

Tuning Surface Properties of Poly(butylene terephthalate) Melt Blown Fibers by Alkaline Hydrolysis and Fluorination

Zaifei Wang, Christopher W. Macosko, and Frank S. Bates*

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, United States

S Supporting Information

ABSTRACT: The wetting properties of poly(butylene terephthalate) (PBT) melt blown fibers were tuned by alkaline hydrolysis and subsequent fluorination. Fiber mats were exposed to a NaOH methanol solution for controlled periods of time at several temperatures, resulting in surface hydrolysis (h-PBT). Subsequent simple solution chemistry was applied to the h-PBT fibers, leading to fluorination of the surface (f-PBT) and the transformation of the wetting properties of the material. Electron microscopy revealed that hydrolysis leads to a textured surface that is retained in the fluorinated product. Sessile drop wetting measurements demonstrated superhydrophilicity for the h-PBT fiber mats and sticky superhydrophobicity with the f-PBT fiber mat.

KEYWORDS: melt blowing, PBT, hydrolysis, fluorination, superhydrophilicity, sticky superhydrophobicity



1. INTRODUCTION

Poly(butylene terephthalate) (PBT) is a strong semicrystalline thermoplastic. It has excellent thermal properties and chemical resistance, good dimensional stability, low moisture absorption, and good electrical and mechanical properties. Because of its facile processability, PBT is widely used in a variety of applications, most commonly in durable products that are formed by injection molding or extrusion, such as electronic equipment, automotive parts, medical devices, and textiles.¹

As a cost-effective engineering material, nonwoven fibers of PBT have been used for filtration medium,² composite materials,^{3–8} and tissue scaffolds.^{9–12} They can be fabricated by melt blowing,¹³ electrospinning,⁵ melt spinning,¹⁴ and forspinning.¹⁵ Among these techniques, melt blowing is of particular interest, because it does not require solvent and is economical. A typical melt blowing process starts with extrusion of a molten polymer through a die. Jets of hot air entrain the molten polymer filament and rapidly extend its length with concomitant reduction in diameter. A significant flow of ambient air, which is entrained by the hot jets, leads to rapid cooling of the fiber below its solidification temperature (i.e., glass transition temperature or crystallization temperature). Thus, fibers are formed between the extrusion temperature and solidification temperature, and finally fiber mats are collected on a static or continuous screen.

Although PBT nonwoven fibers have found uses in a variety of fields, the associated surface properties, such as wetting, biocompatibility, and adsorption, may not meet the requirements for certain targeted applications. Therefore, surface modification plays an important role in improving the surface properties and enhancing the performance of PBT nonwoven fibers. Several techniques have been applied to impart either enhanced hydrophilicity or superhydrophobicity to PBT or other polymeric fibers, such as coating with hydrophilic/

hydrophobic chemicals or particles,^{16–19} physical vapor deposition,^{20,21} chemical vapor deposition,²² addition of low-surface-energy additives through blending,²³ copolymerization,^{24,25} surface grafting,^{26,27} layer-by-layer deposition,²⁸ sol-gel technique,^{29,30} and plasma treatment.^{7,31–35} Another method for modifying the surface wetting properties of polyester materials is alkaline hydrolysis, which has been extensively studied with poly(ethylene terephthalate) (PET) fabrics.^{36–43} However, to the best of our knowledge, this approach has not been applied to modify PBT nonwoven fibers, possibly because PBT woven fabrics are more resistant to aqueous sodium hydroxide solutions than PET woven fabrics.³⁸

In this paper, we report the modification of PBT melt blown fibers by hydrolysis using sodium hydroxide (NaOH) and subsequent fluorination, as illustrated in Figure 1. PBT melt blown fibers were fabricated in our lab and subsequently soaked in NaOH solutions. After hydrolysis, a simple fluorination reaction was conducted. The effects of NaOH hydrolysis on fiber surface morphology, average fiber diameter, mass loss, and structural integrity of the fiber mats was evaluated. Sessile drop measurements revealed that superhydrophilicity was achieved by hydrolysis and sticky superhydrophobicity was obtained by subsequent fluorination. This approach, hydrolysis followed by simple fluorination, offers a facile way to tune the wetting properties of PBT and other polyester fibers.

2. EXPERIMENTAL SECTION

2.1. Fabrication of Melt Blown PBT Fibers. PBT pellets (Celanex 2008, Ticona) were dried at 100 °C for 12 h under vacuum and then melt blown at 265 °C using a previously described lab-scale

Received: April 22, 2014

Accepted: June 26, 2014

Published: June 26, 2014

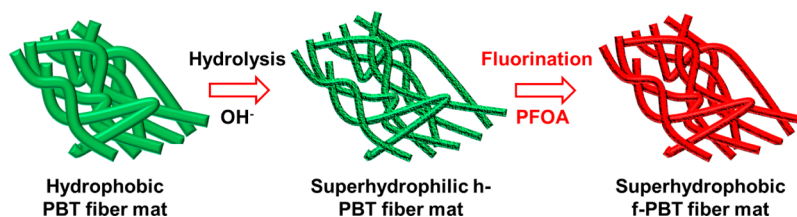


Figure 1. Schematic of the modification of melt blown PBT fibers by alkaline hydrolysis and subsequent fluorination.

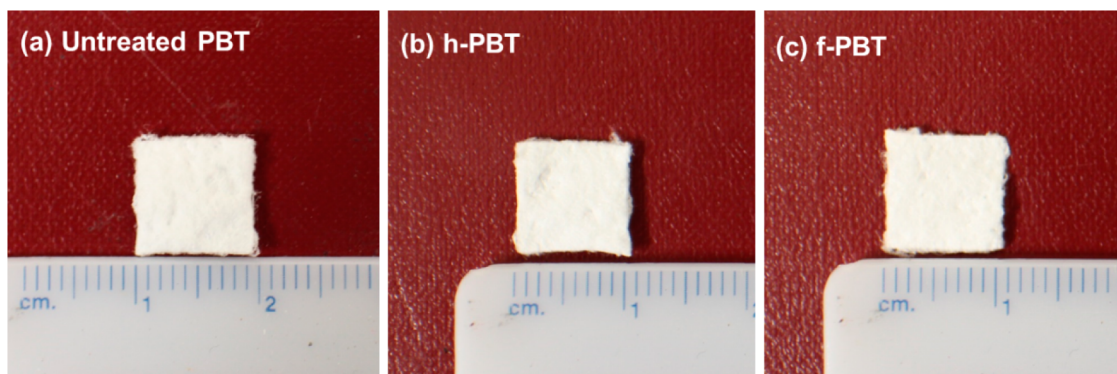


Figure 2. Fiber mat of (a) untreated PBT (b) h-PBT treated at 45 °C for 20 min (c) f-PBT.

apparatus.¹³ The melt blowing die containing five 0.2 mm diameter holes is a modified version of a commercial design.⁴⁴ A stainless steel screen fitted with a blower, located 35 cm away from the melt blowing die, was used to collect the blown fibers, which were generated at a polymer flow rate of 0.18 g/(min-hole) and an air volumetric flow rate of 4.5 SCFM. The air pressure at die exit was kept at about 6 psi.

