

Flame-Retardant Cotton Fabric Prepared by Admicellar Polymerization of a Phosphorus-Containing Monomer Using a Cationic Surfactant

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Abstract:

A flame-retardant coating was developed on cotton fabric through admicellar polymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC) using cetylpyridinium chloride (CPC) as a cationic surfactant. The adsorption behavior of CPC on cotton fabric was investigated at 30 and 60 °C to determine suitable conditions for admicellar polymerization. The adsorption of CPC increased with increasing temperature and a critical micelle concentration (CMC) of approximately 0.65 mM was obtained. Cotton fabrics coated at 60 °C exhibited higher phosphorus content than fabrics coated at 30 °C, indicating enhanced polymer deposition. Thermogravimetric analysis revealed increased char formation and modified thermal degradation behavior in treated fabrics. The onset degradation temperature decreased due to phosphorus-catalyzed dehydration, whereas the char yield increased significantly. Auto-flammability tests demonstrated substantial improvement in flame retardancy, and the treated fabric containing 7.8 mg phosphorus g⁻¹ cotton exhibited self-extinguishing behavior. The flame-retardant effect was retained after home laundering. The results demonstrate that admicellar polymerization is an effective technique for producing durable phosphorus-containing flame-retardant coatings on cotton fabric.

Keywords: Admicellar polymerization; Cationic surfactant; Cotton fabric; Flame retardancy; Phosphorus-containing polymer; Cetylpyridinium chloride

1. Introduction

Cotton is one of the most widely used natural textile fibers because of its comfort, biodegradability, renewability, and excellent moisture absorption properties. However, its high flammability restricts its use in protective textiles and other safety-related applications. Therefore, the development of durable and environmentally acceptable flame-retardant finishes for cotton fabrics continues to attract considerable research interest.

Phosphorus-containing flame retardants are particularly attractive because they promote dehydration and char formation during thermal degradation, thereby reducing the generation of combustible volatile products. Among phosphorus-containing monomers, 2-methacryloyloxyethyl phosphorylcholine (MPC) contains a phosphorylcholine functional group capable of enhancing condensed-phase flame-retardant action.

Admicellar polymerization is a surface-confined polymerization technique in which surfactant aggregates adsorbed on a substrate serve as nanoreactors for polymer formation. This technique provides a convenient approach for depositing thin polymeric films on textile substrates with low chemical consumption and controlled surface coverage.

In the present study, flame-retardant cotton fabric was prepared by admicellar polymerization of MPC using cetylpyridinium chloride (CPC) as a cationic surfactant. The adsorption behavior of CPC on cotton fabric was investigated at different temperatures and the resulting coated fabrics were characterized through phosphorus content determination, thermogravimetric analysis, and auto-flammability testing.

2. Experimental

2.1 Materials

Cetylpyridinium chloride (CPC), 2-methacryloyloxyethyl phosphorylcholine (MPC) and azobisisobutyronitrile (AIBN) were purchased from Sigma-Aldrich (India). All chemicals were used as received without further purification. Plain woven cotton fabric (110 g m^{-2}) was purchased from Amartex Industries Limited, Panchkula, Haryana, India. The fabric specifications were: warp count, 40/1 Ne; weft count, 40/1 Ne; fabric weight, 110 GSM; ends per centimeter, 34.64; and picks per centimeter, 29.92.

2.2 Determination of Adsorption Isotherm

The adsorption isotherms of CPC on cotton fabric were determined at 30 and 60 °C. A cotton fabric specimen measuring 20 cm × 5 cm was immersed in 30 mL of CPC solution of known concentration and adsorption was allowed to proceed for 12 h at the selected temperature. The amount of surfactant in the supernatant was measured using a UV–visible spectrophotometer (Varian Cary 5000). The surfactant adsorption isotherm was obtained by plotting the amount of adsorbed surfactant versus supernatant concentration.

2.3 Admicellar Polymerization Process

2-methacryloyloxyethyl phosphorylcholine (MPC) monomer was polymerized on cotton fabric using cetylpyridinium chloride (CPC) as the cationic surfactant. A piece of cotton fabric measuring 20 cm × 5 cm was placed in a vial containing 1.5 mL of CPC surfactant solution. The surfactant concentration used was 0.65 mM. The vial was wrapped with aluminum foil, and the lid was screwed on and sealed with paraffin film. Two separate vials were prepared. One vial was maintained at 30 °C for 12 h, while the second vial was maintained at 60 °C for 12 h to allow adsorption of the surfactant onto the cotton fabric. Then to initiate the polymerization reactions, 100 mM MPC monomer and 3ml of 0.01M AIBN as initiator dissolved in isopropyl alcohol were added to both vials and shaking was continued for 8 h at 75 °C. Upon completion of the polymerization reaction, the vials were removed from the water bath and allowed to cool to room temperature. The coated cotton fabric samples were removed from the vials and dried first in air and subsequently in an oven at 60 °C overnight.

The coated samples prepared using adsorption temperatures of 30 and 60 °C were designated as CF-MC(T₁) and CF-MC(T₂), respectively. After home laundering, the corresponding samples were designated as CF-MC(T₁)_L and CF-MC(T₂)_L.

