Manufacturing of polymer continuous nanofibers using a novel co-extrusion and multiplication technique

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A novel co-extrusion and two-dimensional multiplication technique was developed for continuous production of nanofibers using melt-processable polymers. This solvent-free and environment-friendly fiber fabrication approach has significant advantages over existing solvent-based techniques such as electrospinning. The flexibility of the co-extrusion processing for nanofiber fabrication is demonstrated using three examples. Multicomponent extrudate strands of polycaprolactone (PCL)/polyethylene oxide (PEO), polyamide 6 (PA6)/polyethylene terephthalate (PET) and polyethylene (PE)/polypropylene (PP) were fabricated for nanofiber production.

PCL nanofibers were produced by removal of PEO component using water as a solvent. PCL fibers down to 70 nm thickness were successfully produced using this approach. In contrast, a mechanical separation approach was used to produce fibers from PA6/PET and PE/PP systems. Both systems resulted into formation of mixed fibers. A post processing technique was utilized to increase the fiber orientation and mechanical properties. An order of magnitude improvement was observed in mechanical properties after orientation. This novel fabrication approach has enabled solvent-free production of nanofibers at large scale for various applications such as scaffolds, filtration media and others.

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1. Introduction
Nanofibers are usually defined as the fibers with at least one dimension of 100 nm (nm) or less. However, the fiber industry extensively uses the term “nanofibers” on those with dimensions of less than 1 μm [1]. In fact, the majority of the published work to date related to “nanofibers” refers to fibers that have diameters between 0.1 and 1 μm. Polymer nanofibers with diameters in the nanometer to submicron size range (0.01–1 μm) have significant advantages over the conventional fibers including large surface area to volume ratio and flexibility in surface functionalization [2]. Therefore membranes fabricated from these nanofibers have wide applications in both biomedical and non-bio-related areas, such as scaffolds used in tissue engineering [4–6], dressings for wound healing [3], drug delivery media [7], medical implants [8], filtration media [9–14], textiles, composite reinforcement [15], precursors to carbon fibers, and ballistic-resistant materials [16].
formed on a substrate, leading to insufficient mechanical strength that limits its applications to areas where mechanical performance is not an essential requirement [27].

Rotary jet spinning is a new technique developed to produce polymer nanofibers from polymer solutions that are ejected from high-speed rotating nozzles. Fibers are elongated by centrifugal forces and solidify as solvent evaporates [28,29]. Varying nozzle geometry, rotation speed, and polymer solution concentration can control fiber morphology, diameter, and web porosity. Nanofibers with diameters ranging from 150 nm to 3 \( \mu \text{m} \) have been generated by this process. Recently, another technique termed “gas jet process” was created to fabricate polymer nanofibers with diameters ranging from a few tens of nanometers to a few micrometers from polymer solutions [30]. With the aid of high velocity expanding gas jets, single or multiple polymer solution(s) can be turned into liquid jets, which are thereafter stretched and thinned down into polymer nanofibers. However, similar to electrospinning, these processes have limited applications due to the toxicity related to the organic solvents used and limited mechanical performance.

Without the aid of solvents, fibers with diameters as low as 500 nm can be fabricated from polymer melts using a technique termed “melt blowing”. In melt-blowing, a jet of hot air is applied at the orifice of the extrusion line, and fibers can be blown down to the nanoscale [31]. However, this technique is only applicable to the preparation of nanofibers from polymer melts that have a low chain overlap concentration [32], and is used mostly to produce microfibers [33]. Another disadvantage is the usage of a modular die with a small orifice and air jets with pressure of 3500 psi or more, which leads to high cost and difficulty in scale-up applications.

To address the performance issues of current nanofiber technology, we developed a novel processing technique to prepare polymer nanofibers that utilizes a forced assembly co-extrusion and two-dimensional multiplication technique followed by an orientation and separation procedure. Using this fabrication strategy, nanofibers can be produced with superior mechanical properties as well as nanoscale cross sectional sizes. This innovative mode of fiber manufacturing avoids the use of organic solvents or complicated constructions, such as pressurized air channels at the orifice or rotary spinning devices. It is also an extremely flexible technique since the entire extrusion line is built with a series of basic multipliers [34], and the assembly can be customized to achieve the desired fiber structure. These valuable advantages present opportunities of scale and throughput limited by the conventional technologies.
2. Experimental

2.1. Vertical layer co-extrusion processing

A layer-multiplying co-extrusion system was used to produce polymeric nanofibers [34]. The co-extrusion system consisted of 2 extruders, an A/B feedblock, a surface layer feedblock, and a series of vertical as well as horizontal multipliers. A unique extrusion line was designed using traditional extruders and multipliers, and a two-dimensional multiplication technique was applied. Fig. 1 is a detailed schematic of the extrusion line assembly with its four essential components.

