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THE USE OF SODIUM BIRNESSITE AS A CURING AGENT FOR LIQUID POLYSULFIDE SEALANT

PORTFOLIO SUBMITTED FOR THE DEGREE OF
ENGINEERING DOCTORATE (Eng.D.) IN ENVIRONMENTAL TECHNOLOGY

by

ANDY. D. HOULSON

CENTRE FOR ENVIRONMENTAL RESEARCH, BRUNEL UNIVERSITY

February 2000

VOLUME 1

ABSTRACT

Manganese (IV) oxide phases are widely used as curing agents for polysulfide sealants. The manganese based curing agents, however, do not give a reproducible cure and this results in material waste. As the market for insulating glass applications is increasing, efficient curing becomes more significant both commercially and environmentally.

The research described in this portfolio focuses on using a laboratory synthesised manganese (IV) oxide phase, sodium birnessite, as a polysulfide curing agent. The synthesis and full characterisation of sodium birnessite is described and its curing ability measured in terms of the following properties of the cured polysulfide: rate of cure, surface condition, hardness build-up, stress-strain data, low and high temperature properties, and moisture transmission. The results obtained are compared with those of polysulfides cured with a good commercial product. Different concentrations of curing agents, and types and concentrations of accelerators, plasticisers and inert diluents were investigated to optimise the curing process, reduce material use and product wastage. Sodium birnessite is an active and reliable curing agent when used at half of the concentration of the commercial agent in the presence and absence of inert diluents. Diluted sodium birnessite (1:1 with inert diluent) cures polysulfide to levels comparable in terms of stress-strain properties, moisture transmission rate, hardness, surface condition, low- and high- temperature properties, and degree of polysulfide cross linking to that achieved with commercial agent. The mechanism of the curing of polysulfide with sodium birnessite, as with all curing agents is conversion of mercaptan groups -S-H into disulfide linkages (-S-S-). Sodium birnessite is a mixed oxidation state compound and its synthesis results in the inclusion of Mn^{2+} in addition to Mn^{4+} ions in the manganese oxide based lattice. A rationale for the improved curing ability of sodium birnessite is presented. It is based on the ability of Mn^{2+} to create vacancies in the Mn^{4+} sub-lattice thus increasing the mobility of the Mn^{4+} in the structure and its transport to the surface of the curing agent where the oxidation-reduction reaction responsible for the cure takes place.

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VOLUME 1 THESIS and other supporting documents

CHAPTER 9 Investigation into the curing mechanism of polysulfide using sodium birnessite

VOLUME 2

Six month reports

Number 1 to Number 8

List of abbreviations used in this document

DBU	1,4-Diazabicyclo(2.2.2)octane
FTIR	Fourier Transform Infra Red Spectrometry
LP32C	Morton International Liquid Polysulfide Polymer
MVTR	Moisture Vapour Transmission Rate
NaB	Sodium birnessite
PPH	Parts Per Hundred
TMTD	Tetramethylthiuramdisulfide
XRD	X-ray diffraction

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Thanks especially to mum for her encouragement and to my family - who this is dedicated to-

Objective of executive summary

The objective is to summarise research carried out for the Engineering Doctorate and to introduce the structure and content of the portfolio.

EXECUTIVE SUMMARY

Introduction to the Engineering Doctorate (EngD)

The Engineering Doctorate is a four year research degree that was set up in 1992 by the Science and Engineering Research Council (SERC) (now EPSRC) in response to industry needs for more industrially orientated research students. The EngD is equivalent to a PhD where the student has to make a contribution to knowledge although with a greater focus on the links between industry and the environment as well as academic research. A mission statement from the Eng.D handbook is: "The Brunel/Surrey Engineering Doctorate aims to create graduate Research Engineers with the necessary background knowledge, skill and experiences to understand the relationship between the environment, technology and business and to apply this understanding to the development, promotion and execution of corporate strategy."

The EngD is distinguished by its programme of compulsory courses which the Research Engineer (i.e a student registered for the EngD degree) attends and which have the following aims:

(a)To provide a state of the art view of the relationship between Engineering and Environment (including the sociological aspects) which can be used in the research projects

(b) To provide professional development in the key business skills and competencies

(c) To close any gaps in the knowledge required to undertake the research project.

All of these modules are assessed by individual assignments and it is a requirement that they are successfully completed. The modules taken over the 4 year period and successfully completed are as follows:

Year 1

Communication and Leadership (Induction course)

Clean Technology and the Environment

Life Cycle Assessment

Risk perception and communication

Environmental Legislation

Research methods.

Year 2

Sociology of the environment

Communication and Leadership (Part 2)

Risk Management

Environmental Law

+ 1 compulsory elective

Year 3

Financial Management

Marketing

Year 4

Talking to the media

Environmental Economics

The work is presented as a portfolio which is the vehicle the research engineer uses to explain the 'thesis by portfolio', in contrast to the PhD method of 'thesis by dissertation'. The portfolio approach better approximates the development of research in an industrial context.(1)

The portfolio contains a series of six monthly reports, a thesis describing the intellectual property of the work, and scientific papers. The six month reports are a record of progress toward the ongoing research objectives, and do not necessarily represent the final conclusions but are simply a record of progress toward deliverables.(1) The portfolio also contains this executive summary of not more than 4000 words which :

(1) Sets the portfolio contents within the context of Environmental Technology

(2) Directs the reader to evidence in the portfolio which describes the innovation (s) and contribution (s) to knowledge in the field of Environmental Technology.

It should also be noted that historically once a document is placed into the portfolio it cannot be removed and it is important to take account of subsequent documents detailing amendments.

The structure of the portfolio

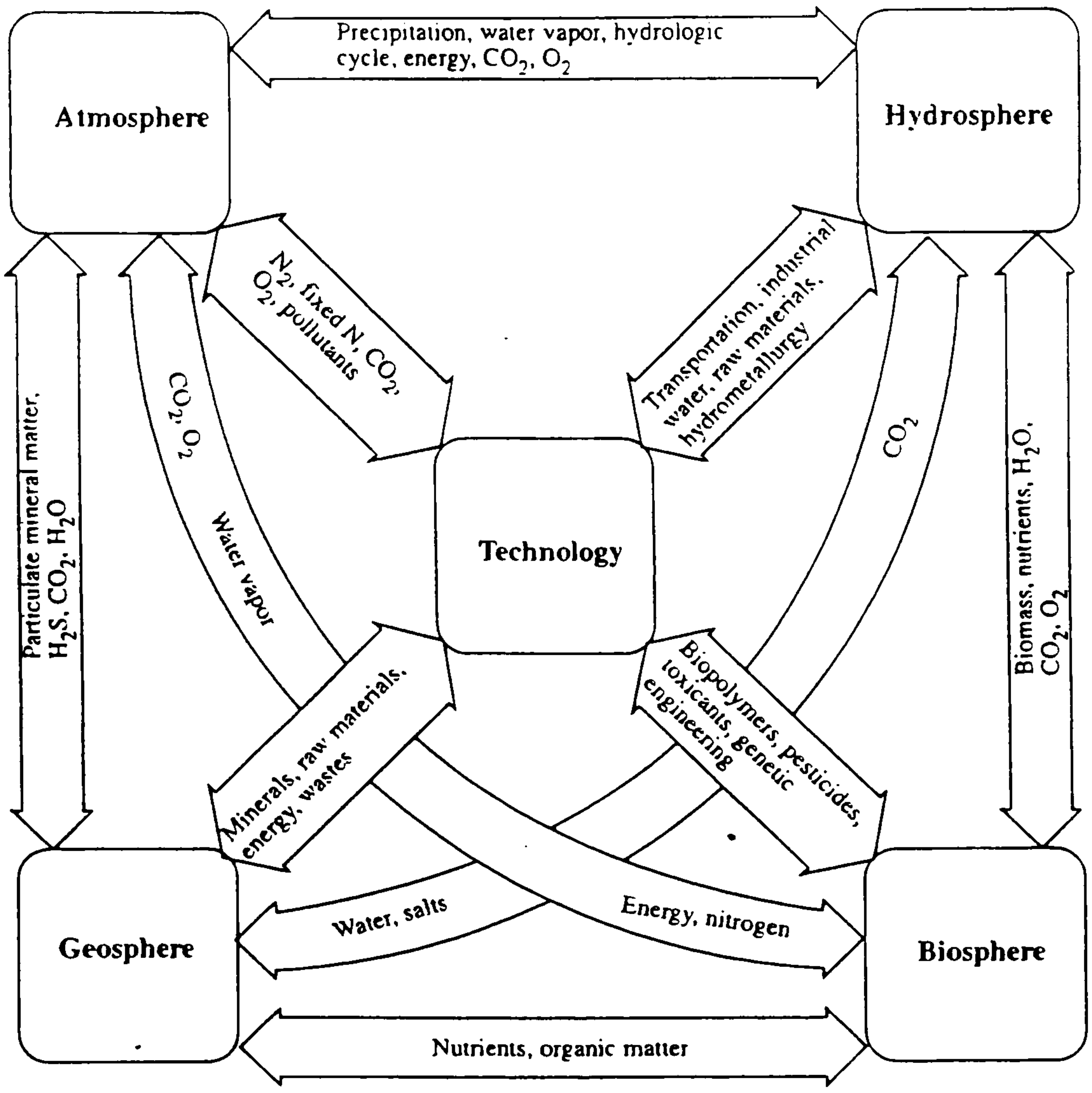
The portfolio is comprised of the thesis that contains the executive summary, a description of the intellectual property of the research, manuscripts prepared for publication, and the poster presented at the Royal Society of Chemistry. Secondly, the portfolio consists of a set of bound six-monthly reports and thirdly, the successfully completed course work for the taught courses.

The portfolio should be read in the order of Executive summary first, then the main body of the thesis which should be read in a similar way to a PhD thesis. The six month reports should only be considered as progress summary notes for each six month period.

An Introduction to Environmental Technology

Environmental technology is "the application of scientific and engineering principles to the study of the environment, with the goal of the improvement of the environment."(2) As Figure 1 shows, there is a very close link between air water and land and their relationship with technology.

Figure 1 The interconnection between technology, earth air and water.(3)



End-of-pipe treatment of environmental problems has been the philosophy of pollution control for over two decades. However a newer philosophy, that of preventative technology is being championed where "processes, operations and products of the industrial system can be redesigned or adjusted so as to avoid or minimise the production of wastes in the first place". Possible benefits of the preventative technology approach include cost savings from reduced end-of-pipe pollution control measures, reductions in energy and maintenance costs, reduction in natural resource requirements, reduction or elimination of pollution control costs, reduced need for occupational health and safety measures, improved worker morale as they take pride in their "green products", and better acceptance by consumers of green products." (4)

In the end, improving both the material efficiency (using fewer materials or less of a single material) and substituting more hazardous materials with less hazardous materials, or even product reformulation, is important in preventative environmental management - i.e acting upstream of environmental problems. It is clear however that product reformulation is not popular within industry because manufacturers are more concerned about loss of product quality than about pollution minimisation. One has to be sure any substituted product does have lower environmental impacts than the substance being substituted for as reflected by whole life cycle impacts.(5) Another aspect of this is in ensuring maximum possible use of products and protecting products from unnecessary decay and obsolescence. The pathway to achieving these effects is as important as the achievement of getting there. It is crucial that the product is tested fully to compare it with the alternatives. In the case of sealants, such as polysulfides used in this research, where the compound has to withstand pollution, rain, stress and strain (for example in insulated glass sealant uses), the testing has to be extensive. Even if a greener alternative can meet these standards, the cost factor is crucial to ensure marketability, but it is an important area for research because the market for double glazing is forecast to increase because of energy efficiency drivers.

EXECUTIVE SUMMARY OF THE 4 YEAR RESEARCH CARRIED OUT.

Evolution of the project.

The original title for this EngD research was: "The use of strontium and manganese chemicals in environmental technology." It was decided however in consultation with supervisors, that by the third year it was preferable to focus the research on one area, namely manganese chemicals in clean technology. This was due to a need to narrow down the research performed in the first two years on both strontium and manganese chemicals. As a result strontium chemicals research was discontinued and subsequent work was focussed on the use of the manganese (IV) oxide phase, sodium birnessite in its curing of liquid polysulfide polymer.

Sodium birnessite is a synthetic analogue of a natural manganese (IV) oxide. It is an oxidising agent and a surface active material because of surface hydroxides, and has been used in the oxidation of organic compounds and in the removal of heavy metals from solution. Work carried out in the Centre for Environmental Research at Brunel University, (6) and some other work carried out on sodium birnessite curing by Cookson(7) identified sodium birnessite as a possible polysulfide catalyst. In the present work, studies have been carried out on the synthesis of sodium birnessite and its use as a polysulfide curing agent. Individual samples of sodium birnessite were characterised by X-ray diffraction and thermogravimetric analysis and composites of identical batches mixed together and sieved to homogenise them. The composite batches were characterised to see they were sodium birnessite using X-ray diffraction, thermogravimetric analysis, particle size measurement and determination of their pH as a 10 % slurry.

The polymerisation studied in this work was of the liquid polysulfide LP32C that is used for insulating glass sealing. A number of factors are important in creating successful insulated glass sealants: they must have good thermal stability, they must have a low moisture vapour transmission rate (MVTR), and be sufficiently hard to maintain the strength of the insulating glass structure. Other important factors are the time taken to create a cured product - too long and the polymer remains sticky and soft, too short and the polymer is unworkable. Another significant factor is that the curing agent for polysulfides has to provide consistent and reliable curing: cure failures must be minimised or eliminated to prevent material and consequent environmental and economic loss.

Full literature and patent searches were carried out at the start of the research and maintained throughout the period of this work. Papers used to decide the methods of investigation of the curing of polysulfide using sodium birnessite were that by Ramaswamy and Sasidharan Achary (8) studying the glass transition temperature, stress-strain properties and thermal stability of cured polysulfide and that of Matsui and Miwa(9) who investigated by infrared spectroscopy the loss of the peak for mercaptan groups in the curing of polysulfide.

The commercial curing agent used as the standard by which to compare sodium birnessite is the best currently available manganese oxide based polysulfide curing agent. The standardised curing experiment used in this work involved the mixing of two components A and B having the following compositions:

PART A		
Liquid polysulfide polymer:	Morton LP32C	(100 pph)
PART B		
Curing agent for the polymer:	Commercial curing agent	(10 pph)
Accelerator for the reaction:	Tetramethylthiuramdisulfide	(0.5 pph)
Plasticiser for the curing agents	Santicizer 278 or Santicizer 261	(10 pph)
TOTAL PART B		***20.5 pph***

(“pph” is parts per hundred liquid polysulfide)

In the case of the use of a commercial curing agent. the material is used at a level of 10 pph - well above the presumed stoichiometric amount of 2 pph RSH:1 part active MnO_2 needed for the reaction with LP32C. This would seem a waste of resources. As a result the current research focuses on looking at the effect of using sodium birnessite at 5 pph and 4 pph to determine whether it is possible to reduce material requirements.

For experiments involving sodium birnessite as the liquid polysulfide curing agent, the standardised curing experiment used in this work involved the mixing of two components A and B having the following compositions:

PART A		
Liquid polysulfide polymer:	Morton International LP32C	(100 pph)
PART B		
Curing agent for the polymer:	Sodium birnessite	(5 or 4 pph)
Diluent for sodium birnessite	$CaCO_3$ / inert MnO_2 or none	(5 or 6 pph)
Accelerator for the reaction	TMTD or DBU or none	(0.5 or 0 pph)
Plasticiser for the curing agents	Santicizer 278 or 261	(10,15,16 pph)
TOTAL PART B		***20.5 pph***

(“pph” is parts per hundred liquid polysulfide)

In the context of this research, environmental technology principles have been applied in a number of areas. Clearly environmental damage can result at the manufacturing stage, at the usage stage and at the disposal stage of a product life cycle. The damage can be to the atmosphere, land or to water. In the manufacture stage, the use of less toxic chemicals can be considered for their effectiveness (this was investigated in the present work by the use of $CaCO_3$ as a replacement diluent) and by studying the effects of using a less toxic accelerator -1.4-diazabicyclo(2.2.2) octane (DBU) compared to the normal commercial accelerator tetamethylthiuramdisulfide (TMTD).

It is a requirement of the Eng.D programme to demonstrate competencies in an environmental technology related topic. The work carried out provides evidence of the following competences:

(1) Expert knowledge of an environmental engineering area

A full literature and patent survey has been carried out into the use of polysulfides and the curing and cured properties of them, and into sodium birnessite and its uses.

(2) Innovation and a contribution to knowledge in the development of environmental technology

The contribution to knowledge is significant. The study described in this work of sodium birnessite as an alternative curing agent is innovation and contribution to knowledge due to the data obtained which is necessary to compare the use of sodium birnessite as a curing agent with the best currently available commercial curing agent. It is important to assess whether sodium birnessite can cure LP32C polysulfide to the same levels as that of the commercial agent to identify whether it can be used as a curing agent for insulating glass applications. The following investigations were made to assess the relationship between the variables of cure mixture (curing agent quantity and type, the presence and quantity of inert diluents, accelerators and plasticisers) and:

(A) The curing profile of sodium birnessite cured polysulfide (compared to that using the best available commercial curing agent) monitored using parallel plate rheometry to and beyond the gel point.

(B) The thermal stability of sodium birnessite cured polysulfide (compared to that of polysulfide cured using the best available commercial curing agent).

(C) The Shore A hardness build up over 7 day periods and the surface tackiness of the sodium birnessite cured polysulfide (compared to that of polysulfide cured using the best available commercial curing agent).

(D) Assessment of the surface condition of the sodium birnessite cured polysulfide(compared to that of polysulfide cured using the best available commercial curing agent).

(E) The measurement of the dynamic mechanical properties (the glass transition temperature) of polysulfide cured with sodium birnessite (compared to that of polysulfide cured using the best available commercial curing agent).

(F) The stress-strain properties of polysulfide cured with sodium birnessite (compared to that of polysulfide cured using the best available commercial curing agent).

(G) The Moisture Vapour Transmission Rate (MVTR) of polysulfide cured with sodium birnessite (compared to that of polysulfide cured using the best available commercial curing agent).

(H) The mechanism of sodium birnessite curing of liquid polysulfide determined by infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy.

OVERALL CONCLUSIONS OF RESEARCH

I. No cure failures have been observed in any experiment using sodium birnessite. This is important because of the percentage of failures found with commercial curing agents and the prevention of material wastage and therefore environmental and economic costs due to failures.

II. The inert diluents and the accelerators on their own do not cure liquid polysulfide, whilst the type of plasticiser has little effect on the rate of curing.

III. The quantity of sodium birnessite used is the most important factor in the curing of polysulfide rather than the pH, water content or presence of accelerator.

IV. Increasing the quantity of sodium birnessite from 4 pph to 5 pph increases the strength of the cured polysulfide.

V. The cured polysulfide stress-strain properties are improved when adding either inert manganese dioxide or calcium carbonate as a diluent.

VI. Inert diluent improves the rate of cure and cured polysulfide strength and Shore A hardness build up. This is believed to be due to separation of the sodium birnessite particles leading to more effective curing agent distribution through the system.

VII. Accelerators do not significantly effect any of the curing and cured properties of the polysulfide other than the rate of curing.

VIII. The DBU accelerator provides a more rapid acceleration of the curing than TMTD and is also less toxic.

IX. The glass transition temperature for all polysulfide samples cured with 5 pph or 4 pph sodium birnessite is virtually the same as for 10 pph commercial agent cured polysulfide, regardless of the quantity or type of inert diluent, plasticizer, or accelerator. This indicates that the same degree of cross linking is achieved.

X. The thermal stability of all samples cured by sodium birnessite at 5 pph and 4 pph is very similar to that of the commercial agent cured polysulfide regardless of the quantity of curing agent, type and quantity of inert diluent, type of accelerator, and quantity and type of plasticiser used. This indicates a similar degree of cross linking of the polysulfide using either the commercial curing agent or sodium birnessite.

XI. Inert diluent diluted sodium birnessite at 5 pph cures liquid polysulfide to at least comparable levels of cure (in terms of Shore A hardness, low and high temperature properties, tensile strength, tack free surface) and provides a more rapid cure than the 10 pph commercial agent cured polysulfide.

XII. Sodium birnessite at 4 pph with 6 pph inert MnO_2 diluent provides similar rate of cure, a higher Shore A 7 day hardness, and strength than the 10 pph commercial curing agent cured polysulfide.

XIII. Sodium birnessite at 4 pph without inert diluent or with inert $CaCO_3$ provides unsatisfactory cured properties of liquid polysulfide compared to the commercial agent (e.g produces a tacky surface on the cured polysulfide after 7 days, making it undesirable). This sets the lower limit of sodium birnessite used alone or with calcium carbonate at 5 pph.

XIV. The Moisture Vapour Transmission Rate through 5 pph inert MnO_2 diluted sodium birnessite (TMTD accelerated) cured polysulfide is at least as low as that of polysulfide cured with 10 pph commercial agent (TMTD accelerated).

Various techniques including infrared spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy have been used in this work to study the mechanism of polysulfide cure using sodium birnessite. Infrared spectroscopy has shown that the reaction between the sodium birnessite and the liquid polysulfide is by the loss of the mercaptan terminals in the polysulfide.

The rapidity of birnessite curing is linked to the reagent concentration not to the three most commonly described variables in polysulfide curing namely pH, water content, and particle size.

The curing reaction of the mercaptan groups in polysulfides with all Mn (IV) oxide phases, including sodium birnessite, depends upon the properties of manganese (IV) as an oxidising agent:

$$Mn^{4+} + 2\,e^- \rightarrow Mn^{2+}$$

In a solid oxide phase this will result in the formation of manganese (II) oxide and the oxidation of oxide ions to supply the electrons to reduce the Mn^{4+} :

$$O^{2-} \rightarrow [O] + 2e^-$$

These reactions lead to the oxidation of the mercaptan groups of polysulfides at the solid-fluid interface. Since the curing reaction is occurring at the manganese (IV) oxide surface, the mobility of the Mn^{4+} in the lattice is important because they have to be transported to the surface to replace any Mn^{2+} ions formed. The improved properties of sodium birnessite found in this work can be rationalised in terms of the formation of vacancies in the Mn^{4+} sublattice that would aid their mobility. Because Mn^{2+} has a d^5 and Mn^{4+} a d^3 outer electronic configuration, Mn^{4+} will have a preference for an octahedral site arising from its crystal field stabilisation energy, while Mn^{2+} will have a zero octahedral site preference. The Mn^{2+} ions are therefore likely to occupy tetrahedral sites leaving vacancies in the Mn^{4+}- O^{2-} sub-lattice which will favour Mn^{4+} migration to the surface and improve the rate of the curing reaction. Consistent with this view is the situation found in the spinel lattices for Mn_3O_4 and Fe_3O_4, i.e the Mn^{2+} $Mn^{3+}{}_2O_4$ and Fe^{2+} $Fe^{3+}{}_2O_4$ lattices. Like Mn^{2+} Fe^{3+} has a zero octahedral site preference because of its d^5 outer electronic configuration while both Mn^{3+} (d^4 configuration) and Fe^{2+} (d^6 configuration) have a preference for an octahedral site. This results in the crystal lattice $Fe^{3+}{}_{TET}$. $Fe^{2+}{}_{OCT}$ $Fe^{3+}{}_{OCT}$ O_4 in which half of the Fe^{3+} (zero octahedral site preference) is replaced by Fe^{2+} and moves into the tetrahedral site. For Mn_3O_4 the Mn^{3+} must occupy the octahedral site leaving Mn^{2+} in the tetrahedral site i.e.$Mn^{2+}{}_{TET}$. $Mn^{3+}{}_{OCT}$ $Mn^{3+}{}_{OCT}$ O_4. In all lattices containing Mn ions in different oxidation states, Mn^{2+} is likely to be forced into the tetrahedral sites by the presence of any other Mn ions including the Mn^{4+} ion in sodium birnessite. This mechanism will produce vacancies in octahedral Mn^{4+} sites that will aid the mobility of this ion.

In the rutile structure all the manganese is present as Mn^{4+} and will occupy octahedral sites but, if the Mn^{4+} is reduced to Mn^{2+} which can move to tetrahedral sites, transport of Mn^{4+} to the surface through the vacancies will be improved. Vacancies in the Mn^{4+} sublattice can also be increased by the deliberate production of mixed oxidation state materials such as sodium birnessite which consist of a close packed oxide lattice containing both Mn^{2+} and Mn^{4+} which should improve the properties of the material as a catalyst. The presence of easily exchangeable sodium ions in sodium birnessite may also help vacancy formation.

The good performance of sodium birnessite as a curing agent for polysulfides is rationalised in terms of the presence of Mn^{2+} in the lattice creating vacancies in the Mn^{4+} sublattice which in turn increases the mobility of Mn^{4+} ions and their transport to the surface of the solid to oxidise the polysulfide.

(3) The appreciation of the industrial context of environmental engineering

The testing carried out on the sodium birnessite curing of polysulfide is that which would be carried out on any curing agent used to cure polysulfide. Where possible, standard testing methods were used.

(4) Project and programme management skills

As the preparation of both the sodium birnessite, and the cure pastes containing the sodium birnessite takes weeks. and the experiments such as the MVTR and the hardness testing take from 1 week to 6 weeks for each experiment. these skills were developed to the full.

(5) Oral and written communication skills

This was demonstrated by the presentation of a poster on the curing of polysulfides at the Annual conference for the Engineering Doctorate in Environmental Technology at Brunel University and the presentation of a paper at the Annual conference for the Engineering Doctorate in Environmental Technology at University of Surrey.

A poster was also presented on the curing of liquid polysulfides using manganese dioxide at The Royal Society of Chemistry. London 1998.

A manuscript has been accepted for publishing in the Journal of Applied Polymer Science based entirely on this Eng.D research.

A manuscript has been accepted for publishing in the Journal of Materials Letters.

(6) Technical organisation skills

The synthesis of sodium birnessite is a lengthy procedure and whilst the chemical was being synthesised. dried and prepared for use (which took roughly 1 year), the time spent waiting for the synthesis of each batch of birnessite was spent performing experiments, with the curing and cured polysulfide.

The equipment used to measure the parameters in this study was for general use rather than specifically for this research project. Technical organisation skills were therefore needed to learn how to use instruments and equipments for the first time. This itself is a fairly lengthy procedure. A research plan also had to be constructed around the days when these equipment were working and available for use. The techniques used included:

X-ray diffraction

Thermal analysis techniques

Video microscopy particle size analysis

X-ray photoelectron spectroscopy

Fourier Transform infrared spectroscopy
Dynamic mechanical thermal analysis
Parallel plate rheometric analysis
Tensile testing

(7) Financial engineering project planning and control

The raw ingredients for creating sodium birnessite involve a manganese (II) salt. This could be manganese chloride, manganese acetate or manganese sulfate. It was decided on financial grounds that manganese sulfate was the cheapest to use, and so all the sodium birnessite synthesised was created using the sulfate. The module, Financial Management, was successfully completed.

(8) The ability to apply skills and knowledge to new and unusual situations

A course for laboratory demonstrators was successfully completed at Brunel University. Also I demonstrated in inorganic laboratory practicals involving experiments studying manganese dioxide for undergraduate chemistry students at Brunel University.

The poster presentation of the research, undertaken during the Engineering Doctorate, at the Royal Society of Chemistry in 1998 "New People New Chemistry meeting" involved answering questions about the technology, and the results obtained.

(9) The ability to seek optimal solutions to complex engineering problems and to search out relevant information sources

In the synthesis of sodium birnessite on hot summer days, one technical problem was frequently encountered. The cylinder containing the NaOH and manganese sulphate reagents bubbled over when oxygen was applied. This was a source of a number of experiments being wasted. The apparatus was thoroughly cleaned but this did not prevent its occurrence. A paper about the nucleation of manganese oxide Mn_3O_4 in suspension at above ambient temperatures indicated that a cooling mechanism for the reaction vessel was required.

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CHAPTER 1

1.1 OVERALL AIM

Work carried out in the Centre for Environmental Research at Brunel University on the curing properties of manganese (IV) oxide phases indicated that sodium manganese (IV) oxides might have potential as polysulfide curing agents. The overall aim of this research is to investigate the use of sodium birnessite in curing a liquid polysulfide polymer and its effect on the cured properties of the polymer in comparison with the best currently available commercial curing agent Riedel-de Haen FA. The investigation focuses on (i) the physical properties of the curing agent, (ii) the effect of additives other than the curing agent on the curing process and the condition of the cured polysulfide polymer and (iii) defining the mechanism of the sodium birnessite curing. The aim of the environmental and economic considerations in this work is the reduction in material use that arises from the reported low efficiency of curing agents for polysulfide sealants, and to ascertain if sodium birnessite is a reliable curing agent.

1.2 INTRODUCTION

The Environment Agency in 1998(1) defined waste minimisation as "the reduction of waste at source" which involves changing processes to reduce and prevent waste and suggests that waste minimisation can benefit industry in four ways:

(a) Cost savings: Production costs can be reduced through improved resource efficiency

(b) Compliance: A proactive approach ensures that the company minimises the possibility of litigation

(c) Risk reduction: Control and reduction of risks and liabilities not only reduce the likelihood of fines and bad publicity but can also boost investor confidence

(d) Market positioning: Eco-friendly products can give supply chain confidence and improve customer relations.

On the cost saving approach, reducing raw material usage can decrease the unit production costs of products and in considering risk reduction, one question that should be asked in industry is "can health and safety risks from handling raw materials be reduced?".(1) The questions relevant to industry expressed by the Environment Agency (1) in terms of market positioning include:

> "(1) Are stakeholders pressing for improvements in the business such as cost savings, improved environmental image or reduced risk of pollution incidents
>
> (2) Would customers prefer a "greener" product- this need not mean higher prices
>
> (3) Can market share be increased or new markets targeted by going green
>
> (4) Can the reputation of the business be enhanced in the sector, getting "first mover advantage" over competitors, by "going green".

With these issues in mind, the research here is focussed on investigating the efficiency of sodium birnessite as a curing agent for liquid polysulfide polymer. Sodium birnessite is a layered manganese dioxide found in nature. The results of the current work show that when synthesised in the laboratory sodium birnessite is active as a curing agent for liquid polysulfide polymers.

A number of properties are important in the curing of the polysulfide. The major one is the rate of curing. Too slow a curing means the cured polysulfide will be too soft after application, whilst too rapid a curing reaction means that the cured product could not be successfully applied to a substrate because it solidifies too quickly.

1.3 MANGANESE AND ITS COMPOUNDS

1.3.1 Introduction

The work described in this thesis is concerned with the development of a manganese (IV) oxide based material. This section provides a general overview of manganese and its compounds.

Manganese was first used by the Egyptians and Romans, in the form of manganese dioxide, to decolourise glass, and was recognised as an element by Scheele in 1771. (2) The element is found in the earth's crust at 1040 ppm by weight and is the 12 th most abundant crustal element. (3) It is also the third most abundant transition metal.(4) The element has 9 isotopes, ^{50}Mn, ^{51}Mn, ^{52}Mn, ^{53}Mn, ^{54}Mn, ^{55}Mn, ^{56}Mn, ^{57}Mn, and ^{58}Mn, the isotope ^{55}Mn being the only natural isotope. (5)

Manganese is present in seawater at 0.002 ppm (5) where it arises mainly through underwater volcanic activity as well as outflows from rivers and accumulation in ferromanganese nodules as hydrated manganese dioxide.(6) In water of low pH and reducing conditions, manganese exists as the hydrated Mn^{2+} ion. However, in alkaline conditions, such as in oxygenated sea water with a pH of about 8, manganese (II) ions oxidise:

$$Mn^{2+} + {}^{1}/_{2}\,O_2 + OH^- \rightarrow MnO_2 + H_2O \text{ (6)}$$

In sediments, under oxidising conditions, manganese is found as $MnO_2.nH_2O$ and under reducing conditions as MnS and $MnCO_3$. (6)

Manganese is an essential element in nature due to its role in photosynthesis.(3) For plants, it is essential for growth and therefore is often used as an agricultural supplement in the form of manganese sulfate. Application is approximately 10 - 100 kg of manganese per hectare annually thus preventing manganese deficiency which causes impairment of chloroplast structures.(2) Manganese is also essential for animals. It is required in bone formation and a deficiency reduces egg production in poultry. (2). Excessive manganese in animals however causes a lack of appetite and slow rate of growth.(2)

In humans, manganese is an essential trace element. An average level of manganese in the human body is from 12-20 mg and a major dietary source is cereals. (2) In drinking water manganese is found in British towns supplied with hard water on average at first-draw levels of 4 $\mu g/l^{-1}$, and in soft water supplied towns at average levels of 20 $\mu g/l^{-1}$. (7) Under the Water Supply (Water Quality) Regulations of 1989, the limit set for manganese in drinking water is $50\mu g/l^{-1}$.(8) Manganese in water can cause staining and taste problems. The European

Community sets a guide level at 20 mg/l for manganese, as at this level laundry and sanitary ware become stained grey-black, whilst The World Health Organisation standard for human health for drinking water quality is 0.5 mg/l.(9)

A deficiency in humans however causes impaired growth, lipid and carbohydrate metabolism difficulties, and skeletal abnormalities. Toxicity due to excess manganese is rare and is mainly due to exposure to dust, or excess mineral supplements. (2)

The absorption of manganese into the body depends on age, type of manganese compound and dietary levels of iron and manganese, whilst the main routes of entrance are the lungs and gastrointestinal tract. The symptoms of the disease of chronic manganese poisoning are psychological and neurological and include bronchitis and hand tremor.(10)

The principal ores of manganese are pyrolusite MnO_2, psilomelane $BaMn_9O_{18}.2H_2O$, cryptomelane KMn_8O_{16} and rhodocrosite $MnCO_3$.(6) World reserves are estimated to be 684 million tonnes, over half of which is found in South Africa.(11) World production of manganese ores is approximately 23 million tonnes per year(3) and the value of the annual production of manganese, as contained metal, was estimated at $1.6 billion in 1995.(11) Of the manganese ore produced worldwide, 90 % is used as ferromanganese, in the steel industry where the average level of manganese in the steel is 0.6%. (2) The role manganese plays in this industry is to scavenge bubble forming oxygen and sulfur in the steel.(6)

The major non-steel use of manganese is in dry cell batteries where it is used as a depolariser. The depolariser oxidises hydrogen formed at the cathode during discharge. The hydrogen has to be converted to water as the build up of hydrogen gas would prevent wetting of the electrodes with the water solution in the battery therefore preventing electrical generation.(2)

Other uses of manganese include manganese dioxide to colour bricks and tiles, and manganese sulfate as a manganese source in fertilisers. Fungicides such as Maneb (Manganese Ethylene Bisdithiocarbamate) are produced from manganese sulfate and are used to control crop and cereal diseases, whilst Methylcyclopentadienyl Manganese Tricarbonyl (MMT) is used as an octane booster in petrol.(2) Environmental pollution can result from the use of the element, for example, from manganese mining and ore processing, the fertiliser industry and from coal burning.(6) Manganese dioxide has also been used, coated on sand, to remove transition metals from solution.(12)

1.3.2 Manganese metal

The metal has an electronic structure of [Ar] $3d^5\ 4s^2$, is in group VIIA, and when pure is a silver coloured, hard, brittle element which melts at 1247°C. Four allotropes of manganese exist: α-Mn, β-Mn, γ-Mn and δ-Mn. The transition from α-Mn to β–Mn occurs at 973K, from β–Mn to γ–Mn at 1352K, and from γ–Mn to δ–Mn at 1413K. (5)

In industry the metal is produced in flake form by the electrolysis of manganese sulfate solution.(3) Manganese is not very reactive with non metals at room temperature. At higher temperatures, manganese is more reactive, for example with fluorine to give MnF_2 and MnF_3. At 1200°C it burns in nitrogen forming Mn_3N_2 and at high temperatures with oxygen forms Mn_3O_4. Manganese also combines directly with boron, carbon, phosphorus, silicon and sulfur although not hydrogen. (13) When finely divided the metal oxidises and may be pyrophoric. (14)

1.3.3 The oxidation states of manganese

Of the elements, manganese has the largest number of oxidation states; from -III to +VII, however the +II state is the most stable. The highest oxidation state corresponds to the total number of 3*d* and 4*s* electrons.(13) The acidity of the compounds increases with their oxidation states, MnO (+II) having a basic character whilst Mn_2O_7 (+VII) is strongly acidic.(3) In nature the oxidation state is usually 2+ or 4+.(15) As oxides and hydroxides manganese exists mainly as the Mn (IV) state.(16) The main source for the manganese oxide formation is from continental weathering or hydrothermal activity under the oceans at mid-oceanic ridges. (17)

1.3.4 The +IV (d^3) oxidation state, its formation, and uses

The +IV oxidation state is found in the most abundant manganese ore, manganese dioxide, MnO_2.(3) Manganese dioxide is produced in nature by leaching of manganese from igneous rocks by alkaline waters and consequent deposition as the dioxide. In acid solution manganese (IV) compounds oxidise to manganese (VI). In alkaline solutions the manganese (IV) is reduced to manganese (II).(4) The manganese (IV) oxide phase used in this work, sodium birnessite, is discussed in Chapter 2.

Under weathering, the rocks that are most likely to result in the formation of manganese oxides are manganese carbonates. Manganese oxides are either formed in-situ by oxidation of the carbonates or are produced through a process of dissolution, lateral and vertical, migration and reprecipitation. The higher oxides and hydroxides of manganese are described by Roy.(16)

Manganese oxides can be formed away from the source of manganese ions. Hydrothermal activity in the oceans can produce buoyant plumes transporting soluble manganese thousands of kilometres, terrestrial hot springs however can produce manganese oxides in-situ. It is in low temperature hydrothermal conditions that the formation of oxides including pyrolusite and cryptomelane occurs, whilst in higher temperature veins, oxides such as hausmannite are formed.(17)

Manganese oxides are important in nature as the extent of reduction and oxidation of the manganese determines its availability to plants and animals as an essential element. Oxidising conditions may reduce manganese availability as Mn (IV) has a lower solubility than Mn (II) causing deficiency, whilst reducing conditions may cause accumulation of toxic levels of soluble Mn (II).(18)

Oxidation of manganese can occur biologically. Crerar et al (19) studied the bacteria, cyanophytes and fungi that in aquatic and terrestrial environments convert soluble Mn (II) oxides to insoluble Mn (IV) oxides. Table 1.1

Table 1.1 Examples of manganese-precipitating organisms (19)

Habitat	**Genera**	**Remarks**
Soils	Corynebacterium	Bacteria
Soils	Pleospora	Fungi
Soils, swamps and lake sediments	Caulococcus	Bacteria
Ocean	Ochrobrium	Cyanophyte

Reduction of manganese in soils occurs under anaerobic conditions. This occurs when bacterial oxidation of organic matter proceeds sufficiently fast for dissolved oxygen to be depleted in the soil. The bacteria then use higher oxides of manganese, such as Mn (IV) as their source of oxygen.(18) The higher manganese oxides can also react with organic components in soils to form Mn (II).(20)

According to McKenzie (18) manganese mineralogy is complicated by the large amount of oxides and hydroxides formed in which Mn $^{2+}$ and Mn $^{4+}$ are substituted. These ions can change valence without changing position and if sufficient ions have been oxidised or reduced, the mechanical structure becomes unstable and a new phase results. This is because the change in Mn-O bond length affects the unit cell size. The various structures of the manganese oxides can be obtained from the connection of MnO_6 octahedra in different ways.

Two main types of structure of manganese dioxide have been found from X-ray studies:3d frameworks and layer structures. Framework structures are composed of either single or multiple chains of MnO_6 octahedra with sharing vertices. Layer structures involve the MnO_6 octahedra being held together by hydrogen bonds due to the water molecules. (21)

The simplest MnO_2 structure is pyrolusite with single chains of MnO_6 octahedra. An example of a double chained manganese dioxide is ramsdellite. Other manganese oxides have a more open structure permitting other cations into the lattices. For example barium in hollandite, $BaMn_8O_{16}.xH_2O$, zinc in chalcophanite $ZnMn_3O_7.3H_2O$, and potassium in cryptomelane

$KMn_8O_{16}.xH_2O$.(22)

Manganese dioxide is present in manganese nodules found in marine environments. A main component of manganese nodules is δ-manganese dioxide. The manganese in these nodules is totally oxidised and is essentially present as Mn (IV)(23). Marine manganese deposits are known to be the most important mechanism in controlling the concentration of heavy metals by adsorption.(24) Manganese oxides in soil are important as the availability of Co is controlled by the amount of manganese in the soil. A deficiency in pastures can result from the ability of manganese oxide to sorp cobalt.(18)

Manganese dioxide is effective at degrading organic compounds. For example hydrous manganese dioxide has been used to completely oxidise phenol.(25) Manganese dioxide has also been used in water treatment. It is effective in removing turbidity and bacteria from water.(26)

1.3.5 Manganese dioxide production for polysulfide curing

With reference to the research performed for the Engineering Doctorate, preparation of manganese dioxides effective at curing polysulfides have been patented. For example patents by Riedel-de Haen involving treating MnO_2 (pyrolusite) with NaOH at 250°C in an autoclave, filtering, washing and spray drying at 195°C.(27)

1.4 SEALANTS AND POLYSULFIDES

1.4.1 Introduction to sealants and polysulfides

Sealants are required anywhere where a leakage could have a negative effect on the function capability of an object. the object could be a house. an automobile or a window for example.(28) Stone age people 10.000 years ago were supposedly the first people to use sealants. where they used clay to block cracks in their houses

Polymers are large molecules composed of smaller units. known as monomers. The word comes from the Greek *poly* meaning many. and *meros* meaning parts.(29) The majority of polymers are organic in origin and are linked together by primary covalent bonds. a variety of secondary bonds including:(1) hydrogen bond (2) dipole interaction (3) van der Waals and (4) electrostatic bonds. If a polymer has covalent chemical bonds in between the polymer chains these are known as crosslinks. The amount of crosslinking has a significant effect on the mechanical and chemical properties of the polymer. As an example, crosslinked polymers will not dissolve. although depending on the amount of crosslinking, the polymer may allow solvent to enter it causing it to swell and soften. Also, crosslinked polymers, such as polysulfides, do not melt as the crosslinks restrict molecular motion and so the polymer irreversibly degrades.(30)

Polysulfides, also called elastothiomers, are the oldest synthetic commercial rubbers in production. They contain no carbon to carbon double bonds and consist of chains of organic sections. and sections which contain more than one sulphur atom.(28) The low percent, 0.5 % in the LP32C polymer. of covalently bonded crosslinks means that the cured compound has good stress-strain properties.(31)

Swiss scientists Karl Lowig and Salomon Weidmann were the first to discover the product. In 1840 they reacted ethylene chloride with potassium trisulfide to form a synthetic rubber. The synthesis was virtually forgotten about until 1924 when in synthesising the antifreeze ethylene diglycol using ethylene dichloride, Dr Patrick of Union Carbide reacted sodium tetrasulfide with ethylene dichloride forming polyethylene tetrasulfide.(28) The new product was called thiokol - after *thio*, Greek for sulphur, and *kolla*, Greek for glue. The synthesis was as follows:

$Cl-CH_2-CH_2-C$ + nNa_2S_4 → $(CH_2-CH_2-S-S-S-S)n$ + $2nNaCl$

1,2-dichloroethane + sodium tetrasulfide → polyethylene tetrasulfide + sodium chloride

The first commercially introduced polysulfide was made by the Thiokol Chemical Corporation of Yardville, New Jersey. The original Thiokol polysulfides were solid and cured using zinc oxide and sulfur.(32) The product was called Thiokol A, and was formed by the reaction of ethylene dichloride and sodium tetrasulfide. The series of polysulfide liquid polymers was started in 1943 with type LP2. Since then other liquid polysulfides including LP32 introduced in 1949 (as used in this research) were introduced. (33) Although the main polysulfides produced are liquid, they are also available as millable solids and water dispersions, and are produced in Germany, USA and Japan.(34) A number of new polysulfide compositions have also been developed to improve the adhesion properties of epoxy resin / polysulfide mixes in coatings and concrete sealers. (35)

1.4.2 The advantages and disadvantages of polysulfide polymers

The advantages of polysulfide polymers have been listed by Ramaswamy and Sasidharan Achary:(36)

(1) Excellent adhesion to a variety of substrates when properly compounded with specific additives

(2) Maintenance of integrity in the seal under extension and compression by relieving the stress under fixed strain through interchange of disulfide linkages

(3) Outstanding fuel resistance because of the sulfur linkages in the chain which enhances the solubility parameter of the polymer

(4) Excellent resistance to ozone, sunlight, and weathering because of the oxygen saturated backbone

(5) Very low gas and vapour permeability.

In addition to this, liquid polysulfides have a low toxicity. The low acute oral toxicity (LD_{50}) is 3.9-5.0 g/kg body weight and little eye or skin irritation with temporary contact means that it has no significant health endangering properties. (28) Despite the polysulfide being of low toxicity, the oxidising (curing) agent may possess harmful properties - such as burns caused when using chromium (VI) oxidising agents.

The sulfur in the polymer determines the resistance to swell in solvents and the chemical resistance, whilst the absence of tertiary carbon reduces the susceptibility of polysulfide to degradation by ultraviolet light and oxygen. The formal group in the polymer gives it flexibility at low temperatures. The lifetime of polysulfides however still depends on the exposure to the environment, such as whether it is north or south facing and the temperature range. The higher the polysulfide content the greater the durability of the sealant.(34)

There is development of the recycling of cured polysulfides too, for example using the degradation of the disulfide links in the backbone with solutions of monomercaptides in toluene.(34) Other examples of cured polysulfide recycling include Markov et al.(37) and Hallisy et al.(38)

Polysulfides however have a number of drawbacks which has helped prevent their wider usage. They include having an unpleasant smell and relatively low heat resistance, and poor physical properties.(29) There is however, a patent for deodorising polysulfide materials. (39)

1.4.3 Uses of polysulfides

Polysulfides are currently commercially important due to their high resistance to oil, solvents, oxygen and ozone. The main use of polysulfides is for double glazing, with smaller uses as aircraft sealants and in construction applications. In construction uses polysulfides have to be produced to adhere to a wide range of materials from aluminium, glass, stone, and stainless steel for example.(40)

Worldwide polysulfide consumption is 31,500 tonnes per year, with Europe accounting for 70 % of this. Its main use is in double glazing sealants and it is forecast that this will increase because of energy saving requirements and so an increased consumption of polysulfides is expected. It is important to investigate ways to produce the polysulfide using less resources. and less toxic materials.(28)

An initial use of the polysulfide was as a rocket fuel in the 1940s although polysulfides were replaced by liquid fuel rockets in the 1950s.(28) Since then it is mainly used as sealant for windows and in aircraft fuel tanks. In aircraft fuel tanks the polysulfides seal the joints keeping them fuel tight under extreme vibration, wing movement and temperature variations.(40) Sealants used for aircraft have polysulfide content of about 60 % by weight, for insulated glass about 22 to 32% and buildings 19 to 30 % by weight. It has been argued that without polysulfides. aviation would not be where it is today as all military and civilian aircraft use polysulfides as sealants and coatings. A Boeing 747 uses over 1 tonne of polysulfides. and manganese dioxide is usually used as the curing agent. In aircraft the uses of polysulfides include:(34)
Sealing integral fuel tanks
Sealing joints and seams in wing and fuselage components
Sealing faying (overlapping) surfaces
Sealing rivets, bolts and other fixings
Sealing pressurised cabins
Sealing access doors
Sealing windshields
Overcoating joints. seams and fixings
Gap filling
Aerodynamic smoothing
Electrical potting

If 1 tonne of sealant is cured with 100 kg (10 pph) of manganese (IV) oxide. and if there is a 20% fail rate for the curing of sealant. this represents 20 kg of wasted manganese (IV) oxide and 200 kg of polysulfide sealant. Reliable curing agents are therefore essential to prevent waste from cure failure.

Manganese dioxide, used as a curing agent for polysulfides, also has a high specific gravity. There exists therefore a need to develop products with lower specific gravities but maintaining the important properties associated with polysulfide sealants.

A smaller use of cured polysulfides is as epoxy matrix modifiers, where they are used as flexibilisers, adhesion promoters, and toughening agents in epoxy matrix systems.(41) Odour free modifications of epoxy resins with epoxy terminated liquid polysulfide have also been developed as flexibilisers of the resin and are described by Rees. (42) (43) Polysulfides have also been developed that have fire resistant properties by producing a carboniferous foam that retards the spread of fire and acts as a barrier against heat.(34)

Polysulfide sealants when well formulated can have a long life. For example, polysulfide sealants used to line the irrigation canals in California were laid in the 1960s and have shown virtually maintenance free performance since.(34) In airfield hard standing areas, polysulfides play an important role by preventing spilt fuel and solvents going into the watertable, and their use is being investigated as sealants against fuel seepage from gasoline service stations in Germany and the Netherlands. Polysulfides are also used as sealants in sewerage works.(44)

The edge sealing of insulated glass is dominated by polysulfides sealants. The reasons for this are:

"Ease of application, both manual and on fast, fully robotic lines
Rapid development of good adhesion to glass and aluminium
Rapid development of modulus and strength
Low Moisture Vapour Transmission Rate (MVTR)
Low diffusion rates for gases
Resistance to water, solvents, and other ingredients in glazing compounds
Resistance to UV through glass, heat and other weathering influences
Flexibility over a wide temperature range
Resistant to the stresses induced by temperature fluctuations and wind load."(34)

There exists however, a need for faster curing of the edge sealant on fast automated production lines. The reason for this is that there is a cost in storing products whilst they wait for the properties to develop fully so they can be safely transported. Polysulfide sealants are also used as sealants for train and bus windows, and sealing between planking in boats. Sealant tapes of polysulfides are used to repair failed sealant joints in buildings. Polysulfides can be used as coatings, for example as 1-2mm layers inside bunds around chemical stores to prevent leaks through ageing bunds.(34) The uses of polysulfide in environmental protection are also described by Rees.(45) Other uses of polysulfides include as a binder for rocket fuel where the pyrotechnics are mixed in a polysulfide which is then cured providing a uniform burn.(34)

An important test for polysulfides is their durability in extension and compression. Polysulfides are favoured in moving joints because of their stress relaxation properties, as it reduces the stress on the adhesive bond when extended. The main source of stress relaxation in the polysulfide is via interchanges in the sulfur to sulfur bonds within the polymer backbone.(46) The source of the resistance to vapour and water permeability is in the high sulfur content of the sample.(29)

1.4.4 The curing of polysulfides

The formulation of sealants today involves two major challenges. These are to (1) reduce raw material costs, whilst (2) improving the performance of their products to meet higher industry standards. Sealants are judged on a number of factors including rheology, durability, and weatherability.(46) The cure chemistry of polysulfides has been reviewed by Lowe.(32) Curing of liquid polysulfides occurs at room temperature in either a one component system or a two component system. One component systems contain the oxidising agent and the reaction occurs when the dried mixture of polysulfide and curing agent comes into contact with atmospheric moisture. The main use of one component systems is in the building sector for window sealing where due to their light colour, calcium peroxide, zinc peroxide, and sodium perborate monohydrate are used.

The two component system contains "component A", the liquid polysulfide, and pigments such as titanium dioxide and fillers such as calcium carbonate, whilst "component B" contains the oxidising agent, fillers, pigments and accelerators. The two components are sold in a container with component B separated from and above component A by a plastic film. The components are then mixed together with suitable mixing equipment before use.

Three types of curing agents can be used. Inorganic, organic and gaseous agents. Various inorganic compounds can be used. Lead compounds, including lead dioxide were used until the 1970s until concerns about toxicity caused them to be phased out. Chromium compounds such as sodium dichromate have also been used in the past but since they have a high toxicity they are little used except for high temperature sealants in aircraft. Gaseous curing, using oxygen is an extremely slow reaction but has been used for the impregnation of leather or textiles with a thin layer of polysulfide.

Metal oxides and peroxides such as calcium and lithium peroxide and barium oxide are also used as oxidising agents for polysulfide curing. Sodium perborate monohydrate is also used in polysulfide curing. Organic oxidising agents including organic hydroperoxide, dioxime, diisocyanate and polyisocyanate can also be used in the oxidative curing of the polysulfides. (28) Metal peroxides are preferred over oxides in curing polysulfides. The reason is that oxides are more likely to form undesirable mercaptides (causing higher heat aging loss) for example:(33)

$$2R\text{-}SH + PbO \rightarrow \text{-}R\text{-}S\text{-}Pb\text{-}S\text{-}R\text{-} + H_2O$$

Different uses are required of the polysulfides. As seen from Table 1.2, manganese dioxide and sodium borohydrate are the most used curatives. (28)

Table 1.2 Preferred applications of the different curing agents

Curing agent	**Application**
Zinc peroxide	Glazing
Sodium borohydrate	Building sealants Glazing
Cumene hydroperoxide	Building sealants
Calcium peroxide	Glazing
Lead dioxide	Building sealants
Manganese dioxide	Insulating glass Building sealants Chemical resistant sealants Tapes

Manganese dioxide was the main replacement for lead dioxide as a polysulfide curing agent because the cured products have better resistance to UV light, greater elasticity and lower toxicity. Manganese has also been used as potassium permanganate but this is not used widely. Flexible insulated glass sealants using liquid polysulfide polymers are exclusively cured using manganese dioxide. (46)

In the construction industry, manganese dioxide is well used as it imparts a higher thermal stability than lead dioxide. It is therefore used extensively in modern aircraft and construction sealants.(46) Almost without exception the curing is performed at room temperature, and with the curing agent dispersed in an organic plasticiser. For insulated glass applications which use activated manganese dioxide, the full properties of the polymer are needed within 36 hours of application at room temperature.(34)

The curing of polysulfides using manganese dioxide occurs as follows: (28)

$$2R\text{-}SH + MnO_2 \rightarrow R\text{-}SS\text{-}R + MnO + H_2O$$

A detailed study of this reaction has been performed. The mechanism of oxidative curing of liquid polysulfide polymers by manganese dioxide was investigated by Coates et al.(47) The reaction proposed involves oxidation of the thiol (RSH) to the appropriate thiyl (RS·) radical with subsequent dimerization to give the disulfide (RSSR):

$$\mathrm{RSH} \xrightarrow{\mathrm{MnO_2}} \mathrm{RS\cdot}$$

$$\mathrm{2\,RS\cdot} \rightarrow \mathrm{RSSR}$$

The reaction involves two or more monomers with reactive terminals, and one of the byproducts formed in this case is water. This process of curing is therefore known as condensation polymerization. (48)

Water is an important part of the polysulfide curing process. In the absence of water, curing of liquid polysulfide can be almost permanently delayed. All of the reactions of the RSH group are influenced by pH, where alkaline conditions catalytically increase reaction rate.(32)

It is known that industrial batches of manganese dioxides however have dissimilar activity. The differences are in the state of the metal-ligand bonds, the nature of localisation of Mn^{4+} ions, the type of MnO_2 crystal lattice, and the content of manganese ions with different degree of oxidation. Minkin et al (49) studied the structure of the MnO_2 by NMR and identified the mobility and nature of the distribution of the Mn^{4+} ions by the width and shape of the NMR lines. The more mobile the Mn^{4+} ions the more active the curing agent. The rate of the reaction is also temperature dependent.(50)

The period of time from after the polysulfide and oxidising agent are mixed to the point at which the mixture viscosity is too high to permit the sample to be applied to the substrate is known as the pot life and can be from a few minutes to many hours. The curing time is defined as the time taken for the polysulfide to reach a hardness of 30 Shore A.(28) The quantity of curing agent used varies in the literature. For example Krishnan and Ninan (51) state that 4 % manganese oxide curing agent is optimal, whilst Ramaswamy and Sasidharan Achary(36) recommend 6 %.

1.4.5 The use of fillers in polysulfides

Fillers can be used to alter the physical properties of the cured polysulfide. These can increase the Shore A hardness of the elastomer.(52) Such fillers include calcium carbonate or natural manganese dioxide ore. If fillers are to be used in polysulfides as chemical resistant seals, an inert filler such as barium sulfate or quartz powder must be used.(28) Aluminium powder can be used to impart softness and a metallic finish to the polysulfide. White coloured fillers include titanium dioxide and fine particle size silica.(53)

Fillers are also incorporated into a sealant for reasons of rheology, cost reduction, reinforcement, and pigmentation. Carbon black is used as a pigmenting agent in polysulfides and is used in reinforcing and at high concentrations. For example, 60 parts by weight in 100 parts of polysulfide produces higher modulus.(46) Fillers with low pH are undesirable for polysulfides. For instance clays depolymerize the polymer structure. (33)

1.4.6 Adhesion additives

In order to be an effective sealant, polysulfides need to adhere well to the substrate. Cured polysulfides show low adhesion to surfaces unless properly compounded due to their low polar character. Adhesion additives are an essential part of the cure mix, as according to Lee (46) the majority of field failures are due to loss of adhesion. Additives need to be incorporated into the cure mix to increase adhesion. Work by Ramaswamy and Sasidharan Achary (36) for example investigated the positive effect of adding the highly polar phenol formaldehyde resin on the adhesion of polysulfide. Hydrocarbons and silanes can also be added to increase adhesion.(46) A formulation has been developed which contains no adhesion promoter but relied on reaction of the polysulfide with the substrate.(54)

1.4.7 The use of plasticisers in polysulfides

These are used to make the compound soft. They can also be used to improve the air release properties of the sealant. Examples include chlorinated paraffins.(53) Plasticisers are important additions as they soften the polysulfide, improve air release from the polymer, permit more filler to be added and lower the modulus.(55) An excess of plasticiser however causes a loss of polymer adhesion to a surface and decreased tear resistance.(53) Plasticisers work by prying apart the polymer chains. causing an increased free volume between the polymer chains. The plasticiser also forms secondary bonds with the polymer chains. reducing the bonding forces between the polymer chains and thus allowing freer translational motion of the polymer molecules and easing flexing and coiling of the molecule too.(56)

Problems have occurred in the past with respect to plasticisers. Plasticisers based on polychlorinated biphenyls (PCB's) were used in the 1950s to 1970s in polysulfides as external sealants. The level of PCBs was up to 20 % weight of the polysulfide. and have been widely used in Sweden and the UK. About 500 tonnes of PCBs may have been used to plasticise polysulfides in the UK, however the PCBs are volatile and are released from the polysulfide especially in hot weather.(57)

1.4.8 The use of pigments for polysulfides

Where required, pigments can also be added, and include titanium dioxide. Carbon black, and iron oxide can also be used. (28)

1.4.9 The use of accelerators in polysulfide curing

The first use of organic accelerators in the curing of rubber was by Oenslager in 1906 using analine in the sulfur vulcanisation of rubber. The purpose of the accelerator was to increase the rate and amount of crosslinking in rubbers.(58) A variety of accelerators exist, and these are divided into groups of similar substances such as the Basic Accelerators which include the Guanidine accelerators such as diphenylguanidine (DPG). Another group is the Thiurams, including thiuram monosulfide and thiuramdisulfide. The Thiurams can act as curing agents in large quantities at 3%, and accelerators at the 0.5 % level.(59) Unlike the Basic accelerators such as DPG, the Thiurams work by donating sulfur to the crosslinking reaction.

Accelerators can be used to increase the rate of the curing reaction, and are usually alkaline compounds such as amines including tri-n-butylamine. According to Ghatge,(53) accelerators tend to be amino compounds, which through their alkalinity speed up the curing reaction. Increasing the accelerator level reduces the amount of curing agent that is needed. If used in large quantities accelerators can also act as curing agents. All accelerators act to shorten the tack free time. The mechanism for acceleration under alkaline conditions has been postulated by Coates et al.(47) Under these conditions thiyl radicals ($RS^{\cdot}$) react readily with thiolate anions ($RS-$) producing disulfide radical anions ($RSSR^{\cdot -}$) which react with oxygen producing disulfide. Activation of oxygen, initially to $O_2^{\cdot -}$ and $HO_2^{\cdot}$ into H_2O_2, leads to further production of disulfide: Figure 1.1

Figure 1.1 The mechanism of acceleration of polysulfide curing under alkaline conditions(47)

$$RSH \xrightarrow{\text{base}} RS^-$$

$$RS- + RS^{\cdot} \rightarrow RSSR^{\cdot -}$$

$$RSSR^{\cdot -} + O_2 \rightarrow RSSR + O_2^{\cdot -} (HO_2^{\cdot})$$

$$RSSR^{\cdot -} + {}^{\cdot}O_2H \xrightarrow{H+} RSSR + H_2O_2$$

$$RSSR^{\cdot -} + H_2O_2 \rightarrow RSSR + HO^{\cdot} + HO^-$$

Increasing the quantity of accelerator can reduce the quantity of curing agent used. Accelerators, in large quantities, can also be used as curing agents too.(53)

1.4.9 The use of retarders in polysulfide curing

The oxidation of mercaptan groups is retarded in acidic conditions.(55) Retarders therefore can be used to slow the rate of reaction. These are acidic substances such as stearic acid and zinc stearate. Other compounds can be used including anhydrides of benzoic and succinic acid, however, stronger acids including maleic and acetic acids are not used as they depolymerize the polysulfide.(53) Retarders have been patented for polysulfide curing, for example Riedel-de Haen A.G(60) using anhydrides of benzoic acid for example.

1.4.10 The mixing of components to cure liquid polysulfide

In industrial applications, mixing of the ingredients is carried out using kneader extruders for example.(55) Mixing is important in polymer processing. It is the "intermingling by mechanical action of two or more initially segregated components." Mixing involves two phenomenon, blending and dispersion. If one of the components, such as agglomerations of particles is cohesive in nature, the scale of the agglomerations needs to be reduced by dispersion or intensive mixing. If no cohesive barriers need to be removed, such as in mixing thermodynamically miscible fluids, then mixing "is determined simply by the history of deformation applied to the fluid, the strain" and the process is called blending. (61)

1.5 THE SCOPE OF THE DISSERTATION

Chapter 2 describes background to the experimental and analytical techniques used in this research. Chapter 3 focuses on the production and identification of sodium birnessite. It also includes the use of other ingredients in the cure mixture, namely, the polysulfide, plasticisers, accelerators, and diluents.

The rate of curing was investigated using an ARES rheometer in dynamic time sweep mode using 25 mm parallel plates. The curing was monitored for a set period of 1 hour to observe the progressive increase in the storage modulus G' and the loss modulus G'' to the gel point. These results are reported for the first time in Chapter 4.

The hardness of the cured product is an important variable to examine as a suitable hardness is needed for the cured polysulfide. The increase in hardness of the polysulfide up to 7 days is therefore industrially important as insulating glass units need to be stored once sealed with polymer until they reach a desired level of hardness (above Shore A 30). The build up of hardness was measured using a Shore A durometer. The industrially recommended measurement of Shore A hardness was also performed whereby readings were taken after 4 hours, 24 hours, 48 hours and 7 days. Chapter 5 contains data reported for the first time on this area.

Thermogravimetric analysis of the cured product is important to measure the thermal stability of the polysulfide compared to the polysulfide cured with the commercial curing agent. The samples of cured polysulfide were therefore analysed for weight loss in a nitrogen atmosphere using a thermal analyser heating the samples from 35°C to 620°C at 10°C per minute. The identification of the glass transition temperature for the cured polysulfide is compared to that for the polysulfide cured with the commercial agent. The low temperature elastic properties of the cured polysulfide, as a cylindrical sample, in tension compression dynamic temperature sweep mode, are also reported. These results are reported for the first time in Chapter 6.

As polysulfide is used as a sealant, the ability to withstand moisture is important. Experiments have been carried out on polysulfide cured with sodium birnessite and the commercial curing agent. The experiment performed was the gravimetric Moisture Vapour Transmission Rate (MVTR) test. These results are reported for the first time in the literature in Chapter 7.

The tensile properties of the cured polysulfide are important to investigate the strength of the cured polysulfide. These properties were measured using an Instron 4106 Universal testing machine, and the samples tested were cut as dumbbell shapes from a sheet of cured polysulfide. These results are reported for the first time in Chapter 8.

Further investigations were carried out into the mechanism of the reaction between sodium birnessite and the liquid polysulfide. X-ray diffraction of the birnessite cured polysulfide was carried out for the first time to identify the phase of manganese dioxide the sodium birnessite had been reduced to after reaction with the liquid polysulfide. Also infrared analysis was performed on all the separate cure paste ingredients and the polysulfide to identify a cure mechanism. The peak of interest being the RS-H (mercaptan) peak which is expected to disappear as the RS-H groups transform to RS-SR groups. It was not possible to use Raman spectroscopy as the cured sample was black and therefore unsuitable for this testing. The use of X-ray photoelectron spectroscopy is reported in this thesis. These results are reported for the first time in Chapter 9.

The final part of the dissertation is conclusions and recommendations for further research. This is reported in Chapter 10.

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CHAPTER 2 EXPERIMENTAL AND ANALYTICAL TECHNIQUES

2.1 INTRODUCTION

The standard cure conditions for polysulfide involve the use of 10 parts per hundred (pph) manganese (IV) oxides curing agent per 100 parts polysulfide. Added to the curing agent in commercial applications are plasticisers and accelerators. Two types of plasticisers Santicizer 278 and Santicizer 261 (a plasticiser of lower viscosity than the Santicizer 278) were also added to the cure paste mix in the work described in this thesis to investigate their effects on the curing of polysulfide. The effects of two different accelerators were also investigated in the sodium birnessite curing system. The accelerator used in commercial curing mixtures with the commercial curing agent is tetramethylthiuramdisulfide (TMTD) and this accelerator was also used in the cure paste with sodium birnessite. A set of experiments were also conducted using an alternative accelerator, namely, 1,4-diazabicyclo(2.2.2)octane (DBU).

The mechanical properties of cured polymers are tested in two modes: (i) by applying oscillating forces, in dynamic tests, to characterise properties resulting from the viscoelastic nature of the polymer (loss and storage modulus or glass transition temperature), and (2) by applying force in one direction (testing tensile strength and indentation hardness). (1) According to Nicholson(1) "in order to characterise a polymeric material completely, data from both kinds of test [dynamic testing and unidirectional testing] are needed." The characterization work carried out in the present work made use of both types of testing.

A number of analytical techniques were used in the course of this research. This Chapter gives a background to the following techniques:

(2.2) Particle size analysis
(2.3) Thermogravimetric analysis
(2.4) X-ray diffraction
(2.5) Parallel plate rheometry
(2.6) Tensile testing
(2.7) Dynamic mechanical testing

(2.8) Shore A hardness testing
(2.9) Moisture Vapour Transmission Rate
(2.10) Infrared spectroscopy

2.2 PARTICLE SIZE ANALYSIS OF CURING AGENTS

Particle size is an important variable affecting the rate of curing of a liquid polysulfide. It is expected that the finer the particles the greater the rate of curing. Particle size analysis was performed on a sample of the commercial curing agent and sodium birnessite samples prepared in this work.

Microscopy is the most common technique used to measure individual particle size and was used in this work because in addition to giving particle dimensions it gives a clear indication of the shape.(2) The analysis of the manganese curing agents was performed using microscopic video analysis which is ideal for particles in the range 0.8 μm to 75 μm.(2) This value is chosen as despite the theoretical lower limit of 0.2 μm at which size a diffraction halo occurs around the particle giving an overestimate. For practical purposes, however, the lower limit of the instrument used was assumed to be 0.8 μm.

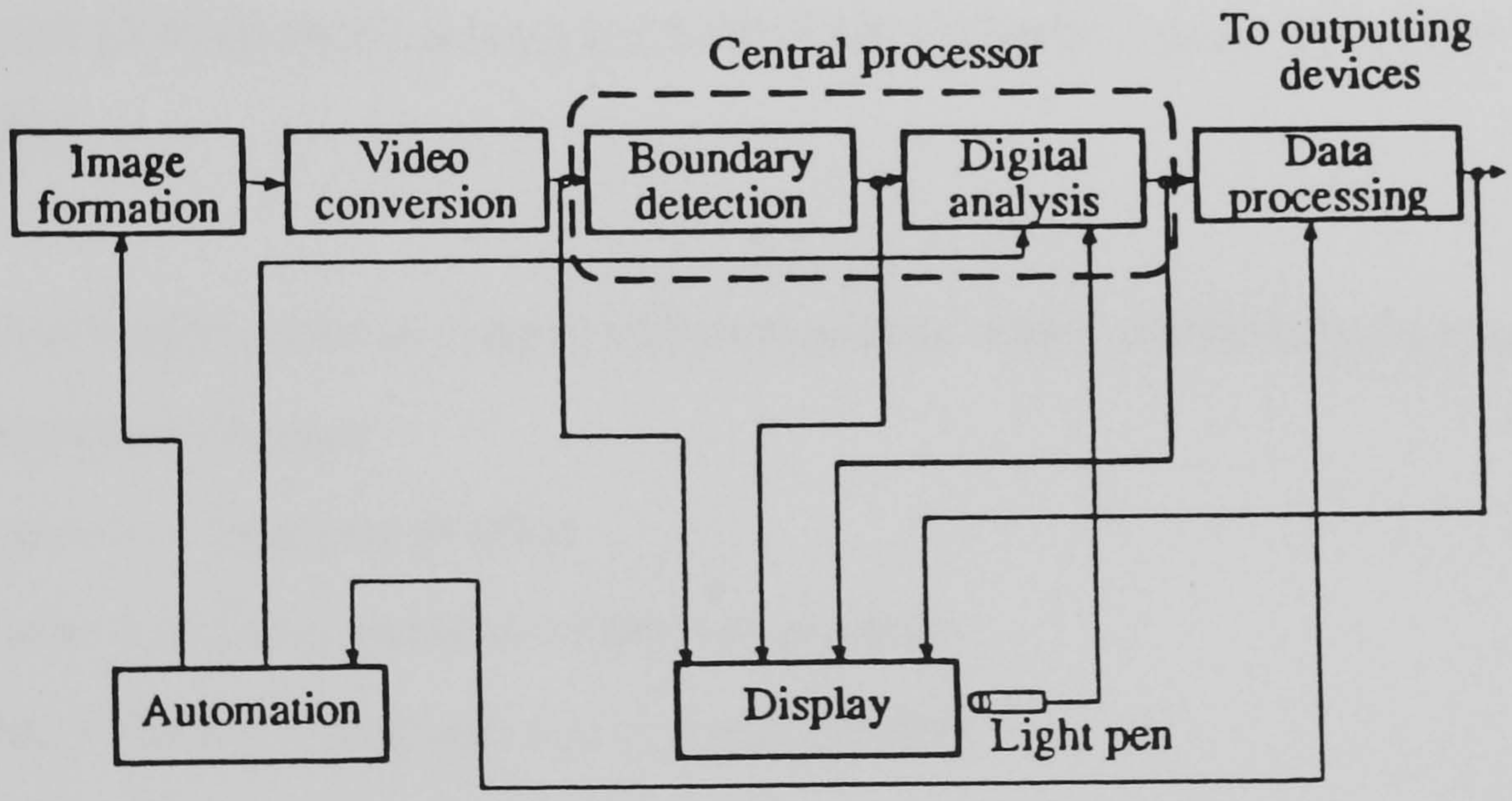
Manual image analysis using a microscope is slow, tedious, and prone to error. The use of automatic or semi automatic equipment is therefore standard. Automatic image analysis is composed of the following steps (2)

(1) Image formation
(2) Image scanning
(3) Feature detection
(4) Feature analysis by count, shape, size or other selected parameter.
(5) Data processing and analysis
(6) Data presentation

Quantitative image analysis involves using a high linearity television camera which is placed onto the conventional microscope. The signals received by the camera are processed using a central processing unit which has circuits that are used to measure, for example, the areas of features and the number of particles.

A visual display of the image under analysis is output to a monitor screen, and interaction with the computer is via a menu driven system. Image editing facilities such as picture enhancement are used to change the grey level and increase the contrast. The image of the particles under analysis is digitised, and can be stored for later analysis. The digital image of the particles is itself composed of picture elements (pixels). The resolution of the image being determined by the number of pixels. The computer then binarizes the image. All pixels below a certain "gray level" become white, the others become black, enabling the particles to be distinguished from the background. A block diagram of a typical image analysis system is shown in Figure 2.1.

Figure 2.1 Block diagram of an image analysing system [(2)]



When performing microscope analysis of a sample, such as in particle size analysis, it is necessary to use an eyepiece graticule calibrated against a stage micrometer placed in the object plane. The stage micrometer is a microscope slide with ruled lines marked in the central area. The stage micrometer is divided up into 100 x 10 μm scale. To calibrate image analysers, such as used in this research, the procedure usually involves indicating the dimensions of an image of a grid or grating of known dimensions on a display screen. Calibration is carried out both perpendicular and parallel to the scan image.(2)

The errors that can occur in particle size analysis include:

(1) Instrument limitations
(2) Improper procedures e.g inadequate dispersion
(3) Operator errors e.g improper instrument set-up or poor calibration
(4) Incorrect sampling

Two sampling errors are possible: (1) Errors due to segregation of the bulk that depend upon the previous history of the powder and which can be minimised by suitable mixing and building up the sample from a large number of increments and (2)Statistical errors which cannot be prevented. Even for an ideal random mixture the quantitative size distribution in samples of a given magnitude is not constant but is subject to random fluctuations." (2) This factor, however, can be reduced by increasing the amount of the sample.

2.3 THERMOGRAVIMETRIC ANALYSIS OF THE CURING AGENTS AND CURED POLYSULFIDE

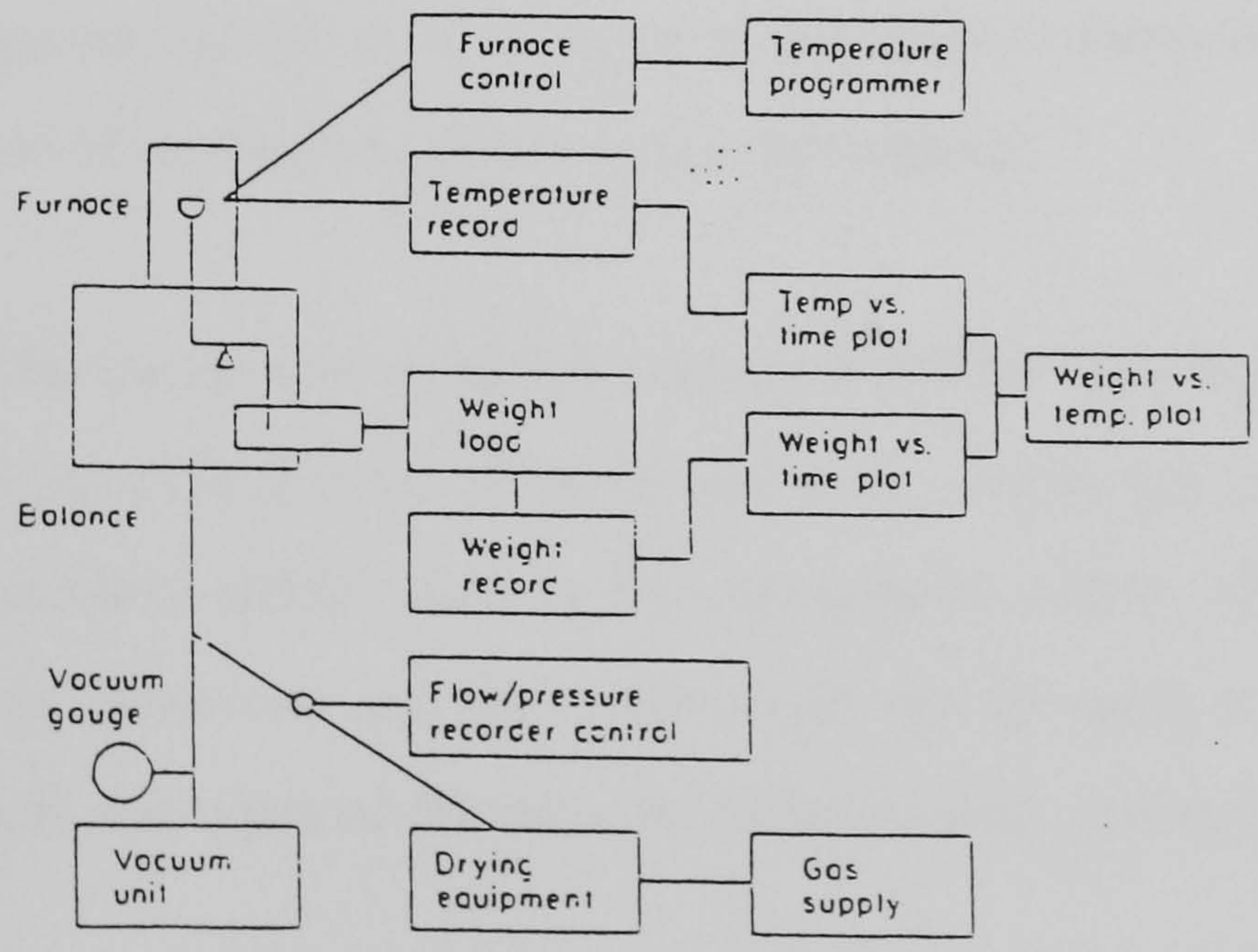
In general, thermal analysis can be used to follow reactions which conform to one or more of the following reaction schemes:
(a) Solid reactant -----> Gaseous product
(b) Solid reactant------> Solid product + Gaseous product
(c) Solid reactant + Gaseous reactant -------> Solid product

The technique involves measuring the changes in weight in a sample which is cooled or heated. The end result is a graph which shows the percentage weight change against temperature. In general since the rate of chemical reactions are temperature dependant, weight losses usually occur at a number of temperatures, resulting in a graph with a series of plateaus and sharp curves.

Thermogravimetric analysis is the most frequently used test to give a quick and quantitative assessment of a plastics components.(3) Thermal analysis was chosen as a technique to study the effect on the product of a number of variables including using the quantities and types of curing agent plasticisers, accelerators and diluents particularly as it is known(4) that the curing agent has an influence on the thermal properties of cured polysulfide sealant. In general for elastomers, any weight loss below 300°C is due to moisture and plasticisers for example while the weight loss between 300°C and 600°C is assumed to result from polymer degradation. The residual weight represents noncombustibles, including metal oxides and inorganic fillers. (3)

Thermogravimetric analysis is performed using a thermobalance. The instrument contains a precision balance, a temperature programmed furnace and a recorder. Small samples are used to achieve the highest resolution of the TGA record. Large samples prevent gaseous reaction products from escaping quickly, and increase the temperature gradient in the sample.(5) Figure 2.2 shows the basic layout of a TGA. Decreasing the heating rate of the sample increases the resolution of the data (5) and the accuracy of the measurement of temperature and weight loss for all of the decomposition steps.

Figure 2.2 The basic layout of a Thermogravimetric analyser (5)



Errors can occur making measurements of weight and temperature inaccurate. Sources of error in TGA include: (5)

(1) Buoyancy effects of sample container
(2) Random fluctuations of balance mechanism
(3) Electrostatic effects on balance mechanism
(4) Condensation on balance suspension
(5) Measurement of weight by balance
(6) Convection effects from furnace
(7) Turbulence effect from gas flow
(8) Induction effects from furnace
(9) The measurement of temperature by thermocouple
(10) Reaction between sample and container

Thermogravimetry has been extensively used to determine the degradation and decomposition of polymers at high temperatures.(6) Studies have been performed by Ramaswamy and Sasidharan Achary(4) on the thermal decomposition of polysulfides cured with various oxidising agents. The cured polysulfide thermal stability depends on both the curing agent used and the polymer backbone composition.(7) Loss of weight also results from the degradation of the polysulfide to monosulfide which is associated with loss of flexibility. The use of manganese dioxide as a curing agent is known to increase thermal stability by reducing the formation of mercaptide groups from mercaptans.(7)

Samples of the curing agents and the cured polysulfide were analysed by Thermogravimetric analysis (TGA) to assess the affect of changing various components of the cure paste. The parameters studied include varying the curing agent and its concentration in the polysulfide using sodium birnessite and the commercial curing agent at various concentrations with varying levels and types of diluents, accelerators and plasticisers.

Approximately 5 mg samples of cured polysulfide were analysed using a Perkin Elmer TGS-2 Thermogravimetric analyser, using a Perkin Elmer heater control, a Perkin Elmer TGS-2 Balance control, and Perkin Elmer Thermal Analysis Data Software. The TGS-2 is capable of controlled heating of the sample, in this case in an open platinum crucible, from 0.3 to 320 °C per minute, although all analysis carried out in this work used a rate of 10°C per minute to obtain accuracy and repeatability. A temperature programme controller is used to operate the furnace at the required temperature. The best sample size for use in this instrument is between 0.5 and 10 milligrams resulting in the best temperature accuracy and repeatability.(8)

2.4 ANALYSIS OF SODIUM BIRNESSITE AND CURED POLYSULFIDE BY X-RAY DIFFRACTION

The main technique to determine the phases present in sodium birnessite produced was X-ray diffraction (XRD). Unlike chemical analysis, XRD reveals the presence of crystalline compounds rather than single elements. The technique is used to study crystalline materials - a crystal being defined as "a solid composed of atoms arranged in a pattern periodic in three dimensions". The size and shape of the unit cell of a crystal is described by its lattice parameters, consisting of the cell edges of length a, b, and c and the angles: α,β, and γ- between them.(9)

X-radiation is measured in Angstroms (10^{-8} cm) and is electromagnetic radiation between the wavelengths characteristic of gamma radiation and ultraviolet radiation.(9) The shorter wavelengths are harder and more penetrative, whilst the longer wavelengths are softer and more easily absorbed.

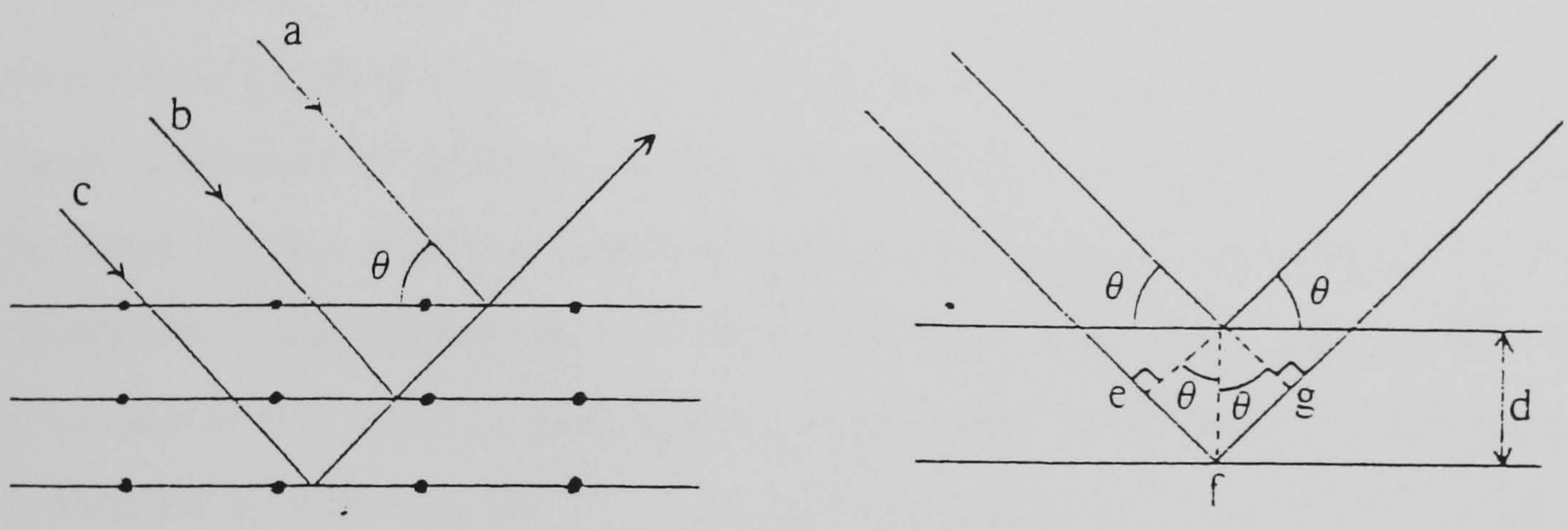
The electrons in orbit around the nucleus of the target atom exist in shells. The principal quantum number n=1,2,3...corresponds to the notation K,L,M etc. Possessing sufficient kinetic energy, an electron hitting the target can knock an electron from the K shell resulting in an excited state atom. An outer shell electron immediately occupies the vacancy, the atom returns to ground state, and the energy emitted as a result is the characteristic K radiation. The critical voltage for obtaining characteristic radiation is therefore that which gives a bombarding electron sufficient kinetic energy to displace an electron from a specific shell. The closer to the nucleus the shell of electrons is, the higher the kinetic energy required for bombarding electrons to dislodge an electron. Therefore K shell electrons require more kinetic energy to dislodge than L or M shell electrons.

Within the X-ray generating tube of a X-ray diffractometer, the high voltage between the anode and cathode draws a stream of electrons from a tungsten filament source and electron collisions with the anode release X-rays in all directions from the rapid deceleration. Above a set critical voltage the X-rays produced are characteristic of the metal anode. This characteristic spectrum of wavelengths consists of sets of lines of increasing wavelength known as K,L,M etc. Usually as the L and M lines of longer wavelength are too easily absorbed, the K lines are used in X-ray diffraction. These consist of $K\alpha 1$, $K\alpha 2$, and $K\beta 1$. For analysis by XRD of non ferrous materials - such as the manganese oxides in this research project - a copper source is used to produce copper $K\alpha$ radiation of 1.542 Å wavelength.

The X-rays produced from the anode pass out of the vacuum in the X-ray tube through X-ray transparent beryllium windows onto the sample being analysed. When the X-rays hit an atom in a crystal, some diffraction of the beam occurs. The degree of scattering depends on the number of electrons in the atom. When the X-rays hit the crystal surface, they will be scattered in all directions. If the angle of scatter is such that the scattered beams are completely in phase then this is termed diffraction. The X-radiation hits the surface of the crystal at a given angle θ - the Bragg angle -between the incident beam and the crystal plane under study. The angular difference between the incident beam and the diffracted beam is 2θ and this is measured by the instrument. The intensity of the diffracted X-rays is measured by a counter which converts the X-ray beam into a pulse of current that is counted. The number of pulses over a set period is directly proportional to the intensity of the diffracted X-rays that enter the detector.

The information obtained from XRD depends upon the diffraction of the X-radiation measured in Å by the grating formed by the regular repeat pattern within the crystal. This diffraction occurs as each atomic electron cloud set into vibration by the X-rays acts as a source of secondary rays of the same wavelength. When X-rays hit the powder, they penetrate the layers, but are also reflected by them. The rays reflected from all the planes take the same direction, if they are in phase with one another constructive interference will result, whilst if they interfere destructive interference will occur. If the difference in path between the rays reflected from successive planes is an integral number of wavelengths reinforcement will occur and a reflected beam forms. In Figure 2.3 the difference in path between rays reflected from successive planes is ef + fg. As ef = fg = (sin θ)d, the condition for successful reflection:Braggs law $n\lambda = 2d \sin \theta$ is met, where n is any integer, d is the interplanar spacing and θ is the glancing angle of incidence.

Figure 2.3 The Bragg angle of reflection [(9)]


(a) Condition for Reflection

(b) Path Difference = 2d.sin θ

From Braggs Law it is clear that a set of planes of a particular spacing can reflect X-rays at only one angle of incidence. Using X-rays of known wavelength, therefore, and measuring the angle of reflectance, θ, the spacing d of the planes of a unit cell of a crystal can be determined.

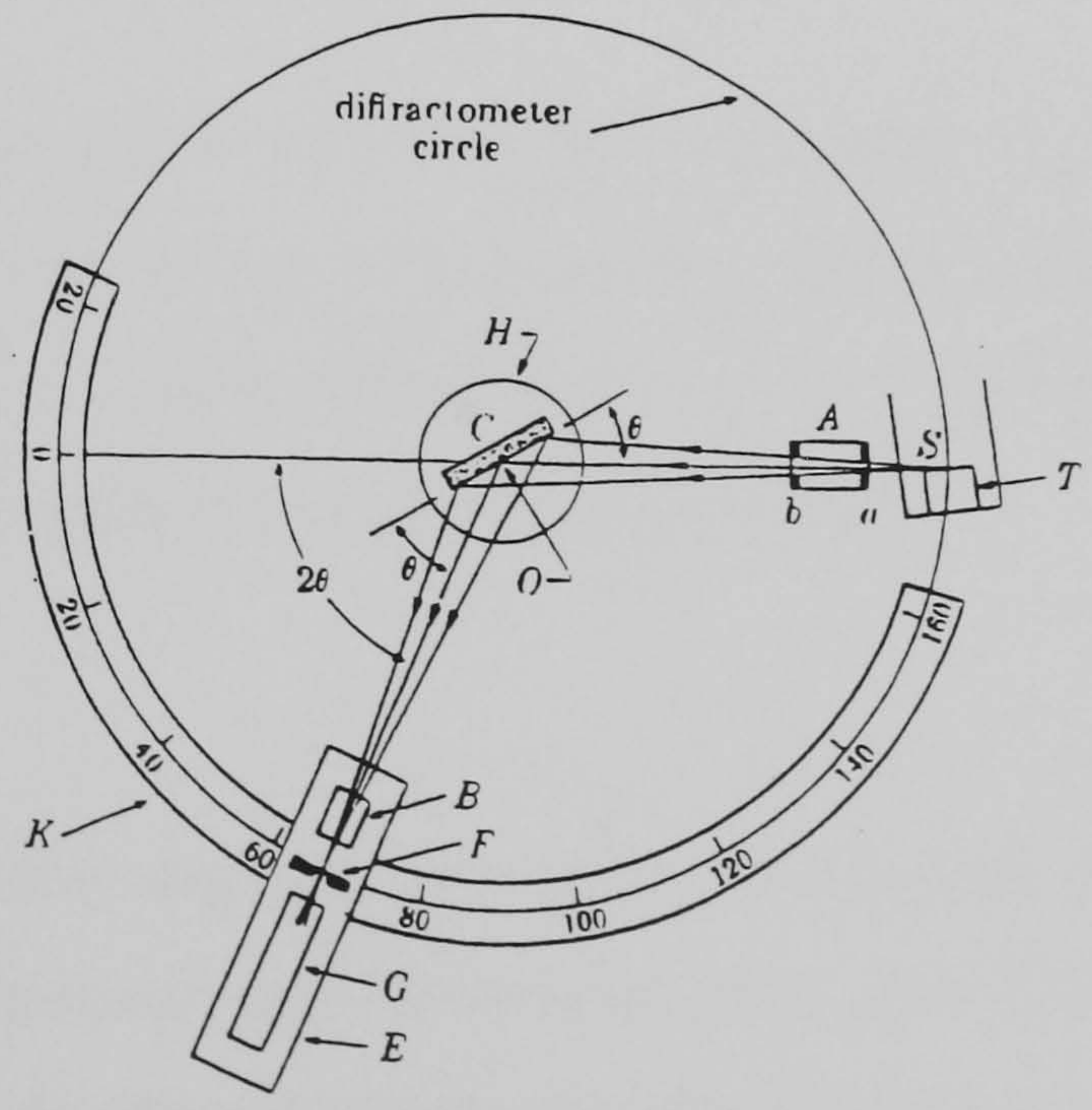
Angular positions of the reflected X-rays are usually recorded in relation to the direction of the undeviated incident beam. For the powder diffraction method used in these experiments the X-ray wavelength λ is fixed whilst the glancing angle θ is variable.

Powder diffraction XRD involves bombarding a powdered crystalline solid with monochromatic X-rays. As the powder contains crystals orientated at all different directions, every set of lattice planes will produce reflection of the incident X-rays as there are many crystals which are orientated so that their hkl planes make the correct Bragg angle with the incident beam. As the correctly oriented crystals all have orientations about the primary beam, the diffracted beams form a cone of half apex angle 2θ(hkl).

The size and symmetry of the unit cell of the crystal structure and the wavelength of the X-radiation used determines the position of the diffraction beams, whilst the intensity of diffracted X-rays depends on the type of atoms in the crystal and the location of the atoms in the unit cell. This principle is used to fingerprint crystalline compounds, and individual components in a mixture. The diffraction pattern (d value) produced can be compared with data of known substances until a match is found.

A diagram of the powder diffractometer is shown - Figure 2.4. A powder specimen C is placed on a flat plate held on a table H - the plate can be rotated on an axis O. The electrons from the tungsten filament hit the target T of the tube, and the X-rays emitted from the target source S. In Figure 2.4, S is normal to the plane of the diagram, and so the sample is parallel to the axis of rotation of the diffractometer O. Diffracted X-rays from the powder are then detected by a counter G after being focused at slit F. The incident and diffracted X-rays are defined and collimated by slits A and B.

Figure 2.4 Schematic of X-ray diffractometer [(9)]



Preferred orientation is a problem that can occur in powder diffractometry. This occurs when the crystals in a sample are not randomly orientated on the sample holder thus causing disagreements between the calculated and observed intensity of characteristic lines of a sample. The problem is partly overcome by carefully placing the powder on the slide compacting sufficiently with a glass slide to cause cohesion although not so much as to cause the surface of the sodium birnessite sample to appear shiny - resulting in preferred orientation.

2.5 MEASUREMENT OF THE PROGRESSION OF CURING OF LIQUID POLYSULFIDE USING PARALLEL PLATE RHEOMETRY

Analysis of the reaction between the polysulfide LP32C and the commercial curing agents and sodium birnessite were performed using an ARES Rheometer. The instrument can be used to measure the viscoelastic properties of polymeric reactions such as the curing of LP32C. It is to be expected that an increase in the amount of curing agent increases the rate of curing, as demonstrated by Fountain and Haas (10) in a study of polysulfide curing using lead dioxide.

One of the methods used to characterise the process of curing of the polysulfide will be the identification of the gel point. According to Rosen, (11) a gel is defined as a "molecule of essentially infinite molecular weight, extending throughout the reaction mass." This is important as once past the gel point the product cannot easily be moulded further.

Viscosity is one of the parameters measured in this experiment. It is the materials flow resistance and is defined by the parameters, shear stress τ and the shear rate γ. The units for rheological measurement are, for viscosity $N.s/m^2$ or Pa.s (1Pa.s = 10 poise). (11) Isaac Newton identified that shear stress is linearly proportional to shear rate:

$$\tau = \eta\gamma$$

The liquids that obey this relationship are Newtonian, and include water and toluene for example. Many liquids are, however, non-Newtonian, as an intensified shear rate increases the resistance to flow for example, shear thickening liquids and certain slurries. Polymer melts and solutions on the other hand are pseudoplastic (shear thinning) where the resistance to flow decreases with shear intensity.(12) Both the shear thickening and shear thinning behaviour of non-Newtonian liquids are time independent, so that after equilibrium is achieved at constant shear rate the same shear stress is observed.

Some liquids breakdown over time. Thixotropic liquids such as ketchup, when sheared at a constant stress, show a decrease in viscosity over time. Rheopectic solutions such as drilling mud used in the oil industry, show the opposite effect where at constant shear stress over time, the viscosity increase. This trend is reversible and if the experiment is repeated, the same results are obtained. For chemically stable polymer solutions or melts however, the equilibrium viscous properties are time independent.(11)

The range of shearing of a polymer affects the flow properties. For instance, at low shear stress rates a "lower Newtonian region" is reached which has zero-shear viscosity. At intermediate shear rates for several decades, the material is pseudoplastic. At very high shear rates, viscosity is η_∞, and an "upper Newtonian region" is reached.(11)

The reason for this is that at low shear rates the molecules are at their most random arrangement, and are not significantly aligned in the shear field and therefore show most resistance to flow. At higher shear stresses, the molecules untangle, aligning in the shear field and their resistance to moving past each other is reduced. At the upper Newtonian regions when the shear rate is severe, the molecules are both untangled and aligned, and have minimum resistance to flowing. At even higher rates of shearing the molecules break down, where the main chain bonds are destroyed. When the shear field is removed, an elastic retraction occurs as the molecules tangle up again.(11)

Polymer melts exhibit a greater shear viscosity than those of other liquids with similar intermolecular forces. The reason for this is that the entangled polymer chains cause shear across any specific plane, drawing chains crossing that plane in other directions.(12) As a result of the entangled structure, polymer melts are viscoelastic in behaviour exhibiting both viscous and elastic characteristics.

2.5.1 The ARES rheometer instrument used in the research

The base unit of the ARES rheometer contains the instrument electronics, system processor, and all the electronics. It interfaces with a PC for instrument operation and data storage and handling. Direct drive DC servo actuators are present in the instrument to apply a deforming strain to the sample. Strain occurs when a stress is applied to a body causing it to change shape or size. The instrument has two air lubricated, and therefore essentially non-compliant Force Rebalance Transducers (FRT) 200 g cm^3 and 2000 g cm^3, to measure the resultant stress in the sample when the actuator applies the dynamic (sinusoidal) shear strain to it. When a body is subject to a balanced set of forces it is known to be stressed. The ARES rheometer is displayed in Figure 2.5.The position of the transducer and motor are shown in Figure 2.6

Figure 2.5 The ARES rheometer system (13)

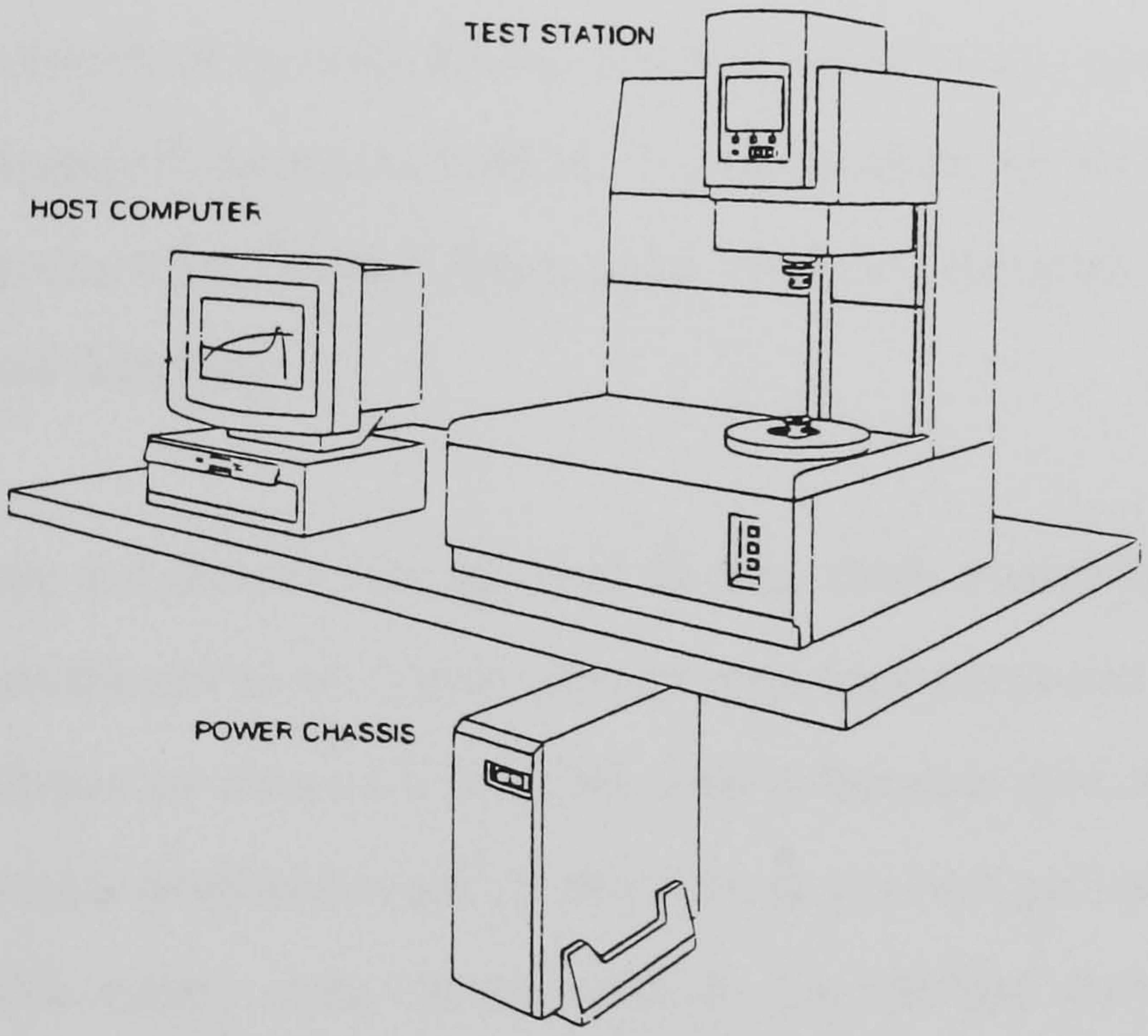
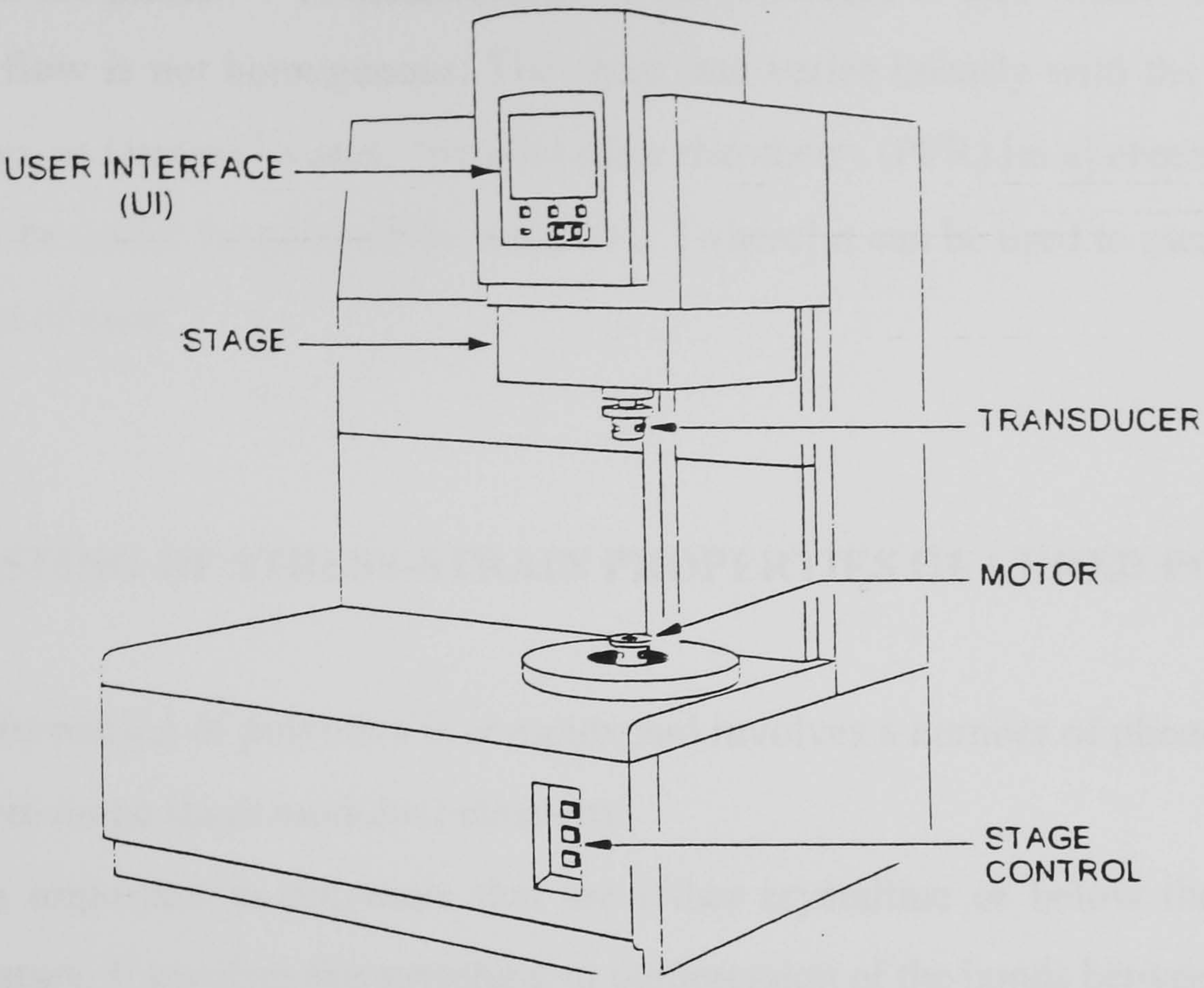


Figure 2.6 The ARES test station [(13)]



An air convection oven with a dual element heater with counter rotating air flow is used to maintain accurate temperature control. The parameters the instrument can measure include the steady shear viscosity, Normal force, shear modulus, complex viscosity, storage modulus, loss modulus, and damping.

The dynamic oscillatory test as used in this work measures the viscosity as the reaction proceeds past the gel point. Unlike steady state measurements, the viscosity can be measured until the polymer becomes a hard solid. This is because *dynamic testing* measurements can be made at a strain amplitude sufficiently low to prevent gel structure disruption as it is being formed. With steady state measurements, the sample under analysis eventually tears or fractures. It should be noted also that the gelation time is sharply dependent on the temperature at which curing occurs (being faster with higher temperatures). As a result, all experiments in this work are performed at a fixed temperature of 25°C.

Dynamic mechanical analysis involves the application of an oscillating strain to a sample. The sample stress that results is then measured.(13) Using parallel plate geometry the normal force and torque are measured when one plate is stationary whilst the other rotates with the sample between the plates.(14) A disadvantage of the technique is that within the gap between the plates, flow is not homogenous. The shear rate varies linearly with the radial position.(15) However, as Usmani(7) states, "parallel plate rheometry (PPR) [is a] characterization method that can be useful for polysulfide sealants ... [where] it can be used to measure rheology as a function of cure"

2.6 TESTING OF STRESS-STRAIN PROPERTIES OF CURED POLYSULFIDE

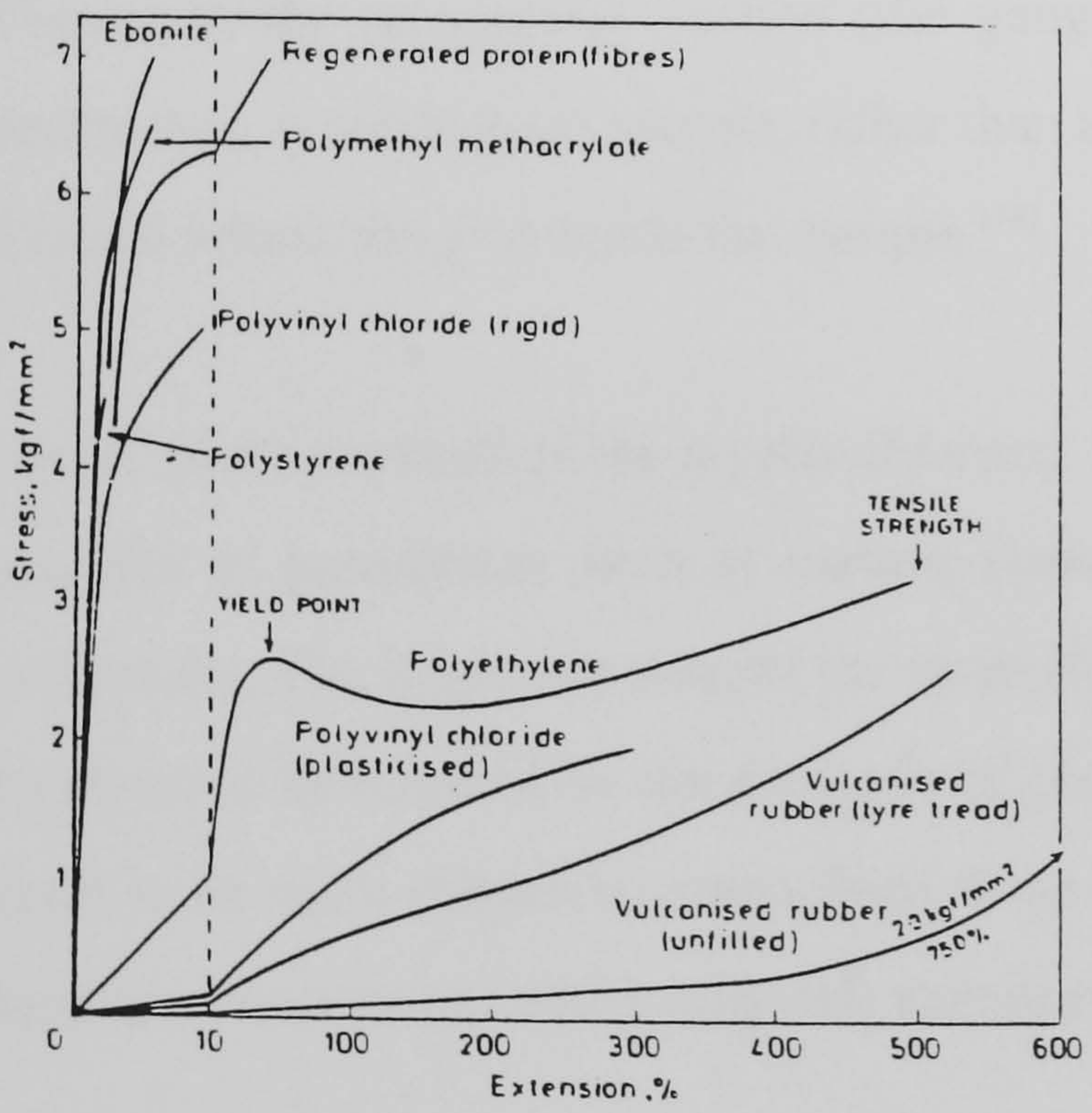
The deformation of polymers is complex and involves a number of phenomena. These are:
(1) Short-range (high modulus) elasticity
This is important in polymers that are either crystalline or below their glass transition temperature. It involves the stretching or compression of the bonds between atoms, and arises when the strain is in phase with the stress (it disappears or appears as soon as the stress is removed or applied respectively). (16)
(2) Long range (rubber like, low modulus) elasticity
This is due to the compression or extension of kinked long chain molecules and is mainly due to the rotation of chain segments about the primary bonds. It means that after applying a deforming force to the polymer, the original undeformed state returns by the motion of the chain segments. The long range rubbery elasticity is time dependent and unlike short range elasticity the strain is more or less out of phase with the stress.
(3) Non-elastic (plastic or viscous) deformation
This occurs when stress is applied to a linear polymer, where the chains are not permanently crosslinked. The result is that the displacement of the molecules is irrecoverable. It is a component of the deformation of any polymer although may be obscured by high modulus elasticity. (16)

A direct tensile force F, which acts on a body of length L, will cause the body to extend by an amount x. A direct compressive or tensile stress will cause a direct strain. Strain can be either elastic which means that the sample returns to its original morphology when the stress is removed, or plastic which is the opposite. Most plastics exhibit both plastic and elastic behaviour. (17)

Youngs modulus relates the parameters of stress and strain (Youngs modulus E = Direct Stress / Direct Strain). The direct stress in the material caused by this force is called the force per unit area measured in Newtons per metre squared (N/m^2). Direct strain is the change in length to the original length. (17)

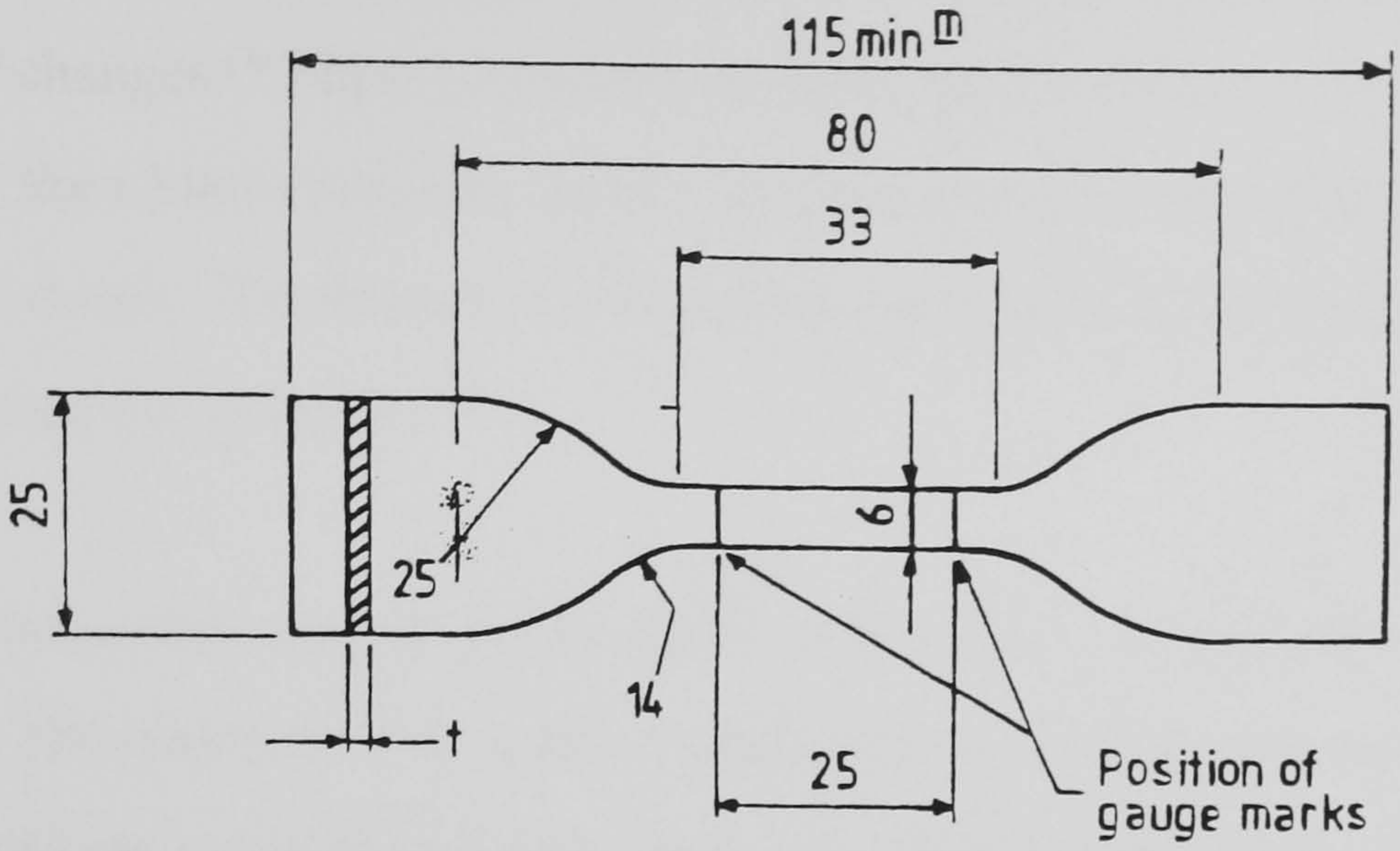
Different types of plastics give different stress-strain curves. The polysulfides tested in this research would be classified as soft and weak for example.(18) Figure 2.7 illustrates various example of stress-strain properties of plastics.

Figure 2.7 Stress-strain properties of various plastics(18)



For stress-strain tests, polymer samples are usually made into a dumb bell shape and forces are applied uniaxially. The testing machine grips either end of the dumb bell shape and these grips are moved apart relative to each other. The dumb bell shaped sample used for testing polymers is shown in Figure 2.8. The grip system is important as it must prevent the sample slipping. The design of the grips and the attachments to the moving crosshead must also ensure that the sample is aligned in the strain direction and there is no bending component. (18)

Figure 2.8 The dimensions of the dumbbell shaped polymer test material used for testing polymers including cured polysulfides(18)



Dumb bell samples are used as this enables the portion where the sample failure occurs to be selected. This is in the rectangular section (the gauge length) which is unbiased by the gripping mechanism. A rectangular sample, rather than a dumb bell, is not used as it is likely failure will occur where the grip holds the sample.(18)

A chart recorder gives a record of the results obtained. It is important to carry out replicates on these samples as parameters such as surface flaws, and internal voids can cause non uniformity of results. The larger the sample the more likely these voids are to occur. Tensile strength is known to be reduced by the presence of plasticisers.(16) This type of experiment therefore tends to be more subject to errors from these sources than dynamic testing such as of glass transition temperature and curing rate monitoring loss and storage modulus. (1)

Extension stress analysis of a polysulfide is important because cured polysulfides must be able to compensate for extension and compression movements in the joints arising from temperature changes and physical movement.(19) Variations in the rate of strain applied to a plastic can influence the test results and influence force-extension values, giving different test results. (17) As the elongation speed increases, the elongation at break decreases, and tensile strength may increase or decrease.(3) Similarly the action of the mixing machine can cause polymer chains to line up and when tested in the direction of the polymer chain alignment, the tensile strength is seen to increase.(3)

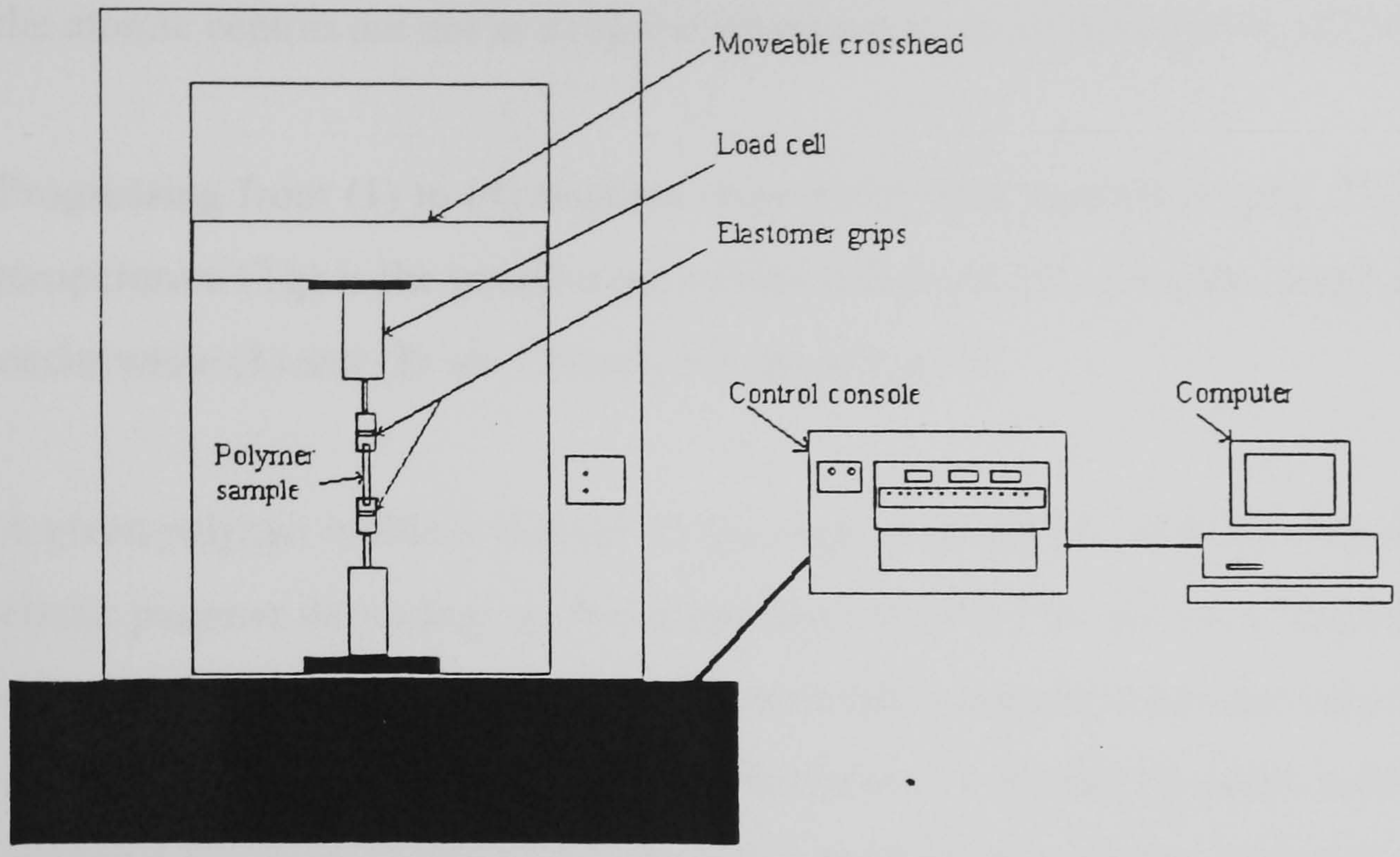
It is important to note that tensile tests should not be carried out on polymers that have already been stretched, as the stress-strain curves of elastomers cannot be replicated after stretching due to material changes.(3) Many polymers, including polysulfides, show no initial straight line relationship in their load-extension curves. In these cases it is not possible to obtain a value for Youngs modulus. The degree of elongation quoted for thermoplastics is known as the percentage elongation at break.(17)

A feature of elastomers such as polysulfides is that they can undergo large and reversible deformations. The reason for this is that curled up polymer chains stretch during deformation although they are prevented from sliding past each other by cross-links and releasing the load allows the molecules to return to their coiled state. In tensile testing of elastomers it is therefore seen that the slope of the stress-strain curve decreases under deformation as the uncurled molecules provide less resistance to movement. Polymer chain breakage results in the fracture of the elastomer.(6)

2.6.1 The Instron 4206 tensile testing apparatus used in this research

The Instron 4206 used for the testing consists of two main components, the crosshead drive and control system applying tensile loading to a specimen, and a load weighing system to measure the loading of a specimen. On the moving crosshead is a load cell, and attached to the load cell is the specimen held between grips. The vertical lead screws move the crosshead up to apply the tensile forces. A console for the testing instrument provides data acquisition, control, and data readout functions for the loading frame.(20) The load cells use strain gauges which detect loads applied to a specimen. The strain gauge consists of an etched foil bonded to an elastic element. Under an applied load, the foil and element deforms and as a result the resistance of the foil is used to determine the load because the resistance is directly proportional to the load. Figure 2.9 shows the Instron 4206 Universal Testing device.

Figure 2.9 Instron 4206 Universal Testing device



2.7 DYNAMIC MECHANICAL ANALYSIS TESTING TO DETERMINE THE GLASS TRANSITION TEMPERATURE OF CURED POLYSULFIDES

The technique of applying sinusoidally oscillating stress to a material and analysing the resultant strain is widely used to characterise polymers. Dynamic mechanical thermal analysis is more sensitive than thermal techniques for measuring macroscopic and molecular relaxation processes, for example the glass transition temperature.(21) All polymers have a glass transition temperature, because all polymers contain some degree of amorphous material, none are wholly crystalline. Not all polymers however have a crystalline melting point as some do not crystallise.(11) The temperature at which a polymer becomes a glassy solid is known as the glass transition point. Above the glass transition temperature, the polymer transforms from a glass-like material with low mobility to a totally mobile rubbery system.

There exist four categories of molecular motion:

(1) Translational motion of entire molecules

(2) Cooperative wriggling and jumping of segments of molecules approximately 40 to 50 carbon atoms in length, permitting the flexing and uncoiling which lead to elasticity

(3) Motions of a few atoms along the main chain (five or six or so) of the side groups on the

main chains

(4) Vibrations of atoms about equilibrium positions, as occurs in crystal lattices, except that the atomic centres are not in a regular arrangement in an amorphous polymer.

Progressing from (1) to (4) requires respectively less thermal energy. The glass transition temperature (Tg) is the temperature at which there is only enough energy for (3) and (4) to occur while (1) and (2) are virtually not occurring.(11)

A given polymer is able to display all the range of properties between a viscous liquid and an elastic polymer depending on the temperature and the time period of the experiment.(22) The dependence of polymer properties on temperature is important because polymers exhibit large changes in properties depending on temperature.(22) At the Tg point, a drop in the storage modulus E′occurs, large peaks also occur for the loss modulus and tan delta curves at this point. The Tg will remain constant at most heating rates but may vary with the frequency of deformation.(21)

The glass transition temperature of polysulfides is dependent on five factors.(11)

(1) The free volume of the polymer, that is the volume that is not taken up by molecules. An equation relates $\nu_f = \nu - \nu_s$ (where $\nu_=$ the specific volume of the polymer mass, and ν_s is the volume of the solidly packed molecules). The larger the free volume, the greater opportunity polymers have to move around resulting in a lowered Tg point.

(2) The strength of bonding between the molecules. The stronger the molecules are bonded together, the more energy it takes to cause motion.

(3) The polymer "internal mobility", which is the freedom to rotate about their bonds. For complete rotation of a chain, the maximum energy is that taken to move one set of the chain substituent groups past another. The Tg increases therefore with increased potential energy.

(4) The chain stiffness affects the Tg. The stiffer the chains, the higher the Tg, as stiff chains have difficulty coiling and folding. Despite being difficult to process because of the high Tg, at high temperatures these polymer are therefore mechanically useable.

(5)The length of the carbon chain affects the Tg point. The shorter the chain length, the more freely the movement of the chains.(11) As only low levels of cross linking monomer are used in the cured polysulfide, it does not affect the glass transition temperature.(7) Increasing the level of crosslinking in the polymer causes a decrease in the free volume in the polymer as chains become closer together, resulting in a rise in the glass transition temperature. (22)

A characteristic notable of elastomers, such as cured polysulfide, is that the glass transition point is below room temperature. In general, polymers change from glass like to rubber like as the temperature is increased or the time of the experiment increases. At low temperatures in the glassy state, the stiffness is related to the change in stored elastic energy on deformation, which is associated with small movements of the molecules from their equilibrium positions.(22)

At increased temperatures in the rubber state, the polymer chains have high flexibility so that in the undeformed state they can adopt conformations which lead to maximum entropy. The presence of chemical crosslinks increases the temperature of glass transition as adjacent chains are brought together reducing the free volume. In polymers with very high crosslinking levels however, movement of large segments of the main chain are not possible and so no glass transition occurs.(22) Low molecular weight additives called plasticisers, which soften polymers, allow changes in molecular conformation to occur more easily and so lower the glass transition temperature and widen the loss peak. Examples of the glass transition temperature of polymers are shown in Table 2.1.

Table 2.1 Examples of glass transition temperatures of polymers(1)

Polymer	Tg (°C)	Contributing feature
Poly (ethylene)	-20	Flexible backbone
Poly (propylene)	+5	CH_3 group inhibits freedom of rotation
PVC	+80	Strong polar attraction between molecules
PTFE	+115	Very stiff backbone

The sodium birnessite cured polysulfide and the commercial curing agent cured polysulfide were analysed by dynamic mechanical analysis. The effect on the modulus of various temperatures was investigated from -60 °C to 30 °C.

Dynamic tests are used to provide information on the appropriate modulus of a plastic. Two types of dynamic testing are used namely the free vibration method and the forced vibration method. The forced vibration method is when the sample is vibrated continuously by external means.(18) During the deformation of a plastic the response is not perfectly elastic and depends on the time scale of the experiment. A plastic, to a first approximation, behaves as a series combination of Voigt and Maxwell elements. The Voigt element consists of a perfectly elastic spring in parallel with a perfectly viscous dash-pot. The Maxwell element consists of a combination of spring and dash-pot. In dynamic tests the behaviour of a plastic is explained by the Voigt element alone if there is no static strain component of deformation. If a stress is applied sinusoidally to the element, at any given time the stress follows the following equation:

$\sigma = \sigma_o \sin \omega t$

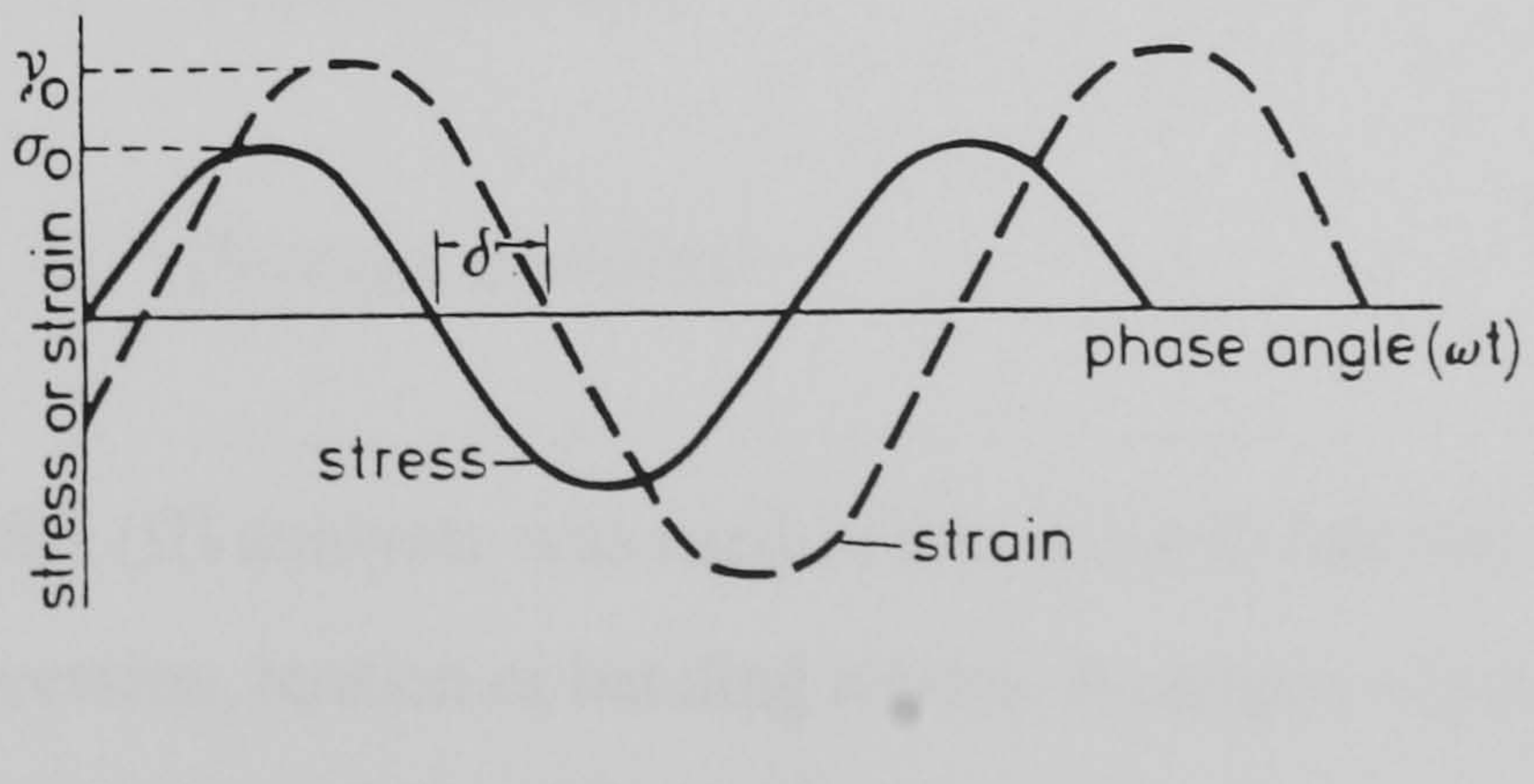
where σ_o is the maximum applied stress

ω is the angular frequency

t is time.

