High-Temperature Electrospinning of Polyethylene Microfibers from Solution

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ABSTRACT: The process of electrospinning uses a high-voltage source to produce an electrostatically driven jet of polymer solution that thins and elongates as it is driven toward an electrically grounded target. The fiber diameters which result from this process are on the order of nanometers to micrometers and can have large surface area to weight ratios. These high surface area fibers offer significant advantages for applications including nanocomposites, filtration media, barrier, and biomedical applications. Consequently, there are many areas of active scientific research currently focused on electrospun polymeric fibers. Because of the major commercial role played by polyolefins, there is significant interest in electrospinning these particular polymers. Polyolefins are not particularly amenable to electrospinning due to solubility and conductivity issues. Linear low-density polyethylene (LLDPE) microfibers were electrospun from solutions of *p*-xylene. Polyethylene readily crystallizes from solution, which requires the solution to be maintained at an elevated temperature throughout the electrospinning process. The polyethylene fibers resulting from the electrospinning process were characterized in terms of surface morphology, compositional and conformational changes, and crystalline structure using FTIR, Raman spectroscopy, FESEM, EDAX, X-ray diffraction, and DSC.

Introduction

Electrospinning of polymeric fibers has been undergoing a renaissance in the past decade due to the relative ease with which nanoscale filaments can be produced. A wide variety of polymers[1−3] have been electrospun into nano- or microscale diameter fibers using a simple laboratory instrument which utilizes significantly less material than required for conventional melt or solution spinning. Many uses of electrospun fibers have been envisioned ranging from high-efficiency filtration[4,5] to scaffolds for tissue engineering.[6]

Most of the polymeric systems which have been electrospun have incorporated some chemical functionality, such as amides, ketones, esters, and acids, among others. Polyolefins are largely absent from the list of hundreds of polymers electrospun so far. Electrospinning polyolefins, in general and specifically polyethylene, is challenging due to their relatively poor solubility in conventional solvent systems used for electrospinning. In general, the polyolefins require temperatures above ambient and nonpolar solvents to dissolve. The resulting polymer solutions have a low dielectric constant with resultant poor conductivity. Polyethylene has previously been electrospun both from the melt at 200−220 °C and from a dilute solution in paraffin at 100 °C by Larrondo and Manley.[7−9] The polyethylene fibers produced had fiber diameters of several microns up to several hundred microns. For the fibers spun from paraffin solutions, the paraffin was removed postspinning by extensive washing in cold xylene. This washing process is a significant complication in the production process as well as providing for the possibility of structural modification of the polyethylene through swelling of the fiber. For these reasons, it would be a valuable development in the electrospinning of polyethylene fibers, if a more flexible solvent system could be employed, such as *p*-xylene. The higher volatility of this solvent would allow for solvent removal during the electrospinning process with resultant structural and morphological development constrained to the spinning process and not in a postspinning treatment. However, electrospinning from *p*-xylene solutions is problematic. The dielectric constants of polyethylene (2.3 at 100 kHz) and *p*-xylene (2.1 at 100 kHz) do not vary significantly with temperature. This leaves the solution with a low dielectric constant and resulting low conductivity, which precludes electrospinning. Overcoming this hurdle requires increasing the dielectric constant of the polymer solution. These limitations have been addressed by introducing temperature control to allow electrospinning above the standard room temperature and the addition of salts[10] to the polymer solution which will raise the dielectric constant of the solution, resulting in higher solution conductivity.

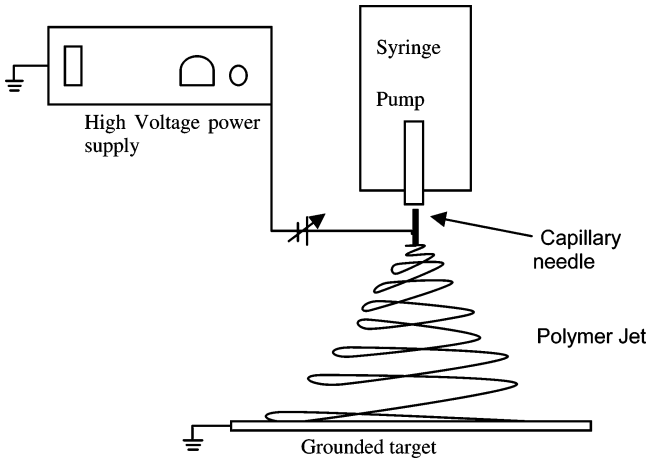

Figure 1. Electrospinning experimental setup.

