Flame-retardant Cotton Fabric Through Graft Copolymerisation

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ABSTRACT

In an attempt to impart flame-retarding properties to the cotton fabric, post-grafting phosphorylation reactions on grafted cotton fabric were carried out. Photochemical graft copolymerisation of 4-vinyl pyridine (4-VP) onto cotton fabric using benzophenone as photosensitiser was carried out. Maximum percentage of grafting *Pg*, (18.50 %) was obtained under optimum conditions; irradiation time 75 min, 0.5 ml of benzophenone, [4-VP]=748.71 x 10^{-2} mole/l and 5 ml of water in the reaction mixture. Aliphatic alcohols of varying chain length decreased percentage of grafting. The pendant pyridine rings of the 4-VP grafted cotton fabric were converted to pyridinium chloride followed by the reaction with acrylamide to give 2-amido-ethylpyridiniumchloride. This was subjected to phosphorylation reaction with PCl_3/petroleum ether. The phosphorylated grafted cotton fabric burns only in the presence of flame with very slow propagation of the flame (only 3.8 cm^2) was found to burn of the total area of 147 cm^2 with 0.12 g of the ash content. Characterisation of gray cotton fabric and modified cotton fabric was carried out by FTIR, thermogravimetric analysis, crease recovery, and moisture absorption studies.

Keywords: Cotton fabric, flame-retardant cotton, graft copolymerisation, 4-vinyl pyridine, phosphorylation, TGA, crease recovery

1. INTRODUCTION

The flammability of cotton and other cellulosic materials has been recognised for many years and there is currently tremendous interest in the development of the textile fibres and fabrics with improved resistance to flammability. Rengasamy[1], *et al.* treated cotton and nomex cotton-blended fabric with flame-retardant finish of phosphoric acid salt containing nitrogen and tested the treated samples for char length, LOI, wash fastness, flame retardant and mechanical properties. Cotton fabric, treated with a novel flame retardant comprising hydroxy-phosphonamides, was tested for flammability behaviour and it was revealed that amides in collaboration with phosphorus work as successful flame retardants[2].

Nakanishi[3], *et al.* investigated the thermal degradation behaviour of cotton fabric treated with compounds containing different kinds of elements that contribute to flame retardation. Giraud[4], *et al.* studied the flame behaviour of cotton coated with polyurethane containing micro encapsulated flame-retardant agent. Sekiguchi[5] worked for durable flame-retardant cotton fabric prepared by partial phosphorylation and metal complexation.

In view of the large interest in developing flame-retardant cotton fabric, the development of flame-retardant cotton fabric involving photochemical graft copolymerisation of 4-VP followed by post-grafting reactions has been reported.

2. EXPERIMENTAL

2.1 Materials

Cotton fabric of Wt $1.24/m^2$, peaks and end 140 cm and 89 cm respectively was used, plain weave (1/1), count of yarn in warp and weft 8/8s cc, twist of warp and weft 252/m and 282/m respectively was used. The fabric was thoroughly washed with a soap solution followed by water, dried and then further extracted with water in a soxhlet apparatus for 24 h to ward off wax and other impurities. The cotton samples were then dried in an oven to a constant weight.

4-Vinyl pyridine (4-VP), (E. Merck) was freshly distilled before use. Acetone solution of benzophenone (S.D. Fine Chemicals) was used as a photosensitiser. Acrylamide (AAm) (E. Merck) and PCl_3 (E. Merck) were used as received. A high-pressure mercury vapour lamp was used as the source of UV radiations.

2.2 Method

2.2.1 Preparation of the Sample

Sample size of the required dimension was cut and the ends were sewed with the thread taken from the same fabric to avoid the loss in weight of the fabric during the course of the reaction.

2.2.2 Graft Copolymerisation

The washed and weighed cotton fabric sample was suspended in a known amount of water. To it was added a known amount of the monomer (4-VP) and the photosensitiser, benzophenone. The reaction mixture was irradiated with the UV lamp for different periods of time. To avoid the rise in temperature, a constant flow of cold water was maintained outside the reaction vessel. After the stipulated time period, the reaction was stopped and the fabric was removed from the reaction mixture. The grafted fabric was washed thoroughly with a mixture of acetone and water (I:1v/v) to remove the homopolymer formed during the reaction. The grafted fabric, free from the homopolymer, was dried and weighed to a constant weight. Percentage of grafting, P_g, was calculated from the increase in initial weight of the cotton fabric as follows:

$$\text{Per cent grafting} = \frac{W_1 - W_0}{W_0} \times 100 \tag{1}$$

where W_1 is the final weight of the fabric after complete removal of the homopolymer and W_0 is the initial weight of the fabric.

