

# FLAME RETARDANCY OF COTTON FABRIC: EFFECT OF COATING OF POLYMERIC FILM CONTAINING PHOSPHORUS BY ADMICELLAR POLYMERIZATION

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## ABSTRACT

The vinyl phosphonic acid a phosphorus-based monomer has been polymerized on the cotton fabric with the aid of a cationic surfactant and 2, 2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA) an initiator with the aim to improve flame retardancy of fabric for the fire safety. The thermal and burning behaviour of treated fabric are studied using thermogravimetry (TG) and limiting oxygen index flammability test (LOI), respectively. This treatment alters the path of degradation of treated cotton fabric sample (CF-PVPA-3) having 1.2% phosphorus, which increased the carbonaceous residue up to 28.2% at 600°C in an inert atmosphere at the expense of flammable products. The LOI value of 28.5 % of treated cotton fabric indicates the attainment of flame retardant property.

**Keywords:** Admicelle, Cotton, Flame-Retardancy, Polymerization, TG.

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## INTRODUCTION

Cotton fabric is the most common and valuable natural textile because of its good strength, high moisture absorbency, and aesthetic value. The textile materials having high surface area are considered the main cause of fire accidents in hot and dry environments. Therefore, the development of flame-retardant cotton fabrics becomes necessary to improve human safety and minimize property losses under many circumstances.<sup>1,2</sup> The Proban and Pyrovatex, two trademarked flame-retardant products, are available at present for cotton fabric and its blends.<sup>3</sup> There are some disadvantages of developed methods such as pad-dry-cure<sup>4</sup>, chemical modification<sup>5</sup>, ionized radiation and plasma graft polymerization<sup>6,7</sup> due to the deteriorating of tensile strength, moisture regains, and stiffness properties of the fiber. In recent years, the focus is on the possibility of formulating environmentally friendly, cost-effective and efficient systems to improve flame retardancy of textile materials. Formation of thin flame-retardant polymeric film on the fibre surface can improve the flame-retardant properties while retaining other important properties of fabric. Admicellar polymerization is a process to form thin layer on fibre surface<sup>8</sup> by physically adsorbed surfactants known as admicelles. The admicelle creation, adsolubilization of monomer and then admicellar polymerization are the three steps to obtain thin polymer layer on the fabric. The coating of very thin polymeric film on several types of substrates such as polystyrene on aluminium<sup>9</sup>, cotton<sup>10</sup> and glass fibres<sup>11</sup>, PTFE on alumina<sup>12</sup>, poly (methyl methacrylate) on polyester<sup>13</sup> and other polymeric films on cotton<sup>14,15</sup> has been carried out by admicellar polymerization for several purposes. In this study, phosphorus based monomer has been polymerized on the cotton using admicellar polymerization method with the aid of cationic surfactant. The thermal stability and flammability behaviour of treated cotton fabric were studied.

## EXPERIMENTAL

### Materials

Vinyl phosphonic acid as monomer, N-hydroxyl methyl acrylamide solution as binding agent, 2, 2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA) and SnCl<sub>2</sub> were procured from Sigma Aldrich (India). Ammonium molybdate and (CH<sub>3</sub>)<sub>2</sub>CHOH from Qualigens; H<sub>2</sub>O<sub>2</sub> (30%) and H<sub>2</sub>SO<sub>4</sub> from Fisher Scientific, hydrochloric acid and diethyl ether were purchased from CDH Chemicals, India. Cetyltrimethylammonium bromide (CTAB) was bought from Himedia Chem., India. Absolute ethyl alcohol was purchased from Molychem, India. Cotton fabrics (110 g/m<sup>2</sup>) was procured from Amartex

Industries Ltd. (India) with specification: warp count-2/30 Ne, weft count 2/30 Ne, GSM-200, end per cm-22.05, pick per cm-20.47. Cotton fabric selected for the coating purpose consists about 10% polyester. These commercial materials were used as received.

### Adsorption Isotherm

Adsorption isotherm of CTAB was carried out using UV-VIS spectrophotometer by exposing a 16×5 cm fabric to 30 mL solution of the surfactant. A surfactant adsorption isotherm was obtained by plotting a graph between concentration of adsorbed surfactant and supernatant concentration. In this method, pieces of cotton fabric samples of weight about 1.84 g each were submerged in 30 mL solutions of surfactant in vials. In a 32 mL vial, the adsorption was permitted to occur at 30°C for 15 h. After 15 hour, cotton samples were put out from each vial and then absorbance of treated and untreated sample was measured using UV-VIS spectrophotometer at 289 nm an experimentally observed maxima. The adsorbed surfactant was plotted against CTAB concentration in the supernatant to obtain isotherm. The 0.8 mM conc. of CTAB just below CMC was noted in isotherm for further process.

