Chiang Mai J. Sci. 2018; 45(5) : 2211-2219
http://epg.science.cmu.ac.th/ejournal/
Contributed Paper

Bifunctional Water-repellent and Flame-retardant Cotton Fabric Coated with Poly(methylhydrogen siloxane) and Ammonium Phosphate

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Received: 1 November 2017
Accepted: 30 April 2018

ABSTRACT

Thermal stability and water repellency of the cotton fabric was improved by coating with hydrophobic and flame-retardant substances. Composition of the flame-retardant substance which is monoammonium phosphate (MAP) or diammonium phosphate (DAP), hydrophobic substance which is poly(methylhydrogen siloxane) (PMHS) and fumed SiO_2 was varied to find the suitable composition that provided high liquid-repellent and flame-retardant properties. The coating was performed by soaking the cleaned cotton fabrics in the coating solution for 2 h followed by padding and drying at 50 °C for 2 h. The optimum coating solution was obtained when weight ratio of the PMHS:MAP:SiO_2 was 10:10:0.5. The coated cotton fabric had water and glycerol contact angles of 134.15±2.85 and 126.35±5.10 degrees, respectively. In addition, it showed the enhanced thermal stability compared to the uncoated sample based on the burning test.

Keywords: bifunctional coating, hydrophobic, water repellent, flame retardant, cotton fabric

1. INTRODUCTION

Cotton has always been the most utilised fabric due to its attractive characteristics such as softness, comfort, warmness and low cost. However, the abundant water-absorbing hydroxyl groups on the cotton surfaces make the cotton fabric absorbent and be easily stained by liquids. In addition, the cotton can be thermally degraded, ignited and burnt. Therefore, many studies have been conducted to modify the cotton's surface to improve the cotton fabric property to meet the specific use. For instance, liquid repellency can be improved by coating the cotton fabric with hydrophobized ZnO nanorod array film [1], hydrophobized TiO_2 [2], hydrophobized SiO_2 [3], organic-inorganic hybrid film [4], or by modification with silane [5]. This approach mimicks surface phenomenon observed on the lotus leaf by enhancing surface roughness of the cotton and/or modifying with the hydrophobic substance [6]. Functionalization of the cotton fabric with graphene oxide nanosheet and polyaniline has been recently reported to obtain conductive and UV blocking properties [7].

An improvement of thermal stability and flame retardancy is another crucial aspect that has been widely conducted to extend the use of a traditional textile to high value-added products. Classic flame retardant for cellulosic material was the halogen-containing substance. However, it has been less acceptable because of health concern. The use of phosphorus-containing flame retardant is preferred over the halogen-containing flame retardant because it does not releases toxic gases during the combustion [8-10]. It has been reported that the amount of phosphorus in flame-retardant cotton has the effect of reducing the decomposition temperature of the treated cotton with an increase in the amount of char formation during thermal degradation [9]. The treated cotton exhibited self-extinguishing behavior. Inorganic oxides such as phosphorus-doped SiO_2 and sol-gel derived oxides have been reported as effective flame retardants [10-11]. In addition, a uniform and tightly anchored thin SiO_2 layer has been directly grown on the cellulose fiber pretreated with NaOH [12]. Such coating increased the temperature at which the fiber started to decompose by 20°C. The intumescent flame retardant of polyacrylamide and exfoliated graphene oxide was coated on the cotton fabric via layer-by-layer assembly [13].

The studies mentioned earlier aimed to modify the cotton fabric with the specific functionality. The studies on multifunctionality are rarely reported. Recently, multifunctional water- and oil-repellent, antibacterial, and flame-retardant coating has been deposited on cellulose fibres by the sol-gel process [14]. Previously, a plasma-induced graft-polymerization (PIGP) process has been employed to treat the cotton fabric to obtain flame and waterproof properties [15]. In this work, a bifunctional coating with hydrophobic and flame-retardant properties was deposited on the cotton fabric by using a simple coating method. The chemicals employed in this study are inexpensive compared to those used in the sol-gel process (e.g. the fluorosilane employed in the Ref. 14), and the coating procedure is much simple compared to the PIGP process).

