EFFECT OF ULTRASONIC WASHING ON THE PROPERTIES OF SUPERHYDROPHOBIC COTTON FABRIC COATED WITH EPOXY COMPOSITE FILM

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Abstract

The objective of this work was to evaluate properties of cotton fabric samples coated with epoxy composite film filled with APTES-modified silica (SiO_2) nanoparticles. The characteristics of superhydrophobic fabrics were investigated as function of the durability of ultrasonic washing. As-prepared samples, the fabric coated with 20 vol% SiO_2 modified APTES exhibited typical characteristic of superhydrophobic material having high water contact angle (WCA) of 152° and low contact angle hysteresis (CAH). The values of WCA and CAH of fabrics slightly decreased with increasing number of washing cycles. But even after 10 washing cycles the samples showed almost spherical drops of common household liquids (water, coffee, juice, honey, and ketchup sauce) on their surface, indicating their excellent self-cleaning ability. Also stains of graphite powder (as model for dust) on the coated fabrics were easily rinsed out with water. Moreover, the coated specimens may have potential to be used for oil/water separation: their separation efficiency was higher than 99%, and was as high as 97% after 10 washing cycles.

Keywords: Aminopropyltriethoxysilane, Silica, Superhydrophobic, Ultrasonic washing, Durability.

Abbreviations	
APTES	Aminopropyltriethoxysilane
ATR-FTIR	Attenuated Total Reflection Fourier Transform Infrared Spectroscopy
CAH	Contact Angle Hysteresis
SEM	Scanning electron microscope
SiO_2	Silica
SiO_2-APTES	Surface modification of SiO_2 with APTES
WCA	Water Contact Angle

1. Introduction

Cotton fabric has been widely used in daily life for many applications such as clothing, decoration, and technical fabrics. It is a well-known fact that cotton fabrics have excellent properties including softness, flexibility, low cost and low density [1-3]. However, overall applications of the cotton fabrics are limited to certain areas due to their high susceptibility to pollution that adversely influence the development for further applications. Thus many research projects have been focused on the enhancement of properties of cotton fabrics [4-7]. To create a self-cleaning surface is the one of the approaches that can effectively protect the cotton fabric from any kind of pollution and stain. In nature, the unique biological organisms such as lotus leave, raspberry and cauliflower exhibit self-cleaning property against any residual dirt or stain [8-10]. So the mimicking of natural hydrophobic surface has attracted much attention by academics and industries to use cotton-based fabrics for advanced applications [11-15].

Generally, the hydrophobicity of artificial surface can be manufactured by two strategies, namely (1) creating sequential roughness on hydrophobic surfaces, [16, 17] and (2) coating a micro/nanostructured anatomy of the surface with low surface energy molecules [5, 6, 18-20]. Based on the results, superhydrophobic cotton fabric exhibiting the water contact angle (WCA) greater than 150° is water repellent [13, 21, 22]. This superhydrophobic surface can clean itself from stains or suspended particles simply by shaking or applying slight movement to the surface [23, 24]. Furthermore, the superhydrophobic cotton fabric has also been successfully used for separation of oil from water [6, 15, 22, 25]. However, most of superhydrophobic materials have low durability under the environmental conditions: the fabricated artificial surface can be easily degraded by light, acid rain, seawater and oxidation [3, 26]. So the durability of superhydrophobic surface is one of the most important issues for an effective and efficient service life [1, 24, 27].

Currently there is very little information on durability of the surface of cotton fabric treated with superhydrophobic silica (SiO_2). Therefore, the main objective of this study was to determine durability and applications of cotton fabric samples coated with superhydrophobic SiO_2 film using dip immersion in presence of epoxy resin. These materials are cost effective and environmentally friendly compared to more common fluorosilane treatment. The use of fluoro-containing chemical reagents should be eliminated or at least minimized because of their toxicity and harm to human health. The performance of the fabric samples was evaluated as function of ultrasonic washing process. The superhydrophobicity of the specimens was investigated by static and dynamic contact angle measurement. The self-cleaning and

oil/water separation characteristics of the samples were also determined qualitatively and quantitatively.