### Admicellar Polymerization

The polymerization of vinyl phosphonic acid monomer on cotton was conceded using 0.8 mM CTAB solution in water with varying vinyl phosphonic acid concentrations using an AIBA initiator. 1.84 g fabric of 16×5 cm size was taken in a 32 mL vial having 30 mL a CTAB solution. Vinyl phosphonic acid (0.30 mM) and the AIBA initiator (0.30 mM) were taken in glass tube (vial). The sealed glass tubes were shaken for 15 hours at 30°C to permit for admicelle formation and monomer adsolubilization into admicelle. After that, the temperature of system was elevated to 80°C for 24 hours to start and finish the polymerization reaction. Then vials were cooled down to ambient temperature after the completion of process. The sample was then removed from vial and rinsed with hot distilled H<sub>2</sub>O to eliminate any remaining labile CTAB. The fabric was air-dried before being dried in a 60°C oven overnight. Various cotton fabric samples were prepared taking different monomer concentrations in the range from 0.30 to 0.43 mM with or without a binding agent (N-(hydroxymethyl) acrylamide). The description of the samples is given in Table-1.

### FTIR and SEM Tests

To analyse the untreated cotton fabric (CF-Control) and cotton fabric treated with PVPA, FTIR spectra were taken using a Shimadzu IR affinity-I FTIR spectrometer. FESEM (7610F Plus/JEOL) with a beam voltage of 20 kV was used to perform morphological analysis on cotton fabric samples sputtered with fine layer of gold.

### Phosphorous Content Determination

The fabric sample (0.1 g) was digested with 2 mL of concentrated sulphuric acid. Then 10 mL of H<sub>2</sub>O<sub>2</sub> (30%) was added to the solution and agitated with a stirrer on a hot plate for one hour. It was then shifted to a 50 mL flask as a clear viscous solution and diluted with distilled H<sub>2</sub>O. The solution was then analysed at 690 nm using a UV Spectrophotometer (Varian Cary 5000). Phosphorus content in per cent was measured of the untreated and treated cotton fabrics (Table-1).

Table-1: Description of Cotton Fabric Samples

Sample	Monomer conc. (mM)	Binding Agent	P (%)
CF-Control	-	-	-
CF-PVPA-1	0.30	Nil	0.46
CF-PVPA-2	0.37	Nil	0.77
CF-PVPA-3	0.43	Nil	1.21
CF-PVPA-1B	0.30	Yes	1.18
CF-PVPA-2B	0.37	Yes	1.72
CF-PVPA-3B	0.43	Yes	2.67

### TG Test

The thermogravimetry (TG) under nitrogen gas flow (100 mL/min) of CF-Control and various treated cotton fabric (CF-PVPA) samples was performed using a TA Instruments DSCQ10 (DSC Thermal Analyzer) by placing 8-10 mg of samples in alumina crucibles. The samples were tested by heating at a rate of 10°C/min from ambient temperature to 600°C.

### Limiting Oxygen Index Test

The Limiting Oxygen Indexer equipment was used to analyse the oxygen index (LOI) of cotton fabric samples as per the ASTM D 2863 standard. For treated and untreated cotton samples of 150x50 mm size, LOI values in volume percent were measured. The cotton sample was lit from upper end and oxygen was controlled until the sample just support burning.

## RESULTS AND DISCUSSION

The quantity of surfactant (CTAB) adsorption (0.8 mM of equilibrium surfactant concentration at 30°C) attained a constant value, which is considered critical micelle concentration. The conc. of CTAB during polymerization is kept below its critical micelle concentration (CMC) value to have extensive coverage on the surface.

### FTIR Test

FTIR spectra (Fig.-1) was carried out to characterize untreated (CF-Control), and treated (CF-PVPA-3B). The spectrum of untreated cotton fabric comprises the bands: 3425  $\text{cm}^{-1}$  (O-H stretching), 2964-2856  $\text{cm}^{-1}$  (C-H stretching), 1410  $\text{cm}^{-1}$  ( $\text{CH}_2$  symmetrical bending), 1340 and 1244  $\text{cm}^{-1}$  (O-H bending), 1096  $\text{cm}^{-1}$  (anti symmetrical bridge C-O-C stretching and in phase, ring stretching), 1016  $\text{cm}^{-1}$  (C-O stretching). Such bands are the feature bands of cotton.<sup>16,17</sup> Polyester moiety in cotton fabric causes an additional band at 1718  $\text{cm}^{-1}$  (C=O str.). Due to overlapping with typical bands of OH deformation (primary and secondary) of cotton seen at 1340, 1244, and 1096  $\text{cm}^{-1}$ , identifying the existence of phosphorus bands is challenging.

