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Design of artificial lotus leaves using nonwoven fabric

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Abstract The apparent contact angles of a droplet deposited on the surfaces of thermal-bonded nonwoven fabrics were presented, and the characteristics required for a superhydrophobic surface were described. For a nonwoven superhydrophobic surface, the Cassie–Baxter model describes the wetting of rough surfaces. Using topological and chemical surface modifications of nylon 6,6 nonwoven fabric, artificial Lotus leaves having water contact angles >150° were prepared. Good agreement between the predictions based on the original Cassie–Baxter model and experiments was obtained. The angle at which a water droplet rolls off the surface has also been used to define a superhydrophobic surface. Superhydrophobic surfaces were prepared by two criteria: a low-surface energy and a properly designed surface roughness.

Introduction

Technologies related to superhydrophobic treatments have recently attracted considerable attention due to their potential applications in medical devices as well as industrial materials [1–8]. A superhydrophobic surface is defined as having a water contact angle >150° and a roll-off angle <5° [9]. The high contact angle is achieved by chemical and topological surface modifications, and the low roll-off angle is obtained by the applied water volume and the contact angle hysteresis, which is the difference between the advancing and the receding contact angles [10]. On a superhydrophobic surface, a water droplet easily rolls off of the surface washing dirt off in the process. This unusual wetting behavior is called the self-cleaning or the Lotus effect although this phenomenon is observed on the other plants' leaves besides the Lotus plant leaves [11]. Since the wettability of a solid surface is determined by two parameters, the chemical composition and the geometrical structure of a rough surface and the combination of these two factors are used for the development of superhydrophobic surface [12].

Nonwoven fabric is a textile material directly produced from fiber webs by bonding and/or interlocking. Although polyolefin and polyester have been the major raw materials for nonwovens, polymers which have more reactive sites such as nylon have begun to actively be used in the nonwoven sector since dyeing and finishing are required to extend the final application of nonwovens. The preparation of superhydrophobic surface using nylon nonwoven is more difficult than the preparation of superhydrophobic polyethylene or polypropylene nonwovens due to the hydrophilicity of nylon. Therefore, we need to apply appropriate surface modifications to achieve superhydrophobicity of nylon nonwovens.

The objectives of this study are to compare the wetting behavior of a rough surface to that of a smooth surface; and to design and prepare superhydrophobic surfaces using textile structures. In this research, a superhydrophobic rough surface is designed using thermal-bonded nonwoven structures and prepared by grafting low surface tension materials such as 1H, 1H-perfluorooctylamine, or octadecylamine onto poly(acrylic acid) (PAA)-grafted nylon 6,6 nonwoven fabric. The wetting behavior of the superhydrophobic nonwoven fabric is compared to that of a flat nylon surface.

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Experimental

Materials

Nylon 6,6 film (M_n: 12 kDa) and nylon 6,6 thermal-bonded nonwoven fabric (weight: 100 g/m^2) were used as smooth or rough surfaces. PAA (M_w: 450 kDa, Aldrich, St. Louis, MO, USA), 4-(4,6-dimethoxy-1,3,5-triazin-2yl)-4-methylmorpholinium chloride (DMTMM, Fluka, St. Louis, MO, USA), sodium thiocyanate (NaSCN, Fisher, Waltham, MA, USA), methanol (CH_3OH, Aldrich), 1H, 1H-perfluorooctylamine ($C_8H_4F_{15}N$, Synquest, Alachua, FL, USA), and octadecylamine ($C_{18}H_{39}N$, Aldrich) were used without further purification.

Grafting of PAA on Nylon 6,6

Since nylon 6,6 has few reactive groups on the surface and we wish to chemically graft an alkyl or fluoroalkyl material to the surface, PAA was first grafted to the nylon surface to increase the number of reactive sites. An aliquot of 1 g PAA was dissolved in 250 mL distilled water at 20 °C. Then 0.5 g nylon film (10 × 10 cm^2) and 0.5 g of each nylon nonwoven fabric (10 × 10 cm^2) were immersed in the PAA solution for 24 h, rinsed in distilled water with stirring for 8 h (repeated thrice with fresh water), wiped with Kimwipes®, and air dried.

An aliquot of 0.1 g DMTMM was dissolved in distilled water with vigorous stirring at 20 °C. PAA-adsorbed nylon materials were immersed in the DMTMM solution to graft PAA to the nylon surfaces. The reaction was allowed to proceed for 2 h. PAA-grafted nylon materials were rinsed in distilled water for 8 h (repeated thrice with fresh solvent), wiped with Kimwipes®, and air dried.

