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Admicellar Polymerization of *Tris*(2-acryloyloxyethyl)phosphate on Cotton Fabric for Flame Retardant Finishing

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To improve the flame retardant property, the admicellar polymerization process was applied to polymerize and coat the *tris*(2-acryloyloxyethyl)phosphate (PTAP) monomer on cotton fabric (CF). The polymerization was completed with the support of a cationic surfactant cetyltrimethylammonium bromide (CTAB) and an initiator 2,2′-azobisisobutyronitrile (AIBN). Thermogravimetric analysis (TGA) and limiting oxygen index test (LOI) were performed to find out the effects on degradation and flammability of modified cotton fabric. One of the modified cotton fabric samples (CF-PTAP) show the decrease in onset temperature caused by acid catalyzed dehydration released from PTAP polymer placed on cotton fabric substrate. The increase in char yield (20.9%) and LOI value (25.0% demonstrated a condensed phase flame retardant action) owing to the presence of PTAP polymer on substrate.

Keywords: Admicelle, Initiator, Cotton, Thermal analysis, Binding agent, Surfactant.

INTRODUCTION

Cotton fabric is the most common and valuable natural textile because of its good strength, high moisture absorbency and appealing value. The textile materials including cotton fabric being organic in nature and having high surface area are thermally degradable and burn easily on heating. Therefore, to increase their wide applicability and safety, many methods [1-5] have been developed in past to modify the textile material to enhance their flammability behaviour.

In recent years, the attention is on the possibility of formulating cost effective, environmentally friendly and efficient systems to improve flame retardancy of textile materials without changing moisture regain, stiffness and other properties of the fibres. A technique known as admicellar polymerization in which a thin polymeric film on fibre surface can be formed by physically adsorbed surfactants of micelle-like surfactant aggregates (admicelles) at a solid substrate [6]. Three-step procedure for forming a thin film on a solid substrate includes the production of admicelles, adsolubilization of monomers in the admicelle and then polymerization *in situ*. The method is said to be quite adaptable and can be used on a number of surfaces. Various applications for the films created by this process have been proposed [7-12].

In this research, formation of a poly *tris*(2-acryloyloxyethyl)phosphate film on cotton fabric has been studied using cationic surfactant. The thermogravimetry analysis (TGA) and limiting oxygen index test (LOI) were performed to see the effects on degradation and flammability of modified cotton fabric.

EXPERIMENTAL

Tris(2-acryloyloxyethyl)phosphate as monomer was synthesized using phosphorous oxychloride, *N*-hydroxyl methyl acrylamide solution as binder, (2,2′-azobisisobutyronitrile) (AIBN), triethylamine, 2-hydroxyethyl acrylate and $SnCl_2$ were from Sigma Aldrich (India). Cetyltrimethylammonium bromide (CTAB), cuprous chloride and Na_2SO_4 were procured from Himedia Chemicals (India). Hydrogen peroxide (30%), H_2SO_4, HCl and diethyl ether were purchased from CDH Chemicals, India. Absolute ethyl alcohol was purchased from Molychem, India. Cotton fabrics with specification: density: 110 g/m^2, warp count: 2/30 Ne; weft count: 2/30 Ne; GSM: 200; end per cm: 22.05; pick per cm: 20.47 was received from Amartex Ind. Ltd. (India) and consists of ~10% polyester. These materials were used as received.

Adsorption isotherm: Cotton fabric samples weighed ~1.8 g were submerged in 30 mL surfactant solutions in a 32 mL vial for 15 h at about 30 ºC. The absorbance of the treated

and untreated samples was evaluated using a UV-VIS spectrophotometer at 290 nm, which was an experimentally observed maximum. The critical micelle concentration value of 0.8 mM of CTAB was observed.

