ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 21, No. 1. 2015

Development of Superhydrophobic Fabrics by Surface Fluorination and Formation of CNT-induced Roughness

Myoung Hee SHIM [1], Jooyoun KIM [2], Chung Hee PARK [1 *]

[1] *Department of Textiles, Merchandising, and Fashion Design, Seoul National University, Seoul, 151-742, Republic of Korea*
[2] *Department of Apparel, Textiles, and Interior Design, Kansas State University, Manhattan, KS 66506, USA*

crossref http://dx.doi.org/10.5755/j01.ms.21.1.5762

Received 21 November 2013; accepted 22 February 2014

Superhydrophobic textile material having self-cleaning function was developed by employing carbon nanotubes (CNTs) and water-repellent agents. Hydrophobic fabrics were prepared on 100 % polyester woven fabrics with various yarn diameters and yarn types. The wetting behavior of fabrics with different treatments was compared for: siloxane repellent, fluorocarbon repellent, and CNT added fluorocarbon repellent. Drawn textured yarn (DTY) fabrics exhibited higher contact angle (CA) than filament yarn fabrics due to the larger surface roughness contributed by the textured yarn. Fabrics treated with fluorocarbon presented larger CA and lower shedding angle than those treated with siloxane, because of the lower surface energy of fluorocarbon repellent. Specimens made of 50 denier DTY and treated with CNT-Teflon AF® showed the most superhydrophobic characteristics in the study, producing the static contact angle greater than 150° and the shedding angle smaller than 15°. CNT on fabric surface contributed to the nano-scale surface roughness to hold the air traps like papillae of lotus leaf, giving superhydrophobic characteristics.

Keywords: superhydrophobic, fabric, contact angle, shedding angle.

1. INTRODUCTION

Application of self-cleaning fabrics is gaining attention [1 – 2] for their convenience of less soiling and reduced frequency of laundering. Among the methods to achieve the self-cleaning textiles, fabrication of textile surface mimicking the lotus leaf has been of particular interest. The superhydrophobic and self-cleaning characteristic of lotus leaf, showing water contact angle (CA) of 161° ±2.7° and CA hysteresis of 2°, are known to be attributed to the binary scale roughness in size of 100 nm to 10 μm [1 – 2].

Hydrophobic property of a material surface is governed by both the chemical composition of the surface and the cooperative effect of nanostructures within the micrometer scale area, so-called the hierarchical roughness [3]. Those two level-roughness structure enable the trapping of air under water droplets, thereby contributing to rolling off of water droplets, and this phenomenon is applicable in engineering a superhydrophobic surface.

The characteristic of superhydrophobicity is often defined by the following. First, the equilibrium water contact angle θ of a surface is greater than 150°. Such high contact angles can be achieved by the combination of low surface energy and geometric surface roughness, while a smooth surface can usually generate an intrinsic contact angle only up to about 120° [4]. Second, water must not stick to the surface, and the droplets should roll off easily, which can relate to the main characteristics of self-cleaning surface.

The wetting behaviour on a rough surface in terms of contact angle of liquid can be explained by the Cassie-Baxter model [5] :

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

where f_1 is the fraction of the solid surface in contact with liquid; f_2 is the fraction of the air in contact with liquid; θ_r^{CB} is the apparent contact angle of liquid on a rough surface in a Cassie-Baxter state; θ_e is the equilibrium contact angle when the liquid droplet sits on a smooth surface; and θ_e' is the equilibrium contact angle when the liquid droplet sits on air.

In the Cassie-Baxter model, smaller f_1 produces larger apparent contact angle θ_r^{CB}, and various techniques have been studied to reduce f_1 by giving the geometrical roughness on surface such as; sol-gel methods [6], templation [7], formation of colloidal assemblies [8], layer-by-layer deposition [9], micelle formation [10 – 11], plasma-enhanced condensed vapor deposition [12], and physical vapor deposition [13]. Most of those efforts to produce superhydrophobic surfaces by forming roughness structure were made for industrial applications, with the theoretical discussions of Cassie-Baxter behaviour. However, there are few studies that examined the validity of the theoretical models applying to the superhydrophobic textile materials or that associated the level of hydrophobicity with different repellent treatments.

