

WETTING BEHAVIOR OF SUPERHYDROPHOBIC FABRICS TREATED WITH CARBON NANOTUBES

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1. Introduction

The self-cleaning of lotus leaves in particular is becoming an interesting topic because of the observed wetting properties of the material surfaces. The water contact angle (CA) of a lotus leaf is $161 \pm 2.7^\circ$ with CA hysteresis of 2° . The structure of a lotus leaf consists of a binary-scale roughness: one around $10 \mu\text{m}$ (rough structure) and the other around 100 nm (fine structure) [1-2]. The superhydrophobic property is believed to be governed by both the chemical composition of the surface material and the cooperative effect of nanostructures within the micrometer-scale areas (the so-called hierarchical structure). The surface structure has two levels of roughness that enable the trapping of air under water droplets, thereby contributing to the rolling water droplet effect that is characteristic of a well-designed superhydrophobic surface.

Two criteria are applied in defining superhydrophobicity. First, the equilibrium water contact angle θ of a superhydrophobic surface must be larger than 150° . Second, water must not stick to the surface, i.e. droplets must roll off easily. Such high contact angles can be achieved by roughening a hydrophobic surface, while smooth surfaces can have an intrinsic contact angle only up to about 120° [3].

Cassie and Baxter extended the Wenzel model to include porous surface. In this model, a liquid sits on a composite surface including solid and air. Cassie and Baxter equation has recently been rewritten as follows [4]

$$\cos\theta_r^{\text{CB}} = \gamma_f f \cos\theta_e + f - 1 \quad (1)$$

Where f is the fraction of the projected area of the solid surface in contact with the liquid and γ_f is the

roughness of the portion of the solid that is in contact with water.

Various techniques have been used to reduce the fraction of the projected area, including sol-gel methods, templation, colloidal assemblies, layer-by-layer deposition, micelles, sublimation of aluminum acetylacetonate, galvanic corrosion techniques, plasma-enhanced CVD, and physical vapor deposition. But, these techniques cannot be successfully applied to textiles.

Y. Lee *et al.* reported that the hierarchically structured surface of long nanofibers on micrometer-scale papillae shows the highest static contact angle and the lowest hysteresis value [8]. Another possibility is employing CNTs, since CNT has the long nanofiber shape. However, it is difficult to grow CNT arrays on common substrates such as plastics and textiles due to van der Waals forces of CNTs bundles.

The purpose of this study is to develop superhydrophobic textiles with self-cleaning function using multi-walled carbon nanotubes (CNTs) and water-repellents which have low surface energy (Teflon AF[®]). The first step is to prepare optimal fabric structure after analyzing the relationship between surface roughness and superhydrophobicity. The second stage is to study the optimal dispersion condition of CNTs into water-repellents and their washing durability of the treatment.

2. Experimental

2.1 Preparation of Materials

The micro structures of surface were prepared by various yarn diameters and yarn types [Table 1], and nanoscaled superhydrophobic surfaces were manufactured by finishing the textiles with CNT nanoparticles using water-repellents (Teflon AF[®]) as a binder.

Table 1. Characteristics of the specimens

Specimen code	Fiber composition	Density
N/P ICF	Nylon/Polyester Islands-in-the-sea Conjugate Fibers	272×136
20F	Polyester 20denier Filament	240×144
50F	Polyester 50denier Filament	192×104
50D	Polyester 50denier DTY	176×112
75D	Polyester 75denier DTY	144×96
75/150D	Polyester 75/150denier DTY	144×80

Teflon AF[®] is based on a copolymer of perfluoro (2,2-dimethyl-1,3-dioxole) and tetrafluoroethylene. A major advantage for substrate casting is its solubility in fluorinated solvents. Therefore, substrates may easily be spin or dip coated. After coating, the material is cured above the glass transition temperature of 160°C for obtaining polymerized, hydrophobic and optical transparent samples.

In this study, CNTs had length of 10-40 µm and diameter of 40-60nm which have the long nanofiber shape (Fig. 1). To improve of the surface hydrophobicity and surface roughness, the textile substrates were treated with Teflon-CNT composites.

Teflon-CNT coated samples were prepared by treating textile substrates with a dispersion of CNTs in Dupont Teflon AF[®] solution. The Teflon AF[®] was dissolved in FC-770 (3M, electronic liquid of perfluorocarbons) solution. And then CNTs were added to the Teflon AF[®] solution in an ultrasonic bath for 30 min to obtain a short-life stable dispersion, and the fabrics were soaked.