2. Materials and Methods

2.1. Preparation of the cotton fabric coated with epoxy composite film

Commercial cotton fabric was supplied by a local manufacturer and has been washed with liquid detergent and dried before usage. Amorphous silica powder (HDK T40) from Wacker Chemie AG was used as filler. The specific gravity of silica powder is 2.20 and its particle size is less than 10 nm. Aminopropyltriethoxysilane (APTES) and acetic acid (99.8%) were obtained from Optimal Tech CO., LTD. and Qrec., respectively. NaOH (97%), methanol (99.99%) and ethanol (99.99%) were purchased from RCI Labscan. Epoxy (Bisphenol A diglycidyl ether) and Jeffamine were supplied by Aditya Birla Chemicals (Thailand) Ltd. (Epoxy Division). The motor oil (Castol active 4T) was purchased from Castol oil.

For preparation of epoxy composite film, the SiO_2 surface was first modified with APTES. So the SiO_2 surface was activated by NaOH (mass ratio SiO_2:NaOH was 5:1.66), and suspended in 125 mL deionized water. After stirring for 24 hr at 60 °C the suspension was neutralized by acetic acid. The obtained powder was washed five times with methanol and dried for 24 hr at 80 °C [28]. Later, 4 g activated SiO_2, 95 mL ethanol and 5 mL deionized water were mixed using sonication for 1 hr followed by adding 2.0 mL of APTES, and the pH value of mixture was adjusted to about 4-5 by 0.8-1 ml of acetic acid. The suspension was kept stirring at 80 °C for 24 hr under reflux. Finally, the SiO_2 modified with APTES was washed again five times with ethanol to remove $C_2H_3NaO_2$, and dried in an oven for 24 hr at 80 °C.

The 0, 10, 20 and 30 vol% SiO_2 modified with APTES and curing agent such a Jeffamine were firstly dispersed in 5 mL acetone by sonication for 5 min. Epoxy was added to the mixture and then stirred for 10 min. The mass ratio between epoxy and Jeffamine was 1:0.45. The cotton fabrics (3 cm × 3 cm) were simply immersed in the obtained mixtures for 10 min [8], and the coated fabrics were cured for 2 hr at 80 °C. For durability test, the coated fabrics were washed by ultrasonicator (DT 255 H Bandelin at 35 kHz and an output power of 160 W) for 30 min.

2.2. Characterization of the samples

Attenuated total reflection-Fourier Transform Infrared (ATR-FTIR) spectroscopy was applied using a Bruker Tensor 27 spectrometer to investigate the surface chemistry of SiO_2 and cotton fabrics before and after the surface modification. The surface morphology of fabrics was observed by Scanning electron microscope (SEM). Surface roughness of coated fabrics was determined by Portable surface roughness measurement surftes model sj-310. The measurement of static and dynamic contact angles was performed by an optical contact angle meter (OCA 15EC) with 5 μL deionized water droplet at ambient temperature [29], and an average of five measurements per sample was taken. The self-cleaning test was adapted from the method described in a previous work [23]. The 0.5 g of graphite powders were placed on the coated fabric and 1 mL of water passed through the surface to determine self- cleaning ability, as illustrated in Fig. 1. The morphology of cotton fabric samples after self-cleaning test were recorded by a digital camera

(Power shot SX10IS, Canon). Oil and water separation tests of the samples were carried out using a mixture of motor oil and water with methyl orange dye in a tube. The coated fabric was immersed into the tube to separate motor oil from water. The separation capacity of sample was calculated depending on the mass of water as depicted in Eq. (1). The averaged values from five samples were reported and the standard deviation error bar was used.

$$\text{Separation capacity } (\%) = (M/M_0) \times 100 \tag{1}$$

when M_0 and M were the weight of water before and after separation, respectively.
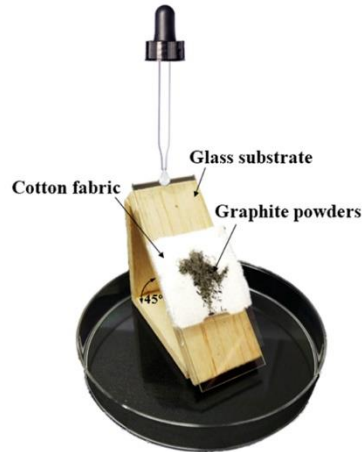
Fig. 1. Schematic of self-cleaning test.

