

Surface characterization of cotton coated by a thin film of polystyrene with and without a cross-linking agent

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Abstract

Thin polystyrene film coated on cotton was successfully formed by admicellar polymerization. Divinylbenzene (DVB) was used as a cross-linking agent to form networked polystyrene to improve film coverage. A wettability test and XPS analysis were used to characterize the coated surface. The optimum amount of DVB was around 1%. At this amount, the film coverage was most complete, as judged by the reduction of the O1s signal in XPS analysis.

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1. Introduction

Thin film coatings are widely used for modification of substrate surfaces. Common methods for applying thin film coatings include chemical vapor deposition, plasma polymerization, physical vapor deposition, and electrochemical deposition. Admicellar polymerization is a method that can be used to create a thin polymeric film on a substrate surface [1]. The method makes use of the formation of a surfactant bilayer on a substrate surface at a surfactant concentration just below the CMC. In the outer surfactant layer, the amphiphilic molecules are oriented with their ionic head groups in contact with the aqueous solution, while the long hydrophobic tails interact to form a hydrophobic inner core (Fig. 1a). An inner layer oriented with the head groups in contact with the substrate completes the surfactant bilayer called an “admicelle.” When an organic monomer is added into the solution, it will be preferentially adsorbed in the core of the admicelle in a process called “adsolubilization,” and

when an initiator is added, the monomer in the admicelle will undergo a polymerization reaction to form a polymeric layer on the substrate surface (Fig. 1b). After the polymerization, surfactant in the upper layer may be removed by washing to expose the polymeric layer on the substrate surface (Fig. 1c).

Admicellar polymerization has been successfully used to coat thin films of a variety of polymers on various kinds of substrates for several purposes, such as hydrophobicity coating on an organic substrate [2,3], hydrocarbon component coating on inorganic materials [4–6], and electropolymer coating on surfaces [7,8]. Recently, the method has been used to form a thin polystyrene film on cotton [2]. The resulting cotton fabric shows good water repellency. Water-repellent cotton has wide applications in tentage material, canvas, raincoats, and furnishing textiles. Polystyrene is known to form a networked polymer with a cross-linking agent such as divinylbenzene (DVB) [9], shown in the reaction scheme in Fig. 2. Many studies have been carried out on various aspects of the reaction [10,11]. In this work the effect of adding DVB to the styrene monomer in the admicellar polymerization process on cotton was studied. After the polymerization, the wettability of the treated cotton sur-

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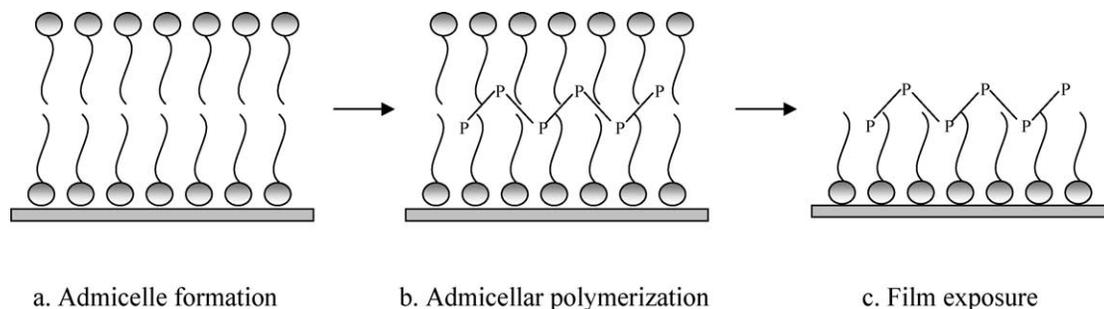


Fig. 1. Admicellar polymerization process.

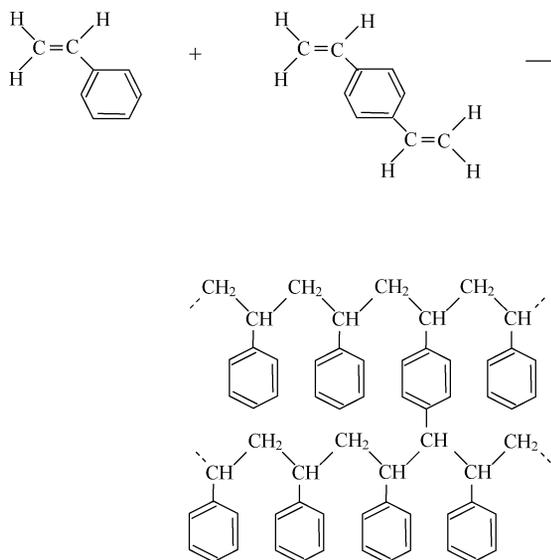


Fig. 2. The reaction of cross-linked polystyrene.

face as determined by the Wilhelmy microbalance technique was correlated to the surface coverage of the polymer as determined by XPS. The wettability of cotton and admicelle-modified cotton using the Wilhelmy microbalance technique was reported previously [12].