2. MATERIALS AND METHODS

2.1 Preparation of Coated Cotton

The bleached 100% cotton fabric was cut into a 10 cm × 10 cm in size. After washing with detergent and distilled water, the cotton fabric was dried at 50°C for 2 h. The coating solutions were prepared by mixing hydrophobic substance which was poly(methylhydrogen siloxane) (PMHS, Dow corning) and fumed SiO_2 (Aerosil® 200, JJ degussa) with retardant substance which was monoammonium phosphate (MAP, 98.0%, Ajax Finechem Pty Ltd.,) or diammonium phosphate (DAP, 98.0%, Ajax Finechem Pty Ltd.). Chemical composition of the coating solution is given in Table 1. The bifunctional coating was performed by soaking the cleaned cotton fabric in the coating solution for 2 h followed by padding and drying at 50 °C for 2 h.

Table 1. Chemical composition of the coating precursors.

Sample No.	Code	Concentration (%w/v)			
		PMHS	MAP	DAP	Fumed SiO_2
1	EX-1	10	10	-	-
2	EX-2	10	-	10	-
3	EX-3	10	10	-	0.5
4	EX-4	10	-	10	0.5

2.2 Characterization

The hydrophobic and oleophobic properties were evaluated by measuring the contact angle against deionized water and glycerol (99.5%, Qrec), respectively, using a goniometer (rame-hart instrument). The measurement was performed on five different locations of the sample. Then, surface free energy was calculated based on the Owen-Wendt equation as follow [16-17]:

$$1 + \cos\theta = \frac{2\sqrt{\gamma_S^D \gamma_L^D}}{\gamma_{LV}} + \frac{2\sqrt{\gamma_S^P \gamma_L^P}}{\gamma_{LV}}\ , \quad (1)$$

and

$$\gamma_S = \gamma_S^D + \gamma_S^P\ , \quad (2)$$

where θ is the contact angle, γ_S^D and γ_L^D are the dispersion component of the solid and the liquid, respectively, γ_S^P and γ_L^P are the polar component of the solid and the liquid, respectively, γ_{LV} is the surface free energy of the liquid, and γ_S is the total surface free energy of the solid. Surface morphology was observed by using a field-emission scanning electron microscope (FE-SEM, JSM 6301F). To access thermal stability, the uncoated and coated samples were directly ignited for 1 s and the ignition source was removed. Then, burning behaviour of the samples was visually observed, and photographs were recorded after 3 s and 10 s and at the completion of burning. In addition, the thermogravimetric analysis (TGA) was carried out on a TGA/DSC1 (Mettler-Toledo) under N_2 atmosphere at the heating rate of 10 °C/min.

3. RESULTS AND DISCUSSION

3.1 Surface Morphology of the Coating

Figure 1 shows SEM images of the uncoated and coated cotton fabrics. The uncoated cotton (Figure 1(a)) has a typical longitudinal fibrous structure and very smooth surface. In contrast, SEM images of the coated fabrics (Figure 1(b)-(e)) show distinct coating feature. All the coated samples have similar morphology regardless of the coating solution employed. The coating features are rough, thus generating a micro-scaled surface structure on the fabric surface. Increasing concentration of the coating solution resulted in the slightly thicker coating. Comparing SEM images of the coating without the fumed SiO_2 (Figure 1(b)-(c)) and of the coating containing the fumed SiO_2 (Figure 1(d)-(e)), there are fine clusters of SiO_2 agglomerates in the coatings prepared from the fumed SiO_2-containing precursors. It is anticipated that the coating can shield the cotton fabrics from atmospheric oxygen that is crucial in the combustion process, resulting in a slower combustion rate. Moreover, the coating which consisted of the siloxane can provide liquid-repellent property similar to the phenomenon observed on the lotus leaf as well.