3. Results and Discussion

3.1. Surface modification of SiO$_2$-APTES coated cotton fabrics

Cotton fabrics with special wettability were obtained via a simple and inexpensive dip coating technique using silica nanoparticles based on epoxy solution. The surface modification of SiO$_2$ with APTES (SiO$_2$-APTES) was confirmed by FTIR. Figure 2 shows the FTIR spectra of APTES, SiO$_2$, and SiO$_2$-APTES. Figure 2(a) exhibits the characteristic of SiO$_2$ at 1073 cm^{-1} and 811 cm^{-1} which were assigned to Si-O-Si and Si-OH, respectively. Figure 2(b) displays the OH band at 368 cm^{-1} which indicated the OH group on SiO$_2$ by treatment with NaOH. The characteristic peak of APTES (Fig. 2(c)) at 1384 cm^{-1} was ascribed to the bending vibration of C-H, whereas 1559 cm^{-1} and 1384 cm^{-1} were assigned to N-H vibrations. The adsorption peak in range of 2886-2960 cm^{-1} was attributed to alkyl (CH$_2$-CH$_3$-) vibrations of APTES. For the spectrum of SiO$_2$-APTES as shown in Fig. 2(d), the peak at 811 cm^{-1} of SiO$_2$ substantially decreased whereas the structure of Si-O-Si at 1073 cm^{-1} still appeared. Furthermore, the adsorption peak of N-H and alkyl groups of APTES were also found at 1500-1700 cm^{-1} and 2935 cm^{-1}, respectively. This observation indicated the high degree of surface condensation between OH groups of SiO$_2$ and APTES. The reaction of SiO$_2$ modified with APTES is demonstrated in Fig. 3. Based on FTIR analysis, it can be concluded that the functional group of APTES was successfully introduced to the SiO$_2$

surface [30]. However, the modification of SiO_2 surface should be further analysed by the high resolution XPS spectra for peaks of C1s and Si2p.
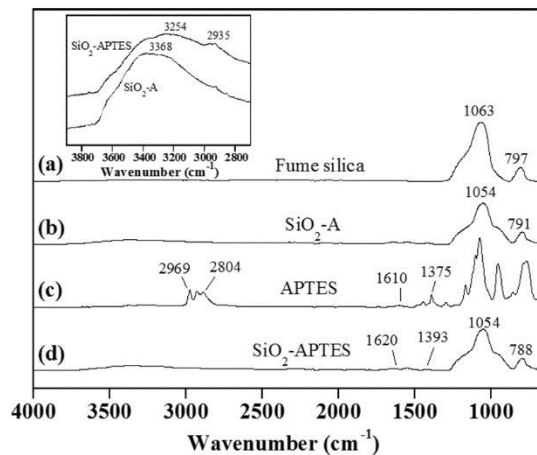

Fig. 2. FTIR spectra of (a) SiO_2, (b) SiO_2-A,
(c) silane (APTES), and (d) SiO_2 modified with APTES.
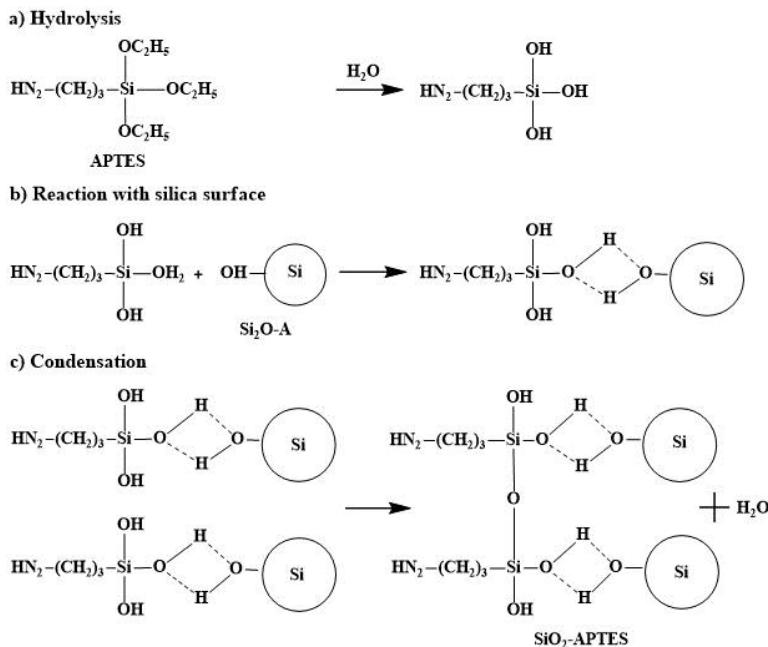

Fig. 3. Surface modification of SiO_2 with aminopropyltriethoxysilane (APTES).