2.4 Determination of Phosphorus Content in Coated Cotton Fabric

Coated cotton fabric (0.1 g) was digested with 2 mL of concentrated sulfuric acid. Subsequently, 10 mL of 30% hydrogen peroxide was added dropwise to the mixture and stirred continuously on a hot plate for 1 h. After complete digestion, the solution was transferred to a 50 mL volumetric flask and diluted with distilled water. The prepared samples were analyzed using a UV–visible spectrophotometer (Varian Cary 5000) by the stannous chloride method for phosphate determination. The phosphorus content was calculated from the phosphate concentration.

2.5 Thermogravimetric Analysis

Thermograms of the samples were obtained using a TA Instruments DSCQ10 differential calorimeter thermal analyzer. Approximately 10 mg of sample was placed in an alumina crucible and heated from ambient temperature to 700 °C under a nitrogen flow rate of 100 mL min⁻¹ at a heating rate of 10 °C min⁻¹.

2.6 Auto-Flammability Test

The burning behavior of cotton fabric samples was studied using a Paramount 45° Automatic Flammability Tester (An ISO 9001:2008 Group) according to ASTM D1230 (Standard Test Method for Flammability of Apparel Textiles). The ignition time was set at 1 s. This test measures the time required for flame propagation through the length of the fabric and the ease of ignition. Fabric specimens measuring 15 cm × 5 cm were exposed to the flame and the burning time and burning characteristics were recorded. The burning behavior of the fabrics was documented using a digital camera.

3. Results and Discussion

3.1 Adsorption Isotherm of CPC Surfactant at Two Different Temperatures on Cotton Fabric

The adsorption isotherms of CPC surfactant on cotton fabric at 30°C and 60°C for 12 h are shown in Figure 1. The estimated critical micelle concentration (CMC) of the CPC surfactant at both temperatures was found to be 0.65 mM. Therefore, based on the adsorption isotherm results, a CPC concentration of 0.65 mM was selected for the subsequent admicellar polymerization reaction.

Figure 1 shows that the adsorption of CPC on cotton fabric increases with an increase in temperature from 30°C to 60°C. The adsorption capacity is considerably affected by rising temperature. The increase in adsorption at higher temperature may be attributed to the decrease in water structuring around the surfactant molecules, which enhances the interaction between CPC molecules and the cotton fabric surface.

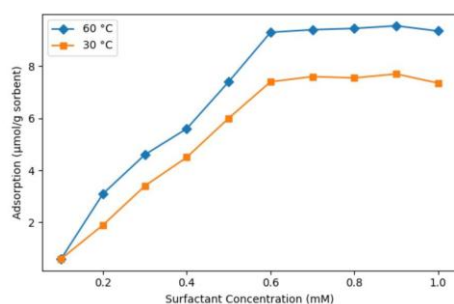


Fig. 1: Adsorption isotherms of CPC surfactant on cotton fabric at 30°C and 60°C

3.2 Determination of Phosphorus Content in Coated Cotton Fabric

The amount of polymer coated on the cotton fabric was determined from its phosphorus content. The phosphorus content values of the coated cotton fabrics are presented in Table 2. The phosphorus content of the coated cotton fabric prepared using CPC adsorption at 30°C was found

to be 4.1 mg g⁻¹ cotton, whereas the phosphorus content of the coated cotton fabric prepared using CPC adsorption at 60°C was 7.6 mg g⁻¹ cotton.

The higher phosphorus content obtained at 60°C indicates a greater amount of polymer deposition on the cotton fabric. As the temperature increased, the adsorption of the CPC surfactant on the cotton surface also increased. In general, the extent of admicellar polymerization increases with an increase in the thickness of the surfactant admicelle layer. Therefore, the enhanced surfactant adsorption at 60°C resulted in a thicker admicellar layer, leading to increased polymer deposition and consequently a higher phosphorus content on the cotton fabric.

3.3 Thermal Analysis

Thermogravimetric (TG) thermograms of pure cotton fabric (CF), treated cotton fabric prepared using CPC adsorption at 30°C CF-MC(T₁), and treated cotton fabric prepared using CPC adsorption at 60°C CF-MC(T₂) were obtained under a nitrogen atmosphere from ambient temperature to 700°C at a heating rate of 10°C min⁻¹. The TG curves are shown in Figure 2, and the corresponding TG data are presented in Table 1.

Figure 2 shows that pure CF undergoes a single stage of thermal degradation in the temperature range of 100–600°C. In contrast, both treated cotton fabric samples, exhibit two stages of thermal degradation. The first stage is attributed to the acid-catalyzed dehydration and depolymerization of cotton, while the second stage corresponds to the thermal degradation of the cotton fabric along with the volatilization of degradation products. The first DTG peak of both treated samples is shifted towards lower temperatures compared to pure CF. This behavior is attributed to acid-catalyzed dehydration induced by phosphoric acid generated from the decomposition of the phosphorus-containing flame-retardant coating. Such early dehydration promotes char formation and enhances flame-retardant performance. The char yield of CF-MC(T₂) was found to be 30.9%, which is higher than that of CF-MC(T₁) (24.0%). The higher char yield of CF-MC(T₂) indicates a greater phosphorus content and improved flame-retardant properties. This enhancement can be attributed to the increased adsorption of CPC surfactant at the higher adsorption temperature, resulting in greater polymer deposition on the cotton fabric.