2.2. NaOH Treatment of PBT Fibers. Melt blown PBT fiber mats were cut into small square pieces (1 × 1 cm and approximately 1 mm thick) and soaked in a methanol solution containing NaOH in a glass vial without stirring. We used methanol as the solvent because alcohols tend to accelerate hydrolysis of polyester.³⁸ NaOH pellets (0.5 g) (Macron Fine Chemicals) were mixed with 2 mL of methanol (Fisher Scientific) and 2 mL of deionized water (pH = 7) and preheated to 45, 50, and 55 °C before soaking the PBT fiber mats for 10, 20, and 30 min. After hydrolysis, the fiber mats were washed three times (1 h soaking each time) with distilled water and then immersed in HCl solution (0.1 mol/L), then washed again with distilled water until neutrality (pH = 7) of the rinse was achieved. Finally, the hydrolyzed PBT (h-PBT) fiber mats were dried in air for 24 h, followed by vacuum drying overnight at 20 °C. All experiments were conducted three times.

2.3. Fluorination of h-PBT Fibers. A piece of h-PBT fiber mat (hydrolyzed at 45 °C for 20 min) was soaked in dimethyl sulfoxide (DMSO) (Sigma-Aldrich) at 80 °C for 24 h. Thirty milligrams of 1H,1H-perfluorooctylamine (PFOA) (Fisher Scientific) and 15 mg of 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM) (Sigma-Aldrich) were dissolved in a mixture of DMSO (6 mL) and methanol (2 mL) with vigorous stirring. The solution was heated to 50 °C and the h-PBT fiber mat was immersed into the solution for 2 h. The fluorinated product, denoted f-PBT, was washed repeatedly with methanol and then distilled water and dried under vacuum for 24 h.

2.4. Characterization of Fibers and Fiber Mats. The square fiber mats were photographed, and the mass was determined using an electric analytical balance (Denver Instrument M-220). Before each measurement, the fiber mats were vacuum-dried overnight at 20 °C. The mass loss (Δm %) was calculated using the following relationship

$$\Delta m\% = \frac{m_0 - m}{m_0} \times 100\% \quad (1)$$

where m_0 is the mass of the unhydrolyzed fiber mat and m is the mass of the h-PBT fiber mat. The porosity (ϵ) and the fiber volume fraction (ϵ_f) were estimated from⁴⁵

$$\epsilon = \left(1 - \frac{w}{A z \rho_{\text{fibers}}} \right) \quad (2)$$

$$\epsilon_f = 1 - \epsilon \quad (3)$$

where ϵ is the porosity of the fiber mat, ϵ_f is the fiber volume fraction, w is the weight of the fiber mat, A and z are the area and thickness of the mat, and ρ_{fibers} is assumed to be the density of bulk PBT (1.4 g/cm³).

PBT and h-PBT fiber mats, dried overnight under vacuum, were analyzed by differential scanning calorimetry (DSC) (TA Instrument Q1000). Heating and cooling scans were controlled from 0 to 250 °C at a constant rate of 10 °C/min. Crystallinity (X_c) was estimated as

$$X_c = \frac{\Delta H_f}{\Delta H_f^\circ} \quad (3)$$

where ΔH_f represents the heat of fusion of the melting peak and $\Delta H_f^\circ = 140$ J/g represents 100% crystalline PBT.⁴⁶

Fiber morphology was determined by a scanning electron microscopy (SEM) (Hitachi S-4700) applied to fiber mats that were coated with gold/palladium for 30 s using a Denton DV-502 sputter coater. For each fiber mat, 25–35 SEM micrographs were taken and 400–500 fiber diameter measurements were made using ImageJ software. Origin Lab software was employed to fit a log-normal function to the distribution of fiber diameters from which the average fiber diameter (d_{av}) and the coefficient of variation (CV) was determined.

X-ray photoelectron spectroscopy (XPS) (Surface Science SSX-100) was employed to determine the surface chemical composition of the h-PBT and f-PBT fiber mats. A monochromatic Al K α source with a spot size of 1 mm was applied at a takeoff angle of 35°, while the pressure of the analysis chamber was maintained at 10⁻¹⁰ Torr. Survey spectra (six scans/sample, 0–1100 eV binding energy) were recorded at a rate of 1 eV/step and the data were processed using Hawk Data Analysis 7 software.

Finally, the wetting properties of the fiber mats were evaluated by sessile drop measurements using a FAMAS interface measurement and

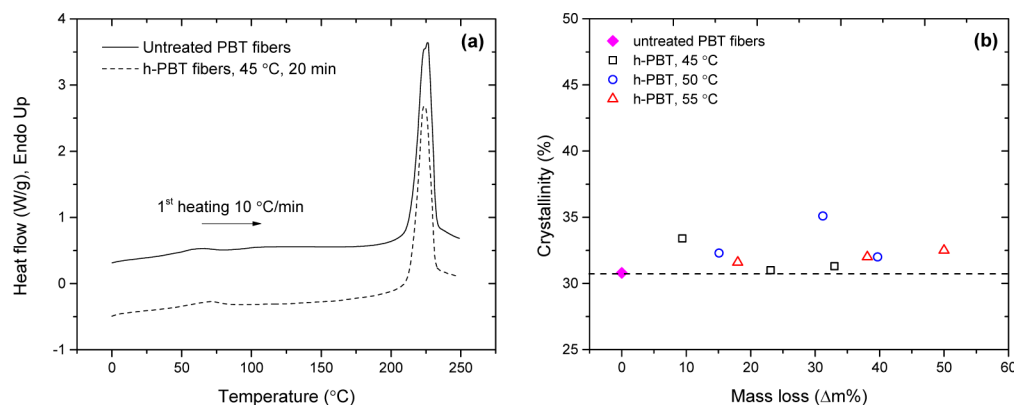


Figure 3. Thermal analysis of (a) PBT and representative h-PBT fibers (b) hydrolysis effect on crystallinity (X_c).

