MICROWAVE ASSISTED MOULDING

OF STARCH-BASED FOAMS

A thesis submitted for the degree of Doctor of Philosophy

by

Jiang Zhou

Department of Mechanical Engineering

Brunel University

June 2004

Abstract

This thesis reports a fundamental study on microwave assisted moulding (MAM), a novel technology where expandable starch based pellets made from extrusion are expanded within a mould cavity into blocks using microwave heating. Foamability or degree of expansion of starch-based pellets during microwave heating was studied comprehensively in terms of: the variation of raw natural materials, the extrusion conditions, the additives and the preconditioning of pellets before foaming. The expansion behaviour, foamed cell structures and mechanical properties of expanded pellets were characterized together with the characterization of microstructure of the extrudate materials and physical properties. Characteristics in microwave assisted moulding of the expandable pellets were then studied in terms of: the interfacial bonding and fusion between foamed pellets, the achievement of uniform heating through a moulded block, the loading of pellets and mould filling during foaming.

It has been found that the degree of free expansion during microwave heating of the starch-based pellets is dependent on the degree of cook of starch during extrusion, the better the distructurization of the native starch granules, the higher the foamability in microwave heating. The maximum expansion ratio achieved in this work is 14, corresponding a foam porosity of 93%. Hydrophilic additives such as PVA and glycerol have adverse effect on the foamability due to combination effects of the melting point of the materials, degree of cook of starch in the pellets and water molecular mobility during foaming. Nucleation agents such as talc powder can refine cell structure of the foams and enhance elastic modulus, strength and energy absorption during compression. Addition of salts enhances microwave heating rate, expansion ratio and plasticization of the foam. Foamed blocks can be made using the MAM technology by adequate mould material, pre-treatment of the pellets, and control of initial loading in the mould cavity. This study paved the way for further development of the MAM technology for moulding of starch-based foams.

Acknowledgements

First of all, I would like to take this opportunity to express my deepest gratitude to my first supervisor Dr Jim Song and my second supervisor Professor Peter Hornsby for their encouragement, guidance and helps throughout this project, especially their efforts in seeking financial aid for my PhD studies. I must also thank Dr. Song for his valuable comments in the completion of the thesis.

I am grateful to Dr. Roger Parker at Institute of Food Research (IFR), my external supervisor, for his valuable suggestions and comments which clarified some key concepts and methodologies used in this thesis. Thanks are also due to Dr. Mary Parker at IFR for her valuable assistance and discussions on differential interference contrast microscopy.

I would also like to thank Laurie Pearson at Heygates Limited for providing the raw materials and organising the access to the RVA facility in the company.

I would like to thank staffs and technicians in the Wolfson Centre for Materials Processing and the Department of Mechanical Engineering at Brunel University, in particular Dr. Karnik Tarverdi, for their support and help in various ways.

Finally, I want to thank my parents for their everlasting support and encouragement. Special thanks must go to my wife, Jingming, and my daughter, Li, for their love, understanding and patience throughout this period of time.

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List of Abbreviations

ABS	acrylonitrile-butadiene-styrene
ASTM	the American Society for Testing and Materials
CPD	critical point dried
DIC	differential interference contrast microscopy
DMTA	dynamic mechanical thermal analysis
DSC	differential scanning calorimetry
D.W.B.	dry weight basis
EAA	ethylene/acrylic acid
EMC	equilibrium moisture content
EPS	expanded polystyrene
EVA	ethylene/vinyl acetate
EVOH	poly (ethylene-co-vinyl alcohol)
FT-IR	Fourier transform infrared spectroscopy
LDPE	low-density polyethylene
MAM	microwave assisted moulding
MC	moisture content
NMR	nuclear magnetic resonance
PCL	polycaprolactone
PE	polyethylene
PEA	poly(ester amide)
PHAs	poly (β-hydroxyalkanoate)s
PHB	polyhydroxybutyrate
PHBV	poly(hydroxybutyrate-co-valerate)
PHEE	poly (hydroxy ester ether)
PLA	poly (lactic acid)
PMA	poly(methyl acrylate)
PS	polystyrene
PTFE	polytetrafluoroethylene
PVA	poly (vinyl alcohol)

PVC	polyvinyl chloride
RH	relative humidity
rpm	revolution per minute
RVA	rapid visco analyser
SANS	small angle neutron scattering
SAXS	small angle X-ray scattering
SEM	scanning electron microscope
SME	specific mechanical energy
TGA	thermal gravity analyser
TMA	thermal mechanical analyser
TMC	total moisture content
TPS	thermoplastic starch
UTS	ultimate tensile strength
WAI	water absorption index
WAXS	wide angle X-ray scattering
WC	water content
WSI	water solubility index
W.W.B.	wet weight basis

Chapter 1

General Introduction

1.1 Background

Plastics are a rapidly growing segment in the municipal solid waste stream. The amount of plastics generation in municipal solid waste in United States has increased from less than 1 percent in 1960 to 10.7 percent in 2000 (U.S. Environmental Protection Agency, 2002). The largest categories of plastics are found in packaging and nondurable goods. In the UK, about 12% of the 27 million tonnes household waste produced annually is from packaging, which is estimated 3.2 million tonnes (Waste Watch Wasteline, 2002). In 2000, the amount of plastic waste generated annually in the UK is estimated to have been approximately 3.5 million tonnes. The biggest use of plastics in the UK is packaging, which accounts for 37% of consumption. (Wasteonline, 2001).

Currently, petroleum-based plastic packaging waste is treated in three main ways: landfill, incineration and recycling/reuse.

Unlike other packaging materials, such as metals and glass, there are considerable practical difficulties and cost in the recycling/reuse of used packaging plastics, especially in sorting and re-processing because of the existence of different additives, such as fillers and plasticizers. Due to the limitations of practice, economic cost and lack of market for low quality recycled plastics, only a small portion of used packaging plastics has been successfully recycled. For instance, recycling rate of post-consumer plastic waste is only 7% in the UK (Wasteonline, 2001).

Incineration with the aim of energy recovery is another option to treat plastics wastes and should be further exploited as plastics have higher calorific value (the amount of heat energy stored in a material) than that of coal, which means they are valuable fuel. However, there is concern in connection with incineration of waste plastics, because incineration may also have negative impact on the environment due to their potentially

hazardous degradation substances emission during incineration or after incineration from ash. In the UK, 8% of post-consumer plastic is incinerated (Wasteonline, 2001).

Landfill is a more convenient and traditional method to dispose the municipal solid waste. In 2001-2002, 78% of domestic waste ended up in landfill sites in the UK (Wasteonline, 2002) and 80% of post-consumer plastic waste went to landfill (Wasteonline, 2001). However, paying regard to the decreasing availability of space for landfills and gas emission, such as methane (a greenhouse gas responsible for global warming and mainly from the organic materials within landfill), it is aware of that any organic/degradable wastes should phase out to landfill. This can help to increase the recycling rate of domestic waste and allow the landfill sites to stabilize more quickly for redevelopment. For instance, a draft UK strategy aims to reduce biodegradable waste entering landfill to 75% of 1995 levels by 2010 (Wasteonline, 2002).

Composting opens another route for organic/degradable waste management, which not only reduces amount of wastes to landfill, but also turns wastes into useful things. To meet the compostability requirement, all the blend components have to fully biodegrade under composting conditions and within the time frame of the composting process. Biodegradable plastic packaging materials make this kind of treatment easier, because it is not necessary to sort the plastic packaging waste out.

On the other hand, it is increasingly being realized that the use of long-lasting plastics for short-lived applications is not entirely justified, especially when increased concern exists about environment problem (such as the litter on street and marine environment) and oil resource crisis. Meanwhile, stringent environmental laws and regulations as well as disposal costs have forced industry to look for other alternatives and recyclable uses. All of these have given driving force for research and development of biodegradable plastics from natural renewable resources to reduce environmental impact of packaging wastes and to utilize sustainable sources of raw materials.

Biodegradable polymers (synthetic or natural) are considered as an alternative to non-biodegradable plastics for packaging applications to reduce the impact of plastic wastes on environment. Biodegradable polymers are referred to those polymers in which their chains can be broken down and assimilated by natural means especially biological

activity. According to ASTM standard (ASTM D6400-99e), biodegradable plastic is defined as a degradable plastic in which the degradation results from the action of naturally occurring micro-organisms such as bacteria, fungi and algae; while compostable plastic is defined as a plastic that undergoes degradation by biological processes during composting to yield CO_2, water, inorganic compounds and biomass at a rate consistent with other known compostable materials and leave no visible, distinguishable or toxic residue.

To date, several synthetic biodegradable polymers have been developed or even have been commercialised, such as poly (lactic acid) (PLA) (NatureWorks™ (trade name), Cargill Dow (producer); LACEA, Mitsui Chemicals), polycaprolactone (PCL) (Tone®, Dow Chemical; CelGreen PH, Daicel Chemical), poly (β-hydroxyalkanoate)s (PHAs) and polyhydroxybutyrate (PHB) (Biopol™, Monsanto). However, the relative high prices, typically 2 – 8 times higher than ordinary plastics (Petersen, et al., 1999), constrain the widespread exploitation of these materials.

Plant-derived materials, such as native starch, a natural polymer, are inherently biodegradable, but they do not naturally possess the properties desired for packaging applications. This leads to two different research approaches: 1) introducing biodegradability into conventional plastics by incorporating starch as biodegradable additives or 2) improving the performances of plant-derived materials by modification. In the first approach, the addition of starch could assist the fragmentation/degradation of discarded products such as bags and films, and may lower the cost of products, the remaining fragments of conventional plastic, however, remain non-biodegradable.

Starch is probably the most abundant and cheapest of the commercially available natural polymer with immense potential for use in the non-food industries. This material has attracted significant interest in recent years. This is not only because starch is produced in large quantities by photosynthetic plants and therefore is annually renewable and relatively cheap, but also because its properties can be modified so that the materials possess a thermoplastic behaviour and then able to be processed using the well developed polymer technologies such as extrusion, thermal moulding and injection moulding.

The hydrophilic nature and lack of toughness are two major constraints that seriously limit the direct use of starch as a material. Although some mechanical properties of starch based plastics are in the same range as that of conventional plastics, a disadvantage of these materials is their sensitivity towards water and ageing. Variation of the water content of the material as a function of changes in relative humidity leads to shifting of the glass transition temperature or crystallisation of amylose and amylopectin, which in turn cause the change in mechanical properties of starch based plastics with ambient humidity and time during the service and storage. Despite this, starch based plastics has found their applications where high humidity is prohibited or long term durability is not needed and rapid biodegradation is crucial. Significant advance in material performance has been achieved and they have been explored with considerable success in applications including trash bags, disposable utensils in fast food industry, packaging foams, and agricultural mulch film. A very successful example is the starch based loose fills produced by direct extrusion foaming, which have been used for cushion packaging applications as a replacement for expanded polystyrene (EPS) loose fills.

To date, however, there are no suitable biodegradable materials available to replace EPS cushioning blocks and moulded pads. This is largely due to the lack of available techniques to produce sizeable and complex biodegradable blocks which satisfy the commercial needs of a competitive packaging market. It is thus desirable to explore and develop new technologies to manufacture moulded block products for this potentially huge market.

Traditionally, synthetic EPS packaging cushion blocks are manufactured by using the steam injection moulding technique. Pre-expanded EPS beads are further expanded within a mould by injection of steam into the mould, which heat the material and react with the blowing agent to expand the cells. The expanded beads fill the mould cavity and fused together until a solid body in formed (Landrock, 1995).

This procedure provides a possible route to produce a foam block from starch materials. It is well known that, starch melt containing about 10% moisture can be puffed into foam structure by rapid heating it using evaporation of superheated water within the material. This phenomenon has been exploited in food industry for snack foods such as

prawn crackers and rice cakes (Guy, 2001a). Similarly, by using microwave heating which has a distinctive advantage over conventional heating, i.e., rapid volumetric heating, extruded starch pellets may be rapidly heated within a mould, the vaporised water in the pellets may expand the pellets to fill the mould and fuse them at contacts into a coherent structure. By adjusting the compositions of the extruded starch pellets, the heating and moulding conditions, a foam block with required cell structures and mechanical properties may be obtained. This novel method is referred to as Microwave Assisted Moulding (MAM) through the rest of this thesis.

1.2 Scope of the research

The objective of the work is to explore the feasibility of the MAM method and develop the technology basis using wheat flour and starch as raw material to produce starch based foam from extruded pellets and to address the scientific and technical problems involved in the development of this novel processing technique. Emphasis will be focused on the fundamental mechanisms associated with the microwave foaming and moulding process in order to understand:

i)   the optimum extrusion condition for producing pellets and the related physical state of starch polymers in these extruded pellets in relation to the best microwave foaming;

ii)   the formulation requirements of the extruded pellets in relation to their microwave foaming behaviour, physical and mechanical properties of the foams;

iii)   the methods to achieve better mould filling, adhesion and uniform temperature profile within the mould.

1.3 Layout of the thesis

This thesis consists of nine chapters. The contents of each chapter are outlined blow:

- Chapter one gives the background, objective and significance of the project.

- Chapter two, the literature review, gives an overview of the background information and related work in this field.

- Chapter three describes the raw materials, additives and the details of experimental procedures.

The results and discussions of the experimental work have been divided into five parts and presented through Chapter four to Chapter eight.

- Chapter four reports the characterisations of degree of cook for the extruded pellets by using various analysis technologies.

- Chapter five presents and discusses the experimental results from the investigations on the microwave foamability of extruded pellets and the influencing factors.

- Chapter six is focused on the effects of different additives on the foamability of extruded pellets.

- Chapter seven reports and discusses several important properties of microwave foamed extruded pellets.

- Chapter eight deals with foam blocks made from the MAM method.

- Chapter nine outlines the conclusions and suggests areas for further work.

Chapter 2

Literature Review

2.1 Starch and its characteristics

2.1.1 Composition of starch

Starch is a natural polymer of D-glucose and is found as a storage carbohydrate in plants. Starch usually has two major components, amylose and amylopectin. Amylose is a nearly linear polymer of α-(1,4) linked D-glucose with a molar mass in the order of several hundred thousands. While amylopectin is composed of short α-(1,4) linked chains connected to each other by α-(1,6) glucosidic linkages. The molecular mass of amylopectin is about 10^8 - 10^{10} g/mol (Blanshard, 1987; Galliard, & Bowler, 1987). The schematic structure of amylose and amylopectin is showed in Figure 2.1 (Mohanty, et al., 2000).
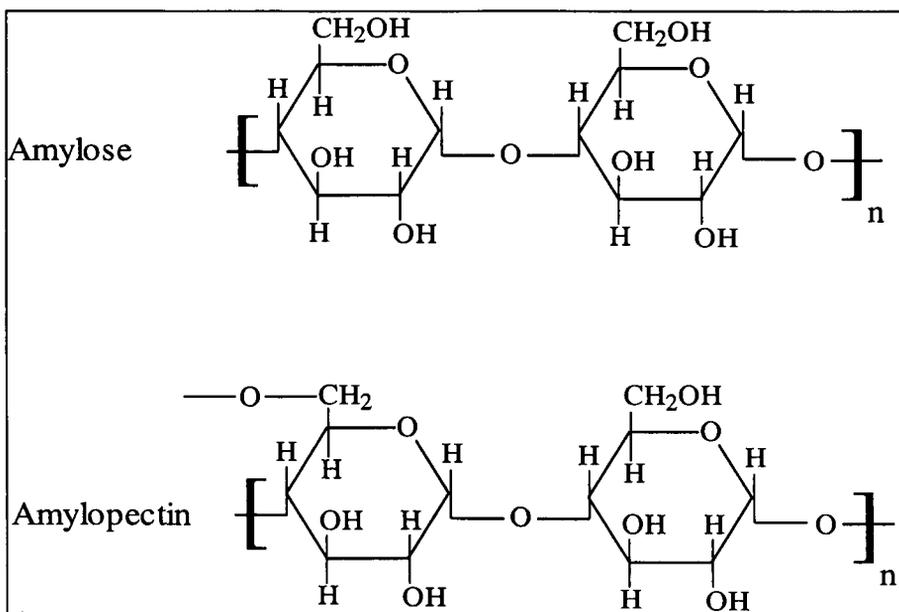
Figure 2.1 The schematic structure of amylose and amylopectin.

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The relative amounts, structures and molecular masses of amylose and amylopectin are determined by means of genetic and environmental control during the biosynthesis process, and therefore wide variation occurs among plant raw materials. Most of starches, such as wheat, maize and potato starch, contain between 20 and 30% w/w amylose. Some waxy starches contain very little (<1%) amylose, and amylomaize starches contain abound 65% amylose (Parker, & Ring, 2001; Ahmad, et al., 1999).

Small amounts of non-carbohydrate constituents such as protein and lipids are usually present in starches, the amounts of lipids and protein could be up to 1.2% and 0.6%, respectively, depending upon the sources of starch (Galliard, & Bowler, 1987; Buleon, et al., 1998). The starches stored under ambient conditions also contain around 10 - 13% water.

2.1.1.1 Composition of wheat flour

As shown in Figure 2.2 (www.professionalpasta.it), wheat grain mainly consists of three distinct parts: bran, the outer covering of the grain; germ, the embryo contained inside the kernel which is rich in enzymes and lipids; and endosperm, the part of the kernel where the starch granules are found, which dominates the composition of flour.
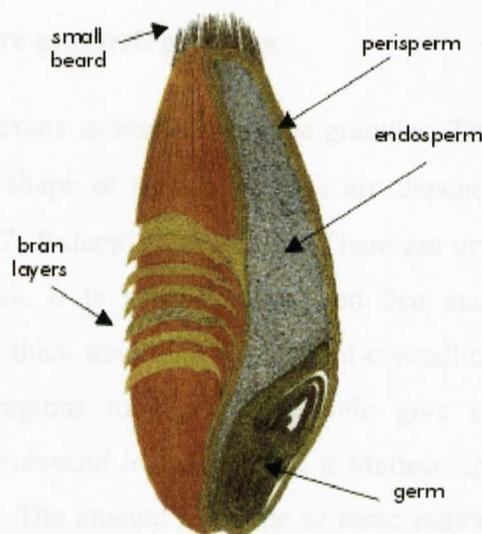
Figure 2.2 Schematic diagram of wheat grain.

Wheat flour is produced by milling the wheat grains into fractions of the inner endosperm and the outer layer of hull. The composition of flour varies with the level of purification process. For most common wheat flour, a large proportion of the hulls has been removed which enriches the starch fraction. Even so, there is still considerable amount of non-starch components, i.e., protein, fibre and lipid in wheat flour. In comparison, a commercially available wheat starch is virtually free from these components. Table 2.1 shows typical composition of materials prepared from wheat grain (Guy, 2001b). In addition, the wheat flour usually contains moisture ranged between 10 – 14 % dependent on the environmental humidity.

Table 2.1 Composition of materials prepared from wheat grain as wt% of dry solids

Component	Whole grain	Flour	Starch
Starch	75	80	90
Protein	12	11	0.2
Fibre	8.0	1.5	0.5
Lipid	2.5	1.5	1.0
Ash	1.5	1.0	0.5

2.1.2 Crystalline structure in starch granules

In its native state, starch exists as semi-crystalline granules. The size (typically ranging from 2 to 100 μm) and shape of starch granules are dependant on the plant origin (Galliard, & Bowler, 1987; Buleon, et al., 1998). There are crystalline and amorphous regions in starch granules. It is generally believed that starch granules consist of alternating 120 - 400 nm thick amorphous and semi-crystalline layers (Buleon, et al., 1998). The crystalline regions in a starch granule give rise to the property of birefringence, which is evidenced in the form of a Maltese cross when viewed under crossed polar microscope. The amount and type of these regions are influenced by the source of the starch. The crystalline structure of native starch can be classified into three main types by their distinct X-ray diffraction patterns: A-, B-, and C-type depending on

starch source. When starch is thermally and mechanically treated, it often exhibits the "V"-type or "E"-type diffraction patterns, which are formed upon complexing of amylose with lipids and other polar organic molecules (Zobel, 1964; Colonna, et al., 1987; Ollett, et al., 1990; Cairns, et al., 1997). Cereal starches give a characteristic A-type diffraction pattern. Tuber starches usually show a B-type diffraction pattern. Certain root and seed starches have C-type patterns. The C-type is believed to be a combination of A- and B-types (Zobel, 1964; Colonna, et al., 1987; Biliaderis, 1992; Zobel, & Stephen, 1995). The main characteristic X-ray diffraction peaks by which the three types can be differentiated readily are listed in Table 2.2. Small deviations from these peak positions may occur due to the sample history and moisture content.

Table 2.2 X-ray diffraction parameters of the three types of native starch

Type	2θ (°)	Intensity
A	15.3	Strong
	17.1	Strong
	18.2	less than strong
	23.5	Strong
B	5.59	Medium
	17.2	Strong
	22.2	Medium
	24.0	less than medium
C	5.73	Weak
	15.3	Strong
	17.3	Strong
	18.3	Medium
	23.5	more than medium

Both A- and B-type crystal lattices consist of double helical structures (Buleon, et al., 1998; Jacobs, et al., 1998; Myllarinen, et al., 2002a). The differences between A and B starch arise from water content and the manner in which the double helices are packed

in the respective crystals (Imberty, et al., 1991; Buleon, et al., 1998). The B-type structure is described as a more loosely packed hexagonal assembly of the helices with a column of water molecules present in the centre of the hexagonal arrangement (van Soest et al., 1996a; Jagannath, et al, 2001), whereas this column of water is replaced by a double helix in the A-type structure. The C-type structure is thought to be an intermediate structure of A- and B-types (van Soest et al., 1996a). The overall crystallinity of the native starch varies from 15 to 45% depending not only on the origin and hydration of starch but also on the technique used to determine it. (Zobel, 1988; Buleon, et al., 1998).

2.1.3 Gelatinisation

Gelatinisation is an irreversible order-disorder transition that starch undergoes when it is heated in the presence of water. Starch gelatinisation is the collapse (disruption) of molecular orders within the starch granule accompanied by a series of events such as water absorption, granular swelling, crystallinity loss, amylose leaching and viscosity development. The gelatinisation process occurs over a limited temperature range for a single granule and a somewhat wider temperature range for a population of granules (Parker, & Ring 2001). The point of initial gelatinisation and the range over which it occurs is governed by the starch concentration, method of observation, botanical origin, and heterogeneity within the granule population under observation (Liu, et al., 1991; Jenkins & Donald, 1998; Maaruf, et al., 2001).

Starch gelatinisation has been studied by several methods based on the observation of changes in structure and properties, micro and/or macroscopic, of starch granules when they are heated in aqueous solution. The techniques include the differential scanning calorimetry (DSC) (Burt, & Russell, 1983; Liu et al., 1991; Noel & Ring, 1992; Cooke & Gidley, 1992; Liu, & Lelievre, 1992; Appelqvist et al., 1993; Le Bail et al., 1993; Jenkins & Donald, 1998; Jacobs, et al., 1998; Fujita, et al., 1998; Maaruf, et al., 2001; Takaya, et al., 2000), nuclear magnetic resonance (NMR) (Cooke & Gidley, 1992), microscopy (Burt, & Russell, 1983; Liu et al., 1991), small angle neutron scattering (SANS) (Jenkins & Donald, 1998) and small and wide angle X-ray scattering (SAXS,

WAXS) (Liu et al., 1991; Cooke & Gidley, 1992; Cameron & Donald, 1993; Le Bail et al., 1993; Jenkins et al., 1994; Jacobs, et al., 1998; Jenkins & Donald, 1998).

Temperature and water content are the primary factors influencing the gelatinisation in addition to the botanical origin of starch. Since the DSC method allows to investigate gelatinisation over a wide range of water content and enables to determine the gelatinisation parameters, such as endothermic peak temperature and enthalpy change, it has been widely used to characterise gelatinisation of starches (Liu, et al., 1991; Jenkins & Donald, 1998; Jacobs, et al., 1998; Fujita, et al., 1998; Maaruf, et al., 2001; Takaya, et al., 2000). In excess water, the DSC endothermic peak temperature of a starch due to gelatinisation is located in the range of 55 - 70°C depending on the botanical source (Jenkins & Donald, 1998). As water content decrease, the second endotherm at higher temperature is developed (Jenkins & Donald, 1998; Barron, et al., 2000; Maaruf, et al., 2001). One explanation for the two endotherms in a DSC observation of gelatinisation is that the swelling of the amorphous regions of the granule at higher water level pulls molecular chains from the surface of crystallities. As water becomes limiting, some part of the crystallites can not be disrupted in this manner, they undergo melting at higher temperature and give rise to the second endotherm (Donovan, 1979; Jenkins & Donald, 1998; Maaruf, et al., 2001).

As structure of a starch granule is complex, and different techniques probe different aspects of the gelatinisation process, it should not be surprising that the descriptions of the processes during gelatinisation are not exactly map onto each other. It was found that the loss of birefringence occurred over a narrower temperature range than the loss of crystalline order determined by DSC (Liu, et al., 1991). A combined study by using SAXS/WAXS/DSC and SANS showed that the results of DSC seem not to tell the whole story of gelatinisation, because the range of crystallinity loss exceeds the range of the DSC endotherm, the gelatinisation process may thus occur over a wider temperature range (Jenkins & Donald, 1998). Even so, the extent of the loss of order as a function of temperature is broadly similar. To further assess loss of order as function of temperature, the heterogeneity in granule and over population of starch should be considered (Parker, & Ring, 2001). The heterogeneity in a population of granules, i.e., granule sizes, size distribution and concentration gradients might affect starch

gelatinisation behaviour. For instance, as the granules that gelatinise first will absorb some of water and swell, the amount of water available for other granules gelatinisation is reduced. Thus, the temperature of gelatinisation will be elevated due to the decrease of water content. This contributes to the temperature range of gelatinisation.

2.1.4 The glass transition temperature of starch

Amorphous polymers (or the amorphous regions in a partially crystalline polymer) exhibit behaviour dependent on a temperature termed as glass transition temperature, T_g. Below this temperature the material is glassy and brittle, above this temperature the material is rubbery and ductile. The glassy nature is due to the frozen molecular mobility of the long chain molecules. The transition from glassy toward rubbery corresponds to the onset of segmental motion in the chains. The increase of molecular motion is indicated by an abrupt increasing of both the coefficient of expansion and the heat capacity as the temperature is being raised. In general, the glass transition temperature is dependent on the thermal history of the material, the molecular weight and molecular weight distribution of the polymer chains, the degree of crystallinity, and the presence of plasticizers. The importance of the glass transition temperature has been recognised in determining the processability of amorphous, synthetic polymers.

The glass transition temperature, T_g, of dry amorphous starch is not normally accessible experimentally because of the thermal decomposition of starch polymers at elevated temperature (Orford, et al., 1989). Water has been shown to act as a plasticizer for starch. The plasticizing effect of water on the phase transitions of starch has been of considerable interest during last fifteen years. Many studies were focused on the glass transition behaviour of a variety of starch-water systems (Hoseney, et al., 1986; Zeleznak, & Hoseney, 1987; Orford, et al., 1989; Kalichevsky, et al., 1992; Yuan, & Thompson, 1994; Thiewes, & Steeneken, 1996; Forssell, et al., 1997; Mousia, et al., 2000). The T_g of starch is strongly dependent on the moisture content, it decreases with increasing of moisture content due to the plasticizing effect of water. The trend in T_g depression by moisture has been observed in rice, wheat and waxy starch (Chung, et al., 2002; Zeleznak, & Hoseney, 1987; Kalichevsky, et al., 1992). By studying the plasticizing effect of different amount of water, the T_g of dry starch was estimated to be

in the range of 240 - 250°C (Biliaderis, et al., 1986). Based upon extrapolation of the glass transition temperatures of malto-oligosaccharides with different degrees of polymerisation, the T_gs of dry amylose and amylopectin were estimated to be about 230°C (Orford, et al., 1989).

It is difficult to make accurate measurements of T_g of the granular starch - water system due to its complexity and heterogeneity. DSC is the most frequently used method, but it is only possible to detect the T_g by DSC within a narrow moisture content range about 13 – 22% (Zeleznak, & Hoseney, 1987). Because the glass transition occurs below room temperature at moisture content greater than 22%, and the transition is too broad and not clearly defined below 13% moisture. Other methods such as dynamic mechanical thermal analysis (DMTA) (Kalichevsky, et al., 1992; Appelqvist et al., 1993; Pereira, & Oliveira, 2000) and nuclear magnetic resonance (NMR) (Kalichevsky, et al., 1992) have also been applied.

There are a number of theoretical approaches to prediction of the composition dependence of the glass transition temperature. The classic thermodynamic theory allows a prediction to be made of the T_g of binary mixtures from the properties of their pure components, which seems to be useful to account for the effect of plasticizer upon the glass transition temperature. In the case of starch and water, the equation is of the form (Kalichevsky, et al., 1992):

$$T_g = \frac{W_1 \Delta C_{p1} T_{g1} + W_2 \Delta C_{p2} T_{g2}}{W_1 \Delta C_{p1} + W_2 \Delta C_{p2}} \tag{2.1}$$

where T_g is the glass transition temperature, ΔC_p is the change in heat capacity of the pure component at its T_g, and W is the weight fraction of the component. The subscripts 1 and 2 denote the two components, water and starch, respectively.

The T_gs of the same starch at native state and gelatinised state could be different. This difference has been observed in wheat starch and rice starch (Zeleznak, & Hoseney, 1987; Chung, et al., 2002). The glass transition temperature of native starch is higher

than that of gelatinised starch and the difference becomes greater as the water content decrease. This may be attributable to the crystalline regions in granules of native starch. It is believed that the crystalline domains, surrounded by the continuous amorphous regions in starch granules, behave as cross-linkages among the amorphous regions (Zeleznak, & Hoseney, 1987), this would suppress the mobility of amorphous molecules. The larger difference in T_g between native and gelatinised starches at lower water content indicates that the constraining effect of crystallites is reduced by the presence of water that acts as a plasticizer.

2.1.5 Pasting characteristics of starch aqueous suspension

In this thesis, the term "starch paste" refers to the viscous slurry obtained by heating and stirring a starch aqueous suspension, and the process from aqueous suspension to paste is known as pasting. The pasting characteristics of starch aqueous suspension are of great significance not only in various applications but also in structural studies. The native starch granules are insoluble in cold water. However, when sufficient heat is applied to a water-starch system, starch granules will swell and the components of starch, mainly amylose, will be released and solubilized, which increase the viscosity of the starch slurry. The resulting paste becomes a macromolecular solution which is composed of water, amylose leaching from starch granules and dispersed swollen starch granules. The more the heat energy input, the greater the extent of granule swelling and the more the leaching of amylose. Viscosity is strongly influenced by the swelling of starch granules (Tattiyakul, & Rao, 2000; Parker, & Ring, 2001). Peak viscosity occurs when the swollen granule reaches its largest size before rupture which induces a viscosity decrease. Fragmentation of the granules causes a decrease in viscosity and change in the texture of the system. As the system is cooled, a gel is formed. For common starches, containing both amylose and amylopectin, when the concentration is low and in the absence of shear, the gel consists of fully swollen amylopectin-rich granules dispersed in an amylose-water matrix. At higher starch concentration, the granules may be partly swollen and tightly packed. If a shear is applied to the system, the granule structure may be destroyed and the behaviour of the gel will depend on the

amount of amylose and amylopectin (Svegmark, & Hermansson, 1991; Parker, & Ring, 2001).

The rheological behaviour of starch pastes and gels is rather complex and dependent on various factors such as botanical source, starch concentration and pasting conditions. Based on viscosity and its relation to shear rate, a fluid can be classified as Newtonian and non-Newtonian. The viscosity of a Newtonian fluid remains constant independent on the shear rate applied. Non-Newtonian fluids are characterised by changes in viscosity with respect to shear rate (Manohar, et al., 1998). In general, most starch pastes are non-Newtonian fluids (Nguyen, et al., 1998; Al-Malah, et al., 2000), their viscosity not only depends on starch concentration and temperature, but also on shear rate, time and shear history (Nguyen, et al., 1998; Nurul I, et al., 1999; Lagarrigue, & Alvarez, 2001).

Various types of rheometers were used to characterise viscosity of starch suspensions and pastes (Abdelrahim, et al., 1995; Lai, 2001; Al-Malah, et al., 2000; Nurul I, et al., 1999; Manohar, et al., 1998). Since the differences in the geometry of the test chambers and heating conditions, the flow field and temperature homogeneity in the samples may be different, the results obtained from different type of rheometers are not easily to be compared with each other (Nguyen, et al., 1998; Lagarrigue, & Alvarez, 2001). In some frequently used commercial instruments, such as the Rapid Visco Analyser (RVA), the shear field is not defined perfectly and shear rate is not uniform within a sample, it only gives out system-specific and empirical viscosity signal from torque rather than true viscosity. These results are useful for investigating the gelatinisation and pasting behaviour of starch, but not suitable for viscosity measurement for process simulation. On the other hand, the standard viscometric instruments equipped with rotational concentric cylinder, or cone and plate geometries have the advantage of well-defined shear fields and can measure relationships of shear stress and shear rate that are independent on the apparatus employed (Nguyen, et al., 1998). However, the sedimentation of particles, the narrow gaps and inefficient heat transfer characteristics (low heating/cooling rates) are additional problems of conventional rheometers for measuring starch pastes as they are heated.

Several models were used to describe rheological behaviour of gelatinised starch aqueous suspension (Abdelrahim, et al., 1995; Bhattacharya, & Bhattacharya, 1996; Stolt, et al., 1999; Rao, & Tattiyakul, 1999; Al-Malah, et al., 2000; Lagarrigue, & Alvarez, 2001). These models are summarised in Table 2.3, where τ is shear stress, and γ is shear rate. Based on the shear rate and shear stress data obtained by standard rheometers, the rheological parameters, such as the consistency coefficient (m) and the flow behaviour index (n), can be evaluated through a linear or non-linear regression method. The power law model is the most frequently used model for describing the rheological behaviour of starch suspensions (Nguyen, et al., 1998; Nurul I, et al., 1999; Stolt, et al., 1999; Manohar, et al., 1998). The consistency coefficient m, a key parameter reflecting viscosity, is very dependent on the type of starch, concentration and temperature. On the other hand, the dependence of flow behaviour index n, a measure of the non-Newtonian behaviour, on the above three factors is not always obvious (Nguyen, et al., 1998; Lagarrigue, & Alvarez, 2001).

Table 2.3 Rheological models for gelatinised starch dispersion

Model	Formula	Parameters
The power-law	$\tau = m(\gamma)^n$	M and n
Herschel-Bulkley	$\tau = \tau_{0HB} + m_{HB}(\gamma)^{nHB}$	τ_{0HB}, m_{HB} and n_{HB}
Bingham plastic	$\tau = \tau_{0B} + \eta_B(\gamma)$	τ_{0B} and η_B
Casson	$\tau^{1/2} = \tau_{0C}^{1/2} + (\eta_C\gamma)^{1/2}$	τ_{0C} and η_C
Mizrahi-Berk	$\tau^{1/2} = \tau_{0MB}^{1/2} + m_{MB}(\gamma)^{nMB}$	τ_{0MB}, m_{MB} and n_{MB}

2.1.6 Retrogradation

Retrogradation is a term used for the reassociation of starch chains (amylose and amylopectin) in gelatinised starch that occurs on cooling or storage and leads to the structural changes from an initially amorphous or disordered state to a more ordered or

crystalline state (Perera, & Hoover, 1999). The process of starch pastes to thicken and to form stiffer gel is also termed retrogradation (Lee, et al., 1998; Parker, & Ring, 2001).

Starch retrogradation is a recrystallisation process, which can only occur in the temperature range between the glass transition temperature and the melting temperature in a dispersed starch system. The kinetics of starch retrogradation exhibit a strong temperature dependence because the nucleation rate increases exponentially with decreasing temperature down to the glass transition temperature, T_g, while the propagation rate increases exponentially with increasing temperature up to the melting temperature, T_m (Silverio, et al., 2000). The rate of retrogradation is expected to be at a maximum approximately mid way between the T_g and T_m. This reflects a balance between the effect of temperature on the driving force favouring crystallisation, and the reduction of mobility as the glass transition is approached (Parker, & Ring, 2001).

The short-term development of crystallinity in starch gels is attributed to the gelation and crystallisation of amylose and takes only a few hours (Fredriksson, et al., 1998; 2000). Therefore, the higher the amylose content the starch has, the greater the gelling capability. Gelling of amylose also gives rise to opacity and syneresis in starch paste. While the long-term reordering that occurs during storage of starch gels is attributed to the recrystallisation of amylopectin which is much slower process over a period of several days or weeks (Miles, et al., 1985; Karim, et al., 2000; Fredriksson, et al., 2000). The influence of the botanical source (Fredriksson, et al., 1998; Silverio, et al., 2000), concentration (Morikawa, & Nishinari, 2000) and storage temperature and duration (Silverio, et al., 2000) on the retrogradation behaviour have been investigated. In general, potato starch exhibits the highest retrogradation enthalpy, and cereal starches the lowest, while pea starch shows intermediate retrogradation enthalpy (Fredriksson, et al., 1998). It was concluded that the longer the length and abundance of the short chain fraction of amylopectin, the greater the tendency to retrograde and crystallise from aqueous solution (Parker, & Ring, 2001).

2.2 Extrusion technology for cooking starch

2.2.1 Extrusion cooking of starches

Extrusion processing technology, often carried out using a twin-screw extruder, has been widely used for the production and property modification of various starch containing products (Kokini, et al., 1992; Guy, 2001c). The thermal energy generated by viscous dissipation during extrusion, combined with shearing results in physico-chemical changes of the raw materials so that the properties of the biopolymer materials are modified. Depending on the energy input, extrusion cooking of starch in the presence of water may result in destructurization of the native granules, gelatinisation of starch, reduction in biopolymer molecular weight, and formation of complexes between starch, lipids and proteins (Singh, & Smith, 1997; Bouvier, 2001). Since extrusion cooking is an important process for processing of foods and biopolymer materials, extensive research works have been carried out for various starches (Kirby, et al., 1988; Della Valle, et al., 1995; Akdogen, 1996; Singh, & Smith, 1997; Guha, et al., 1997; Singh, et al., 1999).

The transformations of starch that occur during extrusion are influenced by extruder characteristics such as extruder type and screw configuration as well as by the processing variables such as extrusion temperature, screw speed, material feeding rate and water content of starch. Temperature and water content have been considered as the two most important variables affecting the physical properties of the extruded starch (Shogren, et al., 1993). These factors are inter-related. For instance, increasing of the screw speed or feeding rate or decreasing of the water content will cause increasing of shear, which in turn leads to temperature rising in the extruder. To assess the intensity of cooking, some researchers use a term, the specific mechanical energy (SME), to characterise the extrusion processes (Ollett, et al., 1990; Brent, et al., 1997; Singh, & Smith, 1997; Miladinov, & Hanna, 2001). Specific mechanical energy may be defined as the energy output of the motor on per unit mass of the extrudate, assuming all the energy is dissipated into the materials. SME can be calculated by either Equation 2.2 (Akdogan, 1996; Miladinov, & Hanna, 2001):

$$\text{SME (J/kg)} = \frac{Torque\,(N \times m) \times Screw\ speed\,(rpm)}{Mass\ flow\ rate\,(kg\,/\,h)} \tag{2.2}$$

or Equation 2.3 (Singh, & Smith, 1997; Guha, et al., 1997; Brent, et al., 1997):

$$\text{SME(J/kg)} = \frac{Screw\ speed \times Motor\ power\,(kW) \times Torque\,(\%)}{Max.\ screw\ speed \times Throughput\,(kg\,/\,h) \times 100} \tag{2.3}$$

Any variable which affects the viscosity of the mixture of materials in the extruder would correspondingly affect torque and SME. SME is significantly dependent on water content, temperature and feeding rate. The gelatinisation of extruded maize grits was found to increase with increasing of the SME during extrusion (Ilo, et al., 1996). It was also found, as expected, that increasing the temperature at constant water content, screw speed, and mass flow rate resulted in a decrease in the torque and SME (Akdogan, 1996).

It is generally recognised that different product types require different process conditions for their manufacture. Since starch extrusion process is also known as extrusion cooking, the term, *degree of cook*, has been used in attempt to describe the intensity of processing a starch mix might receive in the operation of a particular extrusion run (Guy, & Horn, 1988). The evaluation of degree of cook for starch materials will be reviewed in Section 2.4.

Starch extrudates tend to expand upon exiting the extrusion die due to the elastic expansion of the molten extrudates. The stored energy is released during the expansion process, and thus radial expansion of extrudate can be easily observed, which is known as die swell. To avoid foaming of extrudate at the die, extrusion conditions should be optimised as suggested by Simmons & Thomas (1995) for a starch-glycerol-water system:

a) lowering the amount of water injected into the extruder and/or replacing it with certain amount of glycerol;

b) keeping the temperature at the die from 90 to 95°C, which is lower than the boiling temperature of water at atmospheric pressure (glycerol was not expected to contribute to the foaming process since its boiling point is 290°C);

c) venting of water vapour from the extruder's venting ports before reaching the die.

2.2.2 Rheology of molten starch during extrusion

The knowledge on the rheology of starch melts has always been a focus of interest through the development of extrusion cooking processes as it reflects changes in the materials and has important influence on the control of extrusion cooking.

The physical structure of the starch is modified during extrusion. Cleavage of the hydrogen bonding network in the granules leads to the loss of crystallinity (Poutanen, & Forssell, 1996); and the shear forces lead to destruction of the structure of granules. Extrusion cooking of starch may result in a high degree of mixing of the amylose and amylopectin. Molecular chain scission may occur during extrusion, especially for amylopectin molecules owing to their larger size of molecules relative to amylose. All these changes during extrusion cooking can be reflected by the rheological behaviour of the materials. Thus, the control of the end product quality and the choice of optimal processing conditions require a better understanding of the rheological properties of molten starch.

Factors affecting the rheological behaviour of a starchy melt are material composition, temperature, water content, and the thermomechanical history of the material. Recent studies have illustrated how these parameters affect the rheological behaviour of the melt starches (Willett, et al., 1995; Ilo, et al., 1996; Della Valle, et al., 1996).

The water content and shear forces have a highly significant effect on the viscosity of a starch melt. Water acts as a plasticizer for starch based materials, reducing the viscosity and the mechanical energy dissipation during extrusion. The swelling of starch granules increases the viscosity, but the shear stress in extruder can break-up the granules into smaller fragments causing a reduction in melt viscosity.

The viscosity, η, of cereal dough has been found to have a powder-law dependence on shear rate, γ, an Arrhenius dependence on temperature, T, and an exponential dependence on water content, WC (Villar, et al., 1995; Ilo, et al., 1996) shown in Equation 2.4:

$$\eta = K\gamma^{n-1} e^{\Delta H/RT} e^{-kWC} \tag{2.4}$$

where K is the consistency index, n is the power-law exponent, ΔH is the flow activation energy, R is the gas constant, and k is the water dependence constant. Generally, viscosity decreases when temperature and water content increase for a fixed thermomechanical treatment. Viscosity decreases with increasing intensity of treatment and the effect is more pronounced at higher temperatures.

In order to take into account the impact of macromolecular degradation on melt viscosity and its link with the specific mechanical energy (SME), Della Valle et al (1996) proposed a viscosity model shown in Equations 2.5 – 2.7 based on the power law:

$$\eta = K\gamma^{n-1} \tag{2.5}$$

where

$$K = K_0 e^{[(E/R)(1/Ta) - \alpha(WC) - \beta(SME)]} \tag{2.6}$$

and

$$n = n_0 + \alpha_1 T + \alpha_2(WC) + \alpha_3(SME) + \alpha_{12}T(WC) + \alpha_{13}T(SME) + \alpha_{23}(WC)(SME) \tag{2.7}$$

where T_a (°K) is the absolute temperature of the melt, WC is a normalised value (between 0 and 1) of water content, T in °C, and SME in kW h/t. The ratio of the flow

activation energy to the gas constant, E/R, and the coefficients α, β, and α_i are obtained by multiple linear regressions of the experimentally determined values of n and K, which is somewhat tedious and time consuming for the application of the model in practical use.

Several studies on the effects of variables such as water content and extrusion temperature on starch viscosity have been reported. There were considerable variations in the results, reflecting the effects of different types of starches and varying degrees of starch modification during extrusion. Willett et al (1995) reported that the power law index, n, showed a greater dependence on temperature than moisture content for corn starch, and increased from 0.37 to 0.52 as the temperature increased from 120°C to 150°C for the corn starch tested. While Padmanabhan and Bhattachayrya (1993) reported that the power law index n was most dependent on moisture content and molecular degradation of starch during extrusion. The value of n changed from 0.4 to 0.3 for extruded corn meals, as the moisture content decreased from 35 to 25g/100g (dry basis). Most food dough has been shown with n values varying from 0.25 to 0.75 (Lai, & Kokini, 1990). Flow curves for the corn meal under high shear and high temperature extrusion conditions showed severe shear thinning behaviour (n < 0) at lower moisture content (Padmanabhan, & Bhattacharya, 1991). Molecular degradation is believed to be the major factor responsible for n < 0. In general, the consistency K decreases with increasing temperature and increasing water content (Willett, et al., 1995).

It was also found that the viscosity increased as the amylose content in the starch was increased (Villar, et al., 1995). This is because amylose is more entangled than amylopectin, which leads to a higher overall viscosity. By studying the effect of different amylose content on the rheological behaviour of low hydrated molten starches, Della Valle et al (1996) found that the viscosity was more sensitive to moisture content and thermo-mechanical treatment at lower amylose contents, and the main differences observed when decreasing the amylose content were a lower viscosity and less pronounced shear thinning.

2.3 Processing of starch for biodegradable material applications

2.3.1 Physico-mechanical modification of starch

Natural starch exhibits a pronounced macromolecular structure, which is suitable for the production of bio-plastics. However, the native starch itself, without any modification, cannot be processed by conventional processing technology for thermoplastics because it will degrade when heated without forming a melt on its own (Villar, et al., 1995; Simmons, & Thomas, 1995; Matzinos et al., 2001). Therefore, it is necessary to modify the structure of the native starch so that it becomes a so-called *thermoplastic starch.*

The modification of starch is commonly carried out by extrusion under controlled pressure and temperature with water or other plasticizers to destructurize the starch granule structure with the introduction of mechanical and heat energy and to convert it into a homogeneous material that behaves as a thermoplastic (Funke, et al., 1998; Lorcks, 1998). The presence of enough water or other plasticizers is necessary so that the starch will melt below its decomposition temperature and yield a material in which a continuous polymeric phase is formed (Shogren, et al., 1993). Then these thermoplastic materials can be transformed into useful articles using processing technology such as injection, compression or blow moulding.

The type of native starch, moisture content within the starch granules, temperature, pressure, type and amount of plasticizer are significant factors influencing the conversion process. By altering one of these factors, thermoplastic starch with different properties can be prepared (Bastioli, 1998; Matzinos et al., 2001). Therefore, the characteristic extrusion variables differed broadly depending on the type of starch, additives used and the properties of the end products.

2.3.2 Plasticization of starch materials

The role of a plasticizer added to a polymer is to assist flow of the polymer melt and to increase the ductility of the final material. From a thermodynamic point of view, this additive decreases the glass transition temperature, so as to obtain a rubbery material or a material with considerable ductility.

In the production of thermoplastic starches, plasticizers are expected to reduce the intermolecular hydrogen bonds effectively, and to lower the T_g of the products. The nature and amount of plasticizers influence the properties of physically processed starch in two ways: by controlling the degree of destructurization and depolymerization during disruption of the hydrogen bonds, and by acting as softeners in the processed material (Poutanen, & Forssell, 1996).

Water is the most usual plasticizer in starch processing, and the physical properties of starch materials are greatly influenced by the amount of water present. However, its volatility results in changes of moisture content in the materials and hence properties of materials under environment humidity during storage and usage. At mean ambient environment (20°C and 50% RH), the starch material plasticized by water alone typically possess characteristic of a glassy material with glass transition temperature above ambient temperature and often too brittle to be of any use. These materials could be used more extensively if the temperature range corresponding to rubbery plateau were extended by additional plasticizers to include ambient temperature.

Apart from water, a wide range of alternative plasticizers has been studied. These include glycerol (Lourdin, et al., 1997a; van Soest, & Knooren, 1997; Averous, et al., 2000; Myllarinen, et al., 2002b) glucose (Ollett, et al., 1991), sorbitol (Gaudin, et al., 1999; Lourdin, et al., 1997a; Funke, et al., 1998), lactic acid sodium (Lourdin, et al., 1997a), amino acids (Stein, et al., 1999), and urea (Lourdin, et al., 1997a). It had been demonstrated that some of these can effectively reduce the glass transition temperature of the starch material and improve its toughness. The use of glycerol as a plasticizer has also received much attention, especially for the production of thermoplastic starches.

In addition, physical ageing in thermoplastic starch also leads to the material embrittlement. Ageing refers to the change in mechanical properties of starch thermoplastics with time. Generally, modulus and strength of the materials increase and impact strength or flexibility decrease. The exact mechanisms of ageing are still unclear, but it has been attributed to phase separation of plasticizers from starch, starch molecule re-orientation, or crystallisation of amylopectin (van Soest, & Knooren, 1997; Myllarinen, et al., 2002b; Parker, & Ring, 2001).

Therefore, many studies have been focused on the selection and stability of plasticizers during preparation of starch based materials by extrusion or other methods, such as casting, and characterisation of their effects on material properties. Ideally, the plasticizer should be non-volatile; reduce the sensitivity of the material properties of starch to fluctuations in moisture content; and reduce the sensitivity of the materials to ageing through crystallisation (Moates, et al., 2001).

More details about the plasticizers used and their effects on the properties of starchy materials will be reviewed in Section 2.5.2.

2.3.3 Blending and grafting with polymeric materials

2.3.3.1 Blend with polymeric materials

It is known that starch is hydrophilic and the moisture content within the material varies with the relative humidity of the atmosphere in which it is stored. Because of this hygroscopic nature and the effect on the mechanical properties of the material which are relatively poorer than most synthetic plastics, it is often necessary to blend thermoplastic starch with other synthetic polymers for many practical applications. Though some researchers (Fringant, et al., 1996) tried to modify the starch structure, e.g. by acetylation, to reduce the hydrophilic character of the chains, this chemical modification resulted in inferior mechanical properties and greater product cost (Averous, et al., 2000).

Blending starch with polymeric materials is known for several decades. In some of work, starch was only used in granular form as fillers (Griffin, 1977; Willett, 1994; Griffin, 1994) for the sake of giving some biodegradable characteristics to the thermoplastic polymers. However, as starch was blended with polymers in the granular form, only limited amount of starch, about 10% or less by weight (Shogren, et al., 1993), can be incorporated into the mixture without leading to mechanical property deterioration. Starch loading was improved to about 50wt% by using the destructurized (or gelatinised) starches in PVC, ABS and PE (Griffin, 1978; Otey, & Westhoff, 1982). The starch content in these technologies was limited primarily by acceptable level of reduction in mechanical properties.

