CHAPTER III

ADMICELLAR POLYMERIZATION OF STYRENE ON COTTON^{*}

ABSTRACT

Thin-film coating on cotton by admicellar polymerization process was investigated. In this work, styrene was used as the monomer to coat styrene on cotton. The effects of surfactant, styrene, initiator, and electrolyte concentrations on the polymerization process were determined. The polystyrene film formed was characterized by SEM, FTIR, and GPC. The increase in the hydrophobicity of the treated cotton surface was determined by the drop test. Results show that polystyrene thin film was successfully formed on cotton resulting in cotton which can resist wetting by water droplet for longer than 30 min.

Key Words:

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

INTRODUCTION

Thin film coatings have become increasingly important in many areas including MEMS, microelectronics and composites. Several new methods have been invented and intensively studied for thin film coating on many kinds of substrate. Some of these methods, for example, chemical vapor deposition, rely on polymerization of monomer directly on the surface. This way a thin film with thickness below 1 nm can be achieved (1). However, most of these methods require special equipment, and involve working with a gas phase, which is difficult to control. More recently, a new method for thin film coating by admicellar polymerization has been invented (2). Layers of only a few nanometers in thickness

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have been reported for this method (3). The polymerization in this case is conducted in the liquid phase with no special equipment needed, while the monomer may be a gas, liquid, or solid.

Thin film coating by admicellar polymerization generally consists of 3 steps: admicelle formation, monomer adsolubilization, and polymer formation as illustrated in Fig.1.

Step 1- Admicellar formation. Adsorption of surfactants on substrates is a well-known phenomenon. For the adsorption of ionic surfactants on solid surface, the adsorption isotherm curve is typically an S-shaped graph when one plots the log of adsorbed surfactant versus the log of equilibrium concentration of surfactant (4). The S-shaped isotherm can be separated into 4 regions as shown in Fig. 2. In region I, surfactant adsorption is mainly by ion exchange and the amount of surfactant adsorption increases linearly with increase in surfactant concentration. In region II, there is a marked increase in the slope of the graph resulting from interaction of the hydrophobic chains of oncoming surfactant with those previously adsorbed to form admicelles, bilayer aggregates, on the solid surface. In region III, the slope of the isotherm is reduced because adsorption now must overcome electrostatic repulsion between the oncoming ions and the like-charged head groups of surfactants on the surface. Surfactant surface coverage can be limited either by the attainment of CMC below bilayer coverage at low surface charge densities or by the attainment of bilayer coverage below CMC at high surface charge densities (5). In either case, the adsorbed surfactants reach equilibrium in region IV where the amount of surfactant adsorption remains constant with further increase in surfactant concentration. In admicellar polymerization, the surfactant concentration is chosen to be in region III to obtain maximum admicelle formation with no micelles in the solution to avoid emulsion polymerization.

Step 2. Monomer adsolubilization. Many organic monomers are nearly insoluble in water. Thus, at equilibrium, they preferentially partition into the hydrophobic interior of the admicelle in the process called 'adsolubilization'. This process can occur either after the formation of the admicelle or concurrently with surfactant adsorption.

Step 3. Polymer formation. In this step, initiator is added to start the polymerization in the admicelle. Water-soluble initiators are generally used and the initiation reaction is started in the aqueous phase as in the case of emulsion polymerization.

After the polymerization reaction is complete, the upper layer of surfactant can be removed by washing to expose the layer of polymer on the substrate surface. Admicellar polymerization has been successfully carried out in many polymersubstrate systems. Examples are polystyrene on alumina (6) and silica (7), poly (tetrafluoroethylene) on alumina (8), and styrene-isoprene copolymer on glass fiber (9, 10). Most studies are however concentrating on highly porous inorganic materials like silica and alumina. It will therefore be interesting to see if the process also works well with a low surface area and low surface charged organic substrate.