The dash-pot response to the applied stress level is, however, not instantaneous, but is time-dependent. The strain that results, lags behind the stress applied, at an amount depending on the viscous and elastic constants of the element: $\gamma=\gamma o (\sin \omega t - \delta)$ where γo is the maximum strain attained and δ is the phase angle. As shown in Figure 2.10.

Figure 2.10 Stress-strain relationship for sinusoidally varying applied stress.(18)



This model describes polymer behaviour as being due to two simultaneous parts (1) a perfectly elastic part where no energy is lost, and where the applied stress and the resultant strain are in phase and (2) the perfectly viscous part where energy is dissipated as heat and the strain vector is 90° behind the stress. The two moduli resulting are the storage (in-phase) modulus and the loss (out-of-phase) modulus respectively. The storage modulus is given by the ratio of the peak in-phase stress to peak strain. The loss modulus is given by the ratio of the peak out-of-phase stress to peak strain:

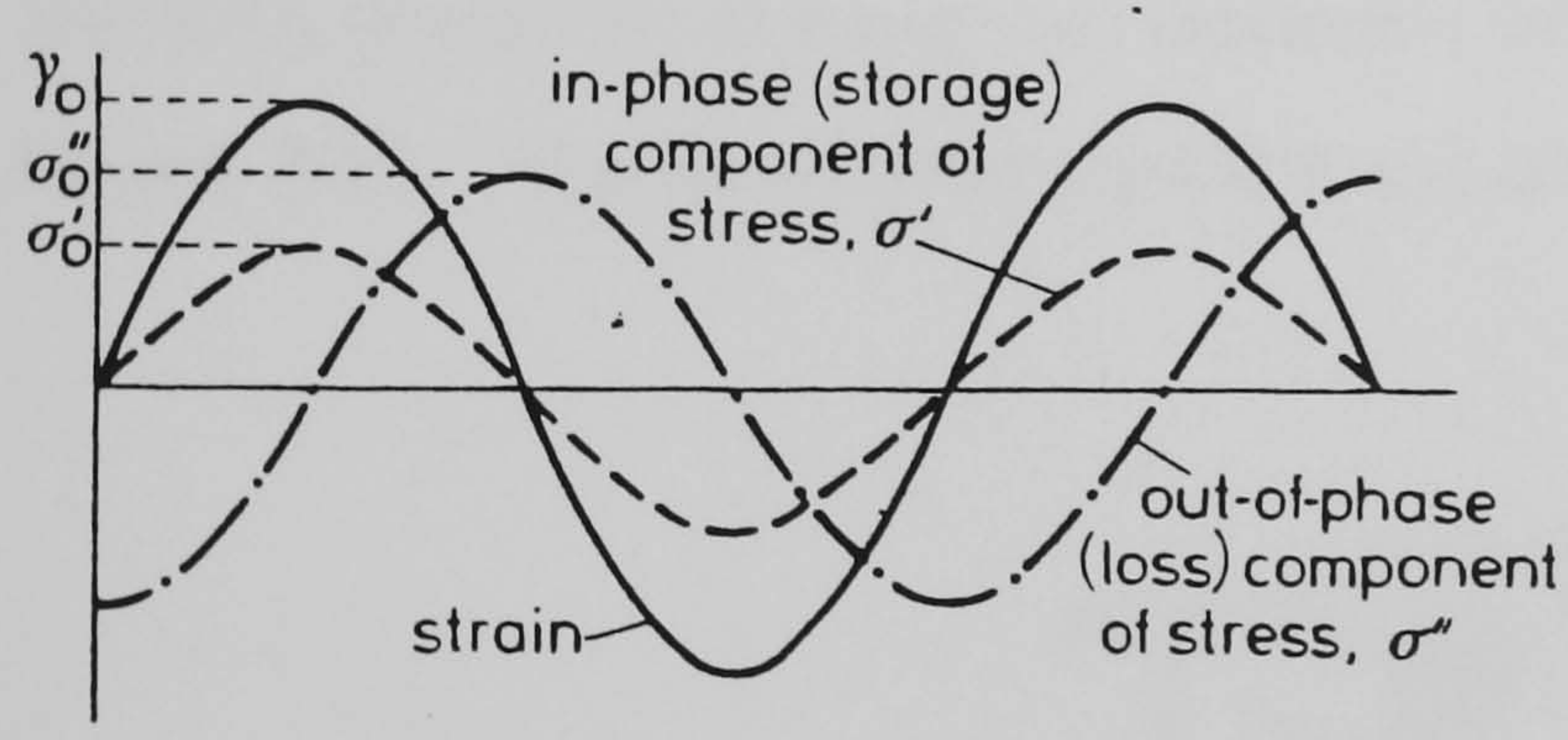
$M' = \sigma'_0 / \gamma_0$

$M'' = \sigma''_0 / \gamma_0$

where M′ is the storage modulus and M″ is the loss modulus.

Figure 2.11 resolves the stress-strain relationship in Figure 2.10 into the two components of storage and loss moduli.

Figure 2.11 The stress-strain relationship of Figure 2.10 resolved into storage and loss components (18)



The tan δ (loss tangent) values shown in the graphs in the results of later Chapters are the ratio of the loss modulus to the storage modulus and are derived as follows: (6)

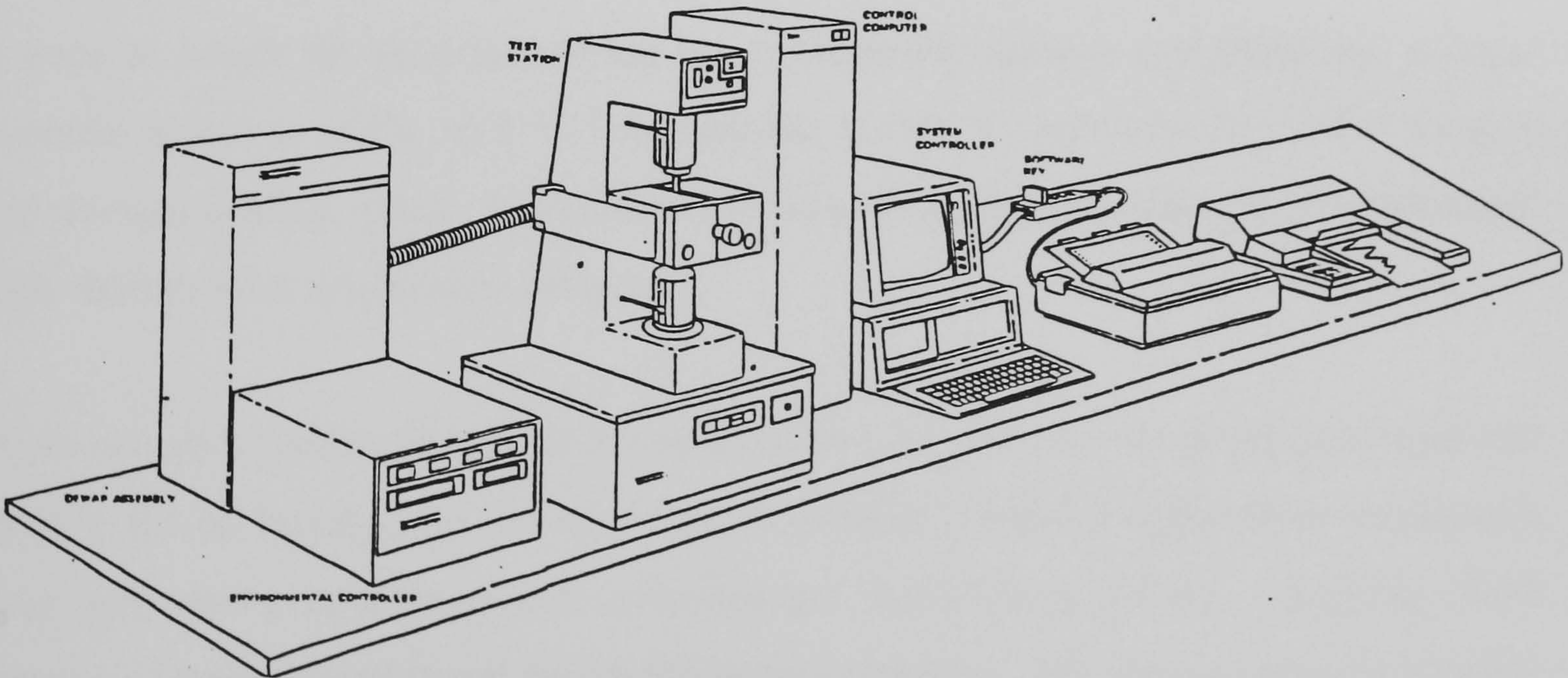
$$\tan\delta = \frac{G'' \text{ or } E'' \text{ (Loss modulus)}}{G' \text{ or } E' \text{ (Storage modulus)}}$$

A Rheometrics RSA (II) analyser was used in this work to test the viscoelastic properties of polymers in compression, tension or bending modes. A sample of polymer is subject to precise compression and detection of the resultant force enables an instant calculation of viscoelastic variables such as the storage and loss moduli E′ and E″ and the complex moduli E*. The real or in phase modulus is E′ whilst the imaginary or out of phase modulus is E″.(22) A computer is used to preset test parameters and repeatable tests and store data. The computer calculates the viscoelastic properties from the data as a function of temperature, time and rate of deformation. These properties provide important information because they can help predict performance of the polymer under, for example, different temperatures.

The testing mode used for this instrument in this work is the Temperature Step mode. This uses a constant frequency and strain level throughout the test at varying fixed temperatures. A start temperature is selected, and incremental temperatures up to the final temperature. The fixed temperatures are held for a preselected time known as a thermal soak, and the measurement made after this soak period.

The sample geometry is important in testing, and for elastomers, cylinders of the material between 3.8mm and 32 mm length and 2.3 to 15 mm width are tested between parallel plates. The RSA II consists of 4 major components (see Figure 2.12)

Figure 2.12 The Rheometrics Solid Analyser II(23)



(1) Test station

This contains the linear servo actuator motor which applies an oscillatory deformation strain to the polymer sample. The amplitude and oscillation of which are user entered into the host computer as strain and frequency values respectively. The actuator is controlled by the central processing unit of the control computer which sets the velocity of the applied deformation force to the sample. The actuator shaft is monitored by a sensor to precisely control actuator shaft movement. The displacement of the shaft from its zero position at the start of the test is proportional to the amount of electrical current received from the actuator shaft sensor.

A transducer, identical to the actuator, but operating in a force rebalance mode, measures force detecting the resultant response in the sample from the effect of the actuator strain on the sample. The transducer detects linear movement of the transducer shaft in a linear variable differential transformer. The transducer loop is used to hold the transducer in a fixed position. To hold the transducer in the same position requires a current, and this current is proportional to the amount of mechanical energy (force) transmitted to the transducer shaft from the sample under testing. The actual sample strain is calculated from this force rebalance transducer.(23) The sample under test is coupled between parallel plates attached to both the actuator and the transducer.

The oven in which the tests are carried out is controlled using a controlled AC voltage convection heater to within +0.5 °C from ambient to 500 °C, and down to -150°C using a liquid nitrogen cooling system. A platinum resistance thermometer within the oven chamber rapidly detects oven temperature changes.

Compressed air is used as the convection medium for oven chamber temperature control and to supply the air bearings for the motor and transducer. Liquid nitrogen from an external storage tank, used to cool the oven is controlled in a 'liquid nitrogen loop', consisting of the computer, a Dewar assembly and the environmental controller. The Dewar assembly contains a double walled flask in which the liquid nitrogen is heated with an immersion heater to above its vapour point of -195 °C, where as a vapour it is used to cool the oven. The cold gas is warmed using a gun heater at the oven entrance chamber.

(2) Control computer

This is used to apply test programs dedicated to specific testing modes, and to calculate the viscoelastic properties of the sample tested. Data from tests is automatically stored by the computer. The stress (material response) of the sample is analysed as a function of the measured force and imposed strain. The computer then calculate the mechanical damping (tan δ), elastic (storage) modulus E′ and viscous (loss) modulus E″.

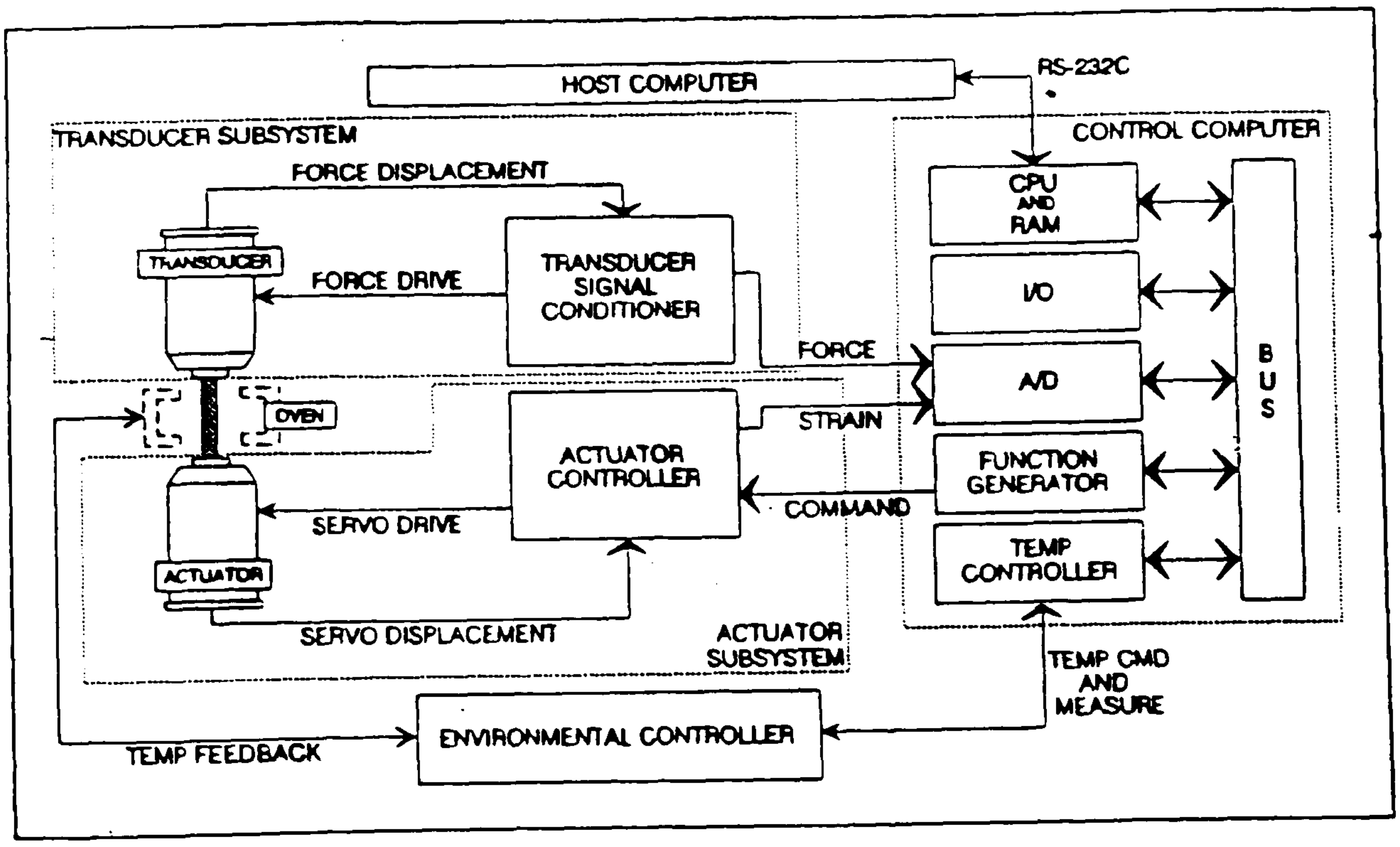
(3) Environmental controller

This unit controls the temperature of the testing oven by application of power and also controls the flow of liquid nitrogen to and through the Dewar assembly.

(4) Host computer

This is used for collecting the data from the control computer to be displayed graphically on screen, transmitted to the printer or stored on floppy disk. A functional block diagram of the system is shown in Figure 2.13.

Figure 2.13 Rheometrics Solids Analyser RSAII Functional block diagram⁽²³⁾



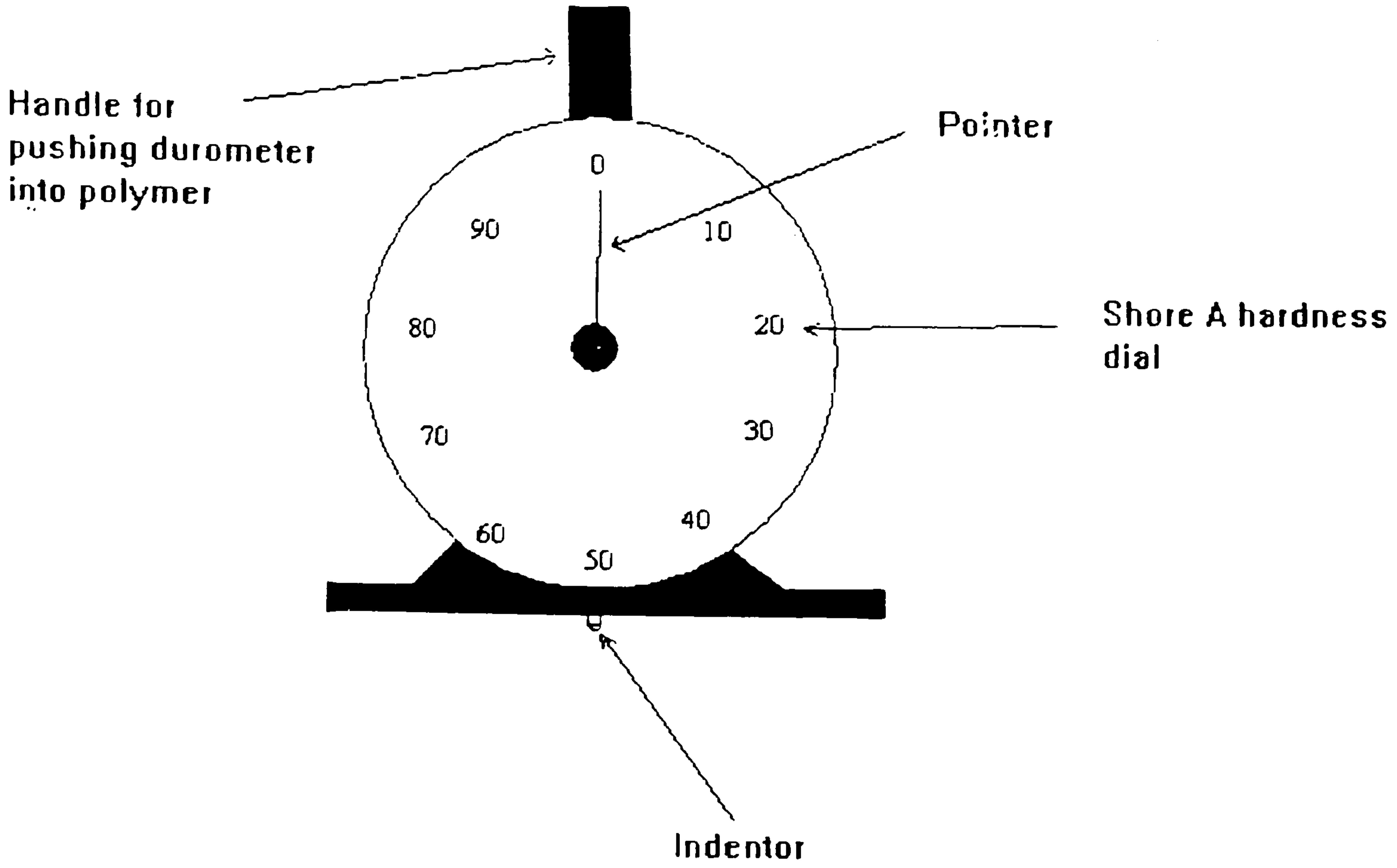
2.8 SHORE A HARDNESS TESTING OF CURED POLYSULFIDE POLYMERS

Hardness is the resistance of a material to "localised plastic deformation".(17) A hardness test therefore involves indenting a material, and expressing the hardness as a function of yield stress σ_y which is required to reach the onset of plastic deformation, and the work-hardening (strain hardening) rate of the material. During plastic deformation, work-hardening occurs when dislocations interact with one another, resulting in deformation becoming more difficult.(12)

Shore A hardness is measured using a Durometer which is a hand held device in which a truncated cone indentor 2.50 mm long and 1.25 mm wide presses into a material surface. Measurements should not be made less than 12 mm from the edge, and the sample should be 5 mm thick.(18) The Shore D hardness technique for harder plastics uses a pointed rather than truncated cone.(18) As a response to the hardness of the surface of the material and the action of a spring and pointer connected to the indentor, hardness is registered.

Shore A hardness meters are used for very soft samples whilst Shore D meters are used for very hard samples.(17) For a Shore A hardness measurement, a polymer hardness of 0 is described as "extremely soft" and 100 is "infinitely hard".(16) Hardness increases with crosslink density, therefore as cured polysulfide has low crosslink density the hardness is low. In a cured polysulfide the deformation of the sample is elastic, and pressure needs to be applied by the indentor into the sample. Unlike metals there is no correlation between a polymer hardness and tensile strength. The reason for this is that hardness measurements are obtained from deformations at the surface of a small section of polymer, whilst tensile properties are obtained from large deformations of the whole mass.(3) Variations in the Shore A readings over time may well be dependent on the measurement technique as it is unlikely that the same area of the polysulfide will be measured for its hardness and therefore readings will vary depending on the degree of curing in the area of sample tested. It is also possible that mixing of the polymer and curing agent may not be complete as inefficiency of mixing can lead to internal voids, and surface flaws for example. The Durometer used to measure Shore A hardness in these experiments is shown in Figure 2.14.

Figure 2.14 The Shore A handheld Durometer



2.9 THE MOISTURE VAPOUR TRANSMISSION RATE MEASUREMENT TECHNIQUE

There are two methods of permeability measurement for plastics, those for water vapour and those for volatile liquids.(18) Both can be measured gravimetrically, and as in this work, Moisture Vapour Transmission Rate (MVTR) is measured by weight loss of water. This value gives an indication as to the ability of a polymer to prevent the passage of water through it. A definition of permeability is "the passage of a gas or vapour through a solid barrier, which is often in the form of a thin film."(16) The permeability of water vapour through a film shows considerable variation depending on the thickness of the film. It is defined as:

$$\text{MVTR} = \frac{g}{At}$$

MVTR=Moisture Vapour Transmission Rate (Units=$g/m^2/24$ hours)
g = mass loss in grams
A = area of exposed surface (m^2)
t = time (days).

The characteristics of sorption and permeation of water vapour through polymers are important in a variety of industries. These include packaging and wastewater treatment.(24) The measurement of these two characteristics are complicated by the high cohesive energy of water and the hydrogen bonding. The transport and sorption characteristics of water vapour is more difficult to measure compared to most other liquids due to the following properties of water:(24)

(1) A tendency to adsorb on high energy surfaces such as glass or metal
(2) A relatively high heat of vaporization
(3) A low saturation vapour pressure
(4) High solubility in many polymers
(5) A tendency to plasticise polymers, with the level of plasticization being a strong function of activity level; and
(6) A tendency to cluster in the polymer at high activities.

The transport of moisture through a high polymer occurs in two ways, interstitially through transient or permanent pores in the polymer, or by sorption or dissolution on one side of the polymer, diffusion across the polymer and then desorption and evaporation on the other side. The passage of moisture increases with temperature, and the presence of plasticisers, and decreases with cross linking and inert fillers.(16)

Providing a sealant is perfectly adhering to the glass and there are no blisters or cracks or continuous pores, then diffusion and permeation depends upon:(25)
(1) The concentration or pressure of the permeating gas/vapour in front of the surface at which it enters the sealant
(2) The adsorption on this surface (= front face)

(3) The transition into the interior of the sealant

(4) The solubility in the sealant

(5) The energy released upon association of the permeant at energetically favourable sites of the polymer sealant

(6) The release energy at these sites and the kinetic energy required for propagation

(7) The size of the free volume between the macromolecular sealant chains

(8) The separation work on the rear side

(9) The concentration of permeant on the rear side

(10) The evaporation or desorption from the rear side surface

(11) The concentration or vapour pressure in the gas volume on the rear side of the membrane.

For water permeation through single phase sealants (such as in those studied in this work) Henry's Law states that for gases such as water the concentration c of gases absorbed at the surface of the membrane is proportional to the partial pressure of the gases. (25)

$c = \sigma \, . \, p'$

(σ is the absorption coefficient)

Diffusion of the vapour through the membrane occurs because of the thermal oscillations or rotations of the polymer chains. The permeation of the moisture therefore increases with temperature and the lower the excitation energy for the freedom of polymer chains to rotate and vibrate the higher the moisture permeation.

Moisture permeates a sealant from a higher humidity atmosphere to a lower humidity atmosphere due to the concentration gradient. This diffusion rate (dQ/dt) can be determined by Ficks first Law:

$dQ/dt \;=\; - D.A.\, dc/dx$

where dQ is an infinitesimal amount of the permeating substance dt an infinitesimal diffusion time

D is the coefficient of diffusion

A the cross-section of the sample

-dc/dx the concentration gradient.(25)

As the membrane thickness varies so does the MVTR, and this can be described by:

$Q = - D.A .t (c2-c1)/l$

where c1 and c2 are the vapour concentrations on the front and the rear of the sealant

Q the quantity of substance that has permeated through the membrane surface A

t the time in a steady diffusion state.

Assuming that Henry's Law applies at the sealant surfaces, the equation can be written:

$Q = - D.\sigma .A .t (p'2-p'1)/l$

where σ is the solubility coefficient

and p′1 and p′2 are the partial pressures of the gas in front and behind the sealant respectively.

As the partial pressure of the water vapour outside the unit will be much greater than that inside, the equation can be simplified to:

$Q = D.\sigma .A .t\, p'1/l$

and to

$Q = P.A .t\, p'1/l$

where

$P = D.\sigma$ is the permeation coefficient

The Moisture Vapour Transmission Rate is directly dependent on the following factors:(25)

(1) The permeation coefficient of the respective sealant P, which is a material constant

(2) The effective seal face A of the sealant which is subjected to the permeation of the moisture

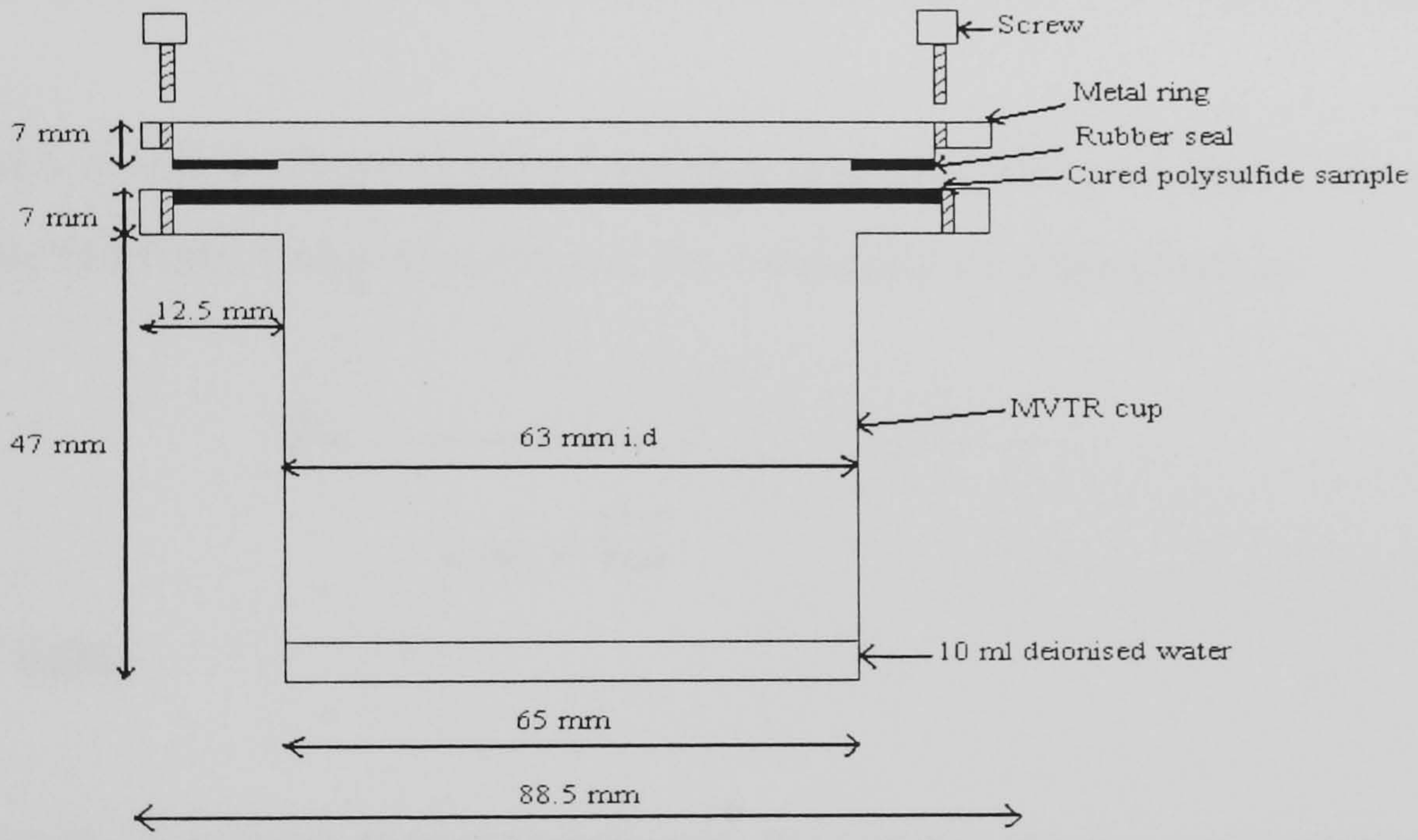
(3) The time t over which the insulating glass unit is exposed to the moisture

(4) The moisture content of the air (water vapour pressure p′1)

(5) The inverse layer depth of the sealant l^{-1}.

Moisture vapour transmission can be measured in a number of ways. One way is to measure the downstream pressure with time and earlier techniques involve gravimetric analysis. For example placing liquid water in a container sealed with a film. As the vapour permeates the film the permeability coefficient is calculated by the rate of loss of weight of the container. An alternative is to place a desiccant in the container and cover it with the polymer film, and the rate of weight gain used to measure the permeability coefficient.(24) Once the rate of water transmission is constant, the rate of change in weight is used in the calculation of the permeation of water vapour through unit area of the test piece in unit time.(18) The MVTR apparatus is displayed in Figure 2.15.

Figure 2.15 The apparatus used to measure Moisture Vapour Transmission Rate



2.10 INFRARED SPECTROSCOPY TO DETERMINE THE MECHANISM OF CURING OF LIQUID POLYSULFIDE BY SODIUM BIRNESSITE

In organic molecules, the vibrational spectra are characteristic of the rotation and vibration of the molecule. If infrared radiation [which has a wavelength of 2.5 to 25 micrometres] is passed through an organic compound, some frequencies of the radiation are absorbed and some are transmitted through the sample. An infrared spectrum can be obtained by plotting the absorbance against the frequency. Incident infrared radiation causes changes in the vibrational and rotational movements of the molecule, and as a result, functional groups which have specific vibration frequencies can be detected, e.g the C-H stretch absorption at around 3000 cm $^{-1}$.(26) The frequency of vibrational modes depends on the force constant which is related to the strength of the bond and the masses of the bonded atoms. To work out the frequency of absorption, calculations are needed: Reduced mass (μ) is used to simplify the calculations and combines the individual atomic masses in the molecule as follows: $1/\mu = 1/m_1 + 1/m_2$

The force constant k is derived from Hookes Law by a proportionality constant. The equation which relates force constant, reduced mass and the frequency of absorption is:

$$\overline{\nu} = \frac{1}{2\pi c\sqrt{k/\mu}}$$

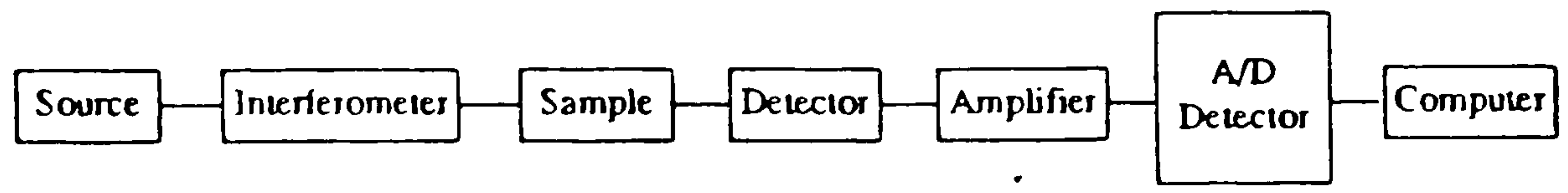
(c is the speed of light)

Infrared spectrometers have three main components, the source, the monochromator and the detector.(26) The source is an electrically heated rod, made of various ceramic materials. The monochromator is a grating, whilst the common detector uses a thermopile using a thermocouple principle of two different metal wires together to create an electric current that is proportional to the amount of infrared radiation falling on the thermopile.(26)The discs for use are KBr, with a useful infrared range of 43500 cm^{-1} to 400 cm^{-1}.(27)

2.10.1 Introduction to the Fourier Transform Infrared Spectrometer (FTIR)

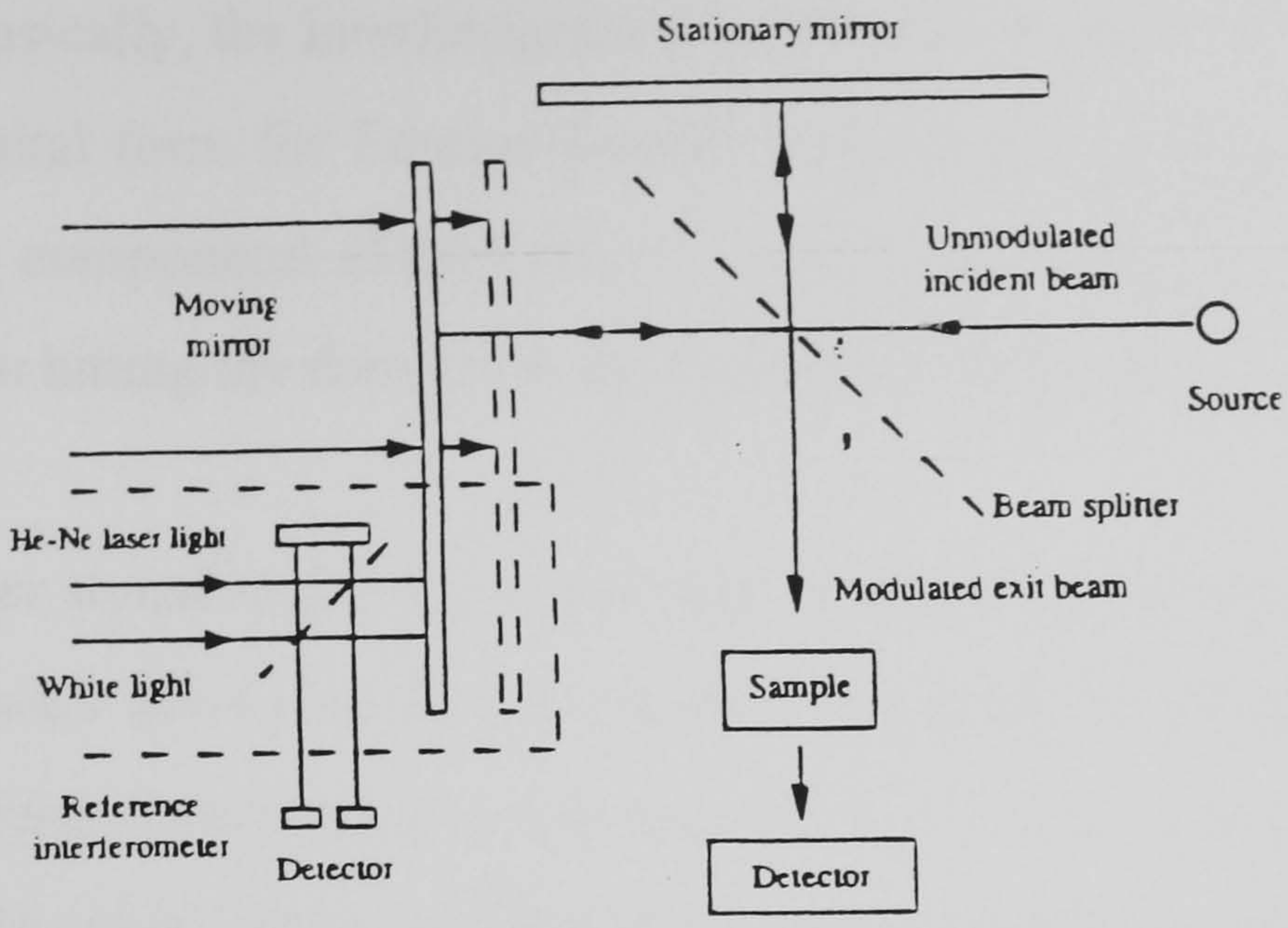
The basis of this instrument is the idea of interference of radiation between two beams resulting in a signal called an interferogram. Interferogram signals are produced as a function of the change of length of beam paths. Fourier transformation mathematically interconverts the variables of both distance and frequency.(27) The basic components of an FTIR are shown in Figure 2.16

Figure 2.16 The components of a Fourier Transform Infrared spectrometer.(27)



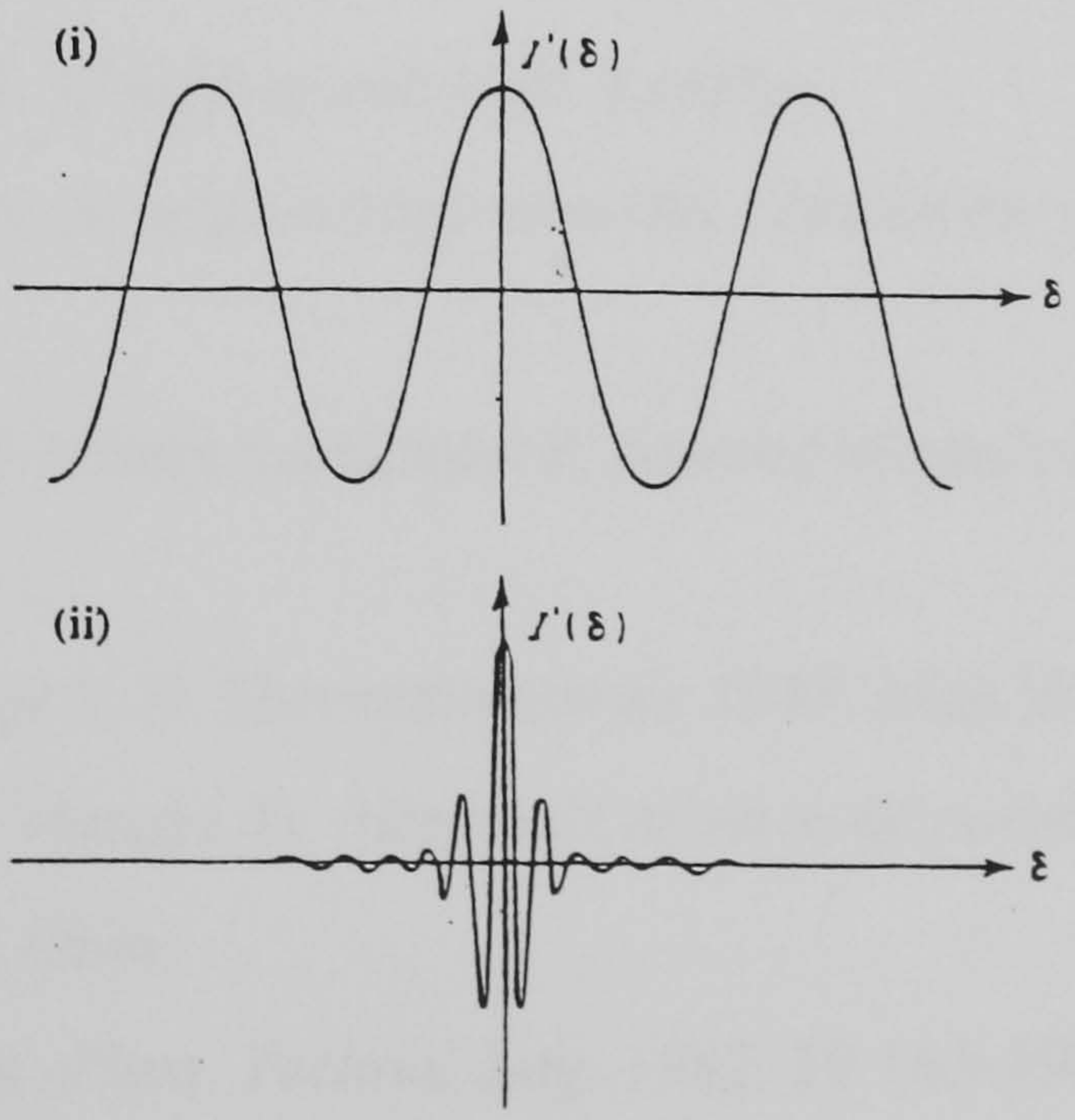
In the FTIR, infrared from a source passes through a Michelson interferometer. The interferometer is named after an American Physicist in 1892. The radiation hits a beamsplitter mirror (made of a disc of KBr covered with germanium), where half the radiation is transmitted to a plane mirror as beam and reflected back to the beam splitter. The other half is transmitted to the moving mirror as a beam and then reflected back to the beamsplitter. Both beams are recombined to form the beam in constructive interference, causing high intensity radiation to reach the detector made of deuterium triglycine sulphate. Half of the beam reflected from the fixed mirror gets transmitted through the beamsplitter and the other half reflects back in the direction of the source. The beam emerging from the interferometer at 90° to the input beam is called the transmitted beam and is detected in the FTIR spectrometer. Having a moving mirror results in an optical path difference between the two arms of the interferometer. Figure 2.17 illustrates the operation of the Michelson interferometer.

Figure 2.17 The Michelson Interferometer(27)



Destructive interference of the transmitted beams is caused by path differences of (n+1/2 λ), whilst constructive interference is caused in the reflected beam. The interference pattern that results is shown in Figure 2.18 for monochromatic radiation that is a simple cosine function and polychromatic radiation is a more complicated form containing all the spectral information of the radiation falling on the detector.(27)

Figure 2.18 Interferograms for monochromatic (i) and polychromatic (ii) radiation(27)



The conversion of an interference pattern to a spectrum is carried out using Fourier Transformation. Basically, the interferogram is in analogue form at the detector. It has to be converted to a digital form for Fourier Transformation to be applied to convert it into a spectrum. The key components of the Fourier Transformation involve relating the intensity of infrared radiation hitting the detector to the spectral power density at a given wavenumber.

The FTIR has better signal to noise ratio per unit time than dispersive infrared instruments. Also as FTIR does not use a slit, all of the source output can be passed through the sample continuously. The large resultant gain in the energy at the detector results in higher signals and better signal to noise ratios. Using a helium-neon laser as a reference in the apparatus results in the accurate determination of the location of the mirror. The precision by which the location of the mirror is known determines the precision of an infrared band position. The other benefit of using FTIR is its speed as the mirror in the machine can move short distances quite quickly, allowing spectra to be taken in milliseconds.

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CHAPTER 3 THE POLYSULFIDE CURING INGREDIENTS

3.1 INTRODUCTION

A variety of manganese oxides have been investigated for their effect on the curing of liquid polysulfide polymer.(1) Goldblatts work investigated the potential of 29 manganese (IV) oxide compounds for polysulfide curing properties. The compounds were divided up into different categories: inert natural MnO_2 ores, activated grades specifically for curing polysulfides (including Riedel-de Haen FA), a synthetic phase (sodium birnessite), battery grade MnO_2, chemically pure (99.999%) grade, and oxidising grades for organics. The tests on these compounds performed by Goldblatt(1) included pH, particle size analysis, moisture content, catalytic performance with potassium chlorate, X-ray diffraction analysis, and polysulfide curing ability.

Some manganese (IV) oxide phases are inactive, or extremely slow polysulfide curing agents, and these include inert natural MnO_2 ore, taking 9 weeks to cure polysulfide, and chemically pure MnO_2.(1) These therefore served as curing agent diluents in the experiments carried out by Goldblatt. Active curing agents were primarily noted(1) for their high pH in contrast to the curing inactive manganese (IV) oxides with low pH and satisfied cation exchange capacity.

In earlier work at the Centre for Environmental Research at Brunel University Goldblatt(1) studied the properties of a wide range of manganese dioxide phases. He developed a method for testing for their activity using their potential ability to catalyse the thermal decomposition of potassium chlorate. He reported that the manganese (IV) oxide phases could be divided into two categories - (1) those which led to the slow decomposition of molten $KClO_3$ and (2) those which catalysed the explosive decomposition of the compound at temperatures below its melting point. Those phases in the second category including sodium birnessite, were considered to be the surface active materials most likely to cure polysulfides and some preliminary curing experiments were consistent with this view.

Research has suggested that not all commercially available curing agents are as reliable as one another.(1) The most reliable and effective commercial curing agent found in work by both the Author, and Goldblatt,(1) identified the Riedel-de Haen "FA Grade" as the best commercial curing agent. The curing using this compound was reproducible and produced a well cured product in terms of curing time and Shore A hardness.

In this context, the experiments involving the curing of polysulfide and testing the cured properties of the polysulfide used the best currently available commercial curing agent, Riedel-de Haen FA Grade, as the commercial curing agent cited by Goldblatt. The comparison was made with the best synthetic manganese (IV) oxide phase identified as sodium birnessite.

3.2 THE CURING AGENT SODIUM BIRNESSITE

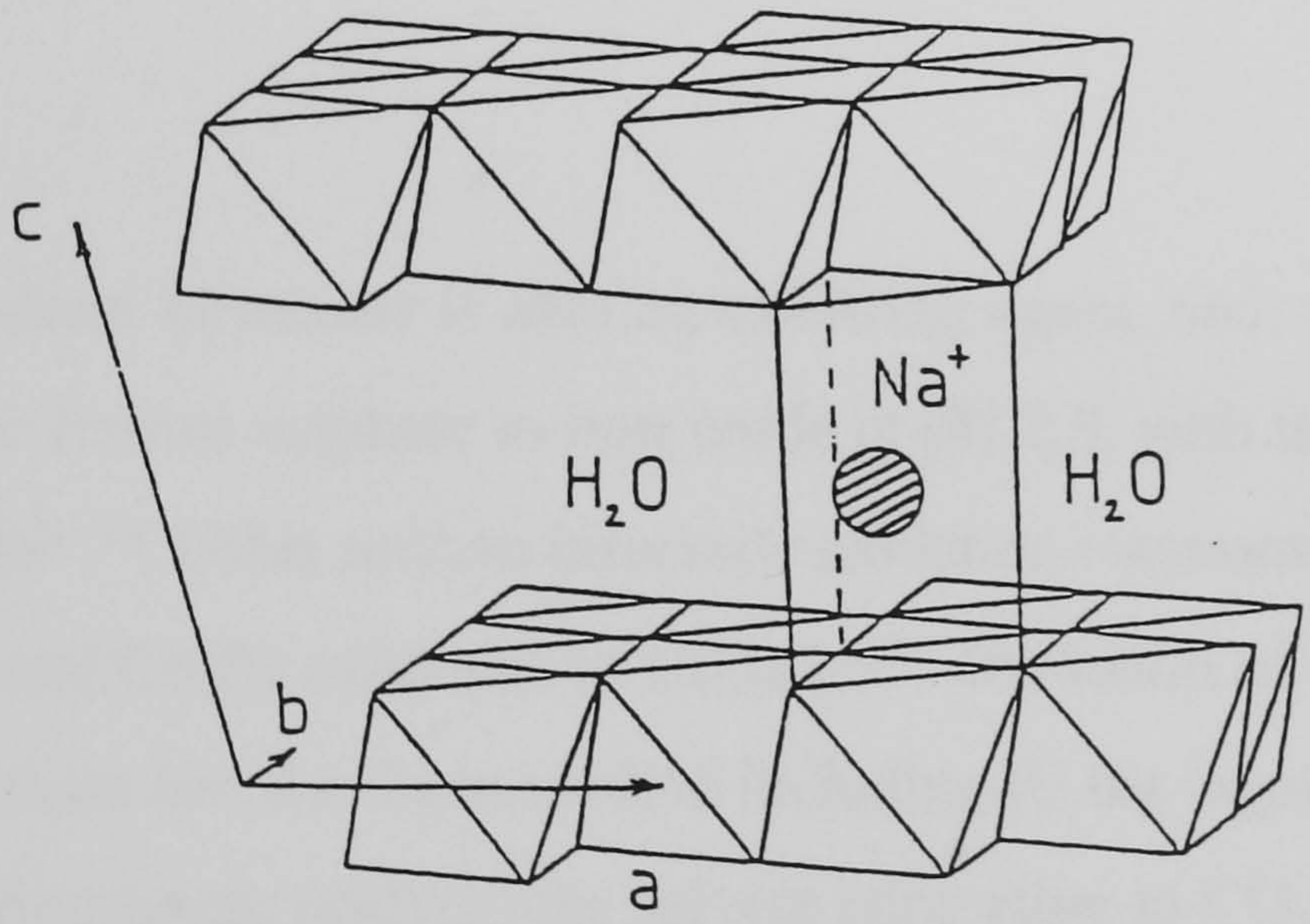
Manganese dioxide in the solid state is based on MnO_6 octahedra. Each manganese ion is coordinated to six oxygen atoms and the structure is built up by sharing of edges of the MnO_6 octahedra forming tunnels and cavities in the lattice. The analytical composition of the synthetic material (Na 6.1%, Mn 54.7%, H_2O 11.3%) suggests that it is based on the formula $Na_2Mn^{II}_2Mn^{IV}_5O_{13}.4.5H_2O$, although the water percentage in the final product can vary. The compound is a hydrated manganese (IV) oxide and has a formula weight of 1455.092. It is a grey black powder which has an average manganese oxidation state of 3.7.(2) In nature it is produced at low temperatures by the oxidation and supergene weathering of manganese rich rocks.(3)

The different anhydrous MnO_2 phases are formed by different sharing patterns for the octahedra. The MnO_2 lattice structures are also capable of incorporating hydroxide ions as replacements for oxide ions and of water or other positive metal ions in the lattice cavities. Sodium birnessite is a sodium manganate (IV) based on the incorporation of Na^+ ions and water in the lattice.

Birnessite is one of the main manganese compounds found in deep sea manganese nodules and was first found in a fluvio-glacial gravel deposit in Birness, Scotland.(3) It can be found both in acidic and alkaline soils,(4) and is one of the most common manganese oxides found in the clay size fraction of soils (<2μm)(5) Birnessite can be present without sodium, and has the formula $Mn_7O_{13}.5H_2O$. If sodium is present, it can be replaced by a variety of cations.(6) The chemistry, structure and other properties of sodium birnessite are however, not well understood according to Golden et al. (5)

Sodium birnessite has a structure composed of sheets of water molecules in between sheets of edge sharing MnO_6 octahedra. The arrangement of octahedral layers occurs every 7 Å on the c axis.(5) Sodium birnessite has a monoclinic symmetry and belongs to a group of manganese (IV) oxide phases having layered structures called phyllomanganates. The lattice parameters of sodium birnessite are a = 5.17,b = 2.85, and c = 7.31 Å and the interlayer distance is 7.11 Å.(7) Figure 3.1 shows the layered structure of sodium birnessite.(7)

Figure 3.1 The structure of sodium birnessite



Birnessite is an important part of desert varnishes, component of soils, and in manganese nodules and is thought to be important in ground water and soil chemistry.(8) The synthetic sodium birnessite is known to act as an ion exchanger.(5)

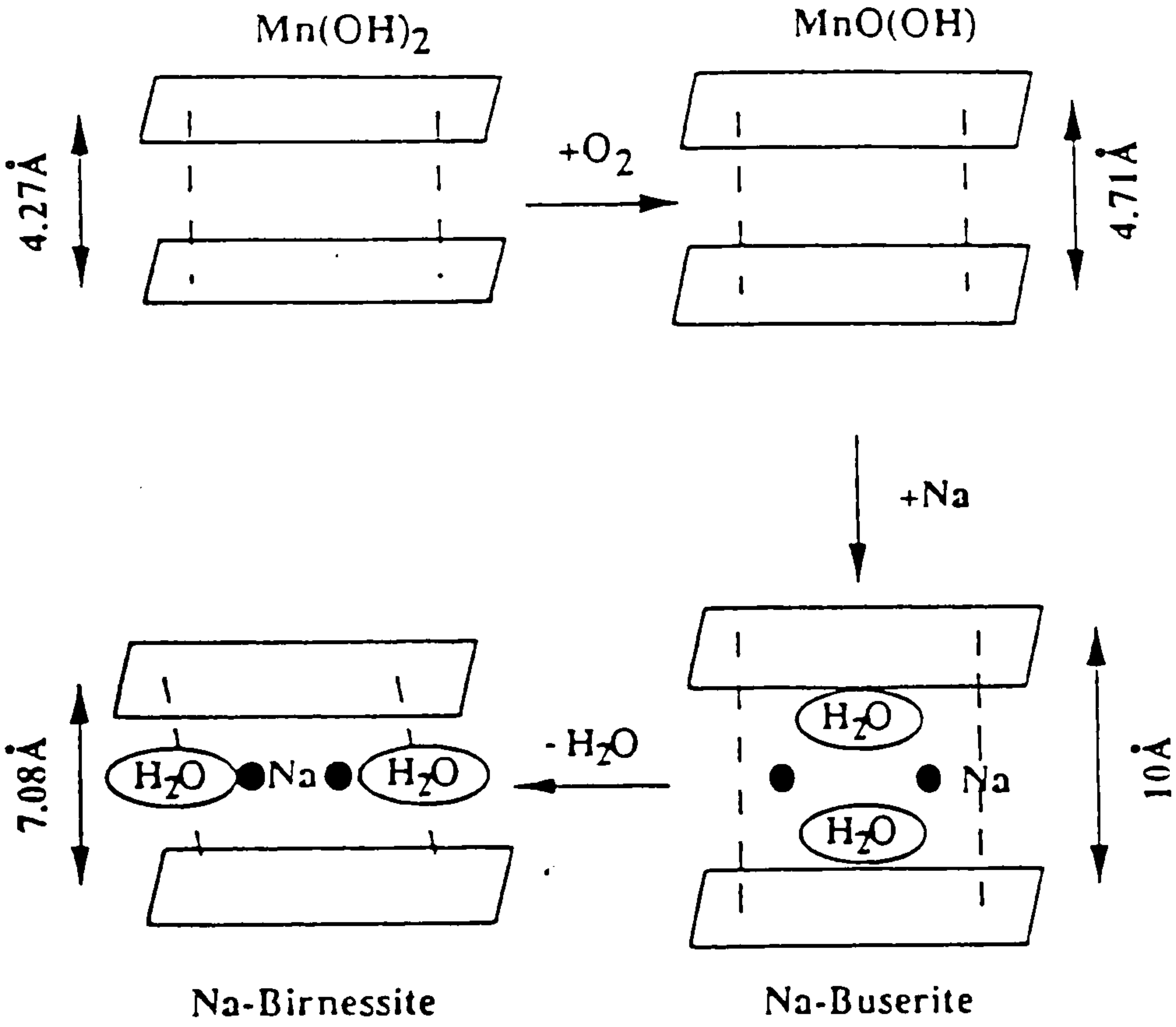
In nature it is a brown black powder with a satiny luster, and is found as fine-earthy and loose aggregates in sediments.(9) In soils birnessite is believed to form from bacterial oxidation or direct oxidation of manganese compounds in soil.(4) Birnessite is found in marine manganese nodules where it incorporates metals such as Fe, Cu, Ni and Zn.(10) Natural birnessite can be found with variable alkali metal content, for example birnessite from Cummington, Massachusetts has a high Ca content whilst that from Birness is rich in Na. Heating sodium birnessite to 120°C removes the chemically bound water, whilst further heating to about 370°C leads to α MnO_2.(9) Heating the birnessite to 1000°C converts it to braunite, Mn_2O_3, and then to hausmannite, Mn_3O_4.(11) The incorporation of ions such as Mg, Ni and Ca into the birnessite structure transforms it into buserite.(5)

Birnessite is known to be effective at binding cations, especially heavy metals.(12) As sodium birnessite is a double layer compound it can bind large amounts of cations and can form surface complexes with metal ions.(5) At pH values above the point of zero charge (pH 1.5 to 2) and up to neutral pH, a negative surface charge on the manganese oxides results in adsorption of cations from the surrounding fluid.(13) The ion exchange properties of birnessite have been studied by Golden et al (5) and LeGoff et al.(7) The sorption of lanthanides onto birnessite in soils was studied by Fendorf and Fendorf(14) for example. Various other researchers have also studied the removal of metal ions from water using sodium birnessite. (15) (16) (17)

Synthetic sodium birnessite is also an oxidising agent, and, for example it can be used to oxidise dilute ferrous sulphate to iron oxide at pH 2.9, with the Mn (IV) in birnessite being reduced to Mn^{2+}.(5) Other sodium birnessite oxidation reactions reported are As(III) oxidation to As(V),(18) and Co(II) oxidation to Co(III).(19) Oxidation of organic compounds in soil by sodium birnessite has also been studied including (i) the degradation of the herbicide 2,4-D (dichlorophenoxyacetic acid) (ii) the solvent ethyl ether to CO_2,(20) and (iii) chlorophenols.(21) (22)(23) The oxidation of dihyroxybenzene by birnessite has also been studied by McBride(24) and other uses of sodium birnessite have been proposed by Luo and Suib. (25)

A patent(26) exists for the manufacture of sodium birnessite. The patent describes the production of birnessite by the passage of oxygen for 4 to 5 hours through a slurry of manganese (II) hydroxide. Pure oxygen is preferable to air as CO_2 gas causes the formation of manganese carbonate and incomplete manganese ion oxidation forming Mn_3O_4 and not birnessite. The manganese (II) hydroxide used in the preparation was formed by the addition of an excess of NaOH to a manganese (II) chloride solution. The presence of alkali in the solution and performing the reaction at room temperature prevents formation of the stable oxide of manganese - hausmannite (Mn_3O_4) which is not a curing agent. Figure 3.2 - shows the suggested steps in the synthesis of sodium birnessite. After the mixture has been oxidised it is then washed and dried under vacuum. Other techniques for synthesising sodium birnessite have been reviewed.(25)

Figure 3.2 The synthesis of sodium birnessite(7)



3.3 THE LABORATORY SYNTHESIS OF SODIUM BIRNESSITE

Natural sodium birnessite is not a good polysulfide curing agent. Laboratory synthesised sodium birnessite is however an active ion exchange compound, and oxidising agent with potential use for curing liquid polysulfides.

An apparatus was developed for the production of synthetic birnessite in this research by a method similar to that originally proposed by Stahli. (27) A 250 ml solution of 5.5 molar NaOH solution in cold deionised water was added to a 200 ml solution of 0.5 M $MnSO_4.H_2O$ in cold deionised water in a polypropylene cylinder of height 360 mm and internal diameter 60 mm. Both solutions were prepared using cold deionised water. The solution was agitated at room temperature (22 $^{+}/_{-}$ 1°C) with a magnetic stirrer bar (30 x 4 mm). Oxygen was bubbled into the solution using a 40 mm (ID) glass funnel with a porosity grade 1 glass frit (porosity $>100 \leq 160$ μm). The metered flow of oxygen was checked regularly to ensure that the flow remained stable at 2.75 L/min for 4 hours.

After a four hour reaction period, the mixture was centrifuged and the supernatant liquor poured off to give a black precipitate that was washed in polypropylene centrifuge bottles with 800 ml double deionised water and thoroughly stirred with a glass rod to mix the water and precipitate. The process of washing and centrifuging was performed a minimum of 5 times per sample to remove excess alkalinity. The apparatus used in this production of birnessite is shown in Figure 3.3.

The damp precipitate which is sodium buserite was then placed in an open polypropylene container and the sample vacuum dried for at least 24 hours at a temperature above freezing and below 30 °C to prevent birnessite decomposition. The sample cannot be heated to remove water as it decomposes to other manganese oxides such as Mn_2O_3. The temperature was monitored using a thermocouple and the drying was achieved using a vacuum pump. The apparatus used to dry the compound is shown in Figure 3.4. Freeze drying was a potential option, but, it is more expensive than drying under vacuum and therefore disregarded. The drying procedure converts the precipitated sodium buserite into sodium birnessite, the desired end product of the synthesis. It is easy to detect incomplete drying of the product as X-ray diffraction (XRD) analysis identifies incomplete conversion of the sodium buserite to sodium birnessite.

Individual batches of sodium birnessite were prepared (called NaB(number)), from these a number of composite samples were prepared and homogenised. Sodium birnessite composite number 2 was prepared from the samples of birnessite preparations NaB 50 to NaB 57. Approximately 80 g of sodium birnessite sample number 3 were prepared by the sieving through an 89 μm sieve of sodium birnessite preparation samples NaB 58,59,61,62,63,64,65,66,67,68. A further batch of sodium birnessite (composite number 4) was prepared by the combination of the prepared samples NaB 71 and 72. These samples were mixed together in mortar and pestle and sieved to below 89 μm and analysed by video microscopy. To ensure that the materials studied in this work are properly characterised samples of sodium birnessite the preparation work took approximately one year.

Figure 3.3 Apparatus used to manufacture sodium birnessite

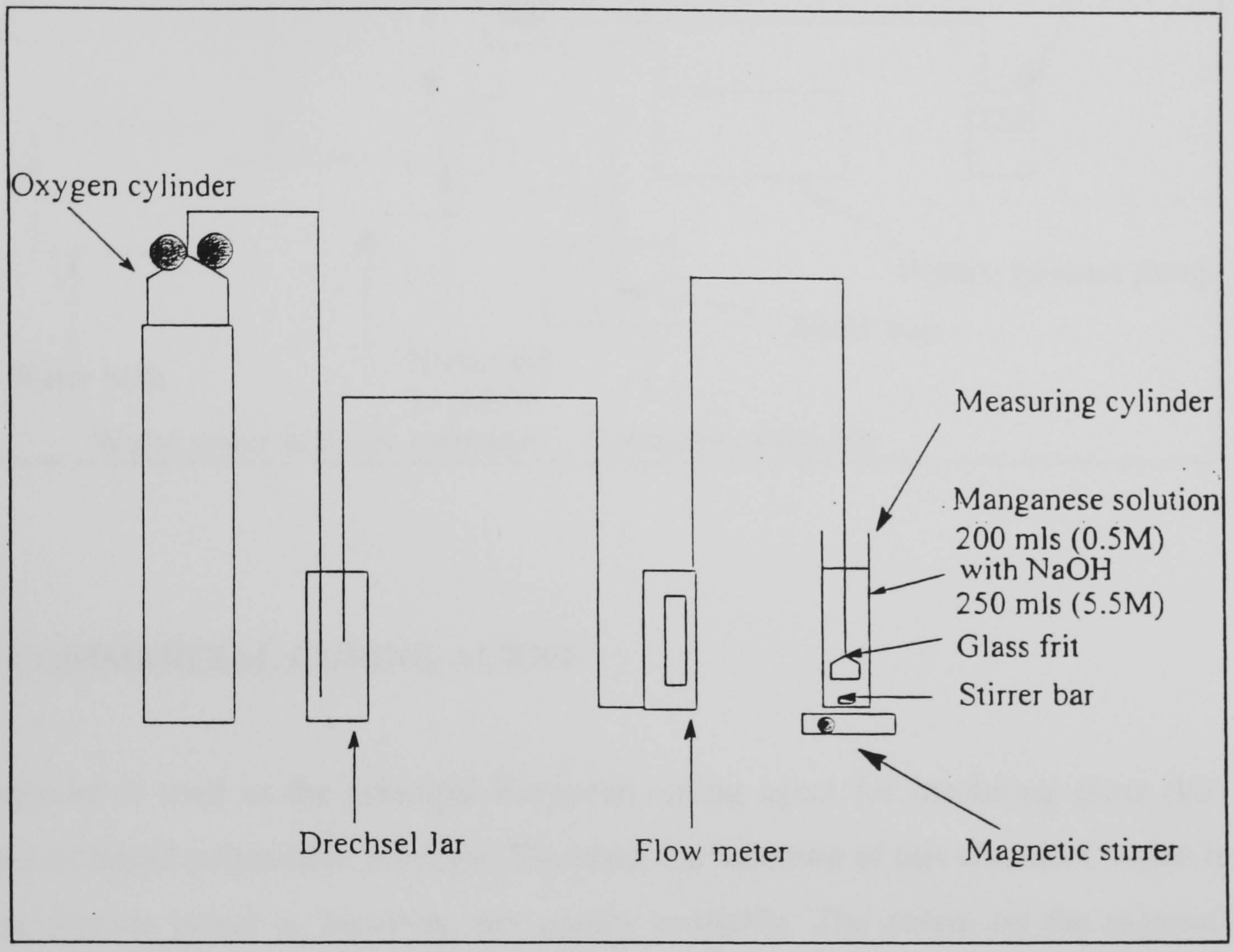
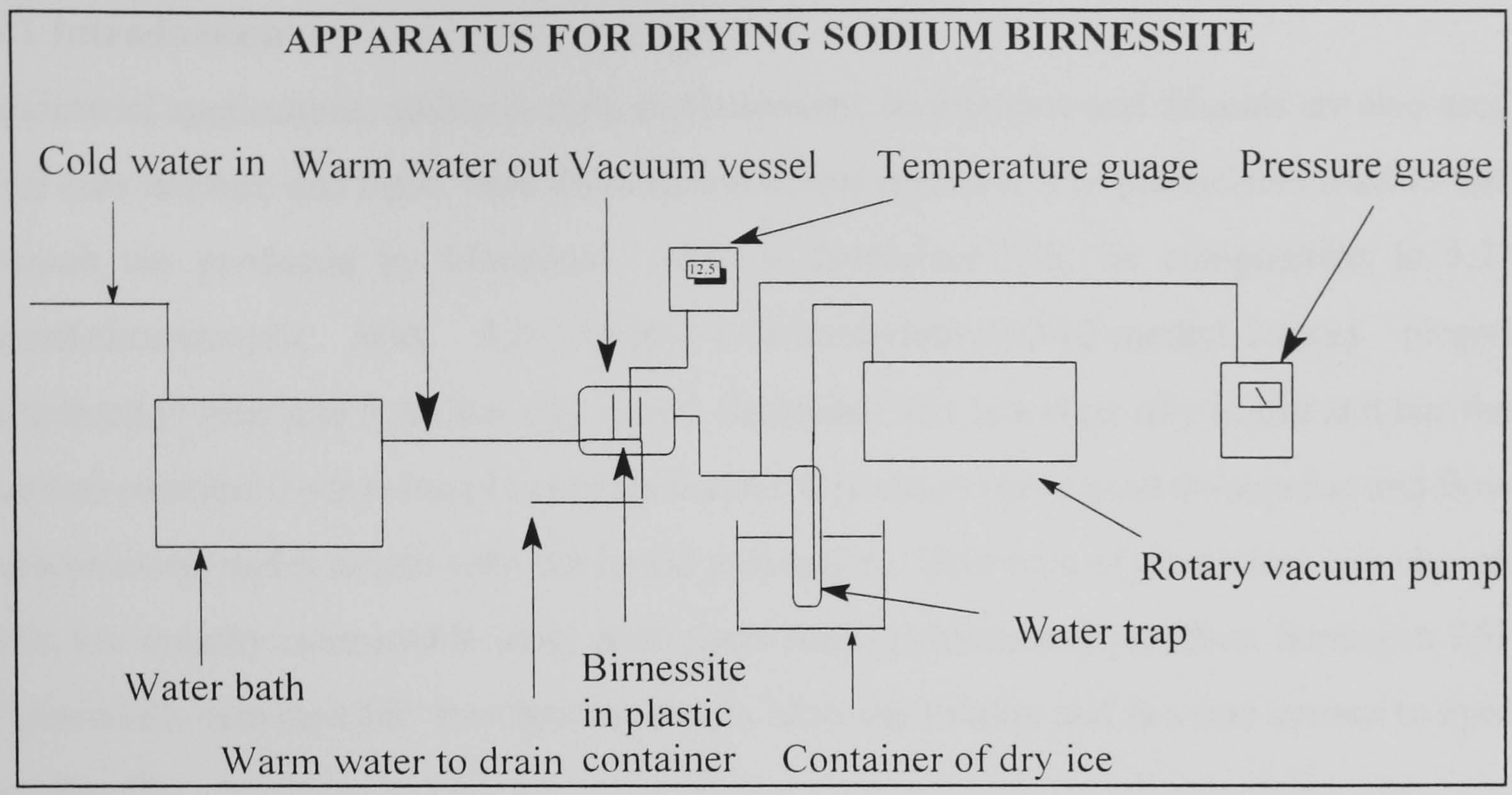


Figure 3.4 Apparatus used to dry sodium birnessite



3.4 THE COMMERCIAL CURING AGENT

This compound is used as the principal European curing agent for insulating glass (IG) applications of liquid polysulfide polymer. The exact manufacture of this chemical which is manganese dioxide based is, however, not openly available. The patent on the material outlines a number of different techniques for its manufacture involving using higher than ambient temperature from 120 to 400°C and pressure of up to 15 bars. The high temperature used to make the commercial agent manganese dioxide are used because the manufacturers claim that operating below 120°C does not result in an activated product.(28) According to Morton (personal communication) (29) the amount of curing agent in commercial sealants is 10 parts per hundred (pph) parts liquid polysulfide.

3.5 ADDITIONAL ADDITIVES FOR THE POLYSULFIDE CURING COMPOSITION

3.5.1 Introduction

In industrial applications, additives such as plasticisers, accelerators and diluents are also used in the cure mixture and these were investigated in this research. The plasticisers used in this research are produced by Monsanto. One is Santicizer 278, its composition is 1,2-benzenedicarboxylic acid, 2,2-dimethyl-1-(1-methylethyl)-3-(2-methyl-1-oxy) propyl phenylmethyl ester and is a clear oily liquid. Santicizer 261 is a clear oily liquid and has the chemical structure 2-ethyl-hexyl-benzyl phthalate. It is used to give good de-aeration and flow characteristics, and is mixed with the liquid polysulfide. This type of plasticiser was chosen for its low toxicity compared to other plasticisers such as chlorinated paraffins. Santicizer 261 is "practically non harmful" by ingestion and by skin absorption, and is a non irritant to eyes and skin.(30)

3.6 THE MnO_2 ORE "IMINI 80" AS AN INERT DILUENT FOR SODIUM BIRNESSITE

An inert ore, which is not active as a polysulfide curing agent was supplied by Twinstar Chemicals Ltd as a filler for polysulfide sealants. The ore was supplied ground to below 8 μm and was sourced from Morocco. The analytical composition of this inert natural manganese dioxide is in Table 3.1.

Table 3.1 The main components of the IMINI 80 natural manganese dioxide ore

Component	**Percentage**
MnO_2	81.0
SiO_2	4.0
CaO	2.6
BaO	2.0
MgO	1.9
Fe_2O_3	1.8
Pb_2O_3	1.0
Al_2O_3	1.0
K_2O	0.5
Na_2O	0.5

3.7 CALCIUM CARBONATE AS AN INERT DILUENT FOR SODIUM BIRNESSITE

It was decided to investigate whether calcium carbonate could be used instead of MnO_2 as a diluent for sodium birnessite in the cure paste. Calcium carbonate is less toxic than MnO_2. It "has no determined acute toxic effects" for inhalation, and no determined toxicological effects for skin contact and ingestion. It is also non oxidising. Environmentally, it "is unlikely to have any long term adverse affect on the environment", and is non toxic to plants and animals, fish, daphnia and algae and soil organisms.(31) In industry, precipitated coated calcium carbonate is used in polysulfides to control slump and reinforce the polymer. Calcium carbonate is coated to neutralize surface charges on the powder making packing easier, and to render it hydrophobic to enable better dispersion and compatibility with organic polymers.(32) Ground calcium carbonates are useful extenders for polysulfides.(33)

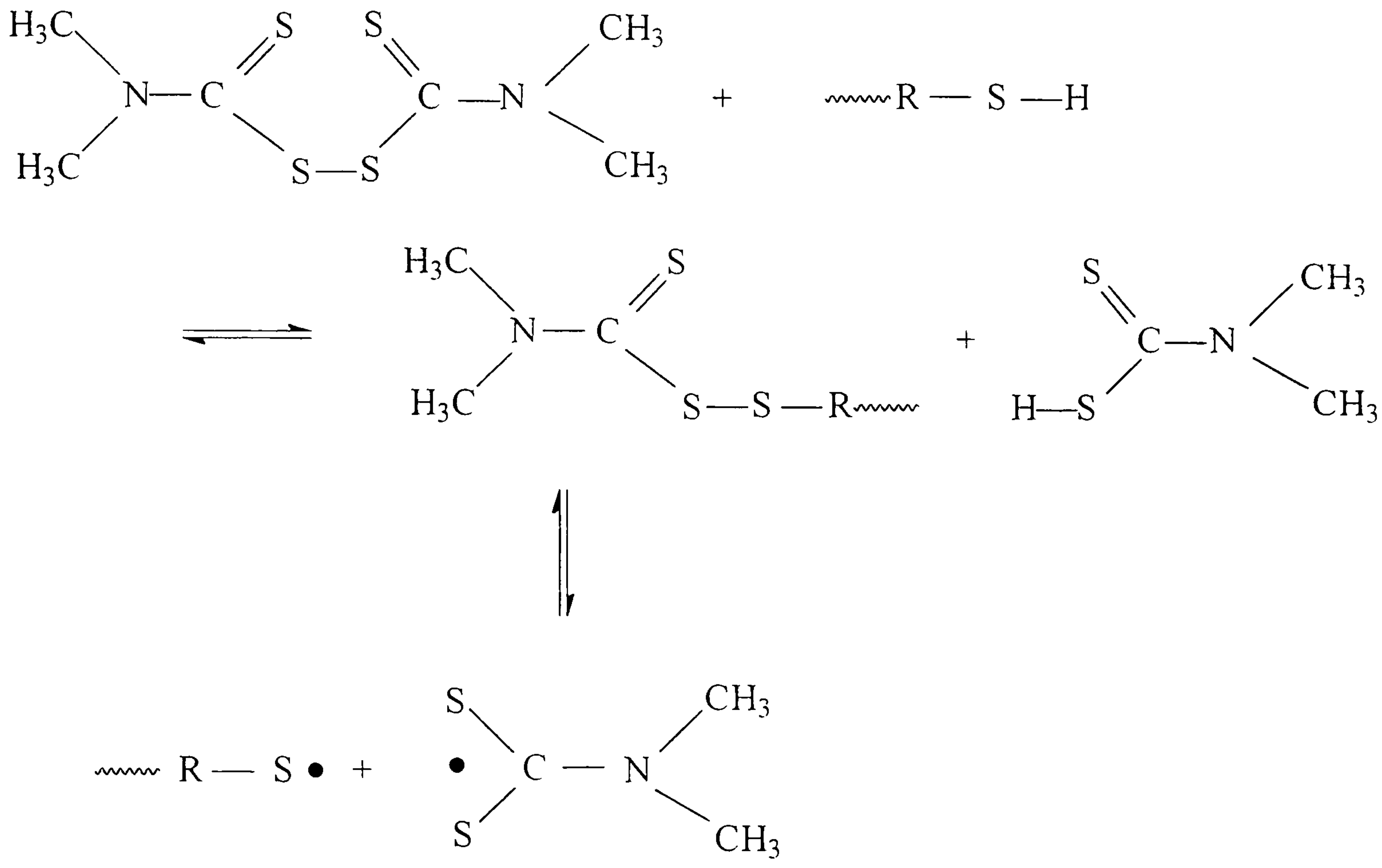
The "Queensfil" calcium carbonate (supplied by English China Clay International) used in this work is specifically for use in polymer applications as a general purpose extender. The particle size is 3% above 20 µm, 12 % above 10 µm and 36 % below 2 µm.(34)

3.8 THE ACCELERATORS USED IN THE CURING REACTIONS.

3.8.1 Introduction

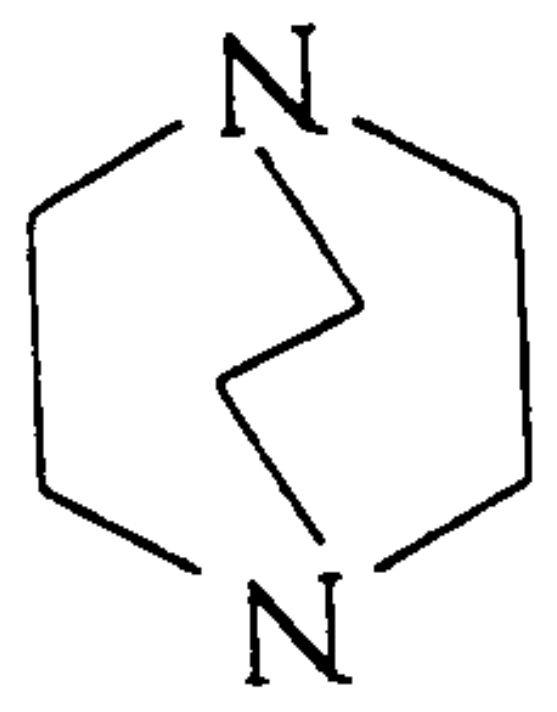
Two accelerators are used in this research: the basic accelerator 1,4-diazabicyclo(2.2.2)octane (DBU) and tetramethylthiuramdisulfide (TMTD). Both are used in industry with the commercial curing agent in the curing of polysulfide. The curing reaction of liquid polysulfide at low levels (0.5 parts per 100 parts liquid polysulfide) using TMTD has been described.(29) See Figure 3.5 .

Figure 3.5 The reaction between TMTD and the liquid polysulfide



The TMTD reaction with the polysulfide mercaptan terminals produces RSH · , a reactive radical species which at low levels, increases the rate of reaction with the mercaptan terminals on the polysulfide chain. The protective species formed however adds to the chain of the polysulfide increasing the chain length and therefore viscosity. The DBU accelerator works due to its basic pH.(29) The structure of DBU is shown in Figure 3.6.

Figure 3.6 The structure of the accelerator DBU



3.9 CHARACTERISATION OF THE COMPONENTS OF THE CURING MIXTURE

3.9.1 Characterisation of sodium birnessite by X-ray diffraction

3.9.1.1 Introduction

The dried birnessite compounds were analysed by X-ray diffraction, to detect major impurity phases such as Mn_3O_4. The instrument used is a Phillips diffractometer, with a copper K α X-ray source emitting a beam of 1.5406 Å wavelength. The data obtained were compared to standard powder diffraction file data to ascertain the components present in the birnessite. The choice of XRD as the analytical technique was based on its ability to detect the presence of crystalline compounds in a sample, sodium birnessite being a monoclinic structure can be detected as can sodium buserite and other manganese oxides. Sodium birnessite has been examined previously by various researchers using this technique.(5)(6)

3.9.1.2 Experimental

Instrumental parameters:

Instrument: Phillips Diffractometer

X-ray radiation source: Cu K α radiation producing X-rays of 1.5406 Å using 36kV and 26mA

Goniometer scan parameters:

Start 2-Theta Angle = 7 degrees

End 2-Theta Angle = 77 degrees

Step size = .02 degrees

Scan Speed= 1 degrees / minute

Experimental error +/- 0.005 in d spacing

The sodium birnessite was packed smoothly onto a viewing slide and placed in the diffractometer. The diffractometer was raised 1 degree per minute from the starting angle of 7 degrees up to the finishing angle of 77 degrees. The data was logged as d spacings, relative intensity counts and angle.

3.9.1.3 Results

Data produced from the X-ray analysis: d-spacing and relative intensity, were compared with data from standards of manganese oxides likely to be in the samples. The standard data were obtained from the JCPOS powder diffraction file. Sodium birnessite has main characteristic d spacing peaks at 7.09 Angstroms (Å), 3.56 Å and 2.51 Å. The 7.09 Å spacing is the distance between the manganese oxide octahedral sheets separated by water.(5) Birnessite is dehydrated buserite. Buserite can therefore be detected by its characteristic d spacing peaks, the main peaks at 10.1, 5.01 and 3.34 Å, and is observed if the precipitate is not dried for over 24 hours or to constant weight (depending on how moist the precipitate is).

The composite samples were analysed for their sodium birnessite content by X-ray diffraction. The literature X-ray diffraction pattern for sodium birnessite is detailed in Table 3.2. The data from X-ray diffraction analysis is shown in Tables 3.3 to 3.8, and the diffractograms in Figures 3.7 to 3.12 for sodium birnessite composite 2,3 and 4 respectively.

Table 3.2 Literature X-ray diffraction pattern for synthetic sodium birnessite.

Dspace	Relative Intensity
7.09	100
5.60	10
3.56	80
2.74	10
2.58	10
2.56	10
2.51	70
2.47	10
2.42	60
2.31	10
2.26	10
2.25	10
2.21	40
2.15	40
2.14	40
2.09	10
1.97	10
1.94	10
1.86	40
1.82	40
1.81	40
1.77	20
1.75	10
1.66	20
1.63	20
1.55	10
1.53	10
1.52	10
1.47	60
1.43	50
1.41	40
1.37	20

Table 3.3 X-ray diffraction data for synthetic sodium birnessite composite number 2

No	Angle	Counts	Dspace	Rel I
1	12.42	3112	7.121	100
2	24.96	1328	3.564	43
3	35.66	520	2.516	17
4	37.	588	2.428	19
5	38.74	118	2.322	4
6	40.62	228	2.219	7
7	41.92	318	2.153	10
8	48.76	191	1.866	6
9	49.96	203	1.824	7
10	56.06	104	1.639	3
11	62.98	195	1.475	6
12	64.46	169	1.444	5
13	65.52	123	1.423	4
14	67.1	109	1.394	4

Figure 3.7 X-ray diffractogram for synthetic sodium birnessite composite number 2

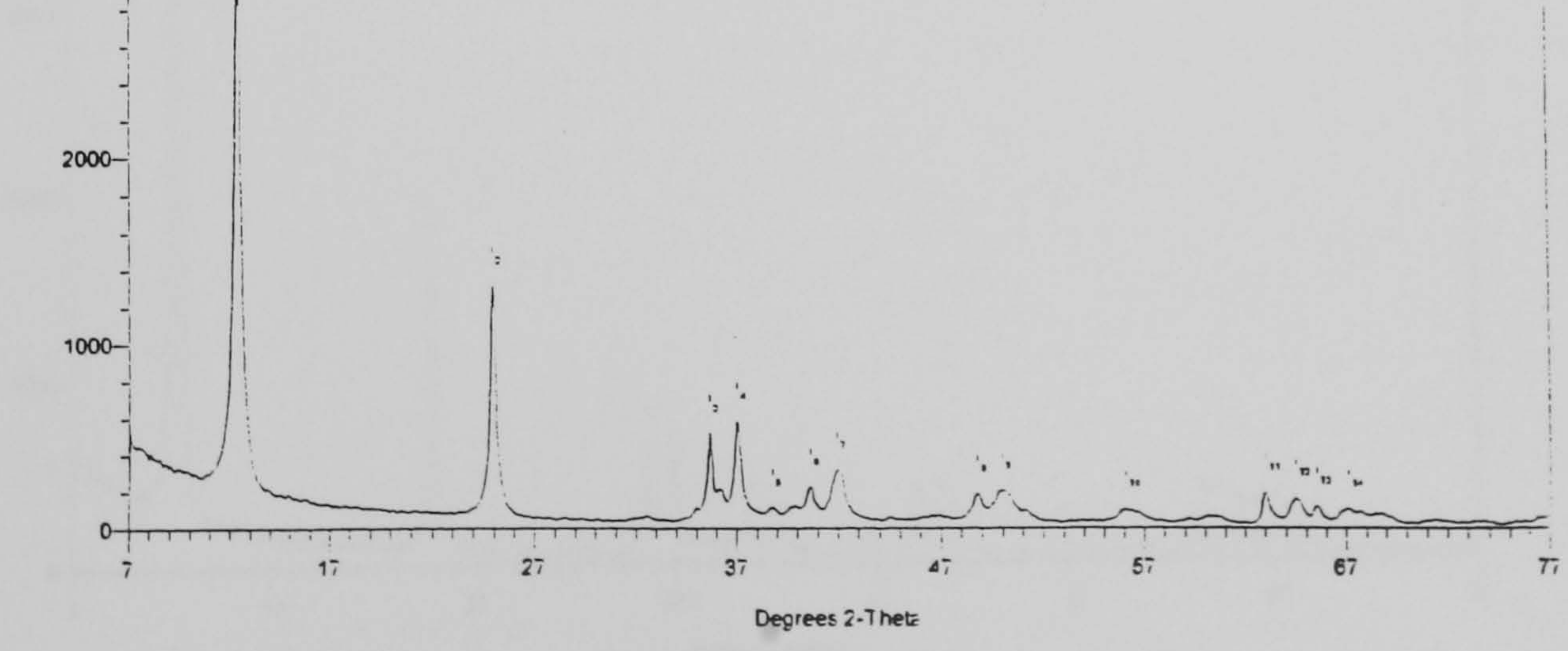


Table 3.4 X-ray diffraction data for synthetic sodium birnessite composite number 2 (replicate experiment)

No	Angle	Counts	Dspace	Rel I
1	12.32	4746	7.178	100
2	24.88	1730	3.576	36
3	35.56	642	2.523	14
4	36.92	740	2.433	16
5	38.66	155	2.327	3
6	40.52	284	2.224	6
7	41.98	411	2.15	9
8	48.66	241	1.87	5
9	49.88	256	1.827	5
10	51.04	125	1.788	3
11	55.92	132	1.643	3
12	62.88	244	1.477	5
13	64.42	211	1.445	4
14	65.38	158	1.426	3
15	66.98	130	1.396	3
16	68.74	104	1.364	2

Figure 3.8 X-ray diffractogram for synthetic sodium birnessite composite number 2 (replicate experiment)

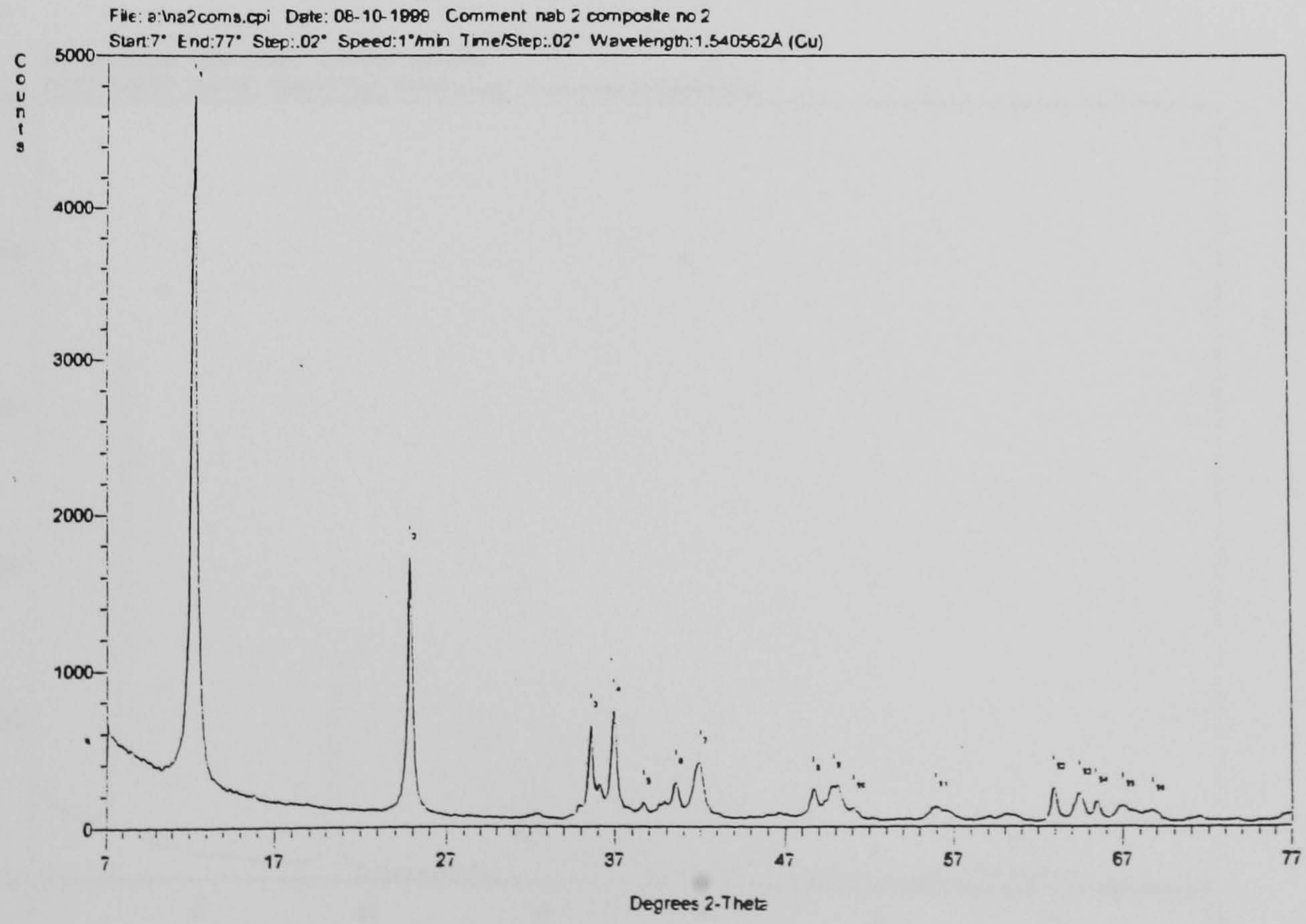


Table 3.5 X-ray diffraction data for synthetic sodium birnessite composite number 3

No	Angle	Counts	Dspace	Rel I
1	12.36	3444	7.155	100
2	24.94	1234	3.567	36
3	35.62	495	2.518	14
4	36.14	288	2.483	8
5	36.98	646	2.429	19
6	40.58	238	2.221	7
7	41.94	339	2.152	10
8	48.82	180	1.864	5
9	49.9	227	1.826	7
10	56.2	109	1.635	3
11	62.96	210	1.475	6
12	64.52	190	1.443	6
13	65.48	149	1.424	4
14	66.9	126	1.397	4
15	68.84	96	1.363	3

Figure 3.9 X-ray diffractogram for synthetic sodium birnessite composite number 3

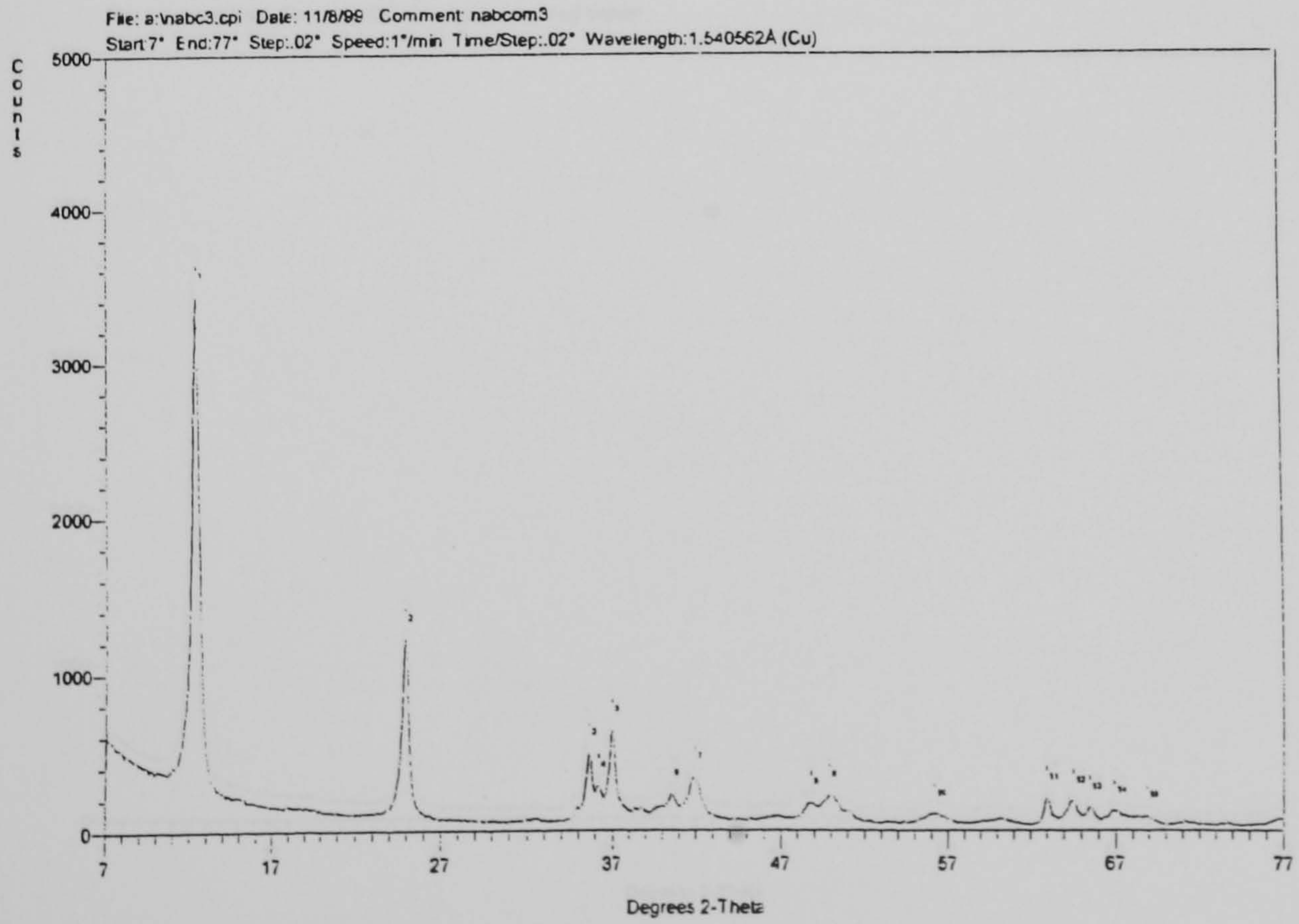


Table 3.6 X-ray diffraction data for synthetic sodium birnessite composite number 3 (replicate experiment)

No	Angle	Counts	Dspace	Rel I
1	12.3	3493	7.19	100
2	24.86	1227	3.579	35
3	35.56	503	2.523	14
4	36.92	617	2.433	18
5	40.54	232	2.223	7
6	41.86	345	2.156	10
7	48.78	180	1.865	5
8	49.78	229	1.83	7
9	56.22	112	1.635	3
10	62.88	208	1.477	6
11	64.48	167	1.444	5
12	65.44	124	1.425	4
13	66.96	114	1.396	3

Figure 3.10 X-ray diffractogram for synthetic sodium birnessite composite number 3 (replicate experiment)

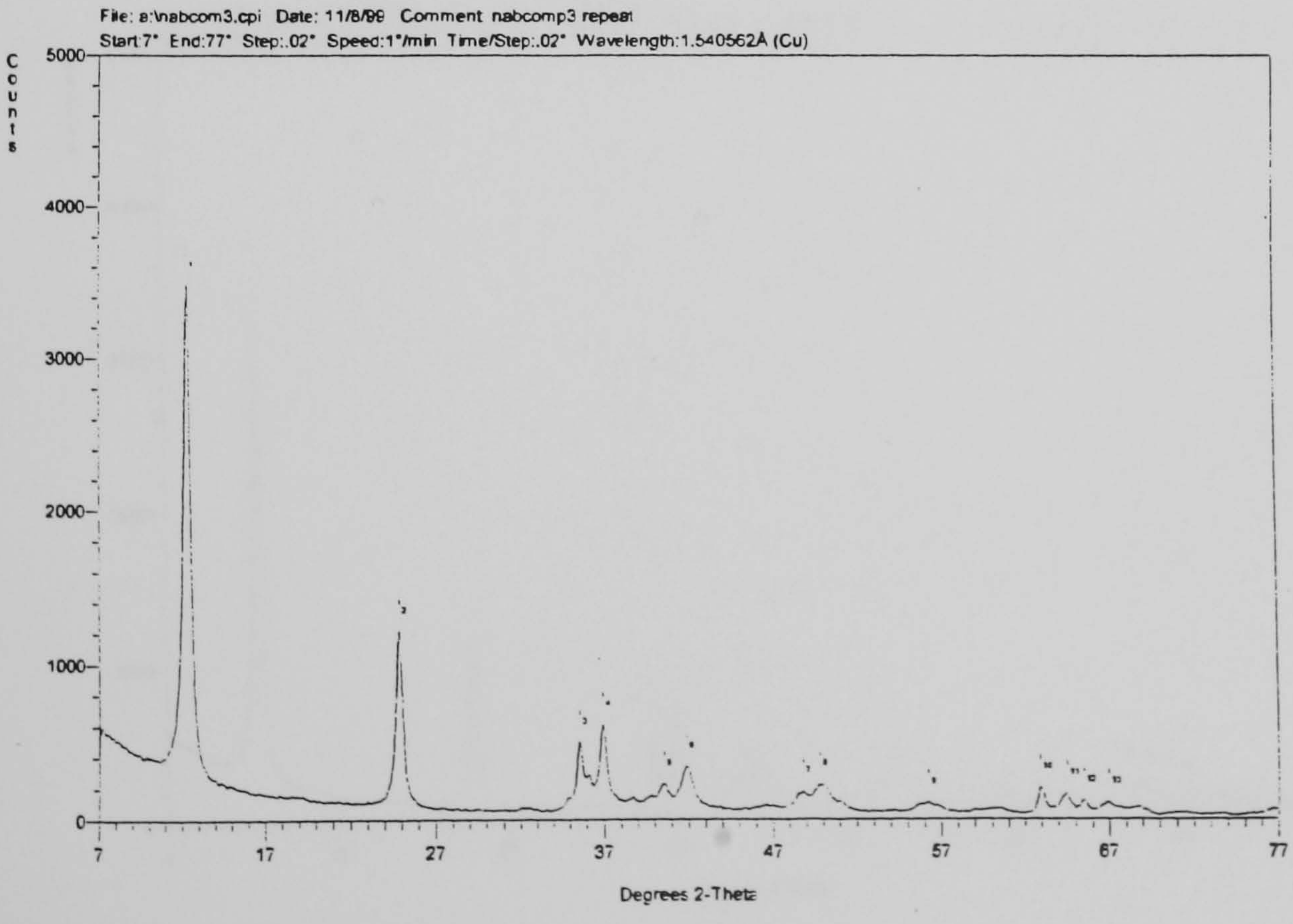


Table 3.7 X-ray diffraction data for synthetic sodium birnessite composite number 4

No	Angle	Counts	Dspace	Rel I
1	12.34	2997	7.167	100
2	24.96	1202	3.564	40
3	35.64	557	2.517	19
4	37.	674	2.428	22
5	40.56	243	2.222	8
6	41.98	363	2.15	12
7	48.82	191	1.864	6
8	49.94	241	1.825	8
9	56.22	109	1.635	4
10	62.98	241	1.475	8
11	64.5	202	1.444	7
12	65.52	164	1.423	5
13	66.82	126	1.399	4

Figure 3.11 X-ray diffractogram for synthetic sodium birnessite composite number 4

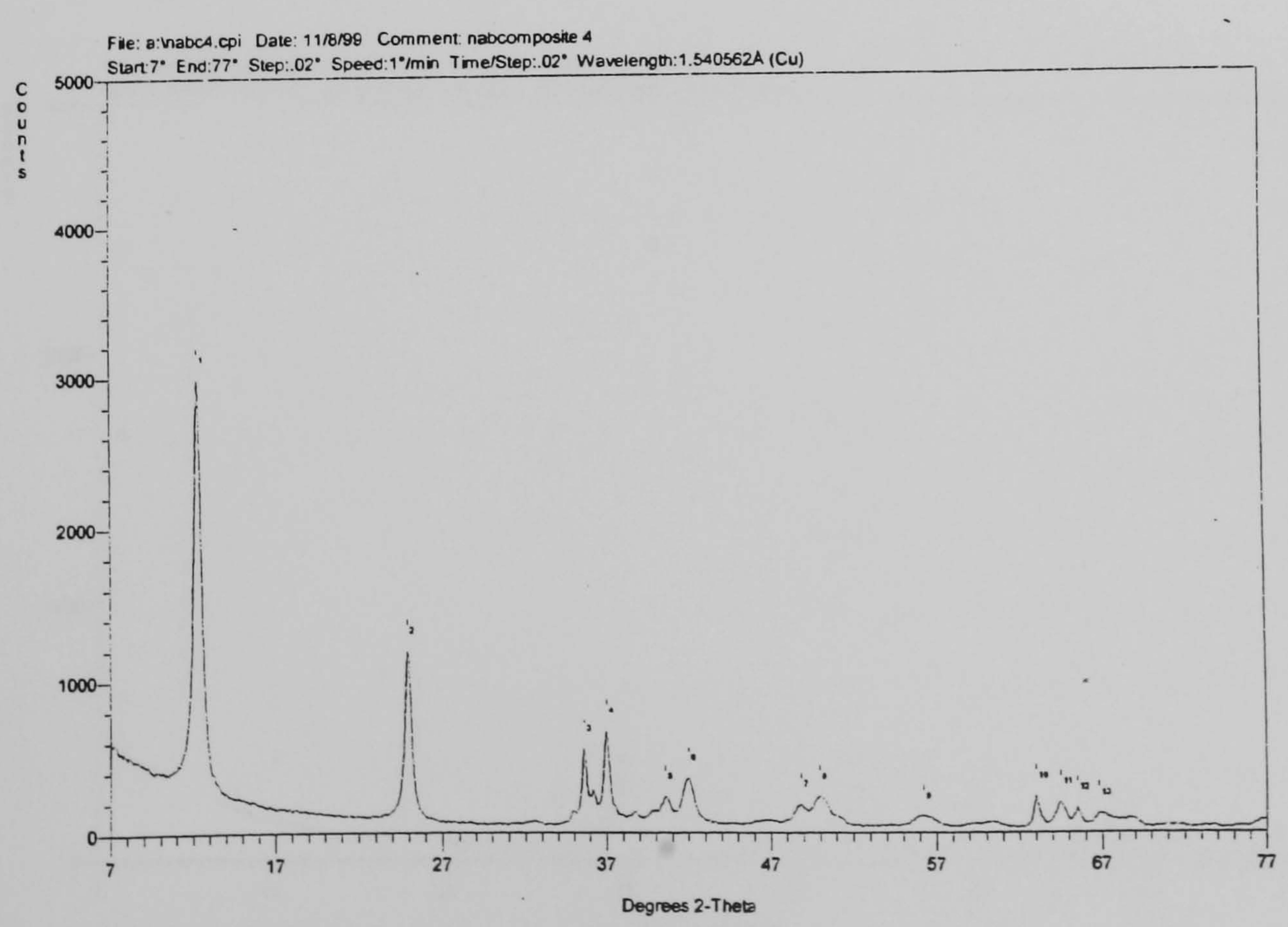
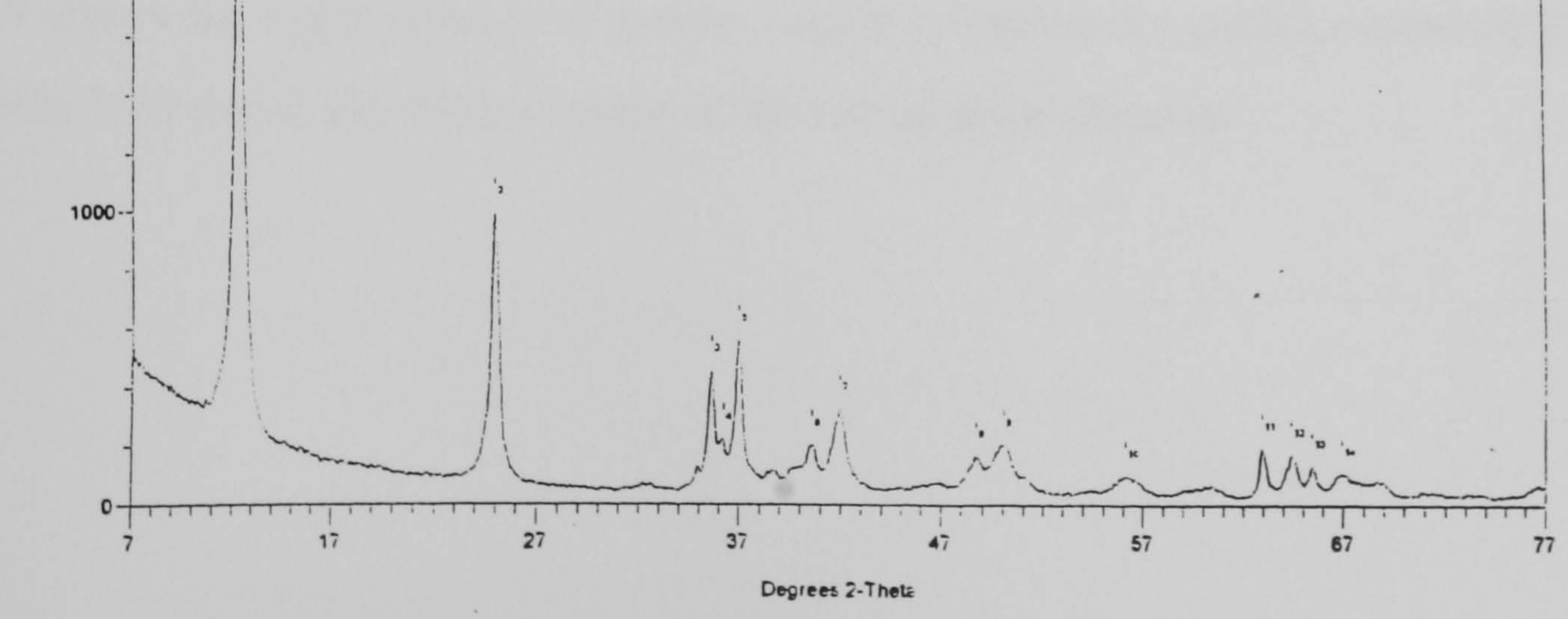


Table 3.8 X-ray diffraction data for synthetic sodium birnessite composite number 4 (replicate experiment)

No	Angle	Counts	Dspace	Rel I
1	12.34	2204	7.167	100
2	24.96	1000	3.564	45
3	35.6	457	2.52	21
4	36.2	227	2.479	10
5	36.96	560	2.43	25
6	40.54	206	2.223	9
7	41.92	327	2.153	15
8	48.68	168	1.869	8
9	50.02	208	1.822	9
10	56.1	101	1.638	5
11	62.9	195	1.476	9
12	64.38	174	1.446	8
13	65.44	134	1.425	6
14	66.92	107	1.397	5

Figure 3.12 X-ray diffractogram for synthetic sodium birnessite composite number 4 (replicate experiment)



File: a:\nabbach4.cpi Date: 11/6/99 Comment: batch 4 sodium birnessite
Start:7° End:77° Step:.02° Speed:1°/min Time/Step:.02° Wavelength:1.540562Å (Cu)

3.9.1.4 Discussion

The X-ray diffraction data produced in this work shows that the sodium birnessite composite samples synthesised are very similar to the standard reference sample. It is therefore assumed that the sodium birnessite composite samples are significantly composed of the known sodium birnessite phase.

3.10 THERMOGRAVIMETRIC ANALYSIS OF CURING AGENT COMPONENTS.

3.10.1 Introduction

Thermal analysis was conducted on the samples of sodium birnessite, commercial curing agent, "Queensfil" $CaCO_3$ and "IMINI 80" inert MnO_2 ore to determine the water content. Manganese oxides have been studied previously using thermogravimetric analysis, for example Agrawal,(35) whilst sodium birnessite in particular by Le Goff et al.(7)

3.10.2 Experimental

In this work the samples were heated at 10°C minute from 35°C to 640°C in platinum crucibles using Al_2O_3 as a reference sample. The atmosphere was flushed with nitrogen. The temperature of 150°C for the point at which weight loss due to water was determined was chosen for this research as research by Le Goff et al (7) revealed that sodium birnessite lost water at two temperatures up to 800 °C, at 85 °C and 150 °C, and so the temperature of 150 °C was chosen so as to be comparable with the published literature.

3.10.3 Results

Table 3.9 shows the water content of various curing component samples measured in this work. Table 3.10 shows the water content of the curing agent diluents.

Table 3.9 Thermal analysis of curing agent compounds to assess water content

Curing agent components	**Weight loss at 150 °C**
Commercial curing agent	***Replicate (1) 9%*** ***Replicate (2) 9%***
Sodium birnessite composite number 2	Replicate (1) 10% Replicate (2) 10%
Sodium birnessite composite number 3	Replicate (1) 11% Replicate (2) 11%
Sodium birnessite composite number 4	Replicate (1) 11% Replicate (2) 11%
Sodium birnessite composite + IMINI 80 inert MnO_2 ore 5pph:5pph Mix	Replicate (1) 6% Replicate (2) 5%
Sodium birnessite composite + IMINI 80 inert MnO_2 ore 4pph:6pph Mix	Replicate (1) 4% Replicate (2) 4 %
Sodium birnessite composite + $CaCO_3$ 5pph:5pph Mix	Replicate (1) 6% Replicate (2) 6%
Sodium birnessite composite +$CaCO_3$ 4pph:6pph Mix	Replicate (1) 4% Replicate (2) 4%

Table 3.10 Thermal analysis of curing agent compounds to assess water content

Inert diluent	Weight loss at 150 °C
"Queensfil" $CaCO_3$ diluent	Replicate (1) 0.01 % Replicate (2) 0.03%
"IMINI 80"inert MnO_2 ore diluent	Replicate (1) 0.2% Replicate (2) 0.1%

3.10.4 Discussion

The results show the sodium birnessite has more water in it than the commercial agent, the "IMINI 80" inert MnO_2 or the $CaCO_3$. Water is known to be an important component of the curing of liquid polysulfide using metal peroxides. Diluting the sodium birnessite with the inert MnO_2 or $CaCO_3$ ore results in a mix with lower moisture content than undiluted birnessite.

3.11 ANALYSIS OF THE pH OF THE CURING AGENT CHEMICALS USED IN THIS RESEARCH.

3.11.1 Introduction and experimental

The pH of the ingredients used in polysulfide curing is important in the polysulfide curing process and also in the finished polysulfide stability. The pH of the manganese chemicals studied in this research were measured by adding 0.5 g of the chemical to 5 ml of freshly deionised water. The pH was measured using a Mettler Delta 320 pH meter.

3.11.2 Results

Table 3.11 shows the pH of the curing agents, and mixtures of sodium birnessite with the inert MnO_2 ore and calcium carbonate. Table 3.12 shows the pH of the inert diluents and Table 3.13 shows the pH of the accelerators.

Table 3.11 The pH of curing agent components investigated

Manganese chemical	**pH of 10 % slurry**
Commercial curing agent	***Replicate (1) 9.65*** ***Replicate (2) 9.73***
sodium birnessite composite number 2	Replicate (1) 10.41 Replicate (2) 10.39
sodium birnessite composite number 3	Replicate (1) 10.11 Replicate (2) 10.20
sodium birnessite composite number 4	Replicate (1) 9.83 Replicate (2) 10.10
sodium birnessite composite +$CaCO_3$ 4pph:6pph mix	Replicate (1)10.43 Replicate (2)10.47
sodium birnessite composite +$CaCO_3$ 5pph:5pph mix	Replicate (1) 10.06 Replicate (2) 9.94
sodium birnessite composite + inert MnO_2 ore 4pph:6pph mix	Replicate (1) 9.91 Replicate (2) 9.83
sodium birnessite composite + inert MnO_2 ore 5pph:5pph mix	Replicate (1) 9.45 Replicate (2) 9.42

Table 3.12 The pH of the inert diluents used as a 10 % slurry in water

Inert diluent	pH of inert diluent as 10 % slurry in water
"Queensfil" $CaCO_3$ diluent	Replicate (1) 8.74 Replicate (2) 8.92
"IMINI 80"inert MnO_2 ore diluent	Replicate (1) 7.05 Replicate (2) 7.63

Table 3.13 The pH of the accelerators as a 10 % slurry in water

Accelerator	pH of accelerator as 10 % slurry in water
DBU	Replicate (1) 11.18 Replicate (2) 11.26
TMTD	Replicate (1) 5.83 Replicate (2) 5.17

3.12 PARTICLE SIZE ANALYSIS OF CURING AGENTS:

3.12.1 Introduction

Particle size analysis was performed on a sample of the commercial curing agent and the sodium birnessite composite number 2 (samples NaB 50-57), number 3 (samples of NaB 58-68) and composite number 4 (samples NaB 71-72). Particle size is an important variable affecting the rate of curing of a polysulfide. It is expected that the finer the particles the greater the rate of curing and so grinding of the curing agent reduces the particles size.(36)

The sodium birnessite composite and commercial curing agent samples were stored in 2 litre plastic containers. As Allen (37) states, "for powder in a container, it is usual to shake the sample prior to sampling in an attempt to achieve a good mix. However, the method of shaking can promote segregation."

3.12.2 Experimental

The instrument used was a Cambridge Instruments Q520 Particle size analyser. A water suspension of a ultrasound treated sample was prepared on a glass slide and covered with a cover glass. According to Allen (37) when adding the particle suspension to a microscope slide, it is important to lower a cover slip gently over the suspension. If the cover slip is pressed to rapidly it causes preferential transfer of larger particles to the edges of the slide, and should be avoided. Ultrasound was used to minimise aggregation of the particles.

The instrument was calibrated using a graticule and computer analysis of randomly chosen areas of the slide was performed to assess the number of particles and their area. It should be noted that the minimum area the particle size analyser could measure was 0.738 μm. The analysis of this sample therefore represents the number of particles above this value, and the mean particle size is only a result of using this instrument.

3.12.3 Results

Tables 3.14, 3.15, 3.16, and 3.17 show parameters of the commercial curing agent and sodium birnessite composite number 2, number 3 and number 4 particle size analysis respectively. Graphs of the cumulative percentage of particle size and particle size distribution for the commercial curing agent and sodium birnessite composite numbers 2,3, and 4 are shown in Figures 3.13 to 3.20.

Table 3.14 Parameters identified using particle size analysis of the commercial curing agent

Sample	Mean particle size μm	Standard deviation	Minimum particle size μm	Maximum particle size μm
commercial curing agent	2.8	1.7	0.74	13.1

Figure 3.13 Particle size distribution for the commercial curing agent

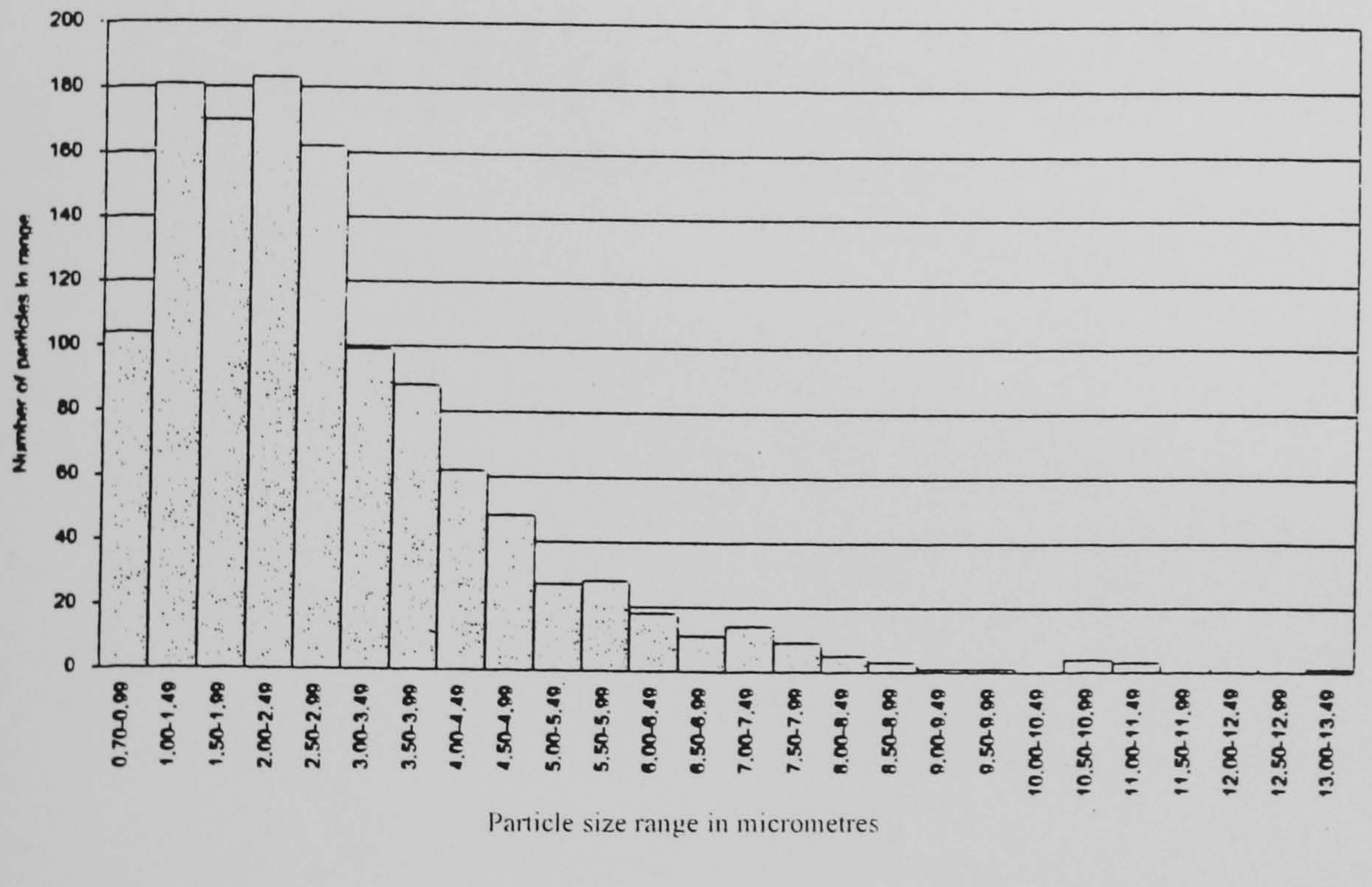


Figure 3.14 Cumulative percentage of particle size for the commercial curing agent

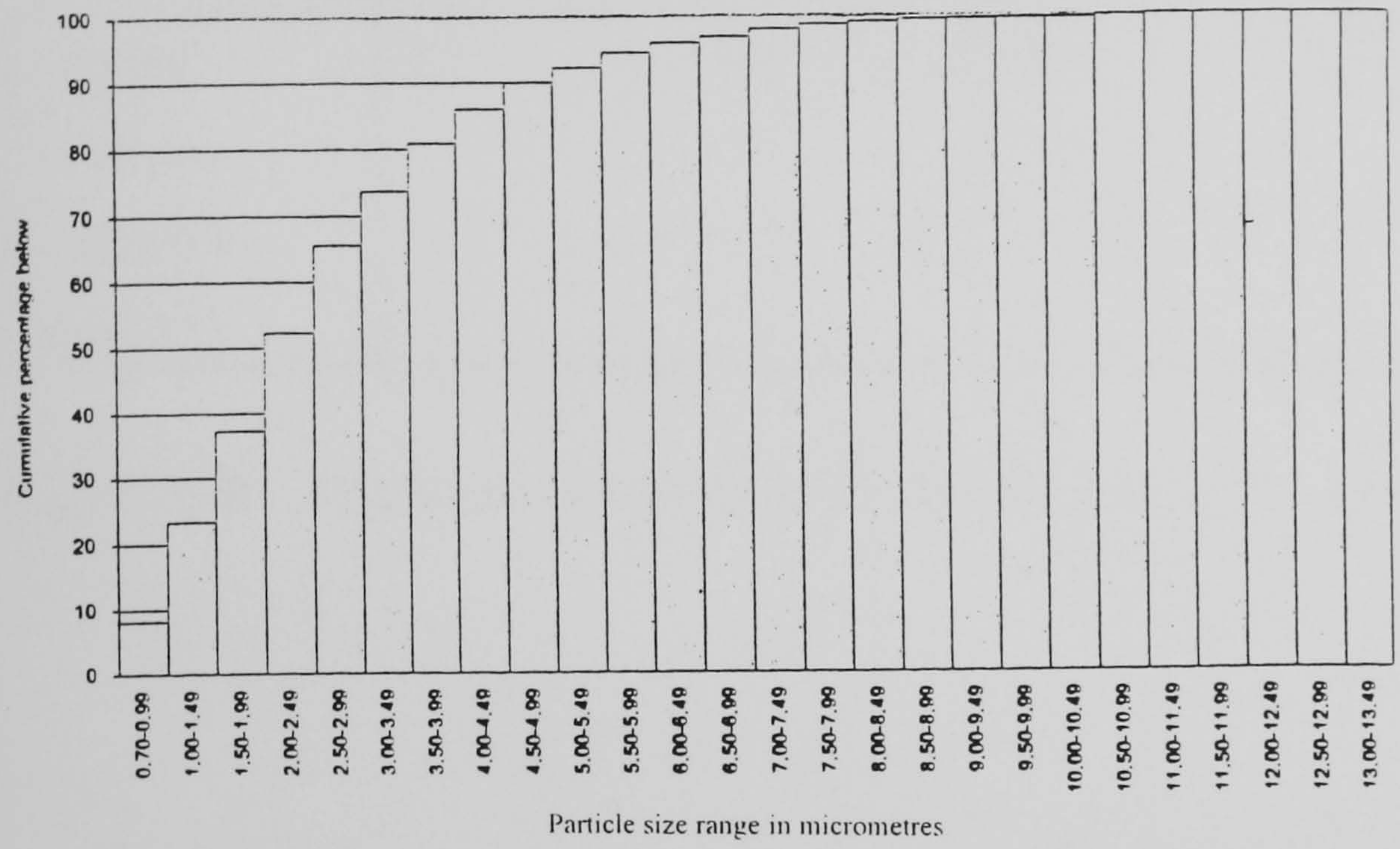


Table 3.15 Parameters identified using particle size analysis of synthetic sodium birnessite composite number 2 (samples NaB 50-NaB 57)

Sample	**Mean particle size μm**	**Standard deviation**	**Minimum particle size μm**	**Maximum particle size μm**
Sodium birnessite composite number 2	2.8	2.4	0.74	19.6

Figure 3.15 Particle size distribution for synthetic sodium birnessite composite number 2

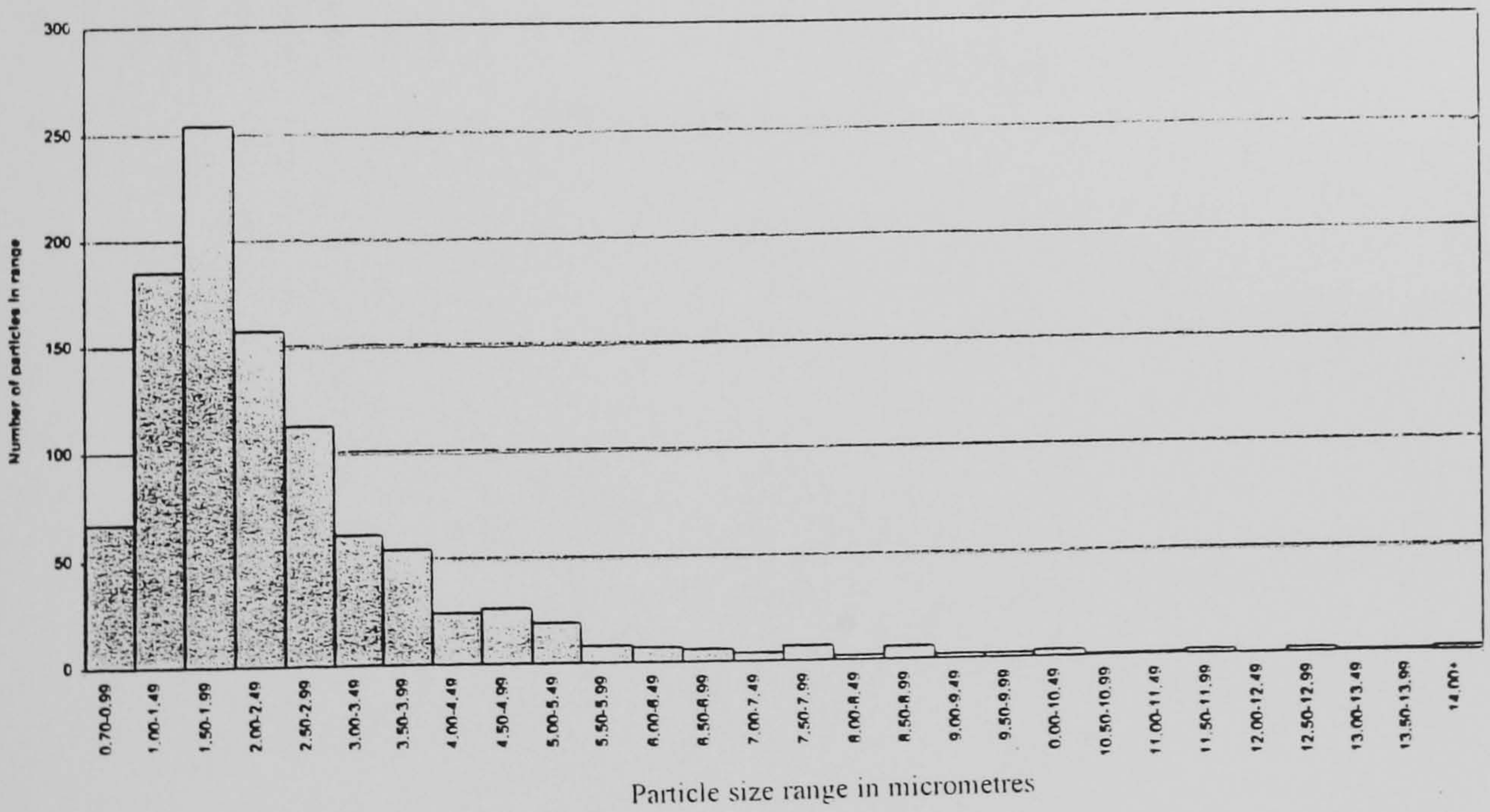


Figure 3.16 Cumulative percentage of particle size for synthetic sodium birnessite composite number 2.