Synthesis of *tris*(2-acryloyloxyethyl)phosphate: *Tris*(2-acryloyloxyethyl)phosphate was synthesized by the reported method [13,14]. In brief, diethyl ether (280 mL) containing 2-hydroxyethyl acrylate (23 mL, 0.2 mol) was taken in 1 L round bottomed flask consisting $CaCl_2$ drying tube followed by the addition of 30 mL of triethylamine (TEA) and 0.332 g of Cu_2Cl_2. Then, a mixture of $POCl_3$ (6.1 mL, 0.066 mol) and 30 mL diethyl ether was added dropwise at 0 ºC over a period of 1 h while magnetically agitated and left for 48 h at room temperature. The triethylamine hydrochloride salt was filtered out and the filtrate was washed with ice-cold water in the separating funnel and then dried over Na_2SO_4. A yellowish viscous liquid of *tris*(2-acryloyloxyethyl)phosphate was obtained with 79% yield after removing the ether under vaccum (**Scheme-I**). FTIR (KBr, ν_{max}, cm^{-1}) = 3109-3039 ($H_2C = CH_2$), 1727 (C=O), 1639-1636 (C=C), 1457-1370 (CH_3), 1272 (P=O), 1195 (P-O-C_2H_5), 1030-985 (P-O-C). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.46 (dd, 3H, *cis* to carbonyl, *J* = 1.32 Hz); 6.15 (dd, 3H, *trans* to carbonyl, *J* = 10.44 Hz); 5.89 (dd, 3H, $=CH_2$, *J* = 1.32 Hz); 4.37-4.41 (m, 6H, OCH_2); 4.28-4.32 (m, 6H, CH_2) ppm.

Admicellar polymerization: The polymerization of *tris*-(2-acryloyloxyethyl)phosphate monomer on cotton substrate was performed using an 0.8 mM CTAB solution with monomer varying concentration using AIBN initiator. The *tris*(2-acryloyloxyethyl)phosphate (0.15 M), CTAB (0.8 mM) and AIBN initiator (0.015 M) were taken into the vial of 32 mL capacity making upto 30 mL aqueous solution in vial. A cotton fabric sample (16 × 5 cm) weighing 1.84 g was placed in the vial. The vials were taped up, then shaken at 30 °C for 15 h to permit for admicelle formation and to transfer monomer into the admicelle. The polymerization was completed by keeping the system at 80 ºC for a day to obtain film of *tris*(2-acryloyloxyethyl)phosphate on the cotton fabric (CF-PTAP). The fabric was cooled, washed with hot distilled water and then dried. Another cotton fabric sample was also prepared using *N*-(hydroxymethyl)acrylamide binding agent (CF-PTAP-B).

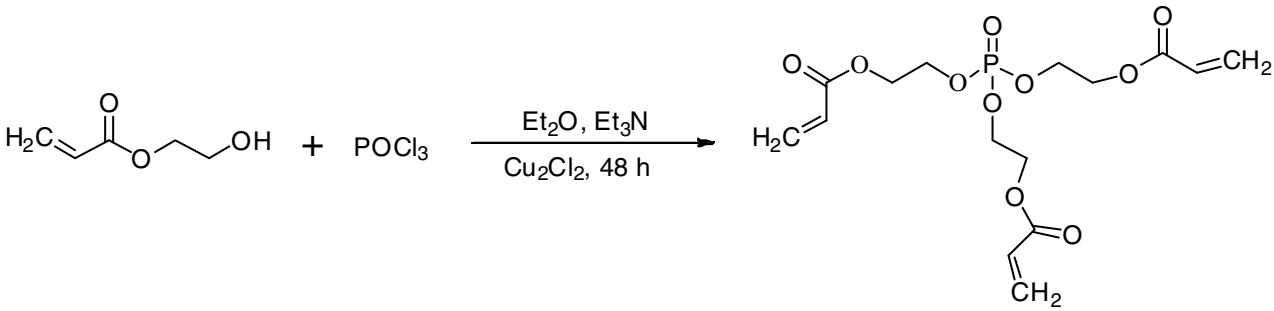
Characterization: FTIR spectra were carried out using Shimadzu IR affinity-I FTIR spectrometer in the range 4000-400 cm^{-1} to characterize the untreated cotton fabric (CF) and treated cotton fabrics (CF-PTAP and CF-PTAP-B). Morphological analysis of cotton fabric samples was carried out by FESEM (7610F Plus/JEOL) with a beam voltage of 20 kV. For SEM analysis, the fabric samples were sputtered with a thin layer of gold. Phosphorus content in per cent (Table-1) was measured of treated cotton fabric samples using UV Spectrophotometer (Varian cary 5000) at 690 nm as per reported procedure [15]. The CF-PTAP and CF-PTAP-B samples give 1.62 and 2.34% of phosphorus, respectively.