Textiles represent an interesting class of materials that can benefit greatly from the process of admicellar polymerization. Polymer modified coated textiles constitute a very diverse range of materials with extremely wide applications (11). Textiles can be modified to enhance water-repellency, soil-resistance, and flame retardancy, to name just a few (12). Among these, modified coated cotton has by far the highest share of all the coated textiles. Cotton is a natural cellulosic fiber with 1,4-D-glucose as its repeat unit. (Fig. 3) As with most surfaces with no formal charges, the fiber acquires a negative charge when in water (13, 14). This is a consequence of the fact that cations are usually more hydrated than anions and so have a greater tendency to reside in the bulk aqueous medium, whereas the smaller, less hydrated and more polarizing anions have the greater tendency to be specifically adsorbed (15). In addition, cotton also contains a small number of carboxylic acid groups (-COOH) which ionize to yield an anionic charge in neutral solution. Bleaching, an oxidizing process, normally results in fibers with a greater number of the carboxyl groups (16). The zeta potential of bleached cotton has been reported to be -16 mV and its point of zero charge is around pH 2-3 (16, 17).

The adsorption of surfactant on the substrate surface is controlled by several parameters including the electro-chemical nature of the substrate, the type of surfactant molecule, the pH of solution, and added counterion. Charge on the substrate surface can be manipulated to be either positive or negative by adjusting the pH of the contacting aqueous solution because both hydronium and hydroxide ions are potential determining ions for substrates. The solution pH at which the surface exhibits a net surface charge of zero is called the point of zero charge or PZC. At pH values below the PZC, the surface becomes protonated and more positively charged; above the PZC, the surface is negatively charged. Consequently, anionic surfactants adsorb well below the PZC and cationic surfactants above the PZC. Cotton can therefore be expected to adsorb an anionic surfactant well at low pH and a cationic surfactant at high pH. With a relatively low concentration of ionizable groups however, this effect should not be as pronounced as substrates used previously for admicellar polymerization. Addition of an electrolyte will also help to reduce the charge on the surface which may affect the adsorption of ionic surfactants. In the case of cotton, addition of electrolyte will reduce the negative charge on the surface and the repulsion between the charges on the head groups of the oncoming ions, hence adsorption of an anionic species will be enhanced (18).

In this work, admicellar polymerization of styrene on cotton was carried out using an anionic surfactant. Application of polystyrene to cotton fabric extends the use of admicellar polymerization to porous, fibrous, organic substrates and provides an alternative approach for the surface treatment of cotton.

EXPERIMENTAL

Materials

A plain weave, medium-weight (150 g/m² superficial area), cotton fabric was purchased from Boonchauy Co. Ltd. The fabric was desized, scoured, and bleached at the factory. 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 the UV absorption of the last washing liquid.

Styrene monomer (99% purity) was provided by Eternal Plastic Co. Ltd. The inhibitor was removed by washing with 10% NaOH according to the method described by Collins, et al. (19).

Linear alkylbenzene sulfonate (LAS) (49.94% concentrated aqueous solution) was provided by Unilever Thai Holding Ltd. The carbon chain length is between 8-12 atoms and the average molecular weight is 344.

Sodium persulfate, hydrochloric acid, sodium chloride, and pinacyanol chloride were purchased from BHD Laboratory Supplies, Merck, Alex Chemicals, and Sigma Co.Ltd., respectively. Divinyl benzene was purchased from Aldrich Co.Ltd. The surfactants and all the chemicals were used as received.

Determination of the amount of LAS adsorbed on cotton

A solution of LAS of the desired concentration, pH, and salt concentration was first prepared. The pH of the solution was adjusted with HCl and NaOH solution. A 20 mL aliquot of the solution was then pipetted into a 24 mL vial containing a 1 g piece of cotton fabric. The sealed vial was then placed in a thermostat water bath at 30°C and shaken at 75 rpm for a set time. For equilibrium adsorption, the set time was 24 hrs. The adsorbed LAS on cotton was calculated by taking the difference between the initial and final concentration of LAS. The concentration of LAS in solution was determined by Cecil UV spectrophotometer model CE 2040. The wavelength of maximum absorption for aqueous solution of LAS was found at 225 nm with a molar extinction coefficient of 1.185x10⁴ Lmol⁻¹ cm⁻¹ from the calibration curve.