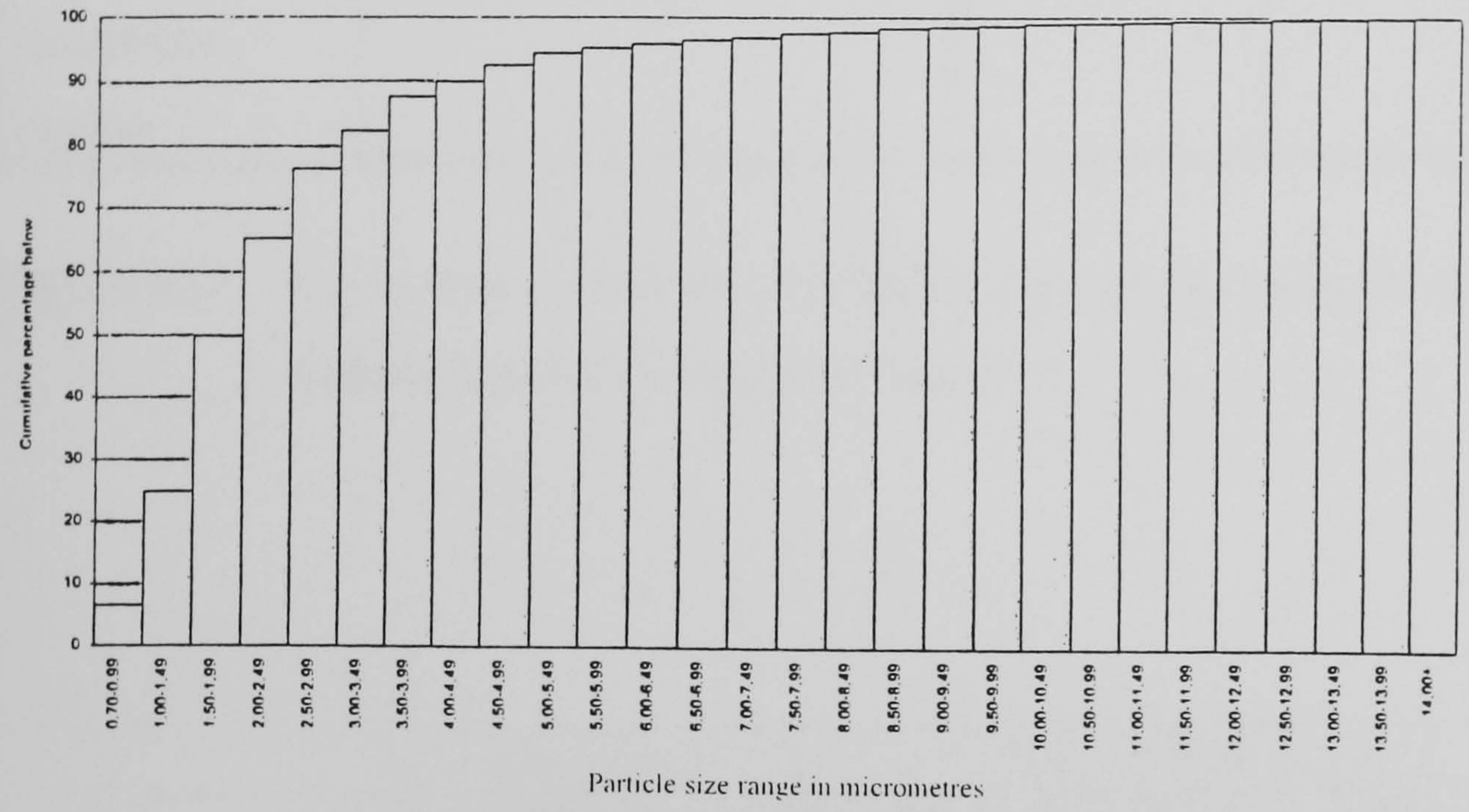


Table 3.16 Parameters identified using particle size analysis of synthetic sodium birnessite composite 3 (NaB 58 -NaB68)

Sample	**Mean particle size μm**	**Standard deviation**	**Minimum particle size μm**	**Maximum particle size μm**
Sodium birnessite composite number 3	1.9	1.7	0.4	19.2

Figure 3.17 Cumulative percentage of particles in given size range for synthetic sodium birnessite composite number 3

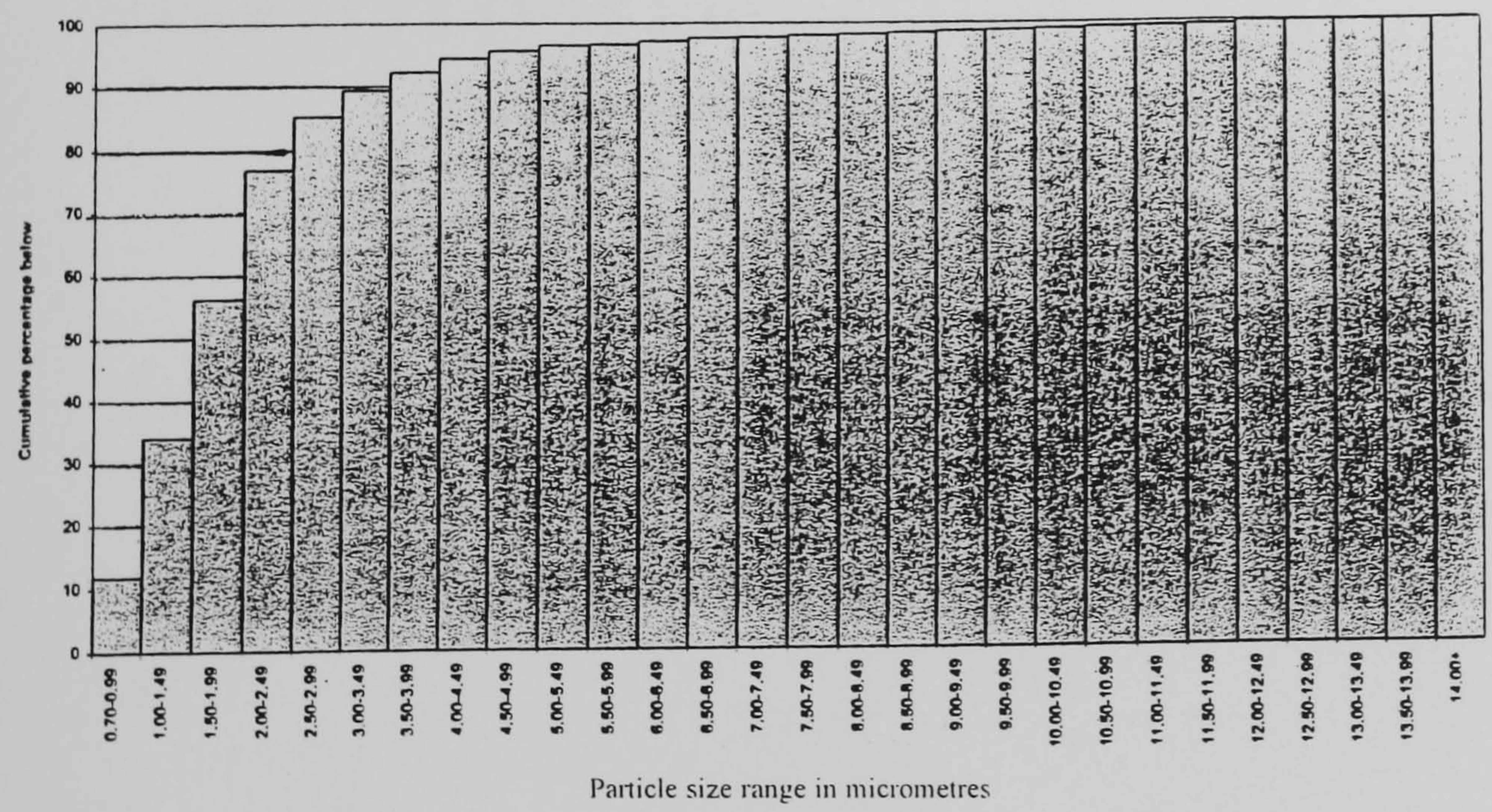


Figure 3.18 Number of particles in given size range for synthetic sodium birnessite composite number 3

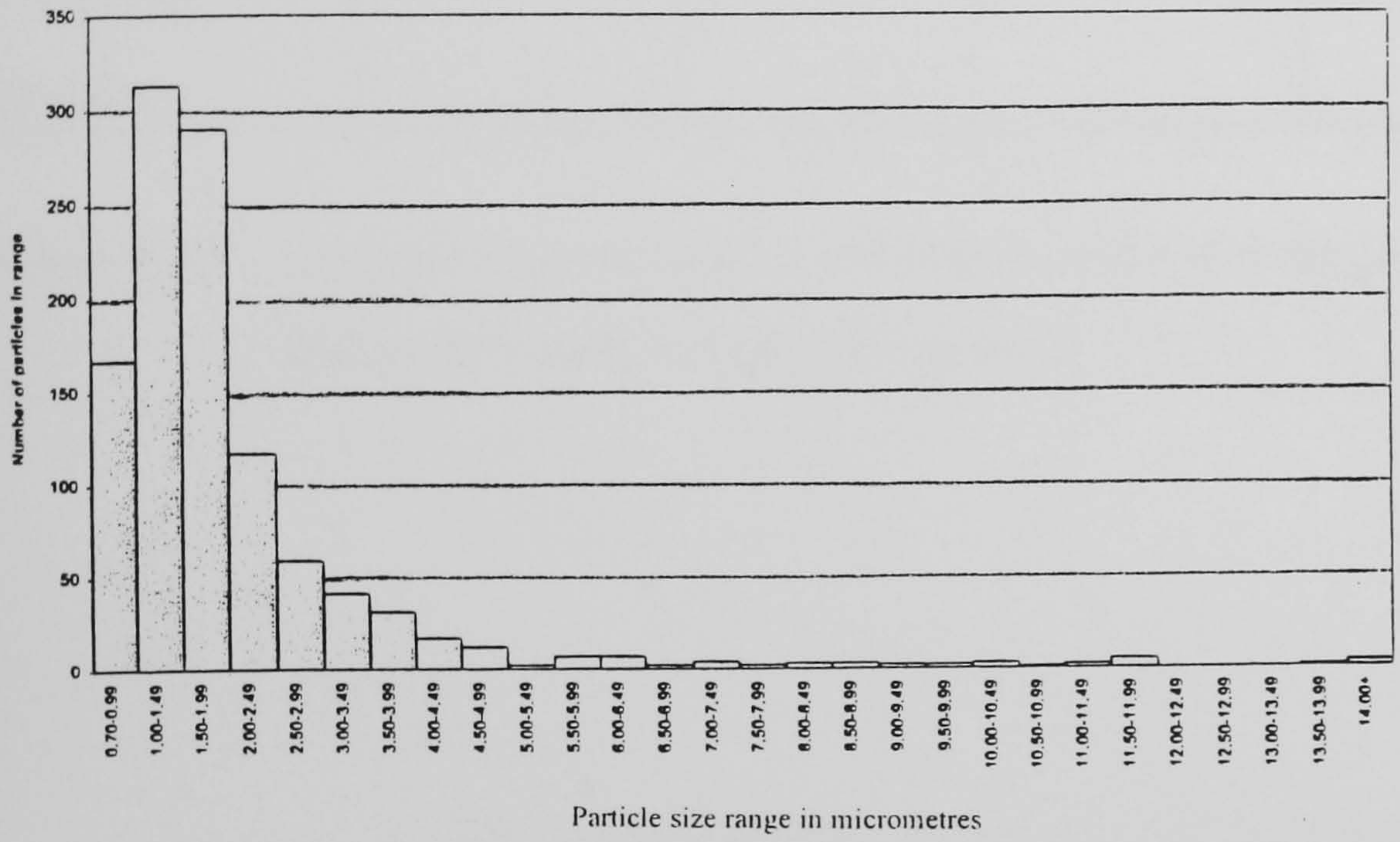


Table 3.17 Parameters identified using particle size analysis of synthetic sodium birnessite composite 4 (NaB71-NaB72)

Sample	Mean particle size µm	Standard deviation	Minimum particle size µm	Maximum particle size µm
Sodium birnessite composite number 4	1.8	1.3	0.7	17.4

Figure 3.19 Cumulative percentage of particles in given size range for synthetic sodium birnessite composite number 4

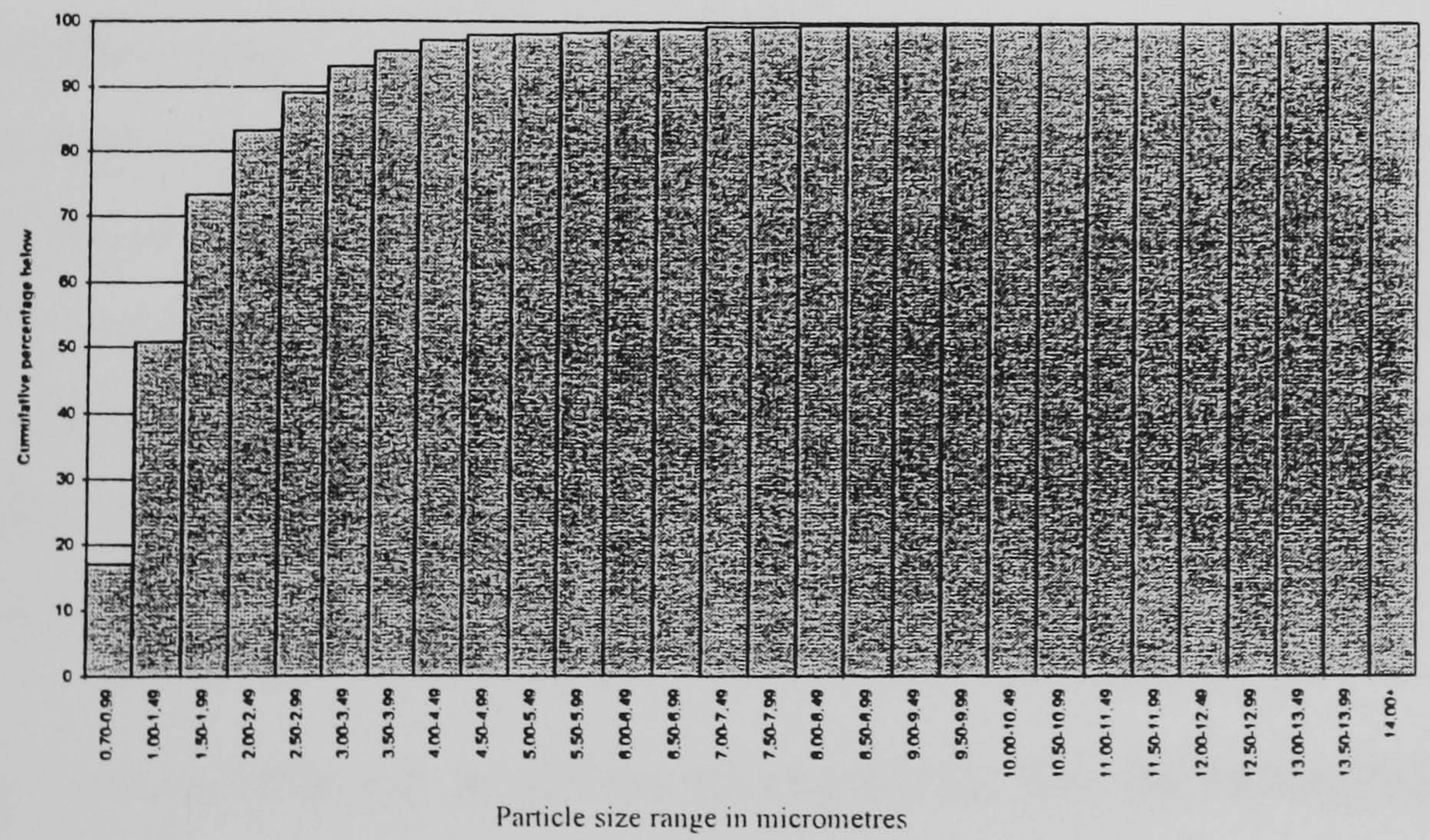
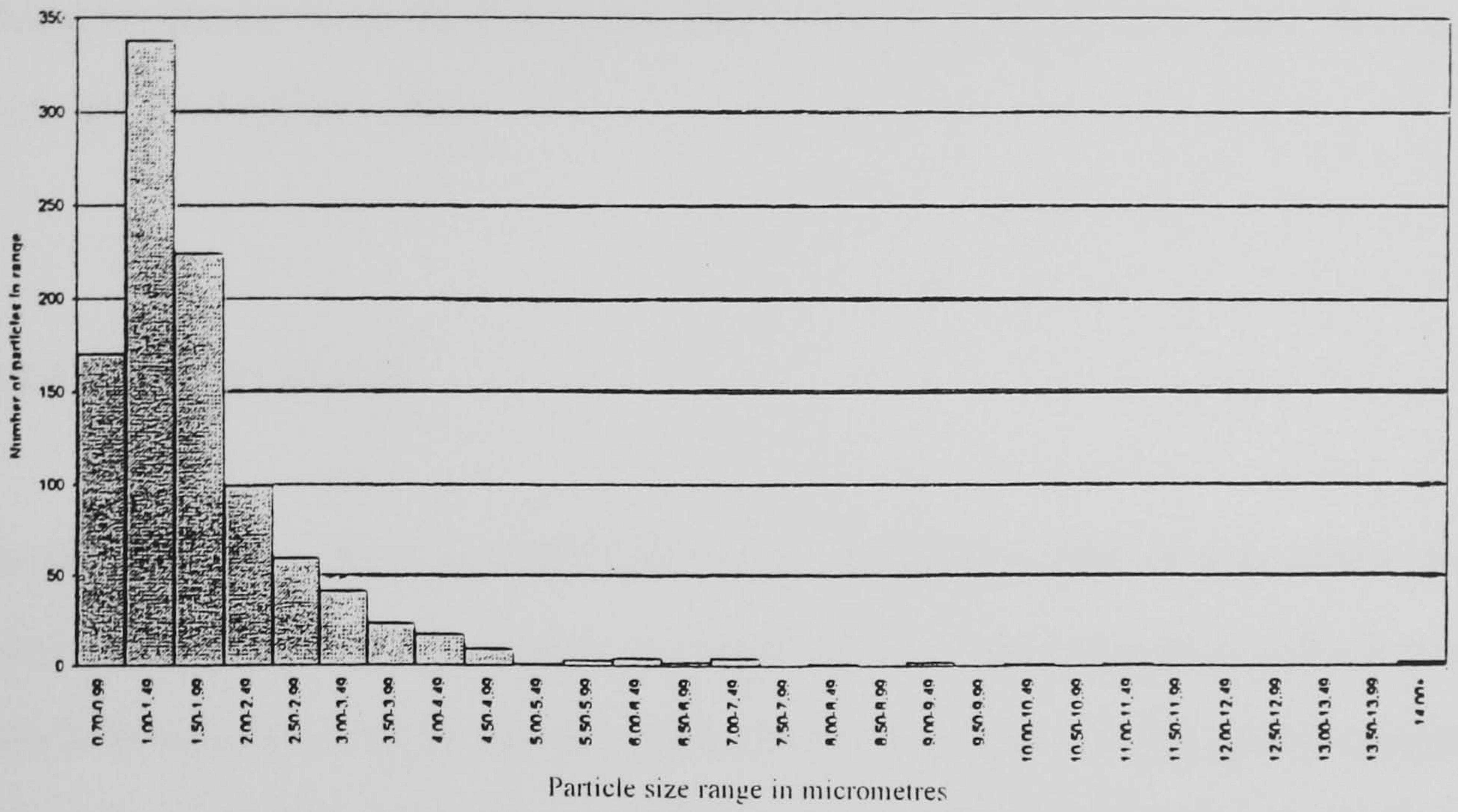


Figure 3.20 Number of particles in given size range for synthetic sodium birnessite composite number 4



3.12.4 Discussion

From these graphs, for the commercial curing agent, 90 % of the particles are between 0.7 μm and 4.99 μm. For sodium birnessite composite number 2, 90 % of the particles are between 0.7 μm and 4.49 μm. These results were confirmed using Transmission Electron Microscopy. For sodium birnessite composite number 3, 90 % of the particles are between 0.7 μm and 3.99 μm and for sodium birnessite composite number 4, 90 % of the particles are between 0.7 μm and 2.99 μm.

3.13 ANALYSIS OF SODIUM BIRNESSITE TO DETERMINE MANGANESE CONTENT

Acid digestion of a manganese dioxide sample and reaction with sodium oxalate reduces the Mn^{4+} to Mn^{2+} and when titrated with potassium permanganate is used to determine the Mn^{4+} content of a MnO_2 sample. Titration of a standardised $KMnO_4$ solution with digested sodium birnessite which had been reacted with sodium oxalate revealed that sodium birnessite had a reproducibly determined Mn^{4+} content of 43%. X-ray photoelectron spectroscopy (XPS) showed the presence of Mn^{4+} and Mn^{2+} in the sodium birnessite composite prepared in this research. The data from the titrations and the XPS supports the assumption from the proposed sodium birnessite formula that of the 54.7 % Mn in sodium birnessite, two in every seven Mn atoms are in the Mn^{2+} state.

3.14 CONCLUSIONS

The pH of the cure mixture is thought to be important in the curing of the liquid polysulfide, where the alkalinity of the cure compounds (to a certain extent) accelerates the reaction. The sodium birnessite is more alkaline than the commercial curing agent, and one could assume from this alone that the rate of curing using sodium birnessite could be greater than the commercial curing agent on this factor alone.

Both the DBU accelerator and the calcium carbonate are alkaline. This would be expected to have an accelerating effect on the rate of polysulfide curing. The particle size of the sodium birnessite composites 2, 3 and 4 and the commercial curing agent however are similar which makes a more comparable comparison of the curing agents curing ability. The water content of the curing agents and diluents is shown in this work to have a range of values. Moisture content is important to increase the rate of curing of polysulfides.

With reference to the quantities of the ingredients used in the cure mixtures for the experiments performed in the following Chapters, it should be noted that for the combined quantity of accelerators, diluents, plasticisers, and curing agent, *the total amount of the cure paste used in each experiment is 20.5 parts cure paste per 100 parts liquid polysulfide. This is an industrial standard recommended by Morton International, the manufacturers of LP32C liquid polysulfide.*

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CHAPTER 4 THE CURING OF LIQUID POLYSULFIDE WITH SODIUM BIRNESSITE AND THE COMMERCIAL CURING AGENT MONITORED USING PARALLEL PLATE RHEOMETRY

4.1 INTRODUCTION

Initial experiments showed that sodium birnessite is a rapid polysulfide curing agent and therefore it needs to be diluted with inert components such as MnO_2 or $CaCO_3$. These diluents were chosen as they show very low curing activity. The reaction between the polysulfide LP32C and the commercial curing agent, and also the diluted sodium birnessite was monitored using an ARES Rheometer. The instrument can be used to obtain viscoelastic properties of polymeric reactions such as the curing of LP32C. It is to be expected that an increase in the amount of curing agent would increase the rate of curing, as demonstrated by Fountain and Haas (1) in a study of polysulfide curing using lead dioxide.

Goldblatt (2) demonstrated the rapidity of curing of polysulfide using various manganese oxides and monitored them using a Brookfield steady state viscometer. Mathur and Peterson(3) also used a Brookfield viscometer while Hanhela et al(4) studied the manganese dioxide curing of liquid polysulfide using an oscillating disc curemeter.

In addition to raw material control, an important factor in producing a reliable sealant is the requirement for precise mixing of the curing agent into the sealant base to ensure a quality product with respect to adhesion, strength, and other cure related properties.(1) Rheology control is important as sealants can be used for vertical and horizontal applications. Self levelling grades of sealant are used for horizontal seals and non slumping grades using non thixotropic calcium carbonate adding body to polysulfide used for vertical joints.(5) An optimal level of curing agent to get these required cure properties is 10 pph curing agent in 100 pph of polysulfide.(1) Mixing of the polysulfide and cure paste mixture was performed with an electric drill stirrer in this research, a technique similar to that used by Matsui and Miwa.(6)

Very little has been published in the literature about the curing of liquid polysulfides. The results of a study on the effect on the storage modulus G′ of adding an (unnamed) accelerator to an (unnamed) manganese dioxide curing agent showing the progression of cure over time was reported by Lowe.(7) There are also very few publications describing the use of parallel plate rheometry for polymers although one example is the paper by Chiu and Wang. (8) The number of less commonly used techniques that have been used to measure curing of polysulfides includes the vibrating needle curemeter,(9) cone and plate rheometry,(10) oscillating disc curemeter(4) and the moving die curemeter.(11)

Industrial definitions for the time scale of the curing vary. The pot life for example is defined as the time to reach double the initial uncured viscosity. As LP32C viscosity is 46.5 Pa s, at 25° C the pot life (also termed the pour time or application time) is when the sample reaches 92.2 Pa s. It is defined as the time the mixture is capable of being transferred to the site. (usually 20-40 mins or 10^2 Pa s). The work life is the time in which the curing polysulfide sample can be re-worked on site after being applied, usually a minimum of 1-2 hours and a maximum of 4-5 hours or under 10^4 Pa s. The gel point, defined as when the material is incapable of flow, is 10^4 Pa s.

4.1.1 The liquid polysulfide investigated in this research

The liquid polysulfide polymer investigated is Morton LP32C, introduced in 1949 and manufactured by Thiokol/Chemical division. It is a polymer of 1,2,3 trichloropropane and 1,1'-[methylenebis(oxy)]bis (2-chloroethane) reduced with sodium sulfide (Na_2Sx). It has an average molecular weight of 4000, and a sulfur content of 37-38 %.(12) The terminal groups of the polymer segments are mercaptan (-SH) groups and it is these mercaptan groups that are converted into disulfide S-S bonds by the curing agent. At 25°C, LP32C has a viscosity of 46.5 Pa s and specific gravity of 1.29.(13) It is a non-Newtonian liquid and has the composition :

$$HS\text{-}(C_2H_4\text{-}O\text{-}CH_2\text{-}O\text{-}C_2H_4\text{-}Sx)_{23}\text{-}C_2H_4\text{-}O\text{-}CH_2\text{-}O\text{-}C_2H_4\text{-}SH$$

The work described in this Chapter is designed to set into context the amount of curing agent needed to produce a solid polysulfide within a workable time span and to identify the effects of the presence of different quantities and different types of accelerator, diluent and plasticiser on the rate of the curing reaction.

4.2 DYNAMIC FREQUENCY SWEEP AND DYNAMIC STRAIN SWEEP TESTING OF UNCURED LP32C POLYSULFIDE

4.2.1 Introduction

Before testing the curing of a polysulfide sample it is necessary to perform dynamic strain and frequency sweeps on the polymer without curing agents added. This is to identify the strain amplitude and the frequency that will result in no disruption to the polymer structure. These data enable monitoring of the curing reaction of the polysulfide with oxidising agents and in this research are performed at a strain and frequency that does not break down the polysulfide structure. The dynamic frequency sweep involves testing the sample dynamically isothermally at the same sinusoidal strain rate but at increasing frequency. The ARES rheometer motor actuator begins all tests at the zero motor position and drives symmetrically about motor zero to the strain set by the user defined test parameters.

4.2.2 Experimental

A sample of LP32C is placed between the two 25mm diameter parallel plates, in the sample oven. At 25°C, a strain and frequency sweep is performed. The level at which sample breakdown would occur can be seen from the graphical output when there is a non linear plot of strain levels. The strain level used for the subsequent test monitoring the cure of the LP32C with manganese dioxide curing agents would be lower than this value. For strain, a plate gap of 1.50 mm was chosen and the strain on the LP32C was increased from 0 % to 50 % at a 1 % strain increment. The frequency was kept constant at 6.28 rad/s. For the Dynamic Frequency Test a gap of 1.50 mm was chosen to separate the 25 mm diameter parallel plates, and the frequency stepped up from 0.1 rad/s to 100 rad/s at a strain of 5 %.

The ARES rheometer was calibrated using the two techniques (1) torque calibration, and (2) Normal force calibration for the transducer. The motor was calibrated using strain calibration, and the motor and transducer calibrated using phase angle calibration. A standard sample of known viscosity. a silicon resin- polydimethylsiloxane. was used to check the instrument in Dynamic frequency sweep mode in which measurement of the storage modulus G′ and loss modulus G″ were measured against increasing frequency (rad/s). identifying the crossover point. Temperature calibration was performed using a thermocouple

4.2.3 Results

The types of results for the Dynamic Strain Sweep and Dynamic Frequency Sweep analyses are shown in Figure 4.1 and Figure 4.2 .

Figure 4.1 Dynamic Strain Sweep for uncured polysulfide LP32C at 25°C

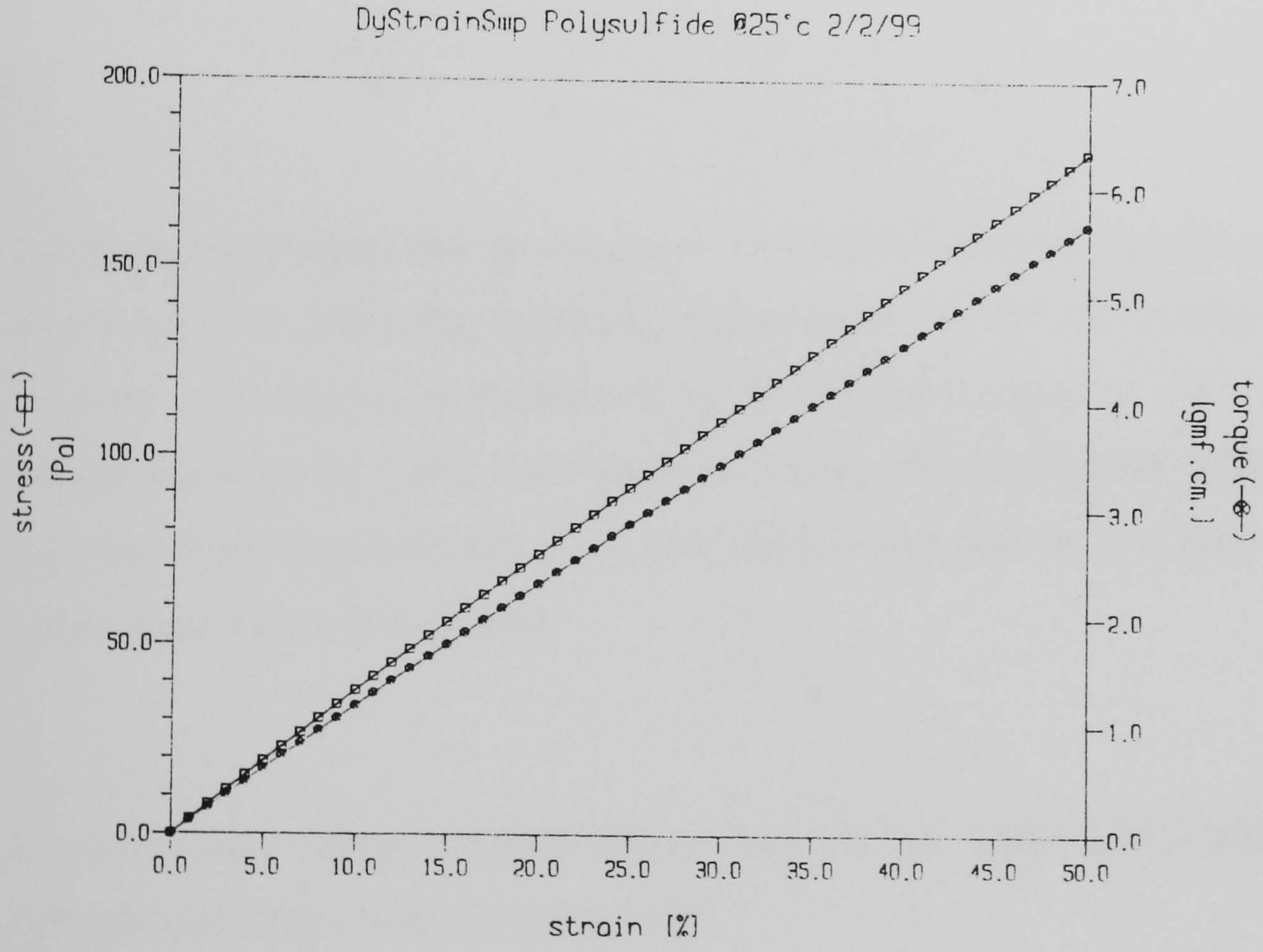
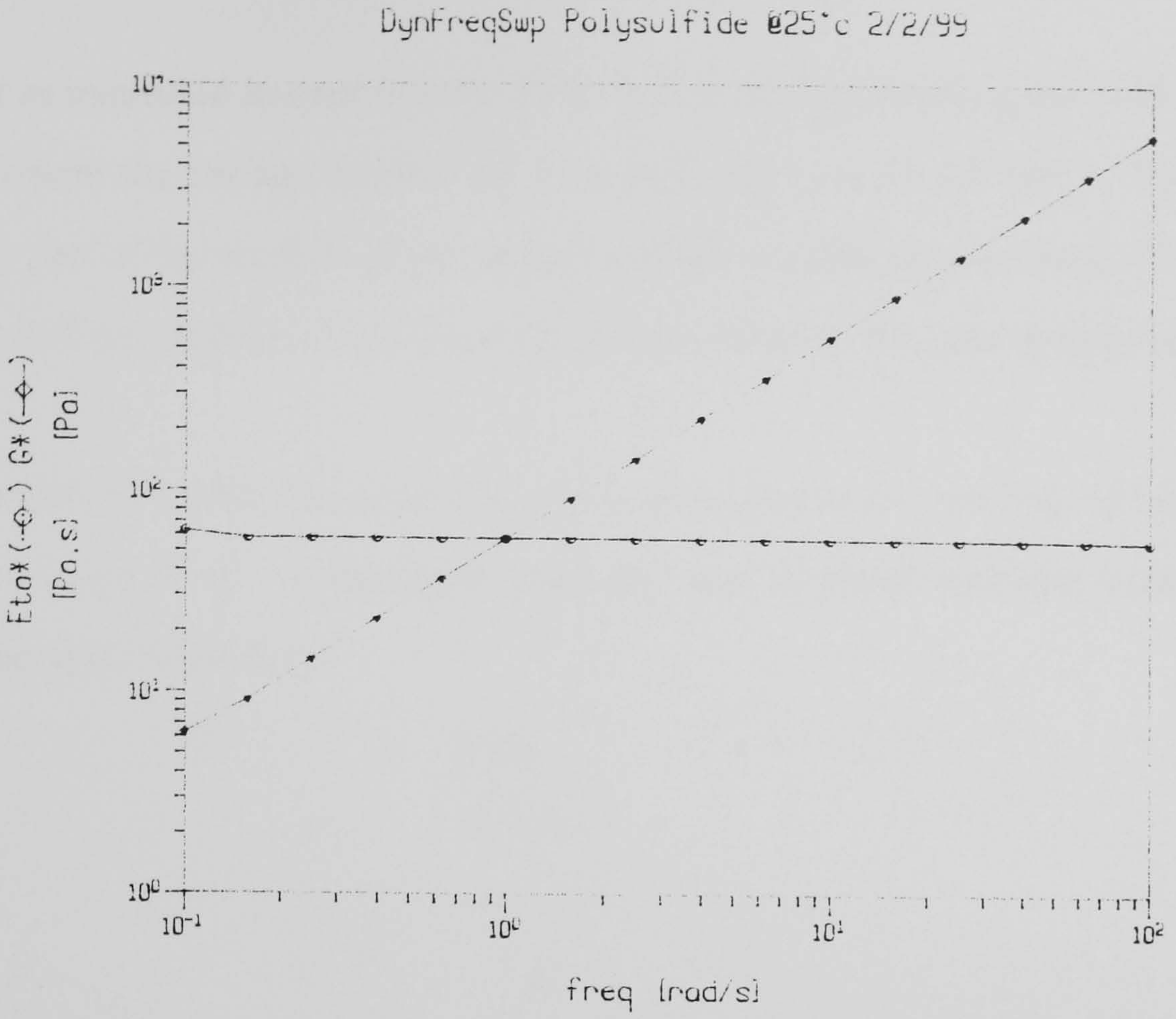


Figure 4.2 Dynamic Frequency Sweep for uncured polysulfide LP32C at 25°C



For the Dynamic Strain Test, the maximum level which would not result in sample breakdown was found to be 13% strain. For the Dynamic Frequency Test, no breakdown in the LP32C structure was detected at frequencies up to 100 rad/s under the test conditions. These parameters of strain (13%) and frequency testing (100 rad/s) were therefore used in the Dynamic Time Sweep testing of the polysulfide cured with the manganese dioxide curing agents described in this Chapter.

4.3 DYNAMIC TIME SWEEP ANALYSIS USING THE ARES RHEOMETER TO MONITOR THE CURING OF LP32C.

4.3.1 Introduction

The Dynamic Time Sweep analysis is used to measure the moduli or viscosity at constant temperature, strain and frequency.(14) The end result of this is to ascertain the gel point. This is the point in time at which the "mixture is incapable of flow, and in molecular terms refers to the point at which an infinite network is formed", i.e. the point at which the liquid turns into a rubbery state.(15)

The *gel point* as measured in experiments described in this thesis using the ARES Rheometer is the point where the storage moduli (G') exceeds the loss moduli (G''). The value of G' represents the part of the stress in phase with the strain, divided by the strain: $G' = \sigma_1/\varepsilon_0$. This quantity is called the storage modulus and is proportional to the recoverable energy.

The shear moduli $G''$is the loss modulus and is proportional to the loss of heat energy per cycle.(16) The value of G'' is the peak stress 90° out of phase with the strain ($\sigma_1 \tan \delta$), divided by the peak strain (ε_0):

$$G'' = \sigma_2/\varepsilon_0 = \frac{\sigma_1 \tan \delta}{\varepsilon_0}$$

The magnitudes of the $G'$and G'' vary according to the polymer state. When in the glassy state, $G'$is high and good elasticity is evident because the lack of movement of polymer molecules means the imposed movement experiences little damping. As a result virtually no strain energy is lost as heat.

Where G' is low, the viscous element contribution is larger and there is a greater delay in response to an applied stress. As a result of this damping, much strain energy is lost as heat. The complex modulus G^* is the combination of G' and G''. The equation to relate the three is:

$$G^* = G' + i\,G''_2$$

$$(i = \sqrt{-1})$$

In industrial applications, the curing agent and accelerator, fillers, etc. are suspended in a plasticiser. The following experiments involve the use of a plasticiser to carry the curing agent components. From personal communication with Morton International (17) it was suggested that a stoichiometric reaction of active manganese dioxide with LP32C involves 2.3 pph of manganese dioxide reacting with 100 pph of LP32C polysulfide.

A number of early preparations of the curing agent / plasticiser mixture were made up and stored in polyethylene cups. However, after a few days of storage of the prepared curing agent suspensions, the plasticiser began to dissolve the cups and a number of preparations had to be discarded and further samples prepared in sealed glass containers.

4.4 DYNAMIC TIME SWEEP ANALYSIS OF CURING OF LP32C USING THE COMMERCIAL CURING AGENT AND ACCELERATOR

4.4.1 Experimental

A cure mixture using 10 pph of the commercial curing agent was investigated in these experiments, the composition of the cure mix is shown for each experiment. The tetramethylthiuramdisulfide (TMTD) is a commercial grade accelerator supplied by Robinson Brothers Limited and is the industrially preferred accelerator used in the commercial curing agent curing systems. A dynamic time sweep analysis of the curing reaction was performed using a Rheometrics ARES rheometer. The mixing time was reduced to 5 minutes due to the homogenous (liquid into liquid) nature of the Part A (the liquid polysulfide) and part B (the cure paste). The gel point of the reaction was determined and results are shown in Tables 4.1 and 4.2 and Figures 4.3 to 4.6.

The quantity of curing agent and polysulfide used was LP32C (100 pph) mixed with 10 pph of curing agent. After the 10 minute mixing using an electric stirrer at constant speed, a small portion of the curing polymer mixture was placed on the lower of the two parallel plates and the time measured using the instrument parameters:

Instrument used: ARES 3A Rheometer

Mode of operation: Dynamic Time Sweep

Temperature of measurement: 25°C

Plates used: 25 mm diameter stainless steel parallel plates.

Gap between plates: 1.500 mm

Transducer: 200 g cm^3

Strain: 5.0 %

Frequency: 6.28 radians/second

Time per measurement: 60 seconds

4.4.2 Results

As with the results given in the other Chapters, the study of the curing reaction using the commercial curing agent are given first followed by the results obtained using sodium birnessite to enable a comparison between the commercial curing agent and the sodium birnessite. Tables 4.1 and 4.2 give data for the reaction times using the commercial curing agent, whilst Figures 4.3 to 4.6 display the changes in moduli of the curing samples.

Descriptions of the amount of material present in the curing mix are given as pph (part per hundred parts polysulfide). The total experiment time was from the start of mixing of the polysulfide with the cure paste until the gel point. Each experiment is replicated.

Experiments using the commercial curing agent:

Experiment 4.1 Experiments involving cure paste mixture using the commercial curing agent and TMTD accelerator

Cure paste mixture:

Part A

Liquid polysulfide polymer	LP32C:	100 pph

Part B

Curing agent:	Commercial curing agent:	10 pph
Plasticiser:	Santicizer 278:	10 pph
Accelerator:	Tetramethylthiuramdisulfide (TMTD)	0.5 pph

Table 4.1 Gel points for LP32C polymer cured with 10 pph commercial curing agent and 0.5 pph TMTD accelerator in 10 pph Santicizer 278

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
10 pph commercial curing agent + 0.5 pph TMTD in Santicizer 278 plasticiser	Replicate (1)11 Replicate (2)11	(1)38 (2)40	(1) 48 (2) 50

Figure 4.3 Polysulfide curing profile using 10 pph commercial curing agent with TMTD in 10 pph Santicizer 278 plasticiser

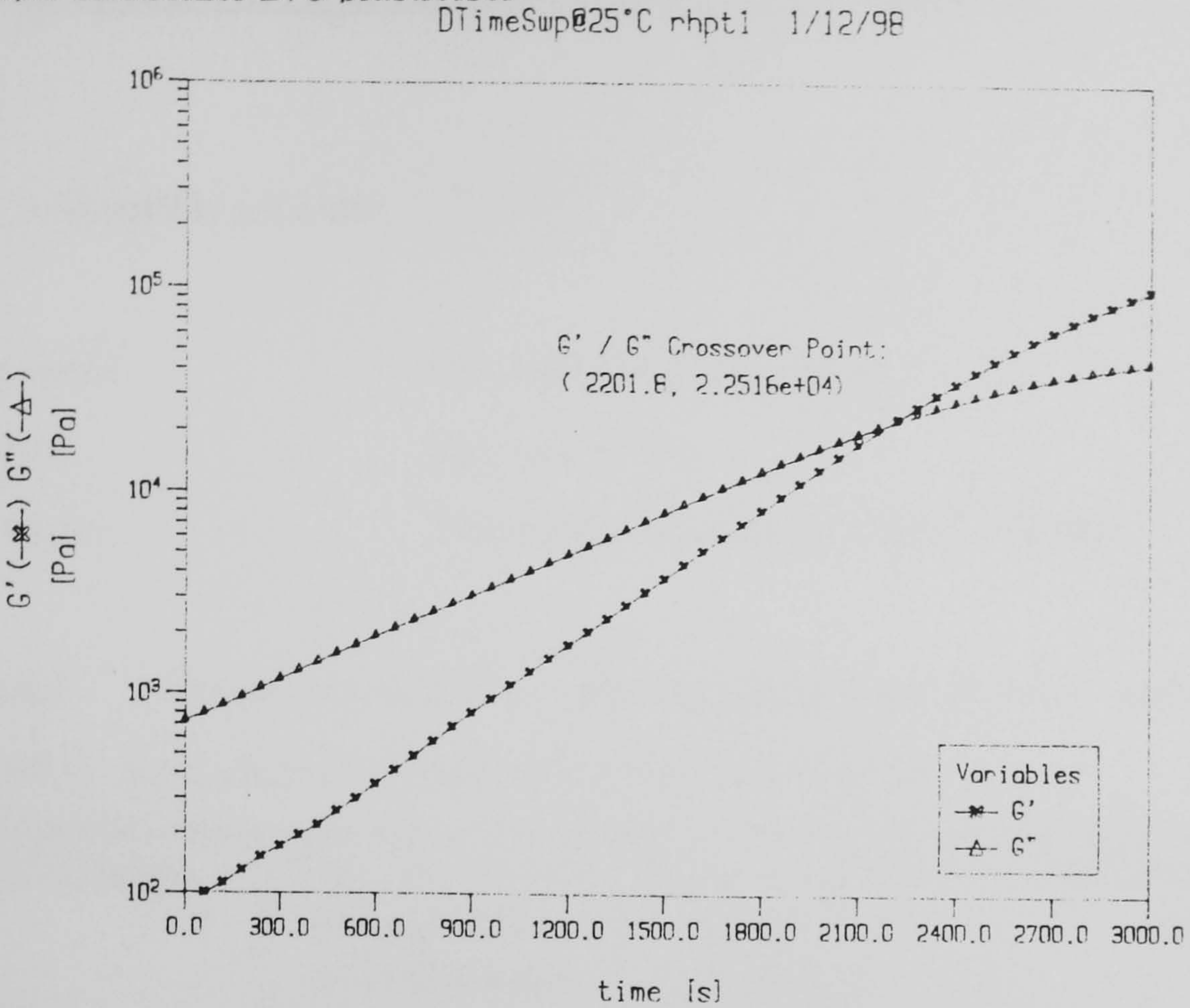
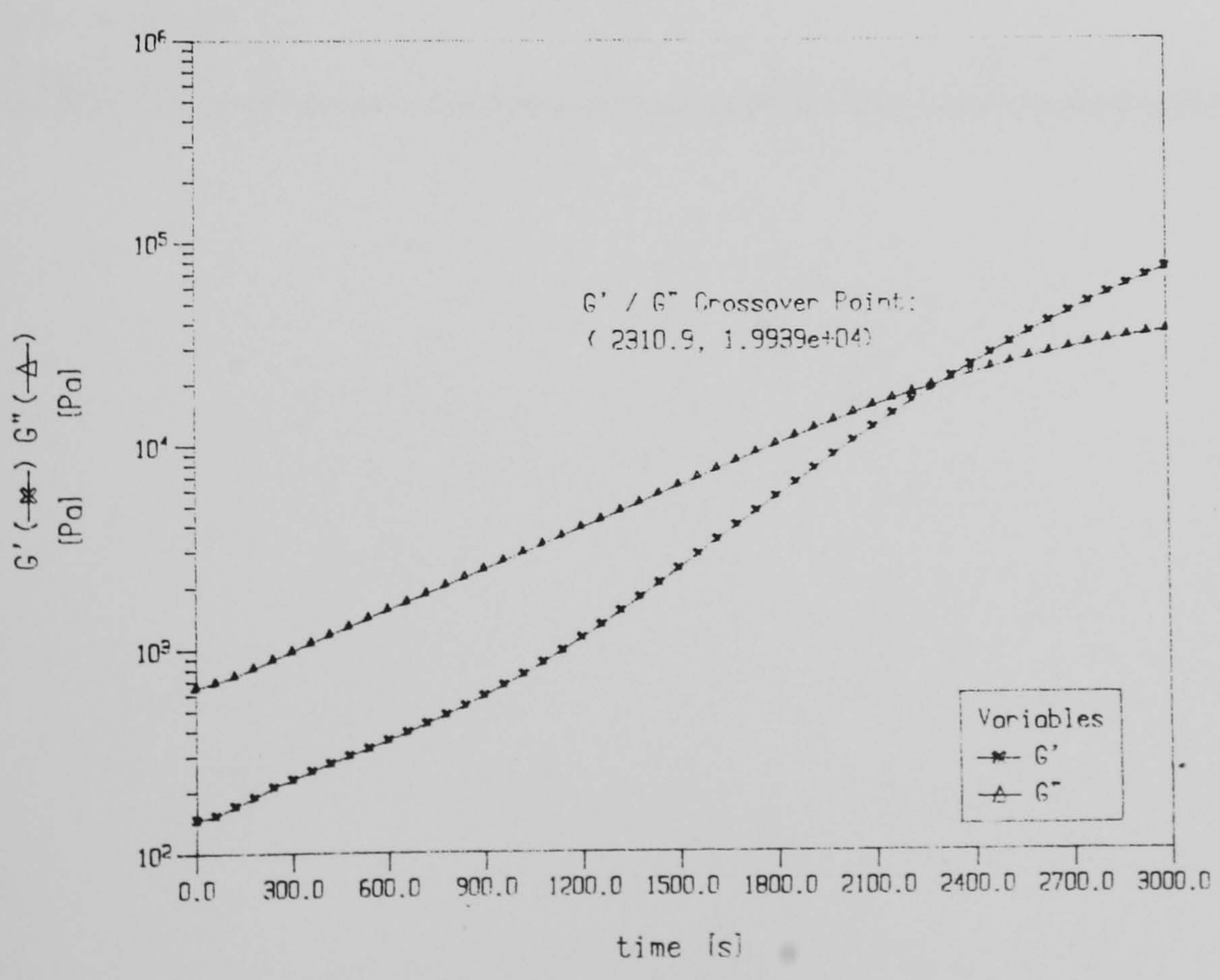


Figure 4.4 Polysulfide curing profile using 10 pph commercial curing agent with TMTD in 10 pph Santicizer 278 plasticiser (replicate)



Experiment 4.2 Experiment involving cure paste mixture containing 10 pph commercial curing agent plus TMTD accelerator in Santicizer 261 plasticiser

Part A:

Liquid polysulfide polymer	LP32C:	100 pph
Part B:		
Curing agent	Commercial curing agent:	10 pph
Plasticiser	Santicizer *261*:	10 pph
Accelerator	Tetramethylthiuramdisulfide (TMTD):	0.5 pph

Table 4.2 Gel points for LP32C polymer cured with 10 pph commercial curing agent, plus TMTD accelerator in 10 pph Santicizer 261 plasticiser

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
10 pph commercial curing agent + 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser	Replicate(1)15 Replicate(2)15	(1)30 (2)23	(1) 45 (2) 38

Figure 4.5 Polysulfide curing profile using 10 pph commercial curing agent with 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser

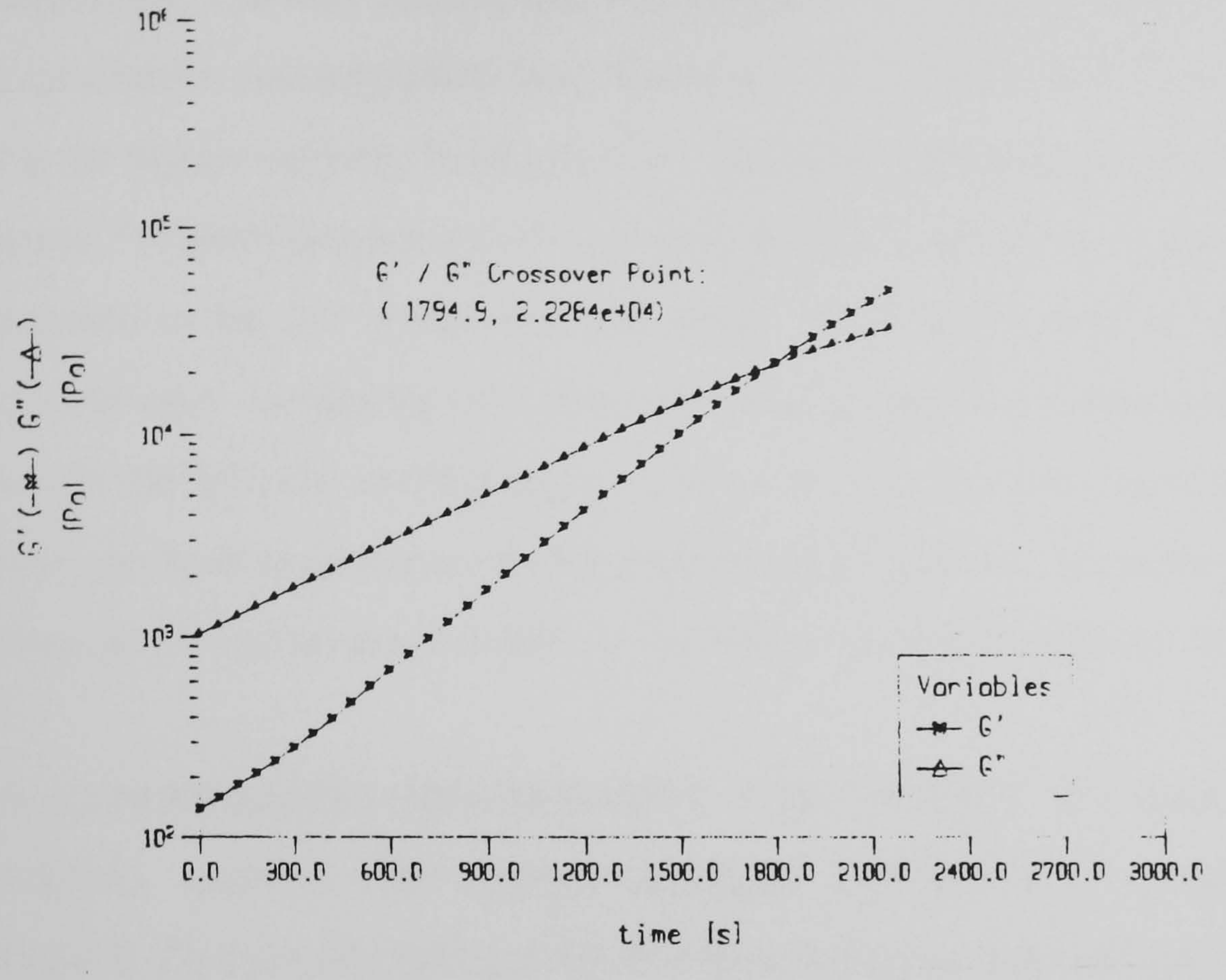
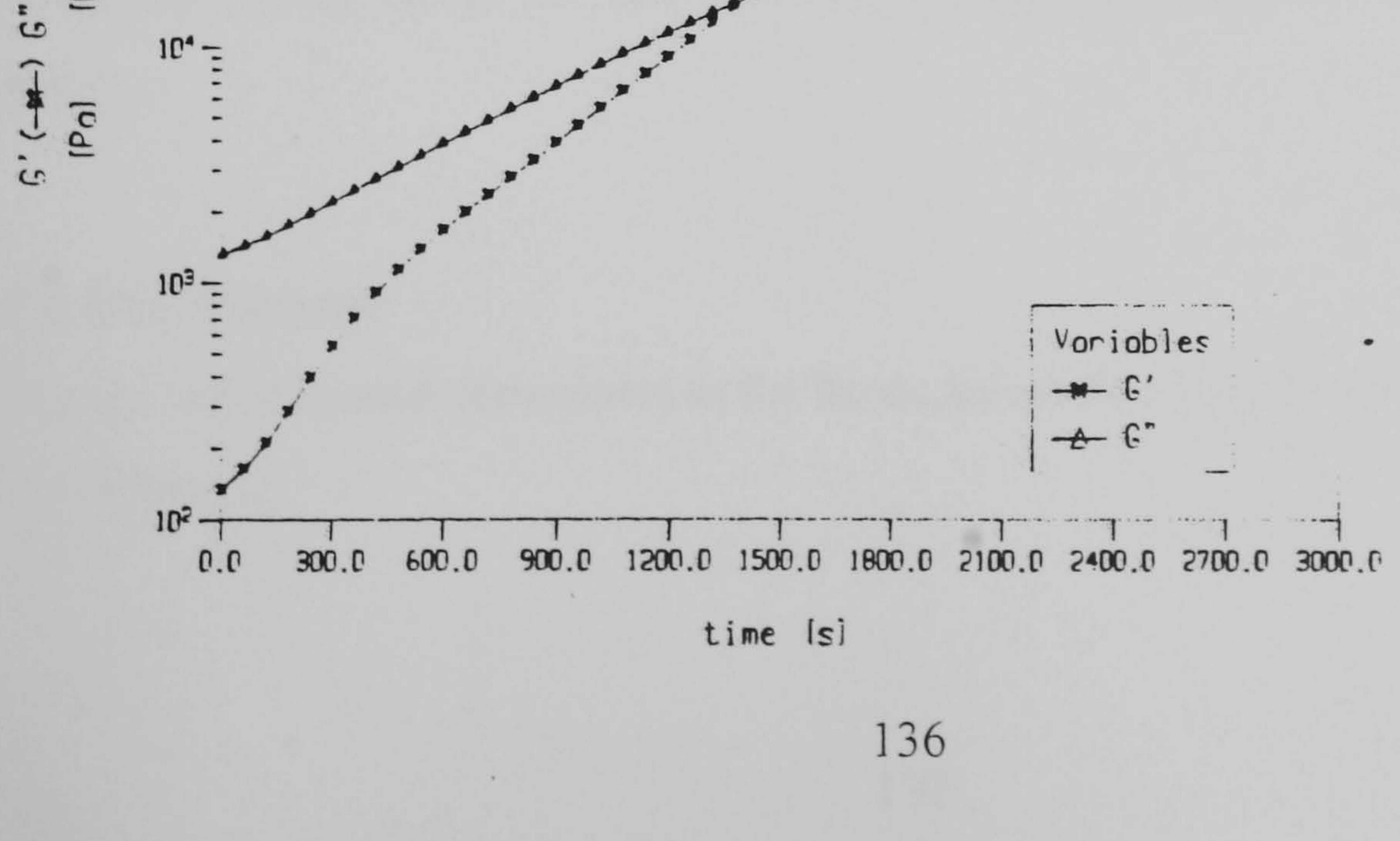


Figure 4.6 Polysulfide curing profile using 10 pph commercial curing agent with 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser (replicate)



4.4.3 Discussion

The results of the experiments using the commercial curing agent show it cures polysulfide reproducibly. The only variable that was changed in the experiments was the plasticiser. The use of a lower viscosity plasticiser, Santicizer 261, resulted in a shorter gel time than when using the higher viscosity Santicizer 278 plasticiser. A possible reason for this is that the more viscous 278 plasticiser mixture is very thick and more difficult to disperse in the polysulfide compared to the 261 plasticised cure paste. These results will be taken as the reference standard when comparing data obtained using sodium birnessite as the curing agent. As a result of the difficulty in obtaining a smooth cure paste using the more viscous Santicizer 278 plasticiser, apart from one set of experiments using Santicizer 278 as the plasticiser for sodium birnessite, all further experiments use the lower viscosity Santicizer 261 plasticiser.

4.5 EXPERIMENTS MONITORING THE EFFECT ON LP32C OF USING NO CURING AGENT OR USING SODIUM BIRNESSITE CURING AGENT AND EITHER TETRAMETHYLTHIURAMDISULFIDE OR NO ACCELERATOR.

4.5.1 Introduction

As sodium birnessite is such an active curing agent,(2) a 1:1 dilution of the sodium birnessite with inert MnO_2 was tested. The following experiments involve using sodium birnessite as a curing agent at different concentrations, with some experimental mixtures containing no curing agent at all. The experiment results listed begin with tests using no curing agent, or no accelerator or no curing agent diluent. These are followed by results showing the use of different combinations of the various cure mixture components to ascertain the effect on polysulfide curing of the sodium birnessite curing agent with or without the other cure additives.

4.5.2 Experimental

The same experimental procedures as for the experiments using the commercial curing agent were followed.

4.5.3 Results

Experiments involving no curing agent but using accelerator and inert MnO_2 diluent:

Experiment 4.3 Experiment involving a cure paste mixture containing only inert manganese dioxide diluent and TMTD accelerator in Santicizer 261 plasticiser:

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C:	100 pph

Part B

Curing Agent:	NONE	0 pph
Curing agent diluent:	Inert manganese dioxide	5 pph
Accelerator:	Tetramethylthiuramdisulfide (TMTD)	0.5 pph
Plasticiser:	Santicizer 261	15 pph

Table 4.3 Gel points for LP32C polymer using 5 pph inert manganese dioxide with 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
5 pph inert MnO_2 + 0.5 pph TMTD in 15 pph Santicizer 261 plasticiser	Replicate(1) 10 Replicate(2) 10	(1) No curing (2) No curing	(1) No curing (2) No curing

Figure 4.7 Polysulfide curing profile for 5 pph inert manganese dioxide with 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser

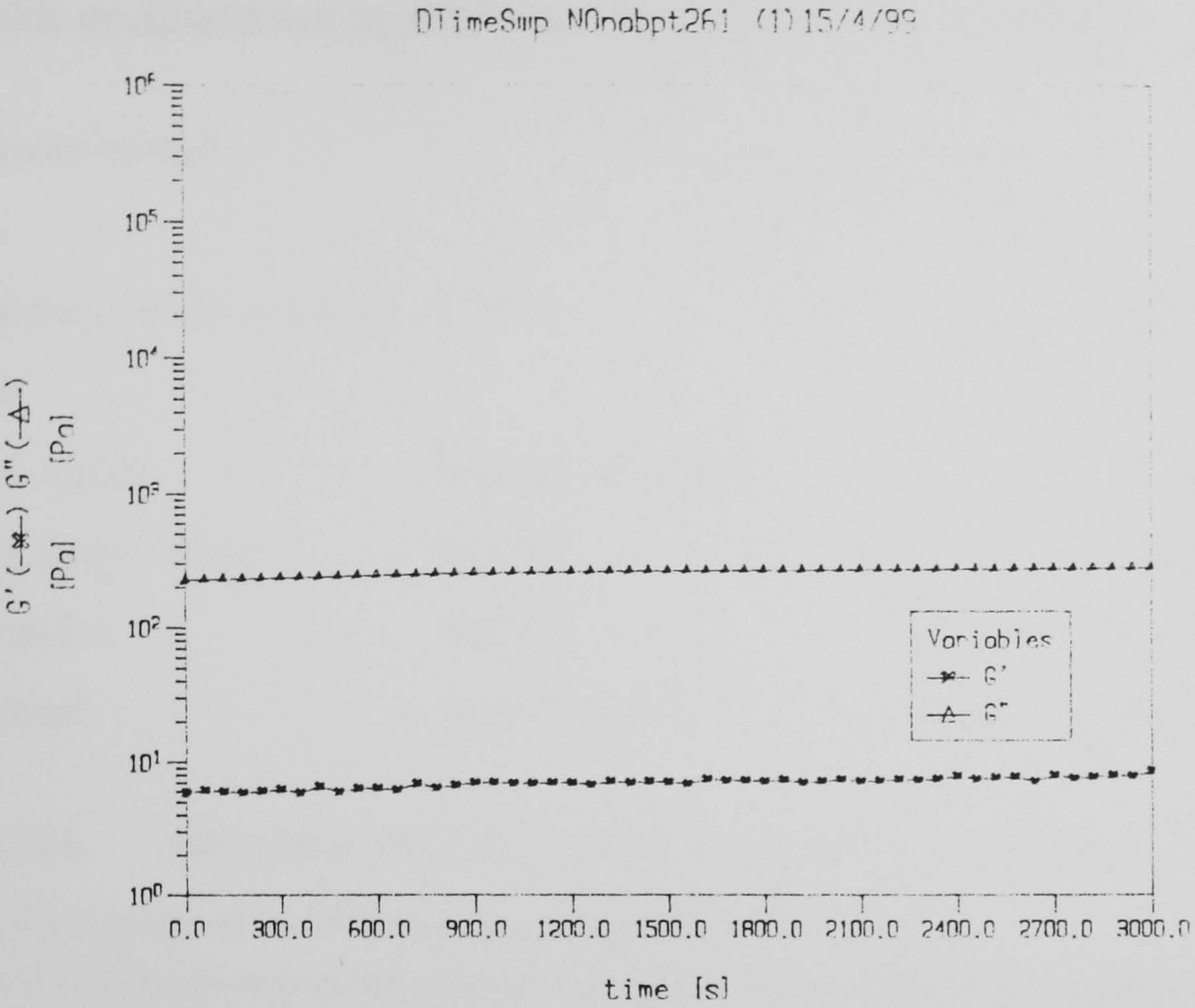
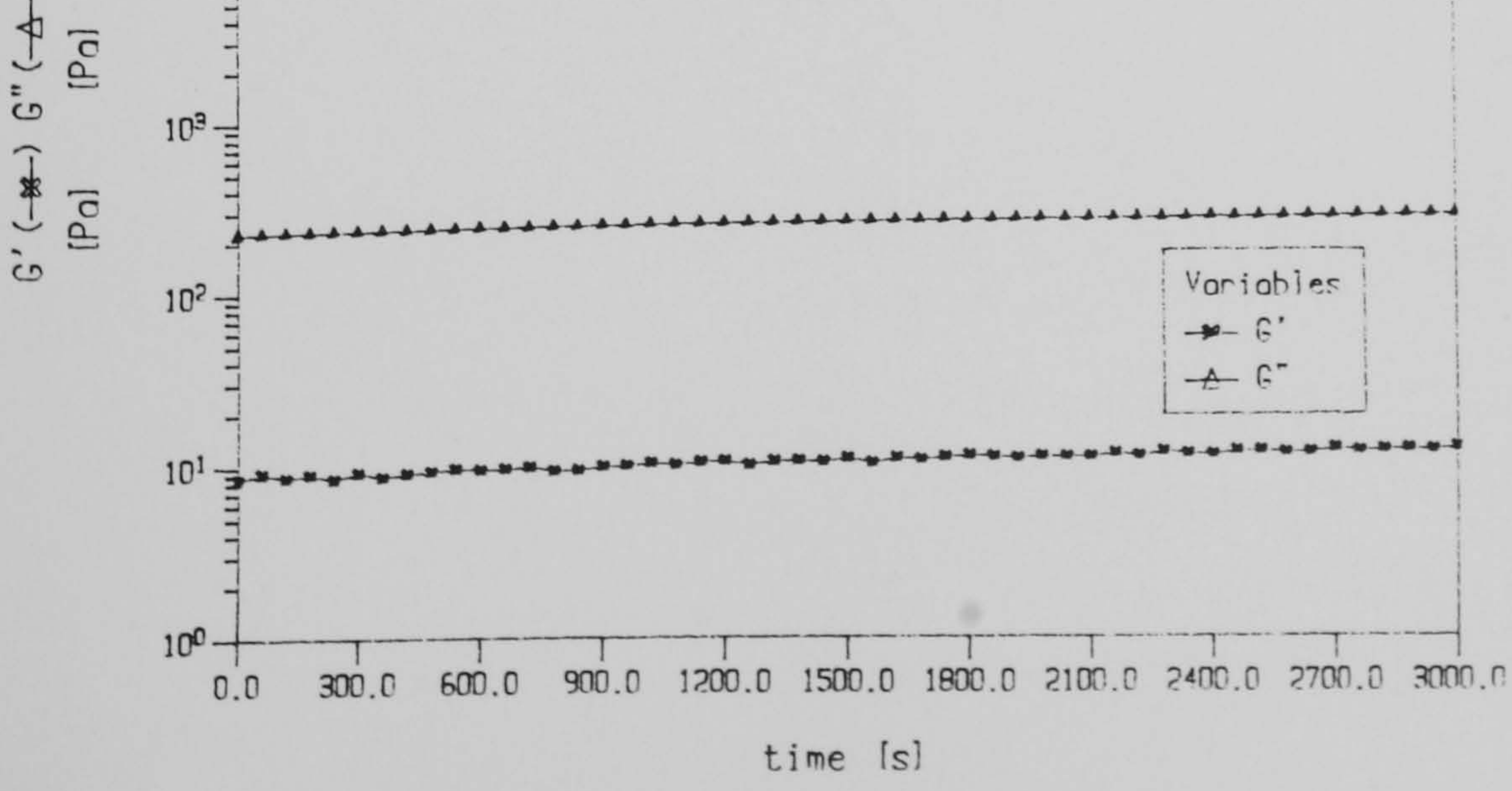


Figure 4.8 Polysulfide curing profile for 5 pph inert manganese dioxide with 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser (replicate)



Experiments involving sodium birnessite as the curing agent but no accelerator:

Experiment 4.4 Experiment involving a cure paste mixture which used 5 pph sodium birnessite no diluent and no accelerator in Santicizer 261 plasticiser

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C:	100 pph

Part B

Curing Agent:	Sodium birnessite	5 pph
Curing agent diluent:	NONE	0 pph
Accelerator:	NONE	0 pph
Plasticiser:	Santicizer 261	15.5 pph

Table 4.4 Gel points for LP32C polymer cured with 5 pph sodium birnessite, undiluted and unnaccelerated in 15.5 pph Santicizer 261 plasticiser

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
5 pph sodium birnessite in 15.5 pph Santicizer 261 plasticiser	(1)10 (2)10	(1)26 (2)24	(1) 36 (2) 34

Figure 4.9 Polysulfide curing profile using 5pph sodium birnessite no accelerator and no diluent in 15.5 pph Santicizer 261 plasticiser

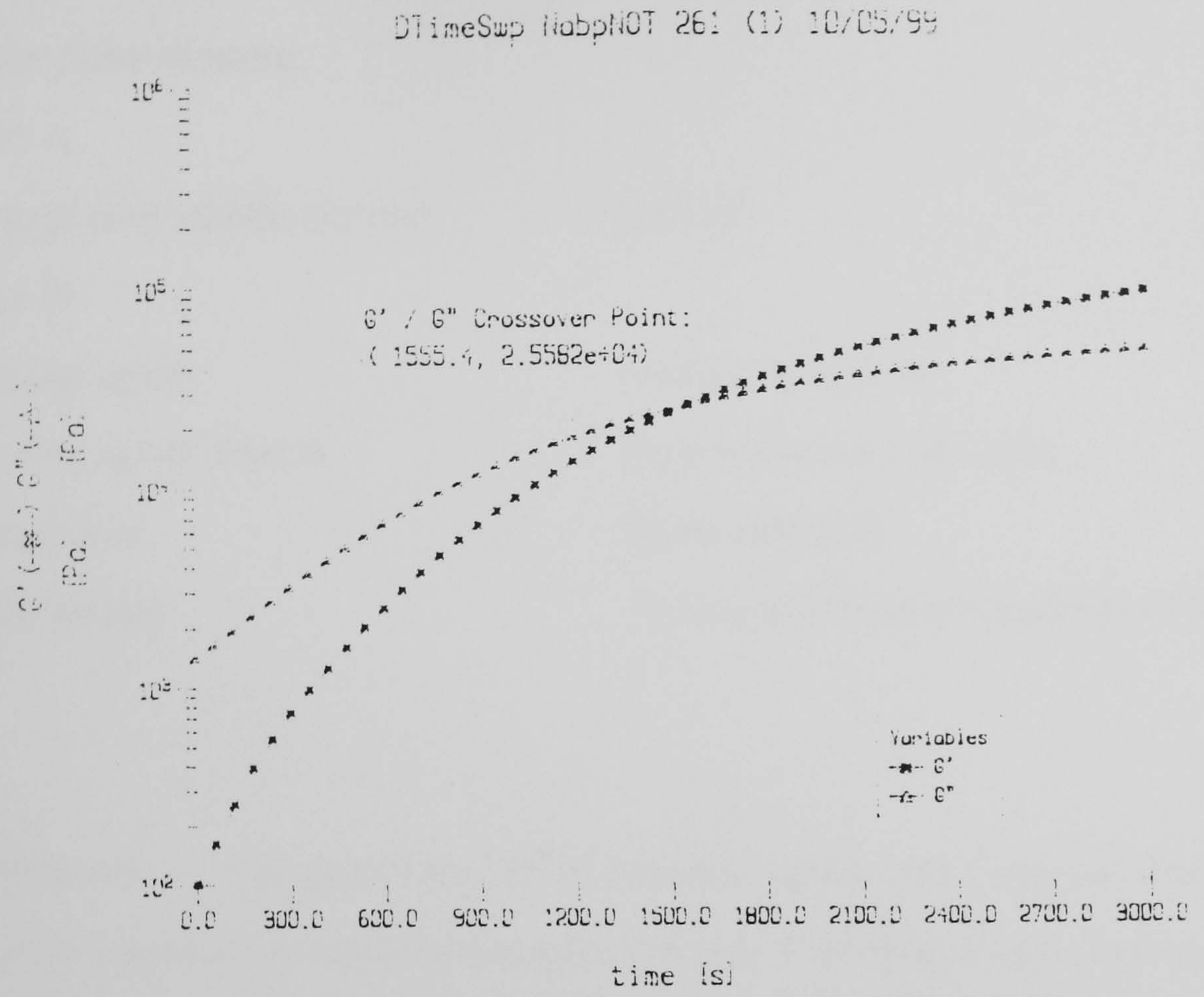
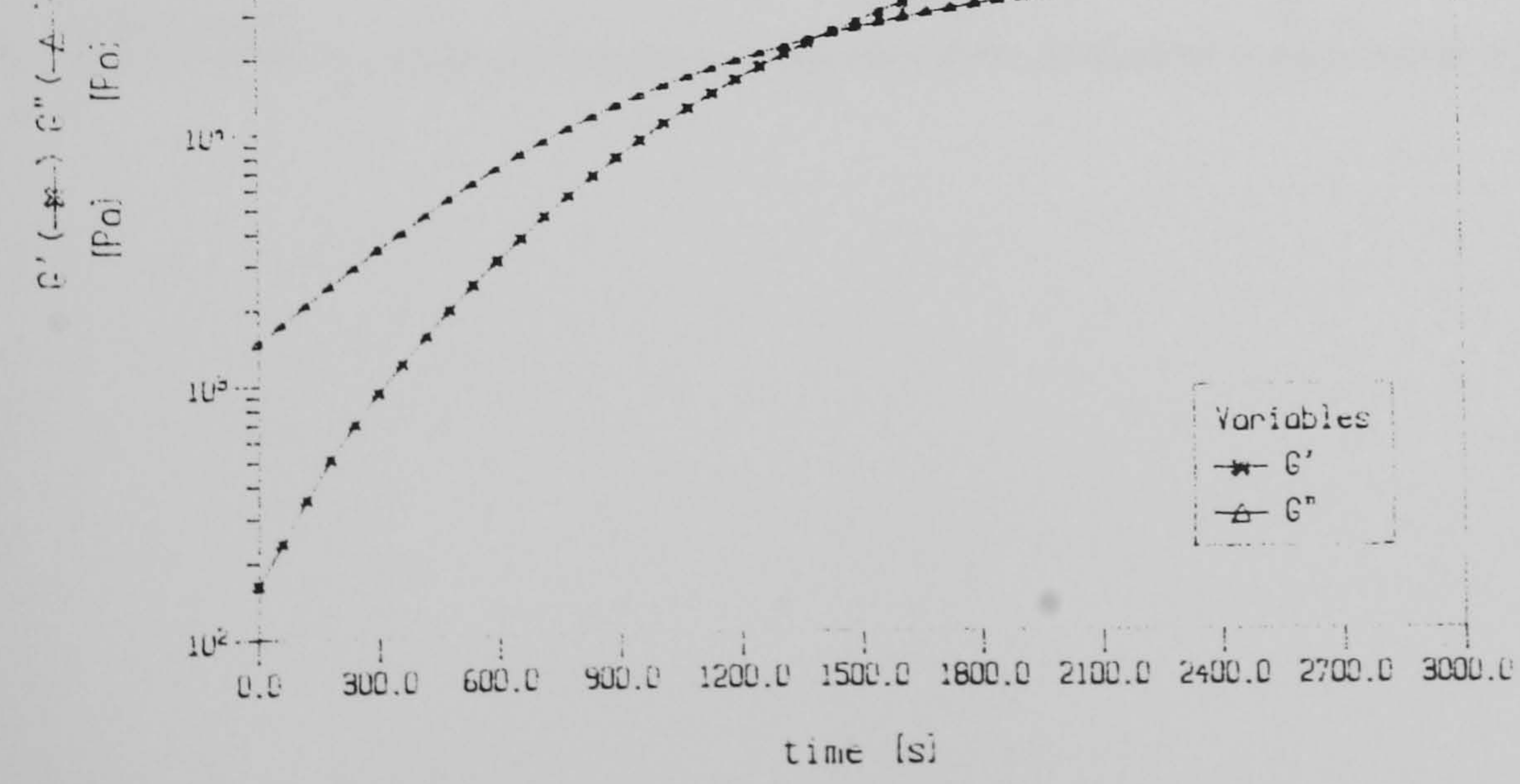


Figure 4.10 Polysulfide curing profile using sodium birnessite. no accelerator and no diluent in 15.5 pph Santicizer 261 plasticiser (replicate)



Experiments using sodium birnessite as a curing agent with TMTD accelerator

Experiment 4.5 Experiment involving cure paste mixture containing sodium birnessite, inert manganese dioxide diluent and TMTD accelerator in Santicizer *278* plasticiser

Cure paste mixture:

Part A

Liquid polysulfide polymer	LP32C:	100 pph
Part B		
Curing agent	Sodium birnessite:	5 pph
Curing agent diluent	Inert manganese dioxide:	5 pph
Plasticiser:	Santicizer 278:	10 pph
Accelerator:	Tetramethylthiuramdisulfide (TMTD)	0.5 pph

Table 4.5 Gel points for LP32C polymer cured with 5 pph sodium birnessite with 5 pph inert manganese dioxide diluent plus 0.5 pph TMTD in10 pph plasticiser Santicizer 278

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
5 pph sodium birnessite in 5pph inert MnO_2 with 0.5 pph TMTD in 10 pph 278 plasticiser	(1)11 (2)12	(1)22 (2)20	(1) 33 (2) 32

Figure 4.11 Polysulfide curing profile using 5 pph sodium birnessite with 5 pph inert manganese dioxide diluent plus 0.5 pph TMTD with plasticiser Santicizer 278

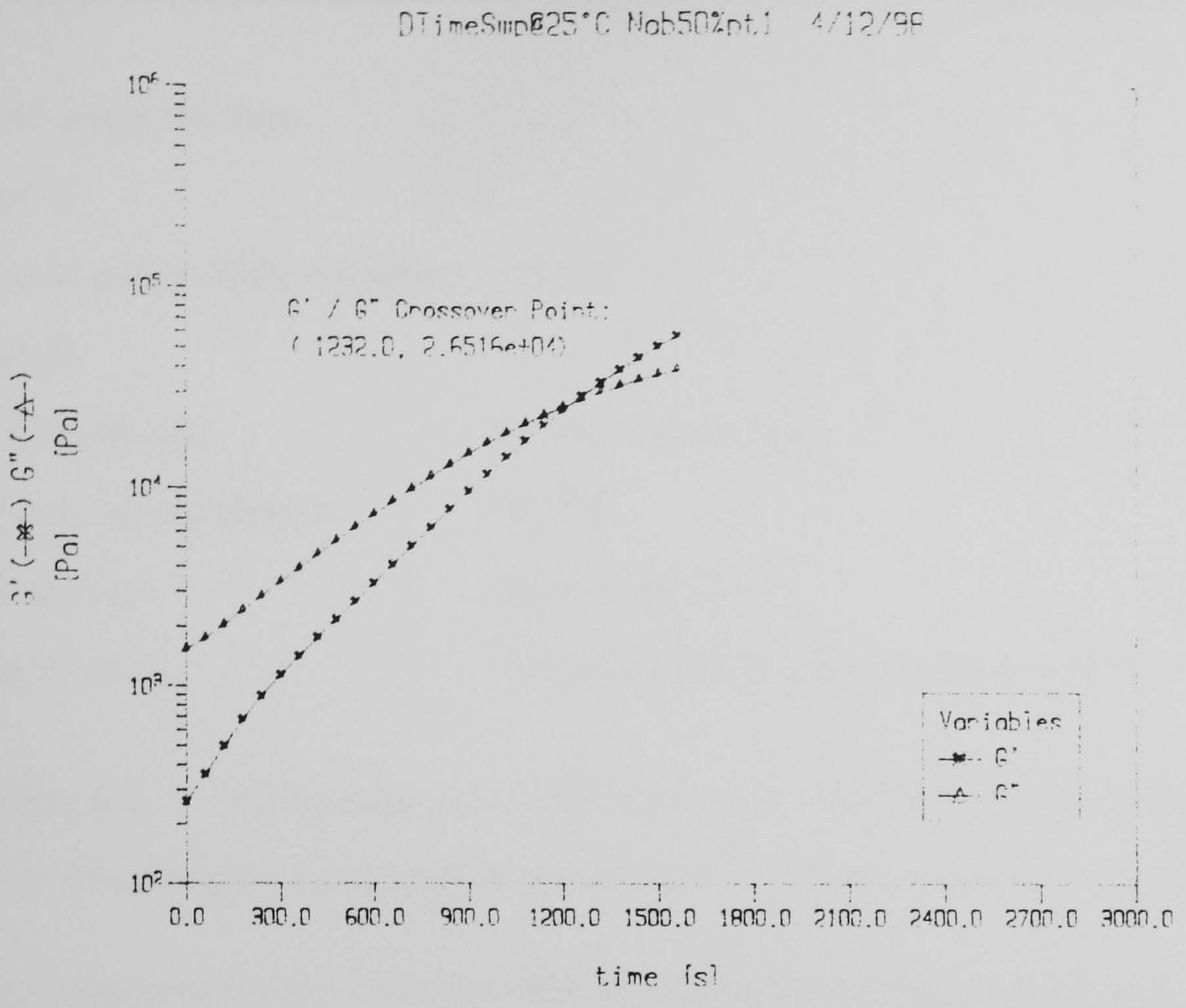
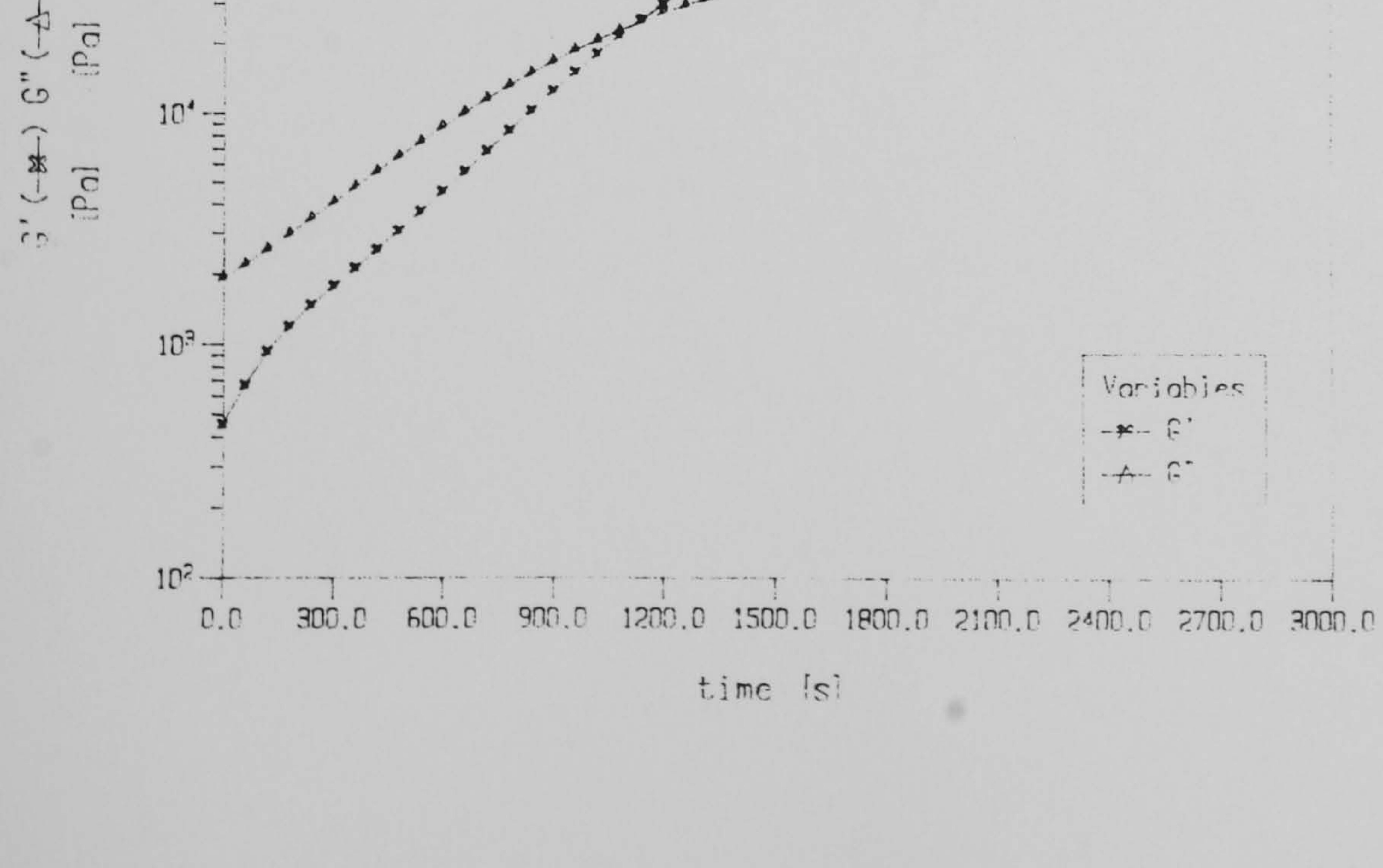


Figure 4.12 Polysulfide curing profile using 5 pph sodium birnessite with 5 pph inert manganese dioxide diluent plus TMTD with plasticiser Santicizer 278 (replicate)



Experiment 4.6 Experiment involving a cure paste mixture containing no curing agent diluent but containing TMTD accelerator in Santicizer 261 plasticiser

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C	100 pph

Part B

Curing agent:	Sodium birnessite	5 pph
Curing agent diluent:	NONE	0 pph
Plasticiser:	Santicizer 261	15 pph
Accelerator:	Tetramethylthiuramdisulfide (TMTD)	0.5 pph

Table 4.6 Gel points for LP32C polymer cured with 5 pph sodium birnessite with no inert diluent, plus with TMTD accelerator in 15 pph plasticiser Santicizer 261

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
5 pph sodium birnessite composite +0.5 pph TMTD in 15 pph Santicizer 261 plasticiser	(1)15 (2)15	(1)36 (2)31	(1) 51 (2) 46

Figure 4.13 Polysulfide curing profile using 5 pph sodium birnessite with no inert diluent. 0.5 pph TMTD accelerator plus 15 pph plasticiser Santicizer 261

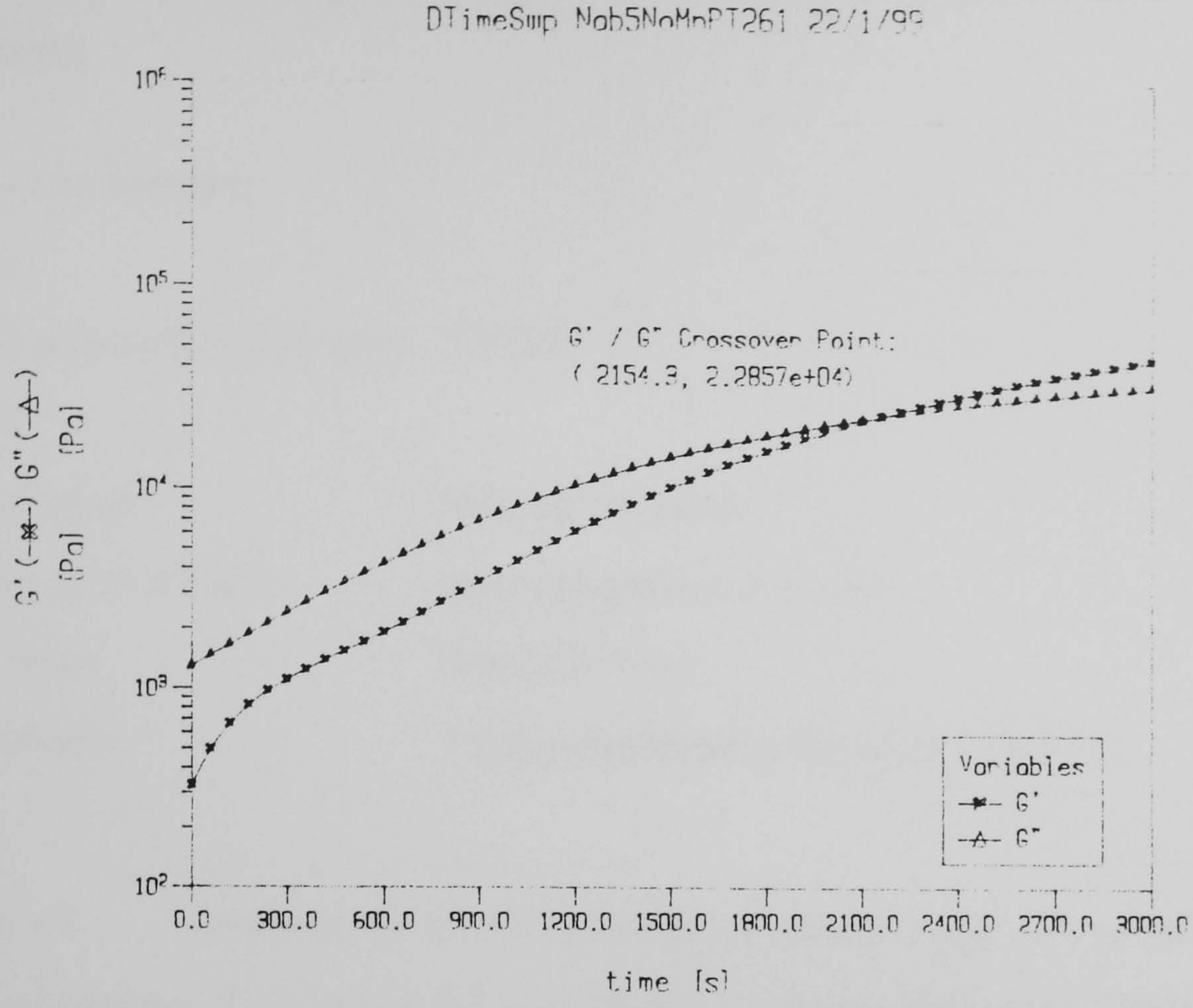
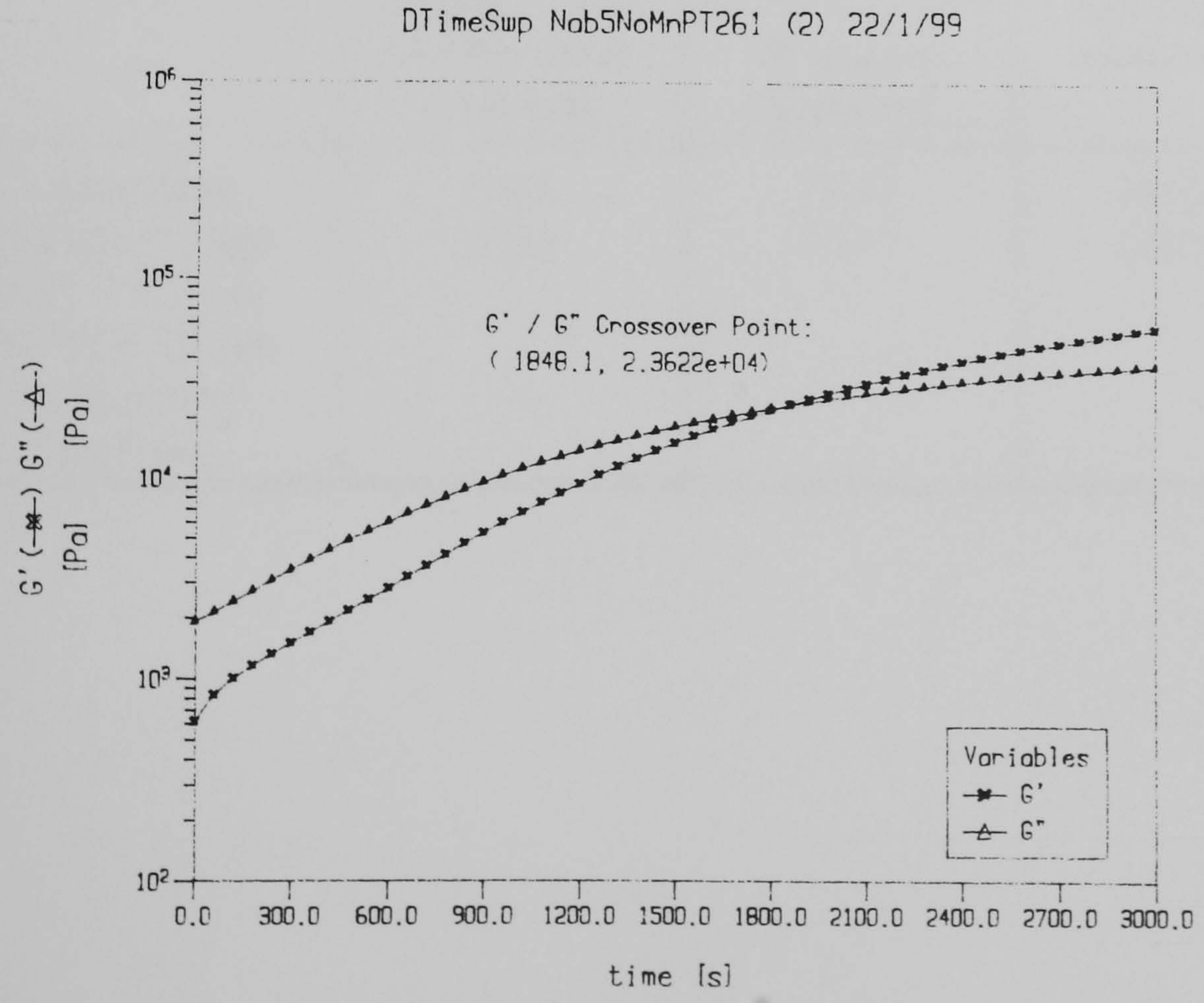


Figure 4.14 Polysulfide curing profile using 5 pph sodium birnessite with no inert diluent. 0.5 pph TMTD accelerator plus 15 pph plasticiser Santicizer 261(replicate)



Experiment 4.7 Experiment involving 5 pph sodium birnessite cure paste mixture containing inert manganese dioxide diluent and TMTD accelerator in Santicizer 261 plasticiser

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C	100 pph

Part B

Curing agent:	Sodium birnessite:	5 pph
Curing agent diluent:	Inert manganese dioxide:	5 pph
Plasticiser:	Santicizer *261*:	10 pph
Accelerator:	Tetramethylthiuramdisulfide (TMTD):	0.5 pph

Table 4.7 Gel points for LP32C polymer cured with 5 pph sodium birnessite with 5 pph inert manganese dioxide plus 0.5 pph TMTD in 10 pph plasticiser Santicizer 261

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
5 pph sodium birnessite + 5 pph MnO_2 + 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser	(1)15 (2)15	(1)19 (2)17	(1) 34 (2) 32

Figure 4.15 Polysulfide curing profile using 5 pph sodium birnessite with 5 pph inert manganese dioxide, 0.5 pph TMTD plus 10 pph plasticiser Santicizer 261

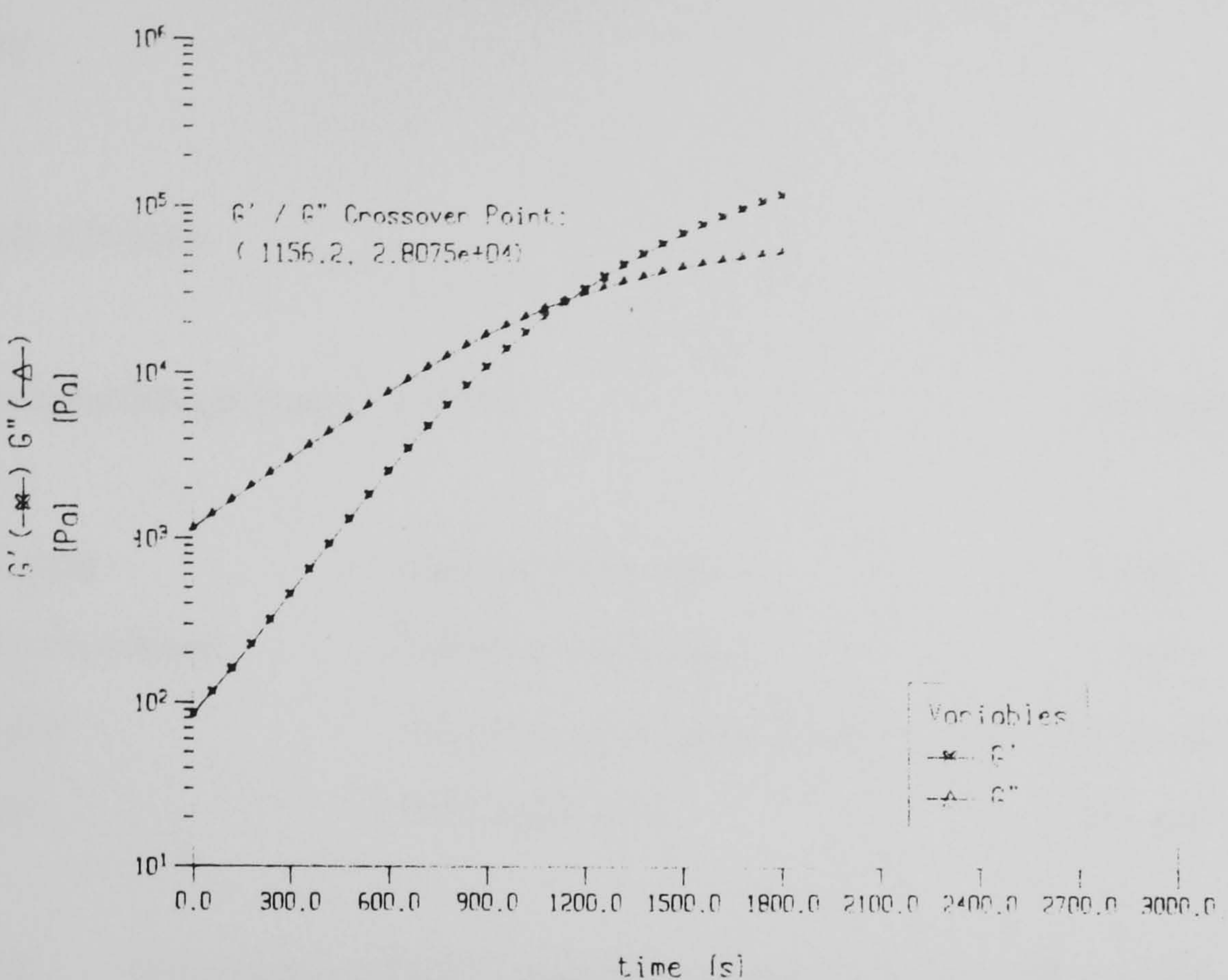
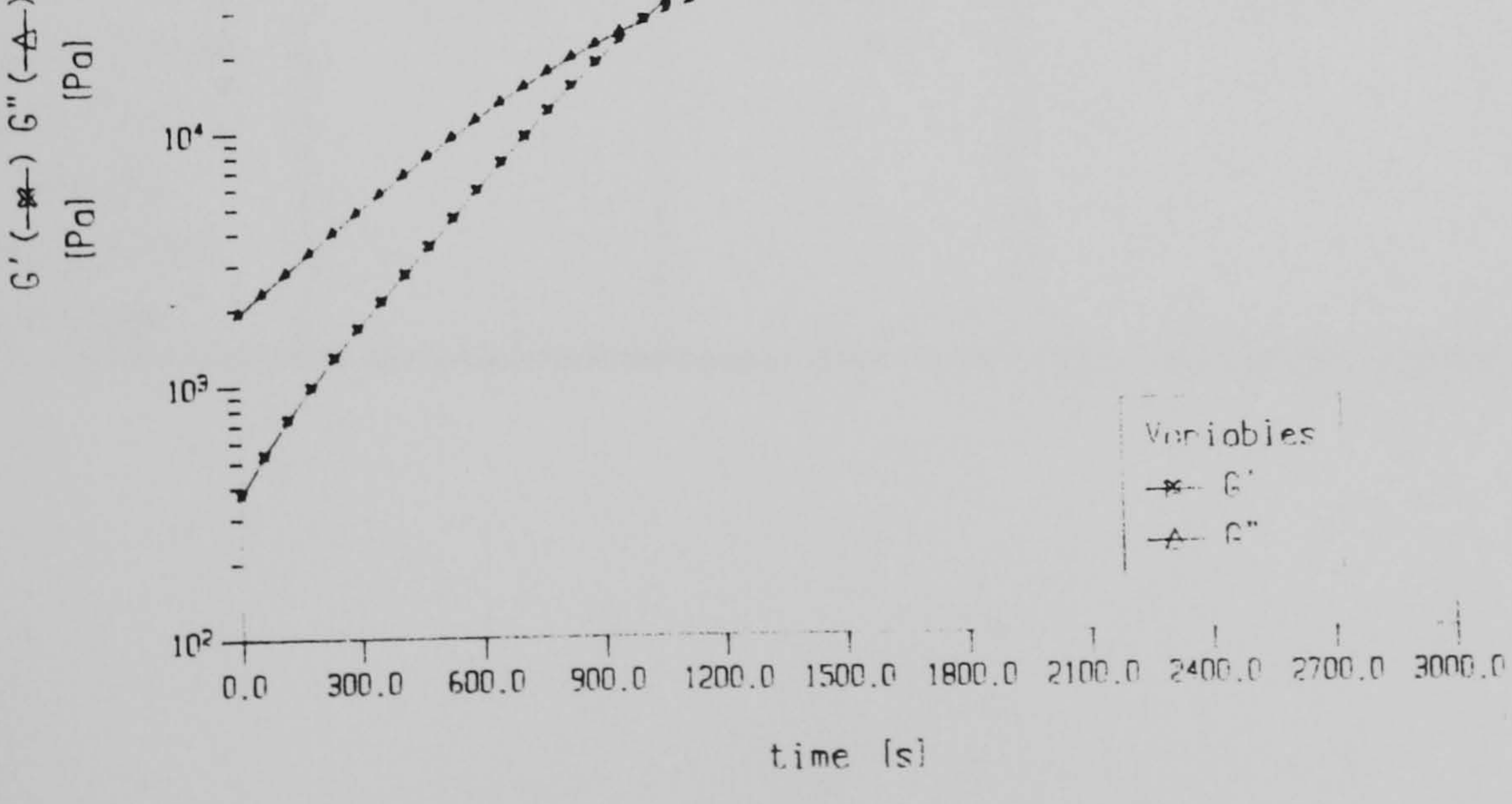


Figure 4.16 Polysulfide curing profile using 5 pph sodium birnessite with 5pph inert manganese dioxide diluent, 0.5 pph TMTD, plus 10 pph plasticiser Santicizer 261(replicate)



Experiment 4.8 Experiment involving a cure paste mixture which used sodium birnessite, 5 pph calcium carbonate as a diluent and TMTD accelerator in Santicizer 261 plasticiser

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C:	100 pph

Part B

Curing Agent:	Sodium birnessite	5 pph
Curing agent diluent:	Calcium carbonate	5 pph
Accelerator:	Tetramethylthiuramdisulfide (TMTD)	0.5 pph
Plasticiser	Santicizer 261	10 pph

Table 4.8 Gel points for LP32C polymer cured with 5 pph sodium birnessite plus 5 pph calcium carbonate and 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
5 pph sodium birnessite + 5 pph calcium carbonate +0.5 pph TMTD in 10 pph Santicizer 261 plasticiser	(1)15 (2)15	(1) 10 (2)10	(1) 25 (2) 25

Figure 4.17 Polysulfide curing profile using 5 pph sodium birnessite, 5 pph calcium carbonate diluent with 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser

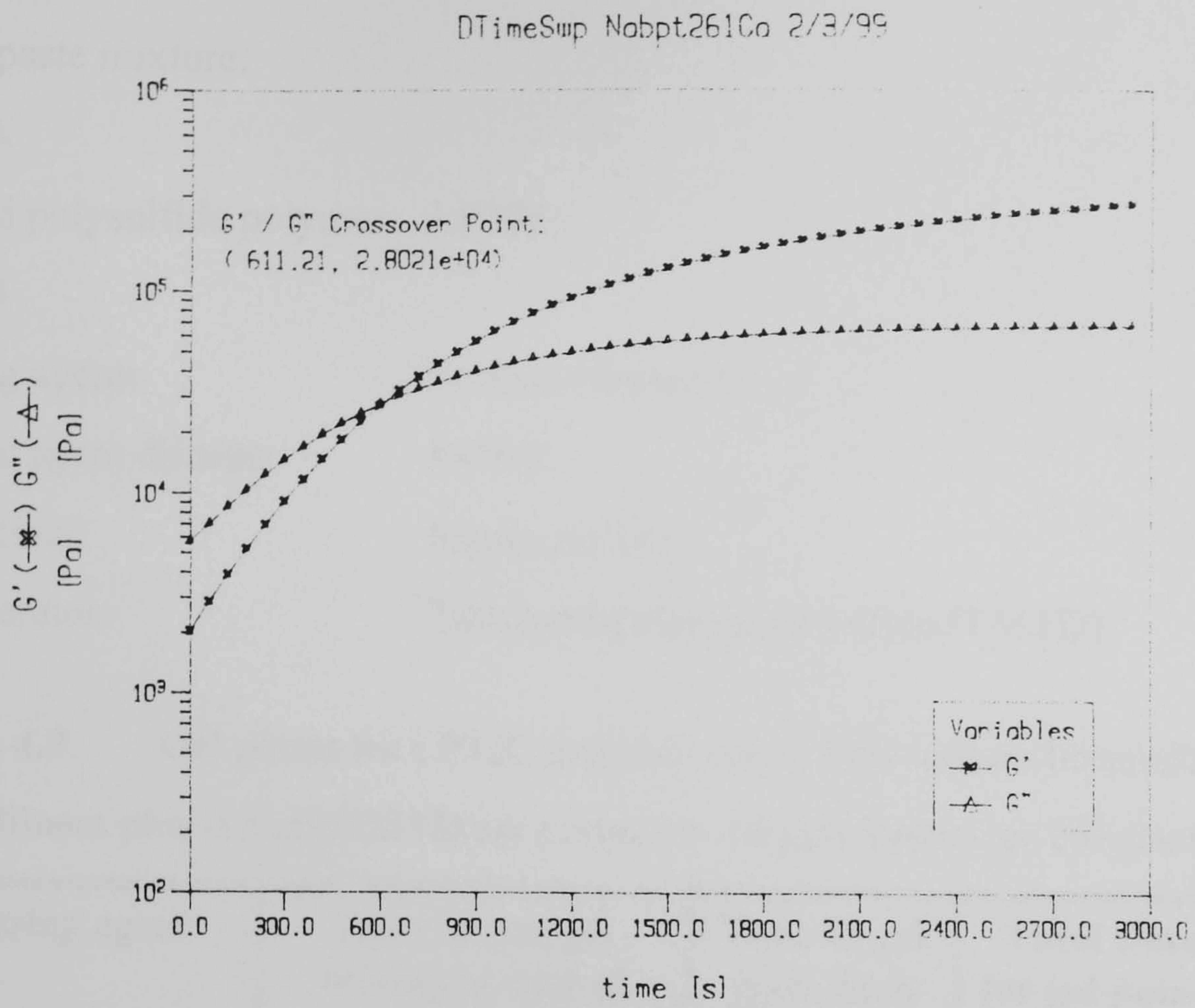
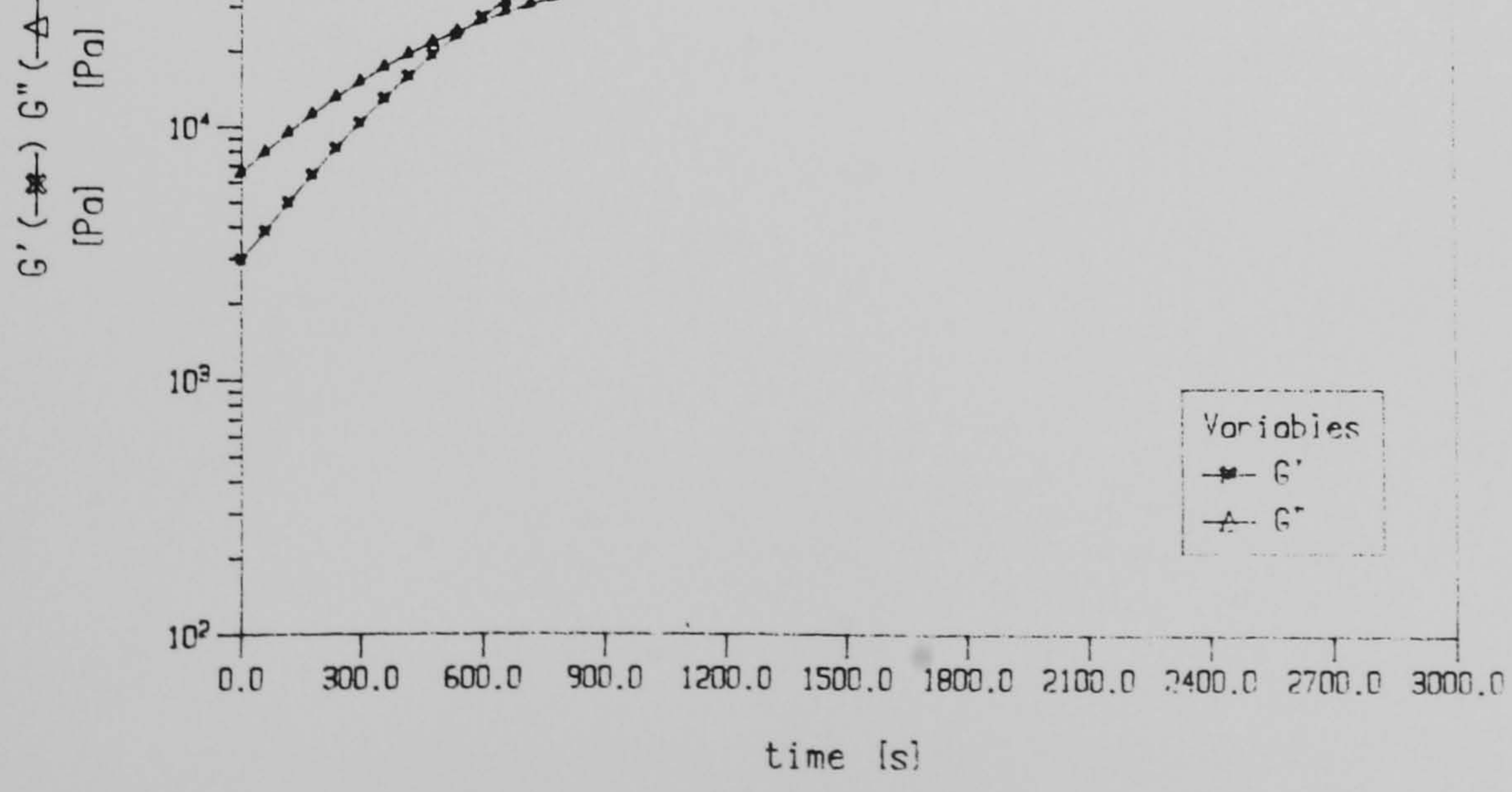


Figure 4.18 Polysulfide curing profile using 5 pph sodium birnessite, 5 pph calcium carbonate diluent with 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser (replicate)



Experiment 4.9 Experiment involving a cure paste containing 4 pph sodium birnessite, no curing agent diluent but containing TMTD accelerator in Santicizer 261 plasticiser.

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C:	100 pph

Part B

Curing agent:	Sodium birnessite:	4 pph
Curing agent diluent:	NONE:	0 pph
Plasticiser:	Santicizer 261:	16 pph
Accelerator:	Tetramethylthiuramdisulfide (TMTD):	0.5 pph

Table 4.9 Gel points for LP32C polymer cured with sodium birnessite at 4 pph with no inert diluent plus 0.5 pphTMTD accelerator in 16 pph Santicizer 261plasticiser

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
4 pph sodium birnessite + 0.5 pph TMTD in 16 pph Santicizer 261 plasticiser	(1)15 (2)15	(1)111 (2)108	(1) 126 (2) 123

Figure 4.19 Polysulfide curing profile using 4 pph sodium birnessite, no inert diluent plus with 0.5 pph TMTD in 16 pph Santicizer 261 plasticiser

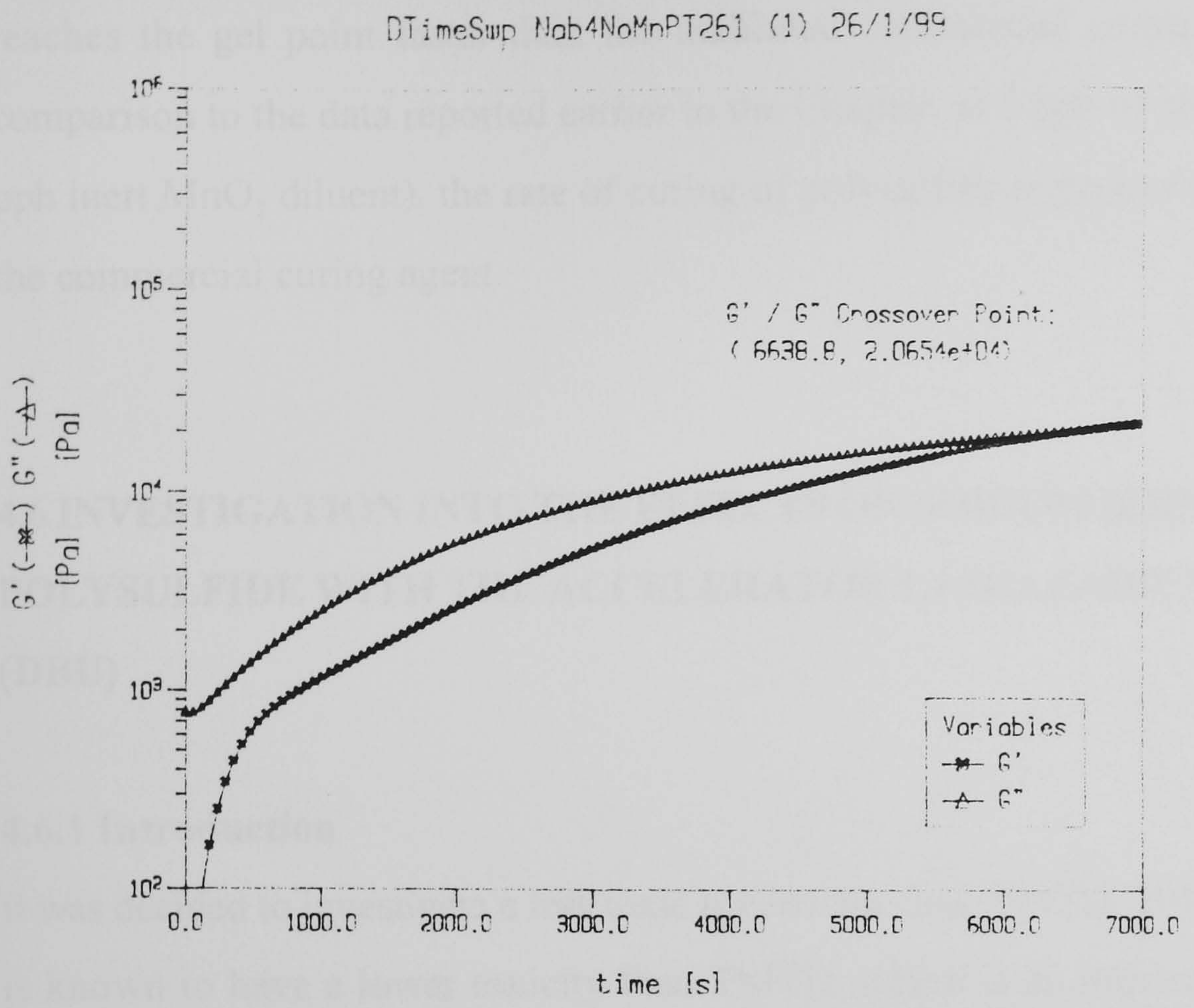
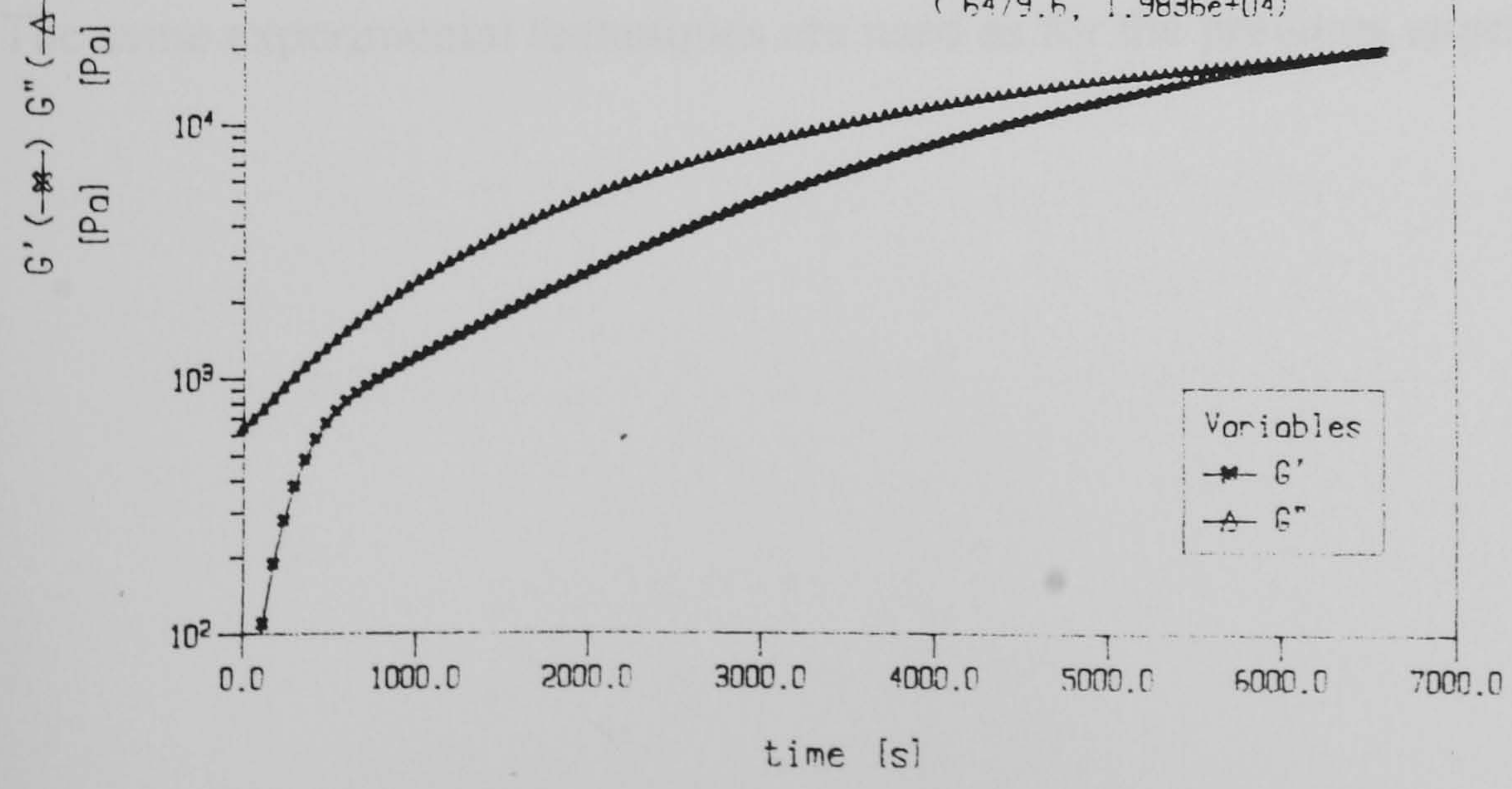


Figure 4.20 Polysulfide curing profile using 4 pph sodium birnessite, no inert diluent plus with 0.5 pph TMTD in 16 pph Santicizer 261 plasticiser (replicate)



4.5.4 Discussion

From these results it can be seen that the inert MnO_2 diluted sodium birnessite curing mixture reaches the gel point faster than the undiluted commercial curing agent. Importantly in comparison to the data reported earlier in the Chapter. at 5 pph of sodium birnessite (with 5 pph inert MnO_2 diluent). the rate of curing of polysulfide is greater than that using 5 pph of the commercial curing agent.

4.6 INVESTIGATION INTO THE EFFECTS ON SODIUM BIRNESSITE CURING OF POLYSULFIDE WITH THE ACCELERATOR 1,4-DIAZABICYCLO(2.2.2)OCTANE (DBU)

4.6.1 Introduction

It was decided to investigate a less toxic accelerator than TMTD. DBU, a 'basic accelerator', is known to have a lower toxicity than TMTD, which is an important consideration in the environmental and health and safety aspects of the polysulfide sealant formulation. The accelerator, although more expensive than TMTD, is used in cure pastes with the commercial curing agent, and it works because its alkalinity in the liquid polysulfide helps form RS- ions which react with RS radicals forming the desired R-S-S-R linkages.(17) The amount of 1,4-diazabicyclo (2.2.2) octane (DBU) accelerator used in this work was kept at 0.5 pph: the same as for the TMTD.

4.6.2 Experimental

The same experimental techniques are used as for the previous experiments.

4.6.3 Results

Experiments involving no curing agent but using DBU accelerator and inert $CaCO_3$ diluent:

Experiment 4.10: Experiment involving a cure paste mixture containing only inert $CaCO_3$ diluent and DBU accelerator in Santicizer 261 plasticiser:

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C:	100 pph

Part B

Curing agent:	NONE	0 pph
Curing agent diluent:	Calcium carbonate	5 pph
Accelerator:	1.4-Diazabicyclo(2.2.2)octane (DBU)	0.5 pph
Plasticiser	Santicizer 261	15 pph

Table 4.10 Gel points for LP32C polymer with added 5 pph inert $CaCO_3$ with 0.5 pph DBU in 15 pph Santicizer 261 plasticiser

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
5 pph inert $CaCO_3$ + 0.5 pph DBU in 15 pph Santicizer 261 plasticiser	Replicate(1) 10 Replicate(2) 10	(1) No curing (2) No curing	(1) No curing (2) No curing

Figure 4.21 Polysulfide curing profile using no curing agent. 5 pph inert $CaCO_3$ with 0.5 pph DBU in 15 pph Santicizer 261 plasticiser

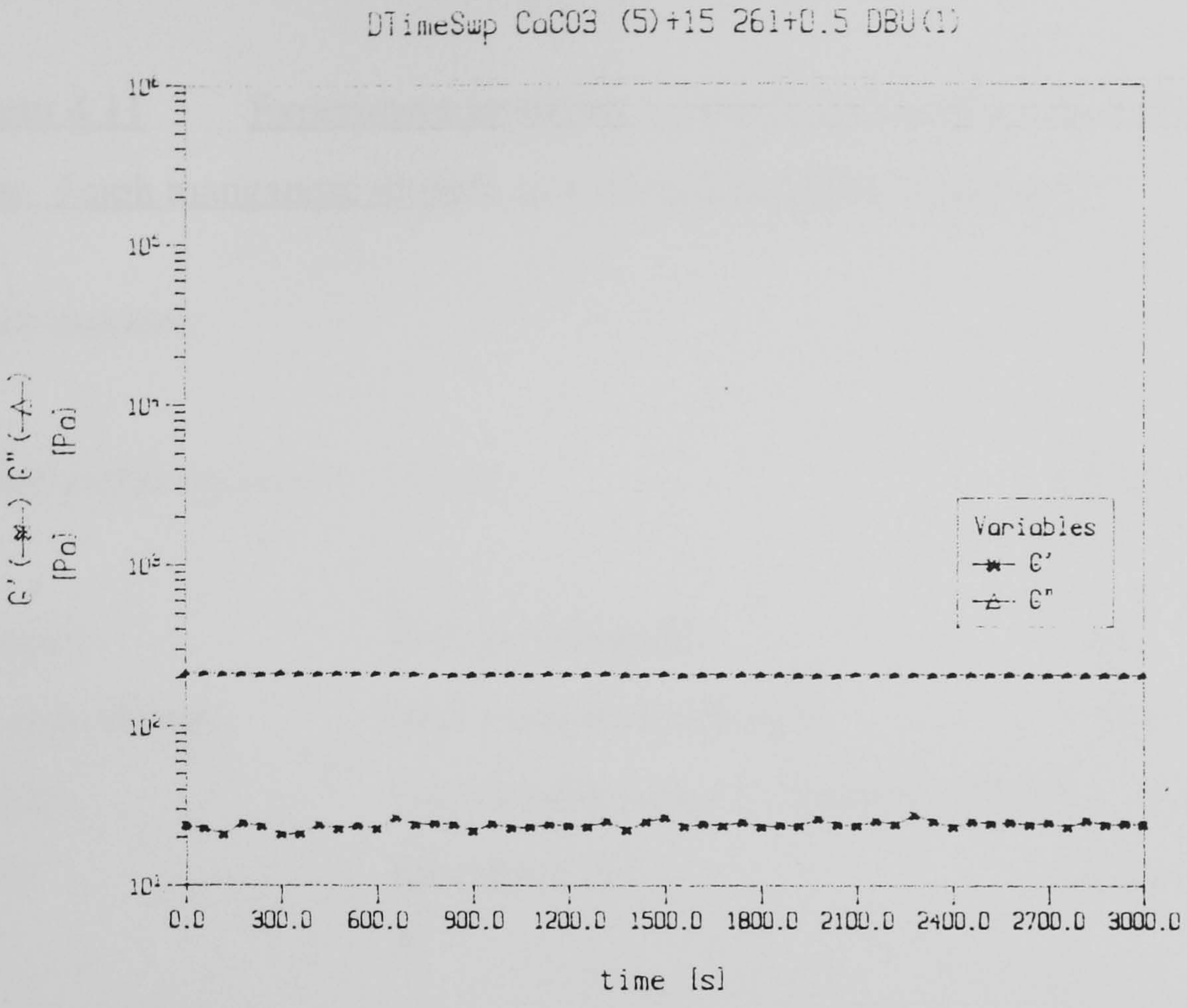
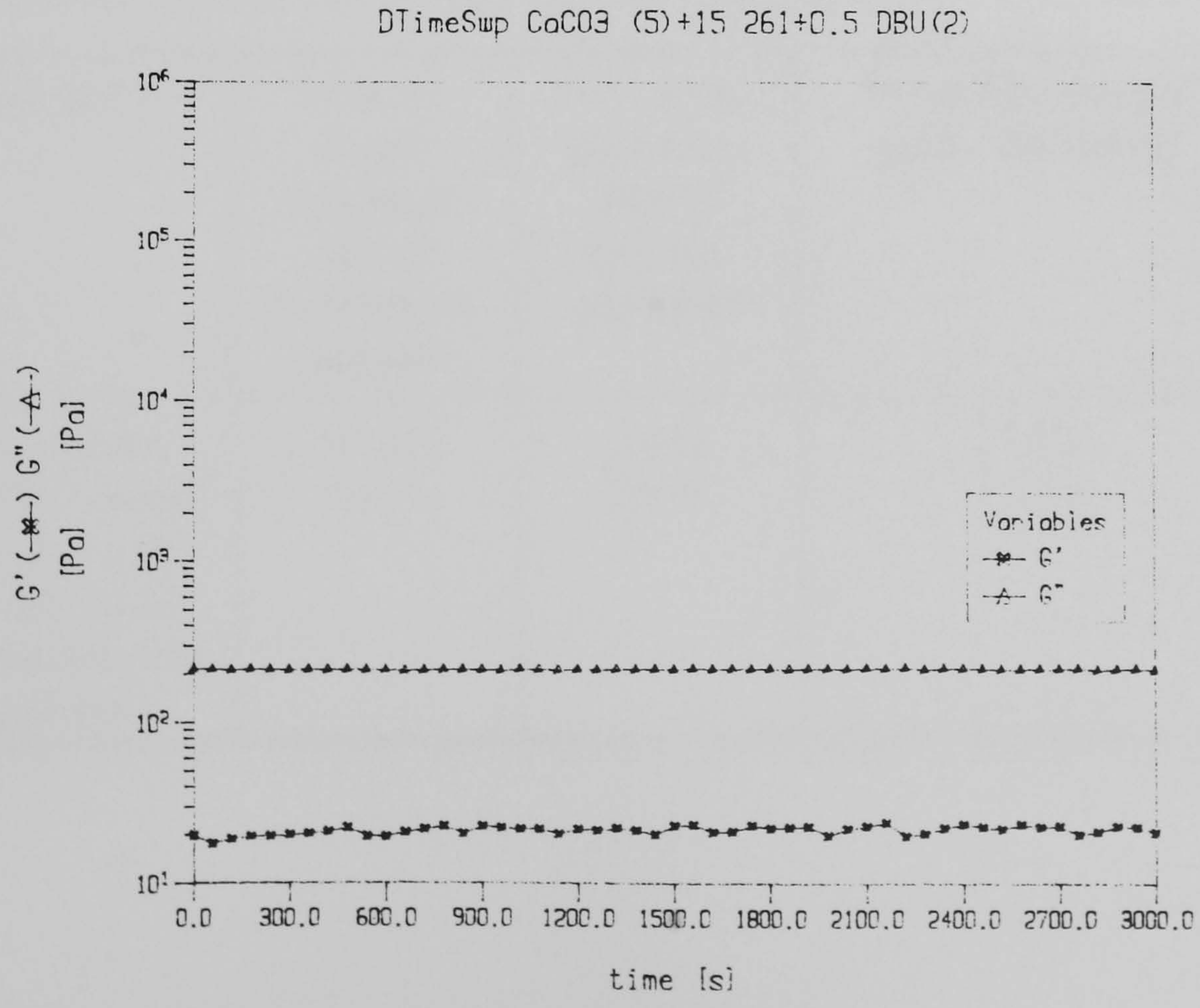


Figure 4.22 Polysulfide curing profile using no curing agent. 5 pph inert $CaCO_3$ with 0.5 pph DBU in Santicizer 261 plasticiser (replicate)



Experiments using sodium birnessite curing agent, inert MnO_2 diluent and DBU as the accelerator:

Experiment 4.11 Experiment involving a cure paste mixture which used 5pph sodium birnessite, 5 pph manganese dioxide as a diluent and DBU accelerator

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C:	100 pph

Part B

Curing agent:	Sodium birnessite	5 pph
Curing agent diluent:	Inert manganese dioxide	5 pph
Accelerator:	1,4-Diazabicyclo(2.2.2)octane (DBU)	0.5 pph
Plasticiser	Santicizer 261	10 pph

Table 4.11 Gel points for LP32C polymer cured with 5 pph sodium birnessite plus 5 pph inert manganese dioxide with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser.

