CHAPTER V
FORMATION OF ULTRATHIN POLYSTYRENE FILM TO PRODUCE HYDROPHOBIC COTTON BY *IN-SITU* REACTION POLYMERIZATION*

ABSTRACT

Thin film polystyrene was formed on cotton fabric using linear alkylbenzenesulfonate (LAS) adsorbed on fabric as a template. The film was formed by using three main reaction steps consisting of LAS adsorption, styrene monomer solubilization into the bilayer of LAS adsorption, and polymerization of styrene monomer *in-situ* LAS adsorbed. Two types of initiator, $Na_2S_2O_8$ and AIBN, were used to produce hydrophobic cotton. The polystyrene film formed on cotton was characterized by FTIR, GPC and SEM. The hydrophobicity of the treated cotton surface was determined by the drop test, and the water adsorption of untreated and treated cottons was examined using the Wilhelmy microelectronic balance technique. The results show that polystyrene thin film was successfully formed on cotton resulting in a hydrophobic cotton. The effects of initiator types on hydrophobic character show that using organic initiator, AIBN, is more efficient than using ionic initiator, $Na_2S_2O_8$, as shown in the lower amount of initiator and styrene monomer required for making hydrophobic cotton.

Key Works:

Admicellar polymerization, cotton, thin-film, coating, polystyrene

INTRODUCTION

Commercial water repellent cotton fabric is commonly produced by depositing a film

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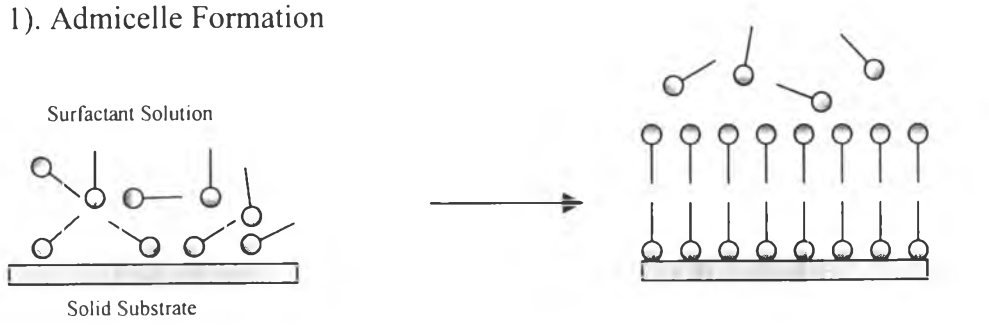
* The content of this Chapter has appeared previously (T. pongprayoon, N. Yanumet and E. A. O'rear in 9th APCChE Congress and CHEMECA 2002, , paper no 427, Christchurch, New Zealand)

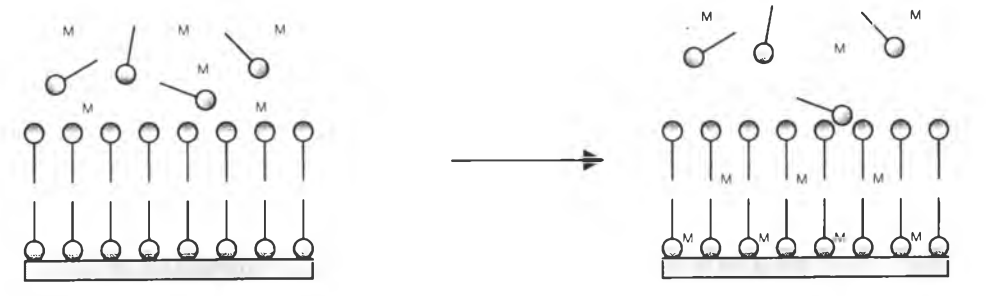
of hydrophobic substance on the fabric. Silicone and fluorochemicals are examples of chemicals used for this purpose. The simple method is to apply a solution of water-repellent agents onto the fabric by the pad-dry-cure process to ensure uniform coating. This method has several disadvantages, including high machinery cost, high energy requirement for drying, and a relatively thick film has to be applied to ensure uniform coating, making the fabric stiff and heavy. Drawbacks to other methods include poor stability, expensive ingredients and an oily feel. Moreover, some processes raise serious environmental concerns such as the utilization of toxic transition metals. The objective of this work was to investigate the alternative technique for making hydrophobic cotton. *In-situ* reaction polymerization of organic monomer in the core of bilayer surfactant adsorbed onto a substrate surface is a novel method for applying thin polymeric film on a substrate surface. This method was patented in the late eighties by Harwell, J. H., and O'Rear, E. A. in US[1]. This process is called admicellar polymerization. It consists of three main steps, surfactant adsorption to form a bilayer on the substrate surface called the admicelle formation step, monomer solubilization into the bilayer of admicelle called the monomer adsolubilization step, and polymerization of the monomer in the admicelle called the *in-situ* polymerization step. The three steps are illustrated in Fig 1.

