

Comparison of three methods for generating superhydrophobic, superoleophobic nylon nonwoven surfaces

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Abstract This research deals with creating a superhydrophobic/superoleophobic surface by preparing a metastable Cassie–Baxter (CB) surface. To create a CB surface it is essential to have low surface energy and properly constructed surface morphology. We have explored three different techniques to achieve superhydrophobicity and superoleophobicity using hydroentangled nylon nonwoven fabric: pulsed plasma polymerization of 1H,1H,2H,2H-perfluorodecyl acrylate (PFAC8), microwave-assisted condensation of 1H,1H,2H,2H-perfluorodecyltrimethoxysilane (FS), and FS condensation through wet processing. Nonwoven fabric materials prepared using these three techniques were superhydrophobic and superoleophobic as shown by their very high contact angles for both water (contact angles of 168–174°) and dodecane (contact angles of 153–160°). The measured contact angles agree with the predicted values obtained through designing a CB surface.

Introduction

A surface is defined as superhydrophobic if the water contact angle exceeds 150° [1–3]. If the same (>150°) contact angle is obtained with oil, the surface is said to be superoleophobic [4]. Often low-molecular-weight alkanes are used as “oils” to probe oleophobicity since they are non-polar, low-surface-energy liquids (LSEs). Although many authors suggest that the definition of superhydrophobic behavior includes low roll-off angles (<5°) without specifying drop volumes or weights [1, 2], Lee and Michielsen [5] reported that the roll-off angle depends on the weight of the liquid. Since the drop size to be used for determining the roll-off angle has not been defined, we do not use roll-off angles in our definition of superhydrophobic or superoleophobic surface, but rather discuss the relationship between the contact and roll-off angles. This study focuses on creating superhydrophobic and superoleophobic surfaces that have water and dodecane contact angles greater than 150°. The self-cleaning ability obtained as the result of superoleophobic surface properties of the material helps rid the surface of oil contamination.

High contact angles are achieved by reducing the surface energy of the solid surface and increasing its roughness in an appropriate manner, thus reducing wetting. The Wenzel [6] and the Cassie–Baxter (CB) [7] models are often used to describe the wetting behavior of rough surfaces [8–12]. In the Wenzel model, the liquid completely fills the grooves of a rough surface and completely wets the surface, whereas in the CB model, a liquid sits on top of a composite surface consisting of air pockets and the top of the rough surface. The apparent contact angle on a CB surface, θ_r^{CB} , can be described as [7]:

$$\cos \theta_r^{CB} = f_1 \cos \theta_e - f_2 \quad (1)$$

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where θ_e is Young's contact angle for a flat surface of the same composition, f_1 is the ratio of the surface area of the liquid in contact with the solid to the total projected area, and f_2 is the ratio of the surface area of the liquid in contact with air to the total projected area. If $f_2 = 0$ in Eq. 1, that is, there are no air pockets between the liquid and the surface, then the liquid completely wets the surface. In this case the surface behaves as a Wenzel surface and the apparent contact angle becomes the apparent Wenzel contact angle, θ_r^W [6]:

$$\cos \theta_r^W = r \cos \theta_e \quad (2)$$

where r , the roughness factor, is the ratio of the area in contact with the liquid divided by the projected area. For a rough surface, $r > 1$. In other words, if $f_2 = 0$ in Eq. 1, then r in Eq. 2 equals f_1 of Eq. 1. According to the Wenzel model (Eq. 2), if θ_e is $<90^\circ$ and the roughness factor is increased, the apparent Wenzel contact angle decreases to 0° . However, in the CB model the apparent contact angle increases irrespective of the initial contact angle when the roughness is increased. Whether the material follows the Wenzel model or the CB model at equilibrium depends on which system has the lower free energy. According to Marmur's analysis, a surface can exhibit true superhydrophobicity or superoleophobicity with a particular liquid only if the contact angle between them is obtuse, $\theta_e > 90^\circ$ [13]. However, for some systems it has been observed that the lowest free energy is predicted by the Wenzel model [14, 15] but the observed behavior follows the CB model. For example, $\theta_e < 90^\circ$ for many liquids on nylon, but they still exhibit apparent contact angles greater than 90° . This condition is called the metastable CB state. Whenever a water droplet is placed on a hydrophilic surface or an oil droplet is placed on an oleophilic surface (θ_e is $<90^\circ$) and the surface behaves as a CB model, a metastable CB state occurs. It is not yet clear what determines when a particular surface will exhibit metastable CB behavior, but such surfaces are useful for shedding oily materials. Another important result from Eq. 1 is the prediction that it is much easier to make a superhydrophobic material than a superoleophobic material, because θ_e (water) $>$ θ_e (oil). This implies that all superoleophobic materials are superhydrophobic, but not the converse.

The objective of this study is to prepare superhydrophobic/superoleophobic hydroentangled nylon nonwoven fabrics. Nonwoven fabrics are engineered fabrics made directly from fiber or fiber webs without first making a yarn. For strength, nonwoven fabrics must be bonded. Hydroentangling is one of the fastest-growing bonding methods in recent years. In this method, fabric is produced by subjecting a web of loose fibers to high pressure water jets. The impact force of the water jets causes the fibers to

entangle, bonding the fibers together by frictional forces [16]. Although polypropylene and polyester have been the major raw materials for nonwovens, polymers such as nylon are increasingly used to produce nonwoven fabrics for different applications [8].