Experimental Section

Materials. Linear low-density polyethylene (LLDPE, 190 000 MW) was purchased from Scientific Polymer Products; *p*-xylene was purchased from Sigma-Aldrich, and *tert*-butylammonium bromide (t-BAB) was purchased from Alfa Aesar. All were used without modification.

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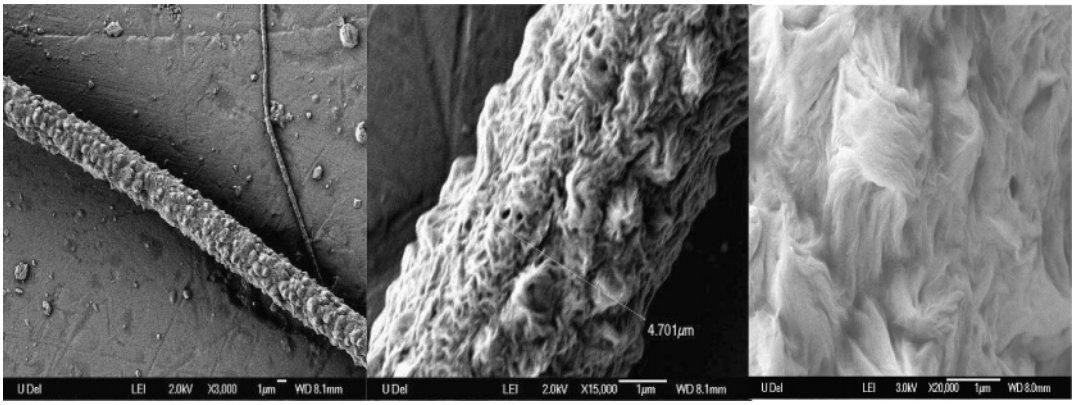

Figure 2. FESEM of LLDPE electrospun fiber at 3K, 15K, and 20K magnification.

Electrospinning Apparatus. A standard electrospinning facility, shown in Figure 1, was employed for all experiments, consisting of a high-voltage power supply (Glassman), a syringe pump to control flow (Orion Sage), and a 3 mL glass syringe (Popper and Sons) with a 21 gauge stainless steel needle (Hamilton). A grounded sheet of aluminum foil was used as a collection target.

Several approaches to maintaining solution temperature above ambient were tried. Initial attempts to keep the polyethylene solutions at processing temperatures using glass fiber heating tape were unsuccessful. This lead to choosing an IR emitter system to maintain the temperature of the solution at 110 °C.

A 7.5 cm by 12.5 cm 500 W 110 volt ceramic infrared emitter with a variable output 110 V controller was purchased from Mor Electric Heating Associates of Comstock Park, MI, and was used as the means to control solution temperature during electrospinning. The emitter was housed in a stainless steel housing with a polished face to reflect any stray heat produced by the emitter. The emitter has a concave face which is oriented to the material to be heated allowing a more focused application of the IR radiation.

The IR emitter system has a very good control response and remains at a given temperature with only minor fluctuations owing to its high mass. The infrared flux on the solution from the emitter is controllable by both the variable output controller and the distance between the emitter and the syringe. The system is scalable and is a noncontact means of heating the solution while still allowing visual monitoring of solution conditions.

Solution conductivity was enhanced by using tetrabutylammonium bromide (t-BAB). This common polymerization initiator dissociates fully in *p*-xylene yielding a dissociated ion pair. Addition of 0.2 wt % salt increased the conductivity of the polymer solution from 0.37 ± 0.04 to 18.76 ± 0.79 μS/cm. This increase in conductivity allowed the solution to be successfully electrospun.

