

Modification of Cellulosic Fabrics to Impart Flame Retardancy Properties

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ABSTRACT: Graft copolymerization of dimethylaminoethyl methacrylate (DMAEMA) onto cotton-cellulose in the fabric form was carried out using a cellulose-thiocarbonate-ammonium persulphate redox initiation system. Effects of the concentration of the monomer, effect of liquor ratio, grafting time, and temperature were studied. The results point out the following important aspects of flame retardation of cellulose fabrics. (1) The graft polymerization of DMAEMA can improve the flame retardant properties of cel-

lulose fabrics. (2) Tertiary amine grafted to cellulosic fabrics is suitable for nitrogen compounds that can effectively operate as synergists. The flame retardant properties of the poly-DMAEMA-grafted-phosphorylated cellulosic materials were found to be excellent even after 25 dry clean washings. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2147–2153, 2012

Key words: graft copolymerization; DMAEMA; redox initiation system; flame retardation; synergists

INTRODUCTION

The grafting of vinyl monomers onto cellulosic materials has gained considerable importance, since it provides substantial information about the kinetics and mechanisms of grafting, as well as making the basic modification required to improve the properties of cellulose.¹ Graft copolymerization of cotton with various monomers can be achieved primarily by free radical initiated processes. Several methods have been developed which differ mainly in the manner of grafting free radicals on the cellulose macro-molecules to initiate the polymerization of the monomers on the grafted chains.

Recently,² we have reported on the use of the cellulose-thiocarbonate-oxidant redox systems for initiating the graft polymerization of various vinyl monomers onto cotton fabrics.³ Hydrosulphide groups (-SH) created along with the cellulose backbone would greatly heighten the reduction power of cotton cellulose. Hence when the cellulose-thiocarbonate is coupled with a strong oxidizing agent such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$ an efficient redox-system, able to initiate vinyl grafting on cotton fabrics is established.

Now in the 21th century, natural and synthetic polymer materials are used in even more areas and under even more demanding environmental condi-

tions. However, five hazards associated with the use of these polymeric materials, which cause the loss of life and property are of particular concern among government regulatory bodies, consumer and manufactures a like.^{4,5} The use of flame retardants to reduce the combustibility of the polymers, and smoke or toxic fume production, therefore becomes a pivotal part of the development and application of new materials. Conversely, the development of flame retardant materials house hotel applications is mainly driven by increasing safety awareness and by environmental issue. It is essential that new flame retardant systems are developed to meet the constantly changing demand of new regulation, standards, and test methods. This work was undertaken with a view to:

- Studying the major factors affecting the graft yield, when cotton fabric is grafted with DMAEMA using a cellulose-thiocarbonate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ redox initiation system.
- Studying the possibility and the ability of the obtained poly DMAEMA-cellulose graft copolymer to further modification to impart flame-proofing properties via treating the grafted cellulose with aqueous solution of phosphoric acid or ammonium dihydrogen phosphate forming ionic stable bonds between the amino groups in grafted cotton and to one of the aforementioned acidic reagents compound. The salt form was done by treatment of grafted cotton with $\approx 25\%$ graft yield. Examining the flame retardancy properties of grafted cotton fabrics

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after repeated washing (25 wash) in tetra chloroethelene because most of detergents contain sodium salt of lauryl sulfonic acid which can form phosphoric acid salt that substitute the amino group of the grafted DMAEMA decreasing the affinity with the fiber and consequently affecting the flame retardancy properties of the treated fabric.

EXPERIMENTAL

Materials

Cotton fabric (poplin, 158 g/m²) kindly purchased from misr hilwan company for spinning and weaving, hilwan, Cairo, and used after purification, by scouring for 2 h at the boil using aqueous solution containing (1%) sodium hydroxide. It was then thoroughly washed and air-dried at room temperature.

Chemicals

DMAEMA, CS₂, NaOH, meta phosphoric acid (H₃PO₄) and ammonium dihydrogen phosphate were of laboratory grade chemicals.

Methodology

Thiocarbonation of cotton fabric

The cotton fabric was impregnated in 1% aq. sodium hydroxide solution and wetting agent, squeezed to 100% pick up then the sample vessel was placed in a shaker containing 1% CS₂ based on weight of fabric and the temperature was kept at 30°C. The content of vessel was continuously shaken throughout thiocarbonation reaction. After 2 h, the fabric was thoroughly washed with cold water until the washing liquor acquired pH 7. The cotton fabric in this form will be referred to as cellulose thiocarbonated.