The adsorption isotherm of an ionic surfactant on a solid surface is typically an S-shaped graph when one plots the log of adsorbed surfactant versus the log of equilibrium surfactant concentration[2]. This curve can be used to obtain the appropriate concentration of surfactant for admicellar polymerization process. This concentration is slightly below the critical micelle concentration or CMC to avoid emulsion polymerization. The important parameters that need to be manipulated are pH value and counterion concentration. Counterions help to reduce the electrostatic repulsion between the oncoming ions and the like-charged head groups of surfactants on the surface to promote the densest adsorption of surfactant[3]. The characteristics of substrate and surfactant type also have an effect on surfactant adsorption. Cotton is a natural cellulosic fiber with 1,4-D-glucose as its repeat unit. It acquires a negative charge when in water[4,5]. Preliminary work has shown that a pH of 4 with 0.15 M NaCl as added counterion can be used to promote the adsorption of an anionic

1). Admicelle Formation



2). Monomer Adsolubilization



3). *In situ* Polymerization

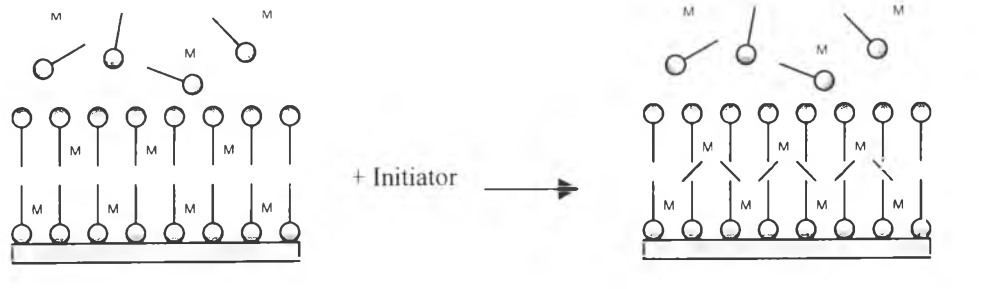


Figure 1. The admicellar polymerization process.

surfactant onto cotton. The admicellar polymerization is started by addition of an initiator. Polymerization occurs in the admicelle bilayer with reaction kinetics similar to that of emulsion polymerization[6]. After the polymerization reaction is complete, the upper layer of surfactant can be removed by washing with water to expose the layer of thin polymer film on the substrate surface. Admicellar polymerization has been successfully used to form thin film of various types of polymer on different substrates such as polystyrene on alumina[7,8] and silica,[9,10] poly (tetrafluoroethylene) on alumina,[11] styrene-isoprene copolymer on glass fiber,[12,13,14] and polypyrrole on alumina[15] and mica[16].

In this work, the admicellar polymerization technique was used to coat polystyrene on cotton to produce hydrophobic, water repellent cotton. Thin polystyrene film on cotton was characterized by FTIR, GPC, and SEM. The hydrophobicity of the treated fabric was also determined by the drop test and the Wilhelmy microelectronic balance technique.

EXPERIMENTAL

Materials

A plain weave, medium-weight (150 g/m^2) bleached cotton fabric was used in this work. Prior to use, the fabric was washed in a washing machine at 95°C several times until it was free from any remaining surfactant as checked by UV absorption of the last washing liquid.

Styrene monomer was purchased from Aldrich Co.Ltd. The inhibitor was removed by washing with 10% NaOH according to the method described by Collins,et al.[17] Dodecylbenzene sulfonate used as linear alkylbenzene sulfonate (LAS) was purchased from Aldrich Co.Ltd. Sodium persulfate and 2,2-azobisisobutyronitrile (AIBN) as initiators were purchased from BHD Laboratory Supplies and Aldrich Co. Ltd respectively. Hydrochloric acid and sodium chloride were purchased from Merck and Alex Chemicals Co. Ltd respectively.

Forming Ultrathin Film on Cotton Fabric by Admicellar Polymerization

Polymerization of styrene on cotton was carried out using 1000 μM LAS at pH 4 with 0.15 M of NaCl. The LAS concentration used was lower than the CMC as shown in the predetermined adsorption isotherm curve in Fig 2. The ratios of styrene:LAS and initiator:styrene were varied to investigate the appropriate condition to produce hydrophobic cotton. Two initiators were used: sodium persulfate and AIBN. At the start of the experiment, a piece of cotton fabric weighing 0.5 g in the square shape of 1.5x1.5 in^2 was placed in a vertical position with no folding or overlapping in a 24 mL vial containing 20 mL of the LAS solution. The desired amount of styrene monomer was injected in the system. Then, the vial was sealed with aluminium foil and the lid was screwed on. All vials were maintained at 30 °C in a shaker bath for 24 hours to allow the LAS adsorption and styrene solubilization in admicelle to reach the equilibrium. The desired amount of 1M initiator solution was then injected into the vial and polymerization was started by placing the resealed vial in the shaker bath at 80 °C for two hours. After polymerization, the vial was cooled down and the fabric was taken out from the vial. The treated fabric was then washed 5 times with hot distilled water at 80 °C for 1 hour each by using a water:cotton ratio of 200:1 by weight to make sure that the outer layer of LAS was completely removed. The fabrics were then dried in an oven at 110 °C for 5 hours before taken out for testing.