Nylon is naturally hydrophilic, so it is essential that the surface be treated with hydrophobic materials to offset the hydrophilicity of nylon. The $-NH_2$ end groups present in nylon facilitate dyeing and finishing of the nonwoven fabric. We report on three chemical modification techniques as approaches for making superoleophobic hydroentangled nylon nonwovens: (a) pulsed plasma polymerization of 1H,1H,2H,2H-perfluorodecyl-acrylate (PFAC8), (b) microwave-assisted grafting of 1H,1H,2H,2H-perfluorodecyl-trimethoxysilane (FS) nanoparticles, and (c) FS grafting via wet processing. Attaching these fluorochemicals to surfaces should reduce the surface energy of the fabric and will potentially generate superhydrophobic and superoleophobic materials.

Experimental

Materials

Nylon 6,6 film (M_n : 12 kDa, Dupont Canada) and hydroentangled nylon nonwoven fabric (Nonwoven Institute, NCSU) were used as the smooth and rough surfaces, respectively. PFAC8 ($C_8F_{17}CH_2CH_2CO_2CH=CH_2$, Fluorochem, Derbyshire, UK), FS ($C_8F_{17}CH_2CH_2Si(OCH_3)_3$, Gelest), tetramethyl orthosilicate (TMOS, $Si(OCH_3)_4$, Aldrich), ammonium hydroxide (NH_4OH , Mallinckrodt Chemical, Raleigh, NC, USA), methanol (CH_3OH , Aldrich), isopropyl alcohol (C_3H_7OH , Fisher), poly(acrylic acid, PAA) ($(C_3H_4O_2)_n$, Aldrich), ethylene diamine (EDA) $H_2NCH_2CH_2NH_2$, Aldrich), 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM, Aldrich), and hydrogen chloride (HCl, Aldrich) were used without further purification. Distilled water (NCSU) and dodecane ($C_{12}H_{26}$, Aldrich) were used for contact angle measurements.

Pulse plasma polymerization of PFAC8 on nylon

The grafting of PFAC8 onto nylon 6,6 film and onto a 100 g/m^2 nylon nonwoven substrate was carried out in a cylindrical, inductively coupled plasma reactor (10 cm diameter and 2700 cm^3 volume) housed in a heated Perspex[®] chamber [17]. Internal pressure was measured using a thermocouple pressure gauge. Prior to each experiment, the reactor was cleaned with an air plasma run at 50 Watts for at least 30 min. The system was pumped back down to base pressure (typically better than 1×10^{-2} mbar) before being raised to

atmosphere to allow insertion of the sample (approximately 12 cm × 20 cm). The sample was placed on a glass shelf situated within the length of the external radio frequency coil (10 turns, center tapped, outside diameter 12 cm). An L-C matching unit was used to minimize the standing wave ratio of the transmitted power between the 13.56 MHz RF generator and the electrical discharge. A radio frequency probe and oscilloscope were used to monitor the RF pulse width produced by a pulse generator. PFAC8 (2 mL) was placed in a monomer tube attached to the air inlet side of the reactor and purified by freeze–thaw cycling prior to use. All connections were grease free.

Whilst the reactor was pumping down, heaters were turned on and the whole reactor (including monomer tube) was heated to 34 °C. Once base pressure had been reached, the monomer was bled into the reactor through a Young's tap to a pressure of approximately 1×10^{-1} mbar, and maintained at this pressure. The monomer vapor was allowed to purge through the reactor for 2 min before the plasma was ignited. Once ignited the plasma was run as a continuous wave plasma (30 W) for 30 s in order to deposit a priming layer to improve adhesion. After 30 s, the pulse generator was switched on and a pulsed plasma polymer deposition carried out for 20 min using a stable pulse envelope as indicated by the oscilloscope.

A typical pulse sequence used was 40 μs on 20 ms off. After the plasma treatment, the monomer vapor was allowed to purge through the reactor for an additional 2 min before the system was isolated from the monomer vapor and pumped down to base pressure. Once base pressure was reached, the plasma chamber was slowly raised to atmospheric pressure, and the samples were removed. A schematic of the pulsed plasma polymerization apparatus is shown in Fig. 1.

Microwave-assisted grafting of FS onto nylon

In the microwave-assisted grafting, FS was partially condensed prior to treating a nylon nonwoven fabric. 1 mL of a 1% aqueous solution of ammonium hydroxide was added to 9 mL of a 4% solution of FS in isopropyl alcohol. A 10 cm × 10 cm (3 g) strip of hydroentangled nylon nonwoven fabric was immersed in this solution and then padded to remove excess liquid, yielding approximately 80% (w/w) wet pick-up and cured in a microwave oven (Panasonic NN-SD967S) at 2.45 GHz, 1.25 kW for 30 s. The FS-grafted nylon nonwoven was sonicated in isopropyl alcohol for 10 min, rinsed with water for 30 min, and air dried.

Grafting FS onto nylon through wet processing

A 4 g/L aqueous solution of PAA was prepared with continuous stirring. A 20 cm × 20 cm piece of nylon 6,6

film (Dupont Canada) and a 20 cm × 20 cm piece of hydroentangled nylon nonwoven fabric were immersed, padded, and cured at 150 °C for 5 min to graft PAA onto them. The PAA-grafted fabric was then immersed in a 4 g/L EDA aqueous solution for 24 h with continuous shaking. After 24 h, 0.5 g DMTMM in 10 mL of methanol was added to the mixture and the reaction was allowed to proceed for 2 h. The fabric was washed with methanol for 8 h. The EDA-g-PAA-g-nylon fabrics were drawn and padded through dilute HCl solution (0.1 M) and dried at 100 °C for 2 min. The fabrics were rinsed with tap water and dried at room temperature.