Determination of the adsorption isotherm

The adsorption isotherms of LAS on cotton were obtained by exposing 1 g of cotton to 20 mL LAS solution of known initial concentration. The mixture equilibrated at 30°C for 24 h in a sealed 24 mL vial. The pH of the solution was pre-adjusted and NaCl pre-added as in the above experiments. The amount of LAS in supernatant was measured by UV spectrometer at 225 nm. The initial LAS concentration in this experiment was varied from 15 - 10000 μ M which covered the regions below and above the CMC of LAS. In the case where the isotherm was

obtained in the presence of styrene, the desired amount of styrene was injected into the system using a microsyringe, the vial was then resealed and the system was again allowed to equilibrate at 30°C for 24 h. Two styrene amounts were used: 4 and 10 μ L. In this case, since styrene also absorbs UV radiation strongly, the initial and final concentration of LAS were determined by HPLC using an Econosphere C₁₈ column and a UV detector. The mobile phase consisted of 25% distilled water and 75% methanol. The flow rate of mobile phase was 7 ml/min. The retention time was 1.5 to 1.8 min. and the wavelength for UV detection was set at 225 nm.

Determination of styrene adsolubilized in the admicelle

Experiments were carried out using 20 ml of 1000 μ M LAS solution in a 24 ml vial containing 1 g of cotton fabric at pH 4 and 0.15 M NaCl at 30 °C. The amount of styrene injected was varied from 1, 2, 4 to 6 μ L. The initial and final concentrations of LAS and styrene in the mobile phase were determined by HPLC using the same procedure as described above. For styrene, the retention time was 4 to 4.5 min and the wavelength for UV detection was set at 249 nm.

Admicellar polymerization

Polymerization of styrene on cotton was carried out using 1000 μ M LAS at pH 4 with the desired amount of NaCl. LAS:styrene ratio, and initiator:styrene ratio. The initiator was sodium persulfate. At the start of the experiment, a piece of cotton fabric weighing 1 g was placed in a 24 mL vial containing 20 mL of the LAS solution. The vial was placed in a shaker bath set at 30°C for 24 h to allow the LAS adsorption to reach equilibrium. After this period, styrene monomer was injected into the vial and the adsolubilization was allowed to reach equilibrium in 48 h at 30° C. The desired amount of initiator was then injected and the temperature raised to 70°C to initiate the polymerization reaction. After 2 h, the fabric was taken out from the vial and washed with distilled water to remove the outer layer of LAS, followed by washing with ethanol to remove the unconverted styrene monomer from the

cotton surface. The fabric was given a final rinse with water and placed in an oven at 110°C until dry, before it was taken for examination.

Determination of surface area of cotton

A cotton fabric weighing 0.5 g was cut into very small pieces and degassed at 100 °C overnight. Its surface area was then determined by nitrogen absorption BET measurement on a Quanta Chrome model Autosorb-1 (20).

Hydrophobicity testing

The hydrophobicity of the fabric was determined by placing a drop of water on the cotton surface using a dropper and the time taken for the water droplet to disappear was determined. The fabric was judged hydrophobic when the time taken for the droplet to disappear was greater than 30 min.

Characterization of the coated film

GPC, FTIR, and SEM were used to characterize the polystyrene film. For GPC and FTIR, the coated film on treated cotton was extracted by boiling in THF. After evaporating off the solvent, the remaining polymer was coated on a silinide disk for analysis on FTIR (Bruker Instrument model FRA 106/s). The MW and MWD of the extracted polystyrene were also determined by GPC. SEM micrographs were taken from gold–coated fabric samples using a Jeol SEM model JSM 5200.

RESULTS AND DISCUSSION

Determination of the optimum conditions for LAS adsorption on cotton

The rate of LAS adsorption on cotton

LAS adsorbs readily on cotton at 30°C and pH 4 (Fig.4). The initial LAS

concentration used was 5 mM which is well above its CMC of around 1.2 mM (4). The adsorption was found to increase rapidly until about 10 h after which it started to slow down and became constant at 6.0 μ mole/g.cotton after 24 h. Therefore, in subsequent experiments, the adsorption step was carried out for 24 h to ensure the establishment of the equilibrium.