To remove nongrafted PAA, the nylon materials were rinsed in a 1-M aqueous sodium thiocyanate (NaSCN) solution with stirring (repeated twice with fresh solution), rinsed in distilled water for 8 h (repeated thrice with fresh solution), and heated in water for 3 h at 65 °C. Then, the nylon surfaces were wiped with Kimwipes® and air dried. Scheme 1 shows the grafting procedure of PAA onto nylon 6,6.

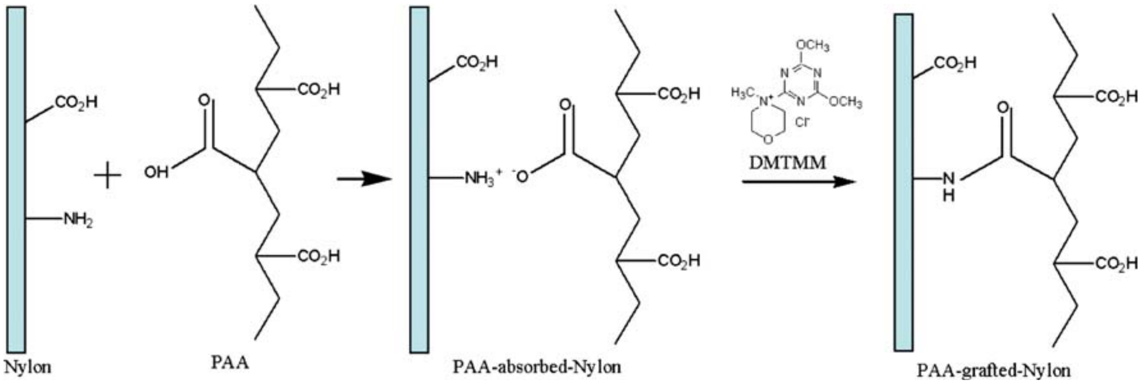
Grafting of fluoroamine or alkylamine on PAA-grafted nylon 6,6 surface

An aliquot of 0.05 g 1H, 1H-perfluorooctylamine or 0.03 g octadecylamine was dissolved in a 10-mL methanol at 20 °C. Then 0.15 g PAA-grafted nylon film (5 × 6 cm^2) and 0.3 g of each PAA-grafted nylon nonwoven fabric (5 × 6 cm^2) were immersed in the 1H, 1H-perfluorooctylamine (or octadecylamine) solution for 24 h with stirring to allow adsorption of 1H, 1H-perfluorooctylamine (octadecylamine).

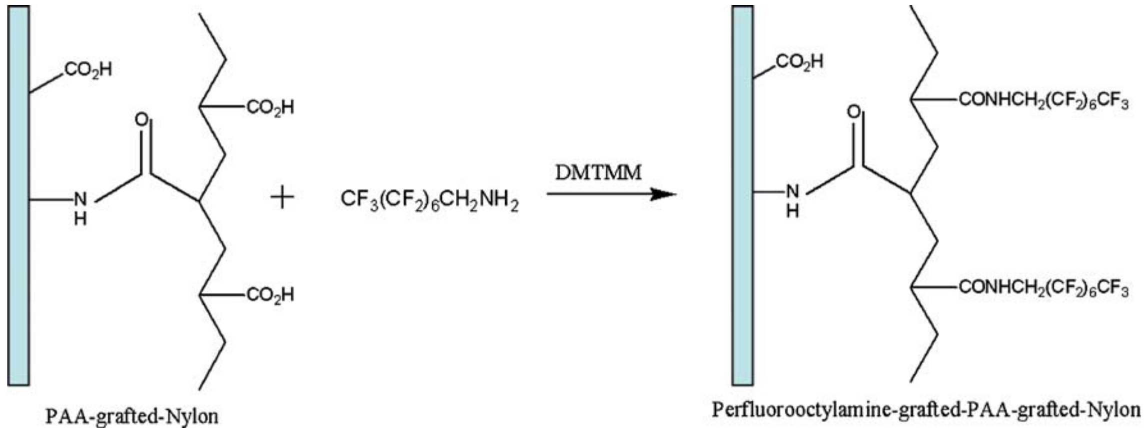
An aliquot of 0.03 g DMTMM was dissolved in methanol with vigorous stirring at 20 °C. 1H, 1H-perfluorooctylamine-adsorbed PAA-grafted nylon materials were immersed in the DMTMM solution to graft 1H, 1H-perfluorooctylamine, or octadecylamine to the PAA on nylon 6,6 surfaces. The reaction proceeded for 2 h. The 1H, 1H-perfluorooctylamine-grafted PAA-grafted nylon, and octadecylamine-grafted PAA-grafted nylon materials were rinsed in methanol for 8 h (repeated twice with fresh solvent), rinsed in distilled water for 8 h (repeated twice with fresh solvent), wiped with Kimwipes®, and air dried. Scheme 2 shows the procedure for grafting 1H, 1H-perfluorooctylamine onto PAA-grafted nylon 6,6.