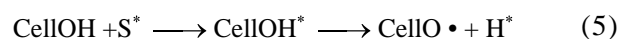#### 2.2.3 Quaternisation of Cotton-g-poly (4-VP) Samples

The grafted cotton fabric, i.e., cotton-g-poly (4-VP) was suspended in methanol and diluted. *HCl* was added in stochiometric proportions under stirring. The reaction mixture was kept at 60 ºC under constant stirring. During the course of stirring, an excess of ethylenic reagent, acrylamide (AAm), was added to convert the pendant pyridinium chloride groups into 2-amido ethyl pyridinium chloride.
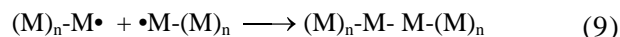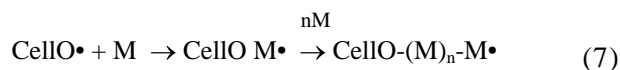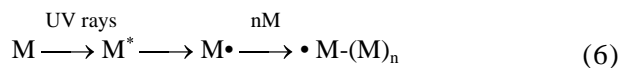

$$\tag{2}$$

$$\tag{3}$$
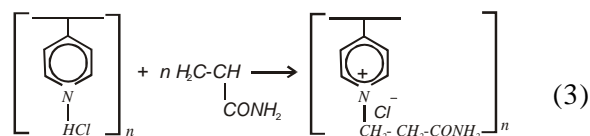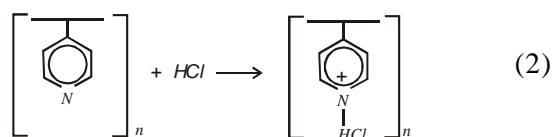
3. RESULTS AND DISCUSSION

Synthesis of graft copolymers of cotton cellulose essentially involves generation of active sites on the backbone polymer where suitable monomer can be graft copolymerised. In the present study, photochemical graft copolymerisation of 4-VP was carried out onto cotton cellulose using benzophenone as photosensitiser. The following probable mechanism is suggested for graft copolymerisation of 4-VP onto cotton fabric by photochemical method:

Initiation and propagation

$$S \xrightarrow{\text{UV rays}} S^* \tag{4}$$

$$\text{CellOH} + S^* \longrightarrow \text{CellOH}^* \longrightarrow \text{CellO} \bullet + H^* \tag{5}$$

$$M \xrightarrow{\text{UV rays}} M^* \longrightarrow M\bullet \xrightarrow{\text{nM}} \bullet M\text{-}(M)_n \qquad (6)$$

$$CellO\bullet + M \xrightarrow{\text{nM}} CellO\, M\bullet \rightarrow CellO\text{-}(M)_n\text{-}M\bullet \qquad (7)$$

$$CellO\bullet + \bullet M\text{-}(M)_n \longrightarrow CellO\text{-}M\text{-}M_n \qquad (8)$$

$$(M)_n\text{-}M\bullet + \bullet M\text{-}(M)_n \longrightarrow (M)_n\text{-}M\text{-} M\text{-}(M)_n \qquad (9)$$

where Cell OH = cotton cellulose, M = monomer, S = sensitiser

Percentage of grafting was studied as a function of various reaction parameters and the results are explained in the light of the proposed mechanism.

3.1 Effect of Irradiation Time

Figure 1 represents the results of effect of time of irradiation on percentage of grafting of 4-VP. The P_g was found to increase with increasing irradiation time, giving maximum (7.11 %) in 75 min. Further increase in the irradiation time decrease the percentage of grafting. This may be due to increase in temperature, leading to various chain transfer and termination reactions and preferred homopolymer formation due to prolonged irradiation.
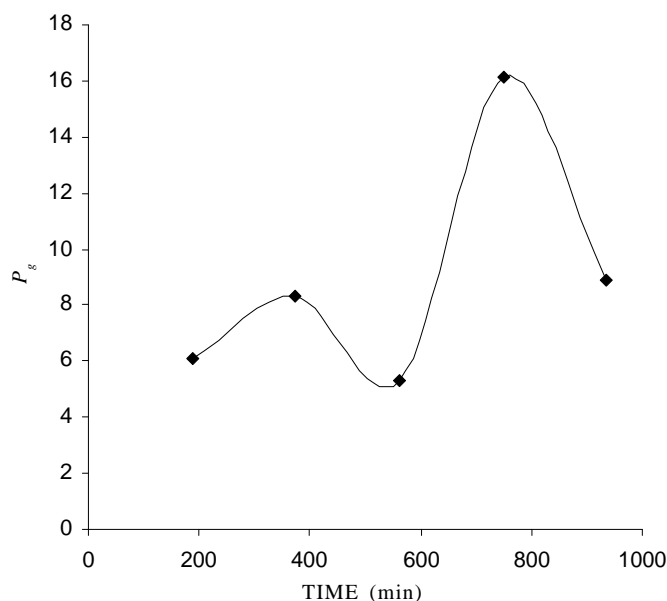
3.2 Effect of Amount of Photosensitiser