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
5 pph sodium birnessite + 5 pph inert MnO_2 + 0.5 pph DBU in 10 pph Santicizer 261 plasticiser	(1) 10 (2) 10	(1) 13 (2) 15	(1) 23 (2) 25

Figure 4.23 Polysulfide curing profile using 5 pph sodium birnessite plus 5 pph inert manganese dioxide with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser

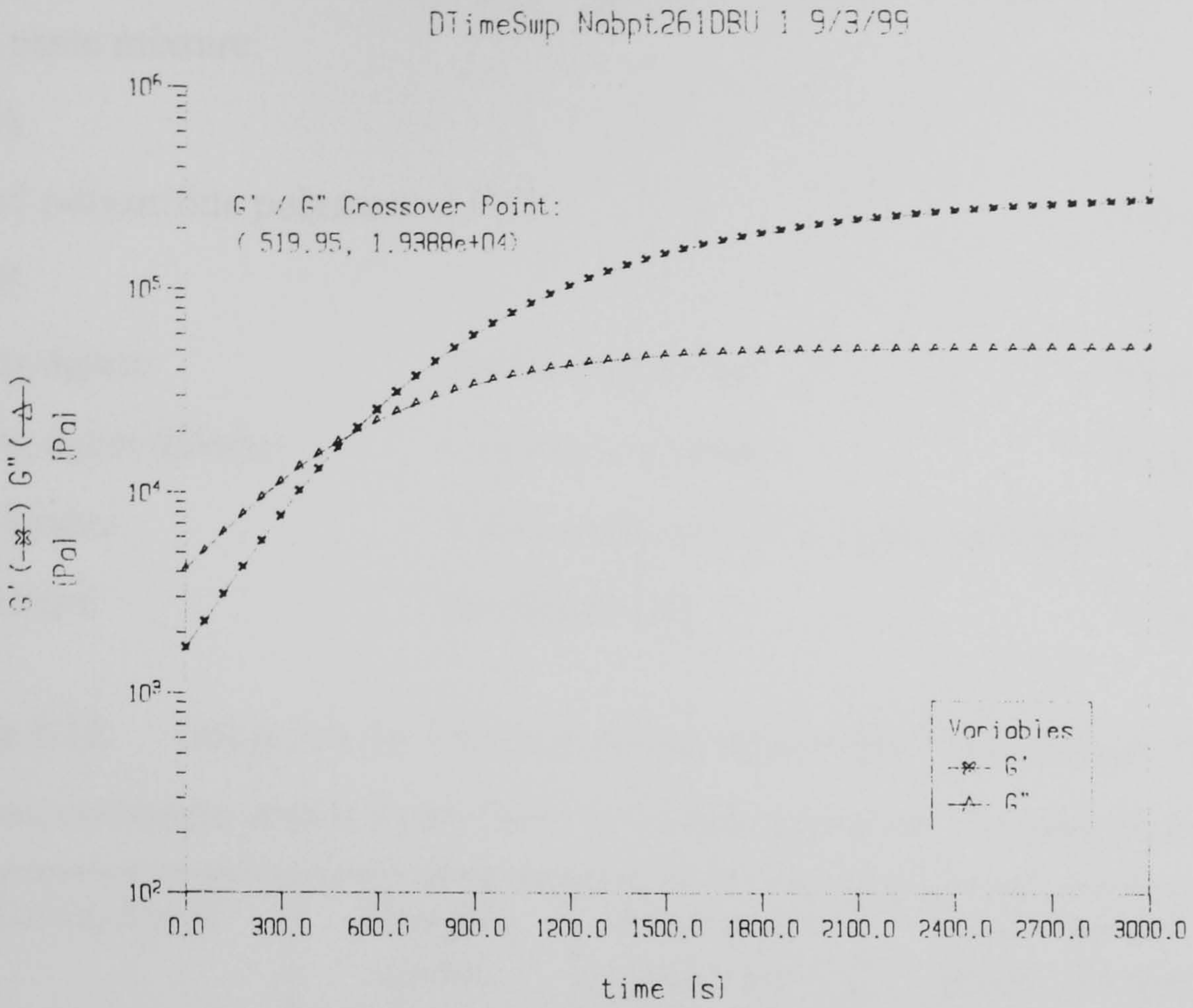
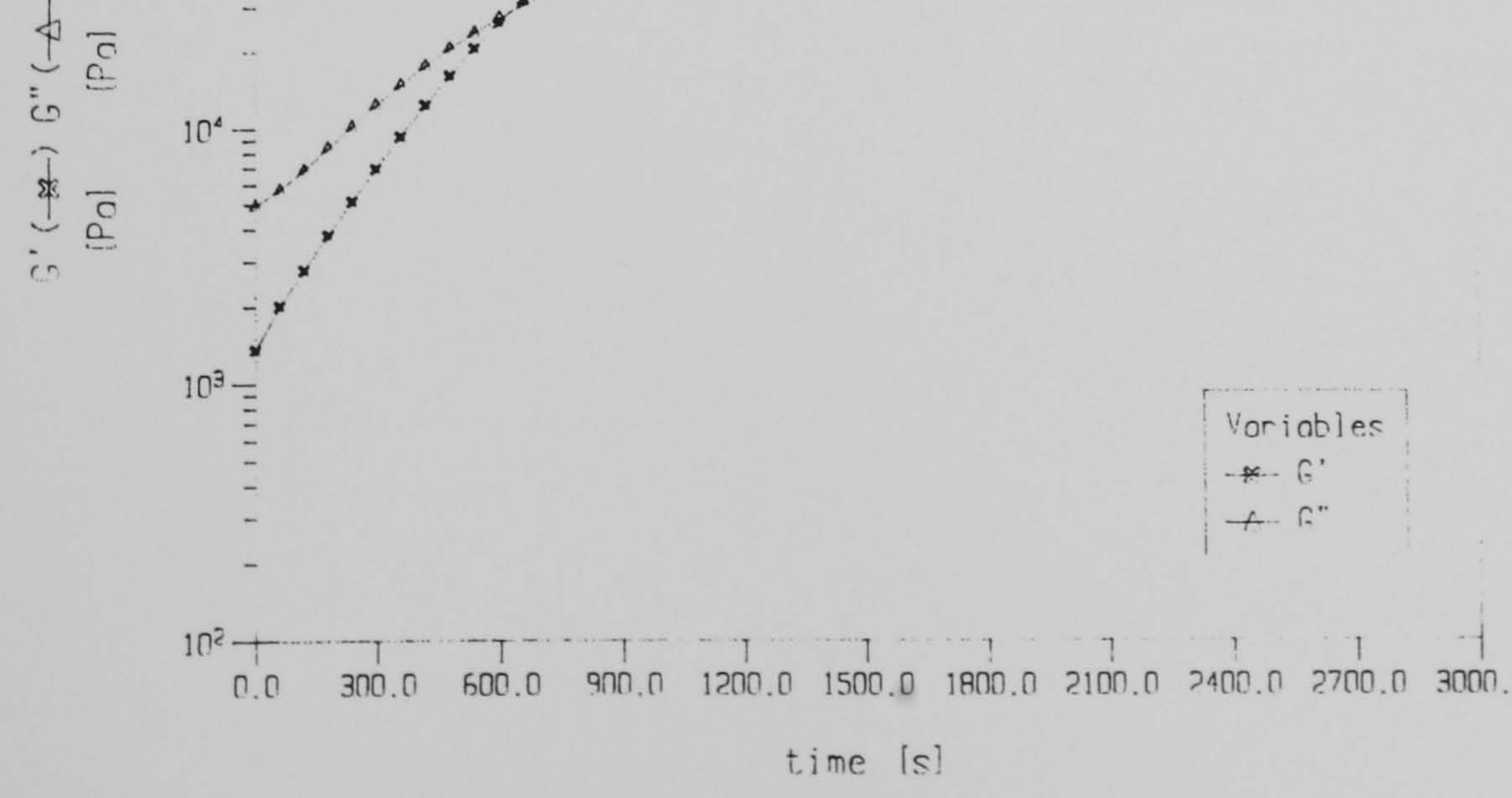


Figure 4.24 Polysulfide curing profile using 5 pph sodium birnessite plus 5 pph inert manganese dioxide with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser (replicate)



Experiment 4.12 Experiment involving a cure paste mixture which used 5 pph sodium birnessite, 5 pph calcium carbonate as a diluent and DBU accelerator

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C:	100 pph

Part B

Curing agent:	Sodium birnessite	5 pph
Curing agent diluent:	Calcium carbonate	5 pph
Accelerator:	1,4-Diazabicyclo(2.2.2)octane (DBU)	0.5 pph
Plasticiser:	Santicizer 261	10 pph

Table 4.12 Gel points for LP32C polymer cured with 5 pph sodium birnessite plus 5 pph calcium carbonate with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
5 pph sodium birnessite + 5pph $CaCO_3$ + 0.5 pph DBU in 10 pph Santicizer 261 plasticiser	(1) 10 (2) 10	(1) 5 (2) 5	(1) 15 (2) 15

Figure 4.25 Polysulfide curing profile using 5 pph sodium birnessite plus 5 pph calcium carbonate with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser cured LP32C polymer.

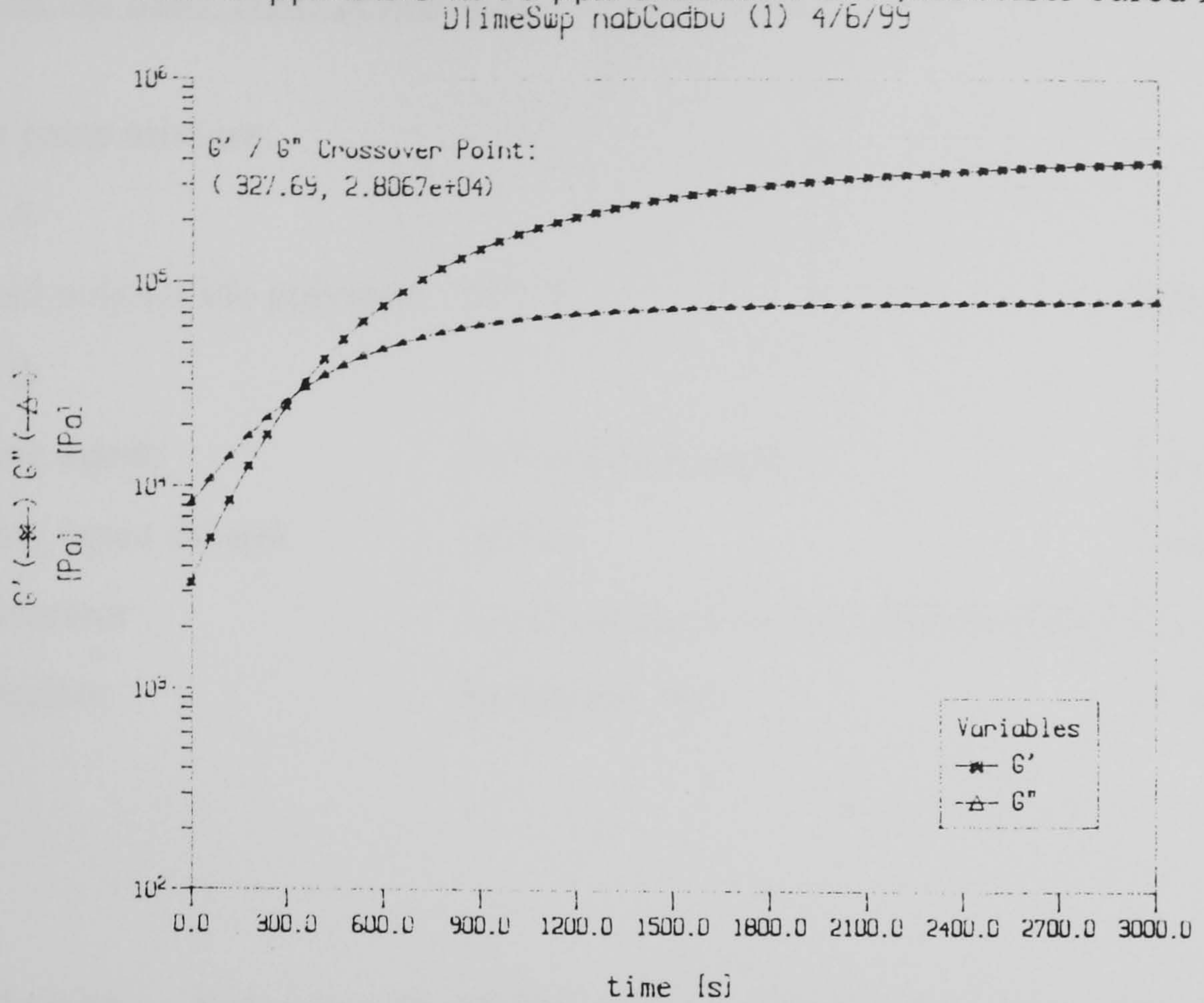
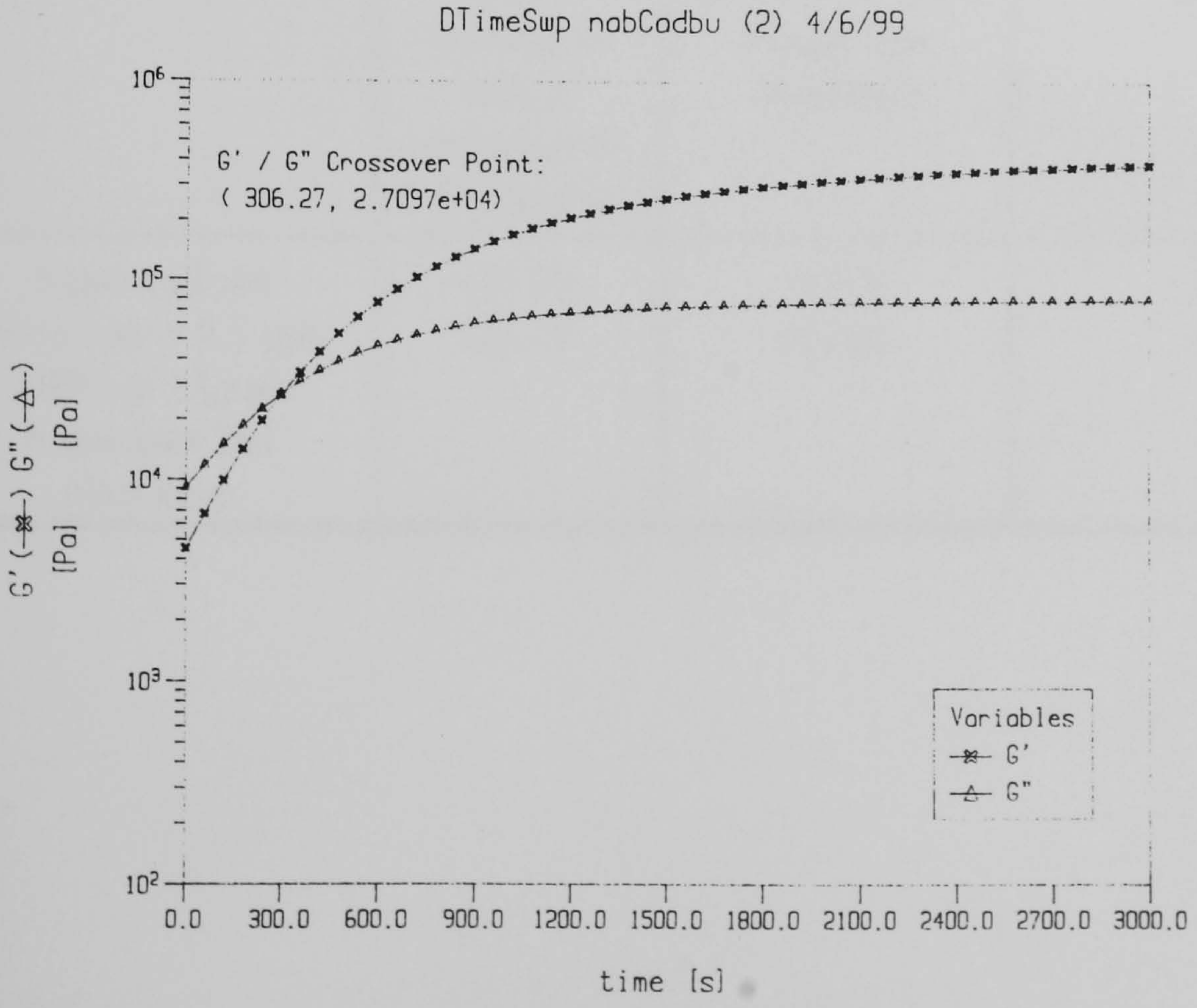


Figure 4.26 Polysulfide curing profile using 5 pph sodium birnessite plus 5 pph calcium carbonate with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser cured LP32C polymer (replicate)



Experiment 4.13 Experiment involving a cure paste mixture which used no curing agent diluent but used DBU accelerator

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C:	100 pph

Part B

Curing agent:	Sodium birnessite	5 pph
Curing agent diluent	NONE	0 pph
Accelerator	1,4-Diazabicyclo(2.2.2)octane (DBU)	0.5 pph
Plasticiser	Santicizer 261	15 pph

Table 4.13 Gel points for LP32C polymer cured with 5 pph undiluted sodium birnessite with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
5 pph sodium birnessite + 0.5 pph DBU in 15 pph Santicizer 261 plasticiser	(1) 10 (2) 10	(1) 16 (2) 26	(1) 26 (2) 36

Figure 4.27 Polysulfide curing profile using 5 pph sodium birnessite, no inert diluent and with 0.5 pph DBU in 15 pph Santicizer 261 plasticiser

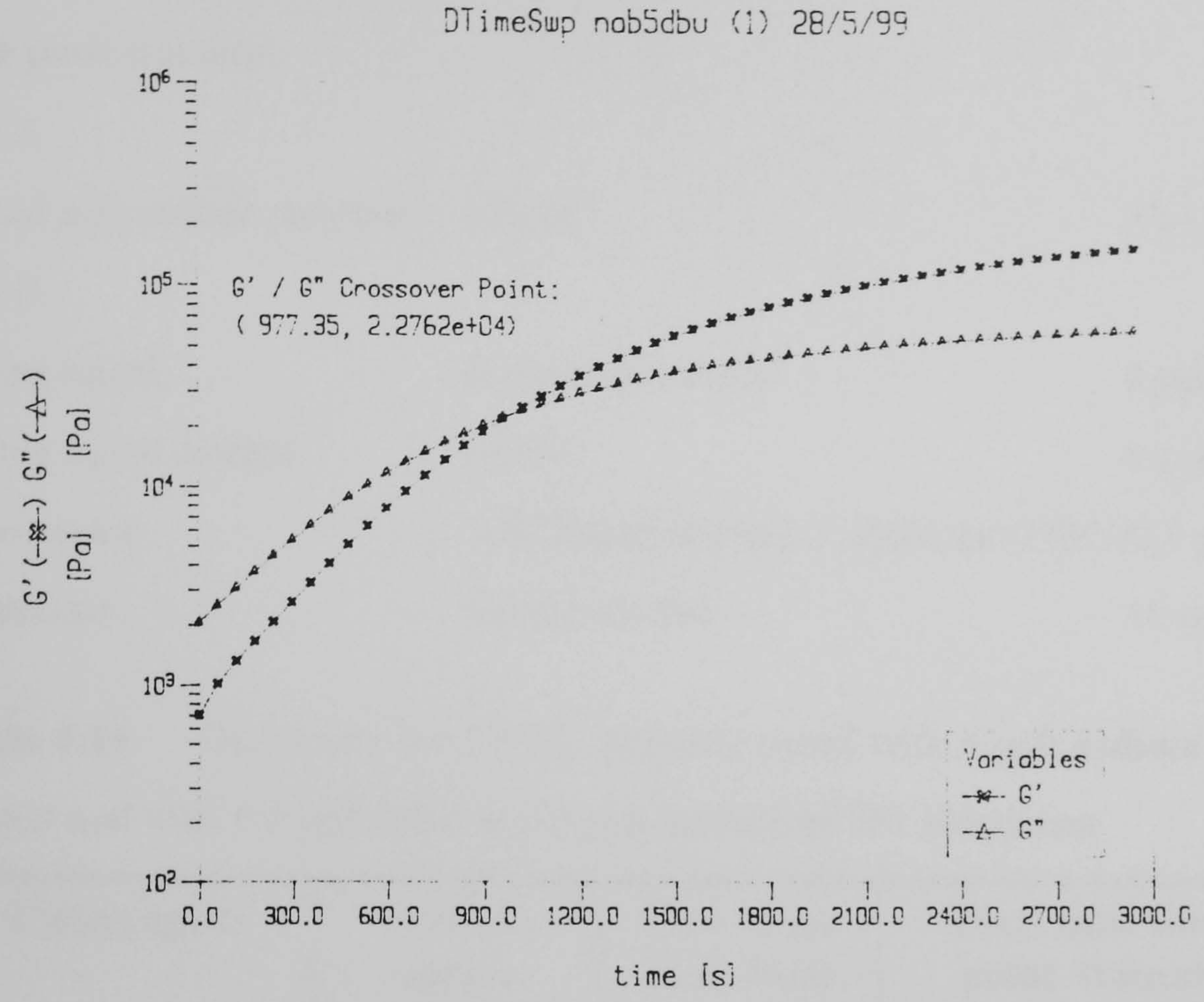
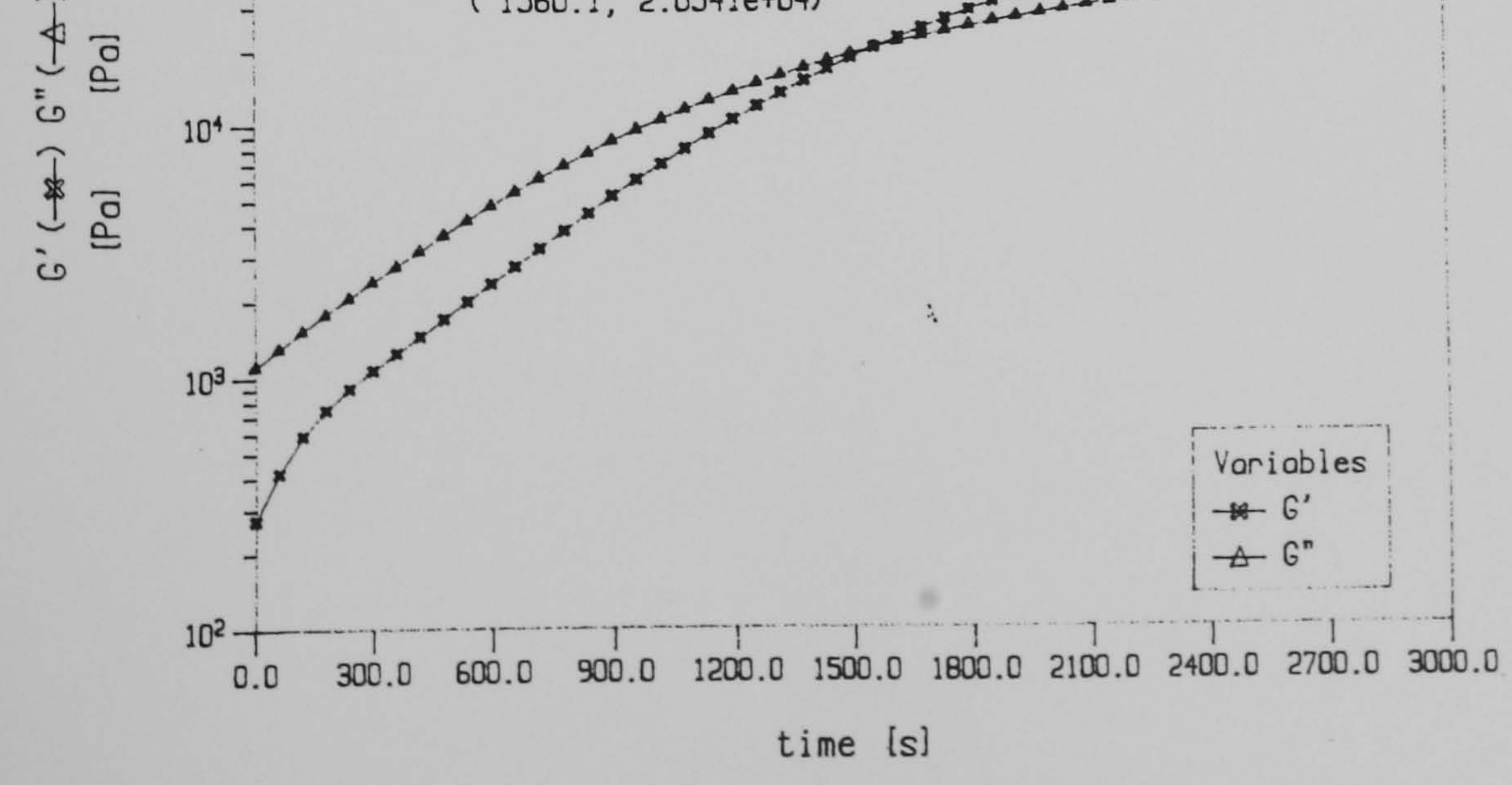


Figure 4.28 Polysulfide curing profile using 5 pph sodium birnessite, no inert diluent and with 0.5 pph DBU in 15 pph Santicizer 261 plasticiser (replicate)



Experiment 4.14 Experiment involving a cure paste mixture which contains 4 pph sodium birnessite, no curing agent diluent with DBU accelerator:

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C:	100 pph

Part B

Curing agent:	Sodium birnessite	4 pph
Curing agent diluent:	NONE	0 pph
Accelerator:	1.4-Diazabicyclo(2.2.2)octane (DBU)	0.5 pph
Plasticiser:	Santicizer 261	16 pph

Table 4.14 Gel points for LP32C polymer cured with 4 pph sodium birnessite, no inert diluent and with 0.5 pph DBU in 16 pph Santicizer 261 plasticiser

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
4 pph sodium birnessite + 0.5 pph DBU in 16 pph Santicizer 261 plasticiser	(1) 10 (2) 10	(1) 46 (2) 45	(1) 56 (2) 55

Figure 4.29 Polysulfide curing profile using 4 pph sodium birnessite, no inert diluent and with 0.5 pph DBU in 16 pph Santicizer 261 plasticiser

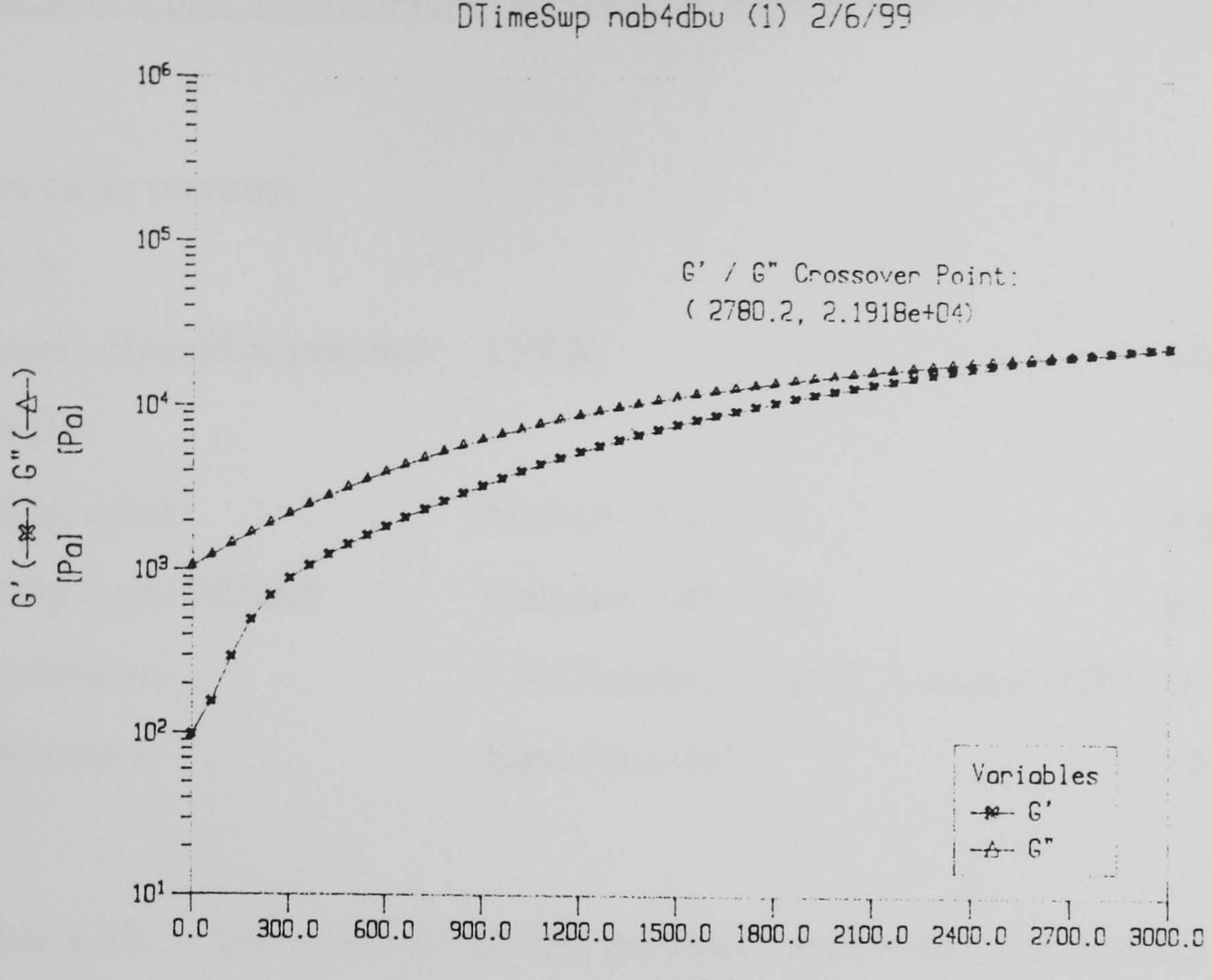
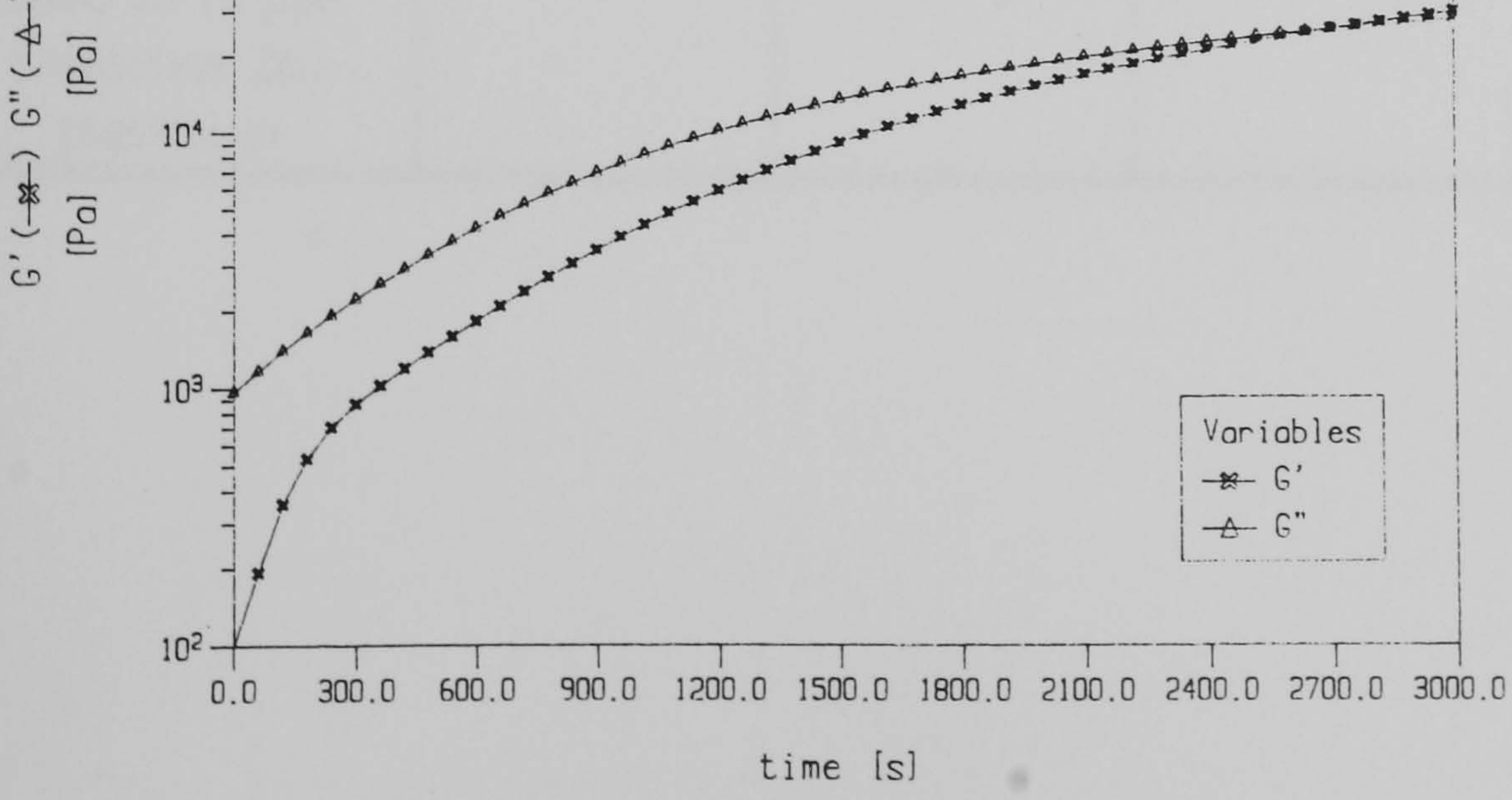


Figure 4.30 Polysulfide curing profile using 4 pph sodium birnessite, no inert diluent and with 0.5 pph DBU in 16 pph Santicizer 261 plasticiser (replicate)



Experiment 4.15 Experiment involving a cure paste mixture which used 4 pph sodium birnessite 6 pph inert calcium carbonate as a diluent and DBU accelerator

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C:	100 pph
Part B		
Curing agent:	Sodium birnessite	4 pph
Curing agent diluent:	Calcium carbonate	6 pph
Accelerator:	1,4-Diazabicyclo(2.2.2)octane (DBU)	0.5 pph
Plasticiser:	Santicizer 261	10 pph

Table 4.15 Gel points for LP32C polymer cured with 4 pph sodium birnessite plus 6 pph inert $CaCO_3$ with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
4 pph sodium birnessite +6 pph $CaCO_3$ +0.5 pph DBU in 10 pph Santicizer 261 plasticiser	(1) 11 (2) 10	(1) 35 (2) 35	(1) 46 (2) 45

Figure 4.31 Polysulfide curing profile using 4 pph sodium birnessite plus 6 pph inert $CaCO_3$ with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser

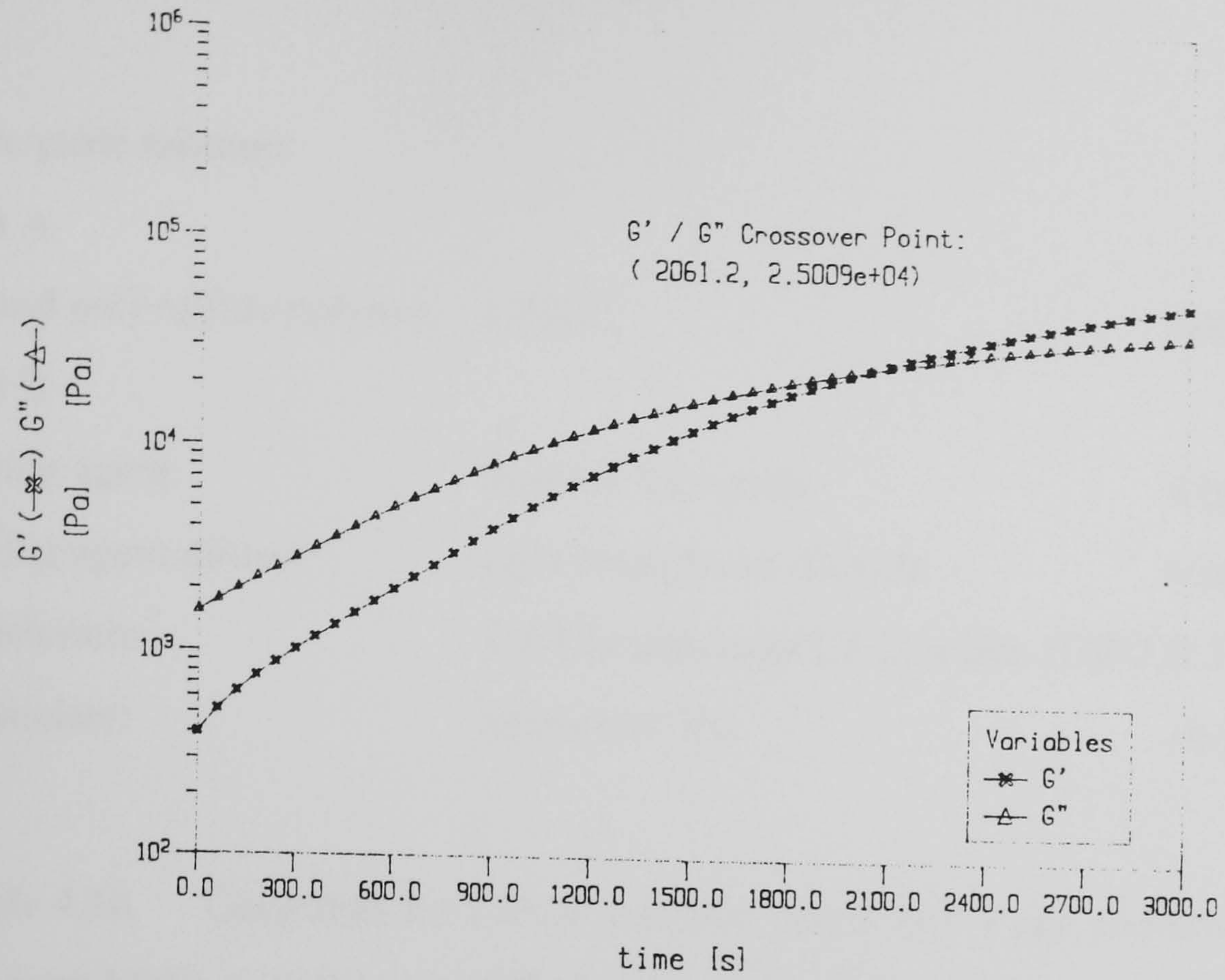
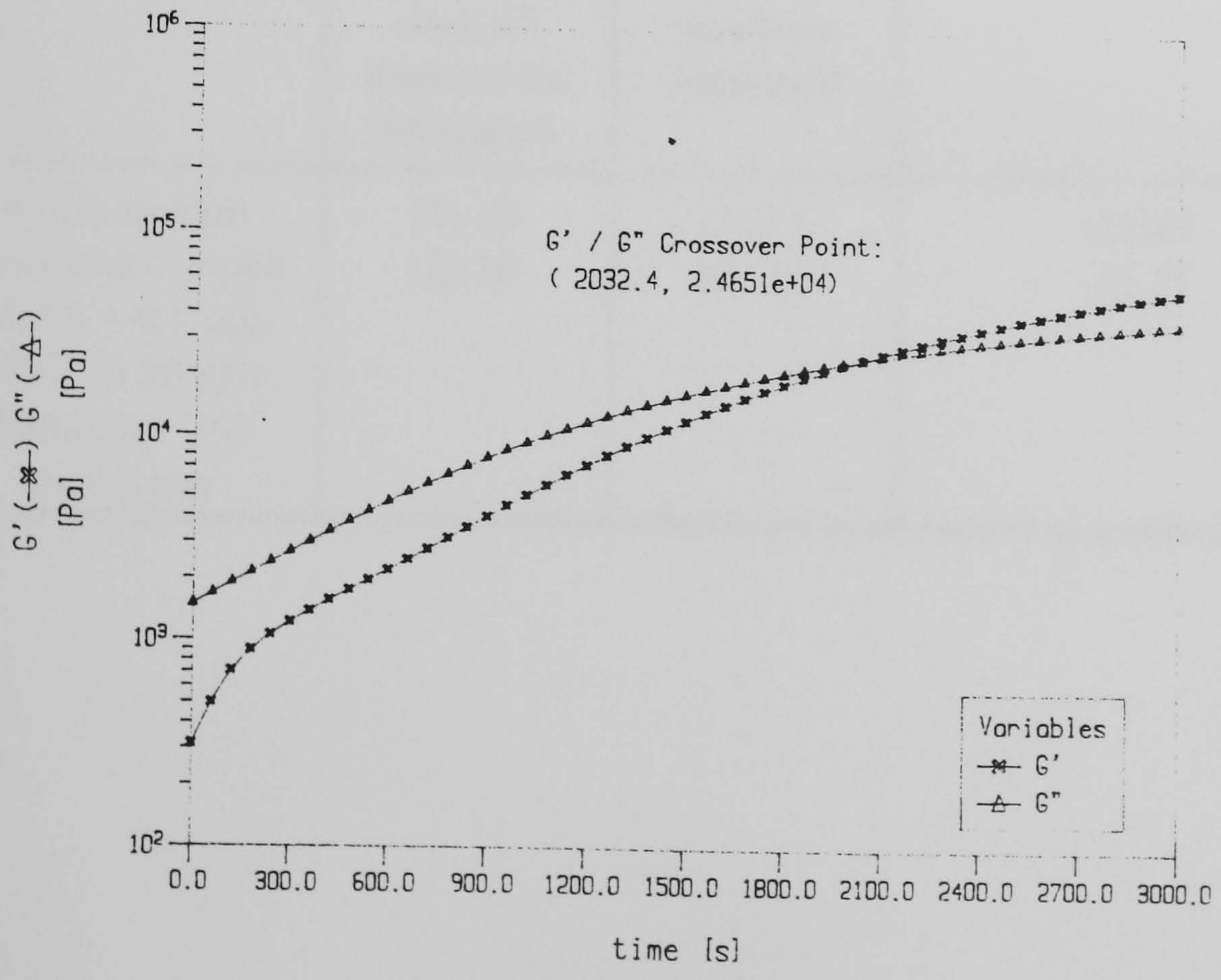


Figure 4.32 Polysulfide curing profile using 4 pph sodium birnessite plus 6 pph inert $CaCO_3$ with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser (replicate)



Experiment 4.16 Experiment involving a cure paste mixture which used 4 pph sodium birnessite 6 pph inert MnO_2 as a diluent and DBU accelerator

Cure paste mixture:

Part A

Liquid polysulfide polymer:	LP32C:	100 pph

Part B

Curing agent:	Sodium birnessite	4 pph
Curing agent diluent:	Inert manganese dioxide	6 pph
Accelerator:	1,4-Diazabicyclo(2.2.2)octane (DBU)	0.5 pph
Plasticiser:	Santicizer 261	10 pph

Table 4.16 Gel points for LP32C polymer cured with 4 pph sodium birnessite plus 6 pph inert MnO_2 with 0.5 pph DBU in 10 pph Santicizer 261

Curing agent	Time for sample mixing to start of experiment (minutes)	Time to gel point from start of reaction (minutes)	**Total time for gel point (minutes)**
4 pph sodium birnessite + 6 pph MnO_2 + 0.5 pph DBU in 10 pph Santicizer 261 plasticiser	(1) 10 (2) 10	(1) 13 (2) 11	(1) 23 (2) 21

Figure 4.33 Polysulfide curing profile using 4 pph sodium birnessite plus 6 pph inert MnO_2 with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser

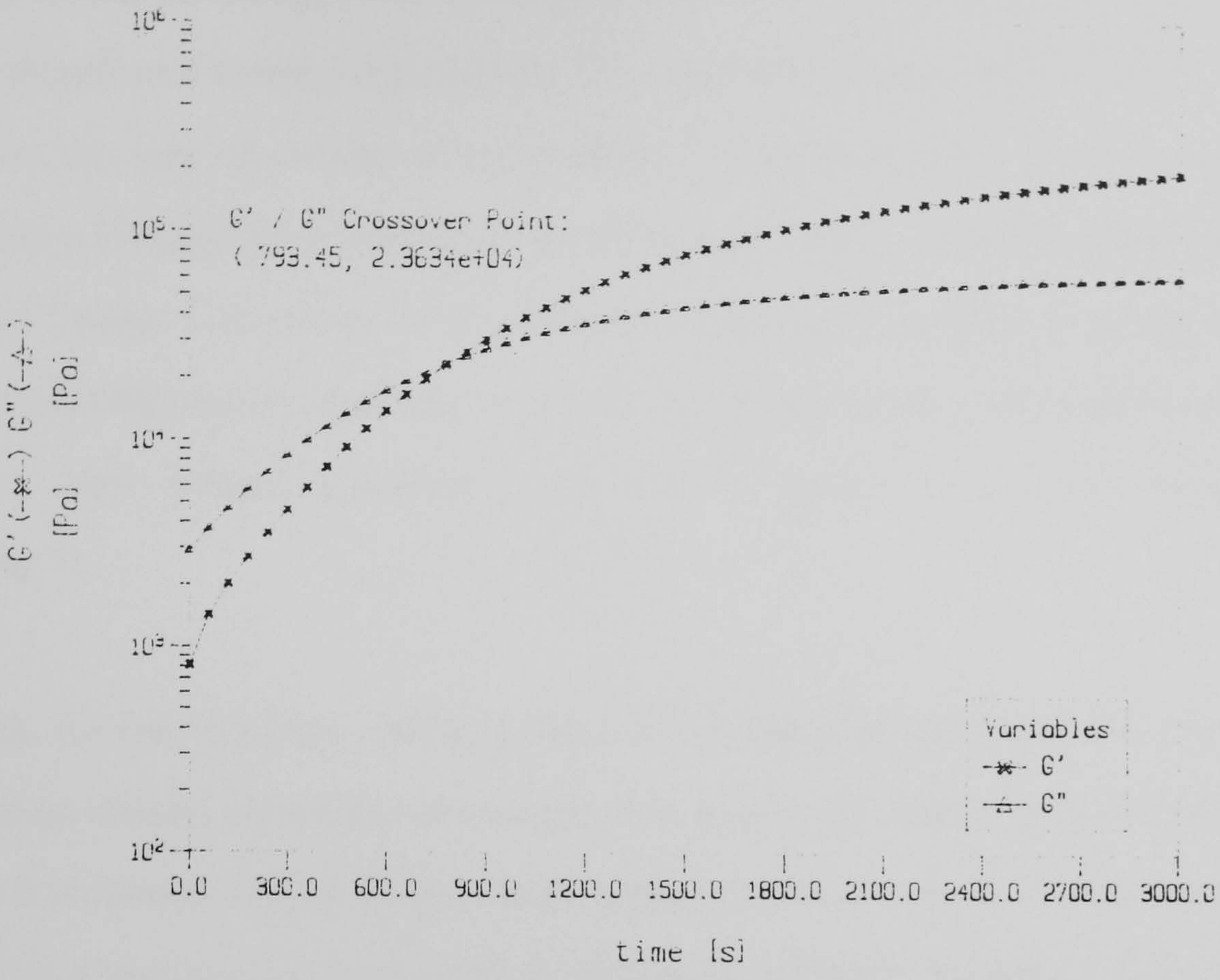
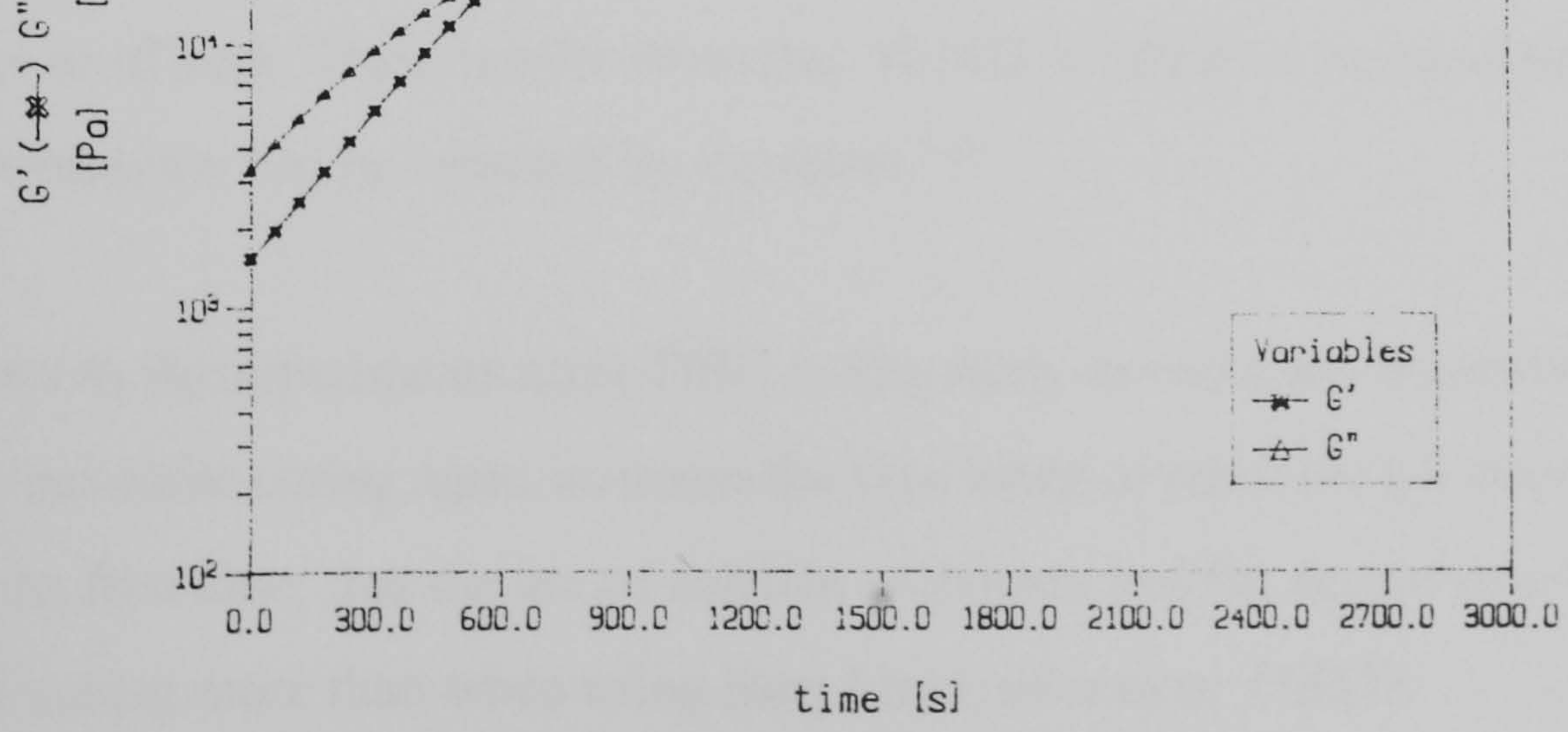


Figure 4.34 Polysulfide curing profile using 4 pph sodium birnessite plus 6 pph inert MnO_2 with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser (replicate)



4.7 DISCUSSION

Preliminary results have suggested that sodium birnessite could be an active polysulfide curing agent, and therefore it formed the topic of this research. Very little has been published in the literature on the rate of curing of polysulfides using manganese dioxide. Goldblatt (2) for instance used a Brookfield Viscometer in preliminary studies in the Centre for Environmental Research at Brunel University to monitor the curing of liquid polysulfide with a range of manganese dioxide phases. Sodium birnessite has been found to be a rapid curing agent and the use of inert diluent manganese dioxide to retard the curing reaction has been investigated.(2)

In this work, for the first time, studies have been performed using parallel plate rheometry in dynamic time sweep mode to investigate the curing of liquid polysulfide using sodium birnessite. It is found in these polysulfide curing reactions, using 10 pph commercial curing agent, or 5 or 4 pph sodium birnessite, the gel point occurs at roughly 2×10^4 Pa, the same as for the commercial curing agent cured polysulfide reactions, indicating a similar degree of crosslinking. Data in this work are included from the reaction propagation phase up to the termination phase, just after the gel point.

The results confirm that the curing of the polysulfide is due to the sodium birnessite, because singly and together the TMTD accelerator and the natural MnO_2 ore in the absence of sodium birnessite do not have any measurable curing effect over the time period studied. The inert MnO_2 in combination with the sodium birnessite and TMTD seems to have only a small effect on increasing the rate of cure above that found using sodium birnessite alone at 5 pph with no accelerator or diluent. These results show that TMTD is effective in increasing the reaction rate, supporting the results obtained by Cookson.(18)

With respect to the experiments using DBU in this work, as expected, decreasing the quantity of sodium birnessite curing agent increases the time taken to reach the gel point. These results show for the first time, that the use of calcium carbonate and the accelerator DBU increases the rate of curing more than when using inert MnO_2 diluent or TMTD.

Environmentally, it is important to reduce toxic components in the cure paste. These preliminary results indicate that DBU, which has a lower toxicity than TMTD, is not detrimental to the curing reaction rate, but is in fact complimentary to it. Furthermore, the lower toxicity and cost of calcium carbonate compared to manganese dioxide, again without detriment to the curing reaction rate, is a benefit.

From results in Chapter 2 analysing the curing agents and accelerators, the higher pH of sodium birnessite than that of the commercial curing agent may account for the quicker time to gel point using birnessite at 5 pph. The higher moisture content of the sodium birnessite than the commercial curing agent as identified in Chapter 2 would also increase the rate of reaction between the polysulfide and the sodium birnessite. Despite the higher pH of the 4 pph sodium birnessite diluted with 6 pph MnO_2 or 6 pph $CaCO_3$, compared to 5 pph birnessite diluted with 5pph of MnO_2 or 5pph $CaCO_3$, this work shows that *the sodium birnessite content* of the curing agent mix is *more important than the pH* of that mix.

The reason for the DBU and the calcium carbonate accelerating the cure faster than is the case for TMTD or manganese dioxide is the higher alkalinity of the former components than the latter. Chapter 2 details their respective pH values. Alkalinity as mentioned previously increases the rate of the curing reaction. The effect that inert manganese dioxide has on the curing rate is not easily explained. It is not a curing agent alone, but when mixed with sodium birnessite increases the cure rate. It is possible that the sodium birnessite becomes more greatly distributed in the polysulfide, maybe on the surface of the natural manganese dioxide

The reproducibility of results for the time for polysulfide to reach its gel point showed consistency of curing using separately prepared sodium birnessite cure pastes. This is a positive sign indicating the consistent curing ability of the birnessite. Cure failures have not been observed in this work for either sodium birnessite or the commercial curing agent cured polysulfide reactions. This is both an environmentally and economically important finding to minimise waste production.

4.8 REFERENCES

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CHAPTER 5 MEASUREMENT OF THE "SHORE A" HARDNESS OF CURED POLYSULFIDE.

5.1 INTRODUCTION

Hardness measurement of polysulfides using Durometers has been described in the literature. for example by Ramaswamy and Sasidharan Achary (1) and Goldblatt. (2) In the work described in this thesis Shore A hardness was measured at set times of 4 hours, 24 hours, 48 hours and 7 days after samples of liquid polysulfide were mixed with various cure pastes. The mixtures of curing ingredients and polysulfide used were the same as those in the work reported in the previous Chapters, using the commercial curing agent, sodium birnessite, Santicizer 278, and 261 plasticisers, TMTD and DBU accelerators, and the inert diluents calcium carbonate and manganese dioxide. Polysulfide sealants can be formulated to have a wide range of hardnesses for example, from Shore A of 12 for road sealants to 50 for insulated glass sealants.(3)

5.2 EXPERIMENTAL

A CV Instruments Analog Durometer was used to measure the sample hardness at room temperature. The instrument was first calibrated on a CV instruments Durometer calibration block. The cured polysulfide sample, at least 5 mm thick, in the plastic weighing vessel was placed on a horizontal, flat, hard surface. The Durometer was held vertically ensuring the point of the indenter was kept at least 12 mm from any edge of the test specimen. The presser foot was applied to the test specimen with the foot kept parallel to the surface and sufficient pressure applied to ensure firm contact. A reading on the dial was taken after applying pressure for three seconds and readings were taken in triplicate. A subjective assessment, by touch, of the surface condition of the 7 day cured polysulfide was then made as to whether the surface was tacky or fully cured.

5.3 RESULTS OF MEASUREMENT OF HARDNESS

The results of Shore A hardness measurements are tabulated in Tables 5.1 to 5.14. The build-up of Shore A hardness is shown in graphs (Figures 5.1 to 5.14) The annotation pph in the Tables of results refers to parts per hundred polysulfide. Test samples which did not include a curing agent did not result in a cured polysulfide and so were not included in the data reported in this Chapter. The results of the polysulfide hardness tests for the commercial curing agent are followed by those for the sodium birnessite cured polysulfide. A section on the surface tack condition of the cured polysulfides is included.

Results for experiments using the commercial curing agent to cure polysulfide

5.3.1 Experiment monitoring hardness build up using 10 pph commercial curing agent, TMTD accelerator and Santicizer 278 plasticiser:

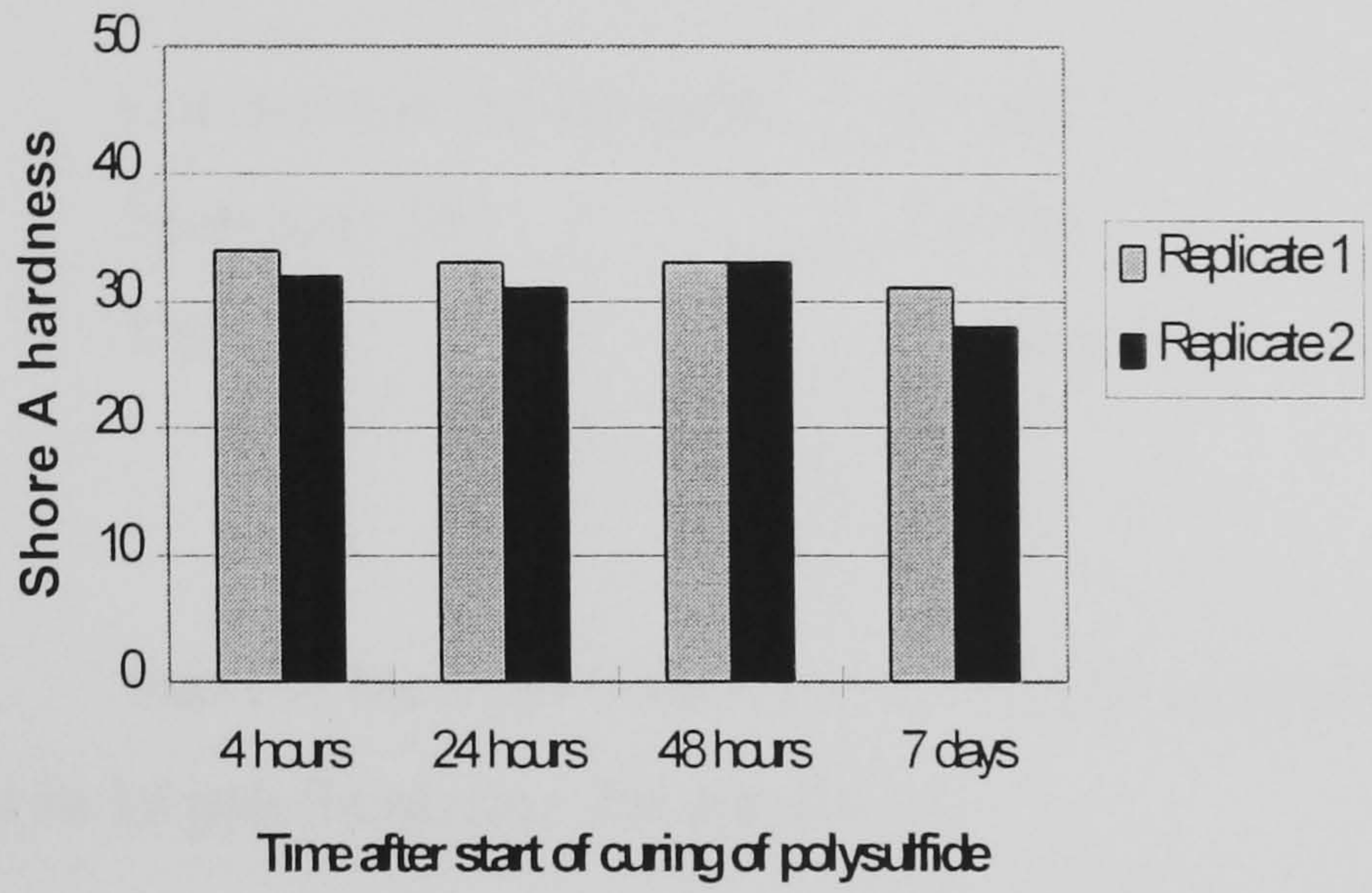
Cure mixture components:

Part A:		
Polysulfide	LP32C	100 pph
Part B:		
Curing agent	Commercial curing agent	10 pph
Plasticiser	Santicizer 278	10 pph
Accelerator	TMTD	0.5 pph

Table 5.1 Shore A hardness build-up using 10 pph commercial curing agent, TMTD accelerator and 10 pph Santicizer 278 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	35,35,32 $\bar{x}=34$	32,32,34 $\bar{x}=33$	33,32,33 $\bar{x}=33$	29,30,33 $\bar{x}=31$
Shore A hardness Replicate (2)	32,32,32 $\bar{x}=32$	31,31,30 $\bar{x}=31$	33,32,33 $\bar{x}=33$	29,29,27 $\bar{x}=28$

Figure 5.1 Graph showing build up of Shore A hardness using the commercial curing agent, TMTD accelerator and 10 pph Santicizer 278 plasticiser



5.3.2 Experiment monitoring hardness build up using the commercial curing agent and TMTD accelerator in Santicizer 261 plasticiser

Cure mixture components:

Part A

Polysulfide	LP32C	100 pph

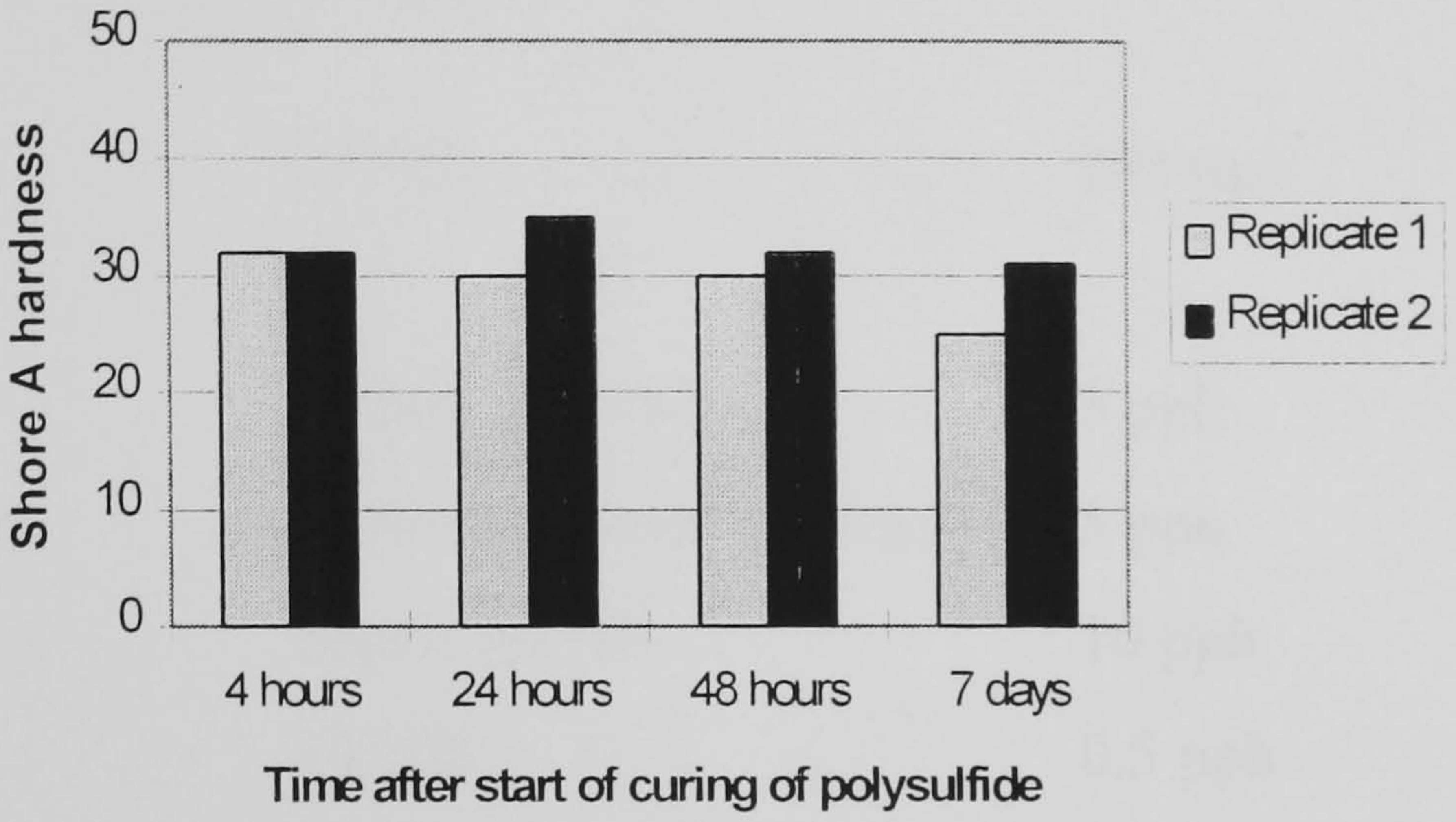
Part B

Curing agent	Commercial curing agent	10 pph
Plasticiser	Santicizer 261	10 pph
Accelerator	TMTD	0.5 pph

Table 5.2 Shore A hardness build-up using 10 pph commercial curing agent and TMTD accelerator in 10 pph Santicizer 261 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	32,32,32 $\bar{x}$=32	30,30,29 $\bar{x}$=30	30,30,29 $\bar{x}$=30	26,26,24 $\bar{x}$=25
Shore A hardness Replicate (2)	32,32,33 $\bar{x}$=32	35,35,34 $\bar{x}$=35	32,32,33 $\bar{x}$=32	32,31,31 $\bar{x}$=31

Figure 5.2 Graph showing build up of Shore A hardness using 10 pph commercial curing agent and TMTD accelerator in 10 pph Santicizer 261 plasticiser



Results for experiments involving sodium birnessite, TMTD accelerator and inert MnO_2 diluent for polysulfide curing

5.3.3 Experiment monitoring hardness build up using 5 pph sodium birnessite 5 pph inert MnO_2 diluent with TMTD accelerator in 10 pph Santicizer 278 plasticiser

Cure mixture components:

Part A:

Polysulfide	LP32C	100 pph

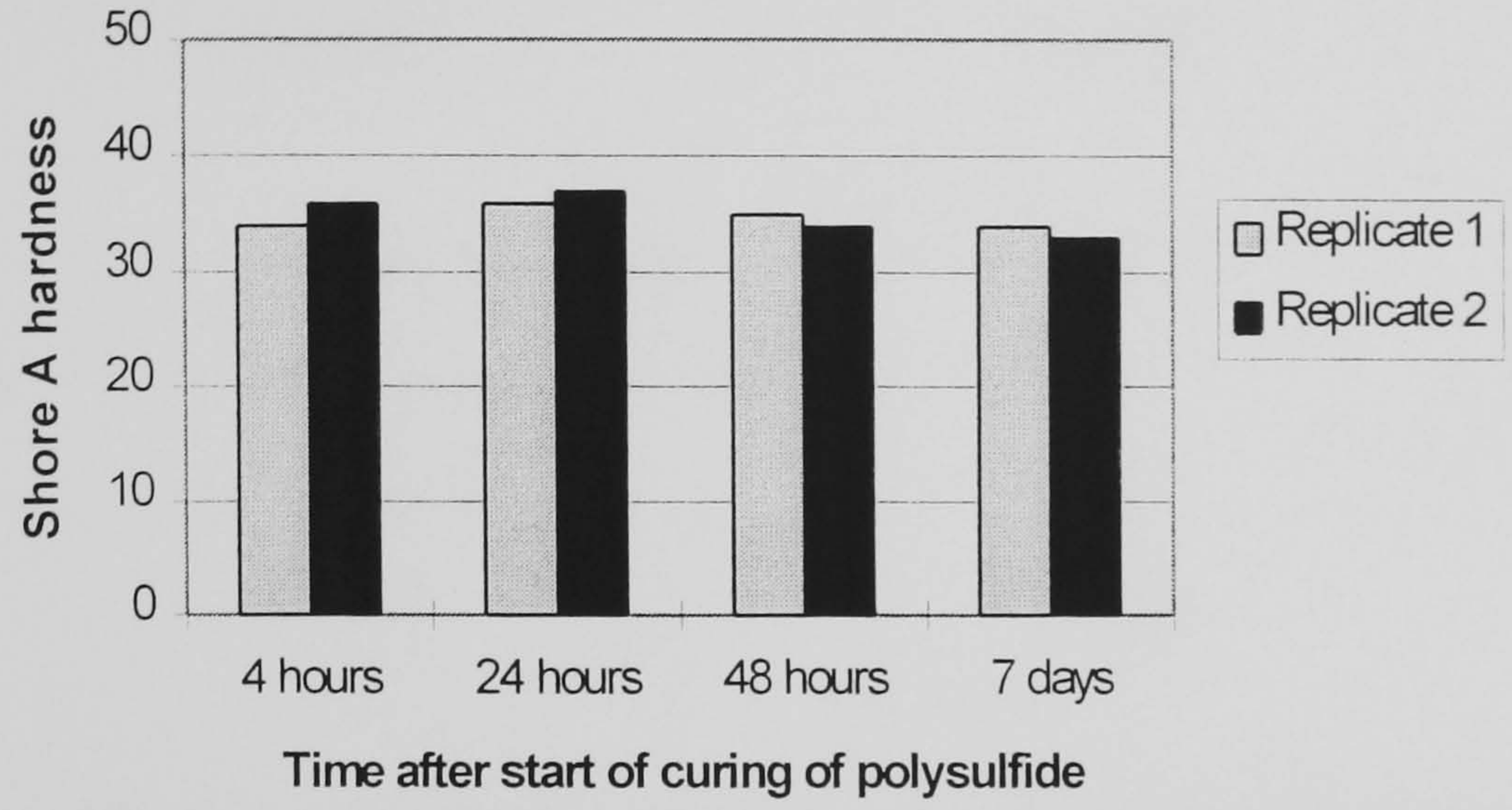
Part B:

Curing agent	sodium birnessite	5 pph
Curing agent diluent	inert manganese dioxide	5 pph
Plasticiser	Santicizer 278	10 pph
Accelerator	TMTD	0.5 pph

Table 5.3 Shore A hardness build-up using 5 pph sodium birnessite 5 pph inert MnO_2 diluent with TMTD accelerator in Santicizer 278 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	36,34,33 $\bar{x}$=34	36,36,36 $\bar{x}$=36	33,37,35 $\bar{x}$=35	34,34,35 $\bar{x}$=34
Shore A hardness Replicate (2)	35,37,37 $\bar{x}$=36	36,37,38 $\bar{x}$=37	33,35,33 $\bar{x}$=34	30,34,34 $\bar{x}$=33

Figure 5.3 Graph showing build-up of Shore A hardness using 5 pph sodium birnessite 5 pph inert MnO_2 diluent with TMTD accelerator in 10 pph Santicizer 278 plasticiser



5.3.4 Experiment monitoring hardness build up using 5 pph sodium birnessite 5 pph inert manganese dioxide diluent with TMTD accelerator and Santicizer 261 plasticiser

Cure mixture components:

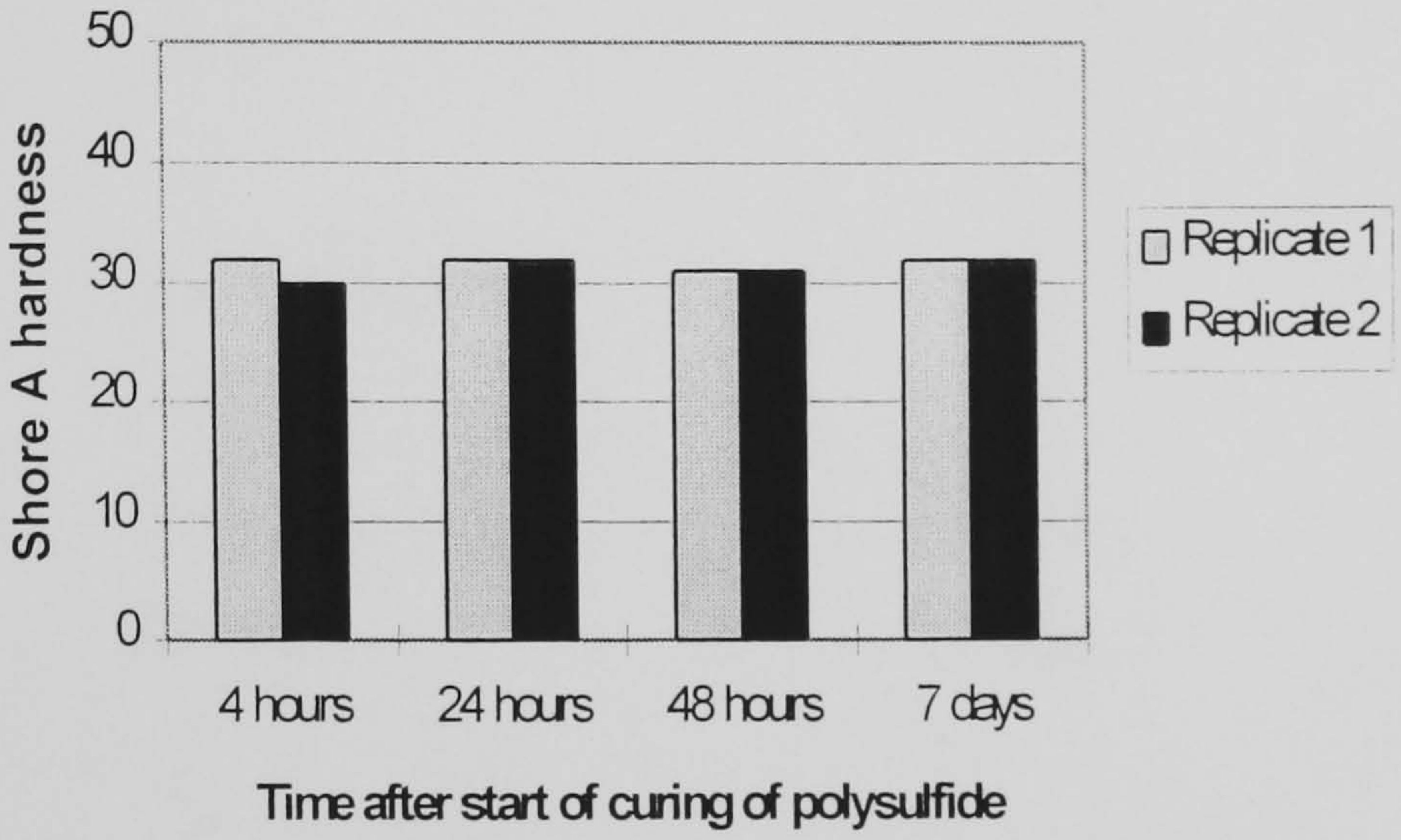
Part A:

Polysulfide	LP32C	100 pph
Part B:		
Curing agent	sodium birnessite	5 pph
Curing agent diluent	inert manganese dioxide	5 pph
Plasticiser	Santicizer 261	10 pph
Accelerator	TMTD	0.5 pph

Table 5.4 Shore A hardness build-up using 5 pph sodium birnessite 5 pph inert manganese dioxide diluent with TMTD accelerator in 10 pph Santicizer 261 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	30,32,33 $\bar{x}$=32	32,33,32 $\bar{x}$=32	30,30,32 $\bar{x}$=31	33,32,30 $\bar{x}$=32
Shore A hardness Replicate (2)	31,32,28 $\bar{x}$=30	31,31,33 $\bar{x}$=32	32,32,30 $\bar{x}$=31	33,30,33 $\bar{x}$=32

Figure 5.4 Graph showing build-up of Shore A hardness using 5 pph sodium birnessite 5 pph inert manganese dioxide diluent with TMTD accelerator in 10 pph Santicizer 261 plasticiser



Experiments involving sodium birnessite with TMTD accelerator and no curing agent diluent

5.3.5 Experiment monitoring hardness build up using 5 pph sodium birnessite no curing agent diluent with TMTD accelerator in 15 pph Santicizer 261 plasticiser

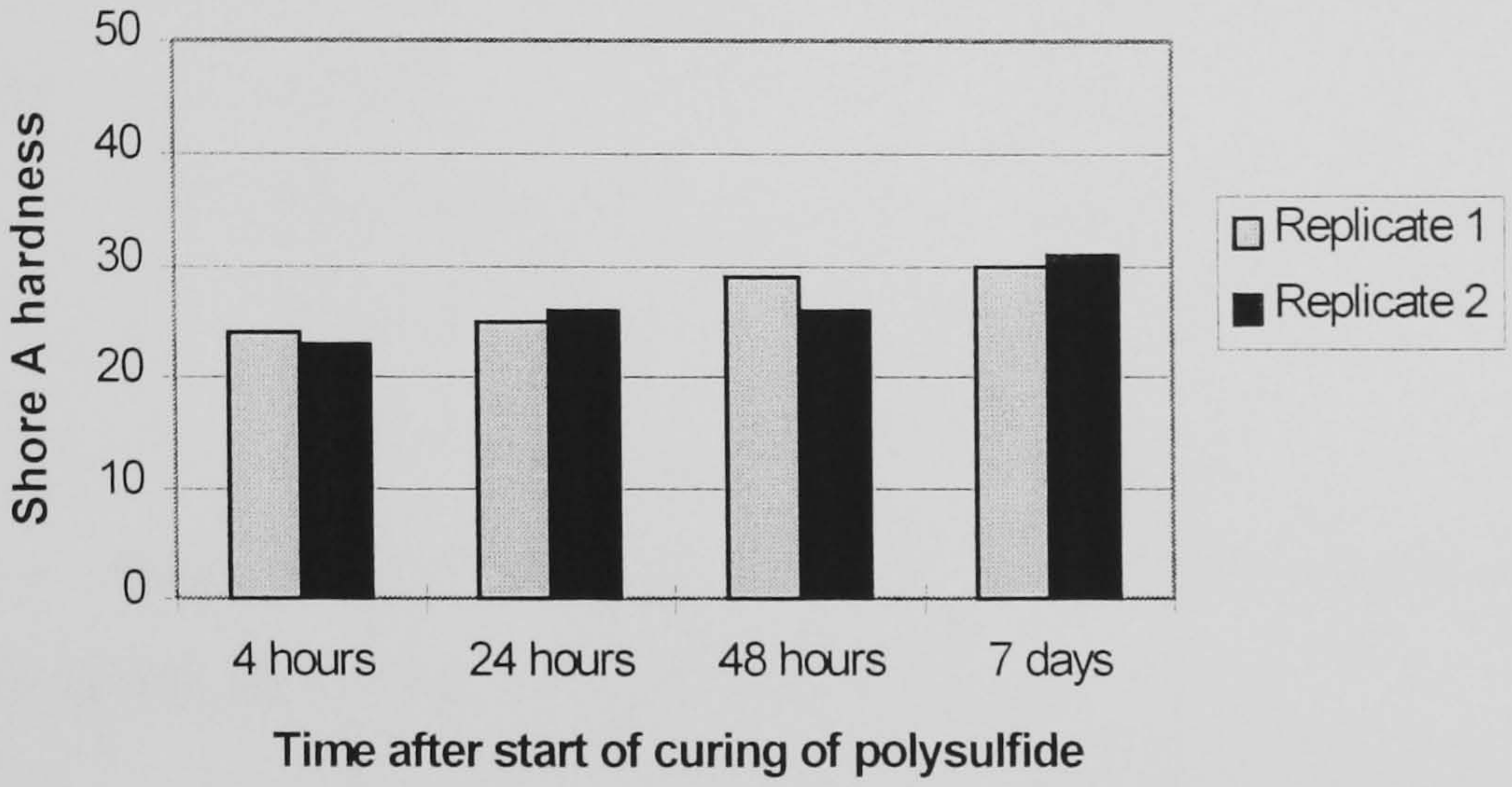
Cure mixture components:

Part A:		
Polysulfide	LP32C	100 pph
Part B:		
Curing agent	sodium birnessite	5 pph
Curing agent diluent	NONE	0 pph
Plasticiser	Santicizer 261	15 pph
Accelerator	TMTD	0.5 pph

Table 5.5 Shore A hardness build-up using 5 pph sodium birnessite no curing agent diluent with TMTD accelerator in 15 pph Santicizer 261 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	23.24.24 $\bar{x}$=24	28.23,23 $\bar{x}$=25	28,29.30 $\bar{x}$=29	29.31,30 $\bar{x}$=30
Shore A hardness Replicate (2)	23.22.23 $\bar{x}$=23	24.27,26 $\bar{x}$=26	23.26,30 $\bar{x}$=26	30.31,32 $\bar{x}$=31

Figure 5.5 Graph showing build up of Shore A hardness using 5 pph sodium birnessite no curing agent diluent with TMTD accelerator in 15 pph Santicizer 261 plasticiser



5.3.6 Experiment monitoring hardness build up using 4 pph sodium birnessite no inert diluent with TMTD accelerator in 16 pph Santicizer 261 plasticiser

Cure mixture components:

Part A:

Polysulfide	LP32C	100 pph

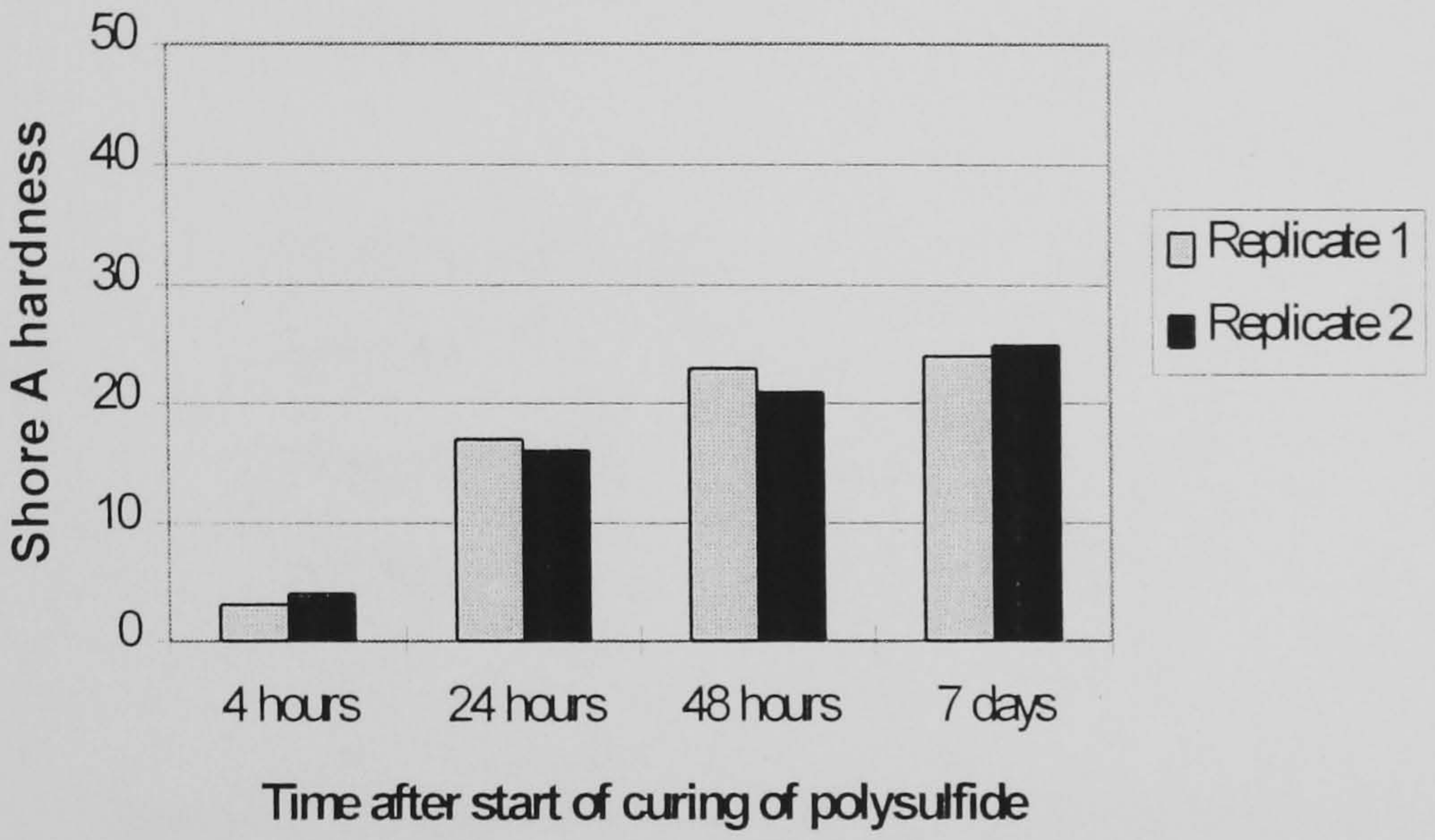
Part B:

Curing agent	sodium birnessite	4 pph
Curing agent diluent:	NONE	0 pph
Plasticiser	Santicizer 261	16 pph
Accelerator	TMTD	0.5 pph

Table 5.6 Shore A hardness build-up using 4 pph sodium birnessite no inert diluent with TMTD accelerator in 16 pph Santicizer 261 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	2.3.3 $\bar{x}$=3	17.18,17 $\bar{x}$=17	23.23,23 $\bar{x}$=23	23.24,25 $\bar{x}$=24
Shore A hardness Replicate (2)	5.3.3 $\bar{x}$=4	16.15.16 $\bar{x}$=16	19.23.21 $\bar{x}$=21	24,25,26 $\bar{x}$=25

Figure 5.6 Graph showing build up of Shore A hardness using 4 pph sodium birnessite no inert diluent with TMTD accelerator in 16 pph Santicizer 261 plasticiser



Experiments involving sodium birnessite and no curing agent diluent or accelerator

5.3.7 Experiment monitoring hardness build up using 5 pph sodium birnessite no curing agent diluent with no accelerator in 15.5 pph Santicizer 261 plasticiser

Cure mixture components:

Part A:

Polysulfide	LP32C	100 pph

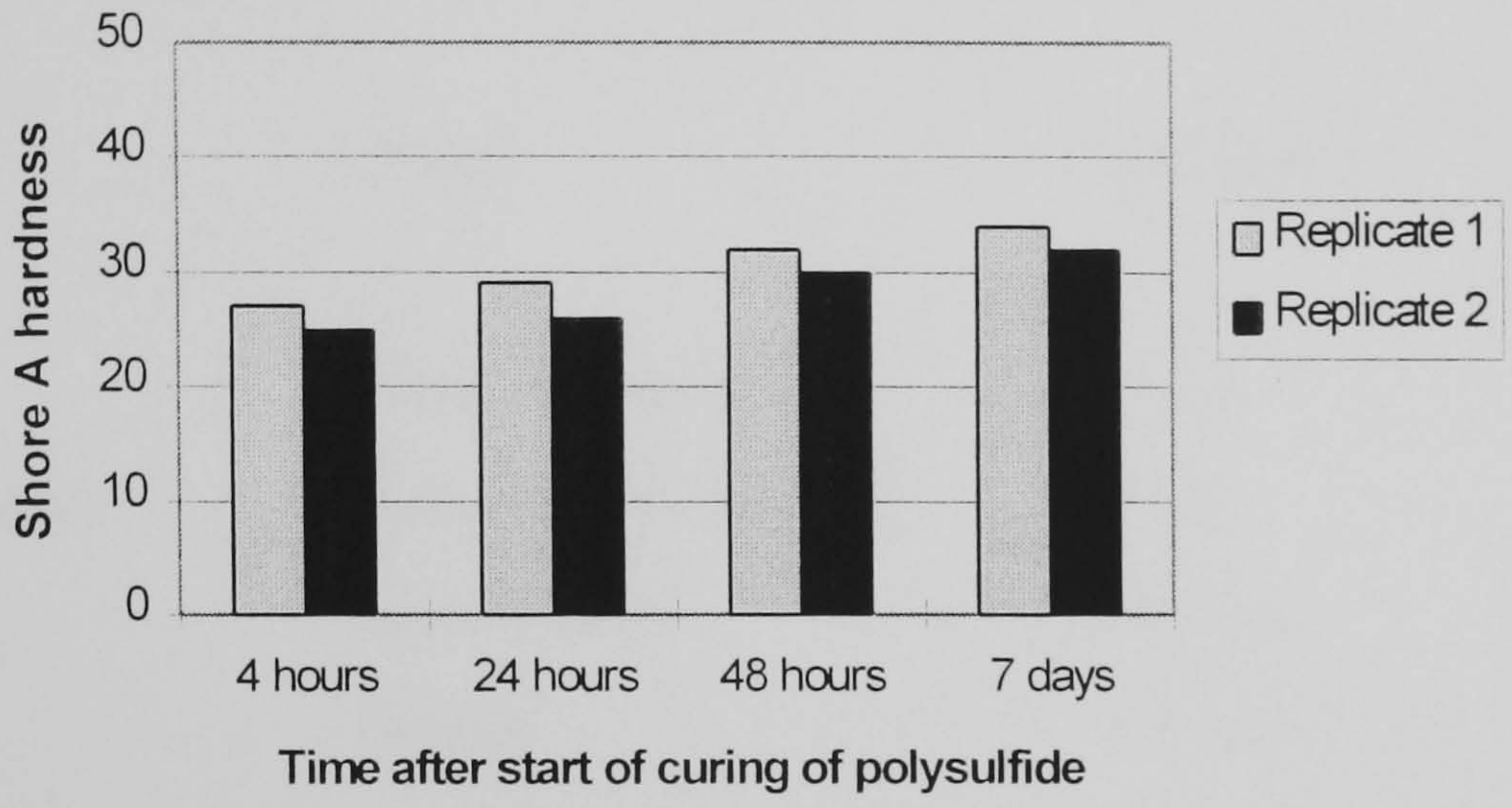
Part B:

Curing agent	sodium birnessite	5 pph
Curing agent diluent	NONE	0 pph
Plasticiser	Santicizer 261	15.5 pph
Accelerator	NONE	0 pph

Table 5.7 Shore A hardness build-up using 5 pph sodium birnessite no curing agent diluent with no accelerator in 15.5 pph Santicizer 261 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	25,29,27 $\bar{x}$=27	28,29,29 $\bar{x}$=29	31,31,33 $\bar{x}$=32	33,33,36 $\bar{x}$=34
Shore A hardness Replicate (2)	23,24,27 $\bar{x}$=25	25,27,26 $\bar{x}$=26	31,29,30 $\bar{x}$=30	30,33,33 $\bar{x}$=32

Figure 5.7 Graph showing build-up of Shore A hardness using 5 pph sodium birnessite no curing agent diluent with no accelerator in 15.5 pph Santicizer 261 plasticiser



Experiments using sodium birnessite, TMTD and calcium carbonate diluent

5.3.8 Experiment monitoring hardness build up using 5 pph sodium birnessite diluted with 5 pph calcium carbonate and using TMTD accelerator in 10 pph Santicizer 261 plasticiser

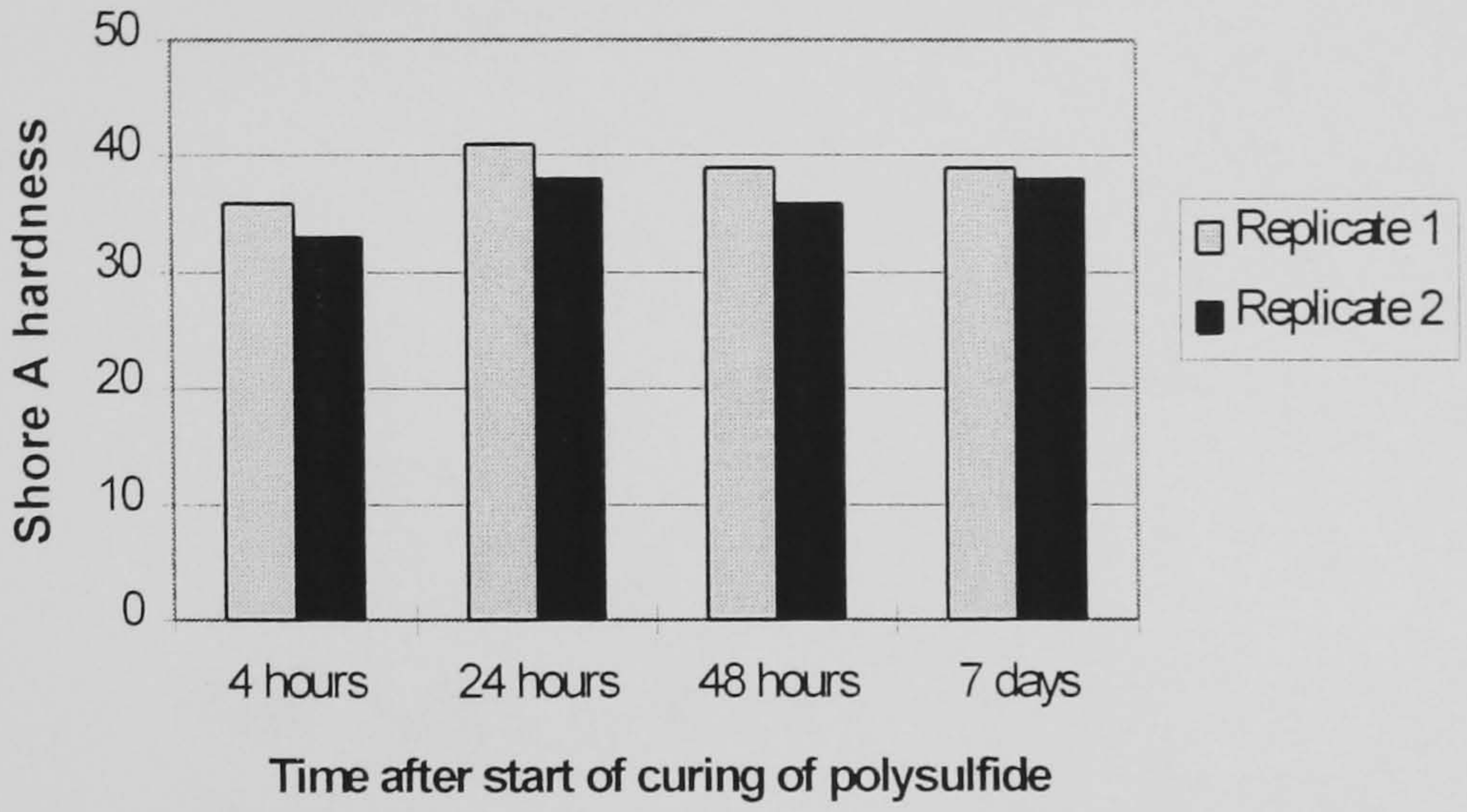
Cure mixture components

Part A:		
Polysulfide	LP32C	100 pph
Part B:		
Curing agent	sodium birnessite	5 pph
Curing agent diluent:	calcium carbonate	5 pph
Plasticiser	Santicizer 261	10 pph
Accelerator	TMTD	0.5 pph

Table 5.8 Shore A hardness build-up using 5 pph sodium birnessite diluted with 5 pph calcium carbonate and using TMTD accelerator in 10 pph Santicizer 261 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	35,35,37 $\bar{x}$=36	41,41,42 $\bar{x}$=41	38,39,40 $\bar{x}$=39	39,39.38 $\bar{x}$=39
Shore A hardness Replicate (2)	34,33.33 $\bar{x}$=33	37,39,38 $\bar{x}$=38	36,33,38 $\bar{x}$=36	39.37.37 $\bar{x}$=38

Figure 5.8 Graph showing build-up of Shore A hardness using 5 pph sodium birnessite diluted with 5 pph calcium carbonate and using TMTD accelerator in 10 pph Santicizer 261 plasticiser



Results for experiments involving sodium birnessite DBU accelerator and inert manganese dioxide diluent for polysulfide curing

5.3.9 Experiment monitoring hardness build up using 5 pph sodium birnessite 5 pph inert manganese dioxide diluent with DBU accelerator in 10 pph Santicizer 261 plasticiser

Cure mixture components:

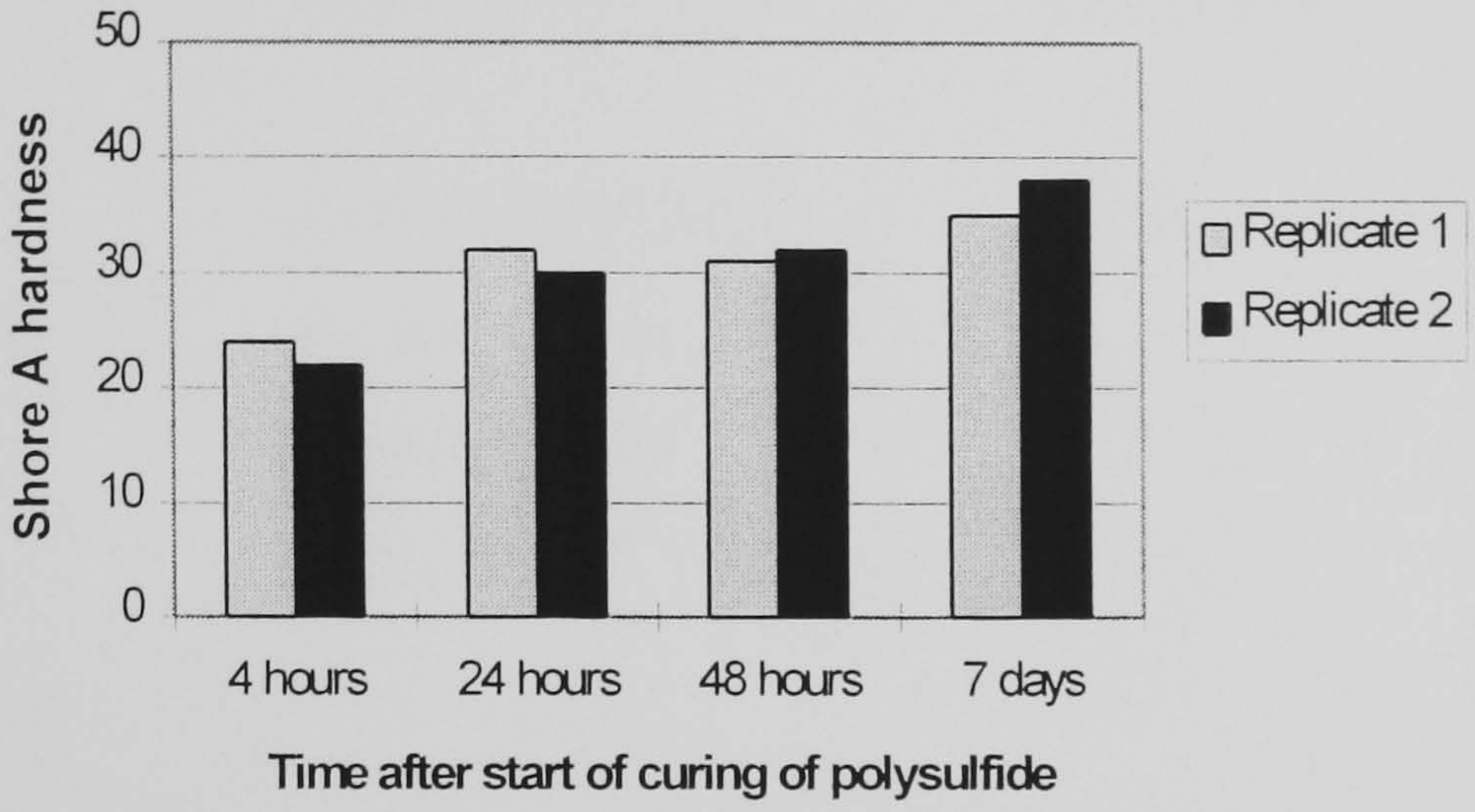
Part A:

Polysulfide	LP32C	100 pph
Part B:		
Curing agent	sodium birnessite	5 pph
Curing agent diluent	inert manganese dioxide	5 pph
Plasticiser	Santicizer 261	10 pph
Accelerator	DBU	0.5 pph

Table 5.9 Shore A hardness build-up using 5 pph sodium birnessite 5 pph inert manganese dioxide diluent with DBU accelerator in 10 pph Santicizer 261 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	25,24,22 $\bar{x}$=24	33,33,30 $\bar{x}$=32	31,33,28 $\bar{x}$=31	35,35,35 $\bar{x}$=35
Shore A hardness Replicate (2)	25,19,22 $\bar{x}$=22	30,30,31 $\bar{x}$=30	31,33,33 $\bar{x}$=32	40,37,37 $\bar{x}$=38

Figure 5.9 Graph showing build-up of Shore A hardness using 5 pph sodium birnessite 5 pph inert manganese dioxide diluent with DBU accelerator in 10 pph Santicizer 261 plasticiser



5.3.10 Experiment monitoring hardness build up using 4 pph sodium birnessite 6 pph manganese dioxide diluent with DBU accelerator and Santicizer 261 plasticiser

Cure mixture components:

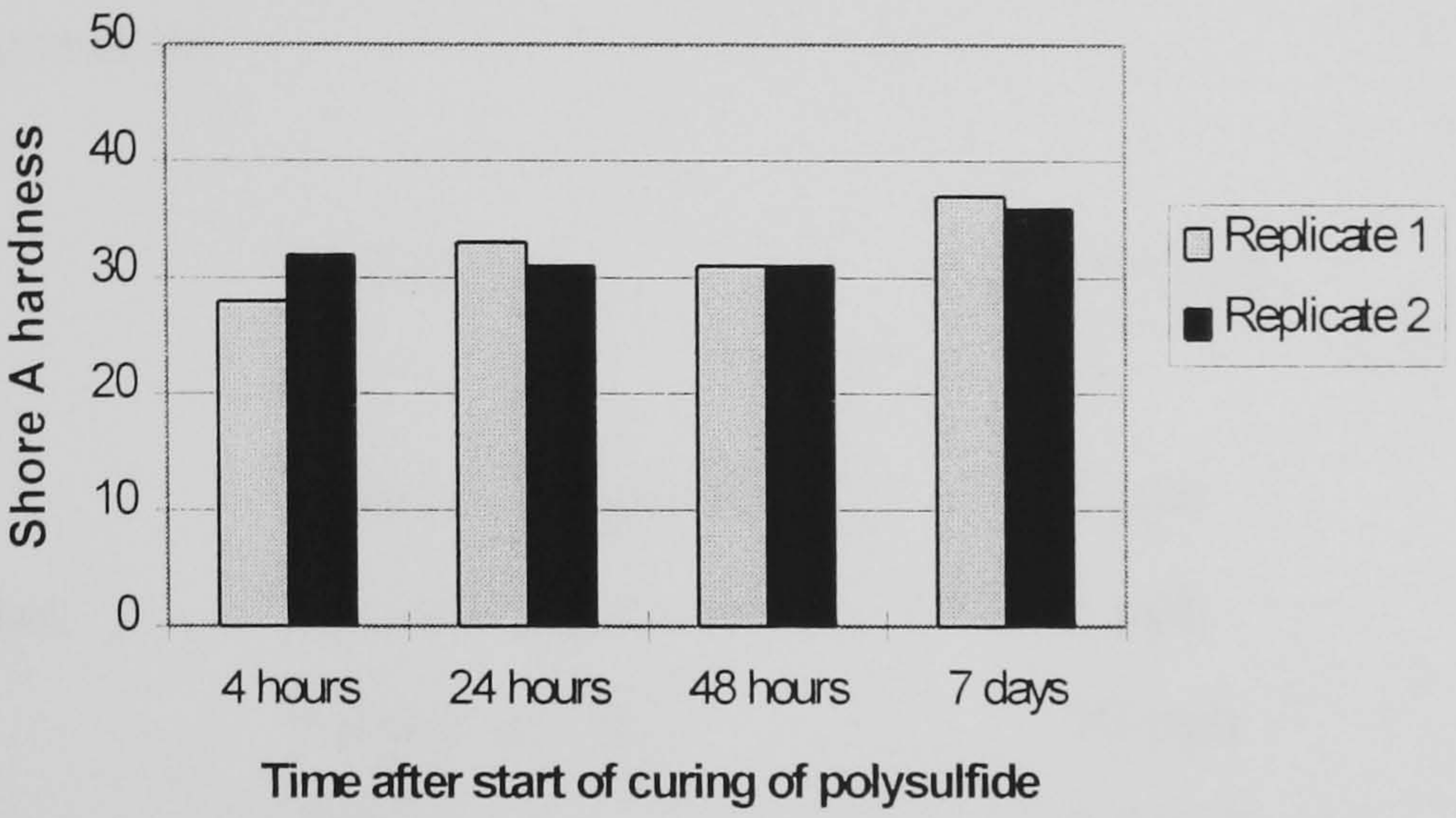
Part A:

Polysulfide	LP32C	100 pph
Part B:		
Curing agent	sodium birnessite	4 pph
Curing agent diluent	manganese dioxide	6 pph
Plasticiser	Santicizer 261	10 pph
Accelerator	DBU	0.5 pph

Table 5.10 Shore A hardness build-up using 4 pph sodium birnessite 6 pph manganese dioxide diluent with DBU accelerator in 10 pph Santicizer 261 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	29,29,25 $\bar{x}$=28	32,33,35 $\bar{x}$=33	33,29,32 $\bar{x}$=31	36,37,38 $\bar{x}$=37
Shore A hardness Replicate (2)	32,31,34 $\bar{x}$=32	31,30,32 $\bar{x}$=31	31,32,31 $\bar{x}$=31	35,36,37 $\bar{x}$=36

Figure 5.10 Graph showing build-up of Shore A hardness using 4 pph sodium birnessite 6 pph manganese dioxide diluent with DBU accelerator in 10 pph Santicizer 261 plasticiser



Results for experiments involving sodium birnessite, DBU accelerator and calcium carbonate diluent for polysulfide curing

5.3.11 Experiment monitoring hardness build up using 5 pph sodium birnessite 5 pph calcium carbonate diluent with DBU accelerator and Santicizer 261 plasticiser

Cure mixture components:

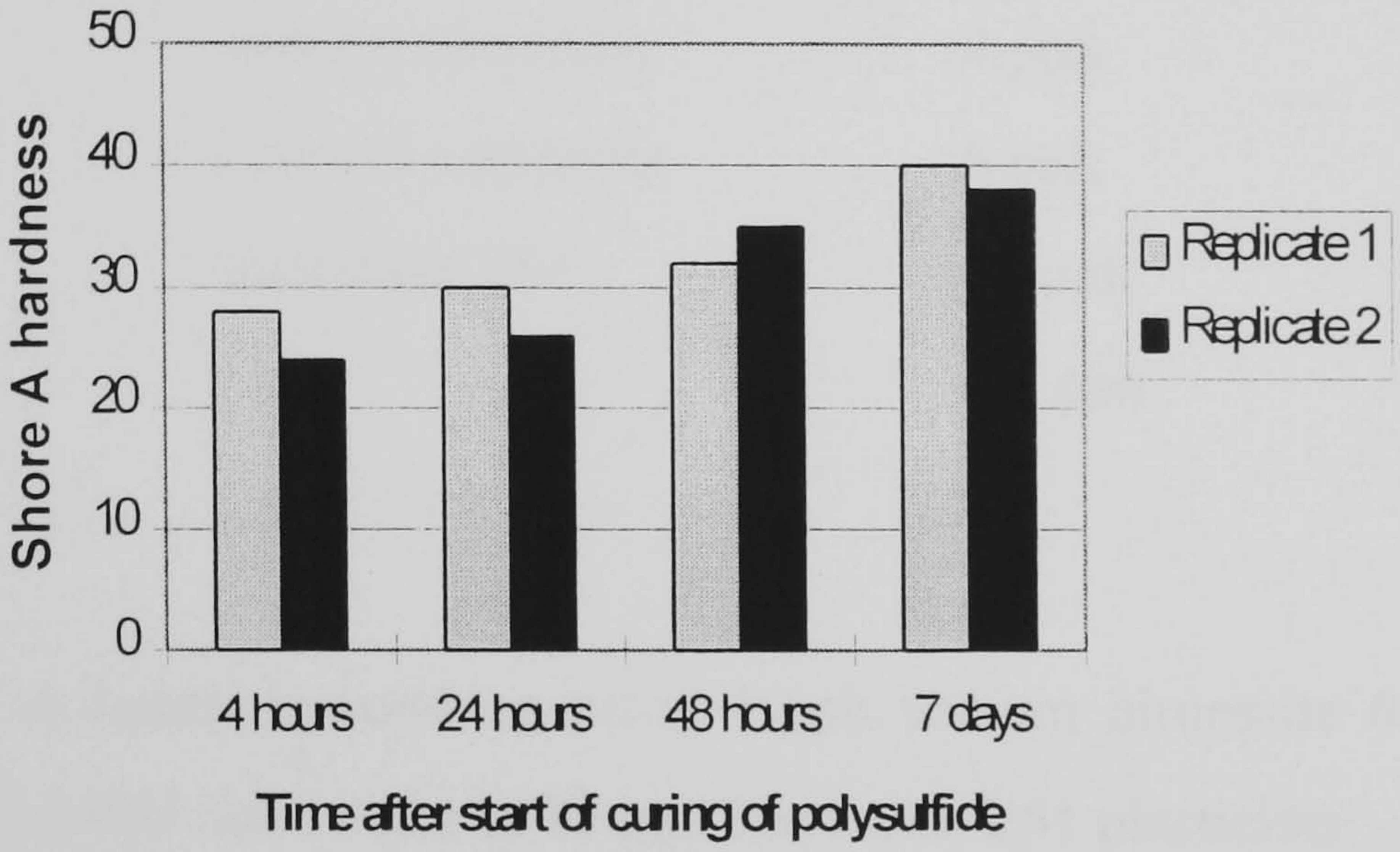
Part A:

Polysulfide	LP32C	100 pph
Part B:		
Curing agent	sodium birnessite	5 pph
Curing agent diluent:	calcium carbonate	5 pph
Plasticiser	Santicizer 261	10 pph
Accelerator	DBU	0.5 pph

Table 5.11 Shore A hardness build-up using 5 pph sodium birnessite 5 pph calcium carbonate diluent with DBU accelerator in 10 pph Santicizer 261 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	28,32,23 $\bar{x}$=28	29,29,31 $\bar{x}$=30	35,31,31 $\bar{x}$=32	38,42,40 $\bar{x}$=40
Shore A hardness Replicate (2)	21,28,23 $\bar{x}$=24	26,26,26 $\bar{x}$=26	35,34,37 $\bar{x}$=35	41,35,37 $\bar{x}$=38

Figure 5.11 Graph showing build-up of Shore A hardness using 5 pph sodium birnessite 5 pph calcium carbonate diluent with DBU accelerator in 10 pph Santicizer 261 plasticiser



5.3.12 Experiment monitoring hardness build up using 4 pph sodium birnessite 6 pph calcium carbonate diluent with DBU accelerator in 10 pph Santicizer 261 plasticiser

Cure mixture components:

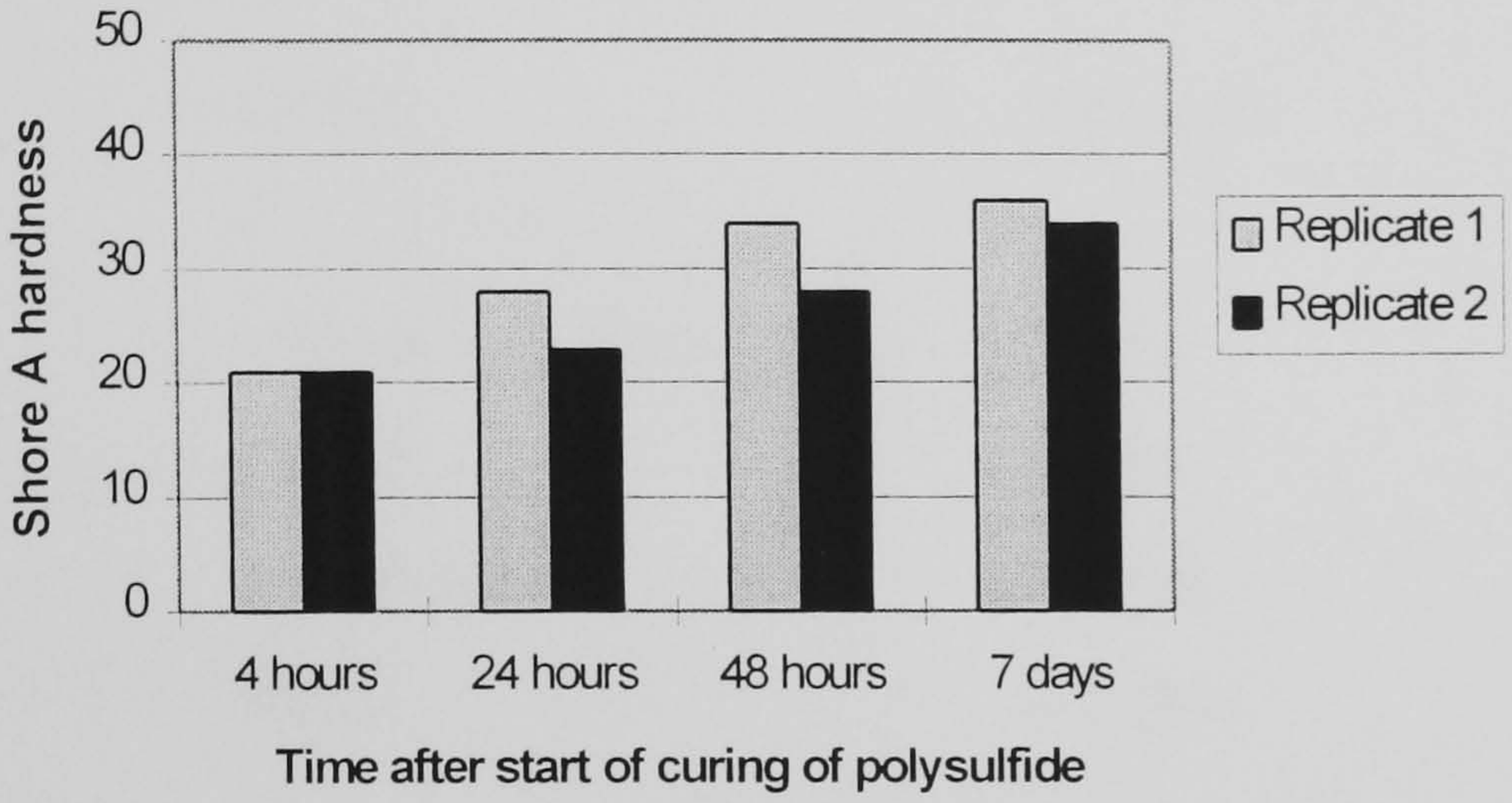
Part A:

Polysulfide	LP32C	100 pph
Part B:		
Curing agent	sodium birnessite	4 pph
Curing agent diluent	calcium carbonate	6 pph
Plasticiser	Santicizer 261	10 pph
Accelerator	DBU	0.5 pph

Table 5.12 Shore A hardness build-up using 4 pph sodium birnessite 6 pph calcium carbonate diluent with DBU accelerator in 10 pph Santicizer 261 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	21,21,22 $\bar{x}$=21	28,29,26 $\bar{x}$=28	33,33,36 $\bar{x}$=34	37,34,37 $\bar{x}$=36
Shore A hardness Replicate (2)	21,21,21 $\bar{x}$=21	24,24,21 $\bar{x}$=23	28,28,29 $\bar{x}$=28	37,32,34 $\bar{x}$=34

Figure 5.12 Graph showing build-up of Shore A hardness using 4 pph sodium birnessite 6 pph calcium carbonate diluent with DBU accelerator in 10 pph Santicizer 261 plasticiser



Results for experiments involving sodium birnessite DBU accelerator and no diluent for polysulfide curing

5.3.13 Experiment monitoring hardness build up using 5 pph sodium birnessite no curing agent diluent with DBU accelerator in 15 pph Santicizer 261 plasticiser

Cure mixture components:

Part A:

Polysulfide	LP32C	100 pph

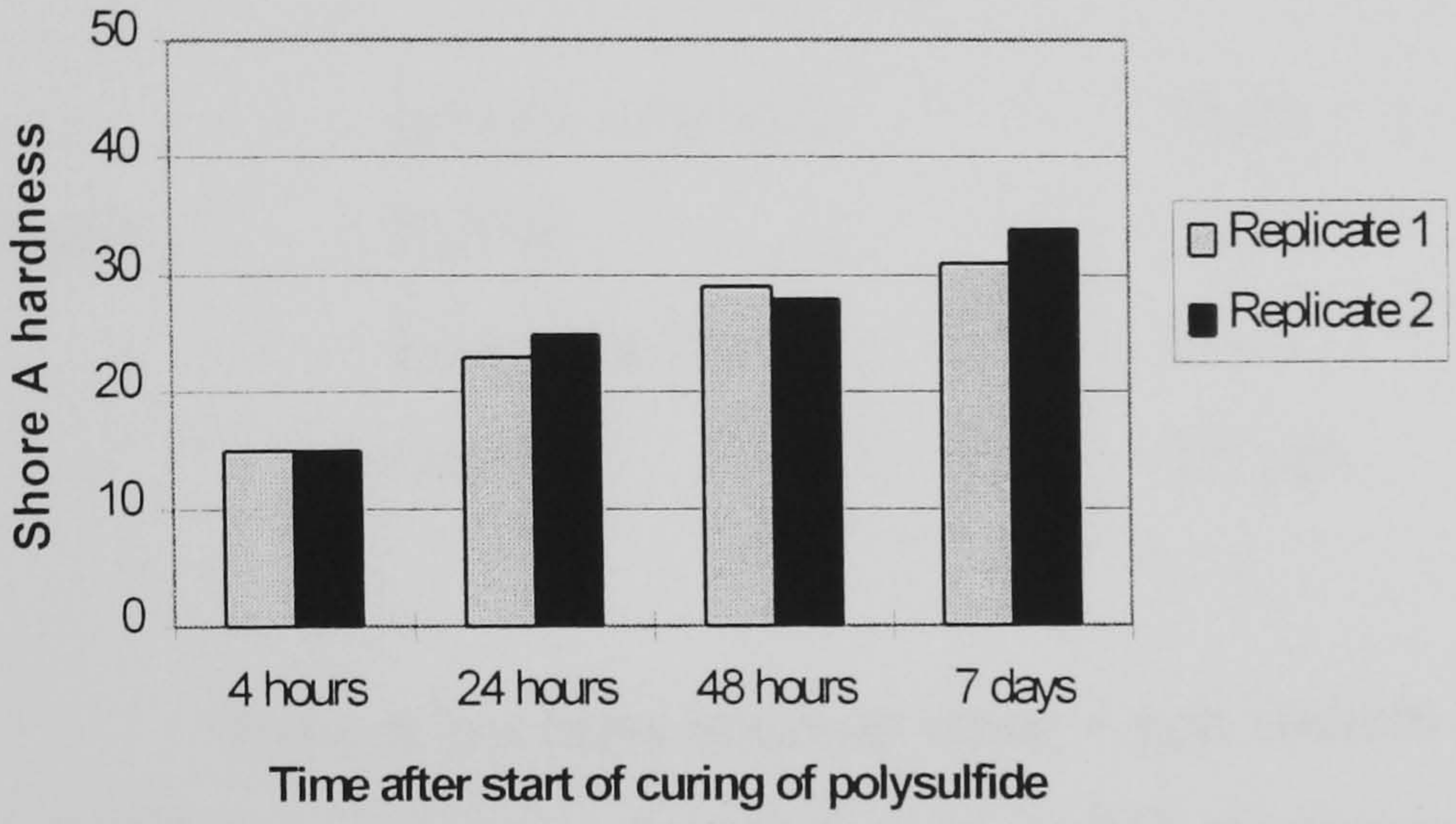
Part B:

Curing agent	sodium birnessite	5 pph
Curing agent diluent	NONE	0 pph
Plasticiser	Santicizer 261	15 pph
Accelerator	DBU	0.5 pph

Table 5.13 Shore A hardness build-up using 5 pph sodium birnessite no curing agent diluent with DBU accelerator in 15 pph Santicizer 261 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	15,13,17 x̄=15	23,23,23 x̄=23	32,28,27 x̄=29	29,31,32 x̄=31
Shore A hardness Replicate (2)	12,13,20 x̄=15	24,26,26 x̄=25	28,28,29 x̄=28	34,31,36 x̄=34

Figure 5.13 Graph showing build-up of Shore A hardness using 5 pph sodium birnessite no curing agent diluent with DBU accelerator in 15 pph Santicizer 261 plasticiser



5.3.14 Experiment monitoring hardness build up using 4 pph sodium birnessite no curing agent diluent with DBU accelerator and Santicizer 261 plasticiser

Cure mixture components:

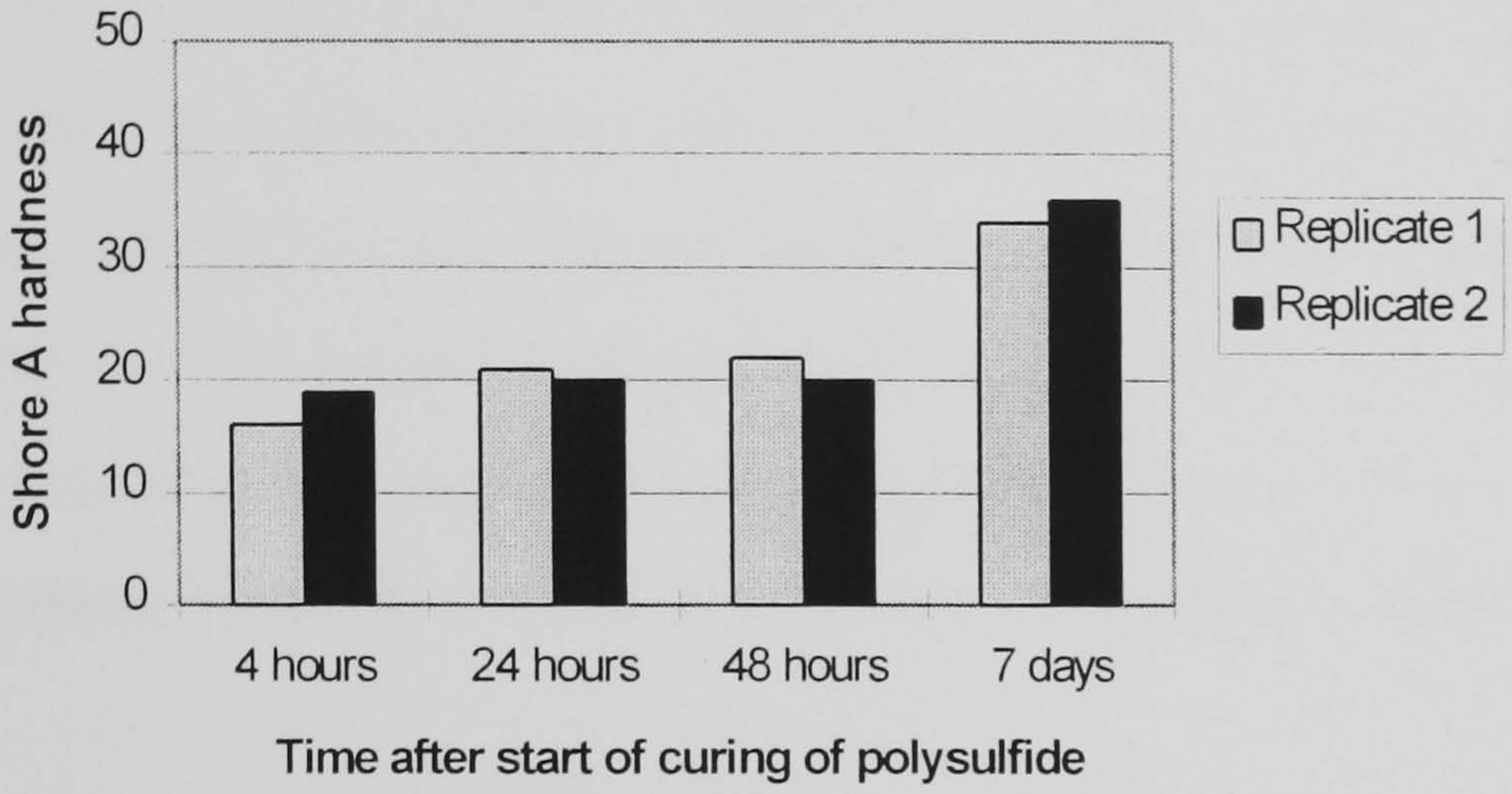
Part A:

Polysulfide	LP32C	100 pph
Part B:		
Curing agent	sodium birnessite	4 pph
Curing agent diluent	NONE	0 pph
Plasticiser	Santicizer 261	16 pph
Accelerator	DBU	0.5 pph

Table 5.14 Shore A hardness build-up using 4 pph sodium birnessite no curing agent diluent with DBU accelerator in 16 pph Santicizer 261 plasticiser

	Time			
	4 hours	24 hours	48 hours	7 days
Shore A hardness Replicate (1)	16,16,16 $\bar{x}$=16	20,20,23 $\bar{x}$=21	23,23,21 $\bar{x}$=22	37,33,32 $\bar{x}$=34
Shore A hardness Replicate (2)	20,19,18 $\bar{x}$=19	17,19,23 $\bar{x}$=20	21,20,19 $\bar{x}$=20	37,36,36 $\bar{x}$=36

Figure 5.14 Graph showing build up of Shore A hardness using 4 pph sodium birnessite no curing agent diluent with DBU accelerator in 16 pph Santicizer 261 plasticiser



5.4 RESULTS FOR STUDY OF SURFACE CONDITION

It was found by subjective assessment of the polysulfide that the commercial curing agent consistently produced a tack free polysulfide surface 7 days after the curing reaction was started. At 5 pph concentration, the sodium birnessite with all combinations of plasticiser, inert diluent and accelerator also produced polysulfide with tack free surface. At 4 pph sodium birnessite however, the surface of the polysulfide was found to be tacky after 7 days. The level of tackiness on the polysulfide samples which used calcium carbonate as the inert diluent, or with no diluent at all was, by the subjective assessment, the greatest. This suggests that 5 pph of sodium birnessite is the minimum useable level to achieve commercially viable cured products. It is commercially important for the polysulfide surface to be tack free as soon as possible after curing to ensure dust etc. does not contaminate the surface finish.

5.5 DISCUSSION

All of the cure mixtures tested at the 5 pph concentration of sodium birnessite, showed that this curing agent diluted with inert manganese dioxide or calcium carbonate and using TMTD or DBU as accelerators gives a Shore A hardness of greater than 30, the commercially acceptable minimum for insulating glass sealants. Even using no accelerator the sodium birnessite cured polysulfide has hardness over 30 after 7 days.

With sodium birnessite at 4 pph most test mixtures also give a satisfactory Shore A hardness. The only test mixture that led to a Shore A hardness of less than 30 after 7 days contained 4 pph sodium birnessite, no diluent, and using TMTD accelerator. Changing the accelerator to DBU however, increases the 7 day Shore A hardness to above 30, but up until 7 days the hardness is too low. Using a diluent, at 6 pph either as inert manganese dioxide or calcium carbonate, increases the hardness of the sample within 48 hours to above 30 which is a benefit of using the diluent.

All tests discussed in this chapter were carried out in the absence of fillers to reduce the number of variables. and even under these circumstances Shore A hardnesses of over 30 are achieved. In commercial uses. the cured polysulfides do contain fillers and this will increase the hardness. For example. Ramaswamy and Sasidharan Achary (1) obtained Shore A hardness of 58 with their manganese dioxide cured polysulfide. A reason for this is that in their cure mixture, 40 g of titanium dioxide, and 10 g of silica were added as fillers. Other workers (3) report that using 60 pph thermal black as a filler results in a Shore A hardness of up to 70. Unfilled LP32C polysulfide, however. cured with 7.5 pph of active manganese dioxide ("D Grade" from Diamond Shamrock Corporation) and 0.1 pph of sulfur additive. was reported to have a Shore A 7 day hardness of 39.(4) Usmani, (5) reports that the hardness of unfilled cured LP32C polymer (as used in these experiments) was Shore A 30, and Hanhela et al (6) reported a hardness of 36. This work on sodium birnessite and the commercial curing agent cured polysulfide is in agreement with the results obtained by Thiokol (4), Usmani (5) and Hanhela et al (6) as the level of Shore A hardness is similar.

With respect to the surface tack condition, this work shows that although the polysulfide surface was tack free using either the commercial curing agent or sodium birnessite, only when sodium birnessite was used at 5 pph a consistently tack free surface after 7 days was observed. At 4 pph sodium birnessite, the polysulfide surface was found to be tacky.

5.6 CONCLUSIONS

Manganese dioxide diluted sodium birnessite cured polysulfide has similar hardness build up to that of the commercial curing agent cured polysulfide, and a tack free surface despite being present at half the concentration of the commercial agent. From this work it appears that the optimal level of sodium birnessite to use as a curing agent is 5 pph. At 4 pph, the finished polysulfide product had a surface tackiness which is not commercially acceptable. These results are important in that they indicate the nature of the formulation of a polysulfide cure paste required to ensure that the optimal Shore A hardness is reached over a 7 day period.

5.7 REFERENCES

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CHAPTER 6 THERMOGRAVIMETRIC ANALYSIS (TGA) AND MEASUREMENT OF THE GLASS TRANSITION TEMPERATURE OF CURED POLYSULFIDES

6.1 INTRODUCTION

6.1.1 Introduction to thermogravimetric analysis of polysulfides

These experiments were conducted to assess the thermal stability of polysulfide cured with sodium birnessite, and compare this with the thermal stability of polysulfide cured using the commercial curing agent. The reason for this is that it is important that sodium birnessite cured polysulfide should have a similar thermal stability to that of polysulfide cured using the commercial curing agent.

Manganese oxides are known to reduce mercaptide (S-Mn-S) formation, and as a result manganese oxide formulated sealants provide service up to 250 °F.(1) However, the upper service temperature for most polysulfides is around 90 °C.(2)

The thermal degradation of polysulfide causes weight loss, and loss of flexibility because of the formation of a monosulfide structure. Thermal instability can also be caused by the addition of metal oxides to the polysulfide because the mercaptan groups react with the metal oxides, although this can be reduced by adding small amounts of sulfur.

Bertozzi (3) discussed the thermal stability of cured polysulfides. Above 150° C the terminal thiols react with the backbone formal groups to form thioformals and hydroxyl groups. The main decomposition process is a free radical oxidation at the formal group resulting in the formation of formic acid. This formic acid attacks other formal groups releasing formaldehyde. The polymeric mercaptan groups are then reduced to disulfide groups by the formic acid which is oxidised to formaldehyde. Increased quantities of hydoxyl groups formed by the hydrolysis of formals then react with thiols to form monosulfide links which harden the polysulfide.

Radhakrishnan and Rama Rao (4) and Rao and Radhakrishnan (5) studied the decomposition products of pyrolysis of cured polysulfide whilst Ramaswamy and Sasidharan Achary (6) studied the thermal decomposition of polysulfides. The temperature of initial decomposition of the polysulfide has been studied by Ramaswamy and Sasidharan Achary(6) who reported that 10 % weight loss occurs at 270 °C, 20 % at 280 °C, 30 % at 292 °C, and 40 % at 295 °C. The temperature of the maximum rate of decomposition of MnO_2 cured polysulfide is given in the literature as 300 °C. (6)

This Chapter contains details of thermogravimetric analyses of uncured liquid polysulfide, and all of the samples that produced a cured polysulfide at 4 pph or 5 pph of sodium birnessite or 10 pph of the commercial curing agent.

6.1.2 Introduction to the measurement of the glass transition temperature of cured polysulfide

The glass transition temperature of polysulfides depends on the liquid polysulfide used and the compounding ingredients. Polymers with glass transition temperature above room temperature are brittle, for example Perspex, whilst polymers, such as cured polysulfides, with glass transition temperatures below room temperature are more flexible. It is the formal linkages ($-O-CH_2-O$) in the polysulfide that gives it low temperature flexibility. (2) Dynamic Mechanical Thermal Analysis (DMTA) studies on cured polysulfides have been reported, for example on one part polysulfides by Allen(7) and Startsev and Baranovskaya,(8) and on two part polysulfide systems cured with manganese dioxide by Ramaswamy and Sasidharan Achary.(6) Research by Severina et al(9) showed that the presence of fillers has very little effect on the glass transition temperature of cured polysulfides due to the low level of interactions between the surface of the filler and the polymer.

