"The last thing one knows in constructing a work is what to put first".

Blaise Pascal (1623–1662), *French philosopher, mathematician, and physicist.*
Pensées.

CHAPTER 1

INTRODUCTION

1.1 SCOPE AND STRUCTURE OF THE THESIS.

The present work is concerned with the investigation of the deformability of the dispersed phase of a binary polymer blend into elongated continuous domains. More specifically, the project explores the possibility of producing continuous fibres of an intrinsically electro-conducting polymer embedded in an insulating polymer matrix so as to form an anisotropically conducting composite. Furthermore, the research included the experimentation with different polymer systems.

The thesis begins providing a technical perspective on the research conducted together with a statement of the objectives of the project. These are provided in the present chapter, which is followed by a chapter outlining fundamental concepts and a review of the literature related to this study that includes conductive polymers, flow of polymer melts and the theory of droplet deformation and breakup, among others.

The raw materials used are described in chapter 3, which also gives an account of the criteria used in their selection. Chapter 4 is concerned with the characterisation of the raw materials. This provides details of the techniques employed, including X-ray diffraction, gravimetry, infrared spectroscopy, thermal analysis, rheology, conductivity measurements and microscopy. The results obtained from the characterisation analysis together with their discussion are also presented in the same chapter. From the results, those from the rheological analysis were determinant in selecting the most suitable polymer system.

Chapter 5 is dedicated to the preliminary experimentation with different systems, compositions and compounding techniques, including manual mixing, roll milling, extrusion and melt mixing. The forming process, that is, ram extrusion, as well as the experimentation with different processing parameters is also described in chapter 5. Chapter 5 is of fundamental importance since this is where the criteria for selecting the most appropriate compounding technique and forming process conditions are reviewed.

The production of different blend compositions of the selected polymer system, using melt mixing under improved processing conditions is described in chapter 6. This chapter also includes sections concerned with the characterisation of the blends, namely morphological and electrical. The forming of the blends is reported in chapter 7, which also includes the morphological and electrical characterisation of the extrudates.

This work also includes the mathematical modelling of the conductivity behaviour with respect to the blends' composition. This is presented in chapter 8, which describes the two approaches followed: percolation theory and a generalisation of effective media theories.

Although conclusions are presented in each of the chapters (i.e., when relevant), it is in chapter 9 where these are compiled. The recommendations for further work are also included in this chapter.

The references, spanning from 1962 to 2001, include journal papers, patents, technical data sheets, standard test methods, textbooks, and PhD and BSc theses, among others. They are indicated throughout the text with numbers between square brackets, running in numerical order, and listed in citation order at the end of the thesis.

Finally, the appendices, presented in the last section of the thesis, include some charts from the rheological analysis together with some of the products of the research, namely a journal paper and reprints from conference proceedings. As a common feature, all the chapters dealing with experimental or analytical methods include the description of the methods, results and their discussion.

1.2 TECHNICAL PERSPECTIVE.

The scientific developments that occurred at the end of the last century have dramatically changed the way in which polymers are envisaged nowadays. For example, there was general agreement that polymers, unlike metals, do not conduct electricity. In fact, some polymers are used as insulation round the copper wires in ordinary electric cables. In spite of this, the winners of the 2000 Nobel Prize in Chemistry were rewarded for their revolutionary discovery that polymers can in fact, after certain modifications, be made electrically conductive.

The winners of the Nobel Prize, Heeger, McDiarmid and Shirakawa, made their inspired findings at the end of the 1970s and subsequently developed conductive polymers into a research field of great importance for chemists, physicists and materials scientists. The area has also yielded important practical applications. For instance, conductive polymers are used in, or being developed industrially for antistatic

substances, photographic films, shields for computer screens against electromagnetic radiation and smart windows that can exclude sunlight, among many other applications.

It is therefore in the field of antistatic materials that a binary polymer blend displaying a morphology of electro-conductive polymer fibres embedded in an insulating matrix could find practical applications, more specifically in carpet and textiles industries. Static charges can be built up on many materials by friction, separation, or induction processes [1], for example whenever two different materials, such as shoes on a carpet, are rubbed together. Once charge is generated, the nature of the material will determine how that charge is dissipated, either by leaking away slowly or conducting suddenly (perhaps damagingly) through another product. Static control seeks to prevent damage caused by the sudden discharge of this electrostatic potential from one body to another, which in the more severe cases can destroy sensitive electronic components or cause explosions in dusty or solvent laden atmospheres.