The effects of pH on the adsorption of LAS on cotton

The amount of LAS adsorbed on cotton rises with acidity over a pH range of 2-10 at an initial LAS concentration of 5 mM (Fig.5). The results show that the amount of LAS adsorbed on cotton decreased as the pH increased from 10.0 μ mole/g cotton at pH 2 down to 2.0 μ mole/g cotton at pH 10. The results agree well with the increase in negative zeta potential of cotton with increase in pH as found by Grancaric et al. (13).

The effect of electrolyte on the adsorption of LAS on cotton

The amount of LAS adsorption changes in the presence of different concentrations of NaCl at pH 2 and 4 (Fig.6). In this experiment, the initial concentration of LAS was 5 mM and the amount of NaCl was varied over the range of 0-0.2 M. The results show that the adsorption of LAS on cotton at both pHs increased sharply with NaCl concentration in the range 0.05-0.15 M. but the increase moderated at higher NaCl concentration. The Na counterions help to reduce the negative charges on the fiber surface and reduce the repulsion of surfactant head groups resulting in greater LAS adsorption when NaCl is added. Similar results were obtained by Wu et al. (6). In this work the amount of LAS adsorption on cotton was found to increase from around 6.0 µmole/g.cotton at pH 4 with no salt addition to around 18.0 µmole/g.cotton at pH 2 with 2.0 M NaCl. The results indicate that the surface was far from saturation in the absence of salt.

In admicellar polymerization, a high coverage of LAS in the admicelle formed on cotton surface is needed for maximum coating of the surface. Based on the above results, an acidic bath with addition of NaCl was shown to give greater adsorption of LAS on cotton.

Determination of the adsorption isotherm of LAS on cotton

Adsorption isotherm in the absence of styrene

The adsorption isotherms of LAS on cotton at pH 2 and 4 and a salt concentration of 0.15 and 2.0 M are presented in Fig.7. It can be seen that the adsorption isotherm of LAS on cotton conforms to curve shapes typical of the adsorption of an ionic species on a solid substrate. The amount of LAS adsorbed on cotton was found to initially increase sharply with an increase in LAS concentration. As the LAS concentration increased further, the slope started to decline leading eventually to a constant value. To determine if this point corresponds to the CMC of the system, the solutions around this point were tested with pinacyanol chloride. A drop of pinacyanol chloride solution was added to the surfactant solution. Pinacyanol chloride dissolving in surfactant solution below the CMC showed a red color, while above the CMC, it dissolved in the micelles and formed a blue color (21). The results show that the point at which the slope became constant in each case indeed corresponded to the CMC of the system. This agrees with the suggestion that, for low surface charge substrate, the amount of bilayer coverage on the surface is limited by the attainment of CMC (4).

Table 1 summarizes the CMCs of the various systems and the amount of LAS adsorbed on cotton at the CMC. Increasing the amount of salt led to a decrease in the CMC, as expected, due to reduction in the repulsion of the head groups on the surfactants (4). Despite this, the LAS adsorption was found to increase with the amount of salt at both levels of acidity. Increase in pH led to an increase in the CMC, but in this case, the amount of LAS adsorbed on cotton was much reduced. The results clearly show that the surface charge and the presence of salt have much greater effects on LAS adsorption than does the position of the CMC.

Adsorption isotherm in the presence of styrene

Addition of an organic monomer such as styrene into a surfactant solution has been known to enhance the adsorption of surfactant on the substrate (6). In the present work, the adsorption isotherm of LAS on cotton in the presence of 4 and 10 μ L of styrene at pH 4 and with 0.15 NaCl was studied. The amount of styrene used was in excess of the solubility of styrene in solution which has been quoted as 0.07 g/L at 25 °C (22). The results in Fig. 8 show that the adsorption of LAS increased in the presence of styrene while the CMC of the system did not change much from the value of 1050 μ M in the absence of styrene. The results show that the presence of styrene enhanced LAS adsorption on the substrate as shown by previous workers (6).

