Development of flame retardant cotton fabric through grafting and post-grafting reactions

Inderjeet Kaur*, Vibha & Rajneesh Sharma
Department of Chemistry, H P University, Shimla 171 005, India

Received 24 February 2006; revised received and accepted 5 December 2006

Low energy UV radiation induced graft copolymerization of methacrylamide (MAAm) onto cotton fabric has been carried out using benzophenone as photosensitizer to introduce functionalities that can react with phosphorus containing compounds to impart flame retardancy. The flammability behaviour of the grey cotton, cotton-g-poly (MAAm) and phosphorylated cotton–g-poly(MAAm) fabrics has been studied on a manual flammability tester. Maximum percentage of grafting (116.1%) is achieved at 75 min irradiation time; 176.47×10⁻² moles/L [MAAm]; 5 mL photosensitizer; and 3 mL reaction medium. The grey cotton and cotton-g-poly (MAAm) fabrics react with phosphorous trichloride and diethylphosphite to introduce phosphorous element, thus imparting flame retardancy. Phosphorylated grafted fabric shows improved flame retardant behaviour in comparison to grafted fabric, which is better than the grey fabric. All the fabric samples have been characterized by FTIR, thermogravimetric analysis and crease recovery behaviour.

Keywords: Cotton fabric, Crease recovery, Flame retardancy, Graft copolymerization, Phosphorylation, Thermogravimetric analysis

IPC Code: Int. Cl. D06M14/00

1 Introduction

Cellulose is known to be an excellent material under normal conditions but often fails to perform under hostile environment. Their utility is therefore hindered in the fields where high performance properties are required. Hence, over the years cotton fabric has been successfully modified through graft copolymerization to improve upon certain properties and to impart flame retardancy. Deo and Gotmare successfully attempted grafting of acrylonitrile onto grey cotton to impart high water absorbency. Zaharan and Mahmoud studied grafting of methacrylic acid onto cotton fabric in an aqueous medium with potassium peroxydiphosphate and cellulose thiocarbonate redox initiation system. Zohdy et al. studied the thermal stability of polyester and cotton-polyester graft copolymers obtained by direct radiation grafting of individual and mixed vinyl monomers. Graft copolymerization reaction of water emulsified methylmethacrylate with pre-irradiated jute fibre has also been studied. Thermal behaviour of cotton yarn was investigated after its graft copolymerization with AAm using emulsion polymerization technique. Yang et al. studied in situ copolymerization of cotton with itaconic acid and crosslinking cotton with poly(itaconic acid). Giraud et al. studied the flame retarding behaviour of cotton coated with polyurethane containing micro-encapsulated flame retardant agent. Synergistic behaviour of phosphorus-bromine in polyester-cotton fabric treated with tetrabromobisphenol-A (TBBA) and diammonium phosphate (DAP) was studied and maximum synergism was obtained when the concentration of TBBA was equal to DAP. Nair studied the methods of improving the durability of phosphorylated cotton towards washing to widen its frontiers of application. Post-grafting reactions of glycidylmethacrylate (GMA) grafted cotton fabric with ethylenediamine followed by orthophosphoric acid were carried out by Reddy et al. to produce fire retardant cotton fabric. Studies on thermal stability of polyester containing phenyl phosphonate units for flame retardant fibre was carried out by Tang et al. FTIR analysis of gases evolved from cotton and flame retarded cotton fabric pyrolysed in air was carried out by Horrocks et al. Kandola et al. studied the influence of treatment of flame retardant cotton on the mechanism of cotton pyrolysis.

Although cotton is being used as the chief textile fibre, its main weakness, such as tendency to wrinkle,
low degree of water repellency and poor flame, crease and abrasion resistance, limits its use in application areas where these properties are desired. The present study is therefore aimed at developing flame retardant cotton fabric through graft copolymerization followed by phosphorylation reactions on the grey and grafted fabrics. The flammability behaviour of all the samples has been studied on the Shirley manual flammability tester.

