



Electrospun poly(butylene terephthalate) fibers: Entanglement density effect on fiber diameter and fiber nucleating ability towards isotactic polypropylene



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ABSTRACT

Electrospun poly(butylene terephthalate) (PBT) fibers were prepared from trifluoroacetic acid (TFA)-based solvent. Rheological studies revealed the concentration (ϕ , volume fraction) dependence of zero-shear viscosity (η_0) to be $\eta_0 \sim \phi^{3.87}$ in the entangled solution regime, and the entanglement concentration (ϕ_e) was 7.84 vol.%. Effects of η_0 on the straight jet-end diameter (d_j) and fiber diameter (d_f) were investigated; two scaling laws existed for PBT/TFA solutions, i.e., $d_j \sim \eta_0^{0.06}$ and $d_f \sim \eta_0^{0.73}$. Moreover, d_f can be scaled with entanglement density and solution plateau modulus (G_N) through $d_f \sim (\phi/\phi_e)^{2.6} \sim G_N$. Results of differential scanning calorimetry and wide-angle X-ray diffraction revealed that as-spun PBT fibers were not amorphous but contained imperfect small α crystallites. During stepwise annealing, crystal perfection gradually occurred, and well-ordered, α -form crystal was developed at temperatures above 160 °C. When electrospun PBT fibers were embedded in isotactic polypropylene (iPP) matrix, fiber surface-induced crystallization readily occurred to develop a transcrystalline layer of iPP monoclinic crystals at the interface. Similar effects were found for electrospun fibers of poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PTT). The conventional method of counting iPP nuclei occurring on the fiber surface to determine fiber nucleation rate was infeasible because of the fine fiber diameter. A new approach to characterize the nucleating ability of polyester fibers with submicron diameter was developed. By measuring the intensity of depolarized light during cooling from the melt, the initial temperature (T_i) for iPP transcrystallization was determined and compared. Based on the derived T_i , the nucleating ability of electrospun fibers toward iPP followed the order PBT > PET ~ PTT. This finding was consistent with isothermal crystallization results. Moreover, the maximum temperature for PBT fiber to induce crystallization of iPP was ca. 157 °C, which was 20 °C higher than those of PET and PTT fibers. The remarkable nucleating ability of PBT fibers was likely associated with epitaxial crystallization and the large substrate crystal dimension in the matching direction, as revealed by atomic force microscopy.

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1. Introduction

Poly(butylene terephthalate) (PBT) is one important member of aromatic polyesters. Compared to the other two polyesters, which are poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PTT), PBT possesses a higher crystallization rate and novel elasticity of crystals. When crystallized, PBT chains will form two different modifications, the α - and β -form [1]. Both α - and β -form possess the triclinic lattices with different chain

conformations in the crystal; the former has the glycol residue with a *gauche-trans-gauche* sequence, whereas the latter has the glycol residue with an all-*trans* sequence. The sufficient deformation of α -form leads to the formation of β -form through the chain stretching in the crystals. Reversible crystal transformation back to the α -form occurs after releasing the applied deformation [2–4]. In addition, PBT can also form a mesomorphic phase, which has an intermediate structure between crystal and amorphous. The mesomorphic phase has a smectic structure, which may act as a precursor for crystallization [5,6]. In the melt-quenched PBT film, Konishi et al. [5] have shown the presence of nodular structure (mesophase) based on small-angle X-ray scattering. The mesophase is in the metastable

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state and may transform into the usual triclinic structure by heating at temperatures above 208 °C.

Fine polymer fibers with diameters of 0.2–1.0 μm become available by electrospinning. The final fiber diameter mainly depends on three major processing variables (solution flow rate, applied voltage, and tip-to-collector distance) and on the solution properties (viscosity, conductivity, and surface tension). Several review articles have addressed the detailed processing mechanism and potential applications of electrospun nanofibers [7–9]. Among all these parameters, solution viscosity is rather important in determining the final diameter of as-spun fibers. The electrospinning solution with entangled chain network is generally required in producing bead-free nanofibers. Thus, the entanglement density (# entanglement strands per unit volume) in the electrospinning solution should be fully addressed to understand the solution rheological effect on the fiber diameter. Neat PBT fibers electrospun from different solvent systems, such as trifluoroacetic acid (TFA) [10], hexafluoropropanol [11], and cosolvent of dichloromethane/TFA [12], have been obtained. Moreover, the electrospun PBT fibers containing nanofillers of POSS [13] and carbon nanotube [14] have been validated to improve the thermal stability for certain applications. Previous papers have focused on the effects of processing variables on final fiber diameter without discussing the relationship of fiber morphology with solution rheology. To better understand how to manipulate the electrified jets to produce fibers with small diameters, a systematic study on the correlation of the cone-jet-fiber morphology is essential. More importantly, a detailed investigation on the crystalline structure of electrospun PBT fibers via X-ray scattering is not yet available. Some controversial results [10,13] regarding whether the as-spun fibers is amorphous or semicrystalline have been reported. When heated, the as-spun PBT fibers exhibited no cold crystallization event until final crystal melting [12,13]. This feature implied that PBT chains in the as-spun fibers were likely not in the amorphous state at all. Electrospun PBT fibers with superior chemical resistance can be applied not only in the filtration of physiological fluids and hot chemicals but also in the tissue engineering as scaffolds for nerve cells [10].

