NONWOVEN FILTERS via A NOVEL, CONTINUOUS MELT COEXTRUSION PROCESS

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Abstract

A novel melt co-extrusion process with two-dimensional multiplication technology created a fiber-film mat with polymer layer dimensions comparable with conventional fibers. When the layers were exfoliated using a high pressure water jet delamination technique a fibrous filter media were fabricated. The filter media made from polypropylene (PP) / polyamide 6 (PA6) system exhibited microscale fibers with uniform fiber distribution and superior mechanical properties. Previously, improved filter surface area and porosity, and decreased the mean pore size was demonstrated with increasing film draw ratio prior to delamination. In current work, applications of this filter for water removal in fuel filters are demonstrated. In addition, PolymerPlus has also demonstrated fabrication of continuous large filter media sheets demonstrating scalability. This melt process based flexible technology can be extended to other melt-processable polymers for various liquid or gas filtration applications.

Introduction

Filtration is widely used process in applications ranging from drinking water filtration to complicated industrial processes. Many non-woven filters are typically used in applications 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. Typically, non-woven filters are fabricated using wet-laid or dry-laid technologies for their easy processability and low cost [1]. In the wet-laid process, the fibers, commonly natural cellulose fibers from plants, are randomly dispersed in water, form 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, followed by chemical or thermal bonding. Because these technologies are applicable to short fibers, weak mechanical properties (brittle nature) of the resulting filters lead to decreased 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) resulting into large pore size and low porosity. Other techniques to produce nonwoven filters include electrospinning and melt-blowing process. 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. However, this is a low process throughput process used in only a select polymers and has a low process throughput. An extrusion based melt blowing technique is used to produce fibers having diameters generally in 1-2 um in a single step. [3] 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 with 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 into a weak crystal orientation of polymers. Melt electrospinning (a solvent-free process) technique has also been investigated over last few years as an alternative to electrospinning technique. Unlike earlier mentioned technologies, melt electrospinning has production scale-up challenges as more investigation is needed to address this issue. [5] Similar to co-extrusion based fiber production technology, this technology is still in its infancy with many recent publications dedicated to understand and develop new fiber materials.

In its patented technology, Case Western Reserve University and PolymerPlus have demonstrated modification of conventional coextrusion process, which is typically used for film production [6], to create two-dimensional film product containing hundreds of thousands of polymer layers resembling fiber/ribbon like structures which can be separated to create fibrous mats. [7, 8, 9, 10]. This novel processing technique has been investigated to control fiber size and distribution, and pore size and distribution. Because the coextrusion process uses two or more polymers, non-woven filter matrices produced consisted of fibers from multiple polymers creating composite structures. It is interesting to note that by changing the relative composition of the two polymers, fiber size distributions of the component fibers and hydrophilicity can also be controlled. Furthermore, the process can also be modified to create filters from only one polymer. For example, PCL fiber system produced from PCL/PEO system was achieved by systematically dissolving PEO component. Examples of
two component system include polyamide 6 (PA6)/polyethylene terephthalate (PET), and polyethylene (PE)/polypropylene (PP), which exhibited micro to nano-size fibers with superior mechanical properties and large surface areas due to ribbon like rectangular cross sections [7,8,9].

In the present study, example of non-woven filter media of Polyamide-6 (PA6)/Polypropylene (PP) for fuel/water separation are discussed. The structure and properties of PP/PA6 based filter media were measured and compared with a commercial fuel filter. An approach of continuous filter media fabrication is also summarized to demonstrate scalability of the process. This new approach of filter fabrication via coextrusion process will be useful in wide range of applications.

Experimental

Co-extrusion process and two-dimensional multiplication: A conventional layer multiplication with two extruders, melt pumps, feedblock, layer multiplying dies and film/sheet die was used for processing fiber-film sheets. Previously described two-dimensional layer multiplication process was used to create PP/PA6 films containing 8192 vertical layers separated into 32 alternating sections, further separated by horizontal PS layers, as schematically shown in Figure 1. The innovation of using the layer multiplying dies created the “fiber-film” structures described in Figure 2 to create filter media. Fabrication of PP/PA6 sample was used for demonstrating improved fuel filtration efficiency as compared to commercial filter media. In addition, films containing 16384 vertical layers in 16 alternating stacks were used to demonstrate modified filter fabrication steps to achieve large filter media sections.

Figure 1. Coextrusion of PA6/PP fiber-films with PS as a separating layer.

