Journal of Metals, Materials and Minerals, Vol.20 No.2 pp.79-83, 2010

Preparation and Properties of Superhydrophobic Cotton Fabrics

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Abstract

In this study, superhydrophobic cotton fabric was prepared by coating maleic-anhydride grafted poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS-g-MA) triblock copolymer solutions containing calcium carbonate ($CaCO_3$) particles. SEBS-g-MA solutions were prepared using single solvent (toluene and tetrahydrofuran (THF)) and mixed solvent (toluene: ethanol (EtOH) and THF: EtOH). Cotton fabrics were treated with the prepared solution using padding technique. All coated fabrics exhibited a water contact angle (WCA) of more than 100°. Optimum WCA values were observed when THF and 90:10 toluene: EtOH were employed. In case of $CaCO_3$ particles addition, 6% W/V $CaCO_3$ could impart the highest WCA value of 154°. However, the durability of the coatings was decreased after washing test as witnessed by the decrease in WCA value. Interestingly, fabrics' WCA values after rubbing test were found higher than those before testing due to rougher fabric surface. Finally, coating of SEBS-g-MA onto cotton fabric insignificantly affected the color appearance of coated fabric, judged by an insignificant change in CIE L*a*b* values.

Key words: Superhydrophobic, Cotton fabric, Maleic-anhydride grafted poly[styrene-b-(ethylene-co-butylene)-b-styrene

Introduction

The main characteristics of solid surface are wettability, which means ability of liquid to cover a surface.[1] It can be divided into two main groups: hydrophobic and hydrophilic. The wettability of the surface is measured by using contact angle measurement. Contact angle (CA) is the angle indicating liquid spread on the surface. Generally, a CA of less than 5° means superhydrophilic surface while a CA between 5° and 90° means hydrophilic surface. In the case of hydrophobic surface, 90° to 149° CA is called hydrophobic surface, and a CA of more than 150° is known as superhydrophobic surface.[2] Normally, there are two methods to create a superhydrophobic surface, which means making the hydrophobic surface rough as well as coating low surface energy materials onto the rough surface.[3] Recently, there are many methods to produce a rough surface as, for instance, plasma fluorination of a polymer surface (Woodward et al., 2006), sol-gel(Shirtcliffe et al., 2003), and phase separation techniques.[6]

In this work, the rough surface was prepared from coating maleic-anhydride grafted poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS-g-MA) solution on cotton fabric with the following solvents: tetrahydrofuran (THF), toluene, and a mixture of both of these solvents with ethanol. The effect of solvent types and compositions to CA was investigated. Another way to generate a rough surface is adding calcium carbonate ($CaCO_3$) particles to the solution using toluene as a solvent. The amount of $CaCO_3$ affecting the CA was determined. Furthermore, CA of all fabrics after fastness test and color of fabric were investigated.

Materials and Experimental Procedures

Materials

Woven cotton fabric (40 count cotton) was donated from Evergreen Industries Co., Ltd., Thailand. Maleic-anhydride grafted poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS-g-MA) triblock copolymer (Kraton FG1901X) was supplied by Toyota Tsusho (Thailand) Co., Ltd., Thailand (29wt% styrene grafted with 1% MA). Calcium carbonate ($CaCO_3$) particles with an average particle size in the range of 40 to 50

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nanometers (NPCC 601) were supplied from Behn Meyer Chemical (T) Co., Ltd., Thailand. Tetrahydrofuran (THF), ethanol, and toluene were purchased from Fluka, USA.

Solution Preparation

The concentration of SEBS-g-MA solution was prepared at 2%W/V by using different types of solvent, i.e. THF, toluene, toluene:ethanol (EtOH), and THF:EtOH. The ratio of each solvent with EtOH was prepared from 100:0, 90:10, 80:20 and so on until polymer chip refused to be dissolved. The mixture was stirred with magnetic bar at room temperature until it was completely dissolved (about 5 hours). After that, the solution was coated on glass slide and cotton fabric for further characterization.

The clear solution of 2%W/V SEBS-g-MA in pure toluene was mixed with 1-10% W/V $CaCO_3$ particles. The solution was stirred at a speed of 800 rpm with IKA RW20 digital mechanical stirrer (IKA® Works (Asia) Sdn Bhd, Malaysia) for 5 minutes before coating on glass slide and fabric.

Characterization

Contact angles (CA) were measured on a CAM-PLUS Tantec (Tantec Inc., USA) at room temperature. All specimens were measured for a CA of about 5 points; subsequently their average values were calculated. Scanning electron microscopy (SEM) images were obtained using a 4510-Jeol scanning electron microscope (Jeol Ltd. Japan). CIE L*a*b* of fabric was measured by Datacolor Check II spectrophotometer (Datacolor, USA). Fastness including wash-fastness (WF) and rub-fastness (RF) were carried out to the ISO 105-C02:1998(E) and ISO 11640:1993, respectively. After fastness test, the specimens were measured for CA again.