Scanning electron microscopy

The rough surface nylon nonwoven fabric was examined with a scanning electron microscope (SEM), Hitachi S-3200N, operated at 5 and 10 kV and magnifications from ×25 to ×2000. Image J 1.34s (National Institute of Health) was used for image analysis of SEM pictures. On a rough



Scheme 1 Grafting PAA onto nylon 6,6



Scheme 2 Grafting 1H, 1H-perfluorooctylamine onto PAA-grafted nylon 6,6

surface, the fiber diameters and the distances among adjacent fibers were measured using this program.

Contact angle measurements

The contact angle on the prepared surfaces was measured from sessile water drops using a lab-designed goniometer at 20 °C. The weights of the applied droplets of distilled water were 10, 50, 100, 250, and 500 μL. Mean values were calculated from at least four individual measurements each on a new spot. The roll-off angle was measured by placing a specimen on a level platform mounted on a rotation stage, Newport 495, and inclining the specimen. A water droplet was placed onto the surface, and the angle of the stage was recorded when the drop rolled off.

Results and discussion

The wetting behavior of a solid surface is controlled by both the surface tension and the roughness of the surface. To form a superhydrophobic nonwoven surface, the fiber surface has to have a low surface tension, and the fabric has to have an appropriate geometric structure. First, we modified a nylon film to generate a low-surface-tension surface.

Wetting properties of hydrophobic film

A water droplet ($\gamma_{\mathrm{L}}^{\mathrm{d}} = 21.8, \gamma_{\mathrm{L}}^{\mathrm{p}} = 1.4$, and $\gamma_{\mathrm{L}}^{\mathrm{H}} = 49.6$ dyne/cm) placed upon a clean, smooth nylon surface ($\gamma_{\mathrm{S}}^{\mathrm{d}} = 40.8$ and $\gamma_{\mathrm{S}}^{\mathrm{H}} = 6.2$ dyne/cm) should have a contact angle $\theta_{\mathrm{e}} = 72°$ according to Eq. 1 [13].

$$\begin{aligned}\gamma_{\mathrm{L}}(1+\cos\theta_{\mathrm{e}}) &= \gamma_{\mathrm{L}}^{\mathrm{d}}(1+\cos\theta_{\mathrm{e}}) + \gamma_{\mathrm{L}}^{\mathrm{p}}(1+\cos\theta_{\mathrm{e}}) \\ &\quad + \gamma_{\mathrm{L}}^{\mathrm{H}}(1+\cos\theta_{\mathrm{e}}) \\ &= 2\left(\sqrt{\gamma_{\mathrm{S}}^{\mathrm{d}}\cdot\gamma_{\mathrm{L}}^{\mathrm{d}}} + \sqrt{\gamma_{\mathrm{S}}^{\mathrm{p}}\cdot\gamma_{\mathrm{L}}^{\mathrm{p}}} + \sqrt{\gamma_{\mathrm{S}}^{\mathrm{H}}\cdot\gamma_{\mathrm{L}}^{\mathrm{H}}}\right) \quad (1)\end{aligned}$$

The values of the water contact angles measured on clean nylon film in this study are $65° \le \theta_{\mathrm{e}} \le 73°$, in good agreement with the predicted value as shown in Table 1. Figure 1 presents a water droplet sitting on a smooth nylon film; the equilibrium water contact angle on this surface is 70°.

To make the nylon film surface hydrophobic, we need to attach a low-surface-tension material to the nylon surface. However, nylon has very few reactive sites, so first we must modify the surface to increase the number of reactive sites. Using the procedure developed by Tobiesen and Michielsen [14], we first grafted PAA onto the film and had PAA used as a mediator between nylon 6,6 and low-surface-tension material such as fluoroamine or alkylamine due to the high density of carboxylic acid groups along the backbone of PAA. The carboxylic acid groups of PAA are covalently grafted to the amino groups of nylon 6,6 using a triazine-based condensing reagent, DMTMM. Since PAA is more hydrophilic than nylon, the water contact angle on PAA-grafted nylon film should be less than 72°. As shown in Table 1, the water contact angles measured on smooth PAA-grafted nylon film made as described in "Experimental" were found to be $43° \le \theta_{\mathrm{e}} \le 50°$.

