CHAPTER IV
IMPROVING HYDROPHOBICITY OF COTTON FABRIC BY ADMICELLAR POLYMERIZTION*

Abstract:

Cotton fabric was coated with thin film polystyrene formed by using dodecyl benzenesulfonate (DBS) adsorbed on fabric as a template that is called admicellar polymerization technique. This technique consists of three main reaction steps, DBS adsorption, styrene monomer solubilization into the bilayer of DBS adsorption, and polymerization of styrene monomer *in-situ* DBS adsorbed. Sodium persulfate ($Na_2S_2O_8$) was used as an initiator to polymerize polystyrene on cotton surface. FTIR was used to characterize polystyrene film extracted by THF. The hydrophobicity of the treated cotton surface was determined by the drop test, and the water absorption of untreated and treated cotton was examined using the Wilhelmy microelectronic balance technique. The morphology of untreated and treated cotton was obtained by AFM. The results show that polystyrene thin film was successfully formed on cotton resulting in hydrophobic cotton.

1. Introduction

Cotton is a natural fiber that has high water absorption and rapidly transports moisture away from the human body. In textile fabric, cotton is the best fabric for transporting water to make more comfortable feeling for the wearer. Generally, making water repellent cotton fabric has the effect on lacking moisture transportation. This is the aim of this work to make hydrophobic cotton maintaining a good property of original cotton. Admicellar polymerization was selected to make hydrophobic cotton as the alternative method and first published in the journal of colloid and interface science by Pongprayoon, T., et al, (2002).

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Commercial water repellent cotton fabric is commonly produced by depositing a film of hydrophobic substance on the fabric. Silicone and fluorochemicals are examples of chemicals used for this purpose. The traditional method is to apply a solution of water-repellent agents onto the fabric by the pad-dry-cure process to ensure uniform coating (Higgin, E.G., 1963). 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 heavy and oily. 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, admicellar polymerization, to make 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, (1988). Admicellar polymerization process 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 surfactant concentration at equilibrium (Rosen, M. J., 1989). 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 (Scamehorn, J.F., et al, 1982). The characteristics of substrate and surfactant type also have an effect on surfactant adsorption. Cotton is a natural cellulose fiber with 1,4-D-glucose as its repeat unit. It acquires a negative charge when in water (Grancaric, A. M., et al, 1997 and Aspland, J.R., 1991). Admicellar polymerization has been successfully used to form thin film of various types of polymer on different substrates such as polystyrene on alumina (Wu, J., Harwell, et al, 1988), and silica (O'Haver, J., et al, 1994 and Waddell, W.H., et al, 1995), polypyrrole on alumina (Cho, G., et al, 2000) and mica (Yuan, W., et al, 2001), poly(tetrafluoroethylene) on alumina, (Lai, C., et al, 1995) and styrene-isoprene copolymer on glass fiber (Glady, B.P., et al, 1998, and Barraza, H.J., et al, 2001).

In this work, the admicellar polymerization technique was used to coat polystyrene on cotton to produce hydrophobic cotton. The hydrophobicity of the treated fabric was also determined by the drop test and the Wilhelmy microelectronic balance technique. Thin polystyrene film on cotton was identified by FTIR and morphology of untreated and treated cotton was also performed by AFM.

2. Experimental

2.1 Materials

A plain weave, medium-weight (150 g/m^2 superficial area) bleached cotton fabric was used. 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 at 225 nm of the last washing liquid.

Styrene monomer was purchased from Aldrich Co.Ltd. Before using, it was washed with 10% NaOH to removed inhibitor following the method described by Collins,et al (1973).

Dodecylbenzene sulfonate (DBS), a surfactant in the group of linear alkylbenesulfonate (LAS) used to form admicelle, sodium persulfate used as initiators, hydrochloric acid for adjusting pH, and sodium chloride were purchased from Aldrich Co.Ltd., BHD Laboratory Supplies Co. Ltd., Merck and Alex Chemicals Co. Ltd respectively.