Grafting procedure

Unless otherwise indicated, the thiocarbonated cotton fabric was pretreated in an aqueous ferrous sulfate (0.25%) in a bottle kept at room temperature for 30 min. with continuous shaking to avoid the heterogeneity deposition all over the sample surface. After impregnation, the sample was washed repeatedly with distilled water and squeezed between two filter papers before introducing it into the polymerization solution. The sample was placed in a glass vessel containing the polymerization solution [specific concentration of ammonium persulphate and the monomer at PH (1.5–2)]. The material to liquor ratio was 1 : 25. The glass vessel was kept in a thermostat water bath at a definite temperature and time. The sample was kept under continuous shaking during

the polymerization reaction. At this end, the so-treated sample was quickly removed from the polymerization solution, thoroughly washed with distilled water, the homopolymer formed was repeatedly extracted with hot water. Then the sample was treated with excess aqueous solution of NaOH or Na₂CO₃ to get rid of nitrate salt located on the sample before phosphoralization.

Phosphoralization

The poly DMAEMA-cotton copolymer was reacted with excess aqueous solution of metaphosphoric acid or ammonium dihydrogen phosphate in stoppered glass bottle. The reaction was carried out at room temperature for 1 h. The sample was then thoroughly washed with distilled water and dried at 50°C.

TESTING AND ANALYSIS METHOD

Nitrogen content

Nitrogen content of the grafted fabric was determined by making use of the Kjeldahl method.⁶

Phosphorous content

The phosphorous content of the treated fabrics was determined as described in method.⁷

Flammability test

The property of flame-retardancy was monitored as described in the vertical burning test-method.⁸

Tensile strength test

As described in the tensile strength test method.⁹

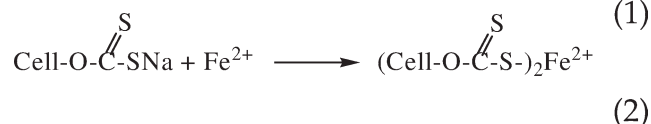
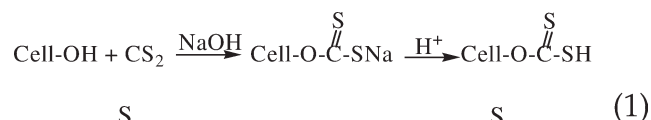
Crease recovery test

As described in the crease recovery test method.¹⁰

RESULTS AND DISCUSSION

Tentative mechanism

Cellulose reacts with carbon disulphide to yield cellulose thiocarbonate as shown by the mechanism suggested by eq. (1) as follows¹¹:



