

Improvement in the Flame Retardancy of Cotton Fabric by Admicellar Polymerization of 2-Acryloyloxyethyl Diethyl Phosphate Using an Anionic Surfactant

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ABSTRACT: The phosphorus-containing acrylate monomer, 2-acryloyloxyethyl diethyl phosphate (ADEP), was synthesized and applied to cotton fabric by using admicellar polymerization. Sodium dodecylbenzene sulfonate was used as the anionic surfactant. The film of polymerized monomer (PADEP) formed on the cotton surface was characterized by FTIR-ATR spectroscopy and SEM. Thermal and flame retardant properties of PADEP-coated cotton were investigated by TGA and flammability tests. Results showed that PADEP polymer film was successfully formed on the cotton fabric. The TGA and DTG analyses showed that the phosphorus-containing PADEP lowered

the decomposition temperature of the treated fabric resulting in a higher char yield than in the case of untreated cotton. The flammability tests showed that the treated cotton had much improved flame retardancy property after the treatment. The treated fabric also retained its good pliability and soft touch with good air permeability. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3859–3866, 2008

Key words: cotton fabric; admicellar polymerization; anionic surfactant; phosphorus-based flame retardant; phosphorus-containing monomer; flame-retardant cotton fabric

INTRODUCTION

Cotton is known to be the most common fiber used in many applications such as clothing, upholstery, bedding, and curtains. However, it is also a highly combustible fiber. Flame retardant finishing of cotton fabrics and garments becomes necessary to improve human safety under many circumstances.¹ Many flame retarding agents are halogen-based, which are harmful to the environment and also toxic in nature because these halogen compounds impart flame retardancy by a vapor phase mechanism of free radical scavenging with toxic gases being evolved in the process.² In an attempt to avoid generation of the toxic and corrosive halogenated gases, the trend is toward halogen-free, phosphorus-based compounds as the flame retarding agents for cotton.^{3–5} Phosphorus-based compounds act as flame retarding agents in a condensed phase by increasing char formation; hence there is hardly any chance for evolution of toxic gases during combustion.⁶

Many techniques have been developed for imparting flame retardant properties to cotton fabrics including pad-dry-cure,⁷ chemical modification,⁸ ionized radiation graft polymerization,⁹ and plasma induced graft polymerization.¹⁰ However, there are some disadvantages to these methods due to their deleterious effects on bulk properties of the fiber such as lower tensile strength and moisture regain, and fabric stiffness. Formation of an ultrathin phosphorus-containing polymer film on the fiber surface with the use of a suitable surfactant can overcome these limitations. However, the uses of surfactant-based methods, like admicellar polymerization, to improve the flame retardant properties of cotton fabric, have not been examined in the literatures.

Admicellar polymerization is a method that can be used to form an ultrathin polymer film on a substrate surface.¹¹ There are three basic steps to admicellar polymerization as shown in Figure 1: admicelle formation, adsolubilization of the monomer into the admicelle, and admicellar polymerization to form a thin polymer film on the substrate surface. After the polymerization is complete, an additional step, step four, is used to remove the outer-layer surfactant by washing with water, to leave the polymer film exposed on the substrate surface.

Admicellar polymerization has been successfully used to coat thin polymer films on various kinds of

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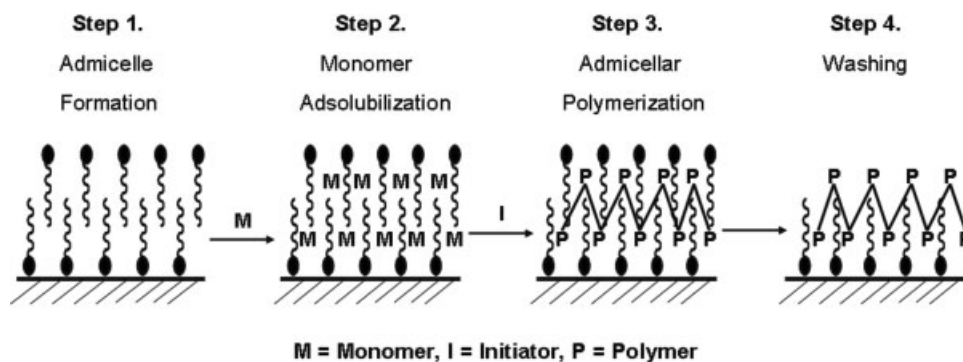


Figure 1 Schematic of the steps in admicellar polymerization.

substrates for several purposes. Examples are polystyrene on cotton,¹² poly(methyl methacrylate) and polystyrene on aluminum,¹³ poly(tetrafluoroethylene) on alumina,¹⁴ poly(methyl methacrylate) on cellulosic fibers¹⁵ and polyester fabric,¹⁶ and polystyrene on glass fibers.¹⁷ In this research work, a phosphorus-containing acrylic monomer was coated onto cotton surface by admicellar polymerization using an anionic surfactant. The thermal and flame retardancy properties of the coated cotton were then studied.