Figure 2 shows a four step process of coextruded fiber-film fabrication process for subsequent exfoliation to create final filter media products. An example of PP/PA6 film structure is discussed. In Step I, PP and PA6 resins fed through extruders and melt streams are combined in a feedblock to form a two-horizontal-layered structure. The polymer melt streams are redirected to create a vertical layer structure as shown in Step II. Subsequent layer multiplication process was carried out using 18 layer multiplication elements to create $2^{18}$ (262,144 layers) vertical PP/PA6 layers, followed by addition of PS material on the top and bottom as shown in Step III. The melt flow was subsequently horizontally multiplied for 5 times in Step IV to create film structure, referred to as fiber-film. It is obvious that the layer thickness was dependent on the number of layer of multiplication steps used during processing. For example, the estimated fiber thickness decreased from ~100 µm at 512 x 32 layers to 6 µm at 8192 x 32 number of layers. The number of layer multiplying dies defines the number and dimensions of the fibers created in the final structure. For a 16384 x 16 layered structure, 19 layer multiplying elements prior to addition of PS material and 4 horizontal layer multiplying elements after PS addition were used. It should be noted that additional decrease in the layer thickness can be achieved by using fiber-film orientation step, as used in 8192x32 sample discussed in this paper. The process flexibility of the coextrusion technology has been used to create fiber structures ranging from few micrometer thickness to few tens of nanometers. [7] Furthermore, fiber thickness reduction of 5 to 10X was achieved by using orientation approach prior to exfoliation process.

Figure 2: Demonstration of various steps involved in two dimensional multiplication of the constituents.
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 as described in other publications. [7, 8, 9] For PP/PA6 system, the orientation temperature above glass transition temperature of PS and below the melting temperature of PP and PA6 were selected. A two-step orientation process with initial orientation at 130 \(^\circ\)C at 1000 \%/min draw rate followed by orientation at 155 \(^\circ\)C at 100\%/min was used to achieve a final orientation of 4.5X in 8192x32 fiber-films.

Fiber-film exfoliation: The oriented fiber-film mats were stacked in cross-ply manner to create 2-, 3- and 4-ply exfoliated structures. The stacked structures were exfoliated using high pressure water jets to achieve breakdown of the PS separating layers, delamination of PP and PA6 fibers and mechanical interlocking of the fiber ribbons to create a filter-media samples. Due to limitations of water jet exfoliation unit, only sections up to 8" x 8" could be created. However, recent process modification allowed combination of these exfoliated mats to create continuous sheets. An example of 3 ft. long continuous exfoliated fiber mat is shown in this paper. The filter mats were characterized for pore size, porosity and filtration performance in fuel/water mixtures.

Detailed experimental procedure is described in Reference 5.

Fuel Filtration Test: A custom fuel filtration test set-up was designed according to SAE1488 guidelines to evaluate filtration efficiency of the filter media. The set-up is designed for one-pass tests and no recycle flow line was installed. The system comprised of 10 L tank containing fuel/water mixture, a centrifugal pump to emulsify the solution, a peristaltic pump to transfer the liquid, a flowmeter and customized filter holder with drainage, pressure gauge, upstream and downstream sample ports. The fuel/water mixture containing 2500 ppm water was used for testing filter efficiency. Further detailed experiment description can be found in Reference 8.

Results
Multilayer coextrusion process and uniaxial stretching processes followed by exfoliation step was used to create filter media. The starting fiber-film structure consisting of 8132 x 32 layer structure was oriented by uniaxial stretching via a two-step orientation process to achieve 4.5x orientation. Stretched PP/PA6 fiber-film samples were stacked as 2-, 3- or 4-ply sheets in cross-ply manner in exfoliation step to create fibrous filters. The filter media structure was compared with a commercial grade polyester/cellulosic paper-based composite filter.

The structural differences between the two filters – 2-ply PP/PA6 filter and commercial filter - are shown in SEM images, Figure 3. The commercial filter is comprised of two layers, the top layer containing meltblown PET fibers, while the bottom layer is a cellulosic fibrous substrate. Meltblown PET fibers in the top layers were in the range of 7 µm and the cellulose fibers were measured in 5 to 20 µm size range. In contrast PP/PA6 filter is a composite filter containing PP and PA6 fibers. A wider fiber size distribution ranging from 8 to 49 µm was observed for 2-ply filter, while 4-ply filter showed reduced pore size range of 4 to 25 µm, as summarized in Table 1. The overall surface are of the 2-ply PP/PA6 fibrous filter was 2.92 ± 0.03 m\(^2\)/g as compared to 0.23 m\(^2\)/g surface area of commercial filter of similar overall thickness of 0.74 mm. The PP/PA6 fibrous filter media showed smaller mean pore size and higher porosity as compared to commercial filter. A 4-ply PP/PA6 filter shows reduced mean pore size range, while similar porosity of 87%. It should be noted that the fiber production process is reproducible as demonstrated in several examples over last few years. The samples and results discussed have also been reproduced several times.

