

Flame retardant coating on cotton fabric with phosphorus containing polymeric film by admicellar polymerization

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In this study, 2-methacryloyloxyethyl phosphorylcholine monomer has been polymerized using azobis-isobutyronitrile initiator on the surface of cotton fabric by admicellar polymerization with the assistance of anionic surfactant (dodecylbenzenesulphonic acid sodium salt) along with NaCl as electrolyte. The polymeric film formed on cotton surface has been characterized by FTIR and SEM. FTIR spectrum shows additional bands at 1720 cm^{-1} (C=O str.), 1258 cm^{-1} (P=O str.) and 1078 cm^{-1} (P-O-C str.) of phosphorus based polymer formed on cotton fabric. Thermal behaviour in nitrogen atmosphere is also studied which shows that onset temperature of degradation of treated cotton fabric decreases by $37\text{ }^{\circ}\text{C}$ and char yield increases by 21.7% at $600\text{ }^{\circ}\text{C}$. The burning behaviour of treated cotton fabric is investigated by 45° auto flammability and limiting oxygen index tests. The pure cotton fabric burns the entire length of 15 cm sample in 11.8 s but treated cotton fabric self-extinguishes in auto flammability test. The durability of treated cotton fabric has also been studied up to two home launderings.

Keywords: Admicellar polymerization, Anionic surfactant, Cotton fabric, Flame retardancy, Phosphorous based polymer

1 Introduction

Cotton is the most commonly used natural textile fibre as it is good absorbent, comfortable and aesthetic. But it is prone to burning¹ on ignition and heating at high temperature, which remains an obstacle to its wider use. In order to meet today's demands for fire safety, cotton in the form of finished fabric having better flame retardant property has to be developed. Although many bromine-based flame retardants, currently in use, are relatively efficient but they have ecological drawbacks. There is preference for phosphorous containing flame retardant²⁻⁴ being environment friendly. The most successful phosphorous based flame retardant systems available for cotton fabric are Proban and Pyrovatex CP⁵. Cotton cellulose undergoes thermal degradation on heating and produces a major combustible volatile compound, namely levoglucosan (1,6-anhydro- β -D-glucopyranose)⁶, which is responsible for propagation of fire. The phosphorous based flame retardants generally act in condensed phase, and increase the carbonaceous residue at the cost of combustible volatile products. The surface layer of protective char also acts as a barrier between flame and cotton fabric which results in the extinguishment of combustion⁷.

Several other methods have been reported to make cotton fabric flame retardant, such as chemical modification⁸, pad-dry cure⁹, graft polymerization by ionized radiation¹⁰, plasma treatment¹¹ and intumescent systems¹². However, there are some disadvantages to maintain some desirable fabric properties such as strength, softness, air permeability, stiffness and aesthetic appearance of the cotton fabric. In this study, admicellar polymerization¹³⁻¹⁵ is used to develop flame retarded cotton fabric with advantage of maintaining physio-mechanical properties of cotton fabric by selecting phosphorous containing monomer. In this technique a very thin layer of polymer is formed on the surface of cotton fabric with the assistance of surfactant adsorbed on the surface. Admicellar polymerization is a three step process. In the first step, admicelle are formed on cotton surface. In the second step, monomer is added, which, in turn, partitions into admicelle, and an initiator is then added to promote polymerization reaction. In the third step, the upper layer of surfactant is removed to expose the polymeric film on the surface.

In this study, 2-methacryloyloxyethyl phosphorylcholine monomer has been polymerized using azobis-isobutyronitrile initiator on the surface of cotton fabric by admicellar polymerization with the assistance of anionic surfactant (dodecylbenzenesulphonic acid sodium salt) along with NaCl as electrolyte. The thermal properties and burning behaviour of cotton fabric

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samples were studied using thermogravimetry (TG) and flammability tests.

2 Materials and Methods

2.1 Materials

2-Methacryloyloxyethyl phosphorylcholine (MPC), N-(hydroxymethyl) acrylamide solution, sodium chloride, lithium chloride, potassium chloride and stannous chloride were purchased from Sigma Aldrich (India). Dodecylbenzenesulphonic acid sodium salt (DBSA) and azobis-isobutyronitrile (AIBN) were purchased from Himedia Chemicals Co. (India); ammonium molybdate and isopropyl alcohol from Qualigens (India); and hydrogen peroxide (30%) and sulphuric acid from Fisher Scientific (India). All these materials were used as received without further purification. Simple woven cotton fabric (110 g/m^2) was purchased from Amartex Industries Limited (Panchkula, Haryana, India). Its specifications are warp count 40/1 Ne, weft count 40/1 Ne, GSM 110, ends/cm 34.64 and picks/cm 29.92.

