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Nanofibers from Melt Blown Fiber-in-Fiber Polymer Blends

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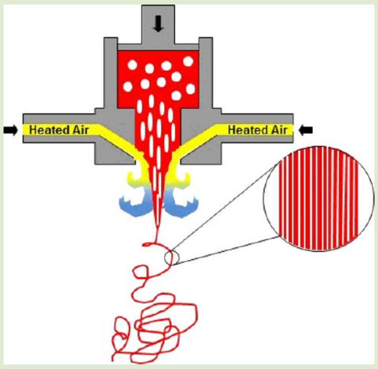
Supporting Information

ABSTRACT: Nanofibers were generated by melt blowing three sets of polymer blends, each comprised of pairs of immiscible components. Blends containing minority phases (25% by volume) of poly(ethylene-*co*-chlorotrifluoroethylene) (PECTFE) in poly(butylene terephthalate) (PBT), PECTFE in poly(styrene) (PS), and PBT in PS were dispersed as droplets in a continuous majority phase and melt blown into long (>100 μm) fibers with average diameters of several micrometers. Electron microscopy experiments revealed that melt blowing transformed the initial spherical dispersions into a nanofiber-in-fiber morphology. Macroscopic mats of nonwoven PBT and PECTFE nanofibers, with average diameters as small as 70 nm, were isolated by selectively removing the majority phase with a solvent. This method provides a potentially inexpensive, high throughput, one-step route to scalable quantities of polymeric nanofibers.



Nonwoven fibers are a \$20 billion industry with wide-ranging applications in filtration, absorbance, hygiene, and apparel.[1−6] Melt blowing produces nonwoven materials rapidly and economically, but the process is limited to fibers with average diameters greater than about 2 μm. Submicrometer fibers dramatically increase the fiber surface area while decreasing the pore size, opening new applications for these products.[7−13] Electrospinning can produce submicrometer diameter fibers, but production is slow and costly and the types of polymers that can be processed is limited.[8] We have shown that the use of high air flow rates during melt blowing can result in fiber diameters of around 0.5 μm or even smaller.[14,15] In this letter we demonstrate that melt blowing immiscible polymer blends, followed by dissolution of one of the components, offers a new and facile approach to generating fibers with diameters as small as tens of nanometers.

Early studies on fibers made from polymer blends were focused on reinforcing mechanical properties of matrix polymers with rigid polymer microfiber fillers.[16−27] Sun and co-workers were the first to create free-standing nanofibers from polymer blends.[28−35] These investigators prepared immiscible binary blends containing cellulose acetate butyrate (CAB) and various thermoplastic polymers and then extruded these blends through a spinneret die, followed by hot-drawing at different draw ratios. They obtained continuous filaments with a diameter of hundreds of micrometers, which subsequently were soaked in acetone to remove only CAB. Fibers from the dispersed thermoplastics were obtained with diameters ranging from hundreds of nanometers to several micrometers. The final average fiber diameter depended primarily on interfacial tension and, to a lesser extent, the viscosity ratio, but it was also strongly influenced by the processing parameters during extrusion and drawing. Application of this extrusion plus hot-drawing technique to produce fibers with average diameters below 100 nm was challenging, requiring a very low fraction of the dispersed phase and high draw ratios.

Another method to create nanofibers is through melt spinning using specially designed spinnerets that combine different materials from separate melt feed streams. These fibers-in-fiber structures are often referred to as "islands-in-the-sea". Research carried out by Choi and Kim, and later by Fedorova and Pourdeyhimi, demonstrated that islands with a diameter on the order of 100 nm could be obtained.[36−38] The smallest fibers obtained using this technique, reported by Nakata et al., were generated by drawing a blend of polyamide (sea) and poly(ethylene terephthalate) (0.7 μm diameter islands) into 44 μm diameter fibers, followed by removal of the polyamide using formic acid.[39] The poly(ethylene terephthalate) islands were drawn down to an average diameter of 39 nm. In addition to requiring a specially designed spinneret and two extruders, this method involves two separate steps with an extremely high draw ratio of about 500 in the second stage.