Historically, horizontal layered film samples with few tens to a few thousands of layers have been successfully co-extruded [34]. For fiber production, fabrication of vertical layered samples is important to control the fiber dimensions. The rationale behind using vertical layered systems is discussed later in this paper. To visualize the vertical layer multiplication process, extrudate samples were collected at four critical processing areas highlighted in Fig. 1. The cross-sectional structures of the materials in the extrusion line were observed utilizing colored co-extruded resins; colo coating was achieved by adding 1 wt% of dyes in various colors via dry-blending with polymer pellets prior to processing. The properties of the polymers used in this study are tabulated in Table 1. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) resins were used as polymer A (in blue, in web version) and polymer B (in red, in web version) in making these visualization samples. Co-extrusion throughput of 30 cc/rev was used to produce these samples. A detachable adapter with channel dimensions ½" by ½" was used at different steps during the co-extrusion processing. The visualization samples were obtained by stopping the extruders and freezing the polymer structures in these adapters. Cross-sectional images were recorded using an Olympus SZH-ILLD optical microscopic after scanning the samples with sand paper.

2.2. Nanofiber production

Three unique A/B polymer systems were extruded to demonstrate processing flexibility and nanofiber production.

a. Polycaprolactone (PCL)/Polyethylene oxide (PEO) – PEO can be dissolved easily using water as a solvent and PCL fibers can be separated.

b. Polyamide 6 (PA6)/polyethylene terephthalate (PET) – It is possible to produce PA6 and PET fibers using conventional techniques such as electrospinning. We will demonstrate a solvent-free fabrication technique of these polymers.

c. Polyethylene (PE)/polypropylene (PP) – Both polymers are polyolefins, and are difficult to be processed by any conventional solvent-based techniques. We will demonstrate a solvent-free fabrication technique of these polymers.

Polycaprolactone (PCL) CAPA 6800 pellets were used as received to produce PCL nanofibers in our study. PCL was extruded with poly(ethylen oxide) (PEO). A PEO blend of Dow POLYOX N80 (Mw = 200 kg/mol) and POLYOX N10 (Mw = 100 kg/mol) was prepared using Haake Rheodrive 5000 twin screw extruder with a weight ratio of 30:70 (N80:N10). The blend was prepared to achieve viscosity match with PCL at the processing temperature of 200 °C. PEO blend was dried under vacuum at 40 °C for 48 h before extrusion to remove any moisture.

Polyamide 6 (PA6) Ultramid BHM36 O1 and polyethylene terephthalate (PET) Polyclear 1101 were co-extruded at 260 °C. Both resins were dried in a vacuum oven at 80 °C for 24 h prior to co-extrusion processing.

Low-density polyethylene (LDPE) Dow 5011 and polypropylene (PP) Exxon Mobil 2252 E4 resins was co-extruded at 230 °C. All these composite materials were extruded through a tape die with width of ½" and height of 0.02", and collected on a chill roll at specific rotational speeds. The PCL/PEO, PA6/PET, and LDPE/PP tapes were orientated in an Instron 5965 tensile unit at specific temperatures and strain rates.

2.3. Nanofiber characterization and analysis

A PerkinElmer Pyris Differential Scanning Calorimetry (DSC) was used to investigate thermal properties. The systems were heated from 0 °C to 300 °C at a heating rate of 10 °C/min, and characteristic temperatures, such as melting and glass transitions temperatures were determined from the first heating scans for all 3 systems. Both as-extruded and oriented samples were characterized using Rigaku MicoMax 200 + S 2D X-ray spectroscopy to determine the degree of polymer chain orientation. Crystal orientation was evaluated by calculating Herman's orientation factors from the azimuthal scans of the nanofibers as:

\[ f_e = \frac{1}{2} \left( 3 \cos^2 \varphi_c - 1 \right) \]

whereas \( \cos^2 \varphi_c \) is the square average of the cosine of orientation angle, \( \varphi_c \), which is the angle between the c axis of the polymer crystal