2 Materials and Methods

Cotton fabric, procured from the local market of Shimla, having the following specifications: weight 1.24 mg/m²; picks/inch 55 and ends/inch 35; plain weave (1/1); count of yarn in warp and weft 8/8s (cc); warp twist 252 turns/m; and weft twist 282 turns/m was used. The fabric was thoroughly washed with a soap solution followed by water and extracted further with water in a Soxhlet apparatus for 24 h to remove any wax and other impurities.

Methacrylamide (MAAm) (E.Merck), 1% acetone solution of benzophenone (S.D.Fine Chemicals) as a photosensitizer, and mercury vapour lamp (230w) as the source of UV radiations were used.

2.1 Preparation of Sample

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

2.2 Graft Copolymerization

Washed, dried and weighed cotton sample of 5cm × 5cm size was suspended in 3-20 mL water and a known amount of monomer MAAm (47.06×10⁻² – 294×10⁻² moles/L) and benzophenone (0.5 – 1.7 mL) were added to the above solution. The reaction mixture was irradiated with UV-lamp for different time periods (45 - 120 min). To avoid any rise in temperature, a constant flow of 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 water 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 (Pg) was calculated from the increase in initial weight of the cotton fabric using the following relationship:

\[
\text{Per cent grafting } = \frac{W_f - W_0}{W_0} \times 100
\]

where \(W_f\) is the final weight of the fabric after the complete removal of the homopolymer; and \(W_0\), the initial weight of the fabric.

2.3 Phosphorylation Reactions

To impart flame retardancy to the cotton fabric, phosphorylation reactions were carried out on grey and grafted fabrics. The formation of grafted and phosphorylated cotton fabric samples was confirmed by FTIR and TGA.

2.3.1 Phosphorylation by PCl₃/Py

Dried and weighed grey and grafted fabrics were suspended separately in pyridine (Py) (10ml) and PCl₃ (4 ml) at 120°C for 6h. After the stipulated time, the fabric was removed and washed thoroughly with distilled water till it became free from pyridine. The fabric was dried at 40-45°C.

2.3.2 Phosphorylation with Diethylphosphite (DEP)

Preparation of DEP

Ethyl alcohol (65.5mL) in CCl₄ (56mL) was placed in a two-necked flask. To this solution, PCl₃ (32.7mL) and CCl₄ (37.5mL) mixture was added drop-wise from the separating funnel (Scheme 1). The reaction flask, fitted with a condenser carrying the guard tube, was kept on a water bath and refluxed for an hour while air was allowed to pass through it continuously to remove hydrogen chloride and low boiling liquid. It was then distilled at a reduced pressure and distillate in the range of 102°-103°C was measured.

Phosphorylation Reaction

Weighed samples of cotton and cotton-g-poly(MAAm) were suspended separately in dimethylformamide (DMF) (10 mL) and DEP (2 mL) mixture in a round bottom flask. The mixture was refluxed for a definite time period. After the stipulated time, the product was taken out and washed thoroughly with DMF followed by water.

\[
P \text{Cl}_3 + 2 \text{C}_2 \text{H}_5 \text{OH} \rightarrow \text{C}_2 \text{H}_5 \text{O} \text{P} \text{H} \text{OC}_2 \text{H}_5
\]

Scheme 1—Preparation of diethylphosphite
3 Results and Discussion

Synthesis of graft copolymers of cotton-cellulose essentially involves generation of active sites on the backbone polymer, where suitable monomer is polymerized. In the present work, photochemical graft copolymerization of MAAm is attempted onto cotton using benzophenone as photosensitizer. The details of the mechanism has already been reported in a similar study carried out during photochemical grafting of 4-vinyl pyridine onto cotton fabric, imparting flame retarding properties.  

3.1 Effect of Irradiation Time

Figure 1 shows the effect of exposure time of UV radiation on $P_g$ of MAAm. Percentage grafting of MAAm increases with the increase in irradiation time, attains the maximum value (45.26%) within 75 min and decreases thereafter. The decrease in $P_g$ after the optimum time is due to the preferred formation of the homopolymer. Prolonged irradiation leads to thermal polymerization and it may also promote various chain transfer and termination reactions, leading to decrease in percentage of grafting.