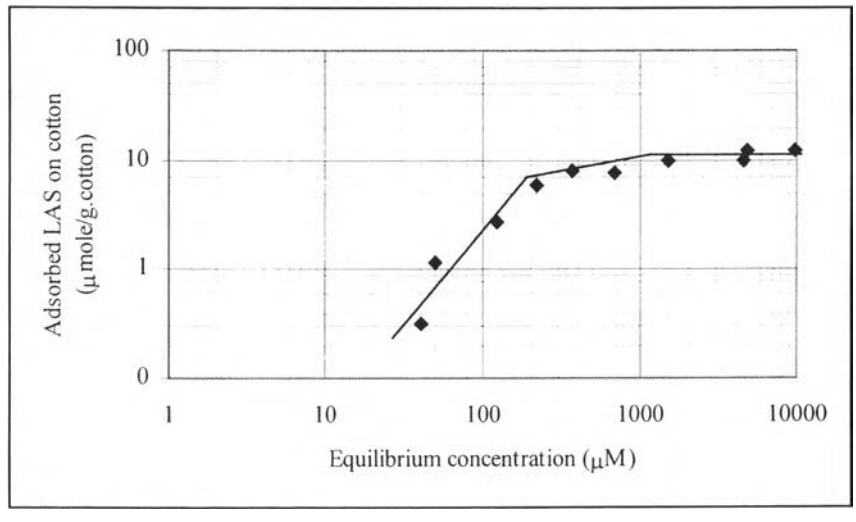


Figure 2. Adsorption isotherm of LAS-styrene-cotton system

Hydrophobicity testing by the drop test

The hydrophobicity of the fabric was determined by placing a drop of water on the cotton surface by injecting 10 μL of distilled water with a 20 μL syringe. The drop was carefully placed onto the fabric with no impact force as shown in Fig 3. The hydrophobicity of the treated fabric was determined by observing the appearance of the droplet after 1 sec and 30 min. Fig 4 illustrates the results of the drop test on fabric with different hydrophobicity. The water droplet on untreated cotton was found to spread over a wide area and disappeared immediately. For fabric with low hydrophobicity, there was some spreading of water droplet after 1 sec but the droplet disappeared within 30 min. For moderate hydrophobicity, there was no spreading after 1 sec but slight spreading within 30 min. For hydrophobic cotton, the water droplet did not spread out and remained spherical after 30 min.

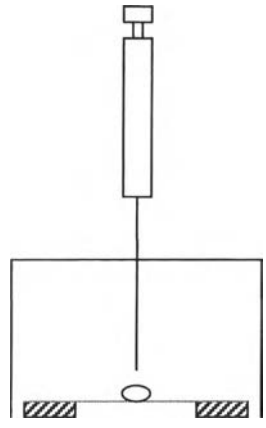


Figure 3. The drop testing

Characterization of the coated film

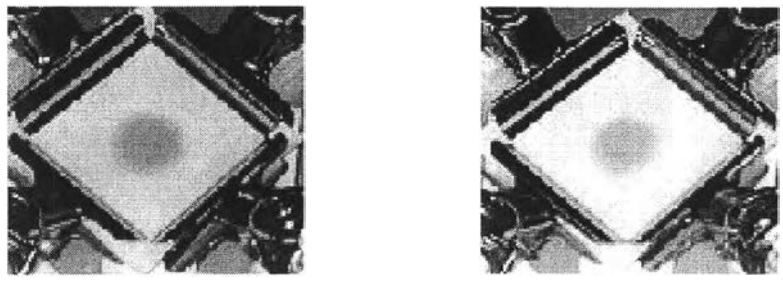
FTIR and GPC were used to characterize the polystyrene film of coated cotton. The polystyrene film on coated cotton was extracted in boiling THF and the extracted THF was concentrated by evaporation for GPC analysis, using a Waters 600E system control, Waters 486 tunable absorbance detector, and Waters 410 differential refractometer. The THF extract was also used for FTIR analysis by coating the sample on a zinc selinide disk, the FTIR spectra was then obtained using a Bruker Instrument model FRA 160/s. The surface of the coated cotton was characterized by SEM using a Jeol SEM model JSM 5200.

Wettability test by Wilhelmy microbalance technique

Individual yarns were taken from the fabric and cut into 8 mm in length for testing. The wettability was measured by dynamic contact angle measuring instrument with a Cahn model DCA-322 using the Wilhelmy microbalance technique. The cotton yarn was attached with wire and hanged on the balance of the machine to determine the force during testing. The instrument is illustrated in Fig 5. After setting the machine, the wicking method[18,19] was applied for use in this work. The yarn was slowly lowered to touch the water surface in the beaker and was held still for 5 min. After

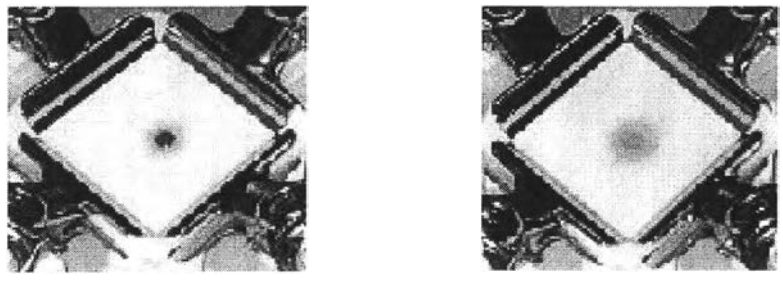
that it was taken up to the previous position. In the experiment, when the yarn touched the water surface, the force immediately increased from zero. This force was termed the initial force. It includes the capillary force and other forces such as surface tension between yarn and water, and water adsorption. The initial force is related to the hydrophobicity of the treated fabric; the higher the initial force, the lower the hydrophobicity.

The other type of force was the force from water absorption. In the experiment, after the yarn was taken up from the water surface the force value did not return to zero because there was some water absorbed in the yarn. This force was the force from the water absorbed in the yarn and it was termed the adsorption force. The adsorption force indicates the ability of the yarn to retain water in its structure after the yarn is lifted from the water surface.



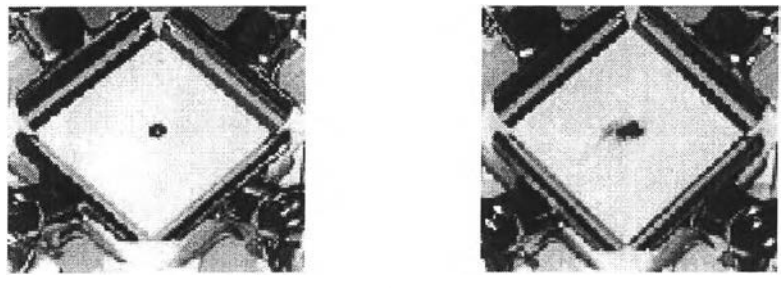
After 1 sec. After 30 min.

(a)



After 1 sec. After 30 min.

(b)



After 1 sec. After 30 min.