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**Table 1**

Properties of the materials used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer</th>
<th>Trade name</th>
<th>( T_m , (^\circ \text{C}) )</th>
<th>( T_f , (^\circ \text{C}) )</th>
<th>Melt flow index or viscosity</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>Dow Chemical</td>
<td>Styron 615APR</td>
<td>Not applicable</td>
<td>101</td>
<td>MFI = 14 g/10 min (200 °C/5 kg)</td>
<td>Not available</td>
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<tr>
<td>PMMA</td>
<td>Arkema Group</td>
<td>Plexiglas V5-100</td>
<td>Not applicable</td>
<td>87.2</td>
<td>MFI = 27 g/10 min (230 °C/3.8 kg)</td>
<td>Not available</td>
</tr>
<tr>
<td>PCL/PED system</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCL</td>
<td>Perstorp</td>
<td>Capa 6800</td>
<td>59.3</td>
<td>Not measured</td>
<td>MFI = 3 g/10 min (190 °C/5 kg)</td>
<td>80,000</td>
</tr>
<tr>
<td>PEO</td>
<td>Dow Chemical</td>
<td>PolyOx WSR N80</td>
<td>63.6</td>
<td>Not measured</td>
<td>Viscosity of a 5% solution at 25 °C = 55−90 cP</td>
<td>200,000</td>
</tr>
<tr>
<td>PEO</td>
<td>Dow Chemical</td>
<td>PolyOx WSR N10</td>
<td>61.3</td>
<td>Not measured</td>
<td>Viscosity of a 5% solution at 25 °C = 30−50 cP</td>
<td>100,000</td>
</tr>
<tr>
<td>PA6/PET system</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA6</td>
<td>BASF Corporation</td>
<td>Ultramid B36 01</td>
<td>218.6</td>
<td>42.2</td>
<td>Viscosity Number (0.5% in 96% Sulfuric Acid) = 218 cm/g</td>
<td>Not available</td>
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<tr>
<td>PET</td>
<td>INVISTA</td>
<td>Polyclear 1101</td>
<td>245.7</td>
<td>73.0</td>
<td>Intrinsic viscosity (1% Solution in Dichloroacetic Acid) = 0.83 ± 0.02</td>
<td>Not available</td>
</tr>
<tr>
<td>PP</td>
<td>Dow Chemical</td>
<td>Styrol 685D</td>
<td>Not applicable</td>
<td>102.7</td>
<td>MFI = 1.5 g/10 min (200 °C/5 kg)</td>
<td>Not available</td>
</tr>
<tr>
<td>LDPE</td>
<td>Dow Chemical</td>
<td>501I</td>
<td>Not measured</td>
<td>108.3</td>
<td>MFI = 1.9 g/10 min (190 °C/2.16 kg)</td>
<td>Not available</td>
</tr>
<tr>
<td>LDPE</td>
<td>ExxonMobil</td>
<td>2252E4</td>
<td>Not measured</td>
<td>163.5</td>
<td>MFI = 4.2 g/10 min (230 °C/2.16 kg)</td>
<td>Not available</td>
</tr>
</tbody>
</table>

*Measured using the PerkinElmer Pyris Differential Scanning Calorimetry (DSC) instrument at Case Western Reserve University.
*Provided by the corresponding manufacturers.
and the fiber axis. The calculation method of $\cos^2 \phi_c$ varies according to the specific crystal structures, and will be discussed specifically later. The value of $f_c$ varies between $-0.5$ for perfect perpendicular orientation and $1.0$ for perfect parallel orientation [35,36].

Stress–strain curves were obtained for the oriented PCL nanofibers, PA6/PET and LDPE/PP composite nanofiber samples after removing the separating layers. The mechanical tests were conducted using the Instron 5965 tensile unit at room temperature and a test rate of $100\%/\text{min}$. The fiber with a gauge length of 25 mm samples were prepared with their ends embedded in epoxy in order to prevent any slippage from the grips during test. The embedded parts were thereafter microtomed using a Leica EM UC7 ultramicrotome unit at $-140^\circ \text{C}$, and the cross sectional areas were determined using an Olympus S2H-ILLD optical microscope.

The oriented tapes were fibrillated by either dissolving a sacrificial component or separating their components using a high pressure water jet. A customized water pumping system was purchased from Antomizing Systems, Inc to generate such water jets, whose water pressure at nozzles can be adjusted between 0 and 3000 psi. The nozzle orifice has a diameter of 0.010". Both the fiber samples before and after delamination were characterized using Fourier Transform Infrared (FTIR) NICOLET CONTINUUM unit to check the amount of the residue sacrificial component. We also observed the final nanofibers using a JEOL Scanning Electron Microscopy (SEM) to determine the fiber sizes under an emission voltage of 30 kV. The fiber cross-sectional dimensions were measured under SEM for each sample, and the size distribution was generated accordingly.

### 3. Results and discussion

This innovative approach to fabricate robust nanofibers is achieved in three main steps.

I. Extrusion of layered tapes

II. Orientation of layered tapes

III. Separation of fibers from layered tapes using various techniques

We will describe the extrusion procedure in detail first, which is independent of the specific nanofiber system. Since orientation and separation are system dependent, these manufacturing aspects will be highlighted as it relates to the nanofiber composite material.

#### 3.1. Extrusion of layered tapes for fiber production

In the co-extrusion system (Fig. 1), Polymer resins A and B are melt-pumped separately, and layered one on top of the other in the A/B feedblock. “STEP I” refers to the first vertical multiplier that is attached to the feedblock. The dimensions the melt flow channels for two polymers gradually change from $\frac{1}{2}'' \times 1''$ to $1'' \times \frac{1}{2}''$ to create a vertical-looking A/B structure as shown in Fig. 1(I). Each of the vertical multipliers in STEP II cuts the extrusion flow horizontally, and expands the two flow fields vertically so that they are aligned in parallel. The number of vertical layers is doubled during the extrusion through each multiplier. Provided that a total number of $(n-1)$ vertical multipliers are employed throughout STEP II, a melt flow comprised of 2" vertical alternating A and B layers will be produced. To decrease the cross-sectional dimensions of A and B domains via separation, a sacrificial component was introduced to the main extrusion line from both above and below the vertical layer section, as depicted in STEP III of Fig. 1. The sacrificial material can be either a third polymer or the vertical layer materials depending upon the target application.