2.2 Determination of Adsorption Isotherm

The adsorption isotherm of (i) DBSA surfactant, (ii) DBSA with 0.15M LiCl, (iii) DBSA with 0.15M NaCl and (iv) DBSA with 0.15M KCl at pH 4 was obtained by exposing a $20 \text{ cm} \times 5 \text{ cm}$ piece of cotton fabric to 30 mL of the surfactant solution of known initial concentration. The value of pH 4 was set using 0.1M HCl. The adsorption was allowed to take place at $30 \text{ }^\circ\text{C}$ for 15 h in 36 mL vial with the lid sealed with paraffin film. The amount of DBSA in supernatant was measured by a UV-VIS spectrophotometer (Varian Cary 5000) at 224 nm (experimentally observed maxima). A plot of the amount of adsorbed surfactant versus supernatant concentration was obtained which yielded the surfactant adsorption isotherm.

2.3 Admicellar Polymerization Process

2-Methacryloyloxyethyl phosphorylcholine (MPC) monomer was polymerized on cotton fabric using AIBN initiator. A piece of $20 \text{ cm} \times 5 \text{ cm}$ cotton fabric weighing 1.1 g was placed in a 36 mL vial containing a solution of 1.5 mL DBSA (0.55 mM) as surfactant, 1.5 mL NaCl (0.15M) as electrolyte, MPC monomer at concentrations in range 25 - 125 mM, 3 mL AIBN (0.01M) as initiator dissolved in isopropyl alcohol and N-(hydroxymethyl) acrylamide (3.6 mM/g) as binding agent. The pH 4 was set using 0.1M HCl. The vial was then wrapped with aluminium foil and then lid was screwed on and then sealed with paraffin film as well. All vials were placed into a water shaker

thermostat for 15 h at $30 \text{ }^\circ\text{C}$ to allow adsorption of surfactant and for adsolubilization of monomer in the admicelle to reach equilibrium. Then to initiate the polymerization reaction, the temperature was raised to $75 \text{ }^\circ\text{C}$ for 8 h. After polymerization, the vials were removed and cooled down to room temperature. Then fabric samples were removed from the vial and dried first in air and then in an oven at $60 \text{ }^\circ\text{C}$ overnight.

The burning behaviour of these samples was studied by auto flammability test. The fabrics (not burnt) were home laundered in a washing machine using detergent at room temperature ($25 \text{ }^\circ\text{C}$) for 30 min. The samples were then dried in dryer and then in an oven overnight at $60 \text{ }^\circ\text{C}$. These samples were stored in desiccator until required and finally tested for flame retardant behaviour to evaluate their durability. The washed fabrics (not burnt) were home laundered again for flammability test. For untreated cotton fabric (UCF), treated cotton fabric (TCF), and treated cotton fabric after first home laundering (TCF-1), treated cotton fabric with binding agent (TCF-B) and treated cotton fabric after first home laundering (TCF-B1), the fourier transform infrared spectroscopy, scanning electron microscopy, thermal analysis and flammability studies were carried out. The durability of treated cotton fabric samples with MPC monomer (25-125 mM) with and without binding agent was also studied.

2.4 Surface Characterization of Coated Cotton

Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to characterize the surface of untreated, treated and treated cotton after home laundering. FTIR spectra were carried out using the KBr pellet testing techniques on Shimadzu IR affinity-I 8000 FTIR spectrometer in the range $4000\text{-}400 \text{ cm}^{-1}$ for 15 scans with a resolution of 4 cm^{-1} .

Morphological analysis of cotton fabric samples was carried out by SEM using a JOEL JSM 6100 with a beam voltage of 10 kV. These samples were mounted on metal stubs with adhesive tape and sputtered with a thin layer of gold before analysis.

2.5 Determination of Phosphorous Content in Coated Cotton Fabric

Treated cotton fabric (0.1 g) was digested with conc. sulphuric acid (2.0 mL). Then 10 mL of 30% H_2O_2 was added dropwise to the mixture and stirred continuously for 1 h on hot plate. Then completely digested sample was transferred to a 50 mL volumetric flask, and diluted with distilled water. The prepared samples were analysed by UV-VIS spectrophotometer (Varian Cary

5000) using stannous chloride method for phosphate determination¹⁶. The phosphorous concentration was calculated from phosphate concentration.