Among the few studies on self-cleaning textiles, Zimmermann et al. [14, 15] reported the superhydrophobic behaviour of of polyethylene terephthalate (PET) fabric treated with polymethylsilsesquioxane ($CH_3SiO_{3/2}$), where silicone nano-filaments grew on fabric surface to form nano-pillars. However, the durability of nano-filaments was not achieved, losing the superhydrophobic nature after one-time laundering. Liu et al. [16] treated cotton fabric with carbon nanotube (CNT) embedded in polybutylacrylate (PBA) by dip-pad-dry-cure process,

* Corresponding author. Tel.: +82-28806842; fax.: +82-28758359.
E-mail address: *junghee@snu.ac.kr* (C. H. Park)

and the resulting fabric exhibited the contact angle greater than 150°. CNT would be another good candidate to fabricate the nano-scale roughness on fabric surface, yet it would be challenging to uniformly grow CNT arrays on textile substrate due to van der Waals forces of CNTs bundles.

Measurement of static contact angle of water droplet on fabric substrate has been used as to evaluate the superhydrophobicity of fabrics. However, this method could generate measurement errors from the unclear contact boundary between fabric surface and water droplet. Moreover, this measurement is often difficult to differentiate the level of hydrophobicity of specimens, generating very large contact angles [17]. Another measurement, contact angle hysteresis, has also been discussed as challenging to produce an accurate measurement. Thus, alternative methods such as measurement of shedding angle or sliding angle, and imaging analysis of the water drop movement have been suggested [18, 19].

Research on the area of superhydrophobic textile application has been progressed rather recently, and this area needs further studies on theoretical validation and experimental follow-up for fabricating superhydrophobic fabrics. Also, the evaluation method for superhydrophobicity needs to be revisited to provide more practical and relevant analysis to differentiate the level of hydrophobicity of materials.

In the earlier report in our study [20], theoretical validation of the Cassie-Baxter model was provided on the hydrophobic woven polyester fabrics, with the estimation of fabric roughness represented by $f_1 + f_2$ [20]. In this study, a superhydrophobic fabric mimicking the binary rough structure of lotus leaf was fabricated employing CNT and fluoro chemicals, and the effect of fabric roughness and surface energy on superhydrophobicity was investigated. To this end, five different fabrics that were varied in roughness by their yarn size and texture were chosen as substrates for superhydrophobic treatment. Two different repellent agents, siloxane and fluorocarbon compounds having varied surface energy, were used as treatment chemicals. A relevant measurement method to evaluate the superhydrophobicity of fabric was discussed.

2. EXPERIMENT

2.1. Preparation of materials

100 % Polyester woven fabrics having various yarn diameters and yarn types were purchased from Dong Jin Textile Co., Ltd. (Korea). The number given in the specimen code indicates the denier of yarn, and the following alphabet code D and F is to discriminate between the filament yarns with and without the drawn textured yarn (DTY) finishing. The characteristics of fabrics are presented in Table 1. All fabrics were purified as in the following. Fabric specimens were washed with a solution of 5 g/l anionic surfactant and 10 g/l Na_2CO_3 for 30 minutes at 97 °C ±3 °C, rinsed and dried. Dried fabrics were extracted for 8 hours with a mixture of benzene-ethanol (2 : 1 v/v) in a soxhlet, rinsed with 40 °C water, and dried at 105 °C ±2 °C for 20 minutes.

Table 1. Characteristics of the fabric specimens

Specimen code	Fiber composition	Weight (g/m^2)	Density (in cm)
20F	100 % Polyester 20deneir filament	38.12	94×57
50F	100 % Polyester 50deneir filament	66.12	76×41
50D	100 % Polyester 50deneir DTY	65.53	69×44
75D	100 % Polyester 75deneir DTY	83.42	57×38
150D	100 % Polyester 75/150deneir DTY	107.99	57×31

Fabrics with different surface energy were prepared using two different water repellent agents; a silicone agent, polydimethylsiloxane (Phobol RSH®) obtained from Huntsman (USA) and Teflon AF® (DuPont, USA). Teflon AF® is based on a copolymer of perfluoro(2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole) (PDD) and tetrafluoroethylene (TFE). Silicone agent was used as a dilution in deionized water. Fabrics were soaked in the water repellent solution for 10 seconds, dried at 120 °C for 2 min in a drying chamber, then cured at 160 °C for 5 min. Treatment conditions applied were the same for both siloxane and fluorocarbon treatment.