Area occupied by LAS molecules on the cotton surface

From the above results, the maximum amount of LAS adsorption on cotton was found to increase from around 13 μ mol/g cotton in the absence of styrene to as high as 25 μ mol/g cotton in the presence of 10 μ L of styrene at an equilibrium LAS concentration of 3500 μ M, which was well above the CMC of the system. At this point, it seems reasonable to assume that the cotton surface is near saturation. Thus, knowing the accessible surface area of cotton, the surface area occupied by an LAS molecule on the cotton surface can be calculated. The surface area of cotton as determined from BET with nitrogen was found to be 4 m²/g. By assuming that LAS formed a bilayer on cotton, the area occupied by an LAS molecule was found to be 60 A², which is in good agreement with the area occupied by LAS on a liquid/air interface, which has been quoted as between 46-59 A² in the presence of salt (4). The present results therefore show that we can get close to surface saturation in LAS adsorption in the presence of an added hydrophobic adsolubilized species.

Adsolubilization of styrene in the admicelle at constant initial LAS concentration

To study the adsolubilization of styrene in the admicelle, the amount of styrene adsolubilized was determined in the presence of an LAS concentration of around 1100 μ M which is below the CMC of LAS in solution. The initial amount of styrene was varied from 1, 2, 4 to 6 μ L which covered the range below and above the solubility limit of styrene. The partition coefficient of styrene was calculated according to the following equation.

K = (Amount of adsolubilized styrene per adsorbed surfactant molecule)/ (Concentration of styrene in the supernatant)

The results in Table 2 show that the equilibrium LAS concentration decreased from 719 μ M to 479 μ M while the amount of LAS adsorbed on cotton increased from 9.81 to 13.10 μ mol/g cotton as the amount of styrene in the system increased. The K value decreased from 1220 to 268 M⁻¹ as the amount of styrene increased and the LAS:styrene ratio in the admicelle decreased to 2:1. Both the K value and LAS:styrene ratio obtained in this work are in good agreement with those obtained by other workers for another type of substrate (6). The results therefore show that admicelle formation and adsolubilization can be affected in very much the same way on a low surface area, low charged surface as they are in highly charged, high surface area substrates.

Property of the admicellar-treated cotton

Admicellar polymerization of styrene on cotton was carried out using an LAS concentration of 1000 μ M, which is just below the CMC of 1050 μ M at a pH of 4, and NaCl concentration of 0.15 M. Sodium persulfate was used as the initiator and the polymerization time was 2 hours at 70 °C. The hydrophobicity results of both untreated and admicellar-treated cotton were compared by using the drop test. The water droplet on untreated cotton was found to spread over a wide area and disappear immediately, whereas on admicellar-treated cotton, it formed a near spherical droplet which stayed on the fabric surface for more than 30 min. Thus, it can be seen that admicellar-treated cotton shows a marked improvement in water repellency indicating that the cotton surface has been modified.

Identification of the coated film by FTIR

To confirm that polystyrene has been successfully coated on cotton by admicellar polymerization, FTIR spectrum of the extract from treated cotton was taken and compared to that of standard polystyrene and the extract from the untreated sample. From Figure 9, it can be seen that the extract from admicellar-treated sample shows distinctive characteristic peaks of polystyrene at 1455, 1490 and 1600 cm⁻¹. These peaks are absent from the extract 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.

MW of admicellar polymerized styrene on cotton

The MW of styrene extracted from the cotton surface was determined by GPC using tetrahydrofuran as the solvent and the result was compared to that obtained by emulsion polymerization under the same conditions using LAS:styrene and styrene:initiator ratios of 1:10 and 1:1, respectively. The results in Table 3 show that both processes yielded similar MW in the range 200,000 although the polymer from admicellar polymerization also had some molecules with lower MW as can be seen from the chromatograms in Fig. 10. The results indicate a close similarity between admicellar polymerization and emulsion polymerization. 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 in the conditions used for polymerization was far from the conditions needed for surface saturation.

Characterization of the fabric surface by SEM

Fig. 11 shows SEM micrographs of untreated and admicellar-treated cotton surface. 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.