To reduce the static buildup on carpets, antistatic chemicals can be applied to the carpet, or permanent antistatic filaments can be incorporated into the carpet yarns. Antistatic chemicals are generally only effective at certain humidity levels. For example, under low humidity conditions the carpet may allow high levels of static buildup [2]. In addition, antistatic chemicals may be removed by heavy traffic and cleaning. On the other hand, manufacturing carpets by interweaving antistatic filaments, consisting of electrically conducting polymer fibres embedded in an insulating polymer matrix (refer to fig. 1.1), could effectively limit static buildup at any humidity and temperature. Unlike antistatic chemicals, the conducting fibres would be integral to the carpet throughout its life.

One promising approach for manufacturing this type of filament is to generate the electro-conductive fibres in-situ, that is, during the actual forming process of the filaments. This has been the subject of extensive investigation and it has been shown that under appropriate conditions, the dispersed phase of a binary polymer blend can deform into ellipsoids or even short fibres.

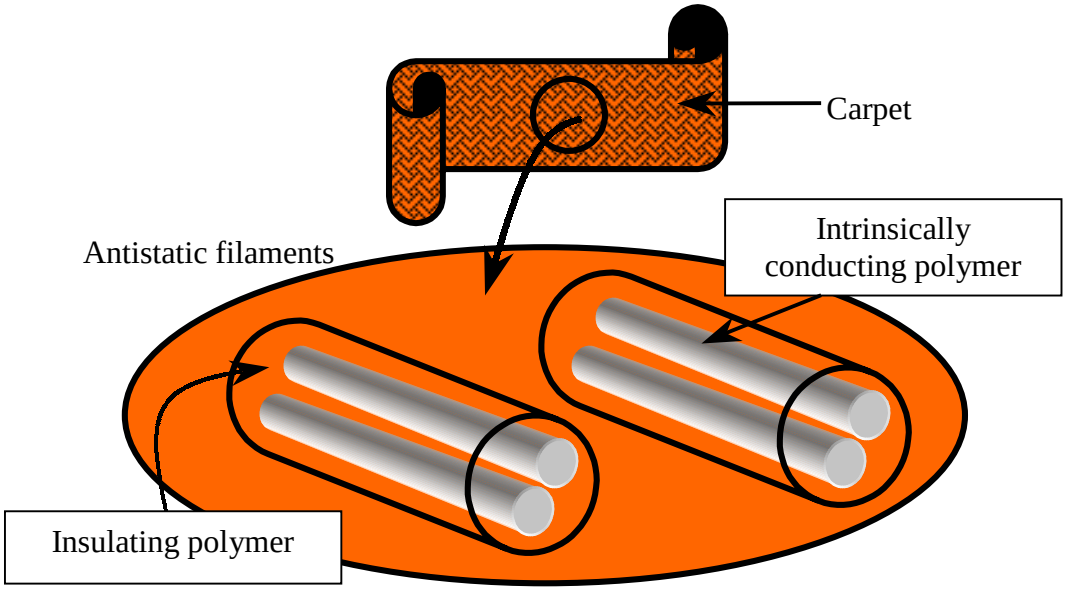

Figure 1.1. Schematic representation of the use of antistatic filaments in the manufacture of carpets.

To produce fibres in-situ, a binary (or higher) polymer blend is required. The phases should be immiscible, with one phase being well dispersed in the other matrix phase. It has been shown that under certain processing conditions and materials' parameters (i.e., processing equipment, type of flow field, shear rate levels, ratio of the viscosity of the dispersed phase to that of the matrix, and interfacial tensions, among others) the action of the matrix on the dispersed phase may be such to extend the dispersed phase into ellipsoids or even fibres. For example it has been demonstrated that during processing by capillary extrusion, elongational flow fields taking place at the entrance of the capillary played an important role in the generation of fibres. On the other hand, there is evidence that when the viscosity of the dispersed phase is lower than that of the matrix it is easier to deform the dispersed phase into elongated domains (the reader is invited to consult the references cited in the relevant sections of chapter 2).

In the present work, an intrinsically electro-conducting polymer was used as the dispersed phase (refer to sections 2.2 and 3.2). Advantages in using such a material over other conducting fillers, like metal particles or carbon black, include the relatively low content needed to yield a high electrical conductive blend. In addition, the material used has the characteristic of lowering the viscosity of the blends, which facilitates their

processability. With respect to the polymer matrix, experimentation was performed with three commercial polymers. Their properties are described in the relevant chapter.

1.3 OBJECTIVES.

The objectives of the present work are the following:

- To establish the feasibility of producing electrically conductive fibres of an intrinsically conductive polymer, fully aligned within a suitable polymer matrix, so as to form an anisotropically conducting composite.
- To explore different processing routes for the production of an anisotropically conducting composite.
- To experiment with different polymer systems in order to find the most suitable one for the production of an anisotropically conducting composite.
- To investigate the behaviour of the electrical conductivity with respect to the content of electrical filler in the composite.
- To analyse the microstructure of the conductive composites.
- To correlate the behaviour of the conductivity with the microstructure of the conductive composite.