After immersing the cotton fabrics in epoxy-based coating solution, the curing process was conducted at elevated temperature to deposit SiO_2-APTES nanoparticles onto the fabric surface. Therefore, the curing process of epoxy composite film incorporated with various contents of SiO_2-APTES on the fabric surface was studied by FTIR as depicted in Fig. 4. The important features in these FTIR spectra are the decrease of peaks at 838 cm^{-1} attributed to C-O-C stretching and 908 cm^{-1} assigned

to C-O stretching due to ring opening of epoxied ring [31, 32]. In addition, the appearance of a peak at 3440 cm^{-1} indicated the crosslink of epoxy. The peaks at 2870-2960 cm^{-1} and 1097 cm^{-1} were assigned to aliphatic C-H stretching and C-O-C stretching of ether linkage, respectively [31, 33]. Moreover, the peak at 1091 cm^{-1} decreased with increasing SiO$_2$-APTES content. This observation implied that the amine groups on modified SiO$_2$ reacted with epoxide ring resulted in the decrease of ether linkage between amine groups of Jeffamine and epoxy, as illustrated in Fig. 5.
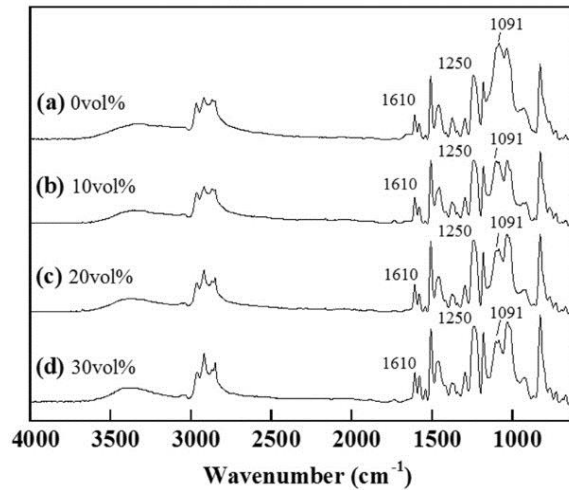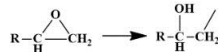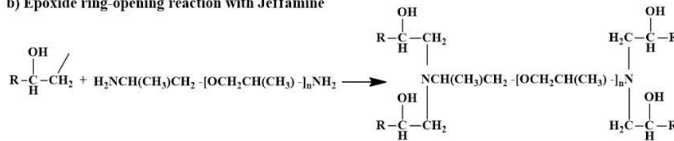

**Fig. 4. FTIR spectra of cotton fabrics coated
with epoxy composite containing various contents of SiO$_2$-APTES.**
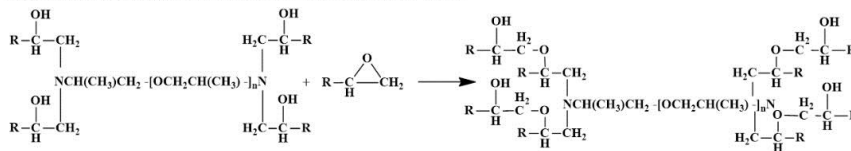
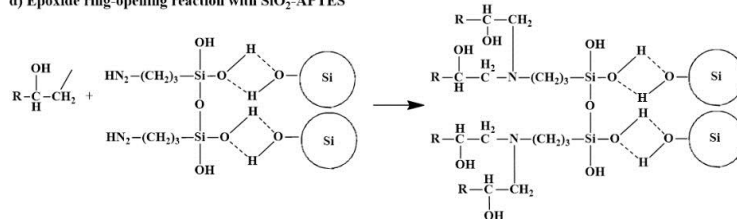**Fig. 5. Reaction of epoxy resin with SiO$_2$-APTES.**