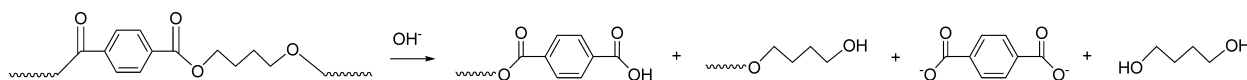


Figure 4. Mechanism of PBT alkaline hydrolysis.

analysis system (Kyowa, DM-CE1). For PBT and the h-PBT fiber mats, the static contact angle (CA) was determined by placing a $5 \mu\text{L}$ water droplet onto the surface of a mat, and images were recorded with a CCD camera. For the f-PBT fiber mats, a $7 \mu\text{L}$ water droplet was used for both static and slide-off angle measurements, and images were captured photographically. Five measurements were taken with each sample.

3. RESULTS AND DISCUSSION

3.1. Size and Integrity of the Fiber Mats. The size and integrity of the PBT fiber mats were relatively insensitive to the conditions of NaOH treatment (i.e., the temperature and duration of the reaction). As shown by the representative photographs in Figure 2, the dimensions of the h-PBT fiber mat treated at $45 \text{ }^\circ\text{C}$ for 20 min are nearly identical to those of the original material. This behavior differs from the situation when PET fabrics are treated with aqueous solutions of NaOH. PET fabrics shrink during NaOH treatment, which has been shown to depend on the crystallinity of the fibers, the duration and the temperature of the treatment, the fiber diameter, and the fabric structure.^{37,43} DSC measurements shown in Figure 3a demonstrate a relatively high degree of crystallinity in the untreated PBT fibers ($X_c = 31\%$), and this value did not change significantly with hydrolysis. In contrast, Hadjizadeh et al.³⁷ reported that recrystallization of melt blown PET fibers ($X_c = 15\%$) during hydrolysis leads to noticeable shrinkage. We attribute the relative stability of the h-PBT fiber mats to several factors, including the higher crystallinity due to fast crystallization,⁴⁷ the mild hydrolysis conditions (i.e., the relatively low NaOH concentration, modest temperature, and short reaction times), and the associated localization of the hydrolysis reaction at the fiber surfaces resulting in the maintenance of the fiber dimensional integrity (see Figure 2). Subsequent fluorination did not affect this property, as shown in Figure 2c.

In addition, thermal analysis indicated that hydrolysis had only a minor impact on the fiber crystallinity, as shown in Figure 3b. Within the experimental uncertainty, X_c increased slightly (ca. 2–4%). In contrast, single poly(lactide) (PLA) or poly(glycolic acid) (PGA) fibers are reported to display a greater increase in crystallinity with hydrolysis.^{48,49}

3.2. Mass Loss and Fiber Diameter. Reacting the melt blown PBT fiber mat with NaOH results in the loss of mass. The most plausible mechanism of PBT alkaline hydrolysis is shown in Figure 4, where hydroxide ions (OH^-) attack carbonyl carbons of the ester linkage, breaking PBT chains and leading to the formation of a carbonate salt of sodium, 1,4-butanediol, and fragmented polymer chains with carboxyl or hydroxyl end groups.⁵⁰

As shown in Figure 5, the mass loss (for $0 \leq \Delta m \leq 60\%$) of the h-PBT fiber mats increases linearly with increasing

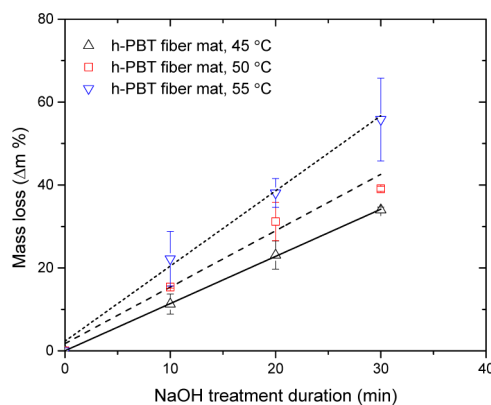


Figure 5. Mass loss (Δm %) of h-PBT fiber mats.

treatment time at a constant temperature, similar to what has been reported during NaOH hydrolysis of PET–cotton spun fabric and PET woven fabrics,^{38,39,51} but contrary to the nonlinear loss of mass reported for PET melt blown fiber mats and single PLA fibers.^{37,48} Alkaline hydrolysis of polyester fabrics and single fibers has been shown to be a surface reaction, where the fiber weight loss increases nonlinearly with respect to the etching time, depending on several factors, including the concentration of OH^- , the fiber surface area relative to the fiber diameter, and the fabric structure.^{36,48,52} We attribute the linear dependence of the mass loss with time ($0 \leq t \leq 30 \text{ min}$) to the relatively constant OH^- concentration associated with the excess NaOH. A more comprehensive

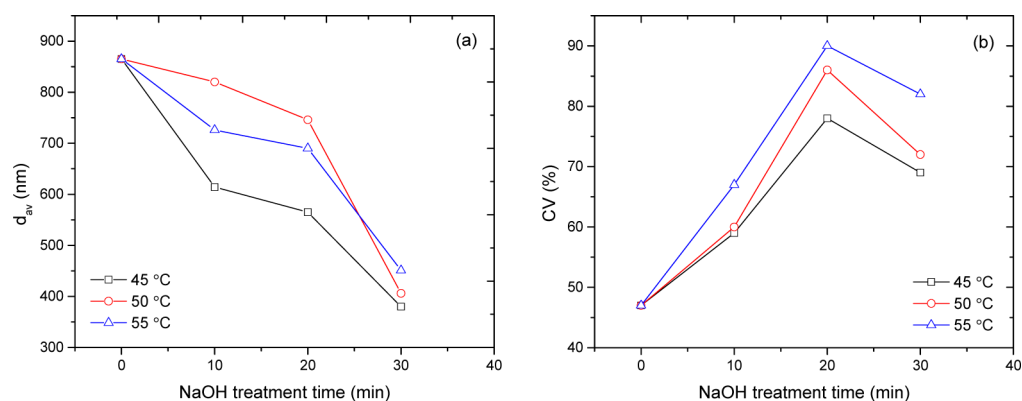


Figure 6. Hydrolysis effect on (a) d_{av} and (b) CV.