In contrast to these previous studies, where nanofibers-in-fiber were obtained through extrusion followed by a separate mechanical drawing, we report a new direct approach to fabricating nanofiber-in-fiber materials, that is, a simple one-step melt blowing of immiscible polymer blends. As illustrated in Figure 1, this technique transforms dispersed spherical domains within a polymer blend into long, small diameter,

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cylindrical domains, dispersed within micrometer scale composite fibers.

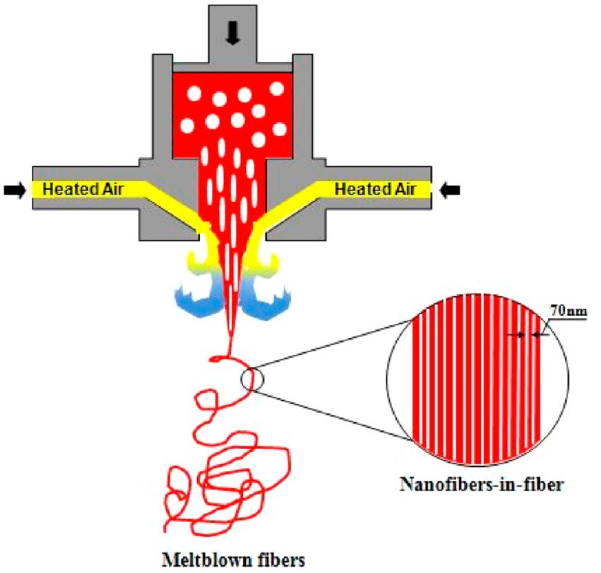

Figure 1. Schematic of nanofibers-in-fiber fabrication by melt blowing.

Polymer blends containing 25 vol% poly(ethylene-*co*-chlorotrifluoroethylene) (PECTFE) and 75 vol% poly(butylene terephthalate) (PBT) were characterized using transmission and scanning electron microscopy (TEM and SEM; descriptions of the materials and experimental procedures are provided in the Supporting Information). As shown in the TEM and backscattered SEM images in Figure 2, PECTFE appears as approximately spherical droplets dispersed in a PBT matrix. The total area of dark (TEM) and bright (SEM) phases are roughly consistent with the bulk mixture stoichiometry. Figure 2C shows the distribution of PECTFE domain diameters obtained by measuring more than 200 droplets in several SEM images using ImageJ software; these range from about 0.5 to 2.5 μm, with a number average diameter of 1.3 μm.

The PECTFE/PBT blend was melt blown at 265 °C and a representative SEM image of the resulting nonwoven fibers is shown in Figure 3, along with a fiber diameter analysis. The number average fiber diameter is about 3 μm, typical for melt blowing. However, the distribution of fiber diameters generated by the blend is somewhat broader than we have reported for single component melt blowing (e.g., pure PBT).[15] This may be associated with the high segregation strength of PBT and PECTFE, which could contribute to instability during the drawing processing.

To investigate the internal morphology, thin sections of the fibers were studied by TEM. Figure 4A shows a representative TEM image of a partial cross-section of a melt blown fiber that was microtomed after being embedded in epoxy. This image clearly shows circular domains of PECTFE dispersed in the melt blown fiber; there may be some accumulation or migration of a small amount of PECTFE toward the fiber surface due to its low surface energy, although this is not evident in Figure 4A. All PECTFE domains in the PBT matrix appear to be well separated from each other.