Next, a 10% (w/w) solution of FS in methanol was prepared. The prepared fabrics were drawn and padded through the solution at 100% wet pick-up and dried at 100 °C for 2 min. The fabrics were drawn and padded through the FS solution a second time. The zero-time control fabric was immediately cured at 150 °C for 5 min while the other fabrics were allowed to cure for 2 h.

Scanning electron microscopy

The nylon nonwoven fabric was examined using a scanning electron microscope (SEM, Hitachi S-3200 N) operated at 5 and 10 kV and magnifications from ×50 to ×50,000. RevolutionTM v1.60b24 (4pi Analysis Inc.) was used for image analysis of SEM images. The fiber diameters and the distances between adjacent fibers were measured. Each sample was observed at five or more different places at random.

Contact angle measurements

The contact angles of water and dodecane on the treated surfaces were measured by the sessile drop method using a lab-designed goniometer at 20 °C. The volumes of the deposited droplets were 10 μL. The range of contact angles was obtained from at least three individual measurements, each on a new spot. The image of liquid droplets on the prepared surface was obtained using a digital camera (Cannon EOS EF-S-18-55IS) attached to a stereo microscope (Meiji Techno EMZ-13TR).

Roll-off angle measurements

Roll-off angles were measured by placing a specimen on a level platform mounted on a Newport 495 rotation stage and inclining the specimen. Drops (50 μL) of water or dodecane were placed on the surface, the stage was rotated and the angle of the stage was recorded when each drop rolled off. The range of roll-off angle was measured at five different spots on the fabric.

Fig. 1 Schematic representation of pulsed plasma polymerization apparatus [17]

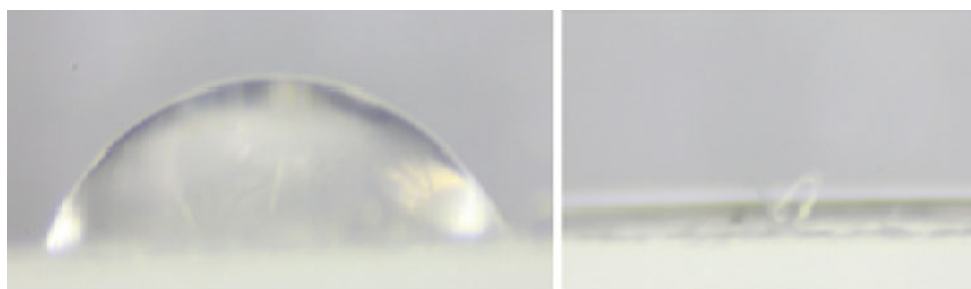
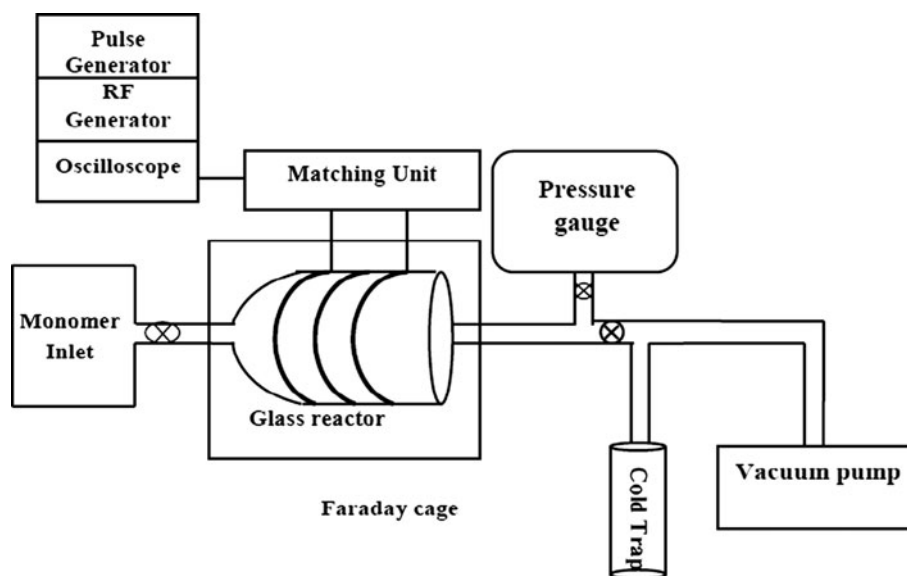


Fig. 2 Water (*left*) and dodecane (*right*) droplets on an untreated nylon film

Results and discussion

Superhydrophobic materials are often prepared by applying fluorochemicals to solid surfaces that are naturally rough or by creating new roughness while attaching fluorochemicals. In this study, we compare three different processes for making superhydrophobic and superoleophobic materials, by attaching identical fluoroalkyl chains, $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{-X}$, which differ only in the X-group used to attach the fluoroalkyl chain to the surface and the method used to cure the fluoroalkyl materials.

Pulsed plasma polymerization of fluoroalkyl acrylates onto nylon surface

When perfluoroalkyl acrylates are introduced into plasma, polymerization of the vinyl double bond can be initiated in the vapor phase and on any nearby surfaces. The perfluoroalkyl acrylate polymerization creates a closely packed covering of trifluoromethyl groups on the surface. When this polymerization was carried out in the presence of nylon films, we observed that Young's contact angle for

water increased from $70\text{--}74^\circ$ for the untreated nylon film to $123\text{--}125^\circ$ for the plasma-polymerized treatment. Similarly, Young's contact angle for dodecane increased from $<5^\circ$ for the untreated nylon film to $78\text{--}81^\circ$ for the plasma-polymerized treatment, as seen in Figs. 2 and 3 [18]. This demonstrates that a hydrophilic flat nylon surface became hydrophobic upon fluorochemical treatment. At the same time, the oleophilic surface became much less oleophilic, but it did not become oleophobic (i.e. the contact angle for dodecane was still less than 90°).