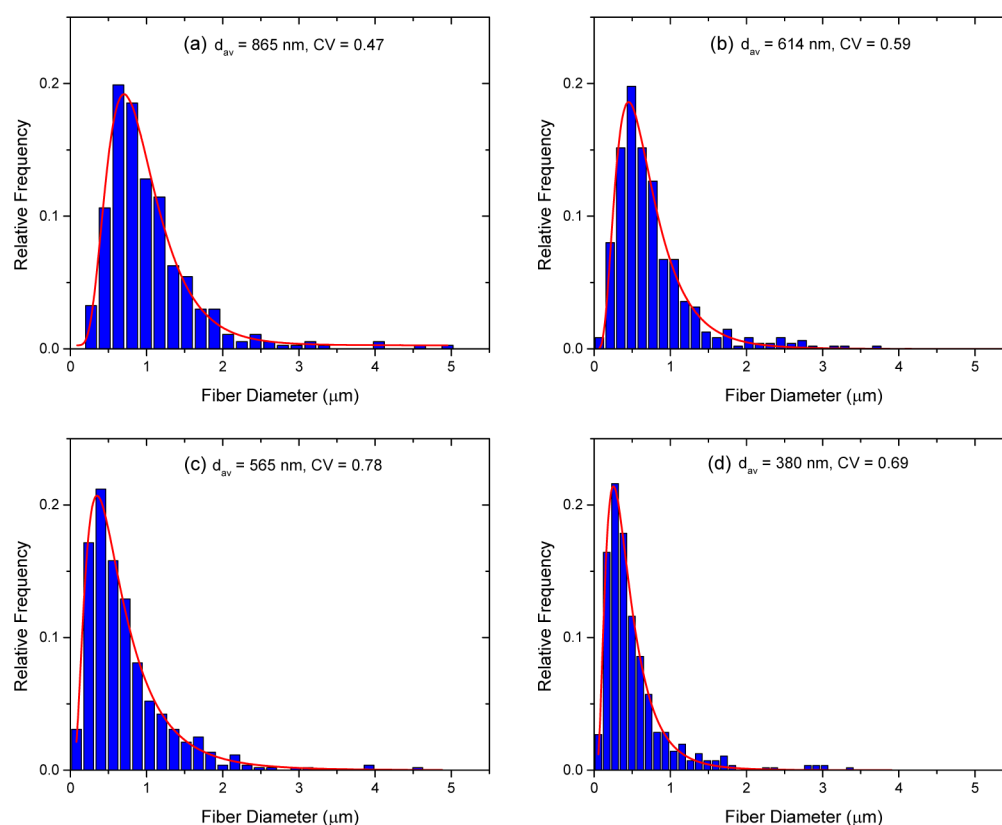


Figure 7. Representative distribution of fiber diameters and associated log-normal function for (a) untreated PBT fibers, (b) h-PBT fibers treated at 45 °C for 10 min, (c) h-PBT treated at 45 °C for 20 min, and (d) h-PBT treated at 45 °C for 30 min.

investigation of these kinetic issues will be reported in the future.

Also shown in Figure 5, the rate of the mass loss increases with increasing reaction temperature, which we attribute to the underlying Arrhenius kinetics.⁴⁸ As the hydrolysis proceeds, the fiber volume fraction (ε_f) decreases from the initial 5.9% for the untreated PBT fiber mat to 2.6% for the h-PBT fiber mats. (see the Supporting Information). This decrease in the fiber volume fraction is due to the mass loss resulting from the fiber surface corrosion as evidenced by no change in the fiber mat size and overall integrity.

Surface hydrolysis also leads to a decrease in fiber diameter and an increase in the distribution of fiber diameters (i.e., the coefficient of variation, CV). As shown in Figures 6 and 7, after 30 min, the average fiber diameter (d_{av}) has been approximately

cut in half with considerably broadening of CV. This behavior supports our hypothesis that NaOH hydrolysis is a surface reaction that proceeds at a constant rate independent of the fiber diameter in the specified reaction periods ($0 \leq t \leq 30$ min). As a consequence, the fractional loss in fiber mass is greater for the smallest fibers, which explains the increase in CV with reaction time, as shown in Figure 6b. Hence, if the reaction was extended to a longer time, the smallest fibers would be completely consumed, eventually degrading the integrity of the entire fiber mat.

Preliminary tensile experiments on the etched fiber mats demonstrate that the mechanical properties are not significantly affected after 10% mass loss (i.e., less than 30% reduction in the tensile strength σ_T and strain at break ε_b), which is beyond the point of full surface wetting modification discussed in the

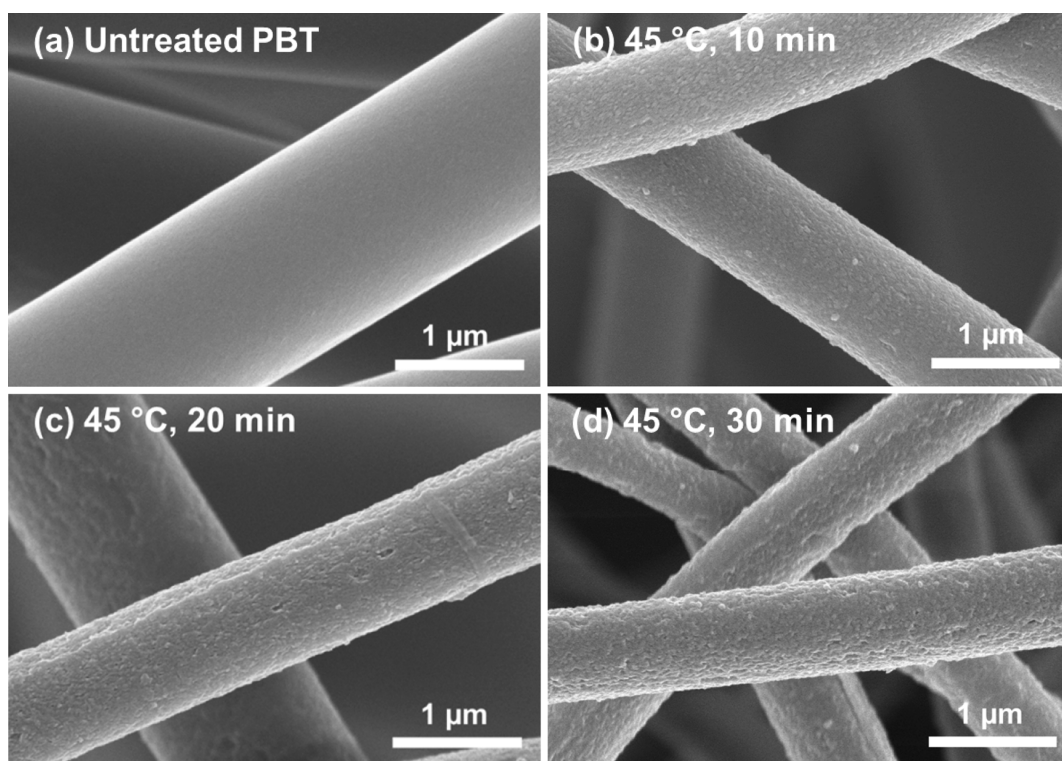


Figure 8. SEM images of (a) untreated PBT fibers, (b) h-PBT fibers treated at 45 °C for 10 min, (c) h-PBT fibers treated at 45 °C for 20 min, and (d) h-PBT fibers treated at 45 °C for 30 min.

following section. A full assessment of the wetting versus mechanical properties correlation will be presented in a future publication.