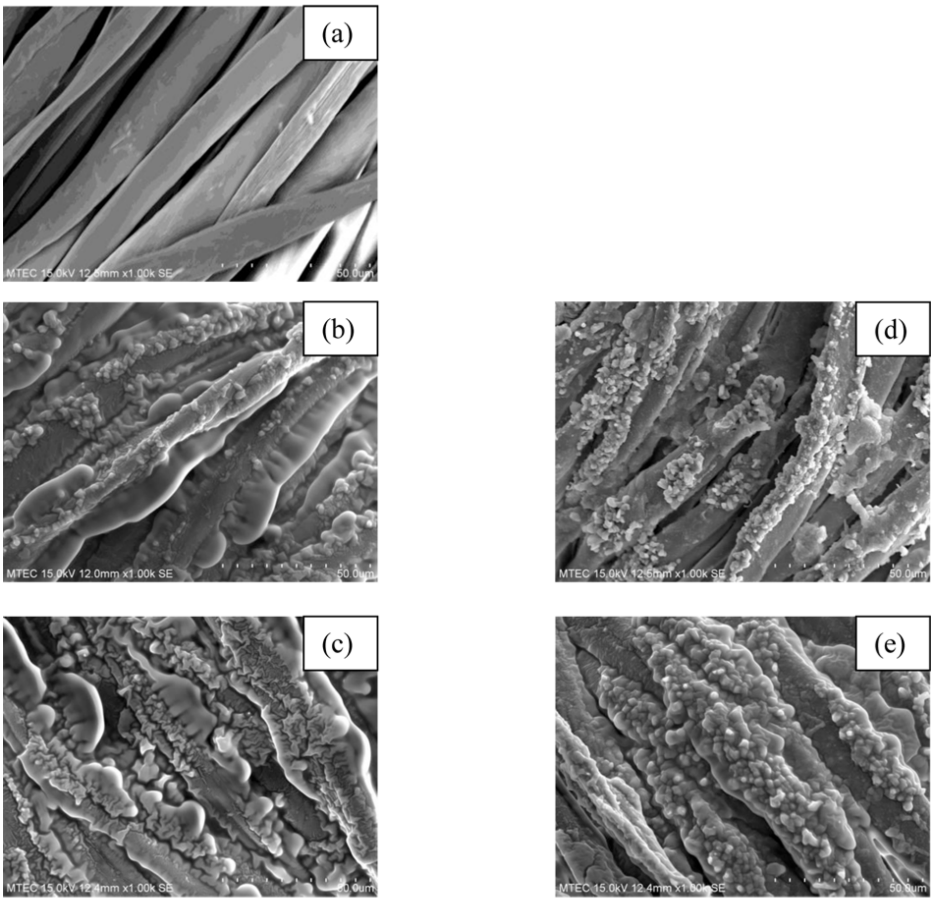

Figure 1. SEM images of (a) the uncoated cotton fabric and (b)-(e) the cotton fabric coated with EX-1, EX-2, EX-3 and EX-4, respectively.

3.2 Liquid Repellency

Table 2 shows the contact angles measured by using de-ionized water and glycerol on the coated fabric, and the surface free energy calculated from the Owen-Wendt equation. The contact angle of the uncoated sample cannot be measured because the water and glycerol quickly penetrated through it indicating its hydrophilic nature. For the coated samples, the water contact angle was in the range of 127-134 degrees, and the glycerol contact angles was in the range of 120-129 degrees. The water contact angle was slightly higher than the glycerol contact angle because water has higher surface tension than glycerol, i.e. 72.8 v.s. 64.0 mN·m^{-2} [18]. A couple observations can be drawn from the results of contact angle measurement summarized in Table 2. Firstly, the values of contact angle of samples EX-1 and EX-2 are in the same range within the experimental error (i.e. 127-130 degrees for water and 120 degrees for glycerol). This observation is also applied for the samples EX-3 and EX-4 (i.e. 133-134 degrees for water and 126-129 degrees for glycerol). These results indicated that the composition employed in this study did not play a significant role on the liquid-repellent property of this mutifunctional coating. Secondly, the incorporation of fumed SiO_2 (samples EX-3 and EX-4) resulted in the improvement of liquid repellency. This result can be explained based on the increased surface roughness of the coating deposited from the precursors containing the fumed SiO_2 as observed in the SEM images in Figure 1. It has been known that the increase of surface roughness can enhance the liquid contact angle [6].

Table 2. Water and glycerol contact angles and surface free energy of the coated cotton fabrics.