EXPERIMENTAL

Materials

2-Hydroxyethyl acrylate (HEA) (97%) and triethylamine (TEA) (99%) were purchased from Fluka. Dodecylbenzenesulfonic acid (DBSA), sodium salt, 2, 2'-azobisisobutyronitrile (AIBN) (97%), and cuprous chloride (CuCl) (97%) were purchased from Aldrich. Absolute ethyl alcohol was purchased from Mallinckrodt. Hydrochloric acid (37%), sulfuric acid (96%), diethyl ether, and sodium chloride were purchased from Carlo Erba Reagenti. Hydrogen peroxide (H₂O₂) (30%) was purchased from Ajax Finechem. Diethyl chlorophosphate (97%) was purchased from Fisher Scientific. All chemicals were used as received.

Plain weave bleached cotton fabric (285 g/m²) was washed several times in a washing machine at 95°C until it was free from any remaining surfactant prior to use.

Synthesis and characterization of the 2-acryloyloxyethyl diethyl phosphate (ADEP)

To 7.1 g (0.06 mol) HEA, dissolved in 75 mL diethyl ether, was added 9 mL TEA together with 0.1 g of CuCl. The system was cooled to 0°C while magnetically agitated. Equimolar diethyl chlorophosphate (9 mL) was added slowly over a period of 1 h. The system was then allowed to attain room temperature and stirred overnight. Precipitated triethylamine hydrochloride was filtered and washed with diethyl ether to remove any remaining product. The filtrate was then washed with ice cold water in a separatory funnel and dried over MgSO₄. Finally, the ether was evaporated off under vacuum to leave a pale yellow viscous oil with 65% yield.¹⁸

The synthesis reaction is shown in Figure 2. The chemical structure of the product was confirmed by the following ¹H-NMR and FTIR analyses:

¹H-NMR (DMSO): 1.1 (CH₃, 6H, t), 3.9 (CH₂, 4H, q), 4.1 (CH₂, 2H, t), 4.3 (CH₂, 2H, t), 5.9 (=CH, 1H, dd, α-carbonyl), 6.1 (=CH, 1H, d, trans to carbonyl), 6.3 (=CH, 1H, d, cis to carbonyl) ppm.

FTIR: 2986-2911 (CH₃), 1728 (C=O), 1636 (C=C), 1448-1370 (CH₃), 1270 (P=O), 1173 (P—O—C₂H₅), 1030-980 (P—O—C) cm⁻¹.

Determination of the adsorption isotherm

The adsorption isotherm of DBSA with 0.15M NaCl at pH 4 on cotton fabric was obtained by exposing a 1.2-g piece of the cotton fabric to 30 mL of the surfactant solution of known initial concentration. The adsorption was allowed to take place at 30°C for

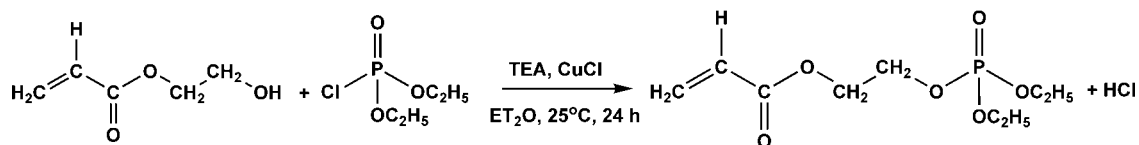


Figure 2 Synthesis of 2-acryloyloxyethyl diethyl phosphate.

15 h in a 36-mL vial. The amounts of DBSA in the supernatant were measured by a UV spectrophotometer (Shimadzu Model UV 2550) at 224 nm. The initial DBSA concentrations in these experiments were varied from 10 to 10,000 μM which covered the regions below and above the critical micelle concentration (CMC) of DBSA. A plot of the amount of adsorbed surfactant versus equilibrium supernatant concentration yielded the surfactant adsorption isotherm.

Admicellar polymerization process

A piece of $6.5 \times 6.5 \text{ cm}^2$ cotton fabric weighing 1.2 g was placed in a 36-mL vial containing a 35 mL solution of 0.6 mM of DBSA, 0.15M NaCl, ADEP monomer at the concentrations of 6.2, 12.4, 18.6, 24.8, and 31 mM, and the initiator, AIBN, to give a 1 : 5 initiator : monomer molar ratio. The vial was then wrapped with aluminum foil and the lid was screwed on and sealed with paraffin film. All vials were placed into a shaker bath set at 30°C for 15 h to allow the surfactant adsorption and monomer adsolubilization in the admicelle to reach equilibrium, then the temperature was raised to 75°C to initiate the polymerization reaction for 24 h. After polymerization, the vial was cooled down and the fabric was removed from the vial and washed in water three times at 80°C for 30 min to remove the outer-layer surfactant. Finally, the fabrics were dried in an oven overnight at 65°C.