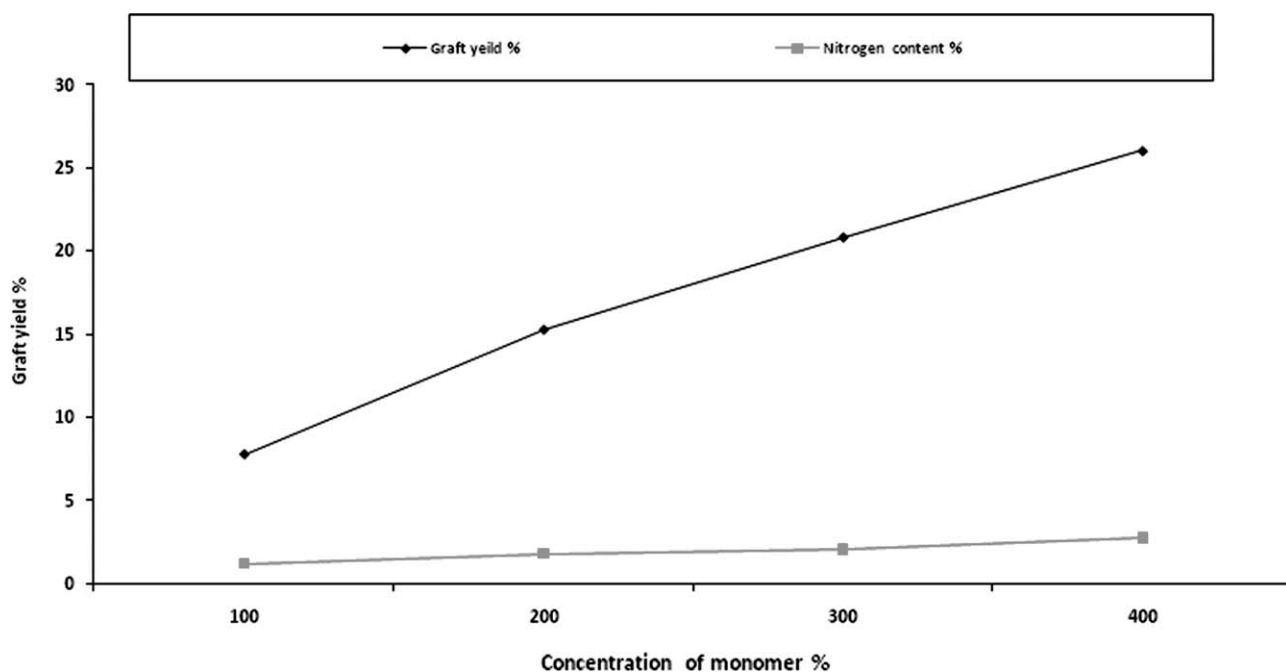
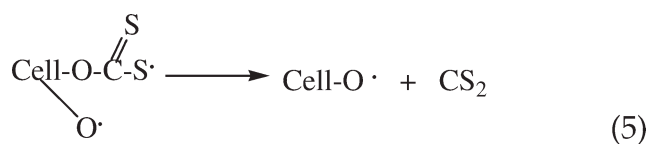
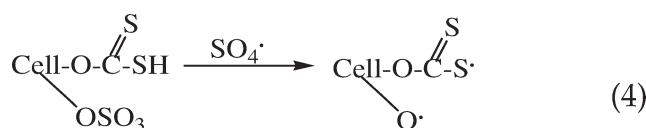
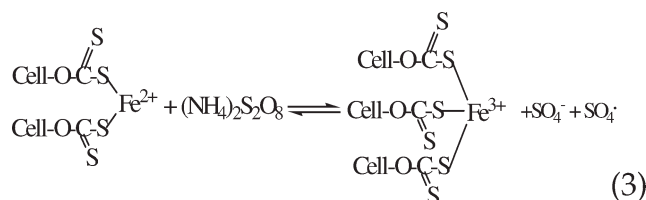
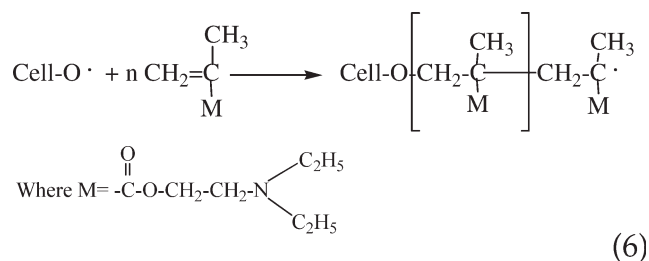


Figure 1 Effect of monomer concentration on graft yield and nitrogen content.

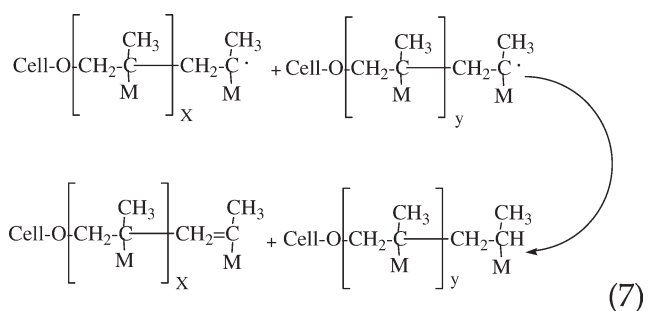


When $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is coupled with cellulose- Fe^{2+} -thiocarbonate, an efficient redox system, able to initiate a vinyl grafting reaction along with cellulose backbone is established. Hence an initiating radical is formed by abstraction of H atoms from the hydro-sulphide groups ($-\text{SH}$) and from OH hydroxyl groups under the influence of HO^- anion. This is followed by subsequent rapid decomposition of the radicals eq. (4) to form stable cellulose macroradicals eq. (5).¹²

In the presence of DMAEMA, the cellulose macroradical ($\text{Cell-O} \cdot$) are added to the double bonds of DMAEMA to initiate and then propagate the grafting reaction onto the cellulose fabric eq. (6).¹²



The propagation chain of cellulose may be terminated via two possible routes, namely, disproportionation eq. (7) and/or recombination eq. (8) between two growing cellulose-polymer chain radicals.