XPS is a powerful technique that is widely used for characterization of substrate surfaces [13,14]. It provides information about the chemical state and concentration of elements composing the outermost surface layer of a solid. The sample depth of this technique is generally less than 10 nm [15]. In this work it was used to characterize films of polystyrene coated on cotton in both qualitative and quantitative analysis. The peak C(1s) was qualitatively used to differentiate characteristic peaks between cotton and polystyrene and confirm that cotton fabric modified by admicellar polymerization was coated with polystyrene. The coverage and film thickness of polystyrene on cotton were quantitatively determined by XPS using the peak of O(1s), which has no signal for pure polystyrene, but occurs in cellulose of cotton. The coverage and thickness of the film were used to comparatively explain the wettability of different cotton samples prepared using various amounts of DVB.

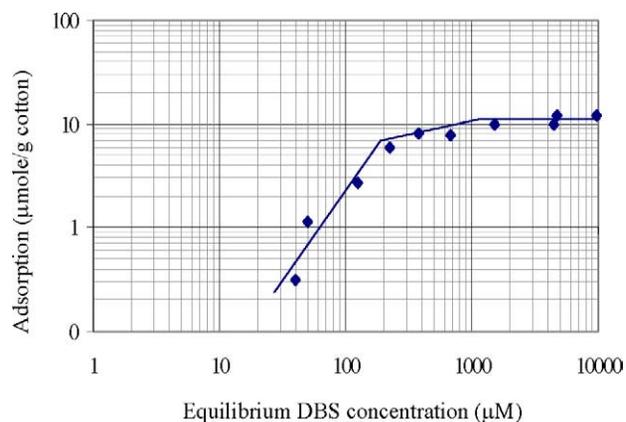


Fig. 3. Adsorption isotherm curve of DBS–cotton system.

2. Experimental

2.1. Materials

A plain weave, medium-weight (150 g/m²) bleached cotton fabric was purchased from Boonchaury Co. Ltd. Prior to use, the fabric was washed several times in a washing machine at 95 °C until it was free from any remaining surfactant, as checked by the UV absorption of the last washing liquid at the wavelength of 225 nm.

Styrene monomer and divinylbenzene were purchased from Aldrich Co. Ltd. The inhibitors in both chemicals were removed by washing with 10% NaOH according to the method described by Collins et al. [16].

Dodecylbenzene sulfonate (DBS), used as the surfactant, was purchased from Aldrich Co. Ltd.

Sodium persulfate, used as an initiator, was purchased from BHD Laboratory Supplies Co. Ltd. Hydrochloric acid and sodium chloride were purchased from Merck Co. Ltd.

2.2. Admicellar polymerization process

The admicelle-enabled surface polymerization was carried out at a DBS concentration just below the CMC, as determined from the adsorption isotherm of the DBS–cotton system in the presence of 0.15 M NaCl at pH 4, as shown in Fig. 3. The concentration of DBS in solution was determined by a Cecil Model CE 2040 UV spectrophotometer at a wavelength of 225 nm, which is the wavelength of maximum

absorption of aqueous DBS solution, with an extinction coefficient of $1.185 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.

From the adsorption isotherm, the CMC was found at $1050 \mu\text{M}$ and so a DBS concentration of $1000 \mu\text{M}$ was chosen for the admicellar polymerization process. The solution was adjusted to pH 4 and 0.15 M NaCl was added into the solution to enhance surfactant adsorption.

To carry out the admicellar polymerization, a 20-ml aliquot of DBS solution was pipetted into a 24-ml glass vial and a 0.5 g square piece of cotton fabric 1.5×1.5 in was placed in the vial in the vertical position with no folding or overlapping. The styrene monomer with 0, 1, 2, and 5 mol% divinylbenzene as a cross-linking agent was pipetted into the vial to give a DBS:monomer ratio of 1:5. Sodium persulfate at an initiator:monomer ratio of 1:1 was then added into the vial. Vials were sealed and maintained at 30°C in a shaker bath for 8 h to allow admicelle formation and adsorption of the monomer in the admicelle. After that, the temperature of the system was raised to and maintained at 80°C for 2 h to effect the polymerization reaction.

After that, the fabric was taken from the vial and washed five times with hot distilled water at 80°C for 1 h each time using a water:cotton ratio of 200:1 by weight to make sure that the outer layer of DBS was completely removed. The fabric was then dried in an oven at 110°C for 5 h before being taken out for further testing.

2.3. Water repellency test by the drop test

An initial characterization of the treated surface was by the drop test. A $10\text{-}\mu\text{l}$ droplet of distilled water was placed on the cotton fabric surface with a $20\text{-}\mu\text{l}$ syringe. The drop was carefully placed on the fabric with no impact force. The fabric was judged water-repellent when the droplet remained spherical on the fabric with no wetting after 30 min.

2.4. Wettability test by the Wilhelmy microbalance technique

Individual yarns were taken from the fabric and cut into 8-mm length for testing. Each yarn was attached to a wire and hung from the Wilhelmy microbalance (Cahn Model DCA-322). The application of this technique was successfully used to gauge the wettability of porous material in prior work [17,18], especially of cotton yarn, to study its wettability, water transport, and water absorption [12]. The instrument was set as shown in Fig. 4. With the microbalance operating under microcomputer control, the yarn was slowly lowered to touch the water surface in the beaker and then held still for 5 min before being withdrawn to the previous position. The results during the operation were recorded in the force–position curve shown in Fig. 5 and the force–time curve shown in Fig. 6. The force–position curve began after the microbalance was zeroed for the weight of the yarn and continued as the yarn touched the water surface, absorbed water, and returned to the starting position. The residual

