NONWOVEN MICROFILTERS PRODUCED BY A NOVEL MELT COEXTRUSION PROCESS

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Abstract

Fibrous filters were fabricated using a novel melt co-extrusion and two-dimensional multiplication technology combined with a high pressure water jet delamination technique. The filters made from polypropylene (PP) / polyamide 6 (PA6) system exhibited micro to nano scale fibers having uniform fiber distribution and superior mechanical properties. Effects of film draw ratio upon co-extrusion on the final filter characteristics were investigated. It was found that increasing the film draw ratio significantly improves the fiber’s surface area and porosity, and decreases the mean pore size. This melt-based, versatile technology is applicable to any melt-processable polymers to produce fibrous filters having tunable properties for various filtration applications.

Introduction

Non-woven fiber based filter materials are widely used in filtration industry such as - fuel/water separation, oil/lube, cabin air filtration in the automotive segment, water and air filtration in consumer, industrial, and oil & gas segments; healthcare, food & beverages segments among others. Conventionally nonwoven filters from staple fibers are produced using wet-laid and dry-laid technologies, based on the several decades old paper manufacturing process, due to their ease of handling and low cost [1]. In the wet-laid process, the fibers, commonly natural cellulose fibers from plants, are randomly dispersed in water, forming a web after removal of water on a drying belt, and are thermally or chemically bonded for an integrated filter structure. The dry-laid process consists of opening and mixing, carding, and web-laying steps. The fibers are eventually bonded together chemically or thermally. These technologies are only applicable to short fibers, which can weaken the mechanical properties of the fiber. In fact, these paper-like fibrous materials generally have very brittle mechanical behavior, thereby potentially reducing its lifetime under high pressure and varying temperature field service conditions. Additionally, these technologies produce large fiber sizes (varying from a few µm to tens of µm) that results in large pore size and low porosity.

Nonwoven filtration materials comprised of continuous fibers have also been developed using electrospinning and melt blowing techniques. In electrospinning [2], polymer solutions are extracted by a strong electric potential through an orifice to form a jet toward a grounded screen. Fast evaporation of the solvent solidifies the polymer, and the continuous fibers land in a random direction on the screen to construct a web. The unsupported fibers are thin (avg 500 nm in diameter) and weak in mechanical properties. Commercially, a composite, Ultraweb® HEPA air filter from Donaldson Corp. is fabricated by depositing electrospun nylon nanofibers onto a thicker fibrous polymer support, pre-produced by wet-laid or dry laid technologies. However, majority of the studies on the electrospun filtration materials still remain in the lab-scale due to several limitations, including low process throughput and limited application to the polymers that dissolve easily in organic solvents. Additionally, the use of large amounts of organic solvents renders it cost-prohibitive and poses significant environment concerns in its recovery and disposal. An extrusion based melt blowing technique [3] is used to produce fibers having diameters generally in 1-2 um in a single step: Polymer melt is extruded from a spinneret, and is attenuated by a surrounding high-pressure hot air jet afterwards. Despite the advantage of the melt-based process, melt blowing is only applicable to polymer melts having a low chain overlap concentration [4]. Fiber mats produced using this technique usually have limited mechanical properties due to inherently high MFI (low MW/MWD) and resulting weak crystal orientation of polymers.

Previously micro/nano scale fiber fabrication was reported using a novel melt-based co-extrusion and
two-dimensional multiplication technology [5, 6] that can easily scale up to production using an industrial film/film co-extrusion process. This processing technique was shown to readily control the fiber size and its distributions while enabling a single component or multi-component, non-woven fiber mix to be processed, without any organic solvents, and from large selection of commercial thermoplastic materials – which were prohibited due to process limitations of current techniques. These fiber systems demonstrated via single component PCL poly(caprolactone) system and two component polyamide 6 (PA6)/polyethylene terephthalate (PET), and polyethylene (PE)/polypropylene (PP) systems exhibited micro to nano scale fibers, superior mechanical properties and large surface areas due to ribbon like rectangular cross sections [5].

In the present study, we investigated the novel co-extrusion/fiber exfoliation process for fabrication of non-woven Polyamide-6 (PA6)/Polypropylene (PP) fibrous mats that is considered suitable for several filtration platforms such as fuel/water separation, air filtration and water filtration. Compared to previous investigation [5], which focused largely on developing the unique fiber fabrication approach, this study systematically investigated the effects of orienting the co-extruded PA6/PP fiber-films systems on fibrous mat density, fiber size, pore size and respective distributions, morphology and surface areas, and mechanical performance. The overall study revealing the processing-structure-properties relationship of PA6/PP based fibrous products should provide a better fundamental understanding of the process for potential filtration applications.

**Experimental**

**Materials**

Extrusion grade polypropylene (PP Pinnacle 1703) and polyamide 6 (PA6 BASF Ultramid B 36 01) were used for co-extrusion and final filter fabrication. The supplier-provided polymer densities are 0.9 g/cm³ and 1.13 g/cm³ for PP and PA6, respectively. Polystyrene (PS Dow 685D) was used as the separating material in the extrusion procedure.