Microwave-assisted FS grafting onto nylon

Microwave radiation greatly accelerates many reactions, including siloxane condensation [19, 20]. Fluorosiloxanes can self-condense to form nano- or micro-particles, which deposit on nearby surfaces [21]. They can also react directly with surfaces and form covalent bonds with them [9, 22]. Thus, they offer great potential to generate a rough, fluorinated surface. For comparison of the effectiveness of the plasma polymerization of fluoroalkyl acrylate to microwave assisted grafting of fluoroalkylsiloxanes, we

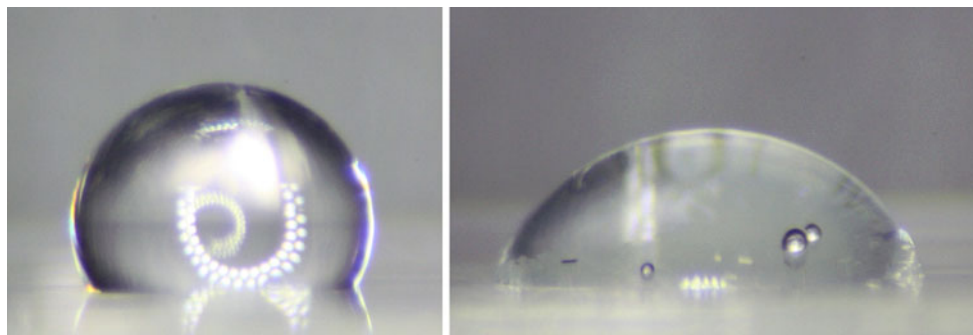


Fig. 3 Water (*left*) and dodecane (*right*) droplets on a pulse-plasma-polymerized PFAC8-grafted nylon film. (Source: Lee et al. [18])

Fig. 4 Water (*left*) and dodecane (*right*) droplets on microwave-assisted FS-treated nylon film

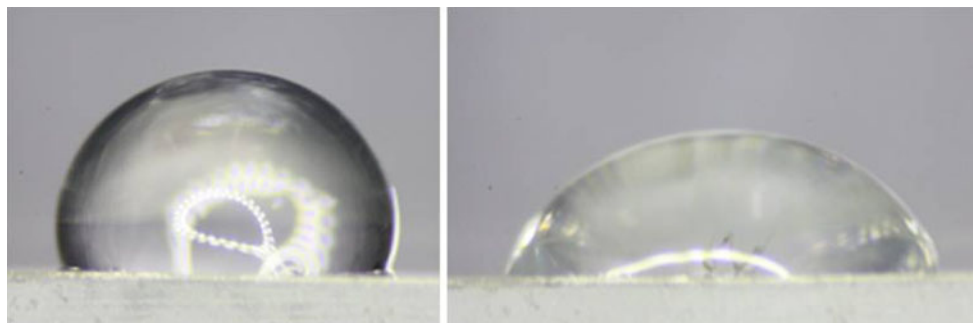
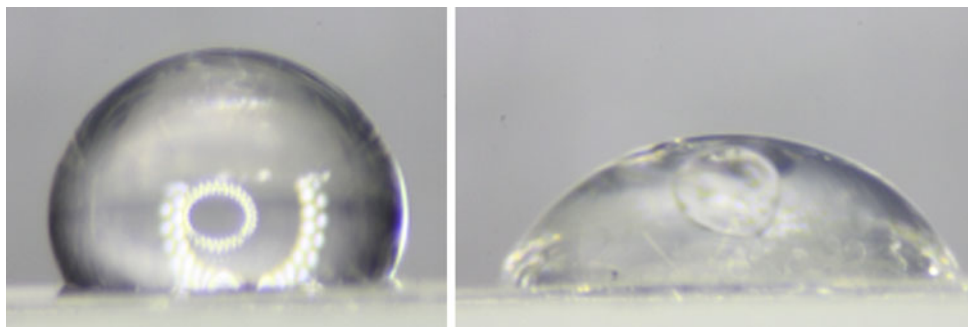


Fig. 5 Water (*left*) and dodecane (*right*) droplets on FS (wet processing) grafted nylon film

applied FS to nylon 6,6 film and used microwaves to assist grafting. Young's contact angles for water on the treated film increased to 124–126° and for dodecane they increased to 70–73° as shown in Fig. 4. These results are very close to those above for the plasma polymerized treatment.

FS grafting onto nylon via wet processing

For comparison to traditional wet processing techniques, FS was applied to nylon 6,6 film by immersing the film in a solution of FS that was allowed to self-condense and react with the film surface at room temperature. However, the number of reactive groups on the surface of untreated nylon is low. To circumvent this problem, additional sites

were added by grafting PAA to the surface followed by condensing EDA with the carboxylic acid groups in PAA. This provided a surface rich in $-\text{NH}_2$ groups [23]. After FS deposition on this surface, Young's contact angle for water was 120–124° and for dodecane was 64–68° (see Fig. 5). These contact angles are nearly identical to those for the plasma-polymerized fluoroalkyl acrylates. The results of all three methods are shown in Table 1.

All three methods reduced the surface energy of the nylon film and led to higher contact angles for both water and dodecane. However, none of these treatments resulted in superhydrophobic or oleophobic materials. To accomplish that goal, the surface roughness must be increased. The work reported below uses hydroentangled nylon fabrics to introduce roughness.