High strength polymer fibers, such as PET and Kevlar fibers [15,16], are frequently incorporated into semi-crystalline polymers to reinforce the mechanical strength for practical application. The addition of fibers in the semi-crystalline matrix may also alter the crystalline structure of matrix. Fiber surface-induced crystallization is likely to develop the so-called transcrystalline layer (TCL), which may improve the interfacial strength [17]. The structure of TCL is different from that of spherulites developed in the bulk. Compared to the conventional fibers with diameters of 10–100 μm, electrospun fibers provide two valuable advantages because of their fine diameter. The first advantage is the enhancement of the fiber modulus with decreasing fiber diameter [18], plausibly due to the improved molecular orientation in the electrospun fibers. Having a high surface-to-volume ratio, electrospun nanofibers are also more effective than the conventional micron-sized fibers to induce the TCL, if applicable. Thus, electrospun fibers are potential fillers for nanocomposites, not only for mechanical reinforcement but also as a nucleating agent to enhance the crystallization rate of the matrix.

In the present study, the effects of PBT solution rheology on the morphologies of the electrified jet and as-spun fibers were studied. TFA alone is found to be an excellent solvent for PBT electrospinning to produce fine diameters. Scaling laws are derived to correlate the fiber diameter with the zero-shear viscosity and polymer concentration based on the entanglement density concept. The crystalline state of PBT in the electrospun fiber during stepwise annealing was also investigated using wide-angle X-ray diffraction (WAXD). By stepwise heating, the submicron-sized fibers provided a unique

geometry to elucidate the crystallization mechanism of oriented PBT chains. The as-spun fibers were found to possess imperfect small crystallites of α form. Upon heating, crystalline perfection was detected at temperatures above 160 °C. In the final section of the paper, the potential application of the electrospun polyester (PBT, PET, and PTT) fibers in nanocomposites is realized by observing the fiber surface-induced crystallization of the isotactic polypropylene (iPP) matrix. The electrospun PBT fibers act as a much better nucleating agent toward iPP matrix than the electrospun PET and PTT fibers to enhance the crystallization rate.

2. Experimental

2.1. Solutions properties and electrospinning process

PBT pellets were kindly supplied by Chang Chung Chemical Co. (Taiwan). Its intrinsic viscosity determined from 60:40 w/w solvent mixture of phenol/tetrachloroethane at 30 °C was 1.20 dL/g, corresponding to an average molecular weight (MW) of 40,500 g/mol based on the Mark-Houwink-Sakurada equation with the reported values of $K = 1.166 \times 10^{-4}$ and $a = 0.871$ [19]. PTT pellets were obtained from the DuPont Co, whereas the electrospinning solvent of TFA (99 vol.% pure) was purchased from the Alfa Aesar Co. Prior to solution preparation, the as-received pellets were dried under a vacuum at 60 °C for 24 h. The advantages of TFA include its high dielectric constant (42.1), low boiling point (72.4 °C), and low surface tension (13.4 dyne/cm). These characteristics favor the production of fine fibers by electrospinning. The intrinsic viscosity [η] of PBT solutions in TFA at 25 °C was determined to be 1.235 dL/g (Supplementary Materials, Fig. S1) using an Ubbelohde viscometer. Solutions with different weight fraction (ϕ_w) were prepared, and the volume fraction (ϕ) was calculated from the pure component density ($\rho_{PBT} = 1.31$ and $\rho_{TFA} = 1.48$ g/cm³), assuming a negligible volume change during mixing. The zero-shear viscosity (η_0) and conductivity of the prepared solutions were measured using a Brookfield viscometer (LVDV-1+, spindle 18, and cup 13R) and a Consort conductivity meter (C832), respectively. To calculate the specific viscosity of PBT/TFA solutions, a solvent viscosity of 0.81 cP was used.

For the electrospinning process, a needle with inner and outer diameters of 0.508 and 0.813 mm, respectively, was used as the spinneret. The prepared solution was delivered by a syringe pump (Cole-Parmer) at a controlled flow rate of 1.0 mL/h to the needle. In the needle, a positive voltage of 9.3 kV was applied by a high-voltage source (Bertan, 205B) to provide a sufficient electric field for electrospinning. To construct a needle-to-plate electrode configuration, a steel net (30 cm × 30 cm) was used as the collector for the electrospun fibers at a fixed tip-to-collector distance of 140 mm. These processing variables were identical with the previous study on the electrospun PET fibers. The detailed processing conditions have been provided in our previous paper [20]. During electrospinning, several CCDs were used to monitor the electrospinning process. The diameter (d_f) of electrospinning jet was measured by a laser scattering technique prior to bending instability. In addition, both solutions of PTT/TFA and PET/TFA at 20 wt% were also electrospun under the same processing variables to prepare PTT and PET fibers for the transcrystallization study of iPP.

2.2. Characterization of as-spun polyester fibers

The morphology of the as-spun fibers was observed using scanning electron microscopy (SEM) system (Hitachi S4100). The fiber diameters were measured within electron micrographs from a population of ~500 fibers, from which the average fiber diameter (d_f), and corresponding standard deviation were determined. The

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