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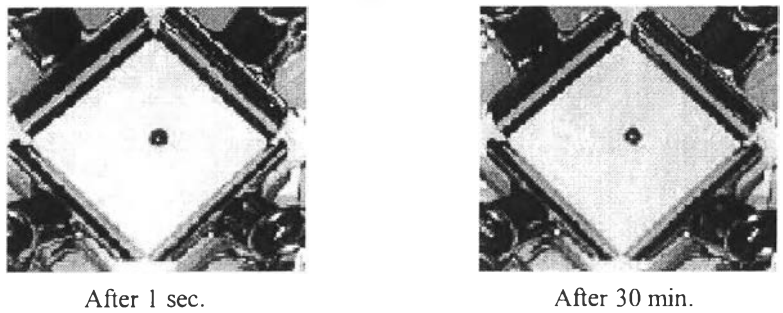


After 1 sec. After 30 min.

(d)

Figure 4. Drop test on fabrics of different hydrophobicity
(a) untreated cotton, (b) low hydrophobicity,
(c) moderate hydrophobicity, and (d) hydrophobic cotton

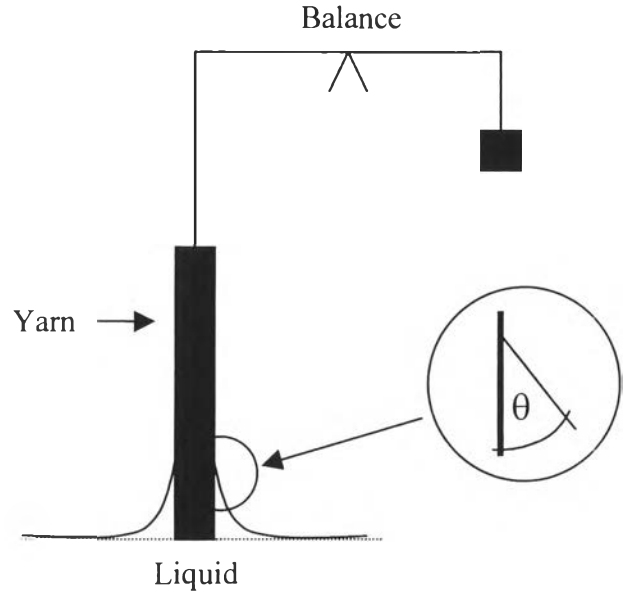


Figure 5. Wilhelmy microbalance technique

RESULTS AND DISCUSSION

The effects of the amounts of styrene and initiator

Using $Na_2S_2O_8$ as the initiator:

The effects of varying styrene:LAS and initiator:styrene ratios are shown in Table 1 (a) and (b) for the drop test and in Fig 6 and 7 for the Wilhelmy microbalance test. The results show that the hydrophobicity of the treated cotton increased with increase in the amount of styrene and initiator. In the case of the drop test, the treated cotton became hydrophobic at a styrene:LAS ratio 5:1 and a styrene:initiator ratio 1:1. In the case of the Wilhelmy test, the adsorption force of the treated samples showed a sudden decrease to almost zero at the same styrene:LAS ratio 5:1 and the same initiator:styrene ratio 1:1 (Fig 7(b) and 8(b)). The results show that there is a close correlation between the drop test and the Wilhelmy test. Well coated cotton has good water resistance as shown by the drop test and low water retention as shown by the Wilhelmy test.

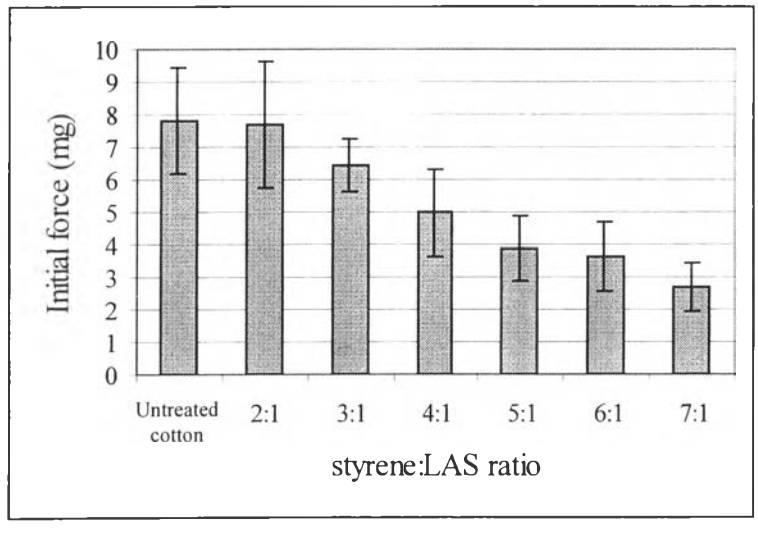
Table 1. Hydrophobicity of treated cotton by the drop test using $Na_2S_2O_8$ as the initiator

a). Effect of varying styrene:LAS ratio

Styrene:LAS ratio	*Hydrophobicity*
1:1	Low
2:1	Low
3:1	Low
4:1	Moderate
5:1	Hydrophobic
6:1	Hydrophobic
7:1	Hydrophobic

b). Effect of varying initiator:styrene ratio

Initiator:styrene ratio	*Hydrophobicity*
0.25:1	Low
0.33:1	Low
0.5:1	Moderate
1:1	Hydrophobic