More recently, thermoplastic starch has been blended with synthetic polymers for two major purposes. One is to improve the properties of thermoplastic starch, such as by adding a small amount polymer to improve the brittleness and water resistance of thermoplastic starch which hinder its more wide spread applications. Another one is to reduce the cost of products of some synthetic biodegradable polymers since starch is inexpensive and biodegradable.

The polymeric materials used to blend with starch are ranged from non-biodegradable conventional plastics to what is known as biodegradable polymers. Conventional plastics such as low density polyethylene (St- Pierre, et al., 1997; Prinos, et al., 1998; Matzinos et al., 2001), polypropylene (Gonsalves, et al., 1991; Zuchowska, et al., 1998) were blended with starch in attempts to preserve the mechanical properties of petrochemical-derived plastics and it was also hoped that, as the starch component degraded, the remaining plastic matrix of the blend would be sufficiently unstable so that it could mechanically fall apart and "disappear". Clearly, this degradation process was not sufficient enough to allow the materials to be classified as completely biodegradable, because the fragments of synthetic polymers will still exist and may cause problem associated with the residues, such as deterioration of soil quality when such materials are used for mulching films.

Other polymers such as poly (ethylene-co-vinyl alcohol) (George, et al., 1994; Simmons, & Thomas, 1995; Villar, et al., 1995; Stenhouse, et al., 1997), poly (ethylene-co-acylic acid) (Fanta, et al., 1992), poly (vinyl alcohol) (Lenk, 1980; Lawton, & Fanta, 1994; Stenhouse, et al., 1997; Lawton, 1996; Shogren, et al., 1998a; Liu, et al., 1999; Willett, & Shogren, 2002), polycaprolactone (Koenig, & Huang, 1995; Averous, et al., 2000), poly (lactic acid) (Park, & Im, 2000; Martin, & Averous, 2001; Willett, & Shogren, 2002), poly(hydroxyester ether) (Zhou, et al., 2001; Willett, & Doane, 2002; Willett, & Shogren, 2002; Walia, et al., 2002) were also used in blends with starches. Some starch-based blends have been commercialised, such as the Mater-Bi™ by Novamont, Italy (Bastioli, 1998) and the Bioplast™ by Biotec, Germany (Lorcks, 1998).

The improvements of mechanical properties of starch materials by blending with polymers will be reviewed in Section of 2.5.3.

2.3.3.2 Grafting with polymeric materials

Due to the hydrophilic nature of starch, blends with hydrophobic plastics have poor mechanical properties as a consequence of lack of compatibility and thus poor interfacial adhesion. Direct grafting of polymeric chains onto the starch backbone is another type of modification of starch, which provides an important method for preparing starch - polymer composites. By grafting two materials together (usually using coupling agents), a primary chemical bonding between two or more phase can be established and so a singular continuous phase containing material may be achieved (Uyama, et al., 1998). Since starch and synthetic polymer are held together by chemical bonding, as opposed to merely existing as a physical mixture in blends, the two dissimilar polymers could be intimately associated, and phase separation is less likely to occur. Such examples are starch-g-polystyrene (Fanta, et al., 1977 & 1983), starch-g-poly(methyl acrylate) (Patil, & Fanta, 1993; Trimnell, et al., 1993), and aliphatic polyester grafted starch (Dubois, et al., 1999).

Henderson and Rudin (1982) reported the tensile and dynamic mechanical properties of extruded and moulded samples of starch-g-polystyrene (S-g-PS) and starch-g-poly(methyl acrylate) (S-g-PMA). For the extruded ribbons of S-g-PS, the ultimate tensile strength (UTS) was 35.3 ± 3.2 MPa; while the UTS was 14.3 ± 1.9 MPa and % elongation at break (%E) was 70 ± 25 for extruded ribbons of S-g-PMA. However, the injection moulded specimens of S-g-PMA had %E of 150 ± 20, but UTS dropped to 12.5 ± 1.2 MPa.

Trimnell et al (1993) reported that the properties of ribbons prepared from extrusion-processed starch-g-poly(methyl acrylate) depended on the combined effects of poly(methyl acrylate) (PMA) level in the graft copolymer, moisture content of the graft copolymer during extrusion, and the temperature at which samples were extruded. The graft copolymers containing 46 and 58% PMA exhibited the highest values for both UTS and %E when extrusion was performed at 180°C and 10% water. The UTS was reduced and %E was increased when the water content during processing was increased to 30%.

2.4 Characterisation of structure and properties of extruded starch

Extrusion technology offers an effective means for the modification and plasticization of starches. A variety of microstructual changes from molecular levels to the macroscopic scales in starchy materials occur during extrusion. Shearing of the molten granules destroys their organised crystalline structure, and the granular starch is converted to a dispersed, amorphous and homogeneous material. The melt and dispersed starch can also recrystallise into several crystal structures depending on the extrusion condition and material composition. Since the physical and mechanical properties of starch-based materials depend on the physical state of starch polymers, it is of particular interest to estimate and characterise the nature and extent of changes in starch polymers induced by extrusion cooking, and their effects on the properties of the materials. In this section, several key methods used for estimating the degree of cook of extruded starch in food industry have been reviewed.

2.4.1 Structural changes of starch after extrusion cooking

In extrusion, starch cooking is achieved by application of both thermal and mechanical energy. Basically, three phenomena may occur at different structural levels (Poutanen, & Forssell, 1996):

- Fragmentation of starch granules;

- Hydrogen-bond cleavage between starch molecules, leading to loss of crystallinity; and

- Partial depolymersation of the starch polymer chains.

Depending on the processing conditions, the extrudates could be composed of residual swollen granular starch (partially broken and partially melted granules), completely molten starch, and recrystallised starch. Therefore, residual native A-, B-, or C-type crystallinity and processing-induced crystallinity (V- and E-types) could be present in the extrudates.

The existence of residual native starch crystallinity in extrudates is due usually to incomplete gelatinisation or melting of starch during extrusion when the energy input is too low (Ollett, et al., 1990; van Soest, et al., 1996a). Therefore, the amount of residual crystallinity is related to processing conditions such as processing temperature or applied shear.

DSC and optical microscopy using crossed polarisers have also been used to investigate the existence of crystal in the starch materials, however, these techniques can not give further information about the types of crystallinity, or structural changes that occur in starch during extrusion processing.

X-ray diffraction has often been used to characterise the crystallinity of native starches and processed starch-based materials, because it provides information about the long-range order of the molecular constituents in polymers, including levels and types of crystallinity.

By X-ray diffraction, two types (V- and E-) of extrusion induced crystalline structures have been observed. These crystallinities are caused by the rapid recrystallization of single-helical structures of amylose during cooling after processing (van Soest, & Vliegenthart, 1997). The amount of these types of crystallinity depends on the processing conditions, as well as the composition of the materials.

The most frequently observed structure is denoted as V-type, which is induced when starches are extruded in the presence of lipids. The V-type structure has a 6-fold left-handed helix in an orthorhombic unit cell or in a hexagonal unit cell (van Soest, et al., 1996a). Another structure termed E-type has been also observed which is characterised by three diffraction peaks slightly displaced from those of the V-type and may be transformed back to the stable V-structure. It has been proposed that the E-type structure is helical and like the V-structure, has six glucose residues per turn. The differences between the two structures have been attributed to different interaxial distances between helices (Shogren, et al., 1993). The E variant is formed under conditions of reduced water availability and higher temperatures and can be converted to the stable V-type by increasing the moisture content of the extrudate (Cairns, et al., 1997).

The diffraction parameters of the processing induced crystallinities in extrudates are summarised in Table 2.4 (van Soest, et al., 1996a; Cairns, et al., 1997).

Table 2.4 The diffraction parameters of V and E type crystals in extruded starches

Type	2θ (°)	Intensity
V	7.1/7.4	Strong
	12.6/13.0	Strong
	19.4/20.0	Very strong
	22.1	Medium
E	6.6/6.9	Medium
	11.6/12.0	Medium
	18.0/18.5	Strong

The processing induced crystallinity depends upon the processing conditions, especially the extrusion temperature and moisture content. It is known that for the crystalline polymers, the crystallinsation phase will form when the material temperature lies between its melting and glass transition temperatures. Water acts as a plasticizer during extrusion. A decrease in water content will cause increasing of T_m and T_g of the starch material being extruded. If, as a result of changes in water content, the extrusion temperature falls below T_m, crystallisation will occur. Directly lowering the extrusion temperature below T_m would also induce crystallisation. The cooling rate and drying rate of the extrudates should also have influence on the formation of crystalline amylose complexes, but no research report was found.

It has been found that the amount of V- type crystallinity is proportional to the amount of amylose (van Soest, et al., 1996a). Starch source and thereby lipid contents are important factors affecting the formation of these processing induced structures. Since the V-type and E-type structures come from the amylose-lipid complexes, none of them have been observed in potato starch (which is lipid free) or in waxy maize starch (which contains no amylose).

2.4.2 RVA characterisation of degree of cook during extrusion

Intact starch granules are generally insoluble in cold water (below ~ 50°C). When starch granules are heated in water beyond a critical temperature, the granules will absorb water and swell; meanwhile the soluble amylose in the granules will leach out into solution. All these will affect the viscosity of starch aqueous suspension. Rapid Visco Analyser (RVA) is a useful tool for rapid evaluation of the pasting characteristics of starches and their products by monitoring viscosity of starch aqueous suspension over a time-temperature profile. The measurement can be accomplished during a short testing time and only a small amount of sample is required.
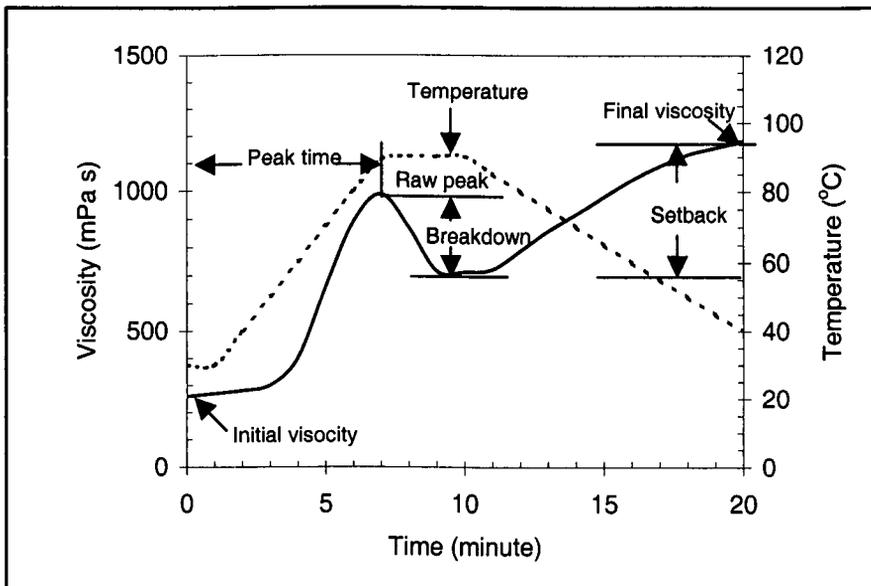
Figure 2.3 Typical RVA curve for a native starch.

Figure 2.3 presents a typical RVA curve for a native starch. The viscosity and temperature profile were recorded with time, and the commonly measured parameters were highlighted. After holding at room temperature for 2 minutes, the solution is heated linearly to 95°C and held at this temperature for 3 minutes, then cooling down to room temperature. During this heating and cooling process, the apparent viscosity calculated from the torque is monitored and recorded. At the early stage of heating, the temperature is below the gelatinisation temperature of the starch, and the viscosity is

low. When the temperature rises above the gelatinisation temperature, the starch granules begin to swell, and viscosity increases. When a sufficient number of granules become swollen, a rapid increase in viscosity occurs. As the temperature increases further, the granules rupture and the more soluble amylose leaches out into the solution. Peak viscosity occurs at the equilibrium point between swelling and polymer leaching. During the hold period of the test, the sample is subjected to a high temperature (usually 95°C) and mechanical shear stress. This will further disrupt the granules and amylose molecules will generally leach out into solution and undergo alignment i.e., orienting themselves in the direction that system is being stirred (Nelles, et al., 2000), which will cause a decline in viscosity known as viscosity breakdown. As the sample is subsequently cooled, retrogradation occurs. This usually causes a degree of gelation within the paste, and viscosity will normally increase to a final viscosity.

The thermo-mechanical reactions such as gelatinisation and molecular degradation occurred during extrusion of starch will subsequently change the behaviour of aqueous suspension of the starch extrudate. Although viscosity of aqueous suspension of a starch extrudate, determined by the commercial RVA, is not appropriate measures of the rheological properties of the starch melt in the extruder, they do reflect physical and structural changes in the extrudate resulted from the extrusion process (Bhattacharya, et al., 1999). Parameters generated from the RVA tests provide a relative measure of gelatinisation, swell, and gelling ability of the extruded starch and thus give some useful information about the degree of cook.

Extrusion cooked starch has different characteristic RVA curve compared with native starch. More than ten characteristics parameters, which have been classified into the time-related parameters, the viscosity-related parameters and the slope-related parameters, can be determined by RVA curves (Ryu, et al., 1993). The viscosity-related parameters as indicated in Figure 2.3, "initial viscosity", "raw peak", and "final viscosity", are most relevant to the degree of cook. The *initial viscosity* is an indication of the extent that the molecular order within starch granules has been disrupted or damaged. A higher value of initial viscosity means that more starch granules have been disrupted so as more granules can swell in could water and more amylose leach into solution. The *raw peak* is originated from the granule swelling and leaching of amylose

due to heating. So it is an indication of amount of starch granules (or residuals) that is available for further gelatinisation. A higher value of raw peak generally means that more intact granules (may be in the form of fragment) exist in the extrudates. *Final viscosity* is an indication of gelling ability which can give some information on the degradation of the starch materials. A lower value of final viscosity usually means the starch molecular chains are more seriously degraded or shortened.

The work of Bhattacharya et al (1999) showed that the initial viscosity of a mixture of wheat and potato flour increased considerably after extruded at a peak temperature of 160°C when the water content increased from 15.5% to 20.7%. The raw peak in the RVA curve was totally disappeared after extrusion. On cooling, there was no marked increase in the viscosity, and the final viscosity of the extruded samples was much lower than the unextruded one, which indicated that the starch was already sufficiently gelatinised and degraded during extrusion. The work of Arambula et al (1998) on extruded corn powder clearly showed that as barrel temperature was increased from 50°C to 100°C, the raw peak disappeared, meanwhile, the initial viscosity increased and the final viscosity decreased.

Apart from the RVA, other rheometers can also be used to evaluate the degree of cook by measuring the viscosity of aqueous suspension of cooked starches. However, as mentioned in Section 2.1.5, care should be taken in determining the conditions of a test and in interpretation of the results. Most starch pastes exhibit non-Newtonian viscosity behaviour, suspensions of cooked starch and gels are usually shearing thinning, showing lower viscosities at higher shear rates, and most starch pastes also display thixotropic behaviour, a reduction in viscosity over time at given constant shear rates. Therefore, there is no absolute measure of starch viscometric attributes, as these depend on the conditions of measurement, such as shear rate, holding times and other parameters used to define the test. Even so, the viscosity of aqueous suspensions does provide indirect information on the structure of starch products. However, due to lack of rheological data and models for cooked starch suspensions, it is rather difficult to relate the estimated degree of cook with the physical state of the starch polymers in the products.

2.4.3 Water absorption index (WAI) and water solubility index (WSI)

WAI and WSI are another two parameters that can be used to evaluate the degree of cook of starches (Kirby, et al., 1988; Govindasamy, et al., 1996; Singh, et al., 1999; Fang, & Hanna, 2001b). The WAI and WSI are usually measured by the method developed by Anderson et al (1969) with some modifications. A certain amount of powder sample (usually 2.5 g or 3.0 g) is dispersed in certain amount of distilled water (usually at solid concentration of 7 – 10wt%). The suspension is then centrifuged at 3000g for 10 minutes. The supernatant is decanted for determination of its solids content by drying and the sediment at wet stage is weighed. WAI and WSI are determined using the expression:

$$WAI = \frac{Weight\ of\ sediment}{Weight\ of\ dry\ solids} \tag{2.8}$$

$$WSI\ (\%) = \frac{Weight\ of\ dissolved\ solids\ in\ supernatant \times 100}{Weight\ of\ dry\ solids} \tag{2.9}$$

It is known that the native semi-crystalline starch granules are insoluble in cold water. However, after extrusion cooking, the starch granules will be disrupted and some amylose will leach out from the granules. When the powder of extrudate is dispersed in cold water, the broken granules will become swollen since water can penetrate the granules and dissolve the amylose. Actually, WAI is an indication of the volume of swollen granules that maintain their integrity in suspension, and WSI is an indication of the amount of amylose leached out from granules in suspension. Both of them directly relate to the granule disruption during a process. Therefore, WAI and WSI readily yield the degree of cook at the practical level without requiring time-consuming biochemical extraction, isolation and characterisation of complex mixtures (Kirby, et al., 1988). But it should be borne in mind that WAI and WSI are not fundamental structural characteristics of the material.

Kirby et al (1988) investigated microstructural changes in starch materials as a function of screw configuration, water content and barrel temperature. Their results revealed the

influence of the specific mechanical energy, SME, on WAI and WSI. Both WAI and WSI were low at low SME. This is attributable to the higher proportion of the intact starch granules which are unable to swell. With increasing SME, due to increase of disrupted granules WAI increased. At the same time, WSI increased with SME too because of the leaching out of amylose. The WAI - WSI relationship, shown in Figure 2.4 (Kirby et al., 1988; Smith, 1992), reached a maximum at an intermediate SME level. Beyond this SME level, the number of swollen starch granules decrease with increasing SME, which caused WAI to decrease, but WSI continued to increase because of more amylose leached out.
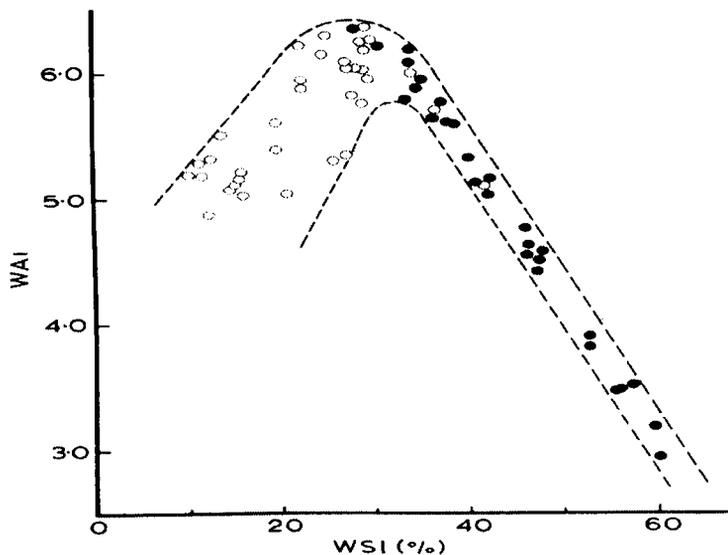
Figure 2.4 WAI against WSI for maize grits showing completely disrupted granules (solid symbols).

2.5 Mechanical properties of starch based materials

Mechanical properties of thermoplastic starch materials are one of the most important concerns for their processing and applications. Therefore, extensive research work has been carried out to characterise the mechanical properties of starch based materials and investigate the ways to improve these properties. Most of work focused on blending

starch with plasticizers and synthetic polymers. This section summarises the mechanical properties of various starch plastics and the effects of added plasticizers and polymers on the mechanical properties.

2.5.1 Mechanical properties of thermoplastic starches

When a native starch is converted to thermoplastic starch (via e.g. extrusion cooking), the mechanical properties of the starch materials are dependent on the processing condition, source of starch (e.g. amylose and amylopectin ratio) and the test environmental conditions.

Moisture content has significantly effect on the mechanical properties of starch materials. Kirby et al (1993) studied the mechanical properties of extruded wheat starch (peak temperature was 170°C) using a three-point bend test. It was found that the flexural modulus and strength of the starch material were a function of moisture content in samples. At a moisture content of 8 - 10%, the flexural modulus, derived from the initial slope of the stress-strain plot, was over 4000 MPa, however, there was a sharp decrease from 2000 MPa to 50 MPa when the moisture content changed from 18% to 20%. It was observed that extruded thermoplastic potato starch (starch was premixed with water and glycerol at composition of starch:water:glycerol = 100:21:30) showed a viscoelastic behaviour characteristic of a polymer with changing of moisture content (van Soest, et al., 1996b). Materials containing less than 9% water were glassy with an elastic modulus between 400 and 1000 MPa. A transition from brittle to ductile behaviour occurred at a water content in the range of 9 - 10%. The rubbery materials, with water content of 9 - 15%, were tough and an optimum ultimate elongation was observed. van Soest et al (1996c) also reported that a sharp decrease in the elastic modulus and tensile stress and an increase in elongation at break were observed at moisture contents of 11 - 13% for a thermoplastic waxy maize starch extruded at 140°C with water and glycerol. These are characteristics of a glass to rubber transition of an amorphous polymer. The materials were brittle below moisture content of 10% with a modulus of approximately 1000 MPa and an elongation at break of less than 20%. The materials with a moisture content of 13 - 20% behaved in a rubbery fashion. The amorphous rubbery materials were soft and weak with moduli of 0 - 10 MPa and tensile

strengths of 0 - 2 MPa, they could be stretched to very high ultimate elongation of 300 - 500%.

The mechanical properties of starch materials also change with time and amylose content as well. Shogren and Jasberg (1994) studied the mechanical properties of extruded high-amylose (70%) and normal cornstarch as a function of time and conditioning humidity. After extruded at 170°C and 20 ~ 30% moisture, tensile strengths for the extruded high-amylose starch ribbons were rather stable with time, changed from 55 to 65, 50 to 55 and staying at 35 MPa after 84 days at 20, 50 and 80% RH, respectively. These were higher than those for normal cornstarch (22 to 25, 40 to 42 and 25 to 15 MPa after 84 days at 20, 50 and 80% RH, respectively). Elongation at break declined gradually with time for the high-amylose starch (from 8 to 6, 15 to 11, and staying at about 11% after 84 days at 20, 50 and 80% RH, respectively), while rapid declines were seen for normal cornstarch at higher humidities (from 5 to 3, 13 to 9, and 8 to 3% after 84 days at 20, 50 and 80% RH, respectively). It has been shown, therefore, that plastic materials prepared from gelatinised or melted high-amylose cornstarch have greater strength and flexibility and slower physical ageing than those prepared from gelatinised normal cornstarch.

The starch molecular mass has also influence on the properties of thermoplastic starches. van Soest et al (1996b) investigated the mechanical properties of extruded thermoplastic starch (made from potato starch) with different mean molecular mass and moisture contents in the range of 5 - 30% (w/w). In the rubbery state of the studied materials (14% moisture content), the elongation at break of the high molecular mass material (~37000 kgmol^{-1}) was 100 - 125%, and the low one (~1900 kgmol^{-1}) only had value of 30 - 50%. The tearing energy of the materials showed a maximum at a moisture content of 9 - 10%, and was 0.15 and 0.1 Jmm^{-2} for the high and low molecular mass materials, respectively. Above water content of 15% the materials became weak and soft and the elongation at break decreased.

2.5.2 Effect of plasticizers

One problem associated with the utilisation of thermoplastic starch products is their embrittlement due to the loss of plasticizing water at low relative humidities and ageing. Although water is a good plasticizer for starch based materials, due to its volatility, a range of other plasticizers have been experimentally studied. This section gives a brief review of the effect of various plasticizers on the mechanical properties of starch based materials.

2.5.2.1 Glycerol

Glycerol has been intensively studied as a plasticizer apart from water for producing thermoplastic starch materials.

Lourdin et al (1997a) studied the use of glycerol as plasticizer for potato starch at different water content. Their results showed that the glass transition temperature of starch films (obtained by a casting method) decreased with increasing content of glycerol at a fixed water content ranging from about 10% to 30% on dry basis. It has been observed that there is a known "antiplasticization" effect in the starch – glycerol system (Lourdin, et al., 1997b): When glycerol content was below 12%, there was appreciable and unexpected decrease in elongation (from 7 to 3%) as plasticizer level is increased, while elongation increased markedly from approximately 3% to about 40% when glycerol content increased above 12%. Therefore, 12% appeared to be a critical concentration for the starch-glycerol system, and the material ductility is "controlled" by glass transition only above this point.

van Soest and Knooren (1997) reported the influence of glycerol and water content on the mechanical properties of extruded potato starch during storage. For the compositions based on the mass ratio of starch:glycerol:water = 100:25:22, the equilibrium moisture content was about 14% (w/w on the basis of total mass) at a controlled environment humidity of approximately 60% RH. The elongation at break decreased and the elastic modulus and the tensile strength increased rapidly during the first week. For the samples stored over one week, only slight changes were observed in

elongation and tensile strength. But the elastic modulus continued to increase during the ageing process from 30 MPa to 70 MPa. These changes of mechanical properties were attributed to the formation of helical structures and crystals, which resulted in a reinforcement of the starch network by physical crosslinking.

Averous et al (2000) reported the mechanical behaviour of a wheat thermoplastic starch plasticized by glycerol. Elastic modulus and tensile strength were seen to decrease with increasing of glycerol content. Depending on the plasticizer content, the elongation at break first increased with the plasticizer content at low glycerol concentrations and then decreased at high glycerol concentrations. The maximum elongation at break, about 126%, was obtained at a glycerol:starch ratio about 0.2.

Myllarinen et al (2002b) studied the effect of glycerol on amylose and amylopectin cast films. It was found that the behaviour of amylose and amylopectin plasticized by glycerol was quite different. The amylopectin films showed more brittle character. Generally, under low glycerol contents, brittleness (judged from elongation at break) of the films increased with increasing of glycerol content compared with glycerol free control samples. But, above 20% glycerol, amylose film showed much larger elongation at break than the low glycerol content films and was still strong, while the amylopectin still produced very low-strength and non-flexible films. The highly plasticized amylose film (30% glycerol) was rather strong showing a tensile stress of 10 MPa (as strong as a polyethylene film), but the corresponding amylopectin film had lost its strength entirely and a liquid-like behaviour being observed.

Water still plays an important role in the plasticization of a starch-glycerol system. It was found that an increase in glycerol concentrations at low levels induced a drop in hydration of film sample of potato starch, while at higher plasticizer levels (>15%) the hydration rate increased (Lourdin, et al., 1997a). This variation of water uptake may have a partial contribution to the antiplasticization effect. By studying the deformation and failure behaviour of extruded sheets produced from wheat starch plasticized with water and glycerol, Kirby et al (1993) found that with increasing water content there was a shift from purely elastic fracture to the inclusion of limited plastic flow. By investigating the mechanical properties of compression moulded thermoplastic starch from native corn, potato, waxy corn and wheat starch with constant weight ratio of

glycerol/dry starch = 0.30, the influence of the amount of water present (from about 11.2 % to 42.2%) during compression moulding was evaluated (Hulleman et al., 1998). It was found that varying the water content in the premixes led to large changes in strain and stress at break. Although there were obvious differences in strain and stress at break (samples were measured after equilibrated 12 - 14 days at 20°C and 55% relative humidity, with moisture content 12.1 - 14.3%) among the materials made form these different starch sources, the maximum of elongation at break for all the materials was observed at water content between 20 - 25% during compression moulding, except that of the potato starch which was observed between 30 - 35%. No significant correlation between the elastic moduli and water content during compression moulding was observed. For the potato, corn, wheat and waxy corn starch, the elastic moduli ranged between 80 - 120 MPa, 20 - 25 MPa, 12 - 20 MPa and 2 - 4 MPa, respectively. Further studies (Hulleman et al., 1999) showed that the amount of B-type crystallinity, either from the residual native starch or recrystallisation of amylopectin, was the major factor influencing the mechanical properties of the compression-moulded, glycerol plasticized potato starches, which depended not only on the composition (amount of water, amylose and native granules) but also processing parameters as such temperature.

2.5.2.2 Other plasticizers

Plasticization of starch has been studied with many other plasticizers besides glycerol, such as glucose (Ollett, et al., 1991), sorbitol (Gaudin, et al., 1999; Lourdin, et al., 1997a; Funke, et al., 1998), lactic acid sodium (Lourdin, et al., 1997a), and amino acids (Stein, et al., 1999).

By studying the changes of the flexural moduli of wheat starch plasticized with glucose and water, Ollett et al (1991) found that there was a sharp change of modulus at a critical water content which was dependent upon the glucose concentration. Increasing the glucose concentration depressed the critical water content. It was concluded that the addition of water and glucose to wheat starch plasticized the material by combined effect on the glass transition.

The work of Lourdin et al (1997a) showed that the T_g of potato starch films was reduced when sorbitol or lactic acid sodium were added as plasticizers. However, the work of Gaudin et al. (1999) showed that although the T_g and tensile strength of wheat starch – sorbitol films decreased with increasing of sorbitol, there was antiplasticization effect up to 27%. Beyond this value, sorbitol acted as a plasticizer and increased the elongation at break with increasing sorbitol concentration. This seems to indicate the poor plasticizing performance of sorbitol as compared with glycerol because much higher concentration is needed to avoid the so called antiplasticization phenomena.

Stein et al (1999) blended twenty natural and synthetic amino acids (5 cyclic and 15 acyclic) with a starch-glycerol mixture and extruded as ribbons. It was found that the amino acids were exceptionally good plasticizers of the starch-based materials, especially cyclic amino acids with nitrogen in the rings. For instance, pipecolic acid increased the elongation at break of the starch-glycerol sample by ten-fold, and piperidinepropionic acid increased the elongation at break nearly by eight-fold. Nipecotic acid and L-proline were also good plasticizers, increasing the elongation at break by six-fold and four-fold, respectively.

2.5.3 Effects of synthetic polymers

It is known that starch is a hygroscopic material and will absorb varying amount of moisture under different environmental humidity conditions. The glass transition temperature of starch varies substantially with the moisture content, which gives rise to the variations in the mechanical properties. The sensitivity of starch materials to fluctuations in moisture content is one of the obstacles to widespread application of the materials. Blending of thermoplastic starch (TPS) with some synthetic polymers, such as poly (vinyl alcohol) (PVA), poly (ethylene-co-vinyl alcohol) (EVOH), polycaprolactone (PCL), poly (hydroxy ester ether) (PHEE) and poly (lactic acid) (PLA) etc. partially mitigates this problem using the relatively low water permeability of these polymers and better mechanical properties such as strength and flexibility.

2.5.3.1 PVA

PVA is produced via polymerising vinyl acetate and then saponifying polyvinyl acetate. Figure 2.5 shows the chemical structure of PVA. $(l + m)$ or n is called polymerisation degree and $l/(l + m) \times 100\%$ is called degree of saponification or hydrolysis (Gohsenol®, 1999). The physical properties of PVA, such as water solubility, molecular weight and modulus depend primarily on polymerisation degree and degree of saponification or hydrolysis.

$$\underbrace{CH_2 - CH}_{l}\underbrace{CH_2 - CH}_{m} \qquad \text{Partially hydrolysed}$$
$$\qquad\quad | \qquad\qquad\quad |$$
$$\qquad\quad OH \qquad\qquad OCOCH_3$$

$$\underbrace{CH_2 - CH}_{n} \qquad \text{Fully hydrolysed}$$
$$\qquad\quad |$$
$$\qquad\quad OH$$
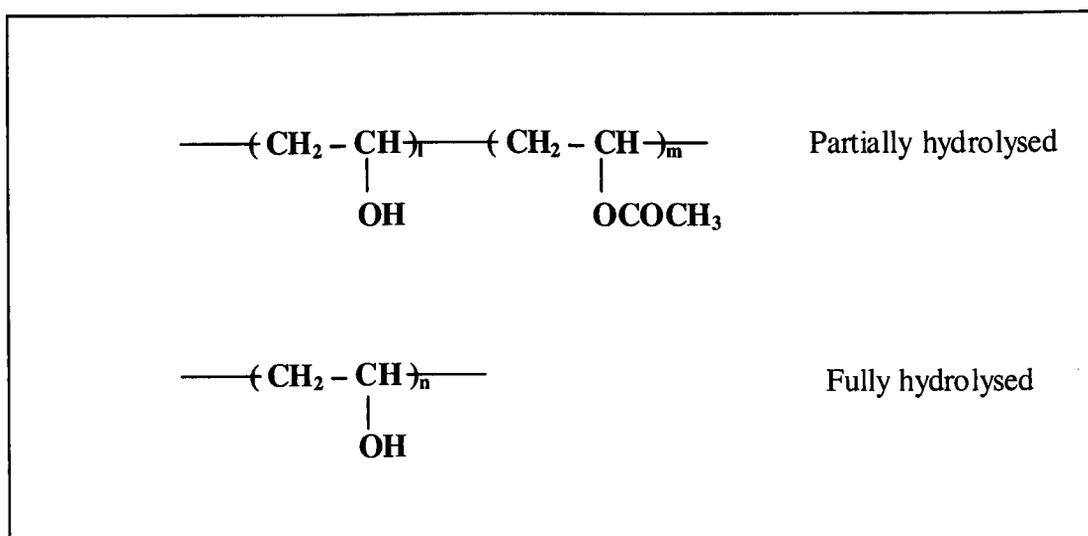
Figure 2.5 Chemical structure of PVA.

Since PVA is a biodegradable polymer (Chandre, & Rustgi, 1998; Mohanty, et al., 2000) compatible with starch in the presence of water, and has excellent strength and flexibility, PVA/starch blend plastics are one of the most popular of the biodegradable polymer blends and widely used in packaging and agricultural mulch films (Ishigaki, et al., 1999). In general, the presence of PVA improves mechanical properties and water resistance of the starch materials.

Shogren et al (1998a) found that the strength, flexibility and water resistance of foams made by baking starch batters inside a hot mould were markedly improved by adding 10 - 30% PVA. The improvement in strength at low humidity was greater using a partially

(88%) hydrolyzed PVA, while strength at higher humidity was improved mostly with a fully (98%) hydrolyzed PVA. Foam flexibility increased with higher molecular weight PVA.

Lawton (1996) investigated tensile strength, elongation at break, tear resistance, and impact strength for starch/PVA cast films. Different types of starch, including normal cornstarch, waxy cornstarch, high amylose cornstarch, wheat starch, potato starch and tapioca starch, were used. The starch type made considerable difference in the properties of the films. Films containing high amylose cornstarch and PVA had good elongations at break, tensile strength, tear resistance and impact strength. Films containing high amylose cornstarch were also more stable at different relative humidities and over time than films made with other starches.

PVA has also been successfully applied to improve the properties of starch foams. Extruded foams based on blends of starch with PVA were patented by National Starch (Lacourse, & Altieri, 1989; 1991; Roesser, et al., 2000). About 8 to 15% of PVA based on the weight of starch, having a degree of hydrolysis of from 88 to 99% was claimed. The addition of PVA was found to give extruded foams good expansion and improved strength and flexibility.

2.5.3.2 Other polymers

Although PVA can improve mechanical properties of starch materials, PVA itself is sensitive to water, which renders starch/PVA blends unsuitable for many high humidity applications. For this reason, poly (ethylene-co-vinyl alcohol) (EVOH) has been explored as an alternative to PVA. EVOH is a good candidate from synthetic polymers for blending with starch, because the hydroxyl groups promote compatibility with starch and ethylene groups can provide hydrophobicity or at least ameliorate the problems associated with the hygroscopic character of starch (Villar, et al., 1995). The products based on starch/EVOH have shown mechanical properties good enough to meet the needs of some specific industrial applications, and their mouldability in film blowing, injection moulding, blowing moulding, thermoforming, foaming, etc. is comparable with that of traditional plastics such as PS, ABS, LDPE (Bastioli, 1998).

George et al (1994) investigated the effect of EVOH concentration on the processability and physical properties of thermoplastic starch plasticized with glycerol and water and explored the effect of starch type on the blend properties. The addition of EVOH to thermoplastic starch improved the injection mouldability and ductility of thermoplastic starch. Though the type of starches exhibited different effect on the processability and physical properties, the blends showed higher elongation at break than the pure plasticized thermoplastic starch but lower modulus and tensile strength. Thermoplastic starch/EVOH blends containing ≥ 50wt% EVOH showed almost as high an elongation at break as the pure EVOH.

PCL is also a biodegradable and hydrophobic polymer for blending with starch materials because of its sufficiently water-resistant (Karlsson, & Albertsson, 1998). Averous et al (2000) studied the properties of wheat thermoplastic starch (TPS) and PCL blends prepared by extrusion and injection moulding. The addition of PCL to TPS matrix overcomes the weaknesses of pure TPS: low resilience (flexibility), high moisture sensitivity and high shrinkage after moulding, even at low PCL concentration, e.g. 10wt%. For pure TPS, the water droplets in contact with the material were very rapidly absorbed because of the hydrophilic nature of the material. However, by measuring the contact angle, it was found that the introduction of PCL at levels as low as 10wt% led to a significant improvement of water resistance of the materials. The results of Averous et al (2000) showed that the effect of PCL on the mechanical properties of TPS depended not only on the PCL concentration but also on the plasticization level of TPS. When the starch matrix had a glassy behaviour, blending with PCL resulted in a decrease of the elastic modulus but improvement of the impact resistance. On the other hand, when the TPS had a rubbery behaviour, PCL increased the modulus of the material.

PHEE is another polymer used to blend with TPS partly due to its character of very low water permeability (Walia, et al., 2002; Willett, & Doane, 2002). It was found that after blending with PHEE, irrespective of the blend concentration, the time for the blends to reach its equilibrium moisture content when conditioned at 50% relative humidity increased from several hours (PHEE-free samples) to almost one month (Walia, et al., 2002). The elastic modulus and tensile strength of the blends increased with decreasing

relative humidity, while the elongation at break decreased. The blends processed at the higher water content (25%) showed higher tensile strength and modulus associated with the presence of fibrillar and laminar morphologies of phases which were oriented in the flow direction (Walia, et al., 2002). Willett and Doane (2002) reported that changing the water content from 1% to 6% during extrusion had no effect on tensile properties of cornstarch/PHEE (60/39) composites. But the tensile properties of starch/PHEE materials were dependent on the total moisture content, TMC (based on the starch/PHEE blends), during the following injection moulding. When TMC was less than approximately 6%, the starch/PHEE materials displayed brittle behaviour, and tensile strength and the elastic modulus gradually decreased as TMC increases. When TMC was over 6%, the starch/PHEE became more ductile and displayed a yield point, and tensile strength and the elastic modulus dropped rapidly, while elongation at break increased. By comparing the effects of moisture content on the tensile properties of the PHEE reported by St Lawrence et al (2001), Willett and Doane (2002) concluded that the changes in tensile properties of starch/PHEE materials with TMC were primarily due to changes in the viscoelastic response of the PHEE matrix.

PLA has received much attention in biodegradable polymers. The materials are derived from renewable starch resource but have many attractive mechanical (strength, stiffness and toughness) and physical (transparency and gas barrier) properties as oil-based polymers. As the price of PLA is rather high compared with conventional plastics, it is used to blend with starch to reduce the material costs and improve the properties of starch-based materials. PLA has been chosen to blend with starch by many researchers (Park, & Im, 2000; Raghavan, & Emekalam, 2001; Martin, & Averous, 2001; Willett, & Shogren, 2002). It was found that even at 10wt% inclusion of native starch granules, the tensile strength was reduced by 40% and modulus by 60% in comparison with pure PLA (Park, & Im, 2000). PLA/TPS blends, however, exhibited superior mechanical properties to those of PLA/native starch blends (Park, & Im, 2000). This suggested that gelatinisation of starch had an effect on the improvement of interfacial adhesion between PLA and starch. By studying the thermal characteristics of TPS (wheat)/PLA blends using DSC, Martin and Averous (2001) found that the T_g value of PLA decreased gradually as the content of TPS in the blend was increased, which indicated that this binary blend was partially miscible. However, the mechanical characteristics of

the blends (tensile strength, elongation at break and impact resistance) showed a marked decrease at lower PLA contents (i.e. 10 and 25wt%), and many data of blends reached values lower than that of pure components, TPS and PLA. It was thought that the poor mechanical properties of TPS/PLA blends might be due to lack of compatibility between the two phases. It seems to suggest that improving compatibility of starch and PLA is an important for further development of aspect starch/PLA materials.

Low-density polyethylene (LDPE) has been blended with starch (St-Pierre, et al., 1997; Matzinos, et al., 2001). However, the purpose of the blending in this case was mainly to take advantage of the biodegradability of starch in attempt to produce a biodegradable packaging material. Since the thermoplastic starch and polyethylene are incompatible to each other, compatibilizer is usually used to increase the compatibility, which contains groups enabling hydrogen bonding with the hydroxyl groups in starch. The most frequently used compatibilizers include ethylene/acrylic acid (EAA) copolymer (Willett, 1994), ethylene/vinyl acetate (EVA) copolymer (Prinos, et al., 1998), and poly(ethylene-g-maleic anhydride) (PE-g-MA) copolymer (Bikiaris, et al., 1998; Matzinos, et al., 2001).

2.6 Structure and properties of foams

Thermoplastic starch has been used to fabricate foams using various technologies so as to produce biodegradable alternatives for synthetic polymeric foams for applications such as cushion packaging, insulation and light weight structures. This section gives a brief overview on the fabrication, structure and properties of conventional polymeric foams and the background information outlined are adapted for that of starch-based foams.

2.6.1 Formation of polymeric foams

The formation of a polymeric foam involves firstly the formation of gas bubbles in a liquid polymer system, a solution or melt, followed by the growth of the bubbles and

eventually the stabilisation of these bubbles as the viscosity of the polymer melt increase, resulting ultimately in a solidified cellular structure.

Gas bubbles can be introduced into a continuous polymer liquid phase by injection or super-saturation of a gas such as air and nitrogen, etc., under elevated pressure (Baumann, 1991). Alternatively, a gas, e.g. CO_2, can be generated within the liquid phase using a specific gas-generating reaction (Bailey, Jr., 1991), or generated by volatilisation of low boiling point solvents e.g. pentane and Freons (Shutov, 1991) or thermal decomposition of chemical blowing agents, e.g. sulfonylhydrazide (Shutov, 1991).

The formation of bubbles within a polymer solution or melt is generally called nucleation. In many cases, a lot of micro-bubbles of air and other contaminants are already present in the system, and serve as sites for bubble growth. However, in practice, new bubbles are still introduced into the system through the approaches described above. The number and size of these gas bubbles are important for foam structure development.

The growth of a bubble is a result of competition between the driving force (the differential pressure of the inside and outside of the bubble) and the resistance (surface tension of the bubble and melt viscosity). Therefore, the rate of growth of a cell in polymer liquid system depends on the aeration of the cell which is determined by the amount of gas diffused into the cell and the internal pressure according to the gas laws and the visco-elastic property of the polymer phase. In addition, the combination and coalescence of two or more smaller bubble can also simply grow a larger cell.

The stabilisation of bubbles in polymer liquid or melt is usually achieved by enhancing the surface tension of the bubbles through increasing the viscosity of the system. The approaches could be chemical reactions that increase molecular weight through polymerisation or cross-linking, or just simply cooling the thermoplastic melts.

There are numerous books (Klempner, & Frisch, 1991; Landrock, 1995; Khemani, 1997) on polymeric foams, covering a wide spectrum of cellular plastics, including manufacture technologies, foaming processes and theoretical modelling.

2.6.2 Structure of solid foams

Solid foam can either consist of closed or open cells. Closed cell foams have a cellular structure in which contiguous cells are isolated and entrapped within a continuous phase. In open cell foams, adjacent cells are interconnected and thus continuous channels are available throughout the solid phase. If made from one material, closed cell foams are generally more rigid, while open cell foams are generally more flexible. Normally a foam can contain a mixture of both closed cells and open cells. Tatarka and Cunningham (1998) used a gas pycnometer to determine the relative amount of open and closed cells in starch foams following standard of the American Society for Testing and Materials (ASTM D2856, Procedure C).

Characterisation of foam morphology can be very complex, mean cell size is a characteristic that can be quantitatively determined and associated with foam morphology. Other features, such as cell uniformity, wall thickness, anisotropy of cell structure and defects can also be informative, but difficult to quantify. The most commonly used methods for the determination of cell size in polymeric foams probably is the standard test from ASTM (ASTM D3576). This method gives an equivalent diameter of cells from an average chord length. Experimentally, the method involves superimposing the image of the foam on a linear scale and measuring the number of cells that intersect a specific length.

2.6.3 Mechanical properties of solid foams

The mechanical properties of solid foams have been studied extensively by Gibson and Ashby (1997). The properties of a foam are related to the cell structure and the properties of the material from which the cell walls are formed. Based on modelling of response of simplified foam structure to loading, series equations which describe the relationship between structure and mechanical properties were obtained, some of them are summarised in Table 2.5 (Gibson, & Ashby, 1997; Smith, 1992).

Table 2.5 Equations for stiffness and strength of foams

Deformation	Open cell foams	Closed cell foams
Linear elasticity	$E/E_w \propto (\rho/\rho_w)^2$	$E/E_w \propto (\rho/\rho_w)^3$
Elastic collapse	$\sigma_e/E_w \propto (\rho/\rho_w)^2$	$\sigma_e/E_w \propto (\rho/\rho_w)^3$
Plastic collapse	$\sigma_p/\sigma_{pw} \propto (\rho/\rho_w)^{3/2}$	$\sigma_p/\sigma_{pw} \propto (\rho/\rho_w)^2$
Brittle crushing	$\sigma_f/\sigma_{fw} \propto (\rho/\rho_w)^{3/2}$	$\sigma_f/\sigma_{fw} \propto (\rho/\rho_w)^2$

In Table 2.5, E is elastic modulus of a foam, E_w is elastic modulus of foam wall material, σ_e is elastic collapse stress of the foam, σ_p is plastic collapse stress of the foam, σ_{pw} is yield strength of the foam wall material, σ_f is brittle crushing strength of the foam, σ_{fw} is modulus of rupture of the foam wall material, ρ is the density of the foam and ρ_w is the density of the foam wall material. Clearly only foam density, one of the many structural characteristics to define morphology of a foam, was used in these equations and hence the predictions should be treated with care, especially in the case of non-uniform and anisotropic foams.

2.7 Starch based foams for packaging applications

2.7.1 Loose fills by extrusion foaming

Extrusion processing technology has been used to develop starch-based foams since the late 1980's (Lacourse, & Altieri, 1989). During extrusion cooking, the starch raw material was converted into a thermoplastic melt and, as the melt exits the die nozzles, the sudden release of pressure causes the melt to become superheated and water vaporise as bubbles. This process enables bubbles to be created and expanded in the extruded melt. The increase in the viscosity of extrudate due to lost of water and cooling stabilise the grown bubbles and leave the extrudate with cellular structure.

The extruded starch-based foam as an alternative to expanded polystyrene (EPS) loose fills (for filling space of packed goods with a packaging) is probably the most

successful application of starch based material in cushion packaging. Several patents on the extruded foams based on starch and blends of starch with various polymers have been filed (Lacourse, & Altieri, 1989; 1991; Bastioli, et al., 1994; Bellotti et al., 1995; Bastioli, et al., 1998a; 1998b; Xu, & Doane, 1997; 1998; Bellotti, et al., 2000). The polymers used to blend with starch included poly(vinyl alcohol), poly(ethylene vinyl alcohol), polycaprolactone, poly(ethylene-co-acrylic acid), cellulose acetate, and hydroxy functional polyesters.

Considerable effort has been made to study the influence of extrusion conditions, moisture content and composition on the physical properties of starch-based foams in recent years (Bhatnagar, & Hanna, 1995a; 1995b; Cha, et al., 2001; Fang, & Hanna, 2001a; 2001b; Willett, & Shogren, 2002).

Bhatnagar and Hanna (1995a) made starch-based foams using corn starch with 25% amylose and polystyrene or polymethylmethacrylate. All formulations were based on a starch to plastic ratio of 70:30. The foams were produced with a commercial twin screw extruder and the extrusion was carried out at 120°C barrel temperature, 140 rpm screw speed and 6% moisture content. These produced foams which performed well compared with commercially available EPS packaging foams used by the loose-fill industry, and also had better functional properties than 100% starch loose-fill.

Fang and Hanna (2000a; 2001a; 2001b) blended polylactic acid, Mater-Bi® ZF03U (MBI) and Easter Bio Copolyester® 14766 (EBC) to regular (25% amylose) and waxy corn starch at different levels (10, 25, 40%). The blends were then extruded into loose fill packaging foams using a co-rotating twin screw extruder with peak temperature of 150°C and screw speed of 150 rpm. It was found that foams produced with waxy starch had greater radial expansions and lower foam and bulk densities (of packed loose fill) than the regular starch. Addition of higher levels of both MBI and EBC reduced radial expansion and increase foam and bulk densities.

Cha et al (2001) produced starch based foams by blending 49% wheat and corn starch (on dry solid basis), 33% synthetic polymers (poly(ethylene-co-vinyl alcohol), polystyrene and poly(styrene/maleic anhydride)), 10.5% total water, 7% blowing agents (methanol) and 0.5% nucleating agent (silicon dioxide) and extruded at 100 - 160°C

with 100 rpm screw speed using a single screw laboratory extruder. It was found that the bulk density of the starch-based foams decreased as the extrusion temperature was increased. The highest expansion occurred when the blends containing normal wheat starch were extruded at 140°C. This was consistent with results of Chinnaswamy and Hanna (1988) for corn starch.

More recently, Willett and Shogren (2002) reported their work on the processing and properties of extruded various starch (corn, wheat, high amylose (70%) and potato) foams with several biodegradable polymers. The addition of PLA, PHEE, or poly(hydroxybutyrate-co-valerate)(PHBV) significantly lowered densities and increased radial expansion ratios of extruded foams. Other polymers studied, such as PCL, poly(ester amide) (PEA) and cellulose acetate also decreased foam density but to a lesser extent. Compressive strength of the foams tested on chips depended primarily on the foam density, not on starch type or polymer additives.

2.7.2 Other forms of starch foams

Although the starch based foams produced by extrusion foaming technology have useful mechanical properties and the loose fill products are already commercial available, it is difficult to produce starch foam products with more complex shapes such as a plate. A number of processes were recently developed for preparing shaped foam articles from starch.