2.6 Thermal Analysis

The thermogravimetry (TG) of untreated cotton fabric (UCF), treated cotton fabric (TCF) and treated cotton fabric after home laundering (TCF-1) were performed using TA instruments DSCQ10 (Differential Calorimeter Thermal Analyzer) by taking about 10 mg of samples in alumina crucibles under continuous nitrogen flow of 100 mL min⁻¹ from ambient temperature to 700 °C at a heating rate of 10 °C min⁻¹.

2.7 Flammability Test

2.7.1 Automatic Flammability Test

The burning behaviour of cotton fabric samples was studied using the Paramount 45° automatic flammability tester (An ISO 9001:2008 group) according to Standard Test Method for Flammability of Apparel Textiles, ASTM D1230-94 (Reapproved 2001). In this study, the ignition time was set at 1 s. The experiments were carried out at the ambient temperature of 30 °C. The fabric sample was dried at 105 °C in an oven for 30 min, cooled down in a desiccator for 50 min and then mounted in a frame and held at an angle of 45°. This test measures the time required for flame to propagate through the length of the fabric and ease of ignition. The specimen (15 cm × 5 cm) was then exposed to flame and then burning time and burning characteristics were recorded. The burning behaviour of fabric was recorded by a digital camera.

2.7.2 LOI Analysis

Limiting oxygen index (LOI) analysis of pure cotton and coated cotton fabric samples was performed using Limiting Oxygen Indexer ISO 4859-2 as per ASTM D 2863. The cotton specimen (15 cm × 5 cm) was ignited at the top. The oxygen concentration was adjusted until the specimen just support combustion. The oxygen concentration is reported as volume percent. In limiting oxygen index test, the higher the LOI values, the better is the flame retardancy of cotton fabric.

2.8 Measurement of Air Permeability and Stiffness of Coated Cotton Fabric

Air permeability of untreated and treated cotton fabric was studied using prolific air permeability tester (IS: 11056-1984). The results of the fabric were expressed in volume of air permeability per minute

per fabric area (m³/min/m²). The reported result was the average of measurements on four samples.

Stiffness of untreated and treated cotton fabrics was studied using the Shirley stiffness tester according to the testing methods for fabric ASTM D 1388. The equipment consists of a horizontal table with a ruler scale on one side and having 45° slope at one end. The fabric sample (15 cm × 2 cm) was placed on the table parallel to the scale. It was then allowed to slide slowly towards the slope until the end of the fabric, extruding from the horizontal table, 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 is the fabric stiffness. The test was repeated thrice for all the samples and an average was taken.

3 Results and Discussion

3.1 Adsorption Isotherm of DBSA Surfactant on Cotton Fabric

The adsorption isotherms of (i) DBSA surfactant¹⁷, (ii) DBSA with 0.15M NaCl, (iii) DBSA with 0.15M LiCl and (iv) DBSA with 0.15M KCl at pH 4 at 30 °C are shown in Fig. 1. The amount of surfactant adsorption attains a constant value at 0.55 mM of equilibrium surfactant concentration (considered as critical micelle concentration-CMC), in case of DBSA surfactant and DBSA + 0.15M NaCl. But in case of DBSA + 0.15M LiCl and DBSA + 0.15M KCl, a constant value of equilibrium surfactant concentration is not clearly observed. The presence of NaCl electrolyte has shown maximum adsorption, hence DBSA with 0.15M NaCl is chosen for adsorption process. In the admicellar polymerization, the concentration of surfactant was kept just below or

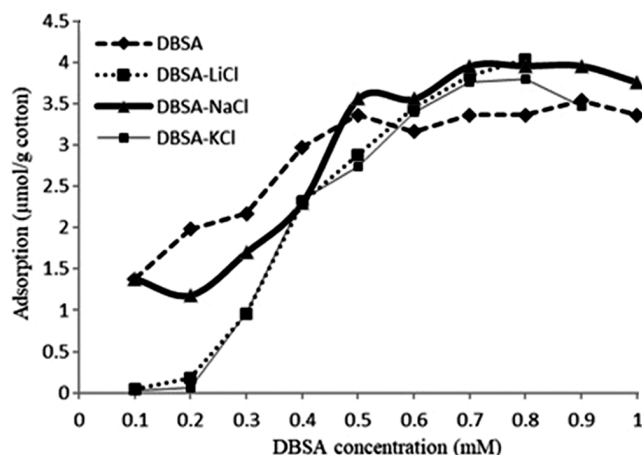


Fig.1 — Adsorption isotherm on cotton fabric of DBSA and DBSA containing 0.15 M electrolytes (LiCl/NaCl/KCl)