Table 1 Comparison of predicted and measured water contact angles on smooth surfaces

Sample	Contact angle (°)	
	Predicted	Measured
Nylon 6,6	$\theta_{\mathrm{e}} = 72$	$65 \le \theta_{\mathrm{e}} \le 73$
PAA-grafted nylon 6,6	$\theta_{\mathrm{e}} < 65$	$43 \le \theta_{\mathrm{e}} \le 50$
1H, 1H-perfluorooctylamine-grafted PAA-grafted nylon 6,6	$\theta_{\mathrm{e}} > 73$	$93 \le \theta_{\mathrm{e}} \le 110$
Octadecylamine-grafted PAA-grafted nylon 6,6	$\theta_{\mathrm{e}} > 73$	$95 \le \theta_{\mathrm{e}} \le 102$

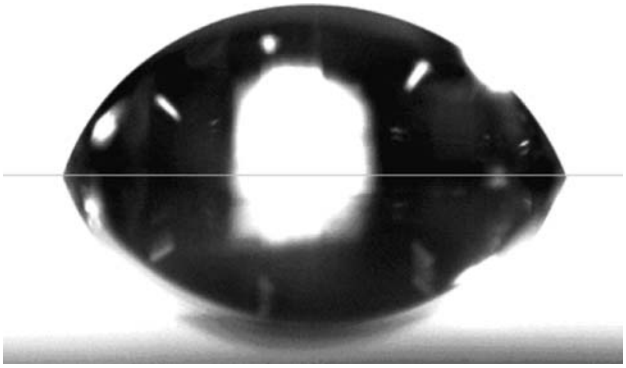


Fig. 1 A water droplet on a smooth nylon surface. *Thin gray line* indicates the film surface

Next, to make the surface hydrophobic, 1H, 1H-perfluorooctylamine, or octadecylamine was grafted onto the PAA-grafted nylon films, again using DMTMM as a condensing agent. When water is placed on a clean, smooth poly(tetrafluoroethylene) surface ($\gamma_S^d = 18.5\ \mathrm{dyne/cm}$), $\theta_e = 117°$. The water contact angles measured on the 1H, 1H-perfluorooctylamine-grafted-PAA-grafted nylon films were $93° \leq \theta_e \leq 110°$ (Table 1). Figure 2 shows a water droplet sitting on a 1H, 1H-perfluorooctylamine-grafted PAA-grafted nylon film; the water contact angle on this surface is 100°.

In the same manner, to make the film surface hydrophobic, octadecylamine was grafted onto the PAA-grafted nylon films as described in "Experimental." Since octadecylamine is more hydrophobic than nylon due to the alkyl groups, θ_e should be greater than 73° and potentially as high as 110° for octadecylamine. The water contact angles measured on the octadecylamine-grafted PAA-grafted nylon film were $95° \leq \theta_e \leq 102°$ as shown in Table 1. Thus, the first criterion for making a superhydrophobic surface has been achieved.

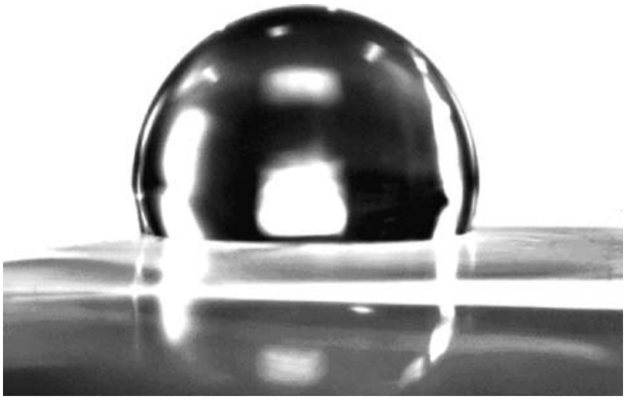


Fig. 2 A water droplet on a 1H, 1H-perfluorooctylamine-grafted nylon surface

Design of superhydrophobic rough surfaces

The wettability of a solid surface can be changed by modifying the structural morphology as well as the chemical composition of the surface [15]. When the surface is roughened, the minimization of liquid surface-free energy results in three possible models: the Wenzel model, the Cassie–Baxter model, and the metastable Cassie–Baxter model. In the Wenzel model, a liquid completely fills the grooves of a rough surface, whereas a liquid sits on top of the solid protuberances of a rough surface in the Cassie–Baxter model. On a metastable Cassie–Baxter surface, a liquid initially sits on top of the surface and is sucked into contact with the rough surface after a certain amount of time which depends on the surface tension and volume of the liquid and the surface tension and morphology of the solid surface. In our recent study, a surface having an initial water contact angle >150° has been developed by modifying only geometrical structure of nylon 6,6 without any chemical treatments. A metastable Cassie–Baxter model is useful when an oleophobic or superoleophobic surface is designed. However, in order to prepare an artificial Lotus leaf having stable superhydrophobicity a "stable" Cassie–Baxter surface has to be designed [15].