**Co-Extrusion and Two-Dimensional Multiplication**

Films containing 8192 by 32 alternating domains of PP/PA6 and 33 PS separating domains with PP/PA6/PS = 45.5/45.5/9 (vol./vol./vol.) composition, schematically displayed in Figure 1, were produced through a continuous co-extrusion and two-dimensional multiplication process. Coextrusion was performed at 255 °C, at which the viscosities of PP, PA6, and PS match with each other. The width of the PA6/PP film was 50 mm and its thickness was maintained at 70 µm. As shown in Figure 1, PP and PA6 resins were melted and conveyed to the feedblock in Step I, where the two are combined to form a two-horizontal-layered structure. This melt flow was vertically multiplied for 18 times. In each vertical multiplication step (Step (I), (II)), the layered structure was cut horizontally from the center into two flow fields, one of which flew to the side of the other so that the two fields were aligned side by side, doubling the number of vertical layers. After generating $2^{18}$ (262,144) vertical PP/PA6 layers, a separating material, PS, was added on the top and bottom (Step (III)), and the flow was horizontally multiplied five times, each of which cut the flow vertically in the center, and stacked the two halves on top of each other to double the number of horizontal sections (Step (IV)). As the final structure consists of continuous PA6/PP closely packed fiber domains, separated by a PS layer, in a co-extruded form, it is regarded “fiber-film” rather than a “conventional film”.

The effect of layer multiplication on estimated fiber size using coextrusion and 2D multiplication technique is illustrated in Table 1. The estimated fiber size decreased from ~100 µm at 512 x 32 layers to 6 µm at 8192 x 32 number of layers. This provides an easy approach for tunability of the fiber size distribution in the final filter product. The 6 µm fibers in the 8192 x 32 layered coextruded films can be further reduced to < 1 µm scale upon orienting the composite fiber-films. This was investigated by orienting the coextruded films to various draw ratios.

**Orientation of Co-Extruded Films**

Orientation of the PA6/PP fiber-film samples was performed to strengthen the fiber components, PP and PA6, thereby resulting into mechanically strong filter mats with nano/micro-scale, oriented fiber mix. It was performed on an Instron 5965 unit from INSTRON (Norwood, MA) equipped with an environmental chamber for high temperature stretching. The selected orientation temperature was above the glass transitional temperature of PS at 102 °C, and below the melting temperatures of PP and PA6 at 161 °C and 218 °C, respectively. The films were oriented at 130 °C and 1000 %/min to draw ratios of 2.7 and 4.0. A second orientation step was done to improve the orientation of PP and PA6 crystals. A maximum draw ratio of 4.5x was achieved by orienting the film with draw ratio of 4.0 at 155 °C, 100 %/min. Properties of the filters
fabricated from the differently drawn films was studied and compared to understand orientation effects.

The oriented and un-oriented filter mats were fabricated from stacked un-oriented and oriented films in cross-ply manner under high pressure water jet [5]. Application of water jet (a) broke down and removed PS separating layers, (b) delaminated the continuous fibers in the extruded fiber-films and (c) assisted in mechanical interlocking of the fibrous ribbons. For this investigation, two strips of PA6/PP fiber-films were cross-plied at 90° and taped down to a steel plate. An aluminum grid of 30 mesh was placed on top for uniform distribution of water jet pressure. The set up was placed 2” below the water jet nozzle and subjected to 1000 psi pressure for 5 min. The two layered set up was inverted, and the same treatment was applied on the bottom layer for another minute. The eventual filter mats were dried overnight in oven at 40°C.

A flow chart illustrating the steps for fabrication of filter mats from coextruded films is shown in Figure 2.

**Results and Discussion**

Fiber size distribution in the water jet exfoliated filter mats was studied under scanning electron microscope (SEM). As seen in Figure 3, the filters produced from the un-oriented and oriented (draw ratio = 4.5) films were composed of well separated PP and PA6 fibers having ribbon-like shapes. Almost all PS layers have been removed, for no PS chunks were observed in the images. Successful removal of PS was also confirmed using FTIR, using a previously established technique [5] that displayed no significant peaks detected at 1453 and 1493 cm⁻¹, designated to the C-C stretching of the aromatic rings. These micro/nano-fibers were well entangled for maintaining the filter integrity. The average fiber lateral dimensions were 8.3 ± 3.8 µm by 1.6 ± 0.58 µm and 2.4 ± 0.80 µm by 0.67 ± 0.20 µm for the filters produced from the un-oriented and oriented tape samples, respectively. This large decrease in the fiber size was attributed to the fiber elongation in the orientation procedure.

