Fabrication and characterisation of polypropylene nanofibres by melt electrospinning and meltblowing

A thesis submitted in fulfillment of the requirements for the degree of

Doctor of Philosophy

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Masters in Textile Technology, 2001

School of Fashion and Textiles
Design and Social Context Portfolio
RMIT University
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Declaration

I, Rajkishore Nayak, certify that:

a. except where due acknowledgement has been made, the work is that of the candidate alone;

b. the work has not been submitted previously, in whole or in part, to qualify for any other academic award;

c. the content of the thesis is the result of work which has been carried out in the School of Fashion and Textiles, RMIT University;

d. any editorial work, paid or unpaid, carried out by a third party has been acknowledged;

e. ethics procedures and guidelines have been followed.

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Rajkishore Nayak

March 2012
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DEDICATION

This work is dedicated to my parents, my parents-in-law, my uncles, my wife and my son.
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Abstract

This research has investigated the scope of fabricating nanofibres of polypropylene (PP) by two different melt processes: melt electrospinning and meltblowing. This study achieved uniform nanofibres of PP by melt electrospinning with the introduction of additives such as sodium oleate (SO) and sodium chloride (NaCl) which increased the electrical conductivity of the polymer melt. Rheology modifiers such as polyethylene glycol (PEG) and polydimethylsiloxane (PDMS) were used to lower the viscosity of the polymer melt which resulted in the decreasing of the fibre diameter. However, the fibres obtained by reducing the melt viscosity were in micrometre or micron (µm) size and less uniform compared to the results obtained with increasing the electrical conductivity. Preliminary studies were undertaken to establish the optimum processing parameters such as temperature, applied voltage, collector distance, melt flow rate and spinneret size prior to the fabrication of nanofibres.

The average fibre diameters achieved by the use of pure polymers of 100, 300, 1000 and 2000 melt flow index (MFI) were in the range of 3.01-14.19 µm. The average fibre diameter was decreased with the increase in the polymer MFI, applied voltage and collector distance. The increase in the melt flow rate and the spinneret size resulted in the increase of the average fibre diameter. The optimal amount of SO and NaCl were 7% and 5% respectively for the fabrication of nanofibres from 1000 and 2000 MFI PP. The lowest average fibre diameters (were achieved from 2000 MFI PP) were 0.371 ± 0.106 µm and 0.310 ± 0.102 µm corresponding to the optimum conditions of SO and NaCl respectively. This research established the fact that there is no effect of the die shape on the cross-sectional shape of the melt electrospun fibres. Unlike other melt processes such as meltblowing, meltspinning; melt electrospinning resulted only in circular fibres by the use of trilobal, tetralobal and multilobal die.

This study demonstrated the scope of fabricating nanofibres by meltblowing with the injection of various fluids such as air, nitrogen (N₂) and water. The use of water worked better in terms of fibre morphology and diameter compared to the use of air and N₂ for the fabrication of nanofibres. The lowest fibre diameter of 0.438 µm was achieved from the 300 MFI PP with water supply.

This study also established the fact that the molecular weight was the predominant factor governing the fibre diameter in melt electrospinning. In contrast, the molecular weight was not the predominant factor governing the fibre diameter in meltblowing. The polymers with the lowest molecular weight resulted in the formation
of the finest fibre in melt electrospinning. However, the lowest molecular weight polymer was really difficult to process in meltblowing and did not produce fibres. The effective collector distances for nanofibre fabrication in the case of melt electrospinning were lower compared to the meltblowing. The polymer feed rate was substantially lower in the case of melt electrospinning (i.e. 0.64 g/hr) compared to meltblowing (i.e. 80 g/hr).

The results of energy dispersive x-ray (EDX) and Fourier transform infrared (FTIR) studies established the presence of additives in the melt electrospun fibres. Similar FTIR and NMR spectra of the polymer and the fibres indicated that there was no chemical change of the fibres fabricated by the application of various fluids and high temperature during meltblowing. The melting points of the fibres fabricated in melt electrospinning and meltblowing shifted to lower values compared to the initial polymer. This change was due to the thermal degradation caused by the high temperature during melt electrospinning and meltblowing.

The degree of thermal degradation was higher in the case of meltblowing due to the higher residual time inside the extruder which was verified by comparing the change in the molecular weights of the fibres fabricated by these processes. X-ray diffraction (XRD) studies showed that all the fibres fabricated by melt electrospinning and meltblowing contained low degree of crystallinity. The crystallinity, tensile strength and modulous of the meltblown fibres were increased with annealing. The fibres fabricated by melt electrospinning and meltblowing showed high values of contact angle indicating the hydrophobic nature. The additives SO, PEG and NaCl were washed away from the fibres fabricated by melt electrospinning. Hence, this research has achieved the goal of fabricating nanofibres and added new knowledge to the field of nanofibres.
Chapter 1 - Introduction

1.1 Scope
Polymers have become an indispensable part of modern life due to their relatively low cost, easy processability, physical, chemical and optical properties [1]. Polymeric fibres with average diameter ranging from 10 to 50 µm are commonly produced as nonwoven webs by traditional methods such as melt spinning, dry spinning and wet spinning [2-4]. A nonwoven web is a sheet or mat of fibres connected together by physical entanglements or adhesion between individual fibres without any knitting or stitching [5]. The nonwoven webs are widely used in various applications such as filtration, wound dressing, hygiene products and protective clothing.

Recently, various engineering fields have given great attention to the formation of nonwoven webs consisting of nanofibres, commonly known as nanowebs. Nanofibres are defined as fibres with diameter of 100 nm or less [6]. However, for the current research, nanofibres will be considered as fibres with diameter less than 1 micrometre (µm). The nanowebs are notable for their characteristic features such as large surface-area-to-volume ratio, extremely small pore dimensions and superior mechanical properties [7]. Due to these features, nanowebs are being investigated in a wide range of applications in areas such as high-performance filtration, wound dressing, vascular grafts, enzyme immobilisation, electrochemical sensing, composite materials, blood-vessel engineering and tissue engineering [8-10].

Existing fibre spinning technologies cannot produce fibres with diameters smaller than 2 µm due to limitations inherent in the process. The process most commonly employed for the fabrication of nanofibres is electrospinning [11, 12]. Electrospinning is a simple and versatile method for the production of continuous micro– and nanofibres from a variety of polymers, as well as inorganic oxide materials [13]. Other processes capable of producing nanofibres include meltblowing, flash spinning, bicomponent spinning, force spinning, phase separation and drawing. In most of these processes, the nanowebs consist of fibres with average diameter ranging from several nanometres to hundreds of nanometres.
The electrospinning process can be classified into two groups: solution electrospinning and melt electrospinning, based on the way the polymer is prepared [14]. In solution electrospinning, the polymer is dissolved in a suitable solvent and the resultant solution is electrospun, whereas in melt electrospinning, additional heating equipment is required for converting the solid polymer into melt for electrospinning [15].

Solution electrospinning has certain limitations, mainly related to the use of solvents, which may require solvent recycling or may be difficult to remove from the sample [16]. In melt electrospinning, as no solvent is used, it is free from the complex and expensive solvent–recycling process. Melt electrospinning is free from the toxicity associated with solvents and additional cost of solvents [17]. Solvent toxicity is of primary concern for tissue–engineering applications. When direct in-vitro electrospinning into body parts or cells is required, solution electrospinning fails to fulfil these requirements due to the toxicity of the residual solvents [17]. Melt electrospinning provides new horizons in electrospinning as it is free from the above technical limitations.

In addition, the productivity of melt electrospinning is higher as there is no loss of mass due to solvent evaporation [18]. Melt electrospinning favours the production of multi-component systems such as blends and composites, as in many cases no common solvent for all the components is available [19]. Theoretical modelling of melt electrospinning is much easier as it is free from the complications associated with solvent evaporation [20]. Thermoplastic polymers such as polyethylene (PE) and polypropylene (PP) are not soluble in solvents at room temperature. Hence, these polymers cannot be used in solution electrospinning. Melt electrospinning is the alternative to address this problem of thermoplastic polymers.

Although there are a large number of publications on solution–based electrospinning, publications on electrospinning of polymer melts are relatively small in number. This is due to more demanding conditions such as the requirements for high temperature and low electrical conductivity of the melt [21]. Apart from these, the difficulty of obtaining nanofibres in melt electrospinning is associated with the high viscosity of the polymer melt. Furthermore, only thermally stable additives can be added to the polymers used in melt electrospinning and the process is associated with electric discharge problem. As a result, melt electrospinning has not drawn much attention from researchers [22].
In addition to melt electrospinning, the other process with potential for the fabrication of nanofibres of thermoplastic polymers is meltblowing [23]. Meltblowing is a simple, versatile and one-step process for the production of fibres/filaments directly from polymers in the nanometre to micrometre range [24]. In the nonwoven industry, meltblowing has become an important technique to produce nonwoven webs of microfibre structure suitable for many applications. Most of the research in the last 20 years on meltblowing has focused on the factors influencing web properties, improving web quality and modelling of the process [25-29]. Limited research has been done on the fabrication of nanofibres by meltblowing [30, 31].

The common polymers used in melt-based industries are the polyolefins (especially PE and PP) due to their commercial importance and versatility for making a wide range of products. Since first synthesised in 1954, PP fibres have been widely used in applications such as medical [32], electrical insulation [33], optical [34], protective clothing [35], thermal insulation [36] and filtration [37] due to their chemical inertness, low surface energy, light weight, lack of heat shrinkage and good mechanical properties [38]. There is a dearth of similar literature for polyolefins in the form of nanofibres. Melt electrospinning and meltblowing are the processes which can produce new horizons in the fabrication of advanced materials from polyolefins. However, these processes have not drawn much attention of researchers due to polyolefins requiring either melting at high temperature or dissolving in a solvent at elevated temperature.

The viscosity of polymer melt is of a magnitude higher than those reported for solutions [21]. This may be a reason why it is difficult to fabricate nanofibres from polymer melt. There are several ways to reduce the viscosity of polymer melts to improve their processability. These include: (i) increasing the processing temperature [22]; (ii) altering the polymer by adjustment in chain configuration; and (iii) use of additives such as surfactants or rheology modifiers [39].

For thermoplastic polymers, a direct correlation exists between melt temperature and viscosity [22]. Higher temperature reduces the viscosity, which results in the fabrication of finer fibres, but increases the risk of thermal degradation [16]. The other approach, of using additives such as surfactants or rheology modifiers to lower the viscosity of the
medium in which they are mixed, has been investigated by several researchers, mainly for the fabrication of microfibres [40, 41]. The thermoplastic polymers such as PP show very low electrical conductivity [42]. The addition of conducting materials can increase the electrical conductivity of the melt [43]. Therefore, in this research the approach of addition of additives to lower the viscosity and improve the electrical conductivity has been adopted for the fabrication of nanofibres.

1.2 Research concepts and hypotheses

This research project investigates the scope of fabricating nanofibres by two different melt processes: melt electrospinning and meltblowing. The main objective is to fabricate uniform nanofibres, and characterise and compare the results of these two processes. The major challenge is to overcome the high viscosity and low electrical conductivity of the polymer melt which prevent the formation of nanofibres. The scope of this research is to derive a suitable means of reducing the viscosity and increasing the electrical conductivity. The possibilities are:

1. Introduction of various fluids (such as air, water and nitrogen) during the meltblowing process to fabricate nanofibres. The hypothesis is to attenuate the melt–jet into nanofibres by creating a high–velocity flow of the mixture of fluids and the polymer melt,

2. Use of additives such as rheology modifiers in melt electrospinning for the formation of nanofibres. The hypothesis is to reduce the melt viscosity and improve the melt processability, so that the polymer melt can flow through the fine orifices. On the basis of the information provided in the literature, it was decided to use the following rheology modifiers: polyethylene glycol (PEG) and polydimethylsiloxane (PDMS),

3. Use of additives in melt electrospinning to increase polymer electrical conductivity. The electrical conductivity of polymers used in melt electrospinning is very poor. The hypothesis is to improve the electrical conductivity of the polymer melt for the formation of nanofibres [44]. Sodium oleate (SO) and sodium chloride (NaCl) were selected to improve the electrical conductivity, as these additives contain ions which can improve the electrical conductivity and are readily available.
1.3 Aims and objectives

The main objective of this research project is to explore means of fabricating nanofibres using the techniques of melt electrospinning and meltblowing. Limited work in this area has encouraged the author to investigate this field. The detailed objectives of the current study are:

1. To fabricate uniform nanofibres of PP by melt electrospinning and meltblowing,
2. To identify the optimum conditions in melt electrospinning such as die temperature, collector distance, applied voltage and polymer flow rate for the fabrication of nanofibres using PP of different melt flow index (MFI) or molecular weights,
3. To investigate the effect of different rheology modifiers (or viscosity–reducing agents) and additives (which increase the electrical conductivity) on the morphological and physical properties in melt electrospinning,
4. To establish the optimum conditions in meltblowing such as extruder and die temperatures, collector distance, type of fluid, flow rates for the fabrication of nanofibres using PP of different MFI or molecular weights,
5. To investigate the effect of various die shapes, other than circular, such as trilobal, tetralobal and multilobal on the resultant fibre cross-section,
6. To investigate the effect of mixing different fluids (air, water and nitrogen) during meltblowing on the morphological and physical properties of meltblowing,
7. To characterise the nanofibres fabricated in melt electrospinning and meltblowing according to their size and morphology,
8. To measure the thermal and crystalline properties including the melting behaviour, crystallinity and types of crystal forms of the fibres,
9. To investigate the mechanical properties of the nanofibres fabricated by melt electrospinning and meltblowing; and
10. To investigate the effect of annealing on the physical and mechanical properties of the fibres fabricated.

1.4 Contribution of the research

The research work focuses on the fabrication of nanofibres by: using additives which modify the rheology and the electrical conductivity of the polymer melt in melt electrospinning; and mixing various fluids into the polymer melt during the meltblowing
process. The resultant fibres were characterised using techniques such as optical microscopy (OM); scanning electron microscopy (SEM); Fourier transform infrared (FTIR); nuclear magnetic resonance (NMR); energy dispersive x-ray (EDX); x-ray diffraction (XRD); differential thermal calorimetry (DSC); thermo gravimetric analysis (TGA); and mechanical characterisation.

In addition, the shear viscosity and electrical conductivity of the melt were analysed to understand the effect of additives on the fibre diameter. The surface wettability of the samples was evaluated by measuring the water contact angle. Hence the completion of this research will contribute new knowledge to the field of melt electrospinning and meltblowing. The effect of die shapes on fibre morphology will add another aspect to melt electrospinning. Furthermore, a fundamental understanding of the limitation of the melt electrospinning and meltblowing process which prevent the fabrication of nanofibres can be gained. Finally, the research will add more knowledge to the field of nanofibre fabrication and characterisation.
Chapter 2 Review of literature: melt electrospinning

2.1 Introduction
Nanotechnology is an interdisciplinary area of science and technology dealing with the materials having dimensions in the range of 0.1–100 nanometres (nm). Recently, nanotechnology has been booming in many important areas such as medicine, engineering, electronics and textiles. In fibrous materials it has predominantly come up in the form of electrospun nanofibres. The process widely used for the fabrication of nanofibres is electrospinning [11, 12] due to its simplicity and suitability for a variety of polymers. Other processes with the potential for the fabrication of nanofibres include flash spinning, bicomponent spinning, force spinning, meltblowing, phase-separation and drawing. In most of these processes, the fibres are collected as nonwoven random fibre mats known as nanowebs, consisting of fibres having diameters from a few nanometres to hundreds of nanometres.

2.2 Electrospinning
Electrospinning is the distortion of a droplet by the application of electric charge. It can be traced back to William Gilbert’s published work in 1600 AD [45, 46]. Electrospinning is based on the principle of electrostatic instabilities in liquids or the distortion of a droplet by the application of electric charge [47]. The earliest and still the most widespread practical application of these instabilities is electrospraying. Electrospinning is mainly employed for the fabrication of fibres with diameters ranging from tens of nanometres to a few micrometres from a number of polymers including both synthetic and natural as well as biopolymers [7, 13, 47-51].

The schematic of an electrospinning device is shown in Figure 2-1 (a). Generally, in electrospinning, a liquid droplet is delivered to the tip of a capillary. When an electric field is applied, charges accumulate on the surface of the pendant droplet formed at the tip of the capillary and create an instability that deforms the hemispherical droplet into a conical shape, referred to as a Taylor cone [52, 53]. At this stage, there is a competition between the Coulombic repulsion of like charges favouring droplet distortion and surface tension opposing droplet division. When the applied electric field strength is sufficiently high, a liquid-jet is continuously ejected from the apex of the cone and travels towards the grounded plate as a barely visible nanoscale fibre (Figure 2-1, b).
The high charge density on the surface of the fine jet leads to electrical instability, making it whip around rapidly. The jet diameter decreases due to stretching (whipping) and evaporation of the solvent.

![Schematic diagram of electrospinning device and Taylor cone](image)

Figure 2-1: Schematic diagram of: (a) electrospinning device and (b) Taylor cone [52, 53].

### 2.2.1 Types of electrospinning

Electrospinning can be classified into two groups: solution electrospinning and melt electrospinning, based on the nature of the polymer used [54]. In the last two decades, research activities in electrospinning were mainly focused on solution electrospinning [43, 55-57], whereas there are few works reported on melt electrospinning [58-60]. However, solution electrospinning of polyolefins, including polyethylene and polypropylene, has been limited due to high solvent resistance and high electrical resistivity [43].

#### 2.2.1.1 Solution electrospinning

In solution electrospinning, the polymer is dissolved in a suitable solvent and the resultant solution is electrospun. Almost all the previous research focus on the fabrication of nanofibres by solution electrospinning.

#### 2.2.1.2 Melt electrospinning

In melt electrospinning, the polymer is heated to melt for electrospinning. Melt electrospinning has many advantages over solution electrospinning. Melt electrospinning is preferred where the problems of solvent recovery and toxicity are a concern. In melt electrospinning, the dissolution of polymers in organic solvents and the subsequent removal of the solvents are not required. Hence, it is free from the extra cost of solvents,
and complex and expensive solvent–recycling equipment. While in-vitro electrospinning directly onto cells is considered, solution electrospinning fails to meet the criteria. This is due to the toxicity of the solvent used in electrospinning, which needs to be fully removed prior to in-vitro use [57]. Electrospinning directly onto cells is possible via melt electrospinning as the fibres contain no residual solvent and are free from the toxicity [17].

Melt electrospinning can commercially fabricate fibres of polymers with no proper solvent at room temperature such as PE, PP and polyethylene terephthalate (PET). In the case of PP, one of the most widely used polymers in commercial spinning it is difficult to find a suitable solvent at room temperature. Hence, melt electrospinning provides an edge over solution electrospinning. Melt electrospinning also favours the production of multi-component systems such as blends and composites, as in many cases no common solvent for all the components may exist [22]. Besides, the modelling of melt electrospinning is much easier as it is free from the complications associated with solvent evaporation.

In spite of these advantages, there has been limited work on melt electrospinning. This may be due to the limiting constraints associated with the process such as: (i) the complex equipment used [61]; (ii) the electric discharge problem associated with the equipment design [18]; and (iii) the intrinsic difficulties associated with the polymer, such as high viscosity and low electrical conductivity [22]. The following section focuses on melt electrospinning (including the components, various configurations, polymers used and fibre diameters obtained).

The designing of equipment for melt electrospinning is complex compared to that for solution electrospinning. A melt electrospinning system is composed of the following components: high-voltage power supply, heating-assembly, syringe pump, temperature controller and collector (Figure 2-2).
2.2.1.2.1 High-voltage supply

Generally, direct current (DC) is used as the source of power supply although it is feasible to use alternating current (AC). Very high-voltage (usually in the range of 10–30 kV) is required for electrospinning. Lyons claimed that the polarity of the electrospinning system is arbitrary and can be reversed depending on the polymer type and final product [62]. The same production efficiency can be obtained without the damage to the extruder by changing the poles. If the spinneret is grounded and the collector is positively charged, the same electric field strength is created compared to the reverse approach.

2.2.1.2.2 Heating assembly

The heating-assembly is designed to melt the polymer to a suitable viscosity which can be electrospun easily. In all the heating assemblies, the major objective is to melt the polymer by providing heat from various sources such as: heating element, heating gun, laser heating and ultrasound heating. The heating-assembly works as a reservoir for the polymer melt. Some of the equipment used by various researchers for melt electrospinning are shown in Table 2-1. A spinneret is connected to the heating-assembly at one end for the production of nanofibres.

2.2.1.2.3 Syringe pump

During the melt electrospinning process, a syringe pump is used to pump the polymer melt at a constant and controllable rate through the spinneret.
2.2.1.2.4 Collector

The collector or the collecting surface is used to collect the electrospun fibres. Surfaces of different geometry and configurations are used as collectors. The collector is mounted on an insulating stand so that its electric potential can be controlled. In melt electrospinning devices, the high-voltage is applied to the collector and the syringe is grounded.

2.2.2 Jet trajectory

There is a remarkable difference between the trajectories of the jet in solution and melt electrospinning. In solution electrospinning, it has been established by numerous studies and models that the jet undergoes bending or whipping instability, which causes drastic stretching and thinning of the fibre [45-48]. However, in melt electrospinning the bending instability is either much weaker and localised [22] or not present at all [42, 49-50]. The weak or lack of bending instability can be attributed to the high viscosity of the polymer melt [53]. In addition, the high surface charge density is also responsible for the occurrence of the bending instabilities in solution electrospinning. As in melt electrospinning, the majority of the polymers are electrically insulating, there is very little or no such instability [63].

Bending instabilities help in the reduction of the jet diameter to the order of nanometres, resulting in nanofibres. Suppression of these instabilities in melt electrospinning will appreciably prevent the stretching and hence result in a fibre diameter mainly in the micrometre range. When the electrospinning temperature is low, fast solidification of the jet is believed to suppress the instability in melt electrospinning [22]. It was found that in melt electrospinning with higher voltages, the bending instability was stronger and more irregular, similar to solution electrospinning [64]. In addition, at lower flow rates, the whipping motion became more vigorous.

2.3 Research on melt electrospinning

The initial work on melt electrospinning was presented in a patent approved in 1936 from Charles Norton from Massachusetts Institute of Technology where an air-blast was used to assist fibre formation [65]. The first scientific publication was reported by Larrondo and Manley [66-68] using thermoplastic polymers in 1981 as a three-paper
series. Of the three papers, only the first one actually demonstrated the formation of fibres from a pendant molten droplet of PE and PP. In this work, they fabricated fibres of greater than 50 µm in diameter from PP of 0.5–2 MFI at collector distances of 1–3 cm and applied voltages of 3–8 kV/cm.

The second paper was the modelling of the flow field in an electrostatically drawn jet using viscous silicone oil in the place of polymer melts. The third paper illustrated the deformation effects of an electrostatic field on a molten polymer droplet of PE or Nylon-12 suspended in hexane. Until these works, it was believed that only fluids and polymer solutions could form such jets under the effect of electrostatic field. This work established the fact that a molten polymer can be drawn electrostatically and was in compliance with Taylor’s formulae for other fluids [53]. Subsequently several researchers worked on melt electrospinning with several configurations using different polymers, which are highlighted in the following section.

2.3.1 Equipment used

A variety of equipment has been used by researchers which may differ by the modes of heating, heating system, material feed and collector design. When designing melt electrospinning equipment, the important thing is the selection of a suitable heating system. A variety of equipment with different means of heating, such as electrical heating by heating elements [22, 69], [63]; laser heating devices [15, 18]; and heating by circulating fluids (i.e. heated air by heat guns [60, 70], circulating oil) have been used. Among these, electrical heating is widely adopted for melt electrospinning as it is easier to design and use [16]. The electrical heating system should be isolated from the high-voltage power supply in order to prevent potential disruptions with the electric field. Therefore in many experiments high-voltage is applied to the collector and the spinneret is grounded. However, a system has been described by Joo et al. [71] which overcomes the issue of isolation from the high-voltage source.

Electrospinning by laser or laser electrospinning has been used by several researchers [44, 50, 59]. A solid polymer sample in the form of a rod or sheet is fed to the laser melting zone, where it is melted. The lasers uniformly and locally heat the sample at the interaction point with the polymer. The polymer is heated instantly and locally in the
laser melting system and therefore can avoid thermal degradation. The electric discharge problem associated with the conventional melt electrospinning can be prevented in laser electrospinning as heating is performed from a distance. The other advantage of laser melting is that the fibres can be fabricated from polymers containing impurities, as nozzles are not used in this equipment. In laser electrospinning, there is no report regarding the temperature of the heating zone, but the power intensity has been reported.

Another approach is heating by a heat gun, which is a simple, safe and inexpensive approach for melt electrospinning. The polymer in powder form is put into a syringe and heated to the appropriate temperature directly by a heat gun. This can prevent the accidental surface contamination of biomaterials with high-temperature circulating fluids. The issues of overheating and undesirable degradation of the polymers with low melting point can be avoided by the use of circulating air from heat guns. The equipment used by researchers in melt electrospinning experiments along with their features is summarised in Table 2-1.