Table 1 Comparison of Young's contact angle of nylon films treated with fluoroalkyls

Treatment	Contact angles	
	Water	Dodecane
No treatment	70–74°	<5°
Plasma-polymerized perfluorodecyl acrylate	120–122°	65–67°
Microwave-assisted FS condensation	124–126°	70–73°
Wet processing of FS	120–124°	64–68°

Treatment of fibers

Figures 6 and 7 present the SEM images of fibers in hydro-entangled nylon nonwoven fabric and after treatment with plasma-polymerized PFAC8, microwave-assisted FS, and wet processing FS. At $\times 5,000$ magnification the wet-processed FS-treated sample appears to have fewer protuberances than the fabrics treated via either plasma-polymerization or microwave-reaction (Fig. 6). Figure 7 shows the rough surface of the three fabrics in greater detail. The plasma-polymerized PFAC8-treated fiber has a sparse distribution of protruding mounds. The microwave-assisted FS-treated fiber shows an undulating surface with crests and depressions. The average distance between two neighboring crests was in the range of 500 nm to 1 μm . On the other hand, the wet processing FS-treated fiber exhibits a very uneven surface with many small protuberances and uniform coverage of the treated fibers. A typical “rocky” structure was observed throughout the surface and the surface appears to have multiple layers of FS condensates. On the other hand, the surface of untreated fibers is very smooth (Fig. 8).

Geometrical modification

To create a stable CB surface, Young's contact angle, θ_e , of a liquid residing on the corresponding flat surface must be greater than 90° [24]. The surface energy of PFAC8

polymer on a flat glass substrate was determined using the liquid geometric mean method proposed by Fowkes in 1964 and Owens and Wendt in 1969. These authors state that the surface tension can be divided into dispersive and polar components [25, 26]. It was found that plasma-polymerized PFAC8 has a very low surface energy ($\sim 9 \text{ mJ/m}^2$). Since the surface energies of nonpolar liquids and solids such as dodecane and the PFAC8 plasma polymer are largely determined by the London dispersion forces, we obtain:

$$\gamma_L(1 + \cos \theta_e) = 2\sqrt{\gamma_S^d \gamma_L^d} = 2\sqrt{\gamma_S \cdot \gamma_L} \quad (3)$$

where the superscript d corresponds to the London dispersion force. Substituting $\gamma_S = 9 \text{ mJ/m}^2$ and $\gamma_L = 25.4 \text{ mJ/m}^2$ into Eq. 3, gives $\theta_e \sim 79^\circ$. Thus, the highest contact angle expected for dodecane on a flat, plasma-polymerized-PFAC8 surface is about 80° , far less than the 150° required for superoleophobicity. Similar results are expected for the fluorosiloxane treatments. Therefore, the surface roughness must be increased to attain the higher apparent contact angles needed for superoleophobicity. We achieve this roughness by using a hydroentangled nylon nonwoven fabric, as shown in Fig. 9. We then applied each of the three treatments discussed above to this fabric.

Despite having a Young's contact angle for dodecane of less than 90° , the PFAC8-plasma-modified nonwoven fabric is both superhydrophobic and superoleophobic, displaying apparent dodecane and water contact angles of $153\text{--}155^\circ$ and $168\text{--}171^\circ$, respectively (Fig. 10). Similar results were achieved for microwave-assisted FS treatment (Fig. 11) and for FS treatment using wet processing (Fig. 12). The measured contact angles for water and dodecane are shown in Table 2. All three treatments give nearly identical contact angles and result in superhydrophobic and superoleophobic materials.

To better understand the results of Table 2, we modeled the structure of the hydroentangled nonwoven fabric as shown in Fig. 13, which represents a cross-sectional view of a liquid droplet sitting on the top layer of the

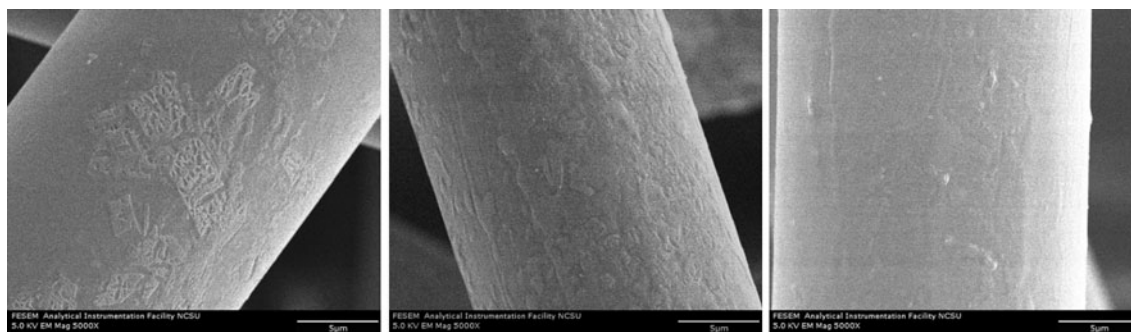


Fig. 6 SEM micrographs of (left) plasma-polymerized PFAC8-treated, (center) microwave-assisted FS-treated, and (right) wet processing FS-treated fibers in a nylon nonwoven. All three samples were imaged at $\times 5,000$ and the bars are 5 μm