The effect of varying the amount of styrene

The effect of varying the amount of total styrene on the wetting time of fabric and MW of resulting polystyrene is shown in Table 4. The LAS concentration was fixed at 1000 μ M while LAS:styrene ratio was varied from 1:3, 1:4, 1:5, 1:6, to 1:7. The results show that the fabric started to become hydrophobic at an LAS:styrene ratio of 1:5. The MW increased slightly as the LAS:styrene ratio increased. However, at the LAS:styrene ratios of 1:6 and 1:7, a second peak in the chromagram was detected which represented a much higher MW polystyrene of well over 200,000. The results show that excess amount of styrene led to high MW polystyrene. It is also possible that some suspension polymerization may have occurred. The polydispersity was low at below 2 in most cases.

The effect of varying amount of initiator

In this experiment, the LAS concentration was fixed at 1000 μ M, LAS:styrene ratio was fixed at 1:4 and 1:5 while the styrene:initiator ratio was varied from 1:0.2, 1:0.5, to 1:1. The results in Table 5 show that, as the amount of initiator increased, the MW of the resulting polystyrene decreased while the time for the droplet to disappear increased. The results show that hydrophobicity of the fabric does not depend on the MW of the polymer coated but depends rather on its amount. In the system using more initiator, more polystyrene was formed leading to higher hydrophobicity.

SUMMARY

This study has shown that admicellar polymerization of styrene can be conducted on cotton fabric. The treated fabric was shown to have a much higher water repellency than the untreated cotton. Hydrophobicity of the treated cotton was found to depend on the LAS:monomer and monomer:initiator ratios.

REFERENCES

- Wahl, G., in "Ullmann's Encyclopedia of Industrial Chemistry", Vol. A26, (B. Elvers and S. Hawkins, Eds.), 681, (1995).
- 2. Harwell, J. H., and O'Rear, E. A., U.S. Patent 4,770,906 (1988).
- 3. Yuan, W. L., Ph.D. Dissertation, University of Oklahoma, 2001.
- Rosen, M. J., "Surfactants and Interfacial Phenomena", 2nd Ed., John Wiley and Sons, New York, (1989).
- Scamehorn, J.F., Schechter, R.S., and Wade, W.H., J. Colloid Interface Sci., 85, 463 (1982).
- 6. Wu, J., Harwell, J. H., and O'Rear, E. A., Langmuir, 3, 531 (1987).
- O'Haver, J., Harwell, J.H., O'Rear, E.A., Snodgrass, L. J., and Waddell, W.H., Langmuir, 10, 2588 (1994).
- 8. Lai, C., Harwell, J. H., and O'Rear, E. A., Langmuir, 11, 905 (1995).
- Glady, B. P., O'Rear, E. A., Penn, L. S., and Pedicini, A., *Polymer Composites*, 19, 579-578 (1998).
- 10. Sakhalkar, S.S. and Hirt, D.E., Langmuir, 11, 3369, (1995).
- Wypych, J., "Polymer Modified Textile Materials", John Wiley&Sons, Inc., New York, (1988).
- Lewin, M. and Sello, S.B.(Eds), "Handbook of Fiber Science and Technology (II): Chemical Processing of Fibers and Fabrics-Functional Finishes", Marcel Dekker, Inc., New York and Basel, (1984)
- 13. Grancaric, A. M., Pusic, T., and Soljacic, I., Text. Chem. Color., 29, 33 (1997).
- 14. Aspland, J.R., Text. Chem. Col., 23, 14 (1991)
- Shaw, D. J., "Introduction to Colloid and Surface Chemistry", 4th Ed.,Butterworth-Heineman, Oxford, (1992).
- Stana-Kleinschek, K., Strand, S., and Ribitsch, V., *Polym. Eng. Sci.*, **39**, 1412, (1999).
- 17. Herrington, T.M. and Midmore, B.R., J. Chem. Soc., Faraday Trans, 1, 80, 1525 (1984)

- Iyer, S. R., and Baddi, N. T., Contribution to the Chemistry of Synthetic Dyes and Mechanism of Dyeing, Symposium Proceedings, University of Bombay (1968).
- Collins, E. A., Bares, J., and Billmeyer Jr., F. W., "Experiments in Polymer Science", Jonh Wiley & Sons, New York, 337 (1973).
- Rouquerol, J. and Sing, R., "Adsorption by Powder and Porous Solids: Principles, Methodology and Applications", Academic Press, London, 166 (1999).
- 21. Nunn, C. C., Schechter, R. S., and Wade, W. H., J. Phys. Chem., 86, 3271 (1982).
- 22. Odian, G., "Principles of Polymerization", 3rd Ed., John Wiley & Sons, Inc., New York, (1991).

