

Antibacterial, Flame Retardant, and Physico-Chemical Properties of Cotton Fabric Graft Copolymerized with a Binary Mixture of Acrylonitrile and 4-Vinylpyridine

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ABSTRACT: Modification of cotton fabric has been carried out through chemically induced graft copolymerization of binary mixture of acrylonitrile (AN) and 4-vinyl pyridine (4-VP) using ceric ammonium nitrate, (CAN) as initiator. Maximum percentage of grafting (151.28%) has been obtained at $[4\text{-VP}] = 0.376 \text{ mol L}^{-1}$ and $[\text{AN}] = 1.221 \text{ mol L}^{-1}$, $[\text{CAN}] = 0.0255 \text{ mol L}^{-1}$ and $[\text{HNO}_3] = 0.9585 \text{ mol L}^{-1}$ in 25mL of water at 70°C in 180 min. Post quarternization and phosphorylation reactions of the grey and grafted cotton fabrics have been carried out to study their antibacterial and flame retardant properties respectively. The fabrics have been characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The physico-chemical properties such as wettability, moisture regain, crease recovery and tensile strength of the grey and grafted cotton fabric have also been evaluated. The modified fabric has been shown to exhibit excellent antibacterial and flame retarding properties with improved physico-chemical properties except for the mechanical properties. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40415.

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INTRODUCTION

Cotton, a renewable fibrous material, finds wide range of applicability in textile industry. Although, the synthetic fibers are being used extensively, the cellulosic textile, cotton and modified cotton have proved to be unrivalled natural materials for domestic purposes such as clothing, beddings and furniture. The excellent textile properties of cotton such as wearing comfort, strength, washability, environment friendly and air permeability distinguish it from synthetic fibers and make it suitable to be used in different applications. However, the competence of cotton faces certain shortcomings such as flammability, microbial infection, nonwrinkle proof and poor water repellence, thereby, limiting its use. Flame retardancy and bacterial attack are the most serious complications in several areas such as safety and health care applications. Thus, in order to widen its frontiers of applications, promising researches in genetic engineering of this fiber/fabric are being carried out.

Cotton has been modified through graft copolymerization by both chemical and radiation induced methods using various monomers for use in different applications. Abidi et al.¹ graft copolymerized vinyl laurate monomers onto plasma activated cotton and studied the hydrophobicity treatments of cotton textiles. Water repelling properties were induced upon grafting

silicone containing monomer of varying formulations onto cotton fabrics.² Acrylonitrile grafted cotton was studied for its water absorbency by Deo and Gotmare.³ Mechanical strength was found to be better for *p*-benzoyloxy styrene grafted cotton fibers by the pad-cure method as compared to the fabrics treated with similar mixture by a prior art method.⁴

Nair⁵ studied the methods of enhancing the washability and durability of phosphorylated cotton. Kaur et al.⁶ carried out living radical polymerization and grafting of diethyl (acryloyloxy) ethylthiophosphoramidate onto cotton fabric to impart flame retardant properties. Graft copolymerization of methacrylamide onto cotton fabric to impart flame retardancy was carried out by photochemical method.⁷ To induce flame retardancy to the grey cotton fabric, grafting of glycidyl methacrylate followed by reaction with ethylene diamine and subsequently with orthophosphoric acid was carried out by Reddy et al.⁸

Abdel-Mohdy⁹ performed graft copolymerization of nitrogen and phosphorus containing monomers onto cotton fabric to develop flame retardant cotton textiles and it was observed that the presence of both nitrogen and phosphorus have synergistic effect on the flame retarding properties of the fabric. Flame retardant cotton fiber was synthesized using plasma-induced graft copolymerization of methacryloyloxyethyl diphenyl phosphate onto cotton surface by Paosawatyanong et al.¹⁰

Gupta and Bajpai prepared acrylamide-*co*-itaconic acid grafted cotton fabric showing antimicrobial activity.¹¹ A new durable antibacterial cotton fabric prepared by free-radical grafting of acrylic acid and itaconic acid and loaded with silver nanoparticles showed potent antibacterial activity to *E. coli*.¹² Selvam et al.¹³ developed antibacterial activity in functionalized cotton fabric by padding ZnO nanoparticles. Effect of grafting of vinyl monomers on thermal stability of polyester and cotton-polyester fabrics was investigated by Zohdy et al.¹⁴

In the present study, we report the modification of cotton fabric by graft copolymerization of binary monomer mixture of 4-VP and AN using CAN as initiator to improve upon the antibacterial and flame resistant properties of the fabric. Both nitrogen and phosphorus elements are known to affect flame retarding properties of the materials. Therefore, introduction of nitrogen by grafting of monomers containing nitrogen as an element (4-VP and AN) and introduction of phosphorus by phosphorylation reaction have been carried out to have the synergistic effect of these elements on the flame retarding properties of the fabric. Antibacterial properties are well established for the quaternary ammonium compounds, and the use of 4-VP as one of the monomers is for the reason that 4-VP can be easily quaternized thus offering the product capable of exhibiting antibacterial properties. In addition to flame retarding and antibacterial properties, physicochemical properties of grey and grafted fabric, Cotton-g-poly (4-VP-*co*-AN) have also been studied and compared.