### 2.3.2 Polymers used

Melt electrospinning can be applied to a wide range of polymers. The first published work on melt electrospinning of PP was by Larrondo and Manley [66] two decades ago. In subsequent work, researchers diversified the materials that can be used in melt electrospinning [41-42, 49, 56, 60-62]. The fabrication of micro- and nanofibres of various polymers such as polylactic acid (PLA) [22] [18], PP [54, 60, 63, 70], low-density PE (LDPE) [69], PET [49-50, 63], polyalirate [15], polycaprolactone (PCL) [72] and PEG47-b-PCL95 [60, 72] by melt electrospinning has been reported by several researchers. The list of polymers used in melt electrospinning has been summarised in Table 2-1.
Table 2-1: Equipment and polymers used in melt electrospinning along with fibre diameters achieved.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Equipment (type &amp; features)</th>
<th>Material property (Mw, MFI, viscosity)</th>
<th>Process parameters</th>
<th>Fibre diameter (µm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>SS chamber with plunger and steel capillary</td>
<td>Unknown</td>
<td>200–220°C</td>
<td>10–420</td>
<td>[66]</td>
</tr>
<tr>
<td>LDPE</td>
<td>Heating rings around piston with temperature controller</td>
<td>MFI 2</td>
<td>315–355°C</td>
<td>5–32</td>
<td>[69]</td>
</tr>
<tr>
<td>PP</td>
<td>Heated syringe, needle, guiding chamber and collector with independent heating systems</td>
<td>Mw 195,100, T=230 syringe, T=280–290 needle</td>
<td>15–40</td>
<td>[35]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ceramic circular heater for syringe and ring-shaped metal heater for part of spin line</td>
<td>MFI 900</td>
<td>T=330–410°C</td>
<td>25–40</td>
<td>[73]</td>
</tr>
</tbody>
</table>
i-PP

Brabender table-top extruder with four heating zones

Mw 190,000  T=200°C  -10 [63]

Mw 106,000  T=200°C  -6.9 [63]

Mw 12,000   T=200°C  -3.5 [63]

SS cylindrical chamber with plunger and steel capillary

Unknown  T=220–240°C  20–180 [66]

ρ (Pa s) 23

ρ = zero-shear viscosity

ρ (Pa s) 75
ρ (Pa s) 33

270°C  35.6 ± 1.7 [60]
270°C  0.84 ± 0.19 [60]

i-PP-15 + 1.5%
atactic PP

Brabender table-top extruder with four heating zones

ρ (Pa s) 33

270°C  0.84 ± 0.19 [60]

sPP

Meltblown electrospinning

Mw 19,600  T=200°C  -21 [63]

Mw 14,000  T=200°C  -13 [63]

ρ (Pa s) 75
ρ (Pa s) 33

270°C  35.6 ± 1.7 [60]
270°C  0.84 ± 0.19 [60]

Meltblown electrospinning
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Characteristics</th>
<th>IV (dL/g)</th>
<th>Laser Power (W)</th>
<th>Density (g/mL)</th>
<th>Temperature Range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene terephthalate (PET)</td>
<td>Rod-like polymer samples, CO₂ laser melting polymer from three directions, rotating collector</td>
<td>0.512–0.706</td>
<td>45 W</td>
<td>1.3</td>
<td>260°C</td>
<td>[15]</td>
</tr>
<tr>
<td>Polyethylene covinyl alcohol (EVOH)</td>
<td>CO₂ line-like laser; sheets of polymer; multiple Taylor cones</td>
<td>4.4 at 190°C</td>
<td>12 W</td>
<td>1.3</td>
<td>230–300°C</td>
<td>[74]</td>
</tr>
<tr>
<td>Polylactide: Polyethylene covinyl alcohol (EVOH)</td>
<td>Rod-like polymer samples, CO₂ laser melting polymer from three directions, rotating collector, heated chamber.</td>
<td>76.9 at 210°C</td>
<td>12 W</td>
<td>1.3</td>
<td>290–300°C</td>
<td>[75]</td>
</tr>
<tr>
<td>Nylon-6</td>
<td>Two heating zones around MACOR shielding, cooling collector</td>
<td>2.61</td>
<td></td>
<td>0.9 &amp; 4</td>
<td></td>
<td>[14]</td>
</tr>
<tr>
<td>Nylon-6/12</td>
<td>Electrical heating to syringe, IR heating to the vicinity of syringe</td>
<td>1.4</td>
<td></td>
<td>0.8–2.2</td>
<td></td>
<td>[74]</td>
</tr>
<tr>
<td>Material</td>
<td>Mw</td>
<td>T (°C)</td>
<td>ΔT (°C)</td>
<td>Ref.</td>
<td></td>
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<tr>
<td>-----------------------------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Polylactic acid</td>
<td>186,000</td>
<td>200</td>
<td>0.5–17</td>
<td>[22]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical heating, 4 zones heating equipment with cooled collector polymer resin</td>
<td>Mw 186,000</td>
<td>225</td>
<td>10–25</td>
<td>[20]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Same as Nylon 6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Same as PET</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ laser melting polymer, rod-like samples with N₂ gas blow to melting area, rotating collector</td>
<td>Mw 186,000</td>
<td>Laser: 6–20W</td>
<td>↓-1</td>
<td>[18]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyalurate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rod-like polymer samples, CO₂ laser melting polymer from three directions, rotating collector</td>
<td>Mw 108,000</td>
<td>Laser: 6–8 W</td>
<td>1–2</td>
<td>[18]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂-PVP sheath loaded with octane</td>
<td>Unknown</td>
<td>68</td>
<td>0.15</td>
<td>[77]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-axial system, electric heater around glass syringe and plastic syringe for sheath material</td>
<td>PMMA (Mw 120,000)</td>
<td>45</td>
<td>Core 0.2–0.4</td>
<td>[19]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>polymethyl methacrylate (PMMA) with CBT</td>
<td>bisphenol A, &amp; CB-unknown</td>
<td>Shell 0.2–0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-axial system, PMMA electrospun from solvent in outer syringe and CBT from melt in inner syringe heated by heating tape</td>
<td>Unknown</td>
<td>Laser power 45 W</td>
<td>0.73 ± 0.2</td>
<td>[74]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyhexamethylene dodecanediamine (Nylon)</td>
<td>Same as EVOH</td>
<td>CO₂ line-like laser; sheets of polymer; multiple Taylor cones</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition</td>
<td>Mw</td>
<td>Temp</td>
<td>Reaction Time</td>
<td>Source</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>------------</td>
<td>------</td>
<td>---------------</td>
<td>--------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% PEG&lt;sub&gt;5000&lt;/sub&gt;-block-PCL&lt;sub&gt;5000&lt;/sub&gt; + 80% PCL</td>
<td>65,960</td>
<td>90°C</td>
<td>1.8 ± 0.8</td>
<td>[78]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% PEG&lt;sub&gt;5000&lt;/sub&gt;-block-PCL&lt;sub&gt;5000&lt;/sub&gt; + 90% PCL PEG47-block-PCL&lt;sub&gt;95&lt;/sub&gt; + 30% PCL</td>
<td>72,980</td>
<td>90°C</td>
<td>2.7 ± 2.0</td>
<td>[78]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ρ = 49</td>
<td>90°C</td>
<td>2.0 ± 0.3</td>
<td>[60]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.27 ± 0.1</td>
<td>[60]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Heated re-circulating water tank attached to glass jacket where syringe is seated

Precise temperature control circulatory system
2.4 Fibre diameter and influencing factors

In melt electrospinning, a range of obtainable fibre diameters have been explained for a variety of polymers. In the majority of recent work, the melt electrospun fibres are in both nanometre and micrometre scales (Table 2-1). The fibre diameter can be controlled by different parameters related to the polymer (i.e. molecular weight [63], MFI [17] and stereoregularity [63]); and the process (applied voltage, collector distance, nozzle diameter, flow rate [63] and temperatures of the spinneret and the spinning region [22]). Apart from these, the ambient conditions such as the temperature and relative humidity (RH) also affect the fibre diameter. The list of factors influencing fibre diameter is given in Figure 2-3.

![Figure 2-3: Schematic of the factors influencing fibre diameter and morphology in melt electrospinning.](image)

In melt electrospinning, accurate dispensing of the polymer to the spinneret and maintaining the homogeneity of the polymer melt are important to achieve consistent fibre diameter [42, 44, 54]. Liu et al. [54] performed an orthogonal-design study to find the dominant factors (such as electric field, collector distance, temperature and polymer MFI) affecting the fibre diameter in melt electrospinning. It was found that the MFI of the polymer was the most influencing parameter affecting average fibre diameter and standard deviation (SD). The importance of the parameters was listed in the following order:

For average fibre diameter: MFI>applied voltage>collector distance>temperature

For SD: MFI> temperature > collector distance> applied voltage
2.4.1 Effects of molecular weight/MFI

Until now it has been found that molecular weight is the most important parameter governing the fibre diameter in melt electrospinning [63]. Higher molecular weight polymers possess higher degrees of chain entanglement and hence lower MFI. As a result, coarser fibre diameters will be formed from these polymers. It has been shown that high-quality fibres can be best made using molecular weights between 40000 to 80000 g/mol, much lower than those of the polymers used for engineering applications [16]. Lyons et al. [63] showed that as the molecular weight decreased continually, the fibre diameter was decreased. In addition, the stereo-regularity of the polymeric chain affects the fibre diameter. For example, isotactic polymers of PP (iPP) produced finer fibres than atactic polymers [63]. This was because in atactic PP the methyl group is randomly positioned with respect to the main backbone and therefore it hardly crystallises. The inability to closely pack due to the steric hindrances may result in large fibre diameters.

2.4.2 Effect of viscosity

The viscosity of the polymer melt is at least one order higher than the viscosity of polymer solution [55, 56]. Higher temperature reduces the viscosity, which results in the fabrication of finer fibres. There are several ways to reduce the viscosity of polymers, such as increasing the process temperature and addition of additives such as rheology modifiers [40, 41]. Due to the high viscosity of the polymer melt, sufficient time is required for stabilisation of the flow rate, especially when a small diameter and/or lengthy spinneret are used. It was found that the higher polymer MFI produced smaller diameter fibre due to the low viscosity [18]. Dang et al. used LDPE with a very low MFI (i.e. 2), which was challenging for melt processing and employed very high temperatures for melt electrospinning.

2.4.3 Effect of applied voltage

The external electric field is a fundamental requirement for electrospinning and an important factor governing the fibre diameter. In melt electrospinning, the only force which is responsible for fibre stretching is the electrostatic force, as there is no solvent evaporation. Melt electrospinning involves the stretching of predominantly non-conducting liquid under the influence of an applied electric field. Several studies have shown that the increase in the applied voltage decreases the fibre diameter [22, 63].
However, a few others have shown a different trend, of a decrease followed by an increase in fibre diameter [79]. The increase in applied voltage reduces the fibre diameter in melt electrospinning as the polymer is subjected to higher dragging force [63, 80, 81]. However, after a threshold value of the applied voltage, the size of the Taylor cone decreases and the fibre diameter starts increasing. This is because after a threshold value, the applied voltage pulls the polymer fluid faster than the flow rate can replace it and hence the size of the Taylor cone diminishes.

### 2.4.4 Effect of collector distance and type

Change in the collector distance influences the fibre diameter. In some experiments, collector distances of <10 cm [60, 82, 83] were used, whereas others were >10 cm [17, 73]. It was found that at shorter collector distances the fibre diameter was coarser, as the jet is not sufficiently thinned before being collected. In addition, a small effect of collector distance on fibre diameter was observed [18, 75]. Interestingly, a trend of decrease followed by an increase in the fibre diameter was observed by increasing the collector distance [69]. As cooling of the fibre is essential for solidification, shorter collector distances can result in slightly molten fibres being deposited, with fusion of the fibres at the crossover point.

Various types of collectors are being used in melt electrospinning. For example, a SEM aluminum stub covered with aluminum foil and Petri dishes were used as collectors and placed at variable distances of 5–30 cm [17]. It was found that the quality of the fibres collected onto the aluminum stub was much better than the fibres collected on Petri dishes. In another approach, glass microscope slides were used as the collector with or without reactive molecules on their surface. The surface modification affected the manner in which the fibres were collected. In addition, collectors such as rotating drums or plates can be used to achieve various patterned structures.

### 2.4.5 Effect of flow rate

Polymer flow rate indicates the amount of polymer melt flowing per unit time. It was found that increase in the flow rate caused more polymer melt being drawn from the nozzle and hence produced coarser fibres [22, 35, 80]. The flow rate used in the melt electrospinning is significantly lower than that of solution electrospinning. A low flow
rate is essential for getting good quality fibres with fine diameter in melt electrospinning [84]. This may be due to the increased charge density at lower flow rates lowers the fibre diameter. The effect of spinning volume per unit time was studied by placing the polymer chip directly on the spinneret orifice during melt electrospinning [63]. As no flow rate was applied, the volume of polymer was continuously reduced, as the fibres were continually fabricated. This resulted in a decrease in the size of the Taylor cone continuously, leading to a decrease in the fibre diameter.

2.4.6 Effect of spinneret size
The diameter of the spinneret used for melt electrospinning is higher compared to that for solution electrospinning, as the flow of high viscous melt through a smaller diameter orifice is challenging. There is strong correlation between the fibre diameter and the spinneret size [22]. However, it was observed that the average fibre diameter decreased initially as the capillary diameter decreased. Once the diameter reached a critical value, the fibre diameter started increasing significantly [69]. This is because the extremely small orifice resulted in high pressure being required to form the Taylor cone, which in turn led to increased flow of the polymer melt to the apex of the capillary, resulting in thicker fibres.

2.4.7 Effect of temperature
The nozzle temperature is one of the most important parameters affecting fibre diameter. It was found that as nozzle temperature increased, both the average fibre diameter and the SD decreased [22, 69]. This is because the increase in the melt temperature decreases the viscoelasticity and thus the final jet gets thinner. Nozzle temperatures above certain values are not applicable, as there are chances of thermal degradation and the elongational viscosity of the melt is not high enough to maintain a continuous jet.

2.4.8 Effect of ambient parameters
The fabrication of electrospun fibres from polymer melt can be influenced by ambient conditions such as relative humidity (RH), vacuum conditions, surrounding gases and temperature. There have been very few studies on the effect of ambient parameters on the fibre diameter in melt electrospinning. The ambient conditions from the tip of the
syringe to the collector can also influence the morphology and diameter of electrospun fibres [14]. It was found that high ambient temperatures in the vicinity of the spinneret made the electrospinning process quicker and produced more uniform fibre [22].

2.4.9 **Effect of electrical conductivity**

The electrical conductivity of a polymer is an important parameter which determines the charge density and is closely related to the attenuating force during electrospinning. The net charge density is mainly affected by the applied electrostatic field and the electrical conductivity of the polymer solution or melt. Almost all the polymers used in solution electrospinning are conductive except few dielectrics. However, the majority of the polymers used in melt electrospinning are not electrically conductive, which makes the process difficult for fibre fabrication [16]. For example, the solution of PP in Decalin had an extremely low electrical conductivity compared to other polar solvents, which made the initiation of electrospinning difficult [85].

2.4.10 **Other parameters**

Kilic et al. [86] studied the effect of polarity on the melt electrospinning process. It was found that inverting the polarity (when the collector is charged and needle grounded) lowers the production rate and results in coarser and less homogenous surfaces. Kessick et al. [87] performed electrospinning by using both AC and DC potential and found that AC potential can reduce the amount of fibre whipping associated with DC potential. In a laser-based melt electrospinning device, the laser power affects the fibre diameter. It has been found that the fibre diameter is large at lower laser power, but it decreases and then becomes constant with increasing laser power [18].

2.5 **Surface morphology**

Surface morphology of the fibres influences the performance of the fibres. Melt electrospun fibres generally appear smooth and cylindrical, with thread-like or ribbon-like structure [35, 54]. There is no solvent evaporation in melt electrospinning, which may lead to inconsistencies on the fibre surface. The smooth surface is due to the partial solidification which occurs rapidly as the jet leaves the spinneret. The material properties affecting the fibre surface morphology are the polymer molecular weight/MFI and the tacticity. Theoretically, the factors affecting melt electrospinning process can
also affect fibre morphology. A minute change in the operating parameters can lead to considerable change in the fibre morphology. The surface morphology of the fibres is also affected by the environmental conditions such as RH and temperature.

Melt electrospun fibres can be deposited either randomly or in an oriented manner to give an aligned nanofibre array. Patterning of the fibres for specific applications can be achieved by altering the collector geometry. Until now only a limited amount of work has been done on the patterning of melt electrospun fibres [58, 72]. In some cases the fibres can consist of two components to form side-by-side or bicomponent structures. Melt electrospinning is poor in generating oriented fibres over significant gaps, probably due to the focused nature of the deposition and elongated jet [60]. The formation of islands of fibres was a common phenomenon while melt electrospinning directly onto metallic collectors, but it did not appear during in-vitro investigations [17].

2.6 Properties of melt electrospun fibres

2.6.1 Mechanical properties

Nanofibres are used for a wide range of applications such as filtration, tissue engineering, reinforcement composites and micro/nano-electro-mechanical systems (MEMS/NEMS). During the service life of these products, various forces are exerted on the fibres, which may result in deformation and even lead to permanent failure. Therefore, the mechanical characterisation of nanofibres is essential to assure the product’s serviceability. As nanofibres are very fine in diameter, commercial equipment cannot be directly used for mechanical testing due to the following reasons: (a) difficulty in manipulation (due to their smaller size, handling of ultrafine fibres without causing any damage is extremely difficult); (b) non-availability of a suitable observation mode; (c) non-availability of an accurate and sensitive force transducer (as the force required to break the nanofibres is in the nano-Newton range, commercial equipment are not suitable for nanofibres); and (d) difficulty in the preparation of single-strand nanofibres.

A variety of techniques are available for the mechanical characterisation of nanofibres such as the tensile test, three-point bending test [76-78], resonance frequency measurements [88], atomic force microscopy (AFM), based cantilever bending experiments [89, 90] and nano-indentation [91, 92]. Commercial mechanical grippers
are not suitable for nanofibres; due to the small size of nanofibres, it is difficult to avoid the slippage or breakage of the fibre at the grips [93]. Another problem associated with tensile testing is misalignment of the sample axis with respect to the load direction, which may lead to premature sample failure. The most convenient method of avoiding these problems is to collect the fabricated fibres on a frame or paper that can be directly mounted on the tensile tester. Tensile testing of nanofibres can be carried out using the Nano Bionix System (MTS, USA) [94, 95].

2.6.2 Thermal properties

The thermal properties of melt electrospun fibres have been investigated by several researchers [22, 59]. DSC studies have shown that the degree of crystallinity of PLA fibres produced by melt electrospinning is very low [22]. Thermal investigations of PEG/cellulose acetate composite have shown that the fibres have good thermal stability and reliability [59]. The fibres imparted balanced thermal storage and release properties and the thermal properties were reproducible after 100 heating–cooling cycles.

2.6.3 Crystalline properties

Crystalline properties are one of the most important factors determining the mechanical properties of the fibre. In general, the elastic modulus of the fibres increases with the degree of crystallinity and results in better mechanical properties. The solvent evaporation in the case of solution electrospinning leads to crystal formation by the solidification of aligned polymer chains [96, 97]. However, the melt electrospun fibres are reported to possess a very low degree of crystallinity and less stable crystal structure due to rapid quenching by electrohydrodynamically driven air flow near the polymer-jet [22, 71, 97]. In solution electrospinning, the solidification rate by solvent evaporation, and in melt electrospinning the cooling rate of the jet, influence the crystalline properties of the fibres [98].

XRD studies have shown that as-spun PLA melt electrospun fibres with 10 µm diameter are mostly amorphous in nature with no distinct crystal peaks [22]. On annealing, the peak strength gradually increased and the peak shifted towards higher temperature depending on the degree of annealing. In another study, high crystallinity values have been reported for LDPE [69].
It has been found that melt electrospun PP fibres cannot maintain oriented structures at room temperature. Therefore, in order to keep the aligned structures at room temperature, a collector cooled below the Tg of PP was used [22]. In another approach, the results from DSC and XRD of PP showed β-form crystals present in solution electrospun fibres, whereas α-form crystals were prevalent in melt electrospun fibres (Figure 2-4)[14]. The fibres changed their morphology to α and γ-form crystals after annealing.

![Figure 2-4: Figure XRD reflection patterns for PP polymers and PP fibres obtained by: (a) solution electrospinning and (b) melt electrospinning.](image)

Cho et al. [14] fabricated Nylon 6 fibres via solution (with formic acid) electrospinning at room temperature and melt electrospinning at elevated temperature. The crystal structure and effect of annealing on the structure were studied by various techniques. The results obtained from DSC, XRD and FTIR indicated that the melt electrospun Nylon 6 fibres predominantly exhibited the metastable γ-crystalline forms and low molecular orientation; whereas the solution electrospun fibres showed both α and γ-form crystals and higher molecular orientation. When the annealing temperature was high, the metastable γ-crystals in melt electrospun fibres easily transformed into stable α-form crystals and the crystals in solution electrospun fibres exhibited higher thermal stability.

### 2.6.4 Other properties

The PP webs prepared both from solution and melt electrospinning exhibited superhydrophobicity with a water contact angle of 151°, which is substantially higher than those of a commercial PP nonwoven web and a compression moulded PP film [14].

26
The enhanced hydrophobicity can contribute to excellent barrier performance without losing permeability when applied to protective clothing.

A number of rheology modifiers have been successfully used for reducing the viscosity of polymer melt. This included metallic stearates, boron nitrides, fluoropolymers, siloxanes and liquid crystal polymers [99]. The commercially available siloxanes and fluoropolymers have high molecular weights. Low molecular weight additives include fatty acids, silicon oils, mineral oils and wax, which are well established in the polymer processing field. It has been found that the low molecular weight additives can provide good results in extrusion at a much lower level of addition than their high molecular weight counterparts. Although the mechanism of viscosity reduction is still under debate, the external lubrication effects of the blend during die flow are generally agreed on [99, 100]. In the case of polyolefins, the main additives used for reducing the viscosity are: sodium oleate (SO) [101], polyethylene glycol (PEG) [102] and polydimethylsiloxane (PDMS) [103].

Although the rheological properties of the polymer melt strongly influence the melt electrospinning, a limited number of studies have given attention to the study of rheological properties. It was found that the average viscosity of PLA melt was one to two orders of magnitude higher than that of PLA/chloroform solution [22]. PLA did not exhibit strong shear thinning over a wide range of shear rates.
3 Chapter 3 Experimental: melt electrospinning

3.1 Introduction
This chapter deals with the materials used, the equipment and the processing parameters applied in the melt electrospinning experiments. It also includes the equipment and test conditions used for the characterisation of the fibres fabricated. The characterisation techniques include scanning electron microscopy (SEM); optical microscopy (OM); energy dispersive x-ray (EDX); nuclear magnetic resonance (NMR); Fourier transform infrared (FTIR); differential thermal calorimetry (DSC); thermo gravimetric analysis (TGA); x-ray diffraction (XRD); and mechanical characterisation. The shear viscosity and electrical conductivity analyses were performed to understand the effect of additives on the fibre diameter. In addition, the surface wettability of the samples was evaluated by measuring the water contact angle.

3.2 Materials
In any melt processing, the polymers with high MFI (hence low viscosity) have the potential to form nonwoven webs consisting of fine fibres [104]. Therefore, in the current work, PP of 100, 300, 1000 and 2000 MFI were used for the melt electrospinning experiments. The list of PP polymers along with MFI, IV and molecular weights used in the current research are listed in Table 3-1.

Table 3-1: List of polymers used for current study.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>MFI</th>
<th>IV (g/dL)</th>
<th>Mw (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.01</td>
<td>100875</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.84</td>
<td>77590</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>0.72</td>
<td>60238</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>0.66</td>
<td>55509</td>
<td></td>
</tr>
</tbody>
</table>

The polymers were selected on the basis of MFI, which is directly related to the melt viscosity. The MFI of a polymer indicates the amount of polymer in grams that flows through a given orifice under a given load at a specific temperature in ten minutes. The MFI was measured according to ASTM-D1238 (at 230°C and a load of 2.16 kg). The higher the polymer MFI, the higher the viscosity of the polymer but the lower the
molecular weight. The MFI of a polymer should be high enough to facilitate the formation of finer fibres in melt electrospinning [54].

3.2.1 Material synthesis

The PP polymers used in the current research are not commercially available. Generally, the molecular weights of PP polymers commercially available are typically high. For example, the molecular weight of commercial polyolefins (such as PE and PP) is often higher than 100,000 g/mol. The use of high molecular weight polymers results in improved mechanical properties (such as tensile strength and fracture toughness) of the extruded article. However, the melt viscosity of the polymer of higher molecular weight is higher which makes the melt processing difficult.

Polymer pellets with 100, 300 and 1000 MFI were prepared in the laboratory by the chain scission of the base polymer (Moplen 241R with a MFI of 30 from Lyondellbasell) using the radical initiator in an extruder [105]. The 2000 MFI PP was purchased from Expert Company (China) and was used as received. The radical initiator used in the chain scission was the combination of 2, 5 dimethyl hexane and 2, 5 bis (tert-butyl peroxide) commonly known as DHBP. The structure of the radical initiator (DHBP) is given in Scheme 3.1.

![Scheme 3.1: The chemical structure of the radical initiator used for the chain scission of PP to produce higher MFI: (a) 2, 5 dimethyl hexane, and (b) 2, 5 bis (tert-butyl peroxide).](image)

The free radicals generated by the decomposition of DHBP remove hydrogen atoms from the tertiary carbon sites, leading to β-scission [105]. Hence the molecular weight is reduced or the MFI is increased, which makes the processability easier for specific melt applications. The mechanism of cleavage is explained in Figure 3-1.
The first step of the mechanism involves generation of peroxy radicals through thermal decomposition of the peroxide:

\[ \text{ROOR} \rightarrow 2\text{RO} \]

The radical then attacks the backbone of the polymer, abstracting a tertiary hydrogen:

\[ \text{RO}^- + \sim \text{CH}_2\text{CH}_2\text{CH} \sim \rightarrow \sim \text{C}^-\text{CH}_2\text{CH}_2\text{CH}_2 \sim \]

The backbone then degrades by β-scission:

\[ \sim \text{C}^-\text{CH}_2\text{CH}_2\text{CH}_2 \sim \rightarrow \sim \text{C} = \text{CH} + \text{CH} - \text{CH}_2 \sim \]

The polymeric radicals then terminate by disproportionation:

\[ \sim \text{CH}_2\text{CH}^- + \text{CH} - \text{CH}_2 \rightarrow \sim \text{CH}_2\text{CH}_2 + \text{CH} = \text{CH} \sim \]

Figure 3-1: β-scission of PP by the radical initiator.

### 3.2.2 Material preparation

The PP polymer was collected as pellets after the β-scission which was used as powder in the melt electrospinning experiments. The pellets were converted to fine powder by cryogenic (liquid nitrogen) grinding [106] in a grinder (Glenmills, Model 500, Figure 3-2). Figure 3-3 shows the images of the PP polymer pellets and powder used for the current research.
The direct use of polymer pellets is not appropriate in melt electrospinning because:

1. The polymer pellets are difficult to feed into the narrow entrance hole of the barrel and also they limit the space inside the melting chamber that acts as a reservoir for the electrospinning melt; and
2. The additives can be mixed uniformly with the powder, rather than with the pellets.

### 3.3 Melt electrospinning apparatus

The basic apparatus used for melt electrospinning experiments is shown in Figure 3-4 and Figure 3-5. It consisted of five major components: temperature controller; high-voltage power supply; heating-assembly; syringe pump; and collector. The temperature controller (BTC 909C) has an accuracy of ± 2°C as measured using a K-type
thermocouple. The maximum processing temperature for 100 and 300 MFI PP was kept at 210°C; and for 1000 and 2000 MFI PP was kept at 200°C (detail in Table 4-2).

A negative voltage (–ve DC) was supplied to the collector plate using a high-voltage power supply (Spellman SL 150) with a voltage range of 0–50 kV. The electrospinning experiments were performed at 36, 40, 44 and 48 kV (detail in Table 4-3). Generally, in solution electrospinning, the high-voltage is applied to the spinneret (barrel) and the collector is grounded. In melt electrospinning, the reverse approach is used in order to: (a) avoid damaging the pump control or heater control units via electric discharges; and (b) protect the temperature sensor from electrical interference. Therefore, the high-voltage was applied to the collector and the spinneret was grounded.

Figure 3-4: Schematic of the apparatus used for melt electrospinning experiments.

Figure 3-5: Image of the apparatus used for melt electrospinning experiments.
The heating-assembly consisted of a stainless steel barrel of 10 mm inner diameter and 125 mm in length. Heating was carried out by electrical heating elements housed inside the barrel. The equipment consisted of a digitally-controlled syringe pump (PHD 2000, Harvard Apparatus) which can precisely control the polymer melt feed rate. The polymer melt was pumped with feed rates of 0.005, 0.0025 and 0.0013 ml/min (i.e. 2.56, 1.28 and 0.64 g/hr) through the single-hole horizontal die. In initial experiments, different dies were used as listed in Table 3-2. The cross-sectional area of the die orifices was determined by using an optical microscope (Olympus-DP72) with a magnification of 40x.

Table 3-2: Specification of the dies used in the melt electrospinning process.

<table>
<thead>
<tr>
<th>Die size (mm)</th>
<th>Die shape</th>
<th>Cross-sectional area of die orifice (µm²) × 10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>C</td>
<td>*</td>
</tr>
<tr>
<td>0.1</td>
<td>C</td>
<td>0.64</td>
</tr>
<tr>
<td>0.15</td>
<td>C</td>
<td>1.62</td>
</tr>
<tr>
<td>0.2</td>
<td>C</td>
<td>2.84</td>
</tr>
<tr>
<td>0.2</td>
<td>CP</td>
<td>2.55</td>
</tr>
<tr>
<td>0.3</td>
<td>CP</td>
<td>6.17</td>
</tr>
<tr>
<td>0.3</td>
<td>C</td>
<td>6.64</td>
</tr>
<tr>
<td>0.2</td>
<td>T</td>
<td>34.03</td>
</tr>
</tbody>
</table>

C: Circular, T: Trilobal and CP: Circular-protruding.

* area could not be measured

The collector was a flat aluminium plate (150 mm (H) × 80 mm (W)) overlaid with aluminium foil on which fibres were collected. The collector was placed at varied distances of 50, 60, 70, 80, 90, 100, 110, 120, 130, 140 and 150 mm depending on the polymer MFI (detail in Table 4-3).

Before starting the melt electrospinning experiments, the barrel was preheated up to the required temperature depending on the MFI of the polymer. The piston was removed and the powdered polymer (about 4 g) was loaded into the barrel and kept for 10 minutes so that a homogenous melt was prepared and a steady state was achieved. The piston was reloaded and the delivery of the polymer melt was initiated. Before collecting the experimental samples, the initial polymer flow rate was set at a higher value and then the experimental value was set. This was done because directly setting the experimental flow rate at the start was at times insufficient to initiate the flow or it took a long time for the flow to be initiated. In addition, a high flow rate was used to expel air from the barrel. After all air bubbles were removed, the flow rate was reduced. When the system
was equilibrated, high-voltage was applied and fibre samples were collected. All the electrospinning experiments were performed in laboratory conditions with a temperature of 20 ± 2°C and RH of 40 to 60%.