With these tentative mechanisms in mind, the factors affecting the graft copolymerization of DMAEMA onto cotton fabric using the cellulose- Fe^{2+} -thiocarbonate- $(\text{NH}_4)_2\text{S}_2\text{O}_8$ redox system were studied.

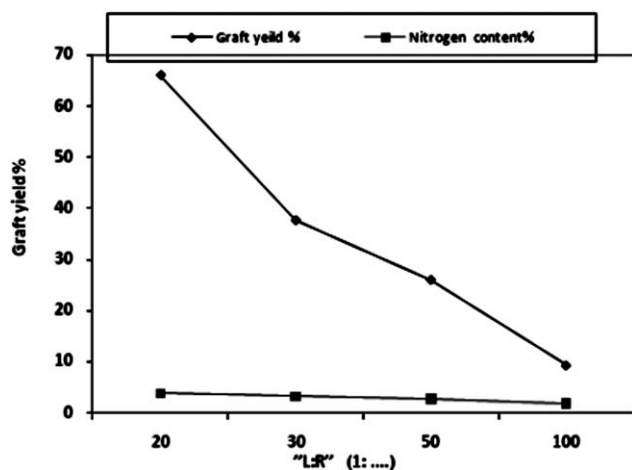


Figure 2 Effect of "L : R" on graft yield of DMAEMA : HNO₃ and nitrogen content.

Monomer concentration

Figure 1, shows the effect of DMAEMA : HNO₃ concentration on the graft yield. When DMAEMA:HNO₃ was polymerized with cotton fabric the graft yield is directly related to the DMAEMA:HNO₃ concentration within the range studied (from 100 to 400% base on weight of fabric). The percentage of grafting increases almost linearly from 7.76% at 100% DMAEMA : HNO₃ concentration to 26.01% at monomer concentration of 400% DMAEMA : HNO₃. At higher concentration of DMAEMA : HNO₃, the gel effect brought about by the solubility of poly

(DMAEMA) in its own monomer seems to be more pronounced. As a result, termination of growing grafted chain radicals by coupling is hindered, while the swelling of cellulose is enhanced.

The relationship between monomer concentration and nitrogen content is shown in Figure 1. Enhancement of grafting by increasing DMAEMA : HNO₃ concentration could be associated with the greater availability of monomer molecules at higher concentration in the proximity of cellulose macromolecules. It is understandable that the active sites on cellulose backbone are mobile. Hence the rate of their reaction with the monomer would essentially depend on the availability of the latter in the vicinity of the cellulose macroradicals and on the mobility of the macroradicals. It is clear that an increase of the monomer concentration increases the percentage of nitrogen content.

The reaction is carried out using different concentrations of DMAEMA : HNO₃ (100, 200, 300, and 400) % in "L : R" 1 : 50 in the presence of each of the ammonium persulphate (1%), [CS₂] (1 mL), ferrous sulfate (0.25%), and NaOH (1%). The pH of the reaction is (1.5–2). The reaction carried out for 2 h at 25°C.

Effect of liquor ratio

Figure 2, shows the effect of L.R. on percentage of graft yield of DMAEMA : HNO₃ monomer and nitrogen content. It is clear that an increase of "L : R" decreases the percentage of grafting within the range of study. The percentage of grafting decreases

