Melt-electrospinning part I: processing parameters and geometric properties

Jason Lyons*, Christopher Li, Frank Ko

Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA

Received 18 August 2004; received in revised form 30 August 2004; accepted 31 August 2004
Available online 11 September 2004

Abstract

The effects of various melt-electrospinning parameters on the morphology and fiber diameter of polypropylene of different tacticities were studied. The effect of the electric field strength at various melt flow indexes of polypropylene on fiber uniformity, morphology, and diameter was measured. It was shown that the molecular weight was the predominant factor in determining the fiber diameter of the collected fibers. Observations prove that the tacticity also influences the fiber diameter. Atactic polymers having molecular chains incapable of crystallization tend to produce larger diameter fibers than isotactic polymers capable of crystallization even at lower molecular weights. The polymer volume, at a given time, supplied to the electric field affected fiber diameter. Those systems supplying the smallest volume, at a given time, produced the smallest fiber diameter.

q 2004 Elsevier Ltd. All rights reserved.

Keywords: Polypropylene; Melt electrospinning; Tacticity

1. Introduction

The utilization of electrostatic forces to deform materials in the liquid state goes back many centuries [1]. Throughout the 20th century, there have been a number of papers dedicated to the study of electrohydrodynamic atomization [2–8]. Electrospinning is simply an extension of this technology applied to higher viscosity fluids. Several researchers [9–16] performed experiments using polymeric solutions and were capable of producing fibers ranging in diameter from a few nanometers to several micrometers. Most of these fibers were being collected as nonwoven, random fiber mats. These fibrous structures can potentially be used in a variety of applications including filtration devices, solar sails, reinforcement, nonwetting textile surfaces, wound dressings, vascular grafts, and tissue scaffolds [16–18]. However, a vast majority of the fibrous structures were produced by solvent based electrospinning. Certain chemicals that are used as solvents to dissolve many of the polymers being electrospun may leave remnants that are not compatible within the industry. In the intent of cleaner processing, environmental safety, and productivity, there is a persistent desire to produce fibers by alternative methods. Thus, in spite of the many potential applications, environmental and health limitations, as well as productivity complications do exist as a result of solvent based electrospinning systems. The use of molten polymers to produce electrospun mats becomes a subject of great interest. In spite of the potential benefits of melt-electrospinning, little progress has been made in the past twenty years. Larrondo and Manley [19–21] were the first to electrospin a molten polymer more than two decades ago. They were capable of spinning polypropylene (melt flow indexes 0.5–2.0) and succeeded in making fibers that were greater than 50 µm in diameter. Their inability to spin sub-micrometer diameter fiber was attributed to the large increase in viscosity that could be many orders of magnitude greater than that of a polymer solution. The electric field strength used in their experiments was 3–8 kV cm⁻¹ at a spinning distance ranging from 1–3 cm. They observed that the polymer melt experienced a large initial decrease in diameter when placed in an electric field and as the electric...
field strength increases, the fiber diameter decreases. Other groups [22,23], and the University of Massachusetts at Dartmouth, have conducted research on melt-electrospinning polymers including poly(ethylene terephthalate) and polyethylene. These groups reported a wide range of obtainable fiber diameters yet limited progress has been made. A full understanding of the melt-electrospinning process, and its potential to replace solution electrospinning, has not yet been realized. It is the object of this study to determine the feasibility of producing electrospun fibers, of varying fiber diameters and morphologies, from the melt and recognize trends revolving around the molecular weight of the polymer, the electric field strength, and the polymer’s tacticity.

1.1. The electrospinning process

Electrospinning is a simple technique for the production of nano to micro scale fibers depending on the medium used. The use of electrospinning to produce fibers from solution, without using pressure, was first reported in a patent issued in 1934 by A. Formhals [25]. This technique incorporates the generation of a strong electric field between the polymeric melt within the extruder and a metallic collecting device. Fig. 1 shows a schematic design of a melt-electrospinning system. As a voltage is applied, a cone forms at the apex of the capillary or spinnerette. At a critical voltage, the electrostatic forces acting on the jet overcome the surface tension and viscoelastic properties of the melt resulting in a fine fiber extruded from the cone residing at the spinnerette. Similar to solution based electrospinning, the main driving force for fiber formation is the attenuation of the spin line under electrostatic forces. While in transit, the jet diameter is continually reduced due to the electrostatic forces acting on it until the point when the viscosity once again overcomes the electrostatic forces as a result of jet solidification from cooling. Unlike similar experiments conducted by other researchers in melt-electrospinning [23,24], these particular experiments did not exhibit a bending instability. The lack of a bending instability may be attributed to the extremely high viscosity associated with the melt as has been demonstrated by Taylor [8] or the small distance that the jet traverses before contacting the collection device. The solidified fibers are deposited randomly on the surface of the grounded collection plate. It has been shown that fiber diameter can be controlled by adjusting the processing parameters such as electric field strength, polymeric viscosity, and flow rate [11–14].