The soaked samples were dried at the temperature of 110°C for 5 min, and then are cured at 170°C for 3 min. The samples were rinsed with water several times to remove the extra CNTs and surfactants. The final samples were dried at 110°C for 3min.

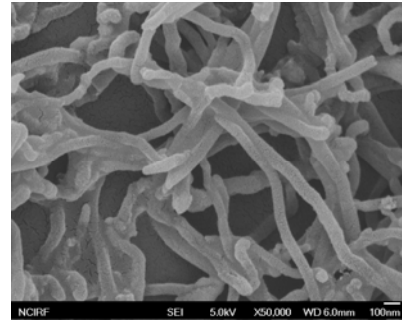


Figure1. Fe-SEM image of carbon nanotubes.

2.2 Evaluation

The appearance and roughness of the specimen surfaces were analyzed using an atomic force microscope and Fe-SEM (jeol. Japan). Contact angle and tilting angle measurement were carried out using a Theta Lite contact angle meter (attension, Finland). Waterproof-breathable properties were estimated by measuring pore size and distribution, air permeability (ASTM D737), water vapor transmission (ASTM E 96).

3. Results and discussion

Various roughnesses of the specimens were obtained by the combination of different yarn diameters and yarn finishings (figure 2). The diameter of a polyester filament ranged from 11 µm to 13 µm. The papillae size of 20F sample was around 100 µm. It was shown that DTY samples could increase the roughness of the surface more effectively, because of its inherent bulky and hairy surface.

The surface morphologies of the samples before and after the coating treatment are shown in Figure 3. The Fe-SEM image of the pristine sample shows smooth surface of the fibers. However, the CNT treated sample was shown to have nano-sized roughness with a layer of CNTs, well deposited on the surface of polyester fibers. Particularly, the sample made of Islands-in-the-sea conjugate fibers had long micrometer-sized papillae that could effectively “hold” the air in place.

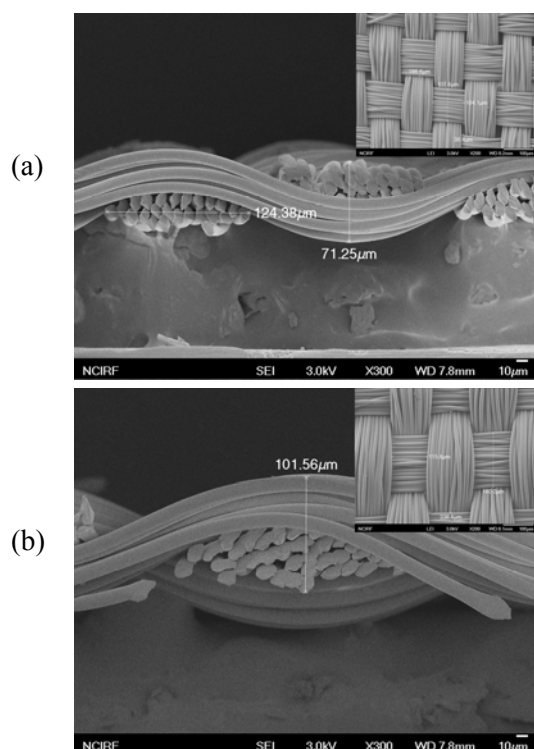


Figure 2. Fe-SEM images of the polyester plain woven fabrics; (a) 20 denier filament, (b) 50 denier filament.

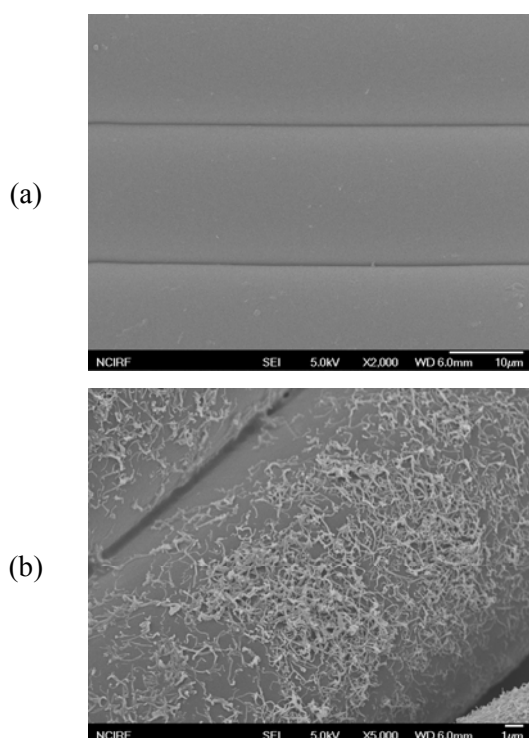


Figure 3. Fe-SEM images of pristine sample (a) and CNTs-Teflon treated sample (b).