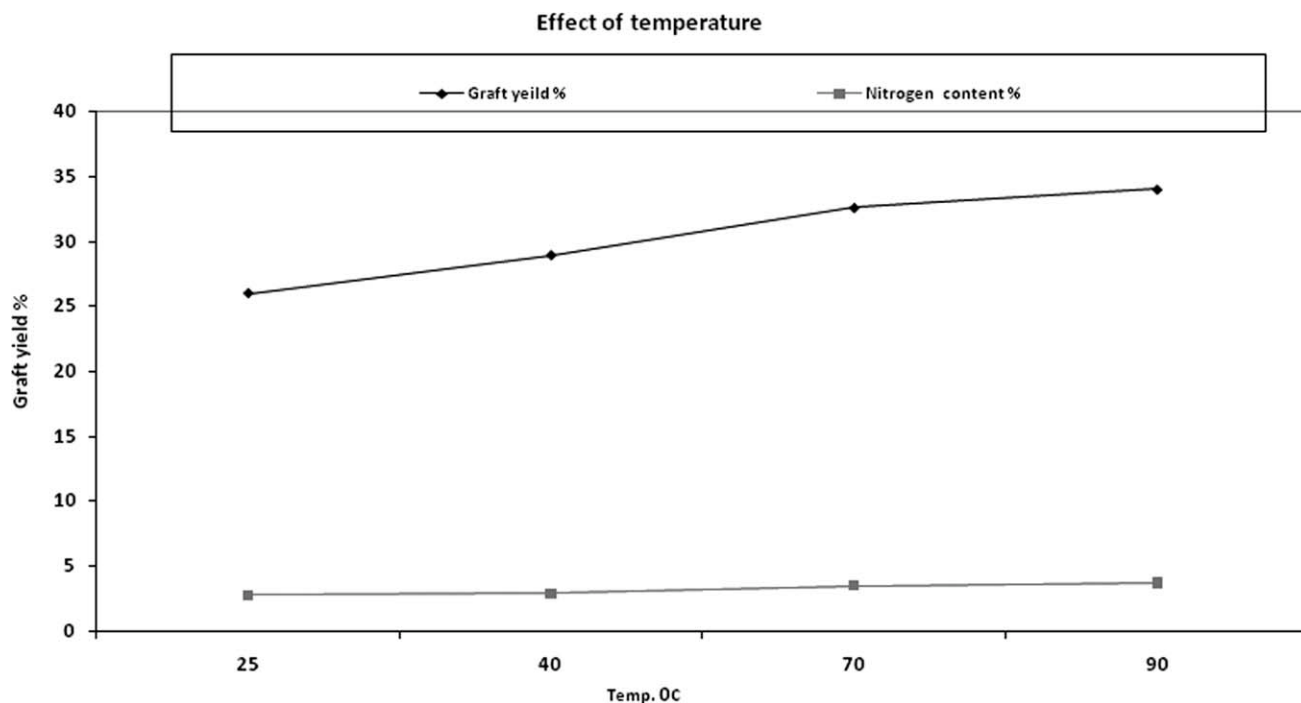


Figure 3 Effect of temperature on graft yield of DMAEMA : HNO₃ and nitrogen content.