1.2. Melt-electrospinning requirements

In conventional textile fiber formation from the melt, small diameter fibers are made through simultaneous control of the spinnerette diameter and the take up speed of the godet rollers. When the fiber passes through the godet rollers, each rotating at a different speed, a shearing action (drawing) occurs on the molecular chains, thus inducing molecular orientation while decreasing fiber diameter as much as 500%. In order to successfully produce nano or sub-micrometer diameter fibers through melt-electrospinning, drawing of the polymer must occur as a result of the electrostatic forces acting on the jet. The forces needed to create a reduction in diameter to the nanometer level are of great interest and are currently being investigated.

2. Experimental

2.1. Fiber spinning experiments

The materials utilized during these experiments can be seen in Table 1. All samples were used as received and they were purchased from Sigma-Aldrich. Polypropylene was chosen because of its relative ease to process from the melt and it large range of available molecular weights ranging from the 10s to the 100s of thousands. In addition, polypropylene is available in different tacticities. By electrospinning different tacticities of polypropylene, the effect of molecular conformation on fiber diameter can be examined.

The polymers were processed through a 3/4” single screw Brabender table-top extruder with four heating zones at 200 °C and a 1.5 mm spinnerette. In these experiments the spinnerette was grounded and the positive charge was applied to a copper collection plate that was placed at varying distances ranging from 2–5 cm. At greater distances, a much higher potential will be required. The electric

![Fig. 1. A schematic diagram describing the melt-electrospinning technique.](image-url)
field strength, expressed in terms of voltage/centimeter, required to extrude a jet from the cone ranged from 6–15 kV cm\(^{-1}\). Higher applied voltages, at short distances, will result in electrical discharge between the spinnerette and the collection plate.

2.2. Characterization

The morphology of the electrospun fibers was examined through field emission environmental scanning electron microscopy (Phillips XL-30 ESEM). A beam strength of 15 kV with a spot size of 3 was used to take the micrographs. The average fiber diameter and the respective distributions were determined from 100 measurements of random fibers at each spinning condition.

3. Results

3.1. Effect of molecular weight on fiber diameter

It was observed that the molecular weight had a significant impact on the feasibility of producing fibers electrostatically at various electric field strengths. With a sufficiently high molecular weight, weaker electric field strengths (\(>10 \text{ kV cm}^{-1}\)) were incapable of producing fibers. Fig. 2 shows the surface morphology of the polypropylene fibers obtained using an applied electric field 15 kV cm\(^{-1}\) at a constant collection plate distance of 2 cm. Polypropylene with a high molecular weight did not form a Taylor cone when placed in the electric field. A fiber nearly the width of the spinnerette hole was slowly pulled to

![Graph showing fiber diameter distribution](image_url)
the collection plate. It was seen that the highest molecular weight polymers formed the largest diameter fibers. It was also observed in all experiments, that a wide variation of diameter was present. In some instances there were standard deviations upwards of 50%. An example of an average fiber distribution is shown in Fig. 3. This distribution shows the fiber diameter distribution of the 12,000 $M_w$ isotactic polypropylene. Fibers that were smaller than 1 $\mu$m have been obtained, however, a majority of the fibers are above 1 $\mu$m. The kurtosis of these graphs show a possible bi-modal distribution that may be attributed to the variation of polymer volumes being supplied to the spinnerette as a result of inconsistent flow rates as such low RPM’s of the extruding screw.

3.2. Effect of electric field strength on morphology and diameter

As a result of the high viscosity of the polymeric melts, it was required to work at considerably large electric field strengths. Each molecular weight polypropylene was electrospun at an electric field strength of 10, 12.5, and 15 kV cm$^{-1}$ at a spinning distance of 2 cm. This field strength is upwards of 10 times stronger than those reported in solution electrospinning. Weaker field strengths were not strong enough to overcome the surface tension and viscoelastic forces of the molten polymer; at higher voltages at this distance, electrical discharge would occur. As expected, it was seen in all samples that the fiber diameter decreased as the electric field strength increases. Fig. 4 shows the relationship between electric field strength and fiber diameter for several of the electrospun polymers. In this figure, the effects of molecular weigh and tacticity can also be seen.

3.3. Effect of polymer volume at the spinnerette tip

In order to supply the appropriate amount of polymer to the spinnerette, it was necessary to have the extruder at the lowest RPM output. At times, the Brabender extruder supplied polymer to the spinnerette faster than the electrostatic forces could carry it away. As a result, it became convenient to place the polymer directly on the spinnerette to melt. In this experiment, the extruder was no longer supplying a continuous volume at a given time to the spinnerette. Thus, it was observed that the Taylor cone continually decreased in size due to the reduction in available polymer and smaller and smaller fibers were produced from the diminishing cone as seen in Fig. 5.