3.3. Fiber Surface Morphology. Hydrolysis influences the topology of the melt blown PBT fiber surfaces, as shown in the SEM images in Figure 8. The relatively smooth surfaces of the untreated PBT fibers are etched by the reaction, resulting in a textured, sponge-like interface. This process resembles the corrosion of a metal surface, where the reaction rate depends on the crystal grain orientation.^{53,54} We postulate that the amorphous and low-crystallinity regions react more readily with OH⁻ than the less accessible ordered crystals, as reported in other studies.³⁶ Preferential fast hydrolysis produces a sponge-like surface, which becomes more dramatic with the extent of mass loss as seen in Figure 8. Interestingly, this behavior has not been reported for NaOH treated melt blown fibers of PBT, which we attribute to quantitative differences in the reactivity and crystallinity of each polyester. We speculate that the detailed rate of etching of the amorphous versus crystalline domains will strongly influence the development of surface roughness and porosity by analogy with the trade-off between fundamental reaction kinetics and morphology, which contributes to the processes operating during the corrosion of metals.^{55–57}

3.4. Superhydrophilicity of h-PBT Fiber Mats. Surface hydrolysis modifies the surface morphology and the wetting properties of the fiber mats. On the basis of the contact angle (CA) criterion used to define hydrophobic materials, $CA_{\text{hydrophobic}} > 90^\circ$,⁵⁸ the unmodified PBT melt blown fiber mats are hydrophobic, where $CA_{\text{PBT fiber mats}} = 126 \pm 4^\circ$ (see Figure 9). We attribute this property to the surface roughness of the fiber mat.⁵⁹ Hydrolysis of the PBT fiber mats significantly enhances the hydrophilicity, as shown in Figure 10, where

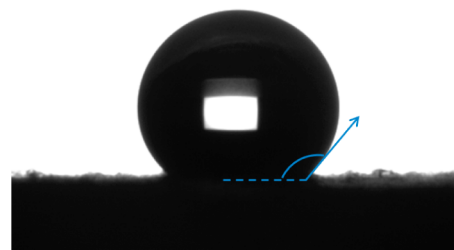


Figure 9. Sessile drop measurement on untreated PBT fiber mat, $CA_{\text{PBT fiber mat}} = 126 \pm 4^\circ$.

water droplets that are deposited are spontaneously sucked into the h-PBT fiber mats. This wickability is directly tied to the presence of polar carboxyl and hydroxyl moieties generated during surface hydrolysis. Another contributing factor is the sponge-like surface and the overall roughness, which adds to the surface area and the hydrophilicity of the fiber mats.^{60,61} In addition, the high porosity associated with the low fiber volume fraction results in capillary phenomenon that enhances the spontaneous spreading and absorption of the droplet. We therefore classify the h-PBT fiber mats as superhydrophilic.⁶²

In detail, the rate at which water is drawn into the h-PBT fiber mats is correlated with the time of NaOH treatment, i.e., water is sucked into the mat treated for 20 min much more rapidly than the one etched for 10 min, as shown in Figure 10, both at 45 °C. However, there was no significant difference between the mats treated for 20 and 30 min, and this trend was duplicated at 50 and 55 °C. We postulate these features reflect the combined effects of the fiber surface roughness, d_{av} , porosity and pore size, and water droplet volume.^{63,64} A comprehensive evaluation of the spreading and wicking kinetics is beyond the scope of this paper.

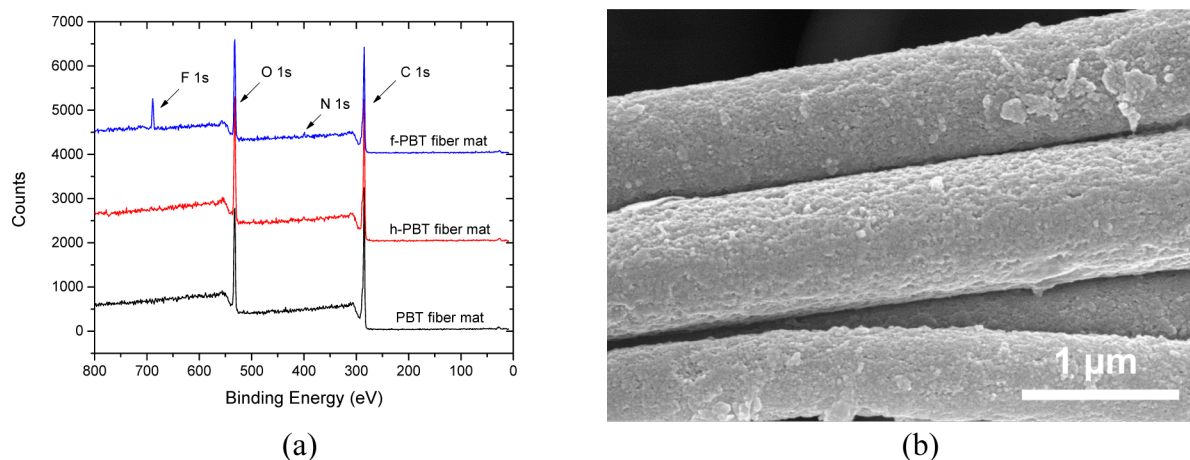


Figure 12. Surface analysis of f-PBT fibers of (a) chemical composition by XPS and (b) physical structure by SEM.