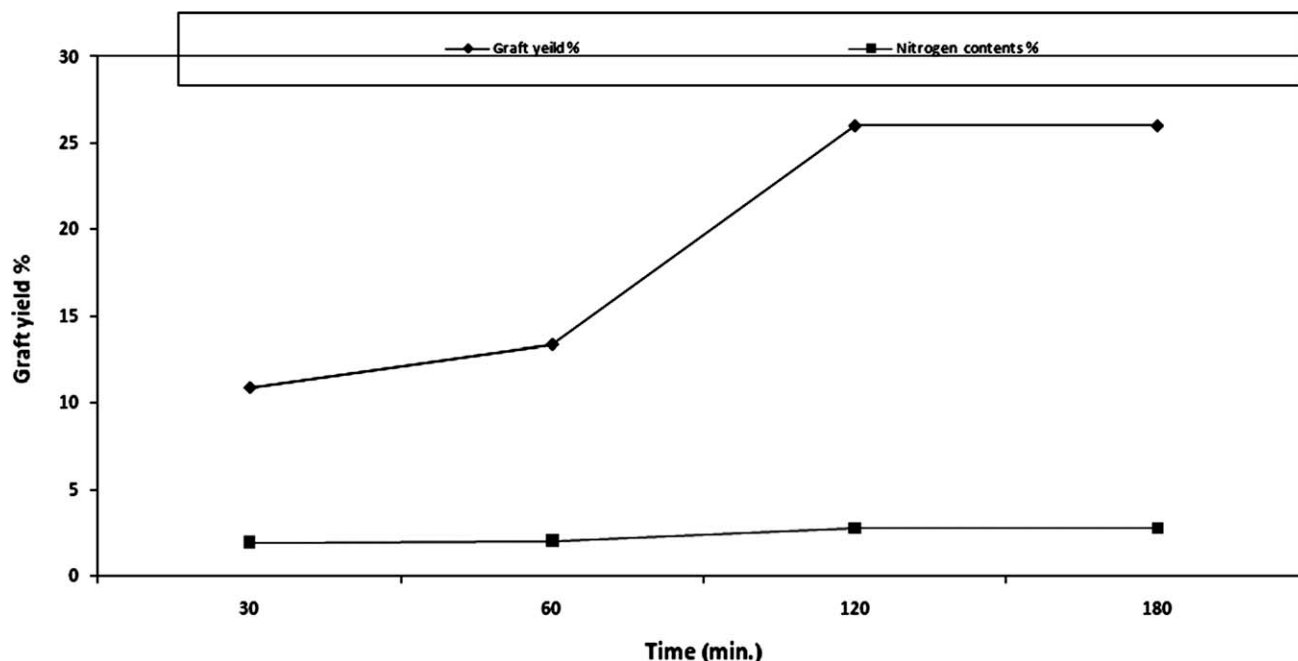


Figure 4 Effect of time on graft yield of DMAEMA : HNO₃ and nitrogen content.

almost linearly from ≈ 66% at L.R. 1 : 20 to 9.26% at L.R. 1 : 100. The relationship between L.R. and nitrogen contents is shown in Figure 2. It is clear that an increase of “L : R” decreases the percentage of nitrogen content. Also, this is rather a direct consequence of dilution of and lower molecular collision among the polymerization ingredients (reactant).

The reaction is carried out using DMAEMA : HNO₃ (400%) in different L : R 1:(20, 30, 50, and

100) in the presence of each of the ammonium persulphate (1%), [CS₂] (1 mL), ferrous sulfate(0.25%) and NaOH (1%). The pH of the reaction is (1.5–2). The reaction carried out for 2 h at 25°C.

Polymerization temperature

Figure 3, shows the effect of polymerization temperature on the graft yield of DMAEMA : HNO₃. The

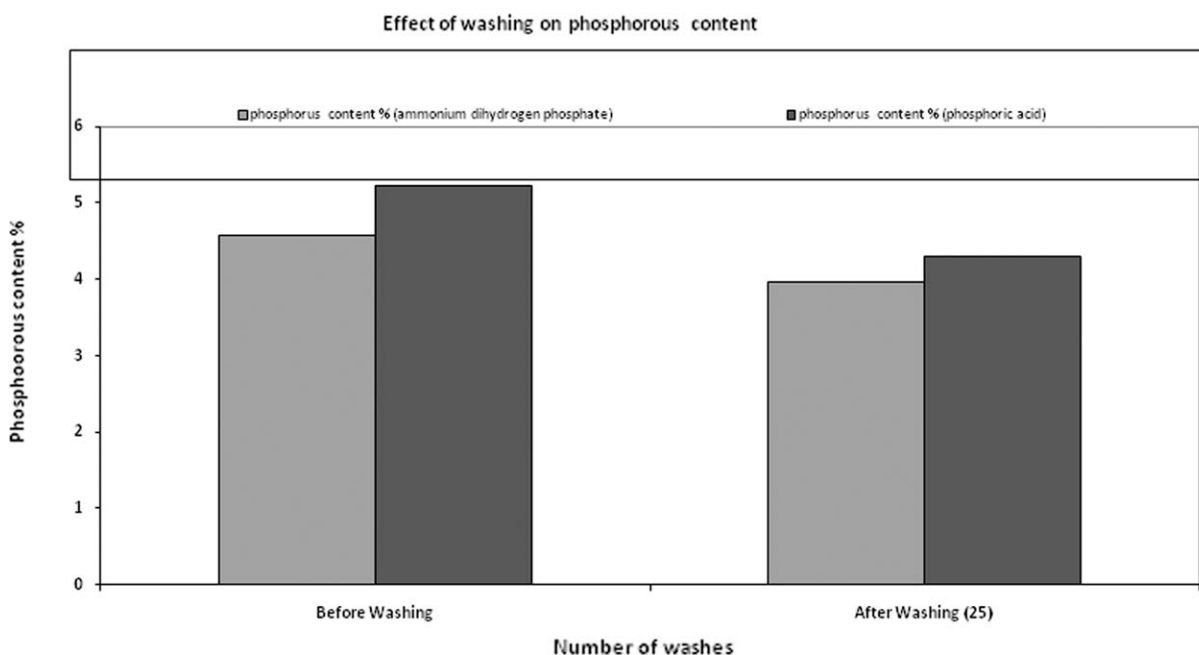


Figure 5 Effect of washing on phosphorus content.