It is essential that the vertical layer height is further decreased to generate fibers with nanoscale dimensions. Therefore, we developed a two-dimensional multiplication technique by using both vertical and horizontal multipliers, which are identical in the channel design but oriented at a 90° differential. After the addition of the separating layers, a series of layer multiplications in the horizontal direction are introduced as shown in STEP IV of Fig. 1. The flow is cut vertically and oriented with one flow field on top of...
the other, \(2^{m+1} + 1\) horizontal sections are generated if a total number of \(m\) horizontal multipliers are placed in STEP IV. The final extrusion flow has a two-dimensional structure comprised of alternating vertical-layered and separating sections that are laid horizontally. This structure has \(2^m\) by \(2^n-m\) alternating micro-lateral-sized domains made of A and B materials, which generate nanofibers after the appropriate orientation and separation procedures.

To produce visualization samples to assess if the desired extrusion and multiplication was achieved, seven \((n=7)\) vertical and two \((m=2)\) horizontal multipliers were used, producing a matrix structure comprised of 32 by 4 alternating PMMA (red, in web version) and PS (blue, in web version) layers isolated by 5 PS separating sections. The PMMA/PS volume composition was 50/50. These cross sectional images are shown in Fig. 2, corresponding to the front cross sections of the four steps depicted in Fig. 1. The extrusion flow at the end of the process has a two-dimensional structure, which is shown in Fig. 2(IV). Both PMMA and PS domains maintain reasonably distinct rectangular shapes, particularly in the center region.

The extrusion technique shows high versatility because the dimensions as well as the thickness/height ratio of the nanofiber cross sections can be adjusted by: 1) changing the number of multipliers used \((n \text{ and } m)\); and/or 2) modifying the composition of either A, B, or C (the separating layer). The generation of smaller fiber dimensions can be controlled by increasing the total number of vertical layers, \(n\). The number of horizontal sections can be altered by \(m\). Increasing \(m\) does not influence the overall fiber sizes, but decreases the layer height at the cost of increasing the layer thickness. For example, if \(n=7\) and \(m=3\), we will obtain a

![Wide-angle X-ray patterns obtained from PCL/PEO strands](image)

**Fig. 3.** Wide-angle X-ray patterns obtained from PCL/PEO strands (a) before and (b) after orientation procedure at 50 °C and 1000%/min to the first step draw ratio of 7.2, followed by a second step drawing at 60 °C and 10%/min to a final draw ratio of 7.7. (c) 2 theta scan and (d) azimuthal scan of the as-extruded and oriented PCL/PEO strands.

**Fig. 4.** Stress–strain curves of the PCL nanofibers before and after orientation.

**Table 2**

<table>
<thead>
<tr>
<th></th>
<th>E (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Herman’s orientation factor ((f_e)) for PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-extruded</td>
<td>0.2 ± 0.01</td>
<td>16 ± 2</td>
<td>0.41</td>
</tr>
<tr>
<td>Oriented</td>
<td>1.6 ± 0.4</td>
<td>240 ± 38</td>
<td>0.96</td>
</tr>
</tbody>
</table>
A composite nanofiber tape that has a cross-sectional structure composed of 8 horizontal sections, each of which has 16 A and B alternating layers. The A/B composition is proportional to the ratio of the thickness of the A layer over the B layer. The fiber lateral sizes are also decreased by increasing the composition of separating sections. Thus, production of one fiber of either A or B with a desired lateral size can be achieved by changing the A/B ratio and the amount of separating materials. One can also modify the fiber architecture via this technique by altering the dimensions of the exit die orifice in either the vertical or horizontal directions. In this study, a tape die with orifice dimensions of ½ wide and 0.02 high is utilized in the multilayer co-extrusion. Tapes with two-dimensional architecture were collected from the tape die, and were attenuated on a chill roll at a chill roll temperature of 60 °C.

3.2. PCL single-component nanofibers

Poly(caprolactone) [PCL] as a bio-compatible and biodegradable polymer is widely used in biomedical applications, such as scaffolds used in tissue engineering, artificial organs, sutures, and wound dressings [37,38]. These synthetic structures are required to have sufficient mechanical properties (Young’s modulus and mechanical strength) so that they can maintain the structural integrity [39]. Several attempts have been made to improve the mechanical properties of electrospun PCL nanofiber scaffolds, including using carbon nanotube fillers [40,41], cellulose nanocrystals [42], and using cross nanofiber bundles [43]. However, no sufficient improvement was obtained to serve the cited purposes. The mechanical properties of our extruded PCL nanofibers can be drastically enhanced using the subsequent orienting procedure.