Solutions of 2−5 wt % of LLDPE were prepared in *p*-xylene by heating the stirred solutions overnight at 115 °C in an oil bath. Once the polyethylene was fully dissolved, 0.2 wt % of t-BAB was added, and the solution was allowed to stir an additional 15 min. The resulting clear solutions were transferred to a 3 mL syringe with a 21 gauge needle attached. Electrospinning was performed with an 8 kV accelerating voltage and a 15 cm working distance. Solution temperature was maintained at 105−110 °C using the infrared heater system with a 5 cm distance between emitter and syringe; the relative humidity was 36%. All fibers were collected on nonstick aluminum foil sheets. Attempts to electrospin using lower salt concentrations were not successful. All fibers were examined using FTIR (Fourier transform infrared apectroscopy, Thermo Nicolet Nexus 670), Raman spectroscopy (Kaiser Optics), field emission scanning electron microscopy (FESEM, JEOL 7400F), energy dispersive X-ray microanalysis (EDAX-JOEL JSM 7400F FESEM at 7 kV), X-ray diffraction, and digital scanning calorimetry (DSC, Perkin-Elmer Diamond DSC at 20 °C/min).

Results and Discussion

Characterization of LLDPE Fibers. The fiber diameter and surface morphology[11−14] of the electrospun fibers were first investigated using FESEM, as shown in Figure 2.

All electrospun LLDPE fibers had diameters of 2−7 μm and possessed a roughened surface morphology. This is a slightly larger diameter than observed for most electrospun fibers. During electrospinning it was noted that there appeared to be less fiber whipping action than observed previously for other fibers. The reduced whipping action could well be the source of the larger diameter fibers due to reduced drawing during spinning. Another possibility could be more rapid onset of crystallization as the solution cools after leaving the Taylor cone. This would also lead to reduced draw during spinning. The exhibited surface morphology may indicate spherulite formation nucleated by the presence of the dissociated t-BAB salt in the solution. The electrospun fibers were soaked in *p*-xylene at 65 °C for 3 days to determine whether the surface morphology was due solely to precipitated salt present on the surface of the fibers. No change in surface morphology was observed after the *p*-xylene soak, suggesting that the surface morphology was not composed solely of t-BAB recrystallized on the surface and was due to morphological structure of the polymer itself. Further investigation of the presence of dissociated t-BAB salt in the electrospun fibers was carried out with EDAX. The bromide counterion of the salt was demonstrated to be present in the as-spun LLDPE electrospun fibers. Prior to characterization by EDAX and FESEM, the polyethylene fibers were coated with a 0.5−1.0 nm layer of gold/palladium to reduce charging in the electron beam. This protective layer results in a large signal from the metals composing the coating in the EDAX spectrum from 1.6 to 3.6 keV. Additionally, a large oxygen peak is seen in the EDAX spectra at 0.5 keV, resulting from processing and handling the electrospun fibers in atmospheric conditions. Since the t-BAB is present in the fiber, but not specifically present on the surface, it is most likely distributed throughout the fiber volume. No further attempts were made to wash out the remaining salt.

Determination of the crystal structure was carried out using X-ray diffraction. Electrospun LLDPE fibers were analyzed at Argonne National Laboratory using a 0.700 Å wavelength synchrotron radiation source with a 20 s exposure. Analysis of the resulting diffraction pattern indicates that the orthorhombic crystal form[15,16] is maintained with *d*-spacings of $a = 7.417$ Å, $b = 4.945$ Å, and $c = 2.547$ Å. Further analysis of the radial scan of the X-ray diffraction pattern indicates the LLDPE fibers are ∼56% crystalline, which agrees well with analysis of the

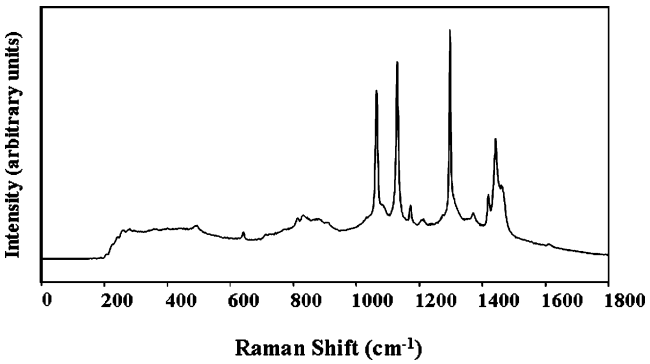

Figure 3. Raman spectrum of electrospun LLDPE fibers indicating similar crystallinity as bulk polymer.