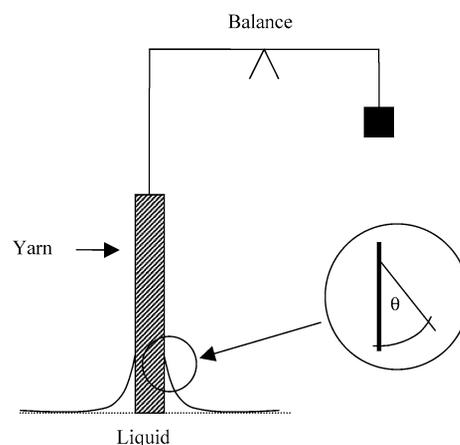


Fig. 4. Wilhelmy microbalance technique.

force after completion of the cycle shows the absorbed water inside the yarn. The force remaining is termed the “absorption force.” From the curve of force and time in Fig. 6, which measured the changing force while the yarn was held on the water surface for 5 min, it can be seen that, as soon as the yarn touches the water surface, the force jumps up due to the wetting of the yarn. This is termed the “initial force” and it is taken to indicate the wettability of the yarn [12].

2.5. Surface characterization by XPS

A small fabric was cut from the prepared sample and placed on the sample holder of an X-ray photoelectron spectrophotometer (XPS), which is a Physical Electronics PHI 5800 ESCA system with a concentric hemispherical analyzer and a monochromatic $\text{AlK}\alpha$ X-ray source (1486 eV). The C1s and O1s spectra of the cotton sample were obtained for the qualification and quantification of the polystyrene film.

3. Results and discussion

3.1. Water repellency test by the drop test

Fig. 7 shows the results of the drop test on unmodified and admicelle-modified cotton. In the case of unmodified cotton (Fig. 7a), the water droplet was found to disappear immediately, with water spreading over a wide area. In the case of admicelle-modified cotton, both with and without DVB cross-linking agent (Fig. 7b), the droplet remained spherical even after 30 min with no spreading, indicating that all modified fabrics are hydrophobic with good water repellency.

3.2. Wettability test by Wilhelmy microbalance technique

The results of this study were measured in terms of the absorption force and initial force from the force–position curve (Fig. 5) and force–time curve (Fig. 6), respectively.

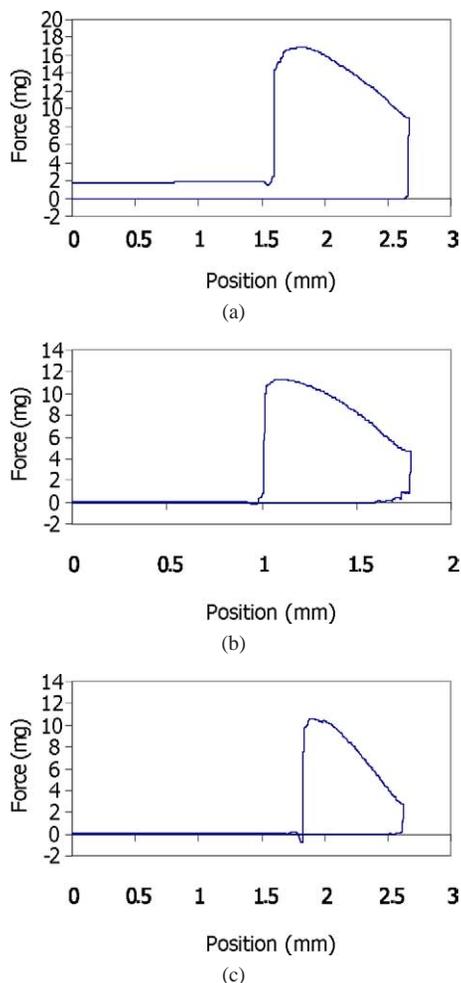


Fig. 5. The DCA curve of the force–position relation of (a) unmodified cotton, (b) admicelle-modified cotton without DVB, and (c) admicelle-modified cotton with 1% DVB.

The characteristics of both curves show clearly different behavior between unmodified and modified cotton with and without the use of DVB. The force–position curve of unmodified cotton shows high residual force or absorption force after the yarn was taken up from water surface (Fig. 5a), whereas the curves of modified cotton with and without the use of DVB show very low absorption forces at the end of the advance/pause/retraction cycle (Figs. 5b and 5c, respectively). The characteristic shape of the force–time curve reveals the change in the force while the yarn was held at the water surface for 5 min. In Fig. 6, results of the unmodified (Fig. 6a) and modified (Figs. 6b and 6c) cotton samples are compared. The force increased dramatically at the starting point and then continued to increase gradually for the unmodified cotton during the pause phase of the cycle. The force–time curves of cotton samples modified both without DVB (Fig. 6b) and with DVB (Fig. 6c) show that the force dramatically increased after the yarn touched the water surface and subsequently remained nearly constant during the pause phase. From this study, it seemed that the unmodified cotton yarn allowed water transfer *into* the yarn while the