To evaluate the axial morphology of the nanofibers, PBT was selectively removed by soaking the fiber mat in trifluoroacetic

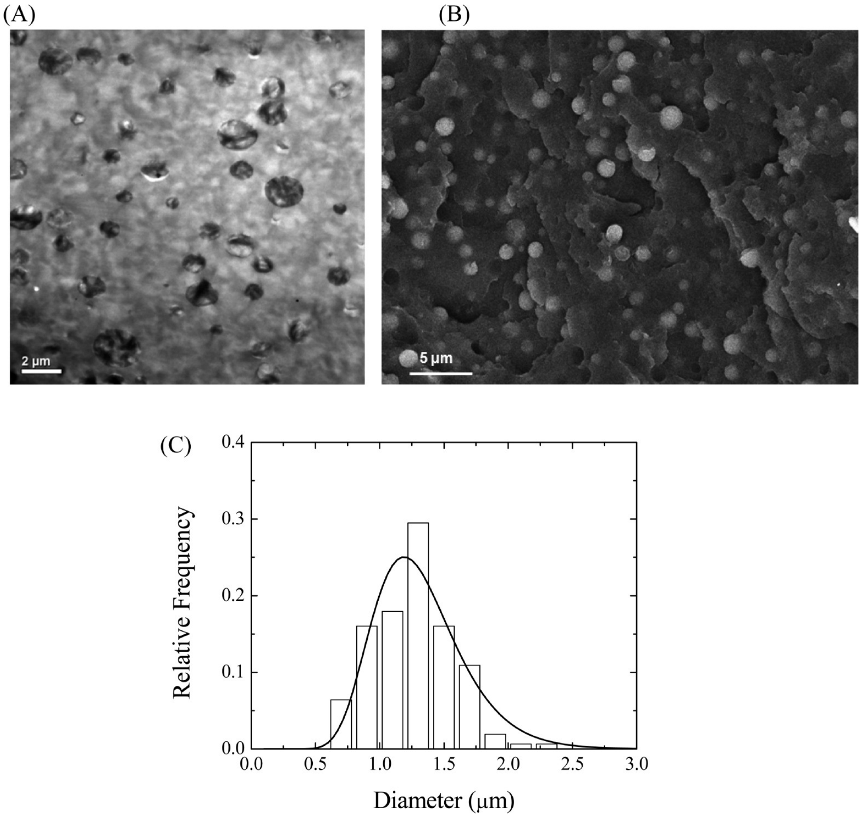

Figure 2. (A) TEM and (B) backscattered SEM images of PECTFE/PBT blend. (C) Statistical analysis of the PECTFE droplet sizes derived from SEM images.

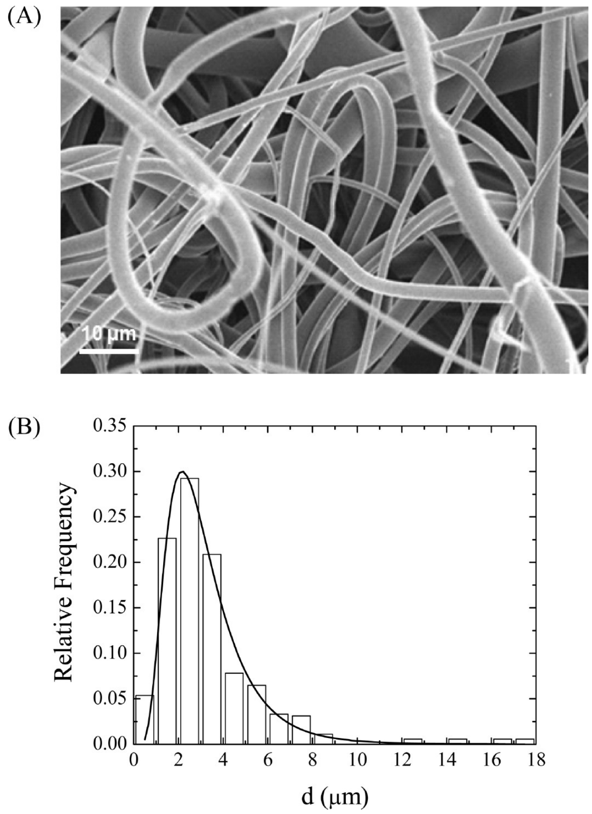

Figure 3. (A) SEM image of melt blown PECTFE/PBT fibers and (B) statistical analysis of the fiber diameters.

