

Bicomponent Fiber Extraction Process for Textile Applications

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ABSTRACT

Tailoring surface properties is important for military applications such as uniforms, shelters, and personal protective equipment. Unique superomniphobic structures for self-cleaning textiles can be created with bi-component fibers. In this work bicomponent fibers were melt extruded using an extractable polymer as one of the two components. Using water to extract the soluble component, fibers with unique core designs were created. The extraction behavior was found to be dependent on temperature, component fraction, and residence time. A continuous extraction process was designed and evaluated for the creation of superomniphobic fibers in a continuous process.

INTRODUCTION

Fabrics and textiles are important for a range of industries including consumer clothing, carpeting, protective uniforms, and upholstery. Textiles that repel oil, dirt, and water significantly reduce cleaning, resist staining, and extend the lifetime of textiles. Creating textiles with superomniphobic properties can address these problems. Superomniphobic surfaces repel a wide variety of low and high surface tension liquids such as water, aqueous and salt solutions, acids, bases, and oils. These types of surfaces cause liquids to repel and flow off of the exterior easily by not permitting wetting of the surface. This is demonstrated by the wetting liquid exhibiting a contact angle greater than 150° [1] Superomniphobic surfaces are created by a combination of surface chemistry and topography [2].

Using superomniphobic textiles for a soldier's uniform and gear allows the capability to provide them with equipment and systems that are easy to clean. It may also provide protection against

hazardous chemicals and environments during combat. Resistance to a variety of liquids provides longevity of uniforms as well.

There are three important factors which contribute to creating superomniphobic surfaces: surface chemistry, micro/nano-scale surface roughness, and geometrical reentrant architecture. Surface chemistry helps to improve a hard surface's ability to resist wetting by low surface tension liquids, where omniphobic materials are both hydrophobic and oleophobic, with contact angles between 90° to 150° [1].

Surface roughness dictates how liquid droplets will behave – either wetting (i.e., Wenzel state) or non-wetting (i.e., Cassie-Baxter state). These micro/nano surface roughness (or features) are found in nature. For example, on a lotus leaf surface [3] or in the unique skin structure of a springtail insect. Geometrical (trapezoidal-shaped) reentrant surface architectures enable the surface to become nonwetting to extremely low surface tension liquids [4]. The unique “micro-hoodoo” surface architecture demonstrated that a man-made super-omniphobic coating is possible, where the contact angle of liquids can be greater than 150°. The key finding was that the ability to resist surface wetting (or liquid robustness) depended on the geometry of the textures. Specifically, if the apparent contact angle was greater than that of the slanted angle of the side wall of the reentrant micro/nano columns, a superomniphobic surface could be created.

As previously explained, reentrant structures provide superomniphobic capabilities [5]. If these structures can be fabricated around a fiber's core, the fiber itself

may become non-wetting. This reentrant structure can be accomplished in a fiber by proper design of a bicomponent fiber where one component can be extracted (*Figure 1*).

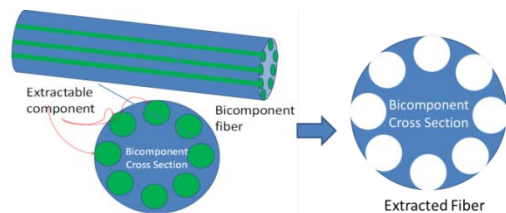


FIGURE 1. Concept of reentrant fiber structure.

A bicomponent fiber is defined by the American Society of Testing Materials (ASTM) as a fiber comprised of two chemically or physically different (or both) polymers [6, 7]. Bicomponent fibers are typically melt spun, using two single screw extruders connected to a spinneret block. The spinneret block contains multiple polymer distribution plates, with the end of the block having a die consisting of 19 holes [8, 9, 10]. The process was first created by DuPont in the mid 1960's, but the approach of using a series of plates to guide the flow of the two polymers was not introduced until 1989. Currently, the United States produces 2.7×10^6 kg of bicomponent fibers annually, with the expectation of growth within the next decade. The leading manufacturers of bicomponent fibers are Hoechst Celanese, Foss Manufacturing, International Polymers Inc., and Fiber Visions [7].