Morton (10) quoted a glass transition temperature range of -40 to -60 °C in their literature on polysulfide. Ramaswamy and Sasidharan Achary(6) however reported a slightly higher Tg point of -32 °C for polysulfide cured with commercially available manganese dioxide, whilst Startsev and Baranovskaya (8) reported -56 °C, and Chun and Gent (11) -55 °C. The storage moduli E′ curves shown in the work presented here provide information on the effect of temperature on the load bearing characteristics of the material. The loss moduli E″ and the tanδ curves help identify regions where specific types of molecular motion effect the mechanical properties of the polymers over fairly narrow temperature bands.(8)

6.2 EXPERIMENTAL

6.2.1 Experimental for thermogravimetric analysis

The thermogravimetric balance used was calibrated for weight loss by monitoring the decomposition of calcium oxalate to calcium peroxide which shows three distinct weight loss steps due to the loss of H_2O, CO and CO_2. Temperature calibration was achieved using the change in weight over temperature of three magnetic metals. Samples of uncured liquid polysulfide, and all the cured polysulfide samples were analysed in replicate. The heating rate, atmosphere used and sample weight used in this work were:

Sample size: 6 mg $^{+}/_{-}1$
Heating rate: 10 °C per minute
Crucible: platinum
Start temp: 40 °C
End temp: 640 °C
Nitrogen flow rate: 30 ml per minute.

6.2.2 Experimental for Dynamic Mechanical Thermal Analysis

The instrument used in the present studies was a Rheometrics Solid Analyser (RSA II). Samples of polysulfide were cured using either sodium birnessite diluted with inert manganese dioxide or calcium carbonate and combinations of plasticisers and accelerators. Polysulfide cured using the best currently available commercial curing agent, with combinations of different plasticisers and accelerators, was also analysed.

As with all the experiments conducted in this research, the total amount of cure paste was 20.5 pph (parts per 100 parts liquid polysulfide). After mixing the polysulfide and the cure paste for 5 minutes a sample was poured into a cylindrical plastic mould and the mixture left to cure for 1 week at room temperature. A sample of the cured polysulfide was then cut from the cure mould using a razor blade to maintain the cylindrical shape and the sample length and radius measured. Samples of the cured polysulfide were cut to obtain a roughly 7 mm long and 8 mm wide cylinder.

The RSA II instrument was set in Dynamic Temperature Step mode, and tension compression testing was performed using the sample on parallel plates from -60 °C to 30 °C. A frequency of 6.28 rad/s and a strain of 0.1 % was used, a 2 °C step increase in temperature and 1 minute measurement time were used. The instrument was calibrated using a standard steel bar to test the elastic modulus in three point bending. The transducer was checked using a 500 g weight, and a thermocouple was used to check the instrument temperature. The instrument measures the elastic modulus and viscous modulus of the polymer at the selected temperatures and, from this data, calculates the glass transition temperature.

6.3 RESULTS

6.3.1 Results for thermogravimetric analysis

Samples of uncured liquid polysulfide were analysed for their thermal stability. These are shown in Figures 6.1 and 6.2, and the data on the thermal decomposition are shown in Tables 6.1 and 6.2. A graphical display of the weight loss of one commercial curing agent cured polysulfide sample and one sodium birnessite cured polysulfide sample is shown in Figure 6.3 and 6.4 respectively. No other Figures are included as the thermograms for every combination of curing agent, accelerator, diluent and plasticiser studied are similar. The numerical results are given in Tables showing the temperature of maximum weight loss, the total weight loss and the cumulative weight loss over a range of temperatures from 30 to 630 °C. The experiments in this work involving thermal decomposition of the commercial curing agent cured polysulfides are displayed first as Tables 6.3 to 6.6, the variable in the polysulfide cure mix changed being the plasticiser, using the more viscous Santicizer 278 and the less viscous Santicizer 261 with a TMTD accelerator. These results are followed by the experiments involving thermogravimetric analysis of sodium birnessite cured polysulfide firstly without accelerator, then TMTD accelerator, and then the DBU accelerator. The results are all replicated and data for replicate measurements for each of the cured polysulfide samples are given in the Tables.

Results for the dynamic mechanical thermal analysis studies

Shown in Tables 6.29 to 6.32

Experiment 6.1

Figure 6.1 Thermal decomposition of the uncured liquid polysulfide polymer

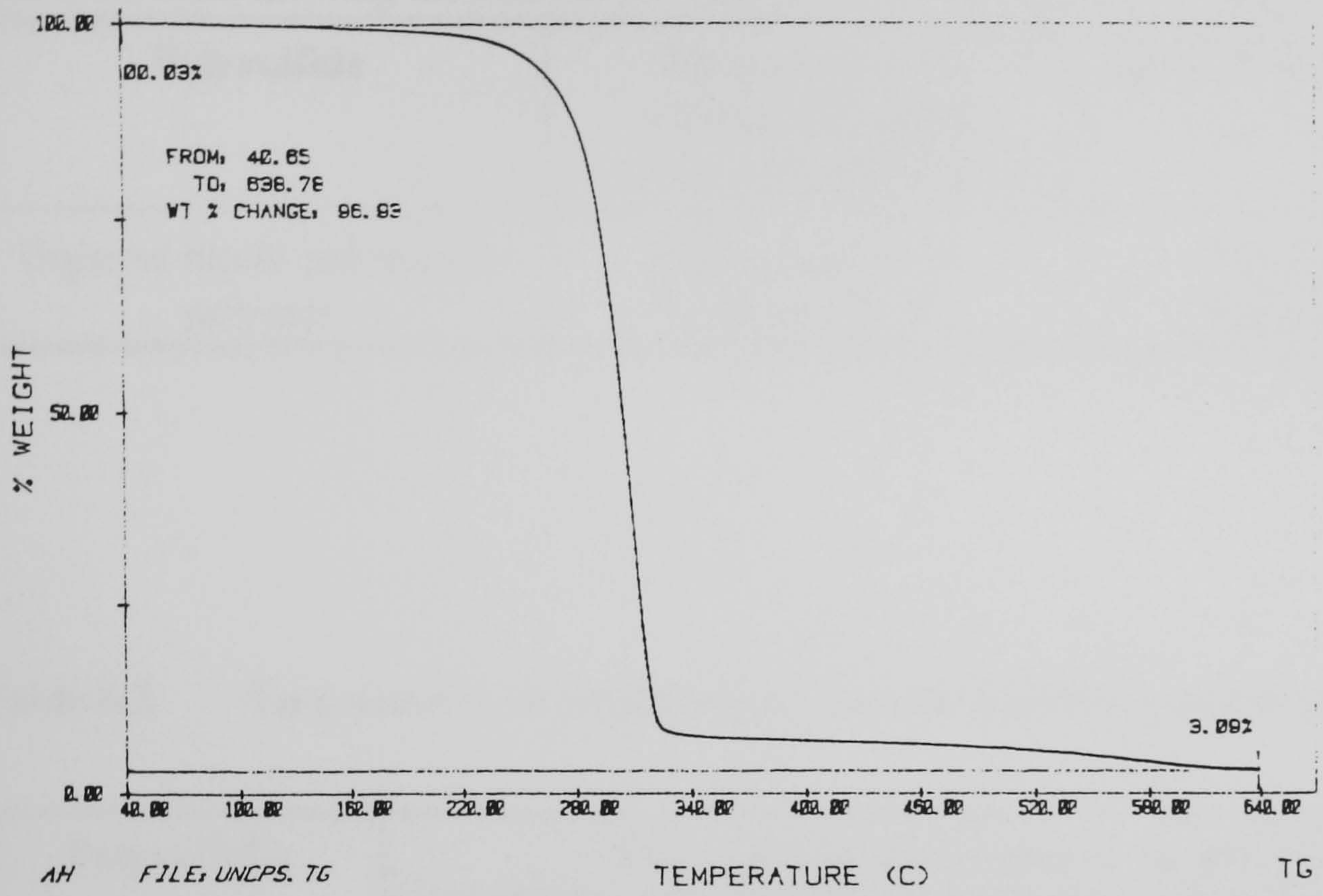
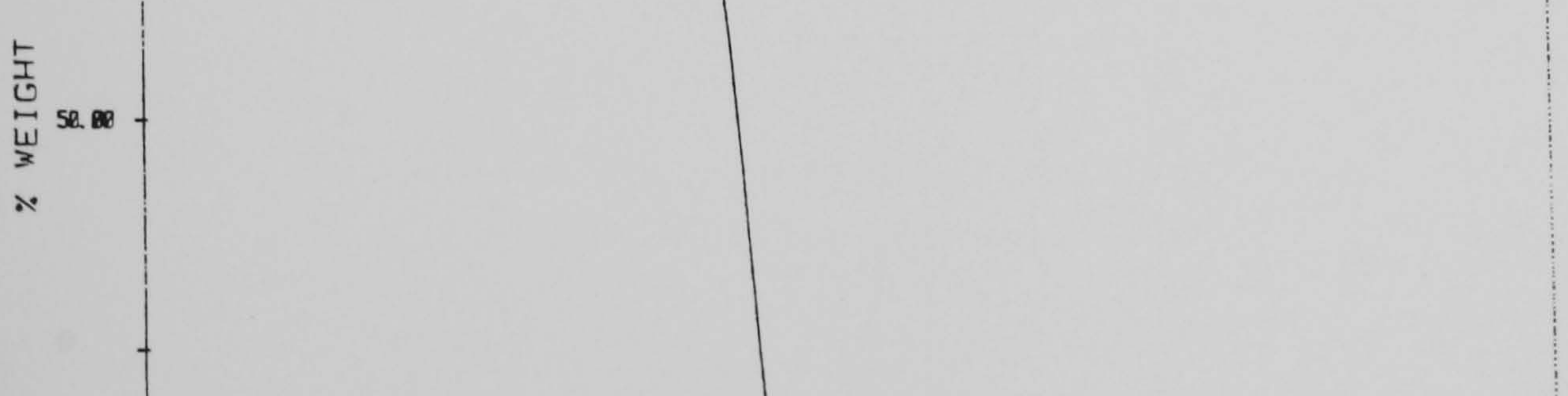


Figure 6.2 Thermal decomposition of the uncured liquid polysulfide polymer (replicate experiment)



Experiment 6.1

Table 6.1 Data showing the thermal decomposition of the uncured liquid polysulfide polymer

Polysulfide	**Temperature of maximum rate of decomposition °C**	**Loss of weight of sample %**
Uncured liquid polysulfide polymer	Replicate (1) 314 Replicate (2) 311	Replicate (1) 97.6 Replicate (2) 96.9

Table 6.2 Temperatures of weight loss of uncured liquid polysulfide polymer.

Polysulfide:	**Temperature of various % weight loss (°C)**						
	10%	20%	30%	40%	50%	60%	70%
Uncured liquid polysulfide	(1)279 (2)276	(1)291 (2)289	(1)298 (2)296	(1)303 (2)302	(1)306 (2)305	(1)310 (2)309	(1)313 (2)312

Figure 6.3 The thermal decomposition of polysulfide cured with 10 pph commercial curing agent 0.5 pph TMTD accelerator, in 10 pph Santicizer 261 plasticiser

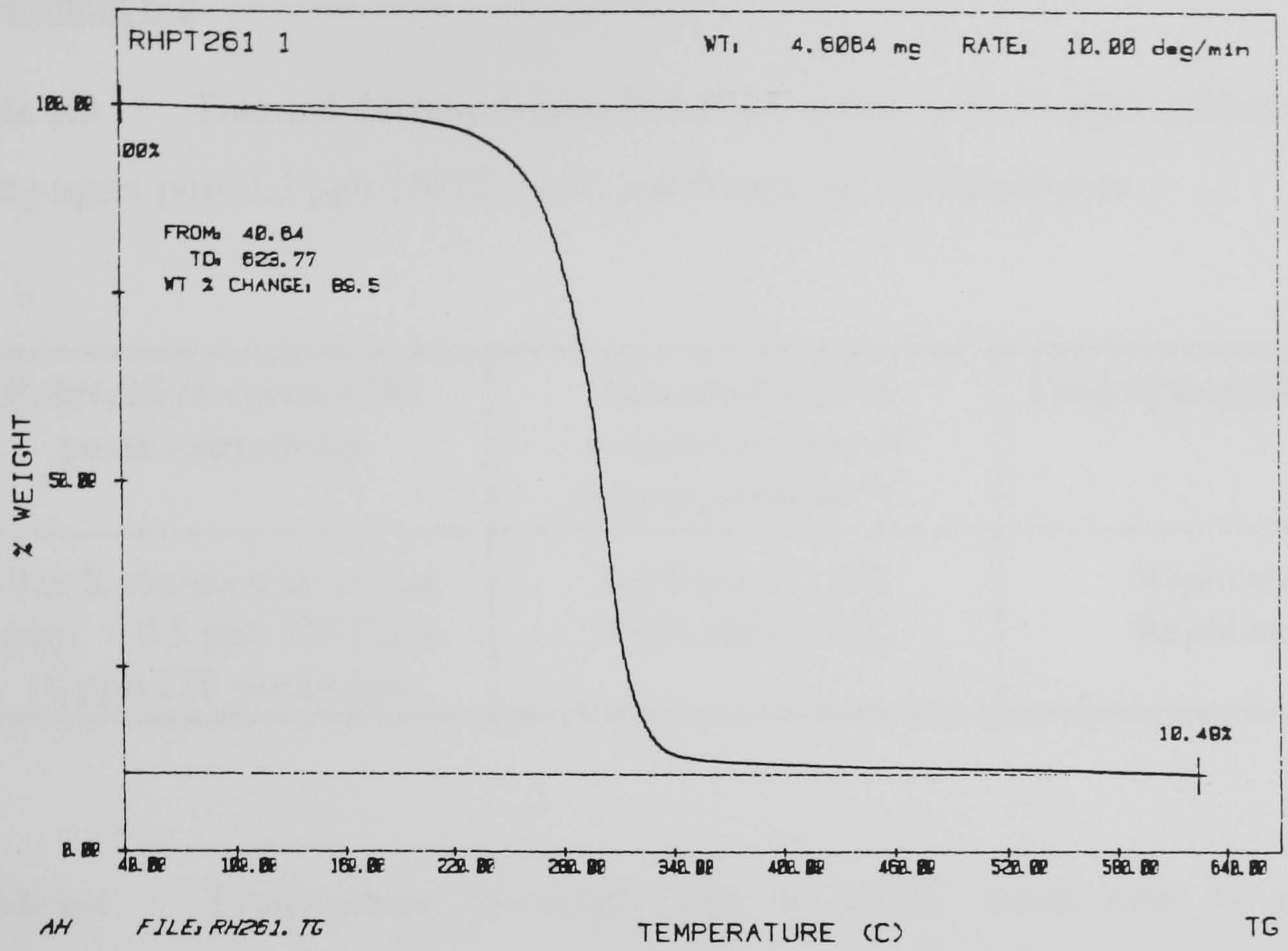
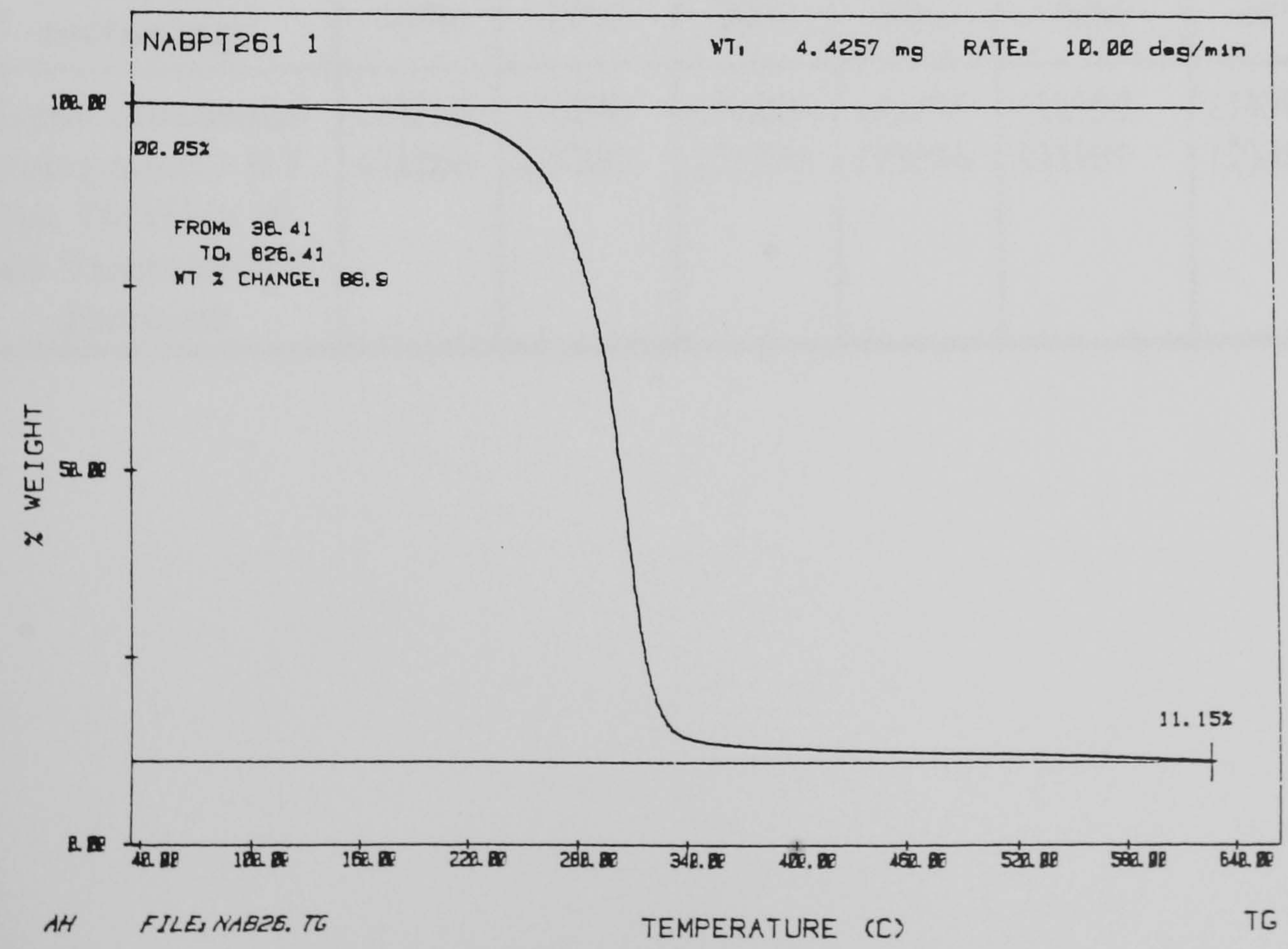


Figure 6.4 The thermal decomposition of polysulfide cured with 5 pph sodium birnessite, 5 pph inert manganese dioxide diluent 0.5 pph TMTD accelerator in 10 pph Santicizer 261 plasticiser



Results of thermogravimetric analysis of the undiluted commercial curing agent cured polysulfide

Experiment 6.2

Table 6.3 Thermal decomposition of LP32C cured with 10 pph undiluted commercial curing agent plus 0.5 pph TMTD in 10 pph Santicizer *278* plasticiser

Polysulfide cured with paste containing	Temperature of maximum rate of decomposition °C	Loss of weight of sample %
10 pph commercial curing agent + 0.5 pph TMTD in 10 pph 278 plasticiser	Replicate (1) 303 Replicate (2) 302	Replicate (1)89.3 Replicate (2)89.7

Table 6.4 Temperatures of weight loss of LP32C cured with 10 pph undiluted commercial curing agent plus 0.5 pph TMTD in 10 pph Santicizer *278* plasticiser

Polysulfide cured with paste containing:	Temperature of various % weight loss (°C)						
	10%	20%	30%	40%	50%	60%	70%
10 pph commercial curing agent + 0.5 pph TMTD in 10 pph Santicizer 278 plasticiser	(1)266 (2)266	(1)280 (2)281	(1)289 (2)289	(1)295 (2)296	(1)300 (2)301	(1)304 (2)305	(1)309 (2)310

Experiment 6.3

Table 6.5 Thermal decomposition of LP32C cured with 10 pph undiluted commercial curing agent plus 0.5 pph TMTD in 10 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	**Temperature of maximum rate of decomposition °C**	**Loss of weight of sample %**
10 pph commercial curing agent + 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser	Replicate (1) 307 Replicate (2) 306	Replicate (1) 89.5 Replicate (2) 89.1

Table 6.6 Temperatures of weight loss of LP32C cured with 10 pph undiluted commercial curing agent plus 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser

Polysulfide cured with paste containing:	**Temperature of various % weight loss (°C)**						
	10%	20%	30%	40%	50%	60%	70%
10 pph commercial curing agent + 0.5 pph TMTD in 261 plasticiser	(1)263 (2)264	(1)280 (2)282	(1)290 (2)293	(1)297 (2)300	(1)302 (2)304	(1)306 (2)308	(1)311 (2)313

Results of thermogravimetric analysis of sodium birnessite cured polysulfide with no accelerator

Experiment 6.4

Table 6.7 Thermal decomposition of LP32C cured with 5 pph of sodium birnessite with no accelerator or inert diluent in 15.5 pph Santiciser 261 plasticiser

Polysulfide cured with paste containing:	**Temperature of maximum rate of decomposition °C**	**Loss of weight of sample %**
5 pph sodium birnessite + NO ACCELERATOR + NO DILUENT + 15.5 pph 261 plasticiser	Replicate (1)308 Replicate (2)310	Replicate (1)93.5 Replicate (2)94.7

Table 6.8 Temperatures of weight loss of LP32C cured with 5 pph of sodium birnessite with no inert diluent and no accelerator in 15.5 pph Santiciser 261 plasticiser

Polysulfide cured with paste containing:	**Temperature of various % weight loss (°C)**						
	10%	20%	30%	40%	50%	60%	70%
5 pph sodium birnessite + NO ACCELERATOR +NO DILUENT + 15.5 pph Santicizer 261 plasticiser	(1)261 (2)254	(1)282 (2)275	(1)293 (2)287	(1)299 (2)296	(1)304 (2)301	(1)307 (2)306	(1)311 (2)311

Results of thermogravimetric analysis of sodium birnessite cured polysulfide with TMTD accelerator

Experiment 6.5

Table 6.9 Thermal decomposition of LP32C cured with 5 pph sodium birnessite with 5 pph inert MnO_2 diluent plus 0.5 pph TMTD in 10 pph Santicizer 278 plasticiser

Polysulfide cured with paste containing:	**Temperature of maximum rate of decomposition °C**	**Loss of weight of sample %**
5 pph sodium birnessite + 5 pph inert MnO_2 ore + 0.5 pph TMTD in 10 pph Santicizer 278 plasticizer	Replicate (1) 308 Replicate (2) 305	Replicate (1) 88.9 Replicate (2) 88.9

Table 6.10 Temperatures of weight loss of LP32C cured with 5 pph of sodium birnessite with 5 pph inert manganese dioxide plus 0.5 pph TMTD in 10 pph Santicizer *278* plasticiser

Polysulfide cured with paste containing:	**Temperature of various % weight loss (°C)**						
	10%	20%	30%	40%	50%	60%	70%
5 pph sodium birnessite + 5 pph inert MnO_2 ore +0.5 pph TMTD in 10 pph Santicizer 278 plasticiser	(1)268 (2)268	(1)285 (2)285	(1)294 (2)294	(1)300 (2)300	(1)305 (2)305	(1)309 (2)309	(1)314 (2)314

Experiment 6.6

Table 6.11 Thermal decomposition of LP32C cured with 5 pph sodium birnessite with 5 pph inert MnO_2 diluent plus 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser

Polysulfide cured with paste containing:	**Temperature of maximum rate of decomposition °C**	**Loss of weight of sample %**
5 pph sodium birnessite + 5 pph inert MnO_2 diluent +0.5 pph TMTD in Santicizer 261 plasticiser	Replicate (1) 308 Replicate (2) 308	Replicate (1) 88.9 Replicate (2) 88.9

Table 6.12 Temperatures of weight loss of LP32C cured with 5 pph sodium birnessite with 5 pph inert MnO_2 diluent plus 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser

Polysulfide cured with paste containing:	**Temperature of various % weight loss (°C)**						
	10%	20%	30%	40%	50%	60%	70%
5 pph sodium birnessite + 5 pph inert MnO_2 diluent +0.5 pph TMTD in Santicizer 261 plasticiser	(1)265 (2)267	(1)282 (2)285	(1)293 (2)295	(1)300 (2)301	(1)305 (2)306	(1)309 (2)310	(1)314 (2)315

Experiment 6.7

Table 6.13 Thermal decomposition of LP32C cured with 5 pph sodium birnessite with no inert diluent plus 0.5 pph TMTD in 15 pph Santicizer 261 plasticiser

Polysulfide cured with paste containing:	**Temperature of maximum rate of decomposition °C**	**Loss of weight of sample %**
5 pph sodium birnessite + NO DILUENT +0.5 pph TMTD in 15 pph Santicizer 261 plasticiser	Replicate (1) 304 Replicate (2) 309	Replicate (1) 93.2 Replicate (2) 93.9

Table 6.14 Temperatures of weight loss of LP32C cured with 5 pph of undiluted sodium birnessite plus 0.5 pph TMTD in 15 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	**Temperature of various % weight loss (°C)**						
	10%	20%	30%	40%	50%	60%	70%
5 pph sodium birnessite + NO DILUENT + 0.5 pph TMTD + 15 pph of Santicizer 261 plasticiser	(1)251 (2)258	(1)275 (2)280	(1)288 (2)292	(1)297 (2)300	(1)303 (2)305	(1)307 (2)309	(1)312 (2)313

Experiment 6.8

Table 6.15 Thermal decomposition of LP32C cured with 4 pph sodium birnessite with no inert diluent plus 0.5 pph TMTD in 16 pph Santicizer 261 plasticiser

Polysulfide cured with paste containing:	**Temperature of maximum rate of decomposition °C**	**Loss of weight of sample %**
4 pph sodium birnessite +NO DILUENT + 0.5 pph TMTD in 16 pph Santicizer 261 plasticiser	Replicate (1) 307 Replicate (2) 306	Replicate (1) 95.9 Replicate (2) 96.2

Table 6.16 Temperatures of weight loss of LP32C cured with 4 pph of undiluted sodium birnessite plus 0.5 pph TMTD in 16 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	**Temperature of various % weight loss (°C)**						
	10%	20%	30%	40%	50%	60%	70%
4 pph sodium birnessite + NO DILUENT + 0.5 pph TMTD in 16 pph of Santicizer 261 plasticiser	(1)257 (2)251	(1)281 (2)279	(1)292 (2)291	(1)298 (2)298	(1)302 (2)303	(1)307 (2)307	(1)311 (2)311

Experiment 6.9

Table 6.17 Thermal decomposition of LP32C cured with 5 pph sodium birnessite with 5 pph $CaCO_3$ plus 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser

Polysulfide cured with paste containing:	**Temperature of maximum rate of decomposition °C**	**Loss of weight of sample %**
5 pph sodium birnessite + 5 pph $CaCO_3$ + 0.5 pph TMTD in Santicizer 261 plasticiser	Replicate (1) 312 Replicate (2) 309	Replicate (1)90.9 Replicate (2)89.0

Table 6.18 Temperatures of weight loss of LP32C cured with 5 pph sodium birnessite with 5 pph of calcium carbonate plus 0.5 pph TMTD in 10 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	**Temperature of various % weight loss (°C)**						
	10%	20%	30%	40%	50%	60%	70%
5 pph sodium birnessite + 5 pph $CaCO_3$ + 0.5 pph TMTD in Santicizer 261 plasticiser	(1)269 (2)262	(1)290 (2)284	(1)301 (2)295	(1)306 (2)302	(1)310 (2)307	(1)314 (2)311	(1)319 (2)316

Results of thermogravimetric analysis of sodium birnessite cured polysulfide with DBU accelerator

Experiment 6.10

Table 6.19 Thermal decomposition of LP32C cured with 5 pph sodium birnessite plus 5 pph of inert manganese dioxide diluent with 0.5 pph DBU accelerator in 10 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	Temperature of maximum rate of decomposition °C	Loss of weight of sample %
5 pph sodium birnessite +5 pph MnO_2 + 0.5 pph DBU in 10 pph Santicizer 261 plasticiser	Replicate (1) 314 Replicate (2) 312	Replicate (1)89.8 Replicate (2)89.7

Table 6.20 Temperatures of weight loss of LP32C cured with 5 pph sodium birnessite plus 5 pph of inert manganese dioxide diluent with 0.5 pph DBU accelerator in 10 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	Temperature of various % weight loss (°C)						
	10%	20%	30%	40%	50%	60%	70%
5 pph sodium birnessite +5 pph MnO_2 + 0.5 pph DBU in 10 pph Santicizer 261 plasticiser	(1)269 (2)271	(1)289 (2)291	(1)299 (2)300	(1)305 (2)305	(1)309 (2)309	(1)313 (2)313	(1)318 (2)317

Experiment 6.11

Table 6.21 Thermal decomposition of LP32C cured with 5 pph undiluted sodium birnessite with 0.5 pph DBU accelerator in 15 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	**Temperature of maximum rate of decomposition °C**	**Loss of weight of sample %**
5 pph sodium birnessite + NO DILUENT + 0.5 pph DBU in 15 pph Santicizer 261 plasticiser	Replicate (1)304 Replicate (2)307	Replicate (1)94.7 Replicate (2)93.2

Table 6.22 Temperatures of weight loss of LP32C cured with 5 pph undiluted sodium birnessite with 0.5 pph DBU accelerator in 15 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	**Temperature of various % weight loss (°C)**						
	10%	20%	30%	40%	50%	60%	70%
5 pph sodium birnessite + NO DILUENT + 0.5 pph DBU in 15 pph Santicizer 261 plasticiser	(1)252 (2)250	(1)277 (2)275	(1)290 (2)289	(1)298 (2)298	(1)303 (2)304	(1)306 (2)308	(1)310 (2)313

Experiment 6.12

Table 6.23 Thermal decomposition of LP32C cured with 4 pph of sodium birnessite plus 6 pph of inert manganese dioxide diluent and 0.5 pph DBU accelerator in 10 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	**Temperature of maximum rate of decomposition °C**	**Loss of weight of sample %**
4 pph sodium birnessite + 6 pph inert MnO_2 with 0.5 pph DBU +10 pph Santicizer 261 plasticiser	Replicate (1)312 Replicate (2)310	Replicate (1)88.7 Replicate (2)88.2

Table 6.24 Temperatures of weight loss of LP32C cured with 4 pph of sodium birnessite plus 6 pph of inert manganese dioxide diluent with 0.5 pph DBU accelerator and in 10 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	**Temperature of various % weight loss (°C)**						
	10%	20%	30%	40%	50%	60%	70%
4 pph sodium birnessite + 6 pph inert MnO_2 with 0.5 pph DBU +10 pph Santicizer 261 plasticiser	(1)266 (2)265	(1)286 (2)286	(1)296 (2)296	(1)304 (2)302	(1)308 (2)307	(1)313 (2)311	(1)317 (2)316

Experiment 6.13

Table 6.25 Thermal decomposition of LP32C cured with 4 pph sodium birnessite and 6 pph calcium carbonate diluent with 0.5 pph DBU accelerator in 10 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	**Temperature of maximum rate of decomposition °C**	**Loss of weight of sample %**
4 pph sodium birnessite + 6 pph $CaCO_3$ with 0.5 pph DBU +10 pph Santicizer 261 plasticiser	Replicate (1)306 Replicate (2)309	Replicate (1)90.6 Replicate (2)89.4

Table 6.26 Temperatures of weight loss of LP32C cured with 4 pph sodium birnessite and 6 pph calcium carbonate with 0.5 pph DBU accelerator in 10 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	**Temperature of various % weight loss (°C)**						
	10%	20%	30%	40%	50%	60%	70%
4 pph sodium birnessite + 6 pph $CaCO_3$ with 0.5 pph DBU +10 pph Santicizer 261 plasticiser	(1)260 (2)262	(1)283 (2)283	(1)294 (2)295	(1)301 (2)302	(1)306 (2)307	(1)310 (2)312	(1)315 (2)317

Experiment 6.14

Table 6.27 Thermal decomposition of LP32C cured with 4 pph undiluted sodium birnessite plus 0.5 pph DBU in 16 pph Santicizer 261 plasticiser

Polysulfide cured with paste containing:	**Temperature of maximum rate of decomposition °C**	**Loss of weight of sample %**
4 pph sodium birnessite +NO DILUENT + 0.5 pph DBU in 16 pph Santicizer 261 plasticiser	Replicate (1)309 Replicate (2)310	Replicate (1)94.5 Replicate (2)93.7

Table 6.28 Temperatures of weight loss of LP32C cured with 4 pph of undiluted sodium birnessite plus 0.5 pph DBU accelerator in 16 pph Santicizer *261* plasticiser

Polysulfide cured with paste containing:	**Temperature of various % weight loss (°C)**						
	10%	20%	30%	40%	50%	60%	70%
4 pph sodium birnessite + NO DILUENT + 0.5 pph DBU in 16 pph of Santicizer 261 plasticiser	(1)256 (2)255	(1)279 (2)276	(1)292 (2)289	(1)299 (2)299	(1)305 (2)304	(1)309 (2)309	(1)313 (2)314

6.3.2 Results for the Dynamic Mechanical Thermal Analysis of polysulfides

Tables 6.29, 6.30, 6.31 and 6.32 summarise the glass transition temperatures for polysulfide samples cured using the commercial curing agent, as well as sodium birnessite with TMTD accelerator, sodium birnessite with DBU accelerator, and sodium birnessite with no accelerator respectively. Each experiment was repeated using a separate sample of polysulfide. The results are given as replicates in the Tables.

Figures 6.5 and 6.6 are graphical outputs of DMTA measurements of polysulfide cured with the commercial curing agent and sodium birnessite with the TMTD accelerator. The Figures show data for the elastic (E′) and viscous (E″) moduli, and the tan δ values over the selected temperature range. Only two Figures are given in the results section as the data for the testing of all the cured polysulfide samples are virtually identical.

Table 6.29 Summary of Glass Transition temperatures of liquid polysulfide cured with 10 pph commercial curing agent and TMTD accelerator

Polysulfide sample cured with:	**Glass transition temperature °C**
10 pph commercial curing agent + 0.5 pph TMTD in 10 pph *278* plasticiser	Replicate (1) -42 Replicate (2) -42
10 pph commercial curing agent + 0.5 pph TMTD in 10 pph 261 plasticiser	Replicate (1) -42 Replicate (2) -42

Table 6.30 Summary of Glass Transition temperatures of liquid polysulfide cured with sodium birnessite and TMTD accelerator

Polysulfide sample cured with:	**Glass transition temperature °C**
5 pph sodium birnessite + 5 pph of MnO_2 + 0.5 pph TMTD in 10 pph *278* plasticiser	Replicate (1) -42 Replicate (2) -42
5 pph sodium birnessite + 5 pph of MnO_2 +0.5 pph TMTD in 10 pph 261 plasticiser	Replicate (1) -44 Replicate (2) -44
5 pph sodium birnessite + 5 pph $CaCO_3$ + 0.5 pph TMTD in 10 pph 261 plasticiser	Replicate (1) -44 Replicate (2) -44
5 pph sodium birnessite + NO DILUENT + 0.5 pph TMTD in 15 pph 261 plasticiser	Replicate (1) -44 Replicate (2) -44
4 pph of sodium birnessite + NO DILUENT 0.5 pph TMTD in 16 pph 261 plasticiser	Replicate (1) -44 Replicate (2) -44

Table 6.31 Summary of Glass Transition temperatures of liquid polysulfide cured with sodium birnessite and DBU accelerator

Polysulfide sample cured with:	Glass transition temperature °C
5 pph sodium birnessite + 5 pph MnO_2 + 0.5 pph DBU in 10 pph 261 plasticiser	Replicate (1) -44 Replicate (2) -44
5 pph sodium birnessite + 5 pph $CaCO_3$ + 0.5 pph DBU in 10 pph 261 plasticiser	Replicate (1) -44 Replicate (2) -44
5 pph sodium birnessite + NO DILUENT + 0.5 pph DBU in 15 pph 261 plasticiser	Replicate (1) -44 Replicate (2) -44
4 pph sodium birnessite + 6 pph $CaCO_3$ + 0.5 pph DBU in 10 pph 261 plasticiser	Replicate (1) -44 Replicate (2) -44
4 pph sodium birnessite + 6 pph MnO_2 + 0.5 pph DBU in 10 pph 261 plasticiser	Replicate (1) -44 Replicate (2) -44
4 pph sodium birnessite + NO DILUENT and 0.5 pph DBU in 16 pph 261 plasticiser	Replicate (1) -44 Replicate (2) -46

Table 6.32 Summary of Glass Transition temperatures of liquid polysulfide cured with sodium birnessite and no accelerator

Polysulfide sample cured with:	Glass transition temperature °C
5 pph sodium birnessite + NO DILUENT + no accelerator in 15.5 pph 261 plasticiser	Replicate (1) -46 Replicate (2) -44

FIGURES SHOWING THE DYNAMIC MECHANICAL THERMAL ANALYSIS (DMTA) OF THE CURED POLYSULFIDES

Figure 6.5 DMTA of polysulfide cured with 10 pph commercial curing agent plus 0.5 pph TMTD in 10 pph Santicizer 261plasticiser

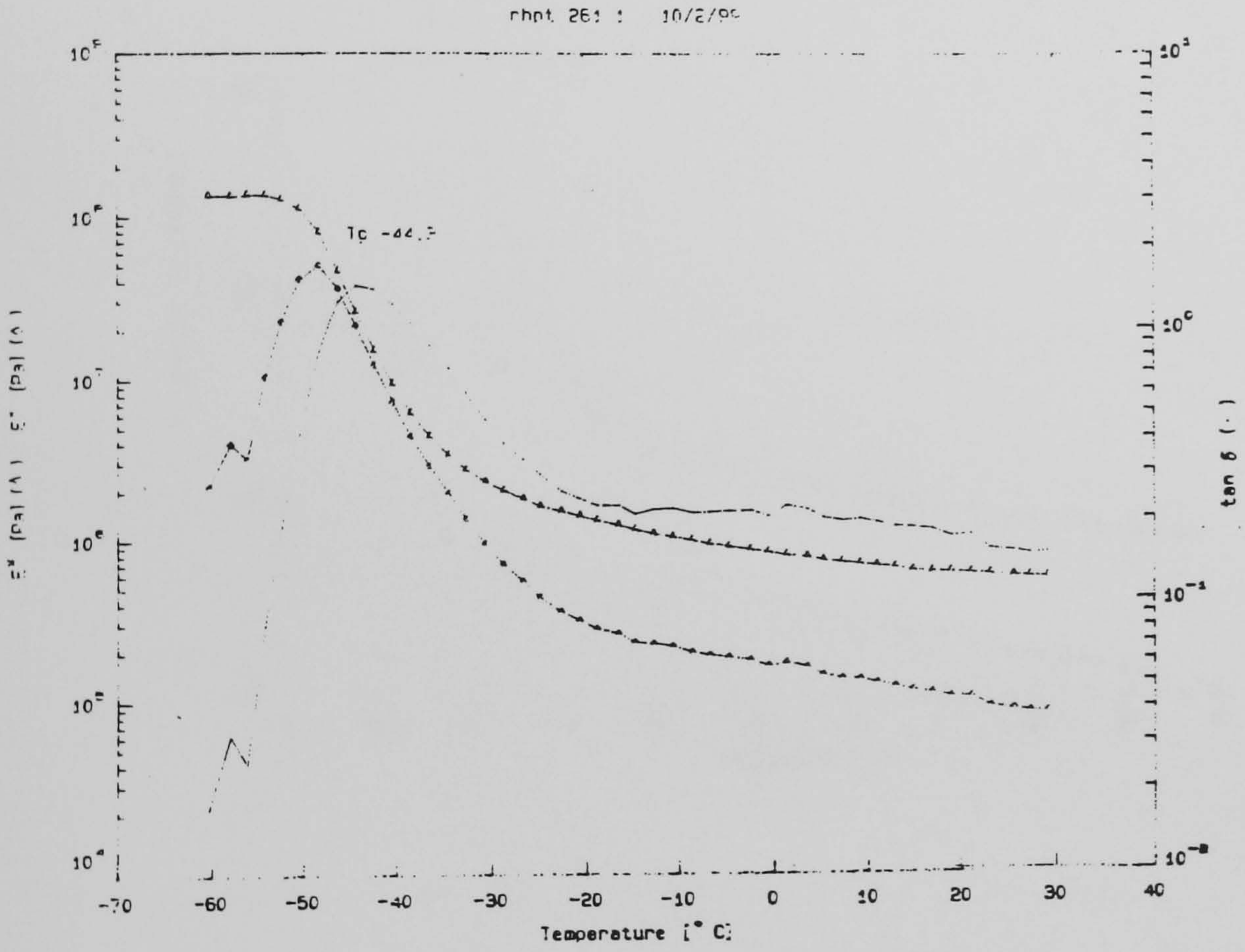
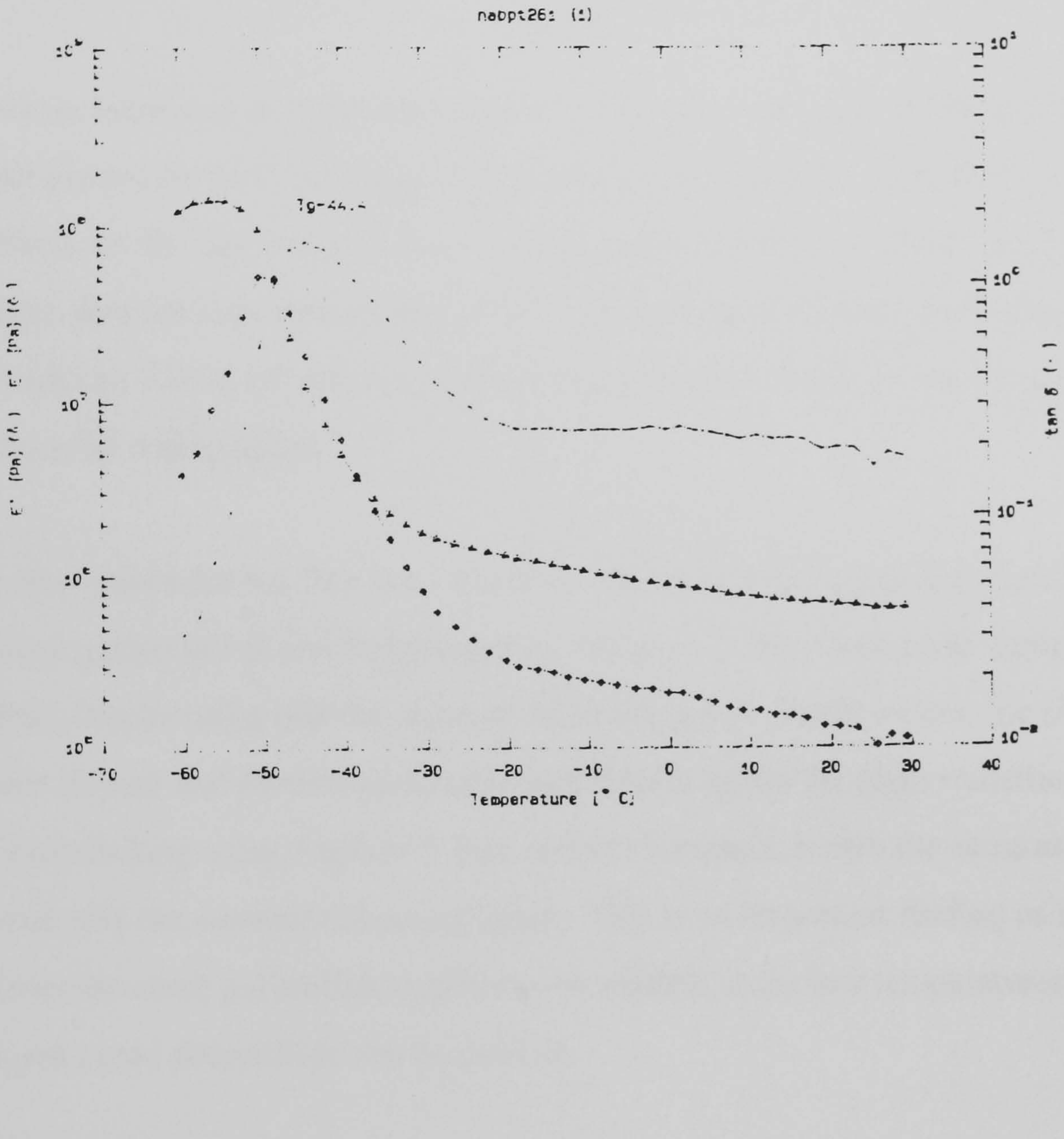


Figure 6.6 DMTA of polysulfide cured with 5 pph sodium birnessite with 5 pph inert MnO_2 diluent plus 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser



6.4 CONCLUSIONS

The data obtained in this work show that the thermal decomposition of the sodium birnessite and the commercial agent cured polysulfide samples are very similar, regardless of the quantity and type of curing agent, inert diluent, accelerator, or plasticiser used. The residual material from the thermal analysis, as shown in the Tables accounts for the amount of inert diluent, and the curing agent present.

The use of sodium birnessite as a curing agent, and the type and quantity of inert diluent, accelerator, and plasticiser used for liquid polysulfide curing appears therefore to have no detrimental effects on the thermal stability of cured polysulfide under these experimental conditions. These data are important as they show that sodium birnessite can produce cured polysulfide which has a level of thermal stability found in polysulfide cured using the best available commercial curing agent.

This research also shows for the first time that the sodium birnessite cured polysulfide has very similar elastic properties at low temperatures compared to the commercial curing agent cured polysulfide, despite using half the quantity of curing agent. Furthermore, the choice of accelerator, inert diluent and plasticiser do not significantly affect the glass transition point. The degree of crosslinking using 4 pph or 5 pph sodium birnessite is also the same as that for polysulfide cured with the commercial curing agent. This is an important finding as it shows that sodium birnessite cured polysulfide appears to be useable at the low temperatures that the commercial agent cured polysulfide can be used at.

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CHAPTER 7 MEASUREMENT OF MOISTURE VAPOUR TRANSMISSION RATE (MVTR) THROUGH CURED POLYSULFIDE SAMPLES

7.1 INTRODUCTION

The market for insulated glass is increasing due to the increased demands for energy efficiency and because of the increasing amount of glass in the facade of new buildings. The MVTR is therefore an important part of the testing of the polysulfide, as the structure of the edge seal is important to ensure long service life of the glass units. Insulating glass units in Europe generally have a double edge seal. The primary seal is made of polyisobutylene (PIB) and acts as a sufficiently impermeable layer to prevent moisture and gas transmission into the glass unit. The secondary seal is made of polysulfide or silicone or polyurethane and bonds the glass panes together as well as providing additional sealing against ingress of moisture and gases.(1) The lower the water vapour permeation of the cured polysulfide the better as it reduces the amount of water entering the insulated glass unit.

The end of the service life of insulating glass sealants is when water vapour condenses on the inside of the glass panes. This can be due to a 'premature failure' of the adhesion of the polymer to the glass, or a 'regular failure' whereby even if the sealant is intact the moisture still diffuses in through the sealant ending up between the glass panes.

A valuable property of polysulfides is that they have a low moisture vapour transmission rate (MVTR) due to the lack of polar groups in the structure. Their MVTR is lower than sealants based on silicones and polyester urethanes.(2) Little research on testing polysulfides, however, for their MVTR has been published.(3)(4)

For insulating glass sealant bases 3 mm thick the MVTR reported by one researcher was 3-6 g/m^2/24 hours.(2) At 20°C the MVTR for 3 mm thick polysulfides is reported to be between 6-8.5 g/m^2/24 hours.(4) Another researcher(3) found results for the MVTR of polysulfide as 3.0584 g/m^2/24 hours (converted to metric units). This is a lower permeability than that found for the cured polysulfides here. However, the Bertozzi[3] polysulfide was prepared with 25 pph calcium carbonate and 10 pph titanium dioxide fillers, unlike in this work.

In this research, samples of polysulfide were cured using the commercial curing agent at 10 pph, and sodium birnessite at 5 pph, diluted with 5 pph inert manganese dioxide. The same accelerator TMTD was used at the same concentration, 0.5 pph, whilst the same plasticiser, Santicizer 261, was used at the same level of 10 pph. Replicate tests were performed. The methodology used for the preparation of samples for use in the MVTR apparatus is similar to that of Massoth and Wolf.[1] Due to the long nature of these experiments (7 weeks per sample including sample preparation and testing) only two replicate experiments were performed. It was decided to keep the accelerator the same to minimise the differences between the experiments.

7.2 EXPERIMENTAL

A 100 g sample of liquid polysulfide was mixed with 20.5 g of a curing mix. The cure paste was prepared using the commercial curing agent: Table 7.1. For a comparison with sodium birnessite diluted with inert MnO_2 cured polysulfide, another cure paste was prepared: Table 7.2.

Table 7.1 Polysulfide cure paste mixture using the commercial curing agent with TMTD accelerator and plasticiser

Part A		
Liquid Polysulfide:	LP32C	100 pph
Part B		
Curing agent	Commercial curing agent	10 pph
Curing agent diluent:	NONE	0 pph
Plasticiser:	Santicizer 261	10 pph
Accelerator:	TMTD	0.5 pph

Table 7.2 Polysulfide cure paste mixture using sodium birnessite curing agent with accelerator, plasticiser and inert MnO_2 diluent.

Part A		
Liquid Polysulfide:	LP32C	100 pph
Part B		
Curing agent:	sodium birnessite	5 pph
Curing agent diluent:	Inert MnO_2	5 pph
Plasticiser:	Santicizer 261	10 pph
Accelerator:	TMTD	0.5 pph

The curing mixture was poured onto a flat metal plate coated with ICI Melinex polypropylene sheet to facilitate quick sample removal and left to cure for one week. Two circular samples were then cut from the cured sheet to fit into the top of the MVTR cups, and their thickness measured. The exposed surface area of both the commercial curing agent and diluted sodium birnessite cured polysulfides were the same at 63 mm.

Distilled water was added to the MVTR cups to the 20 mm level marked inside each cup. The lid of the MVTR cup was then tightly screwed down, and the assembly weighed. The two replicate MVTR assemblies were then placed into a desiccator with silica gel to maintain very low humidity, and the apparatus was kept at room temperature in the laboratory. Measurements of the weight of the MVTR assemblies was made weekly, with the time taken to weigh the samples kept as short as possible.

7.3 RESULTS

The results are shown as Tables, data for the MVTR for the commercial curing agent cured polysulfide is displayed in Table 7.3 and for manganese dioxide diluted sodium birnessite in Table 7.4. A summary of the results is shown in Table 7.5.

Table 7.3 The change of weight of the MVTR assemblies used for the 10 pph commercial curing agent cured polysulfide sample

Time							
	Start	**7 Days**	**14 Days**	**21 Days**	**28 Days**	**35 Days**	**42 Days**	**Weight loss (g)**
Weight of MVTR assembly (g) Replicate A	164.265	164.067	163.795	163.587	163.356	163.073	162.827	**Total weight loss 1.438 g**
Weight change (g)	0	0.198	0.272	0.208	0.231	0.283	0.246	**Mean weekly weight loss 0.240 g**
Weight of MVTR assembly (g) Replicate B	166.765	166.572	166.349	166.149	165.957	165.721	165.517	**Total weight loss 1.248 g**
Weight change (g)	0	0.193	0.223	0.200	0.193	0.235	0.204	**Mean weekly weight loss 0.208 g**

Table 7.4 The change of weight of the MVTR assemblies used for the 5 pph inert MnO_2 diluted sodium birnessite cured polysulfide sample

Time								
	Start	**7 Days**	**14 Days**	**21 Days**	**28 Days**	**35 Days**	**42 Days**	**Weight loss (g)**
Weight of MVTR assembly (g) Replicate A	173.261	172.927	172.683	172.467	172.241	171.743	171.569	**Total weight loss 1.692 g**
Weight change (g)	0	0.334	0.244	0.217	0.226	0.498	0.174	**Mean weekly weight loss 0.282 g**
Weight of MVTR assembly (g) Replicate B	169.486	169.331	169.158	169.034	168.914	168.805	168.689	**Total weight loss 0.797 g**
Weight change (g)	0	0.154	0.173	0.124	0.120	0.109	0.116	**Mean weekly weight loss 0.133 g**

Calculation of MVTR for polysulfide cured with the commercial curing agent

It was decided to use the period of time when the MVTR results appeared to be constant. For both the commercial curing agent polysulfide sample and the sodium birnessite polysulfide sample, this time period was 7 weeks.

The commercial curing agent cured polysulfide experiment replicate A

The exposed surface area of the polysulfide sample is calculated using πr^2

$=\pi \times 31.5^2 = 0.003117\ m^2$

$$\text{as MVTR} = \frac{g}{At}$$

$$= \frac{\text{weight of apparatus at start - weight of apparatus at end of experiment}}{0.003117\ m^2 \times 42\ \text{(days)}}$$

= 1.4380 / 0.130914

= 10.9 g/m^2/24 hours for a polysulfide thickness of 2.77mm

The commercial curing agent cured polysulfide Experiment replicate B

The exposed surface area of the polysulfide sample is calculated using πr^2

$=\pi \times 31.5^2 = 0.003117\ m^2$

$$\text{as MVTR} = \frac{g}{At}$$

$$= \frac{\text{weight of apparatus at start - weight of apparatus at end of experiment}}{0.003117\ m^2 \times 42\ \text{(days)}}$$

=1.2478/0.130914

=9.5 g/m^2/24 hours for a sample thickness 3.04 mm

Calculation of MVTR for polysulfide cured with *sodium birnessite* diluted with inert MnO_2

Sodium birnessite cured polysulfide Experiment replicate A

The exposed surface area of the polysulfide sample is calculated using πr^2

$=\pi \times 31.5^2 = 0.003117 \text{ m}^2$

$$\text{as MVTR} = \frac{g}{At}$$

$$= \frac{\text{weight of apparatus at start - weight of apparatus at end of experiment}}{0.003117 \text{ m}^2 \times 42 \text{ (days)}}$$

$= 1.6921/0.130914$

= **12.9 $g/m^2/24$ hours for a polysulfide thickness of 3.95 mm**

Sodium birnessite cured polysulfide Experiment replicate B

The exposed surface area of the polysulfide sample is calculated using πr^2

$=\pi \times 31.5^2 = 0.003117 \text{ m}^2$

$$\text{as MVTR} = \frac{g}{At}$$

$$= \frac{\text{weight of apparatus at start - weight of apparatus at end of experiment}}{0.003117 \text{ m}^2 \times 42 \text{ (days)}}$$

$= 0.797/0.130914$

= **6.1 $g/m^2/24$ hours for a polysulfide thickness of 4.62 mm**

Table 7.5 Summary Table of results for Moisture Vapour Transmission Rate experiments

Polysulfide cured with:	6 week MVTR $g/m^2/24$ hours	Sample Thickness mm
Commercial curing agent replicate experiment A	*10.9*	*2.77*
Commercial curing agent replicate experiment B	*9.5*	*3.04*
Sodium birnessite diluted with inert MnO_2 replicate experiment A	12.9	3.95
Sodium birnessite diluted with inert MnO_2 replicate experiment B	6.1	4.11

7.4 DISCUSSION

The replicate samples of the commercial curing agent cured polysulfide show similar levels of moisture permeability. However, the MVTR for the cured polysulfide has to be considered with the thickness of each sample being slightly different. Also the thickness of the birnessite cured polysulfide and that of the commercial curing agent may have influenced these results. The samples of sodium birnessite cured polysulfide are thicker than that obtained by the commercial curing agent.

The MVTR for a cured polysulfide is an important factor in determining the suitability of a curing agent for use in polysulfide sealants. The MVTR results for the 5 pph sodium birnessite shows no adverse effect compared to that for the 10 pph commercial curing agent cured polysulfide.

The water vapour permeability of insulating glass sealants is usually quoted only at room temperature. However, MVTR increases with increasing temperature. Further research would be important to investigate the effect of temperature on the MVTR. Wolf(4) states that the temperature loading on insulating glass sealants is high especially on south facing windows.

For comparability with all of the results reported in the literature, the experiments were performed on polysulfide samples 3 mm thick. In industry, however, the secondary layer (the polysulfide layer) is 5-7 mm thick, and therefore this is an important point to bear in mind.(1) Further research on combining the primary sealant polyisobutylene (PIB) with the sodium birnessite cured polysulfide as the secondary sealant would be important to assess the situation as it would occur in a dual phase sealant membrane system. A lower MVTR would be expected using the dual phase sealant membrane than the single phase membrane with PIB / polysulfide sealants typically having MVTR at 20°C of around 1 $g/m^2/24$ hours, with the PIB providing the majority of the protection against moisture vapour ingress.

It should also be noted that, like most of the reported results in the literature these results do not take into account the effect of mechanical loads and aging factors on the edge seals in glazing units.(1) This would be an area for further research.

7.5 REFERENCES

1. Massoth A. and Wolf A. *Kautschuk + Gummi. Kunstoffe.* 1988. **41** 882-887.
2. Lee T.C.P. *Properties and applications of elastomeric polysulfides.* 1999. Rapra review reports. Report 106. Rapra. Shawbury.
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CHAPTER 8 TENSILE TESTING OF CURED POLYSULFIDE POLYMERS

8.1 INTRODUCTION

Tensile testing of the sodium birnessite cured polysulfide is extremely important. For example as a sealant in high rise buildings. joint movement of the gaps between curtain walls may be up to $^{+}/_{-}$ 50% between midnight and midday and summer and winter. (1)

The mechanical properties of cured polysulfide depend on the polymerization conditions. For example the modulus of cured polysulfide was seen to increase with toughening time according to Matsui and Miwa.(1) As a result these experiments are indicative of the tensile properties of polysulfide which has had a longer toughening time (about 3 weeks) than the 7 days used for the Shore A 7 day hardness measurement.

One of the most widely used mechanical tests for sealants is in identifying their stress-strain behaviour.(2) The tensile properties of unfilled polysulfide polymers are poor(3) but it has been shown by Startsev and Baranovskaya(4) that as the temperature of the polysulfide is reduced the strength increases and the elongation at break decreases. It has been suggested in the literature. that the nature of the curing agent affects the mechanical properties of cured polysulfide polymer.(5) Tensile testing of manganese dioxide cured polymers performed by Krishnan and Ninan(5) was on dumb bell shaped samples. although they used only 4 pph of manganese dioxide curing agent in their experiments. The optimum tensile strength properties reported for cured polysulfide in the literature is 6 pph MnO_2 per hundred parts polymer.(2) Ramaswamy and Sasidharan Achary (2) reported that polysulfide cured with 5 pph of manganese dioxide curing agent has a higher tensile strength than polysulfide cured at 4 pph of curing agent. The effect of calcium carbonate on the mechanical properties of LP32 polysulfide cured with manganese dioxide in Santicizer 278 plasticiser has been investigated.(6)

The effects of various parameters (i.e. the amount and type of curing agent. accelerator, plasticiser and diluent) on the properties of polysulfide were investigated in this work using tensile testing of the cured polysulfide.

In preliminary experiments using 4 pph of sodium birnessite as curing agent, it was found that the DBU accelerator was more effective in benefiting the stress-strain properties of the cured polysulfide than TMTD. As a result, more experiments were carried out using DBU than TMTD as an accelerator.

Monsanto (7) reported on the effect of adding increased quantities of Santicizer 261 on the tensile strength of the cured polysulfide. Increasing the Santicizer 261 level increases the elongation at break but reduces the stress at break. The strength at break was found to decrease with increasing levels of plasticiser from 0 pph to 30 pph plasticiser.

Research by Mathur and Peterson (6) found that uncoated precipitated calcium carbonate used with a manganese dioxide curing agent increased the level of reinforcement of the cured LP32C polysulfide. However, using uncoated calcium carbonate was less effective at increasing the elongation than coated calcium carbonate, and coated calcium carbonate was found to have better mechanical properties.

For unfilled polysulfide LP32C, manganese dioxide at 7.5 pph has been reported to result in a cured polysulfide with 290 % elongation. (8)

8.2 EXPERIMENTAL

Samples of LP32C were cured with a variety of cure pastes and poured onto a flat iron plate covered with a "Melinex" polypropylene sheet to ensure easy cured polysulfide removal. The cured polysulfide was stored at room temperature for one week before testing. At least six samples were cut from each sheet using a dumb bell shaped die which has the dimensions which apply to BS 903 pt 2 (1995):Length: 6 mm, Thickness: 3 mm, Gauge length: 33mm.

The Instrument parameters used were as follows:
Grip distance: 80mm
Crosshead Speed: 50 mm min
Load cell: 10 Newtons
Sample grips: Elastomer grips.

Testing was performed on an Instron 4206 Tensile testing machine controlled by a Commodore 1930 computer and the relative humidity and temperature were noted. The instrument was calibrated regularly by the manufacturer Instron, in tension and compression mode. Before each experiment the load measurement was checked using a 20 Newton weight.

8.3 RESULTS

Data are presented as mean values of stress and strain for the six cured polysulfide samples tested in each experiment. Results are summarised in Table 8.1 for the commercial curing agent cured polysulfide, and Table 8.2 for sodium birnessite at 5 pph (TMTD accelerated) cured polysulfide. Table 8.3 and 8.4 provide summaries of results for sodium birnessite at 5 pph (DBU accelerated) cured polysulfides and summary results for sodium birnessite at 4 pph level (TMTD accelerated) cured polysulfide respectively. Table 8.5 compares results for sodium birnessite at 4 pph level (DBU accelerated) cured polysulfide.

Table 8.1 Summary Table of the stress-strain properties of LP32C polysulfide cured with 10 pph commercial curing agent with TMTD accelerator

Sample	Mean Stress at peak MPa	Mean Stress at break MPa	Mean Strain at peak %	Mean Strain at break %
10 pph commercial curing agent + NO INERT DILUENT with 0.5 pph TMTD in 10 pph Santicizer 278 plasticiser	0.373	0.370	263	266
REPLICATE SAMPLE 10 pph commercial curing agent + NO INERT DILUENT with 0.5 pph TMTD in 10 pph Santicizer 278 plasticiser	0.452	0.450	268	269
10 pph commercial curing agent + NO INERT DILUENT with 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser	0.423	0.422	326	327

Table 8.2 Summary Table of the stress-strain properties of LP32C polysulfide cured with 5 pph sodium birnessite and TMTD accelerator

Sample	Mean Stress at peak MPa	Mean Stress at break MPa	Mean Strain at peak %	Mean Strain at break %
5 pph sodium birnessite +5 pph inert MnO_2 with TMTD in 10 pph Santicizer 278 plasticiser	0.509	0.506	220	221
5 pph sodium birnessite + 5 pph inert MnO_2 with 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser	0.579	0.579	234	234
5 pph sodium birnessite + 5 pph $CaCO_3$ with 0.5 pph TMTD in 10 pph Santicizer 261 plasticiser	0.308	0.301	220	231
5 pph sodium birnessite + NO DILUENT with 0.5 pph TMTD in 15 pph Santicizer 261plasticiser (extra 5 pph 261 to replace MnO_2)	0.242	0.237	221	253

Table 8.3 Summary table of stress-strain properties of LP32C polysulfide cured with 5 pph sodium birnessite and DBU accelerator

Sample	Mean Stress at peak MPa	Mean Stress at break MPa	Mean Strain at peak %	Mean Strain at break
5 pph sodium birnessite + 5 pph inert MnO_2 with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser	0.551	0.550	155	155
5 pph sodium birnessite + 5 pph $CaCO_3$ with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser	Not Attempted as curing of polysulfide too rapid	N.A	N.A	N.A
5 pph sodium birnessite + NO DILUENT with 0.5 pph DBU in 15 pph Santicizer 261 plasticiser	0.237	0.231	192	201
5 pph sodium birnessite + NO DILUENT + NO ACCELERATOR in 15.5 pph Santicizer 261	0.205	0.201	273	280

Table 8.4 Summary table of stress-strain properties of LP32C polysulfide cured with 4 pph sodium birnessite with TMTD accelerator

Sample	Mean Stress at peak MPa	Mean Stress at break MPa	Mean Strain at peak %	Mean Strain at break %
4 pph sodium birnessite + NO DILUENT with 0.5 pph TMTD in 16 pph Santicizer 261	0.145	0.136	275	321

Table 8.5 Summary table of stress-strain properties of LP32C polysulfide cured with 4 pph sodium birnessite and DBU accelerator

Sample	Mean Stress at peak MPa	Mean Stress at break MPa	Mean Strain at peak %	Mean Strain at break %
4 pph sodium birnessite plus 6 pph $CaCO_3$ with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser	0.218	0.214	248	255
4 pph sodium birnessite plus 6 pph inert MnO_2 with 0.5 pph DBU in 10 pph Santicizer 261 plasticiser	0.433	0.431	193	196
4 pph sodium birnessite + NO DILUENT with 0.5 pph DBU in 16 pph Santicizer 261 plasticiser	0.204	0.199	206	212

Experiments using the commercial curing agent cured polysulfide:

Figure 8.1 Graph showing stress-strain curve for polysulfide cured with 10 pph commercial curing agent. 0.5 pph TMTD, 10 pph Santicizer 278 plasticiser

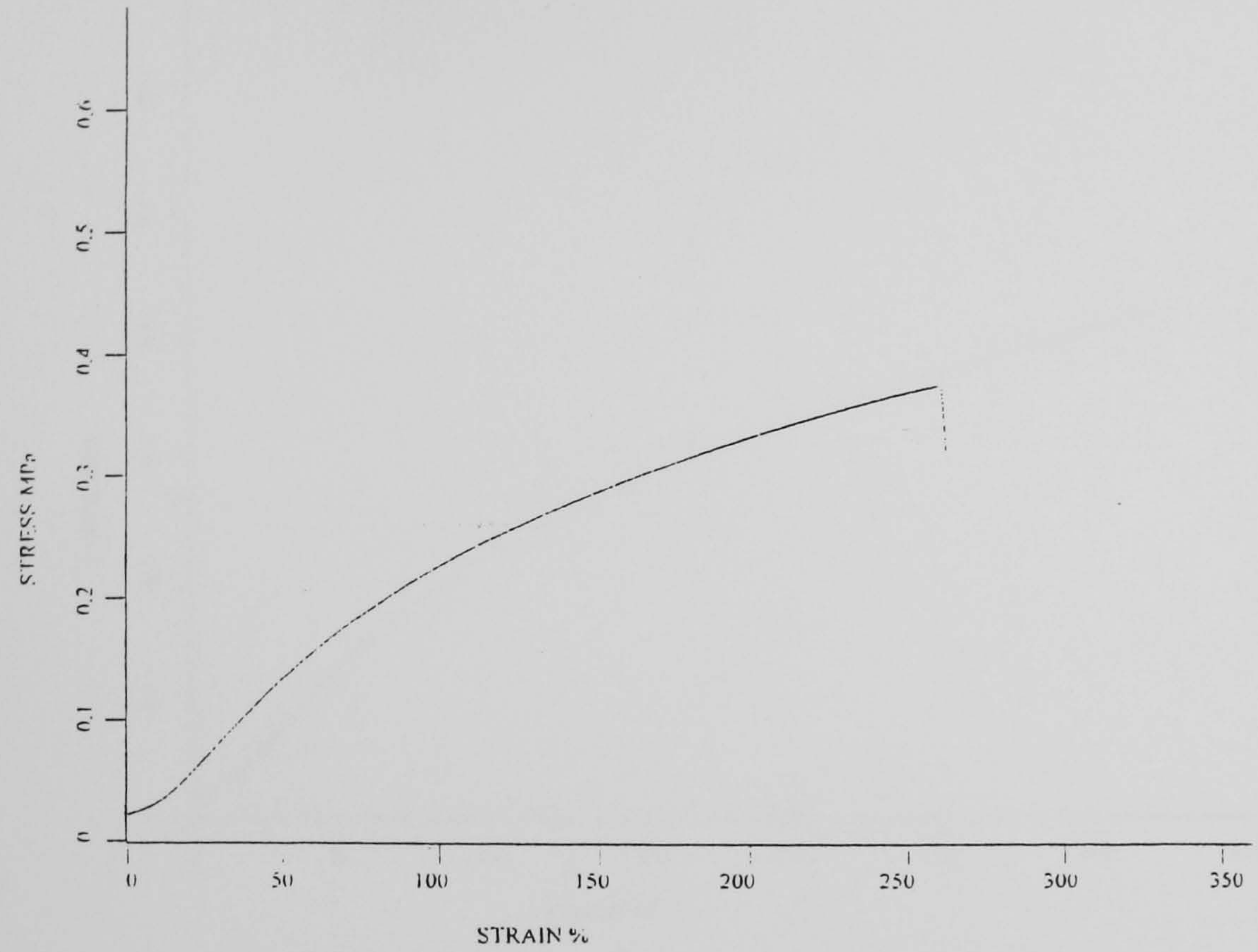


Figure 8.2 Graph showing stress-strain curve for polysulfide cured with 10 pph commercial curing agent, 0.5 pph TMTD, 10 pph Santicizer 278 plasticiser (replicate)

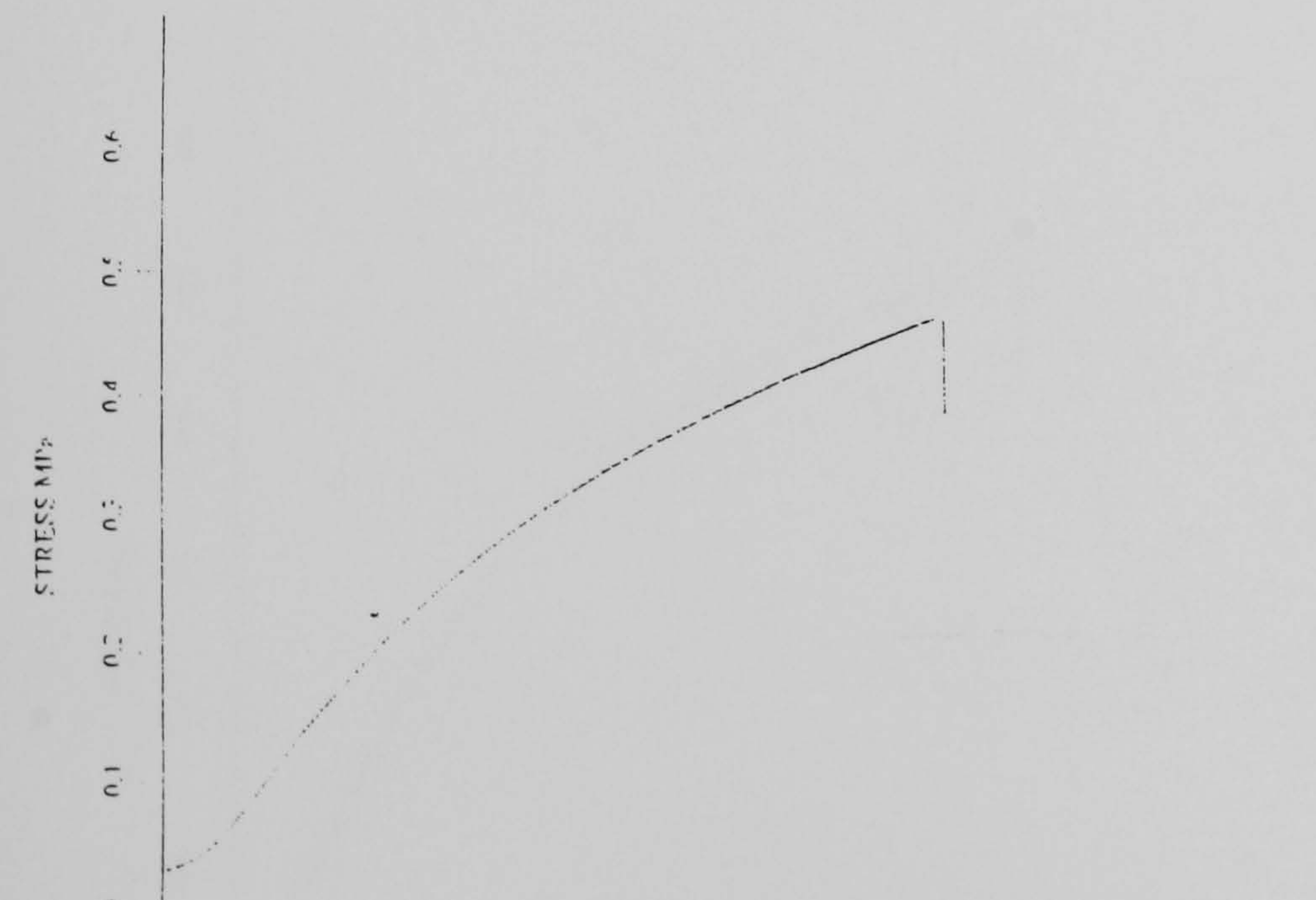
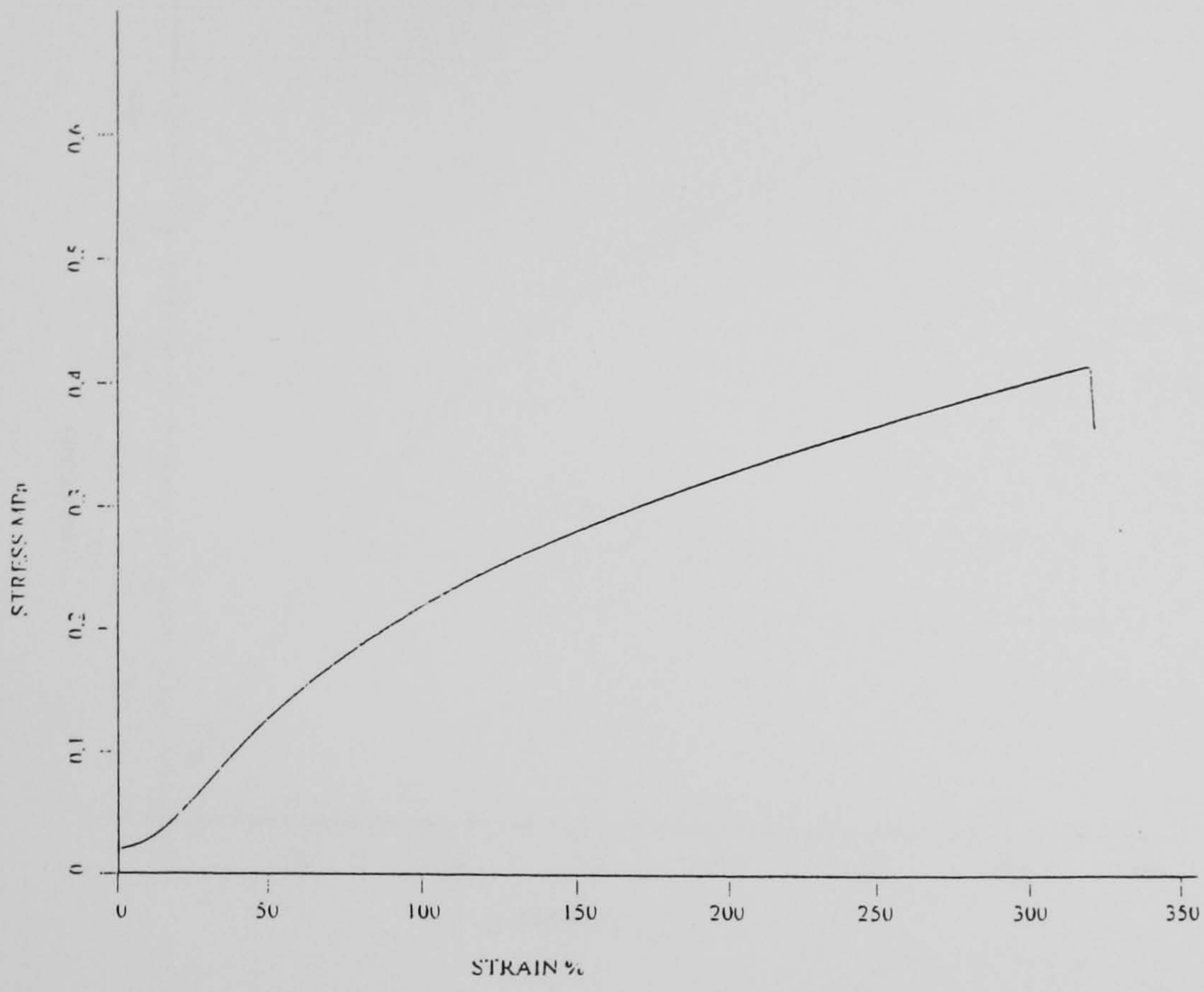


Figure 8.3 Stress-strain graph for polysulfide cured with 10 pph commercial curing agent, 0.5 pph TMTD, 10 pph Santicizer 261 plasticiser



Experiments using sodium birnessite cured polysulfide and TMTD accelerator:

Figure 8.4 Stress-strain graph for polysulfide cured with 5 pph sodium birnessite, 5 pph inert manganese dioxide, 0.5 pph TMTD, 10 pph Santicizer **278** plasticiser

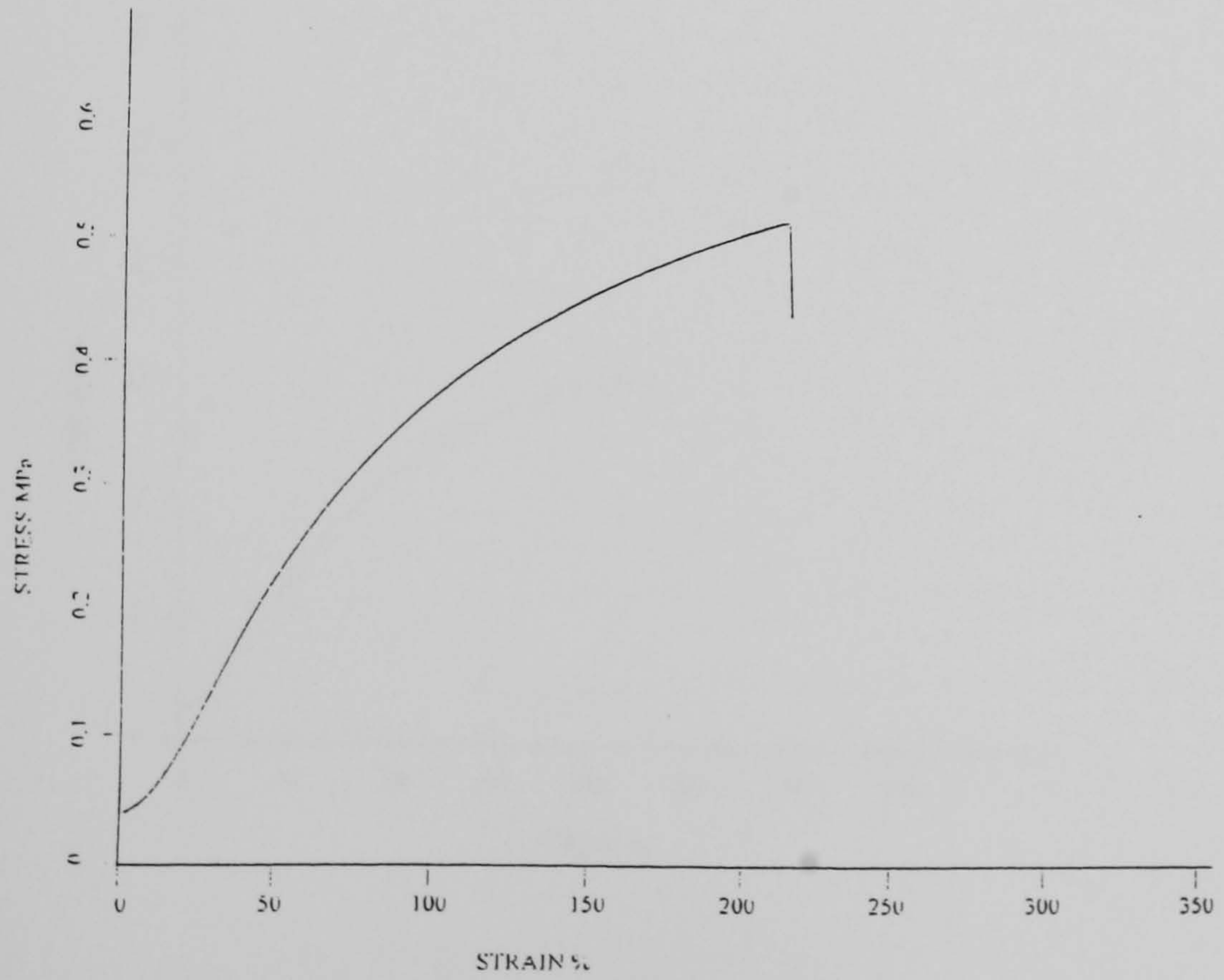


Figure 8.5 Stress-strain graph for polysulfide cured with 5 pph sodium birnessite, 5 pph inert manganese dioxide. 0.5 pph TMTD, 10 pph Santicizer 261plasticiser

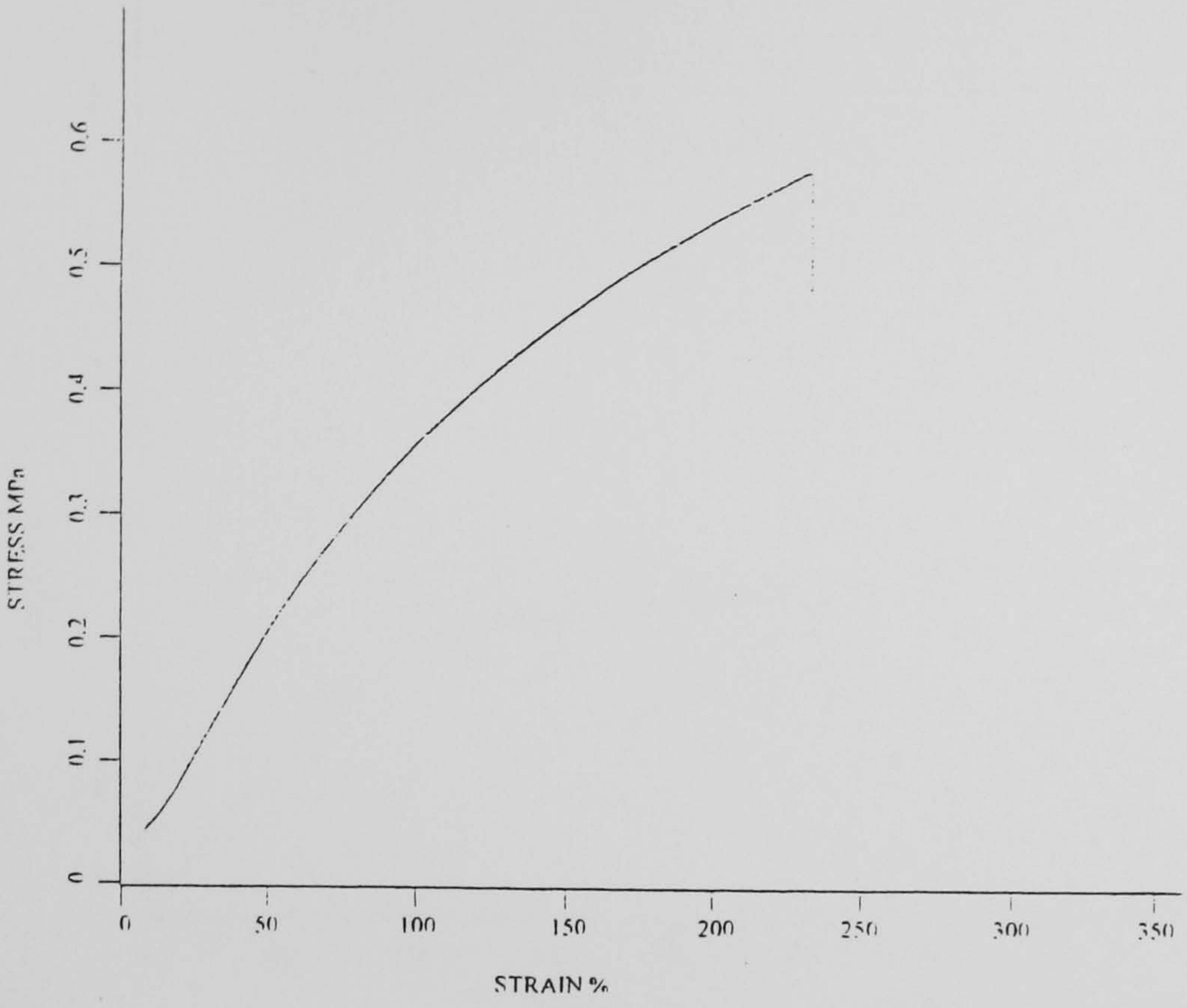


Figure 8.6 Stress-strain graph for polysulfide cured with 5 pph sodium birnessite, 5 pph calcium carbonate, 0.5 pph TMTD, 10 pph Santicizer 261 plasticiser

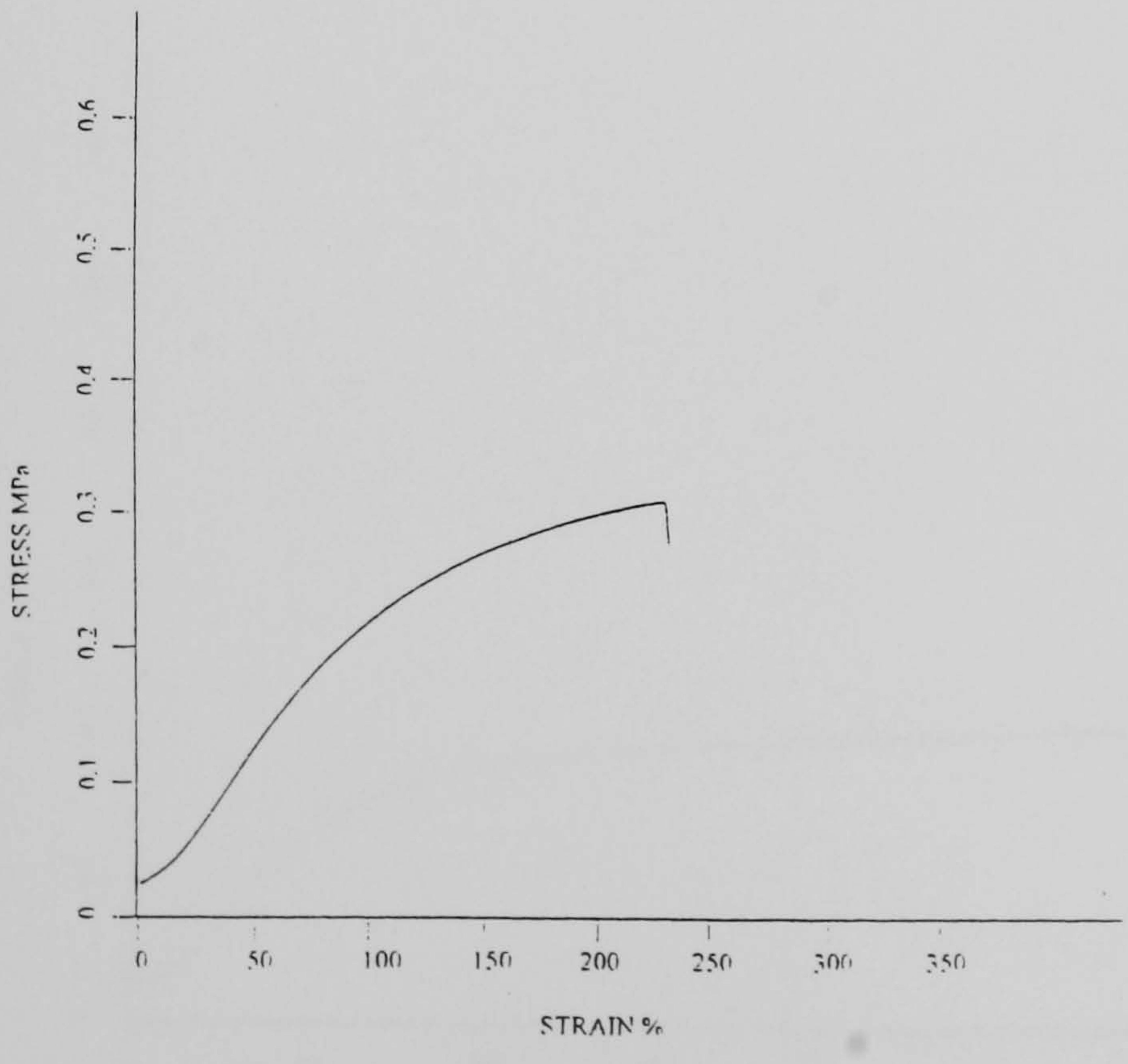


Figure 8.7 Stress-strain graph for polysulfide cured with 5 pph sodium birnessite, no inert diluent, 0.5 pph TMTD, 15 pph Santicizer **261** plasticiser

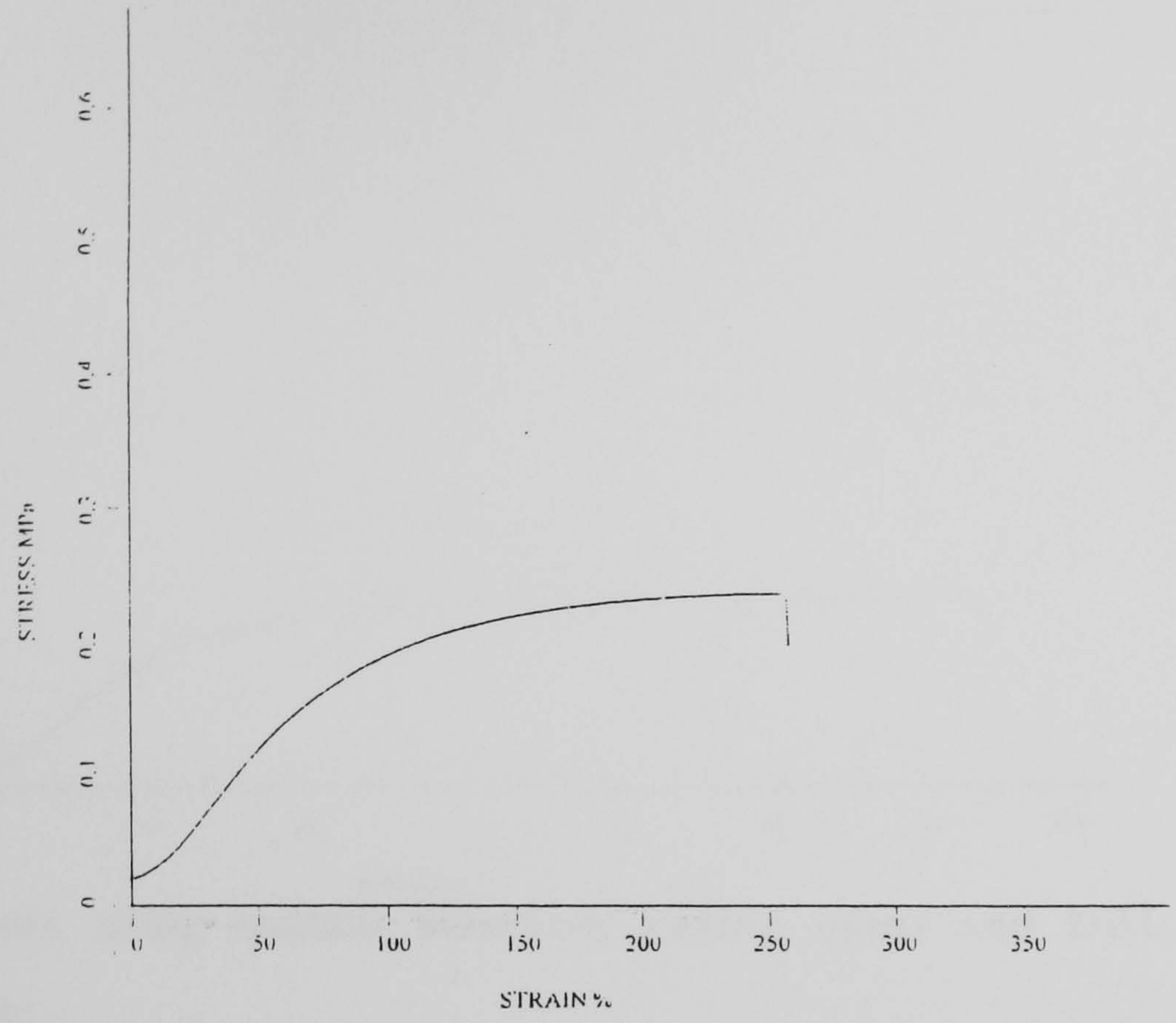


Figure 8.8 Stress-strain graph for polysulfide cured with 5 pph sodium birnessite no curing agent diluent, no accelerator and 15.5 pph Santicizer 261 plasticiser

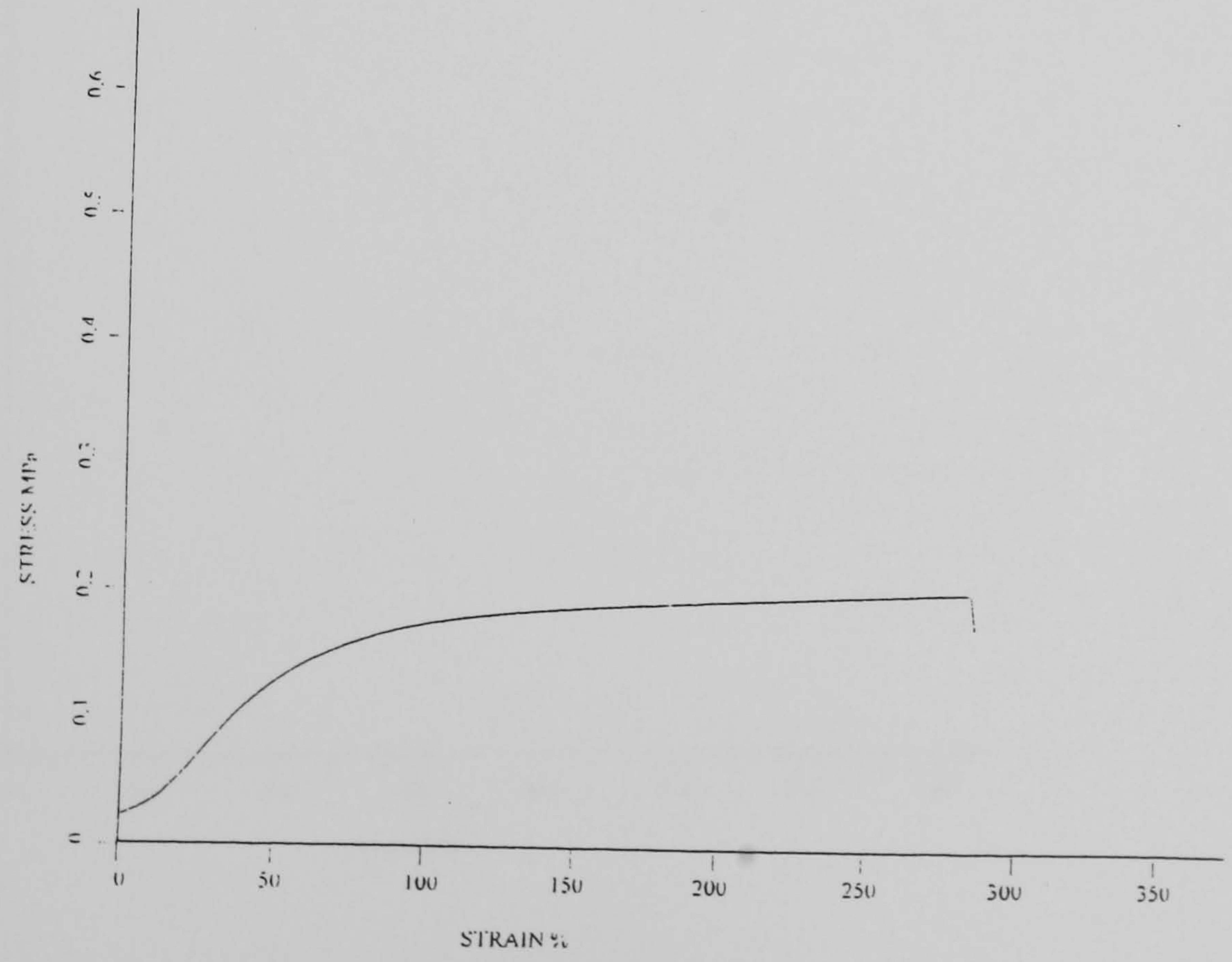
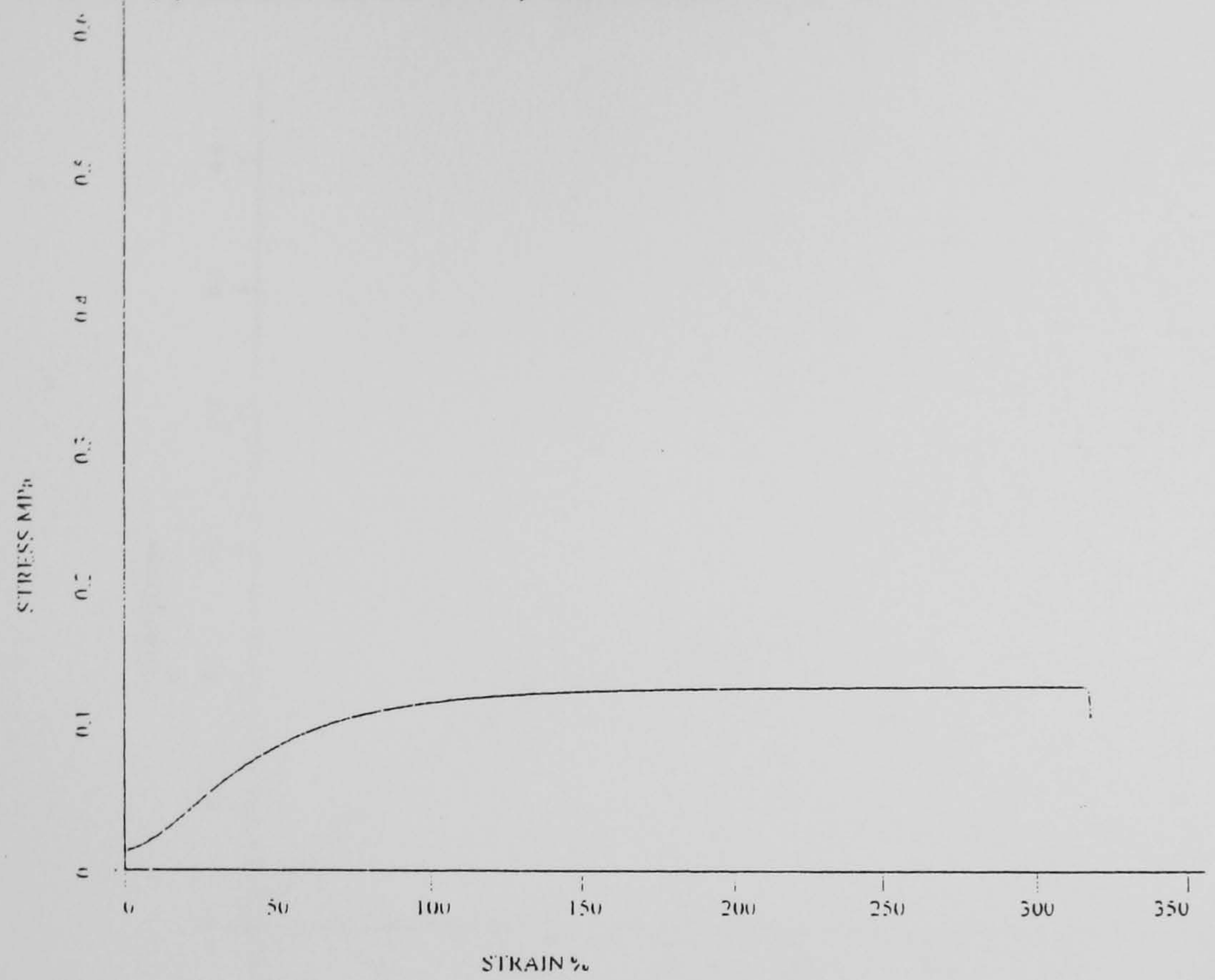


Figure 8.9 Stress-strain graph for polysulfide cured with 4 pph sodium birnessite, 0.5 pph TMTD, 16 pph Santicizer 261 plasticiser



Experiments using sodium birnessite curing agent and DBU accelerator cured polysulfide:

Figure 8.10 Graph showing replicate stress-strain curves for polysulfide cured with 5 pph sodium birnessite, 5 pph inert MnO_2 0.5 pph DBU, 10 pph Santicizer 261 plasticiser

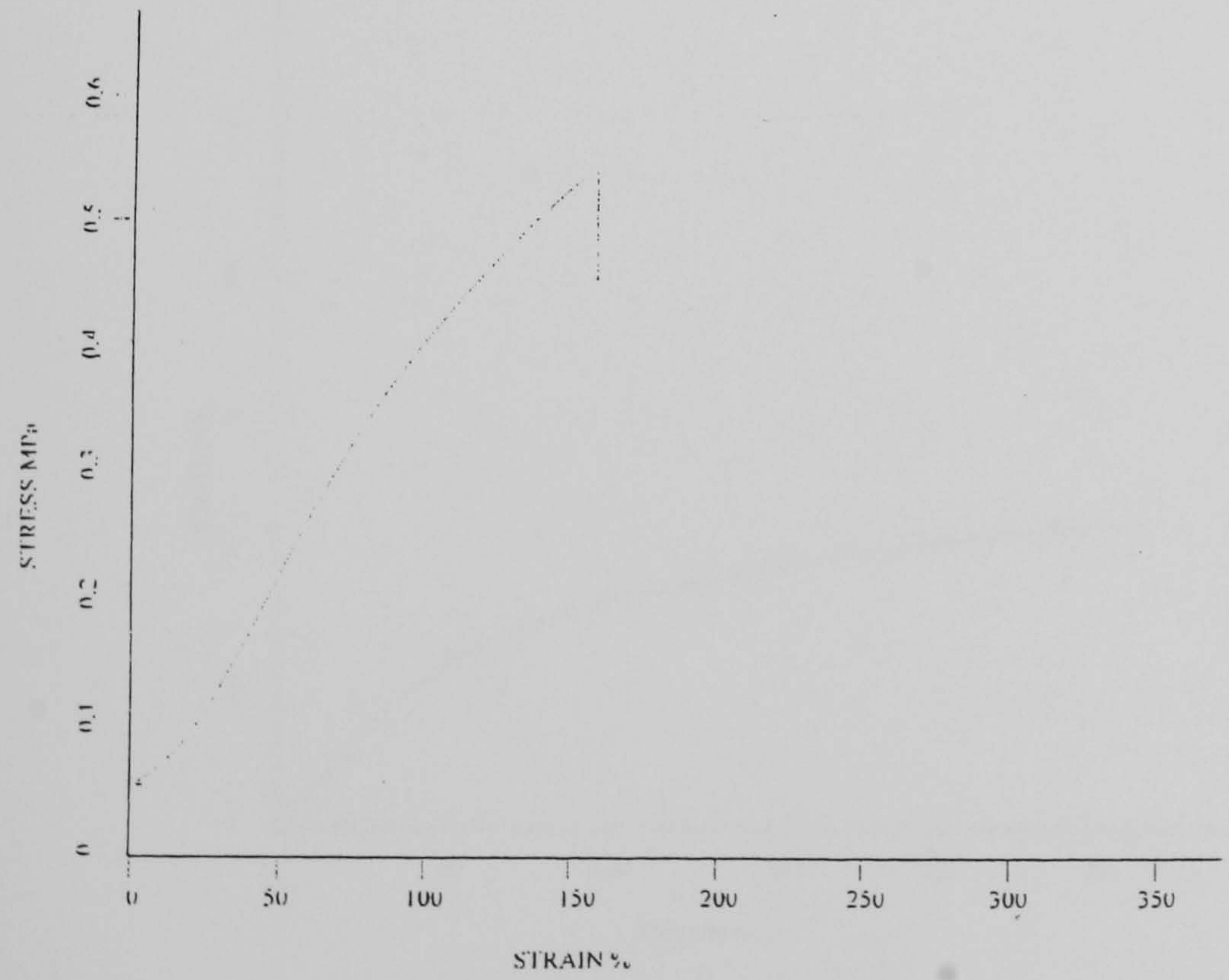


Figure 8.11 Stress-strain graph for polysulfide cured with 5 pph sodium birnessite, no inert diluent, 0.5 pph DBU, 15 pph Santicizer 261 plasticiser

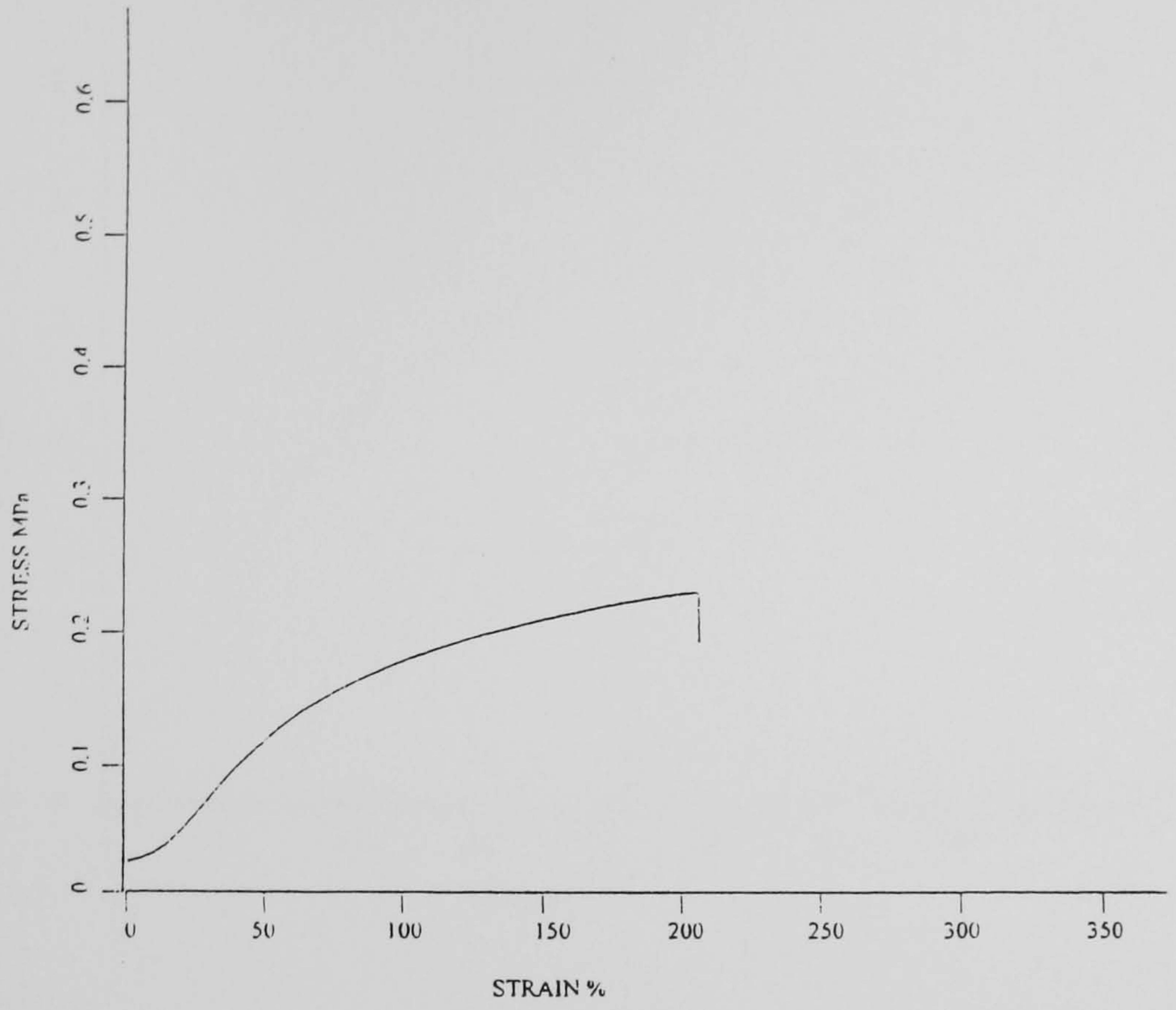


Figure 8.12 Stress-strain graph for polysulfide cured with 4 pph sodium birnessite, 6 pph inert $CaCO_3$ 0.5 pph DBU, 10 pph Santicizer 261 plasticiser

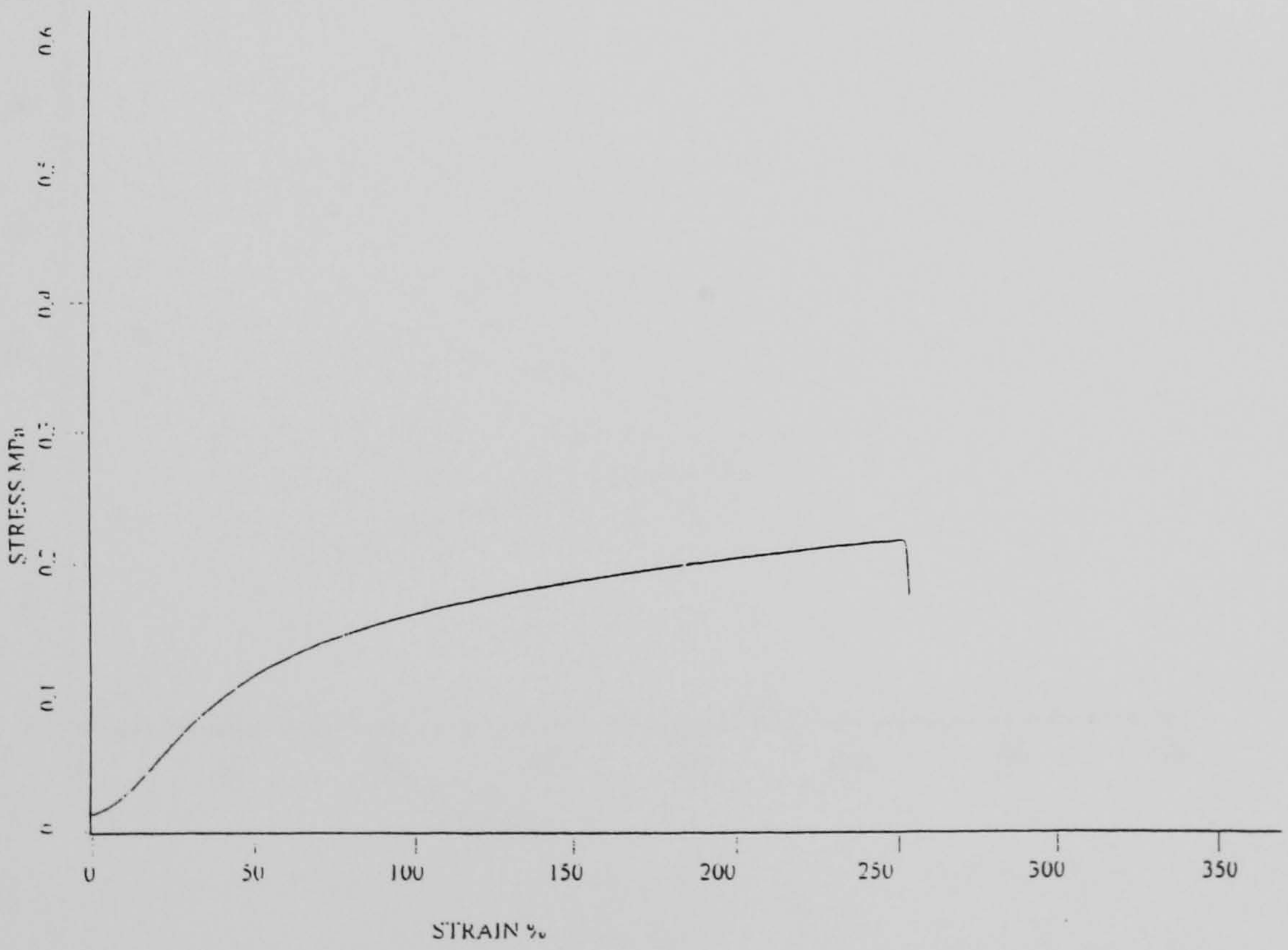


Figure 8.13 Stress-strain graph for polysulfide cured with 4 pph sodium birnessite, 6 pph inert MnO_2 0.5 pph DBU, 10 pph Santicizer 261 plasticiser

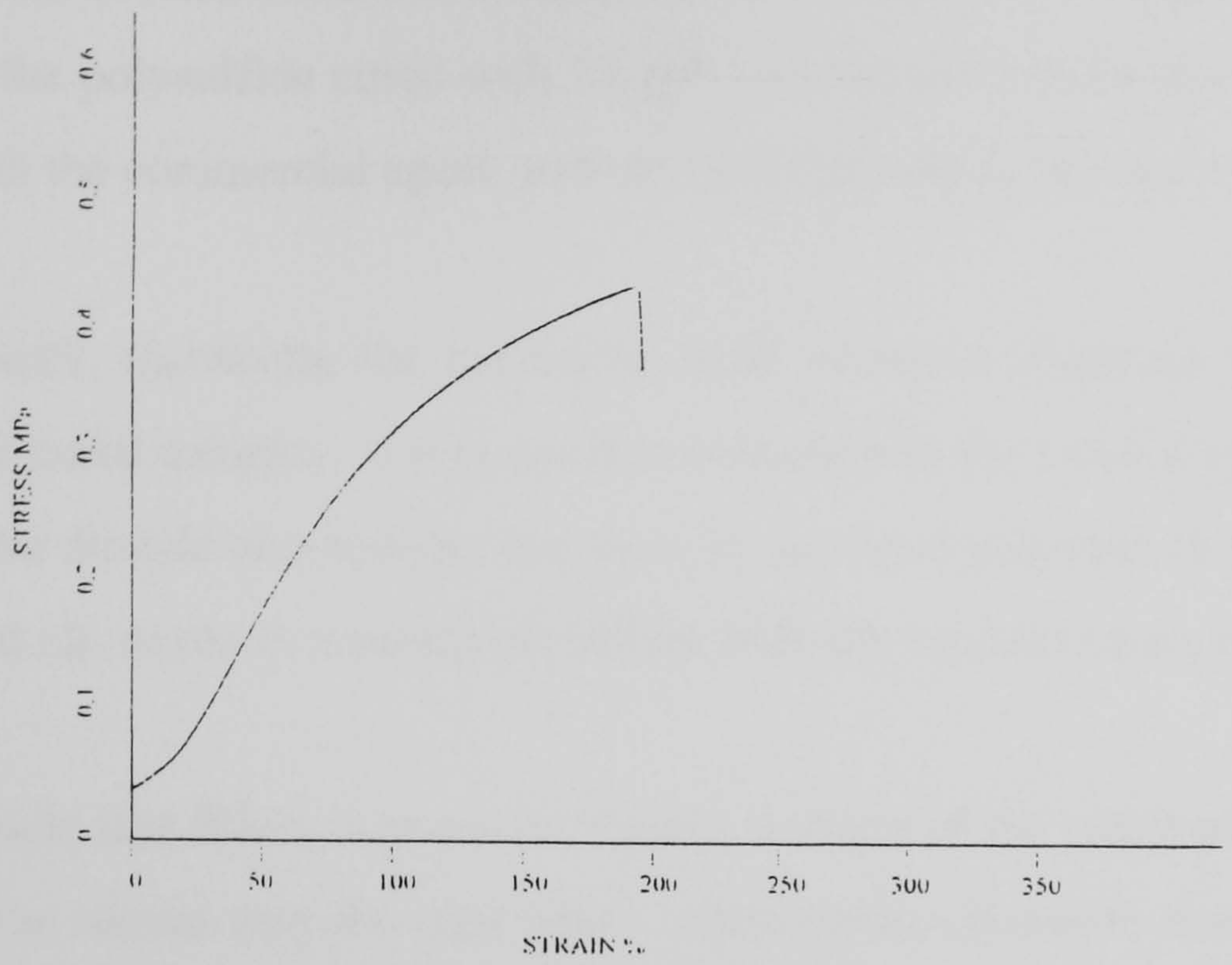
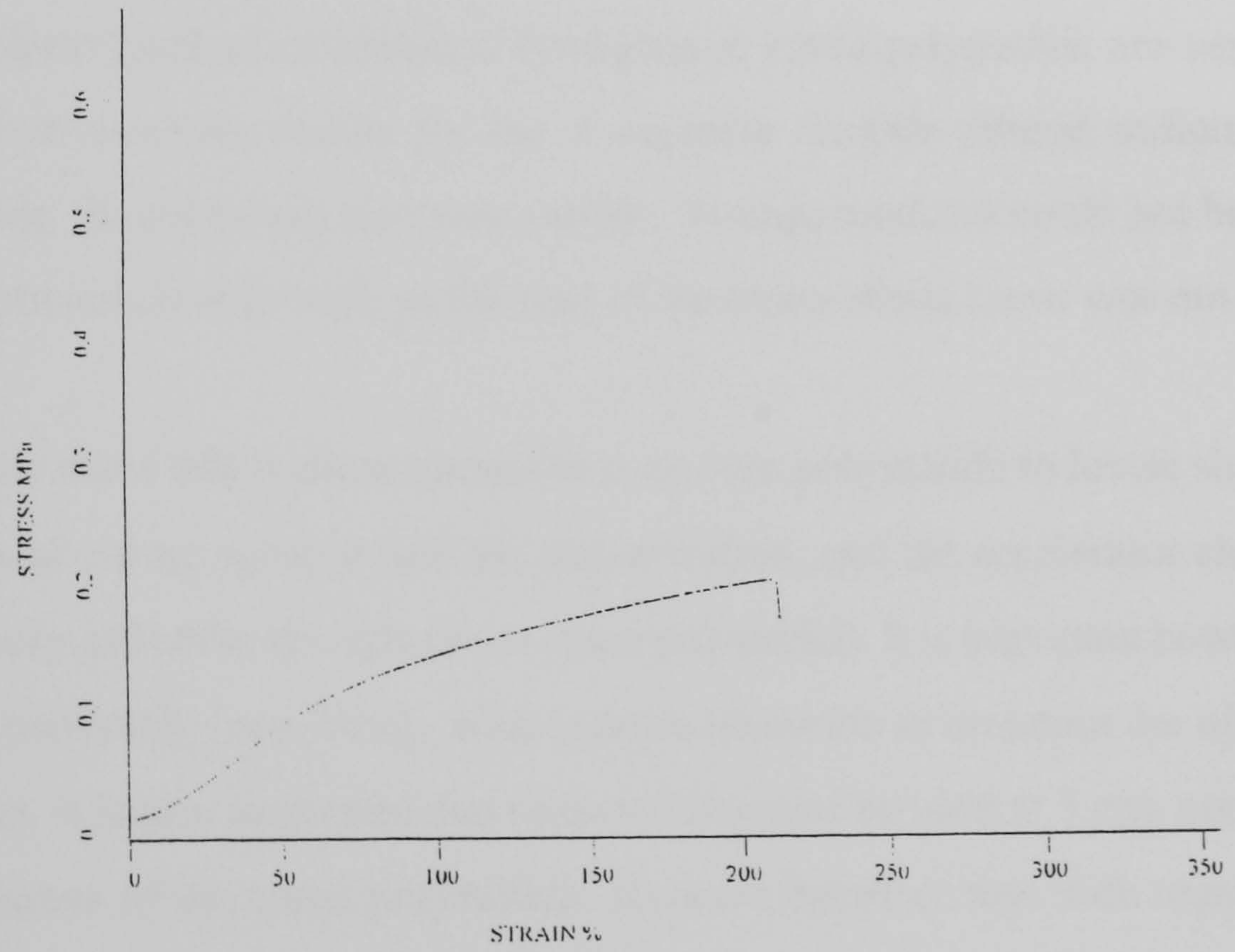


Figure 8.14 Stress-strain graph for polysulfide cured with 4 pph sodium birnessite, no inert diluent, 0.5 pph DBU in 16 pph Santicizer 261 plasticiser



8.4 DISCUSSION

At 5 pph the sodium birnessite cured polysulfide has stress-strain properties very similar to those of the polysulfide cured with 10 pph commercial curing agent and, like polysulfide cured with the commercial agent, sodium birnessite cured sealant also exhibits no yielding.

In this work, increasing the plasticiser level, seems to decrease the strength of sodium birnessite cured samples. Using calcium carbonate in the cured polysulfide instead of inert manganese dioxide also reduces the stress in the cured polymer. However, using no diluent mineral at all results in a cured polysulfide with the weakest stress properties.

Fine particle size fillers increase the tensile strength of the cured polysulfide. (9) This may well be the reason why the inert MnO_2 added to the birnessite results in a higher strength product. Although it may also be due to increased plasticiser to maintain the 20.5 pph level of cure paste added in every experiment to 100 pph of polysulfide.

With regards to replication of results, it is seen from Table 8.1 that the stress-strain properties of a replicate batch of commercial curing agent cured polysulfide are very similar. For the replicate stress-strain results for the manganese dioxide diluted sodium birnessite cured polysulfide, the results are also very similar. Youngs modulus could not be determined from the experiments in this work as the start of the stress-strain curve was not linear.

These data show that sodium birnessite does cure polysulfide to levels similar to that of the commercial curing agent at half the concentration, and the accelerator chosen seems not to significantly affect the strength of the cured polysulfide. It is important however to use an inert diluent, preferably inert MnO_2, with sodium birnessite to maintain the optimal stress-strain properties. It is also important that sodium birnessite be used at 5 pph not 4 pph to maintain the properties of the cured polysulfide. It seems therefore that with regards to stress-strain properties, 5 pph sodium birnessite diluted with 5 pph inert MnO_2 and with an accelerator produces a cured polysulfide that has stress-strain properties that are at least comparable with that of the commercial curing agent cured polysulfide. This is very important commercially.

for example in use as a sealant. as it means that inert MnO_2 diluted sodium birnessite cures polysulfide at 5 pph with no detriment to the sealants stress-strain properties.

8.5 REFERENCES

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CHAPTER 9 INVESTIGATION INTO THE CURING MECHANISM OF POLYSULFIDE USING SODIUM BIRNESSITE

9.1 INVESTIGATION INTO THE CURING MECHANISM USING INFRARED SPECTROSCOPY

9.1.1 Introduction

It has been suggested that further work is needed to fully understand the mechanisms of polysulfide curing with metal oxides.(1) A number of separate analytical techniques were used to propose a mechanism for the sodium birnessite curing of liquid polysulfide. Apart from the parameters of pH, moisture content and particle size, measured in this research, infrared spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy (XPS) were also used. Raman spectroscopy could not be used on the cured polysulfide as the polymer was black in colour.

In this research, it was decided to investigate the curing of the polysulfide using infrared spectroscopy. Infrared spectroscopy is useful for identifying certain mineral phases for example to characterise sodium birnessite.(2) Sodium birnessite has characteristic infrared peaks as identified by Golden et al,(3) these peaks are at 633,512,480, and 421 cm $^{-1}$ The infrared spectra for most manganese oxide minerals depend only on the MnO_6 octahedral framework. (2)

Infrared spectroscopy is also used to characterise polymers, for example, using infrared spectroscopy to measure mercaptan peaks in liquid polysulfides.(4) The S-H mercaptan bond has a characteristic vibration at 2560 cm^{-1}. Matsui and Miwa(5) studied the loss of the mercaptan peak at 2561 cm^{-1} in the lead dioxide curing of liquid polysulfide using Fourier Transform Infrared (FTIR) spectroscopy.

It is possible that the reason for the effectiveness of sodium birnessite in curing polysulfide is that it is the sodium birnessite itself rather than the pH or particle size that effects the cure rate.

9.1.2 Experimental

Equipment:

Nicolet 710 Fourier Transform Infrared Spectroscopy analyser

KBr discs

KBr powder

Sodium birnessite has been studied previously in the form of the pellets made with KBr discs.(3) To 150 mg of anhydrous KBr was added about 0.5 mg of the sample, either sodium birnessite, or the accelerator TMTD were added. After thoroughly mixing in a mortar and pestle the sample mixed with the KBr was evacuated for a few minutes, and then pressed at 10 tonnes under vacuum for 5 minutes. A pure KBr disc was also made to obtain the background spectrum. A very thin layer of LP32C polysulfide was applied to the surface of a KBr disc and after a background reading to subtract atmospheric water and carbon dioxide from the sample spectrum, the sample was analysed. The plasticiser Santicizer 261 spectrum was also investigated as a thin layer over the KBr disc. A mixture of the Santicizer 261, the TMTD and the sodium birnessite were then analysed using FTIR. The cured polysulfide mixture was then analysed within 5 minutes of mixing the cure paste and the polysulfide.

9.1.3 Results

The following peaks were identified at 637, 513, 479 and 421 cm^{-1}. This supports the work reported by Golden et al(3) where peaks at 633, 512, 480 and 421 cm^{-1} are reported, confirming that the manganese dioxide phase in the reaction with the polysulfide is sodium birnessite.

The infrared spectum for the uncured polysulfide is shown in Figure 9.1. Figure 9.2 shows the infrared spectrum for TMTD accelerator, Figure 9.3 shows the infrared spectrum for Santicizer 261 plasticiser. Figure 9.4 shows the infrared spectrum for sodium birnessite, Figure 9.5 shows the infrared spectrum for the cure paste mixture (sodium birnessite, TMTD accelerator, and Santicizer 261 plasticiser). The polysulfide cured with this cure paste mixture is shown in Figure 9.6, the experiment was repeated and shown in Figure 9.7. The spectra are shown whereby the top spectrum in Figure 9.6 and in Figure 9.7 is the uncured liquid polysulfide, and the lower spectrum is the polysulfide cured with the sodium birnessite cure paste mixture. The lack of any peaks for the TMTD accelerator, the Santicizer 261 plasticiser and the sodium birnessite at 2560 cm $^{-1}$ shows that the mercaptan peak loss is not masked by other groups.