In order to generate PCL fibers that have lateral size on the nanoscale, a removable sacrificial material (PEO) was co-extruded with PCL due to its solubility in water. The extrusion process was conduct 200 °C, and the melt flow contains 4 PCL/PEO vertical layered sections with each comprised of 256 alternating layers, separated by 5 PEO separating sections. The PEO separating sections constitute 67 volume percent of the flow, and the PCL/PEO composition within the vertical layer sections is 10/90. This architectural manipulation generates a structure of 512 PCL micron-sized square fibers (ribbons) each individually surrounded by PEO. The PCL ribbon lateral dimensions were determined after dissolving the PEO component by maintaining the as-extruded sample tape in stirring water at room temperature for 15 h. The widths and thicknesses were ranged mainly from 2 to 5 μm and

![IR absorbance spectra](image)

**Fig. 5.** IR absorbance spectra of the as-extruded PCL/PEO sample and the final PCL nanofibers after the removal of PEO.

![SEM images](image)

**Fig. 6.** SEM images of PCL nanofibers at the magnifications of (a) 370×, and (b) 9000×; (c) thickness distribution and (d) width distribution of the obtained PCL nanofibers.
0.4–1 μm, respectively. Several fibers with widths bigger than 5 μm also existed, and could be attributed to incomplete removal of PEO.

An orientation procedure was designed to: 1) produce oriented and strengthened PCL fibers; and 2) largely decrease the cross sectional dimensions of the PCL fibers to the nanoscale. The extruded PCL/PEO strands were first oriented at 1000%/min and 50 °C to a draw ratio of 7.2. This strain rate and orientation temperature were chosen to achieve as the highest draw ratio possible without fiber breakage. A second orientation step was conducted at 60 °C, near the melting temperature of PCL, and at 10%/min to a final draw ratio of 7.7.

Analysis of the wide-angle X-ray scattering patterns of the as-extruded and oriented nano fiber composite sample indicates that the PCL crystals were highly oriented during orientation. Prior to orientation (Fig. 3a), the two-dimensional scattering patterns show four concentric (two overlapping) isotropic rings, corresponding to the crystal planes of PEO (120), PCL (110), and PEO (032)/PCL (200).

Azimuthal scans of all the reflections (not shown here) represent random orientation of PCL and PEO crystals in as-extruded samples. In comparison, the oriented sample shows sharp peaks on the equator at 2θ = 21.3° and 23.4° referring to PCL (110) and (200) planes, respectively, as shown in Fig. 3(b). The calculation of \( \cos^2 \varphi_c \) is based on the strongest (110) peaks due to PCL’s orthorhombic crystal structure using the following equations [44]:

\[
\cos^2 \varphi_c = 1 - 2 \cos^2 \varphi_{110} \tag{2}
\]

\[
\cos^2 \varphi_{110} = \frac{\int_{0}^{2\pi} I_{110}(\varphi) \cos^2 \varphi_{110} \sin \varphi_{110} d\varphi}{\int_{0}^{2\pi} I_{110}(\varphi) \sin \varphi_{110} d\varphi} \tag{3}
\]

whereas \( I_{110}(\varphi) \) is the X-ray signal intensity of the (110) reflection as a function of orientation angle. The Herman’s orientation factor (\( f_c \)) was calculated to be 0.41 and 0.96 for the as-extruded and oriented PCL nanofibers, respectively. Considering \( f_c = 1 \) represents a fully oriented sample, the crystal orientation of these PCL nanofibers is highly aligned along the fiber axis during the orientation process.

### Table 3

<table>
<thead>
<tr>
<th>Constituent Polymers A/B</th>
<th>( d_A (\text{J}^2 \text{cm}^{-1} \text{J}^{-1}) )</th>
<th>( d_B (\text{J}^2 \text{cm}^{-1} \text{J}^{-1}) )</th>
<th>Processing Temperature (°C)</th>
<th>( \chi )</th>
<th>( d_i (\text{nm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6/PET</td>
<td>27.8 [49]</td>
<td>21.9 [50]</td>
<td>255</td>
<td>0.92</td>
<td>0.47</td>
</tr>
</tbody>
</table>

**Table 3** Parameters in the calculation of PA6/PET interphase thickness.

Fig. 7. 2D wide-angle X-ray scattering of PA6/PET/PS composite tapes (a) as extruded, (b) after the 1-step orientation procedure; (c) after 1st step of the 2-step orientation procedure; and (d) after 2nd step of the 2-step orientation procedure.
As-extruded sample

After separation step

Table 4

<table>
<thead>
<tr>
<th>Procedure</th>
<th>E (GPa)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-extruded</td>
<td>0.33 ± 0.02</td>
<td>54 ± 9</td>
</tr>
<tr>
<td>Procedure I</td>
<td>2.5 ± 0.4</td>
<td>330 ± 12</td>
</tr>
<tr>
<td>Procedure II</td>
<td>6.1 ± 0.2</td>
<td>480 ± 21</td>
</tr>
</tbody>
</table>

3.3. PA6/PET composite nanoﬁber system

It is also possible to use this approach of nanofiber fabrication to produce ﬁber mixture without using any solvents. The produced composite materials exhibit properties of both components, and usually have signiﬁcant advantages over their single-material analogs. Compared to the dissolvable system, the throughput is largely improved by minimizing the usage of sacriﬁcial materials via a mechanical separation technique effectively excluding the use of any solvents, including benign water.