TABLE I
Flame Retardant Properties of Treated Cotton Fabric

Flammability Area of charred zone in cm ²		Flammability Area of charred zone in cm ²	
Untreated	Flammable	Untreated	Flammable
Treated with phosphoric acid sample	Excellent (less than one)	Treated with ammonium dihydrogen phosphate sample	Excellent (less than one)
After 25 washing	Excellent (less than one)	After 25 washing	Excellent (less than one)

results signify that the grafting of thiocarbonated cellulosic fabric increases with temperature from 25 to 90°C. The increments in the graft yield by raising the temperature within the range studied could be associated with the favorable effect of temperature on polymerization which ascribed to the speedy disintegration of the thiocarbonate group, greater activation energy, enhanced oxidant efficiency, enhancement of the solubility of the monomer and its diffusion from the solution phase to the fiber phase, and a higher rate of initiation and propagation of the graft.

The reaction is carried out using DMAEMA : HNO₃ (400%) in L : R 1 : 50 in the presence of each of the ammonium persulphate (1%), [CS₂] (1 mL), ferrous sulfate (0.25%), and NaOH (1%). The pH of the reaction is (1.5–2). The reaction carried out for 2 h at different temperatures (25, 40, 70, and 90)°C.

Effect of time

Figure 4, represents the influence of reaction time on graft yield. It can be seen that graft yield increases with increasing reaction time and reaches maximum after 120 min. Also, the nitrogen content increases with increasing reaction time and reaches maximum after 120 min. The favorable effect of time on the percent of graft yield is rather expected.

The reaction is carried out using DMAEMA : HNO₃ (400%) in “L : R” 1 : 50 in the presence of each of the ammonium persulphate (1%), [CS₂] (1 mL), ferrous sulfate (0.25%), and NaOH (1%). The pH of the reaction is (1.5–2). The reaction carried out

at (30, 60, 120, and 180) min at temperature of (25°C).

Flame-retardant properties of cellulose-graft poly DMAEMA

In this work the cellulose-graft poly DMAEMA system to which metaphosphoric acid or ammonium dihydrogen phosphate were reacted ionically and added the synergistic effect between phosphorous and nitrogen atoms may be expected. This study focused on how much metaphosphoric acid or ammonium dihydrogen phosphate is added to cellulose-graft-copoly- DMAEMA in addition to how much the modification enhanced the flame retardant properties of cellulose-graft-poly DMAEMA. Figure 5 and Table I show the changes in phosphorous content and flame retardancy properties of PDMAEMA-graft cotton fabric after treatment with phosphoric acid and ammonium dihydrogen phosphate. The results show that the phosphorous content (P) of cotton fabric which treated with phosphoric acid is more than that treated with ammonium dihydrogen phosphate. Also, the figure shows that the phosphorous content of treated fabric before washing is more than after washing 25 times. The flame retardancy properties are good even after successive washing. This finding can be attributed to a strong salt formation between the acid and the tertiary amino group of the grafted DMAEMA.

The sample which give graft yield of DMAEMA 26.01% under previous conditions is treated afterwards with excess of phosphoric acid or ammonium

TABLE II
Mechanical and Physical Properties of Treated Cotton Fabric

DMAEMA	Mechanical and physical properties					
	Phosphoric acid			Ammonium dihydrogen phosphate		
	Crease recovery angle (W+F) ⁰	Tensile strength pascal	Elongation at break %	Crease recovery angle (W+F) ⁰	Tensile strength pascal	Elongation at break %
Untreated (blank)	140	3432327.5	12	140	3432327.5	12
Treated	140	3236194.5	12	140	3236194.5	12
Washed (25)	140	3236194.5	12	140	3236194.5	12

dihydrogen phosphate and then washed with excess of tetrachloro ethylene at 60°C for 15 min.

Flame retardant properties

Table I shows the effect of ammonium dihydrogen phosphate and phosphoric acid on the flame retardancy properties of the finished cotton fabric that's before and after 25 washing. It is clear that the flame retardant properties of the treated fabrics are excellent.

Mechanical properties

Table II shows the effect of washing on the mechanical and physical Properties of treated fabric with phosphoric acid and ammonium dihydrogen phosphate. It is clear that the tensile strength, crease recovery angle and elongation at break of the treated cotton fabric with phosphoric acid and ammonium dihydrogen phosphate are not affected by repeated washing.

CONCLUSIONS

The study revealed that the cellulose could modified by grafting with DMAEMA, which can then be

treated with phosphorous compounds to give high level of flame retardancy.

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