Figure 9.1 Infrared spectrum for uncured liquid polysulfide

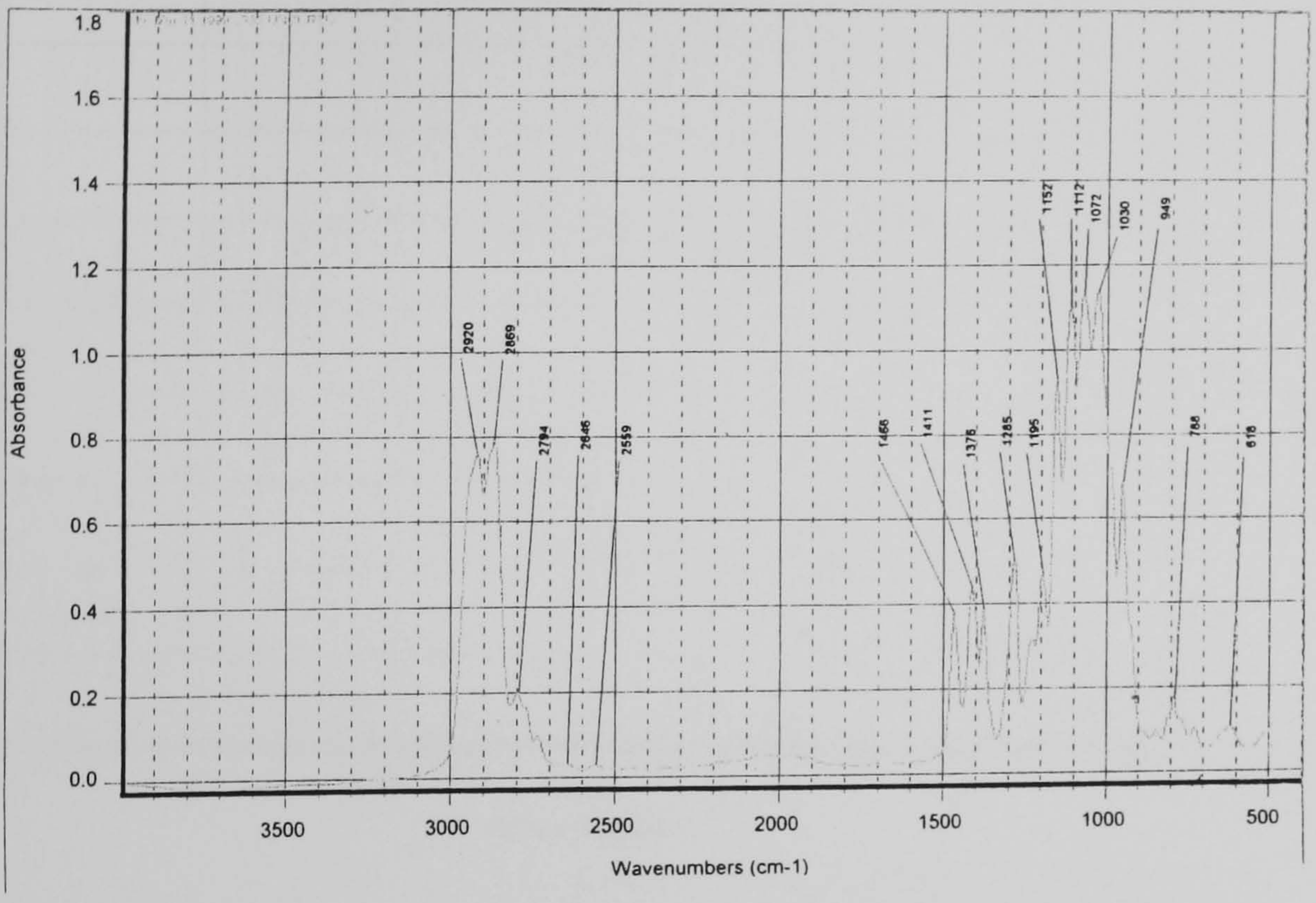


Figure 9.2 Infrared spectrum for TMTD accelerator

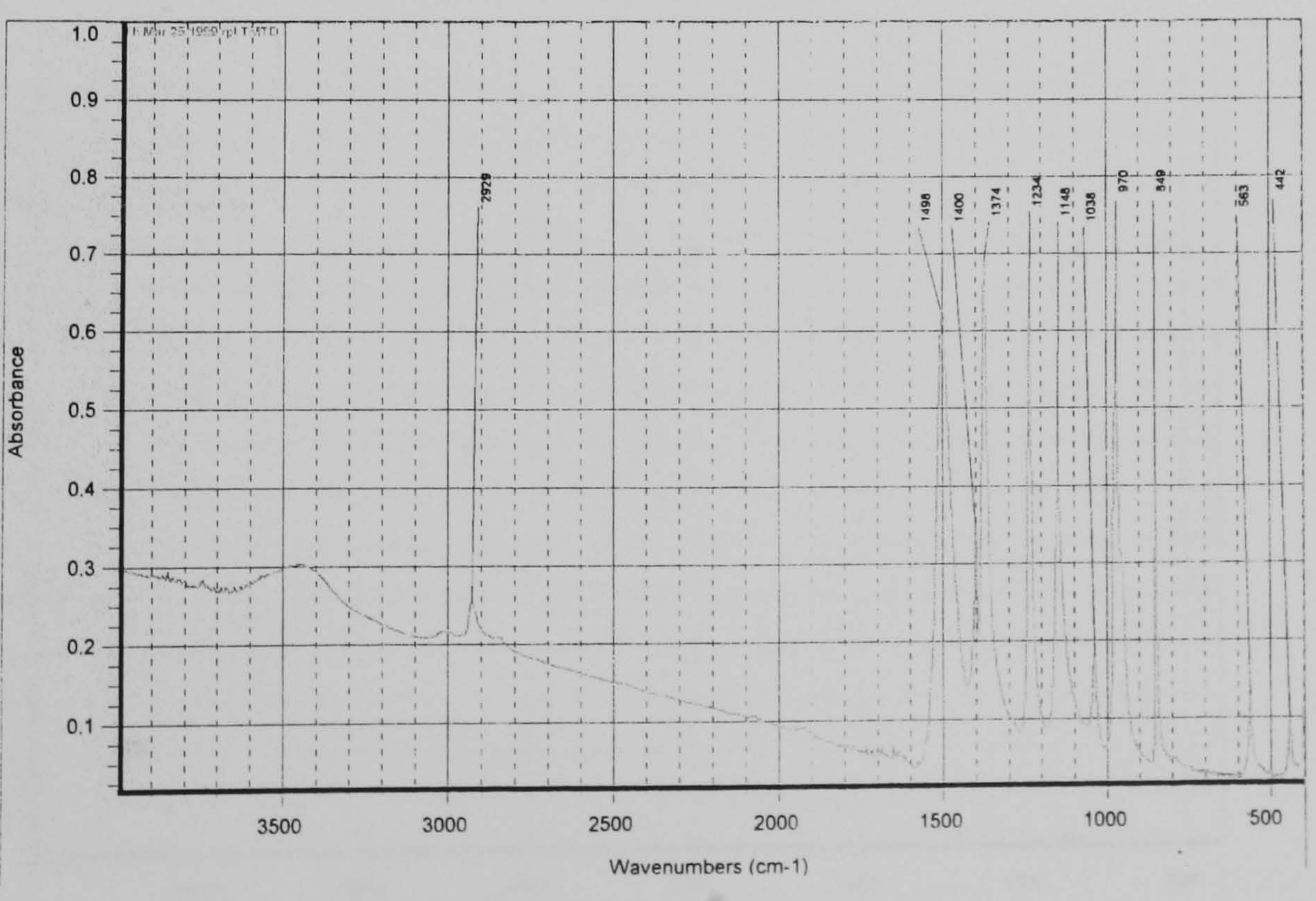


Figure 9.3 Infrared spectrum for Santicizer 261 plasticiser

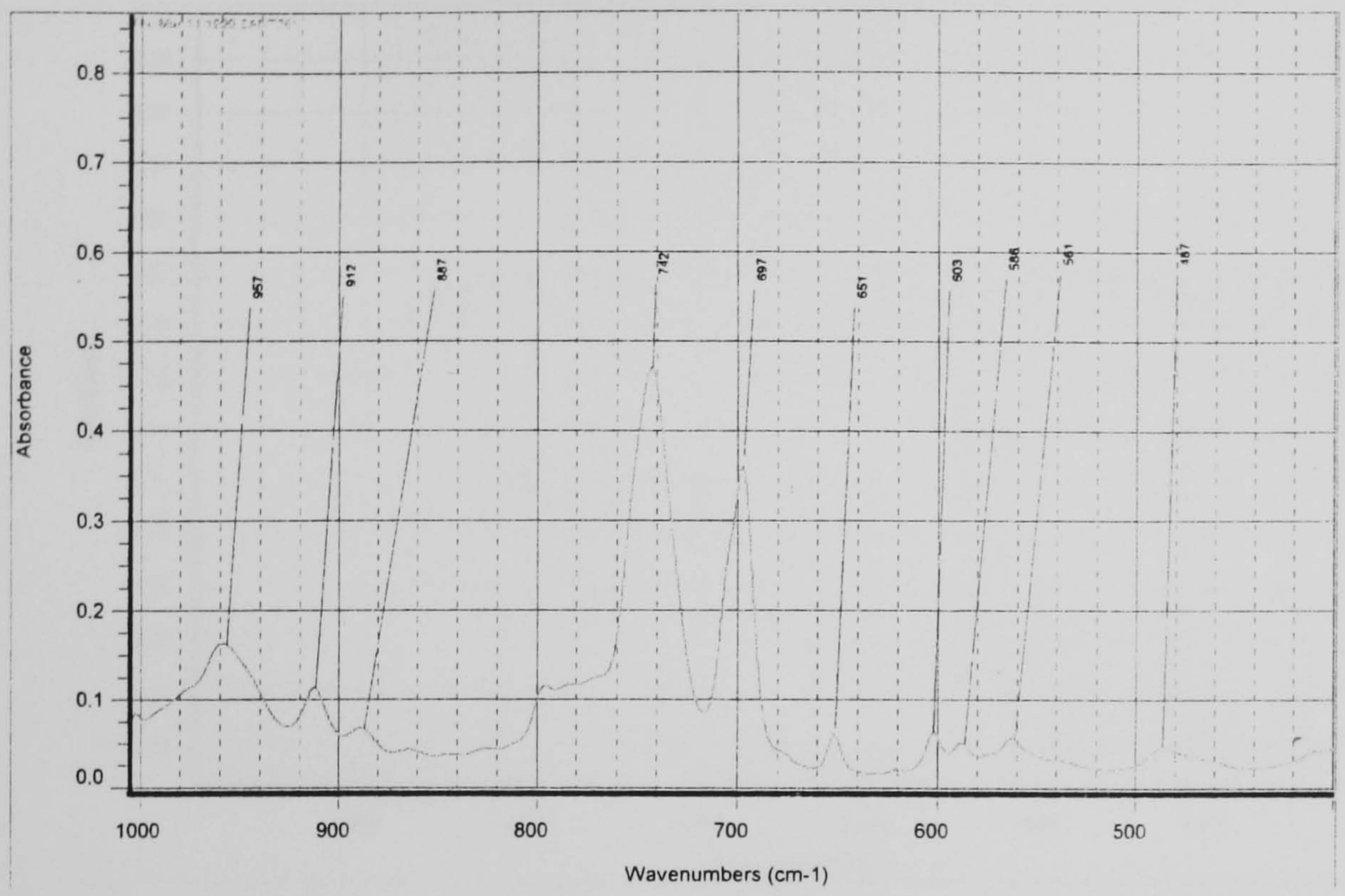


Figure 9.4 Infrared spectrum for sodium birnessite

Figure 9.5 Infrared spectrum for cure paste mixture (sodium birnessite, accelerator, and plasticiser) without addition of liquid polysulfide

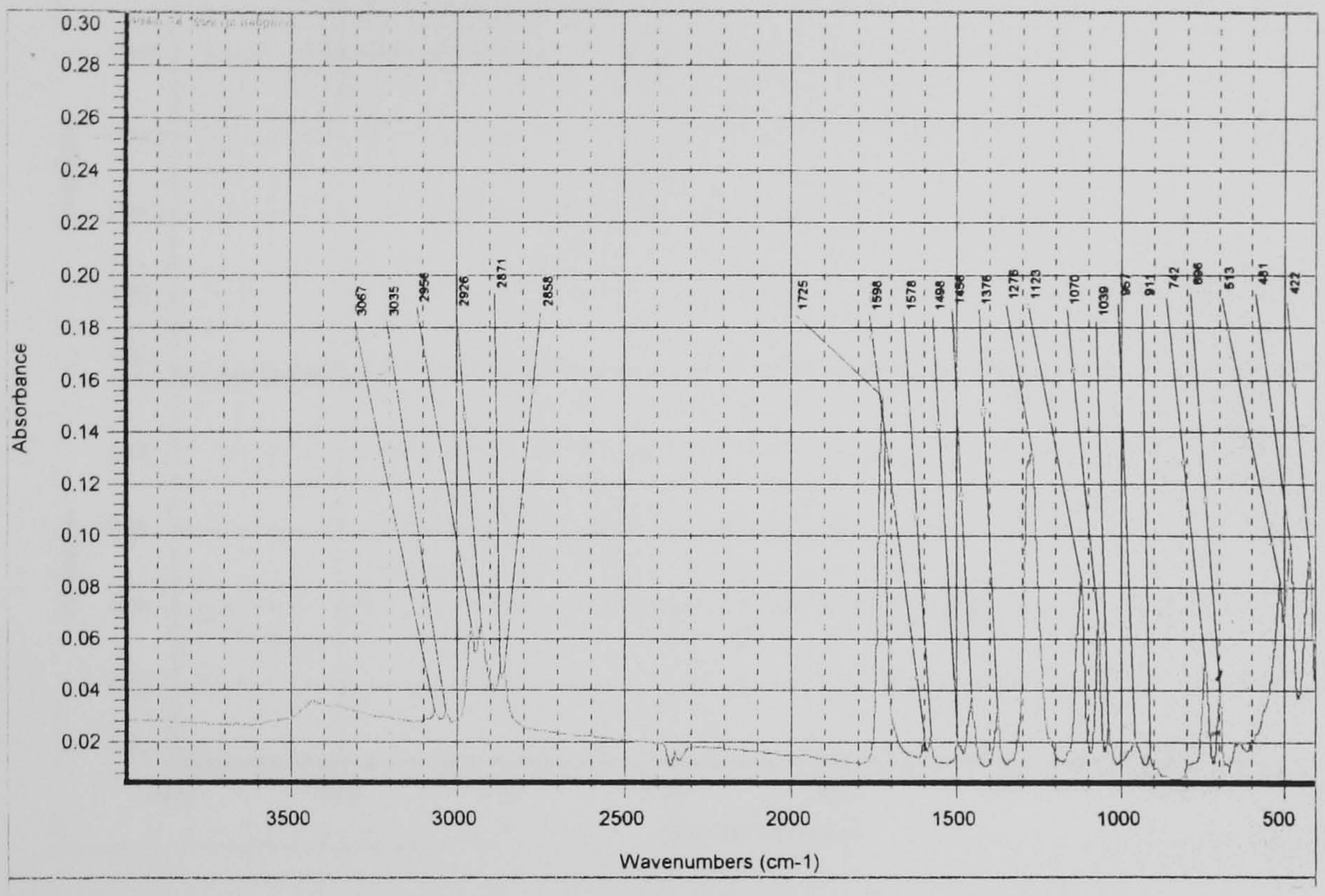
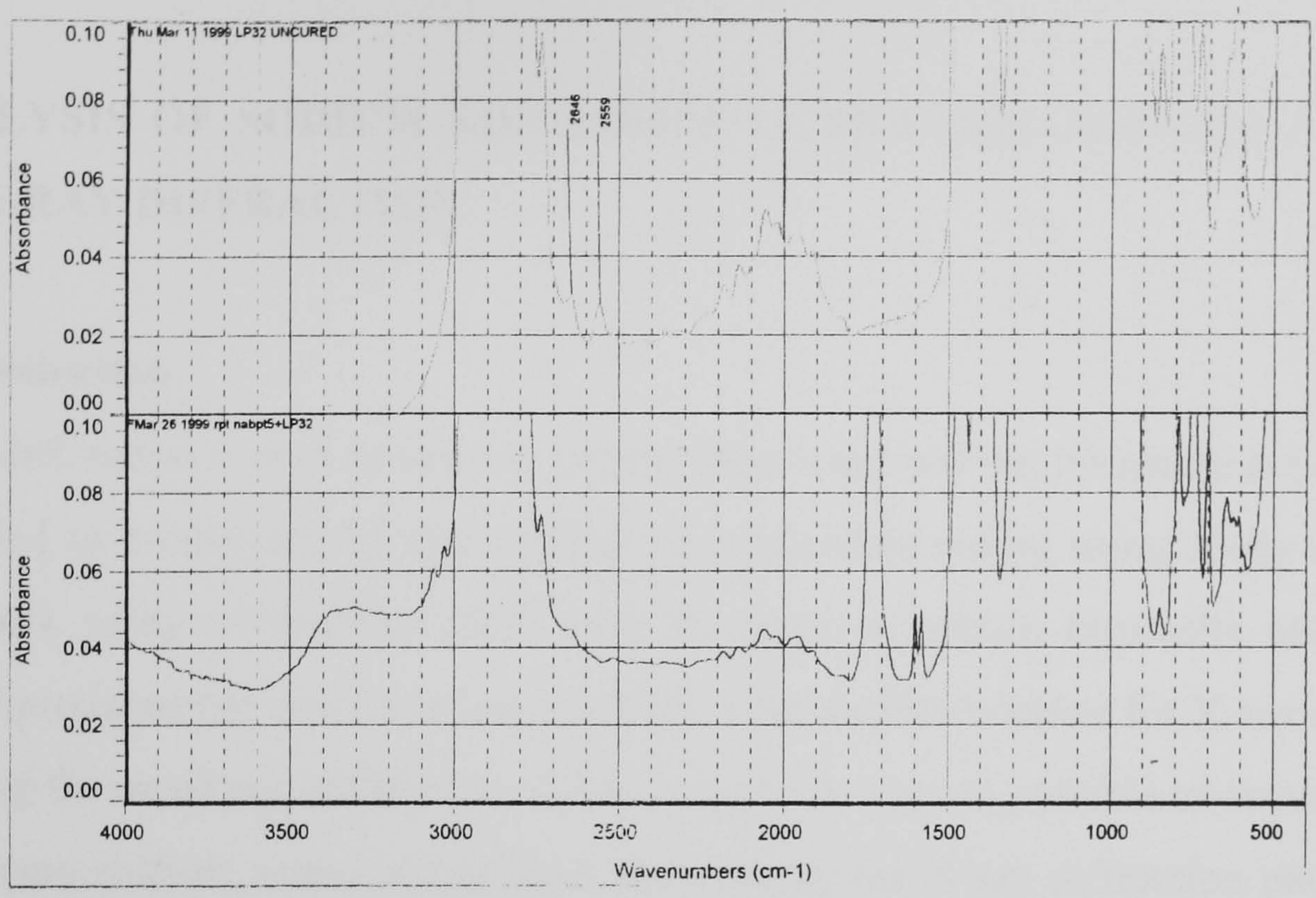


Figure 9.6 Infrared spectrum for cure paste mixture after addition to liquid polysulfide LP32C (top spectrum shows infrared absorbance peaks before curing mix added to polysulfide, whilst bottom spectrum shows infrared absorbance peaks after addition of sodium birnessite curing mixture)

Figure 9.7 Infrared spectrum for cure paste mixture after addition to liquid polysulfide LP32C (replicate experiment) (top spectrum shows infrared absorbance peaks before curing mix added to polysulfide, whilst bottom spectrum shows infrared absorbance peaks after



9.1.4 Discussion

The peaks obtained for sodium birnessite closely match the sodium birnessite peaks identified by Golden et al.[(3)] As expected peaks for the CH, CH_2 CH_3 stretch vibrations are found in the scans between 2850 and 2950 cm^{-1}.

The mercaptan peak in the unreacted liquid polysulfide at 2560 cm^{-1} is visible, and is easily recognised as it is in a region of the infrared spectrum which according to Socrates[(8)] is relatively free of other absorption bands. In the cured liquid polysulfide it has disappeared. This is significant, and indicates that the mechanism involves a reaction with the S-H terminals on the liquid polysulfide. This result was replicated and shown in the results too. The loss of the S-H peak from an infrared spectrum is characteristic of the curing of liquid polysulfide. This has been demonstrated by Matsui and Miwa[(5)] who observed the disappearance of the S-H peak at 2561 cm^{-1} after curing polysulfide with lead dioxide.

These experiments show for the first time that the mechanism by which liquid polysulfide is cured by sodium birnessite is by S-H most likely being converted to S-S. There is an absorption for the RS-SR group in aliphatic disulfides at 520-500 cm^{-1} which could be monitored.(8) The sodium birnessite however has absorption peaks which cover this 520-500 cm $^{-1}$ region. and therefore the formation of RS-SR bonds cannot be monitored.

9.2 ANALYSIS OF SODIUM BIRNESSITE CURED POLYSULFIDE PRODUCT USING X-RAY DIFFRACTION

9.2.1 Introduction

As X-ray diffraction is used to identify crystal phases and sodium birnessite is crystalline it was decided to investigate the end product of polysulfide curing using X-ray diffraction. Earlier work using polysulfide cured with 10 parts of sodium birnessite and no other ingredient produced too rapid a curing to obtain a flat surface suitable for X-ray diffraction. Grinding up the cured polysulfide also did not help as it was not possible to obtain a powder from the very rubbery cured polysulfide. As a result, the X-ray diffraction pattern of the ground up polysulfide produced large amounts of scattering and no meaningful result. It was therefore decided to use a lower quantity of birnessite to reduce the reaction rate and produce a flat surfaced cured polysulfide

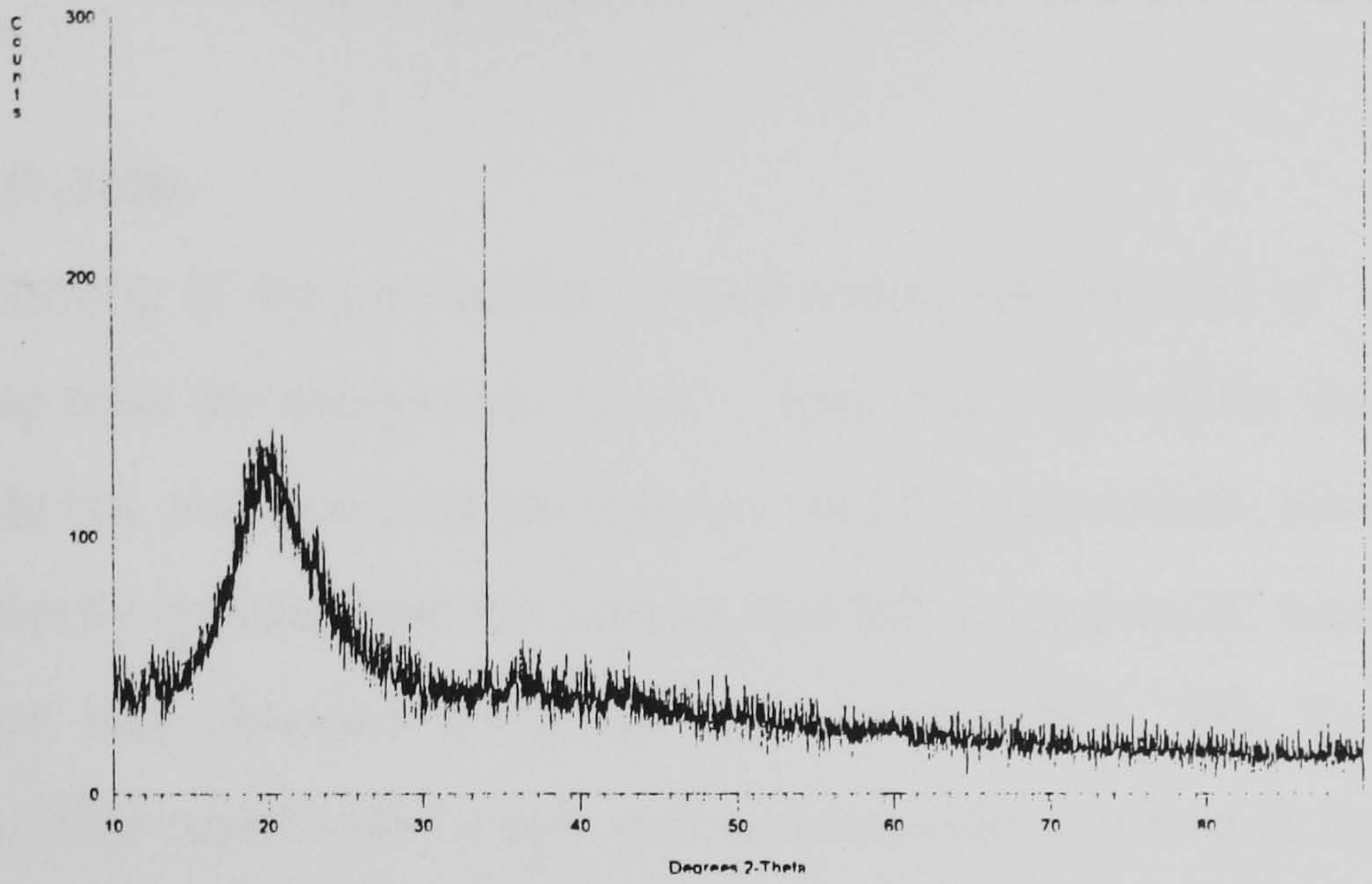
9.2.2 Experimental

A sample of polysulfide was cured using the sodium birnessite cure paste mix as follows

Liquid polysulfide:	LP32C	100 pph
Curing agent:	Sodium birnessite	5 pph
Accelerator:	TMTD	0.5 pph
Plasticiser:	Santicizer 261	15 pph

9.2.3 Results

Figure 9.8 The X-ray diffractogram of LP32C polysulfide cured with 5 pph of sodium birnessite



9.2.4 Discussion

The X-ray diffraction pattern revealed that the sample was amorphous see Figure 9.8. It may well be that any manganese oxides in the polysulfide were in too dilute an amount to be detected. Sodium birnessite being so reactive however cannot be added in quantities greater than the 10 parts used with 100 parts of LP32C polysulfide to achieve this cured product as the rate of reaction precludes the formation of a flat surface to analyse by XRD as the reaction. A ground up sample of sodium birnessite cured polysulfide was found to produce significant noise due to scattering from the uneven surface.

9.3 EXPERIMENT TO INCREASE THE QUANTITY OF SODIUM BIRNESSITE IN THE CURED POLYSULFIDE SAMPLE

As sodium birnessite is very rapid in curing polysulfide - instantaneously when added at 10 parts per 100 parts polysulfide, another approach was needed. It was decided to investigate curing polysulfide chilled to about 0°C in ice water to slow the reaction down.

9.3.1 Experimental

A 5 g sample of polysulfide was chilled to 0°C using ice water. To this was added 0.5 g of sodium birnessite. then mixed thoroughly and placed onto a flat surface to level out. The sample of cured polysulfide was left to cure for 1 week before testing.

9.3.2 Results

The cooling of the polysulfide caused some condensation of water onto its surface during mixing with the manganese dioxide. This would not affect the structure of the manganese dioxide but may speed up the reaction with the polysulfide. However, the rate of curing was sufficiently retarded with the cooling that full mixing could take place and importantly a flat surface was obtained for X-ray diffraction testing. The X-ray diffraction data for the polysulfide cured with 10 pph sodium birnessite is shown in Figure 9.9

Figure 9.9 The X-ray diffraction pattern of LP32C polysulfide cured with 10 parts sodium birnessite

```
No      Angle   Counts  Dspace  Rel I

1       12.418  252     7.122   58
2       25.039  304     3.554   69
3       32.389  209     2.762   48
4       35.581  204     2.521   47
5       36.106  225     2.486   51
6       37.072  201     2.423   46
7       42.133  168     2.143   38
8       60.025  132     1.54    30
```

9.3.3 Discussion

Despite sodium birnessite being detected in the cured polysulfide (Figure 9.9), the results do not indicate the presence of any other manganese oxide resulting from the curing of the polysulfide using sodium birnessite. It would be expected that the end product of the reaction with an active manganese oxide would be MnO. However, even at the level of sodium birnessite used (10 pph when chilled) no MnO was detected. Further research is necessary to identify the manganese oxide phase which results from the sodium birnessite curing of liquid polysulfide.

9.4 OTHER TECHNIQUE USED: X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

This technique is used to identify the charge on metal ions. It would therefore be useful to identify the presence of Mn^{2+} ions for instance in MnO formed by the reduction of sodium birnessite. A sample of sodium birnessite cured polysulfide (with no accelerators, diluents or plasticisers) was attempted to be analysed using XPS (Escalab 210). Due to the volatile nature of the polysulfide, outgassing of volatiles from the polysulfide caused the vacuum to be too low to obtain meaningful results - the results obtained were very noisy. A vacuum of 1 x 10^{-6} mPa was obtained which is 100 times too low for the XPS to carry out the analysis.

9.5 CONCLUSIONS

Overall this research has shown that the mechanism of curing of liquid polysulfide by sodium birnessite is by loss of the mercaptan terminals. It is likely that the mercaptan groups are converted into the disulfide crosslinkages. Because of the location of the peaks for sodium birnessite, the presence of the S-S bonds cannot be detected using the FTIR technique. Further support for the fact that sodium birnessite cured polysulfide has a similar curing mechanism to the commercial curing agent is that it has the same glass transition temperature (as reported in the Chapter on Dynamic Mechanical testing of cured polysulfide) as that of the polysulfide cured using the commercial curing agent. Raman spectroscopy was determined to be unsuitable for analysing the cured polysulfide due to its black colour. The XPS technique was attempted but due to the volatile nature of the polysulfide no meaningful results could be obtained because of the loss of vacuum, due to volatiles, when analysing the cured polysulfide.

9.6 REFERENCES

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CHAPTER 10 CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

10.1. CONCLUSIONS

This thesis contains a description of the properties of a synthetic manganese dioxide phase based on sodium birnessite (a layered manganese oxide which is also found naturally in soils) as a curing agent by comparing its behaviour with that of a standard polysulfide curing agent in terms of the thermal, rheometric, and mechanical properties of the cured polysulfide.

Polysulfides are used in a range of applications. They adhere to glass, steel, wood and concrete, resist solvents and chemicals and are noted for their flexibility and ability to withstand stress and strain. As water-resistant sealants they are used in the construction industry and cured liquid polysulfides dominate the glass sealant industry, where they account for 80 % of secondary and outer seals in insulating glass edge-sealing.

The curing of liquid polysulfide is generally performed in combination with other additives such as plasticisers, fillers, accelerators, and retardants. A variety of agents can be used to polymerise polysulfides including inorganic curing agents, such as metal oxides, organic curing agents, such as cumene hydroperoxide, and gases such as oxygen.(2) Manganese dioxide phases are widely used as curing agents via the oxidation reaction:

$2R\text{-}SH + MnO_2 \text{->} R\text{-}S\text{-}S\text{-}R + H_2O + MnO$

The analytical composition of sodium birnessite is not consistent with all of the manganese being present in the IV+ oxidation state. The composition is consistent with two Mn atoms in every seven being in the II+ oxidation state and with the presence of one sodium atom per three manganese atoms. The analytical composition of the synthetic material (Na 6.1%, Mn 54.7%, H_2O 11.3%) suggests that it is based on the formula $Na_2Mn^{II}_2Mn^{IV}_5O_{13}.4.5H_2O$, although the water percentage in the final product can vary.

Environmental concerns are now favouring the use of manganese dioxide in preference to more toxic polysulfide curing agents. All manganese-containing curing agents are based on manganese (IV) oxide but not all manganese dioxide phases are effective curing catalysts. The results of a study of over twenty manganese (IV) oxide materials carried out in the Centre for Environmental Research at Brunel University showed that curing activity ranged from zero for pure stoichiometric MnO_2, which has the rutile structure, to rapidly curing phases which contain other components such as alkali metals or water. Sodium birnessite was found to be a very active curing agent for liquid polysulfide. Commercially available manganese-based curing agents are usually pretreated, for example under high pressure and in alkaline conditions. Research by Goldblatt (personal communication) also found that some curing agents were unreliable and did not always result in a liquid polysulfide cure. This in industry means having to discard the polysulfides which were insufficiently cured.

An important property in polysulfide curing is the time taken to reach the gel point in order to ensure that the time between application to a substrate is long enough to ensure a good work life in application (between 1 and 4 hours) but not so long that it remains soft and tacky once the job has been finished.

The layered manganese (IV) oxide based phase, sodium birnessite, $Na_2Mn^{II}_2Mn^{IV}_5O_{13}.xH_2O$, gives a liquid polysulfide cure that is too rapid for normal application when added at 10 pph polysulfide. The curing behaviour of sodium birnessite added as 5 pph, 4 pph and as a 5:5 pph mixture with either inert natural manganese dioxide or calcium carbonate has therefore been compared with that of the commercial curing agent at 10 pph. The characteristics of the curing process were followed by rheometry. To minimise the variables that effect the curing of the liquid polysulfide, fillers, retardants, and adhesion agents which are present in commercial cure pastes were excluded from the sealant formulation.

In order to draw conclusions from the results in this thesis, the data described from earlier Chapters are tabulated to make the following comparisons (1) Tables comparing sodium birnessite polysulfide curing experiments with experiments performed using the commercial curing agent, and (2) Tables comparing various combinations of sodium birnessite polysulfide curing mixes with various other sodium birnessite polysulfide curing mixes.

COMPARATIVE RESULTS: (1) TABLES COMPARING SODIUM BIRNESSITE POLYSULFIDE CURING MIXES WITH COMMERCIAL CURING AGENT MIXES

Although two separate *commercial curing agent mixtures* were prepared with Santicizer 278 or Santicizer 261 plasticiser, only experiments using the *commercial agent mixture* containing Santicizer **261** plasticiser are shown compared with experiments involving the sodium birnessite.

Data for the other commercial agent mixture containing the Santicizer 278 are given in earlier Chapters of this Thesis.

Table 10.1 Summary Table of results for experiments using 5 pph sodium birnessite with TMTD accelerator and Santicizer 261 plasticiser compared to 10 pph undiluted commercial curing agent with TMTD accelerator

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite Inert diluent: 5 pph MnO_2 Accelerator: 0.5 pph TMTD Plasticiser: 10 pph Santicizer 261	***Curing agent:10 pph Commercial agent Inert diluent: None Accelerator: 0.5 pph TMTD Plasticiser: 10 pph Santicizer 261***
Time to reach gel point (minutes)	(1) 34 (2) 32	*(1) 45* *(2) 38*
Shore A hardness 4 hours	(1) 32 (2) 30	*(1) 32* *(2) 32*
Shore A hardness 24 hours	(1) 32 (2) 32	*(1) 30* *(2) 35*
Shore A hardness 48 hours	(1) 31 (2) 31	*(1) 30* *(2) 32*
Shore A hardness 7 days	(1) 32 (2) 32	*(1) 25* *(2) 31*
Cured polysulfide surface condition	Tack free	*Tack free*
6 week MVTR $g/m^2/24hours$	(1) 12.9 (3.95mm sample thickness) (2) 6.1 (4.62 mm sample thickness)	*(1) 10.9 (2.77 mm sample thickness)* *(2) 9.5 (3.04 mm sample thickness)*
Glass transition temperature (°C)	(1) -44 (2) -44	*(1) -42* *(2) -42*
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.579	*(1) 0.373*
Stress-strain properties Mean Strain at Break (%)	(1) 234	*(1) 266*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 265 (2) 267	*(1) 263* *(2) 264*

Table 10.2 Summary Table of results for experiments using 5 pph sodium birnessite with TMTD accelerator and the alternative plasticiser Santicizer 278 compared to 10 pph undiluted commercial curing agent with TMTD accelerator

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: 5 pph MnO_2** **Accelerator: 0.5 pph TMTD** **Plasticiser: 10 pph Santicizer 278**	*Curing agent: 10 pph Commercial agent* *Inert diluent: None* *Accelerator: 0.5 pph TMTD* *Plasticiser: 10 pph Santicizer 261*
Time to reach gel point (minutes)	(1) 33 (2) 32	*(1) 45* *(2) 38*
Shore A hardness 4 hours	(1) 34 (2) 36	***(1) 32*** ***(2) 32***
Shore A hardness 24 hours	(1) 36 (2) 37	***(1) 30*** ***(2) 35***
Shore A hardness 48 hours	(1) 35 (2) 34	***(1) 30*** ***(2) 32***
Shore A hardness 7 days	(1) 34 (2) 33	***(1) 25*** ***(2) 31***
Cured polysulfide surface condition	Tack free	***Tack free***
Glass transition temperature (°C)	(1) -42 (2) -42	*(1) -42* *(2) -42*
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.506	*(1) 0.373*
Stress-strain properties Mean Strain at Break (%)	(1) 220	*(1) 266*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 268 (2) 268	*(1) 263* *(2) 264*

Table 10.3 Summary Table of results for experiments using 5 pph sodium birnessite with TMTD accelerator and inert $CaCO_3$ diluent compared to 10 pph undiluted commercial agent with TMTD accelerator

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: 5 pph $CaCO_3$** **Accelerator: 0.5 pph TMTD** **Plasticiser: 10 pph Santicizer 261**	*Curing agent: 10 pph Commercial agent* *Inert diluent: None* *Accelerator: 0.5 pph TMTD* *Plasticiser: 10 pph Santicizer 261*
Time to reach gel point (minutes)	(1) 25 (2) 25	*(1) 45* *(2) 38*
Shore A hardness 4 hours	(1) 36 (2) 33	***(1) 32*** ***(2) 32***
Shore A hardness 24 hours	(1) 41 (2) 38	***(1) 30*** ***(2) 35***
Shore A hardness 48 hours	(1) 39 (2) 36	***(1) 30*** ***(2) 32***
Shore A hardness 7 days	(1) 39 (2) 38	***(1) 25*** ***(2) 31***
Cured polysulfide surface condition	Tack free	***Tack free***
Glass transition temperature (°C)	(1) -44 (2) -44	*(1) -42* *(2) -42*
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.301	*(1) 0.373*
Stress-strain properties Mean Strain at Break (%)	(1) 231	*(1) 266*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 269 (2) 262	*(1) 263* *(2) 264*

Table 10.4 Summary Table of results for experiments using 5 pph sodium birnessite with TMTD accelerator and no inert diluent compared to 10 pph undiluted commercial curing agent with TMTD accelerator.

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: NONE** **Accelerator: 0.5 pph TMTD** **Plasticiser: 15 pph Santicizer 261**	*Curing agent: 10 pph Commercial agent* *Inert diluent: None* *Accelerator: 0.5 pph TMTD* *Plasticiser: 10 pph Santicizer 261*
Time to reach gel point (minutes)	(1) 51 (2) 46	*(1) 45* *(2) 38*
Shore A hardness 4 hours	(1) 24 (2) 23	*(1) 32* *(2) 32*
Shore A hardness 24 hours	(1) 25 (2) 26	*(1) 30* *(2) 35*
Shore A hardness 48 hours	(1) 29 (2) 26	*(1) 30* *(2) 32*
Shore A hardness 7 days	(1) 30 (2) 31	*(1) 25* *(2) 31*
Cured polysulfide surface condition	Tack free	***Tack free***
Glass transition temperature (°C)	(1) -44 (2) -44	*(1) -42* *(2) -42*
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.237	*(1) 0.373*
Stress-strain properties Mean Strain at Break (%)	(1) 253	*(1) 266*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 251 (2) 258	*(1) 263* *(2) 264*

Table 10.5 Summary Table of results for experiments using 4 pph sodium birnessite with TMTD accelerator and no inert diluent compared to 10 pph commercial curing agent with TMTD accelerator.

	CURING AGENT MIXTURES	
	Curing agent: 4 pph Sodium birnessite **Inert diluent: NONE** **Accelerator: 0.5 pph TMTD** **Plasticiser: 16 pph Santicizer 261**	*Curing agent: 10 pph Commercial agent* *Inert diluent: None* *Accelerator: 0.5 pph TMTD* *Plasticiser: 10 pph Santicizer 261*
Time to reach gel point (minutes)	(1) 126 (2) 123	*(1) 45* *(2) 38*
Shore A hardness 4 hours	(1) 3 (2) 4	***(1) 32*** ***(2) 32***
Shore A hardness 24 hours	(1) 17 (2) 16	***(1) 30*** ***(2) 35***
Shore A hardness 48 hours	(1) 23 (2) 21	***(1) 30*** ***(2) 32***
Shore A hardness 7 days	(1) 24 (2) 25	***(1) 25*** ***(2) 31***
Cured polysulfide surface condition	Tacky surface	***Tack free***
Glass transition temperature (°C)	(1) -44 (2) -44	*(1) -42* *(2) -42*
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.136	*(1) 0.373*
Stress-strain properties Mean Strain at Break (%)	(1) 321	*(1) 266*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 257 (2) 251	*(1) 263* *(2) 264*

Table 10.6 Summary Table of results comparing experiments using 5 pph sodium birnessite diluted with inert $CaCO_3$ with DBU accelerator compared to 10 pph undiluted commercial curing agent with TMTD accelerator

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: 5 pph $CaCO_3$** **Accelerator: 0.5 pph DBU** **Plasticiser: 10 pph Santicizer 261**	*Curing agent: 10 pph Commercial agent* *Inert diluent: None* *Accelerator: 0.5 pph TMTD* *Plasticiser: 10 pph Santicizer 261*
Time to reach gel point (minutes)	(1) 15 (2) 15	*(1) 45* *(2) 38*
Shore A hardness 4 hours	(1) 28 (2) 24	***(1) 32*** ***(2) 32***
Shore A hardness 24 hours	(1) 30 (2) 26	***(1) 30*** ***(2) 35***
Shore A hardness 48 hours	(1) 32 (2) 35	***(1) 30*** ***(2) 32***
Shore A hardness 7 days	(1) 40 (2) 38	***(1) 25*** ***(2) 31***
Cured polysulfide surface condition	Tack free	***Tack free***
Glass transition temperature (°C)	(1) -44 (2) -44	*(1) -42* *(2) -42*
Stress-strain properties Mean Stress at Break (MPa)	(1) N.A[1]	*(1) 0.373*
Stress-strain properties Mean Strain at Break (%)	(1) N.A[1]	*(1) 266*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 269 (2) 262	*(1) 263* *(2) 264*

N.A[1] The curing of this polymer was too rapid to obtain samples for these experiments.

Table 10.7 Summary Table of results comparing experiments using 5 pph sodium birnessite diluted with inert MnO_2 with DBU accelerator compared to 10 pph undiluted commercial curing agent with TMTD accelerator

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: 5 pph MnO_2** **Accelerator: 0.5 pph DBU** **Plasticiser: 10 pph Santicizer 261**	*Curing agent: 10 pph Commercial agent* *Inert diluent: None* *Accelerator: 0.5 pph TMTD* *Plasticiser: 10 pph Santicizer 261*
Time to reach gel point (minutes)	(1) 23 (2) 25	*(1) 45* *(2) 38*
Shore A hardness 4 hours	(1) 24 (2) 22	***(1) 32*** ***(2) 32***
Shore A hardness 24 hours	(1) 32 (2) 30	***(1) 30*** ***(2) 35***
Shore A hardness 48 hours	(1) 31 (2) 32	***(1) 30*** ***(2) 32***
Shore A hardness 7 days	(1) 35 (2) 38	***(1) 25*** ***(2) 31***
Cured polysulfide surface condition	Tack free	***Tack free***
Glass transition temperature (°C)	(1) -44 (2) -44	*(1) -42* *(2) -42*
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.579	*(1) 0.373*
Stress-strain properties Mean Strain at Break (%)	(1) 234	*(1) 266*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 269 (2) 271	*(1) 263* *(2) 264*

Table 10.8 Summary Table of results comparing 5pph undiluted sodium birnessite (DBU as the accelerator) with 10 pph commercial curing agent and TMTD accelerator.

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: NONE** **Accelerator: 0.5 pph DBU** **Plasticiser: 15 pph Santicizer 261**	*Curing agent: 10 pph Commercial agent* *Inert diluent: None* *Accelerator: 0.5 pph TMTD* *Plasticiser: 10 pph Santicizer 261*
Time to reach gel point (minutes)	(1) 26 (2) 36	*(1) 45* *(2) 38*
Shore A hardness 4 hours	(1) 15 (2) 15	***(1) 32*** ***(2) 32***
Shore A hardness 24 hours	(1) 23 (2) 25	***(1) 30*** ***(2) 35***
Shore A hardness 48 hours	(1) 29 (2) 28	***(1) 30*** ***(2) 32***
Shore A hardness 7 days	(1) 31 (2) 34	***(1) 25*** ***(2) 31***
Cured polysulfide surface condition	Tack free	***Tack free***
Glass transition temperature (°C)	(1) -44 (2) -44	*(1) -42* *(2) -42*
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.237	*(1) 0.373*
Stress-strain properties Mean Strain at Break (%)	(1) 201	*(1) 266*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 252 (2) 250	*(1) 263* *(2) 264*

Table 10.9 Summary Table of results using sodium birnessite at 4 pph with inert $CaCO_3$ diluent and DBU accelerator compared to the results using the 10 pph undiluted commercial curing agent with TMTD accelerator.

	CURING AGENT MIXTURES	
	Curing agent: 4 pph Sodium birnessite **Inert diluent: 6 pph $CaCO_3$** **Accelerator: 0.5 pph DBU** **Plasticiser: 15 pph Santicizer 261**	*Curing agent: 10 pph Commercial agent* *Inert diluent: None* *Accelerator: 0.5 pph TMTD* *Plasticiser: 10 pph Santicizer 261*
Time to reach gel point (minutes)	(1) 46 (2) 45	*(1) 45* *(2) 38*
Shore A hardness 4 hours	(1) 21 (2) 21	*(1) 32* *(2) 32*
Shore A hardness 24 hours	(1) 28 (2) 23	*(1) 30* *(2) 35*
Shore A hardness 48 hours	(1) 34 (2) 28	*(1) 30* *(2) 32*
Shore A hardness 7 days	(1) 36 (2) 34	*(1) 25* *(2) 31*
Cured polysulfide surface condition	Tacky surface	***Tack free***
Glass transition temperature (°C)	(1) -44 (2) -44	*(1) -42* *(2) -42*
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.214	*(1) 0.373*
Stress-strain properties Mean Strain at Break (%)	(1) 255	*(1) 266*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 260 (2) 262	*(1) 263* *(2) 264*

Table 10.10 Summary Table of results comparing sodium birnessite at 4 pph with inert MnO_2 diluent and DBU accelerator compared to the results using the 10 pph undiluted commercial curing agent with TMTD accelerator.

	CURING AGENT MIXTURES	
	Curing agent: 4 pph Sodium birnessite **Inert diluent: 6 pph MnO_2** **Accelerator: 0.5 pph DBU** **Plasticiser: 10 pph Santicizer 261**	*Curing agent: 10 pph Commercial agent* *Inert diluent: None* *Accelerator: 0.5 pph TMTD* *Plasticiser: 10 pph Santicizer 261*
Time to reach gel point (minutes)	(1) 23 (2) 21	*(1) 45* *(2) 38*
Shore A hardness 4 hours	(1) 28 (2) 32	***(1) 32*** ***(2) 32***
Shore A hardness 24 hours	(1) 33 (2) 31	***(1) 30*** ***(2) 35***
Shore A hardness 48 hours	(1) 31 (2) 31	***(1) 30*** ***(2) 32***
Shore A hardness 7 days	(1) 37 (2) 36	***(1) 25*** ***(2) 31***
Cured polysulfide surface condition	Tack free	***Tack free***
Glass transition temperature (°C)	(1) -44 (2) -44	*(1) -42* *(2) -42*
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.431	*(1) 0.373*
Stress-strain properties Mean Strain at Break (%)	(1) 196	*(1) 266*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 266 (2) 265	*(1) 263* *(2) 264*

Table 10.11 Summary Table of results of experiments using sodium birnessite at 4 pph and no inert diluent compared with experimental results using 10 pph commercial curing agent with TMTD accelerator.

	CURING AGENT MIXTURES	
	Curing agent: 4 pph Sodium birnessite **Inert diluent: NONE** **Accelerator: 0.5 pph DBU** **Plasticiser: 16 pph Santicizer 261**	*Curing agent: 10 pph Commercial agent* *Inert diluent: None* *Accelerator: 0.5 pph TMTD* *Plasticiser: 10 pph Santicizer 261*
Time to reach gel point (minutes)	(1) 56 (2) 55	*(1) 45* *(2) 38*
Shore A hardness 4 hours	(1) 16 (2) 19	***(1) 32*** ***(2) 32***
Shore A hardness 24 hours	(1) 21 (2) 20	***(1) 30*** ***(2) 35***
Shore A hardness 48 hours	(1) 22 (2) 20	***(1) 30*** ***(2) 32***
Shore A hardness 7 days	(1) 34 (2) 36	***(1) 25*** ***(2) 31***
Cured polysulfide surface condition	Tacky surface	***Tack free***
Glass transition temperature (°C)	(1) -46 (2) -44	*(1) -42* *(2) -42*
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.199	*(1) 0.373*
Stress-strain properties Mean Strain at Break (%)	(1) 212	*(1) 266*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 256 (2) 255	*(1) 263* *(2) 264*

Table 10.12 Summary Table of results for experiments using undiluted sodium birnessite at 5pph without accelerator compared to commercial curing agent at 10 pph

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: NONE** **Accelerator: NONE** **Plasticiser: 15.5 pph Santicizer 261**	*Curing agent:10 pph Commercial agent* *Inert diluent: None* *Accelerator: 0.5 pph TMTD* *Plasticiser: 10 pph Santicizer 261*
Time to reach gel point (minutes)	(1) 36 (2) 34	*(1) 45* *(2) 38*
Shore A hardness 4 hours	(1) 27 (2) 25	***(1) 32*** ***(2) 32***
Shore A hardness 24 hours	(1) 29 (2) 26	***(1) 30*** ***(2) 35***
Shore A hardness 48 hours	(1) 32 (2) 30	***(1) 30*** ***(2) 32***
Shore A hardness 7 days	(1) 34 (2) 32	***(1) 25*** ***(2) 31***
Cured polysulfide surface condition	Tack free	***Tack free***
Glass transition temperature (°C)	(1) -46 (2) -44	*(1) -42* *(2) -42*
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.201	*(1) 0.373*
Stress-strain properties Mean Strain at Break (%)	(1) 280	*(1) 266*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 261 (2) 254	*(1) 263* *(2) 264*

TABLES COMPARING SODIUM BIRNESSITE POLYSULFIDE CURING MIXES BETWEEN ONE ANOTHER

Table 10.13 Summary Table of results of experiments comparing the effect of reducing undiluted sodium birnessite concentration from 5 pph to 4 pph

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: NONE** **Accelerator: 0.5 pph DBU** **Plasticiser: 15 pph Santicizer 261**	***Curing agent: 4 pph Sodium birnessite*** ***Inert diluent: NONE*** ***Accelerator: 0.5 pph DBU*** ***Plasticiser: 16 pph Santicizer 261***
Time to reach gel point (minutes)	(1) 26 (2) 36	*(1) 56* *(2) 55*
Shore A hardness 4 hours	(1) 15 (2) 15	*(1) 16* *(2) 19*
Shore A hardness 24 hours	(1) 23 (2) 25	*(1) 21* *(2) 20*
Shore A hardness 48 hours	(1) 29 (2) 28	*(1) 22* *(2) 20*
Shore A hardness 7 days	(1) 31 (2) 34	*(1) 34* *(2) 36*
Cured polysulfide surface condition	Tack free	***Tacky surface***
Glass transition temperature (°C)	(1) -44 (2) -44	*(1) -46* *(2) -44*
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.237	*(1) 0.199*
Stress-strain properties Mean Strain at Break (%)	(1) 201	*(1) 212*
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 252 (2) 250	*(1) 256* *(2) 255*

Table 10.14 Summary Table of results of experiments comparing 5 pph sodium birnessite with inert MnO_2 diluent compared to using inert $CaCO_3$ as a diluent

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: 5 pph MnO_2** **Accelerator: 0.5 pph TMTD** **Plasticiser: 10 pph Santicizer 261**	**Curing agent: 5 pph Sodium birnessite** **Inert diluent: 5 pph $CaCO_3$** **Accelerator: 0.5 pph TMTD** **Plasticiser: 10 pph Santicizer 261**
Time to reach gel point (minutes)	(1) 34 (2) 32	(1) 25 (2) 25
Shore A hardness 4 hours	(1) 32 (2) 30	(1) 36 (2) 33
Shore A hardness 24 hours	(1) 32 (2) 32	(1) 41 (2) 38
Shore A hardness 48 hours	(1) 31 (2) 31	(1) 39 (2) 36
Shore A hardness 7 days	(1) 32 (2) 32	(1) 39 (2) 38
Cured polysulfide surface condition	Tack free	*Tack free*
Glass transition temperature (°C)	(1) -44 (2) -44	(1) -44 (2) -44
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.579	(1) 0.301
Stress-strain properties Mean Strain at Break (%)	(1) 234	(1) 231
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 265 (2) 267	(1) 269 (2) 262

Table 10.15 Summary Table of results of experiments using 4 pph sodium birnessite with inert MnO_2 diluent compared to using inert $CaCO_3$ diluent.

	CURING AGENT MIXTURES	
	Curing agent: 4 pph Sodium birnessite **Inert diluent: 6 pph MnO_2** **Accelerator: 0.5 pph DBU** **Plasticiser: 10 pph Santicizer 261**	**Curing agent: 4 pph Sodium birnessite** **Inert diluent: 6 pph $CaCO_3$** **Accelerator: 0.5 pph DBU** **Plasticiser: 15 pph Santicizer 261**
Time to reach gel point (minutes)	(1) 23 (2) 21	(1) 46 (2) 45
Shore A hardness 4 hours	(1) 28 (2) 32	(1) 21 (2) 21
Shore A hardness 24 hours	(1) 33 (2) 31	(1) 28 (2) 23
Shore A hardness 48 hours	(1) 31 (2) 31	(1) 34 (2) 28
Shore A hardness 7 days	(1) 37 (2) 36	(1) 36 (2) 34
Cured polysulfide surface condition	Tack free	*Tacky surface*
Glass transition temperature (°C)	(1) -44 (2) -44	(1) -44 (2) -44
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.431	(1) 0.214
Stress-strain properties Mean Strain at Break (%)	(1) 196	(1) 255
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 266 (2) 265	(1) 260 (2) 262

Table 10.16 Summary Table of results for experiments comparing 5 pph sodium birnessite diluted with inert MnO_2 with either TMTD accelerator or with DBU accelerator

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: 5 pph MnO_2** **Accelerator: 0.5 pph TMTD** **Plasticiser: 10 pph Santicizer 261**	**Curing agent: 5 pph Sodium birnessite** **Inert diluent: 5 pph MnO_2** **Accelerator: 0.5 pph DBU** **Plasticiser: 10 pph Santicizer 261**
Time to reach gel point (minutes)	(1) 34 (2) 32	(1) 23 (2) 25
Shore A hardness 4 hours	(1) 32 (2) 30	(1) 24 (2) 22
Shore A hardness 24 hours	(1) 32 (2) 32	(1) 32 (2) 30
Shore A hardness 48 hours	(1) 31 (2) 31	(1) 31 (2) 32
Shore A hardness 7 days	(1) 32 (2) 32	(1) 35 (2) 38
Cured polysulfide surface condition	Tack free	*Tack free*
Glass transition temperature (°C)	(1) -44 (2) -44	(1) -44 (2) -44
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.579	(1) 0.579
Stress-strain properties Mean Strain at Break (%)	(1) 234	(1) 234
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 265 (2) 267	(1) 269 (2) 271

Table 10.17 Summary Table of results for experiments comparing 5 pph inert MnO_2 diluted sodium birnessite at 5 pph with either Santicizer 261 plasticiser or with Santicizer 278 plasticiser

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: 5 pph MnO_2** **Accelerator: 0.5 pph TMTD** **Plasticiser: 10 pph Santicizer 261**	**Curing agent: 5 pph Sodium birnessite** **Inert diluent: 5 pph MnO_2** **Accelerator: 0.5 pph TMTD** **Plasticiser: 10 pph Santicizer 278**
Time to reach gel point (minutes)	(1) 34 (2) 32	(1) 33 (2) 32
Shore A hardness 4 hours	(1) 32 (2) 30	(1) 34 (2) 36
Shore A hardness 24 hours	(1) 32 (2) 32	(1) 36 (2) 37
Shore A hardness 48 hours	(1) 31 (2) 31	(1) 35 (2) 34
Shore A hardness 7 days	(1) 32 (2) 32	(1) 34 (2) 33
Cured polysulfide surface condition	Tack free	*Tack free*
Glass transition temperature (°C)	(1) -44 (2) -44	(1) -42 (2) -42
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.579	(1) 0.506
Stress-strain properties Mean Strain at Break (%)	(1) 234	(1) 220
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 265 (2) 267	(1) 268 (2) 268

Table 10.18 Summary Table of results using sodium birnessite at 5 pph with DBU accelerator comparing the effect of using 5 pph inert MnO_2 diluent with using no inert diluent

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: 5 pph MnO_2** **Accelerator: 0.5 pph DBU** **Plasticiser: 10 pph Santicizer 261**	**Curing agent: 5 pph Sodium birnessite** **Inert diluent: NONE** **Accelerator: 0.5 pph DBU** **Plasticiser: 15 pph Santicizer 261**
Time to reach gel point (minutes)	(1) 23 (2) 25	(1) 26 (2) 36
Shore A hardness 4 hours	(1) 24 (2) 22	(1) 15 (2) 15
Shore A hardness 24 hours	(1) 32 (2) 30	(1) 23 (2) 25
Shore A hardness 48 hours	(1) 31 (2) 32	(1) 29 (2) 28
Shore A hardness 7 days	(1) 35 (2) 38	(1) 31 (2) 34
Cured polysulfide surface condition	***Tack free***	Tack free
Glass transition temperature (°C)	(1) -44 (2) -44	(1) -44 (2) -44
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.579	(1) 0.237
Stress-strain properties Mean Strain at Break (%)	(1) 234	(1) 201
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 269 (2) 271	(1) 252 (2) 250

Table 10.19 Summary Table of results using undiluted 5 pph sodium birnessite comparing the effect of using DBU accelerator with using no accelerator

	CURING AGENT MIXTURES	
	Curing agent: 5 pph Sodium birnessite **Inert diluent: NONE** **Accelerator: 0.5 pph DBU** **Plasticiser: 15 pph Santicizer 261**	**Curing agent: 5 pph Sodium birnessite** **Inert diluent: NONE** **Accelerator: NONE** **Plasticiser: 15.5 pph Santicizer 261**
Time to reach gel point (minutes)	(1) 26 (2) 36	(1) 36 (2) 34
Shore A hardness 4 hours	(1) 15 (2) 15	(1) 27 (2) 25
Shore A hardness 24 hours	(1) 23 (2) 25	(1) 29 (2) 26
Shore A hardness 48 hours	(1) 29 (2) 28	(1) 32 (2) 30
Shore A hardness 7 days	(1) 31 (2) 34	(1) 34 (2) 32
Cured polysulfide surface condition	Tack free	*Tack free*
Glass transition temperature (°C)	(1) -44 (2) -44	(1) -46 (2) -44
Stress-strain properties Mean Stress at Break (MPa)	(1) 0.237	(1) 0.201
Stress-strain properties Mean Strain at Break (%)	(1) 201	(1) 280
Temperature (°C) for Thermal decomposition by 10 % of weight	(1) 252 (2) 250	(1) 261 (2) 254

The conclusions drawn from these summary Tables are discussed under two headings: comparison of sodium birnessite with the commercial agent for (1a) sodium birnessite with the TMTD accelerator (1b) sodium birnessite with the DBU accelerator and (1c) sodium birnessite with no accelerator) and (2) comparison of various sodium birnessite combinations with other sodium birnessite cure mix combinations.

(1) COMPARISON OF SODIUM BIRNESSITE CURING OF POLYSULFIDE WITH COMMERCIAL AGENT CURING OF POLYSULFIDE.

(1a)Using the TMTD accelerator with sodium birnessite

- Inert MnO_2 diluted sodium birnessite at 5 pph gives a more rapid polysulfide cure, similar Shore A hardness build-up, similar low and high temperature properties and higher stress at break compared to polysulfide cured with the commercial curing agent at 10 pph. The Moisture Vapour Transmission Rate for cured polysulfide using 5 pph sodium birnessite diluted with 5 pph inert MnO_2 shows no adverse effect compared to that for the commercial curing agent at 10 pph.(Table 10.1)
- The type of plasticiser has very little effect on the rate of curing of liquid polysulfide and cured properties of sodium birnessite cured polysulfide compared to when curing polysulfide with 10 pph commercial curing agent. (Table 10.2 compared to Table 10.1)
- 5 pph sodium birnessite with 5 pph $CaCO_3$ inert diluent gives a faster rate of polysulfide curing, faster Shore A hardness build up and similar low and high temperature properties although it has a lower strength than 10 pph commercial agent cured polysulfide.(Table 10.3)
- 5 pph sodium birnessite diluted with 5 pph inert MnO_2 gives a faster cure, similar low and high temperature properties, faster Shore A hardness buildup and a stronger product compared to that from 10 pph commercial agent.(Table 10.4)
- 4 pph sodium birnessite, using no inert diluent reduces both the rate of curing and Shore A hardness buildup to slower than that when using the commercial cured polysulfide. The 7 day Shore A hardness is below the optimal level of 30. although it has similar low and high temperature properties. It also makes a much weaker cured polysulfide than 10 pph commercial agent. (Table 10.5)

(1b) Using the DBU accelerator with sodium birnessite

- 5 pph sodium birnessite diluted with 5 pph $CaCO_3$. gives a rate of polysulfide curing that is too rapid compared to using 10 pph commercial curing agent. The hardness build-up and low and high temperature properties of the sodium birnessite and commercial agent cured polysulfide are similar though. (Table 10.6)
- 5 pph sodium birnessite diluted with 5 pph inert MnO_2 gives a rate of curing that is faster than the commercial agent, the cured polysulfide strength and the 7 day Shore A hardness are higher than that for 10 pph commercial agent cured polysulfide. The hardness build-up and low and high temperature properties of the 5 pph sodium birnessite and 10 pph commercial agent cured polysulfide are similar. (Table 10.7)
- 5 pph sodium birnessite with no added inert diluent, gives a Shore A hardness build up that is slower than when using the commercial agent. The low and high temperature properties of the sodium birnessite and commercial agent cured polysulfide are similar although sodium birnessite cured polysulfide is weaker than polysulfide cured with 10 pph commercial agent. (Table 10.8)
- 4 pph sodium birnessite with 6 pph inert $CaCO_3$ diluent, gives a rate of curing that is faster, than the commercial curing agent, the Shore A hardness build up is slower, the cured product is weaker than 10 pph commercial agent cured polysulfide. The low and high temperature properties of the sodium birnessite and commercial agent cured polysulfide are similar although the 4 pph sodium birnessite cured polysulfide has an undesirable tacky surface. (Table 10.9)
- 4 pph sodium birnessite with 6 pph inert MnO_2 gives a rate of curing, and Shore A hardness build up faster than using the commercial curing agent. The low and high temperature properties of the sodium birnessite and commercial agent cured polysulfide are similar although sodium birnessite cured polysulfide is stronger than 10 pph commercial agent cured polysulfide.(Table 10.10)
- At 4 pph sodium birnessite with no inert diluent, the rate of curing, the rate of Shore A hardness build up, and polysulfide strength are less than that using 10 pph commercial curing agent, although the low and high temperature properties of the sodium birnessite and commercial agent cured polysulfide are similar. The 4 pph

sodium birnessite cured polysulfide surface is also undesirable being tacky. (Table 10.11)

(1C) Using no accelerator with sodium birnessite

- The rate of curing with 5 pph sodium birnessite and no inert diluent is slightly faster than that using 10 pph commercial agent and the low and high temperature properties of the sodium birnessite and commercial agent cured polysulfide are similar. However, the rate of hardness build up, and the strength of the cured polysulfide is lower than that when using 10 pph commercial curing agent. (Table 10.12)

(2) Comparing various sodium birnessite curing agent mixtures with other sodium birnessite curing mixtures.

- Using the DBU accelerated mixtures, CHANGING ONLY THE SODIUM BIRNESSITE LEVEL FROM 5 PPH TO 4 PPH decreases the rate of curing, the Shore A hardness build up and the strength of the cured polysulfide. The low and high temperature properties of both sodium birnessite cured polysulfides are similar. The cured polysulfide surface also becomes tacky at 4 pph. (Table 10.13)
- Using the TMTD accelerated mixtures using 5 pph sodium birnessite and CHANGING ONLY THE TYPE OF INERT DILUENT FROM MnO_2 TO $CaCO_3$, the rate of curing is increased, the rate of Shore A hardness build up is increased, although the cured polysulfide strength is lowered. The low and high temperature properties of both sodium birnessite cured polysulfides are similar. (Table 10.14)
- Using the DBU accelerator, 4 pph sodium birnessite and 6 pph inert diluent, CHANGING ONLY THE TYPE OF INERT DILUENT FROM MnO_2 TO $CaCO_3$ decreases the rate of curing, reduces the Shore A hardness build up, and reduces the cured polysulfide strength. The low and high temperature properties of both sodium birnessite cured polysulfides are similar, however, using inert $CaCO_3$ as the diluent makes the cured polysulfide surface undesirable as it is tacky. (Table 10.15)
- Using 5 pph sodium birnessite and 5 pph inert MnO_2 diluent, CHANGING ONLY THE ACCELERATOR FROM TMTD TO DBU, results in an increased rate of cure, a slightly decreased Shore A hardness build up, but the same cured polysulfide

strength. The low and high temperature properties of both sodium birnessite cured polysulfides are similar.(Table 10.16)

- Using 5 pph sodium birnessite diluted with 5 pph inert MnO_2 and TMTD accelerator. CHANGING ONLY THE TYPE OF plasticiser FROM SANTICIZER 261 TO 278 has virtually no effect on the curing or cured properties of polysulfide.(Table 10.17)
- Using 5 pph sodium birnessite and DBU accelerator ONLY CHANGING WHETHER OR NOT INERT MnO_2 DILUENT IS USED, shows that adding the inert diluent increases the rate of cure, the cured polysulfide strength, the Shore A hardness build up and the ultimate 7 day hardness. The low and high temperature properties of both sodium birnessite cured polysulfides are similar. (Table 10.18)
- Using 5 pph sodium birnessite with no inert diluent ONLY CHANGING WHETHER OR NOT AN ACCELERATOR IS USED, shows that using DBU, increases the rate of curing with undiluted sodium birnessite, provides a slower Shore A hardness buildup but a slightly stronger cured polysulfide. The low and high temperature properties of both sodium birnessite cured polysulfides are similar. (Table 10.19)

OVERALL CONCLUSIONS

I. **No cure failures have been observed in any experiment using sodium birnessite. This is important because of the percentage of failures found with commercial curing agents and the prevention of material wastage and therefore environmental and economic costs due to failures.**

II. **The inert diluents and the accelerators on their own do not cure liquid polysulfide, whilst the type of plasticiser has little effect on the rate of curing.**

III. **Inert diluent diluted sodium birnessite at 5 pph cures liquid polysulfide to at least comparable levels of cure (in terms of Shore A hardness, low and high temperature properties, tensile strength, tack free surface) and provides a more rapid cure than the 10 pph commercial agent cured polysulfide.**

IV. **Sodium birnessite at 4 pph without inert diluent or with inert $CaCO_3$ provides unsatisfactory cured properties of liquid polysulfide compared to the commercial agent (e.g produces a tacky surface on the cured polysulfide after 7 days, making it undesirable).**

V. Sodium birnessite at 4 pph with 6 pph inert MnO_2 diluent provides similar rate of cure, a higher Shore A 7 day hardness and strength than the 10 pph commercial curing agent cured polysulfide.

VI. The quantity of sodium birnessite used is the most important factor in the curing of polysulfide rather than the pH, water content or presence of accelerator.

VII. Inert diluent improves the rate of cure and cured polysulfide strength and Shore A hardness build up. This is believed to be due to separation of the sodium birnessite particles from each other and therefore their being more effectively distributed through the system.

VIII. The greatest influence the accelerators have on the curing of polysulfide is in the rate of curing.

IX. The DBU accelerator provides a more rapid acceleration of the curing than the TMTD (it is also less toxic).

X. The glass transition temperature is virtually the same as for the commercial agent cured polysulfide for all samples at 5 pph or 4 pph sodium birnessite, regardless of the quantity or type of inert diluent, plasticiser, or accelerator. This indicates that the same degree of cross linking is achieved.

XI. The thermal stability of all samples cured by sodium birnessite at 5 pph and 4 pph is very similar to that of the commercial agent cured polysulfide regardless of the quantity of curing agent, type and quantity of inert diluent, type of accelerator, and quantity and type of plasticiser used. This indicates a similar degree of cross linking of the polysulfide using either the commercial curing agent or sodium birnessite.

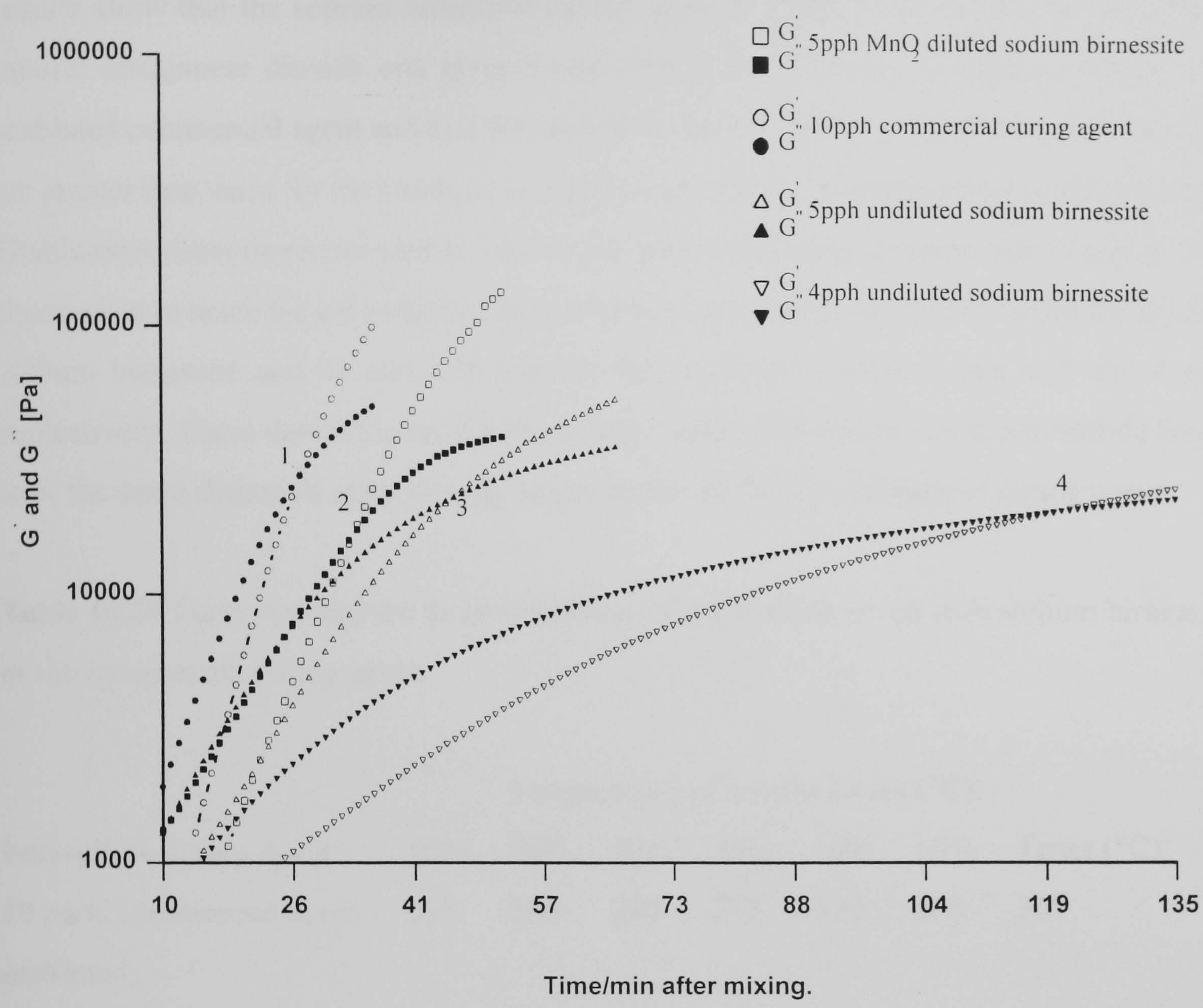
XII. Increasing the quantity of sodium birnessite from 4 pph to 5 pph increases the strength of the cured polysulfide.

XIII. The cured polysulfide stress-strain properties are improved when adding either inert manganese dioxide or calcium carbonate

XIV. The Moisture Vapour Transmission Rate through 5 pph inert MnO_2 diluted sodium birnessite (TMTD accelerated) cured polysulfide appears to be at least as low as that of polysulfide cured with 10 pph commercial agent (TMTD accelerated)

Examples of data comparing some of the effects of different amounts of sodium birnessite curing agent (with TMTD accelerator), and the presence and absence of inert MnO_2 diluent with that when using 10 pph commercial curing agent and TMTD accelerator on the rate of curing of liquid polysulfide are shown in Figure 10.1. Data showing the similar thermal stability and temperature of maximum decomposition (Tmax °C) for a range of sodium birnessite compositions (with TMTD accelerator) cured polysulfides compared to the TMTD accelerated commercial curing agent cured polysulfide is shown in Table 10.19.

Figure 10.1 Comparison of the progression to the gel point of storage modulus G′and the loss modulus G″of the inert manganese dioxide diluted and undiluted sodium birnessite and the commercial agent curing of polysulfide at 25 °C



The gel points of the curing polysulfide systems are obtained from the intersections of the storage modulus G′and the loss modulus G″curves (Numbers 1.2.3.4 on Figure 10.1) The results show that the sodium birnessite curing agent at 5 pph, even diluted with 5 pph of natural manganese dioxide ore, gives a cure that is almost twice as rapid as that for the undiluted commercial agent and that the moduli G′ and G″ for the sodium birnessite reaction are greater than those for the commercial agent curing process throughout the reaction period. Undiluted sodium birnessite used at 5 and 4 pph polysulfide gives a slower rate of curing. The times taken to reach the gel point are 38 min for the commercial agent, 32 min for the diluted sodium birnessite and 51 and 126 min for the undiluted material used at 5 and 4 pph respectively. These data indicate that the diluted sodium birnessite cured polysulfide has at least the same degree of cross linking as that achieved by the commercial curing agent.

Table 10.20 Table showing the thermal stability of polysulfide cured with sodium birnessite or the commercial curing agent.

	Temperature of weight losses (°C):						
Polysulfide curing agent:	10%	20%	30%	40%	50%	60%	Tmax (°C)
10 parts commercial agent undiluted	263	280	290	297	302	306	307
5 parts sodium birnessite diluted with 5 parts inert manganese dioxide	265	282	293	300	305	309	308
5 parts undiluted sodium birnessite	258	280	292	300	305	309	309
4 parts undiluted sodium birnessite	257	281	292	298	302	307	307

The thermal stabilities of the cured polysulfides determined by TGA (Table 10.20) confirm that the sodium birnessite product has at least the same degree of cross linking as that achieved by the commercial agent

Conclusions on the mechanism

Various techniques including infrared spectroscopy. X-ray diffraction and X-ray photoelectron spectroscopy have been used in this work to study the mechanism of polysulfide cure using sodium birnessite. Infrared spectroscopy has shown that the reaction between the sodium birnessite and the liquid polysulfide is by the loss of the mercaptan terminals in the polysulfide.

The rapidity of birnessite curing is linked to the reagent concentration not to the three most commonly described variables in polysulfide curing namely pH, water content, and particle size.

The curing reaction of the mercaptan groups in polysulfides with all Mn (IV) oxide phases, including sodium birnessite, depends upon the properties of manganese (IV) as an oxidising agent:

$$Mn^{4+} + 2\ e- \rightarrow Mn^{2+}$$

In a solid oxide phase this will result in the formation of manganese (II) oxide and the oxidation of oxide ions to supply the electrons to reduce the Mn^{4+} :

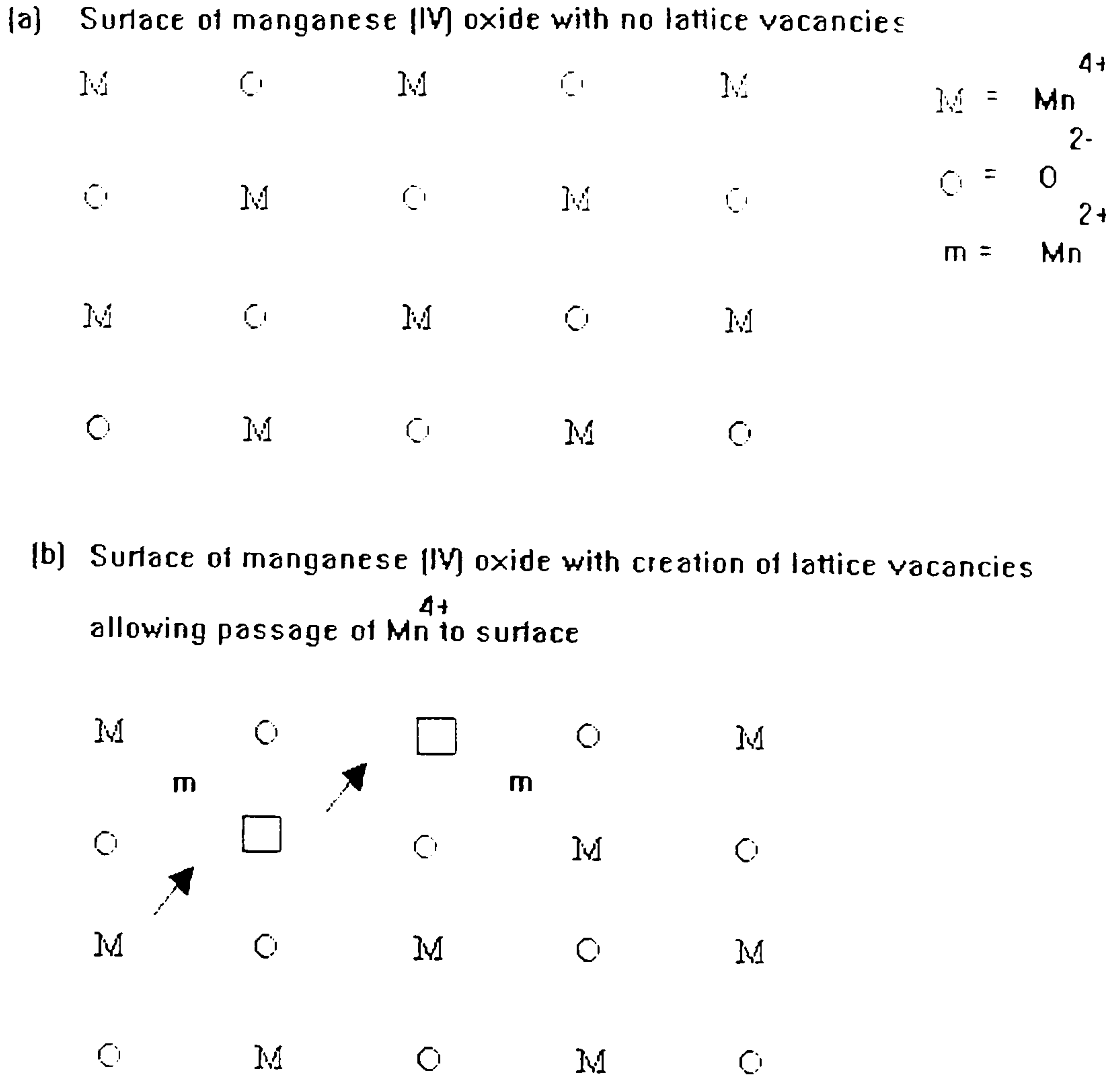
$$O^{2-} \rightarrow [O] + 2e^-$$

These reactions lead to the oxidation of the mercaptan groups of polysulfides at the solid-fluid interface. Since the curing reaction is occurring at the manganese (IV) oxide surface, the mobility of the Mn^{4+} in the lattice is important because they have to be transported to the surface to replace any Mn^{2+} ions formed. The improved properties of sodium birnessite found in this work can be rationalised in terms of the formation of vacancies in the Mn^{4+} sublattice that would aid their mobility. Because Mn^{2+} has a d^5 and Mn^{4+} a d^3 outer electronic configuration, Mn^{4+} will have a preference for an octahedral site arising from its crystal field stabilisation energy, while Mn^{2+} will have a zero octahedral site preference. The Mn^{2+} ions are therefore likely to occupy tetrahedral sites leaving vacancies in the Mn^{4+}- O^{2-} sub-lattice which will favour Mn^{4+} migration to the surface and improve the rate of the curing reaction. Consistent with this view is the situation found in the spinel lattices for Mn_3O_4 and Fe_3O_4, i.e the $Mn^{2+}\ Mn^{3+}{}_2O_4$ and $Fe^{2+}\ Fe^{3+}{}_2O_4$ lattices. Like Mn^{2+}, Fe^{3+} has a zero octahedral site preference because of its d^5 outer electronic configuration while both Mn^{3+} (d^4 configuration) and Fe^{2+} (d^6 configuration) have a preference for an octahedral site. This results in the crystal lattice $Fe^{3+}{}_{TET}$, $Fe^{2+}{}_{OCT}\,Fe^{3+}{}_{OCT}\,O_4$ in which half of the Fe^{3+} (zero octahedral site preference) is replaced by Fe^{2+} and moves into the tetrahedral site. For Mn_3O_4, the Mn^{3+} must occupy the octahedral site leaving Mn^{2+} in the tetrahedral site i.e.$Mn^{2+}{}_{TET}$, $Mn^{3+}{}_{OCT}\,Mn^{3+}{}_{OCT}\,O_4$. In all lattices containing Mn ions in different oxidation states, Mn^{2+} is likely to be forced into the tetrahedral sites by the presence of any other Mn ions including the Mn^{4+} ion in sodium birnessite. This mechanism will produce vacancies in octahedral Mn^{4+} sites that will aid the mobility of this ion.

In the rutile structure all the manganese is present as Mn^{4+} and will occupy octahedral sites but, if the Mn^{4+} is reduced to Mn^{2+} which can move to tetrahedral sites, transport of Mn^{4+} to the surface through the vacancies will be improved. Vacancies in the Mn^{4+} sublattice can also be increased by the deliberate production of mixed oxidation state materials such as sodium birnessite which consist of a close packed oxide lattice containing both Mn^{2+} and Mn^{4+} which should improve the properties of the material as a catalyst.

The good performance of sodium birnessite as a curing agent for polysulfides is rationalised in terms of the presence of Mn^{2+} in the lattice creating vacancies in the Mn^{4+} sublattice which in turn increases the mobility of Mn^{4+} ions and their transport to the surface of the solid to oxidise the polysulfide. Figure 10.2.

Figure 10.2 Lattice vacancies permitting passage of Mn^{4-}



Sodium birnessite however needs to be used at *5 pph* not 4 pph, *with* an inert diluent (preferably manganese dioxide) and *with* an accelerator. This produces a cured polysulfide with properties that are at least comparable with polysulfide cured using the best commercial curing agent. Dilution of the very active sodium birnessite phase from 10 pph to 4 or 5 pph is necessary to slow down the reaction. The preferred choice of accelerator in the usage stage, on the grounds of reduced toxicity and increased 7 day Shore A hardness is the DBU compound rather than the more toxic TMTD.

Overall conclusions

The results of this work have shown that both calcium carbonate and manganese dioxide diluted sodium birnessite are effective curing agent mixes for polysulfides on a number of different parameters of measurement. The research has shown that sodium birnessite can be used at 5 pph (half) the concentration of the best commercial curing agent, with little effect on the thermal stability, glass transition temperature, tensile strength, surface tackiness, build up to 7 day Shore A hardness, and moisture vapour transmission rate.

The properties of polysulfide sealant cured with sodium birnessite diluted with manganese dioxide ore, when compared with the corresponding data for a commercial agent, show that the sodium birnessite formulation gives a more rapid cure, and leads to similar properties for the cured material, except that it has a higher tensile strength and lower elongation at break.

The ability to use less curing agent may offer both environmental and economic benefits but with no observed down side in the parameters investigated in this research. Reduction of the curing agent to 5 pph sodium birnessite seems to cause no detriment in the curing of polysulfide compared to using twice the amount (10 pph) of the best commercial curing agent. It would seem environmentally beneficial to reduce further the birnessite level to 4 pph. However, this reduces the quality of the polysulfide in terms of stress-strain properties, hardness build up, time to reach gel point and the surface tackiness.

There exists a need to reduce the amount of manganese dioxide in other applications of cured polysulfides. These include in aeroplanes, for example on a Boeing 747 where about 1 tonne of cured polysulfide is used, and manganese dioxide is the main curing agent. A potential environmental and economic benefit of using half the amount of curing agent is that the cured polysulfide could be formulated to weigh less.

Overall, this research shows that sodium birnessite can be used at half the concentration of the best current commercial curing agent, producing a sealant that has properties that are comparable, and with less material usage. The curing also occurs without failures which means a reduction in the amount of wasted materials. This represents environmental and economic benefits through reduced material use. The results obtained are also commercially and environmentally relevant as the market for insulated glass (IG) units is expected to increase with increased energy efficiency drives.

10.2 RECOMMENDATIONS FOR FURTHER WORK

It would be useful to assess the time to gel points using a variety of temperatures to assess the effect on the rate of cure of polysulfide using sodium birnessite. A number of other areas for further research work include investigating the bioresistance of the cured polysulfide. Studies of the UV resistance and adhesion of sodium birnessite polysulfides need to be performed to ensure stability when used outside. A life cycle assessment comparing the total material use in making the commercial curing agent compared to the sodium birnessite would be useful too.

The leachability of manganese from the sodium birnessite cured polysulfide would be a factor to investigate as it can cause staining when leached out. The identification of other accelerators for the curing reaction which may improve further the sodium birnessite cure could be studied. The solvent resistance of cured polysulfide is important, and would be an area for further study on the sodium birnessite cured polysulfide.

The effect of the use of fillers in the sodium birnessite cured polysulfide system needs to be investigated too, and possibly the study of retardant chemicals to slow down the birnessite curing reaction to enable the identification of the quantities of birnessite needed to prepare optimal application times suited to its use whether for IG units or other polysulfide applications. Testing of other types of polysulfide polymers with sodium birnessite would also be of use for other applications of polysulfide sealants.

Further work needs to be performed on the mechanism of the curing of polysulfides using sodium birnessite, identifying the end product manganese oxide phase produced in the curing reaction.

Further testing on the properties of cured polysulfides, such as comparing the effects of using the DBU accelerator with that of using the TMTD accelerator in the moisture vapour transmission rate (MVTR) experiments for example could be performed. Also, the effect on the MVTR of using fillers, in the sodium birnessite curing mixture and the effects of weathering on the MVTR of sodium birnessite cured polysulfide would also be a further area to study.

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Curing of a Polysulfide Sealant with Sodium Birnessite

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ABSTRACT: Sodium birnessite ($Na_2Mn_2^{II}Mn_5^{IV}O_{13} \cdot H_2O$), a layered manganese(IV) oxide–based phase, gives a liquid polysulfide cure that is too rapid for normal application when added at 10 pph polysulfide. The curing behavior of sodium birnessite added as 5 pph, 4 pph, and as a 5 : 5 pph mixture with an inert natural manganese dioxide was compared with that of a readily available manganese-based commercial curing agent. The rate of cure at 5 and 4 pph was slower than the commercial agent at 10 pph and led to products with lower tensile strength. The cure with the 5 : 5 pph mixture gave a more rapid reproducible cure than that of the commercial agent, making a product with a higher tensile strength and lower elongation, which indicates better curing and higher crosslinking. The improved performance of sodium birnessite as a curing agent is consistent with the presence of Mn^{2+} in the lattice, creating vacancies in the Mn^{4+}—O^{2-} lattice and increasing the mobility of Mn^{4+} and its transport to the surface of the solid to oxidize the polysulfide. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 000–000, 2000

Key words: polysulfide polymer; manganese dioxide; sodium birnessite; elastomeric sealant

INTRODUCTION

Polysulfides are used in a range of applications. They adhere to glass, steel, wood, and concrete, resist solvents and chemicals,[1] and are noted for their flexibility and ability to withstand stress and strain. As water-resistant sealants they are used in the construction industry, and cured liquid polysulfides dominate the glass-sealant industry, where they account for 80% of secondary and outer seals in insulating-glass edge sealing.

Liquid polysulfide curing is generally carried out in combination with other additives such as plasticizers, fillers, accelerators, and retardants.[1] A variety of agents can be used to polymerize polysulfides including inorganic curing agents such as metal oxides, organic curing agents such as cymene hydroperoxide, and gases such as oxygen.[2] Manganese dioxide phases are widely used as curing agents via the oxidation reaction shown in eq. (1):

$$2R—SH + MnO_2 \rightarrow R—S—S—R + H_2O + MnO$$

Environmental concerns have made manganese dioxide favored over more toxic curing agents. However, not all manganese dioxide phases are effective curing agents, and some can lead to curing failure and material waste. Naturally occurring manganese dioxide is not effective at curing liquid polysulfide, and commercially available manganese-based curing agents are usually pretreated, for example, under high pressure and alkaline conditions.

The curing of liquid polysulfide results in extension of the prepolymer chains. Eventually the

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final Shore A hardness is reached. In insulated glass applications, a Shore A hardness of about 30 is required.[2] Another important property in polysulfide curing is the time needed to reach the gel point, which ensures that the time between applications to a substrate is long enough (between 1 and 4 h) to ensure a good work life of the application but not so long that it remains soft and tacky once the job has been finished.

Using EPR and NMR spectroscopy, Coates et al.[3] studied the mechanism of polysulfide curing with manganese dioxide and suggested that the reaction involves thiol oxidation to the appropriate thiol radical, which dimerizes to make a disulfide:

$$RSH \xrightarrow{MnO_2} RS \quad 2RS \rightarrow RSSR$$

We compared the behavior of a synthetic manganese dioxide phase based on sodium birnessite as a curing agent to that of a standard polysulfide curing agent by looking at the thermal, rheometric, and mechanical properties of the cured polysulfide.

EXPERIMENTAL

The characterization of manganese dioxide–cured polysulfide can be determined in a number of ways, for example, using thermogravimetry and pyrolysis GC[4] rheometry and dynamic mechanical analysis; tensile strength and hardness testing are other important means to study polysulfide curing.[5–6]

The manganese oxide studied in this investigation is a synthetic analogue of the mineral sodium birnessite, which is a layered manganese oxide found naturally in soils. The method of synthesis is similar to that used by Stahli.[7] A 5*M* solution of manganese sulfate in 200 mL of deionized water was added to a 5.5*M* NaOH solution in 250 mL of deionized water. Oxygen was bubbled through this solution for 4 h, resulting in a precipitate, which was separated from the supernatant and dried at room temperature. The product was identified as sodium birnessite using X-ray diffraction and by thermogravimetric analysis. A particle size fraction of the product for use in this study had a mean of 2 μm and a maximum of 14 μm. The commercial manganese dioxide curing agent used in this study also had the same particle size range and was supplied by Twinstar Chemicals Ltd. The pH of an aqueous suspension of the commercial curing agent is 9.65 in comparison with a value of 9.83 for the synthetic sodium birnessite. The analytical composition of the synthetic material (Na 6.1%, Mn 54.7%, H_2O 11.3%) suggests that it is based on the formula $Na_2Mn^{II}{}_2Mn^{IV}{}_5\,O_{13}\dot{s}4.5H_2O$, although the water percentage in the final product can vary.

The liquid polysulfide used in this study was a single batch of Morton LP32C, a polymer of 1,2,3-trichloropropane and 1,1′-[methylenebis(oxy)]-bis(2-chloroethane) reduced with sodium sulfide and having the formula $HS{-}(C_2H_4{-}O{-}CH_2{-}O{-}C_2H_4{-}Sx)_{23}{-}C_2H_4{-}O{-}CH_2{-}O{-}C_2H_4{-}SH$ with an average molecular weight of 4000 and containing 2% terminal —SH groups. At 25°C, LP32C has a viscosity of 46.5 Pa s and a specific gravity of 1.29.

Preliminary curing studies showed that the sodium birnessite as prepared led to a very rapid cure, and for the purposes of this study it was diluted 5:5 with a natural manganese pyrolusite ore, which does not act as a curing agent. A second study used 5 parts and 4 parts sodium birnessite without dilution with natural manganese pyrolusite ore.

Both the commercial and sodium birnessite–pyrolusite curing agents were held in suspension in a phthalate plasticizer, Santicizer 261 (Monsanto), to which was added an accelerator, tetramethylthiuramdisulfide (TMTD), supplied by Robinson Brothers. The cure mixture was sealed and stored for 1 week at room temperature to stabilize it. It was then added to the LP32C polysulfide resin and stirred for 10 min at a constant speed using a electric drill stirrer. To 100 parts of the LP32C was added 20.5 parts of the cure paste. The characteristics of the curing process were followed by rheometry, as well as by thermogravimetric analysis, tensile strength measurement, hardness testing, and dynamic mechanical analysis of the cured polysulfide.

The curing profile was followed using a Rheometrics ARES rheometer with 25-mm diameter parallel plates in a dynamic time sweep mode. The plate gap was 1.50 mm, the strain 5%. and the frequency 6.28 rad/s. The glass transition temperatures of the cured polysulfides were measured on molded cylindrical samples using a Rheometrics RSA II instrument in a compression–temperature step mode from −60 to 30°C.

Hardness of the cured polysulfides was measured on 7-day-old samples using a Shore A Durometer, and thermal decomposition was studied

Table 1 Formulation of Curing System of Liquid Polysulfide

Component A	(i)	(ii)	(iii)	(iv)
Parts polysulfide liquid polymer (LP32 C)	100	100	100	100
Component B				
Curing agent: Commercial agent (pph polysulfide)	10			
or sodium birnessite (pph polysulfide)	—	5	5	4
Curing agent diluent: Natural MnO_2 (pph polysulfide)	—	5	—	—
Accelerator: TMTD (pph polysulfide)	0.5	0.5	0.5	0.5
Plasticizer: Santicizer 261 (pph polysulfide)	10	10	15	16
Total Component B	20.5	20.5	20.5	20.5

on 10-day-old samples using a Perkin Elmer TGS-2 thermogravimetric analyzer. Tensile-testing measurements were performed using an Instron 4109 instrument at a strain rate of 50 mm/min on dumbbell-shaped samples cut from a sheet of 1-week-old cured polysulfide.

The sealant formulations for studies using the commercial curing agent, undiluted sodium birnessite at 5 pph and at 4 pph, and diluted sodium birnessite are listed inTable 1 as (i), (ii), (iii), and (iv), respectively. Fillers, retardants, and adhesion agents that are present in commercial cure pastes have been excluded from the sealant formulation to minimize the variables that affect the curing of the liquid polysulfide.

RESULTS AND DISCUSSION

Curing Profile up to Gel Point

The gel points of the curing polysulfide systems, measured rheometrically at 25°C, were obtained from the intersections of the storage modulus G' and the loss modulus G'' curves (Fig. 1). The results show that the sodium birnessite curing agent at 5 parts, even diluted with 5 parts of natural manganese dioxide ore, gives a cure that is almost twice as rapid as that for the undiluted commercial agent and that the moduli G' and G'' for the sodium birnessite reaction are greater than those for the commercial agent curing pro-

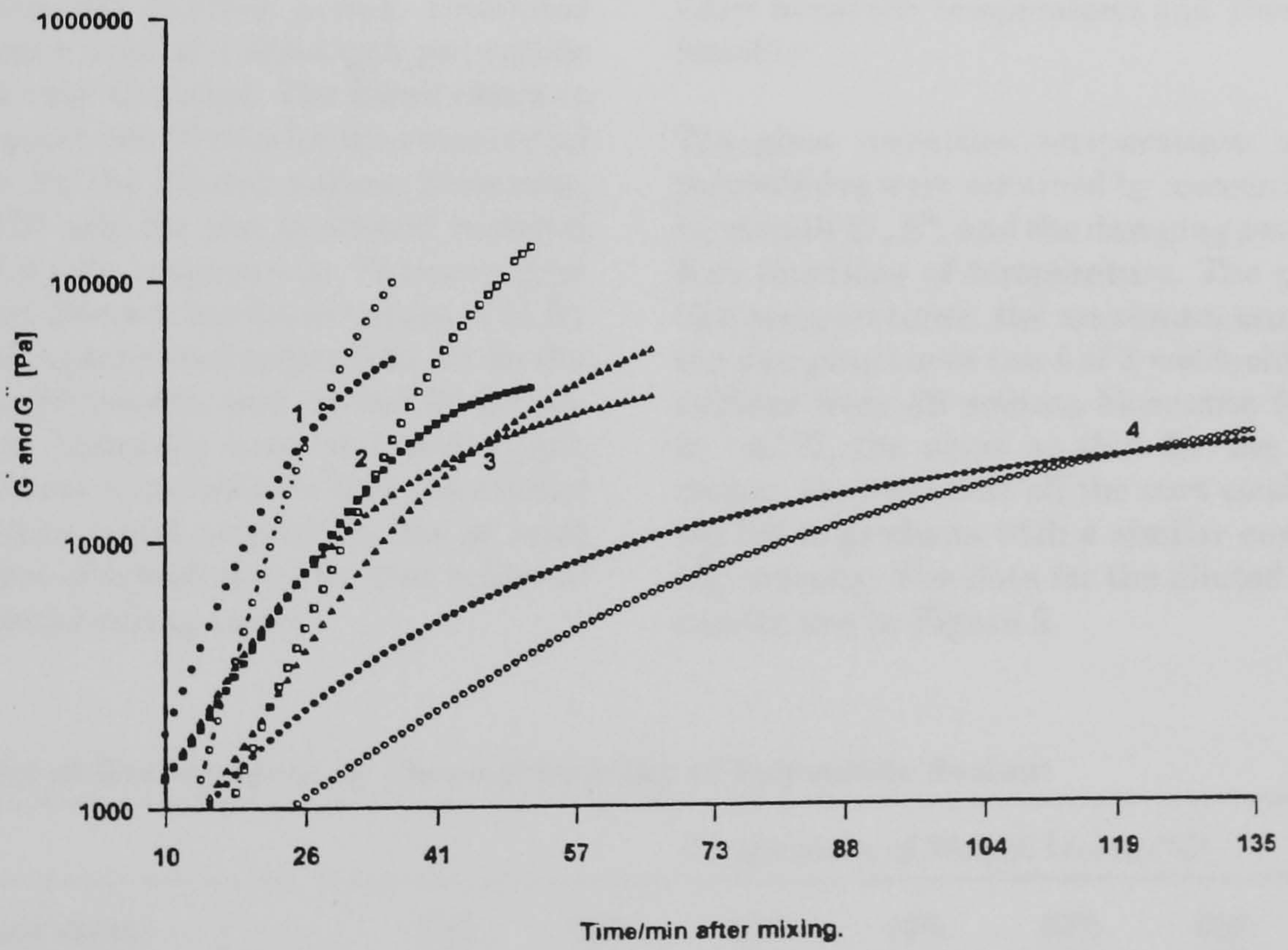

Figure 1 Comparison of the progression to the gel point of storage modulus G' and the loss modulus G' of the diluted and undiluted sodium birnessite and the commercial agent curing of polysulfide at 25°C.

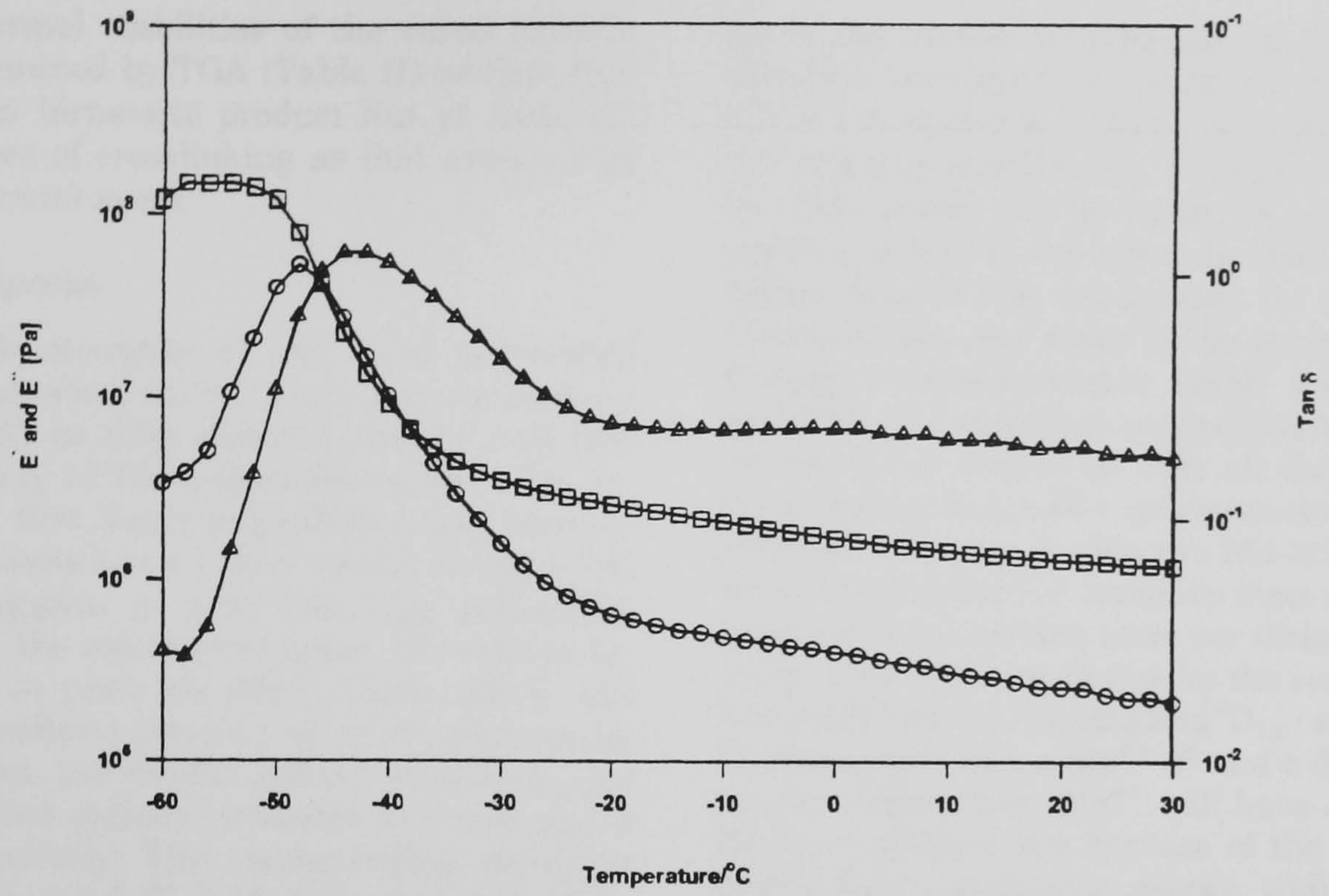

Figure 2 Dynamic mechanical properties of polysulfide sealant cured with 5 parts sodium birnessite diluted with 5 parts natural manganese dioxide ore.

cess throughout the reaction period. Undiluted sodium birnessite used at 5 and 4 pph polysulfide gives a slower rate of curing. The times taken to reach the gel point are 45 min for the commercial agent, 34 min for the diluted sodium birnessite, and 51 and 126 min for the undiluted material used at 5 and 4 pph, respectively. The cures give measured 7-day Shore A hardness values of 31 for the commercial agent cured polysulfide, 31 for the diluted sodium birnessite, and 30 and 25 for undiluted sodium birnessite used at 5 and 4 pph, respectively. These data indicate that the diluted sodium birnessite cured polysulfide has at least the same degree of crosslinking as that achieved by the commercial curing agent.

Glass transition Temperatures and Thermal Stability

The glass transition temperatures of the cured polysulfides were obtained by measuring the elastic moduli E', E'', and the damping parameter, tan δ as functions of temperature. The glass transition temperatures, the maximum temperature in the damping curve tan δ of 3-week-old cured polysulfides from all sodium birnessite formulations is −42°C, the same as that for the commercial curing, showing that all the cure conditions studied led to products with a similar energy-absorbing capacity. The data for the diluted sodium birnessite are in Figure 2. F2

Table II Effect of Curing Agent on Thermal Stability of Polysulfide Sealant

	Temperature of Weight Losses (°C)						
Polysulfide curing agent:	10%	20%	30%	40%	50%	60%	T_{max} (°C)
10 parts commercial agent undiluted	263	280	290	297	302	306	307
5 parts sodium birnessite diluted with 5 parts manganese dioxide	265	282	293	300	305	309	308
5 parts undiluted sodium birnessite	258	280	292	300	305	309	309
4 parts undiluted sodium birnessite	257	281	292	298	302	307	307

Sponsorship for A.D. Houlson is from the EPSRC and Twinstar Chemicals.

The thermal stabilities of the cured polysulfides determined by TGA (Table II) confirm that the sodium birnessite product has at least the same degree of crosslinking as that achieved by the commercial agent

T2

Tensile Properties

The tensile strengths of the cured polysulfide polymers obtained in this study are low because they contain no filler material and the crosslink density using LP32C polysulfide is low.[5] The results show that liquid polysulfide cured with sodium birnessite has a higher tensile strength but lower elongation at peak than the polysulfide cured with the commercial agent. The values for the strain at peak are 326%, 234%, 220%, and 275% for products obtained using the commercial curing agent, the diluted sodium birnessite, and the undiluted sodium birnessite at 5 pph and 4 pph, respectively. The corresponding stress at peak values are 0.42, 0.58, 0.24, and 0.15 MPa, respectively.

CONCLUSIONS

The properties of polysulfide sealant cured with sodium birnessite diluted with manganese dioxide ore, show, when compared with the corresponding data for a commercial agent, that the sodium birnessite formulation gives a more rapid cure and leads to similar properties for the cured material, except that it has a higher tensile strength and lower elongation at break. The speed of the cure with sodium birnessite provides an opportunity to reduce active material consumption by diluting the active agent with inert manganese dioxide or any other suitable inert diluent. This possibly means economic and environmental savings can occur in the usage stage of the polysulfide sodium birnessite life cycle if sodium birnessite is used instead of the commercial agent as a polysulfide curing agent.

All manganese-containing curing agents are based on manganese(IV) oxide, but not all manganese dioxide phases are effective curing catalysts. The results of a study of more than 20 manganese(IV) oxide materials[6] showed that curing activity ranged from zero for pure stoichiometric MnO_2, which has the rutile structure, to rapidly curing phases that contain other components such as alkali metals or water. It seems likely that the activity of the catalyst depends on the mobility of Mn^{4+} in the lattice,[9] which allows easy migration of this ion to the surface to take part in the oxidation-reduction reactions involved in the curing that result in the oxidation of thiol groups and the formation of manganese(II) oxide. Mobility of the Mn^{4+} in an oxide lattice can be increased by deliberately creating defects in the lattice by changing the oxidation state of the manganese, by incorporating hydroxide ions and water in the structure, and by forming nonstoichiometric alkali metal manganates(IV). The analytical composition of sodium birnessite is not consistent with all the manganese being present in the IV+ oxidation state. The composition is consistent with two Mn atoms in every seven being in the II+ oxidation state and with the presence of one sodium atom per three manganese atoms. The best formulation for the sodium birnessite would thus be $Na_2Mn_2^{II}Mn_5^{IV}O_{13} \cdot xH_2O$ ($x = 4$–5). Since Mn^{2+} has a Mn^{4+} d^5 and a d^3 outer electronic configuration, Mn^{4+} will have a preference for an octahedral site because of the value of its crystal field stabilization energy, while Mn^{2+} will have a zero octahedral site preference. The Mn^{2+} ions are therefore likely to occupy tetrahedral sites, leaving vacancies in the Mn^{4+}—O^{2-} sublattice, which will favor Mn^{4+} migration to the surface and improve the rate of the curing reaction. The presence of sodium ions in the material is easily exchangeable, and this may also benefit the maintenance of ideal pH levels during the cure. The results of this work are therefore consistent with the idea that the presence of mobile Mn^{4+} in the Mn^{4+}—O^{2-} lattice is required in order to achieve optimum polysulfide curing.

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PAPER ACCEPTED FOR PUBLICATION IN THE JOURNAL OF MATERIALS LETTERS

Sodium birnessite curing of liquid polysulfide polymers.

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Sodium birnessite is a naturally-occurring manganese (IV) oxide phase that can also be synthesised to give a material that is an effective curing agent for liquid polysulfide polymers. Liquid polysulfides are cured by the oxidation of mercaptan sulfur atoms to give cross-linking disulfides using agents such as manganese dioxide [1 - 3] We have previously shown that sodium birnessite cures polysulfide both rapidly, and reproducibly and that it can be used at lower quantities [1] We now confirm these effects by studies on Shore A hardness build-up and moisture vapour transmission rate, that sodium birnessite can be used in lower quantities than the best commercial curing agents. The mechanism of the sodium birnessite cure is also discussed.

The build-up of Shore A hardness is an important property in polysulfide curing, as the time taken for the polysulfide to reach full cure in insulating glass (IG) applications for example determines how long the IG unit has to be stored before it reaches the minimum recommended Shore A hardness of 30. There is an economic incentive for the build-up of this Shore A hardness to be quick to reduce storage prior to use time. The cured polysulfide hardness was measured using a Shore A analogue indentor Durometer for four liquid polysulfide (LP32C) curing formulations, expressed as parts per hundred (pph) of polysulfide resin, viz 4 pph sodium birnessite, 5 pph sodium birnessite, and 5 pph sodium birnessite diluted with inert MnO_2 and a high performance commercial curing agent at 10 pph. All four formulations contained tetramethylthiuramdisulfide at 0.5 pph as accelerator and the pthalate (Santicizer 261) as plasticiser. The results in Table 1 show the Shore A hardness build-up of polysulfides up to 7 days. Polysulfide cured with sodium birnessite at

5 pph alone and diluted with 5 pph inert manganese dioxide reaches the recommended minimum Shore A hardness of 30 after 7 days comparable to that of the polysulfide cured with the commercial curing agent at 10 pph.

Table 1. Shore A hardness build up in polysulfide cures

	Shore A hardness				
Curing agent	pph	at 4 h	at 24 h	at 48 h	at 7 days
Sodium birnessite	4	3	17	23	24
sodium, birnessite	5	24	25	29	31
sodium birnessite + 5pph inert MnO_2	5	32	32	31	32
Commercial curing agent	10	32	35	32	31

Since water ingress through the polysulfide will shorten the life of an IG unit, low values of Moisture Vapour Transmission Rates (MVTR) are desirable. MVTR data have been obtained for polysulfides cured with 5 pph sodium birnessite (diluted with 5 pph inert manganese dioxide) for comparison with 10 pph of the commercial curing agent data. Circular samples (63mm radius) of room temperature-cured polysulfide were stored in a desiccator over silica gel at ambient temperatures (21 $^{+}/_{-}$ 2°C) and the MVTR determined from weight loss data measured at weekly intervals over a seven week period. The values obtained 13 and 11 g m^{-2} d^{-1} for material cured with diluted sodium birnessite and the commercial agent respectively, are both within the acceptable range.

These data, along with other data on gel point and viscosity data [1] show that sodium birnessite is an effective curing agent for polysulfide at lower active material loadings than can be achieved with a commercial curing agent. Fourier transform infrared analysis confirms the polymerisation reaction to C-S-S-C by loss of the mercaptan S-H vibration at 2560 cm^{-1}. The use of sodium birnessite at 5 pph in the absence of a diluent can give good polysulfide curing and, for example in aircraft manufacture where about 1 tonne of cured polysulfide may be used [4], considerable material savings can be achieved.

The rapidity of birnessite curing is linked to the reagent concentration not to the three most commonly described variables in polysulfide curing namely pH, water content, and particle size.

The curing reaction of the mercaptan groups in polysulfides with all Mn (IV) oxide phases, including sodium birnessite, depends upon the properties of manganese (IV) as an oxidising agent:

$$Mn^{4+} + 2\ e- \rightarrow Mn^{2+}$$

In a solid oxide phase this will result in the formation of manganese (II) oxide and the oxidation of oxide ions to supply the electrons to reduce the Mn^{4+} :

$$O^{2-} \rightarrow [O] + 2e^{-}$$

These reactions lead to the oxidation of the mercaptan groups of polysulfides at the solid-fluid interface. Since the curing reaction is occurring at the manganese (IV) oxide surface, the mobility of the Mn^{4+} in the lattice is important because they have to be transported to the surface to replace any Mn^{2+} ions formed. The improved properties of sodium birnessite found in this work can be rationalised in terms of the formation of vacancies in the Mn^{4+} sublattice that would aid their mobility. Because Mn^{2+} has a d^5 and Mn^{4+} a d^3 outer electronic configuration, Mn^{4+} will have a preference for an octahedral site arising from its crystal field stabilisation energy, while

Mn^{2+} will have a zero octahedral site preference. The Mn^{2+} ions are therefore likely to occupy tetrahedral sites leaving vacancies in the Mn^{4+}- O^{2-} sub-lattice which will favour Mn^{4+} migration to the surface and improve the rate of the curing reaction. Consistent with this view is the situation found in the spinel lattices for Mn_3O_4 and Fe_3O_4, i.e the $Mn^{2+}Mn^{3+}{}_2O_4$ and Fe^{2+} $Fe^{3+}{}_2O_4$ lattices. Like Mn^{2+}, Fe^{3+} has a zero octahedral site preference because of its d^5 outer electronic configuration while both Mn^{3+} (d^4 configuration) and Fe^{2+} (d^6 configuration) have a preference for an octahedral site. This results in the crystal lattice $Fe^{3+}{}_{TET}$, $Fe^{2+}{}_{OCT}$ $Fe^{3+}{}_{OCT}O_4$ in which half of the Fe^{3+} (zero octahedral site preference) is replaced by Fe^{2+} and moves into the tetrahedral site. For Mn_3O_4 the Mn^{3+} must occupy the octahedral site leaving Mn^{2+} in the tetrahedral site i.e.$Mn^{2+}{}_{TET}$, $Mn^{3+}{}_{OCT}$ $Mn^{3+}{}_{OCT}O_4$. In all lattices containing Mn ions in different oxidation states, Mn^{2+} is likely to be forced into the tetrahedral sites by the presence of any other Mn ions including the Mn^{4+} ion in sodium birnessite. This mechanism will produce vacancies in octahedral Mn^{4+} sites that will aid the mobility of this ion.

In the rutile structure all the manganese is present as Mn^{4+} and will occupy octahedral sites but, if the Mn^{4+} is reduced to Mn^{2+} which can move to tetrahedral sites, transport of Mn^{4+} to the surface through the vacancies will be improved. Vacancies in the Mn^{4+} sublattice can also be increased by the deliberate production of mixed oxidation state materials such as sodium birnessite which consist of a close packed oxide lattice containing both Mn^{2+} and Mn^{4+} which should improve the properties of the material as a catalyst. The presence of easily exchangeable sodium ions in sodium birnessite may also help vacancy formation.

The good performance of sodium birnessite as a curing agent for polysulfides is rationalised in terms of the presence of Mn^{2+} in the lattice creating vacancies in the Mn^{4+} sublattice which in turn increases the mobility of Mn^{4+} ions and their transport to the surface of the solid to oxidise the polysulfide.

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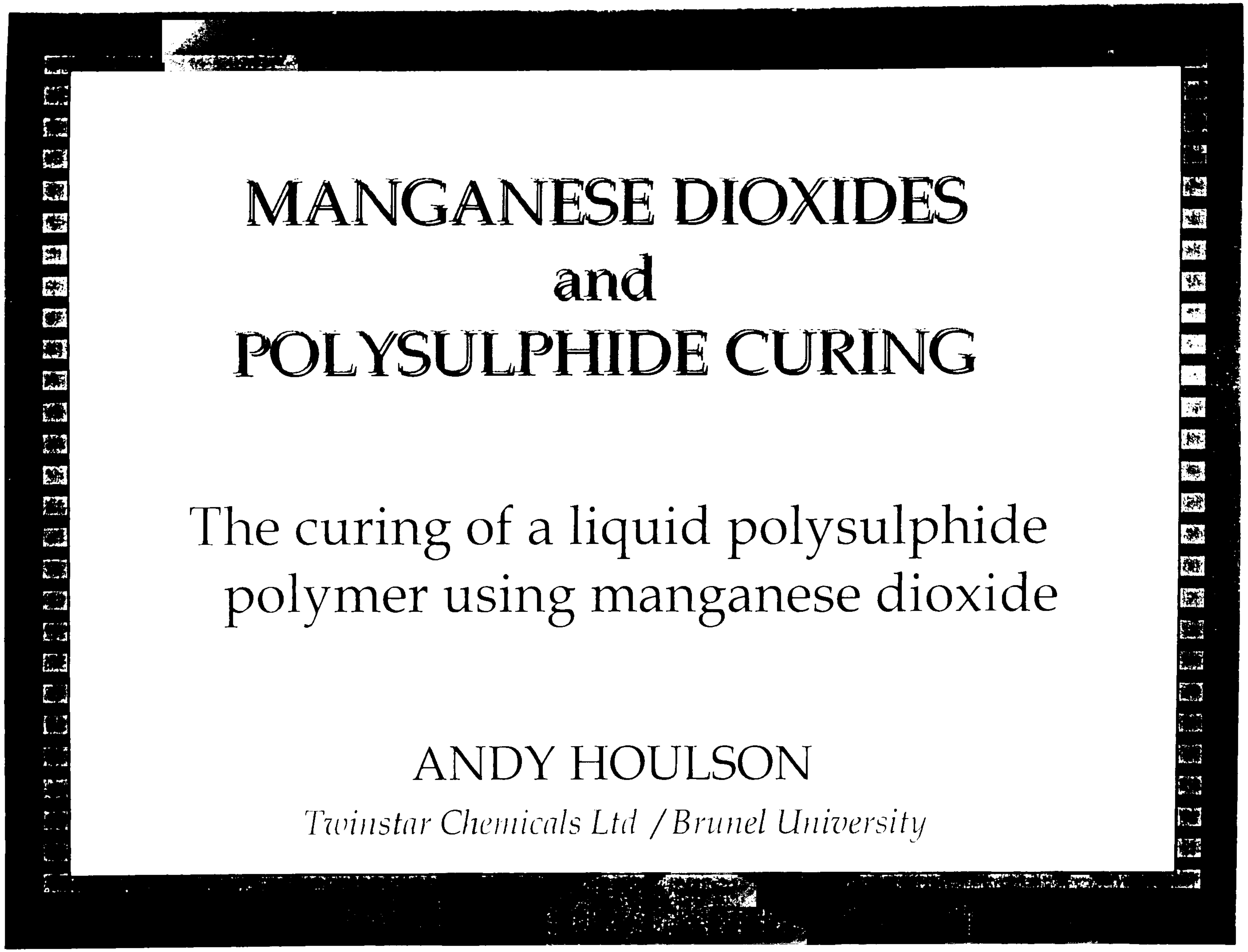


MANGANESE DIOXIDES
and
POLYSULPHIDE CURING

The curing of a liquid polysulphide polymer using manganese dioxide

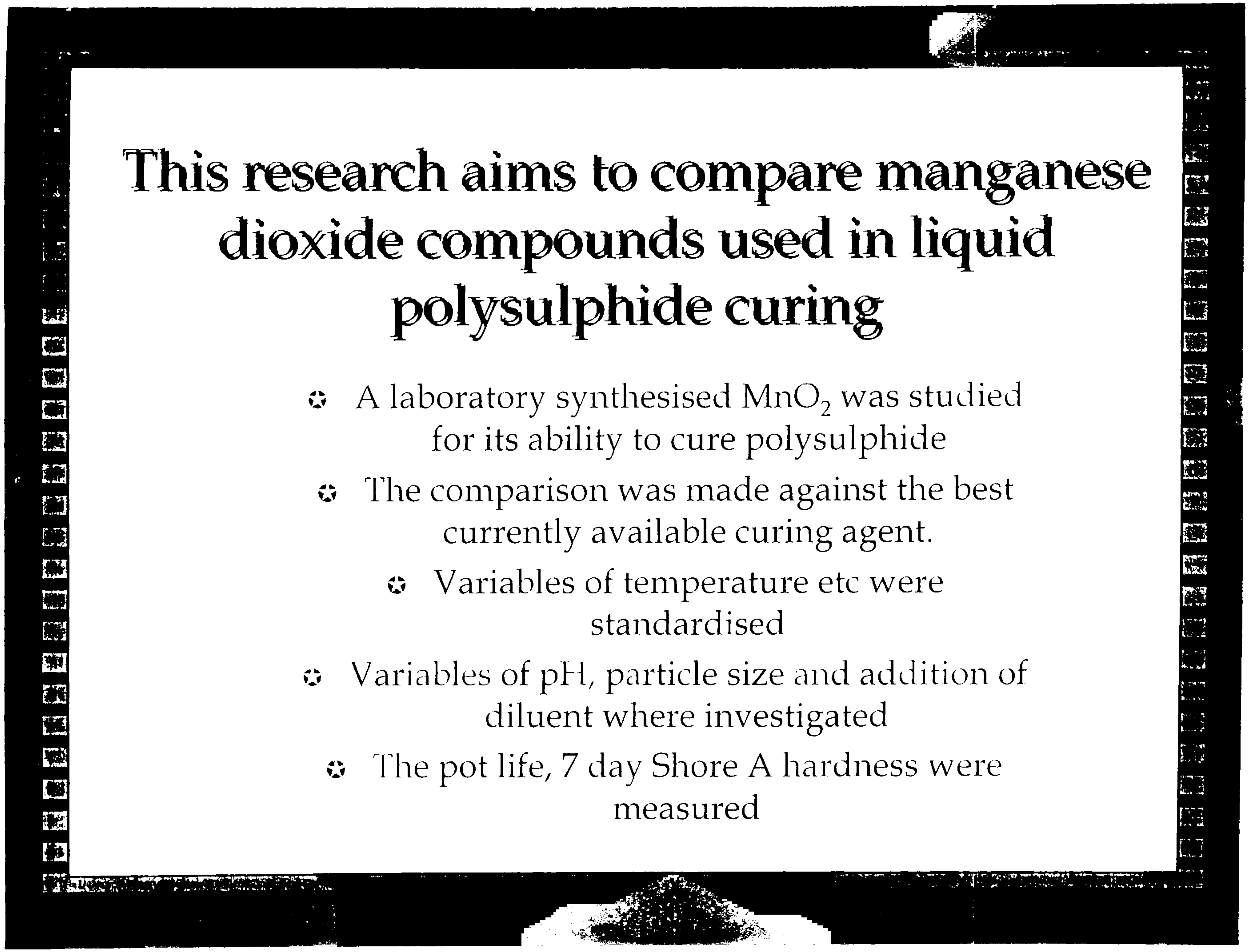
ANDY HOULSON

Twinstar Chemicals Ltd / Brunel University

Facts about Aliphatic Polysulphides

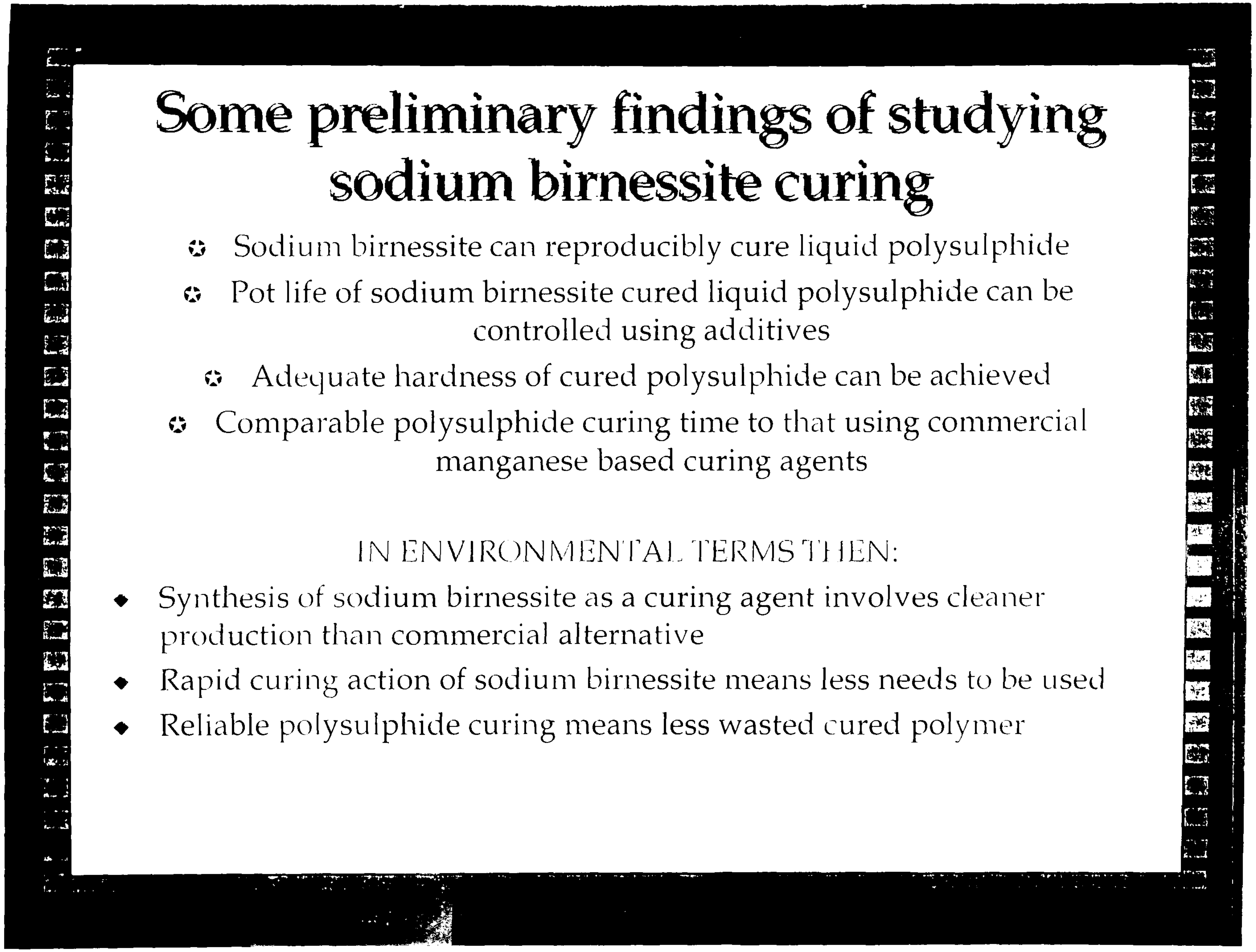
- The oldest commercial rubber in production
- Consist of carbon chains which contain terminal mercaptan groups
- 39,700 tonnes per year of aliphatic polysulphides produced worldwide
- Used in **double glazing,** 14,000 tonnes worldwide annual use and increasing
- Used in **aircraft building**, 12,700 tonnes worldwide annual use
- Used in the **construction industry**, 4,300 tonnes worldwide annual use

A cured aliphatic polysulphide:



This research aims to compare manganese dioxide compounds used in liquid polysulphide curing

- A laboratory synthesised MnO_2 was studied for its ability to cure polysulphide
- The comparison was made against the best currently available curing agent.
- Variables of temperature etc were standardised
- Variables of pH, particle size and addition of diluent where investigated
- The pot life, 7 day Shore A hardness were measured



Some preliminary findings of studying sodium birnessite curing

- Sodium birnessite can reproducibly cure liquid polysulphide
- Pot life of sodium birnessite cured liquid polysulphide can be controlled using additives
- Adequate hardness of cured polysulphide can be achieved
- Comparable polysulphide curing time to that using commercial manganese based curing agents

IN ENVIRONMENTAL TERMS THEN:

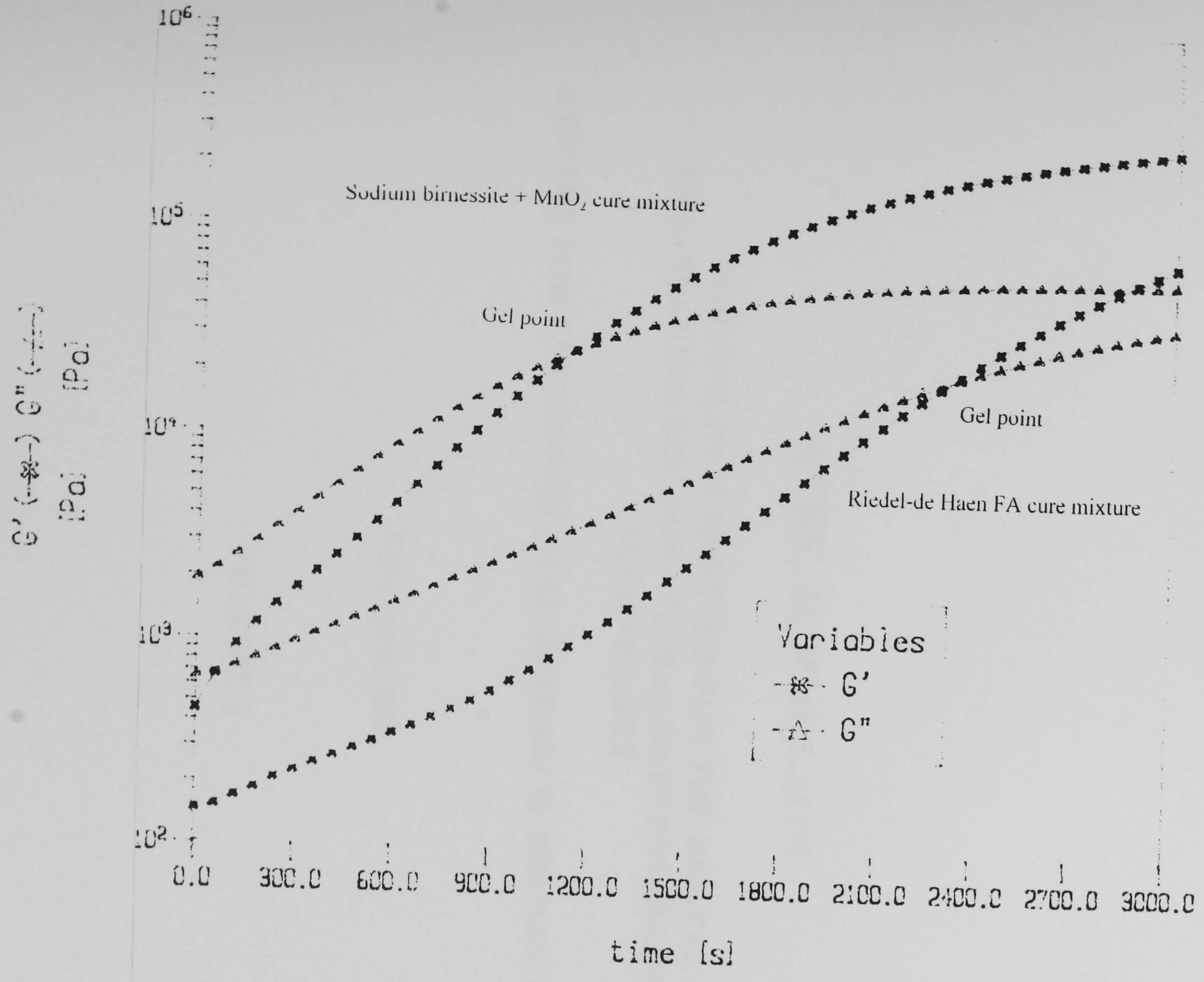
- Synthesis of sodium birnessite as a curing agent involves cleaner production than commercial alternative
- Rapid curing action of sodium birnessite means less needs to be used
- Reliable polysulphide curing means less wasted cured polymer

Investigation of curing reaction rate using dynamic testing

- Dynamic time sweep rheometric testing of the polymer curing using an ARES Rheometer at 25 ° C
    - Parallel plate setup
- Identifies the change in time of loss modulus and storage modulus, and the gel point of the reaction between manganese dioxide and liquid polysulphide

Results

- These graphs display how the two moduli G' and G'' measured during the cure reaction eventually intersect to indicate the gel point of the polymer
- Sodium birnessite curing of polysulphide over time
- Best commercial curing agent available curing of polysulphide over time


10^6
10^5
10^4
10^3
10^2
G' (-✱-) G" (-▲-)
[Pa] [Pa]
Sodium birnessite + MnO_2 cure mixture
Gel point
Gel point
Riedel-de Haen FA cure mixture
Variables
-✱- G'
-▲- G"
0.0
300.0
600.0
900.0
1200.0
1500.0
1800.0
2100.0
2400.0
2700.0
3000.0
time [s]

THE USE OF SODIUM BIRNESSITE AS A CURING AGENT FOR LIQUID POLYSULFIDE SEALANT

ANDY. D. HOULSON

PORTFOLIO SUBMITTED FOR THE DEGREE OF
ENGINEERING DOCTORATE (Eng.D.) IN ENVIRONMENTAL
TECHNOLOGY

CENTRE FOR ENVIRONMENTAL RESEARCH, BRUNEL UNIVERSITY

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VOLUME 2

VOLUME 2 SIX MONTH REPORTS

TABLE OF CONTENTS

Readers note: The six month reports are a record of progress toward the ongoing research objectives, and do not necessarily represent the final conclusions but are simply a record of progress toward deliverables. The reader is referred back to Volume 1 containing the thesis and supporting documents.

As the 6 month reports represent a chronological progression of work during the 4 year research period. the title name of each report is therefore not the same as the portfolio title: "The use of sodium birnessite as a curing agent for liquid polysulfide sealant."