2.2 Hydrophobic cotton production by admicellar polymerization

Polymerization of styrene on cotton was carried out using 1000 μM DBS at pH 4 with 0.15 M of NaCl that is the appropriate condition studied in previous work (Pongprayoon, T., et al, 2002). The ratios of styrene:DBS and initiator (sodium persulfate):styrene were varied to investigate the preferring condition to produce hydrophobic cotton. At the start of the experiment, a piece of cotton fabric weighing 0.5 g in the square shape was placed in a vertical position with no folding or overlapping in a 24 mL vial containing 20 mL of the DBS solution. The desired amount of styrene monomer was injected in the system. Then, the vial was sealed with aluminum foil and the lid was screwed on. The vials were maintained at 30 °C in a shaker bath for 24 hours for adsorption and adsolubilization steps. Then 1 M sodium persulfate solution was injected into the vial to polymerize styrene by maintaining temperature 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 washed with hot distilled water at 80 °C for 1 hour several times until the outer layer of DBS was completely removed. The fabrics were then dried in an oven at 110 °C for 5 hours before taken out for testing.

2.3 Hydrophobicity testing

2.3.1 Drop test

The drop test was used to observe the hydrophobicity of the fabric by placing a drop of water on the cotton surface. 10 μL distilled water was dropped onto the fabric without impact force by using a 20 μL syringe as shown in Fig 2. The time was taken for 30 min to consider being the hydrophobic fabric by no spreading of water droplet.

2.3.2 Wilhelmy microbalance technique

The samples were prepared as individual yarns by taking out from the fabric and cutting into 8 mm in length. The wettability was measured by the Wilhelmy microbalance technique with a Cahn model DCA-322. The cotton yarn was attached with wire and hanged on the balance of the machine to automatically determine the force during testing with software control. The instrument is illustrated in Fig 3. The wicking method presented by Domingue, J. was applied for use in this work. From operating machine, 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 that includes the forces of capillary flow, surface tension between yarn and water, and water absorption. The initial force is related to the hydrophobicity of the treated fabric; the lower the initial force, the higher the hydrophobicity.

The other force was the force from water absorbed in yarn. In the experiment, after the yarn was taken up from water surface there was little water absorbed inside the yarn. The force of water absorbed was termed the absorption force that indicates the ability of yarn to remain water inside its structure. In the same way of initial force, lower value of absorption shows higher hydrophobicity of cotton.

2.4 Characterization of the coated film

FTIR was used to characterize the film coated on cotton. The coated film was extracted in boiling THF and the extracted THF was concentrated by evaporation. The THF extract was 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 spectrum was interpreted to conform the polystyrene formed on cotton.

The surface of untreated and treated cotton was characterized by AFM. A piece of fiber was removed from the cotton yarn and stuck on a mica plate by melted polymer to image its surface by AFM (NanoScope III, Multimode Scanning Probe, Digital Instruments). The instrument was operated in 'height' mode under ambient condition with a standard silicon nitride tip. The commercial hydrophobic cotton and coated cotton with over quality of styrene were also observed to show the significantly different surface from untreated cotton.

3. Results and Discussion

3.1 Hydrophobicity by drop test

The drop test results were illustrated as Fig 4 that shows the different droplet character onto untreated and treated cotton surface. For untreated cotton, water droplet disappeared immediately and spread to cover a wide area after dropping in a second. The water droplet photos of treated cotton taken after 30 min were different and they can be identified as three characters. For fabric considered as low hydrophobicity, the droplet made a sphere on fabric and it disappeared within 30 min by spreading some water droplet. For moderate hydrophobicity, the droplet can be maintained within 30 min by having slightly spreading water droplet. For hydrophobic cotton, the water droplet did not spread out and remained spherical shape after 30 min.

3.2 Welhylmy method results

Welhelmy method by using Cahn microbalance machine yielded the changing force in two type curves, the force and position curve and the force and time curve, while it was operating.

The initial force was read from the recorded data of force and time relationship at the moment the yarn touched water surface and the force immediately increased from zero. For untreated cotton, this force was highest because untreated cotton acts as hydrophilic cotton that water can transfer in yarn very well and also be very well absorbed inside its yarn, while this force of hydrophobic cotton was low. The initial force of untreated cotton was about 8.00 mg much higher than that of hydrophobic cotton treated by admicellar polymerization, approximately 3.00 mg. Another force, absorption force, was read from the relationship between force and position that the yarn was raised from water surface to back to the position at starting test. If the force returns to zero, it indicates that no water was absorbed inside the yarn, which acts as completely hydrophobic surface. This is further evidence of hydrophobic character due to repelling water from its surface. On the other hand, if this force is still high, it mains that the yarn is hydrophilic. From this experiment, the absorption force of untreated cotton was higher about 1.60 mg, while this force of hydrophobic, admicellar-treated cotton was about 0.05 mg that closed to zero.