The Wenzel model explains how roughness contributes the wetting behavior of a surface. In Wenzel's approach, the liquid contact angle at a rough surface can be described as $\cos\theta_r^w = r\cos\theta_e$, where θ_r^w is an apparent contact angle on a Wenzel surface, and r is the ratio of the total wet area of a rough surface to the apparent surface area in contact with the water droplet [16]. Since r is always >1 for a Wenzel surface, the surface becomes more hydrophilic if θ_e is smaller than 90° while the surface becomes more hydrophobic if θ_e is greater than 90°. Prior to designing a Cassie–Baxter nonwoven surface, we make the surface hydrophobic and define an appropriate Wenzel roughness which has to be greater than certain number depending on θ_e. As a numerical example, for a material with a smooth surface water contact angle of 110°, the Wenzel roughness, r, must be >2.5 for the apparent contact angle to exceed 150°. However, an appropriate roughness cannot be designed with only r in the Wenzel model since this number is not involved to the shape of the rough surface. Therefore, we need an extended form of the Wenzel model, which is the Cassie–Baxter model.

In the Cassie–Baxter model, a liquid sits on a composite surface made of two different materials. In this approach, the liquid contact angle at a rough surface can be described as $\cos\theta_r^{CB} = f_1\cos\theta_{e1} + f_2\cos\theta_{e2}$ where $\cos\theta_r^{CB}$ is an apparent contact angle on a Cassie–Baxter surface, f_1 is the surface area of the liquid in contact with Material 1 divided by the projected area, and f_2 is the surface area of the liquid in contact with Material 2 divided by the projected area

[17]. If this composite is a porous rough surface, f_1 is the surface area of the liquid in contact with the solid surface divided by the projected area, and f_2 is the surface area of the liquid in contact with air trapped in the pores of the rough surface divided by the projected area. Since $\cos\theta_e$ of air is equal to -1, Cassie and Baxter suggested that:

$$\cos\theta_r^{\mathrm{CB}} = f_1 \cos\theta_e - f_2 \tag{2}$$

When there is no trapped air the surface behaves as a Wenzel rough surface, and f_1 is identical to the value of r in the Wenzel model. Recently, Eq. 2 has been rewritten as follows:

$$\cos\theta_r^{\mathrm{CB}} = r_f f \cos\theta_e + f - 1 \tag{3}$$

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 [18]. According to Eq. 3, the Wenzel model is a special case of the Cassie–Baxter equation where $f = 1$ and $r_f = r$. In Eq. 3, the contributions of surface roughness and of trapped air are much clearer than in Eq. 2. However, according to Marmur, the minimization of the free energy requires that, for a hydrophobic surface with $f = 1$, $\theta_e = 180°$. Since the only material known with $\theta_e = 180°$ is air or vacuum, f cannot be equal to 1. In other words, the Wenzel model is invalid for hydrophobic surfaces. In order to develop superhydrophobic surfaces, we need to use a different approach, namely the Cassie–Baxter model.

Although most studies of the Lotus effect have been carried out on hard materials using the Cassie–Baxter model, textile materials having a rough surface such as woven, knit, or nonwoven structure can also be superhydrophobic if the surface is properly designed in accordance with Eq. 3. How can we design proper geometrical structures? Figure 3 shows a rough surface having pillars. In a unit of this rough surface, the top area of each pillar which directly contacts with water is a^2; the projected area is $(a + 2D)^2$; the Wenzel roughness, r, is $1 + 4ah/(a + 2D)^2$; f_1 in the Cassie–Baxter model is $a^2/(a + 2D)^2$; and f_2 is $1 - a^2/(a + 2D)^2$. Therefore, the Wenzel and the Cassie–Baxter equations for this surface are:

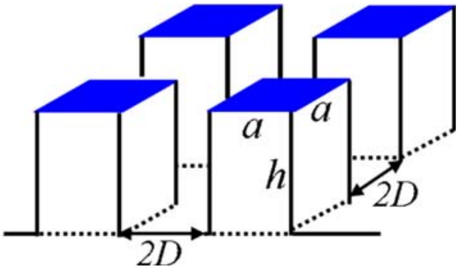


Fig. 3 A model rough surface. The top area of a pillar is a^2, the distance between two pillars is $2D$, and the height of the pillars is h

$$\cos\theta_{\mathrm{r}}^{\mathrm{W}} = r\cos\theta_e = \left[1 + \frac{4ah}{(a+2D)^2}\right]\cos\theta_e \tag{4}$$

$$\begin{aligned}\cos\theta_{\mathrm{r}}^{\mathrm{CB}} &= f_1\cos\theta_e - f_2 \\ &= \left(\frac{a}{a+2D}\right)^2\cos\theta_e - \left[1 - \left(\frac{a}{a+2D}\right)^2\right]\end{aligned} \tag{5}$$

