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Novel elastic nanofibers of syndiotactic polypropylene obtained from electrospinning

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ABSTRACT

Uniform nanofibers of syndiotactic polypropylene (sPP) with diameters between 140 and 350 nm were successfully obtained from high-temperature solution electrospinning. Effects of sPP concentration and fiber-collecting method, either by a stationary plate or by a rotating disc, were investigated. The internal structure of the as-spun nanofibers was characterized via wide-angle X-ray diffraction (WAXD), small-angle scattering (SAXS), Fourier transform-infrared (FT-IR) spectroscopy, and differential scanning calorimetric (DSC) analysis. Based on the WAXD results, the as-spun nanofibers exhibited both all-trans mesophases and helical form I crystallites. Mesophase was the dominant phase of the sPP nanofibers obtained from the 5 wt% solution, whereas form I was the dominant phase of those obtained from the 8 wt% solution. For the more viscous solution, the enhancement of form I was attributed to the less effective stretching during processing, which induced oriented but amorphous chains in the sPP nanofibers deposited on the collector. Post crystallization of the un-crystallizing chains at ambient temperature that yielded more form I was evidenced by the in situ FT-IR probes. For the aligned nanofibers collected by a rotating disc, the amount of mesophase increased due to additional stretching force on the solidifying nanofibers. Under cyclic tensile deformation, the aligned sPP nanofibers exhibited low permanent set and intermediate hysteresis with a mechanical behavior similar to particle-filled elastomers.

1. Introduction

Syndiotactic polypropylene (sPP) is a semi-crystalline polymer that has a very complex polymorphic behavior in the solid state [1–6]. De Rosa and Auriemma [7] classified four major crystal modifications of sPP, namely, forms I, II, III, and IV, and a mesomorphic phase (mesophase) [5,6]. Forms I and II possess chains with *TTGG* helical conformation in the orthorhombic lattices, whereas form III and the mesophase have all-trans conformation. The most stable form I rests on a packing of antichiral helices, whereas form II rests on a packing of isochiral helices. Given the differences in chain conformation, the chain periodicity is 0.74 nm for forms I and II and 0.51 nm for form III and the mesophase. The rare appearance of form IV is obtained by exposing the cold-drawing of melt-quenched sPP samples in form III to organic solvent vapors [2]. The chain conformation for form IV is $T_6G_2T_2G_2$ with a higher chain periodicity of 1.16 nm. When the sPP samples are stretched with form I/II or the mesophase, the crystal transformation is likely to occur to produce form III. At this stage, the applied mechanical energy are stored in the extended amorphous chains between crystallites as well as in the deformed crystalline lattices through the reversible

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transformation of chain conformation or chain packing [8–10]. However, form III is unstable in the unstrained state. When the strains are released, all-trans form III transforms into helical form II (not the most stable form I) or the initial mesophase prior to stretching to allow recovery of the stored energy. This reversible transformation through chain conformation in the non-amorphous region provides the sPP with excellent elasticity, low hysteresis, and small permanent set compared with other semi-crystalline polyolefins. Compared with conventional elastomers whose elasticity is solely associated with entropy change, the cyclic tensile behavior of sPP demonstrates that the enthalpy relevant with the crystalline phase may be involved in the elastic behavior of sPP. This unique behavior makes sPP samples promising materials for elastic fiber applications.

Electrospinning is an important process to prepare polymeric fibers with a sub-micron diameter. The final fiber diameter mainly depends on three processing variables (i.e., solution flow-rate, applied voltage, and tip-to-collector distance), and on three solution properties (i.e., viscosity, conductivity, and surface tension). The detailed processing mechanism and potential applications of derived nanofibers have been addressed by several review monographs [11–13]. Studies have obtained many different electrospun fibers mainly through a room-temperature process. sPP is difficult to dissolve in common solvents at ambient temperature. High-temperature electrospinning is generally required to obtain sPP fibers because of its limited solubility. Sufficient chain entanglements in the electrospinning solution are essential to produce bead-free fibers. To date, only a few studies have obtained sPP nanofibers through solution electrospinning. A tri-component solvent [14,15] of cyclohexane or decalin, acetone, and dimethylformamide was used to dissolve sPP at 60–70 °C to balance the solution properties for processing. Subsequently, electrospinning was performed at 35–40 °C to obtain sPP nanofibers with diameters between 530 and 760 nm. However, the quality of the as-spun sPP fibers was not sufficiently good because they had curled-shaped and twisted ribbon-shaped fibers. Based on the wide-angle X-ray profiles of random sPP fibers, the authors concluded that the crystal structure of the as-spun fibers is a mixture of forms I and III, and form I is the dominant crystal structure [14]. The presence of form III in the electrospun sPP fibers should be studied further because it seems inconsistent with previous findings, which indicated that form III is stable only in the stretched state [7].