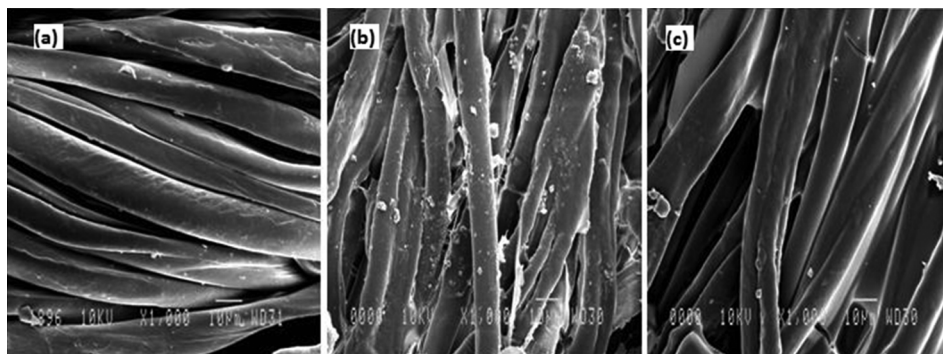


Fig. 2 — SEM images of (a) UCF, (b) TCF and (c) TCF-1 at $10\mu\text{m}$ ($\times 1000$)

near its CMC to ensure significant coverage. Surfactant concentrations above CMC are not recommended because emulsion polymerization may occur in aqueous phase¹⁸. Therefore, from the adsorption isotherm, a concentration of 0.55 mM DBSA which is near the CMC is chosen for the admicellar polymerization reaction.

3.2 Surface Characterization of MPC-Treated Cotton Fabrics

3.2.1 FTIR Studies

FTIR spectra has been used to characterize untreated (UCF), treated (TCF) and treated cotton after first home laundering (TCF-1). The spectrum of UCF consists of following bands: 3422 cm^{-1} (O–H str.), 2902 cm^{-1} (C–H str.), 1434 cm^{-1} (CH_2 symmetrical bending), 1319 cm^{-1} (C–H and O–H bending), 1157 cm^{-1} (C–O–C antisymm. str.) and 1035 cm^{-1} (C–O str.). These are characteristics band of cellulose¹⁹. In TCF, additional bands at 1720 cm^{-1} (C=O str.), 1258 cm^{-1} (P=O str.)²⁰ and 1078 cm^{-1} (P–O–C str.) are seen. These additional bands indicate that a layer of phosphorus based polymer is formed on cotton fabric. In TCF-1, a band at 1258 cm^{-1} (P=O str.) remains intact with the bands of cellulose. But a band at 1078 cm^{-1} (P–O–C str.) is not seen indicating removal of some phosphorus content from fabric after first home laundering.

3.2.2 SEM Studies

SEM microphotograph [Fig. 2(a)] of UCF shows clean and smooth surface. SEM micrograph [Fig. 2(b)] shows the presence of polymer film on the treated cotton fabric in case of TCF. This also indicates that the polymer film is ultra thin since the fine structure of untreated surface is still visible on treated fibre surface. The surface of TCF-1 [Fig. 2(c)] is appeared smooth as compared to treated cotton fabric but not as smooth as untreated cotton fabric, indicating that some polymer remains on the surface of cotton fabric.