Thermal analysis: Thermogravimetric (TGA) analysis of cotton fabric (CF) and treated cotton fabric (CF-PTAP and CF-PTAP-B) samples was executed using TA Instruments DSCQ10 (Differential Calorimeter TA) by taking about 8-10 mg of samples in alumina crucibles under continuous N_2 flow of 100 mL/min from room temperature to 600 ºC at a heating rate of 10 ºC/min.

Limiting oxygen index test: Limiting oxygen index (LOI) analysis of the fabric samples was performed using Limiting Oxygen Index instrument as per ASTM D 2863 standard. The LOI values in volume percent were measured for fabric samples of 150 mm × 50 mm size. The oxygen concentration was adjusted until the specimen just support combustion.

RESULTS AND DISCUSSION

Adsorption isotherm: Surfactant concentrations exceeding CMC are not recommended to surety substantial coverage



Scheme-I: Synthesis of *tris*(2-acryloyloxyethyl)phosphate

TABLE-1
TGA AND FLAMMABILITY DATA OF COTTON FABRICS IN N_2 ATMOSPHERE

Sample	Phosphorus (%)	Temp. range (°C)	DTG (°C)	$T_{10\%}$ (°C)	Char yield (%)	LOI (%)
Cotton fabric (CF)	–	100-370 370-600	346 440	327	6.1	18.5
CF-PTAP	1.62	100-225 225-320 320-600	266 413	250	20.9	25.0 (22.8)
CF-PTAP-B	2.34	100-375 375-600	330 435	325	24.0	28.5 (26.2)

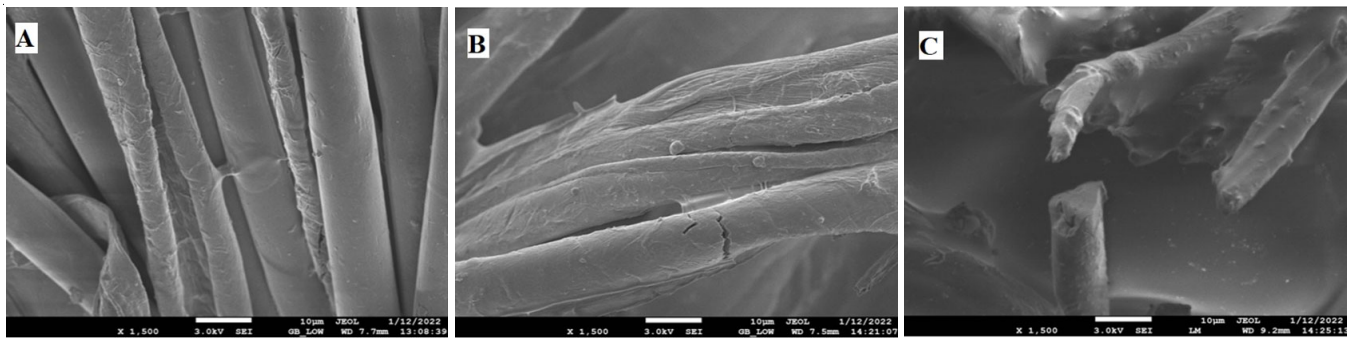


Fig. 1. SEM images of CF-PTAP (A) and residues of CF-PTAP at 250 °C (B) and 300 °C (C) at X1500 magnification

and avoid emulsion polymerization in the aqueous phase. At 0.8 mM of equilibrium surfactant concentration at 30 ºC, the amount of CTAB surfactant adsorption reached a constant value, which was considered as critical micelle concentration (CMC).

^{1}H NMR studies: The ^{1}H NMR spectrum of *tris*(2-acryloyloxyethyl)phosphate shows multiplet of methylene proton α to –O–P(=O) and β to –OC(C=O) at 4.28 to 4.32 ppm and multiplet of methylene proton α to –OC(C=O) and β to –O-P(=O) at 4.37 to 4.41 ppm and shows three doublet of doublets due to acrylate groups at 5.89, 6.15, 6.46 ppm.