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Condition		СМС	Adsorbed LAS		
рН	[NaCl], M	(µM)	(µmoles/g. cotton)		
2	0.15	950	14.5		
2	0.20	720	16.0		
4	0.15	1050	10.5		
4	0.20	900	14.0		

Table 1. The CMC of LAS solution in the presence of cotton at different conditions

Table 2. Adsolubilization of styrene-LAS-cotton system

Cotton	[LAS]ini	[LAS]fi	LAS	Vstr	[str]ini	[str]fi	Styrene	K	LAS/str
			adsorption				adsolubilization		
(g)	(µM)	(µM)	(µmole/g cotton)	(µL)	(µM)	(µM)	(µmole/g cotton)	(M ⁻¹)	
0.9847	1200	719	9.8	1	377	238	2.82	1220	3.46
0.9831	1120	605	10.5	2	881	642	4.87	725	2.15
0.9937	1050	540	10.3	4	1760	1480	5.62	374	2.01
0.9984	1130	479	13.1	6	2320	1980	6.92	268	1.90

Table 3. MW of polystyrene from emulsion and admicellar polymerization

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

Sample	LAS:styrene	Time for water	Mn	Mw	PD
		droplet to disappear	1		
1	1:3	5 sec	4,392	4,938	1.12
2	1:4	12 min	4,614	5,354	1.16
3	1:5	>30 min	4,958	5,930	1.20
4	1:6	>30 min	4,996	5,988	1.20
			124,489	298,639	2.40
5	1:7	>30 min	5,085	6,129	1.21
			129,627	257,281	1.99

<u>Table 4.</u> Effect of LAS:styrene ratio on hydrophobicity and MW, for a ratio of styrene:initiator = 1:1

Table 5. Effect of styrene:initiator ratio on hydrophobicity and MW

Sample	LAS:styrene	Styrene:initiator	Time for water droplet to disappear	Mn	Mw	PD
1	1:4	1:0.2	12 sec	8,519	11,515	1.35
2	1:4	1:0.5	78 sec	5,022	6,131	1.22
3	1:4	1:1	12 min	4,614	5,354	1.16
4	1:5	1:0.2	8 min	10,893	16,615	1.53
5	1:5	1:0.5	30 min	6,488	8,392	1.29
6	1:5	1:1	> 30 min	5,631	6,594	1.17

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1) Admicelle Formation



2). Monomer Adsolubilization



Figure 1. The admicellar polymerization process.



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Figure 2. Typical adsorption isotherm of surfactants on solid surface



Figure 3. Molecular structure of cellulose



Figure 4. Rate of adsorption of LAS on cotton (Temp = $30 \text{ }^{\circ}\text{C}$, [LAS] = 5 mM)



Figure 5. Effect of pH on adsorbed LAS on cotton (Temp = 30 °C, time = 24 h, [LAS] = 5 mM)



Figure 6. Effect of electrolyte on the amount of LAS adsorption on cotton (Temp = 30 $^{\circ}$ C, time = 24 h, [LAS] = 5 mM)



Figure 7. Adsorption isotherms of LAS on cotton (Temp = 30 °C, time = 24 h.)



Figure 8. The adsorption isotherms of LAS on cotton in the systems with and without styrene (Temp = 30 °C, time = 24 h, pH = 4, [NaCl] = 0.15 M)



Figure 9. FTIR spectra of polystyrene, treated and untreated cotton



Figure 10. GPC chromatograms of polystyrene from emulsion and admicellar polymerization



(a)



(b)

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