### 3.4 Additives

Initial experiments in melt electrospinning with pure polymers resulted in fibres with micrometre diameter. On the basis of the information provided in the literature, it was found that the addition of additives or rheology modifiers can lower the viscosity of the medium in which they are mixed and reduce the fibre diameter [40, 41]. Therefore, two rheology modifiers, polyethylene glycol (PEG-300, from Ega Chemie) and polydimethyl siloxane (PDMS, from United Chemical Technologies Inc.) were selected to reduce the viscosity. Similarly, the addition of conducting material can increase the electrical conductivity of the melt, which can help in reducing the fibre diameter [41]. Therefore, sodium oleate (SO, from British Drug House) and sodium chloride (NaCl, from Merck KGaA) were used to increase the electrical conductivity. All the additives were used as received in varying amounts of 4, 7 and 12%. The list of additives along with the chemical structures is shown in Table 3-3.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Supplier</th>
<th>Mw</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium oleate (SO)</td>
<td>CH₃(CH₂)₇(CH₃)₇OONaNa</td>
<td>British Drug House</td>
<td>304.44</td>
<td>Solid (powder)</td>
</tr>
<tr>
<td>Polyethylene glycol (PEG)</td>
<td></td>
<td>Ega Chemie</td>
<td>300</td>
<td>Liquid</td>
</tr>
<tr>
<td>Polydimethyl siloxane (PDMS)</td>
<td></td>
<td>United Chemical Technologies Inc.</td>
<td>Not available</td>
<td>Liquid</td>
</tr>
<tr>
<td>Sodium chloride (NaCl)</td>
<td>NaCl</td>
<td>Merck KGaA</td>
<td>58.44</td>
<td>Solid (crystal)</td>
</tr>
</tbody>
</table>

### 3.5 Annealing

It has been shown that annealing substantially modifies the microstructure of PP and hence the crystallinity [107]. Annealing can also improve a polymer’s melting point and heat of fusion [108]. The increase in the crystallinity affects the mechanical properties.
For annealing, any temperature above the crystallisation temperature and below the melting temperature can be selected. In this study in order to study the effect of annealing on the thermal and crystalline properties of the fibres, the samples were subjected to annealing at 120°C for 30 minutes in a hot air oven. The samples were cooled to room temperature after annealing.

3.6 Characterisation

3.6.1 SEM
The surface morphology of the fibres was analysed by field emission scanning electron microscopy (Philips XL30 FE-SEM) with an accelerating voltage of 30 kV. The fibres were placed on stubs and coated with iridium by using a sputter coater (Polaron SC5750). The current in the sputter coater was set at 50 mA for 20 secs, giving an approximate coating thickness of 100 angstroms. The fibre diameters were measured by an image processing software (Image J, NIST) using the SEM images. The average fibre diameter was determined from at least 150 measurements taken from 10 SEM images.

3.6.2 Optical microscopy
The cross-sectional area of the dies was measured by an optical microscope (Olympus-DP72) with a magnification of 40x. The dies were mounted on the stage of the microscope with the orifice facing upwards. The images of the die orifice were captured by a camera and the cross-sectional area was calculated for each die.

3.6.3 EDX
The EDX microanalysis was used to investigate the presence of the additives in the electrospun fibre samples by analysing various elements of the additives (such as sodium (Na), silicon (Si), and chlorine (Cl)). The Philips XL30 FE-SEM used for analysing the surface morphology was also used for the EDX. An accelerating voltage of 30 kV was used for all the specimens. To determine the distribution of the additives on the fibre, x-ray net counts were obtained at random locations on the stub with a collection time of 500 sec. All the fibre samples were carbon coated before the EDX analysis.

3.6.4 NMR
The chemical structure of a polymer subjected to high temperature may be substantially different from the original (due to chain scission, branching and cross linking during
processing). When subjected to high temperature, there may be reduction of molecular size and the formation of extra chemical groups in the case of PP [109]. NMR was used to study the chemical composition of the fibres before and after melt electrospinning. $^{13}$C NMR spectra were collected from the solid state NMR experiments performed on an NMR spectrometer (Bruker BioSpin Av500) operating at 125.8 MHz. Samples were packed into a 4 mm ZrO$_2$ rotor and spun at 5 kHz in a standard-bore 4 mm broadband MAS probe. Data were processed in Bruker BioSpin TopSpin v3.0.

### 3.6.5 FTIR

In addition to NMR, FTIR was also used to determine any changes in the chemical structure by the effects of high temperature, high-voltage and various additives during melt electrospinning. The FTIR spectra were collected by a spectrometer (PerkinElmer Spectrum-400) to determine the functional groups of the fibres. The number of scans per sample was 8 and the FTIR spectra were collected in the wave number region of 4000–650 cm$^{-1}$. The spectra indicate the absorbance of a material as a function of wave number.

### 3.6.6 DSC

DSC can be used to analyse the physical and chemical transformations that occur with a thermal treatment and measured as a function of temperature [110]. The sample and the reference material (which undergoes no phase change in the temperature range being studied) are heated at a constant rate inside two separate cells containing the junctions of a differential thermocouple. The thermal change in the sample is then measured against the reference material.

The thermal behaviour of the PP polymers, as-spun fibres (fibres fabricated without additives) and fibres fabricated with additives by melt electrospinning, were analysed by DSC (Mettler Toledo, DSC821$^e$) fitted with a sample robot. Aluminum crucibles (40 µL) were used for containing the samples and as the reference pan. About 5–10 mg of the sample was heated from room temperature to 250°C at a heating rate of 10°C/min followed by cooling to room temperature at the same rate. As polyolefins show significant difference between the first and second DCS heating cycles [111], the samples were subjected to a second heating cycle similar to the first. These samples were run in the non-isothermal mode of the equipment. The heating rate of 10°C/min
was selected as it has been reported to be an optimum rate that does not influence the shape and character of the melting endotherm of PP [112].

3.6.7 TGA

TGA was used to obtain information on thermal stability of the samples using thermal analysis equipment (Mettler Toledo (TGA/SDTA-851e) fitted with a sample robot. TGA provides information on the thermal degradation of the polymers during any melt processing. In TGA, about 5–10 mg of the sample was heated in a ceramic crucible from room temperature to 800°C at a heating rate of 10°C/min under nitrogen atmosphere. The resulting weight loss as a function of temperature was analysed and compared for relative thermal stability.

3.6.8 Molecular weight or intrinsic viscosity

In addition to the TGA, thermal degradation of polymers was determined from the change (decrease) in the molecular weight of the polymers before and after the melt electrospinning. The molecular weights of the polymers and fibres were determined from the IV values. IV was determined using the solvent Decalin (Decahydronaphthalene) at 135°C in a calibrated viscometer (Ubbelohde). The molecular weights (M) of polymers were calculated from the IV \([\eta]\) using the Mark Houwink equation:

\[
[\eta] = K M^a \quad \text{Equation 3.1}
\]

where K and a are constants with \(0.5 \leq a \leq 0.8\). For PP, the values of K and a are \(2.38 \times 10^{-4}\) and 0.725 respectively [113].

3.6.9 XRD

The degree of crystallinity of the fibres affects their physical properties. Hence, investigation of the degree of crystallinity can help to understand the physical properties of the fibres. The crystalline properties of the melt electrospun fibres were analysed by XRD (Bruker D8 Advance Diffractometer with CuKα radiation, 40 kV, 40 mA). The diffractometer was equipped with a Lynx-Eye silicon strip detector to obtain the XRD patterns. The samples were scanned over the 2θ range of 5 to 30° with a step size of 0.02° and a count time of 0.4 secs per step. Analyses were performed on the collected XRD data using the Bruker XRD search match program “EVA™” and the crystalline phases were identified using the ICDD-PDF4+ 2010 powder diffraction database.
The XRD diffractograms were used to evaluate the crystalline fraction of the fibres fabricated by melt electrospinning. The crystalline and amorphous scatterings in the diffractogram were separated from each other by using the technique described in detail in the literature [114]. Figure 3-6 shows the XRD diffractogram with appropriate separation between the crystalline and amorphous sections by drawing a line connecting the minima between the crystalline peaks. The scatter intensity above this line (Ic) is from the crystalline region, whereas the scatter intensity below this line (Ia) is from the amorphous region. The integrated area of the crystalline reflections (Ac) and amorphous background (Aa) were used for the estimation of crystallinity. The areas (Ac and Aa) were estimated by curve fitting method using MATLAB 10 software.

![X-ray diffractogram showing the relative crystalline and amorphous areas for the estimation of crystallinity.](image)

The degree of crystallinity of the samples was calculated from the following equation [115]:

$$
Crystallinity \% = \left( \frac{Area \ of \ crystalline \ fraction}{Area \ of \ crystalline \ fraction + Area \ of \ amorphous \ fraction} \right) \times 100
$$

$$
= \frac{Ac}{Ac + Aa} \times 100 \quad \text{Equation 3.2}
$$

3.6.10 Shear viscosity

The viscosity of a polymer melt is an important parameter affecting the fibre diameter. In addition, rheology modifiers were used to reduce the viscosity of the polymer melt in melt electrospinning. The degree of viscosity reduction is dependent on the amount of
the rheology modifier, operating temperature and shear rate. Therefore, it is essential to measure the viscosity of the polymer melt. The shear viscosity was measured using a rheometer (Ares) equipped with parallel plates at various temperatures in the dynamic mode. The shear viscosity of pure polymers and polymers with additives were determined over a wide range of shear rates (0.1–100 s⁻¹). Disc samples of about 1 mm thickness were prepared by using the heat press for the tests. Frequency scans were performed with temperature ranges between 180–210°C at 20% strain.

3.6.11 Electrical conductivity

The electrical conductivity of a polymer melt determines the charge density and is closely related to the attenuating force during melt electrospinning. The electrical conductivity of pure polymers and polymers with additives (SO and NaCl) were measured at elevated temperatures by an electrometer (Keithley 2612). The configuration used for the measurement of the electrical conductivity is shown in Figure 3-7. A circular polymer disc was used, which was prepared by using the heat press. The polymer disc was melted by band heaters to specific temperatures. Two electrodes (separated by 5 mm) were dipped in the melt and connected to the electrometer. The electric current flowing between the electrodes was measured by applying a variable voltage (0–50 volt).

![Figure 3-7: Configuration used for the measurement of electrical conductivity.](image)

3.6.12 Mechanical characterisation

Various forces are exerted on the nanofibres during their use, which may result in deformation and lead to permanent failure. Therefore, the mechanical characterisation of
nanofibres is essential to ensure product serviceability. The mechanical property of single nanofibres fabricated by melt electrospinning with additives was tested in the Chatillon tensile tester (Chatillon TCD 200) with a load cell of 30 g. The gauge length was 10 mm and the traverse speed was 2.5 mm/min. A single nanofibre was carefully removed from the aluminium foil by using a travelling microscope, which was mounted on a square paper using double face tape and PVA wood glue/Aquadhere as described in Figure 3-8. During the tensile testing, the paper was cut on both sides after it was mounted to the jaws and only the fibre was held by the jaws for tensile testing.

![Figure 3-8: Preparation of single nanofibre for tensile testing in Chatillon tensile tester.](image)

**3.6.13 Surface wettability**

It is well known that PP polymer is hydrophobic in nature (i.e. nonwettable by water). The fabrication of fibres by melt electrospinning using different additives can change the surface wettability of the fibres. The water contact angle was used as a measure of surface wettability. The water contact angle was measured with a pocket Goniometer (PG-3, Fibro System) by using 4 µL deionised water drop. PG software was used to measure the contact angle 5 seconds after the drop was applied. The average results of 10 readings per sample were used as the contact angle.
Chapter 4 Results and discussion: melt electrospinning

4.1 Initial experiments with pure polymers

The apparatus used for melt electrospinning experiments (Figure 4-1) consisted of five major components: high-voltage power supply; temperature controller; electrical heating-assembly; syringe pump; and collector. A negative-voltage DC was applied to the collector placed at variable distances and the syringe (barrel) was grounded. The polymers were heated by electrical heating and the temperature was controlled by a temperature controller. A syringe pump was used for controlling the feed rate of the polymer melt.

![Figure 4-1: Schematic of the equipment used for melt electrospinning experiments.](image)

4.1.1 Establishing the processing parameters

Almost all the previous research on melt electrospinning using PP was with high molecular weights (i.e. >100000). Hence, the average fibre diameters achieved were mainly in the micrometre range [35, 57, 61, 67, 72] or nano to micrometre range [22, 72, 116]. In my research, polymers of low molecular weights (i.e. ≤ 100000) were selected to fabricate nanofibres. The polymers were selected on the basis of MFI (which is reciprocal to the molecular weight). PP of 100, 300, 1000 and 2000 MFI were used for the melt electrospinning experiments. The list of PP polymers along with MFI, IV and molecular weight used in the study are listed in Table 4-1.
Table 4-1: List of polymers used in the melt electrospinning experiments.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>IV (g/dL)</th>
<th>Mw (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.01</td>
<td>100875</td>
</tr>
<tr>
<td>300</td>
<td>0.84</td>
<td>77590</td>
</tr>
<tr>
<td>1000</td>
<td>0.72</td>
<td>60238</td>
</tr>
<tr>
<td>2000</td>
<td>0.66</td>
<td>55509</td>
</tr>
</tbody>
</table>

Initially, systematic studies were performed with all the pure polymers in powder form. Subsequently, additives were mixed thoroughly with the polymer prior to the experiments. The optimum processing conditions, such as the temperature, applied voltage, collector distance, melt flow rate and size of the die or spinneret, were established by systematic study.

4.1.1.1 Temperature

In melt electrospinning, the processing temperature should be high enough to facilitate the formation of finer fibres [22]. In my work, the processing temperatures during melt electrospinning were kept at about 30–50°C higher than the melting point (Tm) of the polymers, for easy processing. The maximum processing temperature to avoid thermal degradation was established experimentally for each polymer, listed in Table 4-2. The lower MFI polymers (i.e. 100 and 300) were able to withstand higher processing temperatures compared to higher MFI polymers (i.e. 1000 and 2000). In this case, the 100 and 300 MFI polymers produced fibres at 210°C without any thermal degradation, whereas 1000 and 2000 MFI polymers started degrading at 210°C. Therefore, the maximum processing temperature for lower MFI polymers (i.e. 100 and 300 MFI) was kept at 210°C and for higher MFI polymers (1000 and 2000 MFI) was kept at 200°C. Temperatures below 180°C were too low for the melt electrospinning experiments. No fibres were fabricated at temperatures of 170°C and 175°C irrespective of the polymer MFI.

Table 4-2: Processing temperatures used in melt electrospinning of PP polymers.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Maximum processing temperature (°C)</th>
<th>Experiments performed (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>210</td>
<td>180, 190, 200, 210</td>
</tr>
<tr>
<td>300</td>
<td>210</td>
<td>180, 190, 200, 210</td>
</tr>
<tr>
<td>1000</td>
<td>200</td>
<td>180, 190, 200</td>
</tr>
<tr>
<td>2000</td>
<td>200</td>
<td>180, 190, 200</td>
</tr>
</tbody>
</table>
4.1.1.2 Applied voltage

The range of applied voltages in melt electrospinning was mainly 4–30 kV [23, 49, 53, 55, 57, 186-189] while some reported values are >30 kV [55, 59, 70]. In this work, the experiments were performed with a range of applied voltages (i.e. 36, 40, 44 and 48 kV) and the operating voltage for each polymer was established. It was found that higher applied voltages resulted in the formation of the finest fibres. Therefore, the final experiments with additives were performed at the highest applied voltage (48 kV). As the maximum output voltage of the high-voltage power supply was 50 kV, the maximum applied voltage was kept at 48 kV. The applied voltages for fibre formation were so selected to avoid electric discharge, which was dependent on the collector distance (discussed in the following section).

4.1.1.3 Collector distance

Collector distance plays a vital role in controlling the fibre diameter in melt electrospinning. Most researchers have used collector distances of 100 mm or less [15, 35, 60, 63, 68, 74, 76, 78, 117] with a few using higher than 100 mm [70, 72, 200-201]. In this work, it was observed that very low collector distances resulted in electric discharge. Similarly, it was difficult to fabricate any fibres at very high collector distances due to insufficient electrostatic drag. The collector distances were increased in steps of 10 or 20 mm for various experiments. The list of applied voltages and collector distances used in initial experiments for each polymer MFI is given in Table 4-3.

Table 4-3: Applied voltages and collector distances used for melt electrospinning.

<table>
<thead>
<tr>
<th>Applied voltage (kV)</th>
<th>Effective collector distances (mm) for fibre fabrication</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 MFI</td>
</tr>
<tr>
<td>36</td>
<td>50°, 70, 90, 100°</td>
</tr>
<tr>
<td>40</td>
<td>60°, 80, 100, 110°</td>
</tr>
<tr>
<td>44</td>
<td>80°, 100, 120°</td>
</tr>
<tr>
<td>48</td>
<td>80°, 100, 120°</td>
</tr>
</tbody>
</table>

*: minimum collector distance to avoid electric discharge and °: maximum collector distance for fibre formation

4.1.1.4 Melt flow rate

In melt electrospinning, the melt flow rate is an important parameter affecting the fibre diameter. The flow rate indicates the amount of polymer melt flowing per unit time through the orifice. It has been found that an increase in the flow rate produced coarser fibres [23, 42, 67]. The flow rates used in the melt electrospinning are significantly lower than those of solution electrospinning [16]. In this work, flow rates of 0.005,
0.0025 and 0.0013 ml/min (i.e. 2.56, 1.28 and 0.64 g/hr) were used in the preliminary experiments. The final experiments were performed at 0.0013 ml/min as this resulted in the lowest fibre diameter. The flow rates were selected on the basis of the data provided in the literature [60, 116].

4.1.1.5 Spinneret size

In melt electrospinning, the flow of the melt through small diameter orifices is challenging due to the high viscosity of the melt [78]. In this work, a variety of die profiles such as circular, trilobal, tetrablobal, multilobal and circular-protruding with different diameters were used in initial experiments.

On the basis of the preliminary experiments, it was decided to perform the final experiments with the conditions given in Table 4-4. These conditions were selected as they resulted in the fibres with finest diameter without any thermal degradation or electric discharge. Although different dies such as 0.3 mm circular (C), 0.2 mm trilobal (T), 0.3 mm circular-protruding (CP) and 0.2 mm CP were successfully used for fibre formation in preliminary experiments, the 0.2 mm CP die was mainly employed for the final experiments. This was selected on the basis of the results of the finest fibre diameter in preliminary experiments and the least chance of clogging of the die.

Table 4-4: Processing parameters established by preliminary experiments for melt electrospinning.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Maximum processing temp. (°C)</th>
<th>Applied voltage (kV)</th>
<th>Collector distances</th>
<th>Flow rate (ml/min) or (g/hr)</th>
<th>Die type</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>210</td>
<td>48</td>
<td>As in Table 4-2</td>
<td>0.0013 (0.64)</td>
<td>0.2 CP</td>
</tr>
<tr>
<td>300</td>
<td>210</td>
<td>48</td>
<td>As in Table 4-2</td>
<td>0.0013 (0.64)</td>
<td>0.2 CP</td>
</tr>
<tr>
<td>1000</td>
<td>200</td>
<td>48</td>
<td>As in Table 4-2</td>
<td>0.0013 (0.64)</td>
<td>0.2 CP</td>
</tr>
<tr>
<td>2000</td>
<td>200</td>
<td>48</td>
<td>As in Table 4-2</td>
<td>0.0013 (0.64)</td>
<td>0.2 CP</td>
</tr>
</tbody>
</table>

4.1.2 Initial results: effect of polymer MFI

After the establishment of the processing parameters by preliminary experiments, initial experiments were performed with the pure polymers only (100, 300, 1000 and 2000 MFI) without any additives. Fibres were fabricated for all the processing parameters listed in Table 4-4 and the diameters were measured by Image J software using the SEM images. However, all the pure polymers resulted in fibres with average diameter in the micrometre range. Hence, the effect of all these processing parameters on fibre diameter is not discussed in detail. Some of the results for the lower MFI PP (100 and 300 MFI) and higher MFI PP (1000 and 2000 MFI) are discussed in the following section.
SEM images of the fibres fabricated from 100 and 300 MFI PP are shown in Figure 4-2. It can be observed that the melt electrospun fibres are circular and varying diameter.

Figure 4-2: SEM images of the fibres fabricated by melt electrospinning of PP: (a) 100 MFI and (b) 300 MFI (melt electrospinning was performed at a temperature of 210°C, applied voltage of 48 kV and feed rate of 0.0013 ml/min using the 0.2 CP die).

Figure 4-3 shows the graphical representation of the average diameter of fibres produced by melt electrospinning of 100 and 300 MFI PP. It can be observed that the fibre diameters are in the micrometre range for both the polymers (14–25 µm for 100 MFI and 8–15 µm for 300 MFI) irrespective of the temperature and collector distance. The average diameter of fibres produced from 300 MFI PP was finer compared to 100 MFI PP.

Figure 4-3: Average diameter of melt electrospun PP fibres fabricated from: (a) 100 MFI and (b) 300 MFI (melt electrospinning was performed at a temperature of 210°C, applied voltage of 48 kV and feed rate of 0.0013 ml/min using the 0.2 CP die).
SEM images of the fibres fabricated from 1000 and 2000 MFI PP are shown in Figure 4-4. It can be observed that the melt electrospun fibres are also circular and varying diameter.

![SEM images of fibres](image)

(a)     (b)

Figure 4-4: SEM images of the fibres fabricated by melt electrospinning of PP: (a) 1000 MFI and (b) 2000 MFI (melt electrospinning was performed at a temperature of 200°C, applied voltage of 48 kV and feed rate of 0.0013 ml/min using the 0.2 CP die).

Figure 4-5 shows the graphical representation of average diameter of fibres produced by melt electrospinning of 1000 and 2000 MFI PP. It can be observed that the fibre diameters are also in the micrometre range for both the polymers (3–10 µm for 1000 MFI and 3–8 µm for 2000 MFI). In addition, it can be observed that the results are missing for 1000 MFI PP at a collector distance of 150 mm. The missing results for 1000 MFI PP indicated insufficient electrostatic drag at high collector distance to form any fibres from the pure polymers. However, the same collector distance was effective for 2000 MFI PP to produce fibres. This can be attributed to the lower viscosity of 2000 MFI PP polymer.
Figure 4-5: Average diameter of melt electrospun PP fibres fabricated from: (a) 1000 MFI and (b) 2000 MFI (melt electrospinning was performed at a temperature of 200°C, applied voltage of 48 kV and feed rate of 0.0013 ml/min using the 0.2 CP die).

It was also observed (from Figure 4-3 and Figure 4-5) that as the collector distance was increased, the fibre diameter decreased. This is in accordance with previous findings [73] and can be attributed to further attenuation of the fibres with increased collector distance. Furthermore, higher temperatures resulted in the formation of finer fibres for all the polymers. This is due to the reduced viscosity at higher temperature resulted in the formation of finer fibres. However, there are limitations in increasing the melt temperature, because beyond certain temperatures the polymer starts degrading. The polymer degradation was visually observed by the colour change of the polymer melt from clear melt to yellow melt with some black particles. These black particles accumulated near the fine die exit and finally led to the blockage of the die without any further fibre fabrication. Table 4-5 shows the list of minimum average fibre diameters achievable from various pure PP polymers by melt electrospinning.

Table 4-5: Minimum average fibre diameters fabricated by melt electrospinning from pure PP polymers.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Minimum avg. fibre diameter (µm)</th>
<th>Standard deviation (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>14.19</td>
<td>5.76</td>
</tr>
<tr>
<td>300</td>
<td>8.23</td>
<td>4.21</td>
</tr>
<tr>
<td>1000</td>
<td>3.39</td>
<td>1.12</td>
</tr>
<tr>
<td>2000</td>
<td>3.01</td>
<td>1.07</td>
</tr>
</tbody>
</table>

From the above results and discussions, it can be concluded that the fibre diameters obtained from pure PP polymers were in the micrometre range irrespective of the polymer MFI. The initial results provided the evidence of formation of finer fibres from
the polymers with higher MFI (hence lower viscosity). A possible reason which prevented the fabrication of nanofibres from pure polymers in melt electrospinning was the high viscosity of the polymer melt. Therefore, the shear viscosities of the polymers were determined over a wide range of shear rates, which is discussed in the following section.

4.1.3 Effect of viscosity

The shear viscosity curves for different PP polymers are shown in Figure 4-6. The shear viscosity for 100 and 300 MFI PP was measured at 210°C whereas it was measured at 200°C for 1000 and 2000 MFI PP. The temperatures were selected as these were the maximum temperatures to prevent thermal degradation. It can be observed from the figure that the shear viscosity decreased with the increase in the polymer MFI, which in turn resulted in finer fibres.

Figure 4-6: Shear viscosity curves of different PP polymers: (a) 100 and 300 MFI at 210°C, and (b) 1000 and 2000 MFI at 200°C.
The viscosity of the polymer melt depends on many factors, such as molecular weight of the polymer, melt electrospinning temperature, heating time and presence of viscosity-reducing agents. As the processing temperature plays an important role in governing the polymer viscosity, the temperature dependence of the melt viscosity of PP polymer was investigated. The shear viscosity was tested for all the polymers at the different temperatures used for melt electrospinning. The shear viscosity curves of lower MFI polymers are shown in Figure 4-7, and the higher MFI polymers are shown in Figure 4-8.

Figure 4-7: Shear viscosity curves of PP polymers of at different temperatures: (a) 100 MFI and (b) 300 MFI.
Figure 4-8: Shear viscosity curves of PP polymers of at different temperatures: (a) 1000 MFI and (b) 2000 MFI.

It can be observed that the shear viscosity of the melt decreased as the processing temperature increased, irrespective of the polymer MFI. The shear viscosity was lowest at 210°C for 100 and 300 MFI PP, whereas it was lowest at 200°C for 1000 and 2000 MFI PP. Therefore, the lowest diameters of fibres fabricated at higher temperatures can be attributed to the lowest viscosity. A similar phenomenon of reduction in the shear viscosity of PLA melt with temperature was observed by Zhou et al. [22]. The shear viscosity values for different polymers at a shear rate of 50S⁻¹ have been shown in Table 4-6 and the graph in Figure 4-9.
Table 4-6: Shear viscosity values of PP polymers at different temperatures (at a shear rate of 50S⁻¹).

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Shear viscosity values (Pa.S) at different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>180°C</td>
</tr>
<tr>
<td>100</td>
<td>243.5</td>
</tr>
<tr>
<td>300</td>
<td>192.5</td>
</tr>
<tr>
<td>1000</td>
<td>142.5</td>
</tr>
<tr>
<td>2000</td>
<td>79.0</td>
</tr>
</tbody>
</table>

* 1000 and 2000 MFI PP degrades at a temperature of 210°C.

In addition, to the above observations on fibre diameter and viscosity, other important observations on the effects of flow rate, die size and shape on the fibre diameter are worth mentioning, and are discussed in the following section.

![Graph of shear viscosity values](image)

Figure 4-9: Shear viscosity values of polymers at different temperatures.

### 4.1.4 Effect of melt flow rate

The effect of melt flow rate on fibre diameter was analysed by changing the polymer flow rate from 0.005 to 0.0013 ml/min (i.e. 2.56 to 0.64 g/hr). Figure 4-10 shows the effect of melt flow rate on the fibre diameter at different applied voltages. It can be observed that as the flow rate decreased from 0.005 ml/min to 0.0013 ml/min, fibres with smaller diameters were fabricated. At higher flow rates, more polymer melt was delivered through the die, which was difficult to stretch by the same amount of applied voltage, hence resulting in coarser fibres. As the objective of the current research is to fabricate fibres with the smallest diameter by melt electrospinning, the lowest flow rate of 0.0013 ml/min was selected for the study. Flow rates lower than 0.0013 ml/min were
not sufficient to produce any fibres in melt electrospinning. Furthermore, it could be observed that the fibre diameters decreased as the applied voltage was increased.

Figure 4-10: Effect of melt flow rate and applied voltage on average fibre diameter of melt electrospun PP: (a) 100 MFI, (b) 300 MFI, (c) 1000 MFI and (d) 2000 MFI (melt electrospinning was performed at a temperature of 210°C (for 100 and 300 MFI) and 200°C (for 1000 and 2000 MFI) using the 0.2 CP die).
4.1.5 Other observations

Some other important observations noticed during melt electrospinning and worth mentioning are discussed in this section. It was observed that the main driving force in melt electrospinning for fibre formation is the electrostatic attraction, similar to solution electrospinning. This was observed when the high-voltage supply was turned off; the deposition of fibres on the collector immediately ceased, indicating that the electrostatic force plays the main role in fibre attenuation. It was also observed that the jet diameter was continuously reduced during its path to the collector as the electrostatic forces acted on it until the end-point. In all the experiments, a single fibre was formed by the melt electrospinning process from the Taylor cone at the apex of the die.

4.1.6 Effect of die size and shape

In melt electrospinning, the flow of the polymer melt through the small die orifice is challenging due to its relatively high viscosity. The die size is one of the important parameters affecting the fibre diameter. Although some previous work has shown a direct relation between the die size and fibre diameter [69], no work has been done to study the combined effects of die size and shape on fibre size and morphology. In this study, the combined effects of die size and shape on the fibre diameter and morphology was investigated by using the different dies as listed in Table 4-7. The cross-sectional area of the dies was determined by using an optical microscope. Although the experiments were performed with all the polymers, the results were analysed only for 1000 MFI PP (at 48 kV, 200°C and feed rate of 0.0013 ml/min) as the other polymers produced similar results and the fibre diameter were in micrometres for all the polymers.