3.2. Surface wettability and morphology of coated cotton fabrics

The hierarchical surface structure is a crucial requirement for a surface to have superhydrophobic property. The surface morphology of uncoated and coated cotton fabrics was observed by SEM as demonstrated in Fig. 6. By comparing the surface morphology of fabrics before and after coating, APTES-modified SiO_2 nanoparticles could be deposited on the surface of the cotton fabrics. Larger, coalesced and higher clusters were observed at higher filler loading. This phenomenon is in perfect agreement with previous literature [10, 34-36]. Figure 7 illustrates the surface roughness of cotton fabrics after coating. The presence of SiO_2 modified APTES in epoxy composite film can induce the roughness of fabrics improving their hydrophobicity [37]. The surface roughness increased with up to 20 vol% filler loading, but remarkably decreased at 30 vol% because of the higher tendency to agglomerate, resulting in lower hydrophobicity.
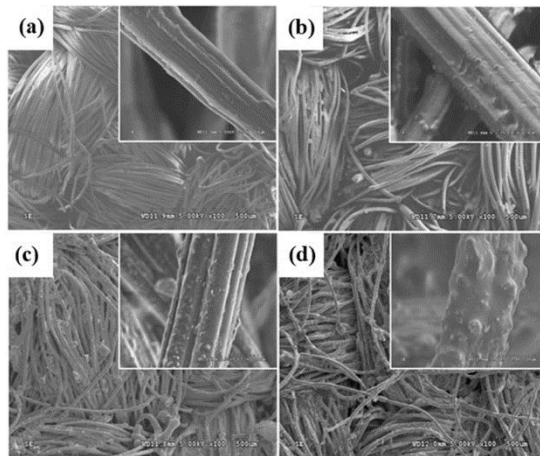

Fig. 6. SEM images of cotton fabrics: (a) uncoated fabric and fabrics coated epoxy composite film containing SiO_2-APTES at (b) 10 vol%, (c) 20 vol%, and (d) 30 vol%.
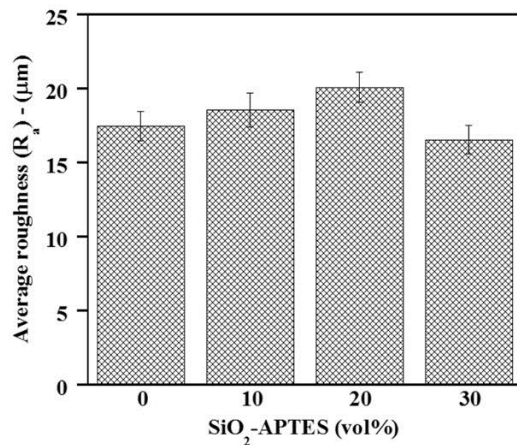

Fig. 7. Surface roughness of cotton fabrics coated with epoxy composite containing various contents of SiO_2-APTES.