According to these equations we can design appropriate roughness and morphology to make the surface superhydrophobic. The Wenzel equation is useful to predict the minimum roughness of the structure in order to prevent water contacting with the substrate; and the Cassie–Baxter equation provides the maximum interfacial ratio between water and the solid surface while keeping an apparent water contact angle >150°. For example, if the side length of pillar, a, is 20 μm, the height of pillar, h, is 1 mm; and the Young contact angle of the surface, θ_e, is 110°, according to Eqs. 4 and 5, the distance between two adjacent pillars has to be between 24 μm and 0.2 mm to make the surface superhydrophobic. If the distance between two pillars is out of range, the surface cannot be superhydrophobic. In the same manner, a superhydrophobic surface can be designed by varying a, h, and θ_e.

Preparation of superhydrophobic nonwoven fabric

Figure 4 shows the top view of melt-blown nylon fabric. R is defined as the radius of fiber, and $2D$ is the average distance between adjacent fibers. Before modeling a superhydrophobic surface with nonwoven fabric, we prove that this nonwoven structure is potential to be a Cassie–Baxter rough surface (Fig. 5). As shown in Fig. 5, the center-to-center distance between two nonwoven webs is considered to be $2(R + d)$; f in Eq. 3 is $R\sin\sigma/(R + d)$; and r_f is $\sigma/\sin\sigma$. According to Marmur, a rough surface can be a Cassie–Baxter surface when $\mathrm{d}(r_f f)/\mathrm{d}f = (\cos\sigma)^{-1}$ and $\mathrm{d}^2(r_f f)/\mathrm{d}f^2 > 0$ since under these conditions there is a minimum surface-free energy on each surface and $\sigma = \pi - \theta_e$ [18].

$$\frac{\mathrm{d}(fr_f)}{\mathrm{d}f} = \frac{\mathrm{d}\left(\frac{R\sigma}{D+R}\right)}{\mathrm{d}\left(\frac{R\sin\sigma}{D+R}\right)} = \frac{1}{\frac{\mathrm{d}\left(\frac{R\sin\sigma}{D+R}\right)}{\mathrm{d}\left(\frac{R\sigma}{D+R}\right)}} = \frac{1}{\frac{\left(\frac{R}{D+R}\right)\mathrm{d}\sin\sigma}{\left(\frac{R}{D+R}\right)\mathrm{d}\sigma}} = \frac{1}{\frac{\mathrm{d}\sin\sigma}{\mathrm{d}\sigma}}$$
$$= (\cos\sigma)^{-1}$$

$$\frac{\mathrm{d}^2(fr_f)}{\mathrm{d}f^2} = \frac{\mathrm{d}\left(\frac{1}{\cos\sigma}\right)}{\mathrm{d}\left(\frac{R\sin\sigma}{D+R}\right)} = \left(\frac{D+R}{R}\right)\frac{\mathrm{d}\left(\frac{1}{\cos\sigma}\right)}{\mathrm{d}(\sin\sigma)}$$
$$= \left(\frac{D+R}{R}\right)\frac{\mathrm{d}\left(\frac{1}{\cos\left(\sin^{-1}t\right)}\right)}{\mathrm{d}t} > 0$$

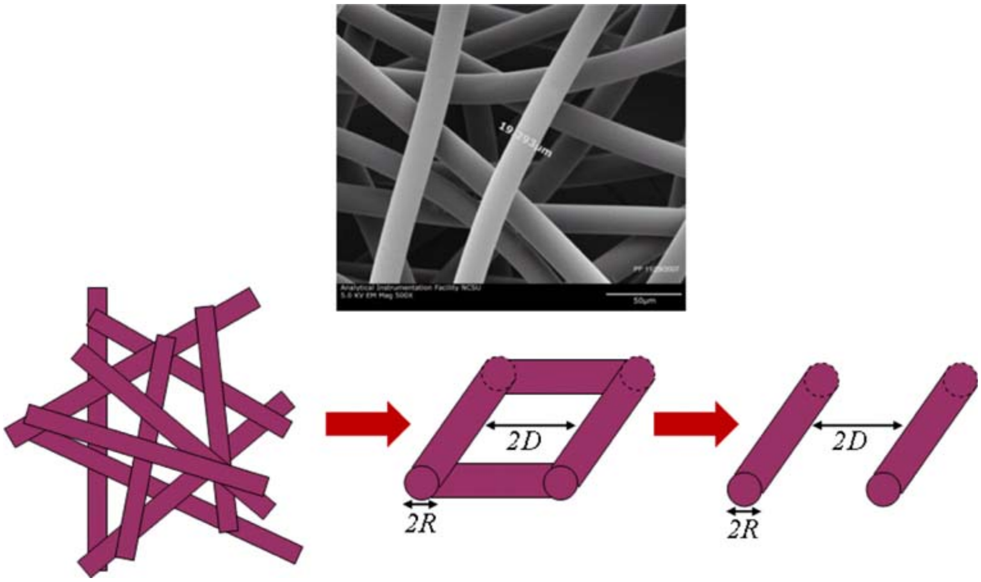


Fig. 4 SEM micrographs of a melt-blown nonwoven fabric (×1,000) and a simplified model used for mechanical modification