The commercial hydrophobic cotton coated with fluorochemical and hydrophobic cotton coated with over quality styrene were also studied in this work. The initial and absorption force of both can not be detected by this test because they floated over water surface. These showed that they did not allow any water transport inside their yarns and did not adsorb any water.

3.3 The effects of quality of styrene and initiator on hydrophobicity

The effects of varying styrene:DBS and initiator:styrene ratios on wettability presented by drop test and Welhylmy methods are shown in Table 1(a) and (b). 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:DBS ratio 5:1 and a styrene:initiator ratio 1:1. In the case of the Wilhelmy test, the absorption force of the treated samples showed a sudden decrease to almost zero at the same styrene:DBS ratio 5:1 and the same initiator:styrene ratio 1:1. 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.

From this table, it can be seen that Welhylmy method can identify the different surface of hydrophobic fabric while drop test was showing the same results. The drop test did not detect any difference in hydrophobicity and wettability of cotton treated by admicellar polymerization that were deemed “hydrophobic”. (i.e. they can all resist wetting by water for more than 30 min).

3.4 The coated film identification by FTIR

The extracted polystyrene film on cotton in THF solution was characterized by FTIR. This confirmed that polystyrene has been coated on cotton by admicellar polymerization shown in Fig 5. The results show that the FTIR spectrum of admicellar treated cotton show character peaks of polystyrene at 1600, 1490, and 1455 cm^{-1} as spectrum (b) that are also distinctively presented in the stand polystyrene as spectrum (a). For untreated cotton shown as spectrum (c), these peaks were not presented. It can be identified that there was polystyrene film coated on cotton by admicellar polymerization.

3.5 AFM images

AFM images show the morphology of untreated cotton and admicellar-treated cottons in Fig 6 (a) and (b). From both, their surfaces look similar; however the hydrophobic test by drop test and Welhylmy methods are clearly different as seen from the former results. These results show that the coated polystyrene film on cotton using the ratio 7:1 of styrene:DBS was ultrathin film. To see the significant change of cotton morphology, the treated cotton using over quality of styrene as the 50:1 ratio of styrene:DBS was observed and the result is shown as Fig. 7. The result shows that polystyrene film was very thick comparing in the same size of AFM image (1 µm.) as Fig. 7(b) with 7:1 styrene:DBS ratio as Fig 6(b). In this condition, hydrophobicity can not be measured. That was similar to the yarn of the commercial hydrophobic cotton that has an oily film completely coated. Its AFM image shown in Fig 8 looks oily by chemical on cotton surface.

4. Conclusions

The results of this work showed that admicellar polymerization has been successfully applied to make hydrophobic cotton and it has a proclivity to be a commercial process with further development. Admicellar treated cotton not only has have high hydrophobicity as shown by the drop test and, but it also allowed some water transport inside its yarn as shown by Wilhelmy test. It can be seen that admicellar treated cotton is coated with a very thin film of polymer confirmed by AFM image.

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Table 1. Hydrophobicity of treated cotton by the drop test and Welhylmy

a). Effect of varying styrene:DBS ratio

Styrene:LAS Ratio	Drop test	Welhylmy method			
		Initial force (mg)		Absorption force (mg)	
		Average	STD	Average	STD
2:1	Low	7.70	1.94	1.38	0.42
3:1	Low	6.44	0.81	1.26	0.22
4:1	Moderate	4.98	1.33	0.46	0.45
5:1	Hydrophobic	3.86	1.01	0.06	0.01
6:1	Hydrophobic	3.60	1.06	0.05	0.02
7:1	Hydrophobic	2.69	0.74	0.05	0.02

b). Effect of varying initiator:styrene ratio

Intiator:styrene Ratio	Drop test	Welhylmy method			
		Initial Force (mg)		Absorption force (mg)	
		Average	STD	Average	STD
0.25:1	Low	7.47	1.77	1.18	0.59
0.33:1	Low	5.75	1.19	0.95	0.33
0.5:1	Moderate	4.61	1.24	0.51	0.36
1:1	Hydrophobic	3.63	0.88	0.06	0.02