The surface wettability of uncoated and coated fabrics was also evaluated as depicted in Fig. 8. Untreated cotton fabrics are highly hydrophilic and can be completely wetted by water. As clearly seen in Fig. 8(a), the anti-wetting surface could be fabricated by coating epoxy composite film with APTES-modified SiO_2 nanoparticles. These coated fabrics demonstrate water penetration resistance and high value of static WCA in range of 133°-152°. The coated fabric displays the highest static WCA of 152° at 20 vol% SiO_2-APTES, whereas adding of 30 vol% filler provides the lower static WCA of 136°. It is likely due to the uniform particle dispersion in matrix having higher hydrophobicity than that the aggregated [38]. This observation is in good agreement with results of surface roughness The obtained static WCA of fabric coated with 20 vol% SiO_2-APTES in epoxy-based coating was comparable with static WCA of coated fabric reported in previous works, i.e., ~147° by using polymer nanocomposite comprising a C-6 perfluorinated acrylic copolymer and acetoxy-cure silicone (PDMS) resin with SiO_2 nanoparticles, 130°-160° by applying different non-fluorinated hydrophobization agents with SiO_2 nanoparticles [39], ~153° by coating zirconia particles mixed hexadecyltrimethoxy silane and stearic acid [25], and 152°-158° by using zirconia particles in water-soluble siloxane emulsion [26]. A superhydrophobic surface means not only a high static contact angle, but also a low contact angle hysteresis (CAH) because the low hysteresis ensures easy rolling off the water droplets, which is favourable for self-cleaning [13, 40]. The CAH is defined as the difference between advancing contact angle and the receding contact angle [41]. The advancing and receding contact angle of water on the surface of fabric coated with epoxy composite containing 20 vol% SiO_2-APTES is demonstrated in Figs. 8(b) and 8(c), respectively. The CAH value was lower than 10°. Thus the fabric with superhydrophobic surface was successfully produced using epoxy-based coating with APTES-modified SiO_2 which achieved a rough surface, a static WCA > 150° and CAH < 10° [13, 40, 41]. Therefore, the addition of 20 vol% SiO_2-APTES in epoxy composite film was found to be the suitable proportion for superhydrophobic surface coating, and was used in further characterization.
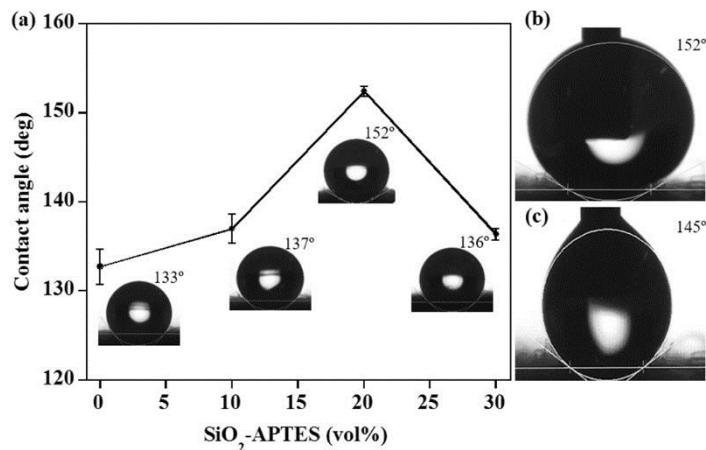

Fig. 8. (a) Static water contact angle of coated fabrics; (b) advancing and (c) receding water contact angles of fabric coated with 20 vol% SiO_2-APTES filled epoxy composite.

3.3. Washing durability of coated cotton fabrics

The durability of superhydrophobic fabrics is one of the most important properties for their reuse [13]. The washing durability of the coated fabric was mostly evaluated using a standard washing laundering machine [41-43]. In this research, washing durability tests of the fabrics were carried out using bath sonication for 30 min. Particularly, this form of washing is much harsher than a normal laundry cycle [10, 35, 44]. The hydrophobicity of coated fabrics was investigated by measuring the contact angle reductions after each washing cycles. The coating microstructure can be rapidly destroyed by ultrasonic treatment, which facilitates the detachment of film coatings and debonding of nanoparticles from fabric surface [10, 45]. Accordingly, the values of static WCA gradually reduced as ultrasonic washing cycles increased, as depicted in Fig. 9(a). Comparing to neat epoxy-coated fabric, the static WCA of fabric coated with SiO_2-APTES epoxy composite was higher for all washing cycles. For both samples, the static WCA remarkably changed after washing, and after 10 washing cycles decreased from 152º to 128º for epoxy composite coating and from 133º to 120º for neat epoxy coating, respectively. Similarly, the WCA of cotton fabrics modified with silica sol nanoparticles and nonfluorinated alkylsilane decreased from 155° to 95° after 30 washing cycles [34], and also the WCA of DDS-SiO_2 and DDS-SiO_2/fluoropolymer coated cotton fabrics greatly decreased from 124° to 69° and from 162° to 153°, respectively, after 30 washing cycles [46]. The surface morphology of coated fabrics after ultrasonic washing was characterized by SEM as provided in Figs. 9(b) and 9(c). The damage of coating on surface was observed after washing. The dynamic contact angles of coated fabric with 20 vol% SiO_2-APTES modified epoxy composite film after washing process are shown in Fig. 10. As expected, both advancing and reducing WCA decreased after ultrasonic washing. However, superhydrophobicity of the coated fabric having high WCA and low CAH was retained after ultrasonic washing which indicated good washing durability.
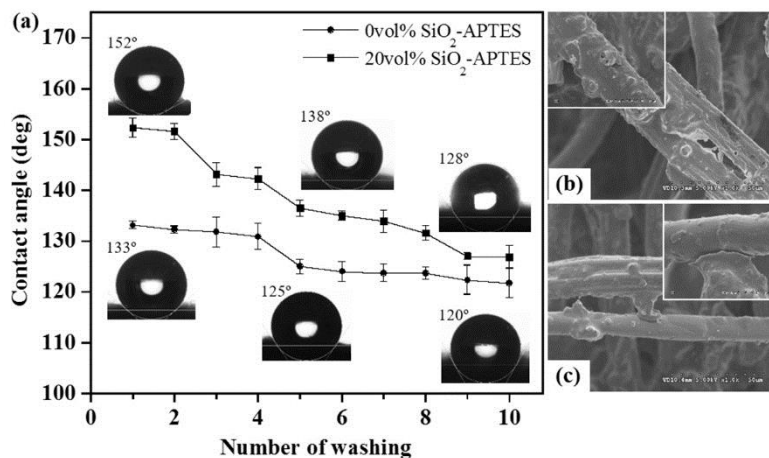