<table>
<thead>
<tr>
<th>Die size (mm)</th>
<th>Die Shape (C/T/CP)</th>
<th>Cross-sectional area of die orifice (µm²) × 10⁴</th>
<th>Fibre formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>C</td>
<td>*</td>
<td>No</td>
</tr>
<tr>
<td>0.1</td>
<td>C</td>
<td>0.64</td>
<td>No</td>
</tr>
<tr>
<td>0.15</td>
<td>C</td>
<td>1.62</td>
<td>No</td>
</tr>
<tr>
<td>0.2</td>
<td>C</td>
<td>2.84</td>
<td>No</td>
</tr>
<tr>
<td>0.2</td>
<td>CP</td>
<td>2.55</td>
<td>Yes</td>
</tr>
<tr>
<td>0.3</td>
<td>CP</td>
<td>6.17</td>
<td>Yes</td>
</tr>
<tr>
<td>0.3</td>
<td>C</td>
<td>6.64</td>
<td>Yes</td>
</tr>
<tr>
<td>0.2</td>
<td>T</td>
<td>34.03</td>
<td>Yes</td>
</tr>
</tbody>
</table>

C: Circular, T: Trilobal and CP: Circular-protruding. Melt electrospinning was performed at 48 kV, 200°C and feed rate of 0.0013 ml/min using 1000 MFI PP.

*The area could not be measured as too small orifice diameter
4.1.6.1 Effect of die size

As smaller nozzle diameters favour the formation of fibres with smaller average diameters [22, 63], initially the experiments were performed with the smallest die size (0.05 mm) before moving to larger sizes. It was observed that the circular dies with 0.2 mm orifice size or lower (i.e. 0.05, 0.1 and 0.15 mm) did not produce any fibre because the high viscosity of the polymer melt prevented the flow through the small orifices. Table 4-7 shows that the cross-sectional area of the orifices in these four dies is smaller than for the other four dies. This might be the reason for the inability of these dies to form any fibres. The syringe pump usually stalled due to the rise in the pressure, since no polymer could exit from the orifices of these dies. However, the other four dies i.e. 0.2 CP, 0.3 CP, 0.3 C and 0.2 T were able to produce fibres.

Figure 4-11 shows the SEM images and fibre diameter distribution plots of the electrospun PP fibres using different dies for 1000 MFI PP. It can be observed from the diameter distribution plots that among all the dies used, the 0.2 T die with the largest orifice produced the coarsest fibre whereas the 0.2 CP die with the smallest orifice produced the finest fibre. Therefore, the nozzle size is an important parameter in the fabrication of fibres with smaller diameter.
Figure 4-11: SEM micrographs showing the effect of die size on the diameter of melt electrospun PP fibres fabricated by: (a) 0.2 CP die, (b) 0.3 CP die, (e) 0.3 C die, and (f) 0.2 T die with accompanying the diameter distribution plots (in micrometres) of fibres fabricated by: (c) 0.2 CP die, (d) 0.3 CP die, (g) 0.3 C die, and (h) 0.2 T die (melt electrospinning was performed at a temperature of 200°C, applied voltage of 48 kV and feed rate of 0.0013 ml/min from 1000 MFI).

From the above results, the presence of nanofibres can be observed only in the case of protruding dies (i.e. 0.3 CP and 0.2 CP). The circular die (0.3 C) with almost the same
cross-sectional area compared to the circular-protruding die (0.3 CP) produced only micro fibres. Similarly, the 0.2 C die with almost the same cross-sectional area compared to 0.2 CP die did not produce any fibre, whereas nanofibres were fabricated in the later case. The nanofibre fabrication in the case of circular-protruding dies is due to the fact that electric field is being concentrated at the end of protrusion, whereas in circular dies (without protrusion) it is distributed over a wider area (Figure 4-12). Hence, more drag force is experienced by the jet from the circular-protruding die, resulting in finer fibres.

![Electric field distribution patterns: (a) circular die and (b) circular-protruding die.](image)

Figure 4-12: Electric field distribution patterns: (a) circular die and (b) circular-protruding die.

Figure 4-13 shows the graphical plot of the effects of different die types on fibre diameter. It can be observed that the 0.2 CP die and 0.2 T die produced the smallest and the largest fibre diameters respectively, corresponding to the smallest and largest cross-sectional area of the dies.

![Graphical plot of die size on average fibre diameter of melt electrospun PP fibres for 1000 MFI.](image)

Figure 4-13: Effect of die size on the average fibre diameter of melt electrospun PP fibres for 1000 MFI (melt electrospinning was performed at a temperature of 200°C, applied voltage of 48 kV and feed rate of 0.0013 ml/min).
4.1.6.2 Effect of die shape

The shape of the die in any melt processing (such as meltspinning and meltblowing) affects the fibre morphology. The effect of the shape of the die on fibre cross-section using dies other than the circular, such as trilobal, tetralobal and multilobal (not listed in Table 4-7), was also investigated, using only 1000 MFI PP. To the best of the author’s knowledge, for the first time it was observed that there is no effect of the shape of the die on the final fibre cross-sectional shapes for PP fibres. The cross-sections of the PP fibres fabricated by different dies are shown in Figure 4-14. It was found that all the dies (i.e. trilobal, tetralobal and multilobal) produced circular fibres, similar to the circular die. Normally in commercial meltblowing, meltspinning or any other melt processing, the fibre cross-section follows the die shape used (i.e. a trilobal die produces trilobal fibres). The shape of fibres not following the die cross-section in melt electrospinning is due to the presence of the Taylor cone, which is essential for electrospinning. When the high-voltage is applied, the polymeric melt is distorted into the form of the Taylor cone [13]. As the electrospinning process starts from the Taylor cone formed at the apex of the die, the die cross-section plays no role in shaping the fibre cross-section.

Figure 4-14: Effect of die shape on the cross-section of the melt electrospun PP fibres fabricated from 1000 MFI PP (melt electrospinning was performed at a temperature of 200°C, applied voltage of 48 kV and feed rate of 0.0013 ml/min): (a) circular die, (b) trilobal die, (c) tetralobal die, and (d) multilobal die.
From the above discussions, it can be concluded that the efforts to fabricate nanofibres in melt electrospinning of pure PP polymers by applying high temperature, high-voltage and very low feed rates only resulted in fibres of micrometre diameter. Therefore, an alternative approach of using different additives to the pure polymers was adopted. The results of using additives are discussed in the following section.

4.2 Experiments with additives
Additives such as SO, PEG, PDMS and NaCl were introduced into the PP melt with the objective of either reducing the viscosity of the polymer or increasing the electrical conductivity, to help in the fabrication of nanofibres. PEG and PDMS were selected for the reduction of viscosity; and SO and NaCl were selected for the increase in electrical conductivity. The results of adding the additives are discussed in the following section.

4.2.1 Effect of additives on fibre diameter
The PP pellets were converted to fine powder by cryogenic (liquid nitrogen) grinding [106] and the selected additives were added and mixed with the PP powder on the basis of percent by weight (4, 7 and 12%) and thoroughly mixed prior to melt electrospinning. The experiments were performed for the entire four polymer MFIs by using the 0.2 CP die, which had previously produced the finest fibres from pure polymers (see Section 4.1.1.5).

4.2.1.1 Fibre diameter from 100 and 300 MFI
It was observed that the minimum average diameters of the fibres formed with the additives using 100 and 300 MFI PP remained within the micrometre range, irrespective of the percentage or type of additives introduced. This can be attributed to the higher degree of polymer chain entanglement in the polymers with lower MFI (hence higher molecular weight) and the inability of the applied electric field to pull individual polymer chains sufficiently well to fabricate nanofibres. Since these two polymers (100 and 300 MFI) with additives formed fibres still in the micrometre range, no further characterisation was performed for them. The smallest average diameters of fibres fabricated from 100 and 300 MFI PP are shown in Table 4-8.
Table 4-8: Smallest average diameters of fibres fabricated by melt electrospinning from 100 and 300 MFI PP with and without additives.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Polymer MFI</th>
<th>Smallest average fibre diameters (µm)</th>
<th>Standard deviation (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With additives</td>
<td>100</td>
<td>6.54</td>
<td>2.14</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>3.36</td>
<td>1.06</td>
</tr>
<tr>
<td>Without additives</td>
<td>100</td>
<td>14.19</td>
<td>5.76</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>8.23</td>
<td>4.21</td>
</tr>
</tbody>
</table>

4.2.1.2 Fibre diameter from 1000 and 2000 MFI

In the case of 1000 and 2000 MFI PP, the addition of SO and NaCl resulted in the formation of nanofibres. These were investigated and fully characterised and are discussed in the following sections. The surface morphology and diameter distribution of melt electrospun PP fibres fabricated with different additives (7%) from 1000 and 2000 MFI PP (at 48 kV, 200°C and feed rate of 0.0013 ml/min) are shown in Figure 4-15 and Figure 4-16 respectively.

![Image of fibre diameter distribution](image1)

(a) Frequency (µm)  
(b) Frequency (µm)  
(c) Frequency (µm)  
(d) Frequency (µm)  

AVG : 3.39  
SDEV : 1.84  
MIN : 0.16  
MAX : 11.87  

AVG : 0.88  
SDEV : 0.61  
MIN : 0.14  
MAX : 3.54
Figure 4-15: SEM micrographs of melt electrospun PP (1000 MFI) fibres with different additives (7%, 48 kV, 200°C and feed rate of 0.0013 ml/min): (a) pure PP, (c) PP with 7% SO, (e) PP with 7% PEG, (g) PP with 7% PDMS and (i) PP with 7% NaCl. Diameter distribution plots of the fibres: (b) pure PP, (d) PP with 7% SO, (f) PP with 7% PEG, (h) PP with 7% PDMS and (j) PP with 7% NaCl.
Figure 4-16: SEM micrographs of melt electrospun PP (2000 MFI) fibres with different additives (7%, 48 kV, 200°C and feed rate of 0.0013 ml/min): (a) pure PP, (c) PP with 7% SO, (e) PP with 7% PEG, (g) PP with 7% PDMS and (i) PP with 7% NaCl. Diameter distribution plots of the fibres: (b) pure PP, (d) PP with 7% SO, (f) PP with 7% PEG, (h) PP with 7% PDMS and (j) PP with 7% NaCl.
It can be observed from above figures that all the additives used in the study helped to reduce the fibre diameter. The fibres fabricated with SO and NaCl were uniform and of nanometre diameter compared to the fibres fabricated from pure PP, PP with additives: PEG and PDMS. Some of the earlier findings have also shown the fabrication of micro and nanofibres by different approaches, which are mentioned in Table 4-9.

Table 4-9: Average fibre diameters obtained in melt electrospinning by different researchers.

<table>
<thead>
<tr>
<th>Name of researcher(s)</th>
<th>Polymer/Features</th>
<th>Fibre diameter (µm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current research</td>
<td>iPP* (Mw: 55509, 60238, 77590 &amp; 100875) (with additives to reduce the viscosity and improve the electrical conductivity)</td>
<td>0.310–25</td>
<td>This study</td>
</tr>
<tr>
<td>Larrondo &amp; Manley</td>
<td>iPP (the objective was to fabricate fibres)</td>
<td>20–180</td>
<td>[66]</td>
</tr>
<tr>
<td>Lyons et al.</td>
<td>iPP (Mw: 12000, 106000, 190000, 580000) (used a Brabender extruder, no syringe pump used)</td>
<td>3.5–466</td>
<td>[63]</td>
</tr>
<tr>
<td>Lyons et al.</td>
<td>aPP+ (Mw: 14000–19600) (used a Brabender extruder, no syringe pump used)</td>
<td>2.25–8.33</td>
<td>[63]</td>
</tr>
<tr>
<td>Dalton et al.</td>
<td>iPP (MFI 44) (SEM stubs and glass slides were used as collector)</td>
<td>8.6–35.6</td>
<td>[60]</td>
</tr>
<tr>
<td>Lee &amp; Obendorf</td>
<td>iPP, (Mw: 195000) (heated collector)</td>
<td>15–40</td>
<td>[35]</td>
</tr>
<tr>
<td>Kong &amp; Jo</td>
<td>iPP (MFI: 900 &amp; 1500) collector vicinity heated</td>
<td>20–40</td>
<td>[73]</td>
</tr>
<tr>
<td>Dalton et al.</td>
<td>iPP+1.5% Irgatec (MFI: 15): no additive with additive</td>
<td>35.6 ± 1.7 0.84 ± 0.19</td>
<td>[60]</td>
</tr>
</tbody>
</table>

* iPP: isotactic polypropylene, ^aPP: atactic polypropylene

It can be observed from the above table that majority of the research achieved microfibres in melt electrospinning using PP. The difficulty in achieving the nanofibres was due to the use of high molecular weight PP, which has high melt viscosity. The approach of reducing the melt viscosity of PP was only adopted by Dalton et al. [60] by adding Irgatec (at 1.5%). The fibre diameter was reduced from 35.6 ± 1.7 µm to 0.840 ± 0.19 µm by the additive. None of the above mentioned research has attempted improvement of the electrical conductivity of the polymer melt. This study focused on the use of additives to: (a) reduce the melt viscosity and (b) improve the electrical conductivity, for the fabrication of nanofibres by melt electrospinning.

The effects of different levels of additives on fibre diameter of 1000 and 2000 MFI PP have been shown in Figure 4-17 and Figure 4-18 respectively. It can be observed from Figure 4-17 (for 1000 MFI) that in case of pure PP and PP with the additives PEG and
PDMS the fibre diameter was in the micrometre range. The addition of PEG and PDMS, helped in the reduction of fibre diameter but was not sufficient to produce nanometre size. Nanofibres were achieved with the addition of SO and NaCl. The effect of increasing the amount of additives from 4 to 12% for 1000 MFI PP on fibre diameter showed a decrease followed by an increase trend in the case of SO. In the case of PEG, the fibre diameter first increased when the PEG concentration was increased from 4 to 7% and then it decreased at 12%. In case of PDMS, a decrease followed by an increase trend was observed when the PDMS concentration was increased from 4 to 7% and 7 to 12% respectively. In the case of NaCl, a decrease followed by an increase trend was observed.
Figure 4-17: Effect of amount of additives (SO, PEG, PDMS and NaCl) on fibre diameter (melt electrospinning was performed at 48 kV, 200°C and feed rate of 0.0013 ml/min): (a) 4%, (b) 7%, and (c) 12% (absence of bars in the graphs indicate no fibres being fabricated).

It can also be observed from the above figures that as the collector distance increased, the fibre diameter decreased. At a collector distance of 150 mm or further, in the case of
pure PP and PP with PDMS additive, no fibre was fabricated. This can be attributed to the insufficient electrostatic drag at very high collector distance of 150 mm.

It can be observed from Figure 4-18 (for 2000 MFI) that in the case of pure PP and PP with the additives PEG and PDMS, the fibre diameter was in the micrometre range, similar to 1000 MFI. The addition of PEG and PDMS helped in the reduction of fibre diameter but not to nanometre size. Nanofibres were fabricated with the addition of SO and NaCl. The fibre diameter decreased and then increased when the amount of SO was increased from 4 to 7% and 7 to 12% respectively. When the amount of PEG was increased from 4 to 7%, the fibre diameter increased and it was decreased when the PEG amount was increased from 7 to 12%. In the case of PDMS, higher fibre diameter was observed with the increase in the amount of PDMS. In the case of NaCl, a decrease followed by an increase trend was observed.
Figure 4-18: Effect of amount of additives (SO, PEG, PDMS and NaCl) on fibre diameter (melt electrospinning was performed at 48 kV, 200°C and feed rate of 0.0013 ml/min): (a) 4%, (b) 7%, and (c) 12%.

In addition, it can be observed that the diameter of fibres fabricated with 2000 MFI PP with additives was finer than that of the fibres from 1000 MFI PP with additives. The collector distance of 150 mm resulted in the formation of fibres for 2000 MFI PP and PP
with PDMS, but did not produce any fibre in the case of 1000 MFI PP and PP with PDMS.

It can be concluded that the addition of the additives helped to reduce the fibre diameter in melt electrospinning. Among the four additives, SO and NaCl, were successful in the fabrication of uniform nanofibres. The possibilities for the reduction in the fibre diameter with the additives are: (i) reduction in the melt viscosity and (ii) increase in the electrical conductivity [16, 21]. Therefore, the effect of shear viscosity and the electrical conductivity of the polymer melts with different additives were evaluated and are discussed in the following section.

4.2.1.3 Effect of viscosity

The shear viscosity curves for 1000 and 2000 MFI PP with different additives (7%) are shown in Figure 4-19. It can be observed that the viscosity of the polymer melt decreased in the presence of PEG and PDMS, while it increased with SO and NaCl, in both the cases of 1000 and 2000 MFI. Similar behaviour was observed with the addition of the additives at 4 and 12%. The decrease in the melt viscosity by adding PEG and PDMS resulted in the fabrication of finer fibres, compared to pure polymers. The magnitude of viscosity reduction was dependent on the amount and type of additives; the processing temperature; and the shear rate.
Figure 4-19: Shear viscosity curves of PP polymer with different additives (7%) at 200°C: (a) 1000 MFI and (b) 2000 MFI.

In addition, the figure shows that in the case of SO and NaCl, the melt viscosity was increased. Hence the reduction in fibre diameter was possibly due to change in the electrical conductivity, which can be attributed to the presence of ions (by the dissociation of these additives) in the polymer melt. Furthermore, it can be observed from viscosity results that PP with additives does not exhibit a strong shear thinning
behaviour over a wide range of shear rates. The shear viscosity of 2000 MFI PP is lower than 1000 MFI.

4.2.1.4 Effect of electrical conductivity

The results obtained from the rheological investigations showed that the viscosity of the polymer melt with the additives SO and NaCl was increased. Hence, the other possibility for the fabrication of nanofibres in melt electrospinning is the increase in the electrical conductivity by the addition of these conductive additives. Therefore, the electrical conductivity of the polymers with SO and NaCl was measured.

In solution electrospinning, the effect of increase in the electrical conductivity of polymer solution on fibre diameter and morphology by the addition of different conductive materials has been investigated by several researchers [41, 118]. However, the study on the effect of electrical conductivity has not been reported earlier in melt electrospinning. It is a well known fact that PP is a good electrical insulator and the amount of current flowing in it is very low at room temperature [119]. Therefore, the addition of additives such as SO and NaCl can lead to an increase in the electrical conductivity of PP.

In order to study the effect of electrical conductivity, the current flowing through PP polymers and PP polymers with additives was measured at elevated temperatures by an electrometer (Keithley 2612). Figure 4-20 shows the change in the electrical conductivity with the addition of SO and NaCl (7%) at different temperatures for 1000 MFI PP. 2000 MFI PP with additives showed similar plots for electrical conductivity and is shown in Appendix A 1.1 and A 1.2. It can be observed from the figure that pure PP polymer melt showed the electrical conductivity in the level of 10⁻¹² S/cm at the highest processing temperature. The electrical conductivity was increased with the addition of SO and NaCl.
The electrical conductivity for PP melt with 7% SO was increased from the level of $10^{-10}$ S/cm to $10^{-8}$ S/cm when the temperature was increased from 180 to 200°C. Similarly, the electrical conductivity for PP melt with 7% NaCl was increased from the level of $10^{-9}$ S/cm to $10^{-7}$ S/cm when the temperature was increased from 180 to 200°C. This is because at lower temperatures, there is little ionic motion. As the temperature increased, the ionic motion between the electrodes increased, resulting in more current flow.

Electrical conductivity in the polymeric materials is governed by the generation and mobility of the charge carriers or ions. The increase in the electrical conductivity with the addition of SO and NaCl can be attributed to the effect of the ions from the dissociation of the additives. At higher temperature, more ions are available, leading to higher electrical conductivity. During melt electrospinning, the ions increased the charge-carrying capacity of the polymer melt-jet. The melt-jet underwent whipping instability during its travel to the collector. The presence of more charges increased the
charge repulsion in the jet. Therefore, the whipping instability of the jet was increased and the jet was subjected to stronger stretching forces, resulting in the formation of finer fibres [41]. In addition, the jet was repeatedly split into smaller jets by the increased charge density, resulting in smaller fibre diameter [120].

The effect of amount of additives on the electrical conductivity of the polymer melt is given in Figure 4-21. It can be observed that as the amount of additives increased from 4 to 12%, the electrical conductivity also increased. The electrical conductivity increased from the level of $10^{-8}$ S/cm to $10^{-6}$ S/cm when the amount of SO increased from 4 to 12%. Similarly, the electrical conductivity increased from the level of $10^{-7}$ S/cm to $10^{-5}$ S/cm when the amount of NaCl increased from 4 to 12%. The amount of current flowing through the polymer melt by the addition of NaCl was higher compared to the addition of SO. The smaller ionic size of NaCl helped to achieve higher mobility of the ions and hence higher current flow. Therefore, the elongational forces experienced by the melt-jet with NaCl was higher than with SO. This might be the reason for the formation of finest fibres by the addition of NaCl.

Figure 4-21: Effect of the amount of additives on the electrical conductivity of PP of 1000 MFI with (a) SO and (b) NaCl (at 200°C).
4.2.1.5 **Optimum concentration of SO and NaCl**

It has been shown that the addition of SO and NaCl resulted in the fabrication of nanofibres. Therefore, the optimum amounts of SO and NaCl to obtain the smallest average fibre diameter were determined experimentally. Both the additives were added to pure PP polymers (1000 & 2000 MFI) in varying quantities as listed in Table 4-10 and the melt electrospinning was performed at collector distances of 120, 140 and 150 mm.

Table 4-10: The amount of additives used to establish the optimum level.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Amount of additives (%)</th>
<th>SO</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>4, 6, 7, 8, 10, 12</td>
<td>4, 5, 6, 7, 10, 12</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>4, 6, 7, 8, 10, 12</td>
<td>4, 5, 6, 7, 10, 12</td>
<td></td>
</tr>
</tbody>
</table>

The average diameters of the melt electrospun fibres with different amounts of additives were measured, graphically shown in Figure 4-22 and Figure 4-23. The figures show that the smallest fibre diameter of electrospun PP fibres was achieved from 7% SO and 5% of NaCl, irrespective of polymer MFI. Therefore, the optimum levels of SO and NaCl were 7% and 5% respectively. The average fibre diameter decreased up to a certain percentage of the additives. When the amount of additives increased beyond this value, the fibre diameter started increasing. The increase in the conductivity after a certain level increases the instability of the melt electrospinning process. This leads to an increase in the fibre diameter after a certain percentage of the additive.
Figure 4-22: Optimum concentration of SO: (a) 1000 MFI and (b) 2000 MFI (melt electrospinning was performed at 48 kV, 200°C and feed rate of 0.0013 ml/min).
Figure 4-23: Optimum concentration of NaCl: (a) 1000 MFI and (b) 2000 MFI (melt electrospinning was performed at 48 kV, 200°C and feed rate of 0.0013 ml/min).

The smallest diameters of the fibres with the optimum amounts of SO and NaCl are listed in Table 4-11. It can be observed that the amount of NaCl required to achieve the lowest fibre diameter was less compared to SO. The size and number of ions depend on the type of the additive used. The charge density is higher when the ions are of smaller radius and thus a higher mobility under the influence of external electric field is obtained. In this case, the lowest size of the ions from NaCl with higher mobility (compared to SO) increased the net charge density on the melt-jet. Therefore, the jet was stretched by a higher amount with NaCl, resulting in finer fibres. The conductivity
results established the fact that the decrease in the fibre diameter was contributed by the conductivity.

Table 4-11: Smallest fibre diameter obtained by melt electrospinning of PP with SO and NaCl.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Smallest fibre diameters (µm) without additives</th>
<th>Smallest fibre diameters (µm) with additives</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>With SO (7%)</td>
</tr>
<tr>
<td>1000</td>
<td>3.39 ± 1.12</td>
<td>0.841 ± 0.232</td>
</tr>
<tr>
<td>2000</td>
<td>3.01 ± 1.07</td>
<td>0.371 ± 0.106</td>
</tr>
</tbody>
</table>

4.3 Characterisation

4.3.1 Elemental composition analysis by EDX

The presence and distribution of SO, PDMS and NaCl in the electrospun PP fibres were analysed by EDX microanalysis. The presence of the additives in the electrospun fibres was determined at randomly selected areas using the EDX spectrum. EDX cannot be used to uniquely identify the elements of PEG as it is a long-chain polymer of carbon (C), hydrogen (H) and oxygen (O). In the EDX spectra (Figure 4-24), the main elements observed in the PP electrospun fibres with SO are C, O, aluminium (Al) and Na. The presence of Na indicates the presence of SO in the fibre structure. The presence of Al can be attributed to the underlying aluminium foil used to collect the fibres, which was present during the EDX analysis.

Similarly, the EDX spectra of electrospun PP fibres with PDMS (Figure 4-25) showed the presence of Si, which is due to the PDMS additive. The presence of Na and chlorine (Cl) indicated the presence of NaCl additive (Figure 4-26). Net counts of these elements can be directly used as an indicator of the relative amounts of the additives in the fibre. Higher net counts suggest higher relative amount of the additives in the fibre.
Figure 4-24: EDX spectra of electrospun PP fibres with (a) 0%, (b) 4%, (c) 7%, and (d) 12% of SO respectively (melt electrospinning was performed at 48 kV, 200°C and feed rate of 0.0013 ml/min).

Figure 4-25: EDX spectra of electrospun PP fibres with (a) 0%, (b) 4%, (c) 7%, and (d) 12% of PDMS respectively (melt electrospinning was performed at 48 kV, 200°C and feed rate of 0.0013 ml/min).
Figure 4-26: EDX spectra of electrospun PP fibres with (a) 0%, (b) 4%, (c) 7%, and (d) 12% of NaCl respectively (melt electrospinning was performed at 48 kV, 200°C and feed rate of 0.0013 ml/min).

Figure 4-27, Figure 4-28 and Figure 4-29 indicate the distribution of the additives in the electrospun PP fibre by EDX mapping. It can be observed from these figures that as the percentage of SO, PDMS and NaCl increased, the amount of the respective elements increased (shown by higher numbers of dots). The EDX mappings also showed the uniform distribution of the additives in the melt electrospun fibre.

Figure 4-27: EDX mapping of electrospun PP fibres with (a) 0%, (b) 4%, (c) 7%, and (d) 12% of SO respectively (melt electrospinning was performed at 48 kV, 200°C and feed rate of 0.0013 ml/min).
4.3.2 NMR results

The process of melt electrospinning involves the application of high temperature and high-voltage. The application of high temperature can lead to chemical changes in the PP polymer by oxidation with atmospheric oxygen. This can lead to chemical changes in the structure of PP by the formation of carboxylic acids, aldehydes or esters [121, 122]. In addition, the additives can be either physically distributed in the fibre or chemically bonded with PP, forming new compounds. Therefore, to investigate whether there is any chemical change by the electrospinning process with the additives, NMR spectra were used. $^{13}$C NMR spectra of the as-spun fibre and fibres fabricated with different additives were recorded for 1000 MFI PP to determine the chemical structure (Figure 4-30).
Figure 4-30: $^{13}$C NMR spectra of fibres fabricated by melt electrospinning with different additives.

It can be observed that the chemical shifts $a$, $b$, $c$ in the figure correspond to the $-\text{CH}_3$, $-\text{CH}$ and $-\text{CH}_2$ groups of PP respectively. The comparison of the NMR spectra indicated that the spectra of the as-spun fibre and fibres fabricated with different additives were similar. The addition of additives does not change the chemical structure of the fibres. This indicated that the additives are only distributed physically in the fibre structure without any chemical reaction. The chemical shifts of the melt electrospun fibres are listed in Table 4-12.

Table 4-12: Chemical shifts of PP.

<table>
<thead>
<tr>
<th>Code</th>
<th>Chemical shift (ppm)</th>
<th>group</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>23.6</td>
<td>$-\text{CH}_3$</td>
</tr>
<tr>
<td>b</td>
<td>28.4</td>
<td>$-\text{CH}$</td>
</tr>
<tr>
<td>c</td>
<td>43.2</td>
<td>$-\text{CH}_2$</td>
</tr>
</tbody>
</table>

**4.3.3 FTIR results**

In addition to the EDX microanalysis and NMR, FTIR spectroscopy was used to further examine the presence of the additives in the fibre structure. The FTIR spectra were compared and peak analysis (shifting, appearance or disappearance of peaks) was
performed to confirm the presence of the additives. The FTIR spectra of PP polymer, as-spun fibre and fibres fabricated with different additives by melt electrospinning are shown in Figure 4-31.

It can be observed that the IR spectra of the PP polymer and as-spun fibre are similar. Similar IR spectra indicate that there was no chemical change of PP by the application of high-voltage and high temperature during melt electrospinning. The presence of SO was indicated by presence of the peaks corresponding to –COO and –C= C stretching. This presence of -C–O–C and –OH peaks was strong evidence that PEG was present on the electrospun fibre.