This study aims to obtain high-quality sPP nanofibers with a uniform diameter via a high-temperature process [16]. The effects of solution concentration and fiber-collecting methods, either by a stationary plate or by a rotating disc, on fiber diameter were investigated. The crystal modification of the as-spun fibers was characterized. Our results showed that both form I and the mesophase coexisted in the sPP nanofibers. The mesophase became dominant when the solution concentration was lower and/or a rotating disc was used as the fiber collector. Based on the tensile hysteresis test, the aligned sPP fibers exhibited an excellent elastic behavior.

2. Experimental section

sPP pellets were purchased from Sigma–Aldrich Co. The sPP samples had an average molecular weight (M_w) of 174,000 g/mol with a tacticity of 93% and a density of 0.9 g/cm^3. Ortho-dichlorobenzene (*o*-DCB) was used as the solvent to prepare the solutions for electrospinning. The density and boiling temperature of the *o*-DCB solvent were 1.3 g/cm^3 and 180.5 °C, respectively. Despite the presence of chain entanglements in the solution, the electrospun products with no fiber-like features were obtained because of the low conductivity of sPP/*o*-DCB solutions. Tetra-n-butyl ammonium perchlorate was added as a salt to enhance the conductivity of the solution. Subsequently, electrospun fibers were readily observed. Weighed amounts of sPP, *o*-DCB, and salt were mixed at 130 °C for 2 h until homogeneous solutions were obtained to prepare solutions with different wt% concentrations. The concentration of the salt was 0.3 wt% relative to the mass of the solvent used. Fig. 1 shows the schematic of the high-temperature electrospinning system. A homemade jacket-type heat exchanger was used to maintain the sPP solution at 80 °C. This temperature was maintained via the circulation of heated silicone oil by a pumping system connected to an oil bath. When the system reached thermal equilibrium, the homogeneous polymer solution was electrospun into fibers based on a previously reported procedure [16]. A needle was used as the spinneret, and the prepared solution was delivered by a syringe pump (Cole–Parmer) at a controlled flow rate of 1 mL/h to the needle, of which a positive voltage of 26 kV was applied by a high-voltage source (Bertan, 205B) to provide a sufficient electric field

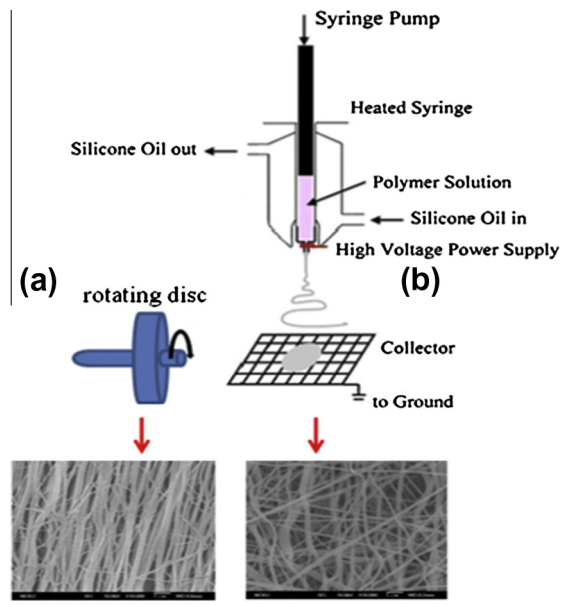

Fig. 1. Schematic drawing of electrospinning process to produce (a) aligned sPP fibers by a rotating disc and (b) non-woven sPP fibers by a stationary plate. The width and diameter of rotating disc are 5 and 100 mm, respectively. The temperature of circulating oil is 80 °C. Typical SEM images of collected sPP fibers are shown.