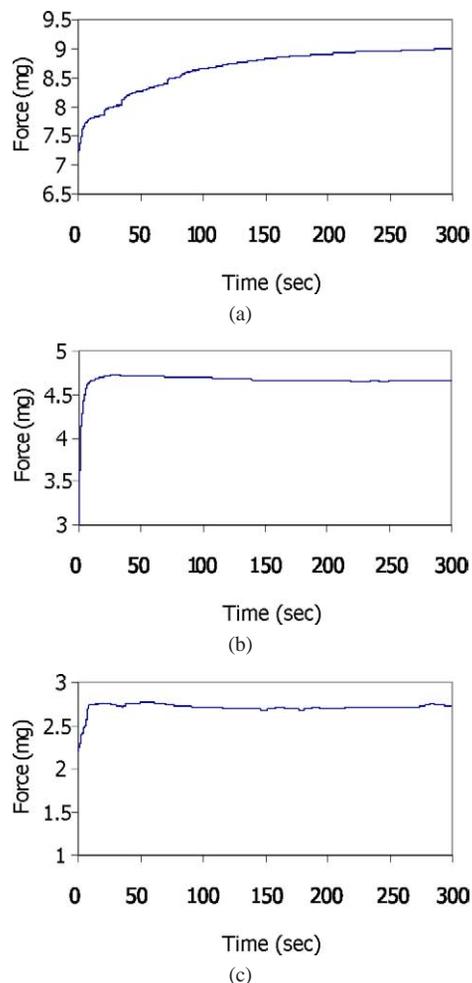


Fig. 6. The DCA curve of the force–time relation of (a) unmodified cotton, (b) admicelle-modified cotton without DVB, and (c) admicelle-modified cotton with 1% DVB.

modified cotton allowed water transfer only *onto* the yarn without absorption. A detailed analysis of similar experiments was published by Pongprayoon et al. [12].

The initial force and absorption force of unmodified and admicelle-modified cotton are compared in Figs. 8 and 9. The initial force and the force from water absorption were used to assess water repellency, from which the optimum amount of cross-linking agent was determined. As shown by the data of Fig. 8, the initial force differed significantly between unmodified and modified cotton. The initial force of unmodified cotton was 7.81 mg, while that of the modified cotton samples ranged from 2.07 to 4.20 mg, depending on the amount of cross-linking agent. Addition of 1% DVB was found to give the lowest initial force, 2.07 mg. From the absorption force in Fig. 9, it can be seen that all modified cotton absorbed very small amounts of water, less than 0.08 mg, while the yarn of unmodified cotton absorbed about 1.56 mg of water. The absorption force of modified cotton with different amounts of DVB is shown in Fig. 10. Again, the sample prepared with 1% DVB shows the lowest absorption force.

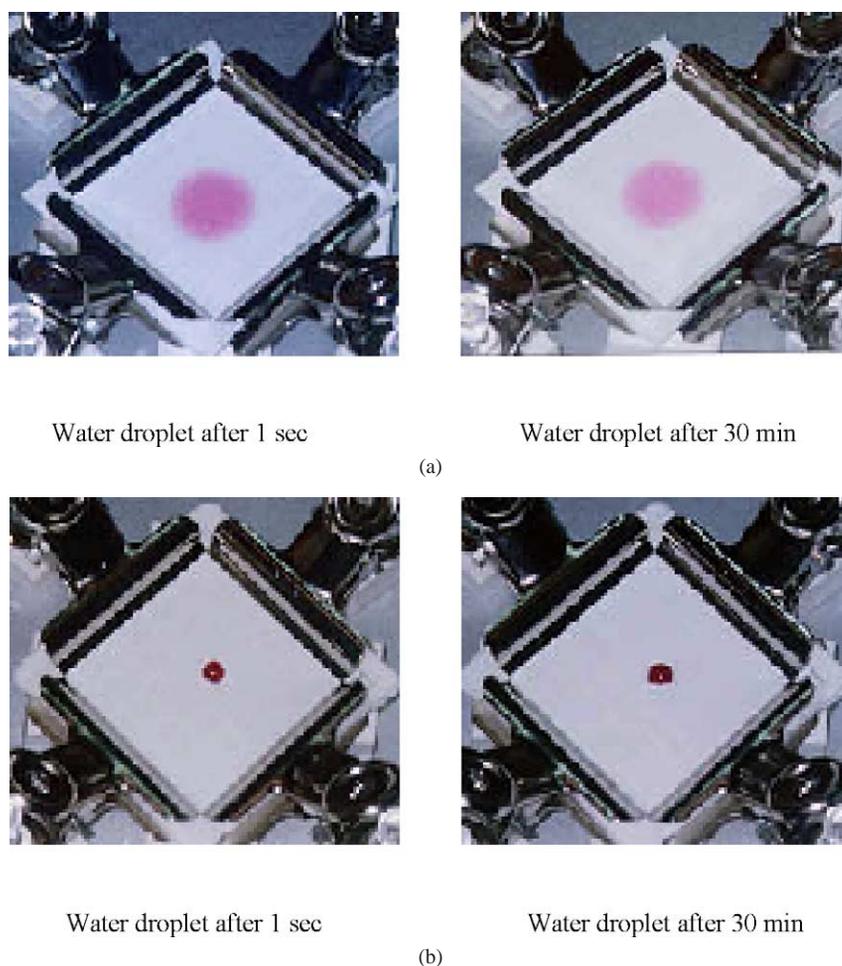


Fig. 7. Hydrophobicity by drop test: (a) unmodified cotton surface, (b) admicelle-modified cotton surface.