Percentage of grafting was studied as a function of amount of photosensitiser comprising of 1 per cent benzophenone solution in acetone and the results are presented in Fig. 2. Maximum P_g (16.10 %) was obtained using 0.5 ml of photosensitiser beyond which P_g decreases. The trend of decrease in grafting at higher concentration of benzophenone is explained by the fact that benzophenone in the excited state has the tendency to abstract hydrogen atom from the system to give photo reduced product, benzhydrol. As a result beyond the catalytic amount of benzophenone, photoreduction of the sensitiser becomes the preferred process, leading to decrease in percentage of grafting.

$$C_6H_5\text{-}C(O)\text{-}C_6H_5 \rightarrow (C_6H_5)_2\text{-}C(O) \bullet \rightarrow (C_6H_5)_2 \text{-}CHOH \qquad (10)$$
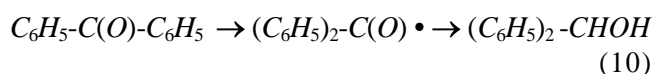
3.3 Effect of Monomer Concentration

Figure 3 represents the plot of percentage of grafting as a function of [4-VP]. Percentage of grafting increases with increasing monomer concentration, giving maximum, (18.50 %), at [4-VP] = 748.71×10^{-2} mole/l. Further increase in the monomer concentration decreases percentage

Figure 1. Effect of irradiation time on P_g of 4-VP onto cotton fabric.
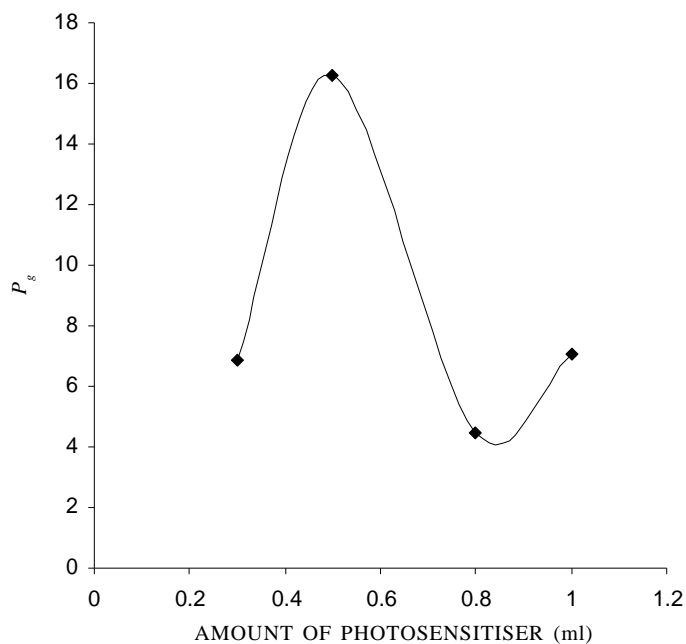

Figure 2. Effect of photosensitiser on P_g of 4-VP onto cotton fabric.

of grafting. This may be due to the fact that at higher monomer concentration, preferential homopolymer formation takes place, which being soluble in water increases the viscosity of the reaction medium. This restricts the mobility of the active sites, thereby lowering the overall percentage of grafting. Also, 4-VP is wasted in the side chain reactions because of its high monomer-transfer value ($C_M = 7 \pm 2 \times 10^{-4}$), thereby decreasing percentage of grafting.