Determination of the phosphorus content on PADEP-coated cotton

Treated fabric samples taken from different parts of fabric specimens were cut into small pieces. Concentrated H_2SO_4 (2 mL) was added to 0.1 g of the sample in a bottle. Then 10 mL of 30% H_2O_2 was added dropwise to the mixture which was stirred by a magnetic stirrer on a hot plate, allowing the reaction to subside between drops. The mixture was then stirred and heated on the hot plate for 1 h. After that, the completely digested sample as a clear viscous solution was transferred to a 50 mL volumetric flask, and then carefully diluted with distilled water. The sample thus prepared was analyzed with a Perkin–Elmer Model PLASMA-1000 inductively coupled plasma/atomic emission spectrometer (ICP/AES) to determine the percent concentration of phosphorus.⁸ As emission spectroscopy can be susceptible to interfering species, validity of the technique was evaluated by preparing control samples with a known amount of phosphorus added to the untreated fabric and its phosphorus content was checked by the method above.

Surface characterization of the modified cotton

FTIR-ATR and SEM were used to characterize the surface of untreated and the PADEP-coated cotton. The polymer film coated on the treated cotton was analyzed on an FTIR-ATR spectrometer (Nicolet model Nexus 670). The surface of the untreated and treated cotton was examined by SEM using a Jeol SEM model JSM 5200-2AE.

Thermal analysis

The thermal properties of untreated and PADEP-coated cotton using 31 mM ADEP were investigated by using a TGA analyzer. The TGA apparatus was a Perkin–Elmer Model TGA 2550 operating under N_2 atmosphere with platinum pan containing 25–30 mg of cotton. The runs were carried out at a temperature ranging from 30 to 600°C at a heating rate of 10°C/min under a continuous N_2 flow of 100 mL/min.

Flammability tests

Burning behaviors of untreated and PADEP-coated cotton fabrics were studied using the Atlas 45° Automatic Flammability Tester according to ASTM D1230.¹⁹ In this study, the ignition time was set at 10 s. The experiments were carried out at the ambient temperature of 30°C and 65% RH. The burning behavior of the fabric was recorded by a digital video camera.

Measurement of air permeability

Air Permeability of untreated and PADEP-coated cotton fabric was studied using the Frazil Type Auto Air Permeability Tester Model AP-360D according to ASTM D737 : 1996.²⁰ The sample test area was 6.9 cm^2 and the air flow rate was automatically adjusted to provide a pressure differential of at least 125 Pa across the fabric sample. The results of the fabric were expressed in volume of air permeability per second per fabric area ($\text{cm}^3/\text{s}/\text{cm}^2$). The reported result was the average from measurements on four samples.

Measurement of fabric stiffness

Stiffness of untreated and PADEP-coated cotton fabric was studied using the 45° Cantilever Type Tester according to the Testing Methods for Fabric JIS L 1096:1999.²¹ The equipment consists of a horizontal table with a ruler scale on one side and having 45° slope at one end. The fabric sample, measured 2 cm \times 15 cm, was placed on the table parallel to the scale. It was then slid slowly towards the slope until the end of the fabric extruding from the horizontal table

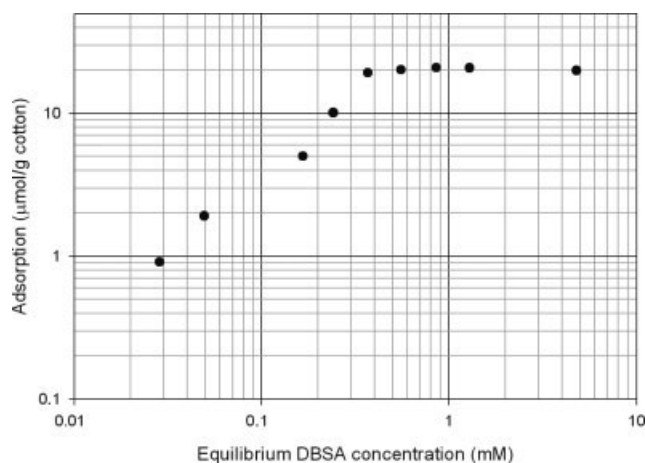


Figure 3 Adsorption isotherm of DBSA on cotton fabric at pH 4, 0.15M NaCl, (Temp = 30°C, time = 15 h).

naturally comes in contact with slope A. The degree of stiffness is indicated by the moving distance of the specimen which was read from the ruler scale. The greater the moving distance, the greater the fabric stiffness was. The reported result was the average obtained from three specimens.