Shogren, et al. (1998b) made thin-walled objects such as plates by heating a starch batter inside a closed mould with temperature of 175 - 235°C based on baking technology in food industry. The foams had a dense outer skin and less dense interior with large, mostly open cells. The overall foam density and strength increased with increasing starch concentration in the batter, the molecular weight and amylose content. It was also found that plates made from potato starch had lower densities and higher flexibilities than those made from corn starch. Due to the high water content within the material (primarily for good mould filling), the baking time, which varies with the size and thickness of the products, are rather long and typically over 60 seconds.

Glenn and Orts (2001a) developed a technology for producing moulded starch foams by using a compression/explosion process based on a similar puffing technique for making rice cakes. A suspension of starch in water (10%, (w/w)) was heated until the viscosity no longer increased then it was chilled (5°C) overnight to allow gelation to occur. The feedstock was prepared in a single screw extruder with feeding a mixture of the starch gel and dry starch powder at a weight ratio 1.8/3.2. Aggregates (1 – 3 mm) were formed and then were conditioned to moisture levels ranging from 8 to 20%. The conditioned aggregates were loaded in an aluminium compression mould heated to 230°C and compressed for 10 seconds under a pressure of 3.5 MPa. The pressure was then released rapidly resulting in an explosive release of steam as the starch feedstock expanded and filled the mould. The starch foam had the general shape of the mould, appeared similar to polystyrene and with mostly closed cells less than 1 mm in diameter. Compared with the baking method, the puffing process is much quicker and typically takes a few seconds.

Glenn, et al (2001b; 2001c) also made some starch-based foam sheets by the baking process and studied the effects of surface laminated films, fibre and $CaCO_3$ on the properties of foams. Foam panels were made by placing a dough sample in the centre of the mould, which was preheated and maintained at 160 - 180°C, then quickly closing and locking the mould. Each sample was baked in the mould for 3 – 5 min. The dough preparation included the following: dispersing fibre (if applicable) in a suspension of starch in water and heating with stirring until the mixture thickened; chilling the mixture at 5°C overnight to allow gelation to occur, extrusion compounding of the remaining dry components with this gel mixture. The properties of the starch/fibre foams, such as density, flexural strength, flexural strain at maximum force, etc., were within the range of that for commercial food containers made of extruded polystyrene or coated paperboard, but the addition of $CaCO_3$ to the starch/fibre foam composites did not improve the foam properties.

At present, there is no report found on moulding of large and complex starch foams cushion packaging blacks. However, multiple ply cushion blocks were fabricated by using extruded starch based foam planks (Lye, et al., 1998). By laminating and gluing

single ply planks in either parallel or cross directions, blocks with good cushioning performance could be made.

2.8 Properties of starch based foams for packaging applications

2.8.1 Density or expansion ratio

Foam density (ratio of mass/volume for a foam) or expansion ratio (volume of a foam/volume of the solid starch before foaming) is the dominant parameter in physical properties of a foam. Since many starch-based foams have often irregular shape and/or rough surface, determination of volume of a foam is the key to obtain the foam density or expansion ratio. Volume displacement method is generally adopted (Tatarka, & Cunningham, 1998; Glenn, & Orts, 2001a; Fang, & Hanna, 2001b), where fine glass beads are used as the displacement medium. Foam specimens with known mass were placed in a graduated cylinder, then filled with a known quantity of glass spheres with certain diameter and packing volume. The total volume of glass spheres and foam specimens were recorded after tapping the graduated cylinder for 1 min. Foam density was calculated from the mass of the foam divided by the displaced volume. Simplicity is the distinctive advantage of this method, but care must be taken in selecting the size of spheres relative to the size of open cells to avoid the entrapment of the spheres into the cells, which gives errors.

The density of extruded starch-based loose fill foam has been found ranging from 0.0167 to 0.0694 (g/cm^3) (Tatarka, & Cunningham, 1998; Willett, & Shogren, 2002), while the density of baked starch foam tray ranged between 0.082 and 0.4 g/cm^3 (Shogren, et al., 1998a, b). Clearly, moisture content should be stated when quoting density of foam as quite different values could be resulted from moisture absorption.

2.8.2 Mechanical properties

Standards for mechanical properties of polymer foams are well established. However, at present there are no generally accepted standard methods for testing mechanical properties of starch based foams. In addition, unlike polymer foam, starch foams are

hygroscopic and thus conditioning before tests is particularly critical to the consistency of the test results. Several parameters have been used for evaluating the mechanical properties of starch foams for cushion packaging applications. The definitions and test methods for these parameters are summarised below.

2.8.2.1 Spring index (resiliency)

Spring index is a measurement of the elastic characteristics of the material and reflects its resistance to permanent deformation as a cushioning material. Indirectly it reflects the ability of a material to recover to its original dimensions after it has been deformed. The measurement of spring index was carried out on a universal testing machine based on the method proposed by Altieri and Lacourse (1990). A cylindrical probe of 6 mm diameter was used to compress the samples, which is initially 20 mm thick, to achieve a deformation of 2 mm at a loading rate of 30 mm/min (Bhatnagar, & Hanna, 1995a, b). Fang and Hanna (2000a, 2001a) used a compression of 80% of sample original thickness to determine the spring index. Two forces were recorded, the initial compression force required to reach the predetermined deformation and the re-compression force to obtain the same deformation one minute after releasing the initial compression. Spring index was calculated by dividing the recompression force by the initial compression force. For an ideal elastic body the ratio of the two forces should be 1. The closer the spring index to 1, the better the resiliency of the material.

Fang and Hanna (2000a, 2001a) also used bulk spring index to evaluate the resiliency of extruded loose fill foams. The test was conducted in the similar way to that used for a single loose fill foam, but the bulk samples were contained within a cylindrical container.

2.8.2.2 Specific compressive stress and compressibility

Specific compressive stress is the compressive stress (pressure) applied to a foam sample to achieve a predetermined amount of compression. Different researchers used different amount of predetermined compression to determine the specific compressive

stress. For example, Bhatnagar and Hanna (1995a, b) used 2 mm (10% of the original specimen height), while Tatarka and Cunningham (1998) used 3 mm (the initial height of specimen varied between 20 and 46 mm) to evaluate the compressibility of a sample. Fang and Hanna (2000a, 2001a) used 80% of the original dimensions to determine the specific compressive stress. It was calculated as the required load divided by cross-sectional area of the probe, and reflects the rigidity of the foams or compressibility. A high value of specific compressive stress means that the material is more rigid or less compressible, and thus has a low compressibility. Despite of a logical flaw, specific compressive stress and compressibility have been used exchangeable in the literature.

2.8.2.3 Stress relaxation test

Stress relaxation tests determine the creep behaviour of foam materials. Wang et al (1995) and Cha et al (1999) employed a stress relaxation test to evaluate the creep properties of starch-based loose fill foams. The samples were contained in a cylinder of 126 mm in diameter and 165 or 150 mm in height. Samples were loaded to 400 N with cross-head speed of 100 mm/min, and the compression of samples was kept constant until the load decreased to approximately 37% of the original value. The decrease of the load was measured as a function of time. The amount of time necessary for this creep process was termed as relaxation time.

2.8.3 Water absorption isotherms

Since the starch-based foams are hydrophilic in nature, their properties are affected by the moisture in the environment. Starch based foams absorb moisture at the high relative humidity and lose moisture to the environment at the low relative humidity. The moisture in the starch-based foams significantly affects their mechanical properties.

Halsey (1948) described the relationship between the equilibrium moisture content (EMC) and relative humidity (RH) as:

$$RH = \exp\{(-A/RT) \times (EMC)^{-B}\} \qquad (2.10)$$

where R is universal gas constant (J/kg mol.K), T is the absolute temperature (K), A and B are constants. Chung and Pfost (1967) developed another empirical equation for the relationship between EMC and RH:

$$RH = \exp[(-A/RT) \times \exp\{-B \times (EMC)\}] \qquad (2.11)$$

which was widely used in the area of hygroscopicity of cereal grains and their products. These equations were also used for evaluation of such relationship for starch-based foams (Cha, et al., 2001). Generally, the absorption isotherms, with increasing relative humidity, were rising curves (Wang, et al., 1995; Fang, & Hanna, 2000b; Cha, et al., 2001).

2.8.4 Friability

Friability is a measure of the fragmentation of foam during handling. It is an important parameter for foams intended for use in loose fill packaging. Friability was measured by tumbling foam samples in a box (190x197x197 mm^3) with small wooden cubes (19 mm edge) for a duration of 10 minutes. (Tatarka, & Cunningham, 1998; Willett, & Shogren, 2002). Friability was determined as the percentage of the foam debris when screened through a 3 mesh and a 5 mesh screens.

2.9 Microwave foaming of starch materials

2.9.1 Microwave heating

Microwave radiation is an electromagnetic wave with frequency between 300 MHz and 30 GHz, or wavelengths from 10 mm to 1 m (Metaxas, & Meredith, 1983). The heating of materials in a microwave field is due to the vibration of polar molecules in the materials. Compared with conventional heating, microwave heating has some distinctive advantages such as rapid volumetric heating and energy saving (Chen, et al.,

1993a), and has been used not only for food stuffs but also for polymer processing and foaming (Chen, et al., 1993b; Teo, et al., 1997).

Microwave heating of materials stems from dielectric power absorption as described by the following equation (Buffler, 1993; Bows, 2000):

$$P_v = 2\pi f \varepsilon_0 \varepsilon'' E^2 \qquad (2.12)$$

where P_v is powder absorbed per unit volume (W/m^3), f is frequency (Hz), ε'' is the dielectric loss factor which depends upon the frequency and the temperature, ε_0 is a constant (8.854 x 10^{-12} F/m) and E is the electric field strength within the material (V/m). The electric field, E, is determined by configuration of a microwave oven, the dielectric properties and the geometry of the material being heated. It should be noted also that the dielectric behaviour of the material is a function of temperature as ε'' varies with temperature.

Once power has been absorbed in a material, the ensuing molecular motion produces a temperature rise. The heating rate is determined by the absorbed power as well as physical and thermal properties of the material, which can be described by the relationship (Buffler, 1993):

$$\frac{dT}{dt} = \frac{P_v V (m^3)}{14.7 \times V (m^3) \times C_p (J/kgK) \times \rho (kg/m^3)} \qquad (2.13)$$

where V is total sample volume, ρ is material density, C_p is the materials heat capacity, and t is the time that microwave power is applied.

On the other hand, the more microwave absorptive a material is (i.e., the higher the loss factor ε''), the less deep microwave energy will penetrate into that material. The measure of how "opaque" a materials is to a microwave field is given by the penetration depth, that is the depth at which the microwave power has fallen to 1/e of its initial

value, and is approximately given by following equation for low-loss materials (ε"<<1) (Buffler, 1993; Bows, 2000):

$$D_p = \frac{4.8\varepsilon'^{1/2}}{f\varepsilon''} \qquad (2.14)$$

where D_p is in cm when the frequency, f, is in Hz, ε' is the dielectric constant.

2.9.2 Microwave foaming for extrusion cooked starches

In the food industry, extrusion cooking is used for producing half-product or pellet snacks, which expanded into foams when heated rapidly using microwave, hot oil or hot air.

Boehmer et al (1992) combined a chlorinated soft wheat flour, corn starch, modified corn starch and whole-grain amaranth flour to form a dry starch mixture half-product expandable in microwave ovens. The ingredients were thoroughly mixed in a ribbon blender, then preconditioned in a paddle mixer with injection of steam and water, to form a mixture with moisture at 22 - 24wt%. This mixture was fed into a twin screw extruder where it was sheared and heated to substantially gelatinize the starches, vented for rapid cooling and moisture release, conveyed and lightly worked at reduced temperature, and then forced through a shaping die and cut into pellets of the desired shape. The pieces were dried in a drying chamber, at an air temperature of 43°C for about three and half to four hours.

Messager and Despre (1998) have developed a new fat-free food product in the form of a pellet, which can be expanded in a microwave oven. The pellets contained 40wt% starch and 9 - 11.5wt% water, having a degree of gelatinisation of 75%. The pellets were made by extruding the mixed ingredients with a water content of 29 - 35wt%, by applying 50 - 400 kWh/tonne of mechanical energy and 10 - 150 kWh/tonne of heat, the extrudate was cut into granules, and passed through a second extruder to obtain pellets

of the desired form. The pellets were pre-dried to a moisture content of 20 - 25wt% and then further dried to reduce moisture to 9 - 11.5wt%.

More recently, Lee et al (2000) investigated the effects of gelatinization and moisture content of extruded starch pellets on properties of microwave-expanded products by preparing extruded pellets from normal corn starch and heating in a conventional microwave oven for about 70 seconds. Their results showed that half-gelatinised extruded pellets had optimum expansion behaviour during microwave heating and the moisture content of the pellets critically affected the expansion behaviour. Maximum puffing efficiency and expansion volume were achieved in the pellets with 52% gelatinization and containing about 11% moisture.

In order to obtain best expansion, it requires the formation of an extrusion-cooked dough of starch and careful drying to form a stable half product. The following factors were found critical and must be controlled to achieve effective expansion in microwave foaming (Guy, 2001a):

- The starch granules should be melted to remove crystallinity but not dispersed more than about 10 – 15%.

- The moist dough must be dried carefully to avoid large moisture difference between the centre and the surface.

Nucleation of bubbles was considered very important to the expansion and the final foam structure. More nucleation sites create a finer textured product. Nucleation was considered to be related to the very small bubbles retained within the structures of starch granules (Guy, 2001a). If the starch granules are highly disrupted during the extrusion, nucleation would be greatly reduced. In addition, rapid air drying at high temperature would form a hard and dry skin on the extruded pellets with moist centres. This would set up strains within the pellets and lead to cracking.

There were no detailed reports about the relationship between the physical state of starch polymer in the pellets and their expansion. Recently, Chen and Yeh (2000) tested the relationship between the glass transition temperature (T_g) and expansion temperature (T_e) of extruded rice pellets using a homemade laboratory-scale oven (probably a

conventional oven). T_g and T_e were determined by DSC and a infrared thermometer, respectively. It was found that T_e increased linearly with T_g and had a correlation coefficient of 0.95, and T_e was 20 – 100°C higher than T_g, which indicated as expected, that the expansion of pellets occurred when the material was at rubbery state. T_g and T_e had similar dependence on the equilibrium moisture content of the pellets and maximum expansion occurred at 10% equilibrium moisture.

Chapter 3

Materials and Experimental Details

3.1 Raw materials and additives

3.1.1 Wheat flours and starch

Two types of wheat flour were used (referred hereafter as Temple and Superfine). These raw materials were supplied by Heygates Limited (Northampton, UK). Based on the information from the supplier, the Temple flour contains 9 - 10% protein and about 11 - 14% moisture, while the Superfine flour contains 7.5 - 8.5% protein and about 11 - 14% moisture. A purified wheat starch, Meritena 200, produced by Amylum Europe NV, Belgium, supplied via Heygates Ltd, was also used as raw material. Figure 3.1 shows the starch particles in these raw materials observed by SEM.
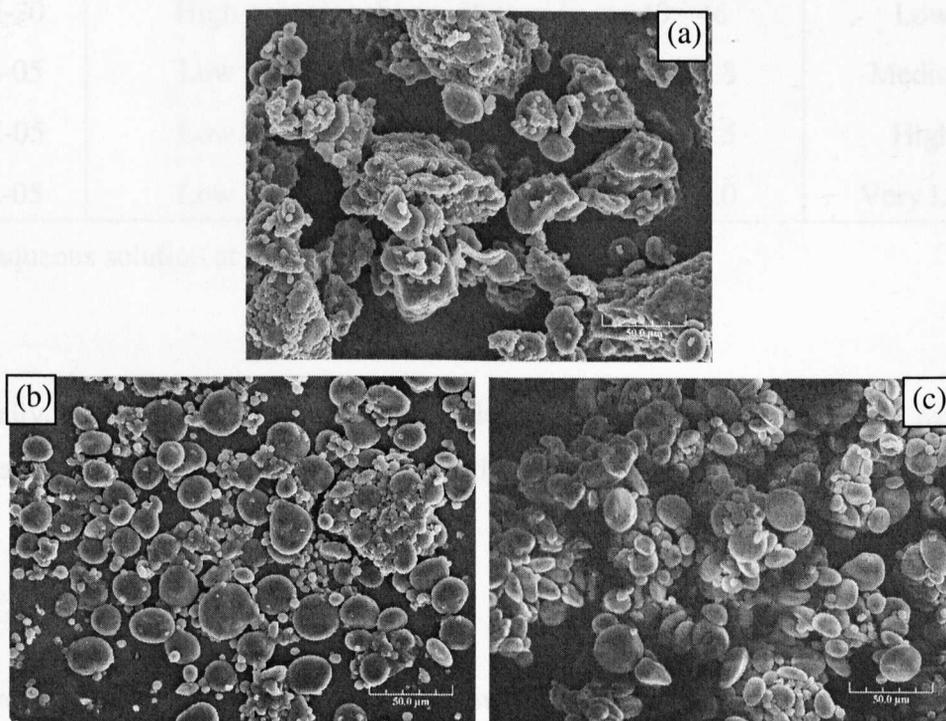

Figure 3.1 SEM micrographs of the particles in the Temple flour (a), the Superfine flour (b) and the purified wheat starch (c).

The actual moisture content in these raw materials was measured as described in Section 3.3.1 when they were used.

3.1.2 PVA

Four grades of PVA (GOHSENOL®, Nippon Gohsei Osaka, Japan) were used as additives in some formulations to blend with the starch materials in order to improve the flexibility of extruded pellets and foams subsequently produced by microwave expansion. Details about the chemical structure of PVAs, polymerisation degree and hydrolysis degree can be found in Section 2.5.3.1. Some information about these four grades of PVAs (manufacturer data) are summarised in Table 3.1.

Table 3.1 Specifications of GOHSENOL PVAs

Grade	Polymerisation degree	Hydrolysis degree (mol %)	Viscosity* (mPa s)	Solubility
GH-20	High	86.5 - 89.0	40 - 46	Low
GL-05	Low	86.5 - 89.0	4.8 - 5.8	Medium
NK-05	Low	71.0 - 75.0	4.5 - 5.5	High
NL-05	Low	98.5 ≤	4.6 - 6.0	Very Low

* 5% aqueous solution at 20°C

Generally, the higher the polymerisation degree, the higher the molecular weight of PVA, and the higher the hydrolysis degree, the lower the water solubility of PVA.

3.1.3 Glycerol

Glycerol (>99.0% purity), product of the Dow Chemical Company (Midland, USA), was selected as plasticizer.

3.1.4 Foaming and nucleation agents

Hydrocerol® BIH (Clariant), supplied by ALFA Chemicals Ltd (UK), was selected as a blowing agent to assist foaming during microwave expansion. Its blowing reaction begins at 160°C. Therefore, the extrusion temperature, when Hydrocerol® BIH is used, should thus be kept lower than 160°C to avoid premature foaming in the extruded pellets. The recommended dosage is up to 1.5% for extrusion and 2.5% for injection moulding.

Talc powder (FINNTALC M50), supplied by Omya UK Limited (Surrey, England), was selected as a nucleating agent. The average particle size of this talc powder is about 22 µm. Figure 3.2 shows these particles.
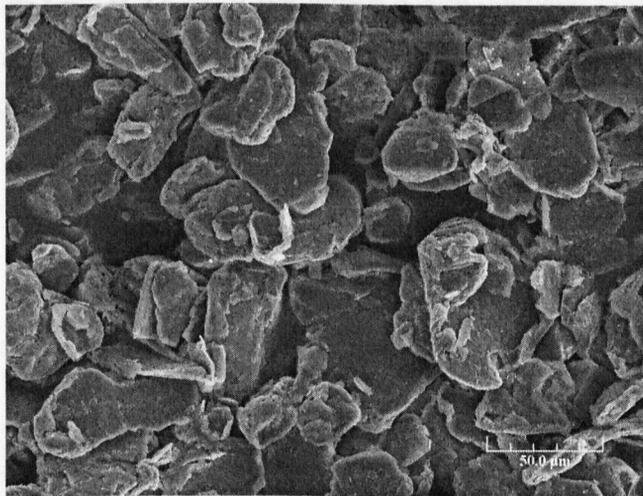
Figure 3.2 SEM micrograph of the particles in the talc powder.

3.1.5 Microwave and moisture absorbents

Calcium chloride ($CaCl_2$) and sodium chloride (NaCl) were selected additives in the extruded starch blends as both microwave energy absorbent during subsequent microwave heating of the extruded pellets and moisture absorbents for plasticizing the extruded pellets and microwave expanded foams. Both $CaCl_2$ (>99.0% purity) and NaCl (>99.5% purity) were Sigma products. $CaCl_2$ was the dihydrate with two molecules of water.

3.2 Extrusion

The extrusion processing was carried out to destructure the starch granules, blend starch materials with additives and produce cylindrical rods for pellets preparation. This section gives a detail description of the extrusion facilities and the extrusion procedures for the different raw materials and various additives.

3.2.1 The extrusion facilities

A Betol (BTS40) twin-screw co-rotating extruder was used to carry out the extrusion processing. The extruder, with total 870 mm long screws, has five barrel sections, each of them is equipped with independently controllable electric heating and water cooling system. The outer diameter of the screws is ϕ 40 mm and hence the length to diameter ratio of the extruder, L/D, is 21.75. A die with a 4 mm diameter circular hole was used. The pressure at the die during extrusion was monitored with a pressure transducer. All extrusion variables, including barrel and die temperatures, die pressure, screw speed and percentage torque were monitored on the control panel. The basic screw configuration from the feed to exit shown in Table 3.2 are used for most extrusion runs unless specified.

Table 3.2 Screw configuration in the extruder

Length (mm)	120		150	90	35	150	120	45	80	80
Pitch (mm)	24		24	24	T	24	16	M	16	16
Barrels	F	Barrel 1		Barrel 2		Barrel 3	Barrel 4		Barrel 5	

T – tri-lobal; M – mix disc; F – feed hopper.

A twin-screw feeder (K-Tron, K-2 modular, Switzerland) was used to feed the starch materials into the extruder through a hopper before barrel 1. The feeder was calibrated to obtain the relationships (linear) between its screw speed and the actual feed rate for

each of the materials used before the experiments, so that the desired formulations can be achieved.

Water or salt solution was directly injected into the extruder through a pipe connected to a port at barrel 2 with a metering pump (N-P 31, Bran+Luebbe, Norderstedt, Germany). The feed rate of the pump was also calibrated before experiments for each liquids used, so as the desired water content in barrel or formulation can be achieved.

3.2.2 Extrusion of wheat flours and purified wheat starch

3.2.2.1 Extrusion of the Temple flour

The Temple flour (moisture content: 10.4%) was fed into the extruder using the feeding system at a rate between 76.4 and 108.2 g/min. The water injection was set at constant rates of either 23.4 or 31.2 g/min. Therefore, the water content in barrel during the extrusion was ranged from 17.8% to 29.0% on wet weight basis, or 26.3 % to 36.4 % on dry weight basis of the flour. The screw speed was fixed at 100 revolution per minute (rpm) based on the experience from preliminary trials. Higher screw speeds would cause foaming of the extrudates. To study the effect of peak barrel temperature on the expansion ratio of the extruded pellets, the temperature at barrel 3 was varied from 100°C to 140°C, while the those at barrels 1, 2, 4, and 5 were kept constants at 60°C, 80°C, 85°C and 75°C, respectively. The temperature of die was set at 50°C. After stable operations were established judged from constant torque and product output, the extrudates were collected. The extrudates were cut manually into cylindrical pellets (about 4 mm long) after the extrudate was cooled to the room temperature. The pellets were then dried naturally in a laboratory atmosphere (~ 23°C and 40 – 50% RH) to moisture content about 12 - 13%. The pellets were then sealed in zip plastic bags for foaming tests.

3.2.2.2 Extrusion of the Superfine flour and purified wheat starch

The Superfine flour and the purified wheat starch were found to be more "sticky" and had poor flowability in the feeding system compared with Temple flour largely due to

the finer particle size of these raw materials. To avoid bridging of the Superfine flour and the starch in the feeding system which would bring in error in the feed rate, the two materials were agglomerated by manually premixing with a predetermined amount of water.

The Superfine flour (moisture content: 10.3%) was premixed with water at the weight ratio of 10/100. The final moisture content in this premixed material was 18.5%. The mixture was sealed in plastic buckets overnight to equilibrate the water distribution.

During the extrusion, the barrel temperatures was set at 60°C/ 80°C/120°C/80°C/70°C from feed to exit, and the die temperature was set at 50°C. The screw speed was kept a constant at 100 rpm. The solid feed rate was fixed at 71.1 g/min and the water feed rate was changed between 7.9 g/min and 15.4 g/min. The water content in barrel was therefore 26.7 to 33.0% (dry weight basis). The extrudates were collected, cut into pellets and stored in the same way as described in Section 3.2.2.1.

The purified wheat starch (moisture content: 9.9%) was premixed with water at the weight ratio of 6/100. The moisture content in the agglomerated mixture was thus 15.0%. The mixture was kept in sealed plastic buckets overnight before use.

During the extrusion, the barrel temperatures was set at 60°C/ 80°C/120°C/80°C/70°C from feeding to die exit, and the die temperature was set at 50°C. The screw speed was kept a constant at 100 rpm. The premixed solid feeding rate was fixed at 52.2 g/min and the water feed rate was adjusted between 12.0 g/min and 20.5 g/min. The water content in barrel was thus 30.9 − 39.0% (on dry weight basis). The extrudates were collected, cut into pellets and stored in the same way as described in Section 3.2.2.1.

3.2.3 Extrusion of the Temple flour with PVA

The peak temperature at barrel 3 and screw speed of extruder were fixed at 120°C and 100 rpm, respectively, all the other settings were the same as that for extrusion of the Temple flour (see Section 3.2.2.1). The Temple flour (moisture content: 13.2%) was fed into the extruder through the feeding port using the K- Tron twin-screw feeder at a rate of 111.9 g/min. Water was injected with the metering pump into a port at barrel 2 at a

rate of 33.0 g/min. Since the feed rates for the Temple flour and water were kept constant during the extrusion, the water content in barrel was 22.8% on wet flour weight basis, or 33.0% on dry flour weight basis. The PVAs were fed, using a second single screw feeder, into the same port for flour feeding. The desired feeding rates were selected so that the weight ratio of the flour (on wet weight basis) to PVAs was controlled at 88/12. The extrudates were collected, cut into pellets and stored in the same way as described in Section 3.2.2.1.

3.2.4 Extrusion of the Temple flour with glycerol

The glycerol was premixed with the Temple flour manually in a weight ratio of glycerol to the flour at 20/100. The mixture was then kept in sealed plastic buckets overnight and then passed through a twin-screw feeder (K-Tron, K-2 modular, Switzerland) to break the lumps and achieve more uniform mixing.

During the extrusion, the barrel temperatures was set at 60°C/ 80°C/120°C/80°C/70°C from feeding to die exit, and the die temperature was set at 50°C. The screw speed was kept a constant at 100 rpm. The solid feed rate was fixed at 133.5 g/min and the water feed rate was adjusted between 20.5 g/min and 33.0 g/min. The water content in barrel was thus 24.1 – 30.7% on dry flour weight basis.

3.2.5 Extrusion of the Temple flour with other additives

3.2.5.1 Extrusion of the Temple flour with foaming and nucleation agents

The foaming and nucleation agents, Hydrocerol® BIH and the talc powder, were premixed with the Temple flour manually in designed concentrations. For the Hydrocerol® BIH, the concentration was 1.5wt% based on the manufacturers recommendation, and for the talc powder the concentrations were 0.8, 1.5 and 2.2wt%. The mixtures were fed into extruder through the K-Tron feeder. All other settings and operations were kept the same as that for extrusion of the Temple flour (see Section 3.2.2.1). The actual water content in barrel during extrusion was 31.3% (dry weight basis).

3.2.5.2 Extrusion of the Temple flour with salt solutions

Water solutions of sodium chloride (NaCl) and calcium chloride (CaCl$_2$) were made by dissolving 140.4 g of NaCl or 275.2 g of CaCl$_2$ in 800 ml of water, respectively, and stored in a solution tank. The extruder was operated at the same settings as that for extrusion of the Temple flour. The flour feed rate was fixed at 93.9 g/min and water feed rate at 33.0 g/min, respectively. Once the extruder was stabilised, the water pump input pipe was diverted from the water tank to the desired salt solution tank. The salt solution feed rate was adjusted to 36.4 g/min for NaCl and 43.2 g/min for CaCl$_2$, respectively. The actual water content in barrel during extrusion of Temple/NaCl and Temple/CaCl$_2$ were 32.7% and 33.0% on dry flour weight basis, respectively. The concentrations of NaCl and CaCl$_2$ in the extrudates were 5.5% and 10.5% (on wet flour weight basis), respectively.

3.3 Characterisation of the raw materials, additives and extrudates

3.3.1 Moisture content determination

About three grams materials, flour, extruded pellets or ground extrudates, were put in aluminium pans and weighed using a balance with an accuracy of 10^{-4} g, then place into a vacuum oven and dried at 85°C for 8 hours and then cooled to room temperature held for another 16 hours under full vacuum. The moisture content (MC) was calculated from the weight loss using the following formula:

$$MC = \frac{W_i - W_f}{W_i} \tag{3.1}$$

where W_i and W_f are the initial weight and final weight of sample, respectively.

3.3.2 Preparation of powder samples

Fine powders were made from dried extruded pellets. 300 grams of pellets from each extrusion conditions were first dried at 65°C for 16 hours then cooled down to room temperature under full vacuum. The dried pellets were ground using a heavy duty coffee maker (Breville Classique Blender, Vine Mill, UK) at medium speed for 1 minute, then the ground materials were passed through a 210 μm sieve to obtain ground powders with particle size under 210 μm, which are refereed to as *ground powders*. The remaining grits (particle size larger than 210 μm) were then further ground using a dry ball miller for 2 hours. Powders were collected by sieving through the 210 μm sieve at 1 hour interval. These powders are refereed to as *ball milled powders*.

3.3.3 X-ray diffraction

Wide angle X-ray spectra of powder samples were collected using a diffractometer employing Cu Kα radiation (PW1050, Phillips). The generator was operated at 36 kV and 26 mA. Samples, as received flour, powdered extrudates or as received PVAs powders, were mounted on a sample stage and scanned over the 2θ range from 3° to 30° or 50° (for PVAs) with step size 0.02° and a scan rate of 0.02 °/sec. The collected data were analysed using the software, Traces (version 3.0, Diffraction Technology Pty Ltd) installed in the machine. The areas under the diffraction peaks (crystallised areas) and total area under the diffraction spectrum were calculated using the "measure peak area" function in the Traces, which automatically generated and subtracted the background pattern from each diffraction spectrum. The crystallinity (%) was obtained from the ratio of the areas of the diffraction peaks to the total area of diffraction spectrum.

3.3.4 Differential scanning calorimetry (DSC)

The calorimetric measurements were carried out using a Perkin Elmer DSC-7. Samples were heated from room temperature to the desired temperature at a heating rate of 10°C/min in nitrogen gas. After the first scanning, the samples were immediately cooled down and rescanned at the same rate.

For measuring the gelatinisation peak, about 1.5 - 3.0 mg dry powder sample was weighed and put into an aluminium DSC sample pan. Distilled water was added until the sample was wetted and uniformly distributed across the bottom of the pan. The pan was then hermetically sealed when the total sample weight reached a desired value. Based on the dry sample weight and the total weight of sample with water, the actual moisture content in the final sample was calculated, which ranged from 60 to 90%.

For measuring the glass transition temperature, the procedure was the same as the measurement for gelatinisation, but no distilled water was added. The powder samples were already in equilibrium with the environmental humidity and had moisture content ranging from 15 to 17%.

For characterisation of the as received PVAs and extruded pellets containing PVAs, about 20 mg powder sample was weighed in an aluminium DSC pan. The pan was covered with an aluminium pan lid. The measurements of glass transition temperature, T_g, and melting point, T_m, were carried out by analysing the observed endothermic stepwise change in the DSC heat flow and determination of the endothermic melting peak.

3.3.5 Thermal mechanical analyser (TMA)

A TMA (TMS-1, Perkin Elmer) was used to measure and analyse thermal expansion of extruded pellets. The top and bottom surfaces of a cylindrical shape pellet were polished on a sample grinder using a fine emery paper (Struers, P#1200) to ensure the two surfaces were flat and parallel. The height of the specimens was between 4.2 ~ 6.2 mm. The sensitivity of probe was set at either 254 μm or 50.8 μm depending on the expansion of specimens, and a static force of 0.5 g was applied. The specimens were heated from room temperature to 100°C with a heating rate of 2°C/min. Changes in probe position (specimen height) were recorded as a function of temperature and plotted by an x-y recorder. The glass transition temperature, T_g, was determined based on the temperature at which a change in the slope of the obtained curves occurred (i.e. the temperature at the intersection of the two portions of the curve). The specimens were

weighed before and after test to determine the moisture loss during the test and average moisture content corresponding to the measured T_gs.

3.3.6 Fourier transform infrared spectroscopy (FT-IR)

The Temple flour as received and ball milled powders samples from extrudates (particle size below 210 μm) were mixed with KBr powder at ratio of 1wt% and pressed into disc. A Nicolet 710 FT-IR Spectrometer was used to record the absorbance spectra. A spectral resolution of 4 cm^{-1} was employed and 64 scans were acquired for each spectrum.

3.3.7 Microscopy observations

Differential interference contrast microscopy (Nikon UFX OPTIPHOT, Japan) was used to observe the morphologies of phases in the extruded pellets. Thin sections (~ 5 μm) were sliced from extruded pellets using a microtome (Leica RM2155, Germany). The sections were placed on micro-slides, then stained with a drop of dilute (1%) iodine-potassium iodide solution. After a short time (~ 15 seconds), the excess solution was suck away using lab tissue.

3.3.8 Determination of WAI and WSI

The water absorption index, WAI, and water solubility index, WSI, were measured using the method described by Anderson et al (1969). A 2.5 g powder sample was dispersed in 25 g of distilled water in a centrifuge tube. A glass rod was used to break up any lumps. After manually stirring for 30 minutes, the suspension was centrifuged at 3000 g for 10 minutes. The supernatant was decanted for determination of its solids content and the sediment was weighed. WAI and WSI were then determined using the Equations 2.8 and 2.9, respectively.

3.3.9 Rapid Visco Analyser (RVA)

A Rapid Visco Analyser (model 3D, Newport Scientific, Australia) was used to measure the changes of apparent viscosity with temperature of the ground extrudates. The test procedure was based on the RVA^{TM} Extrusion Method (Newport scientific method 13, version 4 December 1997). Around 3.0 g of ground sample was weighed and added to 25 ml of distilled water in a new canister (sample weights and water added have been corrected for the sample moisture content to give a constant dry weight concentration). A rubber stopper was used to seal the canister and the suspension was shaken vigorously for 15 seconds to disperse the powder. A programmed heating and cooling cycle was used at constant paddle rotation speed: the sample was equilibrated at 25°C for 2 min, heated to 90°C at a rate of 13°C/min, held at 90°C for 3 min and cooled to 25°C at the same rate. Apparent viscosity and temperature profile were monitored and recorded by a computer.

3.3.10 Haake viscosity

The ground powder samples were first dried at 65°C with full vacuum for 24 hours then at room temperature with full vacuum for 48 hours. Ten grams of dried powder were mixed with 100 ml of distilled water in a plastic bottle and kept for 1 hour during which the suspension was manually stirred at about 15 minutes intervals. A portion of the suspension was removed from the bottle and placed in the MV St cup (cylinder with an interior diameter of 42 mm and height of 95 mm) of Haake Viscotester VT550 (a concentric cylinder viscometer, with 2 mm gap between two cylinders and the inner one of which is rotated) for measurement. The remaining portion within the plastic bottle was cooked in a water bath at 85°C for 1 hour. After the cooked slurries were cooled to room temperature, they were transferred to the cup of the Haake Rheometer for measurement. The apparent viscosity was measured as a function of shear rate which was varied between 2 and 1000 s^{-1}. All viscosity measurements for the slurries before and after cooking were made at room temperature (~ 20°C).

3.4 Foaming tests of the extruded pellets

3.4.1 Moisture conditioning of the extruded pellets

Four saturated salt solutions (LiCl, MgCl$_2$, NaCl or BaCl$_2$) were prepared according to standard practices (ASTM E 104-85) for maintaining constant relative humidities within sealed container. They were placed at the bottom of desiccators to obtained relative humidity of 11, 35, 78 and 93% at room temperature.

In order to investigate the effect of moisture content in the pellets on foaming, some pellets were equilibrated in these desiccators at room temperature for two weeks to modify their moisture content. The actual moisture content of the pellets was determined by drying the pellets in a vacuum oven as described in Section 3.3.1.

3.4.2 Oil bath frying

A compact deep fryer (Midi easy clean fryer F260-E9, DeLonghi, Italy) was used to check foamablity of extruded pellets. Cooking oil was heated to 181°C, then pellets were put into the oil bath. After about 12 seconds, the foamed pellets were removed from the oil bath for a measurement.

3.4.3 Microwave heating

Foaming tests were carried out in a combined microwave oven (Sharp R-8720M, 1000W), which allows both convection hot air heating and microwave heating. The pellets were put in a Pyrex glass Petri dish which was preheated by convection to about 165°C, which was measured by a non-contact infrared thermometer (Raytek®, Raynger® ST6™, Santa Cruz, USA), and located at the centre of the rotating dish in the microwave oven, then heated by microwave at full power (100%). About 30 ~ 65 seconds was required to foam the pellets depending on their compositions. Excessive microwave heating would lead to burning of the foamed pellets.

3.5 Characterisation of foamed pellets and blocks made from the MAM method

3.5.1 Determination of expansion ratio and density

A set of ten pellets were placed in a graduated cylinder before and after foaming tests, then a known volume of 60-mesh solid glass beads (BDH Chemicals Ltd, Poole England) was poured into the cylinder. The total volume of glass beads and pellets (or foamed pellets) were recorded after tapping the graduated cylinder for 1 minute. The volume of pellets (or foamed pellets) was calculated by subtracting the volume of the glass beads from the total volume. The expansion ratio was determined by the ratio of foamed pellet volume to its original volume. The density of the foamed pellets was calculated from the mass of foamed pellets divided by the volume.

To measure the density of the foamed block, it was placed in a container of known volume, and then the container was fully filled with solid glass beads. The block volume was calculated by subtracting the volume of glass beads from the volume of the container. The density of the foamed block was calculated from mass of the block divided by its volume.

3.5.2 Scanning electron microscopy

Foamed pellet samples for scanning electron microscope (SEM) observations were sectioned with a single-edged razor blade. Samples from foamed blocks were sectioned using a handsaw. Samples were then mounted on aluminium stubs with a graphite filled double side adhesive tap, and coated with gold in a SEM sputter coating unit, then examined with a Cambridge Steroscan scanning electron microscope (250 MK2 Cambridge, England).

3.5.3 Measurement of moisture absorption isotherms

For the measurement of moisture absorption isotherms of foamed pellets, the samples were placed in the desiccators containing saturated salt solutions (LiCl, $MgCl_2$, NaCl and $BaCl_2$), and weighed daily until the weight became constant (in about 8 days). These samples then were dried in a vacuum oven under full vacuum at 85°C for 8 hours

then cooled to room temperature and held for another 16 hours. The equilibrium moisture contents (EMC) of foamed pellets at different relative humidities were calculated based on Equation 3.2 using the equilibrium wet weight, W_w, and the dry weight, W_d:

$$EMC = \frac{W_w - W_d}{W_w} \qquad (3.2)$$

3.5.4 Characterisation of mechanical properties of the foams

Mechanical properties of starch-based foams are of major importance for their applications. For the foams relevant to cushion packaging application, their compressive properties may be more important. Therefore, compression tests were carried out to measure some compressive properties, such as compressive modulus of elasticity and compressive strength, of the foams and to investigate the effects of compositions on these properties.

3.5.4.1 Foamed pellets

Samples for compression tests were cut from foamed pellets. A single-edged razor blade was used to cut a foamed pellet into rectangular prism, using a slicing motion to avoid crushing the foam cells. The height of sample was 10 mm, the cross section areas of the samples were dependent on the available size of the foamed pellets, which was governed by their expansion ratio during microwave foaming. It ranged from 45 to 65 mm^2 for Temple/talc pellets which was the smallest ratio and 110 to 160 mm^2 for Superfine flour which was the largest. All the specimens were placed in a controlled environment (20 - 22°C and 50% relative humidity) for ten days before test.

A Hounsfield universal testing machine (Model H10KT, Hounsfield Test Equipment Ltd., Surrey, England) with a 100 N load cell and a 25 mm diameter cylindrical plate

were used to compress the samples to achieve a deformation of 50% of their original dimension at a 10 mm/min loading rate. According to British Standard BS ISO 844:2001 (E), compressive modulus of elasticity of samples was calculated based on the slope of initial linear portion of load-displacement curves. Compressive strength was determined by dividing the peak forces reached in the desired deformation (<10%) by the corresponding cross section area of the samples. For samples where compressive strain larger than 10%, compressive stress at 10% deformation was accepted as compressive strength as suggested in the British Standard. The absorbed energy during deformation was also evaluated by measuring the areas under the load-displacement curves and normalised by dividing them by the initial volume of samples.

Some commercial protective packaging materials, EPS blocks and starch based loose fills were also tested for comparison. The shape of EPS block samples was rectangular prism, with 10mm height and around 60 mm^2 cross section area. The shape of the loose fill sample was cylinder with 10 mm height and about 15 mm in diameter.

3.5.4.2 Foamed blocks

The foamed block with diameter of around 60 mm and height of 22.5 - 23.5 mm were placed in a controlled environment (20 - 22°C and 50% relative humidity) for two weeks before test.

The Hounsfield universal testing machine with a 10 kN load cell and two square compression plates (150 mm x 150 mm) were used to compress the samples to achieve a deformation of 50% of their original dimension at a 10 mm/min loading rate. Compressive stress at 10% relative deformation and compressive modulus of elasticity of the samples were calculated based on British Standard, BS ISO 844:2001 (E).

Chapter 4

Characterisation of Extruded Pellets

Extrusion cooking of starchy materials may cause significant microstructural changes and modification of functional properties. During extrusion cooking under the combined actions of water uptake, heating and mechanical shearing, starch granules swell and gelatinise with loss of their native crystalline structure partly or completely. Subsequently, the swollen granules were disrupted and transformed into a continuous phase of starch polymer melt in which some non-cooked starch granules and granule "ghosts" (swollen, non-birefringent and amylose leached starch granules) may remain. Under severe shearing and heating, starch degradation with molecular chain scission may occur. All these depend upon the severity of the treatment the materials receive during extrusion. Generally, mild treatments occur at high water contents, low barrel temperatures and low screw speeds whereas severe treatments occur at low water contents, high barrel temperatures and high screw speeds. This chapter focuses on the characterisation of some physical properties of the extruded pellets, which are related to their degree of cook. Through these characterisations, it is hoped that a better understanding of the correlation between extrusion conditions and microwave foamability of the extruded pellets can be gained.

4.1 Crystallinity

The crystallinity is an important characteristic in determining the properties of extruded products. Since wide angle X-ray diffraction provides information about the long-range order of the molecular constituents in materials, it has been often used to track structural changes in starch extruded under varied heat, shear, and moisture levels. By carrying out structure investigation of a systematic series of extrudates from wheat flour, it is hoped to gain insight into the effects of extrusion conditions on the final microstructure of the extruded materials.

4.1.1 Influence of extrusion conditions on crystallinity

It was found that the crystalline structures of wheat flour (Temple) change during extrusion. Figure 4.1 shows the X-ray diffraction patterns of the Temple flour extruded at peak temperature of 120°C with different levels of water content in barrel. The extruded samples were powdered with a coffee mill (see Section 3.3.2 for the details). The X-ray diffraction pattern of the raw material is also presented for comparison. The unprocessed wheat flour (Temple) gives the characteristic A-type diffraction spectrum with broad main diffraction peaks located at about 15.2°, 17.3°, 18.0° and 23.1° 2θ degree (Zobel, 1964).
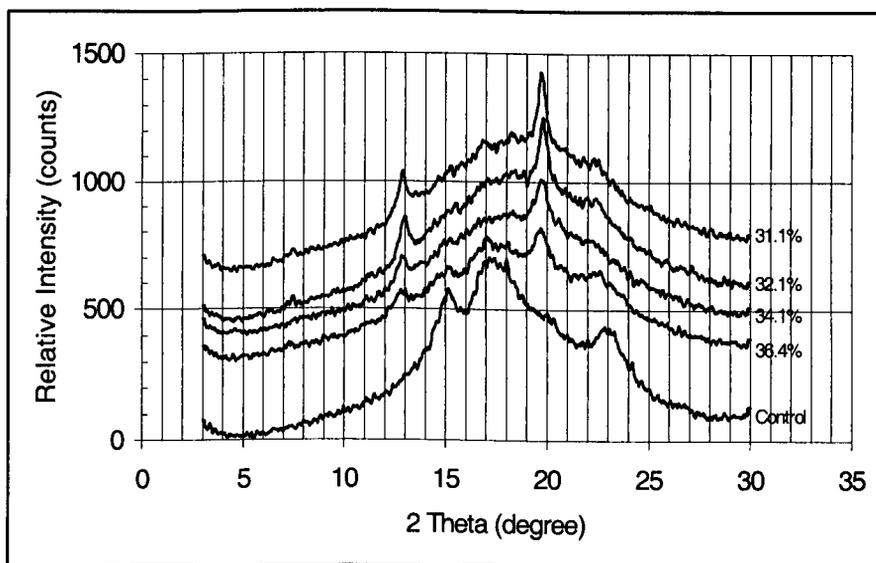

Figure 4.1 X-ray diffraction patterns of the ground powder from the Temple flour extruded at 120°C with different levels of water content in barrel.

As shown in Fig. 4.1, after extrusion at higher water content level, for instance at 36.4% (D.W.B.), a significant reduction of the A-type peaks is observed and some new peaks appear. Since the new peaks located at 12.9°, 19.7° and 22.4° 2θ degree are the characteristic diffractions of V-type structure (van Soest, et al., 1996a), the crystalline structure of the extrudate can be considered as a mixture of V-type and A-type. It should be noted that, with decreasing of the water content in barrel, the A-type

diffraction peaks become weaker, whereas the V-type diffraction peaks become stronger. Since reduction in water content gave rise to increased severity of treatment (i.e. higher melt viscosity and thus higher shear stress in the material during the extrusion when the extrusion temperature and screw speed were kept constant), the residual A-type crystallinity in the native granules was decreased. It can be seen from Fig. 4.1 that when the water content falls to a certain level, approximately below 32.1%, the A-type peaks virtually disappear. This suggests that the native starch granules could not be fully gelatinised at higher water content levels when extruded at 120°C. Optical microscopy using crossed polarizers has confirmed that fragments of native starch granules still exist in those extrudates with A-type diffraction pattern (pictures not shown). On the other hand, as mentioned and discussed in Sections 2.1.2 and 2.4.1, the V-type crystals are complexes of amylose and induced by processing. It has been reported that the relative amount of V-type crystallinity is proportional to the amount of amylose (van Soest, et al., 1996a). Therefore, more V-type crystals would be expected to form in the materials treated with higher shearing if the extrusion has not caused significant degradation of the starch polymer chains, because more amylose would be liberated from the starch granules under severe shearing.
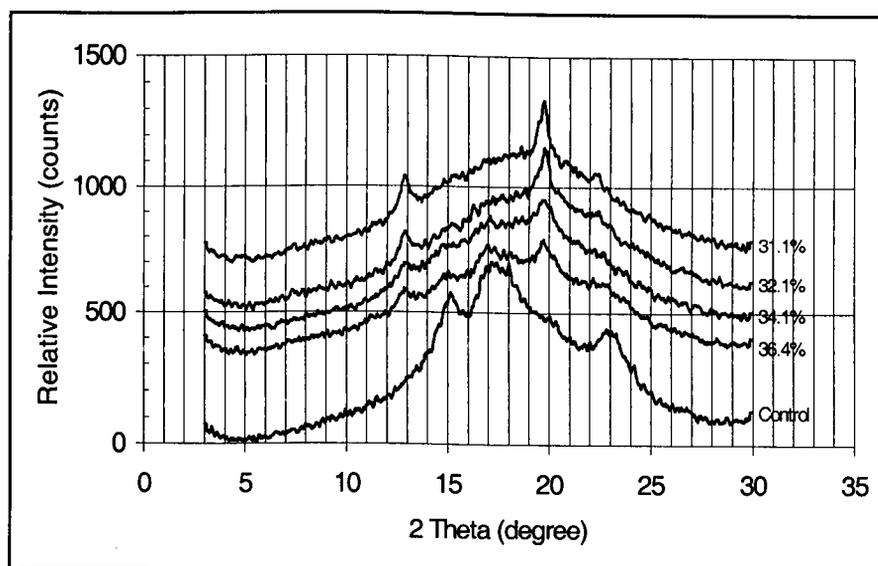

Figure 4.2 X-ray diffraction patterns of the ground powder from the Temple flour extruded at 130°C with different levels of water content.

From the X-ray diffractograms of the Temple flour extruded at 130°C and 140°C presented in Figures 4.2 and 4.3, similar trend can be found in the effect of the water content in barrel on the structures of extrudates: the A-type crystallinity decreases and the V-type crystallinity increases with the reduction of water content. However, it is interesting to note that at 140°C, the native A-type structure was almost destroyed completely at high water content (e.g. 36.4%) and insignificant V-type crystallinity was observed, leading to the X-ray pattern typical of an near amorphous state (Fig.4.3).
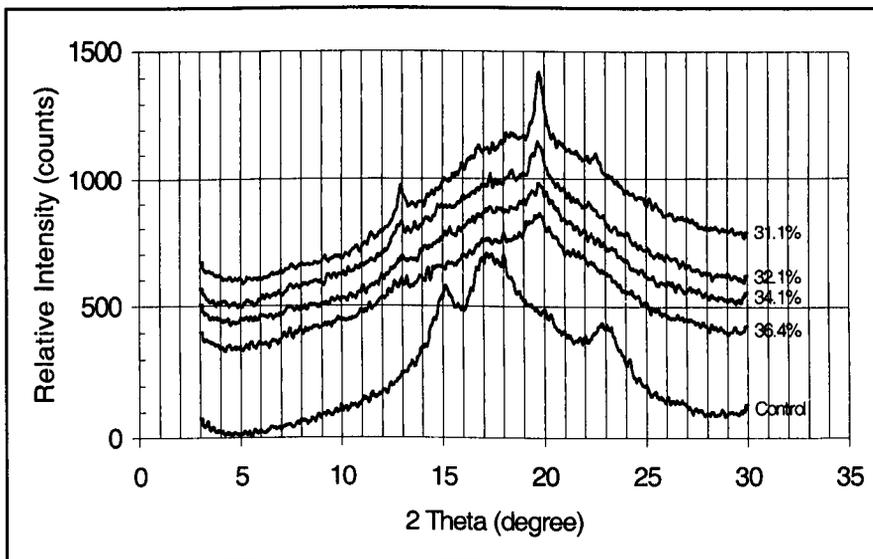

Figure 4.3 X-ray diffraction patterns of the ground powder from the Temple flour extruded at 140°C with different levels of water content.