3.4 Effect of Amount of Water

Percentage of grafting of 4-VP onto cotton fabric was studied as a function of amount of water and the results are presented in Fig. 4. Maximum P_g (18.50 %) was obtained when 5 ml of water was used. Beyond optimum amount of water, P_g decreases. The increase in P_g of 4-VP with increasing amount of water, is due to the increased exposure of the active sites of the cotton cellulose due to hydrogen bonding between the hydroxyl groups of cellulose and the water molecules. Also, 4-VP being soluble in water, can diffuse to the active sites giving rise in P_g. Decrease in P_g beyond optimum amount of water may be due to the dilution of the monomer concentration. The homopolymer, poly(4-VP) being soluble in water raises the viscosity of the medium which inhibits the movement of the growing polymeric chains to the active sites leading to decrease in P_g.
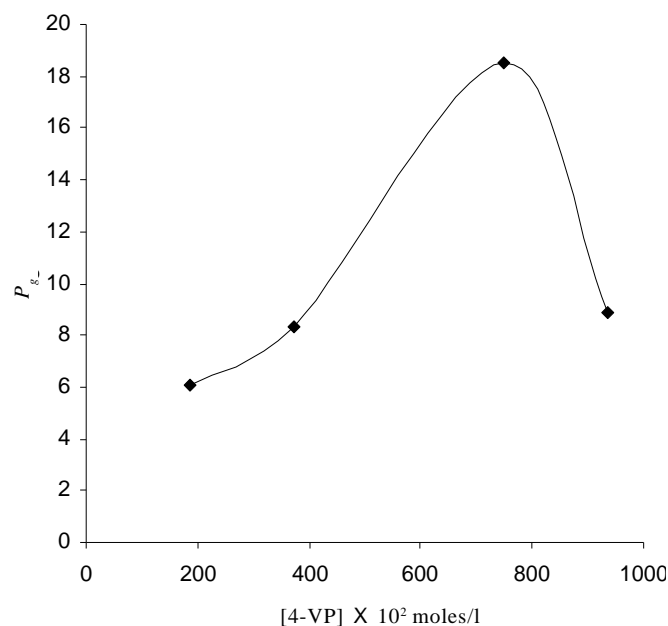
3.5 Effect of Alcohols in Water-Alcohol Solvent System

The effect of addition of aliphatic alcohols (methanol, ethanol, 2-propanol, n-butanol, n-pentanol) to water during graft copolymerisation of 4-VP was studied and the results are presented in Fig. 5. The total amount of mixed solvent system (H_2O + alcohol) was kept constant at 4 ml. The amount of alcohol in the binary mixture was varied. It was observed that the P_g decreases continuously as the amount of alcohol in the solvent system increases and lower P_g in water-alcohol medium was obtained than in pure aqueous medium. The addition of alcohols to water is known to break the hydrogen bonded structure of water and forms the H-bonded structure with water molecule. This affects the interaction of water with the hydroxyl functions of the cellulose and also decreases the autodiffusion of monomer to the active sites. Both these factors lead to decrease in percentage of grafting. The order of reactivity of alcohols towards grafting is:

$$Me\textit{OH} > 2\text{-propanol} > Et\textit{OH} > n\text{-Bu}\textit{OH} > \text{pentanol}$$

As was observed that reactivity decreases with increasing chain length except for 2-propanol. As the size of the chain increases or with the increasing molecular mass, the association degree of alcohol decreases. This is also reflected by their decrease in dielectric constants ($H_2O = 78.35$, MeOH
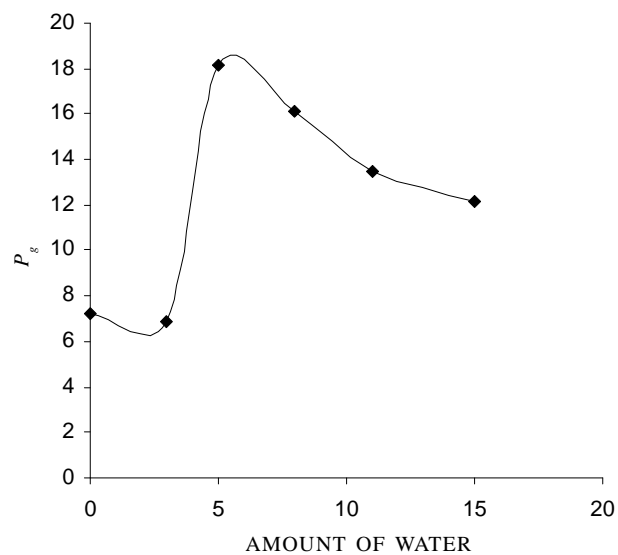

Figure 3. Effect of [4-VP] on P_g of 4-VP cotton fabric.

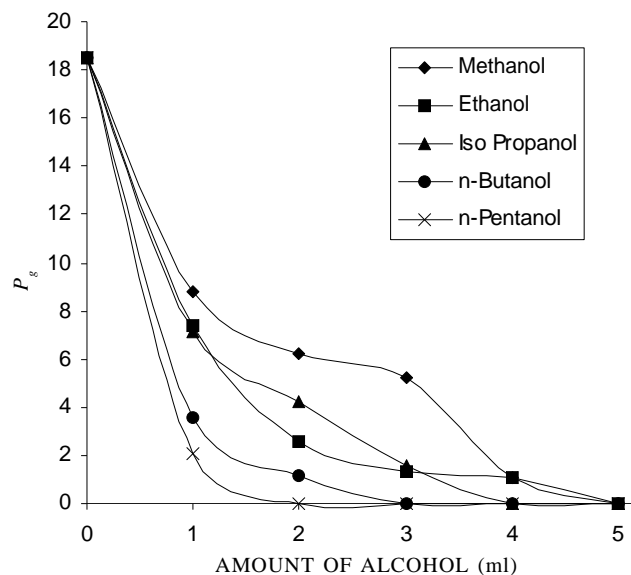**Figure 4. Effect of amount of water on P_g of 4-VP onto cotton fabric.**

Figure 5. Effect of alcohal-water binary mixture on P_g of 4-VP onto cotton fabric.