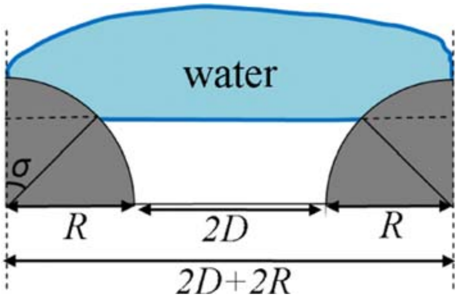


Fig. 5 A water droplet on top of melt-blown nonwoven structure

Substituting for f and r_f into Eq. 3 results in:

$$\cos\theta_{\mathrm{r}}^{\mathrm{CB}} = \frac{R(\pi-\theta_{\mathrm{e}})}{D+R}\cos\theta_{\mathrm{e}} + \frac{R}{D+R}\sin\theta_{\mathrm{e}} - 1 \qquad (6)$$

According to Eq. 6, an apparent contact angle, $\theta_{\mathrm{r}}^{\mathrm{CB}}$, increases with increasing D for $\theta_{\mathrm{e}} > 90^\circ$. Therefore, when a low-surface-tension material such as 1H, 1H-perfluorooctylamine ($\theta_{\mathrm{e}} = 110^\circ$) is grafted on a conventional nylon surface, we can easily achieve superhydrophobicity by increasing the distance between fiber webs as long as the Wenzel roughness, r, is >2.5 which was mentioned above, i.e., $\theta_{\mathrm{r}}^{\mathrm{CB}} > 150^\circ$ when $\theta_{\mathrm{e}} = 110^\circ$, $D > 2.88R$, and $r > 2.5$. Since the average distance, $2D$, measured between fibers of the melt-blown nonwoven fabric in Fig. 4 is $2.8R$, we can predict an apparent contact angle, $\theta_{\mathrm{r}}^{\mathrm{CB}}$, by substituting D into Eq. 6. The predicted $\theta_{\mathrm{r}}^{\mathrm{CB}}$ is 142°, which is close to the measured apparent contact angles $137^\circ < \theta_{\mathrm{r}\ \mathrm{e}}^{\mathrm{CB}} < 143^\circ$ Since it is hard to control D while manufacturing melt-blown nonwovens, we give more roughness to this material by thermal-bonding.

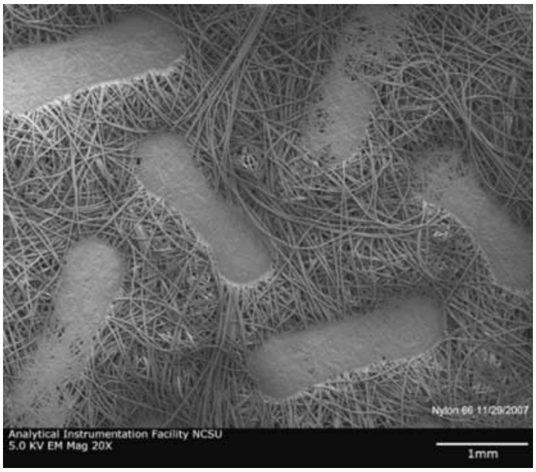


Fig. 6 SEM micrographs of a thermal-bonded nonwoven fabric (×20)

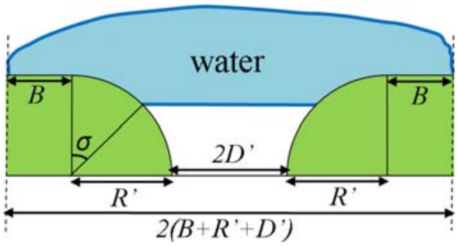


Fig. 7 A water droplet on top of a thermal-bonded nonwoven structure

When the nonwoven structure is more roughened by thermal-bonding, the average $\theta_{\mathrm{r}}^{\mathrm{CB}}$, ~140°, is regarded as θ_{e} of a thermal-bonded nonwoven surface. Based on an SEM image of thermal-bonded nylon fabric in Fig. 6, a thermal-bonded nonwoven rough surface can be modeled as shown in Fig. 7. R' is the radius of a rounded part of a protuberance, $2D'$ is the spacing between the edges of two protuberances, and $2B$ is the width of the flattened portion of each protuberance. In any direction (machine or cross-machine direction), two flattened-cylinder-looking protuberances are placed on the top of the thermal-bonded nonwoven surfaces at a distance, $2D'$, with the adjacent cylinders lying in the same direction. Thus, the unit center-to-center distance is $2(B + R' + D')$. Since f is the fraction of the projected area of the rough surface that is wet by the liquid and r_f is the roughness ratio of the wet area, we obtain $f = (B + R' \sin\sigma)/(B + R' + D')$ and $r_f = (B + R'\sigma)/(B + R' \sin\sigma)$. Therefore,