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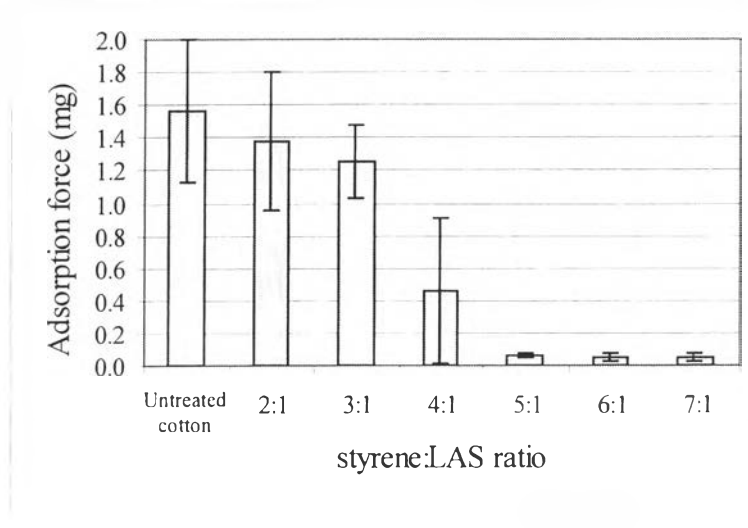
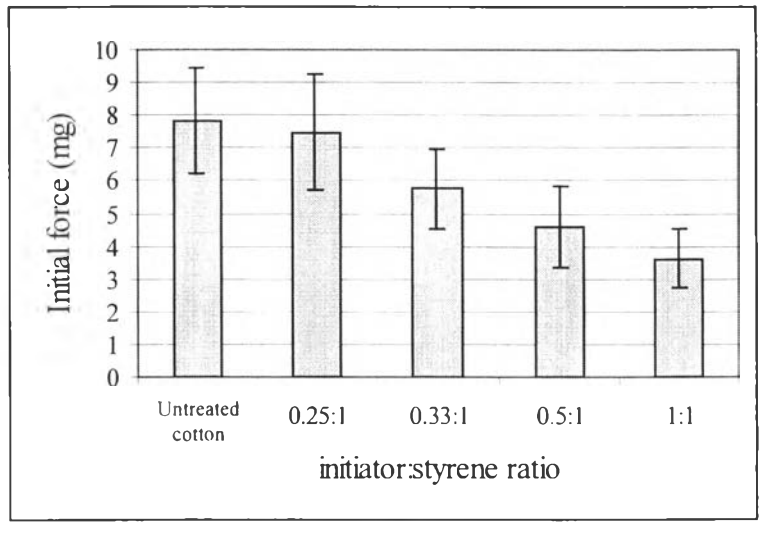


(b)

Figure 6. Effect of varying styrene:LAS ratio using $Na_2S_2O_8$ as initiator by the Wilhelmy test



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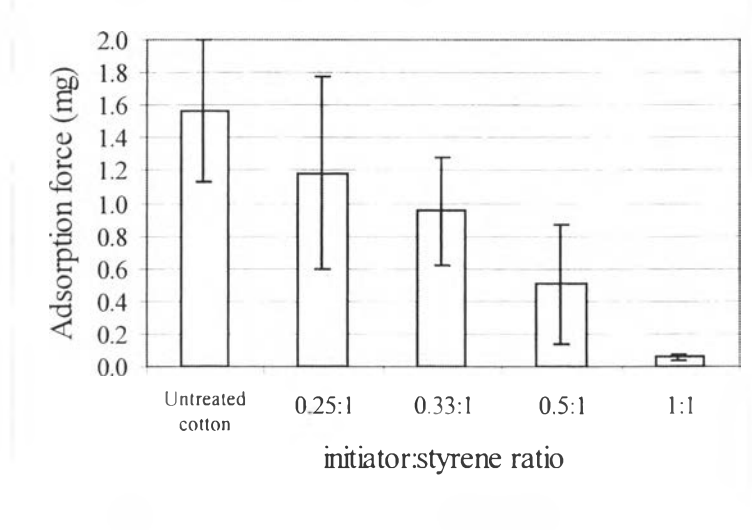


(b)

Figure 7. Effect of varying initiator:styrene ratio using $Na_2S_2O_8$ as initiator by the Wilhelmy test

Using AIBN as the initiator:

In this experiment, the styrene:LAS ratio was varied from 3:1, 4:1, 5:1, 6:1, to 7:1 and the initiator:styrene ratio was varied from 0.04:1 to 1:1. The results of the drop test are shown in Table 2 and of the Wilhelmy test in Fig 8 and 9. The results show that hydrophobicity of the treated cotton increased with increase in the amount of styrene and initiator as in the case of $Na_2S_2O_8$. However, in this case hydrophobic cotton was obtained at a lower styrene:LAS ratio 4:1 and a lower initiator:styrene ratio 0.1:1. Again, the hydrophobic cotton showed almost zero adsorption force in the Wilhelmy test, thus confirming a close correlation between the two test methods. The results also show that AIBN is more efficient in polymerizing styrene than $Na_2S_2O_8$. This is attributed to the fact that AIBN is an organic initiator that can dissolve better in the hydrophobic core of the admicelle whereas $Na_2S_2O_8$ is an inorganic initiator with high water solubility.