= 32.63, EtOH = 24.30, 2-propanol = 18.3, BuOH = 17.7 and pentanol=(13.2). Smaller molecule, e.g., MeOH enters the cavities of the ice-like structure of water to slightly deform the lattice while larger molecules bring about a strong deformation or rearrangement of the lattice. These changes of the reaction medium overall affect the percentage of grafting. High chain transfer constant values of alcohols result in the wastage of the monomer in the side chain reactions, leading to decrease in grafting percentage. Further abstraction of hydrogen from alcohols by benzophenone is a well-known process under photochemical conditions, leading to decreased activation of polymeric backbone.

4. EVIDENCE OF GRAFTING AND PHOSPHORYLATION

4.1 FTIR Studies

FTIR analysis of gray cotton fabric, cotton-g-poly (4-VP) and phosphorylated cotton-g-poly (4-VP) was undertaken. FTIR of gray cotton showed peaks at 3445 cm^{-1} (H-bonded OH), 2819 cm^{-1} (CH_2 str.), 1417cm^{-1} (CH_2 bending), 1152 cm^{-1} (antisym bridge C-O-C), 954 cm^{-1} (stregth of C-O and C-C bond) attached to glucose ring. The cotton-g-poly (4-VP) in addition to these

peaks showed bands due to C=N str. at 1575 cm^{-1} and 1644 cm^{-1} due to C=C bond stretching. The FTIR spectra of cotton-g-Poly (4-VP) quaternised and phosphorylated showed peaks at 3331.62 cm^{1} (NH^2 str.), 1744.47 cm^{-1} (C=Ostr.) and 1461.02 cm^{-1} (C-N str.). 1267.37, 3847.55 (P-OH str.), 1022.52 (P-N str.).

4.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of gray cotton (I), cotton-g-poly(4-VP) (II), grafted and quaternised (III), phosphorylated cotton-g-poly(4-VP) (IV) were carried out on Mettler Star system. The respective primary thermograms are presented in Fig 6. The initial decomposition temperature (IDT) and final decomposition temperature (FDT) and decomposition temperature (DT) at every 10 per cent weight loss of each of the sample are tabulated (Table 1). It was observed from the thermogram that initially gray cotton loses 5 per cent of weight up to 120 ºC due to the desorption of the moisture. Thereafter, it was stable up to 342.85 ºC with 10.34 per cent weight loss, where begins the initial decomposition The fabric degrades rapidly with further rise in the temperature. Final decomposition begins at 388 ºC with 85.36 per cent weight loss, beyond which it degrades incessantly. The temperature difference between every 10 per cent weight loss is less and this difference decreases further and becomes constant with increasing weight loss. However the temperature difference between 80 per cent to 90 per cent weight loss is quite high (98.5 ºC). The per cent residue is also very low (2.14 %).

In the case of 4-VP grafted cotton fabric, an initial loss of weight (3-5 %) between 125-150 ºC due to moisture desorption was observed beyond which it remained stable upto 304.56 ºC where initial decomposition began and continued gradually to final decomposition at 388.6 ºC with a percent weight loss of 80.84 per cent. The decomposition temperature difference for every 10 per cent weight loss was higher than that observed for cotton fabric. Beyond 40 per cent weight loss, the difference in temperature becomes constant. Between 80 per cent weight loss to 90 per cent weight loss the difference increases to 71.95 ºC and the percent
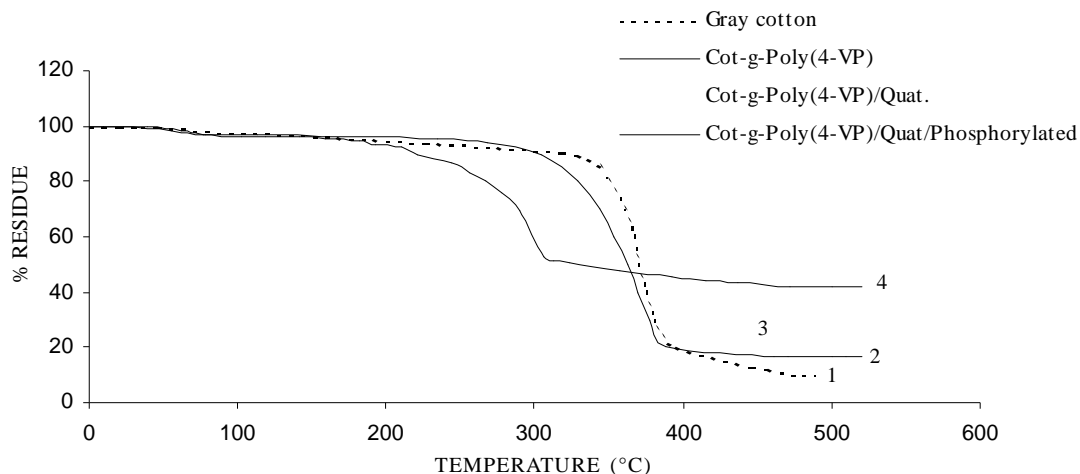
Figure 6. Primary thermogram of gray cotton, cotton-g-poly (4-VP), quaternised cotton-g-poly (4-VP), phosphorylated cotton-g-poly (4-VP).