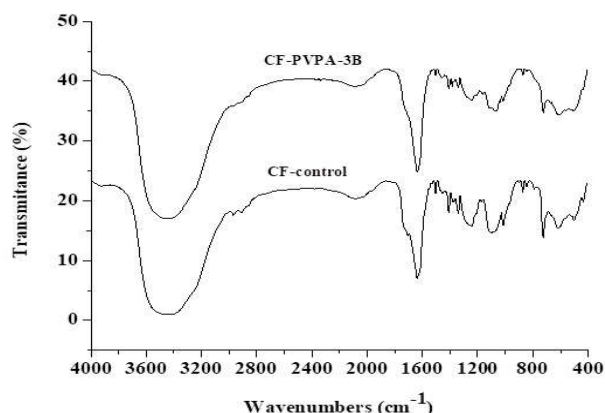


Fig.-1: Characterization of CF-Control and CF-PVPA-3B using FTIR Test

### SEM-EDS Test

SEM-EDS analysis was carried out to investigate the morphology of untreated and treated fabrics. SEM microphotographs of (A) CF-PVPA-3, (B) residue of CF-PVPA-3 at 200°C and (C) residue of CF-PVPA-3 at 300°C are shown in Fig.-2 as a representative. Sample residues were obtained by heating the samples for 10 minutes at 200, 250, and 300°C. SEM images of CF-control shows clean and smooth surface. SEM images of residues of all samples obtained at 200°C show intact fibre without any damage and morphology remains intact. SEM micrograph of CF-PVPA-3 (Fig.-2A) shows the presence of homogeneous coating of polymeric film on the treated cotton fabric and adjoining of the fibres. The presence fine structure of untreated surface also indicates that the coated polymeric film is very thin. SEM images of residue of treated samples formed at 250°C reveals that polymeric material at surface and polyester part of fabric got melted and encapsulated the fibres along with twisting and unfolding of fibres. The SEM images of residue of samples (Fig.-2C) at 300°C show the intensive damage with broken fibres. The increase of P element

content (wt%) observed in SEM-EDS on heating the treated cotton fabric samples indicates that the PVPA a phosphorus based FR acts by condensed phase mechanism.

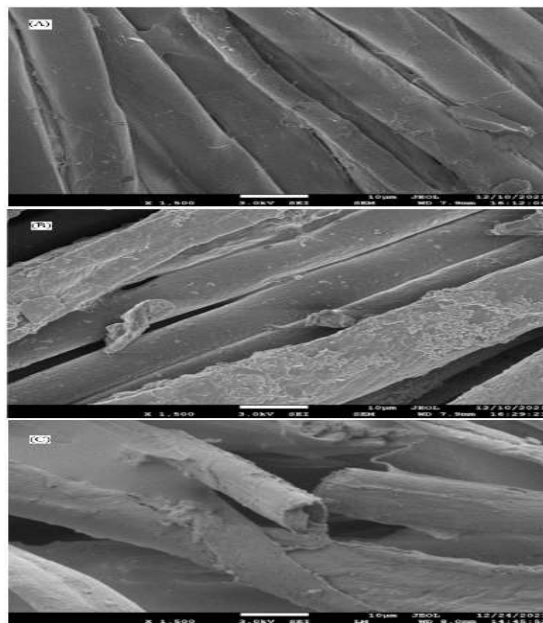


Fig.-2: Characterization of (A) CF-PVPA-3, (B) Residue of CF-PVPA-3 at 200 °C and (C) Residue of CF-PVPA-3 at 300 °C using FESEM Test