Figure 4-31: FTIR spectra of melt electrospun fibres of PP with different additives.

The presence of PDMS was strongly indicated by the peaks at 1090 and 808, which indicate –Si–O–Si stretching and –SiC stretching respectively. It is to be noted that the presence of NaCl cannot be determined by FTIR spectroscopy. However, the presence of NaCl was confirmed by the EDX microanalysis.

In addition to the above spectra, the presence of the additives was confirmed in accordance with the spectra of the additives. Figure 4-32 shows the FTIR spectra of the additives and the melt electrospun fibres fabricated with the additives. The fibres fabricated with additives (SO, PEG and PDMS) show some specific peaks corresponding to the additives, as shown in the figure.
Figure 4-32: FTIR spectra of: (a) PP polymer, pure SO and fibres with SO; (b) PP polymer, pure PEG and fibres with PEG; and (c) PP polymer, pure PDMS and fibres with PDMS.

4.3.4 DSC results

DSC was used to analyse the thermal behaviour of the fibres fabricated by melt electrospinning and to understand the polymer degradation by the decrease of the expected melting point ($T_m$). Figure 4-33 shows the typical thermograms of the as-spun
fibres and the fibres fabricated with SO by melt electrospinning from 1000 MFI PP for different heating/cooling cycles. The DSC thermograms (Figure 4-33, a: 1st heating cycle) indicate that the as-spun fibres exhibited a melting point of 166°C, whereas the fibres produced with varying amounts of SO exhibited melting points in the range of 148–169°C. In addition, only one endothermic peak was observed for the as-spun fibre and fibres with 4% SO, whereas several peaks were observed for the fibres with 7 and 12% SO. The shape of the endotherms became more complex with higher amounts of SO (7 and 12%). The presence of SO in higher amounts shifted the endothermic peak towards higher temperature.
Figure 4-33: DSC thermograms of melt electrospun PP fibres of 1000 MFI PP with varying amounts of SO: (a) 1st heating cycle (b) 1st cooling cycle and (c) 2nd heating cycle.

The cold crystallisation was observed at 110.5°C for the as-spun fibre and in the range of 109–110.5°C for the fibre samples fabricated with different amounts of SO (Figure 4-33, b: 1st cooling cycle). The heating of the fibres for the second cycle is shown in Figure
4-33 (c). Two peaks can be observed for the as-spun fibres and the fibres fabricated with 4% SO. The temperatures corresponding to the double peaks were (155.5, 162.5°C) and (149.5, 158.5) for as-spun fibres and fibres fabricated with 4% SO. Multiple peaks were observed for the fibres fabricated with 7 and 12% SO and the shape of the endotherm became complex (similar to the 1st cycle) with higher amounts of SO. The presence of SO in higher amounts (7 and 12%) also shifted the endothermic peak towards higher temperature.

The typical thermograms of fibres fabricated from 1000 MFI PP with different amounts of PEG, PDMS and NaCl are shown in Figure 4-34, Figure 4-35 and Figure 4-36 respectively. The melting points of the fibre samples (corresponding to the 1st heating cycle) are listed in Table 4-13. It can be observed that in all these cases, there was a decrease of the melting point compared to the as-spun fibre. This change in the melting endotherm indicated a change of the crystalline phase. This also indicated the decrease of the molecular weight, possibly by thermal degradation during electrospinning.
Figure 4-34: DSC thermograms of melt electrospun PP fibres of 1000 MFI PP with varying amounts of PEG: (a) 1st heating cycle (b) 1st cooling cycle and (c) 2nd heating cycle.
Figure 4-35: DSC thermograms of melt electrospun PP fibres of 1000 MFI PP with varying amounts of PDMS: (a) 1st heating cycle (b) 1st cooling cycle and (c) 2nd heating cycle.
Figure 4-36: DSC thermograms of melt electrospun PP fibres of 1000 MFI PP with varying amounts of NaCl: (a) 1st heating cycle (b) 1st cooling cycle and (c) 2nd heating cycle.

The cold crystallisation temperatures (corresponding to the 1st cooling cycle) of the fibres fabricated with PEG, PDMS and NaCl are also listed in Table 4-13. It can be observed that the peak heights for the fibres fabricated with different additives are either equal to or lower than those of the as-spun fibre. From the 2nd heating cycles of these
fibres, two peaks were observed for the as-spun fibres and the fibres fabricated with different amount of additives. The temperatures corresponding to the double peaks are listed in Table 4-13. The as-spun fibres and the fibres fabricated with the additives from 2000 MFI showed similar DSC curves but with different melting and crystallisation temperatures. The figures of the DSC curves are shown in Appendix A 1.3, A 1.4, A 1.5 and A 1.6.

Table 4-13: Thermal properties of melt electrospun fibres fabricated from 1000 MFI PP with various additives.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Fibre samples with</th>
<th>Tm (°C) 1st heating</th>
<th>Tm (°C) 1st cooling</th>
<th>Tm (°C) 2nd heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-spun fibre</td>
<td>166</td>
<td>110.5</td>
<td>155.5, 162.5</td>
<td></td>
</tr>
<tr>
<td>4% SO</td>
<td>152.5, 158.5</td>
<td>110.5</td>
<td>149.5, 158.5</td>
<td></td>
</tr>
<tr>
<td>7% SO</td>
<td>161.5, 164</td>
<td>109</td>
<td>154, 166</td>
<td></td>
</tr>
<tr>
<td>12% SO</td>
<td>148, 158.5</td>
<td>110.5</td>
<td>149.5, 158.5</td>
<td></td>
</tr>
<tr>
<td>4% PEG</td>
<td>158.5</td>
<td>107.5</td>
<td>146.5, 155.5</td>
<td></td>
</tr>
<tr>
<td>7% PEG</td>
<td>163</td>
<td>109</td>
<td>155.5, 166</td>
<td></td>
</tr>
<tr>
<td>12% PEG</td>
<td>166</td>
<td>109</td>
<td>154, 164.5</td>
<td></td>
</tr>
<tr>
<td>4% PDMS</td>
<td>155.5</td>
<td>109</td>
<td>140.5, 149.5</td>
<td></td>
</tr>
<tr>
<td>7% PDMS</td>
<td>155.5</td>
<td>109</td>
<td>142, 154</td>
<td></td>
</tr>
<tr>
<td>12% PDMS</td>
<td>152.5</td>
<td>107.5</td>
<td>137.5, 149.5</td>
<td></td>
</tr>
<tr>
<td>4% NaCl</td>
<td>158.5</td>
<td>107</td>
<td>145, 156</td>
<td></td>
</tr>
<tr>
<td>7% NaCl</td>
<td>161.5</td>
<td>110.5</td>
<td>151, 160</td>
<td></td>
</tr>
<tr>
<td>12% NaCl</td>
<td>161.5</td>
<td>110.5</td>
<td>152.5, 160</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Fibre samples with</th>
<th>Tm (°C) 1st heating</th>
<th>Tm (°C) 1st cooling</th>
<th>Tm (°C) 2nd heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-spun fibre</td>
<td>161.5</td>
<td>112</td>
<td>158.5, 149.5</td>
<td></td>
</tr>
<tr>
<td>4% SO</td>
<td>158.5</td>
<td>112</td>
<td>157, 148</td>
<td></td>
</tr>
<tr>
<td>7% SO</td>
<td>158.5</td>
<td>109</td>
<td>155.5, 145</td>
<td></td>
</tr>
<tr>
<td>12% SO</td>
<td>158.5</td>
<td>109</td>
<td>155.5, 146.5</td>
<td></td>
</tr>
<tr>
<td>4% PEG</td>
<td>157</td>
<td>109</td>
<td>154, 143.5</td>
<td></td>
</tr>
<tr>
<td>7% PEG</td>
<td>158.5</td>
<td>109</td>
<td>155.5, 145</td>
<td></td>
</tr>
<tr>
<td>12% PEG</td>
<td>157</td>
<td>109</td>
<td>154, 145</td>
<td></td>
</tr>
<tr>
<td>4% PDMS</td>
<td>157</td>
<td>109</td>
<td>154, 145</td>
<td></td>
</tr>
<tr>
<td>7% PDMS</td>
<td>155.5</td>
<td>109</td>
<td>154, 145</td>
<td></td>
</tr>
<tr>
<td>12% PDMS</td>
<td>158.5</td>
<td>109</td>
<td>154, 145</td>
<td></td>
</tr>
<tr>
<td>4% NaCl</td>
<td>157</td>
<td>109</td>
<td>155.5, 145.5</td>
<td></td>
</tr>
<tr>
<td>7% NaCl</td>
<td>155.5</td>
<td>109</td>
<td>155.5, 145</td>
<td></td>
</tr>
<tr>
<td>12% NaCl</td>
<td>158.5</td>
<td>109</td>
<td>154, 145</td>
<td></td>
</tr>
</tbody>
</table>

In general, the DSC scans of fibres fabricated with all the additives (except SO) do not show two different peaks corresponding to the polymer and the additives in the 1st heating cycle. The single melting peak in the 1st cycle corresponds to the melting of the PP polymer [123]. However, the complex shape and multiple peaks of the endotherms in the case of SO are due to the complex melting behaviour of SO, which is shown in Figure 4-37. A similar melting phenomenon of complex shape and multiple peaks was observed by Tandon et al. [124] during the melting of SO. The 1st heating scan showed the reducing of the melting temperature and the second heating cycle resulted in the shifting of the peaks towards lower values compared to the 1st in the case of PEG, PDMS and NaCl.
4.3.5 TGA

The thermal stability of the as-spun PP fibres and fibres fabricated with different additives was analysed by TGA. The TGA curves (Figure 4-38) reflect the degree of thermal degradation during melt electrospinning for the fibres fabricated from 1000 MFI PP with additives. The TGA curves show that the PP polymer has the highest thermal stability (indicated by the weight loss starting at the highest temperature) compared to the fibres fabricated by the addition of additives. However, there was no significant difference between the TGA curves of the fibres fabricated with different additives. The curves were very close to each other and therefore the curves cannot be distinctly used to investigate the thermal degradation. Hence, the intrinsic viscosity values were analysed for confirming the thermal degradation during melt electrospinning. The TGA curves for the fibre fabricated from 2000 MFI PP were similar to 1000 MFI and is given in Appendix A 1.7.
4.3.6 Molecular weight or intrinsic viscosity

As TGA results cannot give a clear indication of the degree of thermal degradation by melt electrospinning, the degree of thermal degradation was compared by calculating the molecular weight from the IV values of the fibre samples (Table 4-14). It can be observed that for all the fibres fabricated with additives, the molecular weight is decreased after melt electrospinning, compared to the polymer. This indicated that there was thermal degradation during melt electrospinning with additives.

Table 4-14: Molecular weights (g/mol) of melt electrospun fibres of PP.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Polymer</th>
<th>Fibres with 7% SO</th>
<th>Fibres with 7% PEG</th>
<th>Fibres with 7% PDMS</th>
<th>Fibres with 7% NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>60238</td>
<td>54926</td>
<td>51201</td>
<td>49865</td>
<td>47388</td>
</tr>
<tr>
<td>2000</td>
<td>55509</td>
<td>50508</td>
<td>48603</td>
<td>47804</td>
<td>45436</td>
</tr>
</tbody>
</table>

4.3.7 XRD results

Physical and mechanical properties of the fibres are directly related to the morphology and crystalline structure, which can change during melt electrospinning. In general, the elastic modulous of the fibres increases with the degree of crystallinity and results in better mechanical properties. The presence of the additives in the fibres can alter the crystalline properties. Therefore, investigation of the morphology and crystalline structure is important to understand the performance of the fibres during use. The crystalline structure of the melt electrospun fibres was analysed by XRD analysis and the diffraction patterns for the fibres fabricated from 1000 MFI PP are shown in Figure 4-39.

The diffractograms show the diffraction peaks of the fibre samples fabricated with various additives and also the annealed fibre samples. It can be observed that all the melt electrospun fibres produced with additives contain relatively lower and broader peaks, compared to the higher and sharp peaks of PP polymer and the as-spun fibres. This indicates that the fibre samples fabricated with additives contain low degrees of crystallinity compared to the corresponding as-spun fibre samples. This is due to the samples are not fully crystallised due to their rapid cooling after exit from the die.
In addition, it can be observed that all the melt electrospun fibres fabricated with different additives contain $\alpha$-form crystals. The Bragg reflection peaks at 14°, 17°, 18.5°, 21° and 22° correspond to the monoclinic crystals of PP ($\alpha$-form) with the indexed plane of (110), (040), (130), (111) and (041) [125, 126] and a space group of P2$_1$/c. In the fibre samples fabricated with additives, the $\alpha$-form crystals were predominant and no $\beta$-form or $\gamma$-form was found in any of the melt electrospun samples. Thus the double peaks in DSC during the second scan are related to the process involving $\alpha$-crystals only. During the second heating cycle of DSC, the double endotherm has been attributed to the transitions between different modifications of $\alpha$-crystal form ($\alpha_1$ to $\alpha_2$). The XRD diffractograms of the fibres fabricated from 2000 MFI PP are given in Appendix A 1.8.

It can also be observed that the amount of crystallinity of the fibres increases after annealing. The rapid solidification during melt electrospinning prevents the macromolecular chains from being aligned to form crystallinity. During annealing there is enough time for the macromolecular chains to be relaxed and oriented. Molecular chains in the oriented state are less mobile than in the unoriented state, which leads to high crystallinity.

The amount of crystallinity for the melt electrospun fibres was calculated from the respective areas of the crystalline and amorphous regions (as described in Section 3.6.9).
The crystallinity values (%C) have been summarised in Table 4-15. The crystallinity is affected by the processing parameters, the nature of the additives and the polymer rheology. For the as-spun fibres and the annealed fibres, well defined crystalline peaks were observed, giving higher amounts of crystallinity. It can be observed from the table that the as-spun fibres contained crystallinity of 53%. For the samples fabricated with SO, PEG, PDMS and NaCl, the crystallinity values were 37, 34, 33 and 29% respectively.

Additionally, it can be observed that the fibres show an increase in crystallinity after annealing. The crystallinity values of the fibre samples after annealing were 58, 46, 48, 46 and 41% for as-spun fibres and fibres fabricated with SO, PEG, PDMS and NaCl respectively. All commercial fibres produced in the industry are subjected to drawing and/or heat-setting operations for the crystallites to grow. Therefore, commercial fibres possess high crystallinity compared to the values obtained in the current research.

Table 4-15: Amount of crystallinity of melt electrospun PP fibres fabricated with different additives before and after annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-spun</td>
<td>Before</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>58</td>
</tr>
<tr>
<td>Fibre with SO</td>
<td>Before</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>46</td>
</tr>
<tr>
<td>Fibre with PEG</td>
<td>Before</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>48</td>
</tr>
<tr>
<td>Fibre with PDMS</td>
<td>Before</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>46</td>
</tr>
<tr>
<td>Fibre with NaCl</td>
<td>Before</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>41</td>
</tr>
</tbody>
</table>

4.3.8 Mechanical property

The tensile properties of the single nanofibres were evaluated by Chatillon tensile tester. Ten specimens were tested for the samples fabricated from 1000 MFI PP with the additive SO (7%). Out of the 10 specimens, only 2 were able to break properly at the centre (results given in bold in Table 4-16); 2 samples were broken during specimen mounting and the remaining 6 samples slipped in the jaws instead of breaking.
Table 4-16: Tensile properties of single nanofibres fabricated from 1000 MFI PP with SO (7%) by melt electrospinning.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Elongation at break (%)</th>
<th>Breaking load (cN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.19</td>
<td>0.029</td>
</tr>
<tr>
<td>2</td>
<td>1.4</td>
<td>0.148</td>
</tr>
<tr>
<td>3</td>
<td>3.03</td>
<td>1.369</td>
</tr>
<tr>
<td>4</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>5</td>
<td>3.52</td>
<td>1.945</td>
</tr>
<tr>
<td>6</td>
<td>0.92</td>
<td>0.034</td>
</tr>
<tr>
<td>7</td>
<td>1.41</td>
<td>0.08</td>
</tr>
<tr>
<td>8</td>
<td>1.69</td>
<td>0.085</td>
</tr>
<tr>
<td>9</td>
<td>1.51</td>
<td>0.083</td>
</tr>
<tr>
<td>10</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

* broken during specimen loading

Figure 4-40 shows the load elongation curve of a single nanofibre. The general shape of the load elongation curve is similar to most of the textile fibres. Although comparison of the breaking strength of the fibres fabricated in this study is not possible with other results as the fibre diameters are different and so as the test methods. For a general idea, the breaking strength of a commercial PP fibre was 16.31 cN [127] whereas in this case it is about 1.6 cN.

Figure 4-40: The load-elongation curve of a single nanofibre fabricated by melt electrospinning.

The preparation of a single nanofibre for tensile testing was tedious. In addition, trying with different adhesives to prevent jaw slippage was not successful. Therefore, the alternative approach of testing the dumbbell-shaped specimen from the fibres fabricated by the rotating drum was adopted. Tensile tests of the dumbbell-shaped specimen were successfully performed for the fibres fabricated in meltblowing. However, some
technical difficulties in the tensile tester prevented the experimental work of the fibre fabricated by melt electrospinning. Similar equipment with low load cell was not available in known research places and organisations. Therefore, it was not possible to perform the tensile testing and compare the results with that of meltblowing.

4.3.9 Hydrophobic properties

As mentioned earlier, PP fibres are hydrophobic in nature (i.e. nonwettable by water) [128]. However, the presence of the additives (SO, PEG, NaCl and PDMS) in the fibre can alter the hydrophobicity of the melt electrospun fibres. The additives SO, PEG and NaCl are hydrophilic, whereas PDMS is highly hydrophobic material [129]. Therefore, melt electrospinning with these additives can increase or decrease the hydrophobic behaviour of the fibres. The water contact angle of the fibres fabricated with different additives was used to study the hydrophobic properties. Figure 4-41 shows the graphical representation of the water contact angles of fibres fabricated with various additives.

![Graphical representation of water contact angles of fibres fabricated with different additives from 1000 MFI PP.](image)

Figure 4-41: Water contact angles of melt electrospun fibres fabricated with different additives from 1000 MFI PP.

It can be observed from the figure that the water contact angle is greater than 90° for the melt electrospun fibres, indicating the hydrophobic nature of PP. However, the water contact angles of the fibres were changed with the presence of the additives. The water contact angle for the fibres fabricated with SO, PEG and NaCl decreased, whereas it increased for the fibres fabricated with PDMS. The enhanced hydrophobicity of fibres fabricated with PDMS can contribute to excellent barrier performance without losing
permeability when they are applied to protective clothing. As the additives SO, PEG and NaCl can be washed away and PDMS is still present in the fibre, study of the effect of the amount of PDMS on hydrophobicity is essential.

The change in hydrophobicity with the amount of PDMS is shown in Figure 4-42. It can be observed that the water contact angle increases from 104° to 135° with the increase in the PDMS amount from 0 to 12%. Recently, the fabrication of superhydrophobic fibres by electrospinning has been performed [85]. It has been shown that melt electrospinning of PP can produce near-superhydrophobicity with the addition of PDMS. Hence, melt electrospinning can provide a single-step approach for producing hydrophobicity, compared to other methods which are complicated or need an additional coating process.

The water contact angles of the fibres fabricated from 1000 and 2000 MFI PP with different additives are shown in Table 4-17. It can be observed that the fibres fabricated from 2000 MFI PP are also hydrophobic in nature. The behaviour of the fibres from 2000 MFI PP was similar to that of the fibres from 1000 MFI. No significant difference was observed between the results of 1000 and 2000 MFI PP.
Table 4-17: Water contact angle of the melt electrospun PP fibres fabricated with different additives.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Water contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pure polymer</td>
</tr>
<tr>
<td>1000</td>
<td>104</td>
</tr>
<tr>
<td>2000</td>
<td>108</td>
</tr>
</tbody>
</table>

4.4 Washing of the additives

Among the four additives used for melt electrospinning, three additives (i.e. SO, PEG and NaCl) are soluble in water. Therefore the melt electrospun fibres fabricated with these additives were washed thoroughly with distilled water to remove the additives. The washed samples were dried in a hot-air oven and conditioned in the standard atmosphere before any further testing.

The removal of the additives was analysed by the FTIR spectrum of the washed samples fabricated from 1000 MFI. Figure 4-43 shows the comparison FTIR spectra of the washed fibre samples with the unwashed and as-spun fibres. It can be observed from Figure 4-43 (a) that the peaks at 1560 and 1108 cm⁻¹ disappear in the washed fibre. This indicates the complete removal of SO from the fibre. Similarly, the removal of PEG is clearly evident from the disappearance of the peaks at 1090 and 930 cm⁻¹ (Figure 4-43, b). These results clearly show that the additives did not chemically react with PP, but rather present physically in the fibrous structure.
Figure 4-43: FTIR spectra of electrospun PP fibres fabricated from 1000 MFI PP after washing of: (a) SO and (b) PEG.

As FTIR cannot be used to identify the presence of NaCl, the effect of washing of the fibres fabricated with NaCl was analysed by EDX analysis and the results are explained in Figure 4-44. It can be observed that the peaks corresponding to Na and Cl disappear in the washed fibre. Therefore, the EDX results show the complete removal of NaCl from the fibrous structure.

Figure 4-44: EDX spectra of electrospun PP fibres fabricated with 7% NaCl: (a) before washing and (b) washed fibre.
5 Chapter 5 Conclusions: melt electrospinning

5.1 Conclusions

- Melt electrospinning of pure PP polymers (100, 300, 1000 and 2000 MFI) and polymers with different additives (SO, PEG, PDMS and NaCl) has been successfully achieved. It was found that within limits, an increase in the temperature, applied voltage and collector distance; and a reduction of melt flow rate and spinneret size, resulted in a decrease in the fibre diameter.

- The circular dies of 0.2 mm or lower orifice diameter did not produce any fibres. Fibres were fabricated with the circular dies of greater diameters than 0.2 mm. The circular-protruding die of 0.2 mm was successful in the fabrication of nanofibres with additives. The circular die (0.3 mm) resulted in microfibres only, whereas the circular-protruding die (0.3 mm) resulted in nanofibres with additives.

- It was observed that the cross-sectional shape of the fibres fabricated by melt electrospinning was independent of the die cross-section. All the dies used in the study, such as trilobal, tetralobal and multilobal, resulted in circular fibres, similar to the circular die. This was attributed to the presence of Taylor cone. As the electrospinning process starts from the Taylor cone formed at the apex of the die, the die cross-section plays no role in shaping the fibre cross-section.

- Melt electrospinning of pure polymers with different combinations of temperature, applied voltage, collector distance, melt flow rate and die size resulted in the fibres with micrometre diameter. Polymers with higher MFI resulted in the formation of finer fibres. The fibres were circular in cross-section but of varying diameter, as indicated by high standard deviation values.

- The addition of additives (SO, PEG, PDMS and NaCl) helped in reducing the fibre diameter. In the case of 100 and 300 MFI, the additives resulted in the formation of microfibres only. However, the addition of SO and NaCl to 1000 and 2000 MFI PP resulted in the fabrication of uniform nanofibres. The lowest fibre diameters of 371 ± 106 nm (0.371 ± 0.106 µm) and 310 ± 102 nm (0.310 ± 0.102 µm) were achieved by melt electrospinning of 2000 MFI PP with the additives SO and NaCl respectively.

- In the case of PEG and PDMS, the decrease in the fibre diameter was due to the reduction of the viscosity of the polymer melt. In the case of SO and NaCl, the
decrease in the fibre diameter was due to the increase in the electrical conductivity as the melt viscosity was increased. Therefore, the effect of “the increase in the electrical conductivity” was greater than the effect of “the decrease in the melt viscosity”. Hence, the additives SO and NaCl resulted in the fabrication of nanofibres.

- The electrical conductivity increased with the temperature and the amount of SO and NaCl added. The effect of the increase in the electrical conductivity was greater in the case of NaCl than SO due to the smaller ionic size of NaCl. The optimum concentrations of SO and NaCl were 7% and 5% respectively which resulted in the formation of the lowest fibre diameters.

- EDX microanalysis showed the presence of the additives (SO, PDMS and NaCl) in the fibre. In addition, EDX also provided evidence of the uniform distribution of the additives within the fibre structure. NMR results showed the physical presence of the additives within the fibre. This was also confirmed by the FTIR analysis.

- DSC of fibres fabricated with all the additives (except SO) did not show two different peaks corresponding to the polymer and the additives in the first heating cycle. The single melting peak in the DSC profiles corresponds to the melting of the pure PP polymer.

- XRD studies showed that the fibres fabricated with additives contain lower degrees of crystallinity compared to the as-spun fibre. The amount of crystallinity was increased after annealing. The fibres fabricated with additives contain $\alpha$-form crystals only which is generally the predominant form of PP fibres.

- The preparation of single nanofibres for tensile testing was a tedious process. It was difficult to prevent jaw slippage during the tensile testing of single nanofibres.

- The fibres fabricated from pure PP polymer were hydrophobic in nature. The hydrophobicity was marginally decreased by the addition of SO, PEG and NaCl. The addition of PDMS substantially increased the hydrophobicity of the melt electrospun fibres.

- The additives SO, PEG and NaCl were removed from the fibre by treatment with water. The removal of the additives showed the physical presence of the additives without any chemical reaction with the polymer.
6 Chapter 6 Review of literature: meltblowing

6.1 Meltblowing

Meltblowing is a simple, versatile and one-step process for the production of materials in the micrometre and smaller scale directly from the polymer. The technology of meltblowing was first developed in the 1950s at the Naval Research Laboratory of the United States [38]. The work was carried out with a goal of producing submicron fibres for the collection of radioactive particles in the upper atmosphere. Wente was the first to describe the meltblowing technology to produce microfibres of diameters less than 100 micrometres from thermoplastic polymers [130]. Then, Exxon Research and Engineering (then ESSO) in the 1960s developed equipment to produce a continuous web for battery separators [23].

The nonwoven webs produced by meltblowing have a wide range of applications. The small pore size and high insulating value enable the meltblown fibres to be used for various applications such as filtration media, thermal insulators and battery separators. The meltblown webs are efficient filter materials that can filter particles as small as 0.5 µm [131]. Other applications include waste sorbents, protective garments, medical fabrics, sanitary products, wipes etc.

6.1.1 Equipment

Meltblowing equipment consists of four major components: extruder, die assembly, web formation and winding (Figure 6-1). The equipment can be of two types: (a) horizontal and (b) vertical. The extruder is a heated barrel responsible for the melting of the polymer to achieve appropriate viscosity. The polymer in the form of powder, chips, pellets or granules is gravity-fed from the hopper to the extruder at a certain feed rate and heated in different heating zones. The rotating screw(s) carries the polymer towards the die assembly where it is metered by a metering pump. The metering pump delivers the polymer melt uniformly and consistently to the die assembly [132]. The die assembly is responsible for the production of good quality fibres. In this section the fibre attenuation is achieved by the action of cool air. Subsequently, the fibres are collected as web and forwarded to the winding section.
6.1.2 Fibre diameter and influencing factors

With respect to the average fibre diameter, there is some disagreement among researchers. Some researchers state that meltblowing can produce an average fibre diameter of 2–30 microns [133, 134]. Others state that an average fibre diameter of 30–100 microns can be produced for coarse filtration end-uses [38, 135]. The lowest possible fibre diameters are desirable in the web, as the filtration efficiency increases. However, the commercial meltblowing process cannot produce fibres smaller than 2 microns due to the inability to make sufficiently small spin orifices.

The available literature does not clearly demonstrate the smallest fibre diameter feasible by meltblowing. Although some of the literature states that nanofibres can be synthesised by meltblowing, the minimum average fibre diameter is 1–2 µm [5, 136, 137]. In regard to the fabrication of nanofibres by meltblowing, there are limited works. For example, nanofibres were produced by Ellison et al. [23] using a specially designed single-hole v-slot die of 0.2 mm orifice diameter. Nanofibres of polybutylene
terephthalate, polystyrene and PP with average diameter less than 500 nm were obtained in this study.

It was observed that by increasing the air-to-polymer mass-flux ratio and the processing temperature, the average fibre diameter decreased. In addition to the fibres, some spherical particles were observed in the nonwoven web. The origin of these particles was a result of fibre breakup instabilities driven by surface tension. There was a wide range of fibre diameters achieved in the study (Figure 6-2). Although the average fibre diameter was in the nanometre range, the design of the die used was too complicated.

Figure 6-2: SEM images of meltblown fibres: (a) polystyrene (PS) PS-1, (b) PS-3, (c) PP-1, (d) PP-3, (e) polybutylene terephthalate (PBT) PBT-1 and (f) PBT-2. All scale bars represent 2 mm.