3.2 Effect of Monomer Concentration

Figure 1 represents the effect of variation in concentration of monomer on percentage grafting of MAAm onto cotton fabric. Grafting percentage of MAAm increases with the increase in monomer concentration, giving maximum (85.81%) value at $176.47 \times 10^{-2}$ moles/L [MAAm]. A sharp decrease is observed beyond the optimum value, $P_g$ decreasing to 34.64% at $200 \times 10^{-2}$ moles/L [MAAm] and remaining constant thereafter. The decrease in $P_g$ with increasing monomer concentration may be due to the fact that at higher monomer concentration the preferential homopolymer formation takes place, which being soluble in water increases the viscosity of reaction medium. This restricts the accessibility of growing polymeric chains to the active sites, thereby lowering the overall percentage of grafting.

3.3 Effect of Amount of Photosensitizer

The effect of amount of photosensitizer (1% benzophenone solution in acetone) on $P_g$ of MAAm onto cotton fabric is shown in Fig.1. Maximum $P_g$ (85.8%) is obtained using 0.5mL of photosensitizer beyond which $P_g$ decreases. The decrease in $P_g$ at higher concentration is due to the photoreduction of benzophenone to benzhydrol (Scheme 2). This decreases the number of active sites and hence the percentage of grafting.

3.4 Effect of Liquor Ratio

The grafting of MAAm is also studied as a function of amount of water and the results are given in Fig. 1. Maximum grafting percentage of MAAm (116.1%) is observed when 3mL of water is used.
Further increase in the amount of water decreases the percentage of grafting. This may be due to the reason that the increase in amount of water disturbs the homogeneity of the reaction medium as it interacts with the acetone present in the system. This leads to decrease in diffusion of the monomer to the active sites and also decrease in the reactivity of photosensitizer towards activating the polymeric surface.

This has been further corroborated by carrying out the grafting reaction in the presence of binary solvent system comprising water and organic solvents as additive. Aliphatic alcohols, such as methanol, ethanol, 2-propanol, n-butanol, 2-pentanol, acetone and dioxane, were added to water.

The total amount of mixed solvent system was kept constant at 3mL. Percentage grafting of MAAm is found to be lower in mixed solvent than that in aqueous medium and decreases continuously with increasing the amount of additive. This decrease in percentage grafting is due to the reason that (i) the additives, such as alcohols, acetone and dioxane, break the H-bonded structure of water, leading to decrease in the diffusion of the monomers to the active sites; (ii) the alcohols have high chain transfer constant values and as a result the monomer is wasted in the side chain reactions; and (iii) the abstraction of the hydrogen from alcohols by benzophenone is also a well-known process under photochemical conditions and hence activation process of polymeric backbone is hindered.

3.5 Characterization

Evidence in favour of grafting followed by phosphorylation is based on the following studies.

3.5.1 FTIR Study

FTIR spectra of grey, cotton-g-poly (MAAm), phosphorylated grey and phosphorylated grafted cotton samples were taken on Beckmann spectrophotometer. FTIR spectrum of grey cotton shows peaks at 3445 cm\(^{-1}\) (intermolecular H-bonding), 2819 cm\(^{-1}\) (CH\(_2\) str.), 1417 cm\(^{-1}\) (CH\(_2\) bending), and 1152 cm\(^{-1}\) (anti-symmetric bridge C-O-C).

Cotton-g-MAAm in addition to these peaks shows peaks due to >C=O (1642.6-1675 cm\(^{-1}\)) and -N-H (3350-3400 cm\(^{-1}\)). The phosphorylated grafted samples show peaks due to P=O (1322 cm\(^{-1}\)), P-O-Et (1163 cm\(^{-1}\)), P-OH def. (1281 cm\(^{-1}\)) and C-N str.(1461.02 cm\(^{-1}\)). The presence of specific peaks for a particular group in the modified cotton fabric confirms the formation of the graft and the phosphorylation.