SEM-EDS studies: SEM-EDS analysis was carried out to investigate the morphology of untreated and treated fabrics. SEM micrographs of CF-PTAP, residue of CF-PTAP at 250 ºC and residue of CF-PTAP at 300 ºC are shown in Fig. 1. The residues of samples were obtained by heating the samples at 200, 250 and 300 ºC for 10 min. The surface of the CF is clean and smooth as observed from the SEM images. SEM image of CF-PTAP (Fig. 1a) shows the presence of homogeneous coating of polymeric film on the treated cotton fabric and adjoining of the fibres. SEM images of the residues of all samples obtained at 200 ºC show intact fibre without any damage and morphology remains intact except some swelling of fibre. The fine structure of the untreated surface is still evident on the treated fibre surface, indicating that the polymeric layer is ultrathin. The coated polymeric film is also clearly visible on heating the sample at 200 ºC. SEM images of residue of treated samples formed at 250 ºC (Fig. 1b) reveals that the polymeric material at surface and polyester part of fabric got melted and encapsulated the fibres alongwith unfolding, twisting and furious of fibres. SEM images of the residue of samples (Fig. 1c) at 300 ºC show the severe damage with shattered fibres. An increase in the phosphorus element content (wt.%) observed in SEM-EDS on heating the treated cotton fabric samples indicates that the PTAP a phosphorus based flame-retardant acts by condensed phase mechanism.

FTIR studies: FTIR spectra (Fig. 2) was obtained to characterize untreated (CF), treated (CF-PTAP and CF-PTAP-B). The spectrum of cotton (CF) shows bands at 3425 cm^{-1} (O–H *str.*), 2964-2856 cm^{-1} (C–H *str.*), 1414 cm^{-1} (CH_2 sym. bending), 1347 and 1254 cm^{-1} (O–H bending), 1096 cm^{-1} (broad band, asym. bridge C–O–C *str.* and in phase ring *str.*), 1016 cm^{-1} (C–O *str.*) [16,17]. Additional band at 1720 cm^{-1} (C=O *str.*) is due to polyester moiety in cotton fabric is also seen. In case of spectra of sample of fabric coated with polymeric film

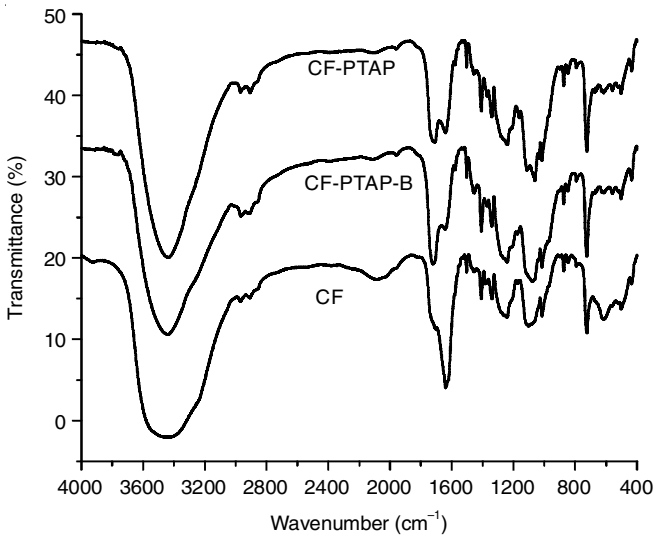


Fig. 2. FTIR spectrum of cotton fabric and treated fabric samples

(CF-PTAP), a band at 1728 cm^{-1} (C=O *str.*) becomes intensified, while at 1254 cm^{-1} (P=O *str.*) overlapped with O–H bending of cotton, appearance of a new band at 1076 cm^{-1} due to P–O–C *str.* indicates the presence of polymeric film on the cotton substrate.