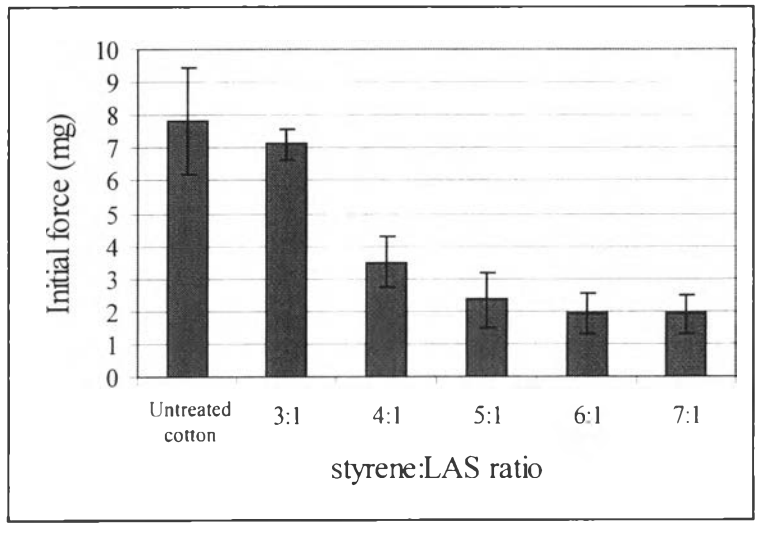
Table 2. Hydrophobicity of treated cotton by the drop test using AIBN as the initiator

a). Effect of varying styrene:LAS ratio

Styrene:LAS ratio	Hydrophobicity
3:1	Moderate
4:1	Hydrophobic
5:1	Hydrophobic
6:1	Hydrophobic
7:1	Hydrophobic

b). Effect of varying initiator:styrene ratio

Initiator:styrene ratio	Hydrophobicity
0.04:1	Moderate
0.05:1	Moderate
0.067:1	Moderate
0.1:1	Hydrophobic
0.2:1	Hydrophobic
0.33:1	Hydrophobic
0.5:1	Hydrophobic
1:1	Hydrophobic



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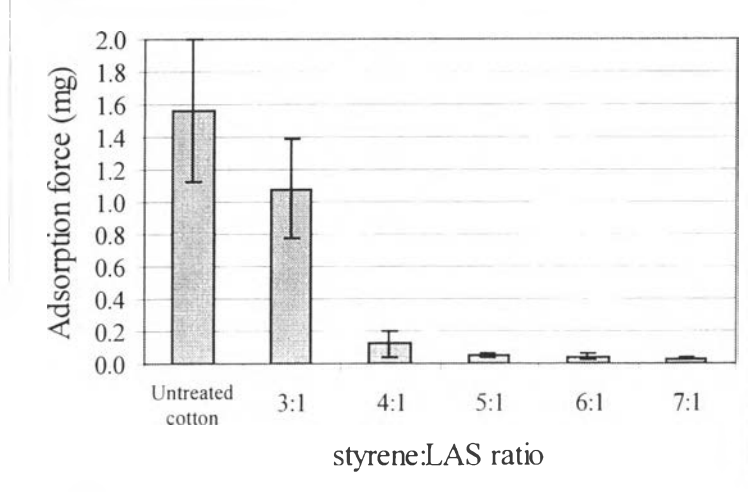
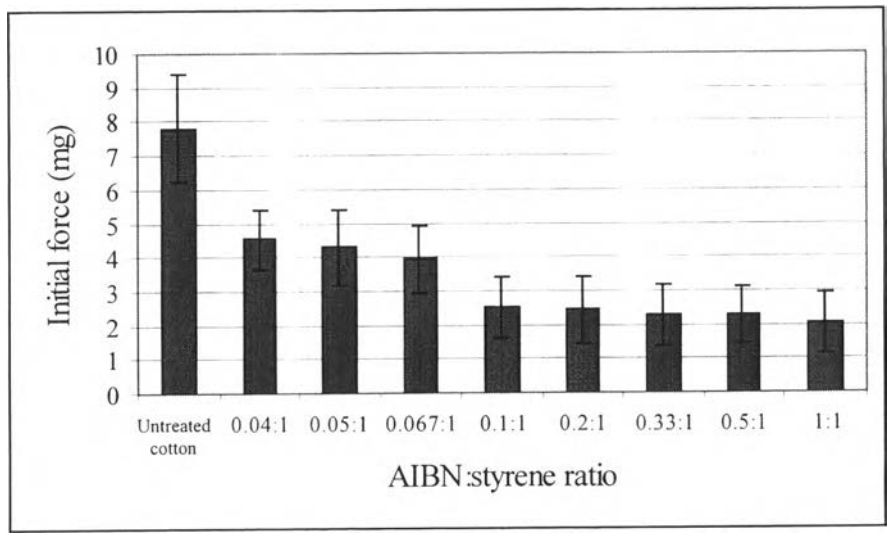


(b)

Figure 8. Effect of varying styrene:LAS ratio using AIBN as initiator by the Wilhelmy test



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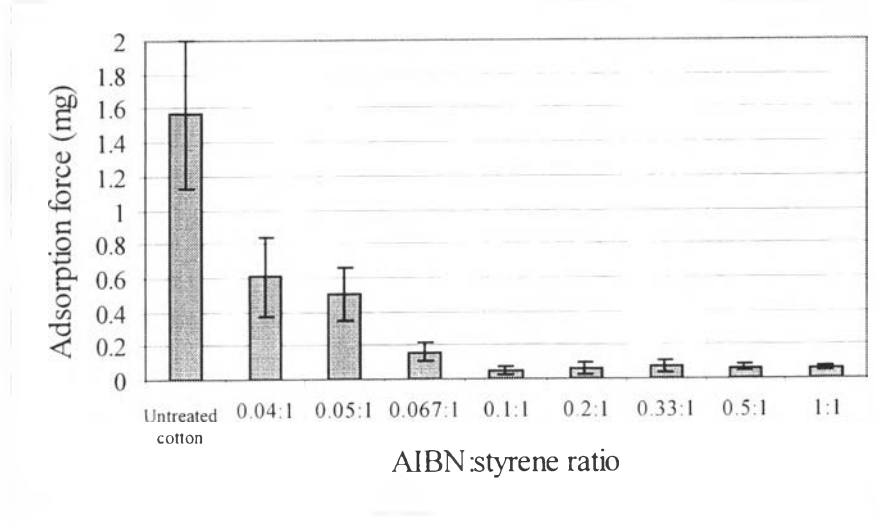


(b)

Figure 9. Effect of varying initiator:LAS ratio using AIBN as initiator by the Wilhelmy test

Identification of the coated film by FTIR

The polystyrene film coated on cotton was characterized by FTIR. The FTIR spectra of standard polystyrene, treated cotton, and untreated cotton were shown in Fig 10. It can be seen that the admicellar-treated sample shows distinctive characteristic peaks of polystyrene at 1455, 1490 and 1600 cm^{-1}. These peaks are absent from untreated cotton. The results thus confirm the presence of polystyrene on the treated cotton. It can be concluded that polystyrene has been successfully admicellar polymerized on cotton.