However, after home laundering, the char yields of both treated samples decreased. The laundered samples, designated as CF-MC(T₁)_L and CF-MC(T₂)_L, exhibited lower char yields due to the partial removal of the phosphorus-containing polymer coating during the washing process.

Table 1: TG data of treated and untreated cotton fabrics

Sample	Stages	Temp. Range (°C)	Weight loss (%)	DTG (°C)	Char at 600°C (%)
CF	1 st	100-600	87.6	340	4.4
CF-MC(T ₁)	1 st	100-300	19.7	250	24.0
	2 nd	300-600	50.5	380	
CF-MC(T ₂)	1 st	100-300	15.6	250	30.9
	2 nd	300-600	51.0	430	
CF-MC(T ₁) _L	1 st	100-600	77.5	310	15.2
CF-MC(T ₂) _L	1 st	100-280	17.7	250	18.1
	2 nd	280-600	61.4	420	

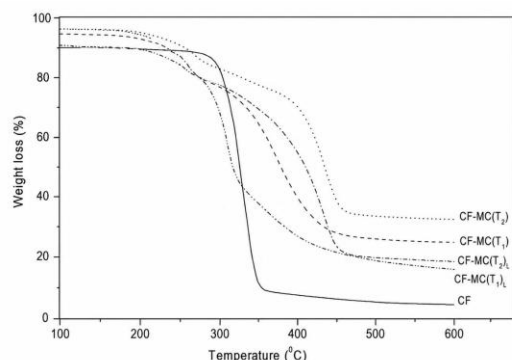


Fig 2. TG curves of untreated and treated cotton fabric samples before and after home laundering in a nitrogen atmosphere.

3.4 Auto-Flammability Behavior

3.4 Flammability Behavior

The flammability behavior of untreated and treated cotton fabric samples before and after home laundering was evaluated using the same ignition time of 1 s. The flame spread parameters of these samples are presented in Table 2. For pure cotton fabric (CF), the flame continued to burn after removal of the ignition source and completely consumed the fabric within 11.8 s, leaving no residue. In the case of CF-MC(T₁), the fabric also burned completely; however, the flame spread time increased to 118 s, indicating improved flame-retardant performance compared to untreated cotton fabric.

CF-MC(T₂) exhibited the best flame-retardant behavior among all the samples. The flame spread was significantly slower, and a char residue of 2.8 cm in length remained after the test, as shown in Figure 3. The formation of char acted as a protective barrier, restricting further combustion of the fabric. The improved flame-retardant performance of CF-MC(T₂) can be attributed to its higher phosphorus content. As the adsorption temperature increased from 30°C to 60°C, the adsorption of CPC surfactant increased, resulting in greater polymer deposition and higher phosphorus incorporation on the cotton fabric. Consequently, the flame-retardant efficiency improved with increasing phosphorus content, leading to enhanced char formation and reduced flame propagation. After first home laundering of treated cotton fabric samples, flame retardancy is decreased because some of the phosphoric polymer layer was washed away.

Table 2: Flammability test and phosphorous content data for cotton fabric samples

Sample	Flame spread time (s)	Char Length (cm)	Pass / Fail	P Content (mg/g cotton)
CF	11.8	BL	Fail	34
CF-MC(T ₁)	52	BL	Fail	250 380
CF-MC(T ₂)	SE	2.8	Pass	250 430
CF-MC(T ₁) _L	150	BL	Fail	310
CF-MC(T ₂) _L	118	BL	Fail	250 420



Fig. 3: Burning behaviour of CF-MC(T₂) cotton fabric sample in auto flammability test.

4. Conclusions

MPC was successfully polymerized on the surface of cotton fabric using CPC through the admicellar polymerization technique. Adsorption isotherm studies demonstrated higher adsorption of CPC at 60 °C than at 30 °C, resulting in greater deposition of the phosphorus-containing polymer on the cotton surface.

Thermogravimetric analysis showed that the onset temperature of degradation of treated cotton fabric decreased due to acid-catalyzed dehydration by phosphoric acid released from the phosphorus-containing polymer. However, the char yield increased significantly at the expense of flammable volatile products. The maximum char yield increased from 4.4% for untreated cotton fabric to 30.9% for treated cotton fabric.

Auto-flammability testing demonstrated that the MPC-treated cotton fabric containing approximately 7.6 mg phosphorus g⁻¹ cotton exhibited self-extinguishing behavior and successfully passed the flammability test. Furthermore, the flame-retardant effect remained durable after home laundering.

The results demonstrate that admicellar polymerization is an effective approach for producing durable phosphorus-containing flame-retardant coatings on cotton fabric.