Figure 4.4 gives the X-ray diffraction patterns of Temple flour extruded at different temperatures with water content of 36.4% (D.W.B.) to illustrate the effect of extrusion temperature on the crystallinity of extrudates. At 120°C and 130°C, some residual A-type crystallinity can be observed after extrusion. While after processing at 140°C, no residual A-type crystallinity can be found and there is only slight trace of the V-type crystallinity. At a fixed water content and screw speed, higher extrusion temperature, to some extent, reduces the melt viscosity as indicated in Eqn. 2.4 and hence lower mechanical shearing in the material. But, the higher thermal energy input into the materials favours its melting and the destruction of crystallinity due to higher mobility

of molecules and greater granule swelling. Therefore, less residual native A-type crystals are present at high extrusion temperature. On the other hand, lower shearing in the melt could reduce the amount of amylose leached out from the gelatinised granules, which in turn decreased the V-type crystallinity. This argument is supported by the observations that, for a fixed extrusion temperature, the lower the water content in barrel, the higher the V-type crystallinity in the extrudates (Figs. 4.1, 4.2 and 4.3).
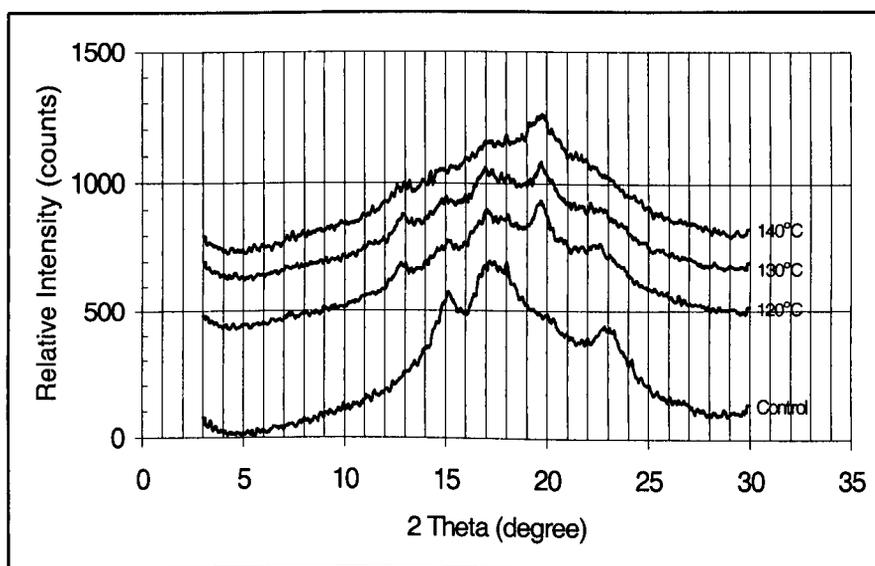
Figure 4.4 X-ray diffraction patterns of the ground powder from the Temple flour extruded at different temperature with identical water content level at 36.4% (dry weight basis).

Figure 4.5 presents the X-ray diffractograms of the Temple flour extruded with water content of 31.1% (D.W.B.) at different temperatures. At this lower water content level, mechanical shearing is dominant and the changes of the extrusion temperature have no significant effect on the X-ray diffraction patterns of extrudates. This suggests that the effect of extrusion temperature on the amount of V-type crystals in the extrudates is dependent on the water content in barrel.
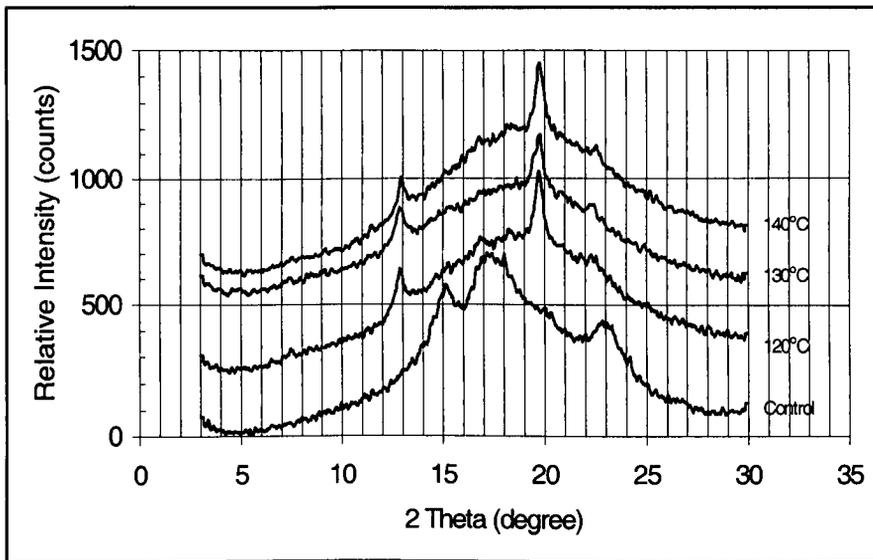
Figure 4.5 X-ray diffraction patterns of the ground powder from the Temple flour extruded at different temperature with identical water content level at 31.1% (dry weight basis).

4.1.2 Influence of powdering methods

All above X-ray diffraction patterns were obtained from the powder samples made by coffee mill (the ground powders). Ball milling is an alternative powdering method for preparation of fine powder samples. The choice of powdering methods raises the question of whether the X-ray diffraction results are likely to be affected by the preparation methods. It has been reported that ball milling can damage the starch granules and cause changes of physical state in starch (Morrison, et al., 1994; Kim, et al., 2001). In order to examine the influence of powdering methods on the X-ray diffraction results, samples powdered by ball milling and collected at 1 hour interval (see Section 3.3.2 for more details) were tested by X-ray diffraction analysis, and compared with those prepared by milling with a coffee mill.

Figure 4.6 (a) shows the X-ray diffraction patterns of Temple flour as received and ball milled for 10 hours. It can be seen that the ball mill significantly decreases the intensity of diffraction peaks and results in a drop in the crystallinity from 13.2% to

8.6%. It was therefore anticipated that the ball milling method would also affect the X-ray diffraction results of the extruded flour in the similar way.
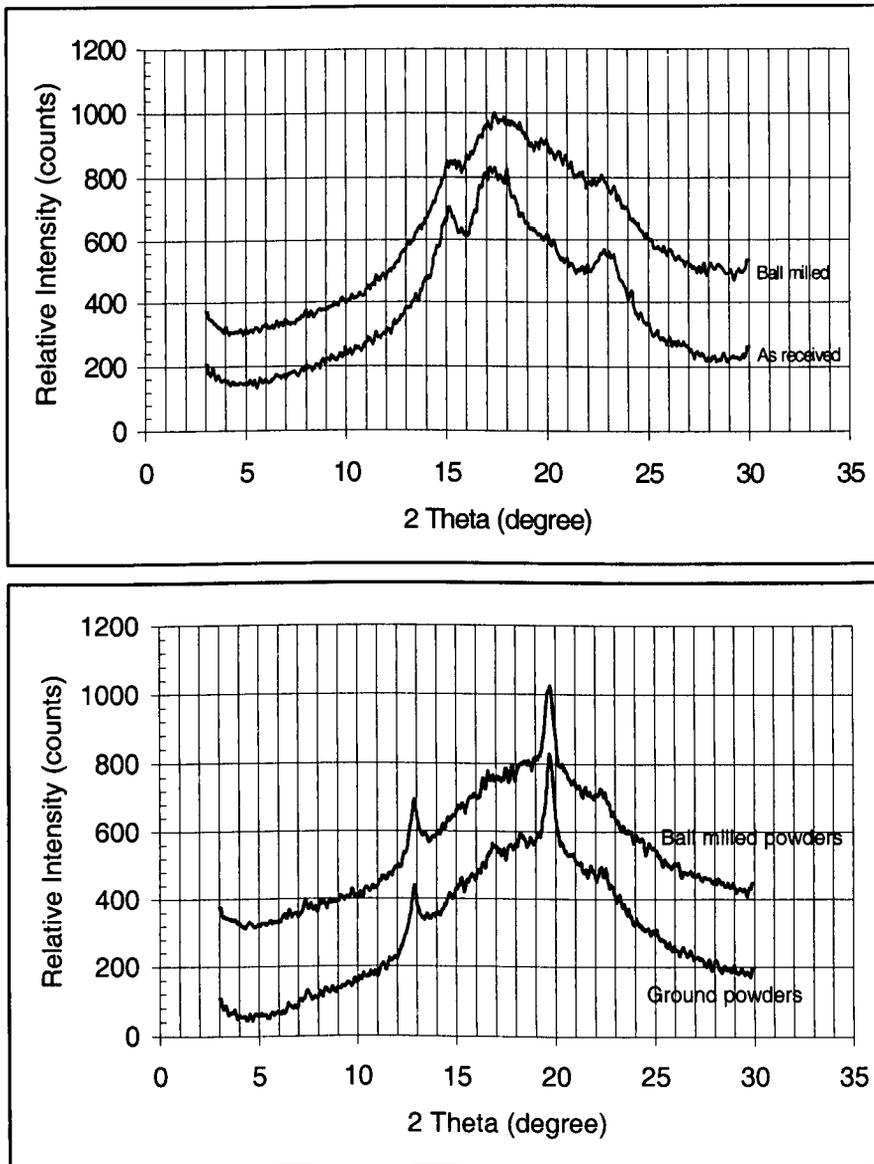

Figure 4.6 Comparison of X-ray diffraction patterns for the Temple flour as received and ball milled for 10 hours (a - top); and extrudate (120°C with 31.1% water content in barrel) powdered by the two different methods (b - bottom).

However, no significant differences have been observed in X-ray diffraction patterns of extrudate samples powdered by coffee milling (ground powders) and ball milling (ball milled powders) as shown in Fig. 4.6 (b). In general, the coffee milling method

simply break up the extrudate pellets by fracturing, while in ball mill, the materials were fractured by impacts between the milling balls and surface wearing by mechanical comminution. Therefore, ball milling is more easily to result in a reduction of crystallinity in flour sample as shown in Fig. 4.6 (a) due to small size of starch granules. However, for extrudate samples, the size of extrudate grits was much larger than the starch granules in flour sample, and the regions of the processing-induced V-type crystallinity are only a small portion of the extrudates which is dispersed in an amorphous matrix. The X-ray diffraction results obtained from these powder samples indicate that the crystalline regions still survive after either cafe milled or ball milled, and the two powdering methods have no significant effect on the X-ray diffraction results for the extruded flour, although ball milling caused a notable decrease of crystallinity in the raw material, which were mainly due to long milling time (10 hours) and small initial particle size of the sample.

Table 4.1 gives the crystallinities of Temple flour extruded at different conditions and powdered by coffee milling and ball milling. Both powdering methods yield similar results. For the extrudates processed at low extrusion temperature and high water content, the total crystallinity has not dropped significantly because of the native A-type crystals remaining in the extrudates. With increasing severity of treatment, the crystallinity reaches a minimum value as the A-type structure has been completely destroyed. Then the crystallinity increases slightly as more V-type crystals are formed.

Table 4.1 The influence of powdering method on the X-ray diffraction results of wheat flour extruded at different conditions

Extrusion Temperature (°C)	Water Content in Barrel (%, D.W.B.)	Coffee Milling		Ball Milling	
		Structure	Crystallinity (%)	Structure	Crystallinity (%)
120	36.4	V and A	10.5	V and A	12.7
	34.1	V and A	5.8	V and A	6.8
	32.1	V	4.9	V	5.8
	31.1	V	6.3	V	6.9
130	36.4	V and A	8.5	V and A	10.3
	34.1	V and A	7.2	V and A	7.9
	32.1	V	5.4	V	6.1
	31.1	V	6.7	V	6.9
140	36.4	V and A	5.5	V and A	5.6
	34.1	V	4.7	V	4.6
	32.1	V	4.7	V	4.6
	31.1	V	6.3	V	6.6

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## 4.2 Differential interference contrast (DIC) microscopy
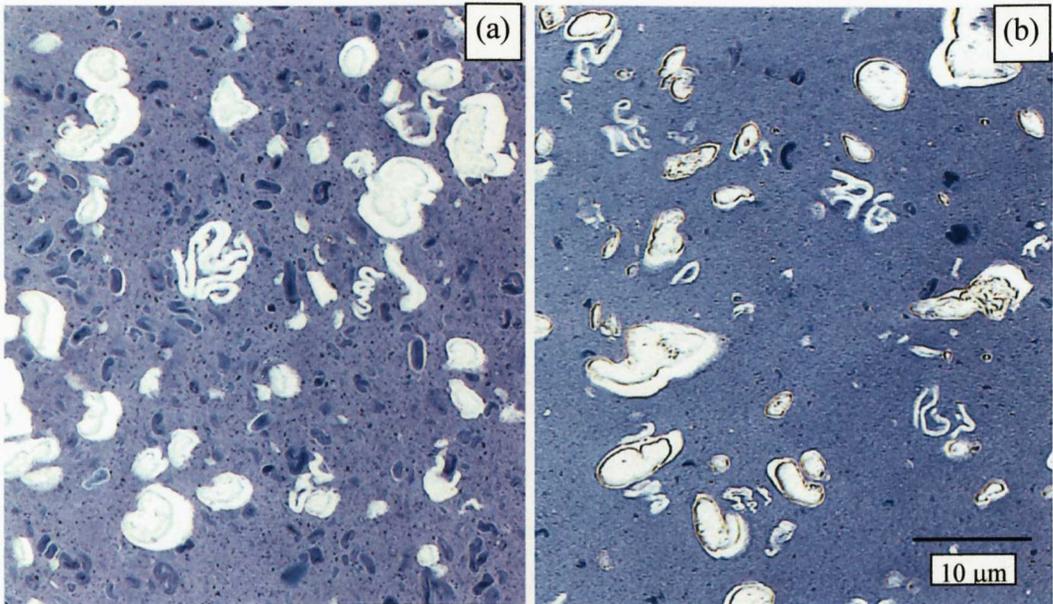
Figure 4.7 Micrographs of DIC for Temple pellets extruded at 120°C with different water contents in barrel (a) 36.4%; (b) 31.1%.

Figure 4.7 presents DIC micrographs for the Temple flour pellets extruded at 120°C with different water contents in barrel (36.4% and 31.1%) after iodine staining. The white particles are identified as gluten (protein) which cannot be stained by iodine but can be stained using toluene blue (prints not shown). The unstained white worm-like structure is believed to be endosperm cell wall. It can be seen in Fig. 4.7 (a), when water content in barrel is high (36.4%), there are many dark blue particles distributed throughout the coarse matrix. However, with decrease of water content level, the numbers of these particles reduce (very few left when water content in barrel was 31.1%, shown in Fig. 4.7 (b)), and the matrix becomes much finer. These dark blue particles are identified as uncooked stained starch granules. It was also found that some starch granules were protected within native cell structure of endosperm and survived in the shearing of the extrusion, even at low level of water content in barrel, such as 31.1% (see Figure 4.8). This provides a confirmation that those dark blue particles are residual of starch granules. The coarse matrix in the extrudate shown in Fig. 4.7 (a) suggests that

the starch granules have not been destructurised sufficiently at this higher water content in barrel, while at low water content in barrel (e.g. 31.1%), the destructrisation of starch granules has been significantly improved.
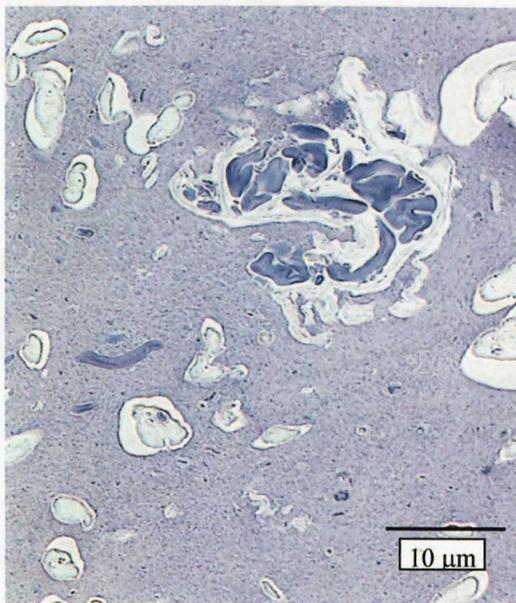

Figure 4.8 Starch granules protected within native cell structure of endosperm in a Temple pellet extruded at 120°C with 31.1% water contents in barrel.

These direct observations have confirmed that starch granules have not been fully disrupted under these extrusion conditions, but with the reduction of water content in barrel, less residual native granular starch exist in the extrudates. This is consistent with the results of X-ray diffraction.

4.3 Enthalpy of gelatinisation

As mentioned in Chapter 2, starch gelatinisation can be assessed by differential scanning calorimetry (Jenkins, & Donald, 1998; Takaya, et al., 2000). Figure 4.9 shows typical DSC scan curves for the Temple flour and its extrudates processed at 120°C with different water contents in barrel. A main endothermic peak accompanying gelatinisation is observed for the as-received Temple flour. The peak temperature and enthalpy on gelatinisation for the as-received Temple flour are 58.2°C and 6.90 J/g. It is

noted that ball milling has considerable effect on the gelatinisation. The gelatinisation endotherm peak has obviously reduced after ball milling. The peak temperature and enthalpy on gelatinisation for ten-hours ball milled Temple flour are 57.9°C and 1.68 J/g. This suggests that ball milling alone is able to destroy partly the original crystalline structure in the native starch. While for the extruded ones (powdered by the coffee milling), the gelatinisation endotherm peaks disappear completely.
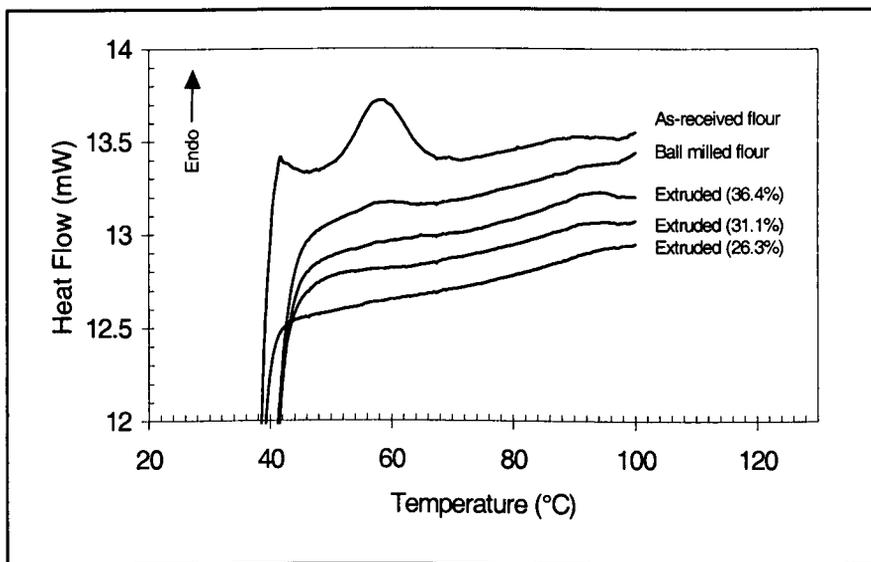

Figure 4.9 Typical DSC scan thermograms of Temple flour and its extrudates extruded at 120°C with different water contents in barrel.

The results obtained from other techniques, such as X-ray diffraction and DIC, have confirmed that there are still some non-gelatinised starch granules in the extrudates especially those with high water content in barrel (see Sections 4.1 and 4.2). However, a similar conclusion cannot be drawn from the DSC results, which suggests that this technique is not sensitive enough to monitor the process of gelatinisation of residual starch granules in the extrudates of the wheat flour used in this study.

It is known that the botanical source of starch affects its DSC gelatinisation characteristics. The enthalpy of gelatinisation for wheat starch is relative small compared with that of other starches. It is only about 70% of maize starch and 50% of potato starch (Jenkins, & Donald, 1998; Ahmad, et al., 1999). In other words, the

gelatinisation of wheat starch only requires a relatively small amount of energy compared with the other starches. It was hoped that by measuring the changes in enthalpy of gelatinisation of extrudates with different extrusion conditions, their degree of cook can be estimated. However, the DSC results shown in Fig. 4.9 suggest that the specific mechanical and thermal energy provided by the extruder under the applied extrusion conditions is so high that the amount of non-gelatinised residual was not detectable. Thus, it may be concluded that determination of enthalpy of gelatinisation by DSC is only suitable for characterising partially gelatinised samples with low degree of cook.

4.4 FT-IR spectrum

It was proposed (Park, & Im, 2000) that gelatinisation of starch could lead to a diminution of hydrogen bonding in the granules. It was possible that the hydrogen bonding between starch polymeric chains was destructured by hydration during gelatinisation. This would cause the OH band shown between 3000 and 3500cm^{-1} became narrow and shifted to a higher wavenumber and the C-O stretching band at 1013 cm^{-1} shifted to 1020 cm^{-1}. Therefore, it was hoped that by measuring the shift of these peaks, the extent of starch gelatinisation could be assessed.

Figure 4.10 shows FT-IR spectra of the as-received Temple flour, the ball milled (ten hours) Temple flour and extruded at 120°C with different water contents in barrel. Based on the FT-IR assignments for starch denoted in Table 4.2 (Park, & Im, 2000), the characteristic peaks appearing between 960 and 1190 cm^{-1} are attributed to C-O bond stretching. The characteristic peak that occurs at 1640 cm^{-1} is believed to be a feature of tightly bound water present in the starch. The peak at 2920 cm^{-1} is characteristic of C-H stretches associated with the ring methine hydrogen atoms. The broad peak appears at 3403 cm^{-1} is due to the complex vibration of hydrogen bonded hydroxyl groups (O-H) which make up the gross structure of starch (Fang, et al., 2002).
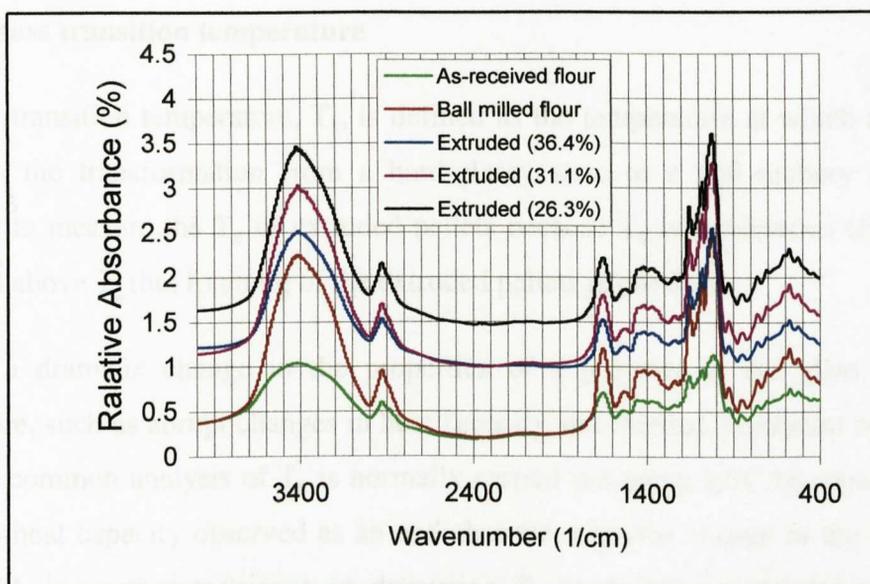
Figure 4.10 FT-IR spectra of Temple flour and extrudates extruded at 120°C with different water contents in barrel.

Table 4.2 FT-IR assignments for starch

Wavenumber (1/cm)	Assignment
2850, 2920	C-H stretching
1640	δ (O-H) bend of absorbed water
1462	CH_2 bending
1445 – 1325	C-H bending and wagging
1243, 1205	O-H bending
960 – 1190	C-O stretching

However, inspection on the spectra in Fig. 4.10 suggests that there is no obvious peak shift occurred after extrusion for the Temple flour. Since the results of X-ray diffraction, DSC and DIC etc. have already confirmed that a gelatinisation does occur in the extruded Temple flour, the spectra in Fig. 4.10 illustrate that FT-IR is not sensitive enough to monitor the process of gelatinisation during extrusion for wheat flour.

4.5 The glass transition temperature

The glass transition temperature, T_g, is defined as the temperature at which a polymer undergoes the transformation from a hard-glassy state to a soft-rubbery one. It is important to measure the T_g of extruded pellets because T_g is a reference temperature point, and above T_g that foaming of the extruded pellets is possible.

There is a dramatic change in the properties of a polymer at the glass transition temperature, such as abrupt changes in heat capacity and thermal expansion coefficient. The most common analysis of T_g is normally carried out using DSC by measuring the change in heat capacity observed as an endothermic stepwise change in the DSC heat flow. TMA is another technique to determine T_g by measuring change in thermal expansion coefficient observed as a slope change in the TMA curve (thermal expansion against temperature). It should be pointed out that both DSC and TMA assume the glass transition event happens over a narrow range of temperature. If the glass transition is very broad it may not be seen with either approach.

4.5.1 Measurement of T_g using DSC

Figure 4.11 presents the typical DSC second scan curves for the Temple flour and its extrudates extruded at 120°C with different water contents in barrel. For all the samples, the moisture content was ranged around 15–17%. It can be seen from Fig. 4.11, there are no detectable endothermic stepwise change in the heat flow. In other words, T_g can not be determined by DSC for these samples. The reason that the glass transition is invisible is probably because the signal is too weak to be detected. Though increasing the amount of sample could enhance the intensity of the signal, it has always led to leakage of moisture or even burst of the sealed sample cell and thus failure of measurements.
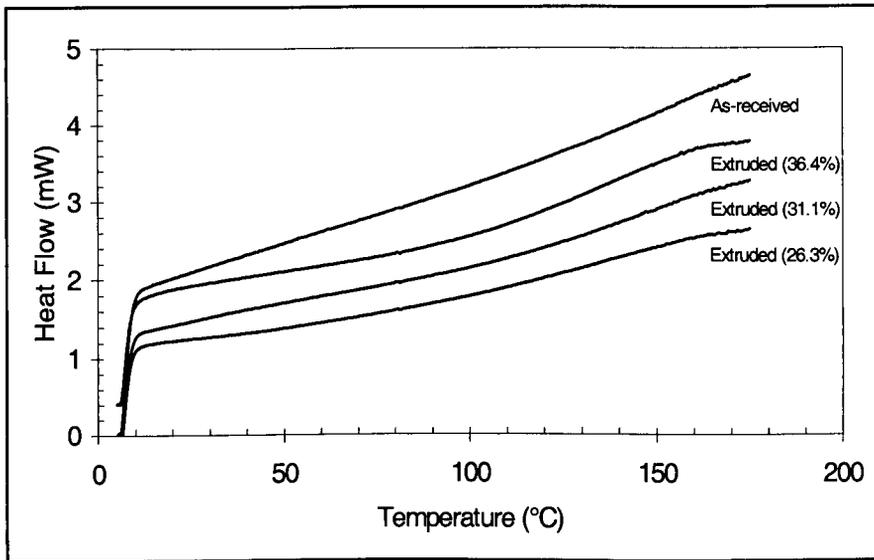
Figure 4.11 DSC second scan thermograms of Temple flour and extrudates extruded at 120°C with different water contents in barrel.

## 4.5.2 Measurement of T_g using TMA
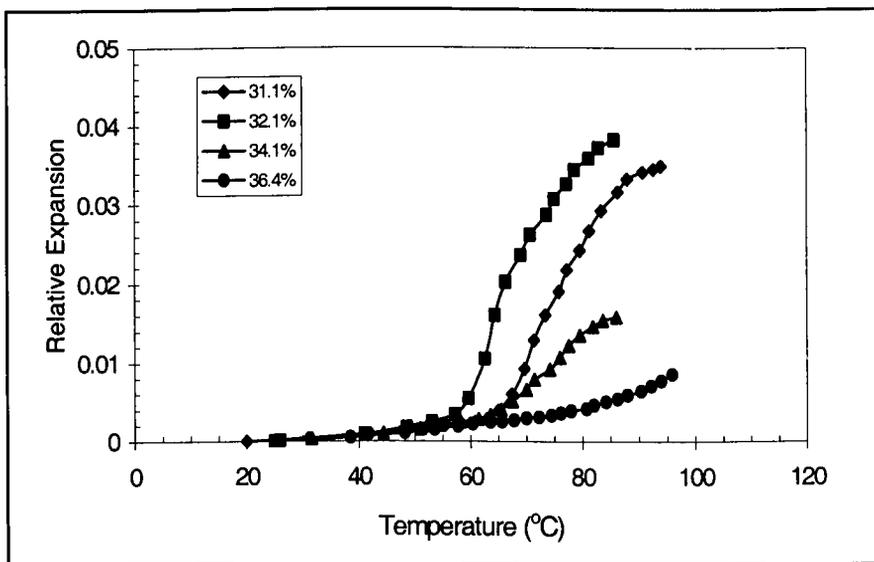
Figure 4.12 TMA curves of Temple flour extruded at 130°C with different water contents in barrel.

Figure 4.12 shows the TMA curves of the Temple flour extruded at 130°C with different water contents in barrel. It can be seen that for the specimens extruded at lower

water content levels (e.g. 31.1% and 32.1%), there is a sudden change in the thermal expansion coefficient (the slope of the curves) at certain temperatures. While for the specimens extruded with higher water content levels, the change in thermal expansion coefficient is not so abrupt, making it more difficult to identify the temperature at which the change takes place.
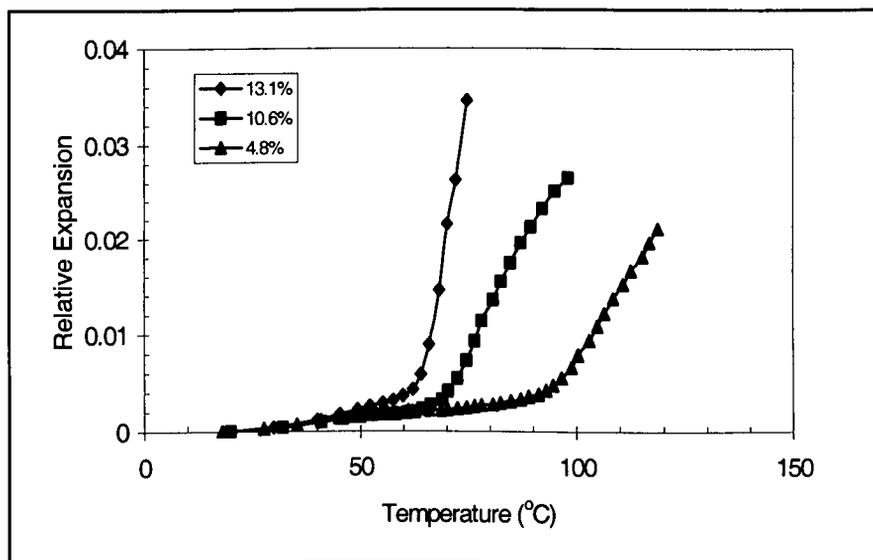

Figure 4.13 Effect of moisture content on the T_g of Temple flour extruded at 120°C with 31.1% water content.

To confirm the observed change in thermal expansion coefficient is originated from the glass transition, the specimens were conditioned at low relative humidity environments to achieve different equilibrium moisture levels. It is well known that the T_g of starch material is sensitive to moisture content and decreases with increasing of moisture content. Figure 4.13 presents the TMA curves for identical extrudate but different equilibrium moisture contents. It can be seen that with decreasing of moisture content in the specimens, the temperature corresponding to the change in thermal expansion coefficient increases as expected for T_g. This suggests that the change in thermal expansion coefficient does result from the glass transition.

Table 4.3 lists the glass transition temperatures, taken as the point at which the linear extrapolations of the two portions of TMA curve meet, for the extruded pellets (Temple flour) with different extrusion conditions.

Table 4.3 Glass transition temperatures for the Temple flour pellets extruded in different conditions

Extrusion Temperature (°C)	Water Content in Barrel (%, D.W.B.)	T_g (°C)	Moisture Content Before Test (%)	Moisture Loss After Test (%)
120	26.3	60	11.0	6.9
	28.5	62	12.5	6.8
	31.1	66	12.3	7.5
	32.1	64	12.3	6.4
	34.1	61	12.8	9.1
	36.4	x	12.3	11.6
130	31.1	65	12.9	6.3
	32.1	59	14.0	8.2
	34.1	x	13.0	7.6
	36.4	x	12.4	11.5
140	31.1	59	12.7	6.8
	32.1	60	12.9	6.9
	34.1	x	12.4	11.5
	36.4	x	12.3	11.9

x – T_g was not detectable.

During the TMA test, the specimens are heated in furnace by radiation and convection, and as specimen temperature increase, moisture would reduce from the specimens. Table 4.3 also lists the moisture content in specimens before test and moisture loss after tests. It is found that after test the specimens in which the T_g is detectable usually lose 50 to 70% of the initial moisture content, while the specimens in which the T_g is not detectable usually lose over 90% of their moisture after exposed throughout the heating process to over 100°C. An exception to this is the specimen extruded at 130°C with 34.1% water content in barrel, its TMA curve was shown in Fig. 4.12. As the T_g of specimens is dependent on the moisture content, moisture change could considerably broaden the temperature range of the glass transition so that T_g could not be identified. On the other hand, low moisture content in specimen could shift the T_g out of the temperature range used in the test.

Due to moisture loss during tests, the measured T_gs are not the same to the moisture content in the specimens before test. As it is difficult to monitor the moisture content in the specimen during the test when the glass transition occurs, TMA cannot establish accurately the relationship between T_g and the moisture content for extruded starch materials although it offer a higher degree of sensitivity as compared to DSC for the detection of the T_g. However, it can be assumed that most moisture loss had occurred near the higher temperature above T_g and thus the actual moisture content can be considered close to the original moisture content in the sample. This gives a fair estimation of the relationship between T_g and moisture content which is still useful as guidelines in practice, e.g. in microwave foaming, which has similar situations where moisture loss also occurs during heating.

4.6 Characterisation of rheological behaviour of aqueous suspensions of powdered extrudates

4.6.1 Results of RVA tests

The effect of extrusion temperature and water content in barrel on the RVA initial viscosity (see Section 2.4.2 for the definition) is presented in Figure 4.14. It clearly shows that RVA initial viscosity increases with decreasing the water content in barrel at all extrusion temperatures. The initial viscosity is less sensitive to water content in barrel at high level of water (>33%), but it increases sharply when water content in barrel lower than 32%.

At a fixed concentration and particle size, the viscosity of a cold aqueous suspension of extrudate is dominated by the swollen powdered extrudate particles which take up water and reduced the space between them. Since the size of native starch granules in the flour used in this work is less than 30 μm as shown in Fig. 3.1, and the powdered extrudate samples were collected by a 210 μm sieve (see Section 3.3.2), therefore, a particle of extrudate powders could be either only a native (or damaged) starch granule or a lump of the melt starch matrix in extrudate, but most probably it should be a lump of a mixture of starch granules with starch melt matrix. As the damaged starch granules and starch melt matrix can swell in cold water, the interaction between these swollen

particles of powdered extrudate gives rise to higher resistance to flow. The increasing of the RVA initial viscosity with decreasing of water content in barrel indicates that more and more native starch granules have lost their crystalline structure and converted into starch melt and can thus swell in cold water as a result of water reduction during extrusion process. At higher water content level (e.g. 36.4%), the effect of extrusion temperature on the RVA initial viscosity is weaker compared with that at low water content level (e.g. 31.1%). Increasing of extrusion temperature generally results in a decrease in the initial viscosity.
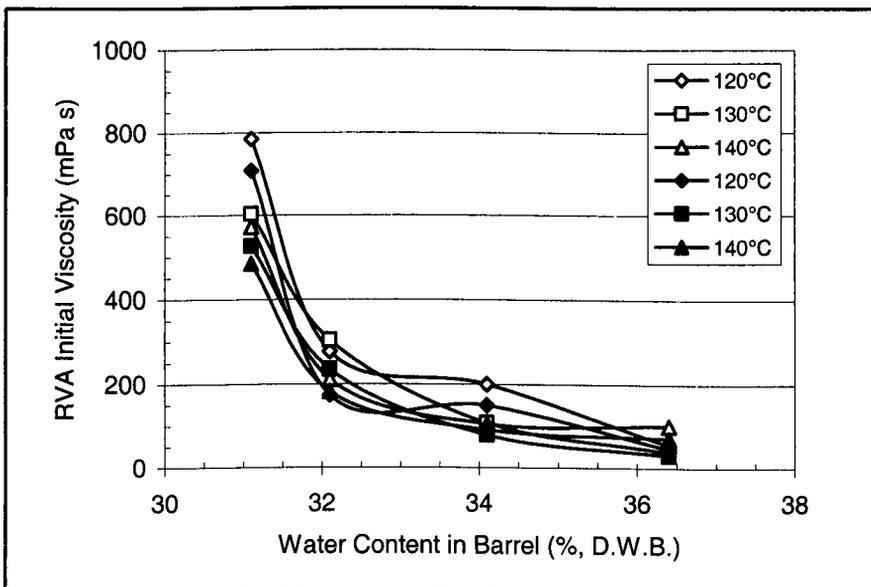

Figure 4.14 Effect of extrusion conditions on the RVA initial viscosity (open symbols – ball milled powders; solid symbols – ground powders).

Figure 4.15 shows the effects of extrusion temperature and water content in barrel on RVA raw peak viscosity (see Section 2.4.2 for the definition). The changes in this parameter with extrusion conditions are much more complex. No clear general trend can be identified. It is noted that the curves for the samples extruded at same condition but powdered by different methods have similar shape, and the ball milled samples have higher values of viscosity compared with those prepared with the coffee milling method (the ground powders). This is sensible as the damage of starch granules and

crystalline structures during powdering process are expected to be different in the two methods, the ball milling process imposed higher comminution actions to the powder samples and hence finer particle dispersion. The similarity in the shapes of the RVA curves from the same extrudate but different powdering methods indicates that the RVA test is reliable, and the "unusual" behaviour should have been resulted from the extrudates themselves.
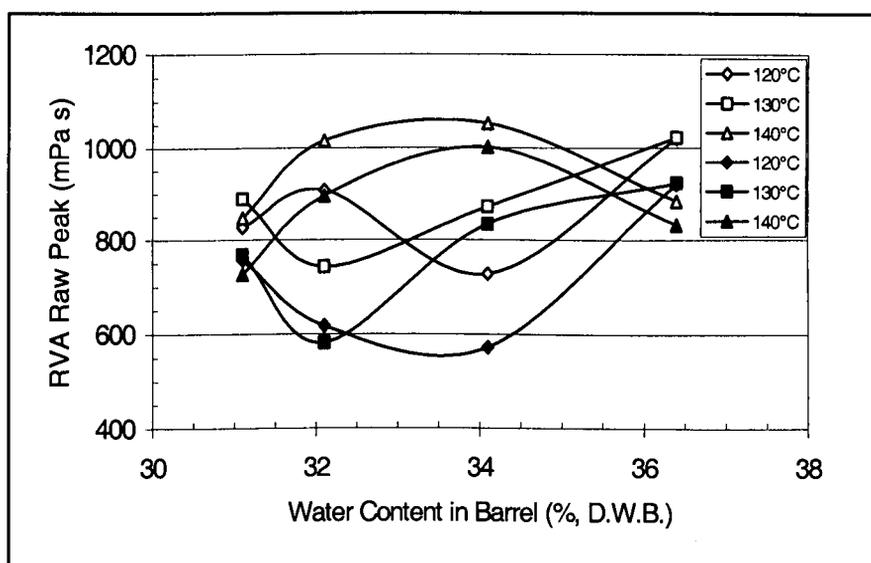

Figure 4.15 Effect of extrusion conditions on the RVA raw peak (open symbols – ball milled powders; solid symbols – ground powders).

Figure 4.16 shows the change of RVA final viscosity (see Section 2.4.2 for the definition) with the extrusion temperature and water content in barrel. Again, there is a similarity in the shapes of viscosity curves for the samples from the same extrudates but prepared using different powdering methods. At extrusion temperature of 120°C, decreasing water content in barrel causes a steady decrease of the final viscosity. However, at extrusion temperatures of 130°C, the final viscosity increases initially with decreasing water content, reaches a maximum at some intermediate water content level and then falls down at lower water content. This behaviour is enhanced at extrusion temperature of 140°C. It is clear that at any given water content level, high extrusion temperature results in higher final viscosity.
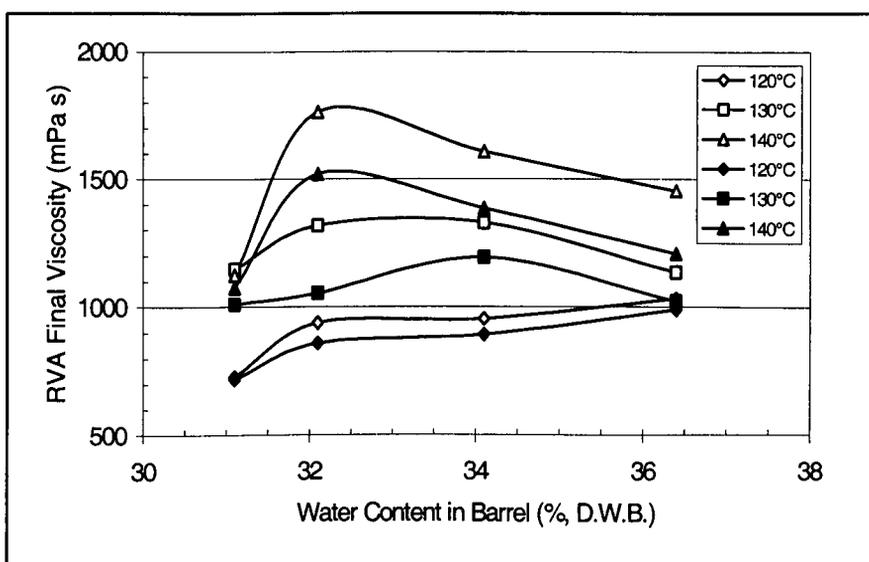
Figure 4.16 Effect of extrusion conditions on the RVA final viscosity (open symbols – ball milled powders; solid symbols – ground powders).

Other obtained RVA parameters are listed in Table 4.4. By comparing the data in Table 4.4 with Figures 4.15 and 4.16, it can be found that the variation of these RVA parameters with water content in barrel and extrusion temperature is broadly similar. The trend of breakdown changing with extrusion conditions is similar to that of raw peak, while the trends of setback and peak time changing with extrusion conditions are similar to that of final viscosity. From the above results and comparison with that of the control flour, it can be concluded that the extrusion processing does affect the RVA parameters significantly, but the influence and the interpretation may be rather complex. Based on these results, it is difficult to evaluate the degree of cook of the extrudates because the changes in the individual parameters cannot be interpreted reasonably and consistently. A conclusion made based on one RVA parameter may be contrary to that made based on another RVA parameter. For instance, based on the dependence of initial viscosity on the extrusion conditions (Fig. 4.14), it could be concluded that with reducing water content in barrel the degree of cook of extrudates is increasing. If this is true, the raw peak should decrease with reducing water content in barrel, because more starch granules should have been gelatinised during extrusion.

But, the RVA raw peak results do not seem to support this (Fig. 4.15) or the understanding and interpretation of the raw peaks have been oversimplified.

Since various RVA parameters reflect different molecular interactions occurring during heating and shearing in a starch suspension, the extent and manner these interactions in relation to the degree of cook of the samples may be different. Although the RVA has been thought to be a technology to assess the degree of cook, most of research work has just described qualitatively the relationship (or variation trends) between degree of cook and some of RVA parameters, or the effects of extrusion conditions on the RVA parameters (Ryu, et al., 1993; Bhattacharya, et al., 1999; Lai, 2001). In order to clearly understand the relationship between the degree of cook of extrudates and the various RVA parameters, further study is still needed, preferably assisted by analytical work in order to provide insight in the structural change in the starch.

Table 4.4 RVA parameters for extruded Temple flour

Extrusion Temperature (°C)	Water Content in Barrel (%, D.W.B.)	Ground Powders			Ball Milled Powders		
		Breakdown (mPa s)	Setback (mPa s)	Peak Time (min)	Breakdown (mPa s)	Setback (mPa s)	Peak Time (min)
120	36.4	680	749	6.13	776	788	5.67
	34.1	374	695	4.87	487	714	4.8
	32.1	409	652	4.73	656	687	4.87
	31.1	560	522	4.2	621	523	4.2
130	36.4	695	794	6.53	771	883	5.6
	34.1	574	933	7.13	583	1039	7.13
	32.1	338	810	7.00	424	999	5.07
	31.1	513	755	5.00	584	843	4.8
140	36.4	587	962	7.13	577	1147	7.13
	34.1	715	1098	7.27	704	1258	7.23
	32.1	525	1150	7.27	571	1319	7.33
	31.1	457	805	4.87	554	831	4.53

4.6.2 Results from Haake rheometer

First, it should be mentioned that all the results from Haake rheometer tests presented were obtained from the powder samples prepared by ball milling. Figure. 4.17 shows the dependence of the apparent viscosity of suspensions on shear rate for the Temple flour extruded at 130°C with different water content in barrel. It is obvious that apparent viscosity decreases with the increase of shear rate, which indicates the shear-thinning behaviour of the suspensions. The results in Fig. 4.17 also clearly suggest that the apparent viscosity of the suspensions of extruded Temple flour increases with increasing of severity of treatment (reducing of water content in barrel while keeping the extrusion temperature and screw speed constant). The suspensions of the extrudates processed at other temperatures (120 and 140°C) also show similar trend (data not shown). Plotting the apparent viscosities of suspensions at a fixed shear rate, for instance 103 s^{-1}, against water content in barrel for the extrudates processed at different extrusion temperatures as shown in Figure 4.18, the trend of the curves are similar to that of RVA initial viscosity in Fig. 4.14.
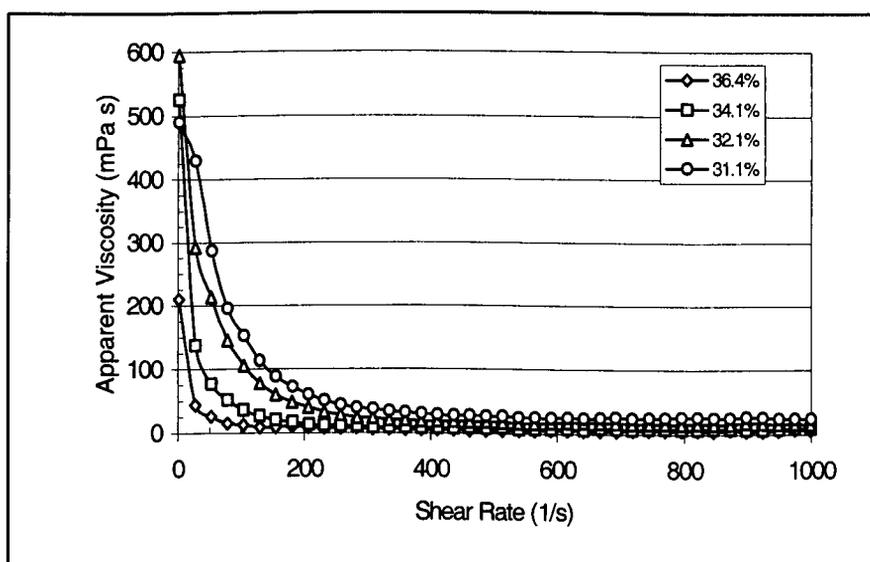

Figure 4.17 Dependence of the apparent viscosity of suspensions on shear rate for the Temple flour extruded at 130°C with different water contents in barrel.
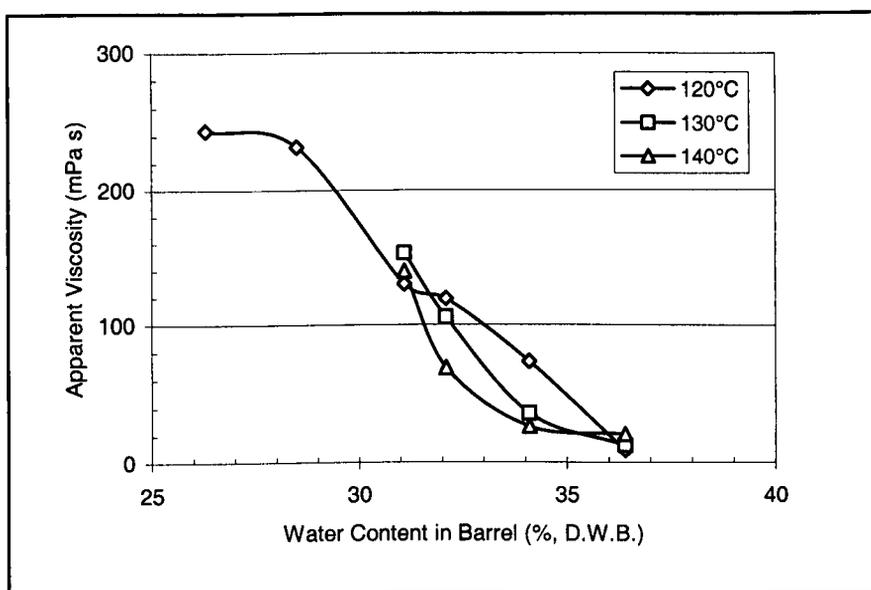
Figure 4.18 Effect of extrusion conditions on the apparent viscosity of suspensions at shear rate of 103 s^{-1}.

It is known that the viscosity of an extruded starch suspension is dependent on the rheological behaviour of swollen extrudate particles (consisting of starch granules and starch melt) dispersed in a continuous phase composed of water and amylose leaching from the starch granules. In other words, the viscosity of an extruded starch suspension reflects a combination of effects from concentration of these swollen particles, from their deformability during interactions and also from the rheology of the continuous phase related to its composition. During the preparation of suspensions in this work, the weight ratio of dry powder of extrudates to water was kept constant, the difference in apparent viscosity of the suspensions is entirely due to the difference in the concentration of the residual starch granules in the powders of extrudates, the extent of extrudate particle swelling, their deformability and the amount of water soluble solid (e.g. amylose leached out from starch granules). As all these are related to the degree of cook, examining the rheological behaviour of extrudate suspensions provides a method to monitor the degree of cook.