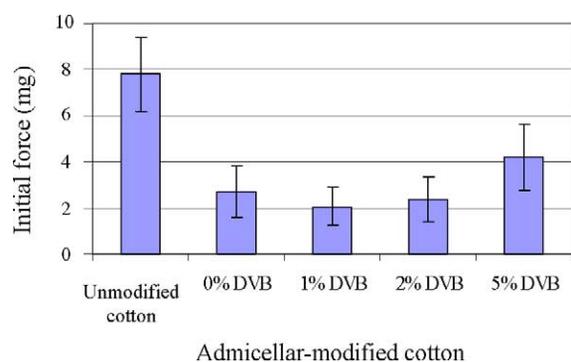


Fig. 8. Cross-linking effect on the initial force.

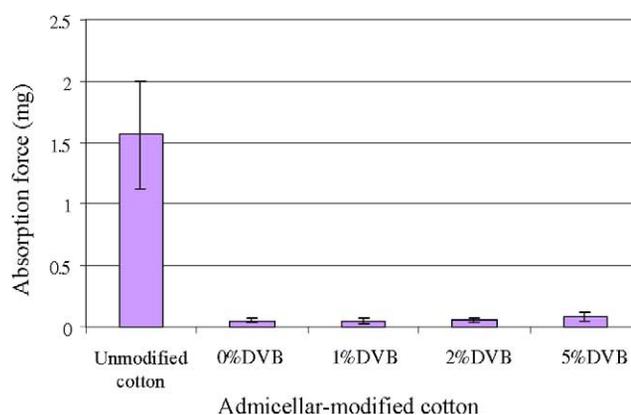


Fig. 9. Cross-linking effect on the absorption force.

Based on the concentrations studied, it appears that the optimum amount of DVB was around 1%.

3.3. Surface characterization of modified cotton by XPS

3.3.1. Qualitative analysis

XPS was used to characterize the surface of modified cotton covered with polystyrene film. The XPS peaks show the characteristic binding energy (eV) of elements. Cotton and polystyrene are hydrocarbon compounds that display

the C(1s) peak of XPS. Fig. 11a shows the C(1s) peak of polystyrene. The pristine polystyrene is fitted with two components centered at 284.5 eV, corresponding to the C–C and C–H bonds, and at 291.3 eV, corresponding to a shake-up satellite of π to π^* of the aromatic ring. The C(1s) peak of cotton is shown in Fig. 11b. It combines three peaks at 284.4 eV of C–C and C–H bonds, 286 eV of C–O bond, and 287.5 eV of O–C–O bond. The polystyrene and cotton

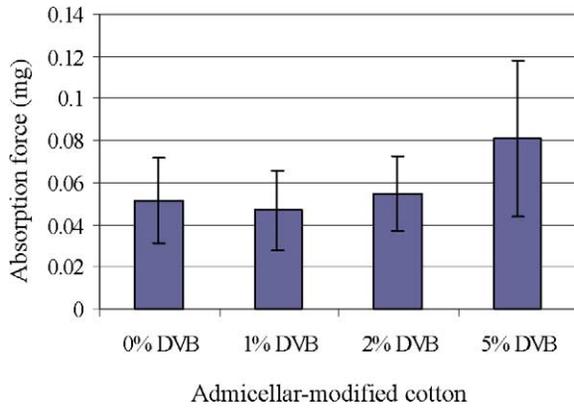


Fig. 10. The effect of varying DVB on the absorption force.

peaks are clearly different. To confirm polystyrene coating on cotton, cotton modified with varying amounts of DVB was characterized by XPS as shown in Figs. 11c–11f. C(1s) peaks of both polystyrene and cotton were present in all modified cotton samples, with the main peak occurring at 284.4 eV in each case; importantly, every sample exhibited the peak of the aromatic ring at around 291.3 eV. The results confirm that polystyrene has been successfully coated onto the surfaces of all modified cotton samples.

3.3.2. Quantitative analysis

Polystyrene film coverage on cotton was calculated from the signal of oxygen, which is one of the main elements of the cellulose molecule of cotton. The other two primary