Bicomponent fibers can be made in many configurations including tipped, side-by-side, micro-denier, and core/sheath [11, 12]. The core/sheath configuration is defined as having the first polymer component (core) fully surrounded by the second polymer component (sheath); the sheath are the smaller multiple cores or channels that run along the length of the fiber. Core/sheath bicomponent fibers are made in applications where the properties must be tailored to specific consumer requirements such as upholstery fabrics and clothing [7]. High surface area fibers for filtration applications are made by spinning core and sheath fibers, then extracting the sheath with an appropriate solvent [13].

Bicomponent fibers for textiles are commonly extruded for the purpose of creating unique cross-sectional geometries [14, 15]. In a core/sheath bicomponent fiber, the core of the fiber may have a unique cross sectional geometry. In order to keep the fiber core architecture supported during melt spinning, the fiber is coextruded with a second

thermoplastic polymer. The second polymer phase acts as the sheath for the fiber core, protecting the geometry until the thermoplastic cools and can maintain its structure [14]. The cross-section of a bicomponent fiber is dictated by several factors: the plate design of the polymer distribution/metering spin pack, matching of the two polymer viscosities, and the interfacial tension between those polymers [9].

To create these unique structures, the sheath is typically a dissolvable polymer. Removing the dissolvable polymer sheath will reveal the fiber core's complex geometry, therefore increasing the fiber surface area. This approach can be used to create superomniphobic fibers (*Figure 1*). The fiber achieves the desired superomniphobic properties once the dissolvable polymer is removed, and additional nanoparticles are added to give an added reentrant level [12]. This requires a polymer sheath extraction process after the fiber is spun.

Core and sheath bicomponent fibers are primarily used to provide a wide range of properties. Another way bicomponent fibers have been utilized is to create a core with high surface area geometries that require an additional thermoplastic polymer sheath [11, 12]. Using the necessary solvent, the sheath component of the fiber is removed to expose the high surface area core.

This research investigates the creation of novel omniphobic fibers through the extraction of one component. The kinetics of extraction was investigated on a batch process and then the entire process was scaled to a continuous process suitable for industry. When developing a continuous extraction process, the dissolving behavior of the polymer sheath must be considered. From a manufacturing standpoint, it is important that the entire dissolvable polymer sheath is completely removed in the shortest time possible. The scope of this paper is to discuss the development of a continuous extraction process for the bicomponent fibers.

EXPERIMENTAL

Bicomponent fibers were prepared with a core of polypropylene (Total Petrochemicals 3762, MFI = 18 g/min.) (PP) or Nylon 6 (BASF, Ultramid B27 12 grade chip, Viscosity #: 148 cm/g, ISO TM 307). The coextruded sheath was made from water soluble polyvinyl alcohol (Nichigo, grade: G-Polymer® OKS 8070p) (GP). This GP was a highly amorphous grade, giving it excellent dissolving characteristics in water [16]. GP also does not tend to foam like common polyvinyl alcohol resins [17].

Table I presents the types of bicomponent fibers used in this study. They included fibers with 16 and 32 segments projecting from the core and slight differences in design (segment pie and segmented gear). The segmented pie geometry has petal-like features around the core, whereas the segmented gear cores have a typical gear-shaped geometry with straight sides and without re-entrant angle structures. The fibers were spun using a Lab-Scale Bicomponent Melt Extrusion Machine (Hills Inc., model: LBS-100). Each extruder had a 0.584 cc/rev melt pump. Two different spin packs were custom designed to create both segmented pie (NSRDEC) and segmented gear (Clemson University) geometries. When the volume output of the two polymers was altered by changing the melt pump speed settings, the resulting cross-sectional shape of the fiber changed. The volume ratios were chosen based on the resulting shape of the fiber and were altered to obtain the optimum shape depending on the polymers and spin pack used in each fiber spinning trial.

TABLE I. Bicomponent Fiber Trials.

Trial	Fiber Core Shape (Material)	Volume Ratio
1	16 Segmented Pie (PP and GP)	1:1, 3:2, 7:3, 4:1, 9:1
2	16 Segmented Gear (PP and GP)	2:1
3	32 Segmented Gear (PP and GP)	2:1
4	32 Segmented Gear (Nylon 6 and GP)	1:1

Extraction Trials

The fibers from Trial 1 were used to optimize the GP extraction parameters (amount of water, water temperature, and residence time in the water bath) in a batch extraction process. First, the relationship between the GP volumes extracted from the bicomponent fibers and the solvent volume (water) was determined with Trial 1 fibers (7:3). For this batch extraction process, a beaker was filled with room temperature water (a thermometer in the water measured the temperature). The water volume ranged from 20 mL to 100 mL, in increments of 10 mL. Pre-weighed virgin fiber samples (61 cm) were placed in the beaker for 30 seconds. The fibers then were removed from the water, dried for 30 minutes, and weighed again. Knowing the densities of each polymer in the bicomponent fiber (1.29 g/cm³ for GP and 0.96 g/cm³ for PP) [11] the change in volume fraction was calculated for the extracted fibers.