Sample No.	Code	Contact angle (deg.)		Surface energy (mJ·m^{-2})
		Water	Glycerol	
1	EX-1	129.60 ± 1.30	120.05 ± 5.75	7.18
2	EX-2	126.80 ± 3.60	120.35 ± 0.35	5.08
3	EX-3	134.15 ± 2.85	126.35 ± 5.10	4.34
4	EX-4	133.00 ± 1.10	128.80 ± 5.70	2.33

Surface free energy of the coated samples summarized in Table 2 is in a range of 2.33-7.18 mJ·m^{-2}. It is known that liquids having the surface tension higher than the surface free energy of the solid will not wet the solid's surface. Comparing the surface tension of water or glycerol and the coated cotton, the surface free energy of the coated cotton is significantly lower than the surface tension of water (72.8 mJ·m^{-2}) and glycerol (64.0 mJ·m^{-2}).

Figure 2 are photographs taken after dropping red dye solution onto the uncoated fabric and the coated fabric, the EX-3 which was selected as a representative of the high liquid-repellent samples. The dye solution quickly penetrated through the uncoated fabrics leaving behind red color marks. In contrast, the dye solution formed spherical droplets on the coated fabric and rolled easily when the fabric was slightly tilted. It is a good indicator of high hydrophobicity and self-cleaning property of the coated cotton fabric. Good wettability of the uncoated cotton fabric is attributed to the abundant hydroxyl groups on the cellulose surface. Therefore, like other natural cellulosic materials, the cotton fabric is highly hydrophilic. Modification of the cotton surface with the coating containing the PMHS making it hydrophobic. The siloxane functional group in the PMHS is hydrolyzed to form silanol groups (Si-OH) [19]. Then, the Si-OH groups react with the hydroxyl group (-OH) of the cotton through the hydrogen bonding. After dehydration, there is the Si-O chemical bonding between the siloxane and to the cotton surface resulting in good adhesion.

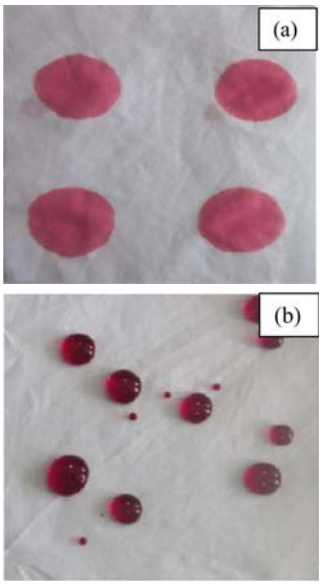

Figure 2. Photographs taken after dropping red dye solution onto the uncoated cotton fabric and the fabric coated with EX-3.

3.3 Thermal Stability

The cotton can be decomposed after prolong exposure to temperature of 150 °C or higher. To investigate thermal property of the uncoated and coated cotton, the samples were ignited and burning behavior was observed. Photographs taken after 3 s, 10 s and completion of the burning are shown in Figure 3. For the uncoated cotton (Figure 3(a)), the burning continued after removing the ignition source. Its burning process was rapid and intense. The whole specimen had been burnt leaving only a small amount of the residue. In contrast, different burning process was observed on the coated cottons (Figure 3(b)-(e)). After removing the ignition source, the flame spread out slowly and was finally self extinguished. A large amount of the unburnt portion can be seen in all of the coated specimens. It is also observed that more flammable volatiles were evolved for the EX-2 and EX-4 compared to the EX-1 and EX-3, indicating that the MAP is more flame retardant than the DAP at the same content. In addition, the incorporation of fumed SiO_2 led to the improvement of thermal property because it was found that the samples containing fumed SiO_2 had lower burning rate.

Figure 3. Photographs showing burning behaviour of (a) the uncoated cotton fabric and (b)-(e) the cotton fabric coated with EX-1, EX-2, EX-3 and EX-4.