For easy delamination of the ﬁber components by mechanical means, the polymers used in each composite system were carefully selected such that there is poor interfacial adhesion, which can be quantiﬁed via calculation of the interphase thickness due to inter-diffusion of the polymer composite polymer layers [45]. Researchers have determined that two polymers that can be easily separated if the interphase thickness is less than 3 nm [45] because of ineffective stress transfer across the interface. In this study, PA6/PET was proposed as a composite nanofiber system that could be potentially used in water ﬁltration applications due to their superior chemical and thermal resistance and mechanical properties [46,47]. As tabulated in Table 3, the interphase thickness of the PA6/PET composite is 0.47 nm, which is indicative of poor adhesion and low energy required for separation of layers.

Twelve vertical multipliers and four horizontal multipliers were used during extrusion, and a tape consisting of 256 by 16 PA6/PET alternating vertical layers was produced. PS was used as the separating layer material since glassy PS has very low adhesion to both PA6 and PET. The volume ratio of PS versus the vertical layer section was 2:1, and the PA6/PET composition in the vertical layer sections was 50/50. To determine the starting lateral sizes of PA6 and PET layers, the PA6/PET ﬁber tape was mechanically delaminated using a high-pressure water jet technique. A jet of pure water at 40 °C under a nozzle pressure of 2200 psi was shot on the as-extruded ﬁber tape, which was afﬁxed on a scaffold. The nozzle was placed 2 inches above the ﬁber strands, and was moved horizontally along the strand at a rate of 1 cm/s for 30 min. During this delamination
step, the PS separating layers were broken into small chunks and washed away. The composite of PA6 and PET micron-sized ribbons was subsequently dried at ambient temperature for 15 h and observed using SEM (not shown here). As expected, the fibers from the as-extruded tape exhibited a rectangular shape. The fiber widths range from 0.1 to 6.6 μm with 90% of the data collected smaller than 4 μm. The fiber thicknesses are observed between 0.1 and 0.6 μm, and over 80% of the thicknesses are smaller than 0.5 μm. The initial PA6 and PET fiber lateral size was expected to be 0.36 μm (thickness) by 2.1 μm (width).

A two-step orientation procedure was targeted to achieve the largest draw ratio as well as the highest enhancement in mechanical behavior. The orientation temperatures in the first drawing step was chosen to be higher than the glass transition temperatures of the three components (73.0 °C for PET, 42.2 °C for PA6, and 102.7 °C for PS), and lower than the cold crystallization temperature of PET (125.0 °C) because thermal crystallization of PET can largely decrease its tenacity and generate early breakage. Several orientation temperatures and strain rates were probed to achieve the highest strain-at-break, which led to a condition of 115 °C and 1000%/min for a draw ratio of 9.0. The fiber composite strand was subsequently oriented at a temperature close to the onset of the system’s lowest melting point to allow high polymer crystal mobility and achieve maximum orientation along fiber axis. This final orientation step was conducted at 200 °C and 10%/min to a final draw ratio of 9.7.

To better understand the extent of orientation of PA6 and PET, we compared the WAXS patterns of the two-step oriented fiber with: 1) the as-extruded composite tape; and 2) the same fiber composite strand that undergoes an orientation at 105 °C and 1000%/min to a draw ratio of 4.0 (e.g. one-step orientation procedure). The WAXS pattern of the as-extruded PA6/PET/PS tape (Fig. 7a) shows an amorphous PS halo with no clear crystal reflection for PA6 and PET, indicating low crystallinity and random crystal orientation of PA6 and PET. Orientation via the one-step method produces two relatively sharp equatorial peaks corresponding to PA6 a002 and a002/202 crystal planes (Fig. 7b). The absence of any PET crystal reflection is indicative of its solely amorphous structure. We can conclude that moderately oriented PA6 crystals and PET in its amorphous phase are obtained for the fibers drawn at relatively low orientation temperatures (105 °C) to a low final draw ratio (4.0).

In comparison, (Fig. 7c), PET crystalline peaks emerge at the equator for the fibers oriented utilizing the two-step procedure. Although not very sharp, these two peaks support the presence of crystalline phase of PET due to the thermal crystallization temperature of PET, which is close to the orientation temperature of 125 °C. The composite fiber tapes subjected to the second drawing step show distinctive PET crystalline equatorial patterns of the (010), (−110), and (100) planes via WAXS (Fig. 7d). We also obtained much stronger equatorial reflections for the PA6 a002 and a002/202 planes. These sharp reflections indicate a high degree of molecular chain orientation along the fiber axis. Due to the overlapping reflections of PA6 (a002/202) and PET (−110), we were unable to determine the exact orientation factor of PA6 and PET. It is proposed that when PET is oriented at a higher temperature and a lower strain rate, the chains receive sufficient energy to move and fold, forming well-aligned crystalline structures and strengthening the composite fiber tape due to the combination of highly oriented PA6 and PET crystals.