Figure 4 shows that the static contact angle of CNT-Teflon treated sample is greater than 164° and rolled off even at slight inclination. Also, the results showed the increasing tendency in superhydrophobicity with the increase of CNT amount. This result revealed that the CNTs with long nanofiber shape maintain the trapped air bubbles. Thus, a more hydrophobic surface was generated because of the reduced the fraction of the solid/liquid interface under the water drop. Also, the washing durability of the treatment was affected by chemical compositions and treatment conditions of the water-repellent.

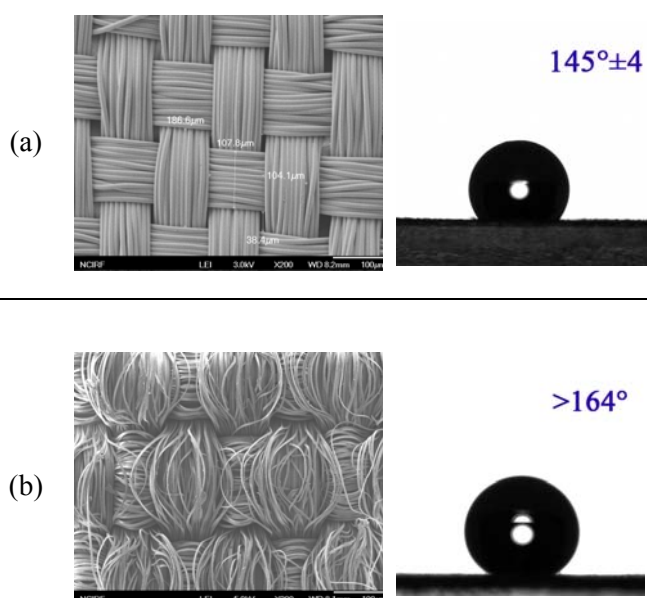


Figure 4. Fe-SEM images of and water contact angles on CNT-Teflon treated samples; (a) 20F, (b) N/P ICF.

References

- [1] M. Sun, C. Luo, L. Xu, H. Ji, "Artificial Lotus Leaf by Nanocasting", *Langmuir*, Vol. 21, pp 8917-8981, 2005
- [2] X. Li, D. Reinhoudt, M. Crego-Calama, "What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces", *Chemical Society Reviews*, Vol. 36, pp 1350-1368, 2007
- [3] T. Verho, C. Bower, P. Andrew, S. Franssila, O. Ikkala, R. Ras, "Mechanically durable

superhydrophobic surfaces”, *Advanced Materials*, pp 1-6, 2010

- [4] A. Marmur, “Wetting on hydrophobic rough surface: to be heterogeneous or not to be?” *Langmuir*, Vol, 19, pp 8343-8348 , 2003
- [5] J. Bravo, L. Zhai, Z. Wu, R.E. Cohen, M. F. Rubner, “Transparent superhydrophobic films based on silica nanoparticles”, *Langmuir*, Vol. 23, pp7293-7298, 2007
- [6] Y. Liu, X. Wang, K. Qi, J. H. Xin, “Functionalization of cotton with carbon nanotubes” *Journal of Materials Chemistry*, Vol. 18, pp 3454-3460, 2008
- [7] Y. Liu, X. Chen, J. H. Xin, “Can superhydrophobic surfaces repel hot water” *Journal of Materials Chemistry*, Vol. 19, pp 5602-5611, 2009
- [8] Y. Lee, S. Park, K. Kim, J. Lee, “Fabrication of hierarchical structures on a polymer surface to mimic natural superhydrophobic surfaces”, *Advanced Materials*, Vol. 19, pp 2330-2335, 2007
- [9] J. Zimmermann, S. Seeger, “Water shedding angle : a new technique to evaluate the water-repellent properties of superhydrophobic surfaces”, *Textile Research Journal*, Vol.79, No. 17, pp1565-1571, 2009