To further probe the effects of orientation, the PA6/PP fibrous filters fabricated from oriented fiber-films were characterized for filter surface area, pore size, and porosity. The effects of approaching nanoscale dimensions, due to tape orientation, was observed in an increased surface area from 1.8 to 4.3 m²/g (2.3x improvement) as shown in Figure 4a. In comparison with electrospun fiber mat having similar fiber sizes, the filters from the co-extruded fibers have around 20-fold larger surface area [7]. This is attributed to the rectangular, ribbon-like micro/nano-fibers produced from the 2D multiplication procedure.

As shown in the plot of the pore size distribution Figure 4b, the filter’s pore size range decreased as the extruded fiber-film draw ratio was increased. The mean flow pore sizes decreased from 16 µm to 8.8 µm, approximately 50% decrease, as the fiber-film draw ratio increased to 4.5x. This trend was in accordance with the study on the relationship between pore size and fibers size for electrospun fiber mats, wherein the mat’s pore size was reported as 3x of the electrospun fiber diameter [8]. In comparison, the pore sizes measured using the same technique ranged from 12 µm to 26 µm, with the mean flow pore size of 17.3 µm, for a commercial grade composite filter composed of a melt-blown polyester fiber top layer and a support layer made from natural cellulose fibers using the wet-laid process [9]. The small pore sizes of the filters fabricated from the un-oriented and oriented co-extruded fiber-films is expected to provide higher filtration efficiency than the commercial filter.

Mechanical properties of the PA6/PP fibrous filter mats fabricated from two different number of layers, 2048 x 64 and 4096 x 64 for un-oriented and oriented films are shown in Figure 5a and b. Orienting the fiber-films significantly increased the tensile strength of fibrous filters. The elastic modulus of the fibers also increased from 7 MPa to 25 MPa as draw ratio increased from 1X (un-oriented) to 4.5X. The area under the stress-strain curve (deformation energy) of the filter mats increased systematically up to 4X film draw ratio and somewhat decreased at 4.5X. Decreased toughness/deformation energy of the strong fibrous mats was expected for taut and highly drawn fibers.

**Conclusions**

Fibrous filtration media were produced using a novel co-extrusion and two-dimensional multiplication technique combined with a water jetting delamination technique. These filters are comprised of uniformly distributed rectangular, ribbon like polypropylene (PP) / polyamide 6 (PA6) micro/nanofibers. The properties of the filters, including fiber surface area, pore size, and porosity, are highly tunable for various filtration applications by adjusting the processing parameters, such as the extent of orientation. The filter’s surface area and mechanical properties significantly improved upon coextruded fiber-film orientation. The mean pore size and density of filters reduced at high draw down ratios.
The melt-based technique of co-extrusion and multiplication is highly versatile, and is applicable to any melt-processable polymer. The tunability of the filter properties by easily adjusting the processing parameters makes these filters excellent candidates for various filter applications.

Acknowledgments

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References


Figure 1. Coextrusion of PA6/PP fiber-films with PS as a separating layer. Demonstration of essential steps in two dimensional multiplication of the constituents.
### Table 1. Effect of Multiplication on Estimated Fiber Size in Coextruded Fiber-Films

<table>
<thead>
<tr>
<th>System</th>
<th>PA6/PP</th>
<th>PA6 or PP fiber size</th>
</tr>
</thead>
<tbody>
<tr>
<td># of Layers</td>
<td>Composition</td>
<td>(µm)</td>
</tr>
<tr>
<td>512 x 32</td>
<td>50/50</td>
<td>98 x 2.8</td>
</tr>
<tr>
<td>2098 x 32</td>
<td>50/50</td>
<td>24 x 2.8</td>
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<tr>
<td>4096 x 32</td>
<td>50/50</td>
<td>12 x 2.8</td>
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<tr>
<td>8192 x 32</td>
<td>50/50</td>
<td>6 x 2.8</td>
</tr>
<tr>
<td>16384 x 32</td>
<td>50/50</td>
<td>3 x 2.8</td>
</tr>
</tbody>
</table>

1. **Easy to tailor for melt extrudable polymers**

**Multilayer Extrusion Films/tapes** → **Uniaxial Orientation (in Instron)** → **Stretched Films** → **DELAMINATION & SEPARATION** → **Fiber mat**

**Fiber size and distribution**
**Surface area & porosity**
**Mechanical properties**

Figure 2. Schematic flow chart of filter mat fabrication steps from the coextruded fiber-films

**As-extruded** → **Draw ratio = 2.7** → **Draw ratio = 4.5**

Fiber width: 8.3 ± 3.8 µm  
Fiber thickness: 1.6 ± 0.6 µm

Figure 3. SEM images displaying the effects of fiber-film draw down on fiber size distribution in PA6/PP filter mats

(a) **Surface Area of PA6/PP Fibrous Filters**  
(b) **Mean flow pore size of PA6/PP Fibrous Filters**

Figure 4. Effect of PA6/PP fiber-film orientation on (a) surface area and (b) mean flow pore size of the filter mats.
Figure 5. Effect of PA6/PP fiber-film orientation on (a) tensile strength and (b) deformation energy of the filter mats.