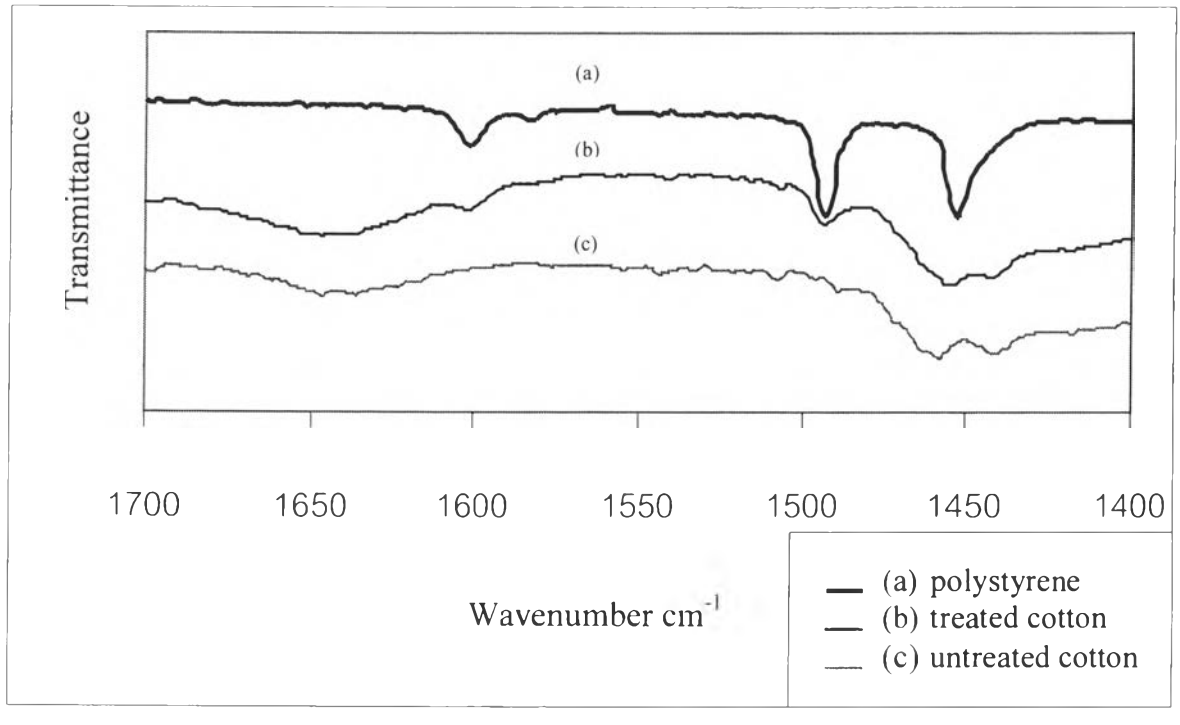


Figure 10. FTIR spectra of polystyrene, treated and untreated cotton

MW Analysis by GPC

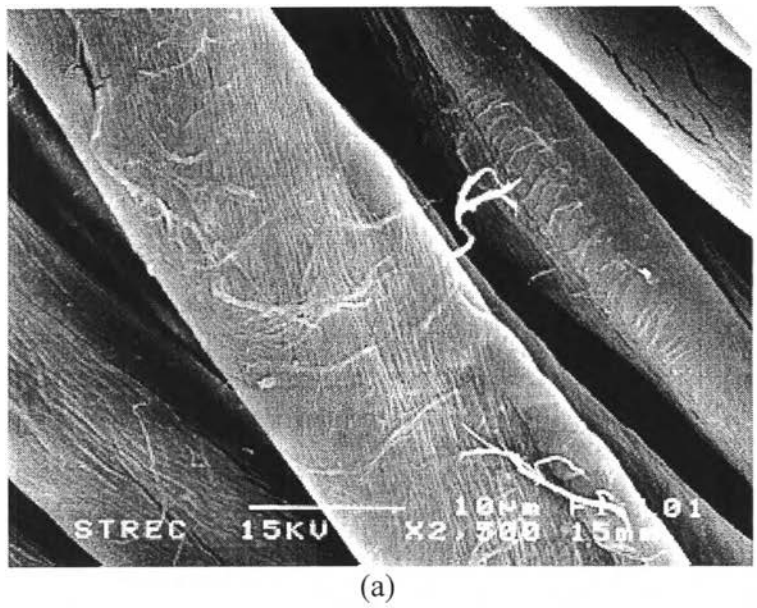
The MW of styrene extracted from the cotton surface was determined by GPC. The result was compared to that obtained by emulsion polymerization under the same conditions using styrene:LAS and initiator($Na_2S_2O_8$):styrene ratios of 10:1 and 1:1, respectively. The results in Table 3 show that admicellar polymerization process yielded MW in the same range as the MW of emulsion polymerization process of 200,000. This indicated a close similarity between admicellar polymerization and emulsion polymerization. It was found that the GPC chromatogram of admicellar treated sample also showed a second peak at a lower MW range of 7000. The polymer in the lower MW range may come from polymerization in isolated patches of admicelle which is possible in this case as LAS adsorption under the conditions used for polymerization was far from the conditions needed for surface saturation.