residue left is 16.96 per cent. The quarternised 4-VP grafted cotton fabric showed similar trends as that of 4-VP grafted cotton but has higher IDT value (342.84 °C) than 4-VP grafted cotton fabric. However, the FDT and DT values at every 10 per cent weight loss were lower while the DT value at 80 per cent weight loss was much higher than either of the two. Percent residue was also higher (18.21 %).

The phosphorylated grafted fabric showed lower IDT, FDT, and DT values than the non-phosphorylated I, II, and III samples. It is well known that the flame-retardant polymers decrease the initial temperature of thermal degradation. The phosphorus

present in the phosphorylated samples (curve 4) increases the thermal decomposition rate, facilitating the char formation. The gaseous pyrolytic products can influence the chain depropagation reactions which usually take place in the flame. This is reflected in the higher temperature difference for every 10 per cent weight loss of the phosphorylated samples. The phosphorylated cotton-g-poly(4-VP) sample also had a much higher per cent residue (42.30 %). The same observations were made by Simionescu, during grafting of rayon fabric in cold plasma conditions[6].

Thus it is observed that both grafting and grafting followed by phosphorylation improve the thermal resistance of the fabric to a great extent, which

Table 1. Thermogravimetric analysis of gray cotton, cotton-g-poly(4-VP), phosphorylated cotton-g-poly(4-VP)

Type of Sample	IDT(°C) at (% Wt loss)	FDT(°C) (% Wt loss)	DT at every 10 % weight loss (°C)									
			10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %	90 %	Residue left (%)
Gray cotton	342.85 (10.34 %)	387.96 (77.45 %)	328.64	348.84	359.94	366.60	369.93	375.48	379.92	385.42	478.40	2.14
Cotton –g-poly(4-VP)	304.56 (5.64 %)	385.71 (80.84 %)	317.73	346.29	357.71	364.29	371.43	378.57	385.72	457.67	-	16.965
Cotton –g-poly(4-VP) Quat.	342.84 (18.8 %)	371.40 (73.32 %)	283.30	338.85	349.96	361.07	369.16	372.18	383.29	483.28	-	18.21
Cotton –g-poly(4-VP) quat./PCl_3	228.56 (6.58 %)	311.65 (49.6 %)	221.52	266.96	289.68	301.04	323.76	-	-	-	-	42.30

indirectly suggests that the samples have flame-resistance properties.

4.2 Crease Recovery Studies

Cotton, because of its cellulosic content, has little tendency to crease or is said to be crease-resistant. Modification of cotton fabric by different methods had been shown to influence the crease resistant property of the cotton. In the present studies, crease-recovery studies of gray cotton and cotton-g-poly (4-VP) were carried out on Shirley's manual Crease recovery tester according to the procedure followed for British Standards BSEN 22313:1992. The crease recovery angles were measured across the length (i.e., warp direction), face-to-face and crease-across (warp direction) end-to-end. The results are presented in Table 2. It was observed from the table that the crease recovery angle in warp and weft directions decreases for the grafted samples, indicating that upon grafting, the fabric has improved upon the ability of fast recovery from creasing.