Fig. 9. (a) Static water contact angle of coated fabrics after ultrasonic washing; morphology of fabrics coated with epoxy composite containing 20 vol% SiO₂-APTES after (b) 1 and (c) 10 washing cycles.
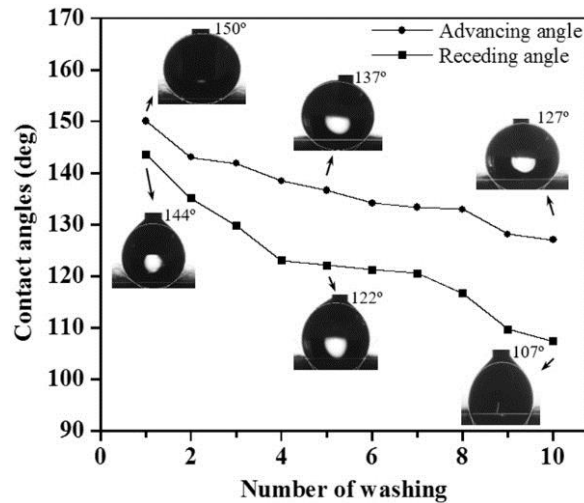
Fig. 10. Advancing and reducing water contact angles of fabric coated with epoxy composite containing 20 vol% SiO$_2$-APTES after ultrasonic washing.

3.4. Self-cleaning ability of coated cotton fabrics

To demonstrate the self-cleaning performance of coated fabric before and after washing, both liquids and solid contamination were tested. Figure 11 displays optical photographs of the common household liquid droplets i.e. water, coffee, juice, honey, and ketchup sauce on the surface of fabric samples. The uncoated fabric rapidly became wetted and colored because of its hydrophilic surface with high absorption ability. Interestingly, the coated fabrics not only show excellent anti-wetting properties with water, but also exhibit high liquid repellency against common household liquids including honey, coffee, orange juice, and ketchup sauce. Moreover, all liquids formed nearly spherical droplets on surface of coated fabric after harsh washing, in agreement with the contact angle measurements (Figs. 9-10).

In Fig. 12, hydrophilic graphite powders were deposited on sample surface before it was rinsed with water through the sample surface according to previously described method [28]. For uncoated fabric, graphite powders could not be removed by water droplets, and the powders still adhered to the surface (Fig. 12(a)). Conversely, coated fabric with high static WCA of 152° and low CAH exhibits excellent self-cleaning ability: the contaminant powder was carried away by the water droplet and rolled down from the surface quickly. Similar findings have also been reported recently in literature [25, 26, 36, 47]. For coated fabric after washing, graphite powders could be removed from the surface as well, but the rolling of water droplets on the surface was slightly slower. This phenomenon is associated with the higher CAH. Superhydrophobic surfaces of enhanced water repellency must correspond to low CAH, generally below 10° [48, 49]. This observation indicated the good self-cleaning property of coated fabrics.