AN INVESTIGATION INTO POTENTIAL USES OF MANGANESE AND STRONTIUM COMPOUNDS IN POLLUTION CONTROL

ENGINEERING DOCTORATE
SIX MONTHLY REPORT - NUMBER 1.

Andy Houlson

1st April 1996

Six monthly report

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Appendices

Andy Houlson, March 1996

Six monthly report

1. Introduction

This report covers the first six month period of research undertaken from October 1995 - March 1996. Further details of the project are given in the Appendices. The thesis to be tested is that manganese and strontium chemicals can successfully be used in pollution control applications. It is also hoped to ascertain whether they can be used in place of more toxic chemicals in various applications such as in glass manufacture.

2. Work undertaken

A literature review has been performed to assess the use of manganese dioxide and strontium compounds in removing organic substances from water. A computer database search of patents covering the use of manganese dioxide and strontium compounds in removing water pollutants has also been carried out. The literature and patenting on manganese dioxide and strontium compounds in water pollution control is very sparse, indicating a good potential for research in a wide variety of fields, both organic and inorganic.

Andy Houlson, March 1996

A sample of manganese dioxide -provided by Twinstar Chemicals- to be used in pollution control experiments has been analysed using Scanning Electron Microscopy. Experiments have also been set up to investigate the efficiency of manganese dioxide in the presence of calcium ions as an adsorber of humic acids - trihalomethane precursors - which may form possible drinking water carcinogens such as chloroform. If initial experiments prove successful, further experiments will be performed using strontium ions to aid in humic acid removal. The removal of the humic acids is detected using a Total Organic Carbon analyser.

Thermogravimetric analysis of seven samples of strontium carbonate used by Twinstar Chemicals have been carried out. The company received information from their Chinese suppliers of the carbonate that impurities may be present which cause difficulty - unwanted carbonate glass formation - in thermal processing of the strontium carbonate to strontium oxide. Investigations have shown differences between samples with some containing sulphur impurities. Testing of the gases evolved -when strontium carbonate is dissolved in hydrochloric acid- with damp lead acetate paper proved positive for all the samples. Analysis for calcium as an impurity in the strontium carbonate was also performed using Atomic Absorption Spectrometry.

An introductory course in Scanning Electron Microscopy was attended. The course over three days involved theoretical aspects of the microscope use, treatment of the samples prior to analysis, analysis of the samples and processing of the photographs. Chemistry department colloquia on aspects of organic and inorganic chemistry have also been attended.

Andy Houlson, March 1996

It is intended to investigate the preparation of glass using strontium compounds instead of barium. Further investigations into the use of manganese dioxide and strontium compounds in removing organic and inorganic compounds in water and air are also planned.

The preparation of sodium birnessite, a manganese oxide compound that is used in the production of polysulphide sealant is being investigated. Determination of experimental parameters to enable a reproducible quality of birnessite is to be performed. A consistent product would then be used for further experiments to assess its ion exchange capacity in water pollution control.

3. Conclusions

Progress has been made on the investigation of the physical properties of compounds of manganese dioxide and strontium carbonate and strontium chloride. The effectiveness of both compounds in water pollution control will be investigated. It seems the scope for further investigation of these chemicals is promising.

Andy Houlson, March 1996

TABLE OF CONTENTS FOR APPENDICES

1.4 THE USE OF STRONTIUM COMPOUNDS IN ENVIRONMENTAL IMPROVEMENT

1.5 ANALYSIS OF STRONTIUM CARBONATE SAMPLES FOR CALCIUM CONTAMINATION

1.6 A STUDY OF MANGANESE OXIDE CHEMICALS AND POLLUTION CONTROL EXPERIMENTS - ALSO INCLUDING EXPERIMENTS WITH CALCIUM AND STRONTIUM IONS.

1.1 AIMS AND OBJECTIVES OF THE PROJECT

The aim of the research is to investigate uses of manganese and strontium compounds in air and water pollution control and clean technology. Strontium for example is non toxic unlike its group II neighbour barium. Uses of strontium that could replace barium, for example in glass making would be a clean technology. The possibility of strontium being used for removing water pollutants is also an area needing investigation. Similiarly, manganese oxides act as catalysts or adsorbers and therefore their potential use in removal of water pollutants is of interest. For the sponsoring company, in the long term, a patentable technique for pollution control or clean technology could bring environmental rewards and may help secure the market of that particular chemical.

1.2 THE SPONSORING ORGANISATION-TWINSTAR CHEMICALS

The company sponsoring the research is Twinstar Chemicals of Kenton, Harrow. It is the largest marketer of manganese oxides in the country and they import and sell many other chemicals including strontium based substances. Twinstar Chemicals is part of the S & D group - Figure 1. The company structure at Twinstar Chemicals - Figure 2.

Figure 1 Twinstar Chemicals and its associated companies

(Source: Twinstar Chemicals)

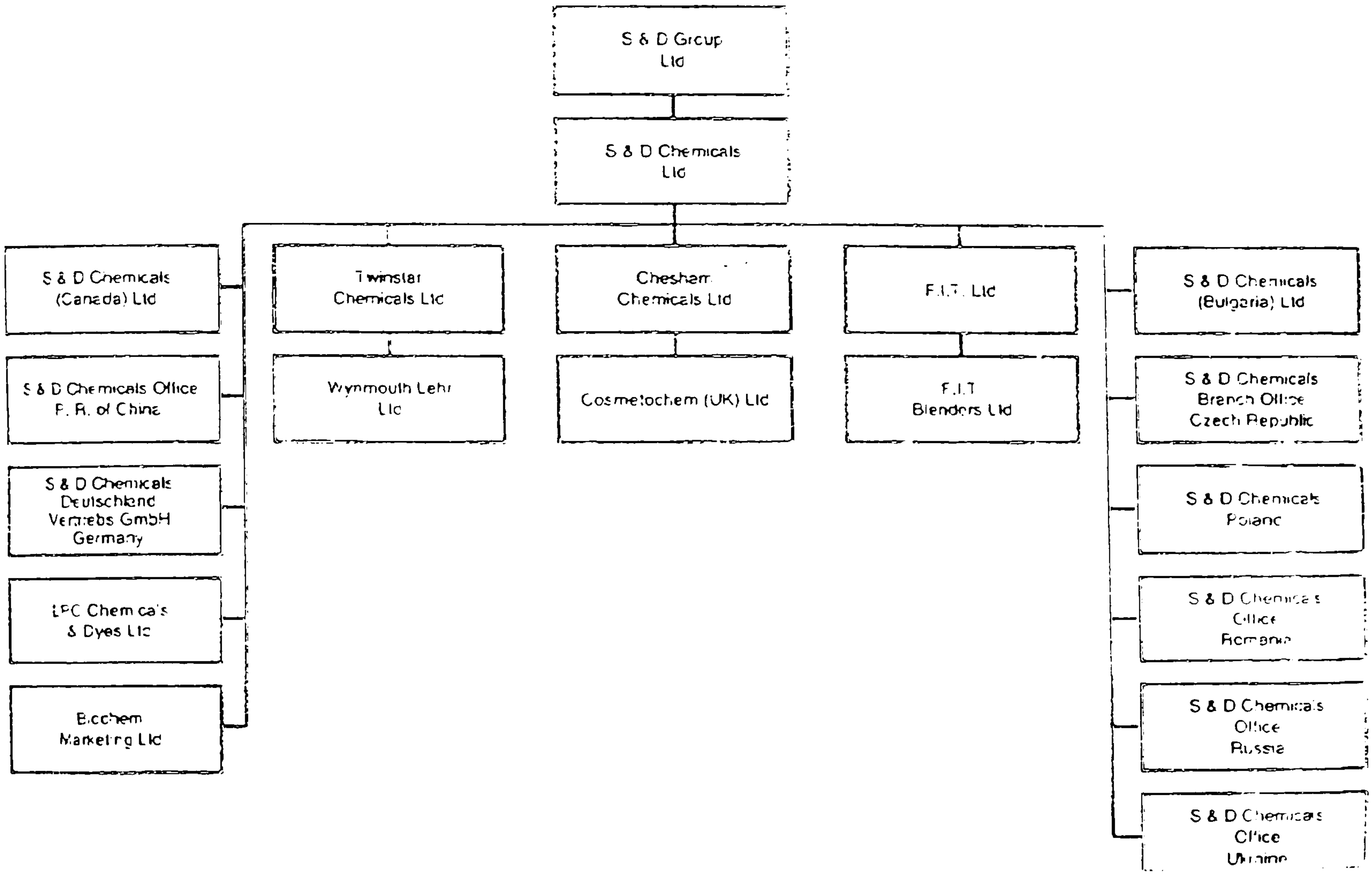
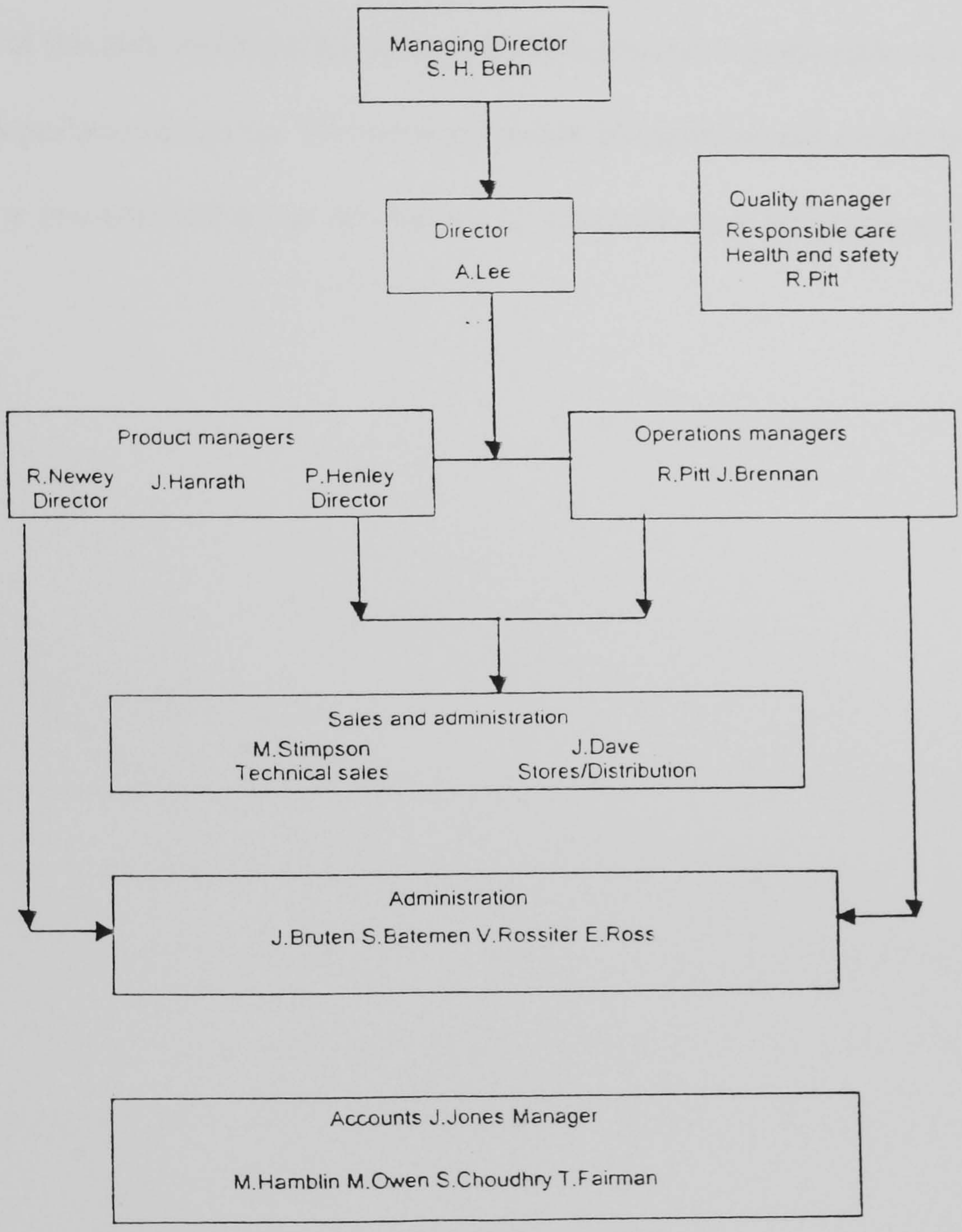


Figure 2 An organisation diagram of Twinstar Chemicals



1.3 THE LITERATURE AND PATENT SEARCH

The main method of obtaining the literature for my experiments is the online computer service 'BIDS' and for patents and for the journal search the online Chemical Abstract service. These techniques have identified suitable experiments to study water pollution control using manganese dioxide and strontium compounds. The results of both a literature and patent search will narrow down my field of research and hopefully direct research towards a marketable or patentable end result for water pollution clean up. The same procedure of literature and patent search followed by setting up a practical will occur for the use of strontium as a replacement for other toxic chemicals.

1.4 THE USE OF STRONTIUM COMPOUNDS IN ENVIRONMENTAL IMPROVEMENT

1.4.1 Introduction to strontium and its compounds

The metal strontium is in group II of the period table - the alkaline earths. (Kirk Othmer 1983) Its compounds therefore resemble the other group II compounds calcium and barium. It is present in the earths crust at 0.02-0.03% averaging 375 ppm in igneous rocks. The scale of mining of the mineral Celestite -strontium sulphate - is low; sometimes being extracted and sorted by hand. (Kirk Othmer 1983) In seawater it is present at about 14 grammes per metric ton and is the fifth most abundant metal in marine waters.(Kirk Othmer 1983)

Strontium metal is a powerful reducing agent and its reactivity is between calcium and barium. The name strontium comes from the discovery and identification of strontium carbonate in 1790 by Crawford and Cruickshank in Strontian, Argyllshire (Parkington 1961) The main two strontium chemicals marketed are strontium carbonate and strontium sulphate. Important uses of strontium compounds are in colour television tube manufacture (especially in North America where high voltage sets require screening with heavy atoms to remove X rays). Other uses include pyrotechnics, pigments, electrical materials, lubricants, and fillers in plastic and rubber. (Kirk Othmer 1983). Strontium compounds are attractive environmentally. They are non toxic and similiar to calcium salts as they are not easily absorbed across the gut. (Kirk Othmer 1983)

Strontium sulphate

Celestite $SrSO_4$ can be found in sedimentary rocks as beds or veins. The colourless, yellow or frequently light blue minerals specific gravity is about 3.97, and hardness on the Moh scale is 3.0-3.5. (Kirk Othmer 1983). Strontium sulphate is fairly insoluble in water (0.0113 g in 100 ml at 0

$^{\circ}$c)(Kirk Othmer 1983) It occurs as white colourless crystals with an index of refraction of 1.622 to 1.631 and a specific gravity of 3.96. Decomposition occurs at 1580°c (Kirk Othmer 1983)

Strontium carbonate

Strontium carbonate exists in its native form as strontianite (which is about 70 % strontium carbonate). Strontium carbonate is formed as a precipitate when a strontium salt solution is mixed with strontium chloride. It is soluble in ammonia salt solutions although not in water and reacts with acids. The carbonate dissolves in water containing carbonic acid forming strontium bicarbonate. (Parkington 1961) The carbonates melting point is 1497^{0}c and decomposition to carbon dioxide and strontium oxide occurs at 1340 ^{0}c The carbonate is a white crystalline solid of specific gravity 3.70. Below 926 ^{0}c it has a rhombic structure, and above a hexagonal structure. (Kirk Othmer 1983)

Strontium carbonates native form is as strontianite found as orthorhombic crystals.(Kirk Othmer 1983). It can be found, amongst other areas, in Schoharie county in New York USA and Westphalia in the Federal Republic of Germany. (Kirk Othmer 1983)

Strontium carbonate can be made by mixing powdered celestite (strontium sulphate) with hydrochloric acid to remove iron oxides and calcium carbonate. After mixing the sulphate with a boiling soda ash solution the carbonate is then washed and dried.(Kirk Othmer 1983). It can also be formed from mixing strontium sulphide solution with carbon dioxide - resulting in the carbonate precipitating out.

More typically celestite is crushed, ground, mixed with coke and heated to strontium sulphide

'Black ash' in kilns (Kirk Othmer 1983). Adding water, and then removing muds by counter current decantation for eventual disposal leaves an after filtration solution of 12 -13 % by weight strontium sulphide. Crystals of strontium carbonate are then formed by adding soda ash, and after filtration the carbonate is dried cooled and screened. (Kirk Othmer 1983)

Strontium carbonates main use is as an X ray barrier due to its large atomic size. At 12-14% strontium oxide it is used in the face plates in colour television screens . Other uses include its role in the glass industry in increasing the firing range of ceramic glazes and glass frits, lowering solubility in acid and reducing pin holing. (Kirk Othmer 1983) It is also used in making zinc with a low lead content in electrolysis. (Kirk Othmer 1983)

Strontium chloride

Strontium halides are used as iodide and bromide replacements in medicine and in toothpaste for sensitive teeth (Kirk Othmer 1983). They are formed by reacting strontium carbonate and acid halide. (Kirk Othmer 1983). Strontium sulphate can also be fused with sodium carbonate to form the strontium carbonate which turns into chloride on washing with water and dissolving in hydrochloric acid (Parkington 1961). Strontium chloride exists as colourless cubic crystals and is water soluble (at 100 ° C 100.8 g dissolve in 100 ml of water) (Kirk Othmer 1983). It has a melting point of 643 ° C and a specific gravity of 3.052 (Kirk Othmer 1983)

1.4.2 Thermogravimetric analysis of Chinese strontium carbonate samples

Thermal analysis involves measuring selected physical properties in samples during a controlled change in temperature. (Dodd and Tonge 1987). Thermogravimetry (TG) is used to measure weight change in a sample over a controlled change in temperature. Energy changes in the sample are measured using Differential Scanning Calorimetry (DSC) or Differential Thermal Analysis (DTA). Both DSC and DTA are used to assess whether the reaction in the sample is endothermic or exothermic, TG is used to quantify the weight loss in a sample. (Dodd and Tonge 1987). The heating rate of the instrument can be varied. The difference in weight change in a solid is quantified by Tg for reactions such as:

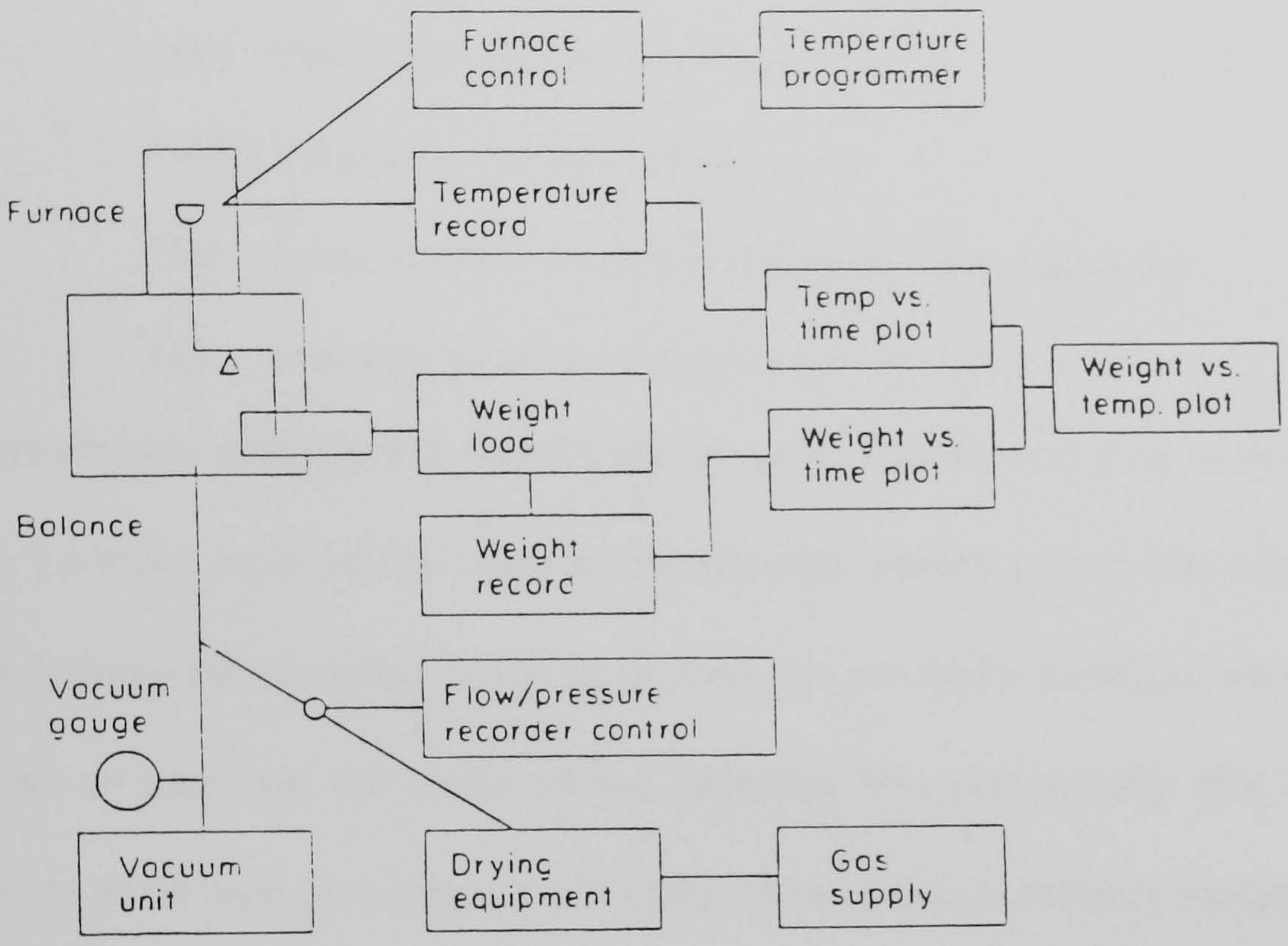
Reactant (solid) ----------------> Product (solid) + Gas.

The DTA results depend on measuring the difference in temperature between an inert reference material and the sample. Exothermic processes occurring in the sample increase the sample temperature relative to the reference, causing a rising peak to form on the printout. Endothermic, downward sloping, peaks are formed when the sample temperature falls below the reference temperature. (Dodd and Tonge 1987). Derivative Thermogravimetric (DTG) records produced by the instrument show the rate of weight loss against temperature. An increased rate of weight loss of the sample with temperature increases the gradient downwards on the graph produced. Decreasing the heating rate decreases the temperature at which the sample decomposes due to an increased time for the sample to decompose. Decreasing the heating rate also increases the resolution of the graphs formed (Dodd and Tonge 1987)

Thermogravimetric analysis is performed using a thermobalance. The instrument contains a precision balance, a temperature programmed furnace and a recorder. Small samples are used as the resolution of the TG record is highest. Large samples prevent the reaction products, if gaseous, from escaping quickly, and also increase the temperature gradient in the sample. (Dodd and Tonge 1987) Figure 3 shows the basic layout of a TG analyser:

Figure 3 The basic layout of a TG analyser

(Dodd and Tonge 1987)



Errors can occur making measurements of weight and temperature inaccurate. For sources of error in TG see table 1 .

Table 1 Sources of error in TG

(Dodd and Tonge 1987)

(*i*) buovancy effect of sample container

(*ii*) random fluctuations of balance mechanism

(*iii*) electrostatic effects on balance mechanism

(*iv*) condensation on balance suspension

(*v*) measurement of weight by balance

(*vi*) convection effects from furnace

(*vii*) turbulence effects from gas flow

(*viii*) induction effects from furnace

(*ix*) measurement of temperature by thermocouple

(*x*) reaction between sample and container

Thermogravimetric analysis was carried out on seven Chinese samples of powdered strontium carbonate. Twinstar reported that some of the samples formed a glass like substance on heating instead of forming the strontium oxide as desired- the company therefore wanted an analysis of the samples to ascertain the cause of the problem. Environmentally this is important as if strontium was to be used on a larger scale some of the natural resource would be wasted due to the glass formation.

Strontium carbonate decomposes to strontium oxide releasing carbon dioxide. During the decomposition structural changes occur - in these experiments between 915 and 936 ^{0}c. These structural changes are usually very reproducable (Dodd and Tonge 1987)

1.4.3 Method

Instrumental parameters:

Thermogravimetric analyser: Stanton Redcroft STA 780 series
Stanton Redcroft UTP
Stanton Redcroft Balance control
Stanton Redcroft DC amplifier
Nitrogen flow rate: 30 %
Sample / Reference holder: Ceramic
Chart rate: 30 cm / hour
Temperature gradient: 45 ^{0}c minute to 670 ^{0}c and then 5 ^{0}c minute to 970 ^{0}c
Maximum temperature: 970 ^{0}c

The instrument printouts show the parameters of sample weight, DTG (Derivative Thermogravimetric data, DTA and Temperature

'Pure' strontium carbonate was prepared by precipitation to provide a standard against the samples. A 100 th mole strontium carbonate (formula weight 266) solution was prepared. To 2.660 g of strontium carbonate was added 50 mls of deionised water. A 100 th mole solution of sodium carbonate (formula weight 103) was also prepared. To 1.030 g of sodium carbonate was added 50 mls of deionised water. The two solutions were mixed together, stirred, and digested over a hot water bath for 3 hours. The precipitate and the supernatant were then vacuum filtered through a number 4 glass sinter. The precipitate was washed with deionised water until no further chloride was released. Addition of a few drops of silver nitrate solution would remain clear (not turning cloudy) when chloride was absent. The precipitate was then scraped using a plastic spatula on a Whatman filter paper, and dried overnight at 120 ^{0}c.

The details of each of the sample analysis - see Table 2

1.4.4 Results

Table 2 Thermogravimetric data for Chinese strontium carbonate samples

Sample Number	Onset Temp of weight loss (^{0}C)	First DTA peak Temp (^{0}C)	Second DTA peak temp (^{0}C)	Initial Sample weight (mg)	Final Sample weight (mg)	Actual weight loss % (from graph)	Theoretical weight loss (mg)*
95/383	860	-	930	22.68	16.10	27.5	29.8
95/589	884	855	918	21.61	15.36	28.0	29.8
95/597	847	-	923	22.21	15.79	28.5	29.8
96/598	844	-	923	23.46	16.84	28.0	29.8
96/600	852	857	929	20.26	14.78	27.0	29.8
96/603	860	858	929	21.25	15.42	27.2	29.8
92/109	876	-	926	20.94	15.07	27.0	29.8
Precipitated SrCO3	852	-	929	21.64	15.21	27.5	29.8

* Calculated by

$$1 - \frac{\text{Formula weight of strontium oxide}}{\text{Formula weight of strontium carbonate}} \times 100$$

$$= 1 - \frac{103.62}{147.63} \times 100 = 29.811$$

An experiment to determine whether the first peak observed in some samples was real or an artifact was performed. Cycling the temperature of the instrument between 800 and 870 ^{0} c - spanning the first DTA peak of interest produced peaks on the DTA graph indicative of exothermic and endothermic energy changes in the sample (depending on whether the sample was heated or was cooling) It was found that the cycling through the temperature at which the phase change was seen to occur showed that the result was not an artifact.

1.4.5 Discussion

Clearly, as detailed in Table 1, ten potential sources of error can occur making the results less accurate. Replicate runs were performed, so possibly errors such as the random fluctuation of the balance mechanism - error source (iii)- may be insignificant. The gas flow was kept constant at 30 % Nitrogen flow rate, and so this error if occuring should be kept constant throughout the experiments. It is hard to quantify the degree of innacuracy in the results of the analysis due to the possible instrumental sources of error. Further experiments in the next 6 months should hopefully identify the first DTA peaks for samples 95/589, 96/600 and 96/603 as shown in the table of results.

1.5 ANALYSIS OF STRONTIUM CARBONATE SAMPLES FOR CALCIUM CONTAMINATION

Analysis of the strontium samples for calcium levels was undertaken using Atomic Absorption Spectrometry.

1.5.1 Measurement of calcium levels in samples using Atomic Absorption Spectroscopy

Flame atomic absorption spectroscopy involves nebulising and then burning an aqueous sample with fuel and oxidant in a flame. (Skoog et al, 1992) In the part of the flame which is at the highest temperature, the sample is turned into ions and atoms in the gaseous phase. At this stage, "excitation of atomic emission spectra" occurs. (Skoog et al 1992). The atoms and ions then absorb and are excited by photons of a given wavelength produced by a hollow cathode lamp. The radiation of the given wavelength which passes through the flame centre is reduced in intensity by the absorption and is then received by a monochromator and then into a radiation detector. (Skoog et al 1992)

Alloway and Ayres (1994)state "at a given wavelength the absorbance [of the incident radiation] is proportional to the number of absorbing species in the light path". On production of a calibration curve using absorbance values from standard solutions and with a known detector response, the analyte concentration is obtained.

Calibration of the AAS is required. As the calibration graph may be curved and not straight (therefore causing an underestimation of metal concentrations) two standards ideally should be used. (Skoog et al 1992). However, Skoog et al (1992) state that "under usual conditions, the relative error associated with a flame absorption analysis is of the order of 1 to 2 %".

The technique does suffer from interference effects, altering the precision of the results. The main effects are spectral interference and chemical interference. Spectral interference occurs due to scattering of incident radiation by particulates produced during atomization in the flame. This also occurs due to interference from other species in the flame absorbing at similiar wavelengths as the analyte. (Skoog et al 1992). Anions present in the sample can form compounds with the analyte causing chemical interference. As the rate of atomization is slowed down, a lower reading of metal level in the sample is produced on the AAS display. (Skoog et al 1992). Spectral interference can be decreased by changing the fuel to oxidant ratio. The intereference can also be reduced by changing the flame temperature or adding an excess of the species causing interference to the sample and standard. Increasing the temperature of the flame reduces chemical interference, as would the adding of releasing agents which react with the interfering substances. (Skoog et al 1992)

1.5.2 Method

A 0.10 g portion of strontium carbonate was dissolved in 10 mls of 2 M HCL. It was noted that samples 96/600 and 96/603 on addition of acid released a gas smelling of hydrogen sulphide. Samples 95/589 and 95/598 released a gas smelling of sulphurous tarry oil. Each of the dissolved samples where diluted to 100 mls in volumetric flasks. Samples were then analysed for calcium content using Atomic Absorption Spectroscopy. A 0.1014 g portion of pure strontium carbonate was dissolved in 2M HCL and to it was added 0.5 mls of a 1000 ppm calcium standard using stock calcium nitrate solution. The standard solution was prepared in a 100 ml volumetric flask.

Atomic Absorption parameters

Instrument: Perkin Elmer 2380 AAS +Perkin Elmer PRS-10 Printer sequencer
Flame: Acetylene/ Air
Wavelength: 422.7 nm

Slit: 0.7 nm

1.5.3 Results

Table 3 Analysis of strontium carbonate samples for calcium levels using Atomic Absorption Spectrometry

Sample	Weight(g)	Mean Calcium concentration (mg/l)	% calcium in sample
'Pure SrCO3	0.1014	5.0 (standard)	-
95/363	0.1026	1.6	0.16
95/589	0.1024	1.7	0.17
95/597	0.1022	0.8	0.08
95/598	0.1019	2.3	0.23
96/600	0.1018	2.0	0.20
96/603	0.1025	2.3	0.22
92/109	0.1026	2.033	0.19

The presence of a sulphur containing compound in the strontium samples was confirmed chemically. Mixing the carbonate powder with 2 M HCl and placing moist lead acetate paper over the mouth of the reaction vessel, all the samples (except the pure SrCO3) evolved a gas containing sulphur revealed by the paper blackening. On later discussion with Twinstar Chemicals, the source of the sulphur could be the powdered coal added to the carbonate in forming strontium oxide.

1.5.4 Discussion

Other impurities are suspected to be present, including sodium carbonate. These results are therefore not discussed at this early stage. The results may clearly also not be accurate. Volumetric errors in producing the solutions and standards, as well as operating the AAS instrument may mean the results are not accurate. As mentioned in 1.5.1, errors in the results simply in operating the AAS may be between 1-2 %.

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1.6 A STUDY OF MANGANESE OXIDE CHEMICALS AND POLLUTION CONTROL EXPERIMENTS - ALSO INCLUDING EXPERIMENTS WITH CALCIUM AND STRONTIUM IONS.

1.6.1 Introduction to manganese oxides

The oxide ores of manganese are found widely. Pyrolusite MnO_2 is the most important and is found in India, West and South Africa, South America and the soviet republic. The other oxide ores of manganese include braunite, Mn_2O_3, manganite MnO,(OH) and hausmannite Mn_3O_4 (Remy 1956). The acidity of the compounds increases with their oxidation states, MnO having a basic character (Remy 1956). Table 4 lists the various properties of manganese oxides. Thermodynamic data for various manganese oxides is shown in Table 5.

Table 4 Various properties of manganese oxides.

Collated from various tables in Kirk Othmer (1995)

			COMPOUND			
	MnO	Mn_3O_4	*a* Mn_2O_3	*B* MnO_2	Mn_2O_7	Mn_5O_8
PROPERTIES:						
Colour	green	black crystals with metallic sheen	black / brown solid	black/grey crystals	dark red oil	black solid
Melting point °C	1945	1560	871-887 dec	535	5.9	550 dec to *a* Mn_2O_3
Density g/cm ^{3}	5.37	4.84	4.89	5.026	2.396	4.85
Crystal system	cubic	tetragonal	rhombic also cubic	tetragonal	NA	monoclinic
Solubility	very soluble in water, slightly soluble in ethanol	water insoluble	water insoluble	water insoluble	very soluble in water, hygro-scopic	water insoluble

Table 5 Thermodynamic data for manganese oxide compounds at 25°C

(From Kirk Othmer 1995)

Substance[a]	Heat of formation, ΔH_f, kJ/mol[b]	Free energy of formation, ΔG_f, kJ/mol[b]	Entropy, S, J/(mol·K)[b]
MnO	−384.9	−362.8	59.8
Mn_2O_3	−956.9	−879.1	110.5
Mn_3O_4	−1386.2	−1281.1	154.0
MnO_2	−520.5	−465.7	53.1

[a] Material is crystalline unless otherwise noted.

[b] To convert J to cal, divide by 4.184; items in parentheses are estimates.

1.6.2 The various types of manganese oxides

MnO Manganese (II) oxide (manganese monoxide)

Manganese monoxide is used as a feedstuff/ fertilizer ingredient (Kirk Othmer 1995) On absorbing oxygen its oxidation state rises to Mn_2O_3

Mn_3O_4 Trimanganese tetra oxide

This is the most stable of the manganese oxides and occurs in nature as hausmannite (Kirk Othmer 1995). In a laboratory it is formed when any manganese oxide is heated in air above 940 to 1000 °C. (Kirk Othmer 1995). Heating Mn_3O_4 to over 1170 °C causes its crystal structure to change from tetragonal to cubic (Kirk Othmer 1995).

Mn_2O_3 (alpha or gamma) manganese sesquioxide/ manganese (III) oxide

This oxide loses oxygen when heated to over 940 °C in air, or 1090 °C in oxygen to form Mn (II) or (IV). (Remy 1956). Manganese sesquioxide exists in two forms - alpha or gamma. In nature, bixbyite is the alpha form Thermal decomposition of manganese dioxide at 500-800 °C in air also forms manganese (III) oxide. Heating the lab produced Mn_2O_3 to 940 °C causes it to be reduced to Mn_3O_4Gamma Mn_3O_4 is produced in the laboratory as it is unstable (Kirk Othmer 1995)

MnO_2 Manganese dioxide /manganese (IV) oxide

Manganese dioxide is an example of a semiconductor that can act as a heterogenous catalyst for oxidation. (Bond 1987). It acts as the main component of the cathode in dry batteries. (Kirk Othmer 1995)

Chemical Manganese Dioxide (CMD)

This is formed in the laboratory under oxidising conditions by decomposition at high temperature of $Mn(NO_3)_2$ or $MnCO_3$, or MnO_4^- ion reduction. CMD is also a byproduct of saccharin manufacture. (Kirk Othmer 1995). The producers of CMD are listed in Table 6.

Table 6 Chemical Manganese Dioxide (CMD) producers

(Kirk Othmer 1995)

Company	Location	Grade, type, or trade name	Capacity, t/yr	Applications
Sedema	Tertre, Belgium	Faradiser M	36,000	batteries
Chemetals Corp.	Baltimore, Md.	HP		ferrites, high purity lower oxides
The Boots Co., Ltd.[b]	Nottingham, U.K.	hydrated manganese dioxide	1,000	batteries
VEB Chemiekombinat[b]	Bitterfeld, Germany	Manganit		batteries
Perstorp Austria GmbH[b]	Vienna, Austria	Permanox		batteries
Shepherd Chemical Co.	Cincinnati, Ohio	808	300	curing of polymer sealants
Winthrop Laboratories[c]	New York, N.Y.	activated MnO_2		organic oxidations

[a] Ref. 159.

[b] CMD comes from saccharin manufacture.

[c] MnO_2 is priced at \$30/kg in 25-kg lots or larger.

Hollandite, psilomelane, cryptomelane, and coronadite are isostructural to alpha a-MnO_2. The a-MnO_2 stoichiometry is not fixed. With a-MnO_2 represented as MnOx, x is between 1.88 and 1.95 (Kirk Othmer 1995) Manganese dioxide is found native as the mineral pyrolusite known as B-MnO2 where in the formula MnOx, x is between 1.95 and 2.00. (Kirk Othmer 1995) Nsutite or Gamma-manganese dioxide is the hydrated form of the compound used for batteries. (Kirk Othmer 1995)

Ramsdellite is an example of Delta-manganese dioxide. one of a group of "amorphous essentially non crystalline hydrous manganese dioxides" including "birnessite, ranceite. takanelite. toddorokite, chalcophanite, and lithioporite" (Kirk Othmer 1995). The stoichiometry is MnOx where x is 1.7 to 2.0 (Kirk Othmer 1995). A temperature of 250 °C changes ramsdellite to pyrolusite. (Kirk Othmer 1995).The progression with temperature from B-MnO_2 to MnO is given in Figure 4.

Figure 4 Effect of temperature on B-MnO_2

(Kirk Othmer 1995)

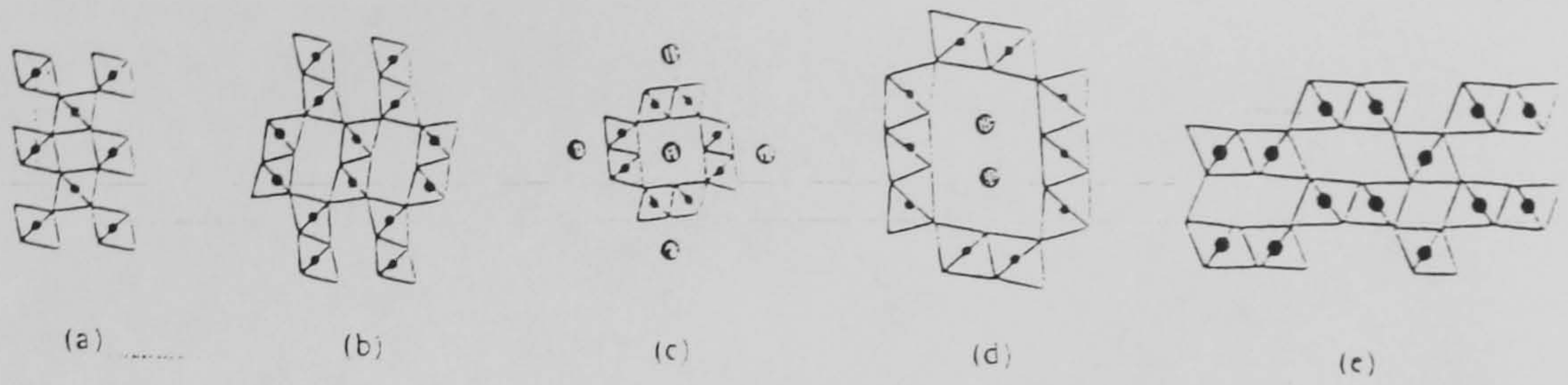
$$\beta\text{-}MnO_2 \xrightarrow{600-700^\circ C} \alpha\text{-}Mn_2O_3 \xrightarrow{900-1000^\circ C} Mn_3O_4 \xrightarrow{>1250^\circ C} MnO$$

Manganese (IV) oxide is not usually of the MnO_2 stoichiometry. It is typically MnO1.7-2.0 as the content of lower valent manganese varies. (Kirk Othmer 1995). A variety of materials approximating to MnO_2 in structure have been prepared in laboratories, and are termed polymorphs. (Wells 1990)

Two main types of structure of manganese dioxide have been found from x-ray studies:3d frameworks and layer structures (Wells 1990)

Figure 5 The framework structures of manganese dioxide:

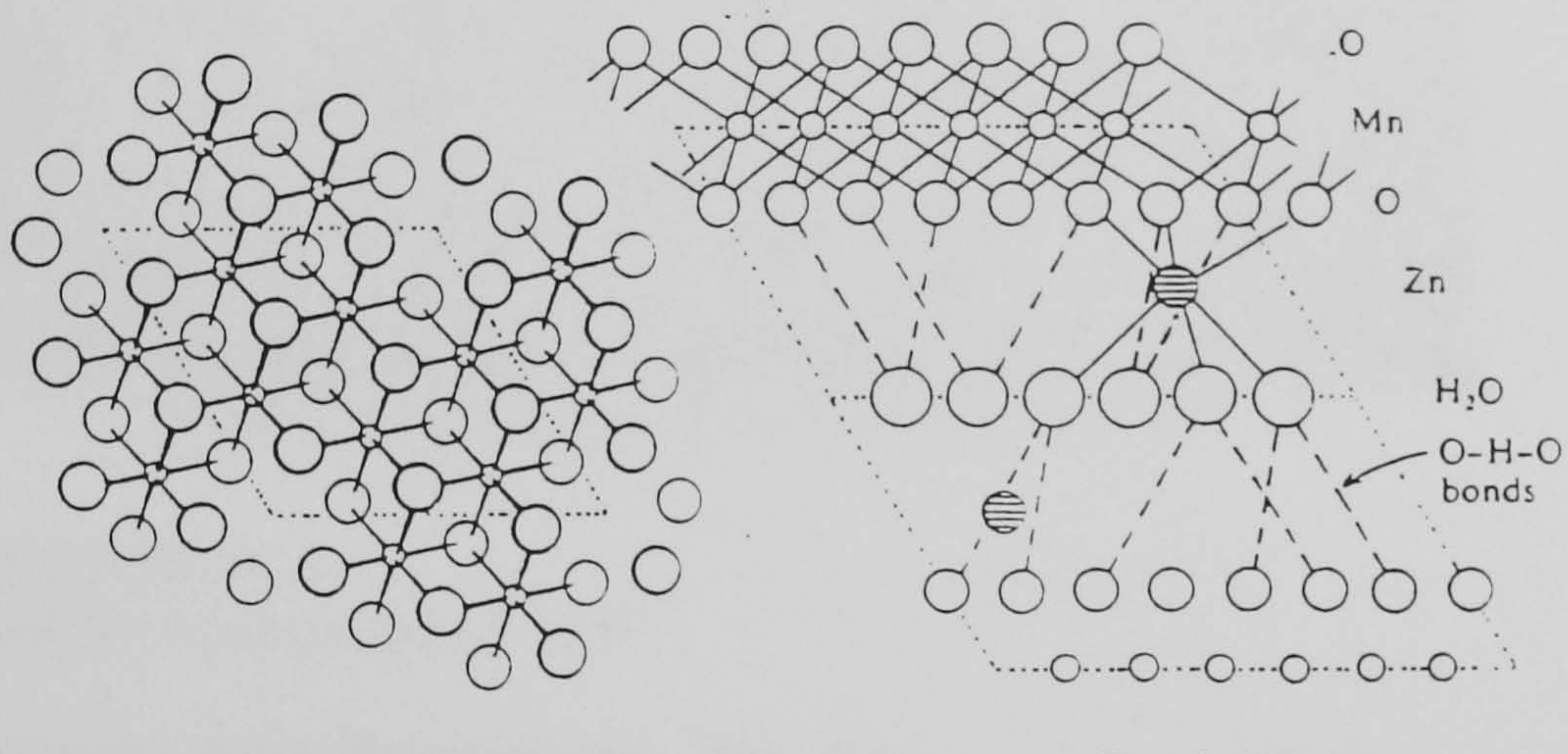
"Single or multiple octahedral chains joined along their lengths by sharing vortices. (Wells 1990)



The structures of (a) β-MnO_2; (b) ramsdellite; (c) α-MnO_2 and hollandite; (b) psilomelane; (e) a 'γ-MnO_2' intermediate between (a) and (b).

Figure 6 The layer structures of manganese dioxide

For example the crystal structure of chalcophanite $ZnMn_3O_7.3H_2O$:(Wells 1990)



Plan of one O-Mn-O layer

Elevation

Electron micrographs were taken of a sample of manganese dioxide from Twinstar Chemicals. The instrument used was a JEOL Scanning Electron Microscope (SEM). The sample of manganese dioxide was crushed mineral, hence the crystalline shaped particles.

Figure 7 Electron micrograph of crushed carbon coated manganese dioxide

Micrograph by Andy Houlson
Carbon coated sample. Magnification 150x

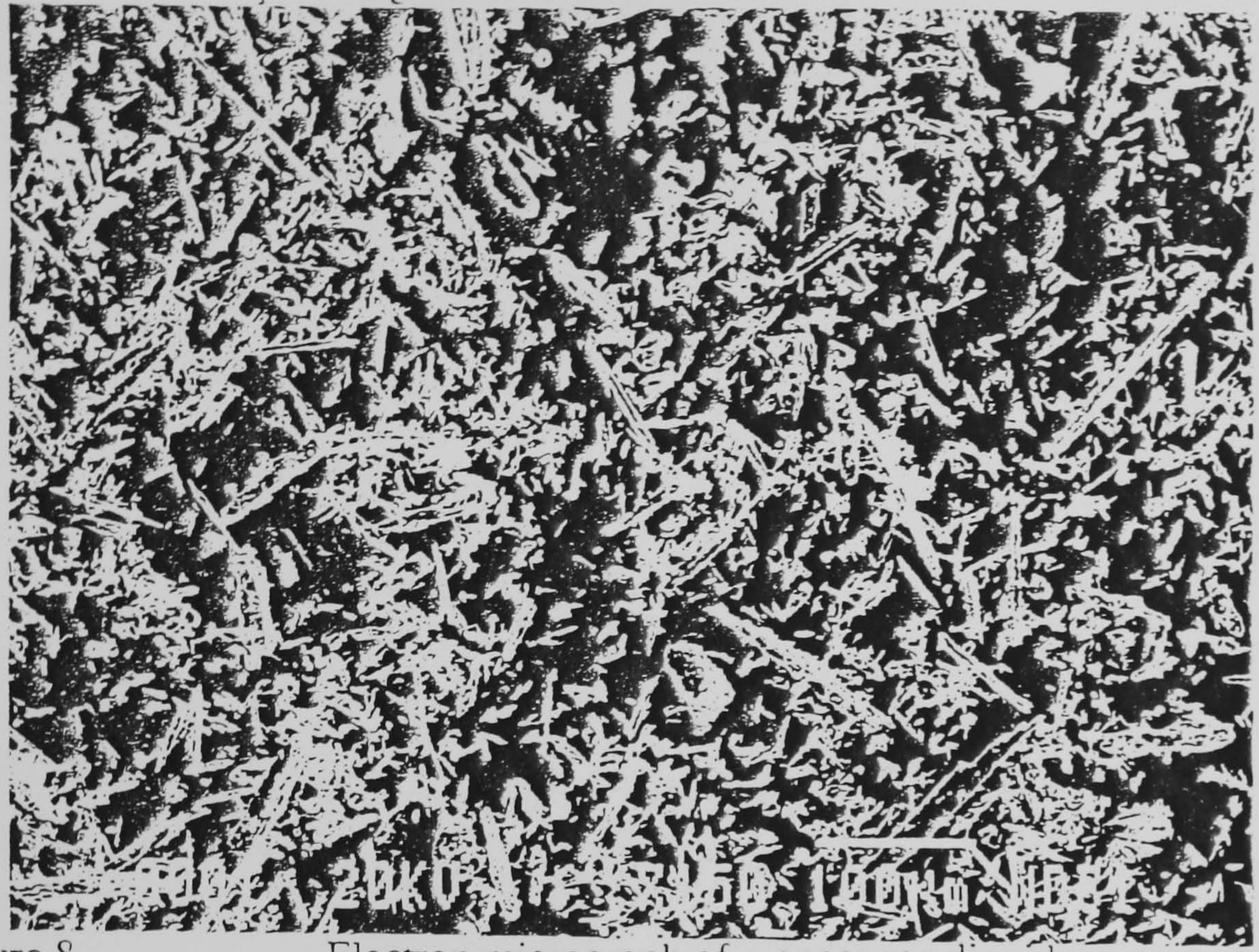


Figure 8 Electron micrograph of manganese dioxide

Micrograph by Andy Houlson
Carbon coated sample. Magnification 4000x

Mn_2O_7 Manganese heptoxide / manganese (VII) oxide

Manganese heptoxide decomposes explosively when contacted with oxidizable agents including alcohol or phosphorous. (Kirk Othmer 1995). Its structure is shown in Figure 9

Figure 9 The structure of manganese heptoxide

Mackay and Mackay (1989)

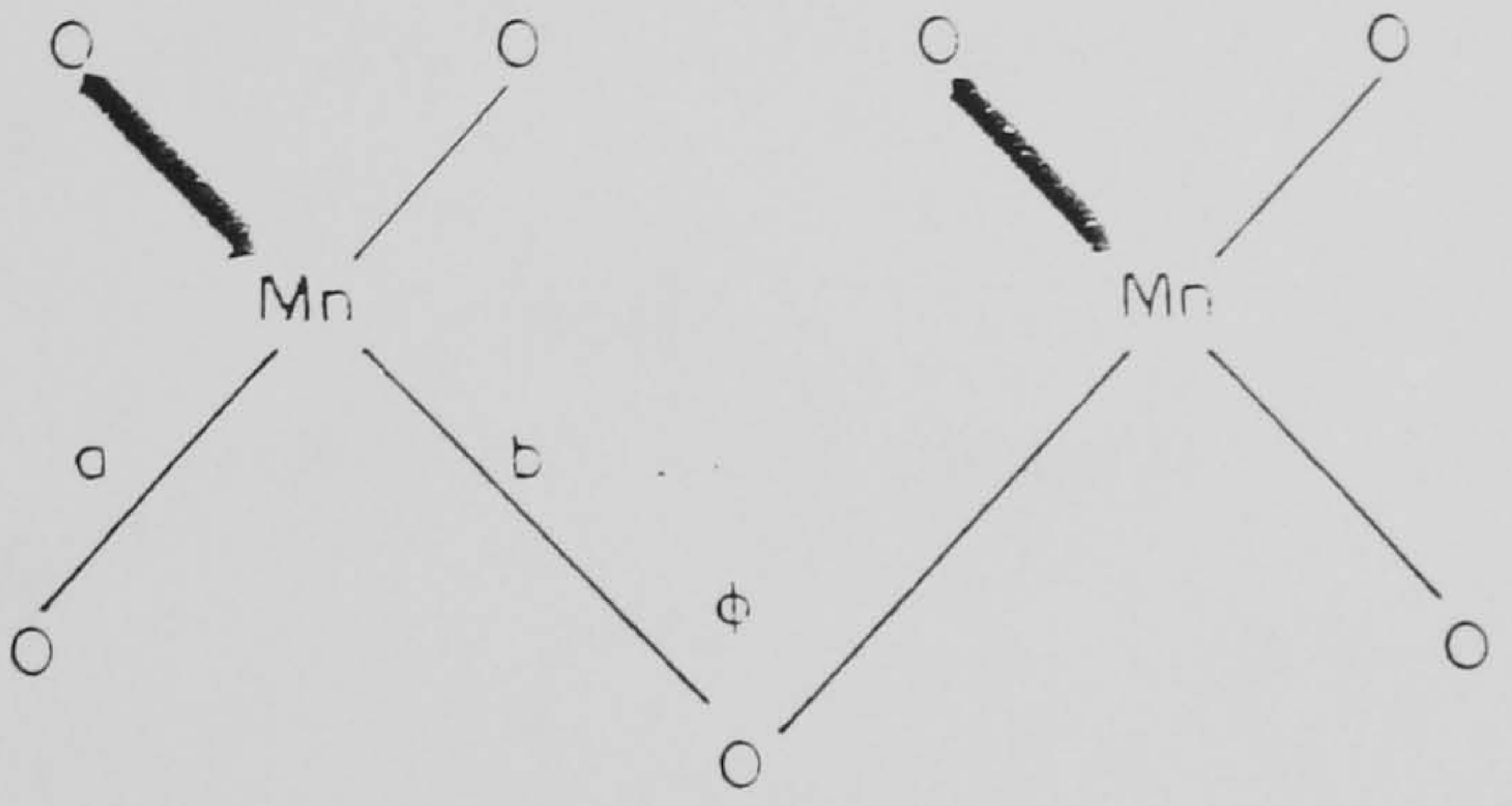


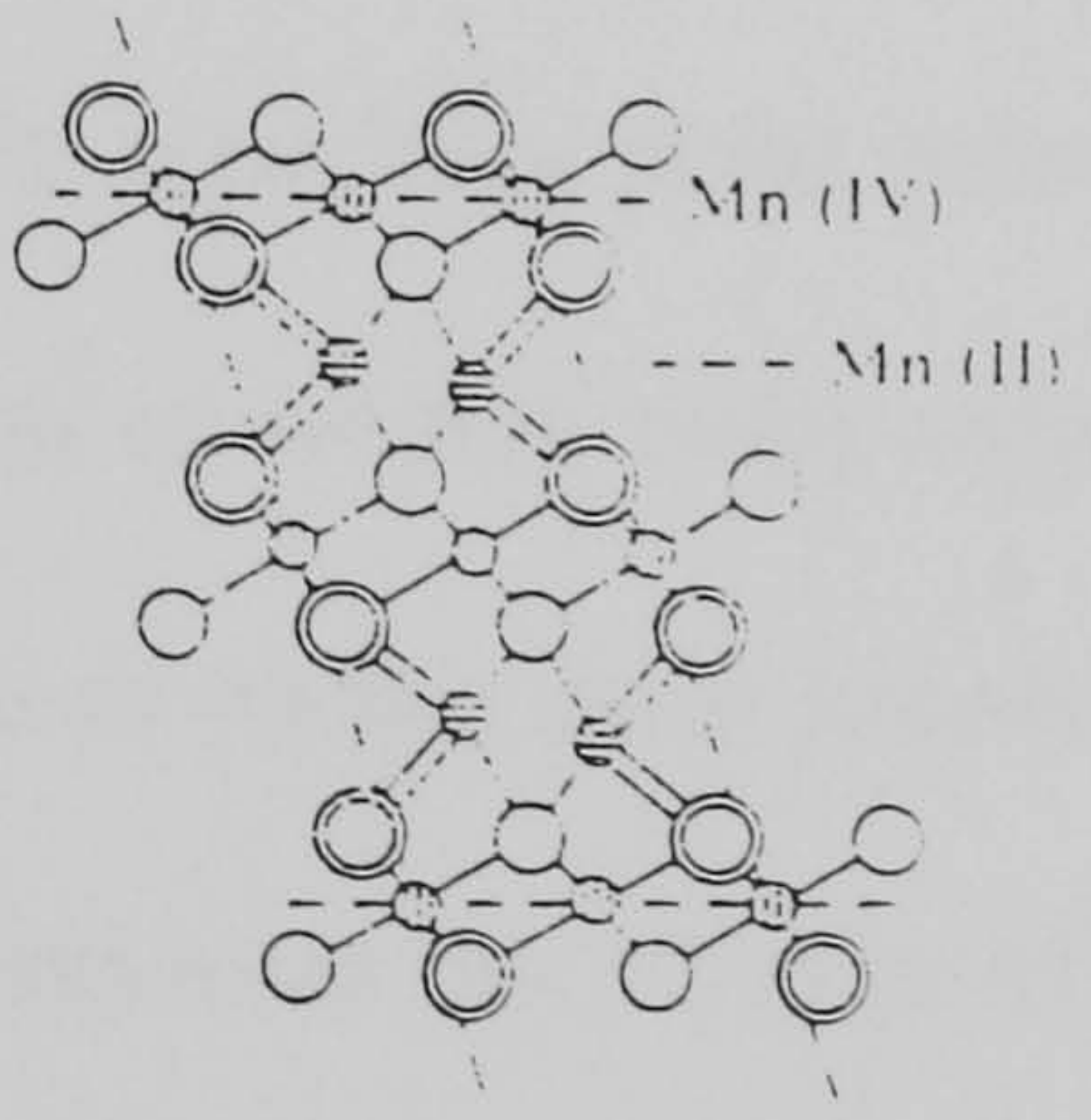
FIGURE 14.21 *The structure of manganese heptoxide.* a = 159 pm. b = 177 pm. ϕ = 121

Mn_5O_8 Pentamanganese octaoxide

The structure of the chemical is shown in Figure 10:

Figure 10 The structure of pentamanganese octaoxide

(Wells 1990)

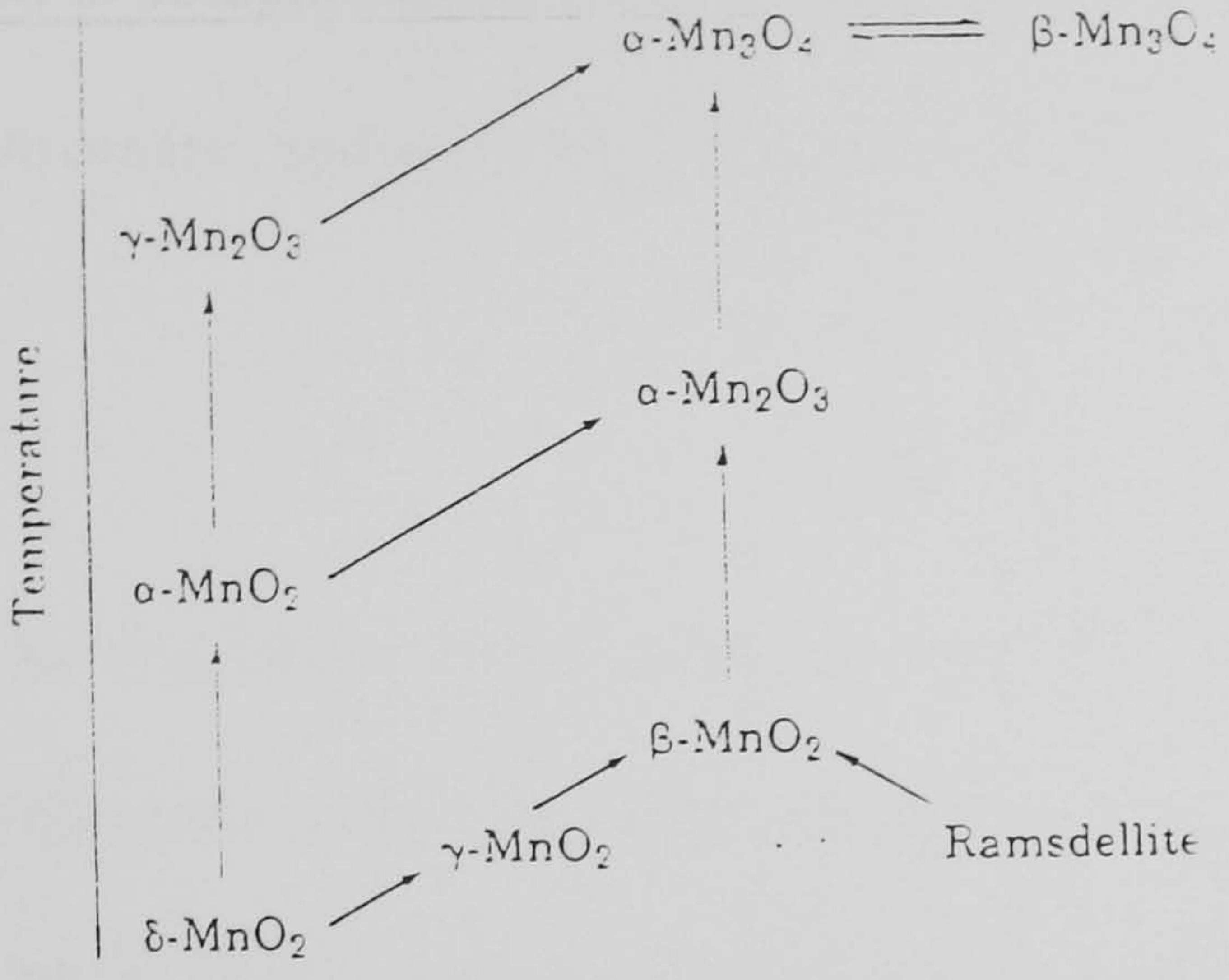


All of the manganese oxides on heating in air to 1000 °C form the compound Mn_3O_4 (Wells 1990).

The formation of Mn_3O_4 see Figure 11.

Figure 11 The formation of various manganese oxides by thermal action

(Kirk Othmer 1995)



1.6.3 Basic facts about water

Water is a tetrahedral molecule with strongly polar hydrogen to oxygen bonds. It is a good solvent of various pollutants especially polar solvents due to the polarity and shape of the molecule, and conversely non or weakly polar substances are not readily dissolved. (Greyson 1990). However, the non polar or weakly polar substances do dissolve at the surface of the water due to airborne non-polar gases alter the polarity of the water surface.(Greyson 1990)

1.6.4 Introduction to organic compounds

Organic compounds contain carbon, and usually hydrogen and in some cases other elements such as nitrogen (O'Neill (1993). Organic compounds are made up of a carbon structure.

Hydrocarbons are composed of just carbon and hydrogen. If the compounds carbon to carbon bonds are single then the compound is termed unsaturated. If double or triple carbon to carbon bonds exist then the compound is saturated.(Schwarzenbach et al 1993). Aliphatic compounds contain only branched or straight carbon chains, whilst compounds containing a single or multiple rings are alicyclic. Aromatic hydrocarbons contain an aromatic ring system. (Schwarzenbach et al 1993).

With polar groups such as OH or NH_2 on the compound, or if the organic compound is ionic, then the substance will show water solubility, without such groups the compound will have low solubility in water. Increasing the molecular mass of related organic compounds also decreases the solubility of them in water. (Reeve 1994). Decreased solubility in water corresponds with an increased solubility in organic compounds. Therefore these organic compounds with low water solubility can accumulate (bioaccumulate) in the fat of creatures in the water. (Reeve 1994). Biomagnification, whereby the compound levels increase in a food chain can occur, for example increasing concentrations from insects eaten by fish to the birds eating the fish. However various organic compounds may be readily degraded or excreted by the organism and so may not be biomagnified (Reeve 1994)

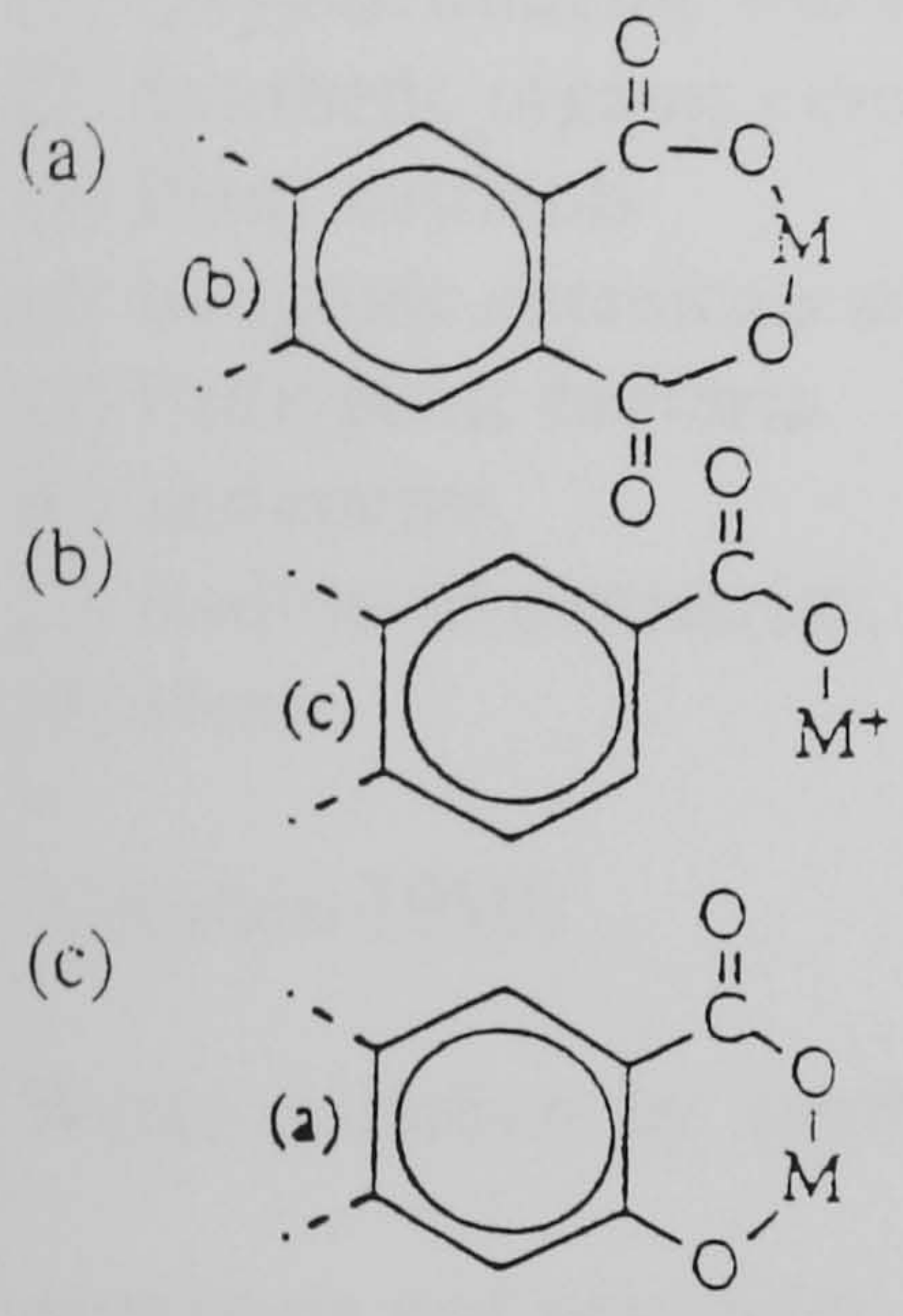
1.6.5 Introduction to humic acid

Humic substances are large complexing agents found in nature and have been known for nearly 200 years. They result from decomposition of vegetation and are resisitant to degradation in the environment. Humic acid is the portion of humic substances that precipitates out from an acidified extract, and can act as an ion exchange species. It is a polyelectrolytic material of formula weight in the tens of thousands. (Manahan 1994) The composition of humic substances is between 45 and 55 % carbon. 30-45 % oxygen. 3-6 % hydrogen. 1-5 % nitrogen and 0-1 % sulphur. (Manahan 1994) Humic acid is insoluble and can act as a cation exchanger. and can chelate with metals in solution. Metal binding can occur through a complexing with two carboxyl groups.complex between metal and carboxyl group or chelation between a phenolic hydroxyl group and carboxyl group. (Manahan 1994)

The chelation of the metal by humic substances is shown in Figure 12

Figure 12 Metal chelation to a humic substance

(Manahan 1994)



(Metal ion = M^{2+})

(a)Complexing with two carboxyl groups:
(b)Complexing with carboxyl group:
(c)Chelation of metal between phenolic hydroxyl and carboxyl group

On their own in water, humic acids can discolour water. (Twort et al 1994). In the presence of chlorine in drinking water treatment, humic substances can form trihalomethanes (THMs). Chloroform, a THM, is a suspected carcinogen. Its formation however can be minimised by removing the humic acid from the water before treating with chlorine. (Manahan 1994). Minimizing chlorine levels whilst maintaining safe disinfection, or using ozone (at the expense of not having residual water disinfection after treatment) also will reduce the formation of THMs. (Harrison 1990). Harrison states that the level of THMs in drinking water however "have not positively" been found to be hazardous.

1.6.6 Water pollution and contamination

A polluted waterway is one that "is ecologically out of balance as a result of contamination" (Greyson 1990). This is important as "the ecological health of a water resource determines its ultimate usefulness to a modern society". (Greyson 1990)

The main groups of water pollutants include

(1) Oxygen utilizing wastes
(2) Synthetic organic compounds
(3) Plant nutrients
(4) Inorganic chemicals and minerals
(5) Pathogenic bacteria
(6) Sediments
(7) Radioactive materials
(8) Heat

(Greyson 1990)

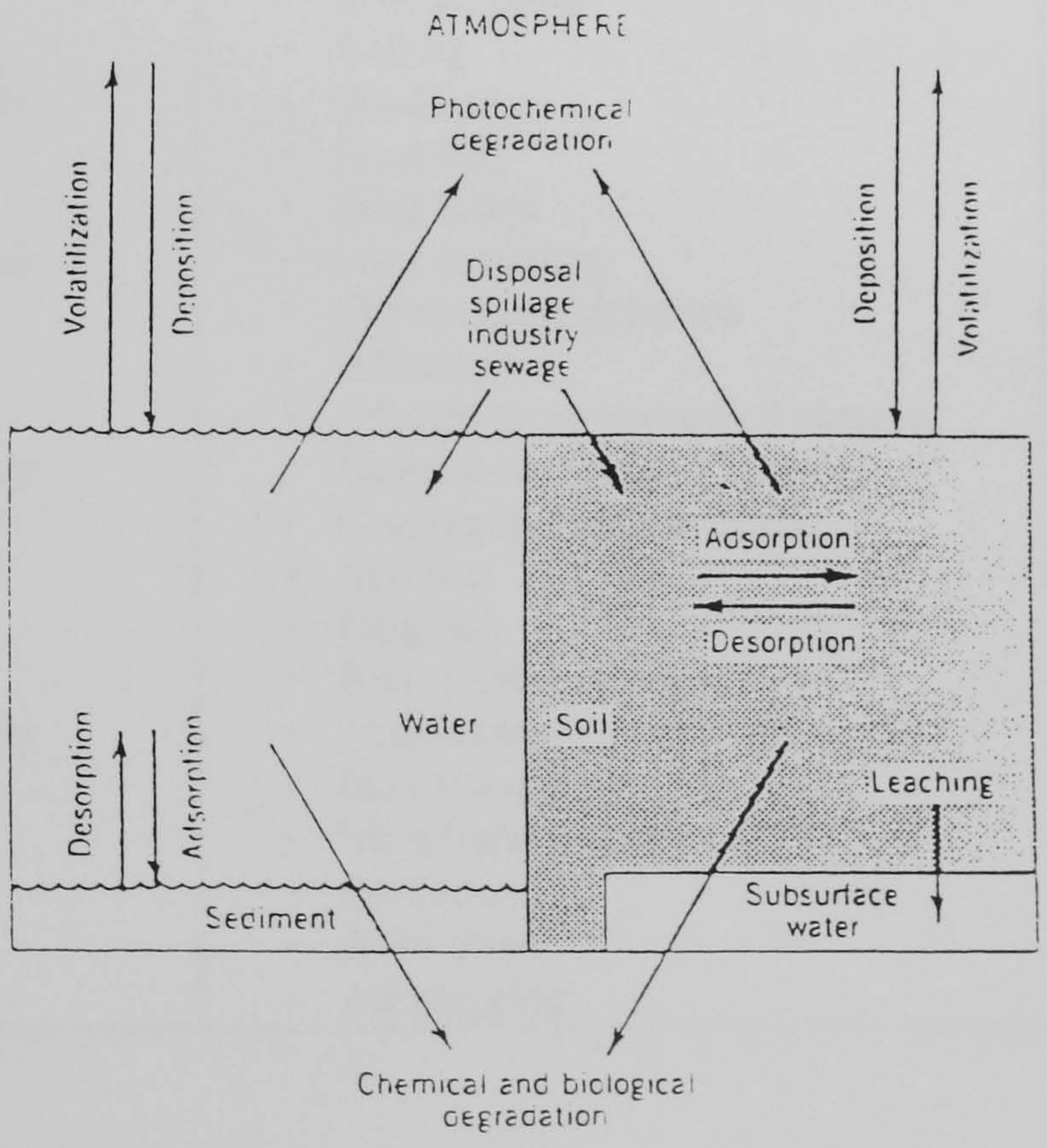
Water pollution by synthetic organic compounds covers industrial solvents and chemicals, detergents and pesticides. (Greyson 1990) Surface waters tend to have more organic pollutants in them compared to groundwater. Urban groundwater tends to have higher levels than rural aquifers however. (Gray 1994). The levels found in each case clearly depend on the presence of industry and other land use. (Gray 1994)

Within the category of organic water pollutants include biodegradable compounds such as organic wastes from farms. Non degradable or slowly degradable organic compounds include aromatic solvents halogenated pesticides and some detergents. (Greyson 1990). Biodegradable substances represent a problem as they can add to the nutrient load of the waterway promoting growth of various possibly unwanted water based organisms. The dissolved oxygen levels of the water contaminated with them can also be reduced denying oxygen to water-based organisms. (Greyson 1990). Non degradable organic substances may present a toxicity threat to organisms, or in the case of detergents cause foaming that prevents oxygen and carbon dioxide diffusion across the water surface.(Greyson 1990)

The organic pollution of water is quite widespread. Over 2000 different compounds have been found in potable water worldwide. In the UK a study of water supplies revealed 343 organic micro-pollutants in the fourteen areas studied. (O'Neill 1993). A total of almost 2 million organic compounds are known. (Montgomery 1985). The transport in the environment and fate of organic chemicals is shown in Figure 12.

Figure 12 The transport and fate of organic compounds in the environment

From Montgomery (1985)



1.6.7 Water pollution regulation

The control of discharges of pollutants into UK waterways is the responsibility of three bodies. Wastewater regulation is covered by the Water Service plcs covering sewerage discharge. Her Majesties Inspectorate of Pollution (HMIP) covers effluent especially from polluting industries. and the National Rivers Authority (NRA) who set controls on most discharges to controlled waters.

1.6.8 The history of water treatment

The history of water treatment is detailed in Table 7

Table 7 Water treatment through time

From Kavanagh (1987)

Period	Process Development
Pre-16th Century	• Coagulation, sedimentation, filtration in batch mode • Boiling
17th Century	• Distillation • Screening • Sand filters
18th Century	• Lime softening • Chemical precipitation • Infiltration • Adsorption on powdered charcoal
19th Century	• Large-scale filtration systems • Coagulation/sedimentation • Aeration • Flotation • Biological processes
20th Century	• Disinfection • Ion exchange • Membrane processes • Oxidation • Adsorption • Air stripping

1.6.9 Removal of pollutants from water

There are four main types of effluent and wastewater treatment: chemical, biological and physical treatment and one classified as other. Table 8 lists the various treatment processes.

Table 8 The main treatment methods for a variety of pollutants

Anon (1993)

Chemical treatment processes	
Catalysis	cyanides, organic wastes, pesticides
Chlorinolysis	chlorinated hydrocarbons
Disinfection	bacteria, colour, pathogens, viruses, solvents
Electrolysis	heavy metals
Flocculation / coagulation	colour, emulsified industrial wastewater, food waste, heavy metals, organics, pesticides, phosphate, suspended solids, turbidity
Hydrolysis	oil sludges, tars, pesticides
Neutralisation	acids, bases, heavy metals, pH
Oxidation	colour, combustible effluents, cyanide, heavy metals, iron, organics, manganese, sulphides
Photolysis	organic wastes
Precipitation	ammonia, food waste, heavy metals, phosphates, suspended solids, tannery waste
Reduction	heavy metals
Biological treatment processes	
Activated sludge	ammonia, BOD, biological wastewater, domestic sewage, food processing waste, organic effluents, nitrate, phosphate, sewage
Anaerobic digestion	biological wastewater, BOD, organic sludges, septic tank wastes, recalcitrant COD, sewage
Composting	biological wastes, BOD, food wastes, sewage sludge
Filter media	colour, suspended solids
Lagoons	heavy metals, leachate
Trickling filters	BOD, COD, colour, cyanides, organic wastes, phenols

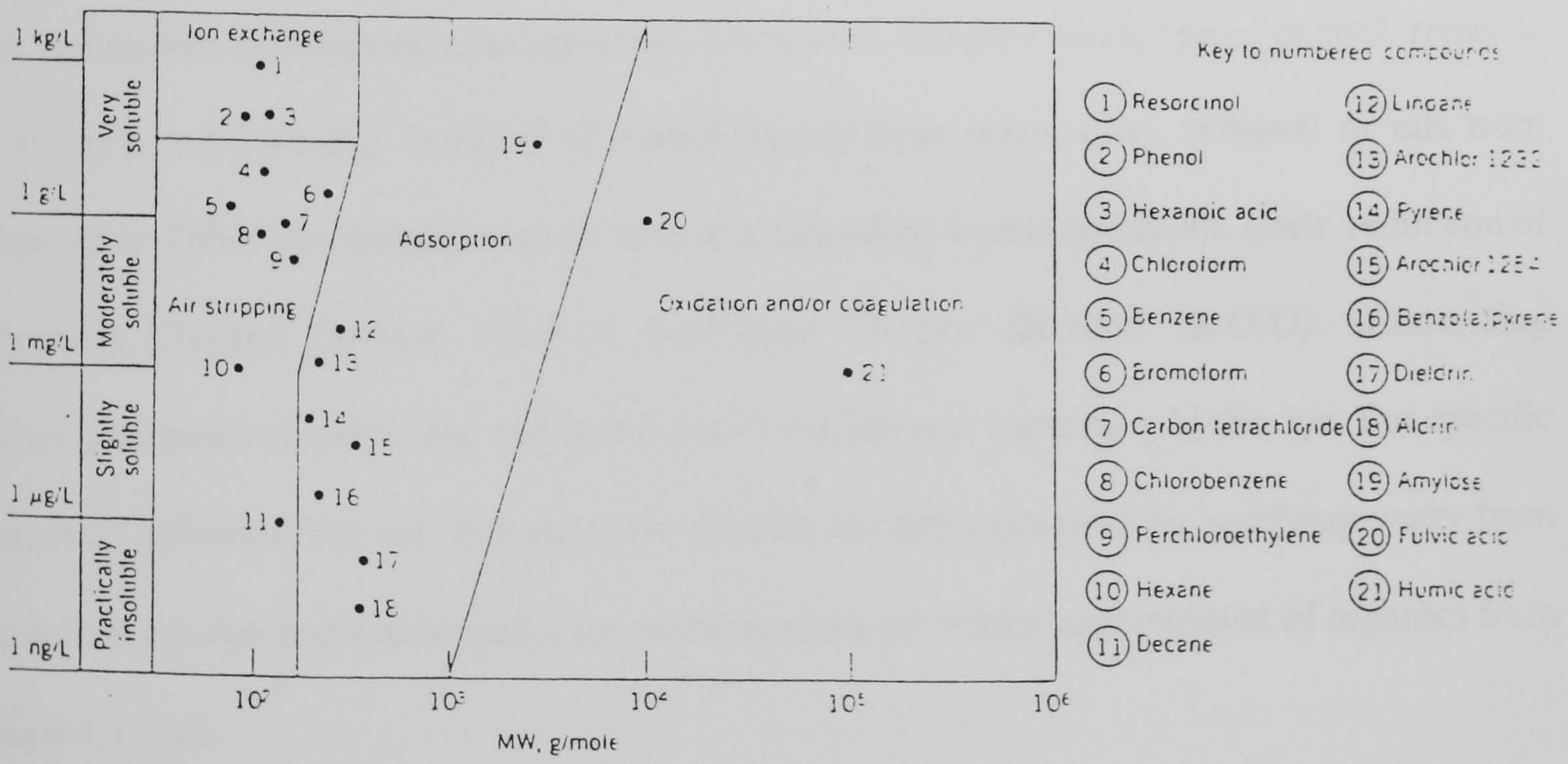
Physical treatment processes	
Adsorption	colour, dissolved organics, fat removal metals, pesticides, phenol recovery, trace elements
Air stripping	ammonia, CO_2, dissolved gases, solvents, volatile organic compounds
Centrifugation	sludge thickening & dewatering, suspended solids
Ion-exchange	colour, heavy metals, inorganics salts, nitrate water treatment, washwater recovery, ultra-pure water preparation
Reverse-osmosis	brackish water, metals, nitrate, wastewater recovery
Electro-dialysis	brackish water, acid mine water
Filtration	carbon tetrachloride, colour, heavy metals, iron, pesticides, sewage, sludges, suspended solids, tertiary treatment, turbidity
Flotation	abattoir wastes, chemical wastes, fuel/oil, grease, heavy metals, suspended solids
Sedimentation	heavy metals, minerals, suspended solids, turbidity
Screens	food wastes, oils, sewage, suspended solids
Solidification	asbestos, hazardous wastes, heavy metals, sludges
Other treatment processes	
Reed bed, coppice	BOD, biological wastewater
Nitrification	ammonia
Ultrafiltration	colloidal slurries

Apart from possible reduction of aquatic oxygen in a waterway where organic substances are discharged the removal of various organic compounds from water is important for other reasons. For example they could be carcinogenic or mutagenic or a promoter.(Harrison 1992). For example bromoform is a mutagen, carbon tetrachloride a carcinogen and phenol a promoter. (Harrison 1992)

Organic compounds are removed from drinking water by reverse osmosis, coagulation, air stripping, adsorption, ion exchange and oxidation. (Montgomery 1985). Figure 13 shows the generalised processes. Adsorption such as on activated carbon is used for removing compounds including PolyAromatic Hydrocarbons (PAHs) and pesticides. Coagulation and oxidation are used for removing humic and fulvic acids. Ion exchange removes highly water soluble compounds including phenols. Volatile organics such as chloroform are easily removed with air stripping. (Montgomery 1985). Humic acids - THM precursors - are usually removed using chemical coagulation at water treatment works. (Twort et al 1994)

Figure 13 Techniques for removing various organic compounds from potable water

Montgomery (1985)



One such treatment process which the chemical of interest, manganese dioxide can perform is adsorption. The process is detailed below:

1.6.10 Adsorption of pollutants.

Adsorption involves molecules in a solvent being held onto the surface of a particle. The forces of attraction to the particle are physical, ionic, and chemical. (Tebbutt 1992) Particles that adsorb well have a large ratio of surface area to volume and are highly porous. Placing an adsorbent in a solvent with dissolved molecules, over time, the amount of molecules will increase on the adsorbent surface. Eventually an equilibrium is reached between the amount of molecules transferred from the solvent to the adsorbent the number of molecules leaving the adsorbent for the solvent. (Tebbutt 1992)

1.6.11 Results of search of patents and articles published involving use of manganese dioxide to remove organic compounds from water

The use of manganese dioxide has been patented for various tasks. Twenty five relevant patents worldwide were located using the computerised 'STN International' worldwide patent database. The patents include removing trihalomethane precursors, complete oxidation of phenol, removal of bacteria and turbidity, removal of carbohydrates from wastewater, removal of oils from wastewater. Other uses include removal of colour caused by humic and fulvic acids, reduction of Chemical Oxygen Demand (C.O.D) Biological Oxygen Demand (B.O.D), deodorizing organophosphorous pesticides and treatment of wastewater containing hydrazine. For specific industrial effluents, the use of manganese dioxide has been patented for purifying water from chromium azo dye production, polymer manufacturing processes, and removal of organics from Bayer Liqours.

A patent reported by Eilbeck and Mattock (1987)detailed that using manganese dioxide in suspension to oxidise phenol in solution is very slow. At 100°c it was found to be 1 mg of phenol removed per gram of catalyst per hour). increasing the temeperature and partial pressure of oxygen increased the phenol removal. Eilbeck and Mattock (1987) state that without a catalyst to aid in organic matter degradation in effluent the presence of oxygen alone is only effective at removing the compounds at high temperatures.

It was reported by Colthurst and Singer (1982) that in experiments to remove trihalomethane precursors manganese dioxide was unable to appreciably reduce these compounds. However, on addition of calcium ions (at 40 mg/l) the formation of precursors was significantly reduced.

The theory outlined in their paper is that anionic polyelectrolytes such as humic acid can bond to manganese dioxide in suspension in water due to divalent cations - calcium ions acting as a bridge between the humic acid and manganese dioxide. On its own a manganese dioxide suspension will not at pH 7 appreciably adsorb much trihalomethane precursors. (Colthurst and Singer 1982). The idea that strontium ions (also group II ions) could be used instead of the calcium as in the Colthurst and Singer (1982) paper is therefore investigated. The study showed up to a 65 % reduction in chloroform formation potential using 40 mg/l calcium, varying concentrations of Mn as MnO_2 and humic acid.

1.6.12 Problems in the use of manganese dioxide for removing organic compounds from water

Manganese can itself cause water pollution problems. Manganese in potable water can cause staining and taste problems. The European Commmunity sets a guide level at 20 mg/l for manganese however as at this level laundry and sanitary ware become stained grey-black. (Gray 1994). The World Health Organisation (WHO) standard set for human health for drinking water quality is 0.5 mg/l. (Gray 1994). Manganese can be removed from water at a pH of 8.5 to 9.0. However, in water treatment works insoluble aluminium compounds used to clarify water by sedimentation will be dissolved out. Increased acidity also means that the dosing of chlorine is tripled when the pH is increased from 8.0 to 9.0. Manganese in groundwater can be complexed out when sodium silicate is added. (Gray 1994)

1.6.13 Results of literature search of experiments published on the use of strontium compounds in water pollution control

Use of the computerised 'STN International' database which searches for patents and journal articles found strontium has been very little used as a pollution control agent. Only one example was found. Cooper, et al patented a system involving the use of semiconductor particles - including $SrTiO_3$ - to degrade oxidizable contaminants under UV light. The purified water is eventually recovered from the semiconductor photocatalyst. This lack of patenting amd articles is a positive sign of the open nature of the field for further research.

1.6.14 Measurement of Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC) in water samples.

Total Organic Carbon is the total quantity organic carbon in compounds in a sample that has been oxidised to CO_2 after the inorganic components have been removed. The most common technique involves reacting the sample at 90-100°C with persulfate oxidising agent. Usually over 98 % of the organic compounds in the sample react to form the carbon dioxide. The carbon dioxide in the solution is purged with nitrogen, and trapped and concentrated for measurement by Non Dispersive Infra Red spectrometry. The amount of CO_2 detected is converted to the concentration of organic carbon in the sample. (OI Corporation 1984)

Total Inorganic Carbon measurements quantify the carbon dioxide, inorganic, organic, and volatile carbon in the sample. The sample solution is acidified and carbon present as carbonate or bicarbonate is converted to CO_2. The carbon dioxide dissolved in the solution is purged with nitrogen, concentrated and trapped for measurement by Non Dispersive Infra Red spectrometry. (OI Corporation 1984)

The OI 700 TOC analyser used in the experiments can analyse samples containing between 4 ppb to 10,000 ppm organic carbon. For inorganic carbon the instrument can quantify levels between 1 ppb and 10, 000 ppm inorganic carbon.

1.6.15 Experiment involving study of the removal of humic acid in water by manganese dioxide, calcium ions, and strontium ions.

1.6.16 Introduction

Experiments investigating the effects of manganese dioxide and calcium / strontium ions in removing the trihalomethane precursor humic acid from solution have been performed.
The first experiments involve the assessment of the ability of the apparatus to produce meaningful and reproducable results - using standards of known organic carbon composition and deionised water.

1.6.17 Methodology

A 500 mg/l humic acid solution was prepared by dissolving 0.5004 grammes of Aldrich humic acid sodium salt in 1000 mls of deionised water. Three portions of 2 mls of the 500 mg/ l solution were then added to three volumetric flasks.

A 1000 mg/l calcium solution was prepared by dissolving 1.828 g analar calcium chloride in 500 mls of deionised water.

Calculations for preparation of Ca solutions

Calculated by Atomic weight Ca = 40.08

Formula weight $CaCl.2H_2O$ =147.02.

Therefore 147.02 / 40.08 = 3.668 g of the chloride contain 1g of Ca. Dissolve 3.668g in 1 Litre produces a 1000mg/l Ca solution. To prepare 500 mls of 1000 mg/l Ca solution, 3.668g / 2 = 1.828 g was used.

A 4 ml portion of the 1000 mg/l calcium solution was added to one 100 ml volumetric flask containing the 2 mls of humic acid. The 100 ml flask was filled to the mark with deionised water to create a 10 mg/l humic acid and 40 mg/l calcium solution. As humic acid is approximately 50 % carbon, the concentration as Total Organic Carbon is approximately 5 mg/l TOC from the 10mg/l humic acid solution.

Calculations for preparation of Sr solutions

A 1000 mg/l stock solution of strontium chloride was prepared by diluting 1.518 g of strontium chloride in 500 mls of deionised water. The calculation of the mass of $SrCl.6H_2O$ needed to prepare a 1000 mg/l solution is as follows:

Atomic weight of Sr = 87.62

Formula weight of $SrCl.6H_2O$=266.62

In a 1 litre solution to make 1000 mg/l Sr. 266.62 / 87.62 =3.0429g are dissolved in 1 litre. In a 500 ml solution of 1000 mg/l Sr 30.429/ 2 = 1.518g are dissolved in the 500 mls. A 40 mg/l strontium ion solution was prepared by diluting 4 mls of the solution in 100 mls of deionised water in a second flask containing 2 mls of humic acid.

The volumetric flask contents were then poured into the conical flasks containing 0.5 g each of manganese dioxide, and the mixtures stirred for two hours on a magnetic stirrer at speed level 2 with temperature measured at the start. A third conical flask containing just the 10 mg/l of humic acid was also stirred for two hours. The manganese dioxide obtained from Twinstar Chemicals was a natural crushed product of particle size 45 um to dust sized with a mean particle size of 0.82 um.

The three samples were then centrifuged at 2000 rpm for 20 minutes to remove the manganese dioxide which would damage the TOC instrument, and the samples analysed for Total Organic Carbon content and Total Inorganic Carbon content.

The temperature of the solutions at the start of the experiment was 22 °C.

The Total Organic Carbon analyser:

The instrument used is a TOC analyser Model 700 OI corporation.
Nitrogen Purge flow rate: 30 psi
Instrumental precision
TOC: greater than +/- 2 % or 2ppb C.
TIC greater than +/- 1 % or 0.5 ppb C.

1.6.18 Results

Preliminary analysis were run to assess the reproducability of results for analysis of distilled water. So far, TOC analysis of deionised water has not produced reproducable results, and further experiments are being planned. Analysis of deionised water from the same source shows variation in TOC from 1 mg/l to 6 mg/l on triplicate analysis. A prelilminary run of the experiment investigating the effects of calcium, strontium and manganese dioxide in removing humic acid from solution have been performed. It appears that calcium ions, as expected, and strontium ions in the presence of manganese dioxide reduce the concentration of humic acid after the two hour experimental contact time on triplicate analysis of the samples by TOC. However, the results have not been included as the humic acid concentration measured by the instrument varies considerably from the actual concentration of 5 mg/l carbon as humic acid (10 mg/l carbon in some triplicate analysis). The experiments will be repeated shortly.

1.6.19 Discussion

The preliminary results indicate there may be a reduction of humic acid levels in water using manganese dioxide and calcium / strontium ions in water. However, further investigation as to the cause of the instrumental problems will take place in the next six months to enable accurate results to be obtained.

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Patent for the use of strontium compounds in water pollution removal

American

Title: Photocatalytic (UV) oxidativbe treatment of water using semiconductor catalysts and seperation by crossflow membrane filtration. Patent Information US 5118422A 920602. Patent

Assignee: Photo Catalytics inc.USA

Patents for the use of manganese compounds in humic acid removal

Japanese

Title: Treatment of water for removal of colour and organic components. Patent Information JP 07163987 A2 950627 Heisei. Patent Assignee: Ngk Insulators Ltd. Japan

Title: Filter medium for water treatment. Patent Information JP 59173191 A2 841001 Showa.Patent Assignee: Matsushitu Electric Industrial Co.Ltd. Japan

Title: Filter medium for water treatment and its preparation. Patent Information JP 59173192 A2 841001 Showa. Patent Assignee: Matsushitu Electric Industrial Co.Ltd. Japan

Title: Filter medium for water treatment. Patent Information JP 59173193 A2 841001 Showa. Patent Assignee: Matsushitu Electric Industrial Co.Ltd. Japan

Title: Water purification apppäratus. Patent Information JP 58216780 A2 831216 Showa. Patent Assignee: Matsushitu Electric Industrial Co.Ltd. Japan

Title: Decolorization in water purification. Patent Information JP 58137492 A2 830815 Showa. Patent Assignee: Matsushitu Electric Industrial Co.Ltd. Japan

German

Title: Water purifying agent. Patent Information DE 3422847 A1 850103 Patent Assignee: Mitsui Mining and Smelting co. Ltd.Japan

Czech

Title: Ferric coagulent for water treatment. Patent Information CS 195208 B 820515 Patent Assignee: Czech

1.7 OTHER ACTIVITIES ATTENDED DURING THE SIX MONTHS

A three day course at the Experimental Techniques Centre (ETC) at Brunel University on Scanning Electron Microscopy was attended. The course involved theoretical background, preparation of samples for electron microscopy analysis, analysis of the samples, and developing the photographs obtained. The course details are outlined below.

Also attended were a variety of Chemistry Department research colloquia held at Brunel. Topics ranged from catalysis to organic compound synthesis.

BRUNEL UNIVERSITY

Experimental Techniques Centre

S.E.M. Preparation and Basic Operation

22nd - 24th January 1996

Day 1

09.30 - 10.15	Introduction to Scanning Electron Microscopy	Dr.R.Bulpett
10.15 - 10.30	Coffee	
10.30 - 10.45	Demonstration	
10.45 - 11.30	Design and Construction of the S.E.M.	Dr.A.J.Reynolds
11.30 - 12.15	Practical.1.	
12.15 - 13.00	Specimen Beam Interactions and Image Formation	Dr.R.Bulpett
13.00 - 14.00	Lunch	
14.00 - 14.45	Specimen Preparation.1.	Dr.A.J.Reynolds
14.45 - 17.00	Practical.2.	

Day 2

09.30 - 10.15	Specimen Preparation.2.	DrR.Bulpett
10.15 - 10.30	Coffee	
10.30 - 10.45	Demonstration	
10.45 - 11.30	Specimen Preparation.3.	Mrs.J.Moses
11.30 - 12.15	Practical.3.	
12.15 - 13.00	Contrast Techniques and Photographic Recording	Dr.R.Bulpett
13.00 - 14.00	Lunch	

14.00 - 14.45	High Resolution S.E.M.	Dr.A.J.Reynolds
14.45 - 15.00	Demonstration	
15.00 - 17.00	Practical.4.	

Day 3

09.30 - 10.15	Additional Contrast and Imaging Techniques	Dr.R.Bulpett
10.15 - 10.30	Coffee	
10.30 - 10.45	Demonstration	
10.45 - 11.30	Introduction to Microanalysis	Dr.A.J.Reynolds
11.30 - 12.15	Practical.5.	
12.15 - 13.00	Applications of S.E.M. (1)	Dr.R.Bulpett
13.00 - 14.00	Lunch	
14.00 - 14.45	Applications of S.E.M. (2)	Dr.A.J.Reynolds
14.45 - 17.00	Practical.6.	

AN INVESTIGATION INTO POTENTIAL USES OF MANGANESE AND STRONTIUM COMPOUNDS IN POLLUTION CONTROL

ENGINEERING DOCTORATE
SIX MONTHLY REPORT - NUMBER 2 .

Andy Houlson

1st October 1996

Six monthly report

Contents

4. Appendices

Andy Houlson, October 1996

1. Introduction

This report covers the second six month period of research undertaken from April 1996 - October 1996. It details module courses attended, conference attendance, work performed in the last 6 months and possible future work on the two areas of this Eng.D: the potential use of manganese and strontium chemicals in environmental improvement.

2. Work undertaken

Literature and patent searches on the uses of sodium birnessite have been performed and add to the literature sources already gathered.

The main area of work has been identifying optimal experimental conditions for the preparation of the potential ion exchanging chemical sodium birnessite. These parameters include:

The reaction time.

The flow rate of the oxygen into the reaction vessel.

The use of either manganese chloride or manganese sulphate as the starting material for creating the birnessite.

The effects of centrifuging or filtering through filter paper on the production process for birnessite.

ADDENDUM

On page two, paragraph one, the sentence containing "centrifuging or filtering the sodium birnessite produces birnessite of consistent quality." is incorrect. Centrifuging the samples produces sodium birnessite of consistent quality, however, filtering the samples results in sodium birnessite of inconsistent quality due to formation of various manganese oxides. For this reason, filtration of samples has been discontinued.

Optimal flow rates, and reaction times for the synthesis have been identified over the last 6 month period. An oxygen flow rate of 2.75 litres per minute has been chosen for the optimal reaction time of 4 hours. Both manganese chloride and manganese sulphate can successfully be used in the synthesis of sodium birnessite, and centrifuging or filtering the sodium birnessite produces birnessite of consistent quality.

The main technique for characterising the reaction precipitate has been by X-Ray diffraction. The technique will only identify components of a mixture if the component is present at above about 5 %. The other technique used was thermogravimetric analysis. Results from both analytical techniques have been used to identify the optimal reaction conditions for sodium birnessite production. Work on the synthesis will be continued to include the use of tap water instead of deionised water to wash the birnessite once it has been precipitated. Work also will investigate the potential role of sodium birnessite to remove metal ions from water will then commence.

The second main area of study is in strontium compounds. The area investigated in the last 6 months involved determination of the substances present as impurities in strontium oxide by the thermal treatment of strontium carbonate. The techniques used in the analysis of the sample include (1) Dionex ion chromatography analysis of the digested carbonate sample for sodium levels and transition elements. (2) determination of the soluble component and (3) basic qualitative physical and chemical tests.

Andy Houlson, October 1996

An oral paper was presented at the Annual Engineering Doctorate Conference on the 10-11 th of September at Brunel University. The conference paper is addended as an appendix to the report.

All the compulsory Eng.D modules have been attended in the last 6 month period. These include the Environmental Audit of the Grundon waste treatment facility at Colnbrook near Heathrow, and the courses: Sociology and the Environment, Risk Perception, and Environmental Measurement.

3. Conclusions

Progress is being made in identifying optimal conditions for the preparation of sodium birnessite, this will continue into the next 6 month period. Investigations will be carried out into the effectiveness of sodium birnessite in metal ion removal from solution. Work on strontium compounds will also be developed in the next period.

Andy Houlson, October 1996

4. Appendices

AN ASSESSMENT TOWARDS THE PROGRESS OF ENG.D COMPETENCIES

Demonstration of competencies in the following areas:

- Expert knowledge of an environmental engineering arca

Presentation of an oral and written contribution to the 1996 Eng.D conference helped meet this criteria. This was followed by a question session at the end of the presentation on my paper.

- Innovation and a contribution to knowledge in the devlopment of environmental technology

The identification of parameters to synthesise sodium birnessite reproducably. The ultimate end use of the product will be as an ion exchanging compound to remove heavy metals from water where the main focus on innovation will occur

- An appreciation of the industrial context of environmental engineering

The technique for developing sodium birnessite is clearly needs to be consider the economic factors if a competitively sellable product is to be produced. The lowest possible reaction period flow rate and filtration costs to achieve a reproducable quality of sodium birnessite are therefore being researched.

- Project management skills

The need to attend course modules, meet deadlines for module assignements, and prepare an Eng.D conference paper and oral presentation means project management is essential. Communication with supervisors and Twinstar Chemicals where necessary to set priorities for study has been important.

- Financial engineering project management and control

Most of the equipment for the projects involving sodium birnessite and the analysis of the strontium carbonate saggar impurity were available and at this stage there was little need for financial planning of the project required. The inoperability of a TOC instrument for measuring organic concentrations in an experiment detailed in the first six monthly report meant that this project has been delayed until the instrument is repaired.

- The ability to apply skills andknowledge to new and unusual situations

The background reading around the sodium birnessite project highlighted the difficulties in sodium birnessite preparation that needed to be understood and resolved. For instance in identifying the impurity sodium buserite (a more hydrated form of birnessite) by using X-ray diffraction.

-The ability to seek optimal solutions to complex engineering problems and to search out relevant information sources

This has been essential for the sodium birnessite project. Optimal solutions have been found through changing experimental variables in the production and drying of sodium birnessite to produce a consistent quality of product.

The relevant information sources have and are been located using the Bath Information Data Services (BIDS) online computer service. The Science Reference Library in Holborn has been used for finding other journal articles on the area of sodium birnessite production.

SPECIFIC AIMS AND DELIVERABLES FOR THE FIRST YEAR OF THE ENG.D

End of Year 1: Specific Aims and Deliverables

Have your research objectives changed? If so, restate your project objectives explaining any changes made. What are your specific deliverables for this year?

Full details of the literature search and the problem (thesis) definition must be included in the RE's first 6 monthly report.

The research objectives of investigating potential uses of manganese and strontium compounds in pollution control are the same as at the start of the Eng. D.

Specific deliverables for this/1st year:

- Full literature search/patent search of Mn/Sr use in pollution control
- Attendance at 1 week Scanning Electron Microscope course
- Analysis of MnO_2 by Scanning Electron Microscope
- Analysis of strontium carbonate by physical/chemical tests to determine contaminants causing glass formation in thermal conversion of strontium carbonate to oxide.
- Preparation of sodium birnessite (manganese oxide) and investigation into different variables for synthesis
- Analysis of sodium birnessite by X ray Diffraction and Thermogravimetric Analysis to identify other manganese oxides present after precipitation.
- Attendance at all course modules
- Oral presentation of paper at Annual Eng. D conference at Brunel University and submission of conference paper.

ANNUAL ENG.D CONFERENCE PAPER 1996

INVESTIGATION INTO THE PREPARATION OF SODIUM BIRNESSITE FOR USE IN REMOVING POLLUTANT IONS FROM WATER

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Twinstar Chemicals, Harrow, Middlesex

ABSTRACT

A successful pollution control agent needs to be of consistent quality. The identification of optimal, and also economically viable production methods needs to be investigated to prove that the chemical is marketable. The substance being investigated is the ion exchanging manganese oxide, sodium birnessite.

1 INTRODUCTION

Some species in water can create a health hazard if injested, or environmental damage if allowed to flow into waterways and to land. The use of chemicals, such as flocculants, to remove pollution from water is common. Research into the use of a chemical such as manganese oxide to remove water pollutants is therefore of environmental and commercial interest.

Sodium birnessite is a naturally occuring manganese oxide found in soils, and manganese nodules and is capable by ion exchange of binding to metals. The natural compound has little ion exchange capacity as it is saturated with other ions such as cobalt. The laboratory produced compound however has greater ion exchange properties - particularly cation exchange capacity.

The compound can be prepared fairly easily in the laboratory by oxidising Mn^{2+} ions with oxygen in alkaline solution. To ensure the method of preparation gives a reproducable quality in the laboratory requires investigation into optimum production conditions such as reaction time and washing and drying protocols. When a reproducable quality of birnessite is produced, it can then be coated onto high surface area material such as perlite and used to remove metal ions from water and effluent.

2 PRODUCTION OF SODIUM BIRNESSITE ($Na_4Mn_{14}O_{27}.9H_2O$) δ-manganese dioxide.

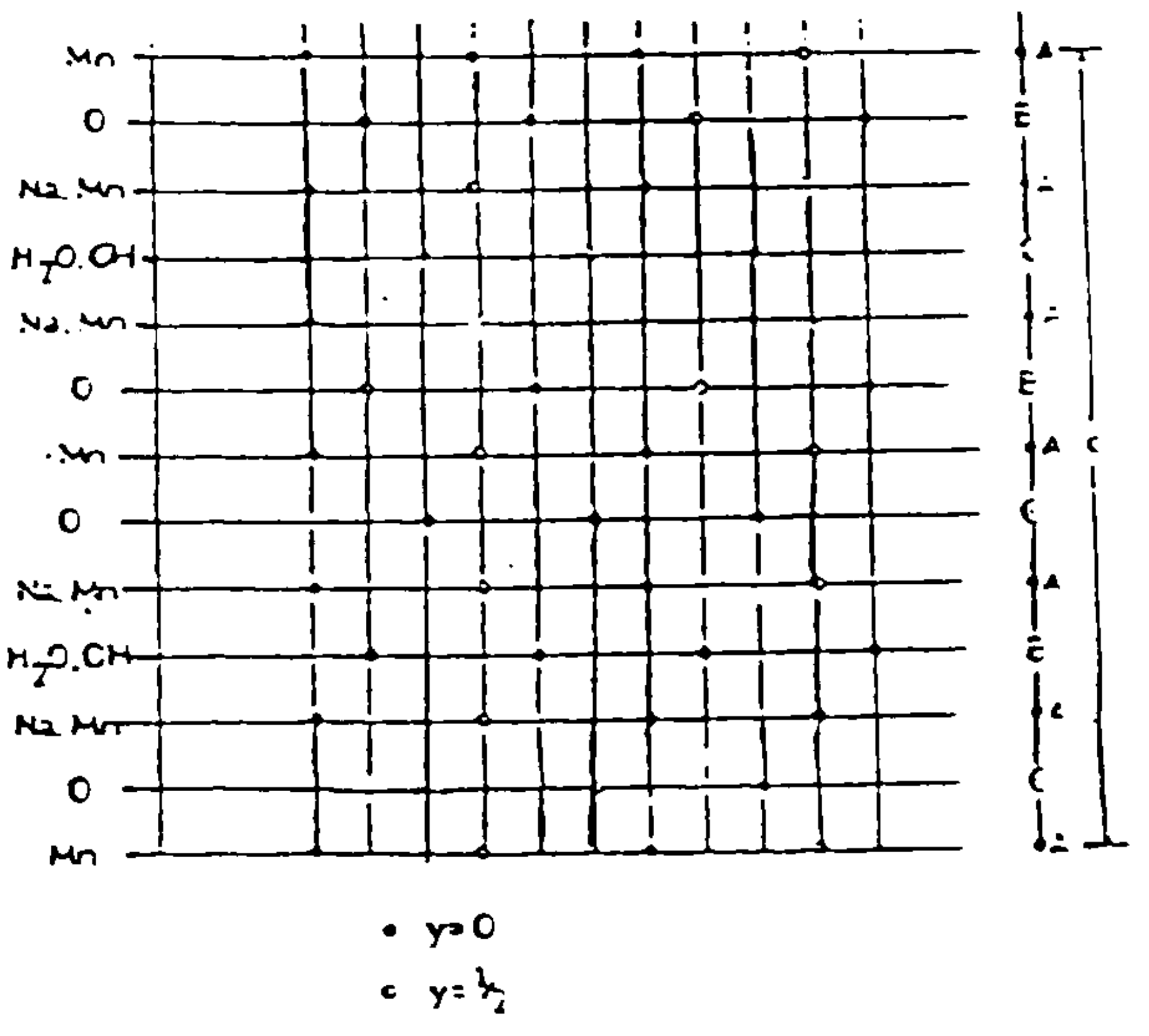
Manganese is the twelfth most common of the elements in the earths crust. (1) It is widely present in the environment with an estimated 1.8×10^5 metric tons world resources, and potential rsources of 1.1×10^5 metric tons. (1) It is a transition metal and exists in oxidation states 2+, 3+,4+,6+, and 7+. In nature the oxidation state is usually 2+ or 4+. (2)

Manganese dioxide is widely used in industry. For example in dry cell batteries, as a colourant in bricks, and glass and an curing agent for polysulfide rubbers. (1) It has a "very low acute toxicity by any route of exposure" as shown by both human and animal studies. (1) Manganese dioxide has an MnO_6 octahedra based structure. Each manganese ion is coordinated to six oxygen atoms. The octahedral shape results from the sharing of edges, tunnels and cavities in the lattice.

Sodium birnessite (sometimes named delta manganese dioxide) is a hydrated form of one of these manganese dioxides. (1). It is composed of 52.9% manganese and 6.3% sodium. (1). It is a grey black powder which has an average manganese oxidation state of 3.7.(3) In nature it is produced at low temperatures by the oxidation and supergene weathering of manganese rich rocks. (2 Birnessite is one of the main manganese compounds found in deep sea manganese nodules and was first found in a fluvio-glacial gravel deposit in Birness, Scotland. (2). It can be found both in acidic and alkaline soils (4)

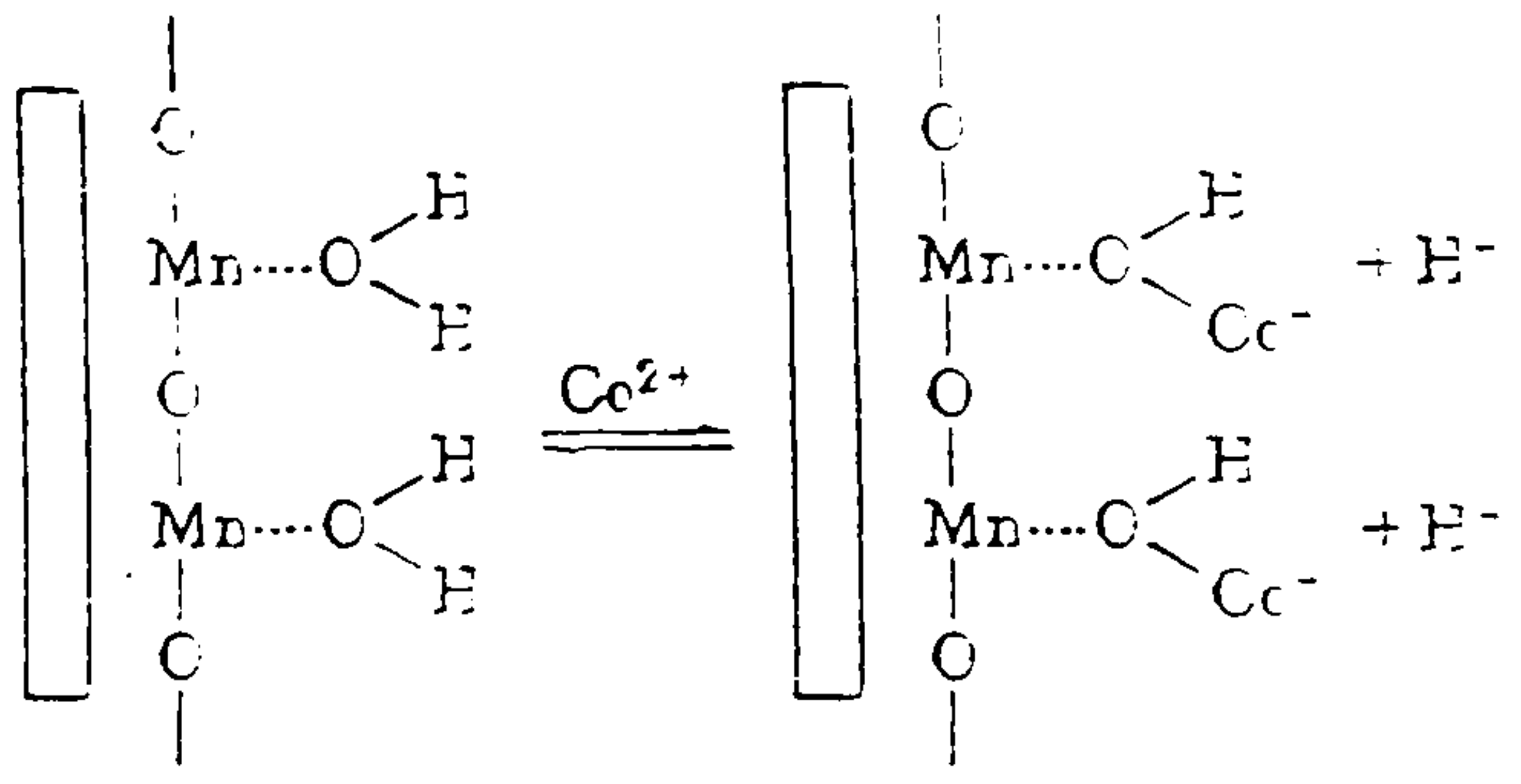
Sodium birnessite can be used in the curing process of polysulpide rubbers, and one of its potential uses could be to replace the oxidising agent currently used, and in doing so reduce the amount of raw materials (the oxidising agent) used to cure the rubber. This would represent a clean technology. As sodium birnessite is a double layer compound it can bind large amounts of cations and due to its negative surface charge (at neutral pH) can form surface complexes with metal ions. (1) The compound can absorb alkaline earth cations such as calcium, strontium and barium, and transition metals such as cobalt, zinc and nickel. (1) Figure 1 shows the layered structure of sodium birnessite. (5)

Figure 1 Sodium birnessite structure



The ion exchange properties of hydrated manganese dioxide (such as birnessite) rely on the hydrated surface species. Once the metal ion is scavenged from solution a hydrogen ion is released. Figure 2. (1).

Figure 2 The ion exchange properties of a hydrous manganese dioxide



Sodium birnessite is formed in the laboratory by the passage of molecular oxygen through a stirred 5.5 M Analar sodium hydroxide (250 mls), and 0.5M Analar manganese chloride or sulphate (200 mls) solution. Sufficient oxygen has to pass through the solution to ensure that the manganese 2^+ are completely oxidised otherwise they form the incompletely oxidised Mn_2O_3 or Mn_3O_4 (hausmannite) phases (3). Hausmannite - beta-manganese dioxide- is a naturally occurring manganese oxide. (3).

After a set reaction period from 2 hours to 10 hours of passing oxygen through the solution, the manganese mixture is centrifuged for five minutes at 3000 rpm to seperate the precipitate from the liquid. The supernatant liquid is discarded and the precipitated birnessite is stirred with double deionised water to remove excess sodium and hydroxide ions from the solution. This procedure of centrifuging and washing is repeated five times. The birnessite is then dried under rotary pump vacuum and kept above freezing point and under room temperature with a warm water pipe running through the vacuum vessel. Drying is performed to a constant weight which takes approximately seven hours. Water removed from the birnessite is trapped using dry ice. The dried birnessite sample can be kept indefinately in sealed sample containers.

There are a variety of variables in the production of the compound. These include the manganese compound used, oxygen flow rate, the reaction period, the amount of washing of the sample and the method by which the product is dried (either in an oven or by vacuum),and the method of filtration. Choice of preparation technique is important as sodium birnessite can be converted to Mn_3O_4 in non-alkaline conditions, when exposed to air, or when the temperatures is above about 100^c c. The ion exchange capacity of the birnessite produced, amongst other factors depends on the temperature of drying.

One of the reaction variables investigated is the reaction period. Reaction times of 2, 3, 4, 6, 7, 8 and 10 hours at 2.75 litres of molecular oxygen per minute flow rate have been used. It was found that the 4 hour reaction period at 2.75 litres per minute produced a birnessite with negligible Mn_3O_4. Therefore it was decided to investigate the lowering of the flow rate to 2 litres per minute and 1.5 litres per minute and also the use of manganese sulphate instead of chloride. The use of filter paper (both glass fibre and paper) to remove the water from the sample is also to be investigated.

The appparatus used in the production of birnessite is shown in Figure 3, and that used to dry the compounds in Figure 4

Figure 3 Apparatus used to manufacture sodium birnessite

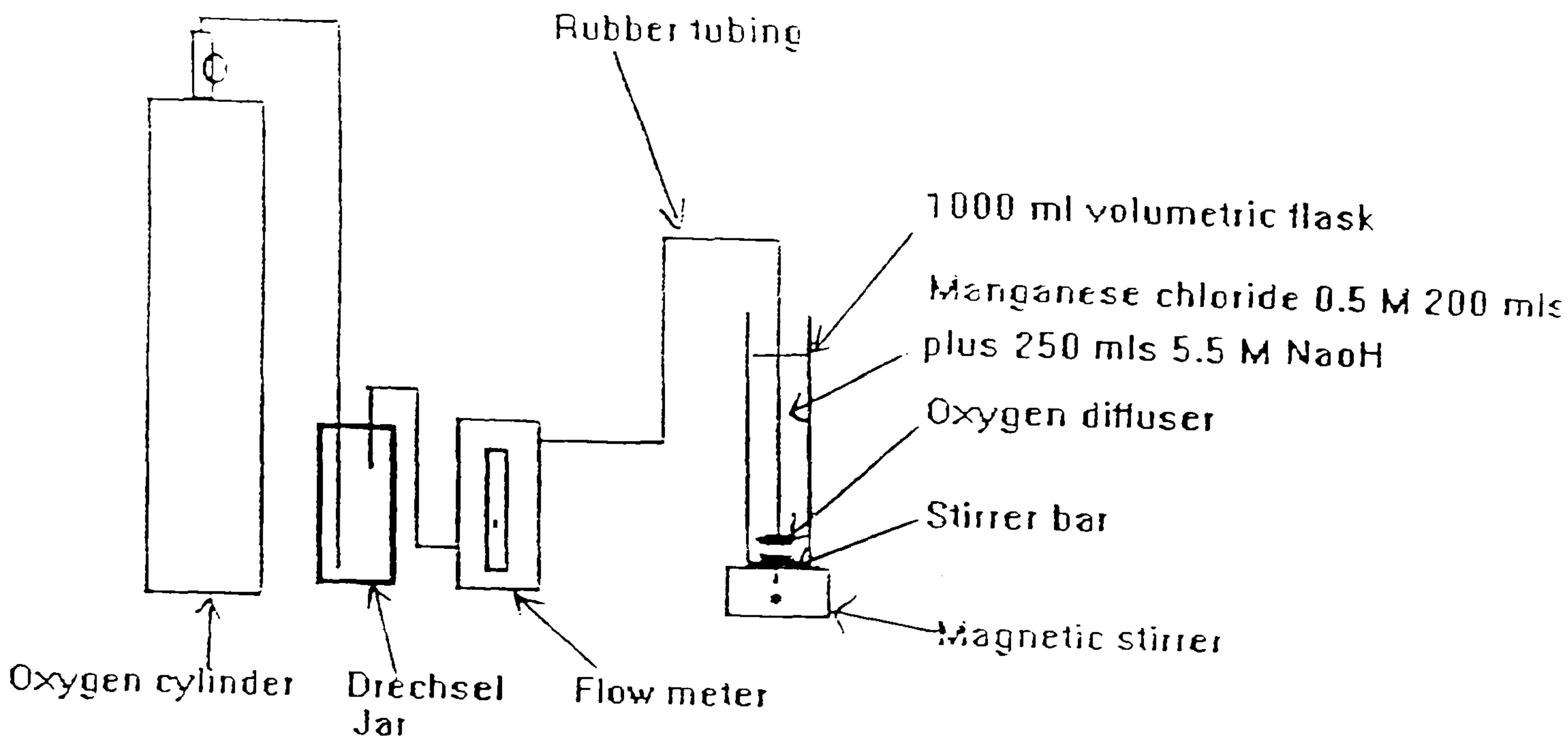
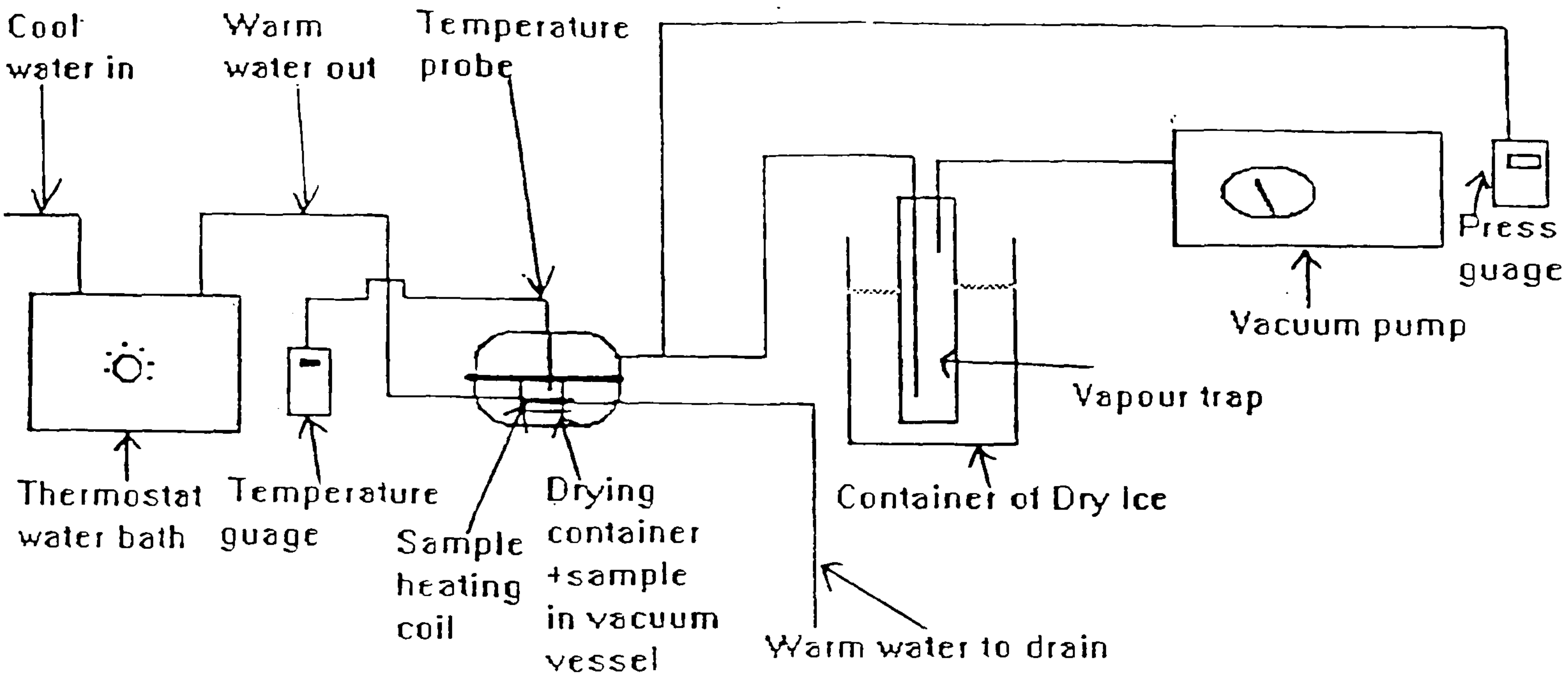


Figure 4 Apparatus used to dry sodium birnessite



The dried birnessite compounds are analysed by X-ray diffraction, to detect major impurity phases such as Mn_3O_4. The instrument used is a Phillips diffractometer, with a copper K alpha X-ray source emitting a beam of 1.5406 Angstroms wavelength.

An X-ray is an electromagnetic radiation existing between the wavelengths characteristic of gamma radiation and ultraviolet radiation and is measured in Angstroms (10^{-8}cm) (6). In comparison to visible light at 6000 Angstroms, the wavelength of X-rays used in X-ray diffraction is between 0.5 and 2.5 Angstroms (6). When X-rays hit an atom in a crystal, diffraction of the beam occurs. The degree of scattering depends on the number of electrons in the atom.

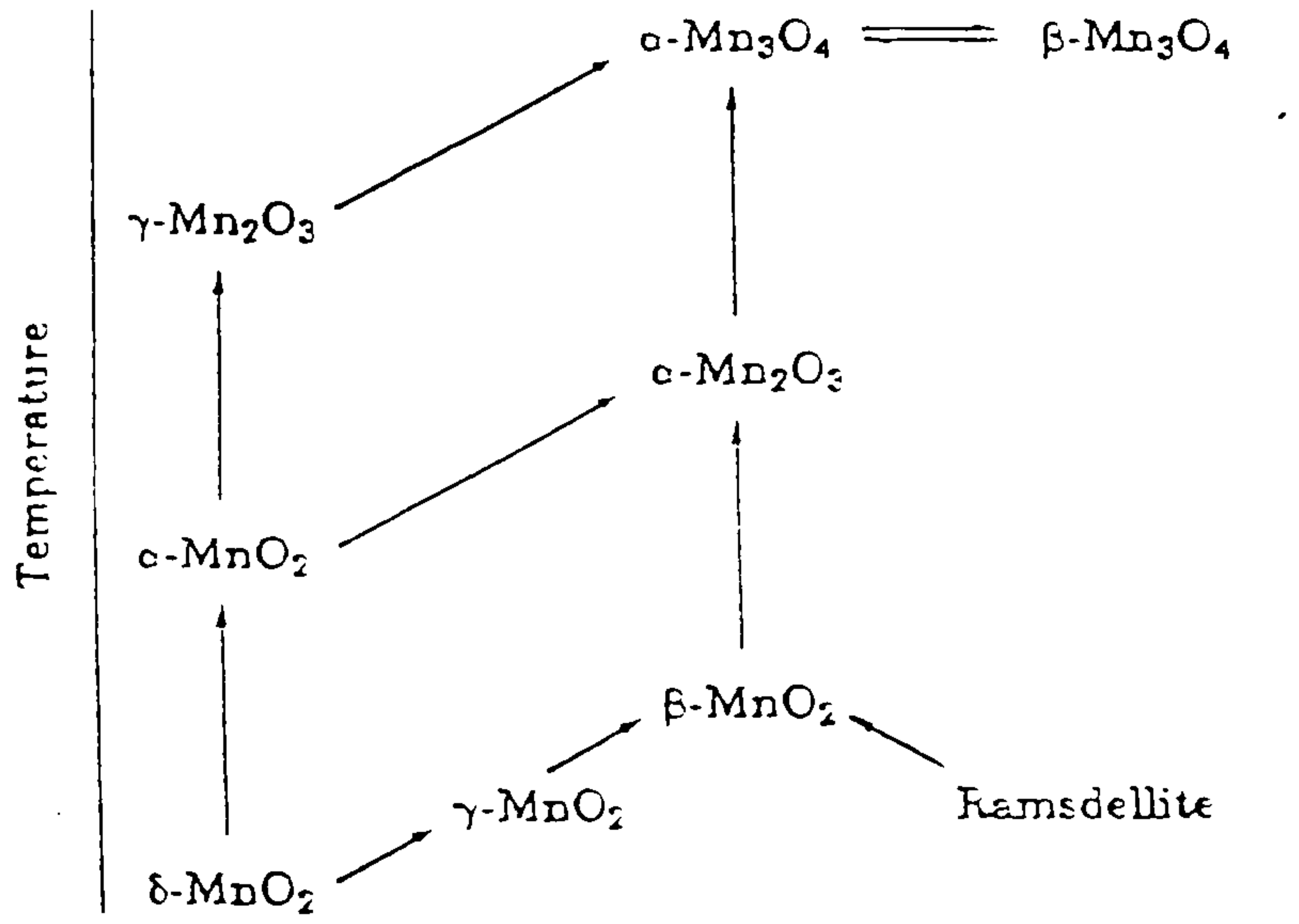
The size and symmetry of the unit cell of the atomic structure and the wavelength of the X radiation used determine the position of the diffraction beams, whilst intensity of diffracted X-rays depends on the type of atoms in the crystal and the location of the atoms in the unit cell. This principle is used to fingerprint crystalline compounds, and individual components in a mixture. The method although sometimes used quantitatively is mainly a qualitative analytical technique. (7) Unlike chemical analysis, the technique reveals the presence of crystalline compounds rather than single elements (6) The diffraction pattern (d value) produced can be compared with data of known substances until a match is found.

Data produced from the X ray analysis were compared with data from standards of chemicals likely to be in the samples. The standard data was obtained from the JCPOS powder diffraction file.

The XRD technique cannot give an accurate quantitative analysis of a mixture of solids without using standards. Therefore one of the samples seen from XRD analysis to be free of the main suspected impurity Mn_3O_4 will be analysed with a given quantity of pure Mn_3O_4 in it. The lack of a XRD peak characteristic of the Mn_3O_4 will indicate the absence of Mn_3O_4 to the detection limit (5%) of the most intense peaks in the diffraction pattern.

Addition of 0.5%, 1 % etc of Mn_3O_4 to a Mn_3O_4 free birnessite sample will create standards for determining the amount of this impurity in the sodium birnessite. Tests on the samples of birnessite by Thermogravimetric analysis have also been performed. Plots of the weight change with temperature of the dried powder indicate the purity of the sample as conversion of the birnessite to more stable oxides occurs at defined temperatures (3) The thermal decomposition of the manganese dioxide is known and can be used in Thermogravimetric analysis to ascertain the presence of contaminants in the birnessite sample produced. Figure 5

Figure 5 The thermal transformation of delta manganese dioxide to Mn_3O_4



Results so far indicate that a reaction period of 4 hours is the minimum that will produce birnessite free of Mn_3O_4, 2 and 3 hour reaction period are insufficiently long, and any reaction over 4 hours is more environmentally expensive involving greater material (oxygen) useage- and therefore less economic.

Experimental parameters that are being investigated include using manganese sulphate instead of manganese chloride. Other investigations will involve varying the volume of water used to wash the samples after production, and investigations into the use of paper filters to remove water from the sample instead of vacuum drying.

Eventually with a technique for producing birnessite at the minimum cost, economically and in raw material useage (i.e clean technology), the compound will be coated onto a high surface area solid such as perlite. Perlite is a natural, silica based igneous rock and is associated with recent volcanic activity. It is non toxic, used in the food industry for filtering fruit juices for example, insoluble and inert and therefore potentially suitable for water pollution control uses. (7) At this stage the surface coated sodium birnessite will be investigated for its properties as a pollution control agent in removing ionic species from water.

Clearly, the compound itself must not pollute the water it is treating and so the efficiency of binding onto the perlite needs careful study. Manganese is naturally found in water at about 60 micrograms per litre. (1). However, at above 20 mg/l in potable water it stains laundry grey black. Similiarly in drinking water manganese has to be below 0.5 mg/l to meet UK drinking water standards. (8). This illustrates the need for careful product development to prevent further pollution problems.

Studies have been performed to ascertain the suitability of manganese dioxide coating onto an inert filler. For example manganese dioxide coated on sand has been used to remove transition metals from solution.(9)

3 CONCLUSION

To ensure a potential pollution control agent is viable, it needs to be reproducably produced. To ensure its financial viability it also needs to be made as cheaply as possible. For example, in reducing the reaction time the amount of resources required are reduced. Studies of optimum conditions for making sodium birnessite are needed to ensure that production of the material has as small an environmental impact as possible at the manufacturing stage. Ultimately, the compound will be coated onto a stable inert solid such as natural perlite or sand. Tests on the efficiency of transition element and group II metal recovery from water will then begin. The contribution to knowledge that this research should provide is whether a reproducable quality of sodium birnessite can be used in pollution control applications.