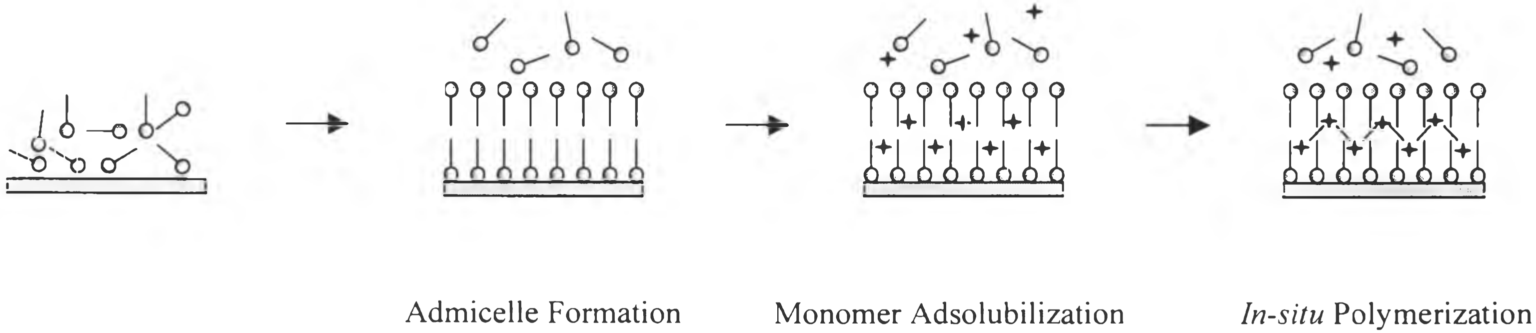


Fig 1. Admicellar polymerization process

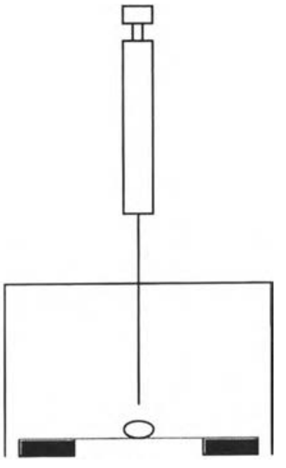


Fig 2. The drop test

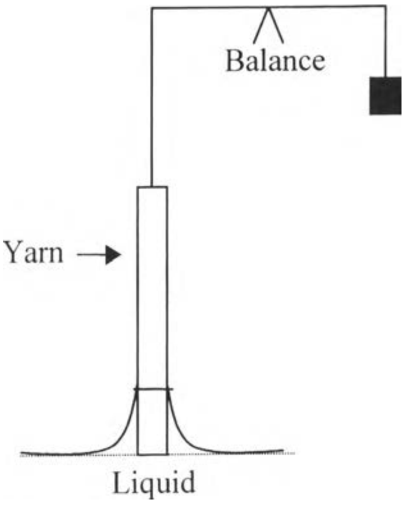
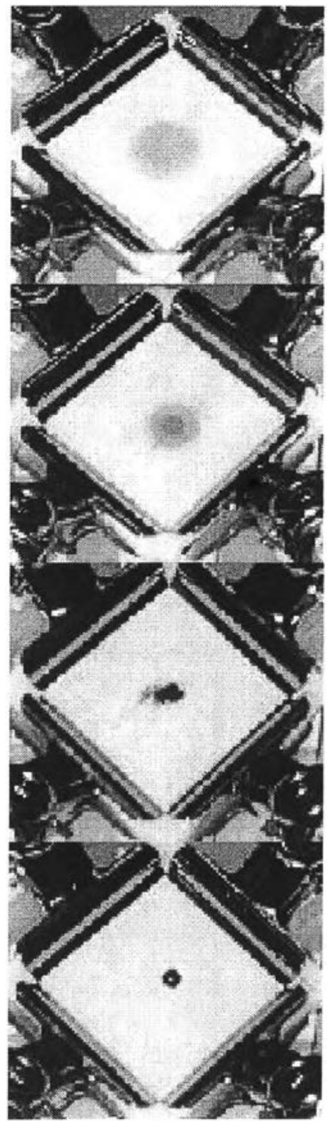