Rough surface in nano to micro scale was fabricated by treating the fabrics with CNT particles. Teflon AF® was used as a binder. CNT with Teflon AF® was prepared by dispersing CNT in Teflon AF® dissolved in FC-75®, liquid perfluoro-2-butyltetrahydrofuran (3M, USA). 1 wt% of CNT in Teflon AF® solution was sonicated in an ultrasonic bath for 20 min to obtain a stable dispersion. Fabrics were soaked in the solution for 10 seconds, dried at 120 °C for 2 min, then cured at 160 °C for 5 min.

From the preliminary experiment with 50D fabric, the soaking in CNT-Fluoro solution was conducted two and four times respectively, where four times of soaking produced higher level of hydrophobicity whoes shedding angle was 4.4°. Two times of soaking produced fabrics with shedding angle of 9.2°. Thus all other experiments were conducted by four times of soaking in CNT-Fluoro solution.

Specimens treated with Phobol RSH®, Teflon AF®, Teflon AF® and CNT were coded as Silicone, Fluoro, Fluoro+CNT, respectively.

CNTs observed by Transmission Electron Microscopy (JEM1010, JEOL, Japan) appeared to have length of 10 μm – 30 μm and diameter of 10 nm – 20 nm (Fig. 1). For uniform and stable dispersion of CNT in the polymer solution, COOH functionalized CNT (Hanwha Inc., Korea) was used.

2.2. Evaluation

Surface roughness of the flat glass slide treated with silicone and fluorocarbon repellents respectively was analysed by Atomic Force Microscopy (NANO Station II, Surface Imaging Systems, Germany) with tapping mode in 4 nm resolution. AFM probe used was PointProbe® Plus Non-Contact/ Tapping Mode – High Resonance Frequency

– Reflex Coating (PPP-NCHR) obtained from Nanosensors™. The tip was in pyramidal shape with the tip radius of curvature being less than 10 nm, and was coated with Al on detector side. The force constant and resonance frequency were 42 N/m and 330 kHz, respectively. The roughness of surfaces treated with different repellents was compared by root-mean-square (RMS) of AFM analysis.

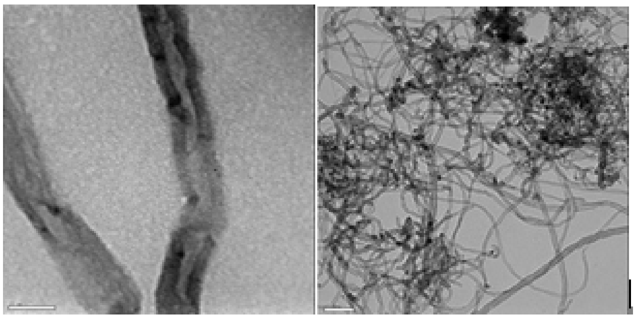


Fig. 1. TEM image of multi-walled CNT: left ×50,000 (scale bar in 100 nm); right ×200,000 (scale bar in 20 nm)

Contact angle and shedding angle of water droplet was measured at room temperature using the goniometer (Attension® Theta Lite, BiolinScientific, Sweden) equipped with cradle, where a sliding angle of the specimen holder can be changed by 0.1°. A fabric specimen was fixed on a glass slide using an adhesive tape for the measurement. For the static contact angle measurement, 3.6 µl ±0.2 µl drops of deionized water were placed on 5 different locations of the surface. The contact angle was recorded within one second upon dropping, and an average of ten different measurements was used for analysis.