Results and Discussion

The results in Figures 1-2 show water contact angle (WCA) of treated cotton fabrics using toluene or THF: EtOH as solvents. Each solution that was treated on fabric showed a higher WCA in comparison with the same coated on glass slide. WCA of solution using THF as a solvent on glass slide, for example, was 104°, whereas WCA on treated fabric was 152° (Figure 3). This result could be explained by the fact that fabric has a rougher surface than glass slide resulting in more air trapped between liquid and fabric than in the case of the glass slide. In the case of toluene: EtOH solvent, the best WCA of this fabric was 90:10 toluene: EtOH ratio showing 150° WCA. For THF: EtOH mixture, fabric using single THF showed the highest WCA of 154° and a gradually decreasing WCA in step with an increasing amount of EtOH. Both toluene and THF can dissolve SEBS-g-MA; however, when the solvent evaporated, the film showed different morphology. The cast film with polymer solution in toluene solvent showed a smooth surface, while cast film with polymer solution in THF showed a rough surface. The possible explanation for this is the solubility parameter (δ) of polymers and solvents (Table 1) which is a numerical value predicting the solubility of materials. Materials with similar values of solubility parameter are likely to be miscible. SEBS-g-MA is a thermoplastic triblock copolymer composed of a hard segment, polystyrene (PS) and a soft segment, poly(ethylene-co-butene) (PES). From Table 1, solubility parameters of toluene ($\delta = 8.9$) and THF ($\delta = 9.1$) are in the range of the PS segment, which are good solvents for this segment. In case of PEB segment, solubility parameters of both toluene and THF are far beyond the range of 7.9-8.1. Both solvents act as precipitators to PEB segments and cause phase-separation.[7] However, THF shows a higher value of solubility parameter than toluene. The larger difference in solubility parameters between the solvent and that of PEB causes larger domain sizes resulting in rougher surface.[7] In the case of adding EtOH into the solution, EtOH is a nonsolvent ($\delta = 12.7$) for this polymer acting as a precipitator. When the EtOH was added in the solution, a white precipitate appeared rapidly resulting in the phase separation that showed the rough surface. When the volumes of EtOH increased, more polymer aggregates would form. However, it does not mean that more aggregates of polymer show higher WCA. The suitable solvent ratios have to be determined to obtain the highest WCA. After wash-fastness test, WCA of treated-fabrics was decreased; however, these fabrics still had hydrophobic properties. For rub-fastness test, the treated fabric showed a WCA that was a little bit higher because rubbing increases the roughness of the fabric.

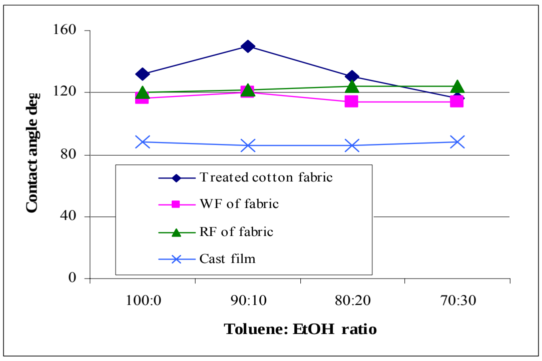


Figure 1. Contact angle of treated cotton fabric using toluene: EtOH solvent (WF = Wash-fastness; RF = Rub-fastness).

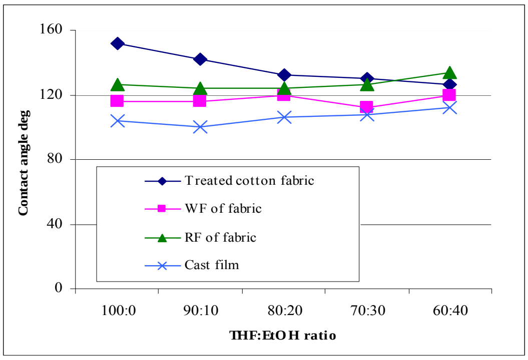
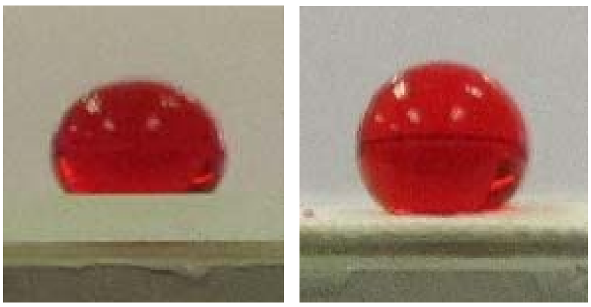


Figure 2. Contact angle of treated cotton fabric using THF:EtOH solvent (WF = Wash-fastness; RF = Rub-fastness).



(a) Glass slide (b) Treated fabric

Figure 3. Water droplets on (a) glass slide and (b) fabric of SEBS-g-MA solution in pure THF.