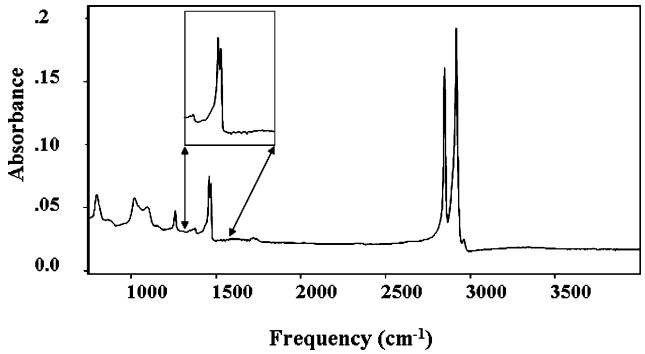

Figure 4. FTIR spectrum of LLDPE electrospun fibers. Inset showing details of splitting of the $-CH_2-$ scissors vibration at 1460−1475 cm^{-1}.

bulk LLPDE from the manufacturer (60% crystalline) and is further supported by Raman spectroscopy. Peak ratioing of the asymmetric and symmetric C−C stretching Raman peaks at 1135 and 1064 cm^{-1}, respectively, indicate 55% crystallinity[17,18] (Figure 3). The orthorhombic unit cell of polyethylene contains two polymer chains. The symmetric C−C stretching vibration of polyethylene at 1064 cm^{-1} is specific to chains in the crystalline region and is indicative of order along the chain axis. The asymmetric C−C stretching vibration at 1135 cm^{-1} is indicative of the less ordered regions of the polymer chain. These bands are consistent with conformations found in crystalline regions of the orthorhombic form of polyethylene.[19] DSC at 20 °C/min indicated an onset of melting at 124.3 °C, in agreement with normal T_m[17]for PE. FTIR analysis (Figure 4) clearly shows the strong CH_2 asymmetric stretching band at 2919 cm^{-1} [20] and the CH_2 symmetric stretching band at 2851 cm^{-1} [20] along with the CH_2 bending doublet at 1473 and 1465 cm^{-1}.[20] The CH stretch positions are indicative of conformationally ordered $-CH_2-$ chains while the splitting of the $-CH_2-$ scissors vibration at 1460−1475 cm^{-1} is clearly indicative of the intermolecular interaction of two chains in an orthorhombic unit cell.[21] These data confirm that the orthorhombic crystalline form and the overall percent crystallinity found in the electrospun material were very similar to those found in the bulk material. The inclusion of the salt and elevated temperature processing during electrospinning have not fundamentally altered the chemical structure and morphology of the polyethylene fibers from that encountered in the bulk or in conventional melt-spun polyethylene.

Conclusions

This investigation has demonstrated the feasibility of electrospinning a polyolefin, polyethylene, from solution with complete solvent removal during the electrospinning process. The approach can be expanded to other polyolefins and may have a significant impact on the production of nanofibers from this entire class of commercially important polymers. LLDPE was electrospun from solution into high surface area micrometer diameter fibers. The addition of a salt was necessary to overcome the issue of low dielectric constant and resulting low conductivity of the solutions. The structure and morphology, crystalline form and degree of crystallinity, of the polyethylene fibers produced by electrospinning were similar to that found for bulk polyethylene or polyethylene fibers produced by melt spinning. The added salt may have contributed to the surface morphology by acting as nucleation sites, but the salt itself is not present on the surface of the fibers.

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