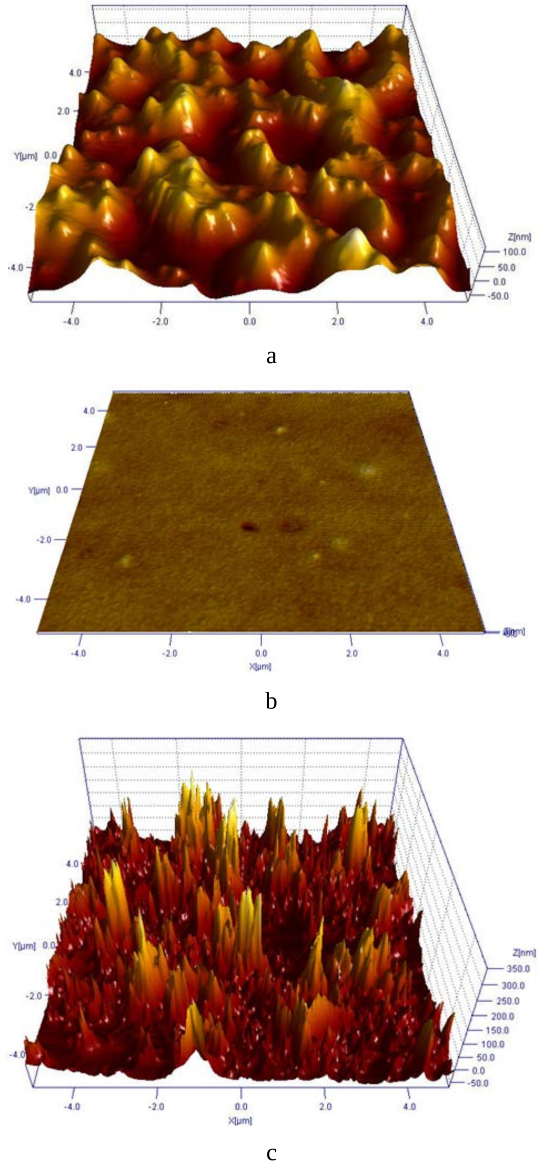
The shedding angle, at which a droplet rolls off 2 cm of distance or greater, was recorded as shedding angle [21]. To have the free fall of a water drop from the syringe, the volume of water drop needed at least 12.5 µl ±0.1 µl. A water drop in 12.5 µl ±0.1 µl was dropped from a 1 cm distance to a specimen surface. The volume of water droplet was 12.5 µl ±0.1 µl, and the distance between the specimen surface and the syringe was set at 1 cm. All measurements were made from 5 different spots in a fabric and the average of 5 measurements was recorded.

For contact angle hysteresis, advancing and receding contact angles were measured from the image captured when a water droplet of 3.5 µl ±0.2 µl contacting with the syringe needle was moved from right to left in 5 mm distance. Smaller contact angle hysteresis means that a liquid drop moves in a shape close to a spherical shape, and the substrate is more hydrophobic. Bouncing image of water droplet from the fabric surface was obtained when the water droplet of 3.6 µl ±0.2 µl was dropped from 1 cm of height. Roughness of the specimen surface was analysed using FE-SEM (Auriga, Carl Zeiss, Germany). Chemical composition of treated fabric surface was measured using X-ray photoelectron spectroscopy (Sigma Probe, ThermoVG, UK) equipped with a monochromatic Al K excitation source. The spectra were collected with 1.0 eV step at 50 eV constant pass energy for wide scan and 0.1 eV step at 20 eV pass energy for narrow scan. Spectroscopic data were processed by Avantage software (ThermoVG).

3. RESULTS AND DISCUSSION

3.1. Morphology of substrates treated with water-repellents

Three different repellent treatments, Silicone, Fluoro and Fluoro+CNT coating were performed on a flat glass slide, and the roughness of coated surface was analyzed by RMS measurement of AFM. In Fig. 2, Silicone treated substrate showed rougher surface than Fluoro treated substrate, because the colloidal form of silicone agents formed aggregates when diluted in water, creating a small scale dull roughness on surface.



a

b

c

Fig. 2. AFM image of flat surface treated with water-repellents: a – Silicone; b – Fluoro; c – Fluoro + CNT

From Table 2, Fluoro showed smooth surface with RMS of about 0.1 nm. Fluoro agent, comprised of PDD and TFE, was well dissolved in perfluoro-2-butyltetrahydrofuran solvent, without forming aggregates. When CNT dispersion in Fluoro was treated on a flat substrate, irregular and sharp roughness was observed from the surface (Fig. 2, c), with a large RMS value. Increased roughness formed by CNT deposition was expected to effectively reduce f_1, the contact area of solid substrate in contact with water droplet, generating the air traps between the geometrical asperities provided by CNTs.

Table 2. The RMS values and static contact angle of water drop on the flat surface treated with water-repellents

	Silicone	Fluoro	Fluoro+CNT
RMS	30.6 nm	0.1 nm	48.9 nm
Static contact angle (°)	114.4	120.6	125.8

3.2. Evaluation of hydrophobicity of treated fabrics

Static water contact angles on a glass slide (flat) and fabrics with different treatments are compared in Fig. 3. From the previous study that estimated the fabric roughness by $f_1 + f_2$ [20], the surface roughness was estimated larger in the order of $50D \approx 75D > 150D \approx 20F > 50F$ [20]; that is, $f_1 + f_2$ was smaller in that order. It can be expected that rougher fabric would have larger static contact angle; however, the contact angle differences by the fabric types were not apparent. On the other hand, the contact angle difference between the untreated and treated specimens was obvious to be monitored.