Table 2. Crease recovery studies

Type of sample	Face-to-face (warp) crease recovery angle (degree)	End-to-end (warp) crease recovery angle (degree)
Gray cotton	130.5	65.5
Cotton-g-poly(4-VP)	108.5	59.8

4.3 Moisture Absorption Studies

Moisture absorption studies of gray cotton fabric and cotton-g-poly(4-VP) were undertaken at 25 ºC, 35 ºC, 45 ºC and corresponding to each temperature, three different humidity levels were studied (RH 65 %, RH 75 %, RH 85 %). The results are presented in Figs 7-9, respectively. The per cent moisture absorption of gray cotton at 25 ºC at respective humidity levels was found to be 2.47 per cent, 2.70 per cent and 2.66 per cent. As the temperature was raised from 25 ºC to 35 ºC and 45 ºC, moisture absorption of gray cotton decreases to 2.20 per cent, 2.60 per cent, 2.30 per cent at 35 ºC and 1.44 per cent, 1.61 per cent, and 0.864 per cent at 45 ºC. Per cent moisture absorption of 4-VP grafted samples at 25 ºC was found to increase

with increase in P_g because of the hydrophilic behaviour of poly (4-VP). Similar behaviour was observed at 35 ºC and 45 ºC, i.e., moisture regain values for the grafted substrate increased gradually with increase in vinyl pyridine graft addon. However, the values are little lower than at 25 ºC.
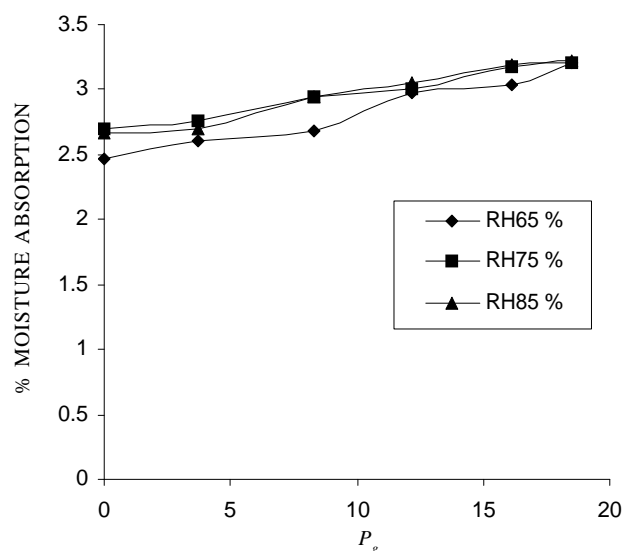

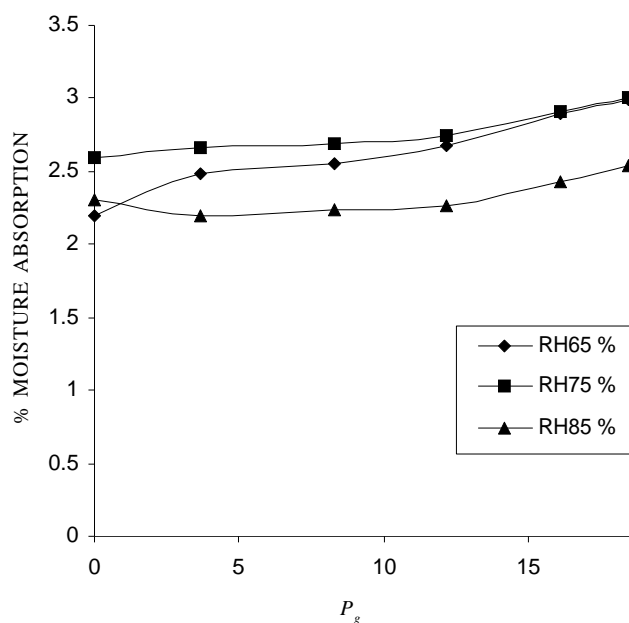**Figure 7. Effect of moisture absorption onto P_g of cotton-g-poly (4-VP) at 25 °C.**

Figure 8. Effect of moisture absorption onto P_g of cotton-g-poly (4-VP) at 35 °C.
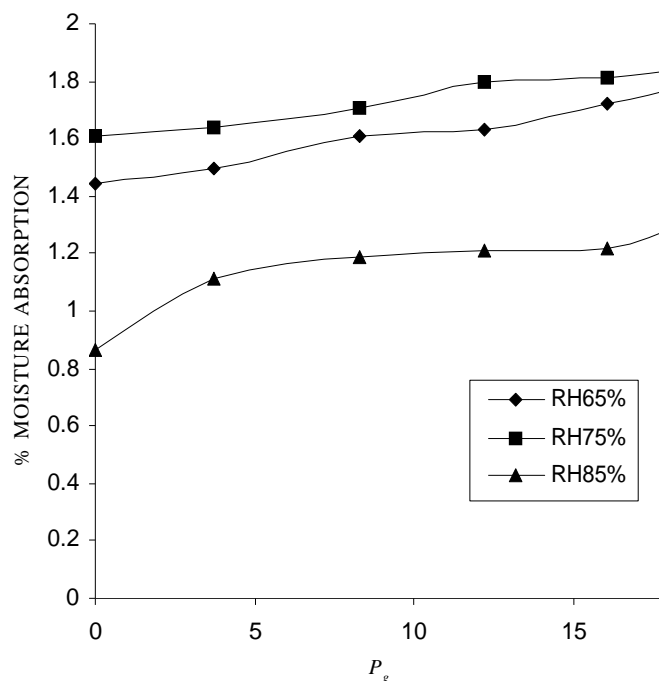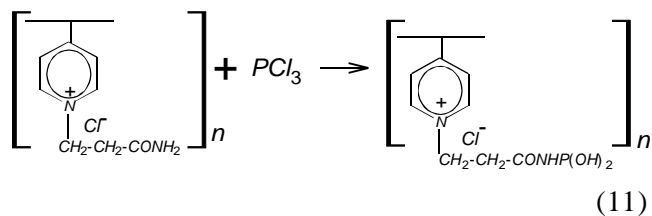
Figure 9. Moisture absorption study of cotton and cotton-g-poly (4-VP) at 45 ºC.