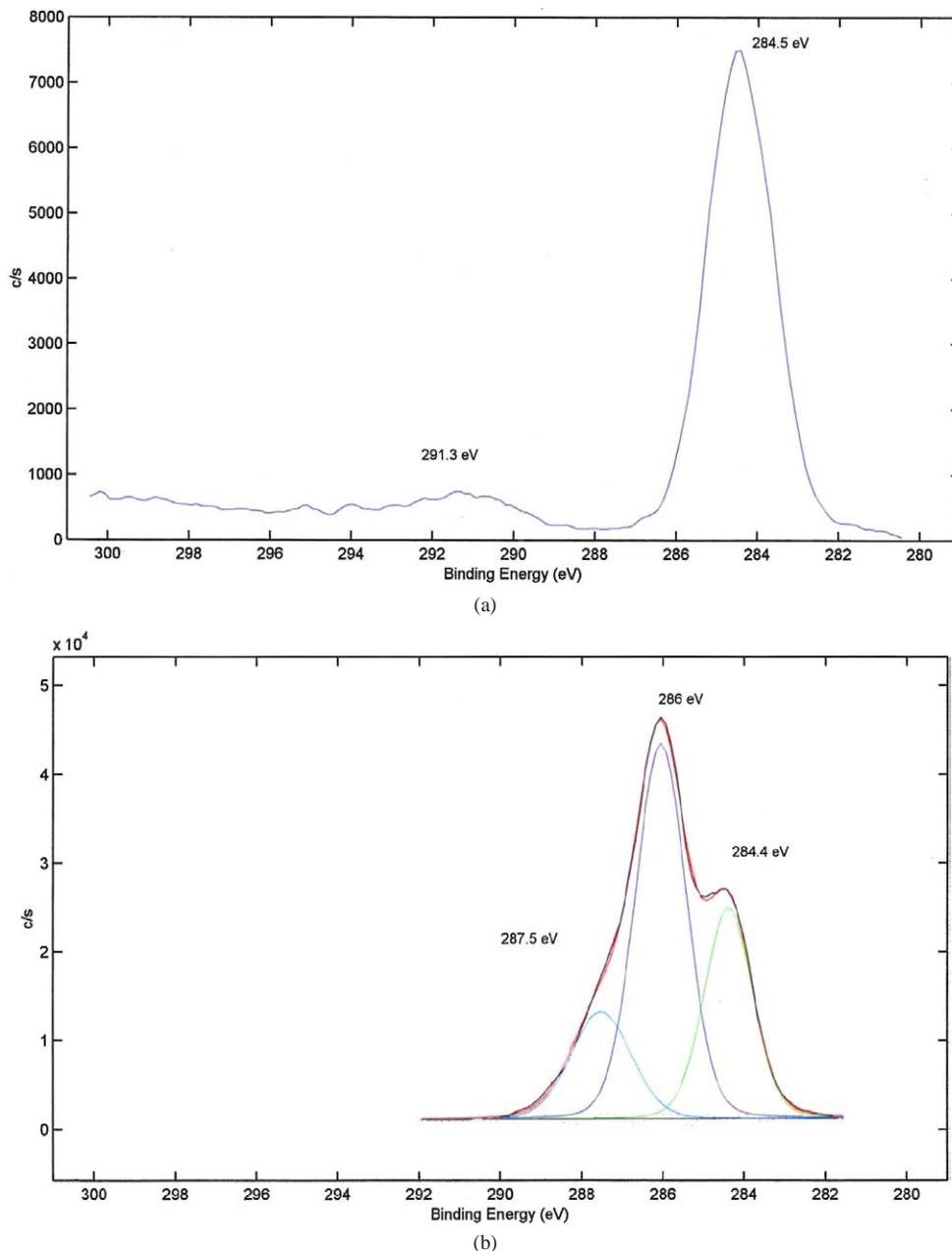
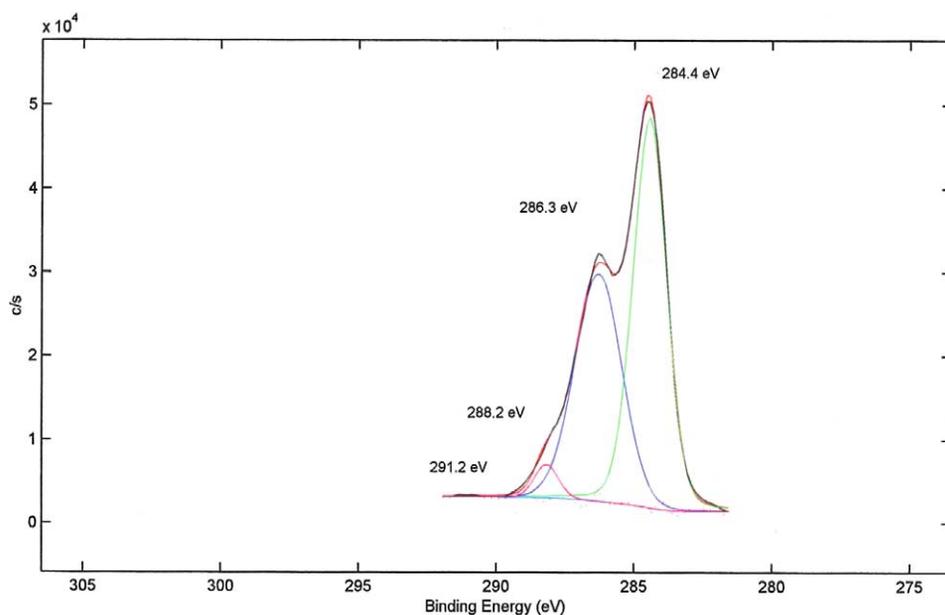
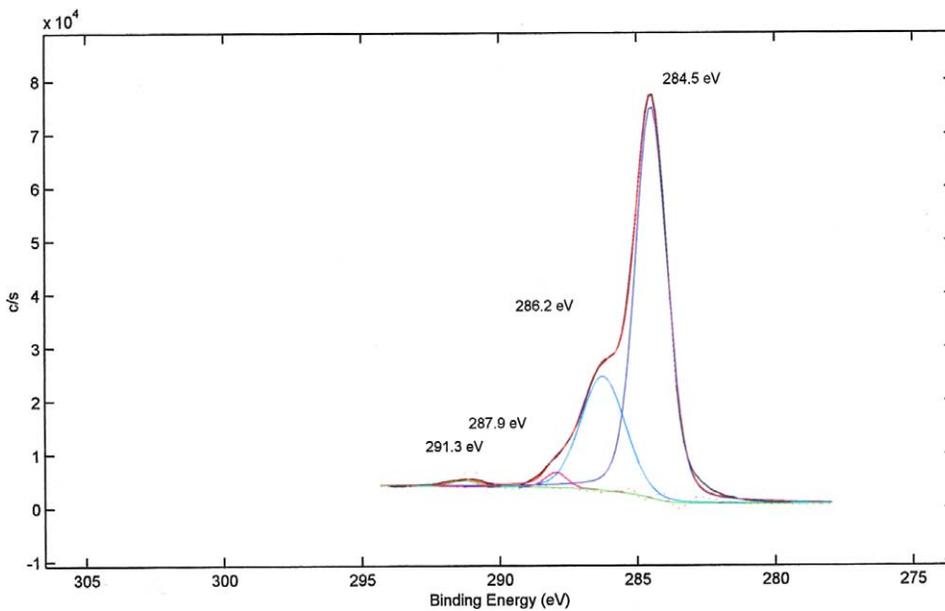