For most of the fabric types, Fluoro treated fabrics presented slightly higher contact angles than Silicone treated fabrics because of the lower surface energy of Fluoro than Silicone, though the differences were negligible for some specimens. Fluoro + CNT specimens showed slightly larger contact angles than Fluoro specimens, which is thought to be attributed to the added roughness by the introduction of CNT particles. However, the static contact angle measurement could not discriminate the level of hydrophobicity among the specimens whose contact angle was near 150°.

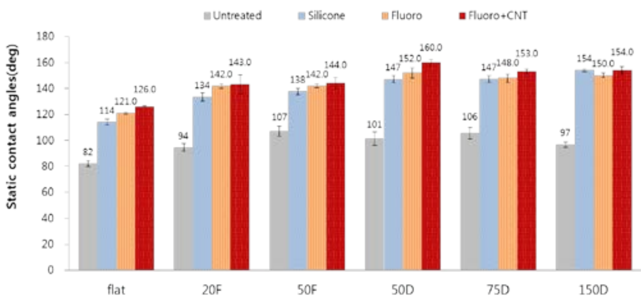


Fig. 3. Static contact angle measurement for the varied fabric types and treatments

As an alternative evaluation method for hydrophobicity, shedding angle at which the water droplet starts to roll off was considered (Fig. 4). It should be noted that the shedding angle greater than 80° could not be practically measured, and the shedding angle of the untreated substrate was recorded as 80°. The level of hydrophobicity for different treatments was better discriminated by shedding angle measurement, producing a smaller shedding angle for more hydrophobic surface. Shedding angle was observed smaller in the order of $50D < 75D < 150D < 20F < 50F$, which roughly corresponded to the order of fabric roughness estimated by $f_1 + f_2$ in the previous study [20]. DTY specimens compared to filament specimens showed smaller shedding angles to roll off the water drop, which implicates higher repellency of DTY fabric surfaces. The texturized yarns in DTY fabrics add the random roughness to filament yarns, providing the small-scale bumps that can effectively hold the air traps when contacting a water drop, thereby contributing to enhanced hydrophobicity of surfaces. Also, fabrics with small yarn size presented more hydrophobic characteristic with lower shedding angles. The measurements also differentiated the hydrophobic properties between Silicone and Fluoro, and between Fluoro and Fluoro+CNT, demonstrating the validity of this mesurement method as an effective and differentiating evaluation of hydrophobicity of fabrics, particularly where the contact angle is near or greater than 150°. In all fabric types, Fluoro + CNT specimens showed shedding angles lower than 10°.

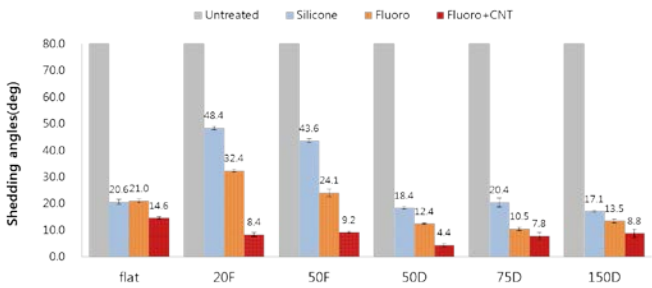


Fig. 4. Shedding angle for the varied fabric types and treatments

Among the static contact angle and shedding angle measurements, 50D fabric treated with Fluoro + CNT showed the highest static contact angle of 160° and the lowest shedding angle of 4.4°. From the measurement of static contact angles, the differences among the specimens were not distinct. However, the shedding angle measurements presented observable tendency of the level of hydrophobicity. The nano-scale roughness contributed by CNT addition on fiber surface was speculated to result in further decrease in shedding angle compared to the Fluoro only treated specimen. It was inferred that the nano-scale roughness created by CNT was effective in holding air traps under nano-scale bumps, reducing the fabric surface area in contact with water droplet, thus exhibiting superhydrophobic characteristic.