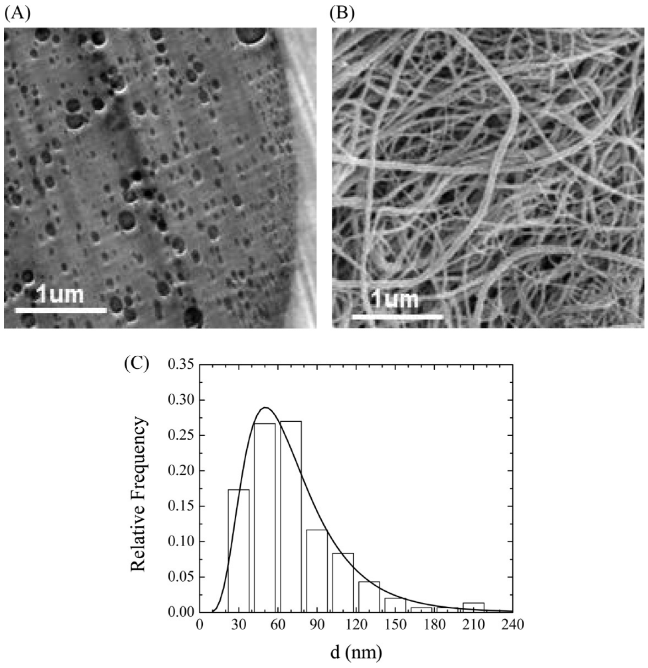

Figure 4. (A) Cross-sectional TEM image of a melt blown PECTFE/PBT fiber. The fiber was embedded in epoxy (white material on right-hand side of the image) to facilitate sectioning. (B) SEM of PECTFE nanofibers following solvent removal of the PBT matrix. (C) Statistical analysis of the PECTFE fiber diameters based on TEM and SEM images.

acid. The extracted mat of fibers constituted about 30 wt % of the original melt blown fibers before soaking, consistent with the weight fraction of PECTFE in the original blend. Fourier transform infrared spectroscopy (see Supporting Information) demonstrated absence of PBT in the solvent-extracted product; the vibrational peak associated with the carboxyl group in PBT (~1700 cm^{-1}) was completely absent. The remaining PECTFE mat was then coated with platinum and examined using SEM. Figure 4B reveals high aspect ratio PECTFE fibers, as evidenced by near complete absence in this and other SEM images of fiber ends. A diameter analysis based on both TEM and SEM images, shown in Figure 4C, shows that the fibers range from about 30 to 200 nm in diameter, with a number average of 70 nm. A simple constant volume calculation dictates that stretching a 1.3 μm diameter spherical droplet into a 70 nm diameter cylinder leads to a 300 μm long fiber, that is, an aspect ratio (length divided by diameter) of more than 4000, consistent with the absence of fiber ends in the SEM images.

To verify the universal aspects of this technology, PBT and PECTFE were individually blended as the minority component (25 vol%) in PS and melt blown into composite fibers, as illustrated in Figures 5A and 6A. Number average fiber diameters of 15.2 μm (PBT in PS) and 13.5 μm (PECTFE/PS) were obtained. These fiber-in-fiber composites are much larger than those produced with the PECTFE/PBT blend (Figure 4B), although the PS-based fiber mats display a more uniform size distribution. Matrix extraction was accomplished by soaking the mat of fibers in tetrahydrofuran, a good solvent for PS, but one that does not dissolve PBT or PECTFE. Complete removal of the PS matrix resulted in PBT and PECTFE nanofibers, as illustrated in the SEM images in Figures 5B and 6B, respectively. These SEM images demonstrate remarkable nanofiber integrity (i.e., uniform diameters and virtually no ends), with average fiber diameters of about 250 nm for PBT and 200 nm for PECTFE. Because the droplet diameters in the precursor blends were about 10–