Brang et al. [138] developed a method and apparatus for the production of polymer nanofibres utilising a plate-edge orifice spinneret with spin holes formed by grooves in the plate(s). The grooves were smaller than 0.005” wide × 0.004” deep and had an L/D ratio of at least 20:1. The polymer flow rate was very low and the average fibre diameter was 0.5 microns. The low throughput caused productivity reduction, which was balanced by increasing the density of the small spinneret orifices. In this case, the design of the plate-edge die was also complicated to design.
Bodaghi et al. [139] fabricated nanofibres by changing the rheology of the polymer in at least the first and second flows of a liquid material in the meltblowing process. The difference in the changed rheology was obtained by using two extruders with different barrel diameters. The changed rheology of the first and second flows was combined to define meltblown fibres. Nanofibres were collected together with any unsplit meltblown fibres to form the nonwoven web. Each meltblown fibre had lengthwise first and second cross-sectional regions formed of the liquid material from the first and second flows respectively. The equipment used by them was too complex and not commercially available. Similarly, Hills Inc. [140] has developed a modified meltblowing technology (using thin-plate extrusion dies) for the production of nanofibres. However, there was no information available on the die design or the processing parameters.

Several pieces of research have shown that the fibre diameter is affected by parameters related to the material and process. Material variables such as polymer type, molecular weight or MFI, form of the polymer (powder, pellets or chips) and presence of additives; and the process variables such as collector distance, polymer flow rate and temperature, air flow rate and temperature and die profile affect the morphology and diameter of the meltblown web. The effects of different material and processing parameters on fibre diameter are discussed in the following section.

6.1.2.1 Effects of material properties

Theoretically, meltblowing technology can be applied to any thermoplastic polymers, although there are some published works with lyocell solution [141, 142]. The compatibility of a polymer in meltblowing is independent of the backbone chemical structure [23]. The most common polymers for meltblowing are polyolefins (especially polypropylene) [143] due to their physical properties, low cost and versatility in making a wide range of products. Among polyolefins PP is dominant due to its relative ease of processing from the melt and availability of a large range of average molecular weights in different tacticity. Other polymers include polyester, polyamides, polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate, polyphenylene sulfide and polyvinyl alcohol (PVA) [144].
Polymers with low molecular weights (hence high MFI) are desirable in the meltblowing process for the formation of finer fibres [5]. Low molecular weight produces low melt viscosity, and hence produces a web with more uniformity. A polymer of high MFI can be processed at lower temperature and decreases the manufacturing cost. It has been shown that the average fibre diameter decreased with the increase in the MFI of the polymer [145]. The average fibre diameter decreased by an amount less than 1 micron when the polymer MFI was increased from 150 to 2000. Another research showed that the fibre diameter did not change substantially with the MFI [146]. This was attributed to the use of different air temperatures for different polymer MFI. Polymers in the form of powder melt better and faster than chips/pellets [132].

6.1.2.2 Effects of process parameters

The collector distance is an important parameter affecting the fibre diameter and properties of the web. The majority of research has shown that the fibre diameter decreases with an increase in the collector distance [145, 147]. However, Lee and Wadsworth [148] indicated that beyond a collector distance of 30 cm, the average fibre diameter was not affected. The effect of the polymer flow rate has been studied by several researchers. It has been shown that increase in the polymer flow rate increases the fibre diameter [130, 145]. This is due to the same amount of drafting force cannot stretch more material to finer diameter.

The increase in the processing temperature decreases the fibre diameter due to the reduction of the melt viscosity [145, 149]. It has been shown that an increase in the airflow rate decreases the average fibre diameter [136, 145]. However, Milligan et al. [149] showed that the fibre diameter is not affected at higher air velocities (275–300 ms⁻¹ and higher). An increase in the air temperature results in a decrease in the mean fibre diameter [130]. However, Chen et al. [145] showed that the effect of air temperature on mean fibre diameter is insignificant.

In meltblowing, the use of smaller orifices resulted in the fabrication of finer fibres [145, 149]. However, there are associated difficulties with smaller orifices [5, 23] such as: (i) the designing of smaller orifices is an industrial challenge; (ii) the higher probability of clogging of smaller orifices; and (iii) difficulty in extruding the polymer through small
orifices as high pressure is required. Kayser and Shambaugh [150] showed that when the capillary diameter that carries the polymer was increased, the fibre diameter decreased slightly. The unexpected result was due to the decreasing area available for air flow resulted in an increase in the air velocity. In addition to these parameters, a few other independent variables affect the fibre diameter, as discussed below.

Shambaugh [151] attempted to provide a universal description for the variation of the fibre diameter in terms of the number of dimensionless groups by analyzing the industrial data on meltblowing. The study showed that the resulting fibre diameter is affected by the air-to-polymer mass-flow rate. Milligan and Haynes [152] performed meltblowing experiments using a single-hole die and concluded that the ratio of air to polymer mass fluxes provided a satisfactory description of the fibre size for a wide range of processing conditions. Bresee and Qureshi [153] stated that the increase in the collector speed (by 83%) increased the fibre diameter only by 0.1 micron, indicating that the collector speed is not an influencing factor. The use of oscillating air [154] and cross-flow air compared to the traditional continuous air flow resulted in a smaller average fibre diameter.

6.1.3 Properties of meltblown fibres

Generally, meltblown webs are characterised by their softness, lightweight, bulk, low porosity, high absorbency, high surface area and poor abrasion resistance [155]. The other feature of meltblown products is the random orientation of the fibres in the web structure. Web uniformity is essential and depends on the uniformity of fibre distribution by the hot air stream, the die design and the vacuum level at the collecting screen [5]. In meltblowing, a low to moderate strength web is produced as the fibres are drawn to the desired diameter while still in the semi-molten state and are rapidly quenched, producing low crystallinity. The lower is the crystallinity, the lower the fibre strength. The meltblown web possesses good barrier, insulating and filtration properties. Several studies have investigated the influencing factors on web properties, as described below.

Choi et al. [156] showed that an increase in the collector distance decreased the tenacity, Young’s modulous and bending rigidity, but increased the elongation at break [156]. It was found that a decrease in polymer flow rate increased the tenacity, yield stress and
initial modulous, and decreased the elongation at break [146]. The tenacity of the web [143, 146], yield stress [146] and initial modulus [146] were increased with the air flow rate, whereas the elongation at break [146] was decreased. Choi et al. [156] also showed that an increase in the air pressure decreased the tenacity, elongation at break, Young’s modulus and bending rigidity. Zhang et al. [143] found an increase in the air temperature increased the tenacity but decreased the elongation at break and hydrostatic head. Milligan et al. [157] showed that the use of cross-flow air compared to continuous air increased the fibre entanglement, air permeability, tenacity, elongation at break and bursting strength.
7 Chapter 7 Experimental: meltblowing

7.1 Introduction
This chapter deals with the materials used, the equipment and the processing parameters applied in the meltblowing experiments. It also includes the equipment and test conditions used for the characterisation of the fibres fabricated. The characterisation techniques included OM and SEM; FTIR and NMR; XRD, DSC and TGA; mechanical characterisation and surface wettability. The shear viscosity was determined to understand the effect of viscosity on the fibre diameter. In addition, the surface wettability of the samples was evaluated by measuring the water contact angle.

7.2 Materials
The same PP polymers used in melt electrospinning experiments (i.e. 100, 300, 1000 and 2000 MFI) were also used in meltblowing experiments. The polymers were synthesised as discussed in Section 3.2.1. The PP pellets were converted to fine powder by cryogenic (liquid nitrogen) grinding [106] similar to melt electrospinning before use. The use of powder helps the feeder in accuracy of feeding and also to achieve a uniform melt in the extruder. The list of PP polymers along with the MFI, IV and molecular weight (Mw) are listed in Table 7-1.

Table 7-1: List of polymers used for meltblowing experiments.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>IV</th>
<th>Mw (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.01</td>
<td>100875</td>
</tr>
<tr>
<td>300</td>
<td>0.84</td>
<td>77590</td>
</tr>
<tr>
<td>1000</td>
<td>0.72</td>
<td>60238</td>
</tr>
<tr>
<td>2000</td>
<td>0.66</td>
<td>55509</td>
</tr>
</tbody>
</table>

7.3 Meltblowing apparatus
Meltblowing experiments were performed on the horizontal melt extruder (JSW- Tex 30) with 40/1 (l/d) ratio, a metering pump and a single-hole die. The meltblowing equipment used is schematically shown in Figure 7-1 and Figure 7-2. It consisted of 11 heating zones as described from C1 to C11 and 4 vent ports.
Figure 7-1: Schematic of the extruder used for meltblowing process: (a) the extruder only, (b) extruder connected with additional devices and (c) die section.

Figure 7-2: JSW extruder used for meltblowing experiments.
The temperature of each heating zone can be regulated independently. The polymer was heated gradually through the various heating zones, as per progressive melt theory [158]. The temperature profiles maintained at various heating zones for the PP polymers during meltblowing experiments are shown in Table 7-2. A single-hole circular die of 0.5 mm orifice diameter was used for the study.

Table 7-2: Processing temperatures (°C) at different heating zones during meltblowing.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>MFI</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>C9</th>
<th>C10</th>
<th>C11</th>
<th>Melt pump</th>
<th>Die</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>130</td>
<td>150</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>190</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>130</td>
<td>130</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>180</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>130</td>
<td>130</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>170</td>
</tr>
<tr>
<td>2000</td>
<td>130</td>
<td>130</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>170</td>
<td>180</td>
</tr>
</tbody>
</table>

The PP pellets were supplied into the extruder from the feeder at a feed rate of 80 g/hr. The low feed rate was selected on the basis that a higher flow rate produces coarser fibres [159]. Due to the low feed rate, the residual time of the polymer in the equipment was high, increasing the chance of thermal degradation. This was avoided by maintaining low temperatures at initial heating zones and gradually increasing it up to the die. The temperature was selected on the basis of initial experiments which were aimed at determining the optimum temperature to avoid thermal degradation. The temperature of each heating zone was measured by the thermocouple located in the heating zone. The processing temperatures of the die for various polymers were kept higher than the melting point (T_m) of the polymers.

Different fluids (water, air and nitrogen) were introduced independently into the extruder at vent port C8 as shown in Figure 7-1. The gases (nitrogen (N_2) and air) used in the experiments were commercial grade (BOC) and used as supplied from the gas cylinders. Deionised water was pressurised and injected by a precision syringe pump (Teledyne ISCO: D-series) fitted with a 4-µm porous metal plug. Deionised water was supplied at 5 and 10 ml/min (i.e. 300 and 600 g/hr) whereas air and N_2 were supplied at 10 g/min (i.e. 600 g/hr). The mass ratios of polymer to fluid were 1:3.75 in the case of air and N_2, and 1:7.5 and 1:7.5 in the case of water supply. The fluid flow rates were established after several preliminary experiments. The fluid flow rates were selected so that there was complete mixing of the fluid with the polymer melt. In addition, a low polymer feed rate helped in better mixing of the polymer and fluid in the extruder. The parameters used in meltblowing experiments are summarised in Table 7-3.
Table 7-3: Processing parameters used in meltblowing experiments.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Die temperature (°C)</th>
<th>Polymer feed rate (g/hr)</th>
<th>Fluid flow rate</th>
<th>Collector distances (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>200</td>
<td>80</td>
<td>10 (600)</td>
<td>5, 10 (300, 600)</td>
</tr>
<tr>
<td>300</td>
<td>190</td>
<td>80</td>
<td>10 (600)</td>
<td>5, 10 (300, 600)</td>
</tr>
<tr>
<td>1000</td>
<td>180</td>
<td>80</td>
<td>10 (600)</td>
<td>5, 10 (300, 600)</td>
</tr>
<tr>
<td>2000</td>
<td>180</td>
<td>80</td>
<td>10 (600)</td>
<td>5, 10 (300, 600)</td>
</tr>
</tbody>
</table>

The pressure inside the extruder was monitored by pressure transducers located at various positions along the extruder length (Figure 7-1). During normal operation of the extruder without any fluid supply, the pressures at different locations were as follows: $P_1 = 0$, $P_2 = 0$ and $P_3 = 0$ kg/cm². (Note: $P_1$ is the pressure at the die section, and $P_2$ and $P_3$ are the pressures at intermediate positions as shown in Figure 7-1, b). While the fluid supply was initiated, the pressure was increased to values such as: $P_1 = 4$, $P_2 = 2–3$ and $P_3 = 2–3$ kg/cm². With the delivery of the fibre through the die, the pressure was dropped to values $P_1 = 2–4$, $P_2 = 1–2$ and $P_3 = 1–2$ kg/cm². However, the pressure at the die section with the fluid supply was always higher by 1-3 kg/cm² than the normal operating pressure (without fluid supply).

Fibre samples were collected on aluminum foils attached to a glass screen, which was placed at distances of 200, 300 and 400 mm from the die exit. Therefore, the variables of the meltblowing process were fluid type, fluid flow rate and collector distance for a specific polymer. A rotating drum collector was also used for the collection of aligned fibres for the mechanical characterisation (detail in Section 7.5.10).

During the meltblowing experiments, the motor was started after the initial set temperatures were achieved in all the heating zones. The set temperatures were kept at 30–40°C higher than the processing temperature (listed in Table 7-2). This was devised because starting the extruder at the processing temperature generated very high torque which prevented the starting of the motor. The starting of the motor was combined with the polymer feed from the hopper. About 20 minutes after the polymer feed, the temperatures of different zones were lowered to match the processing conditions. The extruder was stabilised for approximately one hour before collecting any fibre sample. This was observed by the colour change of the polymer melt from yellow to clear liquid.
In the case of a polymer change, the previous polymer was completely cleaned from the hopper and replaced with another polymer. The equipment was purged with the newly replaced polymer for approximately 2 hours to remove the previous polymers from the heating chambers thoroughly.

7.4 Annealing
It has been shown that annealing substantially modifies the microstructure of PP and hence the crystallinity [107]. Annealing can also improve a polymer’s melting point and heat of fusion [108]. The increase in the crystallinity affects the mechanical properties. For annealing, any temperature above the crystallisation temperature and below the melting temperature can be selected. In this study, in order to study the effect of annealing on the thermal and crystalline properties of the fibres, the samples were subjected to annealing at 120°C for 30 minutes in a hot air oven. The samples were cooled to room temperature after annealing.

7.5 Characterisation

7.5.1 Optical microscopy
The diameters of meltblown fibres fabricated without the injection of any fluid were coarser; hence, the images were captured by an optical microscope (Olympus-DP72) with a magnification of 10x. The fibres were placed on microscope slides, which were then mounted on the stage of the microscope. The images were captured by a camera and the fibre diameters were measured from the images and processed as mentioned above.

7.5.2 SEM
The surface morphology of the fibres was analysed by field emission scanning electron microscopy (Philips XL30 FE-SEM) with an accelerating voltage of 30 kV. The fibres were placed on stubs and coated with iridium using a sputter coater (Polaron SC5750). The current in the sputter coater was set at 50 mA for 20 sec, giving an approximate coating thickness of 100 angstroms. The fibre diameters were measured by an image processing software (Image J, NIST) using the SEM images. The average fibre diameter was determined from at least 150 measurements from at least 10 SEM images for each sample.
7.5.3 NMR
In addition to FTIR, NMR was also used to study the chemical composition of the fibres before and after meltblowing. $^{13}$C NMR spectra were collected from the solid state NMR experiments performed on an NMR spectrometer (Bruker BioSpin Av500) operating at 125.8 MHz. Samples were packed into a 4 mm ZrO$_2$ rotor and spun at 5 kHz in a standard-bore 4 mm broadband MAS probe. Data were processed in Bruker BioSpin TopSpin v3.0.

7.5.4 FTIR
The chemical structure of a polymer subjected to high temperature may be substantially different from the original (due to chain scission, branching and cross linking during processing). When subjected to high temperature, there may be reduction of molecular size and the formation of extra chemical groups in the case of PP [160]. FTIR was used to determine any changes in the chemical structure by the effects of high temperature and various fluids during meltblowing. The FTIR spectra were collected by a spectrometer (PerkinElmer Spectrum-400) to determine the functional groups of the fibres. The number of scans per sample was 8 and the FTIR spectra were collected in the wave number region of 4000–650 cm$^{-1}$. The spectra indicate the absorbance of a material as a function of wave number.

7.5.5 DSC
Differential scanning calorimetry can be used to analyse the physical and chemical transformations that occur by a thermal treatment and can be measured as a function of temperature [110]. The sample and the reference material (which undergoes no phase change in the temperature range being studied) are heated at a constant rate inside two separate cells containing the junctions of a differential thermocouple. The thermal change in the sample is then measured against the reference material.

The thermal behaviour of the PP polymers, as-spun fibres (fabricated without any fluid) and fibres fabricated with fluids by meltblowing were analysed by DSC (Mettler Toledo, DSC821$^\circ$) fitted with a sample robot. Aluminum crucibles (40 µL) were used to contain the samples and as the reference pan. About 5–10 mg of the sample was heated from room temperature to 250°C at a heating rate of 10°C/min, followed by cooling to room temperature at the same rate. As polyolefins show significant difference between the first and second DCS heating cycles [111], the samples were subjected to a second
heating cycle similar to the first. These samples were run in the non-isothermal mode of the equipment. The heating rate of 10°C/min was selected as it has been reported to be an optimum rate that does not influence the shape and character of the melting endotherm of PP [112].

7.5.6 TGA
Thermo gravimetric analysis (TGA) was used to obtain information on thermal stability of the samples using the thermal analysis equipment (Mettler Toledo (TGA/SDTA-851e) fitted with a sample robot. TGA provides information on the thermal degradation of the polymers during any melt processing. In TGA, about 5–10 mg of the sample was heated in a ceramic crucible from room temperature to 800°C at a heating rate of 10°C/min under nitrogen atmosphere. The resulting weight loss as a function of temperature was analysed and compared for the relative thermal stability.

7.5.7 Molecular weight or intrinsic viscosity
In addition to the TGA, the thermal degradation of polymers was determined from the change (decrease) in the molecular weight of the polymers before and after the meltblowing. The molecular weights of the polymers and fibres were determined from the IV values. IV was determined using the solvent Decalin (Decahydronaphthalene) at 135°C in a calibrated viscometer (Ubbelohde). The molecular weights (M) of polymers were calculated from the IV [η] by using Mark Houwink equation:

\[
[\eta] = K M^a
\]

where K and a are constants with 0.5 ≤ a ≤ 0.8. For PP, the values of K and a are 2.38 × 10⁻⁴ and a = 0.725 respectively [113].

7.5.8 XRD
The degree of crystallinity of the fibres affects their physical properties. Hence, investigation of the degree of crystallinity can help to understand the physical properties of the fibres. XRD diffractograms were used to evaluate the crystalline fraction of the fibres fabricated in meltblowing. The crystalline and amorphous scatterings in the diffractogram were separated from each other by using the technique described in detail in the literature [114].

The crystalline properties of the meltblown fibres were analysed by XRD (Bruker D8 Advance Diffractometer with CuKα radiation-40 kV, 40 mA). The diffractometer was
equipped with a Lynx-Eye silicon strip detector to obtain the XRD patterns. The samples were scanned over the 2θ range of 5 to 30° with a step size of 0.02° and a count time of 0.4 seconds per step. Analyses were performed on the collected XRD data using the Bruker XRD search match program “EVA™” and crystalline phases were identified using the ICDD-PDF4+ 2010 powder diffraction database.

Figure 7-3 shows the XRD diffractogram with appropriate separation between the crystalline and amorphous sections by drawing a line connecting the minima between the crystalline peaks. The scatter intensity above this line (Ic) is from the crystalline region, whereas the scatter intensity below this line (Ia) is from the amorphous region. The integrated area of the crystalline reflections (Ac) and amorphous background (Aa) were used for the estimation of crystallinity. The areas (Ac and Aa) were estimated by the curve-fitting method using MATLAB 10 software.

The degree of crystallinity of the samples was calculated from the following equation [115]:

\[
\text{Crystallinity} \, (\%) = \frac{\text{Area of crystalline fraction}}{\text{Area of crystalline fraction} + \text{Area of amorphous fraction}} \times 100
\]

\[
= \frac{Ac}{Ac + Aa} \times 100 \quad \text{Equation 7.2}
\]
7.5.9 Shear viscosity

The viscosity of the polymer melt is an important parameter affecting the fibre diameter in meltblowing. Therefore, it is essential to measure the viscosity of the polymer melt. The shear viscosity of the polymer melt was investigated using a rheometer (Ares) equipped with parallel plates at various temperatures in the dynamic mode over a range of shear rates (0.1–100 s\(^{-1}\)). Disc samples of about 1 mm thickness were prepared by using the heat press. Frequency scans were performed with temperature ranges between 180–210°C at 20% strain.

7.5.10 Mechanical characterisation

Various forces are exerted on the nanofibres during their use, which may result in deformation and lead to permanent failure. Therefore, the mechanical characterisation of nanofibres is essential to ensure product serviceability. The mechanical property of a single nanofibre was extremely difficult to measure due to the problems associated in isolating a single fibre. In addition, slippage at the jaws was observed often in the preliminary experiments with single nanofibres. Therefore, the approach of testing a single nanofibre was avoided and the alternative method of testing a bulk of nanofibres from the nonwoven section was adopted.

The preparation of specimens for tensile testing from the fibres collected on the stationary collector (in the form of a web) was not successful, as the thickness varied along the radial direction. Hence, a rotating drum (Figure 7-4) with traverse was used to achieve uniform thickness of fibres for mechanical characterisation. The fibre samples were collected in the rotating drum overlaid with aluminum foil. The aluminum foil containing the fibres as a nonwoven web was isolated from the drum and taken for sample preparation.
Dumbbell-shaped specimens (Figure 7-5) were prepared (from the nonwoven web) for all the samples, which were then conditioned overnight in the standard atmosphere (temperature of 21 ± 2°C and relative humidity of 65 ± 2%). The length (l) and width (w) of the specimen were 20 mm and 4.8 mm respectively while the thickness (t) was variable. The fibre specimens along with the aluminum foil were prepared by a pneumatic die-cutter. Subsequently, the fibre specimens were separated from the aluminum foil. The thickness of specimens was measured with a fabric thickness gauge (Mitutoyo, Japan) as per ASTM-D 1777.

The mechanical properties of the meltblown fibre samples were performed in a tensile tester (Instron 5500R, Instron, Canton, MA). The load cell used was 2.5 N with a crosshead speed of 10 mm/min and a gauge length of 20 mm. Five specimens were used for each sample and the average values were reported for tensile strength, elongation at break and modulous. Tensile strength was reported as the stress at break for the sample. The stress was calculated by dividing the force with the cross-sectional area of the sample. The cross-sectional area was calculated from the width and thickness of the

Figure 7-4: Rotating drum assembly used to collect uniform thickness of nanofibres for tensile testing in meltblowing.

Figure 7-5: The dumbbell shape of the specimen used for tensile testing in Instron.
sample. The modulus was calculated from the slope of the stress–strain curve in the initial portion where Hooke’s law followed. All these parameters were evaluated for the samples before and after annealing.

7.5.11 Surface wettability

It is well known that PP polymer is hydrophobic in nature (i.e. nonwettable by water). The fabrication of fibres by meltblowing with different fluids can alter the surface wettability (i.e. hydrophobic nature). The water contact angle was used as a measure of surface wettability. The contact angle was measured with a pocket Goniometer (PG-3, Fibro System) by using 4 µL deionised water drop. PG software was used to measure the contact angle 5 seconds after the drop was applied. The average results of 10 readings per sample were used as the contact angle.
8 Chapter 8 Results and discussion: meltblowing

8.1 Initial experiments with pure polymers
The horizontal melt extruder (JSW- Tex 30) with a 0.5 mm single-hole circular die was used for the meltblowing experiment, shown in Figure 8-1. The fluids (air, N\textsubscript{2} and water) were injected independently at vent port C8 of the extruder for the fabrication of nanofibres. The PP polymers of 100, 300, 1000 and 2000 MFI used in melt electrospinning experiments were also used for meltblowing experiments. The fibres were collected on a stationary collector or a rotating drum collector placed at variable distances.

![Figure 8-1: Schematic of the JSW extruder used for meltblowing experiments.](image)

8.1.1 Initial results
Initially, pure polymers were used to fabricate fibres without the injection of any fluid. The as-spun fibres were collected directly on a flat metallic plate. The fibre diameters of the as-spun fibres were measured by the Image J software from the optical images and the average values were calculated. The average diameters of the as-spun fibres obtained from pure polymers of 100, 300, 1000 and 2000 MFI by using the conditions reported in Table 7-2 without any fluid supply are given in Table 8-1.

Table 8-1: Average diameter of as-spun fibres fabricated by meltblowing without any fluid supply.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Fibre diameter ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>739 ± 90</td>
</tr>
<tr>
<td>300</td>
<td>584 ± 53</td>
</tr>
<tr>
<td>1000</td>
<td>467 ± 48</td>
</tr>
<tr>
<td>2000</td>
<td>395 ± 38</td>
</tr>
</tbody>
</table>

It can be observed that the fibres fabricated by meltblowing of pure polymers are several hundred micrometres in diameter. The results indicate that finer fibres can be fabricated from the polymer with higher MFI. Optical images of the fibres fabricated from pure PP polymers without any fluid supply are shown in Figure 8-2.

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Figure 8-2: Optical images of meltblown PP fibres fabricated without any fluid supply from different polymer MFI:s: (a) 100, (b) 300, (c) 1000 and (d) 2000 (each scale bar in the image: 400 µm).

8.2  Effect of fluids
As discussed above, the diameters of the fibres obtained from pure polymers without any fluid injection were hundreds of micrometres. In commercial meltblowing equipment, the fibre diameter is further reduced by the drafting action of air injected into the die section and the drafting rollers after exiting from the die [5]. In the current study, various fluids (air, N₂ and water) were injected independently prior to the die section to attenuate the fibres. The mass ratios of polymer to fluid were 1:3.75 in the case of air and N₂, and 1:3.75 and 1:7.5 in the case of water supply. The fibre attenuation was achieved by the high-velocity of the fluids (supplied at the vent port) as they exited the die of the extruder. The high-velocity of the fluid exerted a drag force on the molten stream, which in turn elongated to fine fibres. The process and mechanism of fibre formation by the injection of fluids are discussed in the following section.

8.2.1 Process of fibre formation with fluid injection
At the beginning, the extruder was stabilised while running with a particular polymer. Once stabilised, the injection of a particular fluid at the vent port was initiated. The appearance and flow of the melt changed as the fluid was introduced to the extruder. The polymer melt exiting the die section as a clear viscous liquid (before the fluid supply) changed to appear white with numerous bubbles with the fluid supply (Figure 8-3 & Figure 8-4). For a better understanding of the effect of fluid supply on the behaviour of polymer melt, the die was removed, as shown in Figure 8-3. It can be observed that the polymer melt with fluid supply contained numerous bubbles.
The other change that was observed with the injection of fluid was in the continuity of the flow of the polymer melt-jet. The melt without any fluid supply flowed as a single continuous jet from the die. However, with the supply of a particular fluid, the melt-jet was often discontinuous, with numerous breaks to the jet after exiting from the die. A similar phenomenon of discontinuity in the flow of mixture of N$_2$–PP melt-jet was observed by Qin et al. [161]. They attributed the discontinuity in the flow to the superheated N$_2$ gas, which caused the nucleation of the bubbles.

The discontinuity of the melt-jet increased with time and the polymer melt appeared to be dripping from the die after 10–15 minutes of the fluid supply. The dripping of the fluid-melt mixture was gradually converted to a discontinuous flow to the collector. Subsequently, the discontinuous flow was converted to a continuous flow of the mixture to the collector. At this stage (after 20–25 minutes of fluid supply) the mixture was flowing with high-velocity to the collector with a hissing sound.
8.2.2 Collection pattern of fibres

The nature of the collection pattern of the fibres was different prior to and after the fluid supply. The collection patterns (Figure 8-5) of the fibres (as a particular fluid was introduced) were analysed by collecting them on a flat plate before and 10 minutes after the fluid supply. It can be observed that the fibres were straight prior to the fluid supply (Figure 8-5, a). When a particular fluid was supplied, coiled fibres were collected (Figure 8-5, b). The coiling of the fibres may be due to the numerous bubbles present in the polymer melt.

![Collection pattern of PP fibres collected after exiting the die](image)

Figure 8-5: Collection pattern of PP fibres collected after exiting the die (a) straight fibres before any fluid supply (corresponding to Figure 8-4, a) and (b) coiled fibres 10 minutes after the fluid supply (corresponding to Figure 8-4, b).