RESULTS AND DISCUSSION

Determination of the adsorption isotherm of DBSA on cotton fabric

The adsorption isotherm of DBSA on cotton with 0.15M NaCl, pH 4, at 30°C is shown in Figure 3. The amount of surfactant adsorption reached a constant value at around 0.6 mM of equilibrium surfactant concentration. This can be compared with the reference value for the CMC of DBSA of 1.2 mM.²² The reduction in the CMC of DBSA is due to the presence of electrolyte in the surfactant solution which decreases electrical repulsion between the surfactant head groups in the micelles. The maximum amount of DBSA adsorption on the cotton fabric was 20 μmol/g cotton. In admicellar polymerization, the concentration of surfactant should be just below or near its CMC to ensure significant coverage while avoiding emulsion polymerization. From the adsorption isotherm, a concentration of 0.6 mM DBSA which is near the CMC was chosen for the admicellar polymerization reaction.

Relationship between monomer concentration and phosphorus content on the treated fabric

In this work, the amount of polymer coated on the treated fabric was determined by its phosphorus content. The results in Figure 4 show that phosphorus content of the treated fabric increased linearly

from 0 to 1.19 mg/g cotton with increase in the monomer concentration in the range 0–31 mM. The amount of monomer adsorbed generally increases with the supernatant concentration by mass action.¹⁴ Therefore, the higher the initial ADEP concentration in the solution the greater the amount of ADEP monomer at the solid-solution interface. As the polymerization reaction proceeds, more monomer can partition into the admicelle and react to form additional polymer leading to an increase in the amount of PADEP coated film on cotton surface.

Surface characterization of the PADEP-coated cotton fabrics

FTIR-ATR spectra

FTIR-ATR spectra of PADEP, untreated and PADEP-coated cotton are shown in Figure 5. We observed in the spectrum of PADEP-coated cotton the presence of a new absorption band at around 1733 cm⁻¹ attributed to the carbonyl (C=O) bond of PADEP. An absorption band in the range of 2989–2911 cm⁻¹ comes from CH₃ asymmetric and CH₂ symmetric stretching of PADEP. It is not easy to identify the P=O and P–O–C vibrations of the PADEP-coated cotton since the absorption bands of the P=O (at 1265 cm⁻¹) and P–O–C (at 1167, 1034 cm⁻¹) appear in the same region as the primary and secondary OH deformation observed in the untreated cotton (at 1367, 1162, and 1057 cm⁻¹). It can be seen that the –OH stretching vibration at around 3430 cm⁻¹ present on untreated cotton is still visible in the treated fabrics; this indicates an ultrathin film coating on the cotton fiber surface by the admicellar polymerization process. The very weak peaks at 1733 cm⁻¹ and 2989–2911 cm⁻¹ exhibited by the treated surface also supported the above observation. Thus, FTIR-ATR spectra indicate that there is

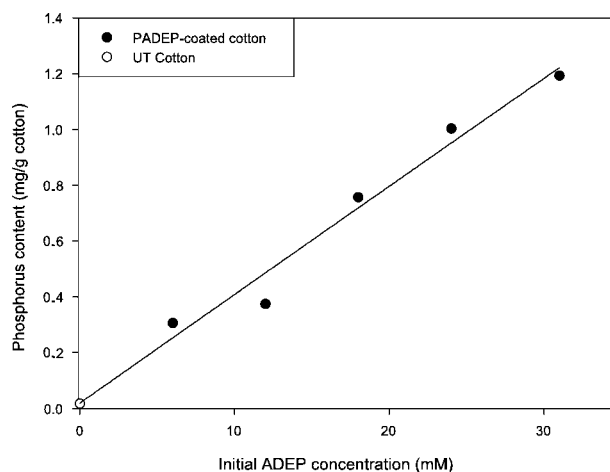


Figure 4 Phosphorus content on the PADEP-coated cotton at varying initial ADEP concentration.

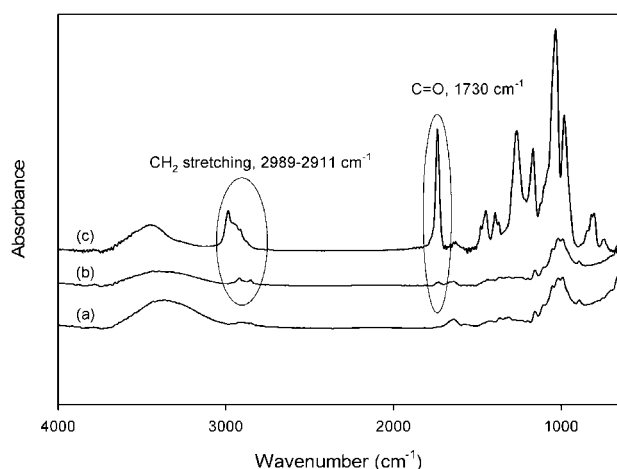


Figure 5 FTIR-ATR spectra of (a) untreated cotton, (b) PADEP-coated cotton, and (c) PADEP.

an ultrathin polymer film of PADEP coated on the cotton surface.