Table 3. MW of polystyrene from emulsion and admicellar polymerization

Type of polystyrene	MW
Emulsion polymerization	200,993
Admicellar polymerization	7,490 - 239,447

Characterization of the fabric surface by SEM

SEM micrographs were obtained to show the film coated on cotton after treated by admicellar polymerization. Fig 11 shows the difference of cotton surface comparing between untreated and admicellar-treated cotton. The admicellar-treated cotton shows clear evidence of a layer of coating on the fiber surface when compared to the untreated fabric. The pictures also show that the coating occurred only on the fiber surface and not in the space between fibers.



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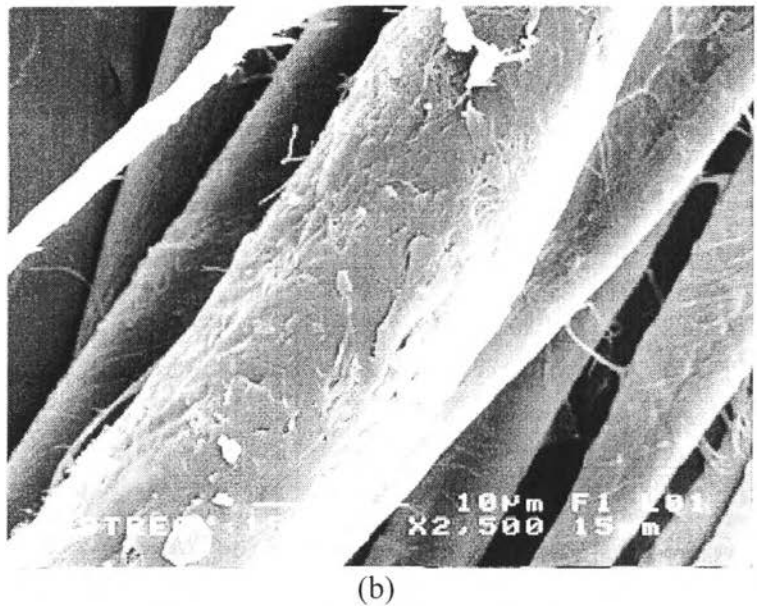

(b)

Figure 11. SEM micrographs of
(a) untreated and (b) admicellar-treated cotton

CONCLUSIONS

Formation of ultrathin polystyrene film to produce hydrophobic cotton by i*n-situ* reaction polymerization called admicellar polymerization has been successfully carried out in this work. The treated samples have high hydrophobicity as shown by the drop test and the Wilhelmy test. When using AIBN as initiator, the amount of styrene and initiator required to produce hydrophobic cotton was lower than when using $Na_2S_2O_8$ as initiator. SEM micropraphs confirm the formation of thin polymeric film on treated cotton surface.

REFERENCES

1. Harwell, J. H.; O'Rear, E. A., U.S. Patent 4 770 906, 1988.
2. Rosen, M. J., In *Surfactants and Interfacial Phenomena*, 2nd Ed., John Wiley and Sons, New York, 1989.
3. Scamehorn, J.F.; Schechter, R.S.; Wade, W.H., *J. Colloid Interface Sci.*, **1982**, 85, 463.
4. Grancaric, A. M.; Pusic, T.; Soljacic, I., *Text. Chem. Color.*, **1997**, 29, 33.
5. Aspland, J.R., *Text. Chem. Col.*, **1991**, 23, 14.
6. Wu, J.; Harwell, J. H.; O'Rear, E. A., *J. Phys.Chem.*, **1987**, 91, 623.
7. Wu, J.; Harwell, J. H.; O'Rear, E. A., *Langmuir*, **1987**, 3, 531.
8. Wu, J.; Harwell, J. H.; O'Rear, E. A., *AIChE J.*, **1988**, 34, 1511.
9. O'Haver, J.; Harwell, J.H.; O'Rear, E.A.; Snodgrass, L. J.; Waddell, W.H., *Langmuir*, **1994**, 10, 2588.
10. Waddell, W. H.; O'Haver J. H.; Evans, L. R.; Harwell, J. H., *J. Applied Polymer Science*, **1995**, 55, 1627-1641.
11. Lai, C.; Harwell, J. H.; O'Rear, E. A., *Langmuir*, **1995**, 11, 905.
12. Sakhalkar, S.S.; Hirt, D.E., *Langmuir*, **1995**, 11, 3369.
13. Glady, B. P.; O'Rear, E. A.; Penn, L. S.; Pedicini, A., *Polymer Composites*, **1998**, 19, 579-578.
14. Barraza, H. J.; Hwa, M J.; Blakley, K.; O'Rear, E. A.; Gragy, B. P., *Langmuir*, **2001**, 17, 5288-5296.

15. Cho, G.; Glatzhofer, D. T.; Fung, B. M.; Yuan, W.; O'Rear, E. A., *Langmuir*, **2000**, 16, 4424-4429.
16. Yuan, W.; O'Rear, E. A.; Cho, G.; Funkhouser, G. P.; Glatzhofer, D. T., *Thin Solid Film*, **2001**, 358, 96-108.
17. Collins, E. A.; Bares, J.; Billmeyer Jr., F. W., In *Experiments in Polymer Science*, Jonh Wiley & Sons, New York, 1973, 337.
18. Domingue, J., In *The Application of Wettability-Based Test Methods to Fiber-Based Materials*, Cahn Instruments, Inc.
19. Chen, D. and McMorran, D., In *Measuring the Wettability of Porous Materials Handling Powder Samples*, Cahn Instruments, Inc.