Figure 4.19 presents the changes of shear stress against shear rate for the Temple flour extruded at 130°C with different water contents in barrel. The most interesting feature in this figure is the shear stress peak at shear rate less than 100 s^{-1}. For the suspension

of extrudate with high water content in barrel (36.4%), this shear stress peak is not obvious and the value of peak is very low, but it increases with decreasing of water content in barrel. The same behaviour has been observed for the extrudates processed at 120°C and 140°C.
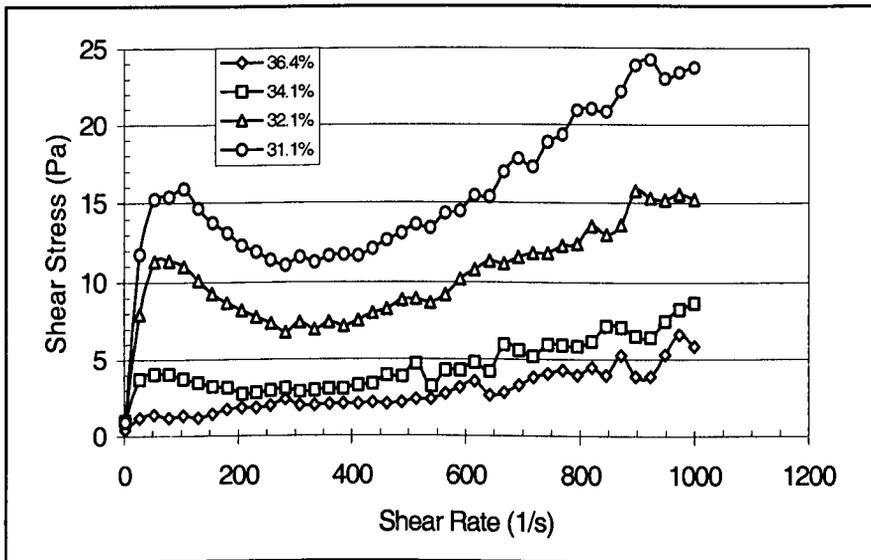

Figure 4.19 Shear stress versus shear rate data of suspensions of the Temple flour extruded at 130°C with different water contents in barrel.

It is known that the native starch granules in flour are hard particles which do not swell much in cold water. As the particles of extrudate powder contain starch melt and starch granules, and with increasing of severity of treatment (e.g. reducing water content in barrel while keeping the extrusion temperature and screw speed constant), fewer and fewer native starch granules left in the starch melt matrix of extrudate, which give rise to the particles of extrudate powder having higher swelling power in cold water. These cause the reduction of water in the surrounding of the swollen particles, meanwhile the swollen particles come into closer with each other and interact to resist shear flow. However, as the swollen particles are deformable, when shear rate reaches a certain level, the swollen particles can be disrupted, which lead to drop in the shear stress and give rise to what is similar to the "yield stress" in the tensile test. Therefore, the shear stress peak should be mainly related to the concentration of swollen particles, the

extent of swelling of these particles in the suspension and the strength of the swollen particles to keep their integrity.

It should be point out that the origin of the shear stress peak at about 75 s^{-1} in Fig. 4.19 is different from that of the raw peak in a RVA test, although the raw peak in a RVA test is also related to the granule swelling. The raw peak in RVA is resulted from the uncooked starch granules which gelatinise and swell during the heating in the test, while the shear stress peak in the Haaker rheometer results is originated from the breakdown of extrudate powder particles which have swollen in cold water during suspension.

Table 4.5 Values of some special shear stress for the suspensions of Temple flour extrudates processed at different conditions

Extrusion Temperature	Water content in Barrel (%, D.W.B.)	Peak (Pa) (At shear rate, s^{-1})	Valley (Pa) (At shear rate, s^{-1})
120°C	36.4	1.41 (27.2)	0.66 (52.7)
	34.1	8.21 (78.2)	4.82 (282.7)
	32.1	12.35 (103.9)	8.93 (282.9)
	31.1	13.54 (78.4)	10.25 (282.9)
	28.5	24.36 (129.6)	20.44 (308.7)
	26.3	25.95 (154.9)	23.72 (283.1)
130°C	36.4	1.38 (52.7)	1.19 (129.4)
	34.1	4.07 (65.8)	2.76 (206.9)
	32.1	11.36 (78.2)	6.77 (283.4)
	31.1	15.37 (78.4)	11.04 (282.9)
140°C	36.4	2.56 (78.2)	1.38 (282.9)
	34.1	2.96 (78.4)	1.97 (231.4)
	32.1	7.95 (78.4)	3.78 (282.2)
	31.1	14.58 (78.2)	9.53 (308.7)

It can be seen from Fig. 4.19, that the peak shear stress increases with decreasing of water content in barrel. Apart from the high water content in barrel, shear stress drops to a minimum before increasing again with the shear rate, i.e., there is a shear stress

valley after the peak. Table 4.5 presents the values of the peak shear stress and the shear stress valley for the extruded Temple flour processed at different extrusion conditions. These data clearly suggest that both the shear stress peak and shear stress valley increase with reduction of water content in barrel at a fixed extrusion temperature and screw speed. However, with increasing severity of treatment, both of these shear stress values are getting close to each other, i.e., the shear stress peak would disappear. This may be because the severe treatment they received during extrusion has weakened the strength of the swollen particles of maintaining their integrity. Therefore, by comparing these two parameters, the peak shear stress and the shear stress valley, the degree of cook of flour extrudates can be estimated.
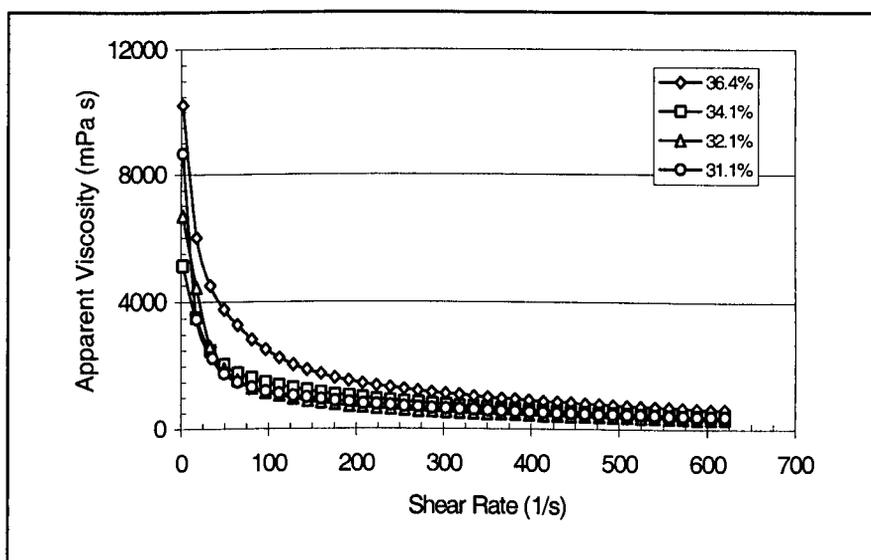
Figure 4.20 Dependence of apparent viscosity of suspensions (pre-cooked at 85°C for 1 hr) on shear rate for the Temple flour extruded at 130°C with different water contents in barrel.

Pre-cooked suspensions behave very differently. Figure 4.20 presents the dependence of apparent viscosity on shear rate of suspensions of the Temple flour extruded at 130°C with different water contents in barrel, the suspensions were cooked at 85°C for 1 hour then cooled to 20°C at which the measurements were carried out. Compared with the viscosity of original suspensions shown in Fig 4.17, it can be seen that the

viscosity of suspensions in Fig. 4.20 has been significantly elevated and the trend of suspension viscosity against the severity of treatment in extruder has been reversed. The same behaviour was found in the suspensions of the extrudates processed at other temperatures (120°C and 140°C).

It is noted that the shear stress peak at low shear rate in shear stress against shear rate plot has disappeared after 85°C cooking (see Fig. 4.21), which indicates the pre-cooking has changed the status of the suspension and the information related to swelling and breakdown of extrudate particles was lost. Thus, compared with that of original suspensions, the rheological behaviour of pre-cooked suspensions may be not suitable for assessing the degree of cook of extrudates.
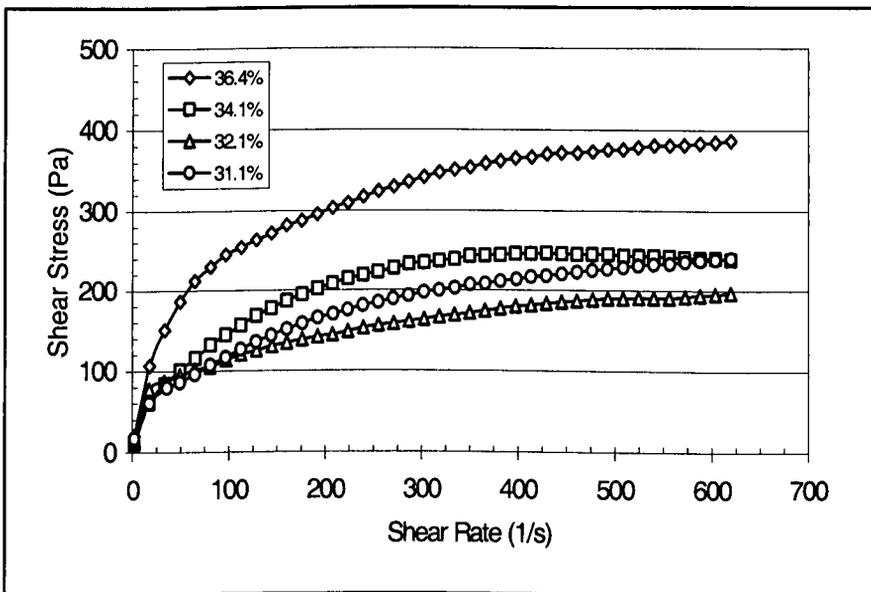

Figure 4.21 Shear stress versus shear rate of suspensions (cooked at 85°C for 1 hr) for the Temple flour extruded at 130°C with different water contents in barrel.

The rheological behaviour of both pre-cooked and original suspensions was assessed using the power law model. It is found that the power law, $\eta = K\gamma^{n-1}$, describes the behaviour of pre-cooked suspensions very well as there is a linear relationship in the ln–ln plot of apparent viscosity against shear rate as shown in Fig. 4.22. The data fit

the model with values of coefficient of determination, R^2, greater than 0.97 in the whole shear rate range applied. Fig. 4.23 gives the ln–ln plot of apparent viscosity if original suspensions of extrudates (extruded at 130°C with different water content in barrel) against shear rate, it can be seen that, only in the range of shear rate between about 52 s^{-1} to 385 s^{-1}, the date have a linear relationship, i.e., fit with the power law. For comparison, the regression parameters of this model, the consistency index K and the flow behaviour index n for the extruded and control Temple flour suspensions (both original and pre-cooked) are presented in Table 4.6.
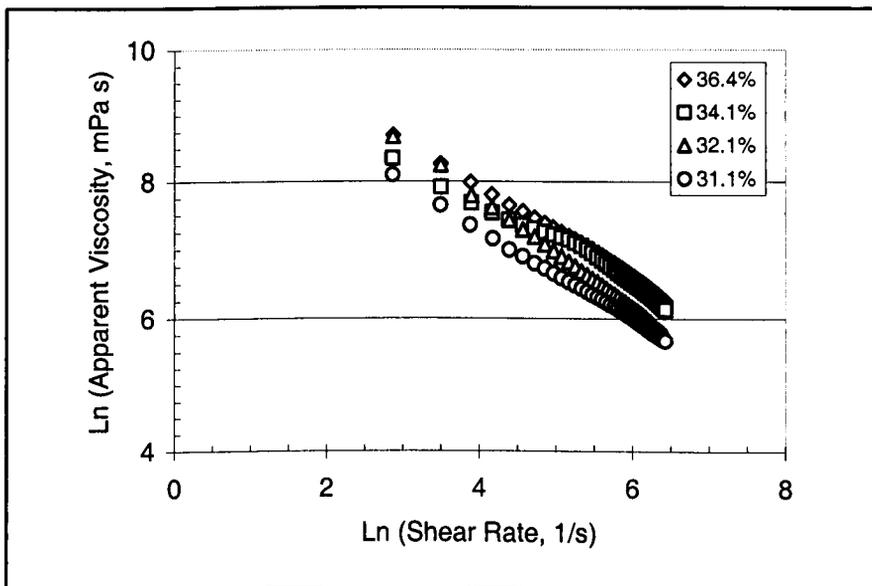

Figure 4.22 Ln-Ln plot of apparent viscosity against shear rate for the pre-cooked suspensions of extrudates extruded at 130°C with different water contents in barrel.

The data in Table 4.6 show that the flow behaviour indices for all the suspensions are less that unity suggesting that these suspensions are non-Newtonian and shear thinning (or pseudoplastic) fluids that display a decreasing viscosity with an increasing shear rate. A greater than unity value of the flow behaviour index means that the substance exhibits a shear thickening (or dilatant) behaviour that display an increasing viscosity with an increase in shear rate, while the viscosity of a Newtonian fluid remains constant regardless of shear rate, i.e., the flow behaviour index equals to unity.
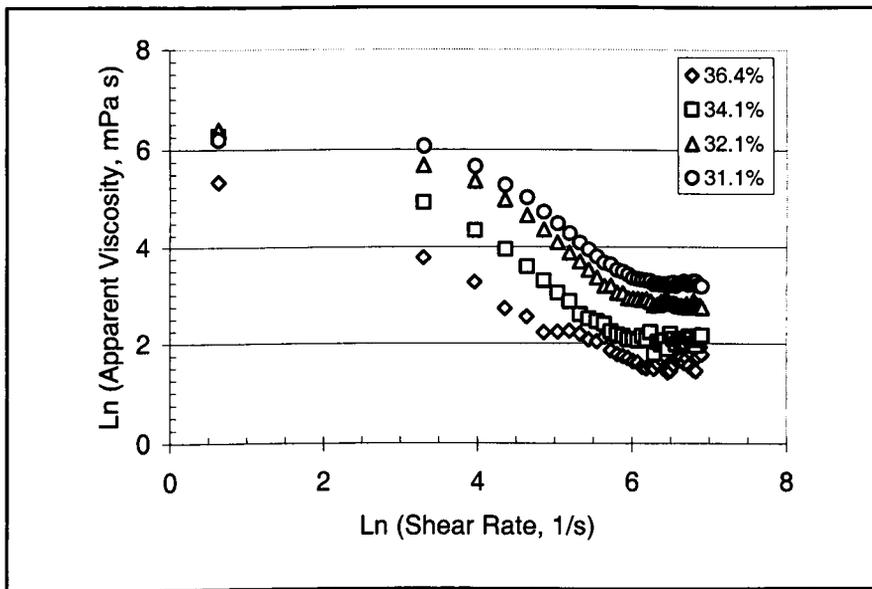
Figure 4.23 Ln-Ln plot of apparent viscosity against shear rate for the original suspensions of extrudates extruded at 130°C with different water contents in barrel.

It can be seen from the data in Table 4.6 that the flow behaviour indices, n, of some original suspensions are negative. Examining the shear stress-shear rate plots of all the original suspensions (such as Fig. 4.19) and comparing with the flow behaviour indices, it was found that all the suspensions with shear stress peak at about 75 s^{-1} have a negative flow behaviour index. It was reported that a corn meal under high shear and high temperature extrusion conditions showed severe shear thinning behaviour (n < 0) at lower moisture content (Padmanabhan, & Bhattacharya, 1991). Molecular degradation was believed to be the major factor responsible for n < 0. In the case of this work, the structure change in the suspensions, i.e., breakdown of the swollen particles of extrudate powders may be the main reason resulting in the negative flow behaviour index.

Table 4.6 Regression parameters of the power law model for suspensions of extruded and control Temple flour at different conditions

Extrusion Temperature	Water Content in Barrel (%, D.W.B.)	Original (shear rate range: 52 –385 s^{-1})			Pre-cooked at 85°C (shear rate range: 20 –620 s^{-1})		
		K (Pa s^n)	n	R^2	K (Pa s^n)	n	R^2
Control	-	0.09	0.47	0.9289	11.57	0.38	0.9987
120°C	36.4	0.18	0.35	0.9739	17.94	0.46	0.9980
	34.1	31.19	-0.32	0.9961	40.46	0.25	0.9823
	32.1	24.44	-0.17	0.9817	21.61	0.34	0.9967
	31.1	19.28	-0.10	0.9907	14.94	0.41	0.9954
	28.5	29.23	-0.06	0.9908	7.81	0.44	0.9972
	26.3	19.23	0.04	0.9897	5.05	0.53	0.9876
130°C	36.4	0.31	0.33	0.9293	41.65	0.33	0.9971
	34.1	8.40	-0.18	0.9920	25.77	0.39	0.9762
	32.1	40.09	-0.30	0.9948	62.26	0.18	0.9989
	31.1	36.50	-0.20	0.9950	21.27	0.34	0.9980
140°C	36.4	4.78	-0.19	0.9495	40.74	0.32	0.9744
	34.1	4.61	-0.14	0.9722	145.22	0.12	0.9885
	31.2	35.99	-0.37	0.9882	95.13	0.20	0.9895
	31.1	39.62	-0.24	0.9931	14.06	0.48	0.9912

4.7 Water absorption index (WAI) and water solubility index (WSI)

It was found that extrusion results in an increase in the WAI above the value of the Temple flour control (1.93 g/g). Figure 4.24 gives the effect of extrusion temperature and water content in barrel on the WAI of extruded Temple flour.
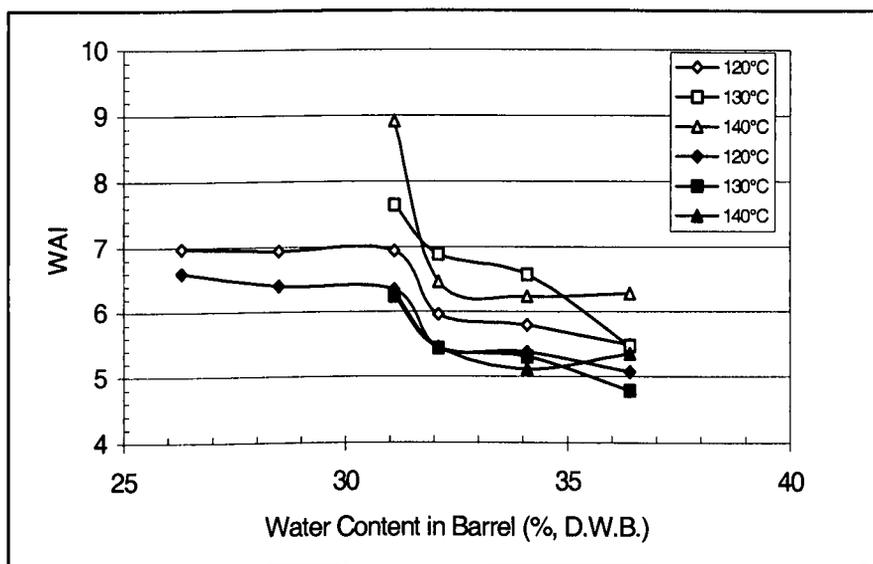

Figure 4.24 Effect of extrusion conditions on the WAI of extruded Temple flour (open symbols – ball milled powders; solid symbols – ground powders).

Examining Fig. 4.24, it can be seen that WAI increases with decrease of water content in barrel at all the extrusion temperatures explored. A common feature of this figure is that there is a sharp increase in WAI over a small water content decrease, between 32.1% and 31.1%. This means that 31-32% water content in barrel is more efficient than others to cook the starch granules in flour with the applied extrusion conditions. This is consistent with the results of the RVA initial viscosity shown in Fig. 4.14. For the extrusion temperature of 120°C, a further reduction of water content in barrel from 31.1% results in little change in WAI. It should be mentioned that the sediments at lower water content levels (28.5% and 26.3%) are obviously softer and less viscous than those at higher water content levels. When decanting the supernatant, the sediments are weakly cohesive and hardly hold their shape meaning that a pipette has to be used to

remove the supernatant. This phenomenon indicates that, in comparison with firmer compacted swollen particles of extrudates with higher water content in barrel, the swollen particle structure has almost lost as a consequence of the decrease of water content in barrel during extrusion in this range. At a fixed water content, WAI has not shown a clear dependency on the extrusion temperature particular for samples prepared with ball milling, in which the intensive mechanical impacts has contributed to the increase of WAI. However, the water content in barrel has more dominant influence on the WAI and the extrusion temperature is not the major factor in the range of processing conditions used in this study. These results are consistent with that obtained in RVA test and Haake rheometer measurements.
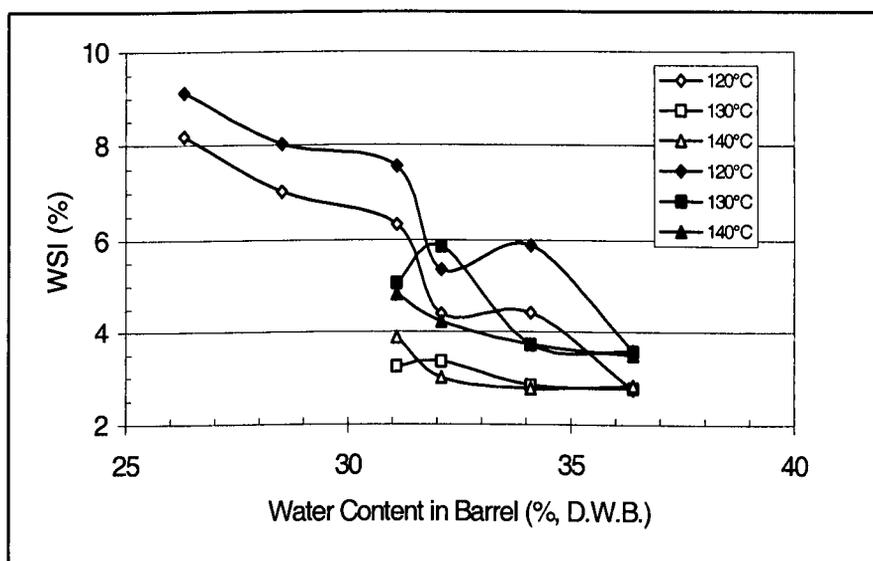

Figure 4.25 Effect of extrusion conditions on the WSI of extruded Temple flour (open symbols – ball milled powders; solid symbols – ground powders).

Figure 4.25 shows the effect of extrusion conditions on the WSI. In general, WSI increases with decrease of water content at a fixed temperature. For given water content, WSI decreases with increasing extrusion temperature. This result is in general consistent with the results obtained by Singh and Smith (1997) in extruded wheat starch. It was showed that WSI increased with decreasing of water content at extrusion temperature between 125°C and 175°C. Complications similar to those in Fig. 4.25

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occurred, WSI went through a maximum when extrusion temperature was about 145°C at lower water content (22 – 26%, W.W.B.), but this trend was reversed, i.e., WSI went through a minimum when the extrusion temperature was about 155°C at higher water content (27%, W.W.B.).

The data presented in Figs 4.24 and 4.25 illustrate that powder sample preparation method has a notable effect on the values of WAI and WSI. The ball mill caused both WAI and WSI increase. This may be attributable to the intensive mechanical impacts and surface wearing by mechanical comminution during ball mill.

Examining the WAI and WSI results obtained by other researchers (Kirby, et al., 1988; Govindasamy, et al., 1996; Guha, et al., 1997; Singh, & Smith, 1997; Govindasamy, et al., 1997), it has been found that the trends of WAI and WSI varied a great deal with the extrusion conditions (temperature, water content and screw speed). The effects of extrusion conditions on the WAI and WSI, reflecting the degree of cook, are synergistic due to the interaction among the extrusion parameters. For instance, elevating the extrusion temperature at constant water content and screw speed should enhance the gelatinisation of starch, however, melt viscosity also decreases with increase in temperature, thus reduces shear stress in the material, which in turn decrease the degree of cook of starch. The degree of cook therefore is dependent on the competition of the two factors. Such competition may be rather complex as reflected by the fluctuation of the WAI and WSI values. Therefore, there is a competitive mechanism between the influence of thermal energy and shear energy on the degree of cook in extrudates. The water content in barrel and screw speed are the main factors that determine how these two types of energies contribute the gelatinisation and disruption of starch granules.

Depending on the extrusion parameters and the interaction among them as well as the composition of the extrudate, thermomechanical processing in an extruder could result in many changes. At molecular level, starch gelatinisation, complexation, melting and degradation may occur. At microscopic level, starch granules may either be sheared into smaller pieces or the surface layer be worn away. The crystalline structure is either wholly or partially preserved within the fragments of the granules. Each change is affected by the combination of processing conditions and their interactions with the extrudate. It is the physicochemical characteristics of the extrudates that affect the WAI

and WSI. Thus, it is not surprising that there are some complex observations of the dependencies of WAI and WSI on the extrusion conditions and starch source.

Analysis of the relationship between WSI and WAI can reveal the type of mechanisms responsible for increased water solubility. Fig. 4.26 shows the variation of WSI with WAI for the extruded Temple flour. Within the experimental region, WSI increases with increasing WAI. This suggests that the increase of water solubility may have resulted from an increasing proportion of granules attaining a state of gelatinisation (Smith, 1992). The simultaneous increase of WAI and WSI is an indication that the starch granules may have not been completely disrupted during extrusion, which is consistent with the results of X-ray diffraction and DIC observations.
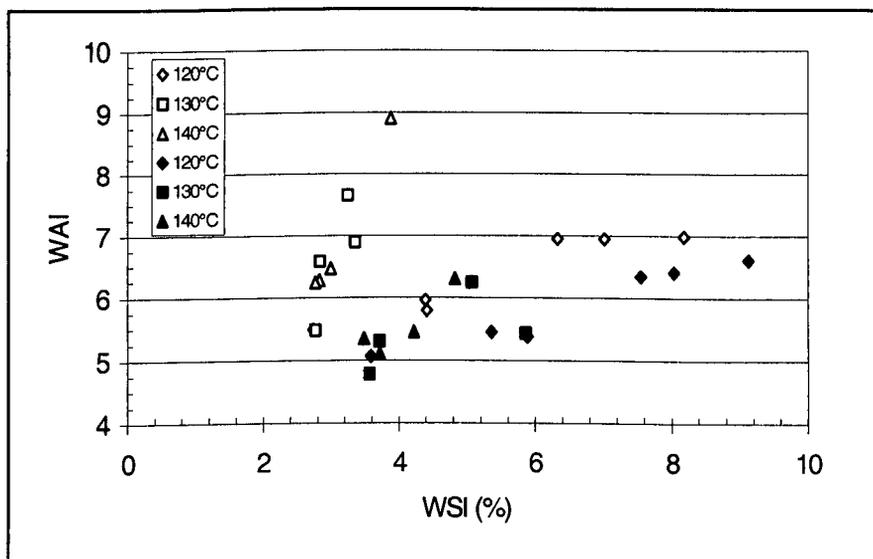
**Figure 4.26 Water absorption index versus Water solubility index (open symbols – ball milled powders; solid symbols – ground powders).**

4.8 Summary

Two crystalline structures have been observed in the extruded wheat flour by using X-ray diffraction. The structures are identified as A-type and V-type crystallinity. The A-type structure is attributable to the residual crystallinity that is present in the native

wheat starch granules. The V-type structure is formed during or after extrusion. The amounts of A-type crystallinity decrease with increasing of treatment severity. While the amount of the V-type crystallinity depends very much on the extrusion temperature and water content in barrel. The powdering methods (coffee milling and ball milling) have influence on the X-ray diffraction results, but not to a significant degree.

Different approaches are compared for characterising the degree of cook of the extruded pellets. FT-IR is not sensitive enough to detect the changes in microstructure of starch granules during extrusion process.

The information obtained from the RVA, WAI and WSI are useful to reflect the structure changes in starch granules during extrusion, it is difficult to quantify the degree of cook of the extrudates, and thus can only be used as relative comparison between samples.

DSC can give information about starch gelatinisation, but only if there exists a certain amount of residual starch granules in the sample and thus cannot be applied to a wider range of degree of cook. X-ray diffraction gives some details of information about microstructure change, but it cannot provide further information about reduction in molecular weight after starch granules are totally disrupted and the material starts thermal-mechanical degradation (over-cook). DIC is the only method to directly observe the destruction of native starch granules, which provides visible images to check the results from other methods, but it also depends existence of residual granules or granular "ghost" (swollen, non-birefringent and amylose leached starch granules). Therefore, DSC, X-ray diffraction and DIC are suitable for characterising the samples with low to medium degrees of cook where only partial destruction or disruption of the granular structure is achieved.

Viscosity measurement by using rheometer seems to be preferable because it allows a wider range of degree of cook to be easily estimated and is potentially quantifiable. It is also capable of indicating over-cook as reduction in molecular weight would result in drop in viscosity.

The change in heat capacity at T_g for the extruded wheat flour is small and hence hardly detectable using the conventional DSC. On the other hand, TMA allows T_g to be measured using linear extrapolations of the thermal expansion curve above and below the T_g and their intersection. Due to the moisture loss during the TMA test, the relationship between moisture content and T_g can not be accurately established.

Although the methodologies used in this work are appropriate and useful, in their own ways in assisting to and interpret the degree of cook in a thermo-mechanical processing of starch materials, it is difficult to establish a straightforward correlation between each individual process condition (parameter) and degree of cook as these conditions affect the structure of the materials collectively. Even so, the results obtained from the used approaches do provide an insight into structure changes at microscopic level and molecular level in starch granules during extrusion, which can be assessed by degree of cook. At the fixed screw speed (100 rpm), decreasing water content in barrel from 36.4% to 26.3% increase degree of cook of the extruded wheat flour (the Temple), while extrusion temperature, ranged from 120°C to 140°C, has no considerably effect on degree of cook compared with water content in barrel.

Chapter 5

Foamability of Extruded Wheat Flour and Starch

5.1 Effect of foaming method

Foaming of extruded starch pellets during rapid heating is due to the expansion of superheated water vapour within the molten matrix. The pre-condition for the pellets to be foamed is that the water within the pellets should be heated well above the boiling point to overcome the restriction to the expansion from the matrix material. This required condition could be achieved by either dropping the pellets into a hot oil bath or by rapid microwave heating the pellets.

5.1.1 Foaming in a hot oil bath

This method allows the control of predetermined foaming temperature and time for foaming to be accurately recorded. It was used to estimate the foaming temperature and heating time as a guide for foaming of pellets. The extruded pellets from the Temple flour were dropped into an oil bath containing vegetable oil heated to 181°C. It was noted that some bubbles occurred at the surface of pellets after about 4 seconds. It took 10 - 12 seconds for the pellets to start foaming and float up. Figure 5.1 shows the expansion ratio (see Section 3.5.1 for the detail) for the Temple flour pellets extruded at different peak temperature and 32.1% water content (D.W.B.) in extruder barrel. It is evident that expansion ratio, the most important measure of foamability, is sensitive to the extrusion conditions when other conditions were kept constant. Extrusion at peak temperature of 120°C gave the best expansion.

The expansion process of the pellets in an oil bath foaming can be divided into three phases (Anonymous, 1998; Lee, et al., 2000). Firstly, temperature increase in the pellets and moisture loss occurs at the surface of pellets. Then secondly, moisture inside the pellets turns to steam by the heat. And finally, as the vapour quickly evaporates, the pellets expand (Lee, et al., 2000). In this process, heating of the pellets is dominated by

thermal conduction. Usually, heat transfer is much faster than moisture transfer in starch materials at ambient temperature (Bouvier, 2001). However, when the temperature of pellets is elevated during oil frying, the heat transfer decreases due to the decreasing of temperature gradient and water diffusivity increases due to temperature rising. To avoid moisture loss and to heat the pellets quickly, fry temperature should be high enough, but too high fry temperature will cause pellet surface burnt and decomposition. In the food industry, it has been found that a temperature of 185 to 190°C in vegetable oil is best for fry expansion of extruded half products (Guy, 2001a).
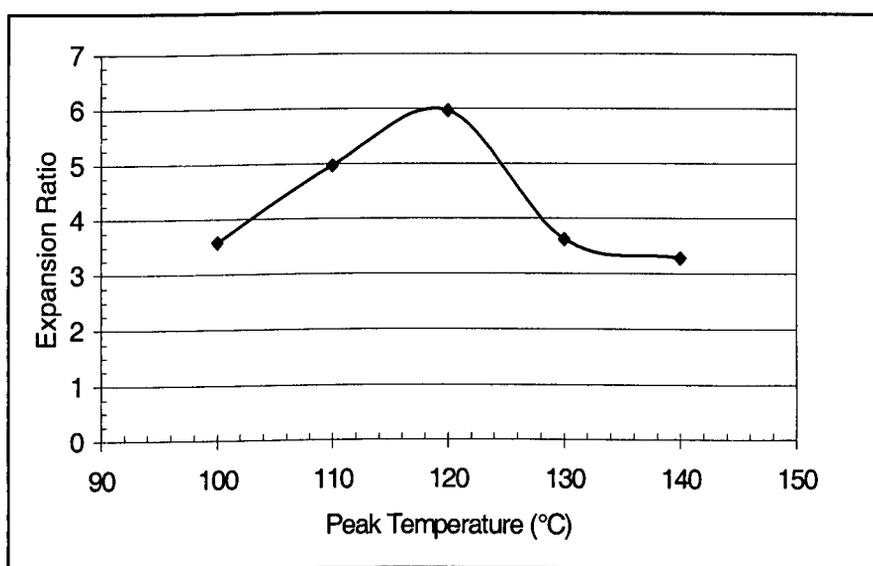

Figure 5.1 Oil fried expansion ratio of Temple flour pellets extruded at different peak temperature with water content of 32.1% (moisture content prior to foaming was about 12%).

5.1.2 Foaming in microwave heating

The extruded Temple flour pellets were heated in a microwave oven (see Section 3.4.3 for the details). It took about 50-65 seconds of heating for the pellets to reach the foaming condition. Each of the pellet foams up in a short period and the variation in completion of foaming is attributable to the variation in pellet size and absorption of the microwaves. Prolonged microwave heating would cause the pellets to be darkened or

burnt. Based on the observations that the pellets became darkened between 200°C and 210°C in TGA tests, the expansion temperature should be lower than 200°C. Figure 5.2 shows the expansion ratio of microwave foamed pellets from the Temple flour extruded with 32.1% water content (D.W.B.) in the extruder barrel at different peak temperatures.
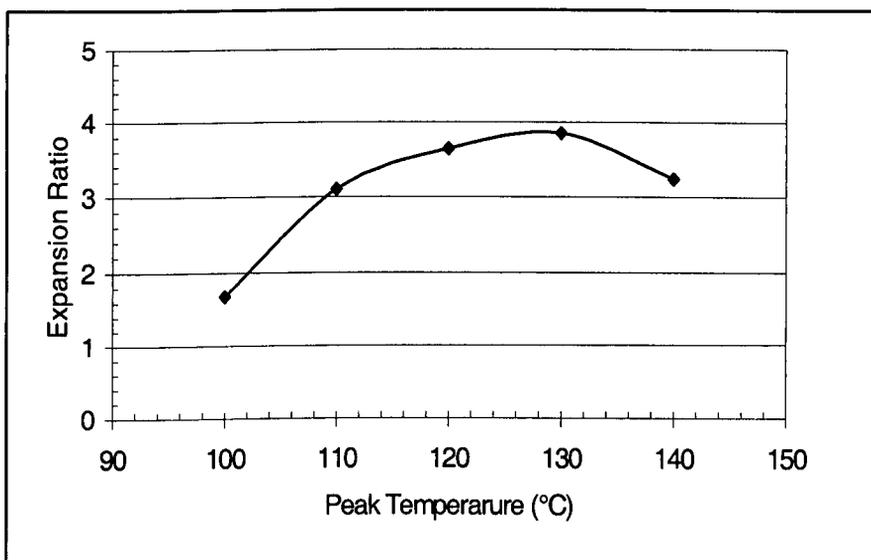

Figure. 5.2 Expansion ratio of microwave foamed Temple flour pellets extruded at barrel water content of 32.1% with different peak temperatures (moisture content prior to foaming was about 12%).

Compared with the hot oil heating, expansion of the extruded pellets by microwave heating, a relatively new foaming process, revealed some different characteristics. Results shown in Figs. 5.1 and 5.2 suggest that for the pellets with the same extrusion conditions, the hot oil heating yield higher expansion ratio than the microwave heating. Moreover, foaming time is much shorter in the hot oil heating than in microwave heating. The mechanism of microwave foaming should be similar to that of oil frying, namely the expansion of water vapour in the starch-based melt. However, there is a key difference in the heating process. Unlike hot oil foaming in which the pellets are dropped in a hot oil and heated from outside, the heating of pellets during microwave foaming is dominated by the absorption of microwave energy and the pellets are volumetrically heated but subject to a heat loss from their surfaces. The difference between the heating time required to start foaming for the two methods indicates that

the heating rate in microwave foaming is much lower than that in hot oil foaming. This probably also is the reason that microwave foaming yielded lower expansion ratio, because water has more time to escape by diffusion before it is boiled off.

5.1.3 Discussions on the effect of foaming methods

The methods for creating cellular structure in starch materials can be divided into two categories. One relies on heating to achieve rapid vaporisation of water at atmospheric pressure (known as temperature jump or T-jump). Foaming by hot oil and microwave heating used here belonged to this category. Another uses pressure drop (P-drop) procedure, which relies on sudden release of external pressure on the materials containing superheated moist. Popcorn puffing and direct extrusion foaming belong to this category.

Water vapour pressure is the driving force to create a foam structure within a starch material either in hot oil foaming or microwave foaming. Despite the difference in the methods of heating (temperature profile in materials hence is different), both hot oil and microwave heating share the same mechanism of foaming. When the material is heated rapidly, the water diffused into a nuclei bubble turns into vapour, and the pressure inside the bubble, P, which depends upon temperature and amount of water in the bubble, increases. It was shown that nucleation is related to very small bubbles already present in the glassy structure (Guy, 2001a). When the temperature, T, reaches a certain level, the material passes through its glass transition and becomes a viscous melt. At this time, if P is sufficiently larger than atmospheric pressure, P_a, to overcome the resistance to expansion, P_r, originated from the flow-induced stress, elastic modulus and surface tension, bubble growth will occur. Therefore, the expansion of bubble depends on the net driving force ΔP:

$$\Delta P = P - P_a - P_r \qquad (5.1)$$

Obviously, all the mentioned material properties related to P_r are influenced by moisture content and temperature. As water vapour escapes, the material may returns to the glassy state due to the increase in T_g, which stabilises the foam structure formed in the material. Moisture content also determines the amount of water vapour available for foaming up the bubbles and the viscoelasticity of the melt. Temperature not only determines vapour pressure but also affects the viscoelasticity of the starch melt. Here, heating rate is important. If heating rate is not high enough, water in the material will diffuse out as in a drying process.

In the T-jump process these is some loss of water during heating and fail to create a large internal vapour pressure compared with extrusion foaming, where the material is encapsulated and pressurised during heating.

In extrusion foaming, the heated extruder barrels allow the water-containing materials to be superheated up to about 220°C without any loss of water and a very high pressure is built up in the material. In the confined space in the barrels, heating temperature determines the vapour pressure within the material. Pressure drop (i.e. from the pressure in barrel to ambient pressure) acts as the driving force for foaming. The superheated water is rapidly vaporised as the pressure is suddenly released when the material exits the extrusion nozzle, which leads to the formation of bubbles throughout the extrudate. Therefore, extrusion foaming can give excellent expansion and fine foam cell structure. Comparison of densities for foams produced by microwave heating and direct extrusion indicates that starch based foams from microwave heating are approximately two to four times denser than that from direct extrusion (see Section 7.1 for more details).

The extent of foaming depends also on the resistance for the bubbles to expand. Viscoelasticity of the starch melt affects its resistance to expansion. The viscoelasticity of starch melt is dependant on the degree of gelatinisation of starch, the melt temperature, water content and additives such as plasticizer. To achieve effective expansion during foaming, sufficient heat should be supplied so that the starch melt in its rubbery state. In the expansion of microwave foaming, there is a transition of material state from a glassy solid to a rubbery melt during the microwave heating, the viscoelasticity of pellets, which depend on material composition, extrusion conditions, temperature and moisture content, play an important role (see Sections 5.2 and 5.3).

However, for given extruded pellets, the heating rate seems a critical factor. The higher heating rate not only gives rise to a larger internal vapour pressure in material due to less water loss, but also brings the material into its rubbery state before it is dried out because water is an effective plasticizer.

5.2 Effects of extrusion conditions

Foaming of extruded pellets relies on the rapid vaporisation of water vapour within a starch melt during heating. In order to create a stable low density foam, the pellets should be well cooked so as to form a melt with sufficient gelatinisation and be viscoelastic enough. Therefore, the physical state of starch polymers in the pellets is one of key factors to control the foaming, the cell structure and properties of foam. It has been reported that the expansion ratio of extruded starch under microwave heating mainly depends on its degree of gelatinisation (Lee, et al., 2000), which in turn is determined by the extrusion cooking conditions. So, it is necessary to investigate the effects of extrusion conditions on microwave foamability of extruded pellets. Among the parameters of the extrusion conditions, the peak temperature, screw speed and water content in the barrel have significant effect on the degree of cook of extrudates. In this Section, the attention was mainly focused on the influence of these three parameters on the foamability of extruded pellets.

5.2.1 Effect of peak temperature

The variations of expansion ratio in microwave foaming for the extruded pellets (moisture content in pellets before microwave foaming was about 12-13%) with different extrusion peak temperatures are shown in Figure 5.3. For water content in barrel above 31%, there was not much difference between the curves of the extrusion ratio against peak temperature. For these cases, the pellets extruded at ~130°C yield the highest expansion ratio compared with those at other peak temperatures. Clearly, for given water content during extrusion, there exists an optimum peak temperature for maximum expansion during subsequent microwave foaming. Pellets extruded at the water content 31% behaved rather differently. At the same extrusion peak temperature,

the expansion ratios of pellets extruded at 31% water content were higher than those extruded at other water contents. Although the optimum peak temperature for 31% water content was not determined due to limited data, it can be expected that the expansion ratio should reach the maximum at somewhere between 100°C and 120°C.
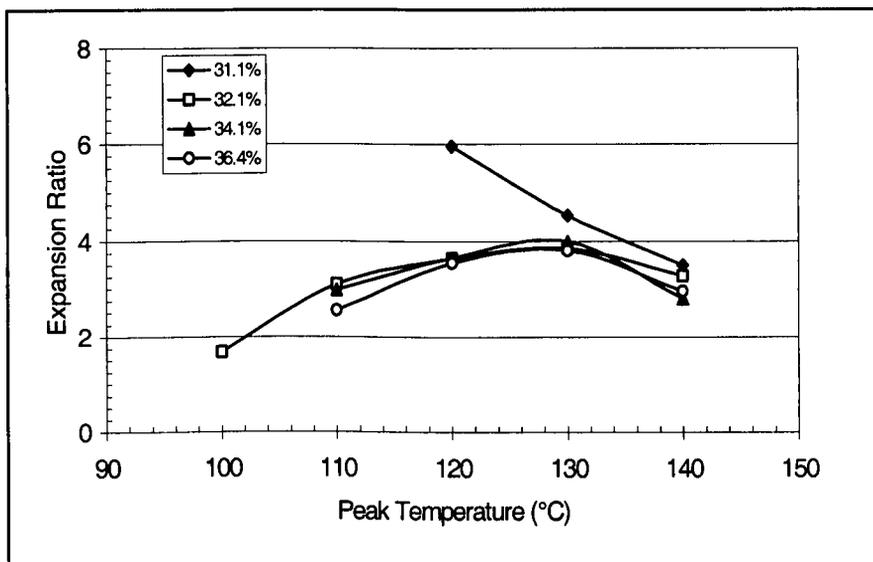

Figure 5.3 Effect of extrusion peak temperature on microwave expansion ratio of extruded Temple flour pellets processed at different water content in barrel.

It was claimed that one of the critical features to yield a successful expansion of extruded products was that the starch granules should be melted to remove crystallinity but not "dispersed" more than about 10 – 15% during the extrusion (Guy, 2001a). It was believed that nucleation of cells is related to very small bubbles retained from the native starch granules. If the starch granules were highly destructurised in an extrusion process, the nucleation sites would be reduced (Guy, 2001a). It was also reported that optimal expansion by microwave heating was achieved when the starch was approximately "half-gelatinized" (Lee, et al., 2000). When the starch has low gelatinisation, the insufficient viscoelasticity and discharge channels between swollen starch granules would unable to build high vapour pressure in the pellets. On the other hand, high degree of gelatinisation would lead to large cells with thick cell walls (Lee, et al., 2000).

Though the degree of gelatinisation of extruded pellets have not been measured in this work, it can be expected that for the pellets extruded at high water contents (>31%), higher degree of gelatinisation may be achieved in the extruded pellets with higher peak temperature when keeping all the other variables constant. Thus, at the lower peak extrusion temperature, the lower expansion ratio of extruded pellets may be attributed to the lower degree of gelatinisation. An optimum peak temperature of ~130°C may have yielded required degree of gelatinisation, but when the peak temperature reaches 140°C expansion ratio decreases because of the excess gelatinisation in the pellets. At low water content, the melt would be high in viscosity and thus high shear and higher gelatinisation would be expected at the same extrusion temperature. The optimum peak temperature had therefore shifted to the lower.

Although the arguments presented agree with the observations in the literature, it is also possible that the starch molecular chains may have undergone degradation at high peak temperature of 140°C, which would reduce the elongation flowability of the material and decrease the expansion ratio. As reported by Chinnaswamy and Hanna (1988), corn starch underwent molecular degradation and expanded less at high barrel temperatures above 140°C.

5.2.2 Effect of water content in barrel

Water content in barrel plays an important role during extrusion cooking and may have significant effect on the degree of cook to the extrudates. Under condition of given barrel temperature and screw speed, water content in barrel determines the severity of a cooking treatment to the starch materials being extruded. Basically, high water content would give rise to low viscosity to the starch melt and thus less degree of shear destructurisation of the starch granules. Reduction of water content would increase the viscosity of the starch material and thus the shear destructurisation of material being extruded. This would elevate the degree of cook of starch in the pellets, which in turn affects the expansion ratio of extruded pellets. If the water content is too low, the poor material flowability would result in high power input, temperature rise and materials degradation, or even block the extruder.
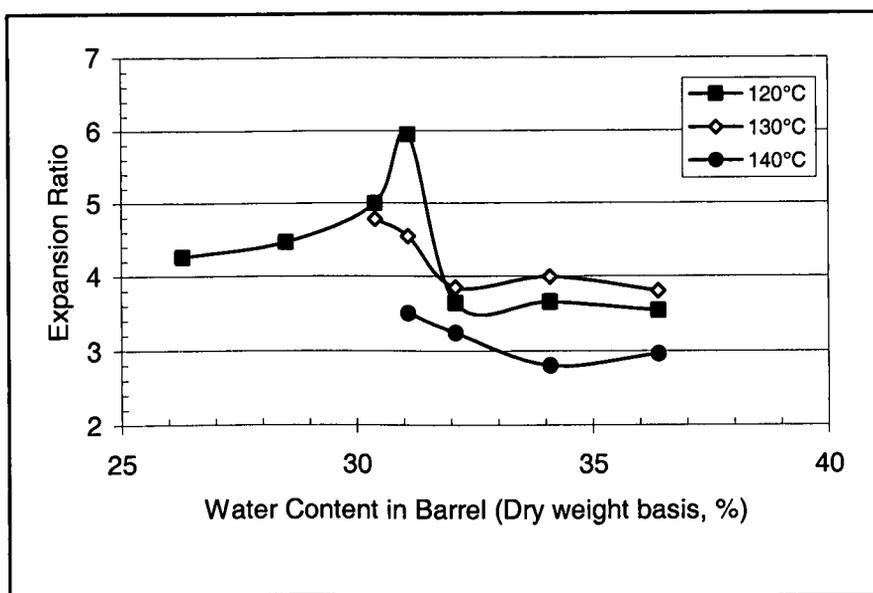
Figure 5.4 Effect of water content in barrel on microwave expansion ratio of extruded Temple flour pellets extruded at different peak temperatures.

The foregoing arguments were supported by the results shown in Figure 5.4. As shown in Fig. 5.4, for the pellets extruded at peak temperature of 120°C, the expansion ratio (moisture content prior to foaming was about 12%) increases from 3.54 to 5.95 when water content in barrel decreases from 36.4% to 31.1% (D.W.B.). However, with further decreasing of water content to 26.3% (D.W.B.), the expansion ratio drops to 4.26. No attempt was made to fully explore the curves for peak temperature of 130°C and 140°C at low water content as the extrudates tended to form bubbles, because the cooling power of the extruder was not sufficient to remove the heat generated by the high shearing of the material. From data shown in Fig. 5.4, it can be seen that about 30-31% water content in barrel (D.W.B.) and 120°C and 130°C peak temperature seem to be the optimum to give better expansion.

5.2.3 Effect of screw speed

Attempt was made to investigate the effect of screw speed on the foamability of extruded pellets, as a change of screw speed would cause variation of both shearing and

residence time of the materials being extruded which in turn affects the degree of cook of extrudates. However, the adjustable screw speed range was proven very narrow. When the screw speed was increased to about 165 rpm, bubbles formed in the extrudates exiting the die, even with the peak barrel temperature set at as low as 110°C. For the peak temperatures of 130°C and 140°C, screw speed above 135 rpm also led to formation of bubbles in the extrudates. The high screw speed had resulted in a severe shearing in extruder, which causes a rapid increasing of temperature in the materials being extruded. When the cooling power of the extruder was insufficient to reduce the material temperature below the boiling point at the die, bubbles would form in the overheated melt. On the other hand, when the screw speed was decreased to 65 rpm, the shear in material was found too low, which gave rise to insufficient cooking for the extrudates extruded at 100°C (peak barrel temperature) with appearance similar to an uncooked dough. To obtain a combination of reasonable high extrusion rate and sufficient degree of cook, the screw speed range for bubble-free extrudates is too narrow to be investigated. A narrow window was found to be 100 – 120 rpm to obtain bubble-free and well-cooked extrudates.

5.3 Effect of moisture content in the pellets

Since microwave foaming of the extruded pellets relies on the rapid vaporisation of moisture, the moisture content in pellets is expected to play an important role in foaming. Therefore, it is necessary to investigate the effect of moisture content in pellets on foaming and identify the optimum moisture content for achieving maximum expansion during microwave heating.