SEM

Representative SEM images of untreated and the PADEP-coated cotton using 31 mM ADEP are presented in Figure 6. Figure 6(b) shows the presence of the polymer film on the cotton surface when compared to the clean, untreated cotton surface in Figure 6(a). The SEM images indicate that the polymer films are ultrathin since the fine structure of the untreated surface is still visible on the treated fiber surface. From the amount of polymer formed on the fiber surface and the surface area of the fabric of $4.54 \text{ m}^2/\text{g}$ obtained from BET with nitrogen, the thickness of the coated film was found to be 2.15 nm. Assuming that the maximum possible thickness of the admicelle is about twice the length of the hydrophobic

tail of DBSA, which is estimated to be about 4 nm, it can be seen that the calculated thickness of the coated film is well within the maximum thickness of the admicelle. Several workers also found their admicellar coated film to have the thickness within this range.^{23–25} These observations are in agreement with the FTIR results and confirm that an ultrathin polymer film has been coated on the cotton fabric by admicellar polymerization. Also, it can be observed that there is no polymer deposition in the interstices between fibers. Hence, good air permeability can be maintained in the treated fabrics.

Thermal analysis

Cellulose is known to undergo thermal degradation via two competing routes.²⁶ The first route which occurs at higher temperature involves depolymerization of cellulose yielding levoglucosan which subsequently pyrolyses to give highly flammable volatiles. The second route which occurs at lower temperature involves dehydration leading to the formation of char and water. Figure 7 compares the DTG thermograms of untreated cotton and the PADEP polymer. For untreated cotton, the decomposition started at temperature above 300°C , giving rise to a main DTG peak at 350°C . In the case of PADEP, the main decomposition occurred at 300°C , which is about 50°C below that of untreated cotton. It is generally agreed that, to be effective, the flame retardant agent should decompose before the substrate to interfere with its burning process. Figure 8 shows the TGA and DTG curves of untreated and treated cotton at different ADEP concentrations. For untreated cotton, the main decomposition temperature was found at 350°C and an 8% residue at 600°C was found from the TGA thermogram. For PADEP-treated cotton, the DTG decomposition peak shifted to a lower temper-

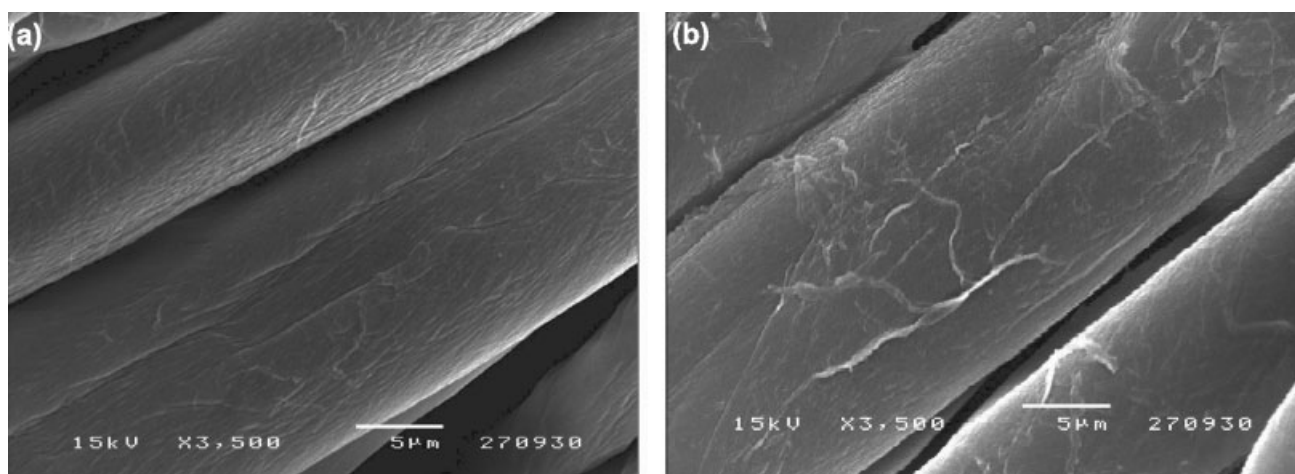


Figure 6 SEM micrographs of (a) untreated and (b) PADEP-coated cotton.