Next, the relationship between dissolved GP volume from the bicomponent fibers with respect to time and temperature (27°C - 38°C) was determined using Trial 1 fibers (7:3). A beaker was filled with 200 mL of water and placed on a hot plate to keep the water at the desired temperature; a thermometer in the beaker measured the temperature. Again, pre-weighed virgin fiber samples (61 cm) were immersed in the water for times varying from 5 to 30 seconds. After the fibers were removed from the water, they were dried and the fiber sample was weighed at each time interval listed in Table II. The volumetric change was calculated as discussed earlier.

TABLE II. Fiber Line Puller Speed Settings.

Puller Speed (m/s)	Water Bath Residence Time (s)
0.31	5
0.16	10
0.10	15
0.08	20
0.06	25
0.05	30

Trials 2, 3, and 4 were used to develop the continuous GP extraction process. A 61-cm-long sample of virgin fibers from each trial was cut and weighed for comparison to their weights after extraction. The fiber spool was then placed in the payoff system to run in a continuous process. The fiber line was pulled through a 1.5-m-long water bath via a Caterpillar Conair puller system (Figure 6). The water bath temperature was held constant at 38°C, while the puller speed was varied to give the desired water bath residence time (Table II). Extracted fiber samples from the continuous process were weighed once the process stabilized.

Fiber Characterization

The extracted fibers were characterized using scanning electron microscopy (SEM). To prepare the fibers for SEM, virgin and extracted samples were placed in a flat mold. The flat molds were then filled with epoxy, embedding the fibers. The epoxy was cured for at least 12 hours at room temperature, providing enough stability for the fibers to maintain their cross-section when the samples were microtomed. A gold coating was applied to the microtomed samples using two two-minute-long passes in a sputter coater (Denton Vacuum). SEM imaging of the coated samples was performed with a JEOL 7401 SEM using 10 kV and an emission current of 10 μA.

RESULTS AND DISCUSSION

Prior to determining the relationship between dissolution of GP with respect to solvent bath residence time and temperature, the minimum amount of solvent necessary for the extraction was determined. At water volumes greater or equal to 40 mL, the volume of dissolved GP was near the ideal volume decrease of 30%. Based on this result, volumes of greater than 100 mL were used for the remaining batch experiments (with 61-cm-long fiber samples).

The effects of temperature and water bath residence time on GP dissolution are presented in for the Trial 1 (7:3) fibers (*Figure 2*). A higher water temperature more rapidly dissolved the GP, but for all temperatures, GP was completely dissolved within 20-30 seconds. Provided the water bath residence times were at least 20-30 seconds, full extraction was accomplished.

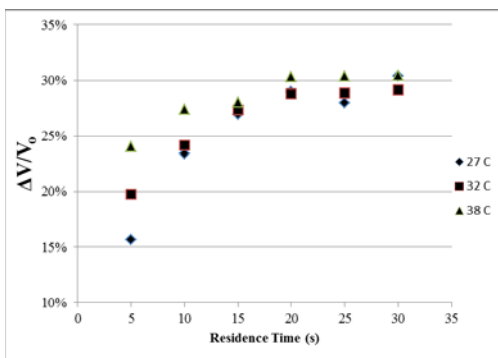


FIGURE 2. Effect of dissolving time and water temperature on GP dissolution. ΔV is the change in volume and V_0 is the original volume.

The relationship between GP dissolution with water bath residence time for Trial 1 fibers (with varying PP-to-GP ratios) at 38°C is shown in *Figure 3*. At higher GP ratios, longer dissolving times were required for complete dissolution. The 1:1 PP-to-GP fiber required the longest dissolving time at 25 seconds. Fibers with ratios of 6:4 and 7:3 reached nearly complete dissolution at 20 seconds. At ratios of 8:2 and 9:1, full dissolution was achieved in only 5 seconds. Even for the highest GP content (1:1), full extraction was accomplished in only 30 seconds.