Based on the data shown in Fig. 5.4, pellets extruded at 120°C, 130°C and 140°C with water content in barrel of 31.1% (D.W.B.) were selected and conditioned to different moisture contents using equilibration with saturated salt solutions. Figure 5.5 shows the relationship between the expansion ratio of pellets and moisture content in the pellets from extruded Temple flour. The data in Fig. 5.5 clearly show the significant effect of moisture content on the expansion ratio. Both low moisture content (i.e. dry pellets) and high moisture content (i.e. wet pellets) gave rise to low expansion ratio, while for all the pellets extruded at different processing conditions, moisture content around 9-10%

resulted highest expansion ratio. The pellets extruded at 120°C and 130°C with 31.1% water content in barrel yield a maximum expansion ratio over 8 in this region of moisture content. These results are consistent with those reported by Lee et al (2000) for extruded corn starch and Chen and Yeh (2000) for extruded rice pellets.
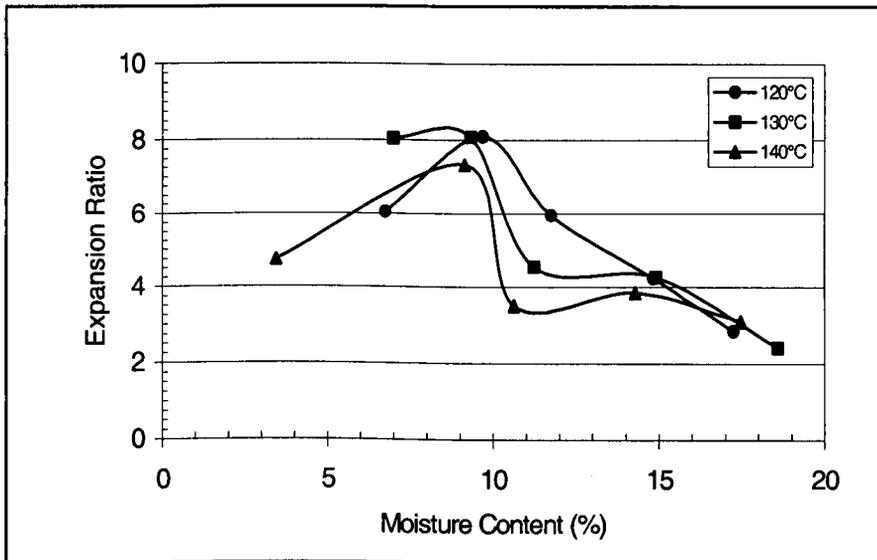

Figure 5.5 Variation of microwave expansion ratio with the moisture content in Temple flour pellets extruded at different temperatures with 31.1% water content.

It is interesting to note that the shapes of the foamed pellets are highly dependent on the moisture content. Figure 5.6 shows the extruded Temple pellets and those microwave foamed at different moisture contents. The original shape of extruded pellets was cylindrical (Fig. 5.6 (a)). At lower moisture content, the shape of foamed pellets is irregular (Fig. 5.6 (d) and (e)) and there are some opened cracks on the surface, exposing internal region of the pellet. The foamed pellets look like puffed popcorns, especially for those with maximum expansion (Fig. 5.6 (d)). The opened cracks on the surface of the foamed pellets indicated that the skin layer of the pellets burst during expansion. This could cause a sudden pressure drop in the pellets to trigger rapid expansion of bubbles and improve foaming. The ideal condition for microwave foaming is such that there should be a vapour pressure build up within the pellets followed by a sudden release of pressure (puffing) during the heating (Lee et al., 2000). The best

expansion at ~10% moisture content may have resulted in a optimum combination of available moisture for building up the internal vapour pressure and the viscoelasticity for holding the pressure to a point when a large number of bubbles can rapidly expand in a single burst. At high moisture contents, the shape of foamed pellets was almost spherical (although the original pellets were cylindrical) and there were no opened cracks on the surface (Fig.5.6 (b) and (c)). This suggested that the material was soft during foaming so that the pellets were able to take spherical shape to minimise the surface energy. The vapour pressure in the pellets induced during microwave heating was relaxed via creeping of the material. These observations suggest that it is difficult to build up a high vapour pressure in the pellets when the moisture content is too high. In other words, too high moisture content of pellets hindered the sudden vapour pressure release due to the lack of ability to hold the pressure.
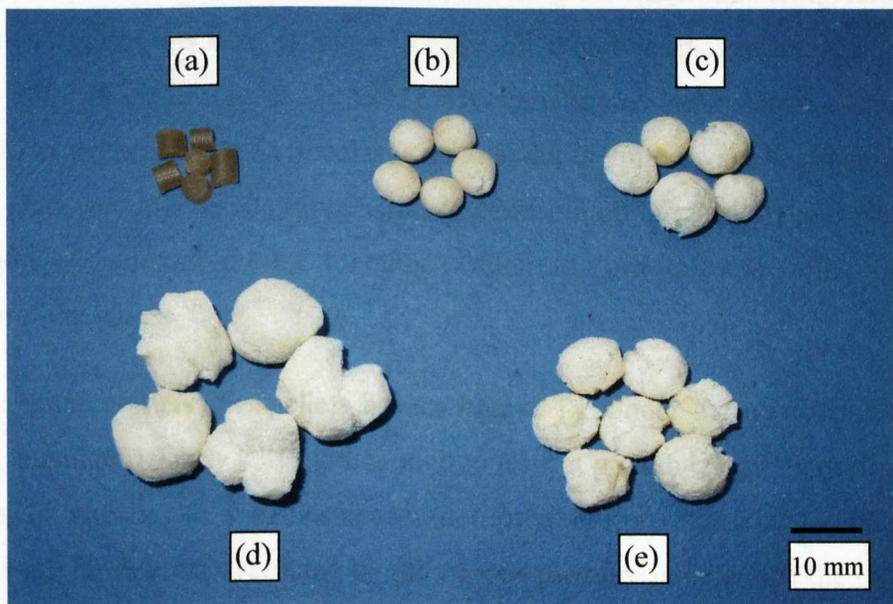
Figure 5.6 Extruded Temple pellets microwave foamed at various moisture contents. (a) extruded pellets; (b) 17.2%; (c) 14.8%; (d) 9.7%; (e) 6.7%.

Since microwave foaming relies on the rapid evaporation of the water and hence the water stored within the pellets (the moisture content) inevitably affect the foaming process. It is easy to imagine that for the pellets with low moisture content, there is insufficient moisture for puffing the pellets, which will result in a low expansion.

Similarly, it is natural to expect that the expansion ratio increase with moisture content and this was indeed the case (see the curves in Fig. 5.5 before the peak expansion ratios are reached). However, the argument simply based on moisture level failed to explain why the expansion ratio declines at higher moisture content over 10%. The change of viscoelastic behaviour of the pellets with moisture content should not be overlooked, because viscoelastic property of extruded pellets plays an important role in microwave foaming.

It is believed that the best expansion of the extruded pellets should occur in a rubbery state. That means the foaming temperature should be above the T_g (or the crystalline melting temperature, T_m, in the case of crystalline starch polymer) of the extruded pellets and below the temperature at which the starch polymers either flow or decompose. The glass transition temperature, T_g, of starch materials is extremely sensitive to the moisture content. Moisture reduces glass transitions temperature in the starch/water system because it plays a role of effective plasticizer (Zeleznak, & Hoseney, 1987; Kalichevsky, et al., 1992). The variation of the moisture content in the pellets lead to a change of the viscoelastic state under the microwave foaming condition due to T_g shift, and this results in variation of contribution of elasticity and plasticity to deformation of material during foaming, which in turn influences the expansion behaviour of the pellets.

At low moisture content, the pellets have a higher T_g. Under the microwave foaming condition, the material may still rigid enough to restrict growth of the vapour bubbles in the pellets. In other words, the resistance to deformation from elasticity and plasticity of material is too large to be overcome by the vapour pressure in cells. On the other hand, when moisture content in pellets is sufficiently high, the material could be in its visco-flow state under the microwave foaming condition and yield readily, which would also give the pellets poor expansion because the water vapour pressure cannot be built up. Only when the moisture content in pellets is at certain levels, the material under microwave foaming condition has such a viscoelastic state which allow the built up water vapour pressure in the bubbles overcome the resistance from elasticity and plasticity and blow up the bubbles, and stabilise the created foam structure.

While we have an incomplete knowledge of the effects of temperature, water content and microstructure on the viscoelastic properties of starch-rich materials, the glass transition temperature is increasingly well studies, it represents a major transition in the material properties and has been shown to correlate with pellet expansion parameters. Chen and Yeh (2000) reported that for extruded rice pellets, expansion temperature (by using hot air to foam) was 20 – 100°C higher than glass transition temperature. However, it should be pointed out that the temperature range of rubberiness, i.e., the width of processing window, depends on the materials and their composition.

In the present work, an attempt was made to measure the glass transition temperatures of the Temple flour pellets extruded at different conditions and with different moisture contents (see Section 4.7). However, no clear T_g was detected in the DSC tests. The results of TMA showed that T_g of some extruded pellets ranged from 56 to 95°C when moisture content was lower than 14%. Attempts were also made to measure the microwave foaming temperature by embedding a thermocouple probe at the centre of an extruded pellet through a drilled hole or by using a non-contact infrared thermometer (Raytek®, Raynger® ST6[TM], Santa Cruz, USA), but proved unsuccessful. The embedded metallic thermal couple probe caused sparks and burning of the thermocouple wire and the starch material in contact with the probe. The infrared thermometer could only measure the average surface temperature on a foamed pellet, which ranged from 65°C to 81°C when measured immediately after switching off the microwave heating. This was clearly not the foaming temperature at the centre of the pellet.

5.4 Effects of pellet size

In order to investigate the effect of particle size of pellets on the expansion ratio of microwave foaming, extruded Temple pellets were broken using a Breville Classique Blender, then passed through a series of sieves, to give particles in the ranges of <0.6 mm, 0.6 - 1.7 mm, 1.7 - 3.35 mm, 3.35 - 6.7 mm and 6.7 - 14.5 mm. Figure 5.7 presents the microwave foaming expansion ratios of the pellets with different particle size ranges.
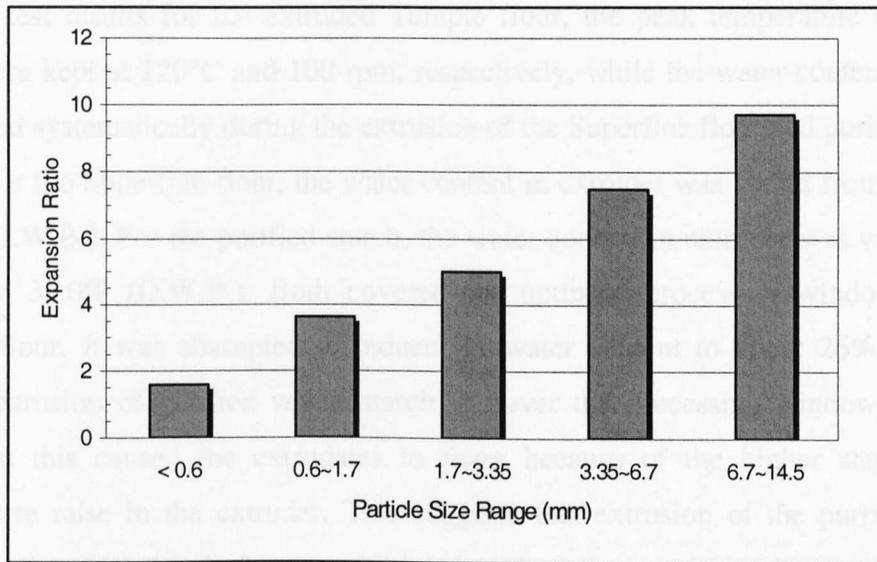
Figure 5.7 Expansion ratios of extruded Temple flour pellets with different sizes.

As shown in Fig. 5.7, the expansion ratio decreases with the decreasing of pellet size. Since the expansion of pellets are caused by rapid releasing of water vapour, and considering the fact that the extrusion conditions and moisture content in all the pellets with different sizes are the same, the difference in expansion ratio must have resulted from the manner in which the moisture evaporated. When the particles are small, i.e., the ratio of surface to volume is large, the pellets tend to be dried without enough moisture aeration during the heating as most of moisture would diffuse out through the surface. This would cause a lack of steam and prevent the building up of internal pressure in the pellets, while the dried particles would possess more resistance to expansion. As the pellet size increases, the length of maximum diffusion path increases and hence the percentage moisture lost due to diffusion decreases. Thus, more moisture would remain in the pellets and then evaporated as a blowing agent to yield a larger expansion.

5.5 Effects of raw materials

Besides the Temple wheat flour, the study on microwave foaming has been extended to two other raw materials, Superfine wheat flour and purified wheat starch. Based on the

foaming test results for the extruded Temple flour, the peak temperature and screw speed were kept at 120°C and 100 rpm, respectively, while the water content in barrel was varied systematically during the extrusion of the Superfine flour and purified wheat starch. For the Superfine flour, the water content in extruder was varied from 26.7% to 33.0% (D.W.B.). For the purified starch, the water content in extruder was varied from 30.9% to 39.0% (D.W.B.). Both covered the optimum-processing window for the Temple flour. It was attempted to reduce the water content to about 26% (D.W.B.) during extrusion of purified wheat starch to cover the processing window of wheat flour, but this caused the extrudates to foam because of the higher shearing and temperature raise in the extruder. This suggests that extrusion of the purified wheat starch requires high level of water addition to reduce the melt viscosity compared with the wheat flour.
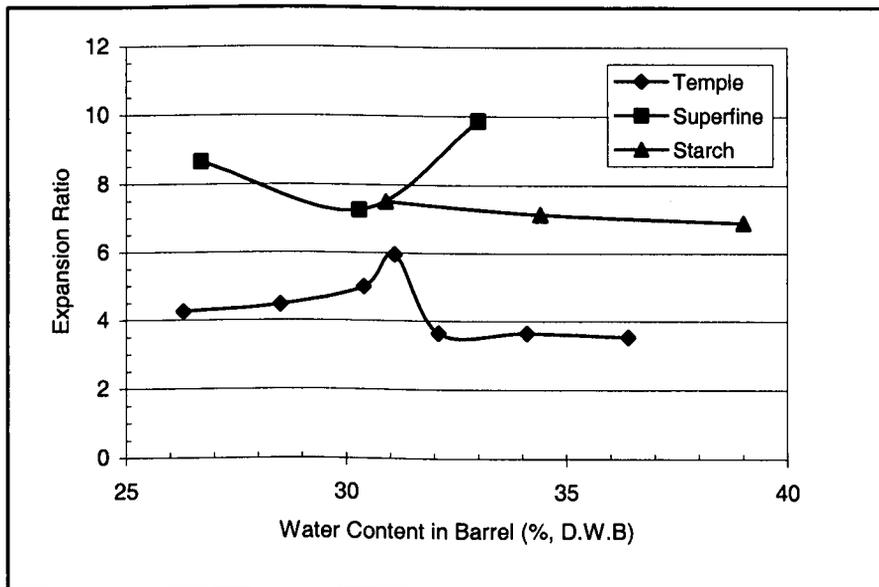
Figure 5.8 Changes of expansion ratios with water content in barrel for the pellets extruded at 120°C with different raw materials.

Figure 5.8 shows the changes of expansion ratio with water content in barrel for the pellets (air dried, moisture content was 15 - 16% for the pellets of Superfine flour and purified wheat starch, and ~12% for the pellets of Temple flour) made from different raw materials extruded at 120°C. As can be seen in Fig. 5.8, both extruded Superfine

flour and purified wheat starch expand better than extruded Temple flour during the microwave foaming process. Unlike Temple flour, however, extruded Superfine flour yield a minimum expansion at the water content of 30.3%. Either increase or decrease water content in barrel from 30.3% resulted higher expansion ratio. While for the purified wheat starch, water content in barrel has no significant influence on the expansion ratio of pellets in the range investigated.

Figure 5.9 presents the relationship between the expansion ratio and moisture content prior to foaming for the pellets extruded at almost identical extrusion conditions (120°C peak temperature, 100 rpm screw speed and around 30.3-31.1% water content in barrel) for all three raw materials. For both flours, about 10% moisture content gives rise to the optimum expansion. For the purified wheat starch, a lower moisture content, about 8% is expected to give the maximum expansion. The largest expansion ratio over 11 has been achieved in the Superfine flour compared with 8 for the Temple flour.
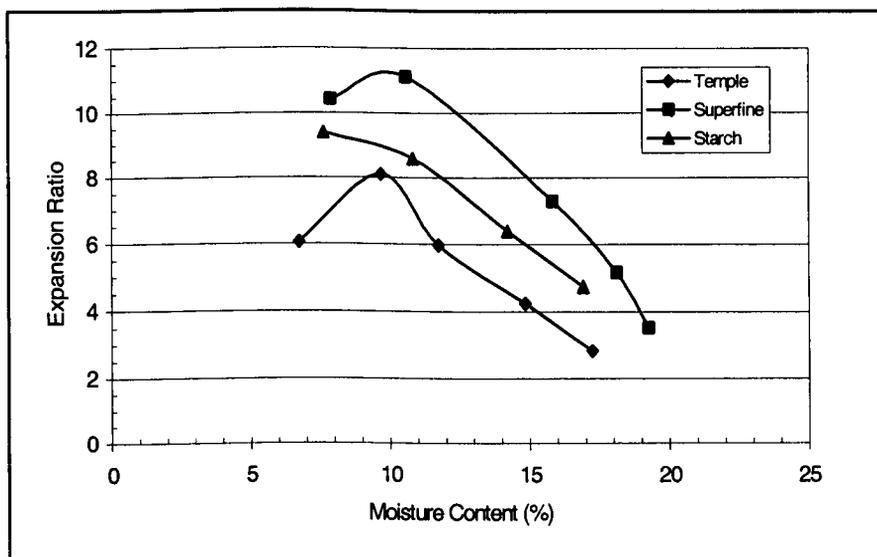
Figure 5.9 Relationship between the expansion ratio and moisture content in the pellets extruded at same condition but with different raw materials.

The foam structure analysis (see Section 7.2 for details) revealed that the higher expansion ratio of the pellets extruded from the Superfine flour and purified wheat starch was associated with large sized cells resulting from fewer number of nucleation sites and/or high elongational flow of the cell wall of the bubbles during growth. This is

probably due to less impurities present in these two raw materials. For instance, bran which could both act as nucleation agent and sites to cause rupture of growing cells. Lower gluten content in the Superfine flour and purified starch may also improve expansion of pellets by allowing higher elongational flow of cell wall of bubbles during bubble growth.

5.6 Summary

Extruded wheat flours (Temple and Superfine) and purified wheat starch pellets can be foamed using a conventional microwave oven. The expansion ratio of extruded pellets is highly dependent on the physical state of the pellets, which is related to the extrusion conditions, the moisture content in the pellets prior to microwave foaming and the type of raw materials. The size of the extruded pellets also has significant influence on the extent of expansion, the bigger the pellets (under 14.5 mm in diameter), the larger the expansion.

The optimum moisture content to yield maximum expansion during microwave foaming is about 10% for the extruded pellets from the wheat flours investigated.

For the Temple flour, the highest expansion ratio foamed by microwave heating is obtained when it has been extrusion cooked at peak temperature of 120°C with 31.1% water content in barrel (dry weight basis) at screw speed of 100 rpm. Although these are machine specific, a similar optimum extrusion condition should be identified experimentally for a chosen extruder which corresponds to a non-extreme extrusion cooking condition. At similar extrusion conditions, Superfine wheat flour and purified wheat starch have higher expansion ratio than the Temple flour. The maximum expansion ratios for extruded Temple flour, Superfine flour and pure starch are 8.1, 11.1 and 9.4, respectively.

Water content in barrel during extrusion cooking and moisture content in the pellets prior to the microwave foaming were found to have significant influence on expansion ratio of extruded pellets compared with other variables, such as extrusion peak temperature and screw speed.

Chapter 6

Effect of Additives on Foaming of Extruded Pellets

This chapter focuses on the effect on foamability (expansion ratio) during microwave heating of various additives used in the extruded pellets. The effects of additives on foam structure and properties will be discussed separately.

6.1 Effect of polymer additive - poly (vinyl alcohol) (PVA)

6.1.1 Characterisations of PVAs

PVAs have been used in starch foams to increase their resilience to compression, flexibility and reduce dust resulting from pneumatic conveying. Four grades of PVA, NK-05, GL-05, NL-05, and GH-20 (GOHSENOL®, Nippon Gohsei Osaka, Japan) with different molecular weights and degree of hydrolysis were used in this work (see Table 3.1). Some basic properties of these PVAs, such as crystalline structure, glass transition temperature and melting point, are characterised in order to understand their effect on the properties of the extrudates.

Particle appearance of these PVA powders is different. GH-20, GL-05 and NL-05 are all angular, while NK-05 is spherical with smooth surface. The particle size range was estimated by observation through SEM to be between 150-800 μm (GH-20), 70-500 μm (GL-05), 20-900 μm (NL-05) and 50-400 μm (NK-05).

Figures 6.1 and 6.2 show the X-ray diffraction patterns and DSC second scan curves for the four grades of PVA. From their similar X-ray diffraction patterns, especially for NL-05, GL-05 and GH-20, it can be said that the crystalline structure in these PVAs should be same though the crystallinity may differ. Compared with other three PVAs, there is a slight difference in the X-ray diffraction pattern for NK-05: the main peak at 19.5° of 2θ degree is relative weak and the small peaks at 11.2° and 22.6° of 2θ degree disappear. This suggests that NK-05 has a slight different crystalline structure. DSC scans show

that the crystal melting peak for NL-05 is sharp and narrow, while crystal melting peaks for other three PVAs are relative flat and wide. This indicates that the crystal integrity among these PVAs is different.
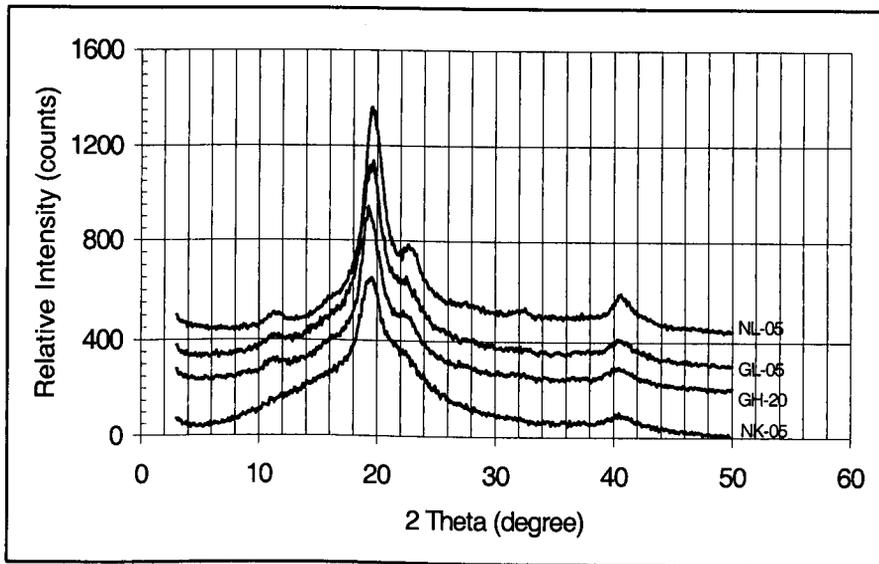

**Figure 6.1 X-ray diffraction patterns for the different grades of PVA.**
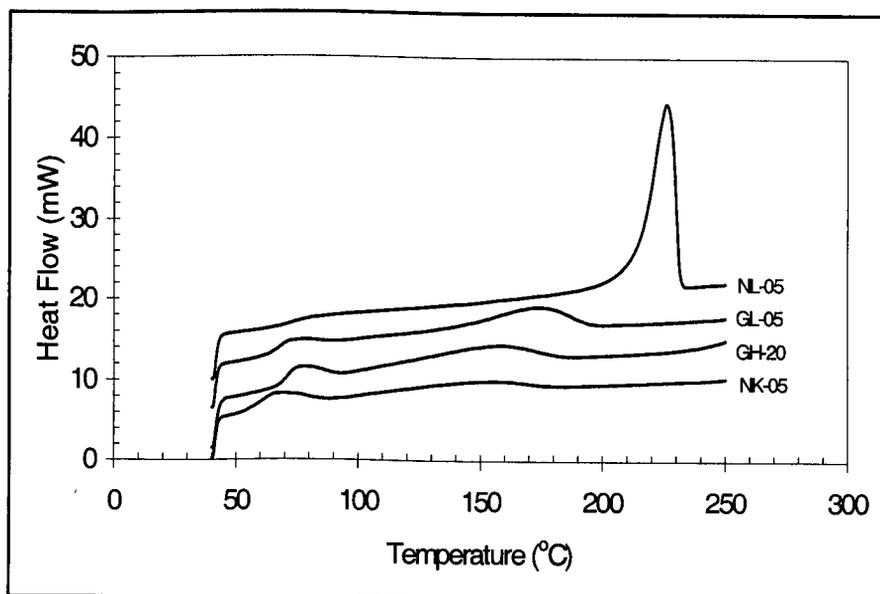
Figure 6.2 DSC second scan curves for the different grades of PVAs.

Table 6.1 lists the obtained glass transition temperatures (T_g) and crystalline melting points (T_m) for these PVAs from the DSC results (see section 3.3.4 for details). It seems that the degree of hydrolysis has more notable influence on the T_g and T_m than the molecular weight. A PVA with higher degree of hydrolysis has higher T_g and T_m, while for those with the same degree of hydrolysis but different molecular weight, such as GL-05 and GH-20, the differences in T_g and T_m are not significant. It is worth noticing that melting temperatures for these PVAs in dry state are between 172 – 230°C, hence should be processed above these temperatures without addition of water.

Table 6.1 Values of T_g and T_m of PVAs determined by DSC

Grade of PVA	T_g (°C)	T_m (°C)
NL-05	75	230
GL-05	65	201
GH-20	67	194
NK-05	57	172

6.1.2 Foamability of Temple pellets extruded with PVAs

Figure 6.3 shows the variation of expansion ratio with moisture content for the pellets extruded with different grades of PVA (see Section 3.2.3 for the details of the extrusion processing). For the purpose of comparison, the results for the Temple flour extrudate without PVAs, i.e. the extruded Temple flour before PVAs added is also included in Figure 6.3.

The expansion ratio of extruded Temple flour reaches 6.6 at moisture content 15.4% and 8.9 at moisture content of 10.3%, which is similar to the previous results (see Section 5.3). However, within the range of moisture content, the expansion ratios for extruded Temple flour with different grades of PVA are significantly lower and are insensitive to the moisture content. The highest one is 4.73 for the pellets extruded with

GH-20 at moisture content about 5%, while the expansion ratios for most other pellets extruded with PVA are only around 2. Since the flour and water feedrates were kept constant before and after the PVAs have been added during the extrusion, the decrease of expansion ratio is clearly attributable to the addition of PVAs.
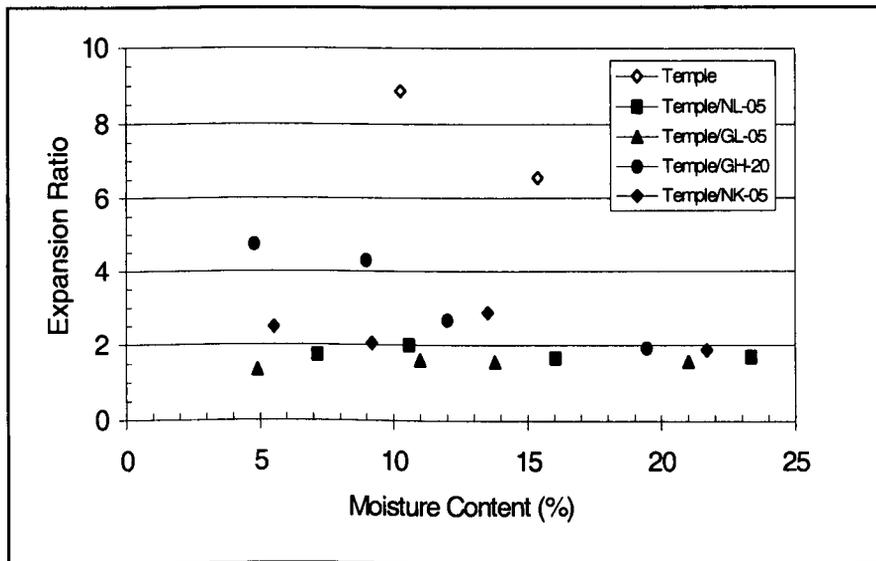
Figure 6.3 Variation of expansion ratio with moisture content for the pellets extruded with different grades of PVA.

6.1.3 Characterisations of extruded pellets containing PVAs

To explore the reasons for the low expansion ratio when PVAs were added, some further characterisations were carried out.

One possible reason is that PVA remains crystalline in the extrudate and restricted expansion at a temperature much lower than the melting point of PVA. Figure 6.4 shows the X-ray diffraction patterns of extruded Temple flour and those extruded with the four different grades of PVA. From the peak located at about 13° of 2θ degree, it can be concluded that a V-type structure has formed in all the extruded pellets. However, compared with Fig. 6.1, it can be found that the peak of V-type structure in extruded Temple flour at about 19.5° of 2θ degree (Fig. 6.4) is almost located at the

same position of the main peak of PVAs. Therefore, it is difficult to identify whether the peak at 19.5° is partially from the PVA or exclusively from the V-type structure thus the crystalline structure in PVA has disappeared.
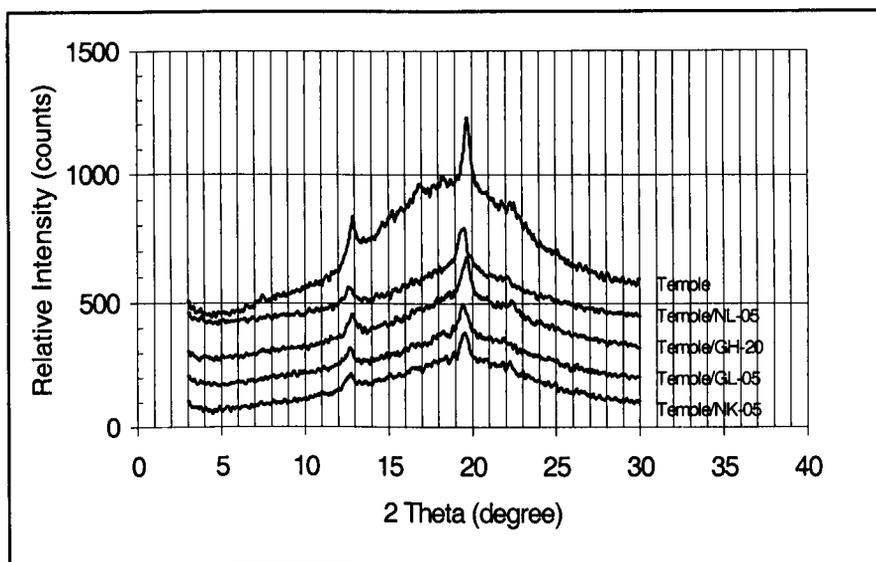

Figure 6.4 X-ray diffraction patterns for the Temple flour extruded at 120°C with 33.0% water content in barrel (dry weight basis) and different grades of PVAs.

Figure 6.5 shows the DSC scan curves for the extruded Temple flour with PVAs. The melting peak of PVAs still exists. This indicates that either the extrusion has not destroyed the crystalline structure in PVAs or the PVAs have recrystallized after extrusion. The latter is more likely the case as PVA is water soluble and during extrusion with added water the crystalline structure may has been destroyed, but recrystallization can take place when the extrudate is cooled. Whichever case it may be, the crystalline structure in PVAs can restrict the expansion of extruded pellets because of its relative high melting temperature. In other words, the temperature reached in the pellets by microwave heating may be not high enough to melt the PVA crystalline structure, or by the time the temperature is over the melting temperature of PVAs, the blow agent (water) has already escaped from the pellets.
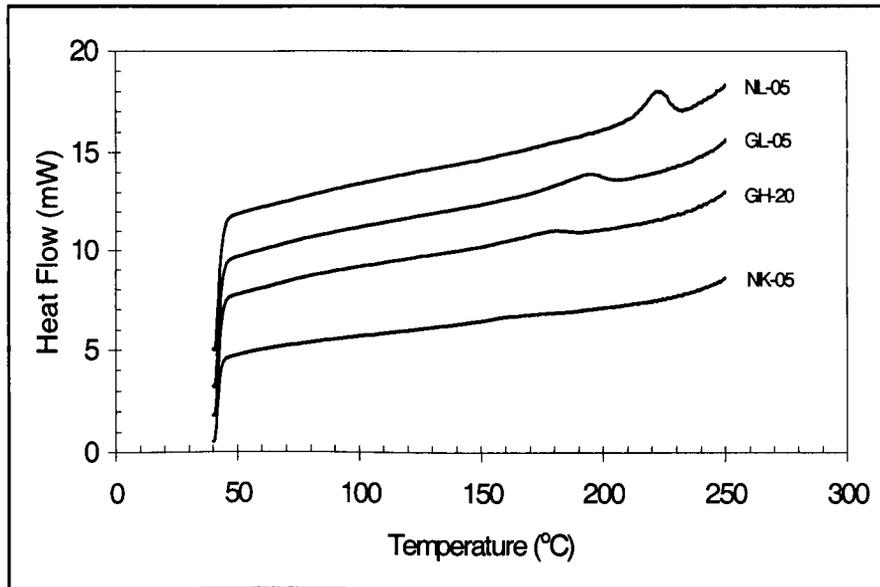
Figure 6.5 DSC second scan curves for the Temple flour extruded with different grades of PVA.

As shown in Chapters 4 and 5, under different extrusion conditions, the expansion behaviour of microwave foamed pellets was different due to the difference in their degree of cook. The extrusion conditions could be changed due to addition of PVAs. This is because the PVAs could act as a lubricant or diluent during the extrusion. On the other hand, the PVAs absorb some water in the barrel and reduce the amount of water available for the starch granule gelatinisation. All these will change the degree of cook of extruded pellets which in turn affects their microwave expansion.

To investigate the changes of degree of cook, WAI and WSI of extruded Temple pellets with different grades of PVA were measured. The results are shown in Figure 6.6. If there were no PVA in the pellets, it is easy to assess and compare the degree of cook of the pellets based on the values of WAI and WSI. However, the presence of PVAs and their difference in water solubility has complicated the situation.

Generally speaking, high degree of cook is reflected by high WAI and WSI values. Although WSI of extruded pellets has increased with addition of PVAs, it should be borne in mind that as PVA is water soluble, the 12wt% PVA in the samples would inevitably increase the value of WSI. The WSI of the control one (extruded Temple

flour) is considerably lower than that of all extruded with PVAs is clearly due to dissolution of PVAs. As the difference in the degree of hydrolysis, the solubility of these grades of PVA in cold water is different, and thus their contributions to the WSI should be different. Theoretically, the higher the degree of hydrolysis and molecular weight, the lower the solubility of PVAs in cold water. Therefore, according to the product technical data (GOHSENOL®, Nippon Gohsei Osaka, Japan), the solubility of these PVAs should follow the order: NK-05 > GL-05 > NL-05 and GL-05>GH-20. It is noted that the pellets containing the PVA with the lowest solubility (NL-05) has the lowest WSI, which suggests that some of or maybe most of the increasing of WSI come from dissolved PVA during the period of measurements. This indicates that for the extruded pellets containing PVAs, the values of WSI cannot be directly used to assess the degree of cook.
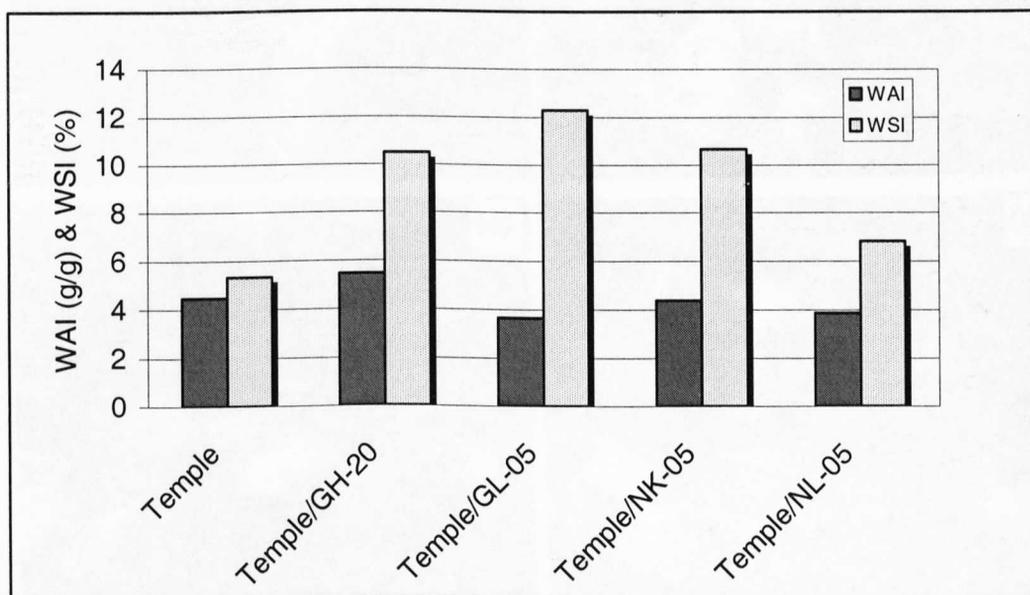
Figure 6.6 WAI and WSI values for the pellets extruded with different grades of PVA.

The values of WAI in Fig. 6.6 seem suggest that the degree of cook in Temple/GH-20 is higher than that in the pellets of Temple/GL-05, Temple/NK-05 and Temple/NL-05. However, without the support of WSI data, this speculation needs further confirmation.

If this is true, it will provide an explanation as why the Temple/GH-20 expanded better than the other three extrudates shown in Fig 6.3.

Figures 6.7 presents the differential interference contrast (DIC) micrographs of extruded pellets with various grades of PVA after iodine staining. Although it is difficult to identify the PVA phase from these observations, the difference in the residual starch granules and starch gel matrix among the pellets with different PVAs provided clear evidences that the degree of cook of starch in these pellets was different.
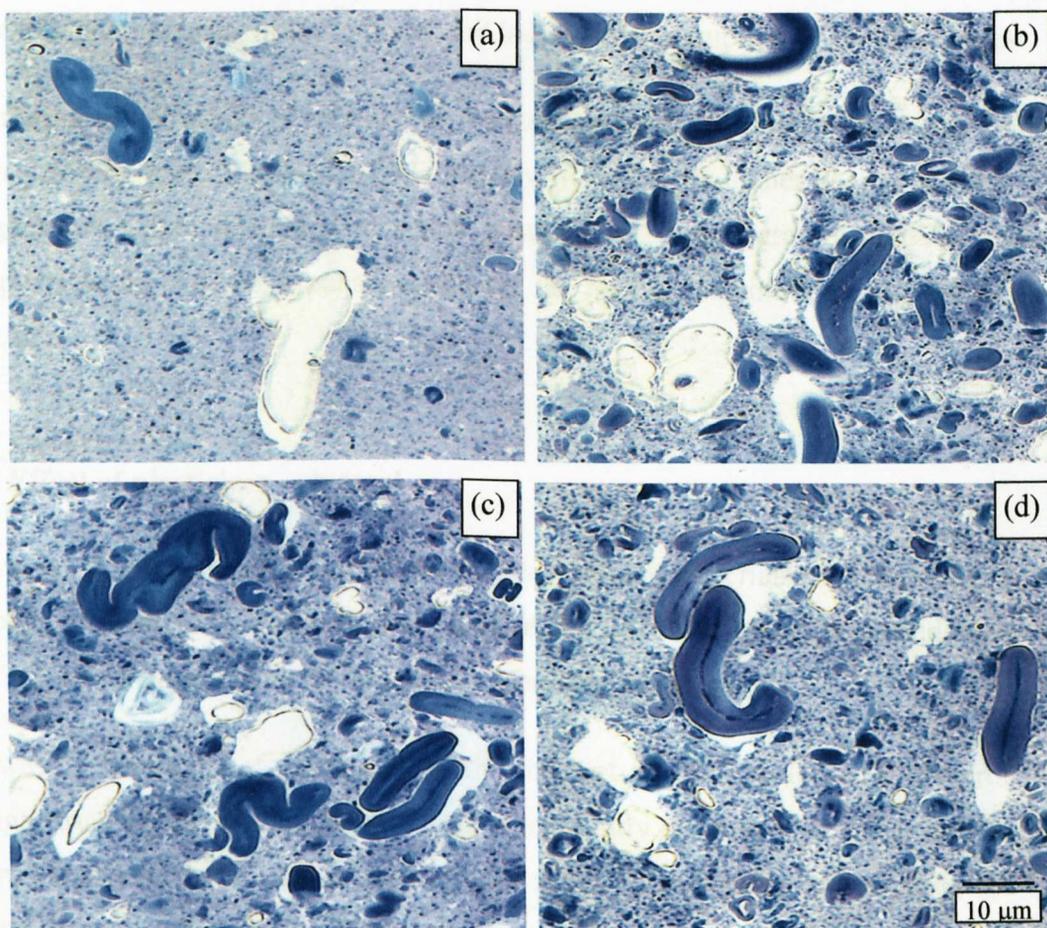
Figure 6.7 DIC micrographs of extruded Temple flour with various grades of PVA, (a) GH-20, (b) GL-05, (c) NK-05 and (d) NL-05.

As can be seen from Fig. 6.7, there is very few residual starch granules (the purple and blue particles) in a fine starch gel matrix for Temple/GH-20 (Fig.6.7 (a)), which is

similar to the extruded Temple flour shown in Fig. 4.7(b). While for the pellets containing other three grades of PVA, there are much more residual starch granules in a coarse starch gel matrix. These results indicated that most of starch granules in Temple/GH-20 were disrupted, while many of starch granules in Temple/GL-05, Temple/NK-05, and Temple/NL-05 were not sufficiently disrupted. This means that the degree of cook in Temple/GH-20 is higher than that in the other three, which confirms the results of WAI measurement. The reason for the higher degree of cook in Temple/GH-20 is probably attributed to the higher polymerisation degree of GH-20 and resulted in its higher molecular weight and viscosity (see Table 3.1), which could give rise to higher shearing in the extruder and led to better disruption of starch granules.

Referring to the results of microwave foamability shown in Fig.6.3, the relative higher expansion ratio of Temple/GH-20 is directly related to its higher degree of cook. This suggests that poor disruption of starch granules, i.e., low degree of cook, is partially responsible for the low expansion ratio for the pellets containing GL-05, NK-05, and NL-05.

6.2 Effect of plasticizer - glycerol

Glycerol is a widely used plasticizer for starch-based materials. In this study, it was expected that by using glycerol as an additive, the flexibility of cell walls and hence that of foamed pellets could be increased for cushioning applications.

However, the results of foaming tests showed that addition of 16.7wt% glycerol (wet weight basis on flour) into Temple flour significantly depressed the expansion ratio of extruded pellets. For all the pellets, extruded at 120°C peak barrel temperature, 100 rpm screw speed and with three different water contents in barrel: 26.2%, 27.9% and 30.7% (D.W.B. on flour), the microwave foaming expansion ratios were under 2 even the moisture content was between 11.3% and 12.3% which is near the optimum for foaming of the Temple alone extrudate. Further attempt to reduce water content in barrel to 24.4%, led to foaming of the extrudate and thus abandoned.

The DIC observations in Figure 6.8 showed the starch granules were very poorly disrupted in all Temple/glycerol pellets. Distorted starch granules were evenly distributed throughout with starch gel background for all the pellets extruded at different levels of water content in barrel. It is obvious that the addition of 16.7wt% glycerol lubricates and dilutes the system, which result in significant reduction of shear in the extruder and lead to survival of the starch granules in the extrudates. It is thus concluded that the significantly lower degree of cook in Temple/glycerol pellets is responsible for the poor expansion.
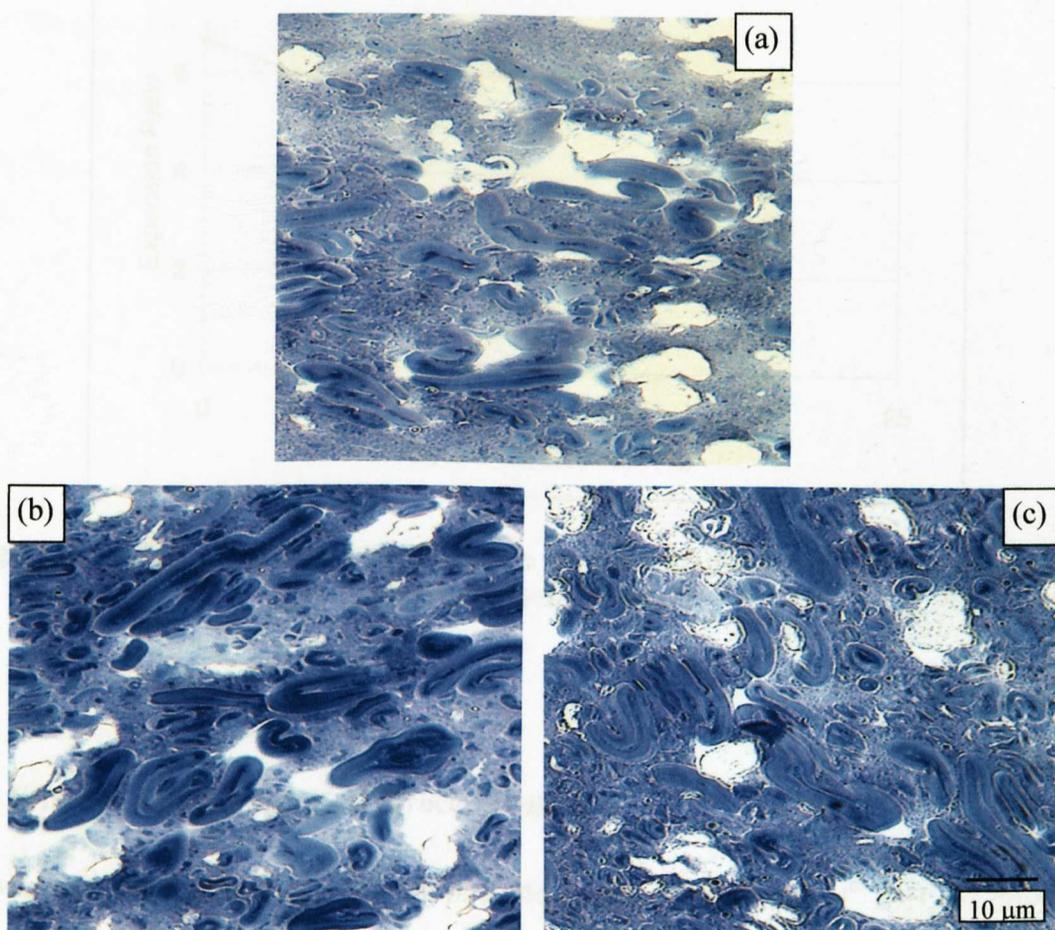

Figure 6.8 DIC micrographs of Temple/glycerol (16.7wt%) extruded with different water content in barrel (D.W.B. on flour). (a) 26.2%, (b) 27.9% and (c) 30.7%.

This view is further supported by foaming tests on another set of pure starch/glycerol pellets, extruded at peak temperature of 120°C, screw speed of 100 rpm, and water

content in barrel abound 37 - 39% (D.W.B.) with three different levels of glycerol concentration, which revealed that expansion ratio decreases with increasing the glycerol concentration as shown in Figure 6.9. Clearly, with other conditions the same, the higher the glycerol content, the more lubrication effects the glycerol has on the extrudates and thus results in poorer disruption of the starch granules and give rise to lower foaming expansion ratios.
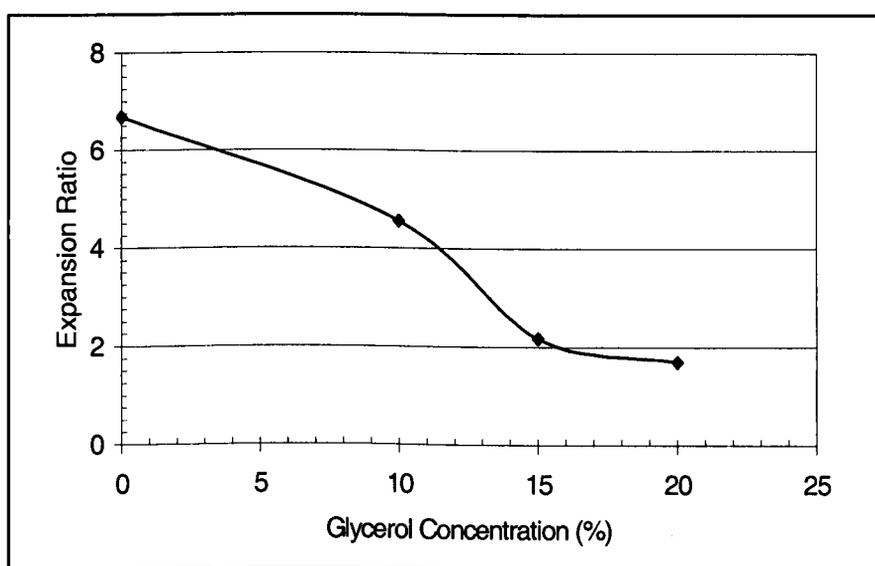
Figure 6.9 Effect of glycerol concentration on the expansion ratio of extruded pure starch/glycerol pellets.

6.3 Effect of blowing agent - Hydrocerol® BIH

It was expected that by using an additional blowing agent, Hydrocerol® BIH, the driving force to expand pellets could be enhanced so that the foamability of extruded pellets could be improved. However, the addition of 1.5wt% of this blowing agent as suggested by the supplier into the Temple flour has no significant effect on the foamability of the extruded pellets. The expansion ratios of Temple/BIH pellets are 6.6 and 8.7 when the moisture contents are 17.5% and 9.6%, respectively. These data are very close to that of Temple flour pellets.

BIH works by decomposition and release of gaseous products at elevated temperature. However, no obvious gas release was observed during the microwave heating of the Temple/BIH pellets. The decomposition temperature of the blowing agent is 160°C, but it takes two to six minutes to evolve larger volume of gas at the decomposition temperature (manufacturer data). The extruded starch pellets foam within one minute during microwave heating, prolonged microwave heating would cause foamed pellets to burn. Thus, even if the decomposition temperature of blowing agent was reached during the microwave heating, the slow decomposition behaviour was unable to release sufficient gas to puff the pellets while they are still ductile enough before water is lost and the material hardens.