Fig. 3 Wilhelmy microbalance technique



Hydrophilic cotton

Low hydrophobic cotton

Moderate hydrophobic cotton

Hydrophobic cotton

Fig. 4 Drop test on fabrics of different hydrophobicity after 30 min dropped

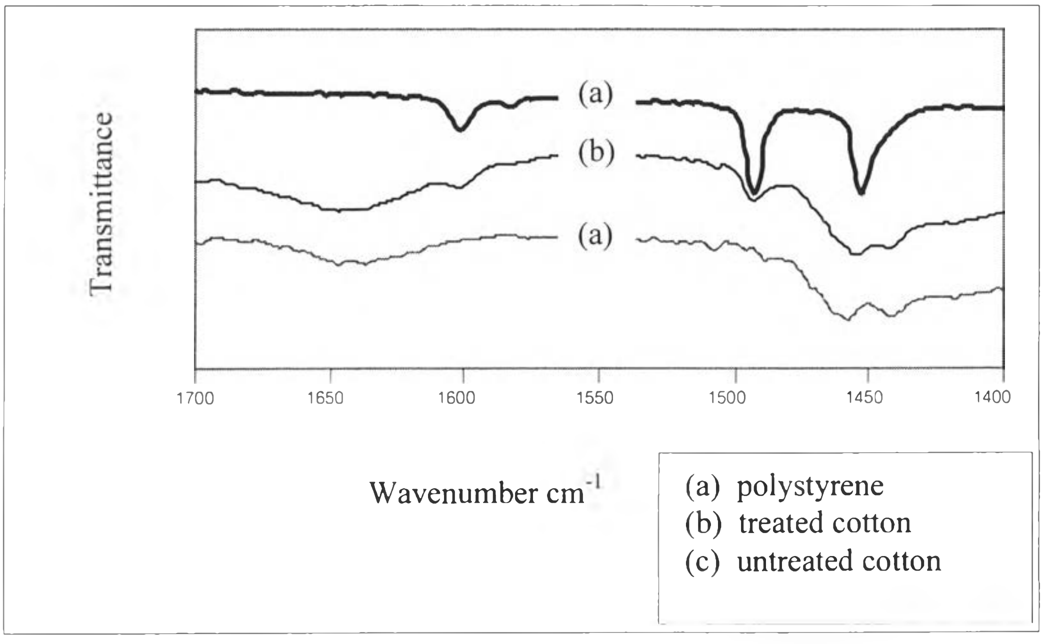


Fig 5. FTIR spectrum

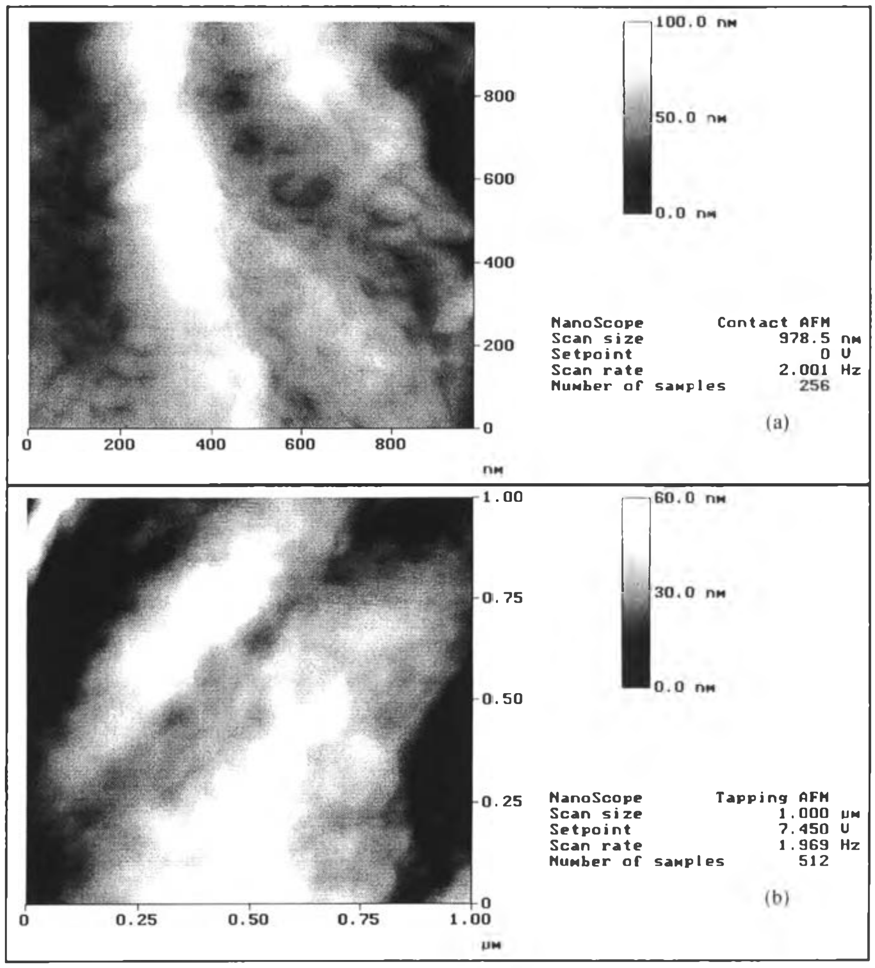


Fig. 6 AFM images sizing 1 µm of;
(a) untreated cotton and
(b) admicellar treated cotton