4.4 Phosphorylation

To impart flame retardancy to the cotton fabric, phosphorylation reactions were carried out on gray fabric, grafted fabric, and grafted and quarterinised fabric. The flammability behaviour of each of the treated fabric was studied and compared. The following procedure was adopted:

In a two-necked flask was placed the weighed specific cotton sample in petroleum spirit. Phosphorus trichloride (15 ml) was added slowly from the separating funnel fitted in one of the necks. The reaction flask, fitted with a condenser carrying a guard tube, was kept on a water bath and refluxed for 1 h. After 1 h, the product was washed thoroughly with water and dried first in air and then in oven and weighed. IR and TGA analyses confirmed the phosphorylation of the grafted cotton fabric sample.

$$\left[\underset{\substack{| \\ N \\ CH_2\text{-}CH_2\text{-}CONH_2}}{\bigcirc} \right]_n + PCl_3 \longrightarrow \left[\underset{\substack{| \\ N \\ CH_2\text{-}CH_2\text{-}CONHP(OH)_2}}{\bigcirc} \right]_n \quad (11)$$

5. FLAMMABILITY OF GRAY COTTON, GRAFTED COTTON, AND PHOSPHORYLATED GRAFTED COTTON

5.1 Qualitative Determination

Qualitative determination of the gray cotton samples and phosphorylated grafted cotton samples was carried out by burning the samples, placed vertically over the candle flame.It was observed that the cotton fabric caught the flame immediately and burnt completely with negligible ash content, the grafted cotton fabric, i.e., cotton-g-poly(4-VP) also burnt completely but the propagation of flame was slow and a small amount of the ash was left behind. On the other hand, the phosphorylated and grafted fabric was found to catch the flame only on the introduction of burning candle. The flame extinguished as the flame source was removed. The ash content was also very high.

5.2 Quantitative Determination

Quantitative determination of flammability of all the samples was carried out on Shirley manual flammability tester, which follows the relevant British Standard BS-5438:1989. standard test. Sample sizes of 80 x 200 mm of gray cotton, grafted cotton fabric, and phosphorylated and grafted cotton were prepared and the tests were preformed as per specifications of BS-5438:1989. The results are presented in Table 3.

The samples were fixed on a template and the flame was applied to the sample from the bottom edge for 12 s and removed thereafter.

Table 3. Flammability tests for gray cotton, grafted cotton, and phosphorylated cotton fabric

Type of sample	Time of flame (s)	After glow (s)	Area burnt (out of total area 147 cm^2)	Ash content (g)
Gray cotton	12	10	Completely burnt	0.02
Cotton-g-poly (2-VP)	12	51	Completely burnt	0.21
Grafted-PCl_3/Py	12	0	3.8	0.12

The gray cotton fabric completely burnt within 10 s of the applied flame. A very negligible amount (0.02 g) of ash was collected. The grafted sample continues to burn for 51 s after the removal of the flame. The whole sample completely burnt with ash content of 0.21 g. In the case of phosphorylated and grafted sample, the sample caught the flame on the introduction of the flame, but when the flame source was removed after 12 s the flame of the sample extinguishes. The propagation of the flame during burning in the presence of the burning source was also very slow. Only 3.8 cm^2 of the area was burnt of the total area of 147 cm^2. The ash content from the burnt area was 0.12 g.

Thus from the above results it may be concluded that

- Grafting of vinyl monomers with nitrogen as one of the element is capable of imparting flame retarding properties to the fabric.

- Phosphorylation of the grafted sample remarkably improves the non-flammability behaviour of the fabric. This is attributed to the synergistic effect of nitrogen and phosphorus introduced during grafting and phosphorylation reactions.

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