4. Discussions

4.1. Molecular weight

From the results, it is evident that the molecular weight plays a significant role in the feasibility of electrospinning polymeric fibers. This finding is comparable and consistent with past research claiming that solution concentration is the most dominant parameter in electrostatic spinning [26]. It was observed that the 580,000 $M_w$ polypropylene resulted in fiber diameters in access of 400 $\mu$m. In addition, it was
observed that the 165,700 $M_n$ isotactic polypropylene and the 5400 $M_n$ atactic polypropylene produced fiber diameters larger than similar tacticity polymers with smaller $M_n$ values. The polymer with the largest $M_n$ will be subjected to the highest degree of polymer chain entanglement. It is therefore more difficult for the electrostatic forces to pull on individual polymer chains. As a result, larger fiber diameter will be formed, as was observed experimentally. As the molecular weight continually decreases, fiber diameter decreases as shown in Fig. 6 for isotactic polypropylene. There were not enough data points to verify the same trend in the atactic samples. Fibers were not produced with electric field strengths less than 15 kV cm$^{-1}$ for the 580,000 $M_w$ isotactic sample.

The molecular weight interaction was not exclusively responsible for determining the collected fiber diameter. As seen in Fig. 2, both atactic polypropylene samples formed larger diameter fibers than all but the 580,000 $M_w$ isotactic sample. Since atactic polypropylene possesses a random positioning of the methyl group off of the main molecular backbone, it is impossible to crystallize. The inability of the polymer chains to closely pack due to steric hindrances may result in larger fiber diameters than those obtained from similar molecular weight polymers capable of crystallization. Therefore, the tacticity of the polymer has a significant effect on the fiber diameter. It is also possible that variations in fiber diameter between polymers of different tacticities are related to the memory effect of the polymer.

4.2. Electric field strength

Consistent with past electrospinning research [10–12], an increase in the electric field strength decreases the average fiber diameter for all of the polymers examined. When a steady amount of polymer is being supplied to the spinnerette, an increase in the electric field strength exposes the polymer droplet to larger forces, therefore further reducing the fiber diameter. It was observed that the angle (from jet axis) of the cone, at the spinnerette orifice, increases as the electric field strength increases as a result of more material being pulled away; consistent with past research [10,11].

It is worthy to note that in some instances, while using the 12,000 $M_w$ polymer, that sub-micrometer fibers were obtained as seen in Fig. 7. In all instances, these fibers are the result of branches from a larger fiber within the sample.
This is conceivable because at the speeds that the jet is traveling, it is not completely solidified once leaving the spinnerette. As the jet travels further into the electric field, it is exposed to stronger field strengths. If the molecular weight of the polymer is low enough, it is possible that a side jet can be created from the molten jet leading to smaller diameter fibers. These fibers did not make up a majority of the sample but they represent the only fibers to break the 1 μm barrier.

The surface morphology, of a majority of the polymers electrospun, consists of smooth cylindrical fibers. It is believed that the smooth surface is in part due to the partial solidification that occurs as soon as the jet leaves the spinnerette. Also, there is no solvent evaporation that may lead to inconsistencies on the fiber surface.

### 4.3. Spinning volume at a given time

In order to study the effect of spinning volume, a polymer chip was placed directly on the spinnerette orifice and melted. Since no flow rate was being applied, the volume would continually reduce as the polymer was transferred to the collection device in the form of fibers. The diameters of the collected fiber as a function of time can be seen in Fig. 5. Similar to increasing the electric field strength a smaller Taylor cone was formed as a result of the decreasing volume. This cone was then exposed to larger field strengths ultimately leading to a decrease in fiber diameter. This observation suggests for the possibility of forming sub-micrometer diameters consistently under specific experimental parameters for certain polymers from the melt if a

---

Fig. 5. ESEM micrographs of 19,600 M<sub>ω</sub> melt-electrospun polypropylene at an electric field strength of 10 kV cm<sup>−1</sup> at 2 cm. (A) 10 s, (B) 20 s, (C) 30 s.

Fig. 6. Graph showing the exponential increase in fiber diameter with increasing molecular weight for isotactic polypropylene.

Fig. 7. Sub-micrometer diameter fibers branching from 12,000 M<sub>ω</sub> isotactic polypropylene.
small enough volume could be supplied to the spinnerette on a consistent basis. This may also explain the large standard deviations that result from the melt-electrospinning process.

5. Conclusions

Electrospinning polypropylene of various tacticities and molecular weight, from the molten state, was successfully completed resulting in fiber diameters from several hundred nanometers to several hundred micrometers depending on the electrospinning parameters and some important observations were made. The surface morphology and diameter distribution of the fibers were studied as a function of various electrospinning parameters including electric field strength, supplied volume, and molecular weight. The molecular weight of polymer was the dominant parameter determining the feasibility of electrostatically producing polypropylene fibers from the melt. Although several trends were observed, many other parameters of the polymer and electrospinning process must be examined including temperature, flow rate, spinnerette diameter, di-electric constant, thermal conductivity, and surface energy. On the basis of observations made in the preliminary study, it would be helpful to develop a model relating fiber diameter to the empirical processing parameters. Also, characterization of the mechanical properties and structural analysis of the collected fibers needs to be performed to gain insight on the structure-properties relationship of melt-electrospun fiber. Accordingly, modeling of the melt-electrospinning process will be the focus of subsequent studies.

Acknowledgements

This work was made possible, in part, by the State of Pennsylvania under The Nanotechnology Institute. Thanks also are extended to the Koerner Fellowship offered at Drexel University for partial assistance in this study. The invaluable assistance of David Von Rohr for ESEM assistance is very much appreciated.

References