Thermal studies: TGA thermograms of CF, CF-PTAP and CF-PTAP-B are shown in Fig. 3. TGA thermogram of CF and treated samples with PTAP show two steps of thermal degradation in nitrogen atmosphere. When cotton fabric (CF) is heated in an inert atmosphere, weight loss happens in two stages due to dehydration and decomposition *via* random chain scission [18], releasing a significant volatile substance mostly levoglucosan and leaving 6.1% carbonaceous residue at 600 ºC. TG thermogram of sample of CF treated with PTAP (CF-PTAP) containing 1.62% phosphorus shows start of weight loss of cellulose at early temperature by about 75 ºC due to phosphoric acid catalyzed dehydration, which is generated from the coated PTAP polymeric film. This treatment modifies the path of degradation of cotton in three stage weight loss, as result of which, the char is increased to 20.9% at 600 ºC, which is desirable and strategic to reduce the flammable volatile products.

TGA thermogram of CF-PTAP-B containing binding agent and 2.34 % phosphorus show two stage weight loss with DTG maxima at 330 and 435 ºC. The onset temperature ($T_{10wt\%}$) of degradation is not much affected due to the presence of binding

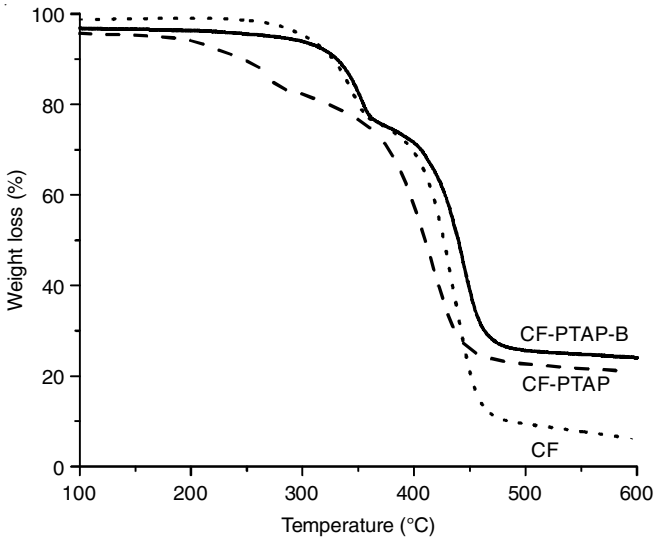


Fig. 3. TGA thermograms of CF, CF-PTAP and CF-PTAP-B in nitrogen atmosphere

agent. But at later stage of heating above 375 ºC, the condensed phase action of flame retardant is observed as the char is increased to higher value of 24.0% at 600 ºC.

The DSC endothermic peak at 356 ºC is attributed to the dehydration of cellulose and beginning of decomposition of cotton. The next broad endothermic peak at 447 ºC is attributed to the major decomposition of cotton cellulose as well as minor component of polyester corresponding to second step of degradation in TG thermogram where major weight loss occurs. The small endothermic peak at 258 ºC is attributed to the melting of polyester a minor component in cotton fabric.

LOI and durability: In the LOI experiment, the oxygen concentration was adjusted until the specimen just supported combustion. The LOI value in volume per cent for CF is 18.5, which is increased up to 25% for CF-PTAP sample without binding agent having 1.62% phosphorus content. The LOI value is further increased to 28.5% for CF-PTAP-B sample having 2.34% phosphorus content with the use of binding agent. This indicates that with the increase of phosphorus content, the higher the value of LOI the better is the flame resistance of the material. The durability of treated sample was also checked after carrying out one home laundry of both the treated samples and measuring their LOI value, which is decreased a little (Table-1). The amount of phosphorous containing polymeric layer on treated cotton fabric is responsible for enhancing char yield and flame retardant finishing.

Conclusion

To develop a cotton fabric flame-resistant, *tris*(2-acryloyloxyethyl)phosphate monomer was synthesized and successfully polymerized on the surface of cotton fabric *via* admicellar polymerization with the help of a cationic surfactant. The existence of polymeric coating on the fabric substrate was confirmed by SEM, FTIR and phosphorus content analyses. The treatment affects the course of degradation of treated cotton fabric sample (*e.g.* CF-PTAP-B) with 2.34% phosphorus by increasing the carbonaceous residue up to 24% at 600 ºC in N_2 environment at the expense of volatile compounds, as revealed from the thermal investigations. As compare to cotton fabric (18.5%), the limiting oxygen index value of treated cotton fabric has increased to 28.5%, indicating that flame-retardant finishing has been achieved.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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