To investigate the effect of fluorination on the wetting properties of the fiber mat, we measured the water contact angle. $CA_{f\text{-PBT fiber mat}} = 156 \pm 5^\circ$, as shown in Figure 13,

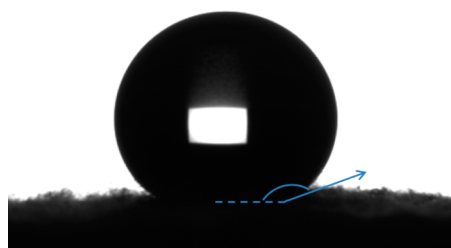


Figure 13. Sessile drop measurement on f-PBT fiber mat, $CA_{f\text{-PBT fiber mat}} = 156 \pm 5^\circ$.

confirming a superhydrophobic surface character.^{67,68} To evaluate the slide-off angle, we tilted, and even inverted, the substrate, yet the water droplet always remained attached to the surface. This demonstrates simultaneous superhydrophobicity and a high level of droplet adhesion for the f-PBT fiber mat. Such sticky superhydrophobicity has been reported on rose petals and peanut leaves.^{67,69,70} We speculate that the sticky behavior of the f-PBT fiber mat results from the nanoscale and microscale roughness associated with the sponge-like surface topology. Presumably, these little “sponge bumps” on the surface of each fiber are not large enough to mimic the lotus leaf, hair-like nanostructure that leads to roll-off superhydrophobicity.⁷¹ Because of this special sponge-like surface roughness, the three-phase contact line of water droplets on the fiber mat is quasi-continuous at the microscale but discontinuous at the nanoscale, creating a Cassie impregnating wetting state also known as the petal effect.^{69,70}

4. SUMMARY

We have described a facile approach to tuning the surface wetting properties of melt blown PBT fibers based on NaOH hydrolysis and subsequent fluorination with PFOA. Hydrolysis leads to mass loss and increased porosity without disrupting the original overall size and integrity of the material. Etching the fiber mat for 30 min reduced the average fiber diameter to less than half its initial diameter (865 nm). At the same time, hydrolysis creates a textured, sponge-like fiber surface decorated with hydrophilic carboxyl and hydroxyl groups.

This combination of chemical and physical surface modification imparts superhydrophilicity. Subsequent reaction with PFOA leads to a sticky superhydrophobic surface. This approach, melt blowing followed by hydrolysis and simple fluorination, should be generally applicable with many types of polyester fabrics. In addition, it offers the opportunity to prepare composite materials, such as hydrophobic/hydrophilic filtration media.

■ ASSOCIATED CONTENT

Supporting Information

A summary of the hydrolysis effects on the average fiber diameter, the fiber diameter distribution, the porosity, and the fiber volume fraction along with the fiber surface morphology of the h-PBT fibers treated at 50 and 55 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*F. S. Bates. E-mail: bates001@umn.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge Cummins Filtration for financial support. Contact angle measurements were performed in the lab of Dr. Conrado Aparicio in the Dental Research Center for Biomaterials and Biomechanics at University of Minnesota, Twin Cities. Parts of this work (SEM, XPS) were carried out in the Characterization Facility, University of Minnesota, which receives partial support from the National Science Foundation through the Materials Research Science and Engineering Center (NSF-MRSEC) program.

■ REFERENCES

- (1) Gallucci, R. R.; Patel, B. R. Poly(butylene terephthalate). In *Modern polyesters: Chemistry and Technology of Polyesters and Copolyesters*; Scheirs, J., Long, T. E., Eds.; Wiley: West Sussex, U. K., 2003; pp 293–322.
- (2) Hutten, I. M. Processes for Nonwoven Filter Media. *Handbook of Nonwoven Filter Media*; Elsevier: Burlington, MA, 2007; pp 195–244.
- (3) Zuo, F.; Tan, D. H.; Wang, Z.; Jeung, S.; Macosko, C. W.; Bates, F. S. Nanofibers from Melt Blown Fiber-in-Fiber Polymer Blends. *ACS Macro Lett.* **2013**, *2*, 301–305.