The cross-sections of the above straight and coiled fibres were prepared by microtome and examined by optical microscope with a magnification of 100x. Numerous void spaces corresponding to the bubbles of different sizes were observed in the structure of the fibres fabricated with fluids (Figure 8-6). The presence of the bubbles in the fibre structure will alter the physical properties of the fibres.
Figure 8-6: Cross-section of PP fibres collected after exiting the die: (a) straight fibres before the fluid supply and (b) coiled fibres 10 minutes after the fluid supply.

The next image was analysed when the fibres started collecting on the screen before stabilisation. In this stage, the collected material consisted of a mixture of beads and fibres. At the initial stage of fibre collection, numerous beads were observed (Figure 8-7) along with the fibres, as stabilisation was not achieved with the fluid supply.

Figure 8-7: Meltblown fibres fabricated in the initial stages on the collector by fluid injection, showing the presence of beads and fibres.

Stabilisation was achieved in 5–10 minutes after the flow of the fluid-melt mixture to the collector. Once stabilisation was achieved with fluid supply, bead-less fibres were collected on the collector. At this stage, the fibres along with the heated gases or steam continuously travelled with high–velocity towards the collector (Figure 8-8). The fibres were collected on the screen while the gas/steam mixed with the atmosphere.
The fibres were collected as webs on the aluminium foil (laid over the collector) in a wide area after stabilisation was achieved. The collection patterns were nearly circular (Figure 8-9), which was similar for all the fluid types. There was a random distribution of the fibres in the web structure. It was observed that the thickness of the web was different along the radial direction, being highest near to the centre and gradually decreasing towards the periphery. These fibres were taken for the morphological investigation and further characterisation.

It is to be noted that there are 2 stages of stabilisation: (a) the 1st stabilisation is achieved before the fluid supply and (b) the 2nd stabilisation is achieved after the injection of a particular fluid. The 2nd stabilisation was used for the collection of experimental samples after the fluid supply. Both stabilisations are essential for the fabrication of good quality fibres in meltblowing.
8.2.3 Mechanism of fibre formation

In this study, nanofibres were fabricated by the injection of different fluids in the vent port. In commercial meltblowing machines, it is not possible to fabricate nanofibres. Therefore, the mechanism of fibre fabrication is different in the study compared to commercial equipment.

In commercial meltblowing equipment the combined drafting action of air (supplied in the die section) and the drafting system (after the die section) results in the formation of fibres several micrometres in diameter [5]. In this study, the drafting system was not used and the drafting by fluids was achieved much ahead of the die section. The drafting action achieved by injecting the fluids at the vent port resulted in the formation of nanofibres. Therefore, the amount of drafting achieved by the fluid injection at the vent port was higher than in commercial equipment. This can be attributed to the underlying differences in the mechanism of drafting when the fluids were independently supplied at the vent port. The mechanism of nanofibre formation in meltblowing with the fluid supply followed 2 modes: (a) mixing mode and (b) fibre formation mode, as discussed below:

1. **Mixing mode:** This mode involved the mechanism of mixing of a particular fluid with the polymer melt and was initiated by the injection of a particular fluid at the vent port. At the initial stages of the fluid injection, the fluid-melt mixture was not homogeneous. The fluid gradually mixed with the polymer melt and the mixing was increased with time. The process of mixing of fluids with the polymer melt was different for different fluids. In the case of air and N₂ injection, there was volumetric expansion due to high temperature inside the extruder (as the gases (air & N₂) at room temperature (~20°C) landed on the melt at high temperature (160–180°C)). The expanded gases occupied more volume, moved towards the die section (as the screw design does not allow backward flow) along with the polymer melt and started mixing with the polymer melt, creating bubbles. Similarly, in the case of water injection, water droplets landed on the polymer melt, which was at a temperature higher than water’s boiling point, and hence created superheated steam. The superheated steam moved towards the die section and mixed with the polymer melt, creating bubbles in the melt.
As the time elapsed, there was complete dispersion of the heated gases or the superheated steam in the polymer melt, resulting in a homogeneous phase with uniform distribution of bubbles in the melt (Figure 8-3). The polymer melts were carried out towards the die section with the screw rotation and delivered at the die. The screw rotation generated mechanical energy, which facilitated the dispersion of the heated gases or the superheated steam into the polymer melt. The complete dispersion of the fluids in the molten polymer is the critical step for the fabrication of nanofibres, which depends on the fluid type and amount; polymer MFI; and the operating temperature [162].

The number of bubbles increased with time as the dispersion of the expanded gas or superheated steam increased. The mixture started to exit from the die and the presence of the fluid was observed by the change of appearance from clear melt to white melt with bubbles. There was a single melt-jet in this mode exiting the die. The formation of bubbles resulted in the reduction of the intermolecular attraction of the polymer molecules, and the long chains were disentangled by the additional free volume created by the fluid supply, hence reducing the melt viscosity. A similar phenomenon of bubble formation was observed by Lan et al. [163] by the injection of supercritical CO₂ (SCC) to a PP melt. The injection of SCC to the extruder resulted in the formation of large-scale micro-bubbles (10–100 µm) with a population density as high as 10⁹/cm³ in the melt. In that study, the injection of SCC was effective in reducing the viscosity of the polymer melt by a certain magnitude, depending on the amount of SCC and shear rate.

2. **Fibre formation mode:** This mode included the formation of fibres by the fluid supply. In this mode, the fibres were collected on the screen by the flow of the fluid-melt mixture at high-velocity from the die exit. The high-velocity flow can be explained on the basis of Bernoulli’s equation, as there is change in the cross-sectional area (CSA) inside the extruder. The CSA is higher in the heating zones of the extruder. In the die section, there is substantial reduction in the CSA (Figure 8-10). Therefore, the fluid-melt mixture, travelling at relatively low velocity in the heating zone, starts moving with high-velocity to keep the amount of material flowing at a constant rate. In addition, the volumetric expansion of the gas/steam helps the fluid-melt mixture to be carried out at high-velocity.
In the fibre formation mode, several fibres were simultaneously collected in the form of a web on the collector. The single jet with bubbles was converted to several fibres. The bubbles were eliminated during the splitting of the melt-jet. The fibres were collected over the aluminium foil attached to the collector. There was sudden cooling of the fibres from the die temperature to room temperature, along with the gas or steam. The gas/steam mixed with the atmosphere, leaving the fibre on the foil.

The results obtained for 2000 MFI PP during the meltblowing experiments were completely different and the fibres fabricated were not as good as the fibres fabricated from other polymers. Unlike the other fibres, it consisted of beads rather than fibres. Therefore, these fibres were not taken for morphological investigation and other characterisation. Detailed discussions of the results for 2000 MFI PP are given in Section 8.2.4.3. The results for the remaining polymers (i.e. 100, 300 and 1000) are discussed in the following section.

### 8.2.4 Morphology and diameter of fibres

#### 8.2.4.1 Fibre morphology

Figure 8-11 shows the SEM images of the meltblown fibres fabricated using different fluids. The type of polymer and fluid not only affected the web morphology, but also affected the fibre diameter. The SEM images indicate that the fibres are not uniform, irrespective of the polymer MFI and fluid types. The coefficient of variation was very high, indicating high variation of the fibre diameter. The web consisted of discontinuous filaments inter-dispersed within the fibrous structure. However, in commercial meltblowing process, the fibre produced by a single-hole die is a continuous filament. An attempt was made to examine the fibre length distribution by a travelling microscope. However, this was not successful as the fibres were long and it was difficult to separate a single nanofibre.
Figure 8-11: SEM micrographs of meltblown PP fibres showing the effect of MFI and fluid type on fibre morphology and diameter: (a, b, c & d) – 100 MFI; (e, f, g & h) – 300 MFI; and (i, j, k & l) – 1000 MFI.

It can be observed from the figure that in the case of 100 MFI polymer and air supply, the fibre morphology was an incoherent fibrous structure, not very clear (Figure 8-11, a) and it was difficult to measure the diameter of the fibres in the web. This could be due to the high viscosity of the 100 MFI restricted the attenuation of the molten jet into distinct fibres. N₂ supply in the case of 100 MFI produced better fibre morphology compared to air. However, in the case of water supply with 100 MFI polymer, distinct fibres were present. In the case of 300 and 1000 MFI, although air and N₂ produced fibres with
distinct morphology, these were less uniform compared to the fibres fabricated by water. These fibres also contained some ribbon-shaped and fused fibres. The application of water produced better fibres with the higher polymer MFI (i.e. 300 & 1000) compared to 100 MFI.

Four types of meltblown PP fibres were observed in this study, as shown in Figure 8-12. In addition to the single distinct circular fibres (Figure 8-12, a), some ribbon-shaped fibres (Figure 8-12, b) and fused fibres (Figure 8-12, c) were also present in the nonwoven web, irrespective of the polymer and fluid type. The presence of ribbon-shaped fibres can be attributed to the spiral flow of the heated gas (air/N₂) or superheated steam inside the extruder due to the profile of the twin screw. The presence of fused fibres can be attributed to the insufficient separation between the fibres due to the sudden cooling of the molten jet by the interaction with the ambient air. In addition, some instances of branching of the fibres were observed (Figure 8-12, d) where a finer fibre emanated from the parent fibre.

![SEM images of meltblown PP fibres](image)

Figure 8-12: SEM images of meltblown PP fibres fabricated with fluids indicating: (a) single circular fibres, (b) ribbon-shaped fibres, (c) fused fibres and (d) branching of fibres (fibres fabricated from 300 MFI with water supply).
8.2.4.2 Average fibre diameter

Figure 8-13 shows the graphical representation of the average fibre diameter at different collector distances for different polymer MFI and fluid types. It can be observed that in the case of 100 MFI polymer, water at 5 ml/min (W5) produced coarser fibres compared to a faster flow rate of 10 ml/min (W10). No values are present in the case of air as no measurable diameter was present for the 100 MFI polymer. On the other hand, N₂ produced fibres with measurable diameter as shown in the SEM images (Figure 8-11). The fibres fabricated with N₂ were coarser than the fibres fabricated with water.

Figure 8-13: Average diameter of meltblown PP fibres fabricated with different fluids: (a) 100 MFI, (b) 300 MFI and (c) 1000 MFI.
It can be observed from the figure that in the case of 300 MFI polymer, water at 5 ml/min resulted finer fibres compared to 10 ml/min. Air and N₂ supply produced coarser average fibre diameter compared to water. The fibres produced by air were coarser than the fibres produced by N₂. Similarly, in the case of 1000 MFI polymer, no noticeable difference was observed for the two different flow rates of water. It could also be observed that as the collector distance increased, the average fibre diameter decreased, irrespective of the polymer MFI and fluid type.

In addition to W5 and W10, the effect of amount of water supply on the fibre morphology was analysed by changing the water supply to 1 ml/min (W1) and 15 ml/min (W15) using 300 MFI PP. The morphology of the fibres collected using W1 and W15 is shown in Figure 8-14. It can be observed that in the case of W1 (Figure 8-14, a), there is insufficient separation between the fibres. This was due to the insufficient driving force generated by the lower amount of fluid supply to split the melt-jet into individual fibres. In the case of W15, the mass of the fibres collected was higher at the beginning and it decreased with time. This can be attributed to more polymer being transferred initially, which could not be replaced by the polymer feed rate. After about one hour, the mass of the fibres collected were stabilised and particles was delivered with few fibres (Figure 8-14, b). The effect of W15 was similar to the effect of a particular fluid supply in the case of 2000 MFI PP, as discussed in Section 8.2.4.3.

Figure 8-14: SEM micrographs of meltblown fibres fabricated from 300 MFI PP with water supply at different feed rates: (a) 1 ml/min and (b) 15 ml/min.

The above results showed that nanofibres can be fabricated by the meltblowing process by injecting various fluids. This can close the gap between meltblowing and electrospinning with respect to the ability to produce nanofibres.
8.2.4.3 Results for 2000 MFI PP

The supply of fluids produced different results in the case of 2000 MFI PP compared to the other polymers. With the 2000 MFI PP, the extruder was stabilised (similar to the experiments with other polymers) after the introduction of the fluids at the vent port. The fibres were collected over the aluminium foil fixed to the stationary collector. Initially large amounts of fibres were collected and the amount decreased with time. This can be attributed to the lowest viscosity of the 2000 MFI PP compared to other polymers (Figure 8-15).

![Figure 8-15: Shear viscosity of different polymer MFI at 200°C.](image)

The high-velocity created by the mixing of fluids carried a large amount of polymer melt initially. As time elapsed, the amount of fibre collected decreased gradually. The SEM images of the fibres fabricated with W5 from 2000 MFI PP at different time intervals are shown in Figure 8-16. It can be observed that the fibres fabricated from 2000 MFI consisted of some fibres and beads in the first 5 min of the fibre formation. As time elapsed, only beads were formed. The fibres collected were bulky at the beginning and the bulkiness decreased as the time elapsed.
The morphology of the fibres collected in the steady state revealed the presence of beads rather than fibres (Figure 8-16). The fibres collected at 60 min, when touched with fingers, were brittle and converted to fine powder. This was due to the insufficient amount of polymer which was overheated as the polymer feed rate could not replace the polymer delivery rate. The amount of polymer feed was lower than the amount of polymer driven by the fluid supply. Hence, the weight of the polymer melt inside the extruder decreased gradually. The reduced weight of the polymer was subjected to the same amount of heat, causing overheating of the polymer.

8.3 Characterisation

This section includes the results of the characterisation techniques used for the nanofibres fabricated by meltblowing with different fluids. The characterisation was performed for all the nanofibres fabricated from different polymers with injection of various fluids. However, in some of the characterisation techniques (such as NMR, FTIR) identical results are obtained. Hence the results were discussed only for 300 MFI PP, as it produced the finest fibre. In some of the characterisation techniques (such as DSC, TGA and XRD), the nature of the results obtained was similar with different peak values. Hence, the results are discussed for 300 MFI PP and the remaining results (for 100 and 1000 MFI PP) are given in Appendix 2.

8.3.1 NMR results

The process of meltblowing involves the application of high temperature to the PP polymer. The application of high temperature can lead to chemical changes in the polymer by oxidation with atmospheric oxygen. This can lead to chemical changes in the structure of PP by the formation of carboxylic acids, aldehydes or esters [121, 122]. NMR spectra of the polymers and fibres fabricated with fluids were recorded to
determine the chemical structure. Figure 8-17 shows the $^{13}$C NMR spectra of 300 MFI polymer, as-spun fibre and fibres fabricated using different fluids in meltblowing. The fibres fabricated from the other two polymers (i.e. 100 and 1000 MFI) show identical NMR spectra.

The chemical shifts a, b, c in the figure correspond to the –CH$_3$, –CH and –CH$_2$ groups of PP respectively. The comparison of the NMR spectra indicated that the spectra of the polymer, as-spun fibre and fibres fabricated with different fluids are similar. Therefore, the injection of fluids did not change the chemical structure of the fibres at high temperature. The chemical shifts for PP are listed in Table 8-2.

Table 8-2: Chemical shifts of PP.

<table>
<thead>
<tr>
<th>Code</th>
<th>Chemical shift (ppm)</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>23.6</td>
<td>–CH$_3$</td>
</tr>
<tr>
<td>b</td>
<td>28.4</td>
<td>–CH</td>
</tr>
<tr>
<td>c</td>
<td>43.2</td>
<td>–CH$_2$</td>
</tr>
</tbody>
</table>

8.3.2 FTIR results

In addition to the NMR, FTIR was also used to determine the chemical structure of the fibres fabricated by meltblowing. The FTIR spectra of PP polymer, as-spun fibre and fibre samples with different fluids from 300 MFI PP are shown in Figure 8-18. All the
bands present in the spectra are the characteristic bands of iPP. The presence of similar spectra of the PP polymer, as-spun fibre and fibres fabricated with fluids indicates that there was no chemical change in PP fibre by the application of various fluids and high temperature during meltblowing. The symmetric and asymmetric stretching, scissors or bending and wagging of –CH₃, –CH₂ groups were observed in the PP polymer, as-spun fibre and fibres fabricated with fluids.

![FTIR spectra of meltblown PP fibres fabricated with different fluids from 300 MFI PP.](image)

In all the samples fabricated by meltblowing, the symmetric stretching vibration of –CH₃ group was observed at 2870 cm⁻¹. The asymmetric stretching vibrations of –CH₃ and –CH₂ groups were observed at 2957 and 2920 cm⁻¹ respectively. –CH₂ wagging vibration was observed at 1303 cm⁻¹. The symmetric and asymmetric scissoring vibrations of the methyl group were observed at 1376 and 1455 cm⁻¹ respectively. IR vibrational assignments of electrospun PP fibres were done by the peaks at 842, 1376 and 2800–2935 cm⁻¹ corresponding to –CH₂, –CH₂ and –CH stretching. The absorption band at 1166 and 974 cm⁻¹ corresponds to the 3/1 helix structure of PP (α-form) which was confirmed by the XRD study. Similar spectra also indicate that the helix structure was not affected by the application of various fluids and high temperature. The fibres fabricated from the other two polymers (i.e. 100 and 1000 MFI) show identical FTIR spectra.

### 8.3.3 DSC results

DSC was used to analyse the thermal behaviour of the fibres fabricated by meltblowing and to discover the polymer degradation by the reducing of the expected melting point (Tm). The DSC thermograms for both the first and second scans of both the polymer and
as-spun fibres for 300 MFI PP are shown in Figure 8-19. The thermograms indicate the heat gain or loss accompanying the phase transition during the DSC run.
The DSC thermograms (Figure 8-19, a) indicate that the PP polymer exhibited a melting point of 164.5°C, the as-spun fibres exhibited a melting point of 165°C, whereas the fibres produced with various fluids exhibited melting points in the range of 151–155.5°C depending on the type of fluid. The melting point of polymers and fibres was the endothermic peak corresponding to the fusion of the crystalline part of the polymer [164]. The melting point of the fibres fabricated with fluids shifted to lower values compared to the PP polymer and the as-spun fibre sample. This change in the melting endotherm indicated a change of the crystalline phase. This could be due to the thermal degradation caused by the high temperature during meltblowing. The thermal degradation was further analysed by the comparison of the TGA and the molecular weight results for the fibres fabricated with and without fluid supply (as discussed in Sections 8.3.4 and 8.3.5 below).

Cold crystallisation was observed at 113.5°C for the PP polymer, 112°C for the as-spun fibre and 107.5°C for all the samples fabricated with different fluids (Figure 8-19, b). It can be observed that single melting peaks were obtained in the first heating cycle, whereas double melting peaks were obtained for the second heating cycle (Figure 8-19, c) irrespective of the fluid types. This can be attributed to the recrystallisation or re-organisation by heating during the DSC experiments [165]. The higher melting endotherm in the double peak corresponds to the fusion of lamellar crystals formed during the process of primary crystallisation, whereas the lower melting endotherm
corresponds to the fusion of crystals grown mainly in inter-fibrillar regions during the secondary crystallisation process.

The temperatures corresponding to the double peaks were (155, 161.5°C) for the PP polymer and as-spun fibre, and (140.5, 151) for the fibres fabricated with fluids. The DSC curves in the second cooling cycle were similar to the first, but the peak height was the same or lower compared to the 1st cycle (Figure 8-19, d). For the fibres fabricated with fluids, the peaks were broader with lower peak heights. The polymers, as-spun fibres and fibres fabricated with fluids from 100 and 1000 MFI PP showed similar DSC curves, but with different melting and crystallisation temperatures. Therefore, the DSC curves for these fibres are shown in Appendix A 2.1 and A 2.2. However, the values of Tm and Tc for the fibres fabricated with different fluids are listed in Table 8-3.

Table 8-3: Thermal properties of meltblown fibres fabricated with different fluid supply.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Fibre samples</th>
<th>Tm (°C) (1st heating)</th>
<th>Tc (°C) (1st cooling)</th>
<th>Tm (°C) (2nd heating)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>As-spun fibre</td>
<td>166</td>
<td>112</td>
<td>157, 163</td>
</tr>
<tr>
<td></td>
<td>With air</td>
<td>148</td>
<td>104.5</td>
<td>136, 148</td>
</tr>
<tr>
<td></td>
<td>With N2</td>
<td>148</td>
<td>104.5</td>
<td>136, 148</td>
</tr>
<tr>
<td></td>
<td>With W5</td>
<td>155.5</td>
<td>107.5</td>
<td>140.5, 152.5</td>
</tr>
<tr>
<td></td>
<td>With W10</td>
<td>155.5</td>
<td>106</td>
<td>140.5, 152.5</td>
</tr>
<tr>
<td>300</td>
<td>As-spun fibre</td>
<td>165.5</td>
<td>110.5</td>
<td>155.5, 162.5</td>
</tr>
<tr>
<td></td>
<td>With air</td>
<td>155.5</td>
<td>107.5</td>
<td>140.5, 151</td>
</tr>
<tr>
<td></td>
<td>With N2</td>
<td>155.5</td>
<td>107.5</td>
<td>140.5, 152.5</td>
</tr>
<tr>
<td></td>
<td>With W5</td>
<td>152.5</td>
<td>107.5</td>
<td>140.5, 152.5</td>
</tr>
<tr>
<td></td>
<td>With W10</td>
<td>154</td>
<td>107.5</td>
<td>139, 149.5</td>
</tr>
<tr>
<td>1000</td>
<td>As-spun fibre</td>
<td>164.5</td>
<td>112</td>
<td>140.5, 152.5</td>
</tr>
<tr>
<td></td>
<td>With air</td>
<td>148</td>
<td>104.5</td>
<td>137.5, 148</td>
</tr>
<tr>
<td></td>
<td>With N2</td>
<td>148</td>
<td>104.5</td>
<td>137.5, 148</td>
</tr>
<tr>
<td></td>
<td>With W5</td>
<td>155.5</td>
<td>104.5</td>
<td>137.5, 148</td>
</tr>
<tr>
<td></td>
<td>With W10</td>
<td>155.5</td>
<td>104.5</td>
<td>140.5, 152.5</td>
</tr>
</tbody>
</table>

8.3.4 TGA

The thermal stability of as-spun PP fibres and fibres fabricated with different fluids was analysed by TGA. The TGA curves (Figure 8-20) reflect the degree of thermal degradation during meltblowing. Although the experiments were performed from room temperature to 800°C, the results are presented in the range 300–600°C for clarity of the image. The TGA curves show that the PP polymer has the highest thermal stability (indicated by the weight loss starting at higher temperature) compared to the fibres fabricated by the supply of fluids. Therefore, the decrease in the melting point (in DSC experiments) after meltblowing with the fluids is due to the decrease of the chain entanglements as a result of decrease in the molecular weight. The weight loss of the
fibres produced by air supply starts at the lowest temperature, which indicates the highest amount of thermal degradation of the fibres. The TGA thermograms of the fibres fabricated from 100 and 1000 MFI PP are shown in Appendix A 2.3.

Figure 8-20: Typical TGA thermograms of PP polymer, as-spun fibre and meltblown fibres fabricated from 300 MFI PP with various fluids.

### 8.3.5 Molecular weight or intrinsic viscosity

In addition to the TGA results, the degree of thermal degradation was also compared by calculating the molecular weights of fibres from the IV values as listed in Table 8-4. It can be observed from the table that the molecular weight of the fibres fabricated with different fluids decreased after meltblowing, irrespective of the polymer MFI. The fibres fabricated with air and N₂ showed higher degradation compared to the fibres fabricated with water. Between air and N₂, air supply resulted in the highest amount of thermal degradation.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Polymer As-spun fibre</th>
<th>Fibres with air</th>
<th>Fibres with N₂</th>
<th>Fibres with W5</th>
<th>Fibres with W10</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>100875</td>
<td>61928</td>
<td>36932</td>
<td>37288</td>
<td>41564</td>
</tr>
<tr>
<td>300</td>
<td>77590</td>
<td>45416</td>
<td>29703</td>
<td>30901</td>
<td>33708</td>
</tr>
<tr>
<td>1000</td>
<td>60238</td>
<td>34372</td>
<td>26158</td>
<td>27065</td>
<td>29657</td>
</tr>
</tbody>
</table>

### 8.3.6 XRD results

Physical and mechanical properties of the fibres are directly related to the morphology and crystalline structure, which can change during meltblowing. The injection of fluids and high temperature in meltblowing can alter the crystalline properties. Therefore, investigation of the morphology and crystalline structure is important to understand the performance of the fibres during use. The crystalline structure of the meltblown fibres
was analysed by XRD analysis and the diffraction patterns for the fibres fabricated from 300 MFI PP are shown in Figure 8-21.

![XRD diffractograms of meltblown PP fibres fabricated with various fluids.](image)

Figure 8-21: XRD diffractograms of meltblown PP fibres fabricated with various fluids.

The XRD study shows the diffraction peaks of the fibre samples fabricated with the fluids and also the annealed samples for 300 MFI PP. It can be observed that all the meltblown samples produced with fluids contain relatively lower and broader peaks, compared to the higher and sharper peaks of PP polymer and as-spun fibre. This indicates that the fibre samples fabricated with fluids contain very low degrees of crystallinity compared to the corresponding as-spun fibre. This is due to the samples were not fully crystallised due to rapid cooling after exiting from the die with the fluid supply. The low degree of crystallinity is in accordance with previous PP meltblown web results [166]. It can be observed that the samples fabricated with air and N₂ are more amorphous than the fibres fabricated with water. The XRD diffractograms of fibres fabricated from 100 and 1000 MFI PP with various fluids are similar to 300 MFI and are shown in Appendix A 2.4.

It can also be observed that all the meltblown fibres contain a mixture of smectic and monoclinic α-form crystals. The Bragg reflection peaks at 14°, 17°, 18.5°, 21° and 22° correspond to the monoclinic crystals of PP (α-form) with the indexed planes of (110), (040), (130), (111) and (041) [125, 126] and a space group of P2₁/c. In the PP polymer and the as-spun fibre sample, the α-form crystals were predominant, whereas the
samples produced by fluids were more smectic. This can be attributed to the faster cooling and smaller size of the crystals formed with a lower degree of perfection during meltblowing with fluids. The monoclinic structure relates to rod-like fibres, whereas the smectic structure relates to ribbon-like fibres. No \(\beta\)-form or \(\gamma\)-form was found in any of the meltblown samples. Thus the double peaks in DSC are related to the process involving \(\alpha\)-crystals only during the second heating cycle of DSC. The double endotherm has been attributed to the transitions between different modifications of \(\alpha\)-crystal form (\(\alpha_1\) to \(\alpha_2\)).

It can also be observed that the amount of crystallinity of the fibres increases after annealing. The crystallinity in as-spun fibres is higher than that for the fibres fabricated with fluids. The rapid solidification during meltblowing prevents the macromolecular chains from being aligned to form crystallinity. In addition, the presence of voids by the mixing of the fluids with the polymer melt also contributes to the low crystallinity of the fibres. The structural orientation and crystallinity are affected by the processing parameters, the nature of fluid supply and the polymer rheology. During annealing, there is enough time for the macromolecular chains to be relaxed and oriented. Molecular chains in the oriented state are less mobile than in the unoriented state, which leads to high crystallinity.

The amount of crystallinity for the meltblown fibres has been summarised in Table 8-5. While calculating the crystallinity, the amorphous section was found to be a very broad peak at the bottom part of each diffractogram. For the as-spun fibres and the annealed fibres, well defined crystalline peaks were observed. It can be observed from the table that the as-spun fibres contained crystallinity in the range of 50–54%. The crystallinity values for the fibre samples fabricated with various fluids (i.e. air, \(N_2\), W5 and W10) were in the range of 25–37%. Additionally, it can be observed that the fibres fabricated with fluids show an increase in the crystallinity after annealing, as indicated in the table. All commercial fibres produced in industry are subjected to drawing and/or heat setting operations for the crystallites to grow. Therefore those fibres possess high crystallinity compared to the values obtained in the current research.
Table 8-5: Crystallinity of the meltblown PP fibres fabricated with different fluids.

<table>
<thead>
<tr>
<th>Fibre sample</th>
<th>Annealing</th>
<th>Crystallinity (%)</th>
<th>100 MFI</th>
<th>300 MFI</th>
<th>1000 MFI</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-spun</td>
<td>Before</td>
<td>54</td>
<td>50</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>61</td>
<td>57</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>Fibre with air</td>
<td>Before</td>
<td>25</td>
<td>30</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>33</td>
<td>44</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>Fibre with N₂</td>
<td>Before</td>
<td>26</td>
<td>32</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>35</td>
<td>45</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Fibre with W5</td>
<td>Before</td>
<td>31</td>
<td>36</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>39</td>
<td>49</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>Fibre with W10</td>
<td>Before</td>
<td>30</td>
<td>37</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>41</td>
<td>48</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>

8.3.7 Mechanical property

Mechanical characterisation of nanofibres is essential to ensure product serviceability. The mechanical properties of the fibres strongly depend on the molecular weight of the polymers, tacticity, processing conditions and degree of crystallinity [167, 168]. It was extremely difficult to measure the mechanical property of a single nanofibre, due to the difficulty in isolating a single nanofibre. The isolation of a single nanofibre was harder in the case of the fibres fabricated in meltblowing, compared to melt electrospinning. Furthermore, frequent slippage at the jaws was observed with single nanofibres. Therefore, the idea of testing single nanofibres was not adopted. The mechanical property of the fibres was measured by preparing dumbbell-shaped specimens from the nonwoven section collected on the rotating drum. The mechanical properties of the nanofibres were affected by several factors, such as polymer MFI, fluid type and annealing, which are discussed in the following section.