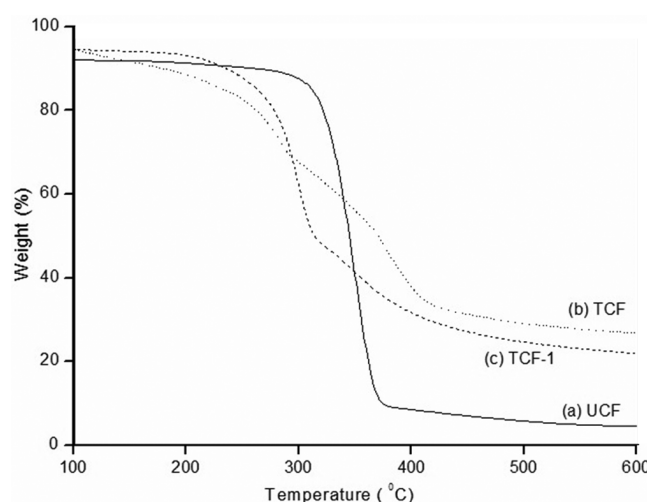


Fig. 3 — TG curves of (a) UCF, (b) TCF and (c) TCF-1 cotton fabric samples in nitrogen atmosphere

3.3 Thermal Analysis

TG and DTG curves of UCF, TCF and TCF-1 are shown in Fig. 3. TG curve of UCF shows only one stage of thermal degradation in temperature range 100–600 °C with weight loss 87.5% in nitrogen atmosphere. On heating cotton fabric, the weight loss occurs due to dehydration and decomposition process through random chain scission, leading to the formation of major volatile product mainly levoglucosan. TG curve of TCF shows two stages of thermal degradation. The first stage (100–330 °C) of degradation of TCF with 33.5% weight loss occurs due to catalysed dehydration, phosphorylation and then dephosphorylation of phosphorylated cotton. The second stage (330–600 °C) of thermal degradation with weight loss of 34.2% occurs due to degradation/pyrolysis of carbon rich residue. The onset temperature ($T_{10\text{wt}\%}$) of TCF is decreased by 37 °C due to acid catalysed dehydration²¹ by phosphoric acid released from decomposition of phosphorous based polymeric flame retardant, and

char yield is increased by 21.7% at 600 °C. This exhibits a typical condensed phase flame retardant activity due to the presence of phosphorous element, leading to higher char yield at the cost of volatile products. TG curve of TCF-1 shows one stage (100-600 °C) similar to the UCF giving rise to less flame retardant action which indicates that some amount of polymeric film is washed away after home laundering.

3.4 Flammability Behaviour

3.4.1 Auto Flammability Test

The auto flammability test of TCF, TCF-1, TCF-B and TCF-B1 samples was carried out at the same ignition time of 1 s and their images are shown in Fig. 4. For UCF, after removing the ignition source, the flame spreads quickly and burned the entire fabric with no residue within 11.8 s. In case of TCF, the flame self-extinguishes leaving a spot of char of length of 2.2 cm as shown in Table 1. In case of treated cotton fabric after home laundering (TCF-1), the flame self-extinguishes leaving a spot of char of length of 9.4 cm. The treated cotton fabric with binding agent (TCF-B) and treated cotton fabric after first home laundering (TCF-B1) show improved results having further reduced spots of char of length of 1.2 cm and 3.6 cm respectively. This shows some of the phosphorous polymer remains on cotton surface

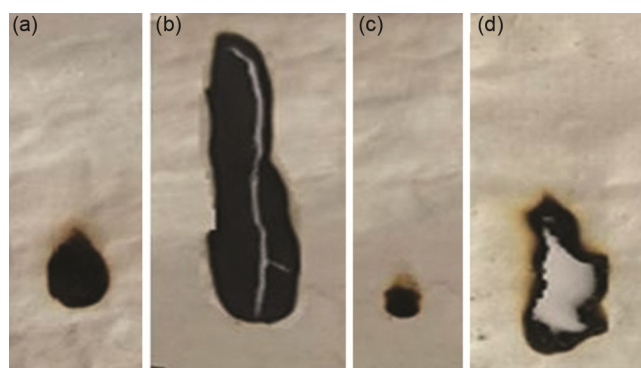


Fig. 4 — Burning behaviour of (a) TCF, (b) TCF-1, (c) TCF-B and (d) TCF-B1 cotton fabric samples after auto flammability test

even after laundering. Improvement in flame retardancy of treated cotton fabric indicates successful coating on cotton fabric by admicellar polymerization of phosphorous based monomer (MPC). The better flame retardancy of treated cotton fabric samples can be explained by the formation of protective barrier layer of char on the surface of cotton fabric during burning process which acted as shield to cotton and prevented it from fire.

3.4.2 Limiting Oxygen Index (LOI)

LOI value for UCF is 18.0 %, which is increased to 24.5 % for TCF and 23.0 % for TCF-1. LOI value is further increased slightly up to 25.5 % with use of binding agent (Table 1). This indicates that polymer layer formed on cotton fabric has provided good flame retardancy even after first home laundering.