Fig. 11. C(1s) peak from XPS: (a) polystyrene, (b) unmodified cotton, (c)–(f) modified cotton using 0%, 1%, 2%, and 5% DVB, respectively.



(c)



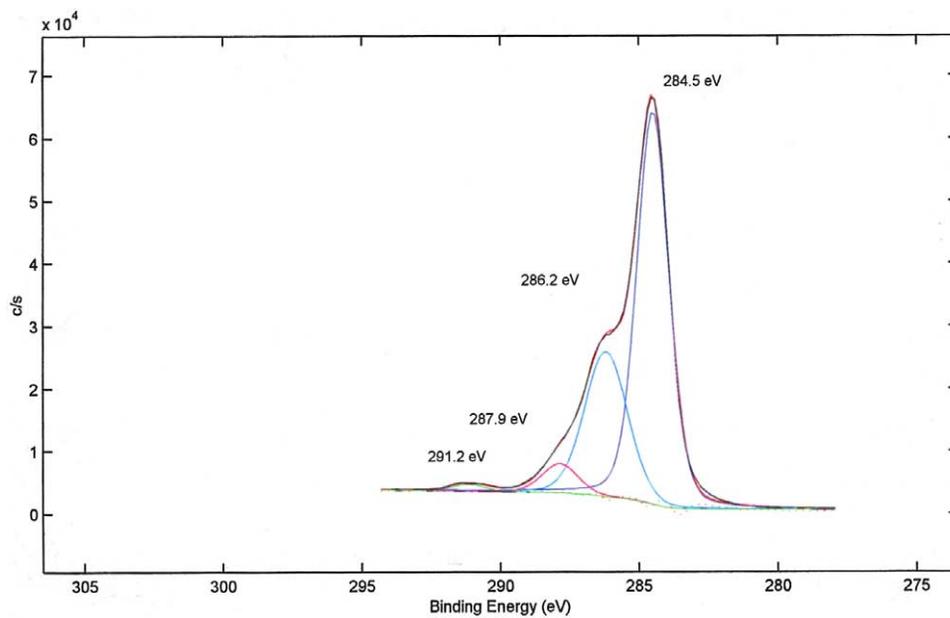
(d)

Fig. 11. (Continued.)

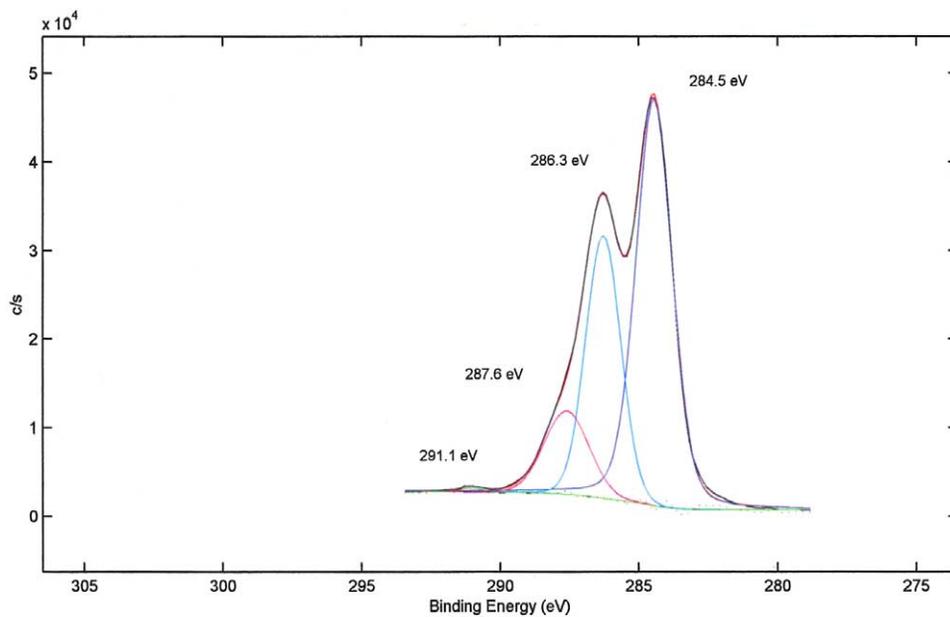
elements are carbon and hydrogen. The main elements of polystyrene are carbon and hydrogen. For this work, the signal of oxygen in cotton was used to estimate the extent of polymer coverage on modified cotton. If cotton is coated with polystyrene, the strength of the oxygen signal should be reduced. From the results in Table 1, all treated cotton fabrics had reduced oxygen signal, but to a different degree depending on the amount of cross-linking agent. While all treated cotton was found to be hydrophobic by the drop test, the extent of reduction in oxygen signal was not the same. The treated cotton with 1% and 2% cross-linking agent had a higher percent reduction in oxygen signal than that with no cross-linking agent and also higher than that with 5% cross-

linking agent. The results are consistent with the wettability tests, which show that the samples with 1–2% DVB have the lowest wettability or highest hydrophobicity. The results indicate that there is a direct correlation between the wettability of the surface and the oxygen signal obtained from XPS, as shown Fig. 12.