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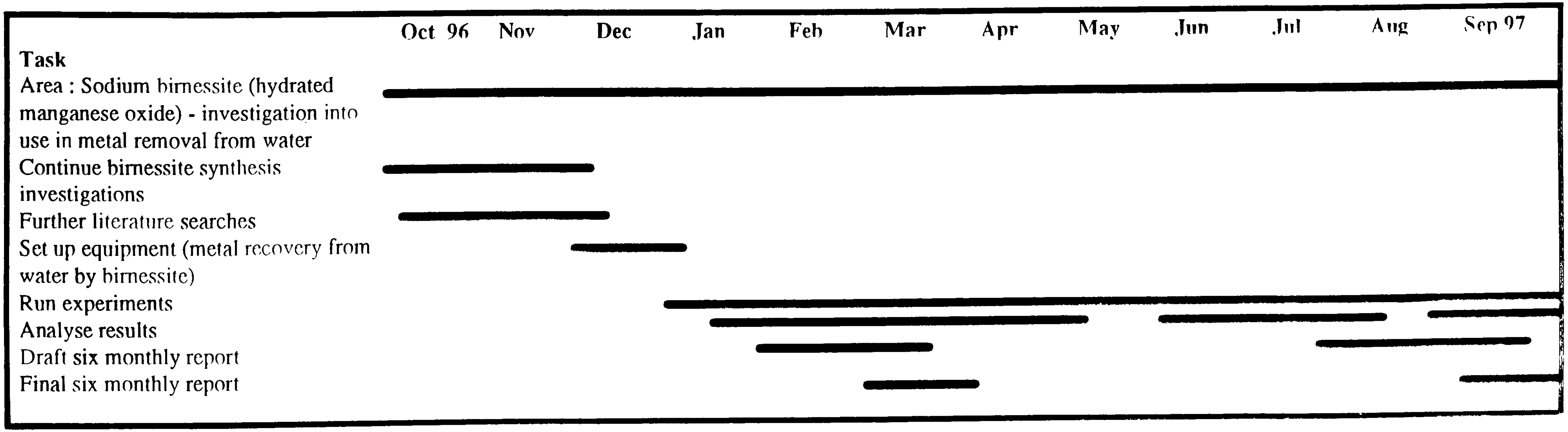
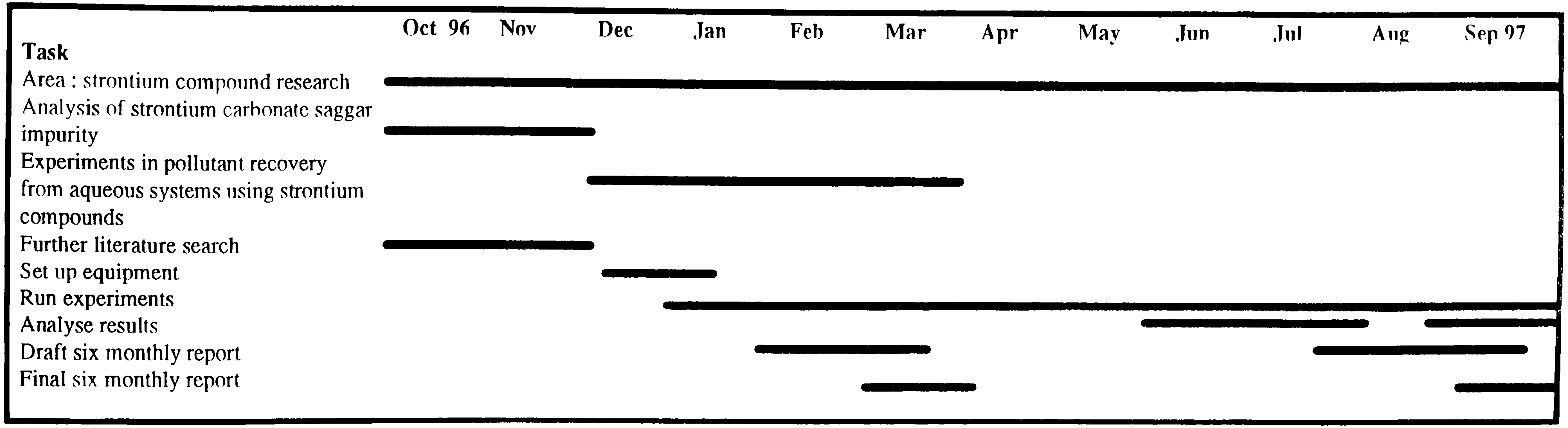
Updated project management plan (october 1996)

Project Gantt chart for October 1996 to September 1997 - manganese compound investigations (sodium birnessite)



Project Gantt chart for October 1996 to September 1997- strontium compound investigations



AN INVESTIGATION INTO POTENTIAL USES OF MANGANESE AND STRONTIUM COMPOUNDS IN POLLUTION CONTROL

ENGINEERING DOCTORATE
SIX MONTHLY REPORT - NUMBER 3 .

Andy Houlson

1st April 1997

Six monthly report

Contents

Andy Houlson, April 1997

1. Introduction

This report covers the third six month period of research undertaken from October 1996- April 1997. It details module courses attended and work performed in the last 6 months and possible future work on the two areas of this Eng.D programme; the potential uses of manganese and strontium chemicals in environmental improvement.

2. Work undertaken

Further literature and patent searches on the structure and chemistry of sodium birnessite have been performed and add to the literature sources already gathered.

Attended the one week course module "Environmental Law".

A compulsory 'elective' module 'Beginners Italian' is being studied to GCSE level.

The main area of work over the period has been on the potential ion exchange properties of sodium birnessite. These studies included:

Completion of synthesis of batch of sodium birnessite samples under the optimal conditions outlined in the previous report.

A selection of birnessite samples were chosen and mixed together to form a 'composite sample' for analysis by x-ray diffraction and thermogravimetry. This analysis shows that the method of synthesis of birnessite is reproducible..

Investigation of removal of copper from aqueous solution using sodium birnessite powder

Further analysis of strontium oxide saggar impurity for strontium levels.

3. Conclusions

Sodium birnessite synthesis is ongoing, this will continue into the next 6 month period. A composite sample of birnessite has also been prepared from samples synthesised up to this period, and characterised by x-ray diffraction and thermogravimetric analysis. Work has been performed in copper ion removal from solution using sodium birnessite. After discussion with Twinstar Chemicals and Professor Donaldson, the copper ion removal experiments have been terminated as it was believed that it would not present a satisfactory enough contribution to environmental technology due to technical problems, and superior alternatives available on the market. Investigations will now be carried out into the effectiveness of sodium birnessite in polysulphide curing where material and energy savings are possible. Work on strontium compounds will also be developed in the next period with a focus on the identification of the strontium oxide saggar impurity and on the use of strontium compounds as replacements for lead and barium compounds.

Andy Houlson, April 1997

4. Appendices

AN INVESTIGATION INTO POTENTIAL USES OF MANGANESE AND STRONTIUM COMPOUNDS IN POLLUTION CONTROL

ENGINEERING DOCTORATE
TWENTY FOUR MONTH REPORT.
(Subsuming the fourth 6 month report)

Andy Houlson

1st October 1997

This EngD research on strontium and manganese chemicals is of commercial and environmental interest because the compounds of both elements have potential applications in clean up and clean technology. The programme consists of work to identify:

(1) Methods for clean production of strontium and manganese chemicals.

(2) Uses of strontium and manganese chemicals in clean technology, potentially replacing environmentally more hazardous processes or chemicals.

(3) Uses of strontium and manganese chemicals in clean up technology to remove undesirable products from waste streams.

Twenty four month report overview

Contents Page

Andy Houlson, October 1997

1. Introduction

This report covers the first twenty four months of research undertaken for the Eng.D degree from October 1995 to October 1997. This report contains summaries on the work performed, compulsory and optional module courses attended and describes possible future work on the two areas of the overall project on uses of strontium and manganese chemicals in environmental improvement. This report subsumes the fourth six monthly report.

2. Work undertaken

Compulsory Eng.D courses attended in the two year period

1ST YEAR:

Engineering Doctorate conference

Induction week (Leadership)

Clean Technology

Project management and Life Cycle Analysis

Hands on Environmental Audit of Grundons Clinical Waste Incinerator, Hillingdon.

Sociology 1

Risk Perception

Environmental Measurement

2ND YEAR:

Engineering Doctorate conference

Risk communication

Environmental Law

Sociology 2

Advanced Leadership

Optional courses attended:

One week Scanning Electron Microscopy course at Brunel University

Brunel University Language Centre. Beginners Italian - Grade A obtained

RESEARCH CONDUCTED WITHIN THE TWO YEAR PERIOD:

The research work described was carried out in conjunction with the sponsors Twinstar Chemicals Ltd on the potential uses of strontium and manganese chemicals in environmental technology. Research has been carried out over the past two years under the following headings:

(1) Full literature and Patent searches on the structure, chemistry and uses of manganese oxide phases including sodium birnessite.

(2) Full literature and Patent searches on the structure, chemistry and uses of strontium compounds.

(3) The synthesis of sodium birnessite.

(4) The methodology for complete characterisation of sodium birnessite using x-ray diffraction, Inductively Coupled Plasma Emission Spectrometry and thermogravimetric analysis.

(5) Studies on the use of sodium birnessite to remove metals from aqueous solution.

(6) Studies on the use of sodium birnessite and a mixture of sodium birnessite and manganese dioxide ore in polysulphide curing.

(7) Studies of the nature of a glassy scale found as an impurity on the walls of a saggar vessel used to produce strontium oxide for Twinstar Chemicals Limited.

(8) Studies on the potential removal of aqueous metal ions using strontium carbonate

(9) Studies on the coating of strontium carbonate onto the mineral perlite

The work under headings (1),(2),(3),(4) and (5) have been completed although the literature data bases for (1) and (2) will be updated over the next two years. Work is continuing on projects (6) to (9)

3. Conclusions

Both strontium and manganese chemicals are a key part of the market operated by the industrial sponsors Twinstar Chemicals Limited. Both groups of chemicals are being investigated for their potential uses in clean up and clean technology processes. It is intended to continue studies on the possible uses of strontium chemicals as either replacements of the more toxic lead and barium compounds and to further investigate its role in clean up technology. Further work on the use of the manganese dioxide - sodium birnessite - in polysulphide curing will also be performed over the next two years.

Andy Houlson, April 1997

TABLE OF CONTENTS FOR 24 MONTH REPORT

IV.1 STATEMENT OF THE OVERALL AIMS AND OBJECTIVES OF THIS RESEARCH IN THE ENG.D PROGRAMME

This statement is a requirement stipulated in the EngD Course Handbook (1997-1998) section 4.4.5

Manganese and strontium chemicals are marketed by Twinstar Chemicals Limited and are of interest either in clean technology or clean up technology. *The project aim is to develop potentially marketable uses of these chemicals and clean technology processes using them in pollution control.*

The manganese compound of interest - sodium birnessite $Na_4Mn_{14}O_{27}.9H_2O$- is a naturally occurring phase based on manganese dioxide and has two potentially valuable properties - as an ion exchanger, and as an oxidising agent in polysulphide curing. These properties are, however, only shown in the synthetic material. Birnessite in its native form is saturated with ions and does not show good exchange or curing properties. A reproducible method for the synthesis of sodium birnessite has developed in the research and the product of this synthesis used to investigate the ability of the material to remove metal ions from aqueous solution and to cure polysulphides. Initial experiments performed in this period on polysulphide curing indicate birnessite is successful in this role and could replace the conventional manganese dioxide curing agent which is synthesised using a more energy intensive process than that for birnessite. The curing appears to be more reproducible than that using the current curing agent, reducing material wastage. These benefits offered by sodium birnessite represent ways in which birnessite incorporates clean technology principles. The polysulphide curing abilities will be the main focus of future research work with sodium birnessite. The sodium birnessite synthesised in this work should lead to a cleaner curing process involving less energy use and less wastage.

Strontium compounds are of interest due to their low toxicity. This means they have a potential role in clean technology and clean up technology. The overall aim of this work is to investigate

(1)The potential of the strontium compounds alone, or coated onto an inert substrate in removing water pollutants - such as metal ions and organics.

(2) To identify potential uses of strontium compounds to replace more toxic barium and lead compounds in commercial use. Barium, in the same group of the Periodic Table as strontium, is a List II substance under the EC Dangerous Substances Directive, and its replacement with strontium in various uses would be a clean technology. Similarly, lead also a List II substance, could potentially be replaced in certain applications by strontium which has common properties.

IV.1.1 Intellectual contribution:

An intellectual contribution will arise from the study of *sodium birnessite as a curing agent for liquid polysulphide*. Utilisation of sodium birnessite instead of the currently used manganese oxide should result in reduced energy usage and more reproducible production of a cured polymer and so would represent clean technology. Little work has been reported in the literature on the use of *strontium compounds in the removal of pollutants from water* or as replacements for lead. The results of such studies would provide an intellectual contribution and clean technology development.

IV.1.2 Methodological approach or approaches to be used:

The methodological approach used in the study of both manganese and strontium compounds will involve:

- Full literature search on the chemistry and uses of the compounds.

- Full Patent search on the uses of the compounds.

-Optimisation of reproducible synthetic procedures for the compounds - particularly of sodium birnessite.

-Testing potential uses of manganese and strontium compounds in the removal of pollutants from aquatic waste streams.

-Testing specific applications of manganese and strontium compounds including:

Polysulphide curing with sodium birnessite

Lead and barium replacement with strontium compounds

IV.1.3 Provisional titles and target refereed journals for two papers to be submitted by the end of the project:

(1) An investigation into the curing of a liquid polysulphide using the manganese dioxide - sodium birnessite.

Target refereed journal: Journal of Applied Polymer Science

(2) The removal of copper from aqueous solution using strontium compounds.

Target refereed journal: Journal of Chemical Technology and Biotechnology incorporating Clean Technology

IV.2 INTRODUCTION TO SPONSORING COMPANY AND INDUSTRIAL CONTEXT

IV.2.1 Twinstar Chemicals Ltd:

Twinstar Chemicals Ltd is a major marketer of a variety of chemicals. The company is based in Kenton, Harrow and is part of the S and D Group multinational. Two of the chemical types it deals with are manganese and strontium compounds. Mr Stuart Behn is the Managing Director of the company and the project industrial supervisor.

IV.2.2 The industrial context of the research:

Twinstar Chemicals Ltd are interested in developing new niches for their products. The use of manganese and strontium chemicals in clean technology and clean up technology would represent both a commercial aspect to the Eng.D, and, research into novel environmental technology applications using these chemicals. Manganese chemicals are of interest in their potential clean technology role. Sodium birnessite - a layered manganese dioxide has been shown to be an effective curing agent for liquid polysulphide. Twinstar Chemicals may be able to market sodium birnessite as a replacement or alternative to the currently used industrial curing agent.

Strontium chemicals are of particular interest as they have a very low toxicity. As a result they have a large potential use either in clean up technology - for example as illustrated by there use in removing metals from solution described in this report. They could also be used in clean technology, for instance replacing more toxic lead and barium compounds. It is clear that Twinstar Chemicals Limited could benefit if new uses for its chemicals are found.

IV.3 PROJECT PROGRESS OVER THE PREVIOUS 24 MONTHS

IV.3.1 LITERATURE REVIEW

The project has involved a thorough literature search on the background to the chemicals of interest. This included obtaining information on the physical properties, and uses of manganese oxides and strontium compounds. Literature searches on the uses of these two groups of chemicals was conducted using the Bath Information Data Services (BIDS) computerised searching system and also the on-line International Patent Search service. Chemical Abstracts was also used to locate papers on the uses of strontium and manganese oxides in pollution control. The literature documentation will be kept up to date and the final version lodged in the portfolio.

IV.3.2 THE STUDY OF THE MANGANESE DIOXIDE CHEMICAL - SODIUM BIRNESSITE

Sodium birnessite is composed of layers of MnO_6 octahedra interspersed between single water layers. It is a naturally occurring manganese dioxide that is found as one of the main manganese components of soil and deep sea manganese nodules. It is known to possess ion exchange capability and is an oxidising agent. Native sodium birnessite cannot be used as an ion exchanging compound as it is already saturated with chelated metal ions. Laboratory synthesised sodium birnessite is an active ion exchange compound, and potential oxidising agent for curing liquid polysulphides.

IV.3.2.1 Sodium birnessite synthesis:

After a full literature and Patent search, work was carried out on the synthesis of sodium birnessite. Sodium birnessite is produced by the passage of oxygen through an alkaline (sodium hydroxide) solution of manganese hydroxide. This creates *sodium buserite* $Na_4Mn_{14}O_{27}.12H_20$, which on vacuum drying is transformed to *sodium birnessite* $Na_4Mn_{14}O_{27}.9H_20$.

Variables investigated in this research on birnessite synthesis included:

(1) Reaction time

(2) Manganese chemical used as starting material- manganese sulphate monohydrate or manganese chloride tetrahydrate

(3) Flow rate of oxygen used

(4) Use of centrifuge or use of filter paper for separating sodium buserite from reaction solution

(5) Number of hours of drying of sodium buserite for conversion to sodium birnessite

Optimisation of the synthesis in the research included investigation of the effect on reproducible birnessite production using different starting ingredients. These included using manganese chloride tetrahydrate, or manganese sulphate monohydrate as starting materials. Both compounds were found to be suitable in the synthesis of a reproducible quality of sodium birnessite. However, financial considerations were critical, and manganese sulphate monohydrate (32.5 % manganese) at £600 per tonne is 5 times cheaper than manganese chloride tetrahydrate (27.8% manganese) at £3000 per tonne (Twinstar Chemicals Limited- February 1997 figures) and so was used in preference.

During the project, the reaction time was also investigated with periods ranging from 2 to 10 hours. The optimum period for reproducible synthesis of sodium birnessite was found to be 4 hours. The optimum flow rate of oxygen into the reaction vessel was found to be 2.75 litres per minute which was sufficient to reproducibly synthesise birnessite. The reaction was kept at room temperature. Economically, the minimum amount of time for the reaction and the minimum oxygen flow rate are the ideal.

Once the sodium buserite has been precipitated in the reaction vessel, it needs to be separated from its aqueous surroundings. Two possibilities were investigated- centrifuging and washing in deionised water, or, filtering through Whatman 541 hardened ashless filter paper. Centrifuging of the product resulted in a reproducible quality of sodium birnessite. Filtration proved to be unsuccessful because it lead to contamination of the product with other manganese oxides-Mn_2O_3. This is due to the longer contact time with air in the filtration process

After the buserite precipitate had been separated from the supernatant it was dried under vacuum to form birnessite. The sample cannot be heated as it decomposes to other manganese oxides such as Mn_2O_3. The total amount of time required to dry the sample under vacuum at between 1 and 30 °C was a minimum of 8 hours. Freeze drying was a potential option, however, it is more expensive than drying under vacuum and therefore disregarded. It is easy to detect incomplete drying of the product as x-ray diffraction (XRD) analysis identifies incomplete conversion of the sodium buserite to sodium birnessite.

IV.3.2.2 The optimum synthesis of sodium birnessite defined in this research:

Within a 1 litre polypropylene measuring cylinder, 250 ml of a 5.5 Molar NaOH solution (55g of NaOH) was added to 200 ml of a 0.5 Molar (16.89 g) solution of manganese sulphate monohydrate. Oxygen was bubbled through the solution using a porosity grade 1 glass frit at a rate of 2.75 litres per minute for 4 hours. After the four hour reaction period, the solution was poured into four 250 ml polypropylene centrifuge bottles and the samples centrifuged for 5 minutes. The supernatant liquor was discarded, the precipitate washed in double deionised water and mixed with 200 ml of double deionised water before centrifuging it again. The centrifuging and cleaning procedure was repeated 5 times to remove excess alkalinity. The damp precipitate was then placed in an open polypropylene container and the sample vacuum dried for at least 8 hours at a temperature above freezing and below 30 °c to prevent birnessite decomposition. The temperature was monitored using a thermocouple and the drying was achieved using a vacuum pump. The drying procedure converts the precipitated sodium buserite into the desired end product of the synthesis, sodium birnessite.

IV.3.2.3 Characterisation of sodium birnessite by x-ray diffraction

All samples of sodium birnessite were analysed using XRD. The data obtained (see Appendices in previous six month reports) were compared to standard powder diffraction file data to ascertain the components present in the birnessite. The choice of XRD as the analytical technique was based on its ability to detect the presence of crystalline compounds in a sample, sodium birnessite being a monoclinic structure can be detected as can sodium buserite and other manganese oxides.

IV.3.3.1 CHARACTERISATION OF SYNTHESISED SODIUM BIRNESSITE BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY

This work was performed within the last 6 months of the EngD research period.

A 100g batch of sodium birnessite was assembled in the research. This was a composite of samples of sodium birnessite prepared during the period that was sieved through a stainless steel 89 micron mesh using an Endecott test sieve shaker. The composite sample of sodium birnessite was analysed for its sodium and manganese content. Analysis was performed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES). The instrument used was a Perkin Elmer 40 Plasma Emission Spectrometer.

IV.3.3.2 Introduction to Plasma Emission Spectrometry

Atomic spectrometry is the most common technique for analysis of trace levels of elements. Atomic emission occurs when an atom either collides with another particle such as an electron, or by absorbing electromagnetic radiation. Excitation of the atom occurs when an electron in its ground state is promoted to a higher energy level further from the nucleus. Returning to its ground state, the atom emits a photon. If the atom absorbs sufficient energy, then the electron is ejected and a positively charged ion results in a process called ionization.

The difference in energy between an upper and lower energy level of a radiative transition will define the wavelength involved in that transition. Each element has its own characteristic absorption and emission wavelengths.

Atomic emission spectrometry involves molecular dissociation into atoms and ionization of the sample elements. The ions or atoms in their excited state then decay to their stable state and emit photons. The emission of particular wavelengths of light is used to determine the elements concentration.

In Plasma Emission Spectrometry, dissociation and excitation occur in a high temperature gas plasma. A plasma is "any form of matter that contains an appreciable fraction (>1 %) of electrons and positive ions in nearly equal numbers, in addition to atoms and neutral molecules" (Boss and Fredeen 1989).

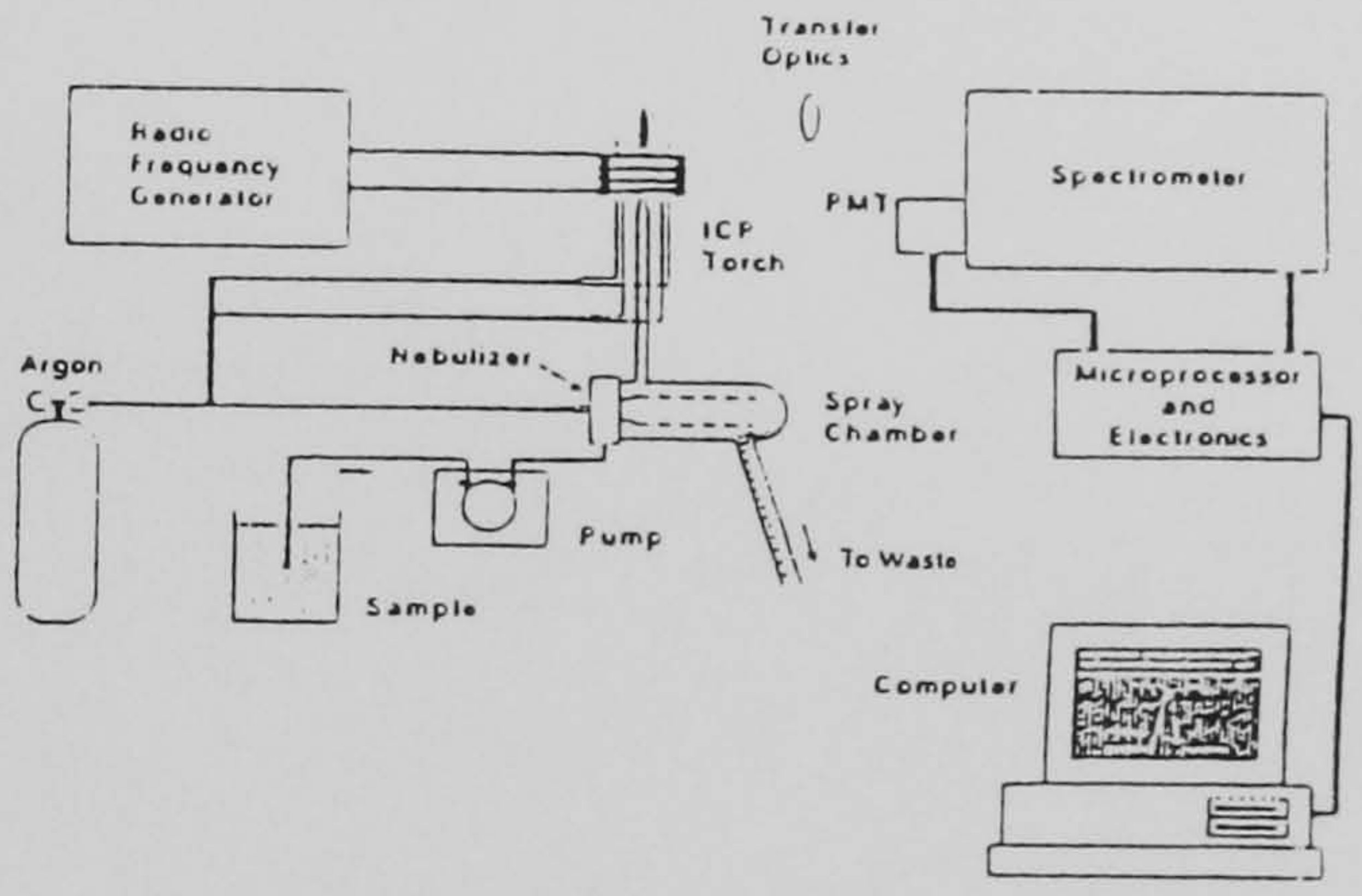
Analysis of sodium birnessite was carried out by argon supported Inductively Coupled Plasma Emission Spectrometry. The instrument relies on argon gas passing through three concentric tubes of quartz, or another similar material. Surrounding the top end of the torch is a copper coil through which radio frequency power of 700-1500 watts is passed. The oscillation caused by the alternating current (at 27 or 40 megahertz) causes radiofrequency magnetic and electric fields to be set up in the top of the torch. When a spark is passed through the gas, some electrons are stripped from the argon. The electrons are then accelerated by the magnetic field. This addition of energy to the electrons is termed Inductive Coupling. When these electrons collide with other argon atoms, further electron stripping results. This chain reaction leads to a brilliant white plasma of argon atoms, argon ions and electrons - the Inductively Coupled Plasma. (Boss and Fredeen 1989)

Samples are introduced into the flame as an aerosol by nebulization and carried to the flame centre by the argon flow. The hot plasma desolvates the aerosol leaving a salt which is then vaporized into a gas and dissociated into atoms. The atoms are then excited and ionized by the collision of analyte atoms with high energy electrons. A benefit of the high temperature flame (6000 ° c in the plasma centre) compared to other atomic emission processes is that the efficiency of excitation and ionization is increased. Furthermore, many chemical interferences found in flames and furnaces are reduced or eliminated. (Boss and Fredeen 1989)

The emission from the sample is then detected. As the excited species in the plasma emit several -polychromatic- wavelengths, these must be separated into individual lines using a monochromator. This permits the identification and measurement of each species without interference from other emission wavelengths. The emissions are captured in a photomultiplier tube. Sample identification is enabled by elements characteristic emission wavelengths, whilst concentration is determined using calibration curves. (Boss and Fredeen 1989). Figure 1 shows the components of an ICP-AES.

Figure 1 The major components of ICP-AES

(Boss and Fredeen 1989)



The technique of ICP-AES can be used to quantitatively and qualitatively analyse 70 elements at levels under 1 milligram per litre. .

IV.3.3.3 Results

	Manganese content	Sodium content
Replicate 1	54.6	6.01
Replicate 2	54.7	6.10
Mean	54.7	6.06

IV.3.3.4 Discussion

The theoretical level of sodium in sodium birnessite is 6.32%. and for manganese 52.86 %. These results by ICP-AES analysis are in accordance with the expected levels of the elements in sodium birnessite.

IV.3.4 USE OF SODIUM BIRNESSITE AS A POLYSULPHIDE CURING AGENT

This research was performed during the last 6 month period from April 1997 to October 1997. Sodium birnessite was used in studies of the curing of polysulphide rubbers. Morton LP32 C liquid polysulphide was cured with sodium birnessite as the active curing agent as an alternative to other commercial manganese oxide phases for which curing is not always reliable. The research has involved studying the effect on polysulphide curing rate of adding different quantities of sodium birnessite to the liquid polysulphide. A study on the effect of adding sodium birnessite mixed with an inert filler - natural manganese dioxide ore has also shown that the curing rate can be controlled by varying the percentage of birnessite with natural ore. The greater the percent of birnessite the more rapid the curing.

The investigation involves studying the reaction between a curing agent - sodium birnessite and a polysulphide. The reaction is measured rheologically and the viscosity calculated in centipoises. (1 mPa.s - millipascal second is equal to one centipoise). Viscosity is the measure of internal friction of a fluid. The greater the friction, the greater the shear or force to move this fluid in relation to another layer. (Brookfield (a) undated)

IV.3.4.1 Introduction to polysulphides

A polysulphide or thioplast / elasto thiomer is a special purpose rubber, and is the oldest commercial rubber in production. Polysulphides contain no carbon to carbon double bonds and consist of chains of organic sections, and sections which contain more than one sulphur atom. They are important commercially due to their high resistance to oil, solvents, oxygen and ozone. The main use of polysulphides is for double glazing, with smaller uses as aircraft sealants and in construction applications. (Kirk Othmer 1995)

The liquid polysulphide polymer investigated is Morton LP32C manufactured by Thiokol/Chemical division. It is a polymer of 1.2.3 trichloropropane and 1.1'-[methylenebis(oxy)]bis (2-chloroethane) reduced with sodium sulphide (Na_2Sx) and has an average molecular weight of 4000. At the end of the polymer segments are mercaptan -SH groups, representing 2% of the polysulphide. It is these mercaptan groups which are converted into disulphide S-S bonds by the curing agent. (Morton undated) At 25 ^{o}c, LP32 has a viscosity of 470 Poise and specific gravity of 1.29. It has the composition:

$$HS\text{-}(C_2H_4\text{-}O\text{-}CH_2\text{-}O\text{-}C_2H_4\text{-}Sx)_{23}\text{-}C_2H_4\text{-}O\text{-}CH_2\text{-}O\text{-}C_2H_4\text{-}SH$$

The sodium birnessite composite prepared in this work was added in various quantities to 8 micron milled natural manganese dioxide ore (pyrolusite). The natural ore does not react with the polysulphide. Sodium birnessite is shown to be the active curing agent and the oxidation reaction of the liquid polysulphide is by chain extension with the oxidising agent:

2R-SH	+	O	->	R-S-S-R	+H_2O
Liquid polysulphide with mercaptan terminal		Oxidizing agent		Disulphide product	

A material sold under the description 'Active manganese dioxide' is used in industry to cure the LP-32 polysulphide at the ratio of 100 parts polymer to 7.5 parts of manganese dioxide. (Morton undated). The sodium birnessite used in this work was prepared in the same ratio for comparison.

IV.3.4.2 Measurement of sample viscosity using the Brookfield Viscometer

This section of the research was performed within the current 6 month period from April 1997 to October 1997.

Sample viscosity was measured in this research as the work life of sodium birnessite cured liquid polysulphides. The work life (application time) is the period during which a curing mix is still soft enough to be re-worked after application to a substrate. The time for a polysulphide sample to cure to a viscosity of 12,000 Poise was chosen as the period of study of work life.

The instrument used to measure viscosity in this work was a dial reading viscometer. Viscosity is measured from the torque required to rotate a stainless steel spindle immersed to a marked level in the sample. The spindle is turned by a synchronous motor through a calibrated spring. Sample viscosity is displayed by a pointer position on a rotating dial, where the spring deflection is indicated by the pointer. The resistance to flow of the spindle increases proportionately with increasing spindle speed. Resistance also depends on the spindle size and shape. The greater the sample viscosity the greater the deflection of the spring.

The reading is from 0 to 100 and five speeds are available to ensure that the reading can be kept within this range. A reading over 100 means a lower spindle rotation speed needs to be selected, below 10, a higher speed needs to be selected. The instrument gives a scale reading of 0-100, however the reading has to be multiplied by a factor depending on the model of viscometer, the spindle and speed combination used. The viscometer is accurate to within +/- 1 % of the spindle/speed combination in use, whilst the reproducibility is to within +/- 0.2%. According to Brookfield (b) (undated) viscosity measurements should involve controlling or specifying the following parameters:

(1) Test temperature
(2) Sample container size
(3) Sample volume
(4) Viscometer model
(5) Spindle used
(6)Test speed or speeds
(7) Length of time or number of spindle revolutions to record viscosity
These parameters have been observed in the following experiments.

IV.3.4.3 Experimental

Approximately 180 g of LP32C was accurately weighed into a plastic cup placed in a water bath held at constant temperature (20-25 °c). The mixture was stirred electrically with a glass rod to ensure the polymer was at the temperature of the bath. Varying mixtures of sodium birnessite and natural manganese dioxide were prepared by grinding them together in a mortar and pestle for 10 minutes to homogenise the mixture. The powder was stirred into the mixture with the electric stirrer, the time noted, and the mixture further stirred for exactly 10 minutes. About 5 g of the manganese oxide and polysulphide reaction mixture was poured from the cup into a plastic weighing vessel and left for one week to measure its hardness and to determine whether the surface was tacky to touch after this time.

The viscosity of the polysulphide manganese oxide mixture was measured every 5 minutes (or longer if the curing reaction proceeded over many hours) using a Brookfield Viscometer with cylindrical spindle number 7. The end point of each reaction was taken as being a sample viscosity of greater than 12,000 centipoise. For very slow reactions containing little (5%) of the oxidising agent sodium birnessite, the reaction was recorded only up to 3 hours (reaching 4000 poise). Mixtures of 5 %, 10 %, 20 % and 30 % sodium birnessite were added to a balance of natural manganese dioxide ore. In every experiment the total amount of birnessite and natural ore was 7.5% of the total weight of the polysulphide. An experiment was also performed using 100% sodium birnessite (no natural manganese dioxide ore added). Additional experiments were performed using a mixture of 10 % of the currently used "active manganese dioxide" curing agent in a balance of (90 %) natural manganese dioxide ore. These experiments were performed to compare the reproducibility of curing liquid polysulphide with sodium birnessite and liquid polysulphide with the "active manganese dioxide".

IV.3.4.4 Results

(1) Sodium birnessite is a very rapid curing agent of liquid polysulphide LP32 - too fast for commercial use.

(2) The material sold as "Active manganese dioxide" is an unreliable curing agent. Using the same "active manganese dioxide" results in variable cure rates.

(3) Sodium birnessite plus inactive natural manganese dioxide ore is a reliable curing agent.

The data is included in the Appendices.

IV.3.4.5 Discussion of results

Sodium birnessite is an effective curing agent. The liquid polysulphide was cured very rapidly using 100 % sodium birnessite (within 10 minutes to 40,000 centipoise) whilst 5 % sodium birnessite mixed with 95 % natural manganese dioxide ore added to liquid polysulphide showed a slower polysulphide oxidation reaching 4000 centipoise in 3 hours. Natural manganese dioxide was unable to cure polysulphide. As was shown with the experiments involving 10%, 20 % and 30 % birnessite, the smaller the birnessite content of the birnessite /natural manganese dioxide ore mix, the slower the curing reaction.

IV.3.4.6 Hardness testing of cured polysulphide samples

Seven days after the experiments were performed, a hardness test was performed on each of the samples poured into the plastic weighing vessels. A CV Instruments Analog Durometer was used to measure the sample hardness at room temperature. The instrument was first calibrated on a CV instruments Durometer calibration block.

The rubber sample in the plastic weighing vessel was placed on a horizontal, flat, hard surface. The Durometer was held vertically ensuring the point of the indenter was kept at least 12mm from any edge of the test specimen. The presser foot was applied to the test specimen with the foot kept parallel to the surface and sufficient pressure applied to ensure firm contact. A reading on the dial was taken after applying pressure for three seconds and readings were taken in triplicate. An assessment was made as to the tackiness of the surface. The end point at which time a sample of cured polysulphide reaches a desired optimum tensile strength or hardness is known as the cure time. An acceptable value according to Goldblatt (personal communication) is between 30 and 40 Shore A hardness. Except for the reaction between natural manganese dioxide ore and polysulphide where no curing was observed, all the experiments involving a sodium birnessite / natural ore mixture resulted in a curing to hardness of over 30 Shore A within 7 days.
See Appendices of this report for data.

IV 3.4.7 Conclusions

Sodium birnessite is found to be a very rapid curing agent. This offers a benefit as the amount of sodium birnessite required to cure the polysulphide can be reduced (to 10 %) and a cheaper filler such as natural manganese dioxide ore can be added as the balance (90%) to the polysulphide / birnessite mixture.

The use of sodium birnessite as a curing agent would represent clean technology. Sodium birnessite production would use less raw materials and energy to produce than the currently used oxidising agent which is prepared using a high temperature process. Sodium birnessite synthesis undertaken earlier in the Eng.D showed that it could be prepared successfully at room temperature. The process for synthesising the currently used curing agent in contrast involves heating a manganese solution under pressure. this clearly would involve large energy expenditure. Utilising sodium birnessite as a polysulphide curing agent instead of the current curing agent would represent a clean technology if successful due to reduced energy usage in preparing the curing agent for liquid polysulphides.

Sodium birnessite use would also represent a clean technology as only a small amount of the birnessite has to be used in the curing process (10 % in a balance of natural manganese dioxide ore) as pure birnessite is an extremely rapid curing agent. Another clean technology benefit of using birnessite is that curing of the polysulphide with sodium birnessite appears to be more reproducible than when the currently marketed curing agent is used. A more reproducible curing would be valuable industrially as less wasteage would occur from polysulphides that failed to cure within the time required for their particular application. A reduction in waste at source represents a clean technology benefit of using sodium birnessite.

IV.3.5 INVESTIGATIONS INTO THE REMOVAL OF COPPER IONS FROM SOLUTION USING SODIUM BIRNESSITE

IV.3.5.1 Summarised experimental

Because sodium birnessite has potential ion exchange capacity, investigation into the removal of copper ions from solution was performed. Portions of 0.1g of the batch of sodium birnessite were added to 100 ml of a 100 ppm copper solution. The solution pH and temperature were measured and the concentration of copper in solution measured after a given contact period. The measurement of copper levels was by Atomic Absorption Spectroscopy. The results are as follows:

IV.3.5.2 Summarised Results

Removal of copper from solution using sodium birnessite suspension

Reaction number	Weight of Birnessite added (g)	Start concn Cu (ppm)	Final concn Cu (ppm)	% Metal removal	Reaction time (hours)	Start pH	End pH
1	0	90	90	0	18	4.26	4.25
2	0.1037	90	35	61	18	4.26	4.98
3	0.1020	90	37.5	58	18	4.18	4.94
4	0.1018	90	40	55	18	4.23	4.96
1	0.1007	90	22.5	75	24	4.57	5.03
2	0.1036	90	20	78	24	4.60	5.12
3	0.1008	90	10	88	24	4.79	5.30
1	0.1098	90	12.5	86	40	4.60	5.23

2	0.1093	90	22.5	75	40	4.54	5.00
3	0.1046	90	25	72	40	4.54	4.92

IV.3.5.3 Discussion

The experiments indicate sodium birnessite is effective at removing copper from solution at this concentration and pH. The experiments however were discontinued after discussion with Professor Donaldson and Twinstar Chemicals Limited for the following reasons:

(1) Removal of the finely powdered birnessite from solution after metal removal is difficult as the birnessite is in a slurry form.

(2) Sodium birnessite is pH sensitive, dissolving in acidic conditions releasing manganese ions.

(3) Manganese ions are released into solution when metal ions exchange onto sodium birnessite.

(4) Alternative metal removal / recovery techniques such as ion exchange resins seem to be more competitive than sodium birnessite in this particular field of environmental technology - as metals can be recovered, the resin reused, and specific resins can be used over a wide range of pH values.

IV.3.6 IDENTIFICATION OF SCALE IMPURITY FOUND ON SAGGAR VESSEL USED TO PRODUCE STRONTIUM OXIDE FROM STRONTIUM CARBONATE

IV.3.6.1 Introduction

Work has been conducted on the identification of an impurity that causes a grey coloured scale to form on the inside of saggar vessels used for strontium carbonate conversion to strontium oxide. The strontium oxide is produced by Thermograde in Staffordshire, and the reason for the formation of the scale is unknown. The impurity formation means a reduction in efficiency of strontium oxide manufacturing process, and therefore a financial and environmental loss. Identifying the impurity in an attempt to avoid its formation would represent cleaner technology. The saggar vessel impurity was analysed by chemical and physical methods. These include Dionex ion chromatography, volumetric titrations, gravimetric analysis, x-ray diffraction, thermogravimetry and x-ray fluorescence. The following information was gained:

IV.3.6.2 Summarised results

Table 1 Analysis of the strontium oxide impurity for its components

Sample component	Method of detection	Present in sample %
Strontium	Titration	64.05
Sodium	Dionex Ion chromatography	0.14
Iron	Dionex Ion chromatography	0.65
Zinc	Dionex Ion chromatography	0.02
Lead	Dionex Ion chromatography	1.2

Cadmium	Dionex Ion chromatography	0.10
Manganese	Dionex Ion chromatography	0.48
Insolubles	Gravimetric analysis	14.23
Total		80.87

Analysis by thermogravimetry of various samples of strontium carbonate showed the presence of an impurity in some of the samples - a reversible DTA peak at between 855 and 858 ^{0} c (shown in bold) in Table 2

Table 2 Table from six month report number 1 detailing the presence of DTA peaks

Sample Number	Onset Temp of weight loss (^{0}C)	First DTA peak Temp(^{0}C)	Second DTA peak temp(^{0}C)	Initial Sample weight (mg)	Final Sample weight (mg)	Actual weight loss % (from graph)	Theoretical weight loss (mg)*
95/383	860	-	930	22.68	16.10	27.5	29.8
95/589	884	**855**	918	21.61	15.36	28.0	29.8
95/597	847	-	923	22.21	15.79	28.5	29.8
96/598	844	-	923	23.46	16.84	28.0	29.8
96/600	852	**857**	929	20.26	14.78	27.0	29.8
96/603	860	**858**	929	21.25	15.42	27.2	29.8
92/109	876	-	926	20.94	15.07	27.0	29.8
Precipitated SrCO3	852	-	929			27.5	29.8

IV.3.6.3 Discussion:

Research is continuing on this project to fully determine the nature of the impurity. Further results will be reported in future 6 monthly reports.

IV.3.7 REMOVAL OF METAL IONS FROM AQUEOUS SOLUTION USING STRONTIUM CARBONATE

IV.3.7.1 Introduction

Research has been conducted by Suzuki et al (1991) into the effectiveness of calcium carbonate in removing metal ions from solution. Trivedi (1997) has also investigated the removal of lead ions from solution by strontium carbonate. It was decided to investigate using strontium carbonate as an exchange compound for other metals in solution.

IV.3.7.2 Experimental

A 100 ppm solution of copper as copper sulphate was prepared. Into a 250 ml polypropylene centrifuge bottle was placed 100 ml of the copper solution. To this was added 0.5g of strontium carbonate. The pH and temperature was measured using a calibrated Mettler Delta 320 pH meter. The samples were then agitated on a flask shaker for three hours. Aliquots of 10 ml of the samples were taken. These were analysed for copper content by flame Atomic Absorption. Samples were taken at periods of 1 hour through the reaction. The strontium carbonate was added as a very fine powder

Strontium carbonate powder size:

<38 microns = 97.5%
38-50 microns= 0.8 %
50-75 microns =1.5 %
75-100 microns= 0.1 %
100-125 microns =0.1%

IV.3.7.3 Results

Experiment to investigate removal of copper from solution using 1 g strontium carbonate and

100 ml 100 ppm Cu as copper sulphate

Weight of strontium carbonate Replicate 1= 1.0165g Replicate 2 =1.0160 g

Time (hours)	Copper content (ppm) Replicate1	Sample pH	Copper content (ppm) Replicate 2	Sample pH	Copper content Average (ppm)
0	90	6.13	90	6.12	90
1	5	6.65	2.5	6.61	3.75
2	0	6.96	0	6.87	0
3	0	7.01	0	7.04	0

Experiment to investigate removal of copper from solution using 0.5 g strontium carbonate and 100 ml 100 ppm Cu as copper sulphate

Weight of strontium carbonate Replicate 1= 0.5009g Replicate 2 =0.5063 g

Time (hours)	Copper content (ppm) Replicate1	Sample pH	Copper content (ppm) Replicate 2	Sample pH	Copper content Average (ppm)
0	90	5.92	90	5.96	90
1	5	6.31	7.5	6.36	6.25
2	0	6.63	2.5	6.69	1.25
3	0	6.84	0	6.96	0

Experiment to investigate removal of copper from solution using 0.25 g strontium carbonate and 100 ml 100 ppm Cu as copper sulphate

Weight of strontium carbonate Replicate 1= 0.2517 g Replicate 2 = 0.2537g

Time (hours)	Copper content (ppm) Replicate 1	Sample pH	Copper content (ppm) Replicate 2	Sample pH	Copper content Average (ppm)
0	90	5.06	90	5.00	90
1	5	5.65	2.5	5.62	3.75
2	2.5	6.27	2.5	6.22	2.5
3	2.5	6.35	0	6.24	1.25

Experiment to investigate removal of cadmium from solution using 0.25 g strontium carbonate and 100 ml 100 ppm Cd as cadmium sulphate

Weight of strontium carbonate Replicate 1= 0.2539 g Replicate 2 = 0.2549g

Time (hours)	Copper content (ppm) Replicate 1	Sample pH	Copper content (ppm) Replicate 2	Sample pH	Copper content Average (ppm)
0	81.4	5.68	81.4	5.66	81.4
1	16.2	6.18	15.6	6.13	15.9
2	10.2	6.32	11.6	6.27	10.9
3	7.1	6.44	7.7	6.38	7.4

Experiment to investigate removal of cadmium from solution using 0.75 g strontium carbonate and 100 mls 100 ppm Cd as cadmium sulphate

Weight of strontium carbonate Replicate 1= 0.7534 g Replicate 2 = 0.7519g

Time (hours)	Copper content (ppm) Replicate 1	Sample pH	Copper content (ppm) Replicate 2	Sample pH	Copper content Average (ppm)
0	81.4	5.63	81.4	5.68	81.4
1	12.7	6.24	12.6	6.29	12.65
2	9.2	6.28	8.8	6.30	9.0
3	5.9	6.34	6.8	6.38	6.36

IV.3.7.4 Discussion

Strontium carbonate seems to be effective in removing metals from solution at the pH values studied. The effect of the strontium carbonate on copper in dilute solution is likely to be exchange precipitation. Strontium carbonate has a solubility of 0.0011g / 100 ml at 25 °c , although the corresponding copper carbonate is less soluble. Exchange precipitation will therefore result in the replacement of Sr^{2+} in the carbonate lattice with Cu^{2+}.

A slurry method for removing metals from solution would not be suitable for industrial use due to the difficulty of removing the powder from the solution. A new technique had therefore to be developed and the possibility of coating of the strontium carbonate onto an inert stable substrate to investigate the potential use of the carbonate in a column system was investigated.

IV.3.8. COATING OF STRONTIUM CARBONATE ONTO AN INERT MINERAL SUBSTRATE

IV.3.8.1 Introduction

The mineral perlite was investigated as a possible substrate on which to coat the strontium carbonate. Perlite is a mineral associated with volcanic activity up to 65 million years ago within the Tertiary and Quaternary periods, and is a glassy rock formed when lava flows, dykes and sills, cool rapidly and trap water and gases within them.(Langford 1979)

Most perlites are pitchstone or obsidian, and have between 1 to 10 % water content which results in the rock expanding on heating. Crude Perlite is grey, brown or black in colour. On heating the mineral to between 800 and 1000°c, to its expanded form, it is white coloured and has a bulk density three to thirty five times less than the original. (Langford 1979)

In industry, expanded perlite is used in acoustic and thermal insulation, filtration of fruit juices, as a filler in plasterboard, and as an absorbent of small oil spills in refineries. The benefits of perlite stem from its inert and stable nature. It is rot proof, not attractive to vermin, and does not degenerate in most conditions according to Langford (1979). Its solubility is under 1% in water and weak acids, and less than 3 % in concentrated mineral acids.

IV.3.8.2 Experimental:

Aldrich natural mined perlite beads were sieved using on brass sieves using a Gallenkamp shaker and the beads between 1.18 and 2.0 mm were selected. The chemical composition of the Aldrich perlite used was as follows:

Oxygen=47.5%
Silicon= 33.6%
Aluminium=7.2%
Potassium=3.5%
Sodium=3.4%
Bound water=3.0%
Magnesium=0.7%
Calcium=0.6%
Iron=0.5%
Traces=0.2%

A slurry of strontium carbonate in water was prepared using 10.0057g of strontium carbonate in 40 ml of double deionised water. To this was added 5.0019g of the 1.18 to 2.0 mm perlite beads. The mixture was simultaneously rotated and dried at 80 °c in a water bath under vacuum until the perlite beads were totally coated in the dried slurry.

The strontium carbonate coated perlite was compared with uncoated perlite using Scanning Electron Microscopy. Sample preparation for Electron Microscopy involved sticking the samples on double sided sticky tape to a 1 cm square SEM stud. The samples were gold plated in a Polaran Equipment SEM coating unit E5000. The Scanning Electron Microscope used was a JEOL JXA 840A Electron Probe Microanalyser.

IV.3.8.3 Results

Photographs of the surfaces of the coated and uncoated surface show that strontium carbonate had successfully covered the perlite surface. Analysis by the Energy Dispersive x-ray analysis equipment of the Electron microscope revealed that the strontium carbonate has coated the surface.

Figure 1 Natural perlite surface detailed under Scanning Electron Microscopy

30 x magnification

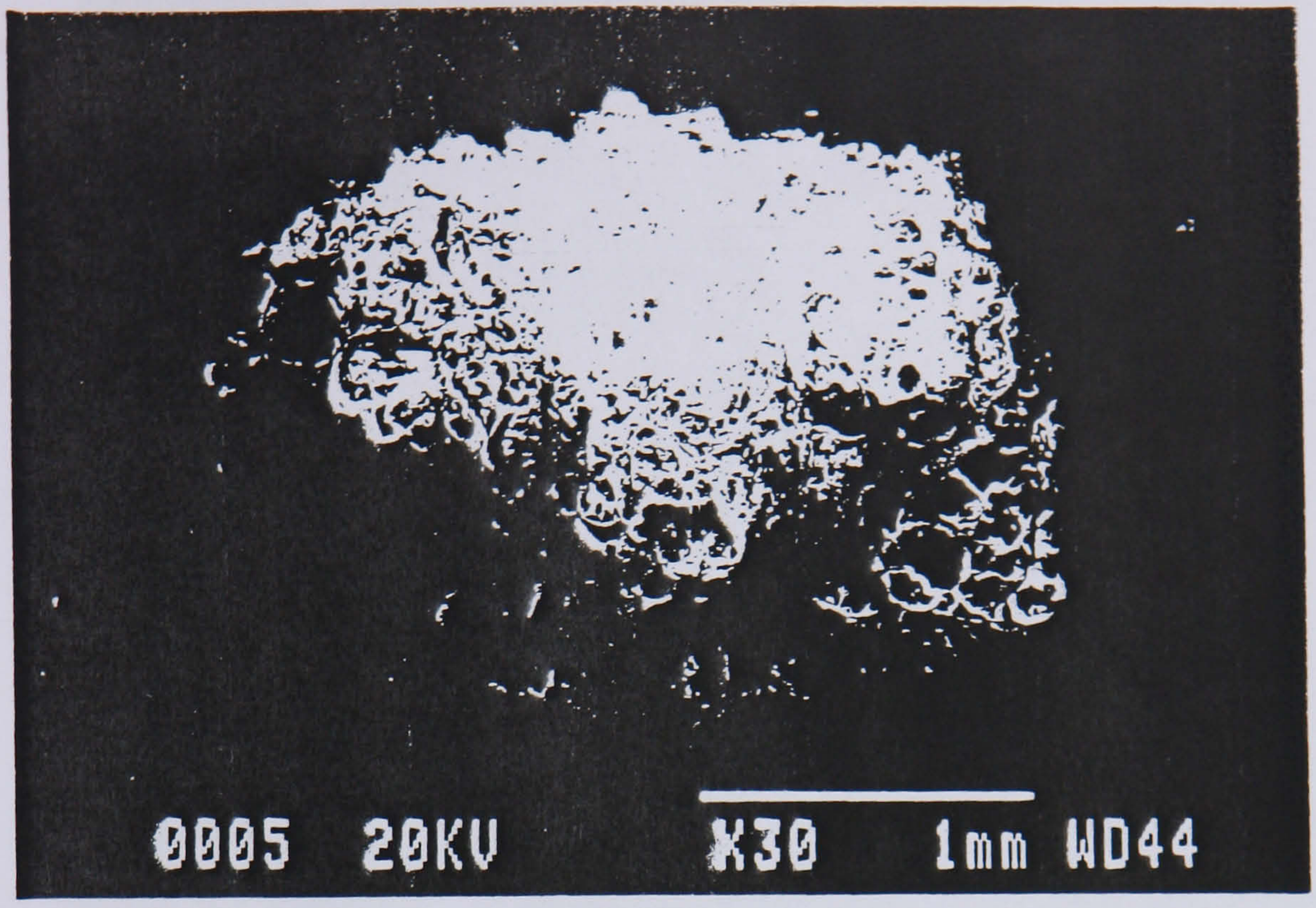


Figure 2 Perlite surface after coating with strontium carbonate

30 x magnification

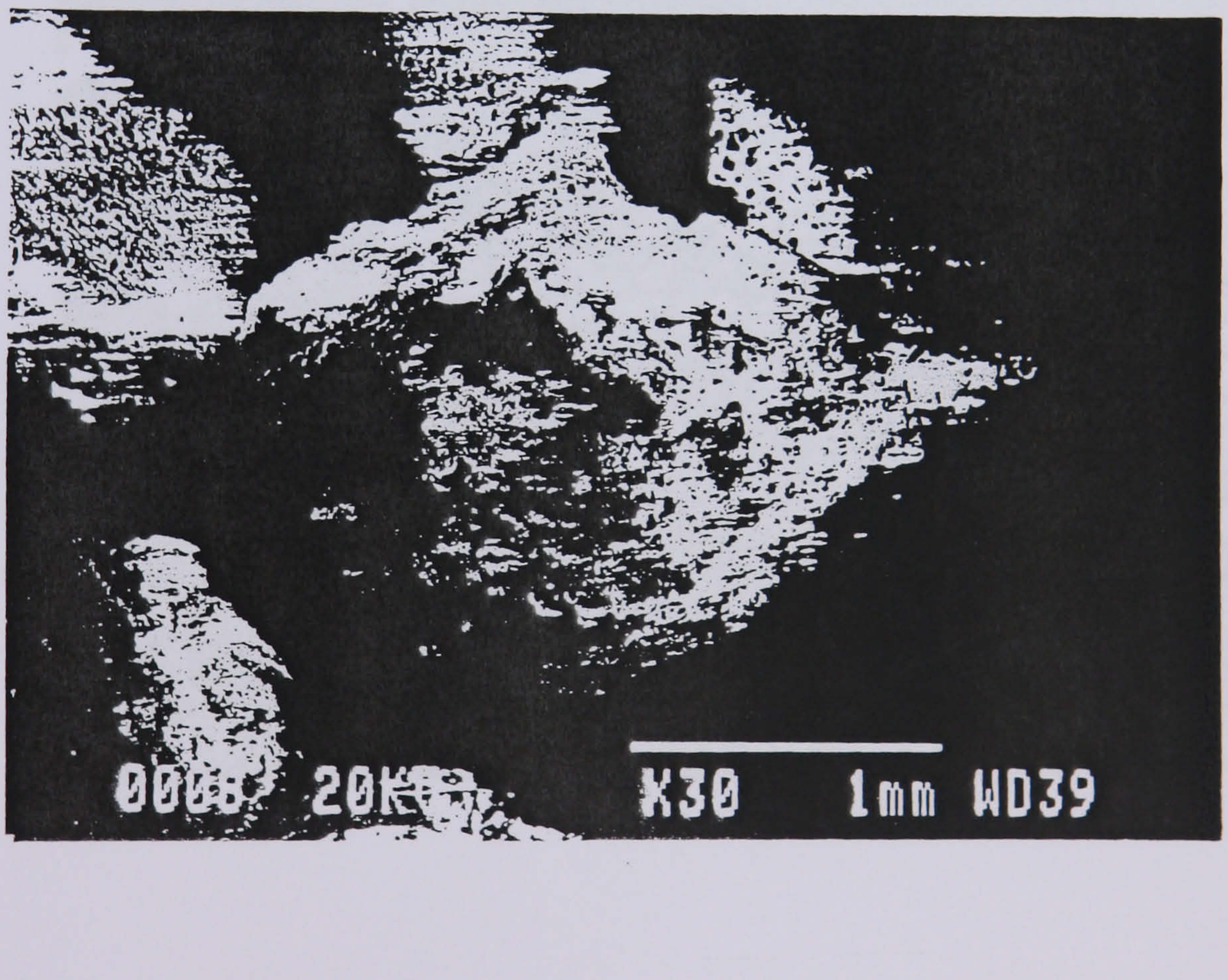
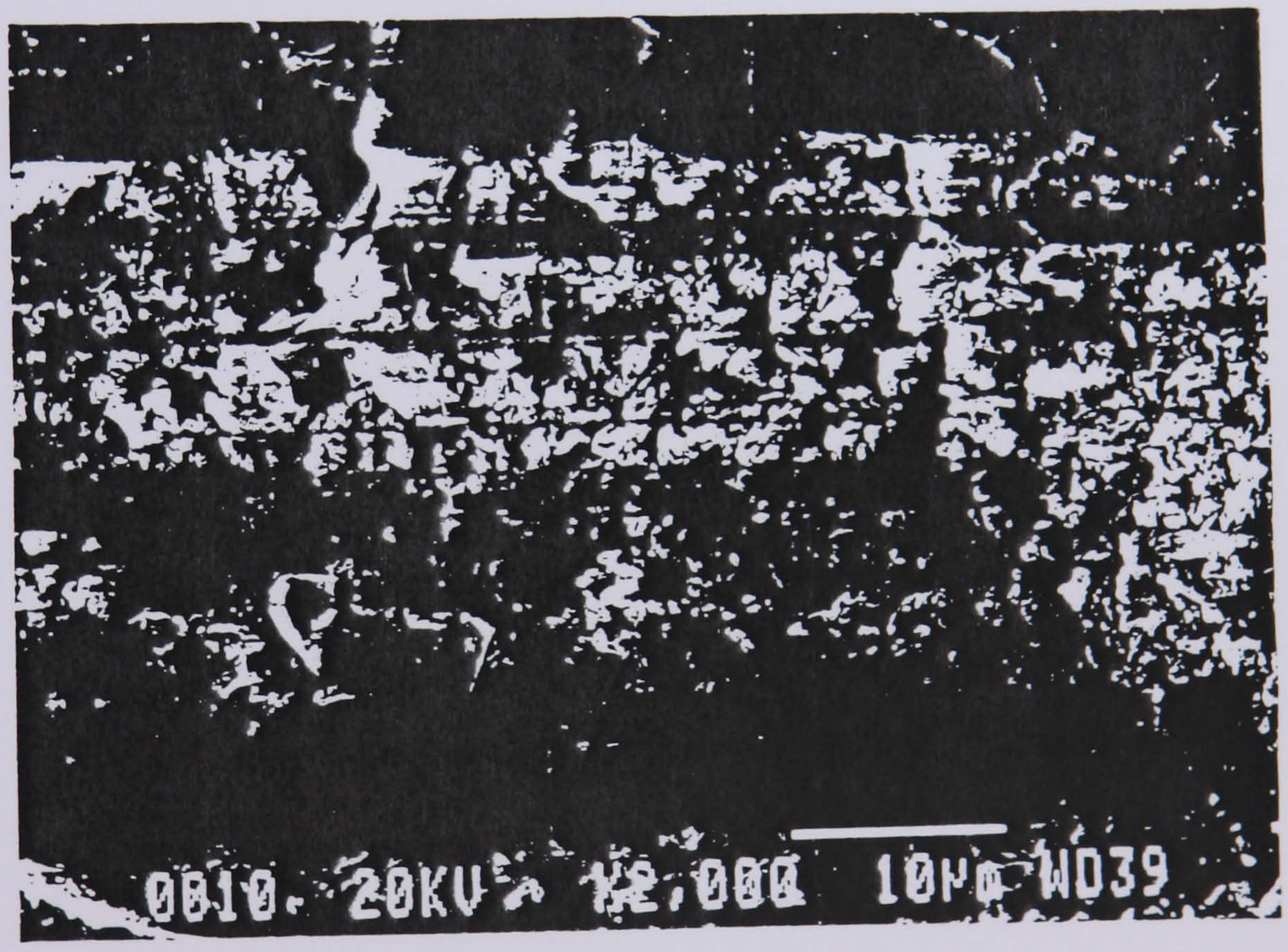


Figure 3 Natural perlite surface detailed under Scanning Electron Microscopy

2000 x magnification

Figure 4 Perlite surface after coating with strontium carbonate

2000 x magnification



IV.3.8.4 Discussion

The electron micrographs appear to indicate a successful coating of strontium carbonate onto the perlite surface. This will be confirmed in the next six month report by Energy Dispersive x-ray analysis to indicate the degree of coating. Further study will be conducted onto the possible use of the strontium carbonate coated beads for removing metal ions from solution

IV.3.9 OVERALL SUMMARY

Work has been undertaken on two chemicals, manganese dioxide and strontium carbonate. The investigation into the synthesis of sodium birnessite has been completed in the period. In synthesising birnessite, consideration has been given to economics. This includes the decision to use manganese sulphate instead of manganese chloride, and using drying under vacuum instead of filtering or freeze drying. Furthermore, study into the minimum reaction time, and minimum oxygen flow rate into the reaction vessel has been conducted. This has ensured a minimal financial investment and environmental impact through minimal use of oxygen.

A study has been performed on the use of sodium birnessite in clean up technology to remove metals from aqueous solution. The use of the synthesised sodium birnessite as a curing agent for polysulphides has also been investigated. Varying the quantities of sodium birnessite as the oxidising agent with natural manganese dioxide ore has resulted in a controllable curing time, either virtually instantaneously with pure sodium birnessite or longer with natural manganese dioxide ore added as a diluent. Twinstar Chemicals Limited are interested in marketing a manganese based polysulphide curing agent that can be used instead of the currently used and expensive curing agent, sodium birnessite mixed with varying quantities of natural MnO_2 ore seems to meet Twinstar Chemical Limited's requirements.

The investigation into the formation of an impurity on the side of saggar vessels used for producing strontium oxide is being performed too. The impurity represents a waste material and a financial loss as the strontium oxide yield is reduced. Identification of the impurity will represent a step forward in clean technology as it may suggest where the impurity originates from.

Studies have been performed into the efficiency of strontium carbonate in removing metal ions from water. The compound is effective at removing copper and cadmium from solution at pH 5-6. Strontium carbonate has also been coated onto an inert substrate. Both the removal of copper and cadmium from solution, and the successful coating of strontium carbonate onto perlite are novel. The coating of strontium carbonate onto perlite using a rotary evaporator technique has been studied using Scanning Electron Microscopy and Energy Dispersive x-ray analysis.

IV.4 SUMMARY OF INTENDED RESEARCH FOR THE REMAINDER OF THE REGISTRATION PERIOD

Work intended for the remaining period include further studies on the use of sodium birnessite as a potential clean technology replacement for the currently used manganese oxide curing agent. The use of strontium compounds in metal ion removal from solution, and an investigation into the replacement of barium compounds with less hazardous strontium compounds will also be carried out. Work is intended to continue on identifying strontium chemicals that could have potential in clean up technology.

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Experiment involving the curing of liquid polysulphide using only sodium birnessite.

Weight of liquid polysulphide=180.6920g. Weight of sodium birnessite = 13.501g. Weight of natural manganese dioxide ore = 0 g (Total weight of sodium birnessite = 7.5 % of weight of polysulphide) Water bath temp=25°c

Time Minutes	Spindle RPM	Viscometer dial reading	Multiplication Factor	Viscosity (centipoise)
Start	-	-	-	-
15	2	100	400	40,000

Experiment involving the curing of liquid polysulphide using a mixture of 30 % sodium birnessite and 70 % natural manganese dioxide ore

Weight of liquid polysulphide=180.2152g.

Weight of sodium birnessite= 4.0595g Weight of natural manganese dioxide ore = 9.4675 g (Total combined weight of sodium birnessite and manganese dioxide ore = 7.5 % of weight of polysulphide) Water Bath temp = 25°c

Time minutes	Spindle RPM	Viscometer dial reading	Multiplication Factor	Viscosity (centipoise)
Start	-	-	-	-
15	50	96	16	1536
20	20	100	40	4000
25	10	86	80	6880
30	5	73.5	160	11760
35	5	99.5	160	15920

Experiment involving the curing of liquid polysulphide using a mixture of 30 % sodium birnessite and 70 % natural manganese dioxide ore

Weight of sodium birnessite= 4.0457g Weight of natural manganese dioxide ore = 9.4662 g (Total combined weight of sodium birnessite and manganese dioxide ore = 7.5 % of weight of polysulphide)

Weight of liquid polysulphide=180.2514g. Water Bath temp = 24^{0}c

Time minutes	Spindle RPM	Viscometer dial reading	Multiplication Factor	Viscosity (centipoise)
Start	-	-	-	-
20	20	55	16	880
25	10	90	80	7200
30	5	72	160	11520
35	5	67	320	21440

Experiment involving the curing of liquid polysulphide using a mixture of 20 % sodium birnessite and 80 % natural manganese dioxide ore

Weight of sodium birnessite= 2.704 g Weight of natural manganese dioxide ore =10.813 g (Total combined weight of sodium birnessite and manganese dioxide ore = 7.5 % of weight of polysulphide) Polysulphide weight=180.2498g. Water bath temp =25^{0}c

Time minutes	Spindle RPM	Viscometer dial reading	Multiplication Factor	Viscosity (centipoise)
Start	-	-	-	-
15	50	85	16	1360
20	20	52	40	2080
25	20	63.5	40	2540
30	20	87	40	3480

35	20	100	40	4000
40	10	61.5	80	4920
45	10	72	80	5760
50	10	84	80	6720
55	10	96	80	7680
60	5	58	160	9280
65	5	65	160	10400
70	5	71.5	160	11440
75	5	78.5	160	12560
80	5	86	160	13760

Experiment involving the curing of liquid polysulphide using a mixture of 20 % sodium birnessite and 80 % natural manganese dioxide ore

Weight of sodium birnessite= 2.709 g Weight of natural manganese dioxide ore =10.8316 g (Total combined weight of sodium birnessite and manganese dioxide ore = 7.5 % of weight of polysulphide). Polysulphide weight=180.6402g. Water bath temp =24 ^{0}c

Time minutes	Spindle RPM	Viscometer dial reading	Multiplication Factor	Viscosity (centipoise)
Start	-	-	-	-
30	20	64	40	2560
35	20	75	40	3000
40	20	91	40	3640
45	10	56	80	4480
50	10	63	80	5040
55	10	72	80	5760
60	10	81	80	6480
65	10	90	80	7200

70	5	51	160	8160
75	5	57	160	9120
80	5	62.5	160	10000
85	5	67	160	10720
90	5	72	160	11570
95	5	77	160	12320

Experiment involving the curing of liquid polysulphide using a mixture of 10 % sodium birnessite and 90 % natural manganese dioxide ore

Weight of sodium birnessite=1.3547 g Weight of natural manganese dioxide ore=12.1974 g (Total combined weight of sodium birnessite and manganese dioxide ore = 7.5 % of weight of polysulphide). Polysulphide weight=180.6848g. Water bath temp=24^{0}c

Time minutes	Spindle RPM	Viscometer dial reading	Multiplication Factor	Viscosity (centipoise)
Start	-	-	-	-
30	50	80	16	1280
35	50	96	16	1536
40	20	58	40	2320
45	20	65	40	2600
50	20	70	40	2800
55	20	77	40	3080
60	20	94	40	3760
65	20	98	40	3920
70	10	54	80	4320
75	10	59	80	4720
80	10	64	80	5120

85	10	68	80	5440
90	10	78	80	6240
95	10	82.5	80	6600
100	10	87.5	80	7000
105	10	92	80	7360
110	5	50	160	8000
115	5	53	160	8480
120	5	59	160	9440
125	5	61.5	160	9840
130	5	64	160	10240
135	5	65.5	160	10480
140	5	68	160	10880
145	5	70.5	160	11280
150	5	73.5	160	11760
155	5	75.5	160	12080

Experiment involving the curing of liquid polysulphide using a mixture of 10 % sodium birnessite and 90 % natural manganese dioxide ore

Weight of sodium birnessite=1.3542 g Weight of natural manganese dioxide ore=12.1896g (Total combined weight of sodium birnessite and manganese dioxide ore = 7.5 % of weight of polysulphide). Polysulphide weight=180.5916g. Water bath temp=24^{o}c

Time minutes	Spindle RPM	Viscometer dial reading	Multiplication Factor	Viscosity (centipoise)
Start	-	-	-	-
20	50	87	16	1392
25	20	46	40	1840

30	20	55.5	40	2220
35	20	69.5	40	2780
40	20	89.5	40	3580
45	20	100	40	4000
50	10	51.5	80	4120
55	10	54	80	4320
60	10	57	80	4550
65	10	63.5	80	5080
70	10	70	80	5600
75	10	75	80	6000
80	10	82.5	80	6600
85	10	88.5	80	7080
90	5	48	160	7680
95	10	50	160	8000
100	5	53.5	160	8560
105	5	57	160	9120
110	5	63.5	160	10160
115	5	68	160	10880
120	5	72	160	11520
125	5	74.5	160	11920
130	5	80	160	12800

Experiment involving the curing of liquid polysulphide using a mixture of 5 % sodium birnessite and 95 % natural manganese dioxide ore

Weight of sodium birnessite = 0.6770 g Weight of natural manganese dioxide ore=12.8311g (Total combined weight of sodium birnessite and manganese dioxide ore = 7.5 % of weight of polysulphide). Polysulphide weight=180.1004g.

Water Bath temp =23^{o}c

Time minutes	Spindle RPM	Viscometer dial reading	Multiplication Factor	Viscosity (centipoise)
Start	-	-	-	-
25	50	56	16	896
30	50	63	16	1008
35	50	69	16	1104
40	50	77	16	1232
45	50	84	16	1344
50	20	36.5	40	1460
55	20	40	40	1600
60	20	42	40	1680
65	20	44.5	40	1780
70	20	46	40	1840
75	20	49	40	1960
80	20	51.5	40	2060
85	20	53	40	2120
90	20	54.5	40	2180
95	20	57	40	2280
100	20	59	40	2360
105	20	61.5	40	2460

110	20	65	40	2600
115	20	67.5	40	2700
120	20	69.5	40	2780
125	20	72	40	2880
130	20	75	40	3000
135	20	77	40	3080
140	20	79	40	3160
145	20	81	40	3240
150	20	83	40	3320
155	20	85	40	3400
160	20	87	40	3480
165	20	90	40	3600
170	20	91	40	3640
175	20	94	40	3760
180	20	100	40	4000

Experiment terminated due to very slow cure rate.

Experiment involving the curing of liquid polysulphide using natural manganese dioxide ore

Weight of sodium birnessite = 0 g Weight of natural manganese dioxide ore=13.5037g (Total combined weight of sodium birnessite and manganese dioxide ore = 7.5 % of weight of polysulphide). Polysulphide weight=180.0198 g.

Water Bath temp =23^{o}c

Time minutes	Spindle RPM	Viscometer dial reading	Multiplication Factor	Viscosity (centipoise)
Start	-	-	-	-

20	20	14.5	40	580
25	20	14.5	40	580
30	20	14.5	40	580
35	20	14.5	40	580
40	20	14.5	40	580
45	20	14.5	40	580
50	20	14.5	40	580

Experiment terminated as no curing evident

Experiment involving the curing of liquid polysulphide using natural manganese dioxide ore

Weight of sodium birnessite = 0 g Weight of natural manganese dioxide ore=13.5037g (Total combined weight of sodium birnessite and manganese dioxide ore = 7.5 % of weight of polysulphide). Polysulphide weight=180.0496g.

Water Bath temp =23^{o}c

Time minutes	Spindle RPM	Viscometer dial reading	Multiplication Factor	Viscosity (centipoise)
Start	-	-	-	-
20	20	14.5	40	580
25	20	14	40	560
30	20	14	40	560
35	20	14	40	560
40	20	14	40	560
45	20	14	40	560
50	20	14	40	560

Experiment terminated as no curing evident

DATA FOR 'SHORE A' HARDNESS MEASUREMENTS:

Sample mixture	Hardness Reading 1	Hardness Reading 2	Hardness Reading 3	Average hardness
100 % sodium birnessite 0% Natural MnO_2 ore	NA	NA	NA*	NA*
30 % sodium birnessite 70% Natural MnO_2 ore	41	39	40	40
20 % sodium birnessite 80% Natural MnO_2 ore	37	40	37	38
10 % sodium birnessite 90% Natural MnO_2 ore	43	41	43	42.3
5 % sodium birnessite 95% Natural MnO_2 ore	41	40	40	40.3

* The hardness reading for 100 % sodium birnessite 0% natural manganese dioxide ore was not possible to take as the polysulphide mixture cured solid within the 10 minutes required to electrically stir the mixture at the start of the experiment. A sample could therefore not be poured into a weighing vessel for Shore A hardness measurement

AN INVESTIGATION INTO POTENTIAL USES OF MANGANESE AND STRONTIUM COMPOUNDS IN POLLUTION CONTROL

ENGINEERING DOCTORATE
SIX MONTHLY REPORT - NUMBER 5.

Andy Houlson

1st April 1998

This EngD research on strontium and manganese chemicals is of commercial and environmental interest because the compounds of both elements have potential applications in clean up and clean technology. The programme consists of work to identify:

(1) Methods for clean production of strontium and manganese chemicals.

(2) Uses of strontium and manganese chemicals in clean technology, potentially replacing environmentally more hazardous processes or chemicals.

Andy Houlson, April 1998

Six month report overview

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Andy Houlson, April 1998

1. Introduction

This report covers the six months of research undertaken for the Eng.D degree from October 1997 to April 1998. This report contains summaries on the work performed, the compulsory module course attended and describes possible future work on the two areas of the overall project on uses of strontium and manganese chemicals in environmental improvement.

2. Work undertaken

Compulsory Eng.D course attended:

Risk management

Research

Research has been carried out over the past 6 months under the following headings:

(1) Further literature and Patent searches on the structure, chemistry and uses of manganese oxide phases including sodium birnessite.

(2) Further literature and Patent searches on the structure, chemistry and uses of strontium compounds.

(3) Studies on the use of both sodium birnessite and the best currently available manganese dioxide curing agent "BCACA" as well as mixture of sodium birnessite, "BCACA" and various manganese dioxide, strontium carbonate, and calcium carbonate fillers in LP32C polysulphide curing.

3 Conclusions

Both strontium and manganese chemicals are a key part of the market operated by the industrial sponsors Twinstar Chemicals Limited. Both groups of chemicals are being investigated for their potential uses in cleaner technology processes. Due to greater potential for environmental benefits, and the increasing market for polysulphides as sealants, research work in this period will now focus on the use of both strontium and manganese chemicals in the curing of liquid polysulphides. The current problem with the use of manganese oxide based curing agents for polysulphides is the large percentage of failures. No efficient curing agents have been developed that achieve a high curing success rate. The result is a considerable generation of waste and loss of raw material.

The research detailed in previous six month reports investigating the nature of a scale produced in the thermal conversion of strontium oxide from strontium carbonate has been suspended. The research into the use of strontium compounds to remove pollutant ions from aqueous solution has also been suspended. This narrowing of the Eng.D research will enable greater focus on the potential role of both manganese and strontium chemicals in polysulphide curing as suggested from comments made by the external examiner in the 24 month viva.

APPENDIX

TABLE OF CONTENTS FOR SIX MONTH REPORT APPENDICES

V.1 INTRODUCTION TO THE INVESTIGATION INTO POLYSULPHIDE CURING USING VARIOUS MANGANESE, STRONTIUM AND CALCIUM CHEMICALS

Previous work was concerned with the synthesis and properties of sodium birnessite. This has been extended over the past 6 months to an investigation into the efficiency of sodium birnessite in curing liquid polysulphide LP32C. Even though sodium birnessite requires less resources to produce than the best currently available curing agent "BCACA", it must also be able to cure liquid polysulphides effectively. This research aims to contribute to environmental technology knowledge by comparing the curing capabilities of sodium birnessite with BCACA.

Natural ground manganese dioxide ores (8 μm) were investigated as the filler material. Sodium birnessite and the commercially used curing agent BCACA were diluted with the inert ores to compare curing efficiency, one week hardness, and tack state after 1 week. It was also decided to investigate the effect on curing, hardness and tackiness of using a battery grade manganese dioxide which was manufactured for Twinstar Chemicals Ltd by autoclaving natural manganese dioxide ore with sodium hydroxide.

Most strontium compounds are known to have a low toxicity. Using an inert strontium compound as a filler could represent a contribution to environmental technology and knowledge. Precipitated strontium carbonate was chosen for this part of the study because precipitated calcium carbonate is widely used as a filler material with LP32C (Lucke 1994) Studies of the use of precipitated calcium carbonate (1μm) were also carried out under identical conditions as that used for strontium carbonate as a comparison with the strontium carbonate.

V.1.1 Experiments to study the effect of various curing agents, fillers and their mixtures on the curing of LP32C

Studies were performed in this period to investigate the curing activity of sodium birnessite and BCACA. To the 180 g of LP32C polysulphide were added 13.50 g of the curing agent mixture. Of this 13.50g, 10 % (1.35g) was the curing agent and 90% (12.15g) was the filler. The rate of curing, cure hardness after 7 days, and cure tackiness were determined as described in previous reports. The activity of the fillers were also determined in the same manner using 13.50g of filler in 180g of LP32C. Mixtures of fillers and active curing agents were then studied to assess their effect on the rate of curing, cure hardness and tackiness. The pH of additives, such as the curing agents and fillers, used in the polysulphide mixture is an important factor as alkalinity increases the rate of polysulphide curing whilst acidity reduces the rate of curing. The pH of the samples of filler and curing agent were measured as a 10 % slurry of sample in deionised water (1g of powder in 10 ml of water). The pH was measured using a Kent Electronic Instruments Limited 3050 pH meter. It should be borne in mind that when considering these results, the preparation for each experiment during this research period, and the viscosity tests themselves are time consuming.

V.2 RESULTS

Data on the effect of undiluted (no addition of filler) curing agents on LP32C have been obtained and the results are shown in Table 1. The data in Table 2 show the effects on curing of adding various fillers to LP32C while the effects of mixing various curing agents and manganese dioxide fillers on the curing of LP32C are described in Table 3. The data in Table 4 show the effects on LP32C curing of adding precipitated strontium carbonate and precipitated calcium carbonate fillers to manganese dioxide curing agents. The pH of the curing agents and fillers in 10 % slurries and the fillers in a 10 % slurry in deionised water are given in Table 5 and 6 respectively.

Table 1 The effect of manganese dioxide curing agents *alone* on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (13.5g in 180g LP32C)	**Filler (0g in 180g LP32C)**	**Filler Treatment**	**Cure time in minutes to 12000 poise with 0% curing agent**	**Cure time in minutes to 12000 poise with 100% curing agent**	**Shore A Hardness after 7 days**	**Tack state after 7 days**
Sodium Birnessite "composite"	None	None	-	<20	Not measured *	Tack free
BCACA	*None*	*None*	-	*<20*	*Not measured* *	*Tack free*

Notes:

* The hardness was not determined as the polysulphide mixture had cured so rapidly it did not present a flat surface required on which to use the Shore A Durometer

Table 2 The effect of manganese dioxide and strontium compound fillers *alone* on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (1.35 g in 180g LP32C)	**Filler (12.15g in 180g LP32C)**	**Filler Treatment**	**Cure time in minutes to 12000 poise with filler**	**Shore A Hardness after 7 days**	**Tack state after 7 days**
None	*Strontium carbonate "96/600"*	Untreated	(1) - (2) -	(1) 0 (2) 0	(1) Tacky (2) Tacky
None	MnO_2 *"IMINI 80"*	Untreated	(1) - (2) -	(1) 0 (2) 0	(1) Tacky (2) Tacky
None	MnO_2 *"No 14"*	Untreated	(1) - (2) -	(1) 0 (2) 0	(1) Tacky (2) Tacky
None	MnO_2 *"No 5"*	Autoclave +Alkali	(1) - (2) -	(1) 24 (2) 31	(1) Tacky (2) Tacky

- No increase in viscosity within 60 minutes as measured by Brookfield Viscometer

Table 3 The effect of manganese dioxide curing agents *mixed* with different manganese dioxide fillers on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (1.35 g in 180g LP32C)	**Filler (12.15g in 180g LP32C)**	**Filler Treatment**	**Cure time in minutes to 12000 poise with 10% curing agent**	**Shore A Hardness after 7 days**	**Tack state after 7 days**
Sodium Birnessite "Composite"	MnO_2 "No 5"	Alkali	(1) 80 (2) 80	(1) 31.5 (2) 31.5	(1) Tacky (2) Tacky
BCACA	*MnO_2 "No 5"*	*Alkali*	*(1) 75* *(2) 110*	*(1) 30.5* *(2) 30.6*	*(1) Tacky* *(2) Tacky*
Sodium Birnessite "Composite"	MnO_2 "No 14"	Untreated	(1) 155 (2) 130	(1) 42.3 (2) 39.6	(1) Tack free (2) Tack free
*BCACA**	*MnO_2 "No 14"*	*Untreated*	*(1) 170* *(2) 140*	*(1) 41* *(2) 35*	*(1) Tack Free* *(2) Tack Free*
Sodium Birnessite "Composite"	MnO_2 "IMINI 80"	Untreated	(1) 280 (2) 345	(1) 33 (2) 28	(1) Tack Free (2) Tack Free
BCACA	*MnO_2 "IMINI 80"*	*Untreated*	*(1) 360* *(2) 320*	*(1) 13.6* *(2) 15.7*	*(1) Tack Free* *(2) Tack Free*

*Experiments conducted by Nick Goldblatt under identical conditions

Table 4 The effect of manganese dioxide curing agents *mixed* with strontium based fillers on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (1.35 g in 180g LP32C)	**Filler (12.15g in 180g LP32C)**	**Filler Treatment**	**Cure time in minutes to 12000 poise with 10% curing agent**	**Shore A Hardness after 7 days**	**Tack state after 7 days**
Sodium Birnessite "composite"	$CaCO_3$	Precipitated	(1) 120 minutes to 1320 poise (2) 120 minutes to 2200 poise	(1) 0 (2) 0	(1) Tack Free* (2) Tack Free*
BCACA	*$CaCO_3$*	*Precipitated*	*(1) 120 minutes to 1520 poise* *(2) 120 minutes to 2600 poise*	*(1) 0* *(2) 0*	*(1)Tack Free** *(2)Tack Free**
Sodium Birnessite "composite"	$SrCO_3$ "96/600"	Precipitated	(1) 140 minutes to 1320 poise (2) 160 minutes to 1360 poise	(1) 0 (2) 0	(1) Tack Free* (2) Tack Free*
BCACA	*$SrCO_3$ "96/600"*	*Precipitated*	*(1) 120 minutes to 1400 poise* *(2) 120 minutes to 1320 poise*	*(1) 0* *(2) 0*	*(1)Tack Free** *(2)Tack Free**

* Surface tack free but bulk of cure mixture still tacky

Table 5 The pH of 10 % slurry of curing agents in deionised water

Curing agent	pH of 10 % slurry
Sodium birnessite "composite"	9.83
BCACA	9.65

Table 6 The pH of 10 % slurry of filler in deionised water

Filler	pH of 10 % slurry
Manganese dioxide "No 5" (alkali treated)	9.66
Manganese dioxide "No 14" (untreated)	6.68
Manganese dioxide "IMINI 80" (untreated)	7.05
Calcium carbonate (precipitated)	8.64
Strontium carbonate "96/600" (precipitated)	8.02

V.3 DISCUSSION

From research conducted earlier and described in previous 6 month reports, both pure sodium birnessite and pure BCACA samples cure LP32C rapidly. In research conducted during this period, the manganese dioxide filler samples "IMINI 80" and "No 14" ore showed no curing (determined using viscometry and the 1 week Shore A hardness test) of the LP32C polymer. Alkali treated manganese dioxide "No 5" filler although not curing the polysulphide rapidly, produced a hard but tacky cure after 7 days.

Despite both the natural "IMINI 80" and "No 5" manganese dioxide fillers not being rapid curing agents as revealed from this research, they do affect the curing reaction of the active oxidising agents, sodium birnessite and BCACA. The alkali treated MnO_2 "No 5" filler acts as an accelerator of the curing reaction due to its high pH as revealed by the results. However, the cured polysulphide is tacky - representing a problem in consumer use and therefore an environmental waste through a curing mixture that is unsatisfactory. Using either sodium birnessite or BCACA with "No 14" manganese dioxide filler produces a sufficiently hard, tack free cured product in 1 week. However, the "No 14" manganese dioxide filler is currently unavailable, and research will now have to be carried out using "IMINI 80".

The untreated filler "IMINI 80" has a lower pH than the alkali treated "No 5" filler despite both having the same particle size of 8µm. As a result, the results obtained in this period indicate that when "IMINI 80" is mixed with sodium birnessite or BCACA it produces a cured product with lower hardness in 7 days than for LP32C cured with sodium birnessite or BCACA mixed with the more alkaline filler "No 5". Clearly choosing the correct filler is significant and is an important factor affecting whether the LP32C cures suitably.

For strontium fillers, precipitated strontium carbonate ("96/600") did not appear to cure the liquid polysulphide. However the carbonate did not mix well with the LP32C and sodium birnessite causing a tacky, soft, cured product which had fine dark lumps of curing agent in it. The rate of cure was considerably slower than with any manganese dioxide fillers. Similarly using the BCACA curing agent with carbonate fillers, the cure rate was very slow and the cured product was soft, tacky and had lumps of curing agent visible.

A similar result was found for using calcium carbonate as a filler where the sodium birnessite or BCACA has a very slow curing effect and produces a tacky, cured polysulphide with lumps of curing agent visible. The reason for this, according to Clark (1998), is that unlike manganese dioxide fillers, strontium and calcium carbonates have no surface hydroxyl groups with which to hydrogen bond with the polysulphide. As a result, a calcium carbonate, or strontium carbonate filler needs to be mixed with wetting agents to enable it to be used effectively as a filler in the LP32C.

V.4 CONCLUSIONS

From this research it appears that sodium birnessite and BCACA cure LP32C similarly. This is important as it may be environmentally more beneficial to use sodium birnessite instead of BCACA.

It is evident from research in this period that variables such as filler *treatment* are significant in the effectiveness of LP32C curing using sodium birnessite or BCACA. This means that these results are specific to these fillers alone, at the reaction temperature of 25^{o}c, and pH of the curing agents. Higher alkalinity fillers increase the cure rate but produce a tacky cure. It seems that sodium birnessite does cure LP32C effectively under these conditions.

The *type* of filler is important too. The precipitated strontium carbonate although not an active curing agent seems to retard the curing of LP32C using either BCACA or sodium birnessite curing agents. The cured polysulphide product after 7 days was too soft for measurements of hardness and was still tacky. A higher percentage of curing agent would therefore be needed to produce a suitably hard cure using this strontium carbonate "96/600" as a filler compared to using manganese dioxide as a filler.

It seems that despite strontium and calcium carbonate being less toxic than manganese dioxide, these carbonates require the addition of a wetting agent to enable them to mix into the polysulphide. The environmental benefits of using a filler which does not require a wetting agent, namely manganese dioxide ore, compared to the fillers, strontium carbonate or calcium carbonate, which require a wetting agent need to be considered. During the next period further research will be conducted in to the curing activity of fillers, BCACA, and sodium birnessite on LP32C.

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AN INVESTIGATION INTO POTENTIAL USES OF STRONTIUM AND MANGANESE COMPOUNDS IN ENVIRONMENTAL TECHNOLOGY

ENGINEERING DOCTORATE
SIX MONTHLY REPORT - NUMBER 6.

Andy Houlson

1st October 1998

Six month report overview

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Andy Houlson, October 1998

1. Introduction

This report covers the six months of research undertaken for the Eng.D degree from April 1998 to October 1998. This report contains summaries on the work performed, the compulsory module course attended and describes possible future work on the two areas of the overall project on uses of strontium and manganese chemicals in environmental improvement.

2. Work undertaken

Compulsory Eng.D courses and conference attended:

Marketing and Finance

Engineering Doctorate Annual Conference at Brunel University

Research

Research has been carried out over the past 6 months under the following headings:

(1) Investigation into the effect on LP32C polysulphide curing using Riedel-de Haen FA grade, Eagle Picher I and II and sodium birnessite with IMINI 80 natural ore diluent

(2) Investigation into the effect on LP32C polysulphide curing using Riedel-de Haen FA grade, Eagle Picher I and II and sodium birnessite with no manganese dioxide diluent added

(3) Investigation into the effect of using pure manganese dioxide (pyrolusite) as a diluent

(4) Synthesis and analysis of sodium birnessite for curing experiments.

3 Conclusions

Adding a filler to the curing agents seems important from this research. The lack of the filler both results in a very soft cure, and a considerably longer pot-life with all the curing agents tested. The removal of this filler would be environmentally friendlier due to the lowered use of manganese dioxide. However, the detrimental effects of a soft cure and long pot life would result. It is important to know why the manganese dioxide filler increases the rate of cure and the cured product hardness. Experiments where therefore performed to begin to identify the component in the filler that was causing the effect on curing. Experiments were performed using curing agent alone, curing agent mixed with the filler and curing agent mixed with a pure manganese dioxide, pyrolusite. Further research is needed to identify the reasons for this finding.

APPENDICES

TABLE OF CONTENTS FOR SIX MONTH REPORT APPENDICES

VI.1.1 Experiments to study the effect of various curing agents, fillers and their mixtures on the curing of LP32C

Studies were performed in this period to investigate the curing activity of sodium birnessite and Riedel-de Haen (BCACA).

In all the experiments using filler and curing agent the percentage by weight of manganese based additives (curing agent and/or filler) is 7.5 % (i.e 13.5g) of the weight of the 180 g of LP32C used in each curing experiment. The percent of the curing mixture represented by the curing agent and the filler is shown as a percentage of this 13.5 g. i.e 20 % curing agent is 2.70g of curing agent in 80 % filler. i.e 10.8 g . Therefore. 2.70g + 10.8 g=13.5g) which is the total percent weight of curing agent + filler or curing agent alone or filler alone.

A further set of experiments involved using 30 % (4.05g) of curing agent and 70 % (9.46g) of filler. This compares with the experiments conducted in the previous six month period which used less curing agent (1.35 g of curing agent i.e. 10 % of the 13.5 g total). The reason for using 20 % and 30% curing agent in these experiments rather than 10 % is that the ratio of 10 % curing agent (either sodium birnessite or BCACA) with 90 % filler. in the case "IMINI 80" filler. was insufficient to produce a sufficiently hard cure within 7 days as measured by Shore A durometry. It was decided to investigate why the IMINI 80 effected the rate of cure and hardness, so a pure manganese dioxide phase, pyrolusite was used as a comparison with the IMINI 80 which is a 8 micron mixture of pyrolusite, sodium birnessite and other inorganic minerals as detailed below.

The chemical analysis of the main components of IMINI 80 is as follows:

Component	Percentage
MnO_2	81.0
SiO_2	4.0
CaO	2.6
MgO	1.9
Fe_2O_3	1.8
Total	91.3

A set of experiments were also conducted using the principal American polysulphide curing agent Eagle Picher I and II. Eagle Picher I is used in the aerospace industry, whilst Eagle Picher II is used in architectural and insulated glass applications.

The rate of curing, cure hardness after 7 days, and cure tackiness were determined as described in previous reports. The activity of the fillers were also determined in the same manner using 13.50g of filler in 180g of LP32C. Mixtures of fillers and active curing agents were then studied to assess their effect on the rate of curing, cure hardness and tackiness. It should be borne in mind that when considering these results, the preparation for each experiment during this research period, and the viscosity tests themselves are time consuming. The pH of the Eagle Picher curing agents I and II and the manganese dioxide phase pyrolusite were measured using a Kent Electronic Instruments Limited 3050 pH meter.

VI.2 RESULTS

Data on the effect of sodium birnessite and Riedel-de Haen FA curing agents on LP32C have been obtained and the results are shown in Tabulated form. Table 1 shows the effect on curing 180g of LP32C using 2.70g of sodium birnessite or Riedel-de Haen FA mixed with 10.8g of IMINI 80 filler. Table 2 shows the effect of 4.05g sodium birnessite or Riedel-de Haen FA curing agent mixed with 9.46g of IMINI 80 effect on curing 180g of LP32C. Table 3 shows the effect of a 20 % curing agent 80 % filler mix of Eagle Picher I and Eagle Picher II with IMINI 80 on LP32 C curing. Table 4 shows the effect of a 30 % mix of Eagle Picher I and Eagle Picher II with 70 % IMINI 80 on LP32 C curing. Table 5 shows the effect of using 100 % curing agent of Eagle Picher I and Eagle Picher II effect on LP32 C curing without filler. Table 6 and 7 show the pH of a 10 % slurry of the Eagle Picher curing agents and the pyrolusite ore. Table 8 shows the effect of pyrolusite on curing LP32C without a curing agent added. Table 9 shows the effect of pyrolusite plus Riedel-de Haen (at 4.05g) curing of LP32C. Table 10 compares the effect of different fillers on Riedel-de Haen curing of LP32C. X-ray diffraction analysis of the manganese dioxide, sold as 99+% manganese dioxide reveals it to be entirely consisting of pyrolusite. The particle size of the pyrolusite is under 149 microns, compared to the IMINI 80 of under 8 microns. See appendix for x-ray diffraction patterns.

Table 1 The effect of 20 % manganese dioxide curing agents *mixed* with manganese dioxide filler "IMINI 80" on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (2.70 g in 180g LP32C)	**Filler (10.8g in 180g LP32C)**	**Filler Treatment**	**Pot life cure time in minutes to 12000 centipoise (m.PaS)**	**Shore A Hardness after 7 days**	**Tack state after 7 days**
Sodium Birnessite "Composite"	MnO_2 "IMINI 80"	Untreated	(1)165 (2)165	(1) 24.6 (2) 29.0	(1) Tack Free (2) Tack Free
Riedel-de Haen FA	*MnO_2 "IMINI 80"*	*Untreated*	*(1) 120* *(2) 115*	*(1) 42* *(2) 42*	*(1) Tack Free* *(2) Tack Free*

Table 2 The effect of 30 % manganese dioxide curing agents *mixed* with manganese dioxide filler "IMINI 80" on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (4.05 g in 180g LP32C)	**Filler (9.46g in 180g LP32C)**	**Filler Treatment**	**Pot life cure time in minutes to 12000 centipoise (m.PaS)**	**Shore A Hardness after 7 days**	**Tack state after 7 days**
Sodium Birnessite "Composite"	MnO_2 "IMINI 80"	Untreated	(1) 55 (2) 40	(1) 41 (2) 42	(1) Tack Free (2) Tack Free
Riedel-de Haen FA	*MnO_2 "IMINI 80"*	*Untreated*	*(1) 35* *(2) 40*	*(1) 42* *(2) 42*	*(1) Tack Free* *(2) Tack Free*

Table 3 The effect of 20 % manganese dioxide curing agent *mixed* with manganese dioxide filler "IMINI 80" on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (2.70 g in 180g LP32C)	**Filler (10.8g in 180g LP32C)**	**Filler Treatment**	**Pot life cure time in minutes to 12000 centipoise (m.PaS)**	**Shore A Hardness after 7 days**	**Tack state after 7 days**
Eagle Picher I	MnO_2 "IMINI 80"	Untreated	(1) 250 (2) 260	(1) 42 (2) 42	(1) Tacky (2) Tacky
Eagle Picher II	MnO_2 "IMINI 80"	Untreated	(1) 420 (2) >480	(1) 43 (2) 42	(1) Tack free (2) Tack free

Table 4 The effect of 30 % manganese dioxide curing agents *mixed* with manganese dioxide filler "IMINI 80" on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (4.05 g in 180g LP32C)	**Filler (9.46g in 180g LP32C)**	**Filler Treatment**	**Pot life cure time in minutes to 12000 centipoise (m.PaS)**	**Shore A Hardness after 7 days**	**Tack state after 7 days**
Eagle Picher I	MnO_2 "IMINI 80"	Untreated	(1) 120 (2) 135	(1) 42 (2) 41	(1) Tacky (2) Tacky
Eagle Picher II	MnO_2 "IMINI 80"	Untreated	(1) 245 (2) 195	(1) 41 (2) 41	(1) Tack free (2) Tack free

Table 5 The effect of 100 % manganese dioxide curing agent on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (13.5 g in 180g LP32C)	Filler (0 g in 180g LP32C)	Filler Treatment	Pot life cure time in minutes to 12000 centipoise (m.PaS)	Shore A Hardness after 7 days	Tack state after 7 days
Eagle Picher I	-	-	(1) 15 (2) 20	(1) 42 (2) 41	(1) Tack free (2) Tack free
Eagle Picher II	-	-	(1) 10 (2) 20	(1) 42 (2) 40	(1) Tack free (2) Tack free

Table 6 The pH of 10 % slurry of curing agents in deionised water

Curing agent	pH of 10 % slurry
Eagle Picher I	9.82
Eagle Picher II	10.96

Table 7 The pH of 10 % slurry of manganese dioxide - pyrolusite in deionised water

Diluent	pH of 10 % slurry
Pyrolusite	5.75

(pH of IMINI 80 from previous 6 month report is pH 7.05)

Table 8 The effect of 100 % filler on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (0 g in 180g LP32C)	Filler 13.5 g in 180g LP32C)	Filler Treatment	Pot life cure time in minutes to 12000 centipoise (m.PaS)	Shore A Hardness after 7 days	Tack state after 7 days
-	Pyrolusite	-	(1) No curing evident (2) No curing evident	(1) 0 (2) 0	(1) Tacky (2) Tacky

Table 9 The effect of manganese dioxide curing agent plus pyrolusite on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (4.05 g in 180g LP32C)	Filler (9.46 g in 180g LP32C)	Filler Treatment	Pot life cure time in minutes to 12000 centipoise (m.PaS)	Shore A Hardness after 7 days	Tack state after 7 days
Riedel-deHaen	Pyrolusite	-	(1) 180 (2) 145	(1) 9 (2) 9	(1) Tack free (2) Tack free

Table 10 The effect of filler plus manganese dioxide curing agent on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (4.05 g in 180g LP32C)	Filler (9.46 g in 180g LP32C)	Filler Treatment	Pot life cure time in minutes to 12000 centipoise (m.PaS)	Shore A Hardness after 7 days	Tack state after 7 days
Riedel-deHaen	IMINI 80	(Natural ore)	(1) 40 (2) 35	(1) 42 (2) 42	(1) Tacky (2) Tacky
Riedel-deHaen	Pyrolusite	(Man made)	(1) 180 (2) 145	(1) 9 (2) 9	(1) Tack free (2) Tack free
Riedel-de Haen	No filler	-	(1) 300 (2) 250	(1) 12 (2) 15	(1) Tack free (2) Tack free

VI.3 DISCUSSION

Using 2.70 g Riedel-de Haen plus 10.8g IMINI 80 (Table 1) and 4.05 g of curing agent plus 9.46g of IMINI 80 the LP32C reaches a sufficient hardness (>30 Shore A) and rapid cure rate. However at the 2.70 g level of sodium birnessite added see Table 1, the cured product is insufficiently hard, and is softer than the Riedel-deHaen cured product. It is only when the quantity of sodium birnessite is increased to 4.05 g (Table 2) that a sufficiently hard cure is obtained. From this experiment, it appears that less Riedel-de Haen can be used than sodium birnessite to get a sufficiently hard cured product.

The Eagle Picher I and II samples from this research are less active curing agents compared to the Riedel-de Haen and sodium birnessite. The Eagle Picher II is the least rapid curing agent. The rate of curing to the pot life (12,000 centipoise) is significantly longer than for the Riedel-de Haen using the same weight of curing agent as the pot life and hardness in Table 2 compared to Table 4 shows. As a result it is decided to suspend work on the Eagle Picher I and II curing agents and focus work on the more active curing agents Riedel-deHaen and sodium birnessite.

The pH of the pyrolusite used, (pH 5.75) is quite close to that of the IMINI 80 natural manganese dioxide ore (pH 7.05). The IMINI 80 from its x-ray diffraction pattern shows that it is mainly pyrolusite, with a significant proportion of sodium birnessite. The x-ray diffraction pattern of the "99+%" manganese dioxide shows it to be pure pyrolusite. It appears that a component of the IMINI 80 is causing the LP32C curing to accelerate, compared to the pyrolusite diluted curing agents. The cause of this difference in using diluents needs to be investigated. The acceleration of the curing using IMINI 80 may be due to presence of sodium birnessite. These results show that at 2.25% curing agent (4.05g in 180g LP32C) curing with Riedel-de Haen is slow and the cured product soft. Adding a manganese dioxide filler significantly increases the rate of curing and increases the hardness of the cured product, and appears to be essential to obtained a pot life of roughly 2 hours for LP32C curing that the construction industry requires.

Table 8 shows that pyrolusite on its own does not cure LP32C. However the results in Table 10 show that the amount of curing agent (Riedel-deHaen FA) can remain constant (at 4.05 g of curing agent), but the filler has a significant effect on increasing the rate of curing and increasing the hardness of the cured polysulphide. The IMINI 80 more strongly effects the rate of curing than the pyrolusite, whilst the pyrolusite increases the rate of cure above that using Riedel-de Haen FA with no filler.

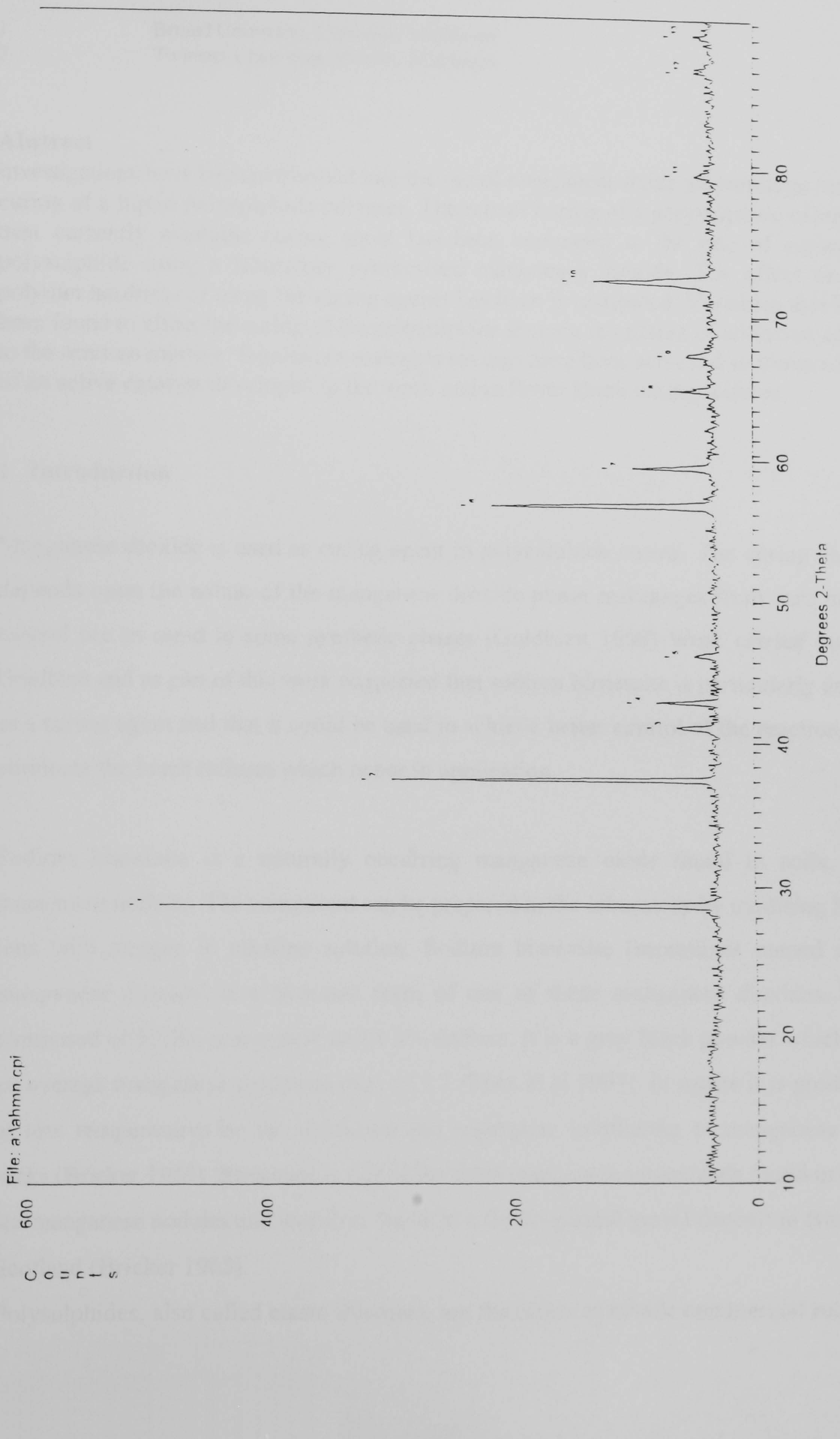
VI.4 CONCLUSION

There is a noticeable effect on the curing reaction when using a natural manganese dioxide filler compared to a pure manganese dioxide filler. Further investigations are underway to determine the precise reasons for the activity caused by the natural manganese dioxide. It will be an important research area to discover precisely what component of the IMINI 80 is responsible for the acceleration of the cure using Riedel-de Haen and this will be a focus for the next six month period. Further research using sodium birnessite as a curing agent will also be conducted during this period.

X-RAY DIFFRACTION DATA - MANGANESE DIOXIDE - PYROLUSITE

No	Angle	Counts	Dspace	Rel I
1	28.69	494	3.109	100
2	37.363	301	2.405	61
3	41.08	66	2.195	13
4	42.823	83	2.11	17
5	46.099	51	1.967	10
6	56.662	220	1.623	45
7	59.371	103	1.555	21
8	64.831	71	1.437	14
9	67.288	56	1.39	11
10	72.349	135	1.305	27
11	79.636	50	1.203	10
12	86.587	50	1.123	10
13	88.981	52	1.099	11

X-RAY DIFFRACTION DATA - MANGANESE DIOXIDE - PYROLUSITE



INVESTIGATION INTO THE USE OF MANGANESE DIOXIDES IN CURING A LIQUID POLYSULPHIDE POLYMER

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Abstract

Investigations have been performed into the use of manganese oxide preparations for the curing of a liquid polysulphide polymer. The rate of curing of a polysulphide using the best currently available curing agent has been compared to the rate of curing of polysulphide using a laboratory synthesised manganese dioxide. The effect on the polymer hardness of using the curing agents has been investigated. Variables that have been found to affect the curing of the polysulphide include the nature of additives added to the reaction mixture. Significant materials savings have been achieved in terms of use of an active catalyst developed in the work and in fewer batch curing failures.

1 Introduction

Manganese dioxide is used as curing agent in polysulphide curing. The curing ability depends upon the nature of the manganese dioxide phase and ranges from zero in the natural ore to rapid in some synthetic phases (Goldblatt 1998) Work carried out by Goldblatt and as part of this work suggested that sodium birnessite is particularly active as a curing agent and that it could be used to achieve better control of the reaction and eliminate the batch failures which occur in application.

Sodium birnessite is a naturally occurring manganese oxide found in soils, and manganese nodules. The compound can be prepared in the laboratory by oxidising Mn^{2+} ions with oxygen in alkaline solution. Sodium birnessite (sometimes named delta manganese dioxide) is a hydrated form of one of these manganese dioxides. It is composed of 52.9% manganese and 6.3% sodium. It is a grey black powder which has an average manganese oxidation state of 3.7 (Shen et al 1993) In nature it is produced at low temperatures by the oxidation and supergene weathering of manganese rich rocks.(Bricker 1965) Birnessite is one of the main manganese compounds found in deep sea manganese nodules and was first found in a fluvio-glacial gravel deposit in Birness, Scotland.(Bricker 1965).

Polysulphides, also called elasto thiomers, are the oldest synthetic commercial rubbers in production. They contain no carbon to carbon double bonds and consist of chains of organic sections, and sections which contain more than one sulphur atom. (Lucke 1994) Liquid polysulphides have a low toxicity. The low acute oral toxicity (LD50) is 3.9-5.0 g/kg body weight and little eye or skin irritation with temporary contact means that it has no significant health endangering properties. (Lucke 1994) Despite the polysulphide being of low toxicity, the oxidising agent, and fillers may possess harmful properties - such as the toxicity of lead for example.

Polysulphides are commercially important due to their high resistance to oil, solvents, oxygen and ozone. The main use of polysulphides is for double glazing, with smaller uses as aircraft sealants and in construction applications. Worldwide polysulphide consumption is 31,500 tonnes per year, with Europe accounting for 70 % of this. (Lucke 1994) It is forecast that the double glazing market will increase due to energy saving requirements and so an increased consumption of polysulphides is expected. (Lucke 1994). It is important to investigate ways to produce the cured polysulphide to minimise resources.

The actual mechanism of oxidative curing of liquid polysulphide polymers by manganese dioxide was investigated by Coates et al (1992) The reaction proposed involves oxidation of the thiol (RSH) to the appropriate thiyl ($RS^\cdot$) radical with subsequent dimerization to give the disulphide (RSSR) as follows:

$$\begin{aligned} \mathrm{RSH} &\xrightarrow{\mathrm{MnO_2}} \mathrm{RS^\cdot} \\ \mathrm{2\,RS^\cdot} &\rightarrow \mathrm{RSSR} \end{aligned}$$

Simplified, the curing reaction using manganese dioxide is as follows:

$$\mathrm{2R\text{-}SH + MnO_2 \rightarrow R\text{-}SS\text{-}R + MnO + H_2O} \text{ (Lucke 1994)}$$

The period of time from after the polysulphide and oxidising agent are mixed to the point at which the mixture viscosity is too high to permit the sample to be applied to the substrate is known as the pot life and can be from a few minutes to many hours. The curing time is defined as the time taken for the polysulphide to reach a hardness of 30

Shore A. (Lucke 1994) Fillers can be used to alter the physical properties of the cured polysulphide. These can increase the Shore A hardness of the elastomer (Bertozzi undated). Such fillers include natural manganese dioxide ore.

The sodium birnessite composite prepared in this work was added in various quantities to 8 micron milled natural manganese dioxide ore (pyrolusite). The natural ore does not react with the polysulphide. Sodium birnessite is shown to be the active curing agent and the oxidation reaction of the liquid polysulphide is by chain extension with the oxidising agent.

Sample viscosity was measured in this research as the work life of sodium birnessite cured liquid polysulphides. The work life (application time) is the period during which a curing mix is still soft enough to be re-worked after application to a substrate. The time for a polysulphide sample to cure to a viscosity of 12,000 centipoise was chosen as the period of study of work life.

The instrument used to measure viscosity in this work was a Brookfield dial reading viscometer. Viscosity is measured from the torque required to rotate a stainless steel spindle immersed to a marked level in the sample. The resistance to flow of the spindle increases proportionately with increasing spindle speed. According to Brookfield (b) (undated) viscosity measurements should involve controlling or specifying the following parameters:

(1) Test temperature
(2) Sample container size
(3) Sample volume
(4) Viscometer model
(5) Spindle used
(6) Test speed or speeds
(7) Length of time or number of spindle revolutions to record viscosity

These parameters have been observed in the following experiments.

IV.3.4.3 Experimental

Sodium birnessite can be used in the curing process of polysulphide rubbers, and one of its potential uses could be to replace the oxidising agent currently used, and in doing so reduce the amount of raw materials (the oxidising agent) used to cure the rubber. This would represent a clean technology. The laboratory synthesis of sodium birnessite is detailed in the 1997 EngD conference paper "Investigation into a pollution control chemical"

A material; BCACA- (the Best Currently Available Curing Agent) sold under the description 'active manganese dioxide' is used in industry to cure the LP-32 polysulphide at the ratio of 100 parts polymer to 7.5 parts of manganese dioxide. The sodium birnessite used in this work was prepared in the same ratio for comparison.

Natural ground manganese dioxide ores (8 μm) were investigated as the filler/diluent material. Sodium birnessite and 'BCACA' were diluted with the inert ores to compare curing efficiency, one week hardness, and tack state after 1 week. The effect on curing, hardness and tackiness of using a battery grade alkaline manganese dioxide which was manufactured for Twinstar Chemicals Ltd was also investigated

The liquid polysulphide polymer investigated in this work is Morton LP32C manufactured by Thiokol/Chemical division. It is a polymer of 1,2,3 trichloropropane and 1,1'-[methylenebis(oxy)]bis (2-chloroethane) reduced with sodium sulphide (Na_2Sx) and has an average molecular weight of 4000, and a sulphur content of 37-38 % (Lucke 1994). The terminal polymer groups of the polymer segments are mercaptan (-SH) groups. The mercaptan groups are converted into disulphide S-S in the curing process. At 25 °c, LP32 has a viscosity of 470 centipoise and specific gravity of 1.29. It has the composition :

$$HS\text{-}(C_2H_4\text{-}O\text{-}CH_2\text{-}O\text{-}C_2H_4\text{-}Sx)_{23}\text{-}C_2H_4\text{-}O\text{-}CH_2\text{-}O\text{-}C_2H_4\text{-}SH$$

Approximately 180 g of LP32C was accurately weighed into a plastic cup placed in a water bath held at constant temperature 20 to 25 °c. The mixture was stirred electrically with a glass rod to ensure the polymer was at the temperature of the bath. Varying mixtures of sodium birnessite and natural manganese dioxide were prepared by grinding them together in a mortar and pestle for 10 minutes to homogenise the mixture. The powder was stirred into the mixture with the electric stirrer, the time noted, and the mixture further stirred for exactly 10 minutes. About 5 g of the manganese oxide and polysulphide reaction mixture was poured from the cup into a plastic weighing vessel and left for one week to measure its hardness and to determine whether the surface was tacky to touch after this time.

The viscosity of the curing polysulphide mixture was measured using a Brookfield Viscometer with cylindrical spindle number 7. The end point of each reaction was taken as being a sample viscosity of greater than 12,000 centipoise.

Experiments were also performed using sodium birnessite and BCACA with no natural manganese dioxide ore added as a diluent and with other manganese dioxide fillers. The method used was as follows:To the 180 g of LP32C polysulphide were added 13.50 g of the curing agent mixture. Of this 13.50g, 10 % (1.35g) was the curing agent and 90% (12.15g) was the filler. The rate of curing, cure hardness after 7 days, and cure tackiness were determined as described later The activity of the fillers were also determined in the same manner using 13.50g of filler in 180g of LP32C. Additional experiments were performed using a mixture of 20 % or 30 % of BCACA in a balance of 80 % or 70 % respectively of natural manganese dioxide ore.

The pH of additives, such as the curing agents and fillers, used in the polysulphide mixture is an important factor as alkalinity increases the rate of polysulphide curing whilst acidity reduces the rate of curing. The pH of the samples of filler and curing agent were measured as a 10 % slurry of sample in deionised water (1g of powder in 10 ml of water). The pH was measured using a Kent Electronic Instruments Limited 3050 pH meter.

Seven days after the experiments were performed, a hardness test was performed on each of the samples poured into the plastic weighing vessels. A CV Instruments Analog Durometer was used to measure the sample hardness at room temperature. The instrument was first calibrated on a CV instruments Durometer calibration block. An acceptable hardness value for commercial use is between 30 and 40 Shore A hardness.

3 Results

Data on the effect of undiluted (no addition of filler) curing agents on LP32C have been obtained and the results are shown in Table 1. The data in Table 2 show the effects on curing of adding various fillers to LP32C while the effects of mixing various curing agents and manganese dioxide fillers on the curing of LP32C are described in Table 3. The pH of the curing agents and fillers in 10 % slurries and the fillers in a 10 % slurry in deionised water are given in Table 4 and 5 respectively.

Table 1 The effect of manganese dioxide curing agents *alone* on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (13.5g in 180g LP32C)	**Filler (0g in 180g LP32C)**	**Filler Treatment**	**Pot life cure time in minutes to 12000 centipoise (m.PaS)**	**Shore A Hardness after 7 days**	**Tack state after 7 days**
Sodium Birnessite "composite"	None	None	<20	Not measured*	Tack free
BCACA	*None*	*None*	*<20*	*Not measured**	*Tack free*

Notes:
* The hardness was not determined as the polysulphide mixture had cured so rapidly it did not present a flat surface required on which to use the Shore A Durometer

Table 2 The effect of manganese dioxide fillers *alone* on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (1.35 g in 180g LP32C)	**Filler (12.15g in 180g LP32C)**	**Filler Treatment**	**Pot life cure time in minutes to 12000 centipoise (m.PaS)**	**Shore A Hardness after 7 days**	**Tack state after 7 days**
None	*MnO_2 "IMINI 80"*	Untreated	(1) ~ (2) ~	(1) 0 (2) 0	(1) Tacky (2) Tacky
None	*MnO_2 "No 14"*	Untreated	(1) ~ (2) ~	(1) 0 (2) 0	(1) Tacky (2) Tacky
None	*MnO_2 "No 5"*	Autoclave +Alkali	(1) ~ (2) ~	(1) 24 (2) 31	(1) Tacky (2) Tacky

~ No increase in viscosity within 60 minutes as measured by Brookfield Viscometer

Table 3 The effect of manganese dioxide curing agents *mixed* with different manganese dioxide fillers on cure rate, tack state and Shore A hardness on LP32C polymer

Curing agent (1.35 g in 180g LP32C)	**Filler (12.15g in 180g LP32C)**	**Filler Treatment**	**Pot life cure time in minutes to 12000 centipoise (m.PaS)**	**Shore A Hardness after 7 days**	**Tack state after 7 days**
Sodium Birnessite "Composite"	MnO_2 "No 5"	Alkali	(1) 80 (2) 80	(1) 31.5 (2) 31.5	(1) Tacky (2) Tacky
BCACA	MnO_2 *"No 5"*	*Alkali*	*(1) 75* *(2) 110*	*(1) 30.5* *(2) 30.6*	*(1) Tacky* *(2) Tacky*
Sodium Birnessite "Composite"	MnO_2 "No 14"	Untreated	(1) 155 (2) 130	(1) 42.3 (2) 39.6	(1) Tack free (2) Tack free
*BCACA**	MnO_2 *"No 14"*	*Untreated*	*(1) 170* *(2) 140*	*(1) 41* *(2) 35*	*(1) Tack Free* *(2) Tack Free*
Sodium Birnessite "Composite"	MnO_2 "IMINI 80"	Untreated	(1) 280 (2) 345	(1) 33 (2) 28	(1) Tack Free (2) Tack Free
BCACA	MnO_2 *"IMINI 80"*	*Untreated*	*(1) 360* *(2) 320*	*(1) 13.6* *(2) 15.7*	*(1) Tack Free* *(2) Tack Free*

*Experiments conducted by Nick Goldblatt under identical conditions

Table 4 The pH of 10 % slurry of curing agents in deionised water

Curing agent	**pH of 10 % slurry**
Sodium birnessite "composite"	9.83
BCACA	9.65

Table 5 The pH of 10 % slurry of filler in deionised water

Filler	pH of 10 % slurry
Manganese dioxide "No 5" (alkali treated)	9.66
Manganese dioxide "No 14" (untreated)	6.68
Manganese dioxide "IMINI 80" (untreated)	7.05

In research conducted during this period, the manganese dioxide filler samples "IMINI 80" and "No 14" ore showed no curing (determined using viscometry and the 1 week Shore A hardness test) of the LP32C polymer. Alkali treated manganese dioxide "No 5" filler although not curing the polysulphide rapidly, produced a hard but tacky cure after 7 days.

Despite both the natural "IMINI 80" and "No 5" manganese dioxide fillers not being rapid curing agents as revealed from this research, they do affect the curing reaction of the active oxidising agents, sodium birnessite and BCACA. The alkali treated MnO_2 "No 5" filler acts as an accelerator of the curing reaction due to its high pH as revealed by the results. The cured polysulphide is tacky however- representing a problem in consumer use and therefore an environmental waste through a curing mixture that is unsatisfactory. Using either sodium birnessite or BCACA with "No 14" manganese dioxide filler produces a sufficiently hard, tack free cured product in 1 week.

The untreated filler "IMINI 80" has a lower pH than the alkali treated "No 5" filler despite both having the same particle size of 8μm. As a result, the results obtained in this period indicate that when "IMINI 80" is mixed with sodium birnessite or BCACA it produces a cured product with lower hardness in 7 days than for LP32C cured with sodium birnessite or BCACA mixed with the more alkaline filler "No 5". The filler "IMINI80" seems to act as a retarder. Clearly choosing the correct filler is significant and is an important factor affecting whether the LP32C cures suitably. The filler IMINI 80 appears from this research to retard the curing of the liquid polysulphide regardless of the active curing agent used.

4 Discussion

Sodium birnessite is an effective curing agent. The liquid polysulphide was cured very rapidly: within 10 minutes to its potlife using 100 % sodium birnessite. Dilution of the sodium birnessite with other components to ensure a longer pot life is therefore necessary in industrial situations. As was shown with the experiments involving 10%, 20 % and 30 % birnessite in a balance of natural manganese dioxide, the smaller the birnessite content of the birnessite /natural manganese dioxide ore mix, the slower the curing reaction. This result was comparable with the curing reaction using the BCACA.

As sodium birnessite is a very rapid curing agent, this offers a benefit as the amount of sodium birnessite required to cure the polysulphide can be reduced (to 10 %) and better controlled using natural manganese dioxide ore can be added as the balance (90%) to the polysulphide / birnessite mixture compared to the other curing agents investigated in this research.

The use of sodium birnessite as a curing agent represents a development in clean technology for two reasons. Sodium birnessite production uses less raw materials and energy to produce than the BCACA which is prepared using a high temperature process. Sodium birnessite synthesis reported in the 1997 Eng.D conference showed that it could be prepared successfully at room temperature. The process for synthesising the currently used curing agent in contrast involves heating a manganese solution under pressure, this clearly would involve large energy expenditure. Utilising sodium birnessite as a polysulphide curing agent instead of the current curing agent would represent a clean technology if successful due to reduced energy usage in preparing the curing agent for liquid polysulphides.

5 Conclusions

From this research it appears that sodium birnessite and BCACA cure LP32C similarly. This is important as it may be environmentally more beneficial to use sodium birnessite instead of BCACA. It is evident from this research that variables such as filler *treatment* are significant in the effectiveness of LP32C curing using sodium birnessite or BCACA. This means that these results are specific to these fillers alone, at the reaction temperature of 25^{o}c, and pH of the curing agents. Higher alkalinity fillers increase the cure rate but produce a tacky cure.

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AN INVESTIGATION INTO POTENTIAL USES OF STRONTIUM AND MANGANESE COMPOUNDS IN ENVIRONMENTAL TECHNOLOGY

ENGINEERING DOCTORATE
SIX MONTHLY REPORT - NUMBER 7.

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Andy Houlson

1st April 1999

Six month report overview

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Andy Houlson April 1999

1. Introduction

This report covers the six months of research undertaken for the Eng.D degree from October 1998 to April 1999. This report contains summaries on the work performed, the compulsory module courses attended and describes possible future work on manganese chemicals in environmental improvement.

2. Work undertaken

Compulsory Eng.D courses and meeting attended:

Distance Learning Finance and Marketing module

Environmental Economics module

Royal Society of Chemistry, London "New People, New Chemistry Meeting" Poster presentation entitled "The curing of a liquid polysulfide polymer"

Research

Research has been carried out over the past 6 months under the following headings:

(1) The use of ARES rheometer in parallel plate rheometry mode and Brookfield Viscometer to investigate the curing profile of liquid polysulfide using sodium birnessite and the Riedel-de Haen FA commercial product.

(2) The investigation of the effects of adding the accelerator tetramethylthiuramdisulfide (TMTD) and plasticizers: Santicizer 261 and Santicizer 278 to the curing mixtures.

(3) Investigation of the glass transition temperature of the Riedel-de Haen FA and sodium birnessite cured polysulfide using dynamic mechanical analysis.

(4) Investigation into the thermal stability of Riedel-de Haen FA and sodium birnessite cured polysulfide using thermogravimetric analysis

(5) Particle size and pH analysis of the Riedel-de Haen FA and sodium birnessite composite

(6) Investigation into the tensile strength of the polysulfide polymers using Instron tensile testing equipment

(7) Investigation into the effects of reducing the level of sodium birnessite curing agent on the properties of the cured polysulfide

3 Conclusions

A number of findings which have not been reported in the literature are reported here on the use of laboratory synthesised sodium birnessite for polysulfide curing. Investigations are focussed on preparing curing mixtures of sodium birnessite to make the results more compatible with commercially used cure pastes for polysulfides. This work has shown sodium birnessite dispersed in plasticizers which are an important component of a cure paste. A commercially used accelerator TMTD used along with sodium birnessite has been shown to produce the desired tack free surface in polysulfide. Using the sodium birnessite in a cure paste with accelerator and plasticizer results in a faster rate of curing (weight for weight) than Riedel-de Haen FA. The curing reaction was monitored by a novel use of parallel plate rheometry at a fixed temperature of 25 °C.

For the first time, results have been reported using dynamic mechanical analysis testing at temperatures from -60°C to 30 °C on cylindrical samples of sodium birnessite cured polysulfide. The glass transition temperature of cured polysulfide remains unaffected by the curing agent used. Tensile testing of sodium birnessite cured polysulfide is also reported for the first time. The stress at peak and break and the strain at peak and break of sodium birnessite and Riedel-de Haen FA grade polysulfide are similar although decreasing the sodium birnessite content reduces the tensile strength. The polysulfide Shore A hardness after 7 days (>30) appears satisfactory for use in insulated glass application.

Andy Houlson April1999

Original research has also been carried out in the six month period to determine the effect of reducing the level of sodium birnessite as a curing agent for polysulfides. As expected the rate of curing decreases when less sodium birnessite is used as does the tensile strength and thermal stability. The glass transition temperature however remains stable.

Various investigations have been performed to investigate the factors that may account for the differences in curing profile and similarity in the cured product properties. Sodium birnessite and Riedel-de Haen FA curing agents have been shown to have similar particle size and similar pH values. The level of water in the sodium birnessite may help account for the difference in the curing although further studies are needed. This research may be useful in determining optimum levels of sodium birnessite using the minimal quantity to ensure a satisfactorily cured product with minimal resource use, leading to both economic and environmental benefits.

AN INVESTIGATION INTO POTENTIAL USES OF STRONTIUM AND MANGANESE COMPOUNDS IN ENVIRONMENTAL TECHNOLOGY

ENGINEERING DOCTORATE

SIX MONTHLY REPORT - NUMBER 8.

Andy Houlson

1st October 1999

Six month report overview

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Andy Houlson, October 1999

1. Introduction

This report covers the six months of research undertaken for the Eng.D degree from April 1999 to October 1999. This report contains summaries on the work performed, the compulsory module course attended and describes possible future work on manganese chemicals in environmental improvement.

2. Work undertaken

Research

Studies have been performed using an alternative curing agent DBU, which show properties similar to that of the TMTD cured polysulfide

The use of calcium carbonate as an inert diluent instead of manganese dioxide for the sodium birnessite curing system has been investigated for the first time. The calcium carbonate did not affect the thermal or mechanical properties of the cured polysulfide and has the benefit over an inert manganese dioxide diluent of being cheaper, non toxic, lighter, and being currently used as a filler in some commercial polysulfide sealants.

Investigation into the moisture vapour transmission rate for sodium birnessite and Riedel-de Haen FA cured polysulfide.

Further tensile testing of samples of polysulfide cured using sodium birnessite or Riedel-de Haen FA.

Further studies have been performed on the use of sodium birnessite at 4 parts per hundred (pph) polysulfide, to ascertain the effects of reducing the birnessite concentration on curing ability and cured polysulfide properties. The research shows that at 4 pph a number of detrimental effects can be seen in the cured polysulfide, for example a tacky surface 7 days after curing.

Studies have been performed into identifying the mechanism of the curing of polysulfide using sodium birnessite using Infra-red spectrometry, X-ray photoelectron spectroscopy, and X-ray diffraction. It has been shown for the first time that sodium birnessite cured LP32 polysulfide by the conversion of mercaptan groups in the polysulfide. From the XRD and XPS techniques however, it was not possible to determine the structure of the manganese oxide produced

Paper accepted for publication

A paper "Curing of a polysulfide sealant with sodium birnessite" based entirely on this research has been accepted for publication in the Journal of Applied Polymer Science.

3. Conclusions

The work in this period has focussed on the use of sodium birnessite as a curing agent for liquid polysulfide polymers. Comparisons of the use of various types and quantities of plasticisers, diluents and accelerators have been made, and this compared to a reference standard, that of the commercial curing agent mix for polysulfides, based on Riedel-de Haen FA. The work has shown for the first time that sodium birnessite is as effective and reliable at curing polysulfide as the commercial agent yet at half the amount. This represents an environmental benefit from preventing waste of resources from cure failures, and a possible economic saving from using less curing agent.

Andy Houlson, October 1999