To probe the effect of orientation on mechanics, tensile stress–strain experiments were performed. As shown in Fig. 8 and tabulated in Table 4, this PA6/PET nanofiber composite exhibits 18.5 times improvement in modulus and 8.9 times enhancement in tensile strength enhancement after the two-step orientation.

The fiber strand was delaminated using a high pressure water jet, and the mechanically-delaminated sample was characterized using FTIR and SEM. In Fig. 9, the FTIR absorption peaks at...
3026 cm$^{-1}$ was attributed to the C–H stretching in aromatics, and the peaks at 1452 and 1493 cm$^{-1}$ were designated to the C–C stretching in the aromatic rings in PS. After delamination, these absorption peaks corresponding to the aromatic groups in the PS were virtually non-existent, suggesting successful removal from the PA6/PET composite.

Shown in the SEM images in Fig. 10a, b, individual PA6 and PET nano fibers were collected from 40 fibers in the images with final cross-sectional dimensions of 0.3–2.4 μm width by 0.1–0.4 μm thickness. The fiber size distributions for both width and thickness are reasonable as shown in Fig. 10c, d. Approximately 80% of the fiber widths are equal or smaller than 1 μm. Exceptions are fibers

Table 5

<table>
<thead>
<tr>
<th></th>
<th>E (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Herman's orientation factor ($f_c$) for PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-extruded</td>
<td>0.29 ± 0.01</td>
<td>13 ± 0.6</td>
<td>0.016</td>
</tr>
<tr>
<td>Oriented</td>
<td>6.1 ± 0.3</td>
<td>370 ± 56</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Fig. 11. Wide-angle X-ray scattering patterns obtained from PP/PE strands with 2/3 PS separating layers (a) before and (b) after orientation procedure at 105 °C and 100%/min to a final draw ratio of 21.7. (c) Radial scan and of the oriented LDPE/PP fiber tape. Azimuthal scans of the (d) PP (110) and (e) (040) reflections for the as-extruded and oriented LDPE/PP fiber tapes.

Fig. 12. Mechanical properties of LDPE/PP nanofiber system before and after orientation.
that have bigger lateral size than 1 μm by 0.4 μm due to incomplete delamination of PA6 and PET fibers. Based upon the fiber size distributions, the expected nanofiber thickness and width are calculated to be 0.24 ± 0.008 μm and 0.76 ± 0.20 μm, respectively. Similar to the PCL nanofibers previously discussed, these PA6 and PET nanofibers have large surface area due to their nanoscale cross sectional dimensions and their rectangular shape, which is advantageous for filtration applications.

3.4. LDPE/PP nanofiber system for filtration applications

The preparation of polyolefin nanofibers, such as PE and PP, has been challenging due to a lack of suitable solvents that are required in conventional nanofiber-making techniques, such as solution electrospinning. Therefore, nanofiber products made with continuous and oriented polyolefinns would have large potential in replacing many of the current nanofiber products made using solvent-based techniques as a result of their lower cost.

A nanofiber system made from LDPE and PP was prepared using our extrusion-orientation-separation technique. The extruded tape is comprised of 256 by 16 alternating vertical layers. The LDPE/PP composition was offset to 30/70 to higher degrees of orientation and PS was used as for the separating layers with a composition of 2/3 in total due to its low adhesion to LDPE and PP. The orientation temperature was selected to be 105 °C, which is slightly above the glass transition temperature of PS (102.7 °C), and lower than the melting point of LDPE at 108.3 °C to achieve the highest draw ratio for high molecular orientation of both LDPE and PP. Several strain rates were tested, and the strain-at-break was found to be the highest when the composites were oriented at 100%/min, allowing us to achieve a draw ratio of 21.7 from the as-extruded tape.

Two-dimensional WAXS patterns of the as-extruded and highly oriented fiber tapes are shown in Fig. 11. The as-extruded tape (Fig. 11a) exhibits an amorphous PS halo referring to the PS separating layers, and four concentric, isotropic rings corresponding to the randomly oriented PP and LDPE chains. After the orientation process, three WAXS reflections at 2θ = 14.7°, 17.1°, and 18.5° on the equator, which are characteristics of PP (110), (040), and (130) planes of its α-form crystals, respectively, are revealed as shown in Fig. 11b, c. Two distinct reflections at 2θ = 21.4° and 23.6° were also observed on the equator referring to LDPE (110) and (200) planes.

As described for the previous extruded nanofiber systems, the extent of molecular orientation was calculated via the Herman’s orientation factor. The degree of LDPE fiber orientation could not be quantified because the PE (110) signal overlaps with the PP (111)/(041) reflections in the azimuthal scan. However, the calculation of PP crystal orientation could be determined (Fig. 11d, e) [48]:

![Graph showing fiber thickness and width distributions](image)

Fig. 13. IR spectra of the LDPE/PP fiber mixture before and after mechanical separation.