- (4) Doan, V. A.; Nobukawa, S.; Yamaguchi, M. Localization of Nanofibers on Polymer Surface using Interface Transfer Technique. *Composites, Part B* **2012**, *43*, 1218–1223.
- (5) Saligheh, O.; Arasteh, R.; Forouharshad, M.; Farsani, R. E. Poly(butylene terephthalate)/Single Wall Carbon Nanotubes Composite Nanofibers by Electrospinning. *J. Macromol. Sci., Phys.* **2011**, *50*, 1031–1041.
- (6) Guo, S.; Ke, Q.; Wang, H.; Jin, X.; Li, Y. Poly(butylene terephthalate) Electrospun/Melt-Blown Composite Mats for White Blood Cell Filtration. *J. Appl. Polym. Sci.* **2013**, *128*, 3652–3659.
- (7) Kim, E. J.; Yeo, G.-d.; Pai, C.-m.; Kang, I.-k. Preparation of Surface-Modified Poly(butylene terephthalate) Nonwovens and Their Application as Leukocyte Removal Filters. *J. Biomed. Mater. Res., Part B* **2009**, *90B*, 849–856.
- (8) Risbud, M.; Nabi Saheb, D.; Jog, J.; Bionde, R. Preparation, Characterization and in Vitro Biocompatibility Evaluation of Poly-(butylene terephthalate)/Wollastonite Composites. *Biomaterials* **2001**, *22*, 1591–1597.
- (9) Catalani, L. H.; Collins, G.; Jaffe, M. Evidence for Molecular Orientation and Residual Charge in the Electrospinning of Poly-(butylene terephthalate) Nanofibers. *Macromolecules* **2007**, *40*, 1693–1697.
- (10) Woodfield, T. B. F.; Malda, J.; de Wijn, J.; Péters, F.; Riesle, J.; van Blitterswijk, C. A. Design of Porous Scaffolds for Cartilage Tissue Engineering using a Three-Dimensional Fiber-Deposition Technique. *Biomaterials* **2004**, *25*, 4149–4161.
- (11) Ikada, Y.; Tsuji, H. Biodegradable Polyesters for Medical and Ecological Applications. *Macromol. Rapid Commun.* **2000**, *21*, 117–132.
- (12) Hollister, S. J. Porous Scaffold Design for Tissue Engineering. *Nat. Mater.* **2005**, *4*, 518–524.
- (13) Ellison, C. J.; Phatak, A.; Giles, D. W.; Macosko, C. W.; Bates, F. S. Melt Blown Nanofibers: Fiber Diameter Distributions and Onset of Fiber Breakup. *Polymer* **2007**, *48*, 3306–3316.
- (14) Chen, S.; Spruiell, J. E. Structure and Properties of High-Speed Melt-Spun Filaments of Poly(butylene terephthalate). *J. Appl. Polym. Sci.* **1987**, *33*, 1427–1444.
- (15) Shanmuganathan, K.; Fang, Y.; Chou, D. Y.; Sparks, S.; Hibbert, J.; Ellison, C. J. Solventless High Throughput Manufacturing of Poly(butylene terephthalate) Nanofibers. *ACS Macro Lett.* **2012**, *1*, 960–964.
- (16) Mari, I. G.; It, M.; Mathieu, B.; De, S. Filter for the Removal of Substances from Blood Products. U.S. Patent 7,524,425 B2, April 28, 2009.
- (17) Ramaratnam, K.; Tsyalkovsky, V.; Klep, V.; Luzinov, I. Ultrahydrophobic Textile Surface via Decorating Fibers with Monolayer of Reactive Nanoparticles and Non-Fluorinated Polymer. *Chem. Commun.* **2007**, 4510–4512.
- (18) De, N.; Oles, M.; Schleich, B.; De, R. Textile Substrates Having Self-Cleaning Properties. U.S. Patent 7,842,624 B2, November 30, 2010.
- (19) Shin, B.; Lee, K.-R.; Moon, M.-W.; Kim, H.-Y. Extreme Water Repellency of Nanostructured Low-Surface-Energy Non-Woven Fabrics. *Soft Matter* **2012**, *8*, 1817–1823.
- (20) Jiang, S. X.; Qin, W. F.; Guo, R. H.; Zhang, L. Surface Functionalization of Nanostructured Silver-Coated Polyester Fabric by Magnetron Sputtering. *Surf. Coat. Technol.* **2010**, *204*, 3662–3667.
- (21) Huang, F.; Wei, Q.; Liu, Y.; Gao, W.; Huang, Y. Surface Functionalization of Silk Fabric by PTFE Sputter Coating. *J. Mater. Sci.* **2007**, *42*, 8025–8028.
- (22) Ma, M.; Mao, Y.; Gupta, M.; Gleason, K. K.; Rutledge, G. C. Superhydrophobic Fabrics Produced by Electrospinning and Chemical Vapor Deposition. *Macromolecules* **2005**, *38*, 9742–9748.
- (23) Hardman, S. J.; Muhamad-sarih, N.; Riggs, H. J.; Thompson, R. L.; Rigby, J.; Bergius, W. N. A.; Hutchings, L. R. Electrospinning Superhydrophobic Fibers Using Surface Segregating End-Functionalized Polymer Additives. *Macromolecules* **2011**, *44*, 6461–6470.
- (24) Zambianchi, I. L.; It, R. E.; Bonaguidi, P.; It, P.; It, M. Filter for the Removal of Substances from Blood Products. U.S. Patent 7,736,516 B2, June 15, 2010.
- (25) Ma, M.; Hill, R. M.; Lowery, J. L.; Fridrikh, S. V.; Rutledge, G. C. Electrospun Poly(styrene-block-dimethylsiloxane) Block Copolymer Fibers Exhibiting Superhydrophobicity. *Langmuir* **2005**, *21*, 5549–5554.
- (26) Fareghi, A. R.; Moghaddam, P. N.; Entezami, A. A.; Avval, M. E. Modification of Hydrophilic Cellulose Fibers by Monolayer Growth of Polystyrene Chains using ATRP. *Iran. Polym. J.* **2013**, *22*, 361–367.
- (27) Bongiovanni, R.; Marchi, S.; Zeno, E.; Pollicino, A.; Thomas, R. R. Water Resistance Improvement of Filter Paper by A UV-Grafting Modification with A Fluoromonomer. *Colloids Surf., A* **2013**, *418*, 52–59.
- (28) Li, H.; Fu, S.; Peng, L.; Zhan, H. Surface Modification of Cellulose Fibers with Layer-by-Layer Self-Assembly of Lignosulfonate and Polyelectrolyte: Effects on Fibers Wetting Properties and Paper Strength. *Cellulose* **2012**, *19*, 533–546.
- (29) Vasiljević, J.; Gorjanc, M.; Tomšič, B.; Orel, B.; Jerman, I.; Mozetič, M.; Vesel, A.; Simončič, B. The Surface Modification of Cellulose Fibres to Create Super-Hydrophobic, Oleophobic and Self-Cleaning Properties. *Cellulose* **2013**, *20*, 277–289.
- (30) Raghavanpillai, A.; Franco, V. A.; Meredith, W. E. Hydrophobic and Oleophobic Surface Modification using Gelling Agents Derived from Amino Acids. *J. Fluorine Chem.* **2012**, *135*, 187–194.
- (31) Fernández-Blázquez, J. P.; Fell, D.; Bonaccorso, E.; Campo, A. d. Superhydrophilic and Superhydrophobic Nanostructured Surfaces via Plasma Treatment. *Adv. Colloid Interface Sci.* **2011**, *357*, 234–238.
- (32) Wei, X.; Zhao, B.; Li, X.-M.; Wang, Z.; He, B.-Q.; He, T.; Jiang, B. CF₄ Plasma Surface Modification of Asymmetric Hydrophilic Polyethersulfone Membranes for Direct Contact Membrane Distillation. *J. Membr. Sci.* **2012**, *407–408*, 164–175.
- (33) Salvagnini, C.; Roback, A.; Momtaz, M.; Pourcelle, V.; Marchand-Brynaert, J. Surface Functionalization of a Poly(butylene terephthalate)(PBT) Melt-Blown Filtration Membrane by Wet Chemistry and Photo-Grafting. *J. Biomater. Sci., Polym. Ed.* **2007**, *18*, 1491–1516.
- (34) Gérard, E.; Bessy, E.; Hénard, G.; Ducoroy, L.; Verpoort, T.; Marchand-Brynaert, J. Surface Modification of Poly(butylene terephthalate) Nonwoven by Photochemistry and Biofunctionalization with Peptides for Blood Filtration. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 5087–5099.
- (35) Liu, H.; Zheng, Y.; Gurgel, P. V.; Carbonell, R. G. Affinity Membrane Development from PBT Nonwoven by Photo-Induced Graft Polymerization, Hydrophilization and Ligand Attachment. *J. Membr. Sci.* **2013**, *428*, 562–575.
- (36) Ng, R.; Zhang, X.; Liu, N.; Yang, S.-T. Modifications of Nonwoven Polyethylene Terephthalate Fibrous Matrices via NaOH Hydrolysis: Effects on Pore Size, Fiber Diameter, Cell Seeding and Proliferation. *Process Biochem.* **2009**, *44*, 992–998.
- (37) Hadjizadeh, A.; Ajjai, A.; Bureau, M. N. Preparation and Characterization of NaOH Treated Micro-Fibrous Polyethylene Terephthalate Nonwovens for Biomedical Application. *J. Mech. Behav. Biomed. Mater.* **2010**, *3*, 574–583.
- (38) Shukla, S. R.; Mathur, M. R. Action of Alkali on Polybutylene Terephthalate and Polyethylene Terephthalate Polyesters. *J. Appl. Polym. Sci.* **2000**, *75*, 1097–1102.
- (39) Dave, J.; Kumar, R.; Srivastava, H. C. Studies on Modification of Polyester Fabrics I: Alkaline Hydrolysis. *J. Appl. Polym. Sci.* **1987**, *33*, 455–477.
- (40) Holmes, S.; Zeronian, S. Surface Area of Aqueous Sodium Hydroxide Hydrolyzed High-Speed Spun Poly(ethylene terephthalate) Fibers. *J. Appl. Polym. Sci.* **1995**, *55*, 1573–1581.
- (41) Kotek, R.; Jung, D.-W.; Kim, J. H.; Smith, B.; Guzman, P.; Schmidt, B. Surface Hydrolysis of Filaments Based on Poly-(trimethylene terephthalate) Spun at High Spinning Speeds. *J. Appl. Polym. Sci.* **2004**, *92*, 1724–1730.