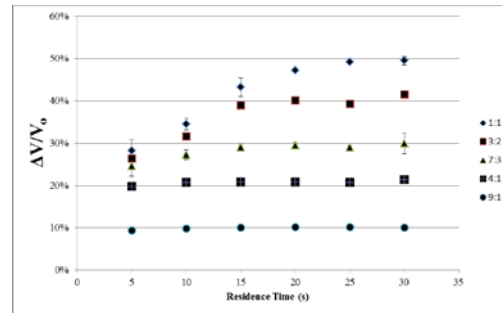


FIGURE 3. GP extraction study for various times and Trial 1 composition ratios at a water temperature of 38°C. ΔV is the change in volume and V_0 is the original volume. Standard error based on five samples.

Microscopy of each Trial 1 fiber's morphology was taken before and after GP extraction (*Figure 4*). The two phase morphology of the virgin fibers provided a unique geometry, with a PP core and reentrant structure, supported by the extractable GP (*Figure 4*, top row). As the ratio of PP to GP increased, the spacing between the fiber's reentrant features decreased, a result of the greater amount of PP in the blend. It was also observed that the fiber's core diameter increased with higher volumes of PP. When comparing the virgin and extracted fiber microscopy images of the Trial 1 fibers (particularly 7:3 and 8:2), the epoxy medium used to reinforce the extracted fibers for microscopy had a low enough viscosity to flow into the reentrant features prior to curing, giving the appearance that no GP dissolved.

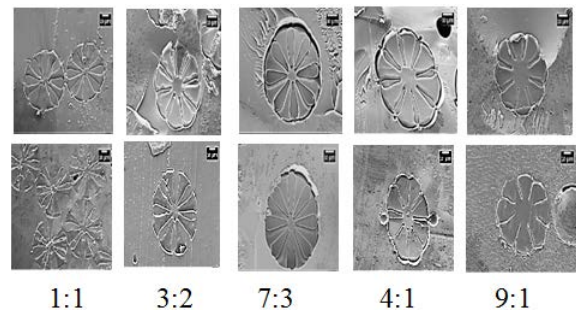


FIGURE 4. SEM images of Trial 1 PP:GP bicomponent fibers of various ratios measured before (top row) and after (bottom row) extraction.

Higher PP-to-GP ratios provided a larger fiber core. The 7:3 fibers seemed to provide high quality reentrant features, but the size of the PP core was rather small. Thus, the extracted fibers may not show good strength properties. When considering mechanical properties, a larger core diameter should give higher mechanical performance. For this reason, the cross section of the fibers was redesigned with a larger core structure (Trials 2-4) (Figure 5). A larger fiber core will be able to contain more reentrant features around the fiber and provide more mechanical integrity.

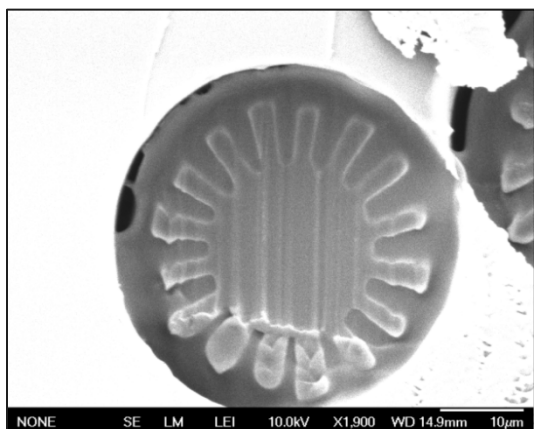


FIGURE 5. Virgin Trial 4 fiber cross-section.

Continuous Fiber Extraction

For a fully scaled manufacturing process, it will be necessary to perform fiber extraction using a continuous process. To develop this process, the use of conventional polymer manufacturing equipment was explored. This equipment consisted of a fiber pay-off system coupled with a puller system that draws the fiber through a 1.5-m-long recirculating water bath that is typically used for cooling in polymer extrusion (Figure 6). The residence time in the water bath was controlled by the speed of the puller. The 30-second-long residence time needed was fairly slow; however, this speed can be easily increased with the use of a longer or multi-pass water bath. The maximum temperature of 38°C was selected based on manufacturing considerations. The continuous extraction process studies compared extraction behavior of the different fiber cross-sectional geometries spun at similar polymer ratios. The first continuous process study (Figure 7) compared Trial 2 and 3 fibers (2:1 ratio). A longer water bath residence time resulted in greater GP dissolution, which was similar to the results from the batch process. After 20 seconds of water bath residence time, the loss in volume became consistent at approximately 33%, indicating full extraction.