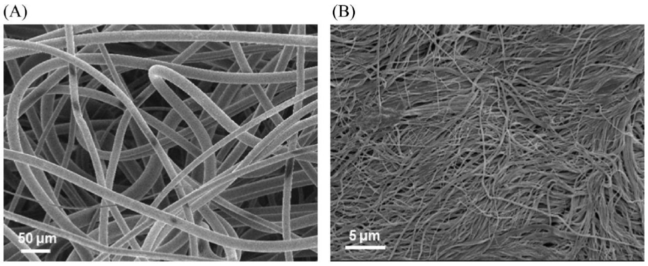

Figure 5. SEM images of (A) 15.2 μm (average) diameter melt blown fibers from PBT/PS and (B) 250 nm (average) diameter PBT fibers obtained after solvent extraction of the PS matrix.

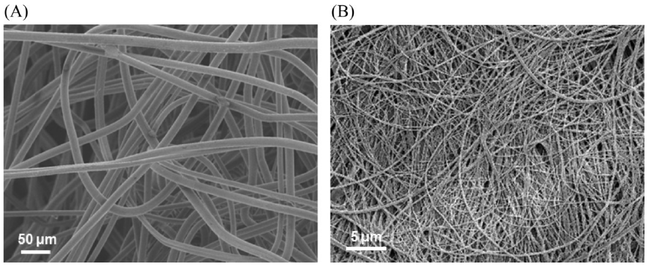

Figure 6. SEM images of (A) 13.5 μm (average) diameter melt blown fibers from PECTFE/PS and (B) 200 nm (average) diameter PECTFE fibers after solvent extraction of the PS matrix.

20 μm, the aspect ratio of these fibers could be more than 10^5, assuming no fiber breakup during the melt blowing process.

The larger diameter fibers produced by melt blowing the PECTFE/PS and PBT/PS blends can be attributed to the relatively high viscosity of the continuous PS phase. The viscosity of the PS melt at the melt blowing temperature is about 400 Pa·s, approximately 1 order of magnitude higher than that of PBT and PECTFE (see Supporting Information). Because PS is the major, continuous component, this higher viscosity predictably leads to increased melt blown fiber diameters.[14] On the other hand, due to the large (ca. 10-fold) viscosity mismatch between PS and the minor components, bigger droplets of dispersed phase were formed during melt mixing in the PS matrix, that is, 10−20 μm with a PS matrix (Figures 5A and 6A) versus 1−2 μm when PECTFE is dispersed in PBT (Figure 4B).[40−42] Both factors result in thicker nanofibers (ca. 200 nm, see Supporting Information) after removing the PS. Nevertheless, the underlying mechanism of nanofiber-in-fiber formation appears to be scale invariant, that is, the drawdown ratio is governed by simple geometric factors, as illustrated in Figure 1. Additional studies aimed at better understanding the principles that govern nanofiber formation and size uniformity are currently underway in our laboratory.

In summary, we demonstrate here a method for producing nanofibers in micrometer scale fibers by melt blowing of immiscible polymer blends. Significantly, this appears to be a versatile technique, applicable to any combination of polymers that phase separate subject to the melt blowing criteria that govern the continuous phase and the ability to generate a discontinuous spherical morphology. After washing away the matrix with a selective solvent, we obtained a nonwoven mat of nanofibers formed from the dispersed polymer. Fluoropolymer fibers with average diameter of 70 nm have been prepared. These nanofiber nonwoven mats have potential applications as reinforcing fibers in polymer composites and as filter media. The fibers-in-fibers can be collected on a supporting porous layer and isolated by washing away the matrix material with a selective solvent, leaving a dense nanofiber mat that may serve as a filtration medium.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and additional analytical results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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