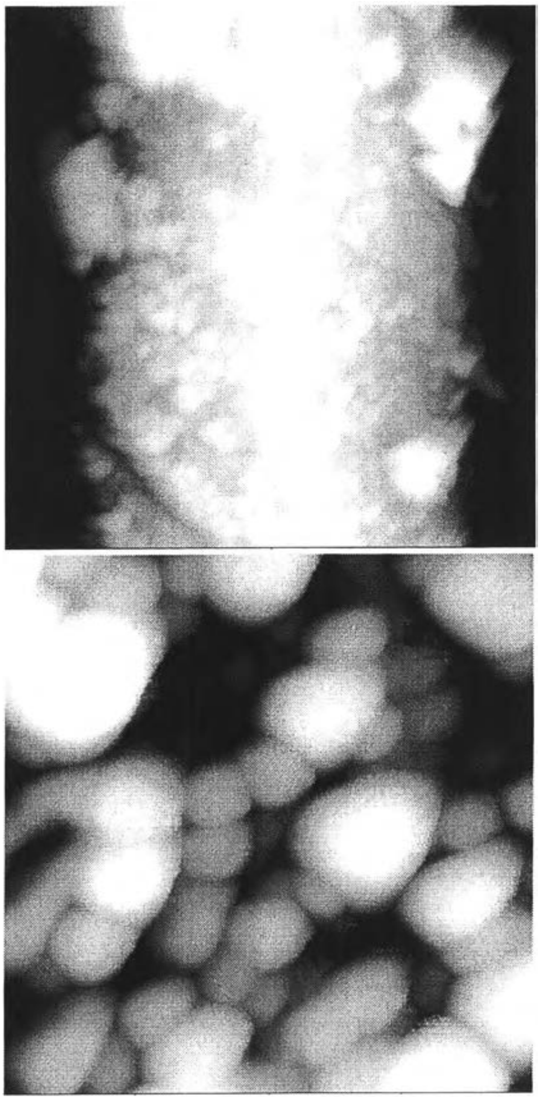


Fig. 7 AFM image of high styrene coated on cotton sizing 5 μm (above) and 1 μm (below)

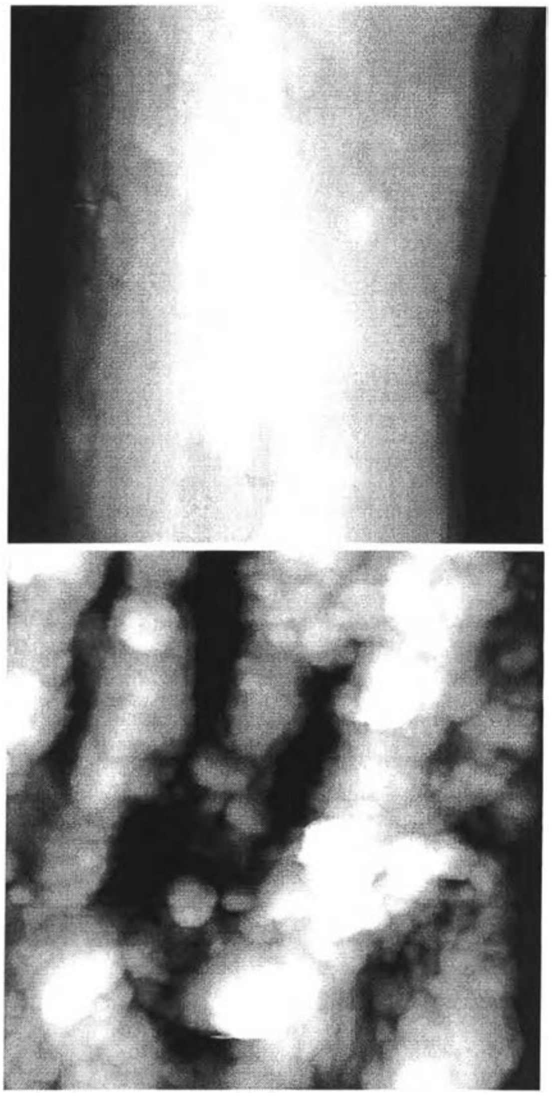


Fig. 8 AFM image of commercial hydrophobic cotton coated by oil chemical sizing 5 μm (above) and 1 μm (below)