3.5.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of grey, grafted and grafted-phosphorylated cotton fabrics was carried out on Schimadzu simultaneous thermal analyzer in air at the heating rate of 10°C/min. Respective primary thermograms are presented in Fig. 2. The initial decomposition temperature (IDT), final decomposition temperature (FDT) and decomposition temperature(DT) at every 10% weight loss of each of the sample are given in Table 1.

It is observed from the thermogram (curve 1) that the grey cotton loses 5% of weight upto 120°C due to the desorption of moisture. Thereafter, it is stable up to 342.85°C with 10.34% weight loss from where begins the initial decomposition. Further rise in temperature degrades the fabric at a faster rate which is indicative from a very small difference in the temperature between each 10% weight loss from 20% to 80%. The temperature difference (107.08°C) between 80% and 90% wt. loss is quite high. Formulation of stable glycosan has been reported for thermal degradation of cellulose. Final decomposition begins at 388°C with 82.84% weight loss, beyond which it degrades constantly.

Primary thermogram of cotton-g-poly (MAAm) (curve3) shows an inflexion between 80°C and 153.26°C due to the moisture desorption. The initial decomposition begins at 317.71°C and continues upto 442°C with 70.70% wt. loss from where begins the final decomposition of the grafted polymer. Table 1 shows that first 10% wt. loss occurs at 138.85°C which is attributed to moisture desorption beyond

![Fig. 2—Primary thermogram of grey cotton, cotton-PCl\(_3\)/Py, cotton-g-poly (MAAm), grafted cotton-PCl\(_3\)/Py, cotton-DEP and grafted cotton-DEP](image-url)
Table 1—TGA of grey, grafted and phosphorylated cotton samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>IDT, °C at (% wt. loss)</th>
<th>FDT, °C at (% wt. loss)</th>
<th>DT (°C) at every 10% wt. loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10%</td>
<td>20%</td>
<td>30%</td>
</tr>
<tr>
<td>Grey cotton</td>
<td>342.85 (13.35)</td>
<td>387.96 (85.36)</td>
<td>331.08</td>
</tr>
<tr>
<td>Cotton-g-poly(MAAm)</td>
<td>317.71 (15.71)</td>
<td>442 (70.70)</td>
<td>138.85</td>
</tr>
<tr>
<td>Cotton-PCl/Py</td>
<td>205.80 (22.13)</td>
<td>241.76 (64.26)</td>
<td>155.68</td>
</tr>
<tr>
<td>Cotton-DEP</td>
<td>261.16 (5.88)</td>
<td>283.52 (38)</td>
<td>266.6</td>
</tr>
<tr>
<td>Grafted cotton-PCl/Py</td>
<td>248.84 (7.42)</td>
<td>451.06 (51.29)</td>
<td>266.6</td>
</tr>
<tr>
<td>Grafted cotton-DEP</td>
<td>313.92 (15.36)</td>
<td>357.72 (50)</td>
<td>167.28</td>
</tr>
</tbody>
</table>

IDT—Initial decomposition temperature, FDT—Final decomposition temperature, and DT—Decomposition temperature.

which the actual decomposition begins. The temperature difference between each 10% wt. loss is much higher than observed for grey cotton and it further increases beyond 60% wt. loss. The DT values and % residue (5.68) are also higher than the grey cotton. The pendent amide groups are known to form stable imides with the loss of ammonia (Scheme 3).

Thus, the grafting of MAAm improves the thermal stability of cotton. Treatment of grey cotton and MAAm grafted cotton fabric with PCl₃ and DEP decreases the initial and final decomposition temperatures, except for MAAm grafted cotton treated with PCl₃/Py, which shows a much higher FDT (451.06°C). The decomposition temperature at every 10% wt. loss for the phosphorylated samples is also much lower than the grey cotton or the grafted cotton fabric. But the temperature difference between each 10% wt. loss is much higher than the temperature difference between DT values of either grey cotton fabric or the grafted cotton fabric. The DT values of PCl₃/Py treated grafted cotton fabric (curve 4) become higher beyond 30% wt. loss with 43% residue while the DEP treated grafted cotton fabric (curve 6) shows higher DT values beyond 50% wt. loss with 10% residue. The cotton fabrics treated with PCl₃/Py (curve 2) and DEP (curve 5) respectively show higher DT at 60% and 50% wt. loss with 35.74% and 44.23 % residue.