Table 1. Solubility parameter of polymers and solvents.[7-8]

Polymer / Solvent	Solubility parameter $(cal/cm^3)^{1/2}$
THF	9.1
Toluene	8.9
EtOH	12.7
PS	8.7-9.1
PEB	7.9-8.1

The amount of $CaCO_3$ particles dispersed in polymer solution that affected the WCA was studied. Figure 4 shows an increase in WCA of treated fabric with an increase of $CaCO_3$ concentration until 6% W/V $CaCO_3$ concentration; from this point on, the WCA was decreased. All treated fabrics had higher WCA than cast film on glass slide. Both wash-fastness (WF) and rub-fastness (RF) of these treated fabrics were decreased compared with the condition before testing. Figure 5 shows the SEM micrographs of untreated fabric, SEBS-g-MA-treated fabric, and 6% W/V $CaCO_3$ in SEBS-g-MA-treated fabric. The smooth surfaces of fabric were obtained from Figure 5(a) and (b). However, polymer-treated fabric (WCA=140°) showed higher WCA than untreated fabric (WCA =0°) because of hydrophobic properties of SEBS-g-MA polymer. After adding $CaCO_3$ particles, a higher roughness of surface was obtained (WCA =154°) shown in Figure 5(c) resulting in superhydrophobic properties.

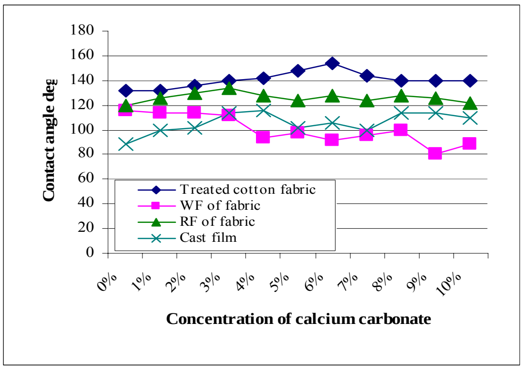
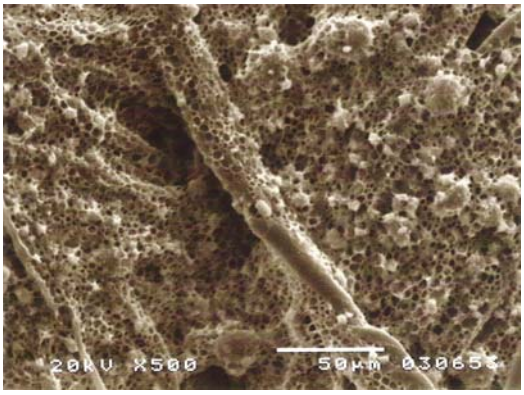


Figure 4. Contact angle of treated cotton fabric with adding calcium carbonate particles (WF = Wash-fastness; RF = Rub-fastness).

(a)

(b)



(c)

Figure 5. SEM micrographs of (a) untreated fabric, (b) SEBS-g-MA-treated fabric, and (c) 6% W/V $CaCO_3$ in SEBS-g-MA-treated fabric.

The CIE L*a*b* values of untreated and treated fabric are shown in Tables 2-3. The L*, a*, and b* values of all treated fabrics showed almost the same as untreated fabric. The result can be explained by the fact that the color of all fabrics was not significantly changed from untreated fabric.

Table 2. CIE L*a*b* values of SEBS-g-MA treated fabrics from various solvents.

Solvent ratio	CIE L*a*b*		
	L*	a*	b*
Untreated	96.01	0.26	2.10
Toluene:EtOH			
100:0	94.05	0.27	3.20
90:10	93.60	0.25	4.51
80:20	93.34	0.24	3.12
70:30	93.95	0.24	3.84
THF:EtOH			
100:0	94.45	0.06	2.95
90:10	95.33	0.12	3.74
80:20	96.52	0.09	2.19
70:30	97.12	0.11	1.52
60:40	95.96	0.14	2.57

Table 3. CIE L*a*b* values of SEBS-g-MA treated fabric with different amounts of $CaCO_3$ particles.

Concentration of $CaCO_3$ (%)	CIE L*a*b*		
	L*	a*	b*
Untreated	96.01	0.26	2.10
1	93.86	0.19	3.63
2	94.37	0.22	4.06
3	93.84	0.14	3.16
4	93.83	0.28	3.06
5	94.35	0.20	3.44
6	94.37	0.19	3.52
7	94.24	0.28	3.47
8	94.27	0.33	3.48
9	94.02	0.27	3.20
10	94.16	0.31	3.41

Conclusions

Superhydrophobic properties resulting from rough surface were prepared from various techniques. In this study, two simple and room temperature techniques were used: using solvent mixture and adding particles into solution. The treated cotton fabric showed excellent hydrophobic properties so that WCA could reach 150° for 90:10 toluene: EtOH ratio, 152° for THF, and 154° for 6% W/V $CaCO_3$ in SEBS-g-MA solution. This finding illustrated that the superhydrophobic property is dependent on roughness of surface and material properties.

Acknowledgements

We would like to thank Miss Pornpen Siridamrong for scanning electron micrographs and also Mr. Wanniwat Wantana for their helpful assistance during this project.

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