Fig. 11. Optical images of the common household liquid droplets on cotton fabric: (a) uncoated fabric, (b) and (c) before and after10 cycles of washing of fabric coated with epoxy composite containing 20 vol% SiO$_2$-APTES, respectively.
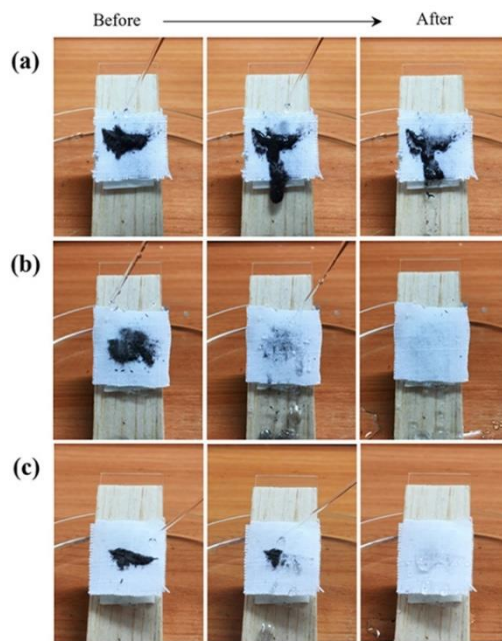

Fig. 12. Self-cleaning ability of cotton fabric samples: (a) uncoated fabric, (b) and (c) before and after 10 cycles of washing of fabric coated with epoxy composite containing 20 vol% SiO$_2$-APTES, respectively.

3.5. Efficiency of motor oil and water separation

Recently, superhydrophobic cotton fabrics were found to be an excellent candidate for removal of oil from water [50-53]. Figure 13 shows oil/water separation of cotton fabric samples coated with epoxy composite before and after washing. The thin layer of oil was observed on top of the mixture. The cotton fabric coated with epoxy composite film was immersed in the mixture, and the water repellency and oil adsorption were observed on the samples. The oil and water contact angle values

were 10° and 152°, respectively. After 10 separation cycles, it can clearly be seen that separation efficiency values were in range of 97%-100% and 94%-100% for the samples without washing and 10 washing cycles, respectively. The separation efficiency decreased after sample washing due to cracking of the coating layer on the cotton surface, as shown in Figs. 9(b-c), causing the oil phase to penetrate the cotton fabric. A similar observation has been reported by Zhou et al. [54]. The obtained separation efficiency of cotton fabric coated with 20 vol% SiO_2-APTES was comparable with the oil/water separation of cotton in previous works, e.g., 94% after 10 cycles separation cotton coated with polyaniline [54], 98-99% cotton coated with titanium dioxide via chemical reaction [55] and 92% of cotton modified by zinc oxide and polystyrene [6]. This result revealed that the samples coated with epoxy composite film could be considered as a candidate for oil purification.
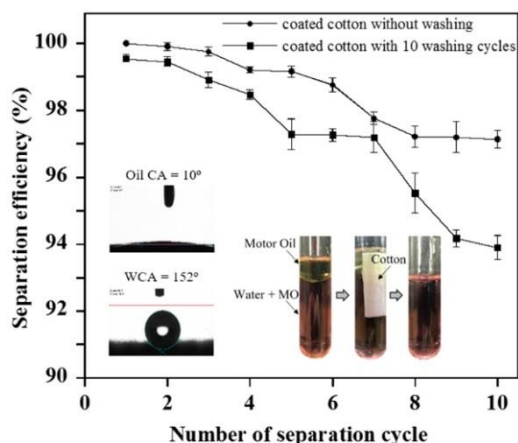

Fig. 13. Oil/water separation efficiency of fabric coated 20 vol% SiO_2-APTES filled epoxy composite film before and after10 cycles ultrasonic washing.

4. Conclusions

Superhydrophobic cotton fabric can be manufactured by coating epoxy composite film filled with 20 vol% APTES-treated SiO_2, which is more cost effective and environmentally friendly compared with the fluorosilane treatment. The coated cotton fabrics still maintained their hydrophobicity with high static WCA and low CAH after harsh washing process. The samples could be protected from common household liquids even after 10 washing cycles. Solid powder such as graphite could also be easily washed off with water when stained on the modified fabric surface. The coated fabric could have potential use for oil/water separation with very high efficiency. The separation efficiency values of the specimens were higher than 94% before and after 10 cycles of washing. Based on the results, the cotton fabric coated with epoxy composite containing 20 vol% of SiO_2-APTES has durability and potential for both self-cleaning and oil/water applications.

Acknowledgements

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