- (42) Tavanai, H. A New Look at the Modification of Polyethylene Terephthalate by Sodium Hydroxide. *J. Text. Inst.* **2009**, *100*, 633–639.
- (43) Kim, E. S.; Lee, C. H.; Kim, S. H. Effects of Pretreatment Reagents on the Hydrolysis and Physical Properties of PET Fabrics. *J. Appl. Polym. Sci.* **2009**, *112*, 3071–3078.
- (44) Keller, J. P.; Buntin, R. R. Melt-Blowing Die for Producing Nonwoven Mats. U.S. Patent 3,825,380, July 23, 1974.
- (45) Barhate, R.; Loong, C. K.; Ramakrishna, S. Preparation and Characterization of Nanofibrous Filtering Media. *J. Membr. Sci.* **2006**, *283*, 209–218.
- (46) Illers, K.-H. Heat of Fusion and Specific Volume of Poly(ethylene terephthalate) and Poly(butylene terephthalate). *Colloid Polym. Sci.* **1980**, *258*, 117–124.
- (47) Chuah, H. H. Crystallization Kinetics of Poly(trimethylene terephthalate). *Polym. Eng. Sci.* **2001**, *41*, 308–313.
- (48) Sun, S.-P.; Wei, M.; Olson, J. R.; Shaw, M. T. Alkali Etching of a Poly(lactide) Fiber. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1572–1578.
- (49) Ginde, R. M.; Gupta, R. K. In Vitro Chemical Degradation of Poly(glycolic acid) Pellets and Fibers. *J. Appl. Polym. Sci.* **1987**, *33*, 2411–2429.
- (50) Goje, A. S.; Chauhan, Y. P.; Mishra, S. Chemical Recycling and Kinetics of Aqueous Alkaline Depolymerization of Poly(Butylene Terephthalate) Waste. *Chem. Eng. Technol.* **2004**, *27*, 790–799.
- (51) Namboori, C.; Haith, M. S. Steric Effects in the Basic Hydrolysis of Poly(ethylene terephthalate). *J. Appl. Polym. Sci.* **1968**, *12*, 1999–2005.
- (52) Kallay, N.; Grancari, A. M.; Tomi, M. Kinetics of Polyester Fiber Dissolution. *Text. Res. J.* **1990**, *60*, 663–668.
- (53) Park, H.; Szpunar, J. The Role of Texture and Morphology in Optimizing the Corrosion Resistance of Zinc-Based Electroplated Coatings. *Corros. Sci.* **1998**, *40*, 525–545.
- (54) Abayarathna, D.; Hale, E.; O'Keefe, T.; Wang, Y.-M.; Radovic, D. Effects of Sample Orientation on the Corrosion of Zinc in Ammonium Sulfate and Sodium Hydroxide Solutions. *Corros. Sci.* **1991**, *32*, 755–768.
- (55) Frankel, G. S. Pitting Corrosion of Metals: A Review of the Critical Factors. *J. Electrochem. Soc.* **1998**, *145*, 2186–2198.
- (56) Burstein, G.; Pistorius, P. Surface Roughness and the Metastable Pitting of Stainless Steel in Chloride Solutions. *Corrosion* **1995**, *51*, 380–385.
- (57) Sasaki, K.; Burstein, G. The Generation of Surface Roughness During Slurry Erosion-Corrosion and Its Effect on the Pitting Potential. *Corros. Sci.* **1996**, *38*, 2111–2120.
- (58) Quéré, D.; Reyssat, M. Non-Adhesive Lotus and Other Hydrophobic Materials. *Philos. Trans. R. Soc., A* **2008**, *366*, 1539–1556.
- (59) Cassie, A.; Baxter, S. Wettability of Porous Surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546–551.
- (60) Quéré, D. Wetting and Roughness. *Annu. Rev. Mater. Res.* **2008**, *38*, 71–99.
- (61) Miwa, M.; Nakajima, A.; Fujishima, A.; Hashimoto, K. Effects of the Surface Roughness on Sliding Angles of Water Droplets on Superhydrophobic Surfaces. *Langmuir* **2000**, *16*, 5754–5760.
- (62) Drelich, J.; Chibowski, E. Superhydrophilic and Superwetting Surfaces: Definition and Mechanisms of Control. *Langmuir* **2010**, *26*, 18621–18623.
- (63) Kissa, E. Wetting and Wicking. *Text. Res. J.* **1996**, *66*, 660–668.
- (64) Patnaik, A.; Rengasamy, R.; Kothari, V.; Ghosh, A. Wetting and Wicking in Fibrous Materials. *Text. Prog.* **2006**, *38*, 1–105.
- (65) Burrell, M. C.; Chera, J. J. Polybutylene Terephthalate (PBT) Spin Cast Films by XPS. *Surf. Sci. Spectra* **1999**, *6*, 5–8.
- (66) Chen, W.; McCarthy, T. J. Chemical Surface Modification of Poly(ethylene terephthalate). *Macromolecules* **1998**, *31*, 3648–3655.
- (67) Balu, B.; Breedveld, V.; Hess, D. W. Fabrication of “Roll-off” and “Sticky” Superhydrophobic Cellulose Surfaces via Plasma Processing. *Langmuir* **2008**, *24*, 4785–4790.
- (68) Lafuma, A.; Quéré, D. Superhydrophobic States. *Nat. Mater.* **2003**, *2*, 457–460.
- (69) Feng, L.; Zhang, Y.; Xi, J.; Zhu, Y.; Wang, N.; Xia, F.; Jiang, L. Petal Effect: A Superhydrophobic State with High Adhesive Force. *Langmuir* **2008**, *24*, 4114–4119.
- (70) Yang, S.; Ju, J.; Qiu, Y.; He, Y.; Wang, X.; Dou, S.; Liu, K.; Jiang, L. Peanut Leaf Inspired Multifunctional Surfaces. *Small* **2014**, *10*, 294–299.
- (71) Bhushan, B.; Her, E. K. Fabrication of Superhydrophobic Surfaces with High and Low Adhesion Inspired from Rose Petal. *Langmuir* **2010**, *26*, 8207–8217.