6.4 Effect of nucleation agent - talc powder
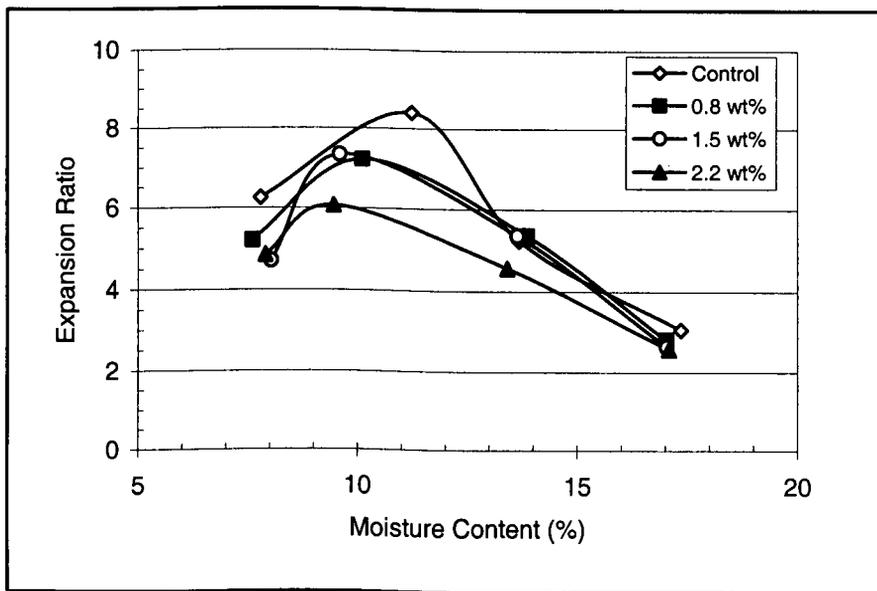
**Figure 6.10 Variation of expansion ratio with moisture content for the extruded Temple pellets with different concentration of talc powder.**

Talc powder has been selected as an inorganic additive as a nucleation agent. It was expected that by adding talc powder the cell structure could be refined and thus the properties of foamed pellets could be improved. Figure 6.10 presents the variations of

expansion ratio at different moisture content for the extruded Temple flour with three concentrations of talc powder. As expected, the addition of talc power did not enhance the expansion ratio. It was reported that addition of talc powder decreased the expansion ratio of starch foams produced from direct extrusion foaming (Bhatnagar, & Hanna, 1996). Nucleation agents may only increase the number of sites for cells to grow, rather than increase total driving force for foaming. In fact, only a few percent of talc powder has resulted some reduction in the expansion ratio of the extrudates. The major effect of talc powder is the refinement of cell structure of foams and hence the physical and mechanical properties of foamed pellets. This will be discussed further in Chapter 7.

6.5 Effect of microwave and moisture absorbents - NaCl and CaCl$_2$

Sodium chloride and calcium chloride are chosen as additives (see Sections 3.1.5 and 3.2.5.2 for the details about the processing) for two purposes. Firstly, it is expected that the addition of these highly polar additives could enhance absorption of microwave energy of the extruded pellets during microwave heating so as to reach the foaming temperature more quickly and to reduce water loss by diffusion and thus improve the foamability. Secondly, salts are moisture absorbent. The addition of salts could assist the foamed pellets to absorb more moisture in ambient humidity environment and hence plasticize the starch foams.

Microwave foaming tests show that the addition of the two salts has significantly improved the foamability of the extruded pellets. Compared with 50-65 seconds to puff the Temple pellets in the microwave oven, it takes only about 30 seconds for the pellets containing either NaCl or CaCl$_2$ to be foamed. The addition of salts has clearly enhanced the microwave energy absorption efficiency and offers an opportunity to shorten the process time. Figure 6.11 shows the significant changes of microwave foaming expansion ratio at different moisture contents for the extruded Temple pellets with and without the addition of the salts. Addition of salts has improved expansion ratio across a wide range of moisture content. A 5.5% addition of NaCl (on wet flour weight basis) gives Temple flour pellets the maximum expansion ratio of 12.9, while 10.5% addition of CaCl$_2$ (on wet flour weight basis) gives the maximum expansion ratio

of 14.3. Compared with that of the Temple pellets without salts, the increase in expansion ratio are 59% and 76%, respectively.
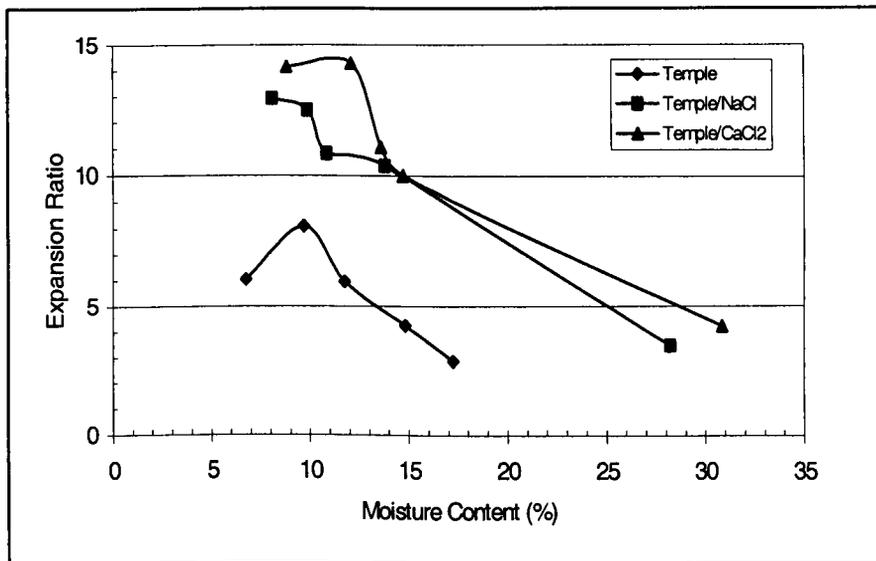
Figure 6.11 Expansion ratio of extruded Temple flour with and without salts at different moisture content.

The influences from the addition of these two salts on the properties of the foamed pellets, such as density, cell structure, moisture absorption isotherms and mechanical properties will be discussed further in Chapter 7.

6.6 Discussions on effects of PVAs and glycerol on foaming

In Sections 6.1 and 6.2, the effects from addition of PVAs and glycerol on low microwave foaming expansion ratios have been reported, and the mechanisms behind it have been discussed in terms of melting point and degree of cook. In this section additional factors in terms of the competition between the driving and resistance forces for foaming are discussed further.

During the microwave foaming of extruded starch pellets, the driving force for foaming is the expansion of the superheated water steam within the material at nucleation sites where water becomes vapour and blows the surrounding material into a bubble cell. The

resistance or restriction force to the expansion of cells comes from the surface energy with creation of new cell wall surfaces and the energy dissipation during stretching of the cell wall materials hence depends on the viscoelastic properties of the melt. The expansion extent of extruded pellets is thus dependent on the competition between them.

It has been observed that some small bubbles had formed within the extruded pellets containing PVAs or glycerol after microwave heating. This suggests that the bubbles have already nucleated but they were unable to grow during the period of heating. In other words, the driving force was not high enough to overcome the resistances to puff the pellets. This could have resulted from either the decreasing of the driving force for expansion or increasing of resistances arisen from the addition of PVAs or glycerol.

To explore the possible causes for the low expansion of the pellets containing PVAs, further investigation was carried out. The extruded Temple flour pellets with about 11% moisture content were soaked in a 15wt% PVA (NK-05) water solution for a few seconds then dried back to about 12% moisture content so that a thin PVA film was coated on the surface of pellets. It was found that the microwave foaming expansion ratio of PVA coated pellets decreased with increasing of the number of the coating times (layers), from 8.9 without PVA film to 7.9 with five coating layers. It should be mentioned that the thickness of coated film on pellets was not uniform due to the slow flow of the solution during the period of drying. These results and the fact that the expansion ratio of extruded Temple/PVAs was only around 2 - 4 indicate that the presence of PVA could restrict the expansion of extruded flour but the modulus and strength of PVA may not be the main factors to cause low expansion.

Glycerol is an effective plasticizer to starch (Lourdin, et al., 1997a; van Soest, & Knooren, 1997; Averous, et al., 2000; Myllarinen, et al., 2002b) and thus in the case of Temple flour extruded with glycerol, the resistance to stretching of cell walls should have reduced compared with that without glycerol addition. Handling the pellets with glycerol it is apparent that they deform at lower stresses. Therefore, the low microwave expansion of Temple/glycerol pellets could not be attributed to the increase of the restriction forces.
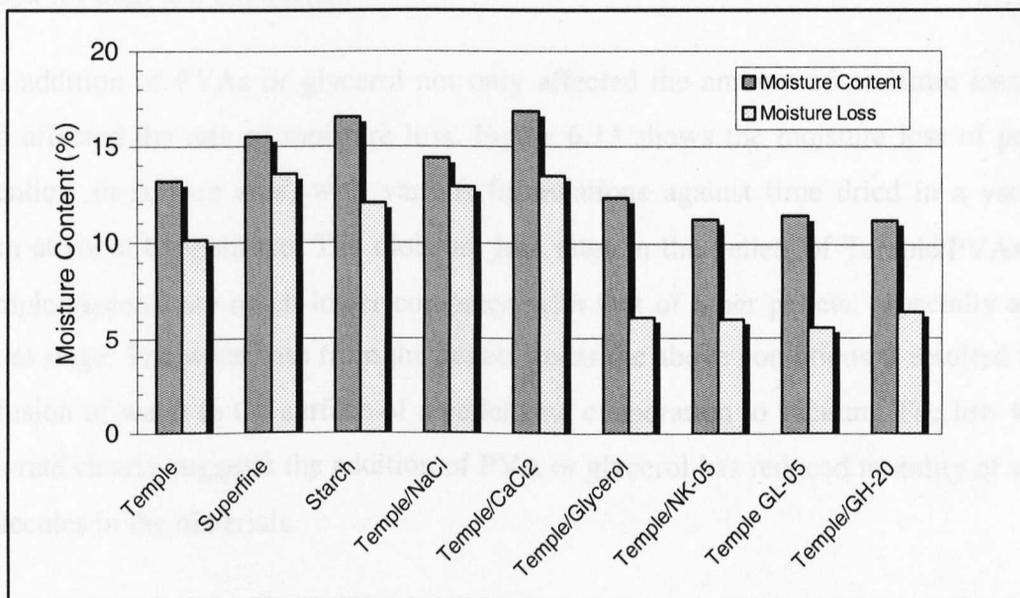
Figure 6.12 Moisture content before microwave heating and moisture loss during microwave foaming of extruded pellets with different formulations.

Since both PVA and glycerol are hydrophilic, the addition of them into starch may have increased the water bonding capability of the materials and give rise to lower driving force for the cell expansion. It is noted that the moisture loss behaviour in the extruded pellets containing PVAs and glycerol are quite different from that of the pellets without them. Figure 6.12 presents the moisture content before microwave heating and moisture loss after microwave heating from cylindrical extruded pellets of identical size with various formulations. The heating periods are: 30 seconds for Temple/NaCl and Temple/CaCl$_2$, 45 seconds for the others. The moisture loss during microwave heating for the extruded pellets containing PVAs or glycerol was much lower than that of other extruded pellets. These results clearly show that for the pellets containing PVAs or glycerol, only about 50% of the moisture in the pellets has evaporated after 45 seconds microwave heating. While for the pellets without these two additives, at least 75% of moisture in the pellets has evaporated (the moisture content in the various pellets is ranged from about 12% to 16%) after microwave heating. Since superheated water is the only blowing agent in all these pellets, the low moisture loss suggests that less water vapour was generated and escaped, therefore, it may be concluded that lack of driving

force (the superheated steam) in the pellets containing PVAs or glycerol is a main reason for their low expansion.

The addition of PVAs or glycerol not only affected the amount of moisture loss, but also affected the rate of moisture loss. Figure 6.13 shows the moisture loss of pellets (identical in surface area) with various formulations against time dried in a vacuum oven at room temperature. The moisture loss rates in the pellets of Temple/PVAs and Temple/glycerol are much lower compared with that of other pellets, especially at the initial stage. The water loss from the pellets under the above conditions is resulted from diffusion of water to the surface of a pellet, and evaporation to vacuum. The low water loss rate clearly suggests the addition of PVA or glycerol has reduced mobility of water molecules in the materials.
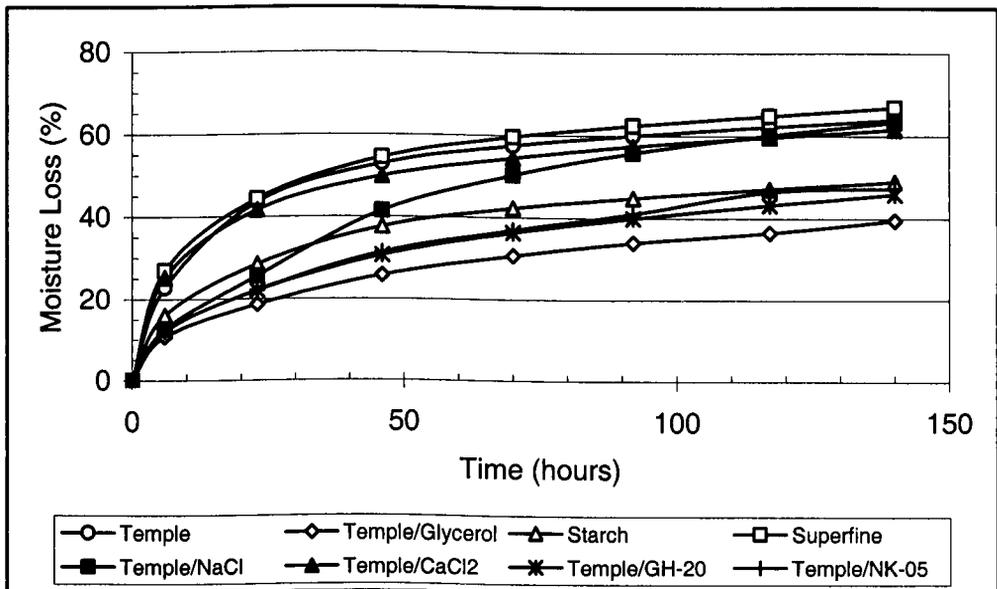

Figure 6.13 Moisture loss of extruded pellets with various formulations against time at room temperature in a vacuum oven.

The above results showed that the addition of hydrophilic additives (PVAs and glycerol) had clear effect on water loss characteristics of the materials in terms of water bonding and mobility of water within the materials. This in turn reduced the driving

force for the foaming, namely the generation of superheated water vapour for nucleation and growth of bubble cells.

In addition, there is probably another reason for the low expansion ratios in the extruded pellets containing PVAs or glycerol, i.e. low microwave energy absorption by the materials and thus low heating rate that can cause less moisture evaporating. It was attempted to measure the difference in temperature rising among the various pellets during microwave heating, but all attempts failed due to the lack of appropriate temperature monitoring technique. However, the results of oil fry test showed that the expansion ratio for the pellets containing PVAs or glycerol remaining low and comparable to that in the microwave foaming. This indicates that the low expansion ratios for these pellets were not resulted from low temperature.

6.7 Summary

Although PVA has been successfully used as a polymeric additive for direct extrusion processing starch foams, it should be borne in mind that there is a large die pressure release (about 6.9 MPa) in that case. The superheated water as the blowing agent has significantly high foaming driving force compared with that for microwave heating. In the microwave foaming of extruded pellets with PAVs, due to lower degree of cook of starch in the pellets and less superheated steam generated during rapid heating, PVA seems not suitable as a additive for extruded wheat flour in microwave foaming processing.

From point of view of polymer physics, a plasticizer is a substance that can depress T_g of polymers. However, as a plasticizer that is suitable for microwave foaming of extruded starch, it should not only keep the cell wall ductile after foaming but also not hinder the extruded pellets expansion during the microwave heating. Although glycerol is a good plasticizer for thermoplastic starch, it does not work for microwave foaming of extruded wheat flour. Because glycerol not only reduced gelatinisation of starch granules during extrusion but also depressed blowing action of water in the pellets during microwave foaming.

There is a mismatch between the period of microwave heating and that needed for complete decomposition reaction of the blowing agent Hydrocerol® BIH in the extruded pellets. To benefit from an additional blowing agent, this mismatch must be overcome by careful selection of blowing agent characteristics.

Although a small amount of nucleation agent, such as talc powder reduce expansion ratio, the resultant refined cell structure may be beneficial. Therefore, such additive should be used when fine cell and more rigid foams are desired.

Sodium chloride and calcium chloride are effective to improve microwave foamability of extruded starch pellets. Both of them not only significantly increased the expansion ratios of pellets but also markedly reduced the foaming time due to their characteristic in microwave energy absorption.

Chapter 7

Physical and Mechanical Properties of Foamed Pellets

7.1 Density of foamed pellets

Like the expansion ratio for characterising foamability of microwave foamed pellets, foam density is also an important physical property to characterise, because both of them directly or indirectly reflect the foam cell structure and thus properties of the foam.

Figure 7.1 shows the dependence of the densities of foamed pellets made from five different formulations on the moisture content within the pellets before microwave foaming. These pellets had almost the same extrusion conditions, i.e., 120°C peak temperature, 100 rpm screw speed and around 30.3-31.1% water content in barrel.
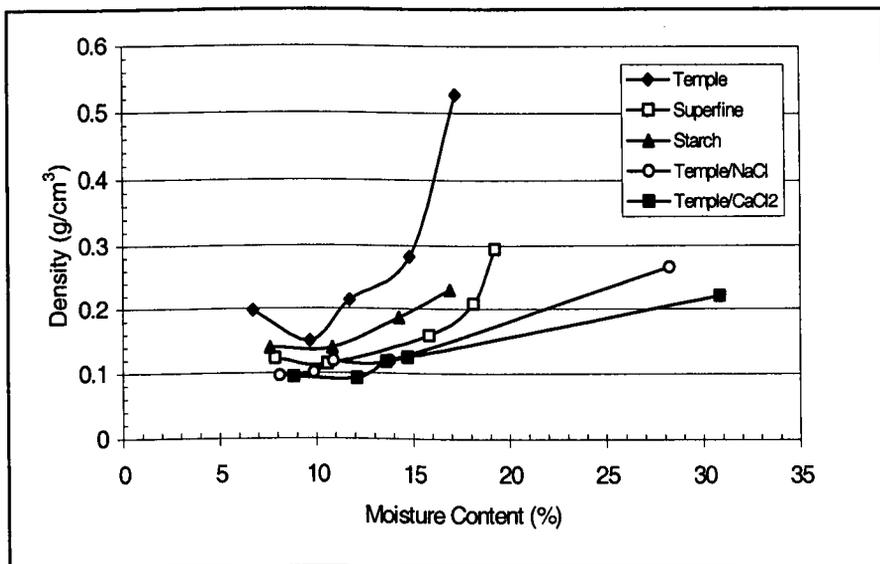
Figure 7.1 The densities of expanded pellets microwave foamed at different moisture contents.

The data in Fig. 7.1 indicate that the lowest density foams for all the individual formulations are achieved when foaming is carried out at about 10% moisture content. However, comparing with the density of commercial starch based loose fills, which ranged between 0.0167 and 0.0226 g/cm^3 (Tatarka, & Cunningham, 1998), the lowest densities of microwave foamed extruded pellets, ranged between 0.114 g/cm^3 (for the Superfine flour) and 0.145 g/cm^3 (for the Temple flour), are still much denser than that of extruded starch foams. This disparity is attributable to the difference in expansion ratio during the foaming process and the existence of denser skin layer in the foamed pellets (see Figure 7.2). The formation of this denser skin layer is likely to have resulted from moisture loss from the surface of a pellet during heating and hence the lack of driving force for foaming.
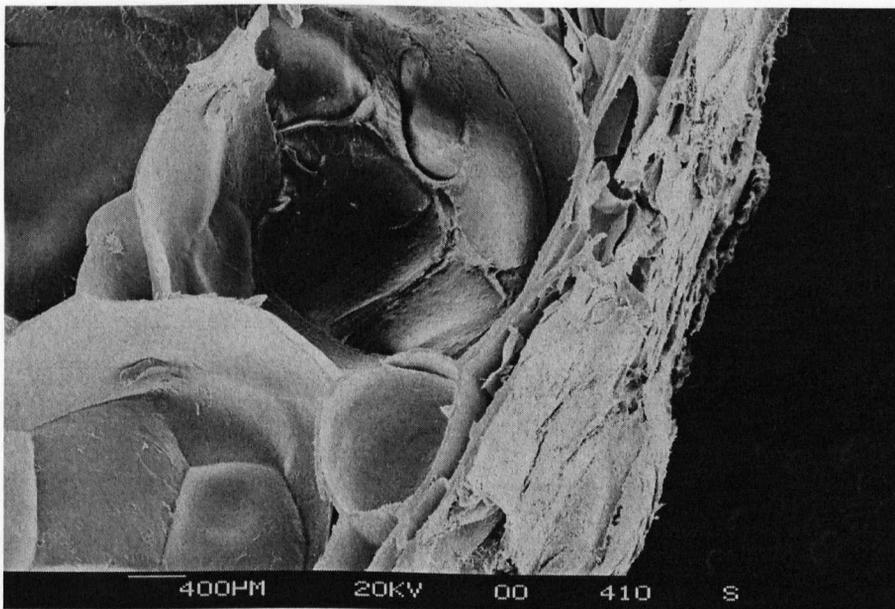
Figure 7.2 The denser skin layer of microwave foamed the Superfine flour extruded pellet.

Addition of salts has increased the expansion ratio of extruded pellets, thus it will also reduce density of foamed pellets. The data in Fig. 7.1 indicate that addition of 5.5% NaCl or 10.5% $CaCl_2$ has significantly reduced the density of foamed Temple flour pellets, from 0.145 g/cm^3 to 0.095 and 0.092 g/cm^3, respectively. Since no attempts were made to optimize the formulation variables, there should be a scope for further

reduction in density. However, it is expected that there should exist an optimum salt concentration, above which the high density of salt will overwhelm the benefit gained by increasing expansion ratio and lead to increase in foam density.

In fact, density of a foam, ρ, is directly related to the expansion ratio, $\alpha = V_f/V_s$, (where V_f is the volume of a foam including voids, and V_s is the volume of solid) by

$$\rho = \rho_s/\alpha \qquad (7.1)$$

where ρ_s is the density of the solid depending on the material composition, ignoring the mass of air in the foam voids (and assuming there are negligible voids in the unexpanded pellets).

Relative density, $\rho_r = \rho/\rho_s = 1/\alpha$, gives a more direct measure of the solid fraction in a foam, and the porosity, β, can be simply expressed by

$$\beta = 1 - \rho_r = 1 - 1/\alpha. \qquad (7.2)$$

Table 7.1 summarized the values of these parameters for the foams from various formulations with maximum expansion during microwave heating to give better insight into how porous these foams are.

Table 7.1 Foam parameters for the microwave foamed pellets from various formulations (maximum expansion)

Foam	Density (g/cm^3)	Expansion ratio	Relative density (%)	Porosity (%)
Temple	0.150	8.1	12.3	87.7
Superfine	0.114	11.4	8.8	91.2
Starch	0.139	9.4	10.6	89.4
Temple/NaCl	0.095	12.9	7.8	92.2
Temple/CaCl$_2$	0.092	14.3	7.0	93.0
Temple/BIH	0.144	8.7	11.5	88.5
Temple/Talc (0.8%)	0.165	7.2	13.9	86.1
Temple/Talc (2.2%)	0.188	6.1	16.4	83.6
Loose fills	0.0167~0.0226[a]	-	1.3~1.7[b]	98.7~98.3

a). After Tatarka, & Cunningham, 1998; b). Calculated using $\rho_s = 1.30$ g/cm^3.

Figure 7.3 presents the means and standard deviations of the densities of microwave foamed pellets (maximum expansion) from various formulations with the denser skin layer removed and at 50% relative humidity. It should be mentioned that the volumes of the samples were calculated from the dimensions measured by a calliper, instead of by measuring with the glass bead displacement method, as the foamed pellets were cut to rectangular prisms and the outside surfaces of the samples were flat. If glass bead displacement method was employed, some glass beads will access the pores and introduce errors to the results. Ten samples were measured for each formulation. The data in Fig.7.3 indicate that after removing the denser skin layer, the densities of some of microwave foamed pellets, such as those made from the Superfine flour, purified wheat starch and Temple/CaCl$_2$, are very close to the upper range of density of some extruded starch foams (Willett, & Shogren, 2002). These results clearly demonstrate the significant contribution of the denser skin layers to the overall high density of the microwave foamed pellets.
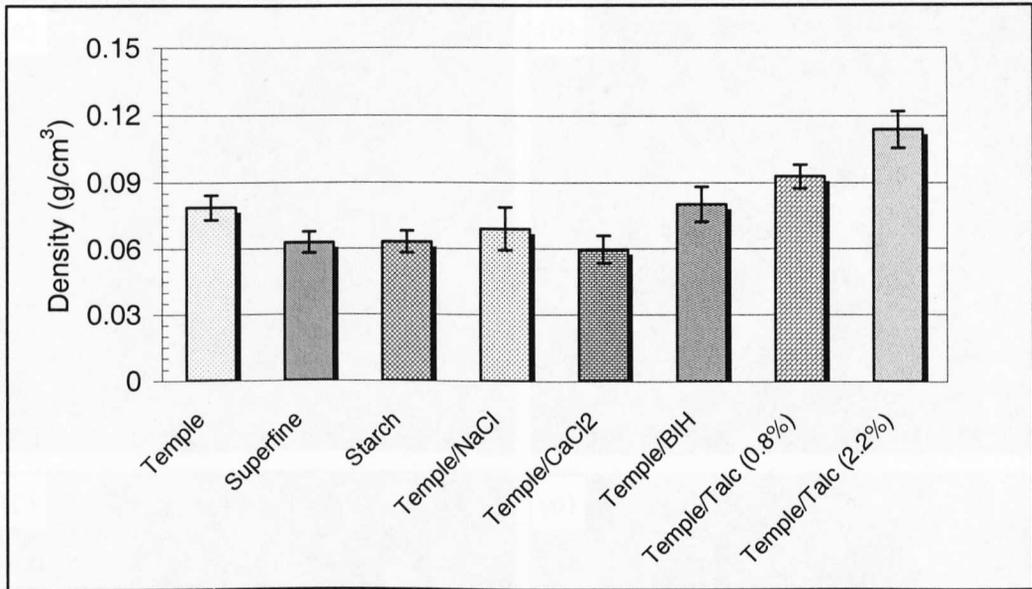
Figure 7.3 Densities of microwave foamed pellets when the denser skin layer is removed.

7.2 Cell structures of foamed pellets

SEM micrographs of cross-sections of foamed pellets with three different raw materials at maximum expansion are shown in Figure 7.4. Examinations have revealed that the cell structures and cell sizes of these three foams are quite different. The sectioned cell sizes are estimated about 0.2 – 2 mm, 0.5 – 3 mm and 1 – 4 mm in diameter for Temple flour, Superfine flour and purified wheat starch foams, respectively. Moreover, the percentage of large size cells in Superfine flour and purified wheat starch foams is much higher than that in the Temple flour foam. The finer cell structure in Temple flour foam is probably due to the presence of bran in the Temple flour, which could act as nucleation agent. The cell wall thickness for Temple flour foam is estimated around 10 to 40 μm, and there is no marked difference from this in Superfine flour and purified wheat starch foams.
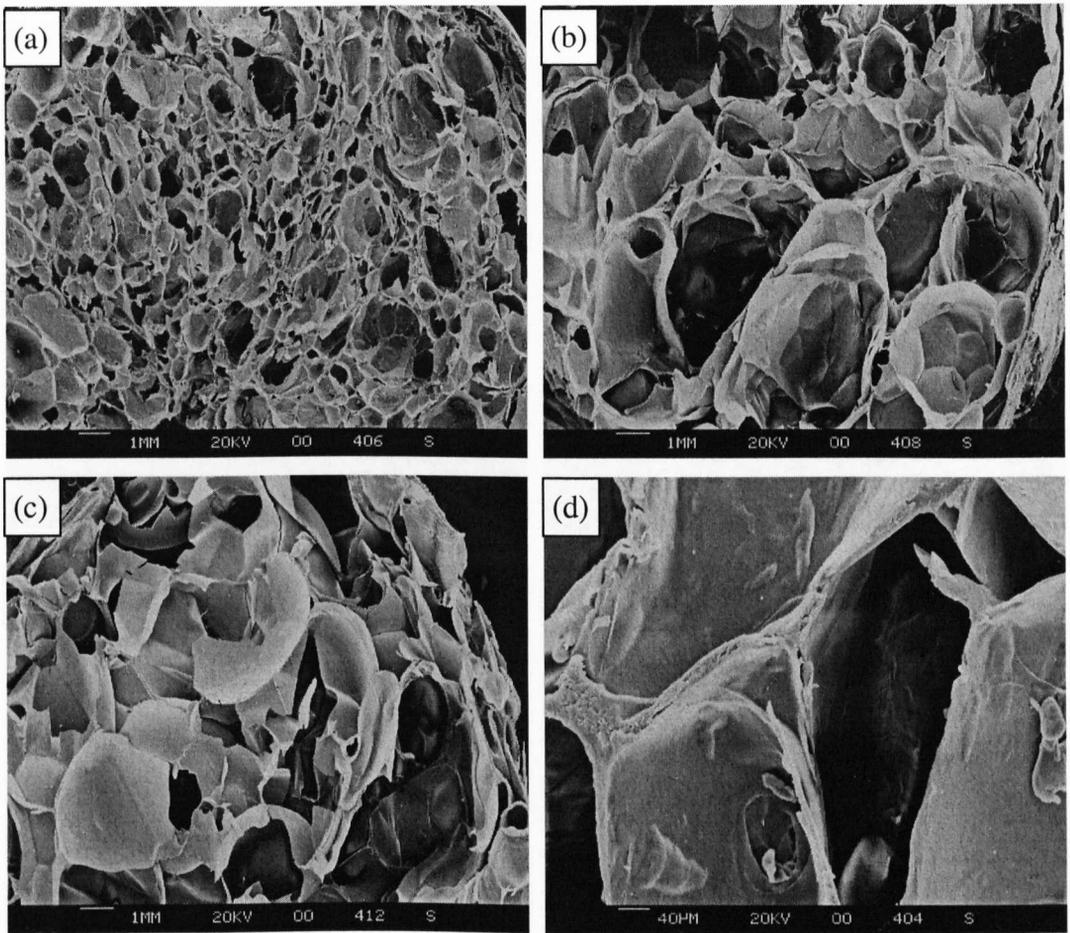
Figure 7.4 Scanning electron micrographs of cross-sections of foamed pellets with different raw materials: (a) Temple flour, (b) Superfine flour, (c) Purified wheat starch, (d) cell wall in Temple foam shown in (a) at higher magnification.

Figure 7.5 presents the SEM micrographs of foamed Temple pellets with different additives. It can be seen that there is no marked change in the foam structure when the blowing agent BIH was used (see Fig. 7.5 (a) and (b)). However, the addition of talc powder has significantly refined the cells of the foam, and the cell sizes decrease with increasing of the talc powder concentration (see Fig. 7.5 (a), (c) and (d)). For the foam with 0.8% talc powder, the cell diameters are estimated to be in the range of 0.2 - 0.8 mm in diameter. While for the foam with 2.2% talc powder, the cell diameters are in the range of 50 μm to 0.5 mm.
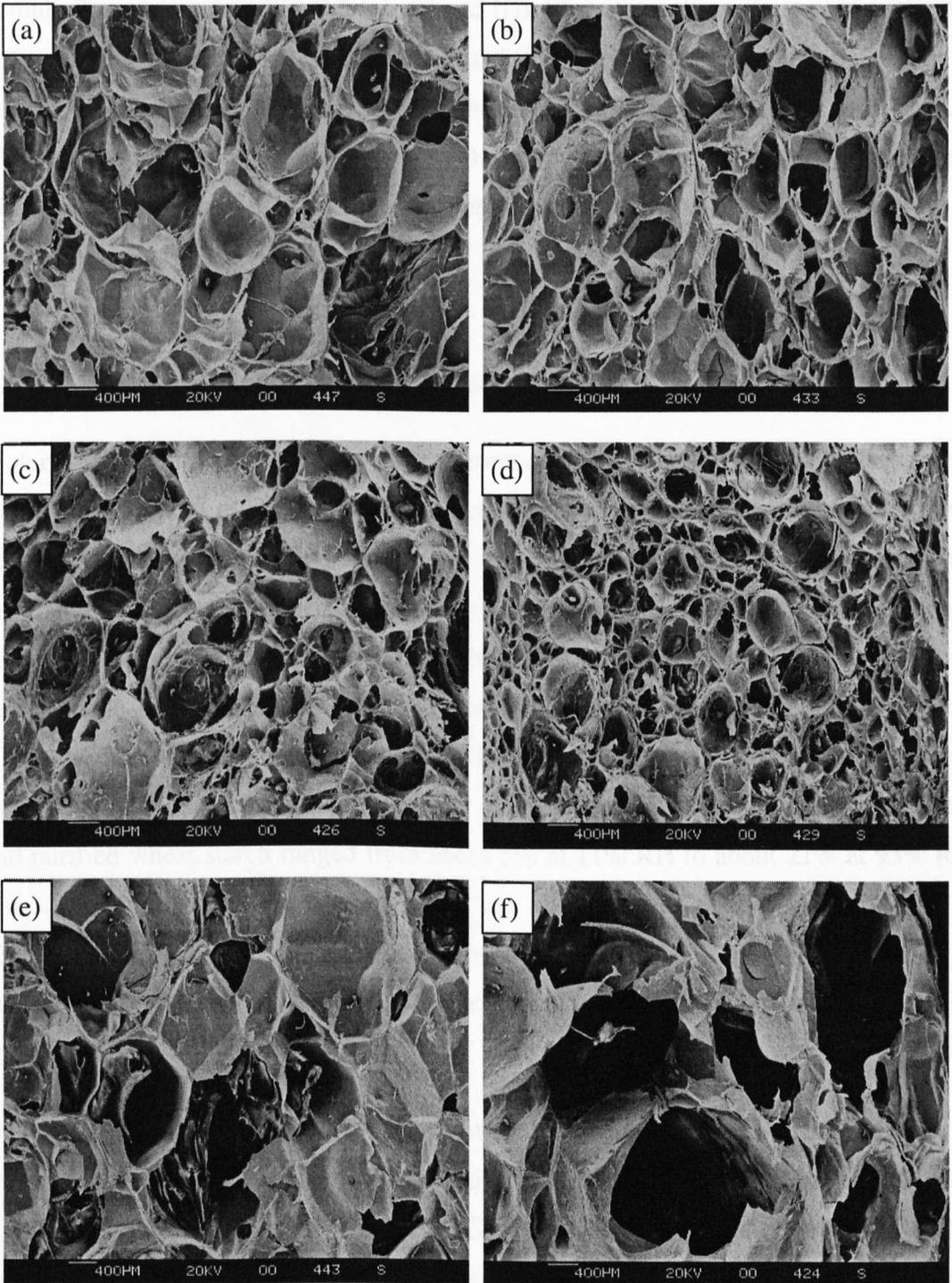
Figure 7.5 Scanning electron micrographs of foamed Temple pellets with various additives: (a) Temple; (b) Temple/BIH (1.5%); (c) Temple/Talc (0.8%); (d) Temple/Talc (2.2%); (e) Temple/NaCl (5.5%); (f) Temple/CaCl$_2$ (10.5%).

The addition of NaCl and $CaCl_2$ gives rise to a marked increase of cell sizes of the Temple flour foams (see Fig. 7.5 (a), (e) and (f)). Since the cell cavity is deep and some cells are interconnected to each other, it is difficult to estimate the cell size range in Temple/NaCl and Temple/$CaCl_2$ foams. The large cell sizes in the foams with the salt additives is thought to be resulted from the more rapid heating and low water loss, which give rise to higher water vapour pressure in the foam cells for them to grow to larger sizes.

7.3 Water absorption characteristics of foamed pellets

Water absorption from the ambient environment after foaming could plasticize the foam, making them more flexible during compression. Water absorption isotherm has been measured at room temperature for foamed pellets made from Temple flour, Superfine flour, purified wheat starch, Temple/NaCl and Temple/$CaCl_2$, the results are presented in Figure 7.6. It was found that the water absorption isotherms are almost the same for the wheat flours (Temple and Superfine) and purified wheat starch. In other words, at the same relative humidity (RH), they have similar absorption properties measured by equilibrium moisture content (EMC). The EMC of foamed wheat flours and purified wheat starch ranged from about 5% at 11% RH to about 21% at 93% RH. The foamed wheat flours and wheat starch can absorb more than twice the moisture at 93% RH than that in an average environment humidity (50% RH). It is interesting to note that the EMC increases almost linearly below 78% RH and then sharply at RH greater than 78%.

Comparing with foamed pellets without salts, the addition of salts raised the capacity of water absorption. Although 5.5% addition of sodium chloride did not change significantly the EMC of the Temple/NaCl foam at lower humidity levels, at higher humidity level, however, this addition did increase the EMC markedly. The addition of 10.5 % calcium chloride has significantly increased (over 50%) the EMC of the Temple/$CaCl_2$ foam at various levels of humidity by comparing with the Temple flour foam. This, as will be discussed in Section 7.4, has a marked influence on the flexibility of the foam equilibrated at typical environmental humidities.
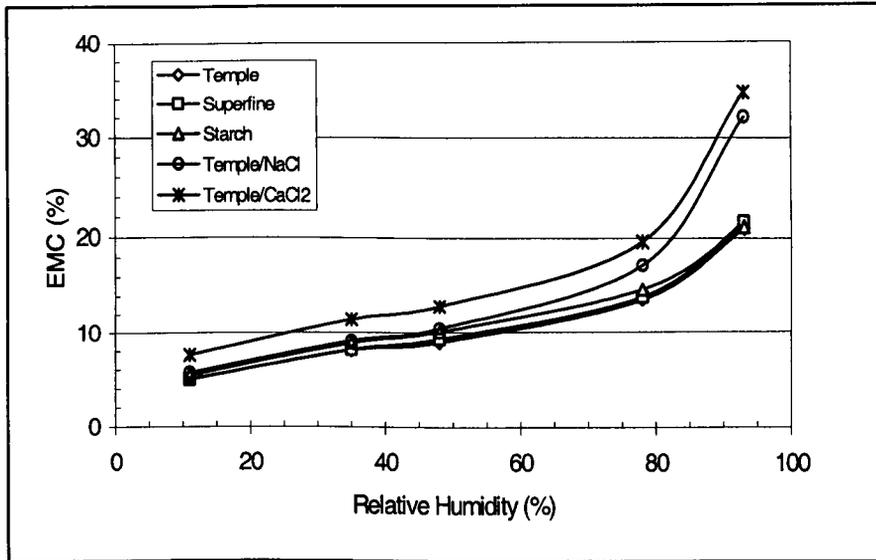
Figure 7.6 Water absorption isotherms for the microwave foamed pellets with different compositions at room temperature.

It has been found that relative humidity not only significantly affects the EMC of the foamed pellets, but also their cell structures. The size of foamed pellets was found to be reduced and became denser when treated at 93% RH during the moisture equilibrium tests, especially for Temple/NaCl and Temple/CaCl$_2$ which were able to absorb more moisture. While at 11 to 78% relative humidities the foamed pellets without salts have hardly any change in size by visual inspection, the foamed pellets with salts have a noticeable shrinkage at 78% RH. This shrinkage in the foam volume at the higher moisture content is clearly caused by the plasticizing effect of the absorbed moisture and the relaxation of tension within cell walls during the foaming process. This phenomenon may be utilized for adjusting the foam density or refining the foam cell structure by treating microwave processed foam in a high humidity chamber to obtain foams with high density and fine cell structures for applications such as high impact cushioning.

7.4 Mechanical properties

Mechanical properties of foams have an important impact on their practical applications. For protective or cushion packaging, it is desirable that foams are able to

absorb impact energy by compression and recover to their original dimensions after impact. Therefore, uniaxial compression tests were carried out to assess mechanical properties relevant to cushioning applications. Details of the specimen preparation and testing are described in Section 3.5.4.1.
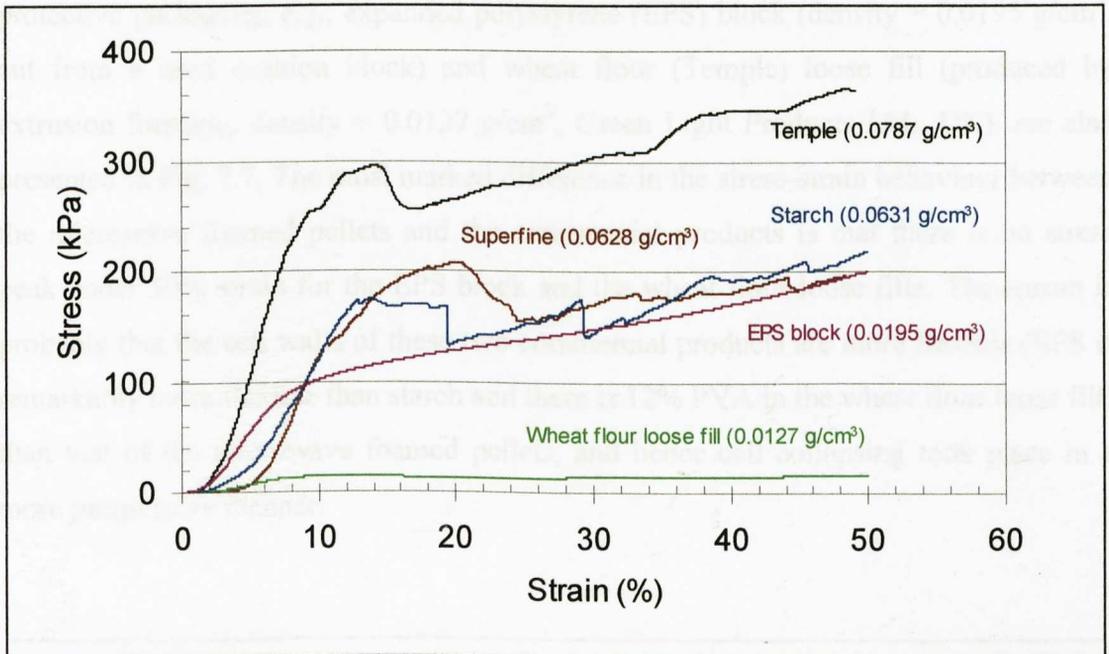
Figure 7.7 Comparison of typical compressive stress–strain curves (22°C, 50% RH) for the microwave foamed pellets made from different raw materials with commercial protective packaging materials.

Figure 7.7 shows the typical compressive stress – strain curves for the microwave foamed pellets produced from different raw materials. Rectangular prisms specimens were cut from foamed pellets and hence the dense skin has been removed. Generally, the stress increases linearly with the strain initially typical for elastic deformation. With further compression, the stress increases non-linearly and reaches a peak value during which, cell buckling can be observed. During further compression, the compressive stress decreases as the result of cell wall collapsing across the specimen at the peak stress. This is followed by a steady increase of the stress as the cell wall collapses throughout the specimen giving rise to an increase in foam density. During this process, for all the samples made from the purified wheat starch and some samples of the

Superfine flour, there are some changes in stress accompanied by noises of cell collapsing. This is not surprising, since the cell structures of these foams are much coarser than the Temple flour foams (See Section 7.2). Collapsing of any individual large cell will have marked effect on the stress.

For comparison, the compressive stress – strain curves of some commercial foams for protective packaging, e.g., expanded polystyrene (EPS) block (density = 0.0195 g/cm^3, cut from a used cushion block) and wheat flour (Temple) loose fill (produced by extrusion foaming, density = 0.0127 g/cm^3, Green Light Products Ltd., UK), are also presented in Fig. 7.7. The most marked difference in the stress-strain behaviour between the microwave foamed pellets and the commercial products is that there is no stress peak under 50% strain for the EPS block and the wheat flour loose fills. The reason is probably that the cell walls of these two commercial products are more flexible (EPS is remarkably more flexible than starch and there is 12% PVA in the wheat flour loose fill) than that of the microwave foamed pellets, and hence cell collapsing took place in a more progressive manner.
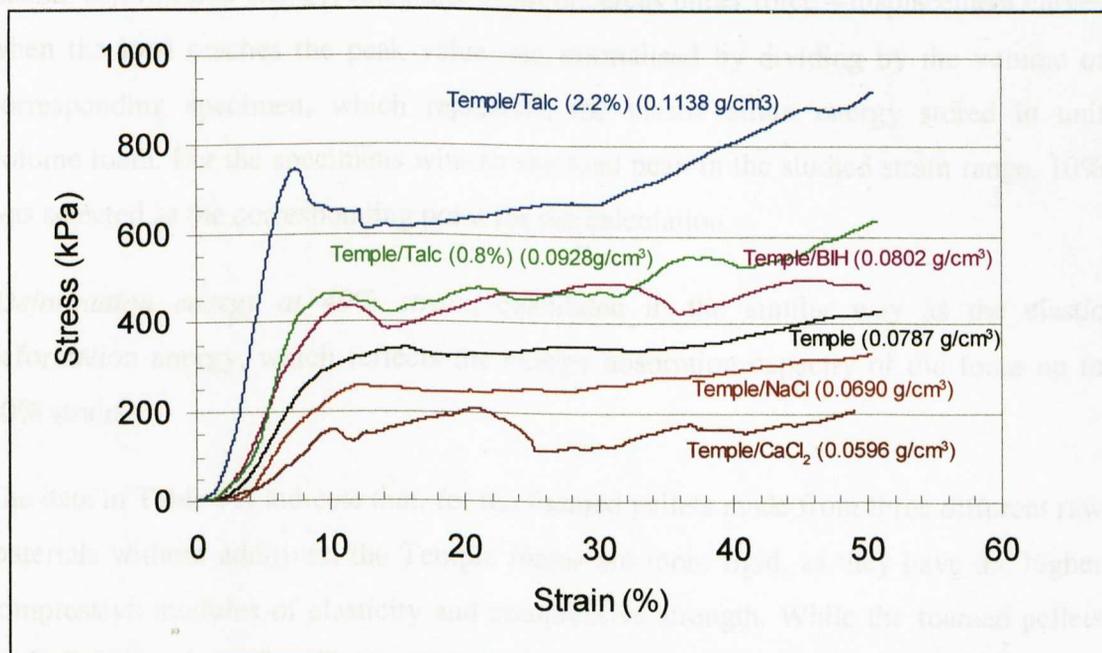
Figure 7.8 Typical compressive stress – strain curves (22°C, 50% RH) for the microwave foamed pellets made from Temple flour and different additives.

Figure 7.8 presents the typical stress-strain curves for the foamed pellets from Temple flour alone and Temple flour with various additives. As can be seen, mechanical behaviour of the foams can be adjusted effectively by controlling the foam cell structure through using different additives.

Table 7.2 summarized the following mechanical properties (mean values and standard deviations) obtained from the compression tests for all foam specimens investigated in this study:

Compressive modulus of elasticity, which reflects elastic rigidity of the foam;

Compressive strength, the peak stress which reflects the maximum load bearing capability of the foam before cell collapsing;

Compressive strain, the deformation at the compressive strength;

Compressive stress at 40% strain, which reflects the load bearing capacity of the foam at 40% strain;

Elastic deformation energy, calculated from the areas under force – displacement curves when the load reaches the peak value and normalised by dividing by the volume of corresponding specimen, which represents the elastic strain energy stored in unit volume foam. For the specimens without the load peak in the studied strain range, 10% was selected as the corresponding point for the calculation.

Deformation energy at 40% strain, calculated in the similar way as the elastic deformation energy, which reflects the energy absorption capacity of the foam up to 40% strain

The data in Table 7.2 indicate that, for the foamed pellets made from three different raw materials without additives, the Temple foams are more rigid, as they have the higher compressive modulus of elasticity and compressive strength. While the foamed pellets made from the Superfine flour and purified wheat starch have comparable compressive modulus of elasticity and compressive strength. These are true reflections of their cell structures as the Temple foams have higher density and finer cells than the other two as presented previously.

Table 7.2 Mechanical properties (22°C, 50% RH) of microwave foamed pellets and commercial protective packaging materials

Sample	Density (mg/cm³)	Compressive Modulus (kPa)	Compressive Strength (kPa)	Compressive Strain (%)	Compressive stress at 40% Strain (kPa)	Elastic Deformation Energy (kJ/m³)	Deformation Energy at 40% Strain (kJ/m³)
Temple	78.7	55 ± 22	314 ± 47	7.9 ± 2.0	377 ± 30	15.4 ± 3.3	129 ± 22
Superfine	62.8	24 ± 6	180 ± 36[a]	-	212 ± 37	11.3 ± 2.5[b]	69 ± 10
Starch	63.1	22 ± 4	161 ± 27	8.3 ± 1.9	241 ± 36	7.8 ± 2.5	68 ± 6
Temple/BIH	80.2	53 ± 19	334 ± 69	7.9 ± 1.6	439 ± 68	16.9 ± 6.2	136 ± 19
Temple/NaCl	69.0	36 ± 16	250 ± 97	8.1 ± 1.2	265 ± 60	12.2 ± 4.6	88 ± 25
Temple/CaCl$_2$	59.6	31 ± 10	174 ± 42	6.3 ± 1.8	175 ± 20	6.9 ± 2.9	63 ± 11
Temple/Talc (0.8%)	92.8	102 ± 17	489 ± 87	5.9 ± 1.1	555 ± 70	18.4 ± 5.5	193 ± 21
Temple/Talc (2.2%)	113.4	142 ± 48	737 ± 187	6.2 ± 1.4	789 ± 127	27.4 ± 7.8	267 ± 50
EPS Block	19.5	16 ± 4	107 ± 8[a]	-	175 ± 8	7.0 ± 0.9[b]	49 ± 3
Loose Fills	12.7	2.5 ± 0.2	15 ± 1.2[a]	-	15 ± 1	1.1 ± 0.1[b]	5.4 ± 0.4

a). Compressive stress at 10% strain; b) Deformation energy at 10% strain

As shown in Figure 7.8 and Table 7.2, the most important factors influencing the mechanical behaviour of the wheat flour based foams were their cellular structure and the composition of starch blend cell walls. Addition of nucleation agent (e.g. talc powder) significantly increased the compressive strength, elastic modulus and elastic deformation energy. Hence, nucleation agents are suitable to refine the foam cell structures to produce more rigid foams with high load bearing capacity and yet able to deform at higher stress levels to absorb impact energy and hence suitable for protecting heavy goods. The addition of salts, on the other hand, decreased all these values markedly except the compressive strain. Due to the larger cells and higher moisture absorption described previously in Sections 7.2 and 7.3, the foams are less rigid and able to be compressed at relatively low stress to absorb impact energy and thus suitable for protect more fragile or light goods.