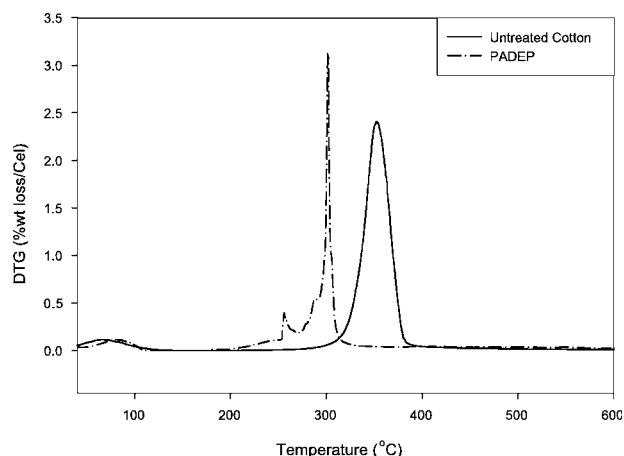


Figure 7 DTG curves of untreated cotton and PADEP.

ature with higher percent remaining residue. Figure 9 shows that the reduction in the decomposition temperature was directly related to the phosphorus content of the treated fabric, decreasing sharply from 350 to 317°C when the phosphorus content increased from 0 to 1.2 mg/g cotton. Figure 10 shows the

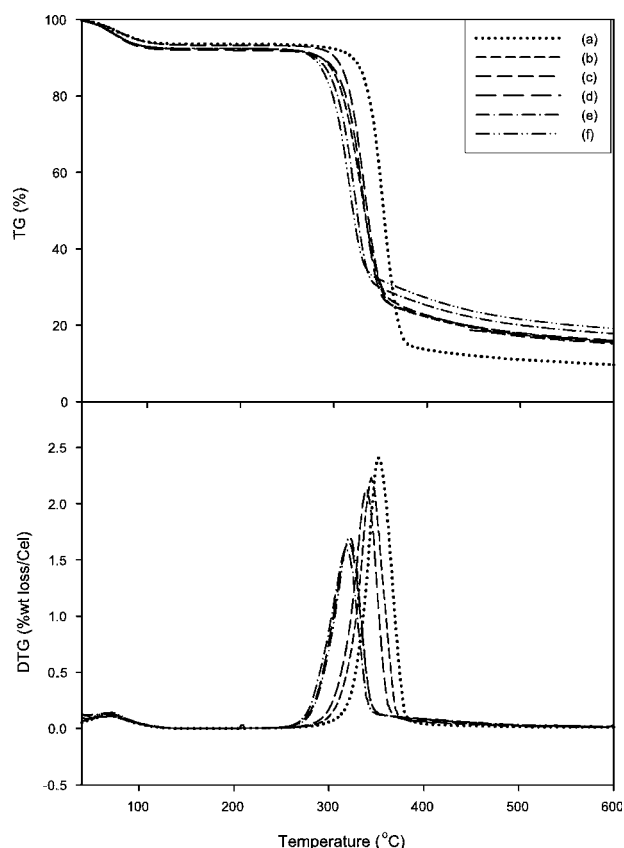


Figure 8 TGA and DTG curves of (a) untreated cotton and PADEP-coated cotton using an ADEP concentration of (b) 6 mM, (c) 12 mM, (d) 18 mM, (e) 24 mM, and (f) 31 mM.

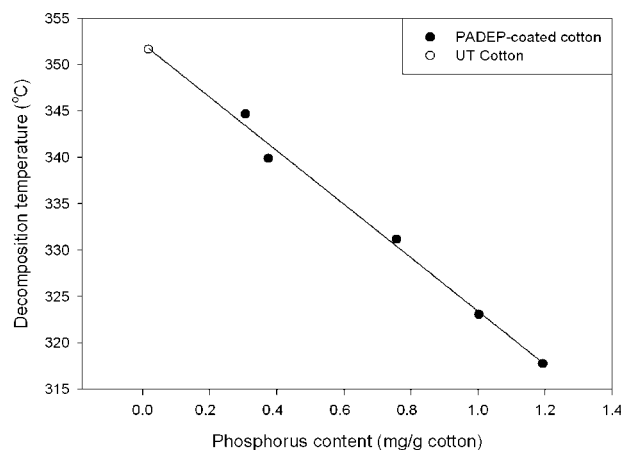


Figure 9 Effect of phosphorus content on the decomposition temperature of PADEP-coated cotton.

correlation between percent remaining residue and phosphorus content of the treated fabric. Again, a direct correlation was obtained with the percent remaining residue increasing sharply from around 8% to 19.4%. Organophosphorus retardants are known to act initially by phosphorylation of cellulose in the C₆ position thus blocking the formation of levoglucosan. At higher temperature, the retardants break down to give phosphoric acid which acts as a dehydration agent leading to a high char yield and a lower decomposition temperature.²⁷ The direct correlation between phosphorus content and the decrease in decomposition temperature as well as the increase in percent remaining residue agrees well with the flame retarding mechanism of phosphorus as described above. The results also show that phosphorus in the flame retardant played a major role in the flame retardancy behavior of the treated fabric.