8.3.7.1 Effect of MFI

The stress–strain curves of the meltblown nanofibres fabricated from PP polymers with different fluids are shown in Figure 8-22. It can be observed from the figure that the mechanical property changed with the polymer MFI. The tensile strength for the fibres fabricated with fluids from 100 MFI PP was lowest compared to the other polymers i.e. 300 and 1000 MFI (Table 8-6). The fibres fabricated from 300 MFI PP showed higher strength compared to the fibres fabricated from 1000 MFI. Generally, in melt processing the fibres fabricated from the polymers with higher MFI (under identical conditions) show lower tensile strength [169]. However, in this study the lowest strength was obtained for the fibres fabricated from the polymer with highest molecular weight. This
can be attributed to the lower degree of crystallinity of the fibres. In addition, the flow behaviours of the polymer melt in the presence of different fluids were different, which affected the macromolecular confirmation and hence the mechanical properties. It can be observed from the table that the modulous values are the highest for the fibres fabricated from 300 MFI PP and the lowest for the fibres fabricated from 100 MFI PP.

Figure 8-22: Stress–strain curves of the meltblown nanofibres fabricated from PP polymers: (a): 100 MFI, (b) 300 MFI and (c) 1000 MFI.
Table 8-6: Tensile properties of meltblown PP nanofibres fabricated with fluids.

<table>
<thead>
<tr>
<th>Polymer MFI</th>
<th>Fibre sample</th>
<th>Annealing</th>
<th>Specimen thickness (mm)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Modulous (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>With air</td>
<td>Before</td>
<td>0.24</td>
<td>0.09</td>
<td>140</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>With air</td>
<td>After</td>
<td>0.21</td>
<td>0.12</td>
<td>128</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>With N₂</td>
<td>Before</td>
<td>0.20</td>
<td>0.11</td>
<td>140</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>With N₂</td>
<td>After</td>
<td>0.20</td>
<td>0.14</td>
<td>131</td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>With W5</td>
<td>Before</td>
<td>0.18</td>
<td>0.15</td>
<td>139</td>
<td>2.78</td>
</tr>
<tr>
<td></td>
<td>With W5</td>
<td>After</td>
<td>0.17</td>
<td>0.19</td>
<td>103</td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>With W10</td>
<td>Before</td>
<td>0.19</td>
<td>0.19</td>
<td>137</td>
<td>2.35</td>
</tr>
<tr>
<td></td>
<td>With W10</td>
<td>After</td>
<td>0.19</td>
<td>0.27</td>
<td>111</td>
<td>2.64</td>
</tr>
<tr>
<td>300</td>
<td>With air</td>
<td>Before</td>
<td>0.22</td>
<td>0.19</td>
<td>140</td>
<td>3.57</td>
</tr>
<tr>
<td></td>
<td>With air</td>
<td>After</td>
<td>0.22</td>
<td>0.21</td>
<td>137</td>
<td>3.80</td>
</tr>
<tr>
<td></td>
<td>With N₂</td>
<td>Before</td>
<td>0.20</td>
<td>0.18</td>
<td>140</td>
<td>3.73</td>
</tr>
<tr>
<td></td>
<td>With N₂</td>
<td>After</td>
<td>0.19</td>
<td>0.20</td>
<td>131</td>
<td>3.96</td>
</tr>
<tr>
<td></td>
<td>With W5</td>
<td>Before</td>
<td>0.17</td>
<td>0.26</td>
<td>103</td>
<td>4.86</td>
</tr>
<tr>
<td></td>
<td>With W5</td>
<td>After</td>
<td>0.16</td>
<td>0.36</td>
<td>104</td>
<td>4.57</td>
</tr>
<tr>
<td></td>
<td>With W10</td>
<td>Before</td>
<td>0.17</td>
<td>0.24</td>
<td>140</td>
<td>4.28</td>
</tr>
<tr>
<td></td>
<td>With W10</td>
<td>After</td>
<td>0.18</td>
<td>0.32</td>
<td>122</td>
<td>4.56</td>
</tr>
<tr>
<td>1000</td>
<td>With air</td>
<td>Before</td>
<td>0.22</td>
<td>0.16</td>
<td>139</td>
<td>3.41</td>
</tr>
<tr>
<td></td>
<td>With air</td>
<td>After</td>
<td>0.22</td>
<td>0.19</td>
<td>140</td>
<td>3.67</td>
</tr>
<tr>
<td></td>
<td>With N₂</td>
<td>Before</td>
<td>0.23</td>
<td>0.15</td>
<td>139</td>
<td>3.13</td>
</tr>
<tr>
<td></td>
<td>With N₂</td>
<td>After</td>
<td>0.23</td>
<td>0.21</td>
<td>139</td>
<td>3.51</td>
</tr>
<tr>
<td></td>
<td>With W5</td>
<td>Before</td>
<td>0.21</td>
<td>0.25</td>
<td>142</td>
<td>4.83</td>
</tr>
<tr>
<td></td>
<td>With W5</td>
<td>After</td>
<td>0.20</td>
<td>0.27</td>
<td>126</td>
<td>4.91</td>
</tr>
<tr>
<td></td>
<td>With W10</td>
<td>Before</td>
<td>0.21</td>
<td>0.24</td>
<td>141</td>
<td>4.09</td>
</tr>
<tr>
<td></td>
<td>With W10</td>
<td>After</td>
<td>0.21</td>
<td>0.26</td>
<td>130</td>
<td>3.93</td>
</tr>
</tbody>
</table>

8.3.7.2 Effect of fluid type

The mechanical properties of the fibres also varied with the type of fluids used. For all the polymer types, the fibres fabricated with air and N₂ resulted in the lowest tensile strength. This can be attributed to the lowest degree of crystallinity, caused by the flow behaviour of the polymer with the presence of different fluids. Meltblown fibres fabricated with N₂ showed higher tensile strength than fibres fabricated with air. However, the difference between them was not significant. The tensile strength of the fibres fabricated with water was highest, which showed significant difference from the fibres fabricated with air and N₂. This can be attributed to the higher degree of crystallinity of the fibre samples. In the case of 300 MFI, W5 resulted in the fibres with highest tensile strength. This can be attributed to the presence of the finest fibres in the dumbbell shaped specimen.

All the fibre samples fabricated with fluids showed very high elongation at break. This can be attributed to the presence of some ribbon-shaped fibres in the web, which get straightened before being ruptured by the load when the load is applied. This phenomenon is like straightening a loop of thread by the application of load. When a
load is applied, the loop starts straightening without any tensile deformation. The tensile deformation starts after the loop is completely straightened. In addition, the high elongation obtained was a result of the orientation of the polymer during tensile deformation. The slow extension rate (10 mm/min) helped the polymer chains to reorient themselves when the load was applied. No significant difference was observed in the elongation at break with polymer MFI and fluid type used. The fibres fabricated with air and N₂ resulted in the lowest modulous values due to the low crystallinity of these fibres.

8.3.7.3 Effect of annealing

In order to investigate the effect of annealing on mechanical property, the samples were annealed in hot air at 120°C for 30 minutes. The effect of annealing on the mechanical properties of the nanofibres was investigated by testing the fibres before and after annealing. The stress–strain curves of the meltblown fibres (fabricated from 300 MFI PP with different fluids) before and after annealing are shown in Figure 8-23. Fibres fabricated from the other polymers (i.e. 100 and 1000 MFI) showed similar stress–strain curves but with different values for tensile strength, elongation at break and modulous as listed in Table 8-6. Therefore, the stress–strain curves for the fibres of these two polymers are explained in Appendix A 2.5 and A 2.6.
Figure 8-23: Stress–strain curves of the meltblown nanofibres from 300 MFI PP (showing the effect of annealing) fabricated with different fluids: (a) air, (b) N₂, (c) W5 and (d) W10.
It can be observed from the above figures and Table 8-6 that annealing marginally increased the breaking strength of the nanofibres (in the web) fabricated with the fluids. This can be attributed to the increase in the crystallinity of the fibres after annealing (Table 8-5). Although the tensile strength of the fibres increased after annealing, it was not significant except in a few cases. It can also be observed that the elongation at break for all the samples decreased after annealing. The modulous values of the fibres fabricated with fluids increased after annealing, irrespective of the polymer MFI.

8.3.7.4  Effect of rotating drum on the mechanical property

The effect of using a rotating drum collector on the mechanical properties of the fibres was analysed and compared with the results of the fibres collected using a stationary collector. Figure 8-24 indicates the SEM images of the fibres collected on the rotating drum and stationary collector. It can be observed that some of the fibres collected on the rotating drum are aligned on the direction of drum rotation. The fibres collected on the stationary collector were randomly distributed. Dumbbell shaped fibre specimens of similar thickness were prepared for both the collector types and were tested in Instron.

![SEM micrographs of the fibres collected on: (a) rotating drum and (b) stationary collector.](image)

Figure 8-24: SEM micrographs of the fibres collected on: (a) rotating drum and (b) stationary collector.

The comparison of the results of tensile test from the rotating drum collector and stationary collector are shown in Figure 8-25. It can be observed that the breaking strength of the fibres collected on the rotating drum collector was higher. The difference between the two groups of results was statistically significant for all the fluid types. This can be attributed to the extra strength contributed by the fibre alignment achieved by using a rotating drum. In the case of the stationary collector, the fibres were randomly oriented. During the tensile test, only the fibres present in the load direction contributed towards the strength. The fibres present at cross direction and not gripped by both the
jaws of the tensile tester did not contribute towards the strength. Therefore, a smaller number of fibres contributed towards the tensile strength. Hence, the tensile strength of the fibre samples from the rotating drum collector was higher.

Figure 8-25: Stress–strain curves of the meltblown nanofibres from 300 MFI PP (showing the effect of rotating drum) fabricated with different fluids: (a) air, (b) N₂, (c) W5 and (d) W10.
8.3.8 Hydrophobic properties

Polypropylene polymers are inherently hydrophobic in nature (i.e. nonwettable by water) [170]. Meltblowing of PP polymers with different fluids may result in the fabrication of hydrophobic fibres. Several pieces of research have been done to make PP fibres hydrophilic [128, 171]. The inert nature of PP prevents any chemical modification by chemical reaction to make the fibres hydrophilic. The standard regain of PP fibre is 0.4%, which indicates the hydrophobic behaviour. In this study, the hydrophobic behaviour was studied by measuring the water contact angle of the fibres. The water contact angle of the as-spun fibre fabricated from 300 MFI PP is shown in Figure 8-26. It can be observed that the water contact angle is > 90°, which indicates the hydrophobic nature of PP fibres.

![Figure 8-26: Image of the water contact angle of meltblown PP fibres from 300 MFI PP.](image)

The water contact angles of fibres fabricated with different fluid supplies are shown in Figure 8-27. It can be observed that the water contact angle for the PP fibres fabricated by meltblowing with different fluids is > 90°, indicating the hydrophobic nature. The water contact angle does not change noticeably for the fibres fabricated by the application of various fluids. The list of contact angles of fibres fabricated in meltblowing with different fluids are given in Table 8-7.
Figure 8-27: Water contact angles of meltblown PP fibres fabricated with different fluid supply from 300 MFI PP.

Table 8-7 Water contact angles of meltblown PP fibres produced with different fluids.

<table>
<thead>
<tr>
<th>Fibre samples</th>
<th>Water contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 MFI</td>
</tr>
<tr>
<td>As-spun</td>
<td>108</td>
</tr>
<tr>
<td>With air</td>
<td>102</td>
</tr>
<tr>
<td>With N₂</td>
<td>100</td>
</tr>
<tr>
<td>With W5</td>
<td>103</td>
</tr>
<tr>
<td>With W10</td>
<td>107</td>
</tr>
</tbody>
</table>

8.4 Processing difficulties with 2000 MFI PP

In the case of 2000 MFI PP polymer, difficulties were encountered during the meltblowing experiments. For example, there was leakage of molten polymer (Figure 4-22) from the interspaces between the covering metallic plates forming the walls of various heating chambers. This phenomenon was observed due to the lowest viscosity of the polymer melt for 2000 MFI polymer. The leakage was increased when the fluid supply was initiated in the equipment. The leaked polymers solidified in the interspaces when the heaters were turned off. In subsequent runs of the extruder, the leakage was aggravated due to remelting of the solidified polymer, which created more gaps.

In addition to the leakage of polymer melt, fluids also leaked in these interspaces. This prevented fibre formation due to insufficient pressure due to the pressure drop at the points of leakage. Once the problem of leakage was observed, switching to the lower MFI PP did not solve the problem. The only way to avoid this problem was burning the polymers off the metallic plates at very high temperature and cleaning the melt...
thoroughly from the walls. The leakage was not observed while the experiments were performed with 100, 300 and 1000 MFI PP.

The other major problem observed in the case of 2000 MFI PP was the blockage of the fluid supply nozzle. The polymer melt for 2000 MFI PP often entered into the small orifice of the nozzle used for the supply of fluids and solidified inside. This blockage also blocked the flow of different fluids to the extruder. This problem was solved by cleaning the nozzle with an airgun, which was a difficult task. The cleaning of the extruder required turning off the twin screws and the polymer feed. While restarting, the extruder was run for a sufficient span of time for stabilisation. Therefore, the experiments with 2000 MFI PP were not easy compared to those for the other polymers. Although this phenomenon was observed with 100, 300 and 1000 MFI PP, it was very rare.
9  Chapter 9 Conclusions: meltblowing

9.1 Conclusions

- The use of pure polymers in meltblowing without any fluid injection resulted in production of fibres with average diameters of several hundred micrometres. Subsequent results showed that nanofibres can be fabricated by meltblowing with the application of various fluids (air, N₂ and water) into the vent port of commercial meltblowing equipment. The nanofibres showed variability in fibre diameter. Four types of meltblown PP fibres were observed in this study: circular, ribbon-shaped, fused and branched fibres.

- The optimum processing conditions for the fabrication of nanofibres from different polymers by using various fluids were established. Injection of water worked better than air and N₂.

- The smallest fibre diameter of 0.438 µm (i.e. 438 nm) was achieved from the 300 MFI PP with the injection of water at 5 ml/min (W5). The molecular weight is an important factor governing the fibre diameter in meltblowing. Generally, lower molecular weight (higher MFI) polymer favours the formation of finer fibres. However, in this study the molecular weight was found to be less influencing. The highest molecular weight polymer (i.e. 100875 or 100 MFI) did not produce fibres with air and produced less uniform fibres with N₂ and water. Similarly, the lowest molecular weight polymer (i.e. 55509 or 2000 MFI) was difficult to process in meltblowing and did not produce fibres. The smallest fibre diameters were obtained from the polymer with a molecular weight of 77590 (i.e. 300 MFI) with W5.

- DSC results showed the presence of single melting peaks in the first heating cycle and double melting peaks in the second, due to re-crystallisation or re-organisation by heating. The melting peaks were shifted to lower values with the use of fluids and this lowering of the melting endotherm was due to the thermal degradation caused by the high temperature.

- TGA results showed that the as-spun PP fibres (fabricated with no fluid injection) showed higher thermal stability compared to the fibres fabricated by the use of fluids. The weight loss of the fibres produced by the injection of air started at the lowest temperature, which indicated the highest amount of thermal
degradation of these fibres compared to N₂ and water. This can be attributed to the oxidative effect of air.

- The decrease of the molecular weight in the case of fibres fabricated by the injection of fluids also indicated thermal degradation after meltblowing which was determined from the intrinsic viscosity values.
- XRD studies showed that all the meltblown PP fibre samples produced with the injection of fluids contain low degrees of crystallinity and a mixture of smectic and monoclinic α-form crystals. The crystallinity was increased with annealing.
- It was found that the fibres fabricated from 100 MFI PP with the injection of fluids resulted in the lowest tensile strength. The fibres fabricated from 1000 MFI were weaker than the fibres fabricated from 300 MFI. For all the polymers, the fibres fabricated with air and N₂ showed the lowest tensile strength. Further, all the fibres fabricated with fluid supply showed high elongation. Annealing of the fibres increased the tensile strength. The strength of fibres fabricated by the rotating drum was higher compared to the fibres fabricated by stationary collector.
- The fibres fabricated with air and N₂ resulted in the lowest modulous values due to the low crystallinity of these fibres. The modulous values of the fibres fabricated by meltblowing with fluids increased after annealing irrespective of the polymer MFI.
- Similar FTIR spectra of the polymer and the fibres indicate that there was no change to the chemical functionality of PP fibres by the application of various fluids and the high temperature during meltblowing. NMR results also showed similar chemical shifts indicating no change to the chemical structure.
- The fibres fabricated by meltblowing showed high values of contact angle indicating their hydrophobic nature. Hydrophobic properties of the as-spun fibres and fibres fabricated with different fluids did not differ significantly fluids do not PP showed different results with various fluids compared to other polymers. The amount of fibre collected initially was higher which decreased gradually. Initially, few beads were present in the fibres which increased gradually.
- Some problems such as the leakage of the polymer at the covering wall of the heating chambers and the blockage of the nozzle (used for the fluid supply) were encountered while processing the 2000 MFI PP due to the low viscosity of this...
polymer melt. However, these problems were rarely observed with the other polymers (100, 300 and 1000 MFI).
Chapter 10 Comparison of results and future suggestions

10.1 Results of the study
In this research the two melt processes i.e. melt electrospinning and meltblowing were successfully employed for the fabrication of nanofibres from polypropylene polymers of different MFI. In melt electrospinning the use of additives (sodium oleate and sodium chloride) resulted in the fabrication of uniform nanofibres due to the increase in the electrical conductivity of the polymer melt. These additives are readily available, cheap and easy to use. Few of the previous research have really achieved the goal of fabricating nanofibres by melt electrospinning. This research explored the possibility of fabricating nanofibres by increasing the electrical conductivity of the polymer melt which has been a neglected area in melt electrospinning. The other important finding of the research is the justification of the fact that fibre cross-sectional shape is independent of the die shape. This has been established for the first time in melt electrospinning.

In meltblowing, the injection of various fluids (air, N₂ and water) at the vent port of a commercial extruder resulted in the fabrication of nanofibres. Limited work has been done in meltblowing for the fabrication of nanofibres mainly by altering the die profile. This study used commercially available die and processing conditions for the fabrication of nanofibres. The polymer feed rate used in meltblowing was substantially higher than melt electrospinning which can solve the issues of low productivity of melt electrospinning.

10.2 Comparison of results for the fabrication of nanofibres
The two melt processes employed in this study differ from each other in principle and mechanism of fibre formation. Furthermore, the morphology and the physical properties of the fibres fabricated by these two processes are also different. These differences are discussed in the following sections.

10.2.1 Differences in the process of fibre formation
The melt electrospinning process involved the application of an external electric field to a polymer melt held in a syringe to produce a single continuous nanofibre from a Taylor cone. The Coulombic attractive force was the main driving force in melt electrospinning;
hence the lower viscosity liquids were stretched to the maximum extent producing finest fibre. On the other hand, the meltblowing involved extruding a polymer melt and driving it out at high–velocity from the die orifice. Several fibres having a distribution of fibre diameters and fibre lengths were formed simultaneously with the supply of the injected fluids. The main driving force for meltblowing was the high–velocity fluid flow at the die exit. This was dependent on the nature of the mixture of the fluid and polymer type.

The effective collector distances for fibre fabrication in the case of melt electrospinning were lower compared to meltblowing. For example the maximum collector distances were 150 mm and 400 mm in the case of melt electrospinning and meltblowing respectively for 2000 MFI PP. The polymer feed rate was substantially lower in the case of melt electrospinning (i.e. 0.64 g/hr) compared to meltblowing (i.e. 80 g/hr).

### 10.2.2 Differences in the material performance

In melt electrospinning, the molecular weight was the predominant factor governing the fibre diameter. The fibre diameter was gradually increased with the molecular weight. The higher molecular weight polymers were not able to produce nanofibres with the additives. The polymer with the highest molecular weight (i.e. 100,875 or 2000 MFI) resulted in the largest fibre diameters. The polymers with the lowest molecular weight (i.e. 55,509 or 100 MFI) resulted in the formation of the finest fibres. In contrast, the molecular weight was not the predominant factor governing the fibre diameter in meltblowing. The highest molecular weight (i.e. 100,875) polymer did not produce good fibres with air injection and resulted in less uniform fibres with the injection of other fluids. Similarly, the lowest molecular weight (i.e. 55,509) polymer was really challenging to process in meltblowing and did not produce good fibres. The lowest fibre diameter was obtained from the polymer with a molecular weight of 77,590 in meltblowing.

Nanofibres were fabricated with the help of additives in melt electrospinning, whereas it was achieved with the injection of various fluids in meltblowing. The additives either lowered the melt viscosity or increased the electrical conductivity for the fabrication of nanofibres. On the other hand, the supply of fluids in meltblowing resulted in the
formation of nanofibres possibly due to the reduction of the melt viscosity and the high-velocity flow of fluid-melt mixture.

10.2.3 Differences in the fibre properties

A single continuous fibre was fabricated in melt electrospinning process, whereas several discontinuous fibres were fabricated in meltblowing. The fibres were collected in different patterns with different additives in melt electrospinning, whereas the collection pattern was similar with different fluids in meltblowing.

The instances of ribbon-shaped fibres and fusing of fibres frequently observed in meltblowing, was not observed in melt electrospinning. Uniform nanofibres were fabricated with the addition of SO and NaCl in melt electrospinning whereas the fibres fabricated by meltblowing were less uniform. The shape of the fibres in melt electrospinning was independent of the die shape due to its formation from the single Taylorcone, whereas the shape of the fibres in meltblowing followed the shape of the die.

The melting points of the fibres fabricated with different additives in melt electrospinning; and different fluids in meltblowing shifted to lower values compared to the PP polymer and the as-spun fibres. This change in the melting endotherm indicated a change of the crystalline phase which was due to the thermal degradation caused by the high temperature during both melt electrospinning and meltblowing. Single melting peaks were obtained in the first heating cycle whereas double melting peaks were obtained for the second heating cycle in both the cases of melt electrospinning and meltblowing.

Thermal degradation was observed in both the processes of melt electrospinning and meltblowing. However the degree of thermal degradation was higher in the case of meltblowing due to the higher residence time inside the extruder. This was verified by comparing the change in the molecular weights of the fibres fabricated by melt electrospinning and meltblowing.
The fibre samples fabricated with different additives in melt electrospinning; and different fluids in meltblowing contain very low degree of crystallinity compared to the corresponding as-spun fibres. This was due to the samples were not fully crystallised after exiting from the die. All the melt electrospun and meltblown fibres contained a mixture of smectic and monoclinic \( \alpha \)-form crystals. Although both the fibres fabricated by melt electrospinning and meltblowing showed hydrophobic nature, the fibres fabricated by melt electrospinning with PDMS showed very high hydrophobicity.

### 10.3 Future suggestions

Melt electrospinning with other additives which reduce the viscosity of PP can result in the reduction of fibre diameter with uniform fibres. Similarly, other electrical conductive additives with different ionic sizes can be used to fabricate nanofibres and to thoroughly understand the effect of electrical conductivity. The aim of the future research should be fabrication of PP nanofibres with average fibre diameters less than 100 nm by melt electrospinning and meltblowing. In melt electrospinning the polymer feed rate used was very low in this study. Therefore, the productivity was very low and not economically viable. Hence, the melt electrospinning equipment with the provision of dies with multiple holes could be investigated to achieve higher productivity. Future research should focus on the production of various types of nanofibres (such as porous, hollow, core/sheath etc.) by melt electrospinning and explore their potentiality in material science.

Both the melt electrospinning and meltblowing experiments should be performed with the provisions of controlled heating of the fibres after exit from the die till the collection of the fibre. The controlled heating can further reduce the fibre diameter and affect the crystallinity and hence the mechanical properties. The study on the use of other thermoplastic polymers such as PET and PE in melt electrospinning and meltblowing should be performed. The amount of research work done on the fabrication of nanofibres of these polymers is limited. The use of supercritical CO\(_2\) in meltblowing can produce different results compared to the fluids used in this study. Supercritical CO\(_2\) has been used in several experiments in extrusion technology with different aims than the fabrication of nanofibres.
The analysis of dynamic viscosity and rheological parameters during the meltblowing experiments with different fluids can provide additional knowledge about the mechanism of nanofibre formation in meltblowing. For this purpose, an in-line capillary rheometer can be used during the meltblowing experiments which can measure the shear viscosity of the fluid-melt mixture.

The tensile characterisation of single nanofibres in both the cases of melt electrospinning and meltblowing can provide better understanding of the tensile properties for direct comparison. Analysis of the size of the spherulites in the crystal structure of PP can provide additional knowledge about the electrical conductivity of the fibres fabricated with the additives in melt electrospinning. Other characterisation techniques such as the analysis of the size and distribution of the pores; the analysis on the performance of the fibres in applications such as filtration and protective clothing can be used to identify the potential applications of these fibres.

10.4 Publications

10.4.1 Journal publications


R Nayak, I L Kyratzis, Y B Truong, R Padhye and L Arnold, “Effect of viscosity and electrical conductivity on the morphology and fibre diameter in melt electrospinning of polypropylene” accepted by Text Res J (Sage publishing, UK).


10.4.2 Conference publications


References


49. Teo W, Ramakrishna S: A review on electrospinning design and nanofibre assemblies. Nanotechnology 2006, 17:R89.


127. Racu C: Influence of physical and mechanical characteristics of polypropylene fibres used for bending with hemp upon the yarn characteristics. In.: Technical University Iasi Romania, Textile Engineering Department; 2001.


Appendix 1: Melt electrospinning

**A 1.1:** Effect of temperature on the electrical conductivity of 2000 MFI PP with additives: (a) SO and (b) NaCl (7%).

(a)

(b)
A 1.2: Effect of the amount of additives on the electrical conductivity of PP of 2000 MFI with (a) SO and (b) NaCl (at 200°C).
A 1.3: DSC thermograms of melt electrospun PP fibres of 2000 MFI with varying amounts of SO: (a) 1st heating cycle, (b) 1st cooling cycle and (c) 2nd heating cycle.
A 1.4: DSC thermograms of melt electrospun PP fibres of 2000 MFI with varying amounts of PEG: (a) 1st heating cycle, (b) 1st cooling cycle and (c) 2nd heating cycle.
A 1.5: DSC thermograms of melt electrospun PP fibres of 2000 MFI with varying amounts of PDMS: (a) 1\textsuperscript{st} heating cycle, (b) 1\textsuperscript{st} cooling cycle and (c) 2\textsuperscript{nd} heating cycle.
A 1.6: DSC thermograms of melt electrospun PP fibres of 2000 MFI with varying amounts of NaCl: (a) 1st heating cycle, (b) 1st cooling cycle and (c) 2nd heating cycle.
A 1.7: Typical TGA thermogram of 2000 MFI PP polymer and melt electrospun fibres fabricated with different additives.

A 1.8: XRD diffractograms of melt electrospun PP fibres fabricated with various additives from 2000 MFI PP.
Appendix 2: Meltblowing

A 2.1: DSC curves of meltblown PP fibres of 100 MFI: (a) 1st heating cycle, (b) 1st cooling cycle and (c) 2nd heating cycle.
A 2.2: DSC curves of meltblown PP fibres of 1000 MFI: (a) 1st heating cycle, (b) 1st cooling cycle and (c) 2nd heating cycle.
A 2.3: TGA thermograms of PP polymer, as-spun fibre and meltblown fibres fabricated with various fluids from: (a) 100 MFI and (b) 1000 MFI.
A 2.4: XRD diffractograms of meltblown PP fibres fabricated with various fluids: (a) 100 MFI and (b) 1000 MFI.
A 2.5: Stress-strain curves of the meltblown nanofibres of 100 MFI PP (showing the effect of annealing) fabricated with fluids: (a) air, (b) N2, (c) W5 and (d) W10.
A 2.6: Stress-strain curves of the meltblown nanofibres of 1000 MFI PP (showing the effect of annealing) fabricated with fluids: (a) air, (b) N2, (c) W5 and (d) W10.