3.3. Contact angle hysteresis

Contact angle hysteresis measures the difference in advancing and receding contact angles immediately before the water droplet starts to roll off at a certain sliding angle; that is, contact angle hysteresis = advancing contact angle - receding contact angle. When the interfacial attraction between the substrate surface and water droplet is small, the water drop forms in more spherical shape, giving a small contact angle hysteresis [22, 23]. However, the measurement is often challenging [17, 19], because it is difficult to catch an image immediately before the water drop starts to roll. Recently a modified method is often used, utilizing a syringe needle to move a liquid drop and measure the advancing and receding contact angles [23, 24].

In this study, the contact angle hysteresis was measured using a syringe needle to move a 3.5 µl ±0.2 µl size water drop in 5 mm distance on a substrate. The image of droplet shape was presented in Fig. 5. On 50D fabric, Fluoro+CNT treated surface (lower image) formed a rounder drop than Fluoro treated surface (upper image), demonstrating the higher level of surface hydrohobicity.

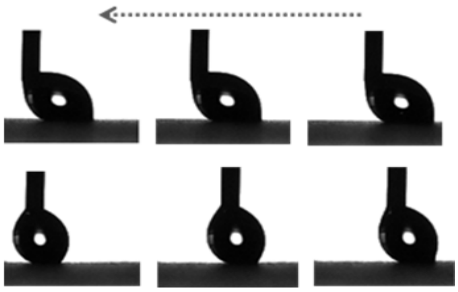


Fig. 5. Contact angle hysteresis of the fabric treated with Fluoro (upper) and Fluoro + CNT (lower)

3.4. Bouncing behavior

Bouncing of water droplet is a unique characteristic of a superhydrophobic surface. When a liquid droplet collides with a superhydrophobic surface in a certain speed, a droplet tends to bounce off rather than adhere to the surface, and this characteristic leads to a self-cleaning property and dry-feel of a surface. The bouncing phenomenon can be explained as in the following; a liquid droplet increases its surface area when colliding with a surface, which leads to the increase of the surface energy of a droplet. When a water drop falls on a substrate, the potential energy produced at collision would be transferred as kinetic energy or be absorbed on the contacting surface. As for a hydrophobic surface where the contact area between the liquid drop and surface is small, the potential energy gets effectively transferred as the kinetic energy, which induces the bouncing of a liquid drop at the superhydrophobic surface [23, 25].

This bouncing phenomenon, closely associated with self-cleaning characteristic, was clearly observed from the 50D treated with Fluoro + CNT (Fig. 6), which demonstrated the feasibility of utilizing this fabric to self-cleaning applications. The very hydrophobic nature, resulted from the low surface energy by Fluoro coating [26] and the roughness added by CNT, generated the bouncing behaviour of a droplet by reducing the contact area between the substrate and the liquid drop.

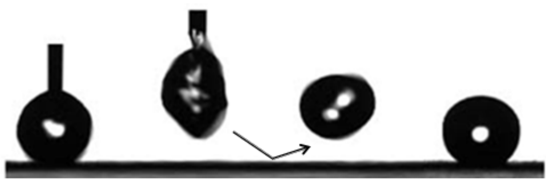


Fig. 6. Bouncing phenomenon on 50D specimen treated with Fluoro + CNT

The chemical composition of 50D treated with Fluoro only and Fluoro + CNT was analyzed by XPS (Fig. 7). Fluoro specimen had the compositions of C 49.44 %, O 17.65 %, Si 0.67 %, F 32.24 %, and the fluorine/carbon ratio was 0.65. Fluoro+CNT specimen had the compositions of C 61.75 %, O 21.04 %, Si 0.74 %, F 16.48 %, where fluorine/carbon ratio was 0.27. The reduced fluorine/carbon ratio for Fluoro + CNT over Fluoro resulted from the increased carbon amount by the CNT addition at the fabric surface. Despite the reduced fluorine ratio in Fluoro + CNT specimen, the surface energy of the substrate would not have increased as the CNT particles would remain as coated by Fluoro compound.