As orientation of the fiber-film was performed prior to exfoliation process, improved mechanical performance was observed in PP/PA6 filters, Figure 3. PP/PA6 based filter media showed increased tensile strength and toughness, while the commercial filters were very rigid and brittle.
Table 1: Summary of PP/PA6 and commercial filters

<table>
<thead>
<tr>
<th>Filter</th>
<th>Filter Thickness (mm)</th>
<th>Surface Area (m²/g)</th>
<th>Pore Size (µm)</th>
<th>Mean Pore Size (µm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/PA6 – 2 ply</td>
<td>0.74</td>
<td>2.92 ± 0.03</td>
<td>8-49</td>
<td>11</td>
<td>87</td>
</tr>
<tr>
<td>PP/PA6 – 4 ply</td>
<td>1.38</td>
<td>--</td>
<td>4-25</td>
<td>5.4</td>
<td>87</td>
</tr>
<tr>
<td>Commercial</td>
<td>0.74</td>
<td>0.23 ± 0.005</td>
<td>12-26</td>
<td>17</td>
<td>84*</td>
</tr>
</tbody>
</table>

*estimated from densities of cellulose and PET

Filtration Performance: Using fuel/water influent containing large quantity of dispersed water droplets with (2.49 ±0.04) x 10³ ppm concentration, PP/PA6 showed a reduced downstream water concentration of (3.7 ± 0.3)x10² ppm, with 85% filtration efficiency. In comparison, commercial filter showed a 62% efficiency with measured water concentration of (9.5 ±0.9) x 10² ppm. Typically, larger water droplets are directly blocked, coalesced, and removed from the main flow, when the size is comparable to smaller than the filter pores. In contrast, the smaller droplets tend to penetrate through the filters. Therefore, physical properties of the filter media are critical in achieving improved performance. Increased efficiency was attributed to reduced pore size in PP/PA6 filters as shown in Table 1. Further characterization of the filters showed comparable water contact angles of 124 and 130 °C for PP/PA6 and commercial filters respectively. Therefore, in addition to reduced pore size, the improved filtration efficiency in PP/PA6 filters was attributed to increased surface area (> 10X).With this example, it was demonstrated that the filter media produced from multilayer coextrusion process can be used successfully for fuel filtration applications.

Production Scale-up: Coextrusion is a continuous process capable of producing thousands of feet of fiber-film rolls as demonstrated at PolymerPlus. However, current limitations of the lab-scale exfoliation unit only allows for production of small exfoliated sheet samples. The exfoliation process can be modified to achieve continuous delamination of fiber-film sheets to achieve large filter media.

To demonstrate production scalability, multiple sections of oriented fiber-films were overlapped and exfoliated to create a 3 ft. continuous filter mat (from 16384 x 16 fiber-film) as shown in Figure 4. This is a significant progress from small samples to continuous sections demonstrating production scale-up feasibility. The measured pore size for this sample ranged from 6 to 18 µm, with porosity of 72 to 75%. It should be noted that the starting fiber-film was not stretched prior to exfoliation step. Continued process optimization and modification are key in technology commercialization.

Conclusions

A novel co-extrusion and two-dimensional multiplication technique was successfully used to create fiber-film structures containing hundreds of thousands of ribbon like layers, which when exfoliated created fibrous mats. Example of composite filter media of PP and PA6 were successfully created and demonstrated for use in fuel filtration application. Mechanically superior filter media than the comparable commercial filter media were achieved. Furthermore, improved filtration efficiency was demonstrated for PP/PA6 filter media. Translation of these results including mechanical properties to actual products require fabricating filter part prototypes for testing and evaluation.

Recently, fabrication of large filter media was shown to demonstrate process scalability of this process. It is interesting to note that the coextraction process can be easily extended to different types of polymers, as shown in several examples in other publications, for wide range of filtration applications.

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