The P-containing flame retardant can produce phosphoric acid (H_3PO_4) by thermal degradation taking place according to the following equation [9, 20-22]:

$$(NH_4)_2HPO_4 \rightarrow NH_4H_2PO_4 + NH_{3(g)}$$
150 °C (3)

$$2NH_4H_2PO_4 \rightarrow (NH_4)_2H_2P_2O_7 + H_2O_{(g)}$$
170 °C (4)

$$(NH_4)_2H_2P_2O_7 \rightarrow 2NH_4PO_3 + H_2O_{(g)}$$
280 °C (5)

$$2NH_4PO_3 \rightarrow P_2O_5 + 2NH_3(g) + H_2O_{(g)}$$
660 °C (6)

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \tag{7}$$

In the presence of phosphoric acid, some of the hydroxyl groups of the cellulose are esterified. Then, the smaller amounts of flammable products are formed. In addition, the relatively large amount of water formed will tend to quench the flame. Also, it has been reported that the fabric can be protected from the heat of combustion by the layer of char formed on its surface.

To investigate the effect of fumed SiO_2, the coated samples containing the MAP as flame-retardant substance (EX-1 and EX-3, without and with fumed SiO_2, respectively) were subjected to TGA and the result shown in Figure 4. Note that only the samples containing the MAP were selected for this analysis because they emitted less flammable volatiles compared to the samples containing the DAP, thus are more promising for practical use. A TGA profile of the uncoated cotton shows a weight loss of 6.46% at 25 - 150 °C and 82.48% at 150 - 600 °C which can be attributed to the loss of moisture and decomposition of the cellulose, respectively. The coating samples show much different thermal degradation profiles. That is, the EX-1 sample shows the weight loss of only 3.79% at 25-150 °C, 8.22% at 150-200 °C and 40.86 % at 200-600 °C. Similarly, the EX-3 sample shows the weight loss of only 3.75% at 25-150 °C and 47.34% at 150-600 °C. These weight losses are attributed to the decomposition of the MAP according to equations (4)-(5). The remaining residues were 11.06, 47.13 and 48.91%, for the uncoated, EX-1 and EX-3 specimens, respectively. It is evident that the residues of the coated specimens were about 4 times higher than that of the uncoated specimen. From previous studies, phosphorous-containing flame retardant provided percent weight loss of remaining residues about 20-24% [9-10]. Moreover, it also should be noted that the EX-3 is more sightly thermally stable than the EX-1 because it consists of the fumed SiO_2 which can enhance thermal stability of the coating [10].

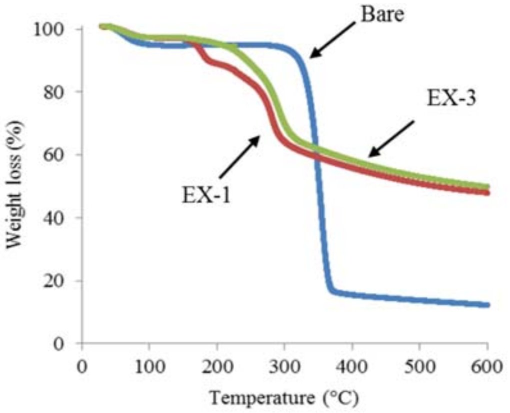

Figure 4. TGA curves of the uncoated cotton fabric and the cotton fabric coated with EX-1 and EX-3, respectively.

4. CONCLUSIONS

Bifunctional coating bearing water-repellent and flame-retardant functionality was deposited on the cotton fabric by simple coating to improve its thermal and liquid-repellent properties. The coating consisted of monoammonium phosphate (MAP) or diammonium phosphate (DAP) employed as a flame-retardant substance and poly(methylhydrogen siloxane) (PMHS) employed as a hydrophobic substance. The incorporation of fumed SiO_2 resulted in the improved properties. At the optimum condition ($PMHS:MAP:SiO_2$ = 10:10:0.5 by weight), the coated cotton fabric had water and glycerol contact angles of 134.15 ± 2.85 and 126.35 ± 5.10 degrees, respectively. Thermal stability of the coated fabric was significantly improved based on TGA results and the burning test.

ACKNOWLEDGEMENTS

This research has been supported by the Nation Metal and Materials Technology Center, the National Science and Technology Development Agency (NSTDA), Thailand (Grant No. MT-B-54-CER-07-277-I).

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