Comparing with the EPS block, some of the mechanical properties, such as compressive modulus of elasticity, compressive stress and deformation energy at 40% strain, of foamed pellets made from the Superfine flour and purified wheat starch were very close to that of EPS block. This suggests that by further optimizing the cell structure and flexibility of cell wall material, it is possible to produce a foam by microwave process so that its mechanical properties match that of EPS block. It should be mentioned that starch loose fills produced by extrusion foaming have very low density, and thus they are suitable for cavity filling in packaging for light weight goods under low compressive stress. While the microwave processed starch foams have relatively high density, they are more suitable for packaging under high compressive stress levels or for heavy goods.

Theoretical modelling on elastic mechanical behaviour of cellular solids (Gibson, & Ashby, 1997) showed that the mechanical properties of foams are closely related to their density. Denser foams tend to have thicker cell walls or higher solid fraction and hence are able to resist deformation better than lower density foams with thinner cell walls or lower solid fraction. Figure 7.9 shows the compressive strength as function of density for all microwave foamed samples studied in this work. As can be seen that there is a strong correlation between sample density and the compressive strength, regardless of the types of raw materials and additives. A similar correlation has also been observed

between the elastic modulus and the foam density, which is shown in Figure 7.10. These suggest that the stiffness of microwave foamed pellets is dominated by the foam density.
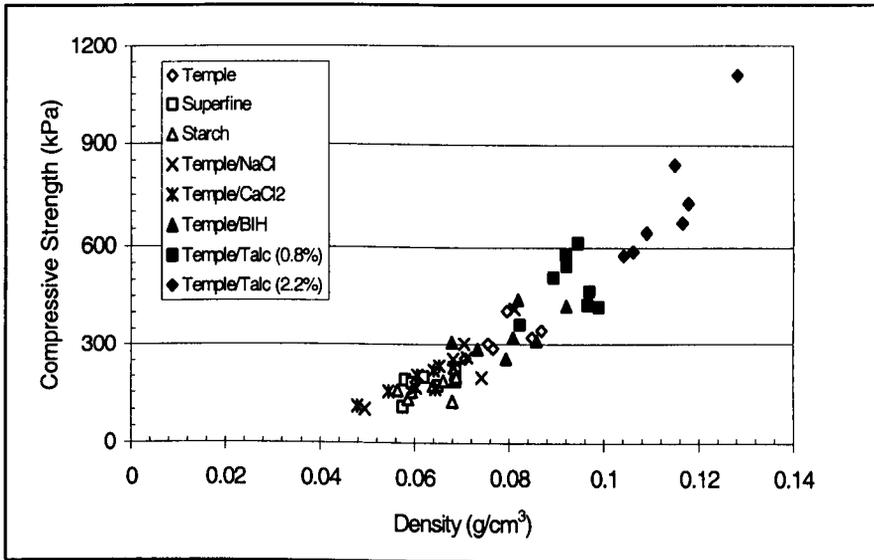

Figure 7.9 Scatter plot of compressive strength and density of microwave foamed pellets with various compositions (22°C, 50% RH).
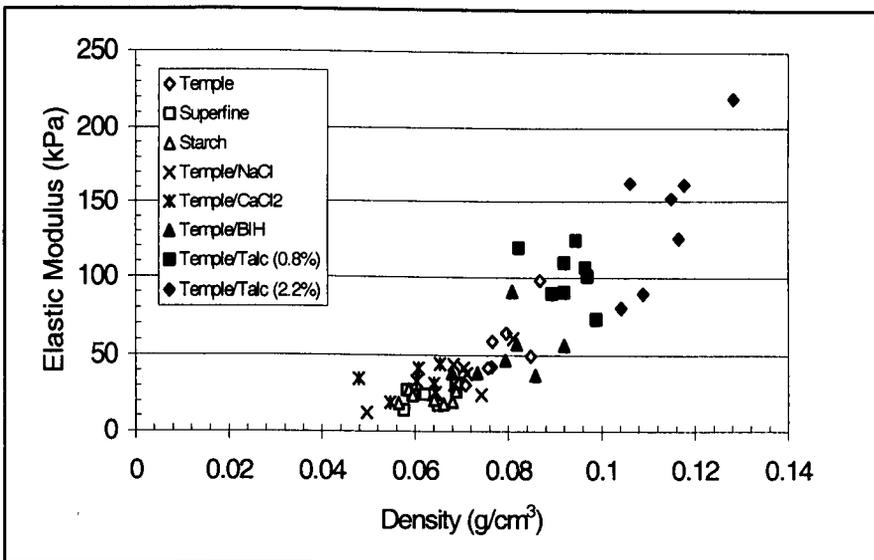

Figure 7.10 Scatter plot of compressive modulus of elasticity and density of microwave foamed pellets with various compositions (22°C, 50% RH).

The data in Figures 7.9 and 7.10 were used to fit a simple power law relationship between mechanical properties, σ, and foam density ρ for solid foams (Warburton, et al., 1992)

$$\sigma \propto \rho^n \qquad\qquad (7.3)$$

The results yield an exponent of 2.3 with a correlation coefficient of 0.8967 for the compressive strength, and an exponent of 2.7 with a correlation coefficient of 0.7889 for the elastic modulus. It was noted that the modulus data (Fig. 7.10) deviated more from the model than the strength data (Fig. 7.9), which is consistent with the report of Hube and Gibson (1988) that the shape anisotropy has a greater effect on stiffness than strength. Considering the non-uniform nature of the starch foams (e.g. Figs. 7.4 and 7.5) and in comparison with the regular model structure of foams (Gibson, & Ashby, 1997), the agreement is good and the correlation has practical utility. The above simplified model only applies to elastic deformation before collapse of cell structures, beyond which the behaviour of foam is governed by the actually architecture of cell structure, including cell connectivity and defects etc., which are not simply represented by a simple factor of density.

No similar relationship has been observed either between the compressive strain and foam density, or between the elastic deformation energy and foam density.

As predicted by the theory equations summarised in Table 2.5, the exponent of the power laws depend upon whether the foams are open or closed cells. In the case of linear elasticity, the exponent is 2 for open cells and 3 for closed cells in the equations describing both stiffness and strength of foams. The obtained values of the exponents between 2 and 3 by regression suggest that the foam cells are mixture of open cells and closed cells. In fact, the SEM observations indicated that the ratios of open cells to closed cells in the foams with different formulations are different. For instance, the foams of Temple/talc are dominated by closed cells, while in the foams of purified wheat starch and Superfine flour, the numbers of open cells are much more than that in

the others. However, techniques, such as Air Comparison Pycnometer (Tatarka, & Cunningham, 1998), to quantify the ratios of open to closed cells was not available and thus no further attempt was made to study this further.

According to the theoretical equations describing stiffness and strength of foams, two approaches could be taken to produce a softer foam, i.e. to reduce the elastic modulus and compressive strength of foams: either change the foam structure to lower densities or soften the properties of cell wall material. The former has been clearly demonstrated in the results shown in Table 7.2, Figures 7.9 and 7.10. While the latter is more challenging as has been demonstrated in the addition of glycerol, soften the solid material may bring in complications for achieving desired foaming conditions.

A good example is the Temple/NaCl and Temple/CaCl$_2$ foams. In comparison with the Temple flour foam, Temple/NaCl and Temple/CaCl$_2$ foams are softer. This may partially attributable to the decrease in density because addition of salt increased the expansion ratio of these pellets. On the other hand, the addition of salts also increased the equilibrium moisture content in the foamed pellets (as shown in Fig. 7.6), which should have softened the cell wall material by plasticization, and hence contributed to the overall softness of the foams.

From the view point of foam structure control, either decreasing the foam density or increasing the number of open cells (i.e. reducing the value of the exponent) can produce a less rigid foam. Thus, the further exploration of microwave foamed pellets should be focused on decreasing the foam density (or to increase the expansion ratio) and/or increasing the number of open cells. In terms of formulation and processing control, selection of additives and foaming process conditions should aim to create higher heating rate, larger water vapour (and/or other gas) pressure, and low melt rheological properties to allow extensive expansion and bubble burst to reduce density and increase fraction of open cells.

7.5 Summary

The physical properties of foamed pellets, such as density, porosity, cell structure, water absorption characteristics and mechanical properties are highly dependent on the raw materials and additives. Addition of salts reduces foam density and plasticizes cell walls, while addition of nucleation agent refines cell structure but increases foam density. Mechanical behaviour of foamed pellets can be adjusted effectively by controlling the cell structure through using different additives. Compressive strength and compressive modulus of elasticity of foamed pellets are closely related to foam density, the relationship can be described by a power law. At room temperature and 50% relative humidity, some mechanical properties, such as compressive strength, compressive modulus of elasticity and deformation energy at 40% strain are comparable to that of a commercial EPS block.

Chapter 8

Microwave Foaming of Extruded Pellets in a Mould

The ultimate aim of developing microwave foamable pellets is the production of foamed blocks for applications such as cushion packaging or thermal insulation. This Chapter describes the key characteristics and developments in foaming of the extruded pellets in a microwave-heated mould cavity as a method for making foam blocks.

8.1 Mould design

In order to manufacture a foamed block from extruded pellets by using microwave heating, free expansion process, which was described previously, needs to be replaced by expansion within a mould cavity. At the later stage of their expansion, the foamed pellets are forced to come into contact with each other to establish sufficient contact and bonding between them to form an integral block. The mould material must be highly transparent for microwave penetration and low in microwave energy absorption. It should have low adhesion to starch materials during moulding and most importantly retain adequate strength at elevated temperature around 200°C.

After several trials of different mould materials, such as glass, plastics (polyethylene and polypropylene), wood and glass fibre reinforced high performance resin, it was found that the PTFE (polytetrafluoroethylene) performed very well, exhibiting all the required properties. PTFE absorb very little microwave energy. It can be effectively preheated by hot air to 180°C without softening, a very important feature for achieving uniform foaming throughout a block (see Section 8.2). Furthermore, the non-stick characteristic to the starch materials allowed mouldings to be released without adhesion. Most of the trial mould materials failed due to excessive microwave energy absorption and softening of the moulds at the foaming temperature. Although glass is transparent to microwaves, it is rather fragile and sticks to the foamed block leading to the difficulties in mould release.

Figure 8.1 shows the PTFE mould used in this work, which were machined from extruded rods and used for moulding foam blocks by microwave heating. The mould consists of three parts: the top and bottom caps of the mould can be screwed on to the cylindrical tube with ϕ58 mm inner diameter and 13 mm wall thickness. ϕ57 mm, discs with different thickness are used to adjust the height of cavity of the mould so that blocks with heights ranging from 22 to 48 mm can be moulded. A ϕ2 mm hole was drilled at the centre of the top cap to allow escape of steam from the mould during foaming, which reduces the internal pressure in the mould to achieve better mould filling.
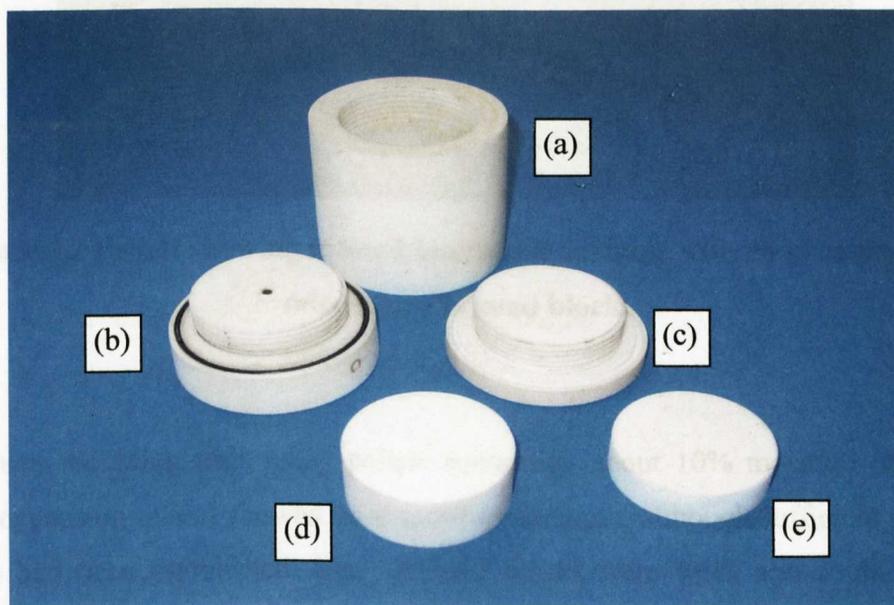
Figure 8.1 PTFE mould used in this work. (a) the central cylindrical tubular mould; (b) & (c) the end caps; (d) & (e) discs for height adjustment of blocks.

8.2 Adhesion of foamed pellets

When pellets are foamed up and are in good contact, the interfaces become multi-faceted with planar contact interfacial surface as shown in Figure 8.2. To form an integral block and have adequate strength, the foamed pellets must 'have' sufficient bending strength at these contact interfaces. Such bonding may be achieved by adhesion when the contact surfaces are sufficiently wet or fusion when interfacial diffusion at the

contacts can be facilitated by sufficient molecular mobility to penetrate across the contact interfaces at the elevated temperature.

10 mm

Figure 8.2 Pellets showing faceted interfacial surfaces with good contacts in microwave foamed block.

Preliminary moulding tests using pellets containing about 10% moisture (those with highest expansion ratios) showed poor interface strength, although sufficient interfacial contacts had been established. The moulded blocks were weak and could be easily broken into foamed pellets, even during release from the mould. This clearly indicated a lack of sufficient bonding at the contacts.

As has been shown in Section 6.6, free expansion of extruded pellets was accompanied by vaporization of a proportion of the water contained within them (Figure 6.12 show that it is less than "most of"). Despite the softening of the pellets during microwave foaming it was insufficient for fusion to occur. Recognising that fusion is a kinetic process, it may be that there is insufficient time during microwave foaming (< 60 s) for fusion to occur at these water contents.

To enhance the bonding strength at the interfaces, maintaining a relatively high water content at the contact surface is crucial, which not only plasticized the materials to achieve more intimate contact but also enhanced the mobility of the starch molecules for interfacial diffusion.

It was found that the interfacial bonding between foamed pellets could be significantly enhanced by wetting the surface of pellets before the microwave foaming. The pellets were soaked in a NaCl solution with a molar concentration of 3 mol/dm^3 for a predetermined time immediately before microwave foaming. It was found that about three minutes soaking gave adequate adhesion between the interfaces. Shorter soaking time than this was insufficient to produce required adhesion, while prolonged soaking time gave rise to a decreased expansion of the pellets and led to dense and hard the foam blocks. This is expected as foamability of pellets has been shown (Section 5.3) to decrease with high moisture content.

The reason to choose the NaCl solution instead of water for soaking is that NaCl has been shown to enhance microwave heating rate and to retain moisture content in the starch materials, which are beneficial for drying off the excessive water in the surface layer yet provide sufficient plasticizing effect for the interface to bond effectively. With other experimental conditions being the same, it was found that pellets soaked in NaCl solution produce better bonded blocks than those soaked in water.

Maintaining plasticized interfaces is considered the key for the successful enhancement of interfacial bounding using the soaking pre-treatment. The layer should be sufficiently thick to avoid drying out of water during the microwave heating and thin enough not to sacrifice the foamability of the interior core material.

8.3 Uniformity of heating and foaming within a moulding

To produce a uniformly foamed structure throughout a microwave foamed block, it is critical to establish a uniform temperature distribution so that pellets throughout the moulding reach the foaming temperature. The consequence of a non-uniform temperature distribution in a microwave foamed block can be drastic – while the centre

may have already burnt, the pellets near the mould surface remain insufficiently foamed, e.g. Figure 8.3

Figure 8.3 A non-uniform foamed block with burnt centre and insufficiently foamed surface.

Assuming the radiation intensity within the mould cavity is uniform and all pellets absorb the same amount of radiation energy, the temperature rise throughout the moulding should be uniform, provided there is no heat exchange at the mould surface. However, this is unfortunately untrue. As the mould absorbs little microwave energy and hence there is less temperature rise, the pellets near the relatively cold mould surface lose heat and their temperature remains lower than those pellets at the centre of the mould as schematically shown in Figure 8.4 (a). If the pellets in a mould are heated by conduction (such as convection in an oven) without microwave radiation, then the temperature profile would be expected as shown schematically in Figure 8.4 (b). A natural solution to non-uniform temperature profile is to combine microwave radiation together with preheating of the mould so as to create a uniform temperature profile as shown schematically in Figure 8.4 (c).
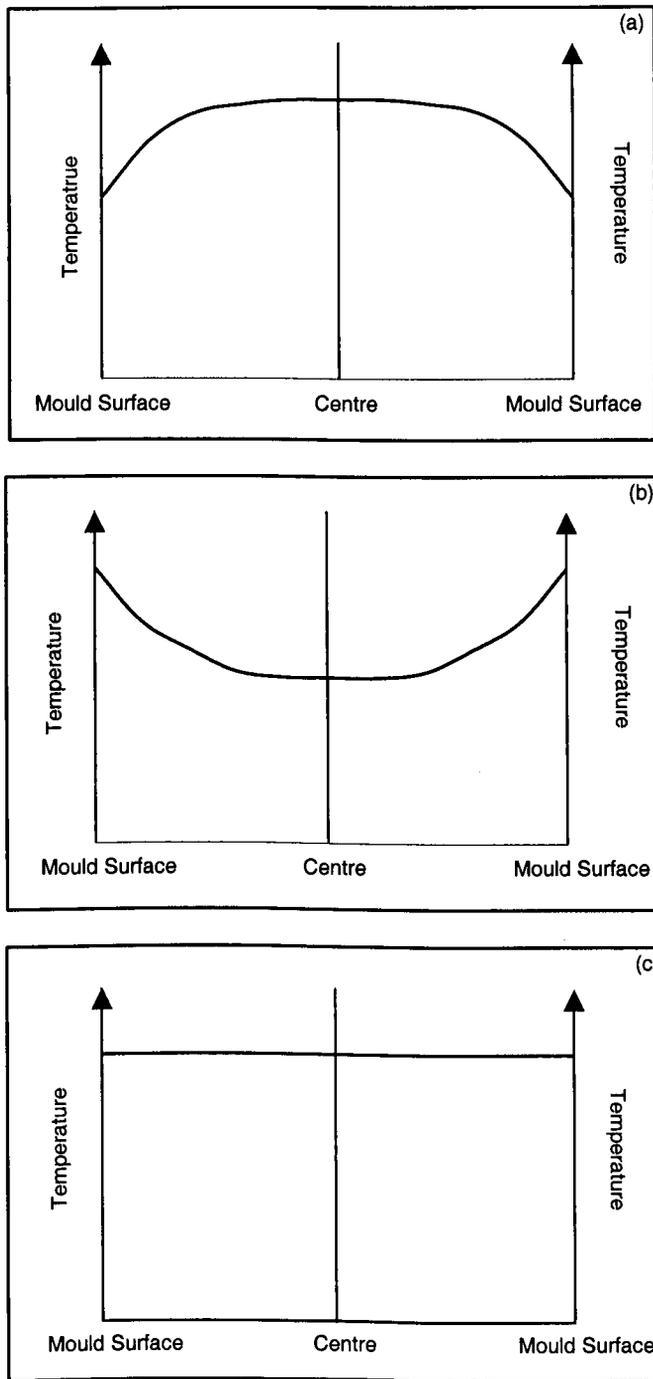
Figure 8.4 Schematic diagrams showing likely temperature distribution with a moulding. (a) Microwave heating in a cold mould, (b) conduction heating in a mould, (c) combined heating of microwave in a preheated mould.

The mould can be preheated to a desired temperature with the convection heating of hot air, a function of the microwave oven. It was found that when the mould surface was heated to about 160°C (measured using a infrared thermometer, Raytek®, Raynger®

ST6™, Santa Cruz, USA), the actual mould surface temperature dropped to about 120°C when the pellets were loaded, and followed by microwave heating to complete the foaming, a uniformly foamed block was produced (Figure 8.5).

Figure 8.5 Uniformly foamed starch based blocks using microwave heating.

8.4 Mould filling and pellet fusion

Since the extruded pellets were expanded in a confined space, the extent to which the mould is filled and indeed the degree of interfacial contacts and bonding between foamed pellets depends on the initial amount of pellets loaded into the mould. Clearly, when the amount of loaded pellets is low, the pellets may expand freely without forming contacts with their neighbours. On the other hand, when excessive amount of pellets are used, the expansion of pellets may be suppressed by the pressure from interfacial contacts with the neighbouring pellets, and results in an insufficiently foamed block.

Therefore, there exist an optimum initial loading of pellets (dependent on the free expansion ratio of pellets), which would allow the pellets: (1) expand sufficiently to reduce the overall foam density; (2) form intimate contact and sufficient bonding with

the neighbouring pellets and fill the available voids within the mould cavity. To satisfy the conflicting requirements of (1) and (2) a compromise must be reached.

To obtain blocks with strong coherent structure, relatively low density and acceptable mould filling, it is necessary to experimentally determine such optimum initial loading for the different types of pellets.

Figure 8.6 shows the effect of initial loading of pellets (measured by the ratio of pellet volume, V_p, to the mould cavity volume, V_m,) on the final mould filling (measured by the ratio of the volume of foamed block, V_b, to the volume of the mould cavity). When the initial loading is lower than 10% for Superfine flour and purified wheat starch pellets, 12% for the Temple flour pellets with salts, and about 14% for Temple flour alone, a coherent foam block cannot be formed (i.e., they are the thresholds for making a block in a mould).
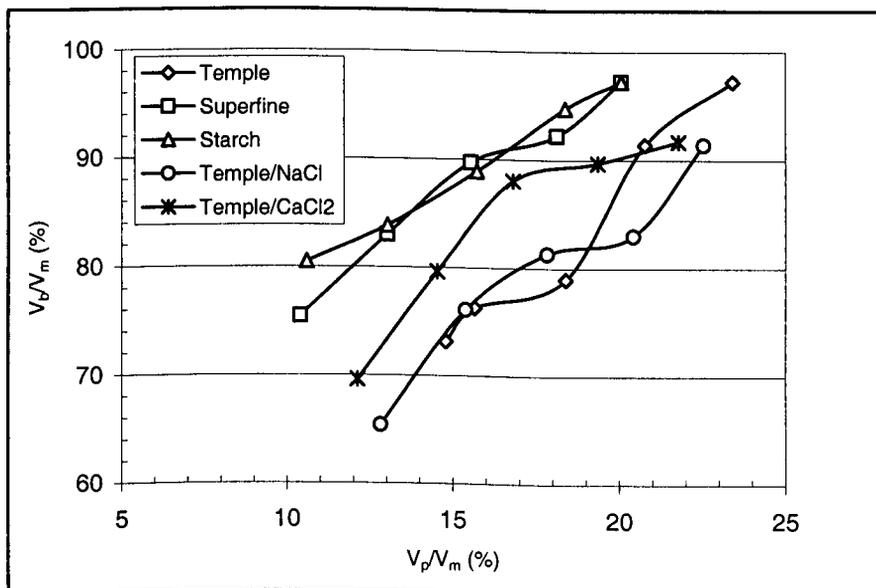
Figure 8.6 Effect of initial loading of pellets on the final mould filling by foamed pellets.

As can be seen from Fig. 8.6, the extent of mould filling increases with V_p/V_m. The extruded pellets made from the Superfine flour and purified wheat starch have better mould filling ability compared with those of other compositions, i.e., with the same

initial loading of pellets, a higher final mould filling can be achieved by using the Superfine flour and purified wheat starch. The addition of salts has significantly increased the free expansion ratio of pellets due to increase of heating rate (see Section 6.5), it also improved the mould filling ability of the Temple flour pellets, especially the addition of 10.5% $CaCl_2$. However, as Temple/NaCl and Temple/$CaCl_2$ pellets have similar or even larger free expansion ratio compared to the Superfine and pure starch pellets, the results in Fig. 8.6 suggest that a high free expansion ratio of pellets does not always correspond to a higher mould filling. This is understandable as mould filling is not only dependent on the expansion ratio of the pellets, but also on the rheological behaviour of the pellets during foaming. Under restriction within a mould, the flowability of pellets during foaming may be more important for achieving a high extent of mould filling.
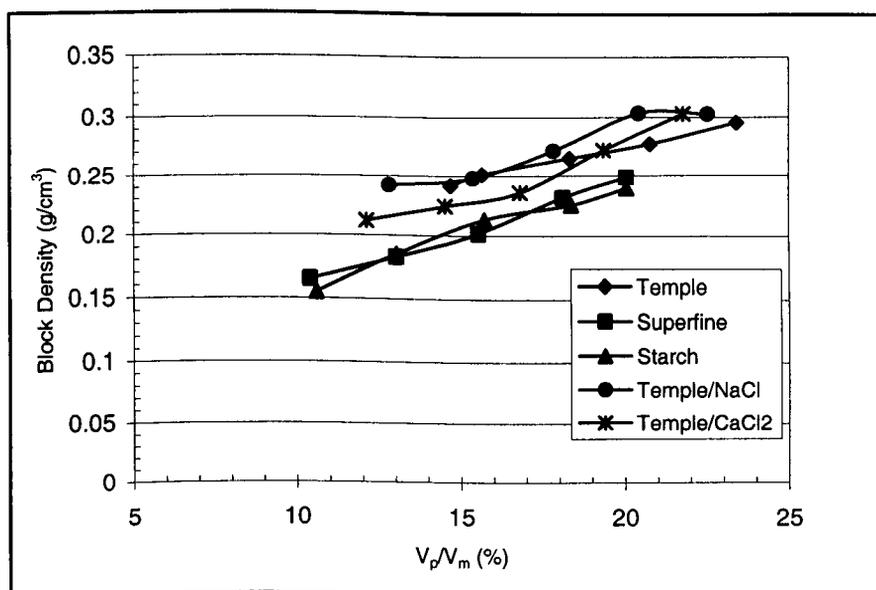
Figure 8.7 Changes of foamed block density with initial loading of pellets of various compositions.

Figure 8.7 shows the changes of density of foamed block with the initial loading of pellets for various compositions. As expected for a fixed volume of the mould cavity, the density of the foamed block increases with the increase of the initial loading of pellets. The blocks made from Superfine flour and purified wheat starch pellets have lower density than the others. However, comparing with the density of free expanded

pellets shown in Fig. 7.1, the density of the foamed block is much higher. The restriction to expansion of pellets from the mould wall and the neighbouring foaming pellets was clearly responsible for this inherent feature of low expansion or high density for the microwave foamed blocks.
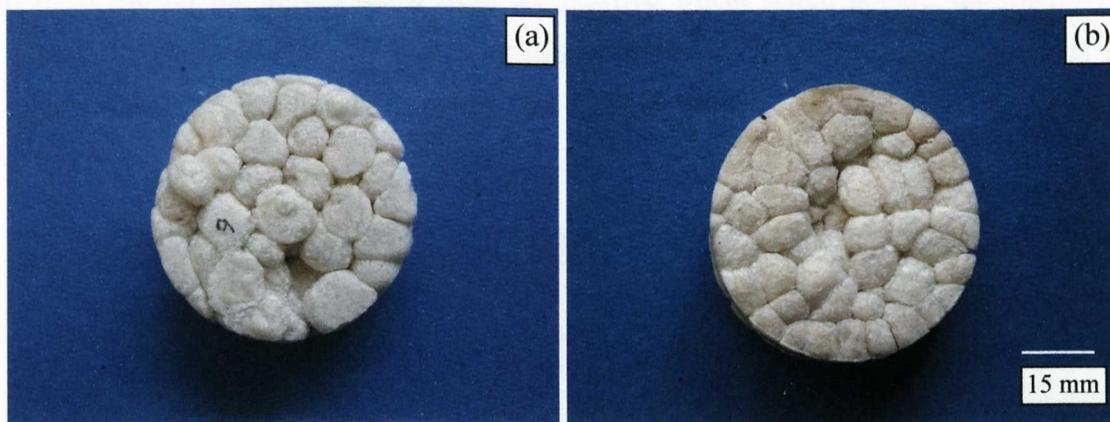
Figure 8.8 The difference in appearance of the external surfaces at the top (a) and the bottom (b) for a Temple flour block.

It was noted that the pellets near the top of the block expanded more than the pellets at bottom, but the foamed blocks could fill sharp corner of the mould better at the bottom (see Figure 8.8). This may be explained by the observation, made in a glass mould, that the pellets at the top started foaming first, probably due to the difference in the penetration of the microwave power. Since there was more free space in the mould in the earlier stages of foaming, the top pellets could expand more freely. These foamed pellets were then pushed up to occupy the available space near the top cap as the pellets under them continued to foam. With the reducing available space in the mould, and the contacts among the foaming pellets, the expansion of the pellets near bottom was restricted, and led to the difference in the extent of expansion or foaming from top to bottom of a block. Furthermore, since the foamed pellets near the top were relative dry because of the moisture loss during foaming, it was more difficult for these foamed pellets to deform at the contacts and fill the mould as well those at the bottom. This would be easily solved, if the exposure to microwave radiation is from variable angles (e. g. from both the top and the bottom of a block), which may be achieved by using an additional horizontal rotation axis.

It has been noticed from the surface appearance of the foamed blocks that the fusion of the foamed pellets is different for those made from the three raw materials. On the surface of the blocks made from the Temple flour pellets, the individual foamed pellets still clearly identified (Figure 8.9 (a)). The addition of salts did not significantly improve the fusion of Temple flour pellets during the microwave foaming (Figure 8.9 (b)). While for the blocks made from the purified wheat starch pellets, the interfaces almost disappear (Figure 8.9 (d)). The extent of fusion for Superfine flour pellets is intermediate, between the starch pellets and Temple flour pellets (Figure 8.9 (c)).
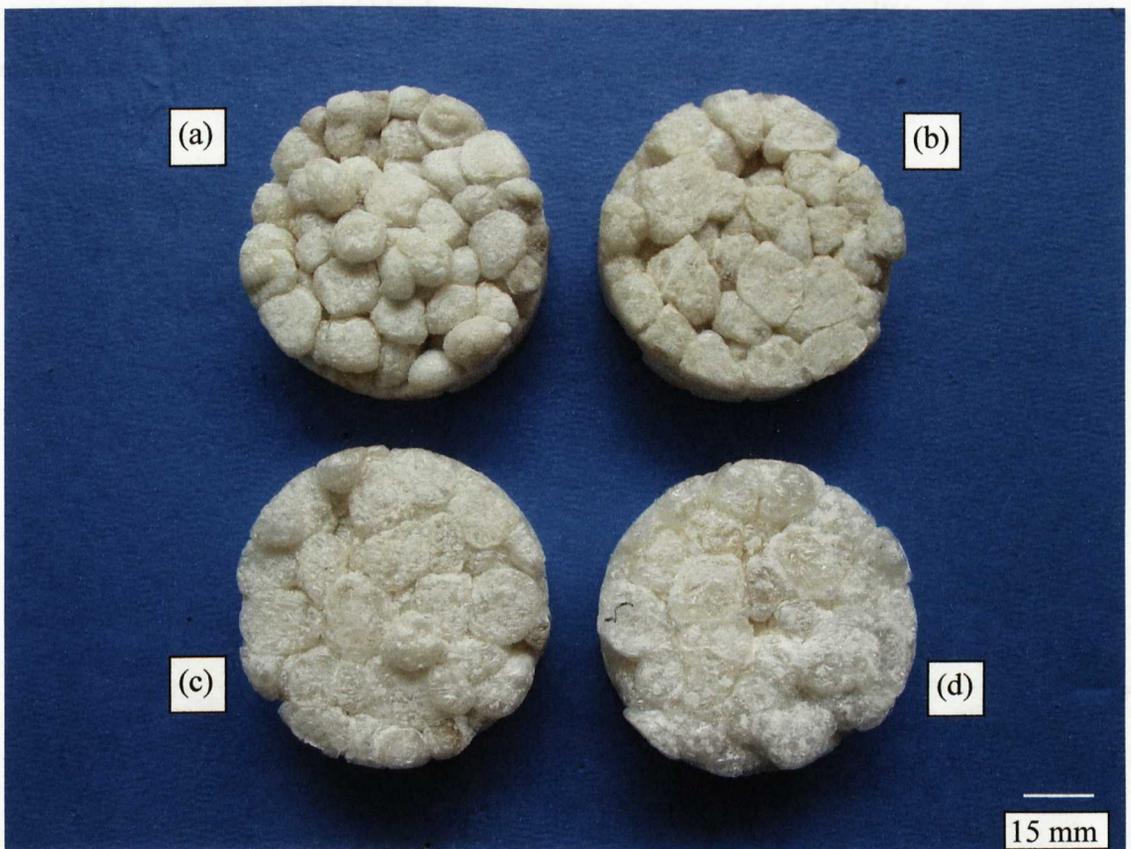
Figure 8.9 Moulding surfaces showing difference in fusion for blocks made from (a) Temple flour; (b) Temple/CaCl₂ (10.5%); (c) Superfine flour; (d) purified wheat starch.

8.5 Properties of the foamed blocks

8.5.1 Cell structures

Figure 8.10 shows SEM micrographs of sections cut along the vertical axis of the disc from foamed blocks made from pellets with different compositions. Although there may exist fusion lines between foamed pellets on the external surface of foamed blocks, most of pellets have been fully fused together in the blocks. Some interfaces between foamed pellets may be identifiable (see Fig.8.10 (a) and (d)), but it is difficult to identify any gaps at the contact areas. No obvious difference in cell structure was observed along the height of blocks, even when the expansion of pellets differ notably at the bottom and top of blocks as described in Section 8.4.
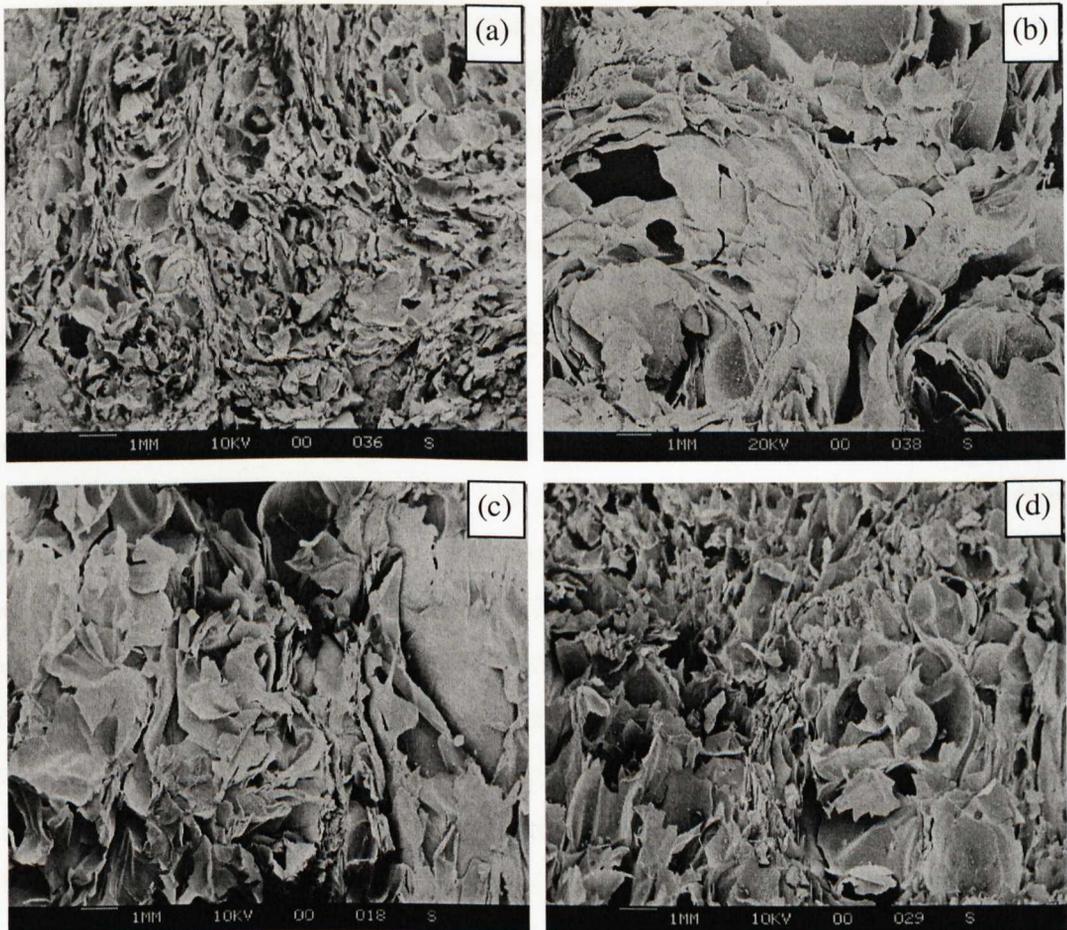

Figure 8.10 SEM micrographs of the sections of microwave foamed blocks made from extruded pellets with different compositions: (a) Temple flour (0.254 g/cm³); (b) Superfine flour (0.215 g/cm³); (c) Purified wheat starch (0.217 g/cm³); (d) Temple/CaCl₂ (0.221 g/cm³).

Comparing Fig. 8.10 with the SEM micrographs of cross section of freely expanded pellets (Figs. 7.4 and 7.5), it can be seen that the differences of cell structures of the foamed block are not only smaller in average cell size, the cell shape was less equiaxial (compared to the almost truncated spheres for the freely expanded foams). The distortion of the cells in foamed blocks indicated that the expansion of pellets was restricted from the contact interfaces or the mould wall during foaming. Since such restriction to expansion is dependent on the free space around periphery of pellets and the area of contacts with the neighbouring pellets, the bubbles in the pellets have an elongated shape with the longer axis parallel to the contact interfaces.

8.5.2 Mechanical properties of the foamed blocks

Figure 8.11 shows the typical compressive stress-strain curves of the microwave foamed blocks measured at 20°C and 50% relative humidity. The initial loadings of pellets into the mould cavity were about 20% for the Temple blocks, and about 16-18% for other blocks. This ensured enough bonding strength among the foamed pellets and acceptable mould filling (about 90%, with the exception of 83% for Temple/NaCl).

Comparing with the compressive stress-strain curves of the freely foamed pellets shown in Figs. 7.7 and 7.8, the marked difference in compression behaviour of these foamed blocks is that the stress peaks for all the samples have disappeared. This is understandable as the cell buckling in individual foamed pellet takes place at different time due to the random orientation of elongated cells. The stress increases linearly with the strain and sharply at the beginning, and followed by a non-linear region in which the foamed block hardened with compressive strain until the tests stop at about 50% strain. To compare the compression behaviour of these blocks with that of freely foamed pellets and EPS block, three parameters have been selected, compressive modulus of elasticity, the compressive stress at 10% strain and deformation energy at 40% strain, which are listed in Table 8.1. The densities, the key factor to influence the mechanical properties for freely foamed pellets, of the foamed blocks are also given in Table 8.1 for comparison.
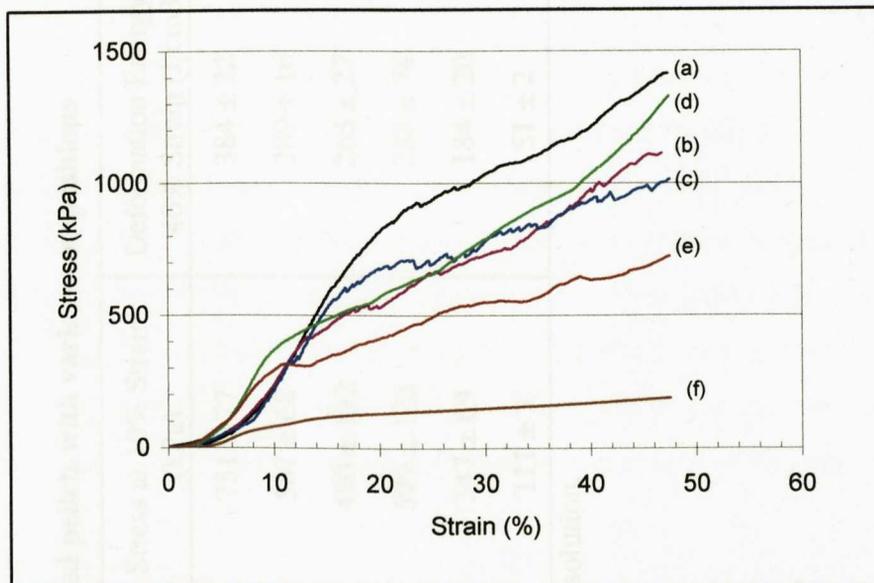
Figure 8.11 Typical compressive stress - strain curves for the foamed blocks made from pellets with different compositions and density: (a) Temple flour (0.254 g/cm³); (b) Superfine flour (0.215 g/cm³); (c) Purified wheat starch (0.217 g/cm³); (d) Temple/NaCl (0.226 g/cm³); (e) Temple/CaCl₂ (0.221 g/cm³); (f) EPS block (0.018 g/cm³).

The data in Table 8.1 show that the blocks with various compositions have similar compressive modulus, noting that there was considerable variation with composition in this parameter for the freely foamed pellets (see Table 7.2). The reason could be attributable to the change in expansion behaviour of pellets when they were foamed in a mould. The mould cavity and initial loading of pellets dominated the expansion instead of pellet formulations. The higher values of compressive modulus and deformation energy, compared with that of the freely foamed pellets, indicates that these blocks are much more rigid and have higher capacity to resist deformation.

8.5 Summary:

Foam blocks using natural materials as feedstock can be produced by the microwave-assisted moulding. Selecting the proper raw materials, combining microwave heating with preheating method, and pre-treatment of pellets are the key issues for fabricating uniform foam blocks with sufficient bonding and fusion among the pellets. The final mould filling and block density are influenced by the initial loading of pellets in the mould cavity and the expansion ratio of the pellets, but the former is dominant. Due to the friction force between the expanding/foaming pellets and the mould wall, the graded formation could alter the cellular structure and hence, the mechanical properties.

Table 8.1 Mechanical properties of microwave foamed blocks from extruded pellets with various compositions

Composition	Block Density (g/cm³)	Relative Density (%)*	Compressive Modulus (kPa)	Stress at 10% Strain (kPa)	Deformation Energy at 40% Strain (J/cm3)
Temple Flour	0.254	19.6	61 ± 7	751 ± 77	384 ± 22
Superfine Flour	0.215	16.5	65 ± 12	567 ± 68	289 ± 16
Starch	0.217	16.8	57 ± 13	480 ± 132	263 ± 27
Temple/NaCl	0.226	17.1	61 ± 8	599 ± 123	288 ± 34
Temple/CaCl₂	0.221	15.8	48 ± 14	347 ± 69	184 ± 20
EPS Block	0.018	-	20 ± 4	111 ± 3	51 ± 2

* Calculated based on pellet density without considering the effect of soaking in the NaCl solution.

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8.6 Summary

Foam blocks using extruded pellets as feedstock can be produced by the microwave assisted moulding method. Selection of mould materials, combining microwave heating with preheating the mould, and pre-treatment of pellets are the key issues for fabricating a uniform foamed block with sufficient bonding and fusion among the pellets. The final mould filling and block density are influenced by the initial loading of pellets in the mould cavity and the expansion ratio of the pellets, but the former is dominant. Due to restriction to pellet expansion from the neighbouring pellets and the mould wall, the pellet formulations have less effect on the cell structure and hence the mechanical properties.

Chapter 9

Conclusions and Suggestions for Future Work

9.1 Conclusions

The aim of this study was to explore the potential of moulding starch-based foams using extruded pellets as feedstock and applying a microwave assisted moulding (MAM) method. It is to address the scientific and technical problems involved in the development of this processing technique and pave the way for producing moulded starch-based foams as biodegradable alternative to oil-base plastic foams for applications such as packaging, thermal and acoustic insulation.

This work have made significant contribution in the scientific understanding of:

a) The requirements for formulation of microwave expandable pellets

b) Optimisation of extrusion conditions

c) Optimisation of expansion in microwave free expansion

d) Optimisation of moulding conditions.

The investigations described in this thesis led to the following conclusions:

1. Extruded wheat flour and purified wheat starch pellets can be foamed by a conventional microwave oven. The expansion of these extruded pellets is highly dependent on composition of the materials, extrusion conditions, the moisture content in the pellets prior to the microwave foaming, and the size of extruded pellets.

- Water content in barrel during extrusion has greater influence on expansion ratio of extruded pellets as compared with other variables, such as extrusion peak temperature and screw speed.

- The optimum moisture content in extruded pellets prior to the microwave foaming to yield maximum expansion during microwave foaming is about 10% for all the extruded pellets investigated.

- Expansion ratio is dependent on size of the pellets. Reduction in pellet size gave rise to decrease in expansion.

- Without additives, the expansion ratio of the pellets made from wheat flours and purified wheat starch at optimum conditions reached 8 –11.

2. Among the characterisation techniques used in this work, X-ray diffraction, rheology of aqueous suspensions, WAI /WSI, microscopy and thermal analysis can all provide information on the thermo-mechanical cooking of starch materials during extrusion, although each has their limitations. Rheology of aqueous suspensions using a rheometer reflect relative degree of cook and allows the assessment across a wider range than most of the other methods. Differential interference contrast (DIC) microscopy was found most effective to directly observe the destruction of starch granules and hence able to visually assess the degree of cook.

3. Hydrophilic additives such as PVAs and glycerol have adverse effects on the foamability of extruded pellets. Both PVA and glycerol lubricate and dilute the materials during extrusion and hence lower the degree of cook of extruded pellets. Moreover, the stronger bonding between water and PVA or glycerol depresses blowing action of water in the extruded pellets during microwave foaming, which lead to poor expansion of the pellets.

4. The physical properties of foamed pellets, such as density, cell structure and equilibrium moisture content can be adjusted effectively by using additives.

- Addition of nucleation agents, such as talc powder, refines the foam cellular structure (cell size decreases and closed cells are dominant) and increases foam density.

- Addition of salts, NaCl (5.5%) and CaCl$_2$ (10.5%), to wheat flour, significantly increase expansion ratio of extruded pellets (from about 8 to 14) and hence markedly reduce the density of foamed pellets (from 0.15 to 0.09 g/cm^3) due to their higher microwave energy absorption capacity which gives rise to higher heating rate during microwave foaming.

- The addition of salts also increases the equilibrium water content of foamed pellets. In the presence of salts the foams absorbs more water from environment which plasticizes and contributes to the overall softness of the material.

5. Mechanical behaviour of the foams can therefore be adjusted effectively by controlling the foam cell structure through using different additives.

- Addition of nucleation agent (e.g. talc powder) assist the formation of more rigid foams. It significantly increases the compressive strength, elastic modulus and deformation energy during compression.

- The addition of salts, on the other hand assist the formation of larger cells and low-density foams and thus more compressible.

6. There are strong correlations between the elastic properties (compressive strength and elastic modulus) of the foams and their density, which can be described by a power law, regardless of the types of raw materials and additives.

7. Foam blocks can be made by the MAM method using an adequate mould material, pre-treatment of pellets and control of initial loading of pellets in the mould cavity.

- PTFE is an appropriate material to make mould for microwave assisted moulding of starch based foam blocks.

- The interfacial bonding between foamed pellets in a block can be significantly enhanced by soaking the pellets in a NaCl solution immediately before microwave foaming.

- Combining convection heating and microwave heating can create a more uniform temperature profile throughout the moulding and give rise to more uniform foaming.

- For a given formulation, there exists an optimum initial loading of pellets, which allow sufficient expansion as well as interfacial bonding to achieve an acceptable extent of mould filling.

- The stiffness of moulded foam blocks is much higher than freely foamed pellets, which is attributable to the restriction in expansion of pellets in a mould cavity.

9.2 Suggestions for future work

Based on the work carried out in this thesis, the following suggestions are made for future research.

Further work at a more fundamental level to elucidate the relationship between physical states of starch polymers in extrudates and expansion behaviour of extrudates during microwave heating are required in order to gain more complete insight into the synergistic effects of extrusion conditions on microwave foamability of starch based extrudates.

Beside the methodologies used in this thesis, dynamic mechanical analysis (DMA) is a technique strongly suggested to be applied for characterizing the extrudates. DMA not only allows accurate determination of T_g (test conducted at room temperature with varying frequency can get rid of the influence of water loss on T_g occurred in TMA), but also provide a approach to assess the viscoelastic properties of extrudates through the storage modulus E' (refers to the energy that is stored by the material during deformation) and loss modulus E'' (refers to the energy this is dissipated during

deformation). Because both E' (elasticity) and E'' (plasticity) strongly relate to the expansion behaviour during foaming, the mechanical spectra (E' and E'') of extrudates with different moisture content against the frequency and temperature may give direct explanation of their microwave foaming behaviour and selection of optimal foaming conditions.

Due to power limitation of the microwave oven used in this work (1000 W), microwave foaming of extruded pellets in a higher range of power need to be examined. Microwave heating at higher power levels may enhance the expansion of extrudates with the compositions investigated in this work and improve the foam properties because of the increasing of heating rate.

Regarding improvement of expansion ratio of the extrudates containing PVAs or glycerol, there are also some further works need to do, e.g., by increasing the severity of treatment during extrusion to disrupt the residual starch granules in the extrudates, which may increase the foamability. This can be achieved by enhancing shearing in extruder through changing screw profile and screw speed provided the extruder has long enough barrels or powerful cooling system to ensure that the temperature of the material in extruder is lower than water boiling point when it arrives at the die exit.

In the aspect of manufacture of extruded pellets to produce softer foams, the further exploration should be focused on decreasing the foam density (or increasing the expansion ratio), increasing the number of open cells (i.e. to control the cell structure), and softening foam cell walls (i.e. to plasticize the material). Selection of additives and foaming process conditions should aim to create higher heating rate, larger water vapour (and/or other gas) pressure, and low melt viscosity to allow extensive expansion and bubble burst to reduce density and increase fraction of open cells.

It is important to study the mechanism and process of microwave foaming of starch based extruded pellets, i.e., to build physico-chemical models for describing bubble nucleation and growth in extruded pellets and the moulding process during microwave heating, which creates foamed blocks. However, this is a very tough task, because the modelling requires the knowledge of the viscpelastic properties of pellets as function of moisture, temperature, pressure and time, water transport behaviour (diffusion and

vaporisation) in the pellets and mould cavity as function of temperature and moisture concentration, dielectric properties of pellets as function of temperature and moisture content, temperature distribution throughout moulding, etc., and some of these are very difficult to measure.

In the aspect of moulding process technology to produce foamed blocks, modification of processing facilities is the key. It is believed that a mould which can hold and suddenly release pressure during microwave heating will help to improve not only expansion of the pellets but also mould filling and fusion of extruded pellets. A microwave oven with a frame which can roll the mould along both vertical and horizontal axes simultaneously or with microwave generators at different positions (such as both top and bottom) will help to increase heating rate and achieve heating uniformity, which in turn improve the quality of foamed blocks.

All these topics mentioned above deserve exploration.

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