![SEM images of the obtained LDPE/PP fiber system](image)

Fig. 14. SEM images of the obtained LDPE/PP fiber system at the magnifications of (a) 2500× and (b) 4000×; Distribution for (c) fiber thickness and (d) fiber width.
\[
\cos^2 \phi_c = 1 - \frac{1.099 \cos^2 \phi_{10} - 0.901 \cos^2 \phi_{040}}{\pi/2} \\
\cos^2 \phi_{hko} = \frac{\int_{0}^{\pi/2} I_{hko}(\phi) \cos^2 \phi_{hko} \sin \phi_{hko} d\phi}{\int_{0}^{\pi/2} I_{hko}(\phi) \sin \phi_{hko} d\phi}
\]

Compared to as-extruded LDPE/PP fiber strand with an orientation factor of 0.016, \( f_c \) of PP was calculated as 0.95 for the oriented fibers, confirming that PP crystals were highly oriented via this method.

As expected, the mechanical properties of the LDPE/PP fiber system were drastically improved as a result of orientation. As shown in the stress–strain curves in Fig. 12 and listed in Table 5, both the Young’s modulus and the tensile strength were largely improved for these LDPE/PP nanofiber system after the orientation procedure with a 21.0 times improvement in Young’s modulus and a 28.5 times increase in the tensile strength were enhanced from 0.29 ± 0.01 to 6.1 ± 0.3 GPa (a factor of 21.0), and from 13 ± 0.6 to 370 ± 56 MPa (a factor of 28.3), respectively.

Separation of the LDPE and PP fibers was also achieved using the water jet approach described for delamination. Water pressure at nozzle was chosen to be 500 psi to prevent breakage of fibers, and the fiber tape was flushed for 10 min under a moving water jet at 1 cm/s. FTIR was used to determine the extent of removal of PS (Fig. 14). For the sample prior to the separation step, the absorption peaks at 1453 and 1493 cm\(^{-1}\) were designated to the C–C stretching of the aromatic rings. A peak at 3026 cm\(^{-1}\) was also observed referring to the C–H stretching of the aromatic structure. Confirmed by the drastically decreased intensity of these three peaks, we were able to achieve nearly complete removal of the sacrificial PS layers.

The produced LDPE/PP nanofiber system was characterized using SEM (Fig. 14). 50 fibers were measured to generate histograms of widths and thicknesses. 75% of the measured fiber widths fall in the range from 0.4 to 1 μm; however, widths as large as 2.5 μm were observed possibly a result of an incomplete PS delamination. Fiber thicknesses were found to range from 0.2 to 0.7 μm, with around 90% of the dimensions to be equal or smaller than 0.5 μm. This distribution of LDPE and PP fiber thicknesses shows a slightly larger span as compared to that for the PA6/PET nanofiber system described earlier due to the offset composition (PP/LDPE = 70/30) used for this sample. Calculated from the size distribution, the average width and thickness are 0.99 ± 0.12 μm and 0.44 ± 0.008 μm, respectively.

4. Conclusions

A novel melt-based co-extrusion and multiplication technique was developed to produce continuous and orientable nanofibers. Using this technique, nanofibers were generated with potential application in biomedical technology and filtration without the aid of organic solvents. This multilayer co-extrusion and multiplication technique was applied to produce single fiber and two-component fiber systems with nanoscale dimensions and rectangular cross sections.

In the single-component PCL nanofiber systems, orientation improved the Young’s modulus and tensile modulus of the PCL nanofibers by a factor of 8 and 15, respectively. Upon dissolution of the sacrificial PEO, the obtained PCL nanofibers exhibited rectangular shape with cross sectional dimensions of 0.07–0.23 μm thickness and 0.2–4.7 μm width. Using the extrusion technique followed by a mechanical separation procedure, a PAG/PET nanofiber system was produced with a thickness and width of 0.1–0.4 μm and 0.3–2.4 μm, respectively. Large mechanical enhancement (18.5 times improvement in Young’s modulus and 8.9 times improvement in tensile strength) was reported for the two-step orientation process, which allowed crystallization of PET and highly orientation of PA6 and PET crystals during drawing. We also demonstrated an advantageous approach to generate nanofibers from polyolefins, such as LDPE and PP, which are not processable using conventional solution-based nanofiber processes. The LDPE/PP nanofibers displayed fiber widths ranging from 0.4 to 2.5 μm, and fiber thicknesses between 0.17 μm and 0.82 μm. Orientation of the composite LDPE/PP bundle offered These LDPE/PP nanofibers have largely improved the mechanical properties: the Young’s modulus and the tensile strength of the LDPE/PP nanofiber bundle were enhanced from 0.29 ± 0.01 to 6.1 ± 0.3 GPa (a factor of 21.0), and from 13 ± 0.6 to 370 ± 56 MPa (a factor of 28.3), respectively.

This melt-based fiber fabrication approach provides a unique opportunity to fabricate continuous nanofibers with superior mechanical properties from any melt processable polymers. It overcomes the processing limitations of other current techniques for preparation of polymer nanofibers with potential in the fiber industry.

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References