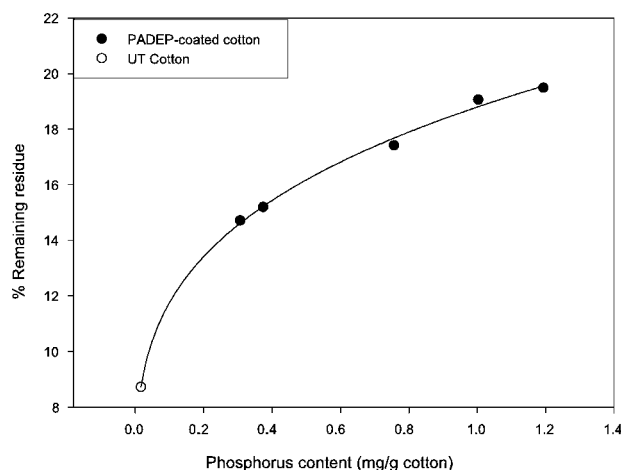


Figure 10 Effect of phosphorus content on the % remaining residue of PADEP-coated cotton at 600°C.

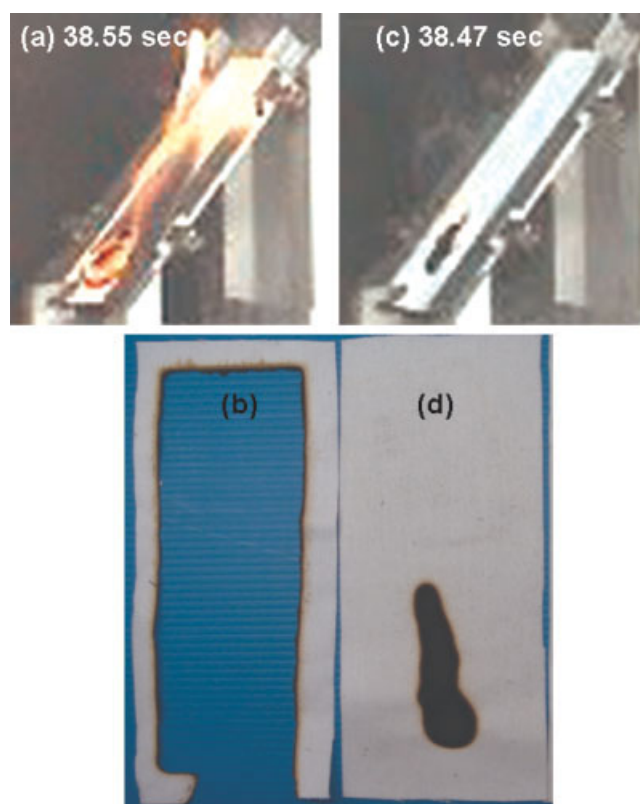


Figure 11 Burning behavior of untreated cotton (a) at 38.55 s, (b) at the end of the burning, and PADEP-coated cotton using 31 mM ADEP (c) at the burning time of 38.47 s, and (d) at the end of the burning. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Burning behavior

The photographs in Figure 11 compared the burning behavior of untreated and PADEP-coated cotton prepared with 31 mM ADEP. In the experiments the ignition time used was 10 s. Figure 11(a,c) compare the burning behavior of the untreated and treated fabric at the same burning time of 38 s. It can be seen that, at this point, the untreated fabric was burning with distinct flame, whereas in the case of treated sample, the char area was formed on the fabric in the burnt area with hardly noticeable flame. It was found that, for untreated cotton, after removing the ignition source, the flame spread quickly and burned the entire fabric with no residue remaining within 71 s [Fig. 11(b)]. In contrast, the PADEP-coated cotton, after removing the ignition source, the flame spread slowly, then extinguished in 53 s leaving an area of char formation [Fig. 11(d)]. The flame spread rate of the untreated cotton was found to be 2.1 mm/s, while that of PADEP-coated cotton was 1.18 mm/s. There was therefore a great improvement in the flame retardancy of the treated cotton. Improvement in flame retardancy with the PADEP coating can be explained by the presence of an

adherent and insulating layer of residual char which built up on the surface of cotton fabric during the burning process. This layer isolates the underlying cotton from the flame and thus makes further degradation by combustion difficult. The flame retardancy observed was also due to the lack of flammable volatiles which were formed in the case of untreated cotton. The good flame retardancy obtained with admicellar polymerization is attributed to the successful coating of an ultrathin uniformed film of a phosphorus-containing flame retarding agent on the fiber surface.

Fabric properties

The air permeability of untreated and PADEP-coated cotton using 31 mM ADEP was 8.58 and 8.12 cm³/s/cm², respectively. The results show that there was only a slight decrease in air permeability of the treated fabric. Methachan et al.²⁸ also found that the air permeability of their admicellar-treated hydrophobic cotton was almost the same as that of untreated cotton fabric. The stiffness of the fabric was determined by the 45° Cantilever Type Tester and the moving distances found for untreated and PADEP-coated cotton using 18 and 31 mM ADEP were 26, 24, and 23 mm, respectively, indicating that the coated polymer film itself was quite flexible leading to a slight decrease in fabric stiffness in the treated samples. In addition, the feel of the treated fabric, as assessed by seven evaluators, was found to have no perceived difference when compared to the untreated fabric. Hence, the ultrathin film, with a weight addition of only 9.75 mg/g cotton, together with the absence of polymer deposition in between fibers or yarns interstices, helps to ensure that the treated fabric retained its good pliability and soft touch with good air permeability.