The thickness of polystyrene film was calculated by using the ratio of cotton and polystyrene intensity. The thickness measurement of coated film by XPS has been applied in previous works [19,20]. The results in Table 2 show that all treated cotton with DVB had thicker films than that without DVB. This is attributed to the formation of a cross-linking network on addition of DVB. The apparent film thickness of



(e)



(f)

Fig. 11. (Continued.)

Table 1
Coverage results from XPS

Sample	Oxygen signal; O(1s)	Reduction in oxygen signal (%)
Cotton	35.94	0.00
Cotton-PS-0% DVB	23.98	33.28
Cotton-PS-1% DVB	16.70	53.53
Cotton-PS-2% DVB	17.00	52.70
Cotton-PS-5% DVB	27.51	23.46

all samples was less than 1.5 nm, which is the approximate length of the hydrocarbon tail group of DBS used to form admicelles on cotton. This suggests that polymerization of

styrene and DVB took place within the very confined space of the admicelle, as shown in Fig. 13. Polystyrene apparently covers the surfaces of individual fibers that compose the cotton yarns or threads in the fabric. This high level of integration of polystyrene and cotton can explain the great reduction in water absorption. It is also consistent with the small thickness of the film, as the polystyrene is dispersed throughout the porous cotton yarn. Both wettability measurements and XPS data indicate an increase in polystyrene coverage of cellulose when 1–2% of cross-linking agent was added and a decrease in coverage at 5% addition. Thus, changes in molecular structure with cross-linking cause both improvement and degradation of water repellency. Addition

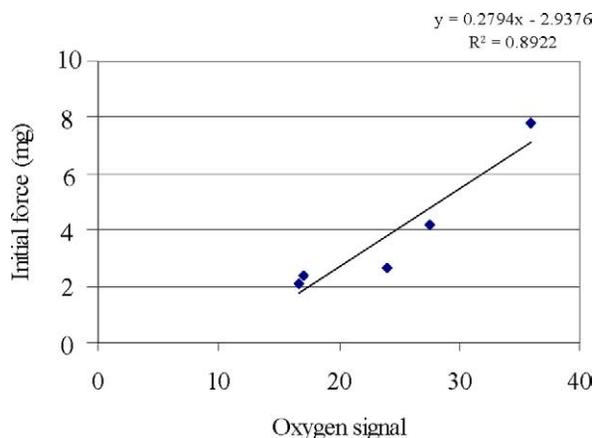


Fig. 12. Relationship between oxygen signal from XPS and initial force.

Table 2
Polystyrene film thickness analyzed from XPS

Sample	Thickness (nm)
Cotton-PS-0% DVB	0.53
Cotton-PS-1% DVB	1.23
Cotton-PS-2% DVB	1.00
Cotton-PS-5% DVB	0.81

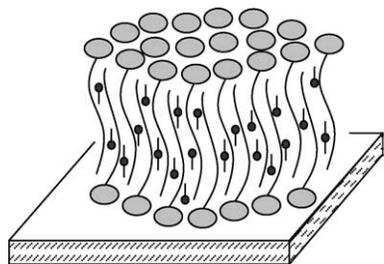


Fig. 13. Three-dimensional presentation of monomer adsolubilization in the core of the admicelle: (♠) styrene, (◊) DVB.

of DVB should increase molecular weight and tend toward a two-dimensional network structure. Attempts to confirm increased molecular weight using GPC were inconclusive. Polystyrene becomes insoluble after cross-linking, so only lower-molecular-weight species could be extracted. However, indirect evidence came from the observation that the amount of extractable sample was less with higher amounts of DVB. Wei et al. recently confirmed the problems in extracting polymer from a surface after admicellar polymerization [21].

Well-known properties can help explain the observed effects of cross-linking in this study. Molecular interactions between polar cellulose and nonpolar polystyrene should not be strongly attractive. Surfactant helps to bridge these two species as polymer is forming and then after admicellar polymerization, but it must compete with the tendency of a linear polymer to coil and attain a zero end-to-end distance.

Coiling will cause polymer to pull up from the substrate. Creation of cross-links ties polystyrene to adjacent polymer molecules in a two-dimensional network that should reduce its ability to retract from the cotton surface. The decrease in coverage at 5% DVB can be understood by the volume change associated with polymerization. Material density increases as monomer converts to polymer, an effect that is even greater with cross-linking. The combined effects of reduced retraction and contraction, with the latter dominating at 5% DVB, can explain the observed trends in polystyrene coverage.

4. Summary

The addition of cross-linking agent led to better coverage of the polymer on the fiber surface, resulting in fiber with improvement in wettability. The optimum amount of cross-linking agent was around 1%. Above this, both the coverage and wettability began to decrease.

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