$$\frac{\mathrm{d}(fr_f)}{\mathrm{d}f} = \frac{\mathrm{d}\left(\frac{B+R'\sigma}{B+R'+D'}\right)}{\mathrm{d}\left(\frac{B+R'\sin\sigma}{B+R'+D'}\right)} = \frac{1}{\frac{\mathrm{d}(B+R'\sin\sigma)}{\mathrm{d}(B+R'\sigma)}} = (\cos\sigma)^{-1}$$

$$\frac{\mathrm{d}^2(fr_f)}{\mathrm{d}f^2} = \frac{\mathrm{d}\left(\frac{1}{\cos\sigma}\right)}{\mathrm{d}\left(\frac{B+R'\sin\sigma}{B+R'+D'}\right)} = \frac{\sin\sigma}{R(B+R'+D')\cos^3\sigma} > 0$$

Again, under these conditions, $\sigma = \pi - \theta_e$. Substituting for f and r_f into Eq. 3 results in:

$$\cos\theta_r^{CB} = \frac{B+R'(\pi-\theta_e)}{B+R'+D'}\cos\theta_e + \frac{B+R'\sin\theta_e}{B+R'+D'} - 1 \qquad (7)$$

According to Eq. 7, when $\theta_e > 90°$, θ_r^{CB} increases with decreasing B and increasing D'. The average of each parameter, B, R', and D', can be measured from photomicrographs, and θ_r^{CB} of this nonwoven material can be predicted by substituting the values of B, R', D', and θ_e (140° as mentioned above) into Eq. 7. The predicted θ_r^{CB} is 160°, and this value is in good agreement with the measured angles which vary between 155° and 165° depending on the location of droplets. Figure 8 shows a water droplet sitting on top of this nonwoven fabric; the apparent water contact angle on the surface is 158°.

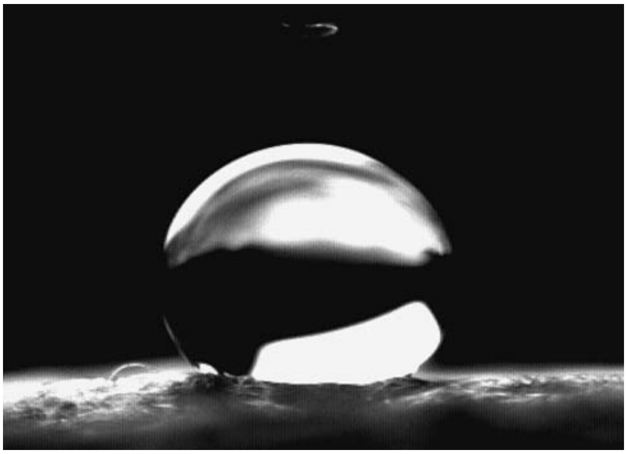


Fig. 8 A water droplet sitting on top of a superhydrophobic thermal-bonded nonwoven surface

Water droplets placed on the Lotus leaves exhibit very low roll-off angles (<5°) while apparent contact angles exceed 150°. The roll-off angles are affected by the surface tension of a solid, morphology, and the size of droplets. For our superhydrophobic thermal-bonded nonwoven fabric, the roll-off angles are less than 5° when the volume of water is 250 μL or more. The advancing contact angles were close to 180° when the droplet began to roll off the surface while the receding contact angles varied between 90° and 155° since the receding contact angles are affected by the local structures of the fabric such as fiber diameters, fiber spacing, and groove sizes.

Conclusion

A superhydrophobic surface is obtained by two criteria: a low surface energy and an appropriate surface roughness which results in water detaching from the surface at a low roll-off angle. In order to make nylon 6,6 superhydrophobic, a low-surface-tension material, 1H, 1H-perfluorooctylamine, or alkylamine was grafted onto nylon 6,6 nonwoven fabric. From the water contact angles measured on flat-modified nylon films, we predicted the apparent contact angle of the nonwoven fabrics. Good agreement between the predicted values and the observed contact angles was obtained. On our superhydrophobic thermal-bonded nonwoven surface, apparent water contact angles were as high as 165° and roll-off angles were less than 5°.

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