### Thermal Studies

TG curves of CF-Control, CF-PVPA-2, CF-PVPA-2B and CF-PVPA-3B as a representative are shown in Fig.-3. TG curves CF-Control and treated samples with PVPA show two steps of thermal degradation in nitrogen atmosphere. On heating cotton fabric control under inert gas flow, the mass loss happens owing to dehydration, chain scission randomly and decomposition resulting in generation of significant volatile product namely levoglucosan leaving 6.1% carbonaceous residue at 600°C. Table-2 reveals that TG curves of samples of CF treated with PVPA without binding agent show early start of degradation of cellulose by about 50 °C because of dehydration catalysed by  $H_3PO_4$  acid generated from PVPA.<sup>18</sup> This treatment alters the path of degradation of CF-PVPA-3, which increased the carbonaceous residue up to 28.2% at 600°C at the expense of vaporizable compounds. TG thermogram of CF-PVPA-3B sample using binding agent show the decrease in onset temperature ( $T_{10wt\%}$ ). This is due to phosphoric acid catalysed dehydration resulting from the disintegration of PVPA coated film. For this sample, the higher char yield (33.6% at 600°C) demonstrates a condensed phase flame retardant action owing to existence of phosphorous, which results in more carbonaceous residue. The DTA data of the cotton control and coated cotton samples is given in Table-2. The endothermic peak at 330°C is attributed to dehydration of cellulose and beginning of decomposition of cotton. The next broad endothermic peak at 385°C is attributed to the major decomposition of cotton cellulose corresponding to second step of degradation in TG curve where major weight loss occurs. The small endothermic peak at 252 and 48 °C are attributed to the melting and decomposition of polyester a minor part (about 10%) in cotton fabric. Table-2 reveals that the second major endothermic DTA peaks of treated cotton fabric samples corresponding to major step of degradation is lowered due to action of flame retardant with increase of carbonization resulting in higher non-flammable residue.

### Effect of Phosphorous Content on LOI

The concentration of oxygen in volume percent was adjusted in LOI experiment until the sample just sustain the burning. The LOI value for CF-Control is 18.5%, but it rises to 28.5% for CF-PVPA-3, which contains 1.21% phosphorus. With the addition of a binding agent, the LOI value for the CF-PVPA-3B sample with 2.67% phosphorus content was enhanced to 36.0% (Table-2). This means that as the phosphorus content increases, the higher the LOI value, the stronger the material's flame resistance. The presence of

phosphorous in polymeric film coated on fabric causes the development of carbonaceous residue by reducing the flammable volatile compounds. Phosphorous amount of the surface of treated fabric is observed in increasing order linearly with the increase of monomer concentration from 0.30 to 0.43 mM. Because of transfer of more monomers into the admicelle available at surface of fabric. Therefore, this leads to increase in LOI value and flame retardancy.

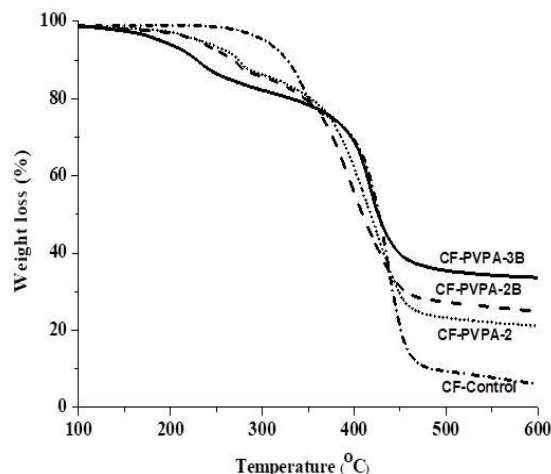


Fig.-3: Characerization of CF-Control, CF-PVPA-2, CF-PVPA-2B and CF-PVPA-3B in Nitrogen Atmosphere using TG Test

Table-2: TG, DTA, and LOI Values of Cotton Fabrics in Inert Atmosphere

Sample	Stage with Temp.(°C)	Weight loss (%)	DTG (°C)	T <sub>10%</sub> (°C)	Residue at 600°C(%)	DTA Endo(°C)	LOI (%)
CF	100-370 370-600	23.4 69.2	346 440	327	6.1	252 330 385, 483	18.5
CF-PVPA-1	100-320 320-600	19.2 61.9	278 437	275	18.2	257 350 472	24.0
CF-PVPA-2	100-315 315-600	13.5 63.9	277 415	274	21.1	256 355 476	26.0
CF-PVPA-3	100-320 320-600	13.9 57.2	265 398	264	28.2	258 350 482	28.5
CF-PVPA-1B	100-320 320-600	13.7 65.5	276 425	274	19.5	256 355 476	27.6
CF-PVPA-2B	100-320 321-600	14.8 59.1	275 400	268	24.8	256 355 476	30.5
CF-PVPA-3B	100-306 306-600	18.1 47.2	231 420	228	33.6	256 383, 407 466	36.0

## CONCLUSION

With the help of a cationic surfactant, the monomer (vinyl phosphonic acid) was successfully polymerized on the cotton fabric using the admicellar polymerization process to improve fabric flame retardancy for fire safety. SEM demonstrated the existence of polymeric film on fabric. Thermal study shows that the treatment alters the path of degradation of treated cotton fabric sample (CF-PVPA-3) having 1.2% phosphorus with the increase the carbonaceous residue up to 28.2% at 60°C in inert atmosphere at the expense of volatile

products. The limiting oxygen index value of treated cotton fabric is increased to 28.5%, which demonstrates the attainment of flame retardant property.

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