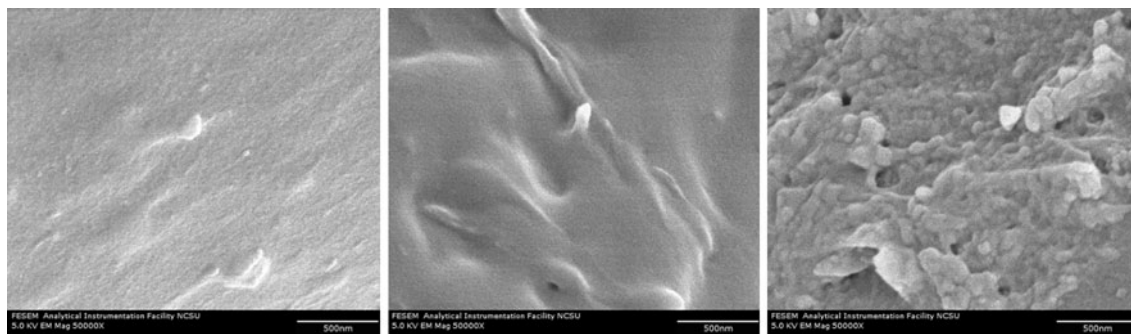


Fig. 7 SEM micrographs of (left) plasma-polymerized PFAC8-treated, (center) microwave- assisted FS-treated, and (right) wet processing FS-treated fibers in a nylon nonwoven. All three samples were imaged at $\times 50,000$ and the bars are 500 nm

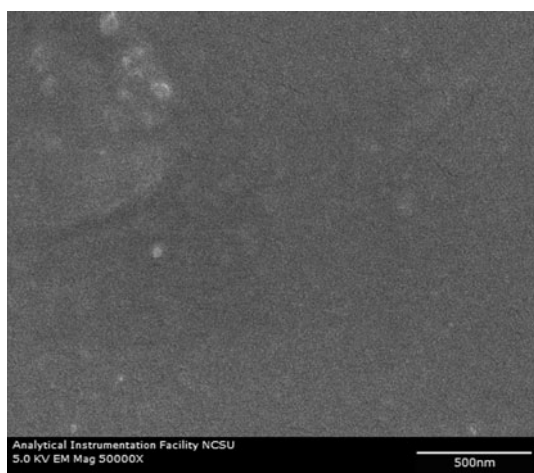


Fig. 8 SEM micrograph of an untreated nylon nonwoven fiber at $\times 50,000$. The bar is 500 nm

hydroentangled nonwoven fabric. Here, R is defined as the radius of the fiber and $2d$ is the distance between two adjacent fibers.

According to Marmur [13], Eq. 1 can be rewritten as follows:

$$\cos \theta_r^{CB} = f r_f \cos \theta_e - 1 + f \tag{4}$$

where f is the fraction of the projected area of the solid surface in contact with the liquid and r_f is the Wenzel roughness in contact with the liquid. (Note that this f is not the same as f_1 in Eq. 1.) Following Lee and Michielsen [23] and referring to Fig. 13, f is given by $R \sin \alpha / (R + d)$ while r_f is $\alpha / \sin \alpha$. According to Marmur, α is equal to $\pi - \theta_e$ when the free energy is a minimum.

Substituting for f and r_f in Eq. 1 results in

$$\cos \theta_r^{CB} = \frac{R(\pi - \theta_e)}{d + R} \cos \theta_e + \frac{R}{d + R} \sin \theta_e - 1 \tag{5}$$

If the apparent contact angle is given by Eq. 5, the drop will exhibit stable CB behavior. However, if the apparent contact angle is given by Eq. 1, but Eq. 5 is not satisfied, the drop will be in the metastable CB state. On closer examination of Eq. 4, we note that r_f and f are both positive, r_f is greater than 1 and f is less than 1. Therefore, if $\theta_e < 90^\circ$, θ_r^{CB} can be $>150^\circ$ only if f is very small (the fibers are very far apart) or if the liquid is in the metastable CB state.

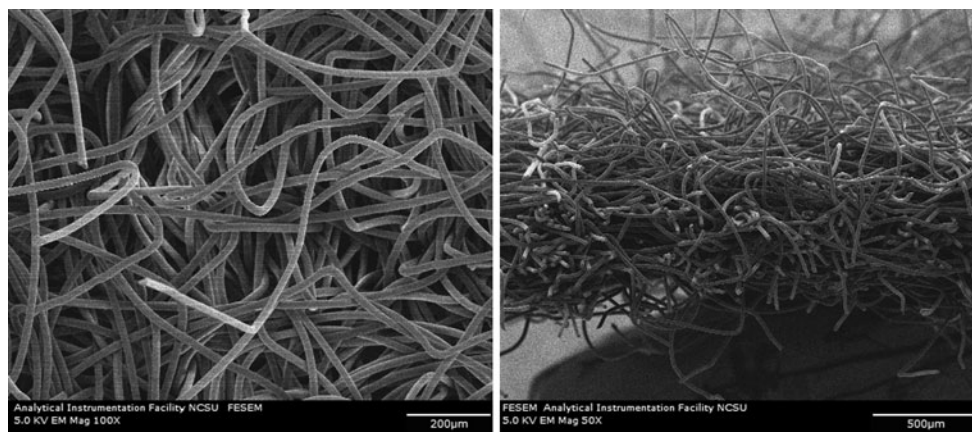


Fig. 9 (left) Top view ($\times 100$) and (right) Cross sectional view ($\times 50$) of hydroentangled nylon nonwoven fabric

Fig. 10 Water (*left*) and dodecane (*right*) droplets on plasma-polymerized PFAC8 on nylon nonwoven fabric