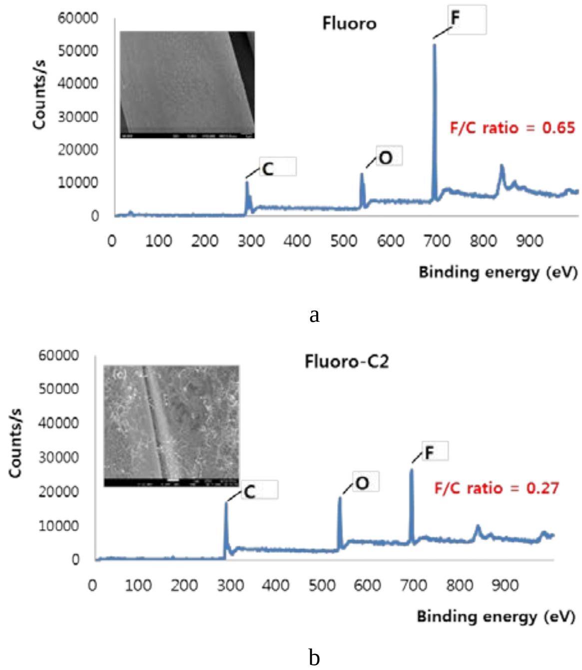


Fig. 7. XPS spectra of 50D fabric treated with: a – Fluoro; b – Fluoro + CNT

4. CONCLUSIONS

The effect of surface energy and fabric roughness on the level of hydrophobicity was investigated. Fabric types, repellent chemicals, addition of CNT were varied to fabricate the different level of hydrophobic polyester woven fabrics. The evaluation method to effectively measure the hydrophobicity of fabrics was examined.

FE-SEM image of Fluoro + CNT treated substrate confirmed the nano-scale roughness introduced by CNT addition. The roughness contributed by CNT augmented the hydrophobic characteristic by reducing the surface area in contact with liquid droplet. Fluoro + CNT treated 50D fabric presented the characteristics of superhydrophobic materials, with the static contact angle of 160° and shedding angle of 4.4°. From this specimen, bouncing behaviour of water droplet was also observed. The results demonstrated that this developed fabric can be utilized as a self-cleaning material.

Of the measurement methods to evaluate the hydrophobicity of fabric surface, shedding angle, rather than static contact angle, was more relevant to differentiate the level of hydrophobicity for a hydrophobic material whose static contact angle was close to or greater than 150°.

This study is meaningful as a groundwork to develop superhydrophobic fabrics by engineering the surface energy and roughness structures. For practical applications to clothing textiles, further evaluation in washing durability and comfort properties need to be performed.

Acknowledgments

This research was supported by the SRC/ERC program of MOST/KOSEF (R11-2005-065) and National Research Foundation of Korea (NRF) Grant funded by the Korean Government (2011-0014765).