These times are similar to those of the batch experiments.



FIGURE 6. Apparatus for continuous GP extraction process: (left) fiber puller system. (center) water bath, and (right) fiber pay-off system.

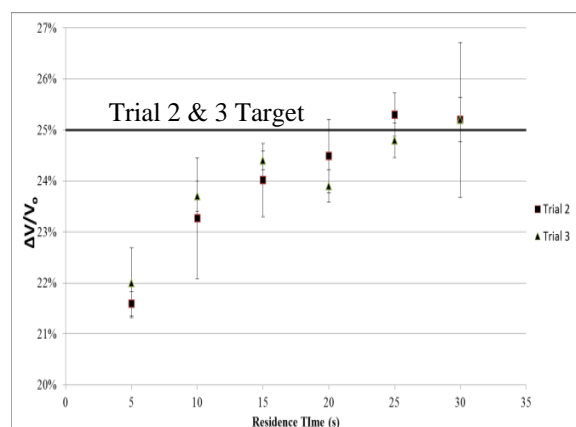


FIGURE 7. Continuous GP extraction study for Trials 2 and 3 fibers at 38°C. ΔV is the change in volume and V_0 is the original volume.

The second continuous process study compared two different geometries: the 16 segmented pie (from Trial 1) and 32 segmented gear (Trial 4) with the same PP-to-GP composition ratio of 1:1 for both batch and continuous processes (Figure 8). Because of the higher GP content, more residence time in the water bath was needed for full extraction (30 seconds) compared to the results from Figure 7. Both batch and continuous processes, however, required the same residence time. The extraction time was independent of fiber cross-sectional geometry provided that the composition was similar. These results indicate the potential of creating superomniphobic fibers in a continuous process.

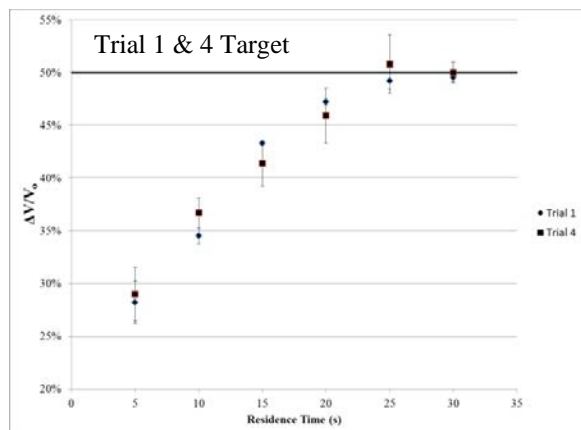


FIGURE 8. Continuous GP extraction study for Trial 4 fibers at 38°C. ΔV is the change in volume and V_0 is the original volume.

CONCLUSION

Bi-component fibers with segmented pie and segmented gear structures were melt extruded using an extractable polymer as one of the components. With water extraction, the soluble component was removed to create unique core designs. The extraction behavior was found to be dependent on temperature, component fraction, and residence time.

Microscopy showed the two phase morphology of the virgin fibers with full extraction revealing the unique geometry of the core, which may provide superomniphobic behavior. As the ratio of PP-to-GP increased, the spacing between the fibers' reentrant features decreased and the fibers' core diameter increased.

Higher water temperature dissolved the water soluble polymer (GP) more quickly, but complete extraction was accomplished within 20-30 seconds. The ratio of PP-to-GP was found to affect the necessary residence time, with higher GP ratios requiring longer dissolving times. The 1:1 PP to GP fiber required the longest dissolving time, however, even for this composition, full extraction was accomplished in just 30 seconds.

A continuous extraction process was designed and investigated. The extraction time for both batch and continuous processes was similar. The extraction time was found to be independent of fiber geometry, but dependent on composition ratio, with higher GP polymer content fibers requiring longer extraction times.

The extraction time depended only on the composition of the fiber. These results indicate the potential of creating superomniphobic fibers in a continuous process.

FUTURE EFFORTS

Work is targeting the creation of a continuous extraction process for knitted fabrics. Early work indicates that a different set of extraction conditions (i.e., time, temperature, and fabric pull speed), and extraction assembly components will likely be required to fully extract the water soluble GP component from the GP-polymer based bicomponent yarns, which are bundles of bicomponent fibers, to achieve an optimal extraction time.

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