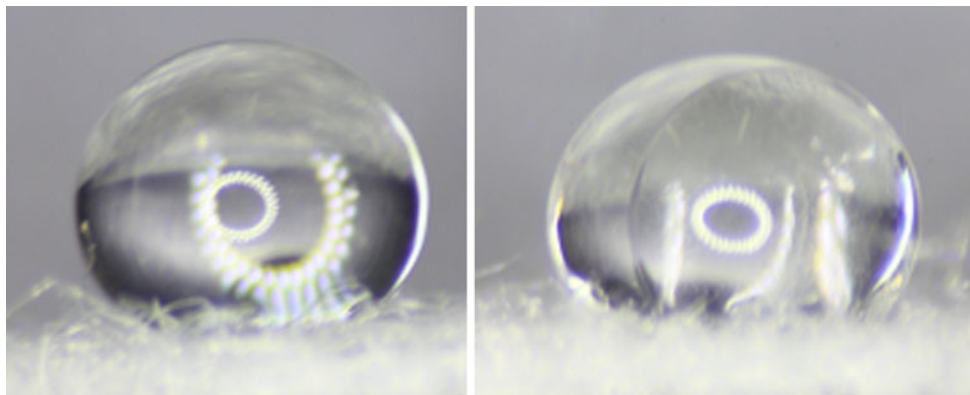


Fig. 11 Water (*left*) and dodecane (*right*) droplets on microwave-assisted FS condensation on hydroentangled nylon nonwoven fabric

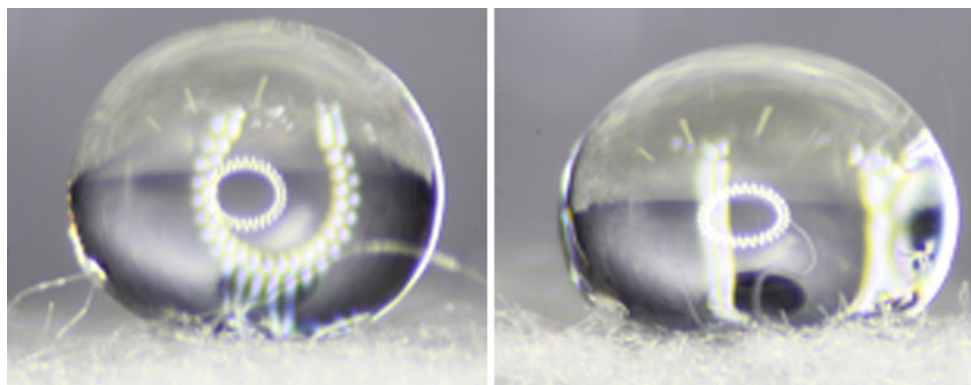
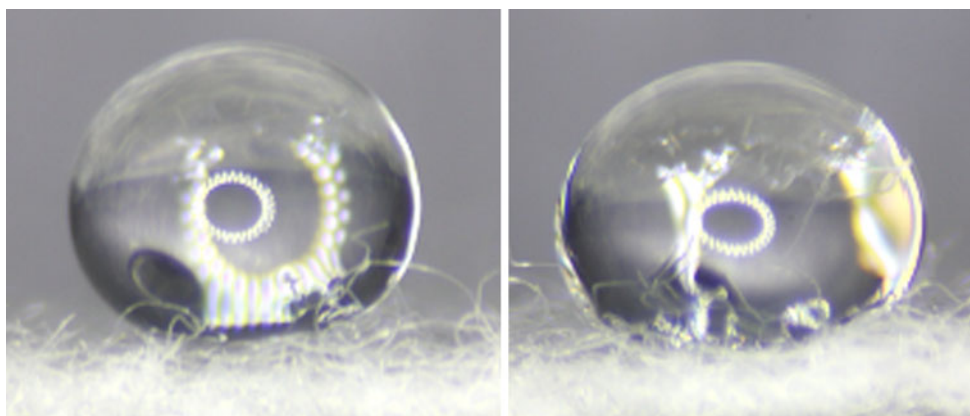


Fig. 12 Water (*left*) and dodecane (*right*) droplets on hydroentangled nylon nonwoven fabrics FS-condensed via wet processing

Table 2 Contact angles of water and dodecane on treated hydroentangled nonwoven fabrics

Treatment	Contact angles	
	Water	Dodecane
Plasma-polymerized perfluorodecyl acrylate	168–171°	153–155°
Microwave-assisted FS condensation	172–174°	158–160°
Wet processing of FS	171–173°	154–156°
Predicted from Eq. 6	~180°	155–156°

The pore ratio of the top layer of hydroentangled nonwoven fabric in Fig. 9 is calculated to be 93% ($f_2 \approx 0.93$), where the pore ratio is

$$\text{pore ratio} = f_2 = 1 - \frac{\text{area occupied by fibers}}{\text{total area}} \quad (6)$$

Because f_2 of Eq. 1 is equal to $1 - (R \sin \theta_e / (d + R))$ from Eq. 5, after substituting $R \approx 10 \mu\text{m}$ and $65^\circ \leq \theta_{e\text{-dodecane}} \leq 67^\circ$ into f_2 , the average value of d can be calculated: $119 \mu\text{m} \leq d \leq 121 \mu\text{m}$. Then, substituting R , d , and θ_e to Eq. 5 results in $150^\circ \leq \theta_{r\text{-dodecane}} \leq 151^\circ$

Fig. 13 A liquid droplet depicted sitting on top of a superhydrophobic/superoleophobic surface. R is the radius of a fiber, $2d$ is the spacing between two adjacent fibers along the liquid–air interface line, α is the fraction of the circle between vertical and the liquid contact point and θ_e is Young’s contact angle. (Source: Lee et al. [18])