REFERENCES

1. **Sun, M., Luo, C., Xu, L., Ji, H.** Artificial Lotus Leaf by Nanocasting *Langmuir* 21 2005: pp. 8917 – 8981.
2. **Li, X. M., Reinhoudt, D., Crego-Calama, M.** What Do We Need for a Superhydrophobic Surface? A Review on the Recent Progress in the Preparation of Superhydrophobic Surfaces *Chemical Society Reviews* 36 2007: pp. 1350 – 1368.
3. **Lee, Y., Park, S. H., Kim, K. B., Lee, J. K.** Fabrication of Hierarchical Structures on a Polymer Surface to Mimic Natural Superhydrophobic Surfaces *Advanced Materials* 19 2007: pp. 2330 – 2335.
4. **Verho, T., Bower, C., Andrew, P., Franssila, S., Ikkala, O., Ras, R. H. A.** Mechanically Durable Superhydrophobic Surfaces *Advanced Materials* 23 2011: pp. 673 – 678. http://dx.doi.org/10.1002/adma.201003129
5. **Marmur, A.** Wetting on Hydrophobic Rough Surfaces: To be Heterogeneous or Not to Be? *Langmuir* 18 2003: pp. 8343 – 8348. http://dx.doi.org/10.1021/la0344682
6. **Hikita, M., Tanaka, K., Nakamura, T., Kajiyama, T., Takahara, A.** Super-Liquid-Repellent Surfaces Prepared by Colloidal Silica Nanoparticles Covered with Fluoroalkyl Groups *Langmuir* 21 2005: pp. 7299 – 7302.
7. **Lee, W., Jin, M. K., Yoo, W. C., Lee, J. K.** Nanostructuring of a Polymeric Substrate with Well-Defined Nanometer-Scale Topography and Tailored Surface Wettability *Langmuir* 20 2004: pp. 7665 – 7669.
8. **Zhang, G., Wang, D., Gu, Z. Z., Mohwald, H.** Fabrication of Superhydrophobic Surfaces from Binary Colloidal Assembly *Langmuir* 21 2005: pp. 9143 – 9148. http://dx.doi.org/10.1021/la0511945
9. **Bravo, J., Zhai, L., Wu, Z., Cohen, R. E., Rubner, M. F.** Transparent Superhydrophobic Films Based on Silica Nanoparticles *Langmuir* 23 2007: pp. 7293 – 7298.
10. **Xie, Q., Fan, G., Zhao, N., Guo, X., Xu, J., Dong, J., Zhang, L., Zhang, Y., Han, C.** Facile Creation of a Bionic Super-Hydrophobic Block Copolymer Surface *Advanced Materials* 16 2004: pp. 1830 – 1833. http://dx.doi.org/10.1002/adma.200400074
11. **Han, J., Xu, X., Cho, K.** Diverse Access to Artificial Superhydrophobic Surfaces Using Block Copolymer *Langmuir* 21 2005: pp. 6662 – 6665.
12. **Riekerink, M. B. O., Terlingen, J. G. A., Engbers, G. H. M., Feijen, J.** Selective Etching of Semicrystalline Polymer: CF_4 Gas Plasma Treatment of Poly(ethylene) *Langmuir* 15 1999: pp. 4847 – 4856. http://dx.doi.org/10.1021/la990020i
13. **Ma, M., Mao, Y., Gupta, M., Gleason, K., Rutledge, G.** Superhydrophobic Fabrics Produced by Electrospinning and Chemical Vapor Deposition *Macromolecules* 38 2005: pp. 9742 – 9748.
14. **Zimmermann, J., Artus, G., Seeger, S.** Long Term Studies on the Chemical Stability of a Superhydrophobic Silicone Nanofilament Coating *Applied Surface Science* 253 2007: pp. 5972 – 5979.
15. **Zimmermann, J., Reifler, F., Fortunato, G., Gerhardt, L., Seeger, S. A.** Simple, One-Step Approach to Durable and Robust Superhydrophobic Textiles *Advanced Functional Materials* 18 2008: pp. 3662 – 3669.
16. **Liu, Y., Chen, X., Xin, J.** Can Superhydrophobic Surfaces Repel Hot Water? *Journal of Materials Chemistry* 19 2009: pp. 5602 – 5611. http://dx.doi.org/10.1039/b822168e
17. **Seeger, J., Reifler, F.** Water-Shedding Angle: A New Technique to Evaluate the Water-repellent Properties of Superhydrophobic Surfaces *Textile Research Journal* 79 2009: pp. 1565 – 1570.
18. **Oner, D., McCarthy, T.** Ultrahydrophobic Surface Effects of Topography Length Scales on Wettability *Langmuir* 16 2000: pp. 7777 – 7782.
19. **Gao, L., McCarthy, T.** How Wenzel and Cassie Were Wrong *Langmuir* 23 2007: pp. 3762 – 3765.
20. **Shim, M. H., Kim, J., Park, C. H.** The Effects of Surface Energy and Roughness on the Hydrophobicity of Woven Fabrics *Textile Research Journal* online first publication: doi: 10.1177/0040517513495945, 2014. http://dx.doi.org/10.1177/0040517513495945
21. **Zimmermann, J., Seeger, S., Reifler, F. A.** Water Shedding Angle: A New Technique to Evaluate the Water-Repellent Properties of Superhydrophobic Surface *Textile Research Journal* 79 2009: pp. 1565 – 1570.
22. **Wang, S., Jiang, L.** Definition of Superhydrophobic States *Advanced Materials* 19 2007: pp. 3423 – 3424.
23. **Minko, S., Muller, M., Motornov, M., Nitschke, M., Grundke, K., Stamm, M.** Two-level Structured Self-Adaptive Surfaces With Reversibly Tunable Properties *Journal of the American Chemical Society* 125 2003: pp. 3896 – 3900. http://dx.doi.org/10.1021/ja0279693
24. **Baldacchini, T., Carey, J. E., Zhou, M. Mazur, E.** Superhydrophobic Surfaces Prepared by Microstructuring of Silicon Using a Femtosecond Laser *Langmuir* 22 2006: pp. 4917 – 4919.
25. **Kalantarian, A., David, R., Neumann, A. W.** Methodology for High Accuracy Contact Angle Measurement *Langmuir* 25 2009: pp. 14146 – 14154.
26. **Seong, H. K., Jeong-Hoon, K., Bang-Kwon, K., Han, S. U.** Superhydrophobic CF_x Coating via in-Line Atmospheric RF Plasma of He-CF_4-H_2 *Langmuir* 21 2005: pp. 12213 – 12217.