The decrease in IDT and the FDT values of the phosphorylated samples is because of the fact that the flame retardants decrease the beginning temperature of the thermal degradation and increase the thermal decomposition rate (lower DT values), facilitating the char formation. The same observations were also made by Simionescu et al.¹⁵ during grafting of rayon fabric in cold plasma conditions.

The TG data thus reveals that the grafting of MAAm onto cotton fabric followed by treatment with phosphorus containing compounds increases the thermal stability of the fabric and hence imparts flame retarding behaviour.

3.5.3 Crease Recovery Studies

Crease recovery studies of grey cotton and cotton-g-poly (MAAm) were carried out on Shirley manual crease recovery tester according to the procedure followed by British Standards BSEN 22313:1992. The crease recovery angle (CRA) was measured across the length (warp direction) face to face. It is observed that the CRA of the grafted sample (70°) decreases from 130.5° (CRA of grey cotton fabric),

Scheme 3—Loss of ammonia from the adjacent pendent amide groups of grafted MAAm
indicating that upon grafting the fabric has improved upon the ability of fast recovery from creasing.

### 3.6 Determination of Flammability

#### 3.6.1 Qualitative Determination

Qualitative determination was carried out by burning the samples, placed vertically over the candle flame. It is found that the untreated cotton fabric burnt immediately with negligible ash content. The grafted cotton fabric also burnt completely but the propagation of the flame is slow and a small amount of ash is also formed. Phosphorylated grey cotton fabric burnt little slowly with very small ash content. The phosphorylated cotton-g-poly(MAAm) fabric is found to catch flame only on introduction of the flame. The flame extinguishes as the flame source was removed.

#### 3.6.2 Quantitative Determination

Quantitative determination of flammability of all the samples was carried out on Shirley manual flammability tester as per the BS5438:1989 standards. Sample size of 80 × 200 mm of grey, grafted and phosphorylated cotton fabrics was prepared and the test was performed as per the standard specifications. The samples were fixed on a template and the burner was positioned in front of, but below, the specimen such that it lies in a plane passing through the vertical centreline of the test sample and perpendicular to its face, with the longitudinal axis inclined upwards at 30° to the vertical towards the bottom edge of the test specimen. The distance between the tip of the burner tube and the bottom edge of the test specimen was 20mm. The burner was preheated for 10 min and the flame height was adjusted at 40±2mm using the gas flow fine control valve. The flame was applied to the sample from the bottom edge for 12s and after that flame was removed. The results are given in Table 2.

It is observed that the grey cotton fabric is burnt completely within 10s of the applied flame. A very negligible amount (0.02g) of ash is collected. However, the cotton–g-poly (MAAm) continues to burn for 22s. after the removal of flame. The whole sample is completely burnt with an ash content of 0.13 g. In the case of grafted phosphorylated cotton, the sample caught the flame only on the application of the flame. But when the flame source is removed after 12s, the burning of the sample is stopped, i.e. flame extinguishes. The propagation of the flame during burning with a burning source in fact is also very slow. Only 5.94 cm² (ash content 0.19g) and 4.85 cm² (ash content 0.23g) of the area of PCl₃ /Py and DEP treated grafted cotton respectively is burnt of the total area of 160 cm².

### 4 Conclusions

#### 4.1 Grafting of vinyl monomer with nitrogen as one of the element has an effect in imparting flame retarding properties to the fabric as observed for cotton-g-poly (MAAm).

#### 4.2 Phosphorylation of cotton and cotton-g-poly (MAAm) improves the flammability behaviour of the fabric. The grafted sample, however, shows improved resistance to burning. This may be attributed to the synergistic effect of nitrogen and phosphorus.

### Acknowledgement

The authors (Vibha and RS) are thankful to the Defense Research and Development Organization, Govt. of India, for the financial assistance to carry out this work.

### References