3.5 Air Permeability and Stiffness Measurement

Table 1 shows the slight decrease in air permeability value of UCF from 200 m³/m²/min to 191.7 m³/m²/min for TCF and to 186.1 m³/m²/min for TCF-B. There is slight increase in fabric stiffness from value 2.0 cm (UCF) to 2.8 cm (TCF) and to 3.0 cm (TCF-B). Therefore, the coated film is found quite flexible and with good air permeability even after adding binding agent and also after first home laundering.

3.6 Effect of Phosphorous content on Flammability Behaviour and Durability

The amount of phosphorous containing polymeric film on treated cotton fabric is responsible for char formation and to make cotton fabric flame retarded. In this work, the amount of polymeric film coated on treated fabric is determined by its phosphorous content. Phosphorous content of the treated fabric is increased linearly as the monomer concentration is increased from 25 mM to 125 mM, and the amount of polymeric film on cotton surface is increased more linearly with the use of 3.6 mM/g binding agent (Table 2). More monomer can partition into the admicelle on increasing the concentration of monomer which reacts to form additional polymer.

Table 1 — Flammability test, air permeability and stiffness data for cotton fabric samples

Sample	Flame spread time, s	Char length, cm	Pass/Fail	LOI, %	Air permeability, m ³ /m ² /min	Stiffness, cm
UCF	11.8	BL	Fail	18.0	200.0	2.0
TCF	SE	2.2	Pass	24.5	191.7	2.8
TCF-1	SE	9.4	Pass	23.0	194.5	2.3
TCF-B	SE	1.2	Pass	25.5	186.1	3.0
TCF-B1	SE	3.6	Pass	24.5	190.0	2.6

SE –Self-extinguished, BL –Burn entire length.

Table 2 — Effect of monomer concentration and binding agent on flame retardancy and durability of cotton fabric

Monomer conc. mM	Treated cotton fabric			1 st home laundering		2 nd home laundering	
	Phosphorus content mg/g cotton	Flame spread time, s	Char length, cm	Flame spread time, s	Char length, cm	Flame spread time, s	Char length, cm
Without binding agent							
25	1.6	20.2	BL	—	—	—	—
50	2.5	32.6	BL	—	—	—	—
75	4.1	48.0	BL	—	—	—	—
100	5.5	SE	2.2	SE	9.4	58.4	BL
125	7.1	SE	1.5	SE	5.2	60.0	BL
With binding agent							
25	1.9	31.2	BL	—	—	—	—
50	3.0	59.6	BL	—	—	—	—
75	4.7	SE	5.8	60.2	BL	—	—
100	6.5	SE	1.2	SE	3.6	SE	8.0
125	8.2	SE	0.8	SE	2.5	SE	7.4

SE –Self-extinguished, BL –Burn entire length.

Therefore, this leads to increase in the amount of polymeric film on cotton surface. If the char length of treated cotton fabric in the auto flammability test decreases, the performance of cotton fabric improves. Table 2 shows that with increase in phosphorous content the char length is decreased, and with the use of binding agent at same amount of phosphorous content the char length is decreased more. In the absence of binding agent, the coating of polymer is not stable to home laundering and subsequent flame retardancy is poor. The treated cotton fabric becomes more durable to home laundering as the phosphorous polymer linkage to cotton fabric provides stronger adherence.

The phosphorous content of 4.7 mg/g cotton is the minimum phosphorous concentration required with binding agent to pass auto flammability test but it is not durable to washing. The treated cotton fabric having phosphorous content of 6.5 mg/g cotton with binding agent self-extinguishes in flammability test, which is durable upto two home laundering.

4 Conclusion

The formation of polymer film on cotton fabric with good air permeability using an anionic surfactant by admicellar polymerization is carried out successfully. FTIR and SEM indicate the presence of phosphorous based polymer layer on cotton fabric. In TG study, the onset temperature of degradation of treated cotton fabric is decreased by 37 °C in comparison to untreated cotton fabric due to acid catalysed dehydration by phosphoric acid released from decomposition of phosphorous based polymeric

flame retardant. The char yield is increased by 21.7 % at 600 °C in inert atmosphere. The auto flammability test shows that treated cotton fabric having phosphorous content of 6.5 mg/g cotton with binding agent self-extinguishes in flammability test which is also durable upto two home laundering.

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