SUMMARY

The formation of a phosphorus-containing polymer thin film on cotton fabric was successfully carried out in this work by admicellar polymerization using the anionic surfactant, DBSA. FTIR-ATR results and SEM micrographs confirmed that a polymer film was successfully formed on the cotton surface. The phosphorus content on the PADEP-coated cotton increased linearly with the ADEP concentration in the range 0–31 mM. The TGA and DTG results showed that the decrease in the main decomposition temperature and the increase in percent remaining residue at 600°C related directly to the amount of phosphorus content on the fabric. The results from the flammability tests showed that PADEP-coated cotton using DBSA as the surfactant and an ADEP concentration of 31 mM exhibited much improved

flame retardancy with char formation on the burnt surface while the untreated cotton burned completely. The treated fabric was found to retain its good pliability and soft touch with good air permeability.

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References

1. Horrocks, A. R. *Polym Degrad Stab* 1996, 54, 143.
2. Schnipper, A.; Smith-Hansen, L.; Thomasen, E. S. *Fire Mater* 1995, 19, 61.
3. Liu, Y. L.; Hsiu, G. H.; Chiu, Y. S.; Jeng, R. J.; Ma, H. *J Appl Polym Sci* 1996, 59, 1619.
4. Horrocks, A. R.; Price, D.; Akalin, M. *Polym Degrad Stab* 1996, 52, 205.
5. Price, D.; Horrocks, A. R.; Akalin, M.; Farooq, A. A. *J Anal Appl Pyrolysis* 1997, 40/41, 511.
6. Zhang, S.; Horrocks, A. R. *J Appl Polym Sci* 2003, 90, 3165.
7. Zhu, P.; Sui, S.; Wang, B.; Sun, K.; Sun, G. *J Anal Appl Pyrolysis* 2004, 71, 645.
8. Wu, W.; Yang, C. Q. *Polym Degrad Stab* 2004, 85, 623.
9. Reddy, P. R. A.; Agathian, G.; Kumar, A. *Rad Phys Chem* 2005, 72, 511.
10. Tsafack, M. J.; Levolois-Grutzmacher, J. *Surf Coat Technol* 2005, 200, 3503.
11. Harwell, J. H.; O'Rear, E. A. U.S. Patent 4,770,906 (1988).
12. Pongprayoon, T.; Yanumet, N.; O'Rear, E. A. *J Colloid Interface Sci* 2002, 249, 227.
13. Matarredona, O. M.; Mach, K.; Rieger, M. M.; O'Rear, E. A. *Corrosion Sci* 2003, 45, 2541.
14. Lai, C.; Harwell, J. H.; O'Rear, E. A.; Komatsuzaki, S.; Arai, J.; Nakawaji, T.; Ito, Y. *Langmuir* 1995, 11, 905.
15. Boufi, S.; Gandini, A. *Cellulose* 2002, 8, 303.
16. Siriviriyannun, A.; O'Rear, E. A.; Yanumet, N. *J Appl Polym Sci* 2007, 103, 4059.
17. Sakhalakar, S. S.; Hirt, D. E. *Langmuir* 1995, 11, 3369.
18. Reghunadhan-Nair, C. P.; Clouet, G. *Eur Polym J* 1985, 25, 251.
19. ASTM D. The American Society for Testing and Materials, Standard Test Method for Flammability of Apparel Textiles, ASTM D 1230-94 (Reapproved 2001).
20. Standard Test Method for Air Permeability of Apparel Textiles, ASTM D 737-96.
21. JIS. Japanese Industrial Standard, Testing Method for Woven Fabric, JIS L 1096:1999.
22. Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley Inter Science: New York, 2004.
23. Wu, J.; Harwell, J. H.; O'Rear, E. A. *Langmuir* 1987, 3, 531.
24. Yuan, W. L.; O'Rear, E. A.; Grady, B. P.; Glatzhofer, D. T. *Langmuir* 2002, 18, 3343.
25. Pongprayoon, T.; Yanumet, N.; O'Rear, E. A.; Alvarez, W. E.; Resasco, D. E. *J Colloid Interface Sci* 2005, 281, 307.
26. Horrocks, A. R. *J Soc Dyer Color* 1983, 99, 191.
27. Langley, J. T.; Drews, M. J.; Barker, R. H. *J Appl Polym Sci* 1980, 25, 243.
28. Methachan, B.; Pongprayoon, T.; Yanumet, N. *AATCC Rev* 2002, 2, 60.