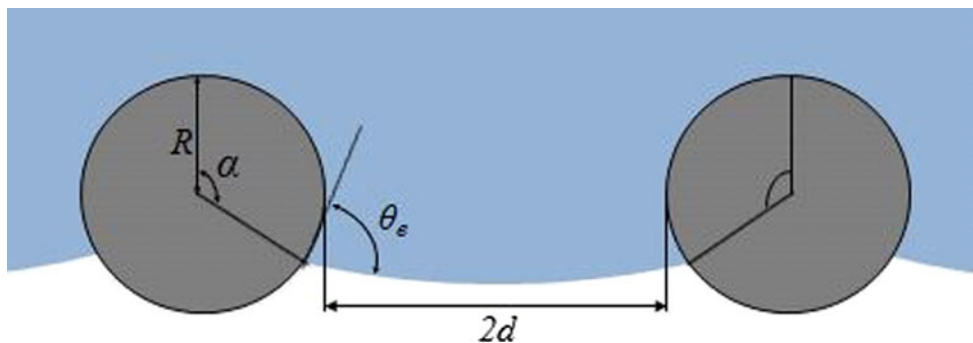


Table 3 Roll-off angles for different treatments on nylon nonwoven

Treatment	Roll-off angles	
	Water	Dodecane
Plasma-polymerized perfluorodecyl acrylate	9–11°	26–29°
Microwave-assisted FS condensation	6–8°	21–24°
Wet processing of FS	8–10°	25–28°

and $\theta_{r-water} \approx 180^\circ$. As shown in Table 2, the measured contact angles for all three treated fabrics are in good agreement with the predicted values.

All three treatments resulted in nearly the same contact angle on flat films. In addition, the measured contact angles for all three treatments are well represented by Eq. 1 considering only the fabric structure and not the nanostructures on the fiber surfaces. This means that the fabric structure and the surface energy of the fluorochemicals are the dominant factors determining whether the material will be superhydrophobic and superoleophobic. The nanostructures observed on the fibers appear to play no role in the apparent contact angles of these materials.

Another method for distinguishing between these treatments is to examine the roll-off angles for liquid droplets. The roll-off angles of water and dodecane were measured by placing the treated nonwoven fabric on a level platform mounted on a rotation stage and inclining the fabric (Table 3). The advancing and the receding contact angles were measured and the roll-off angles were recorded when

the droplet began to move. The contact angle hysteresis (CAH)—the difference between the advancing and the receding contact angles—determines how easily a drop rolls off the surface of the fabric. (See Figs. 14, 15.) The advancing contact angles, θ_A , for both water and dodecane were $\sim 180^\circ$ for all three surfaces when the droplets began to roll off our superhydrophobic/superoleophobic surfaces. It was observed that the receding contact angles, θ_R , of water on the treated nonwoven fabrics were $145\text{--}155^\circ$ whereas for dodecane $\theta_R < 30^\circ$ on the same fabric. The roll-off angles also depend on the weight of the droplet and the surface tension of the liquid since $mg \sin \alpha \approx \gamma_L D (\cos \theta_R - \cos \theta_A)$ where m is the mass of the droplet, g is the gravitational acceleration, α is the roll-off angle, γ_L is the liquid surface tension, and D is the contact diameter of the droplet on the surface [5, 27]. Although the roll-off angles of a $50 \mu\text{L}$ droplet of water and dodecane on the treated nonwoven surface were 21° and 36° , respectively, as shown in Figs. 14 and 15, if the drop volume is reduced to $10 \mu\text{L}$, the drops do not roll off the surface even if the fabric is tilted to the vertical position (90°). This demonstrates a direct correlation between the weight of the droplet and its roll-off angle.

Conclusion

Three methods for preparing superhydrophobic/superoleophobic hydroentangled nonwoven fabrics were carefully studied: pulse plasma polymerization of PFAC8,

Fig. 14 Water rolling off a superhydrophobic/superoleophobic surface

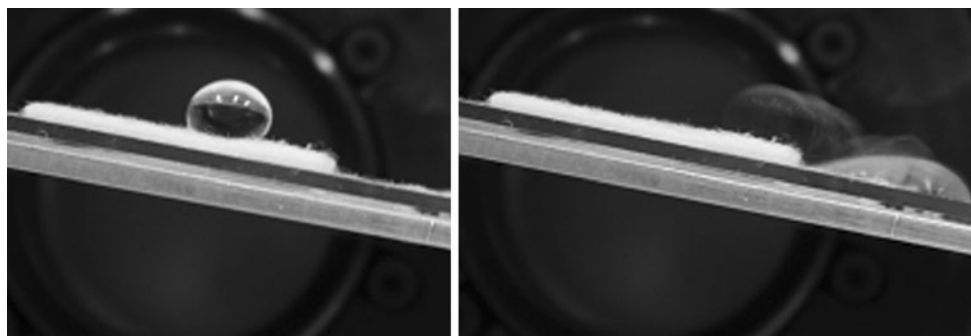


Fig. 15 Dodecane rolling off a superhydrophobic/superoleophobic surface



microwave-assisted fluorosiloxane condensation, and fluorosiloxane condensation via wet processing. The apparent contact angles and roll-off angles for water and dodecane droplets were measured. Although the surface morphology of the fibers treated in each process were quite different, the apparent contact angles were nearly the same, up to 174° for water and 160° for dodecane. In addition, roll-off angles as low as 6° for water and 21° for dodecane were obtained for $50\ \mu\text{L}$ droplet volume. On the other hand, $10\ \mu\text{L}$ droplets of water and dodecane did not roll off any of the surfaces.

Modeling the behavior of liquids on the fluorochemical-treated hydroentangled nylon nonwoven fabric showed that the influence of nanoparticle structures on the apparent contact angles was insignificant. The two controlling parameters were the low surface energy imparted by either of the fluorochemicals used and the structure of the nonwoven fabric (fiber size and spacing).

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