EXPERIMENTAL

Materials and Method

Cotton fabric was purchased from the local Khadi shop. Sodium bicarbonate (Loba Chemie) was used for refluxing. 4-Vinyl pyridine (Merck) was freshly distilled before use and the middle fraction was used. Acrylonitrile (Merck), ceric ammonium nitrate (Nice Chemicals) and nitric acid (SD Fine Chemicals) were used as received. Distilled water was used as the reaction medium. Dimethyl formamide (DMF) (SD Fine Chemicals), pyridine (SD Fine Chemical) and petroleum spirit (SD Fine Chemicals) were used as reaction solvents.

Preparation of the cotton fabric samples and the method of graft copolymerization has been discussed elsewhere.¹⁵

Antimicrobial Activity

The antimicrobial activity of the fabric was quantitatively evaluated against gram-negative and gram-positive bacteria, *Pseudomonas aeruginosa* (PA) and *Staphylococcus aureus* (SA) respectively. The antimicrobial activity of the treated samples was checked by counting colony forming unit (CFU) on nutrient agar plate.

Preparation of Bacterial Culture

A single colony of PA and SA each, was grown in 10 mL of nutrient broth (Beef extract 0.3%, Peptone 0.5%, NaCl 0.8%, pH 7.1) and incubated overnight at 30°C. The cultures were then centrifuged at 10,000 rpm at 5°C for 10 and 5 min, respectively of PA and SA cultures and finally suspended in 10 mL of normal saline (0.8% NaCl solution). The solution is referred to as bsA. The optical density was recorded at 660 nm against normal saline as the blank.

Quaternization of Cotton Grafted Sample. To introduce antibacterial activity to Cotton-g-poly (4-VP-*co*-AN), quaternization was carried out by treating the grafted fabric with methyl 4-hydroxy benzoate. The grafted sample was suspended in a solution of methyl 4-hydroxy benzoate (3 mL) in 100 mL xylene and heated at 40°C for 24 h.

Antimicrobial Filtration Method. The grey and quaternized samples (1 × 1 cm²) were dipped in the bacterial saline suspension, bsA, overnight. The cotton fabric with attached bacteria was removed from bsA and transferred to 10 mL of fresh normal saline solution, referred to as bsB. Now both residual bsA and bsB solutions were shaken over orbital shaker for 2 min and diluted up to 1 × 10⁻⁶ of initial concentration. The diluted suspension (40 μm) of bsA and bsB was separately seeded onto the nutrient agar in the Petri dish. The plates were incubated at 37°C overnight. The number of bacterial colonies in the plate was counted.

The percent bacterial removal of grey cotton fabric and quaternized cotton fabric was calculated by the following formula

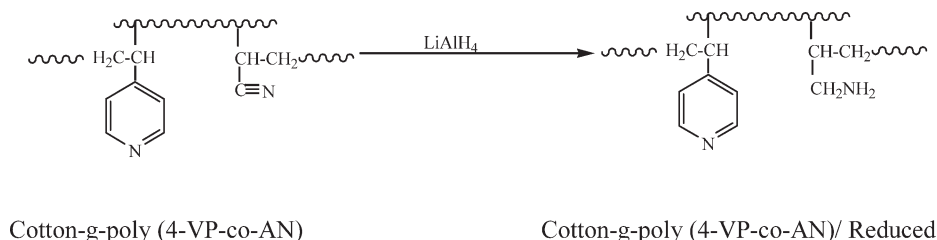
$$\text{Removal percent} = \frac{N_0 - N_1}{N_0} \times 100$$

where N_0 and N_1 , respectively are the total number of CFU in pure cotton fabric and in grafted cotton fabric.

Flame Retardant Properties

Samples of grey cotton and Cotton-g-poly (4-VP-*co*-AN) of size (80 mm × 200 mm), specific for BS 5438: 1989 standard test, have been used for flammability studies. The post grafting phosphorylation reactions were carried out by treating the fabric with phosphorous trichloride (PCl₃)/pyridine and phosphorous oxychloride (POCl₃). Dimethyl formamide (DMF), pyridine and petroleum spirit were used as the reaction solvents.

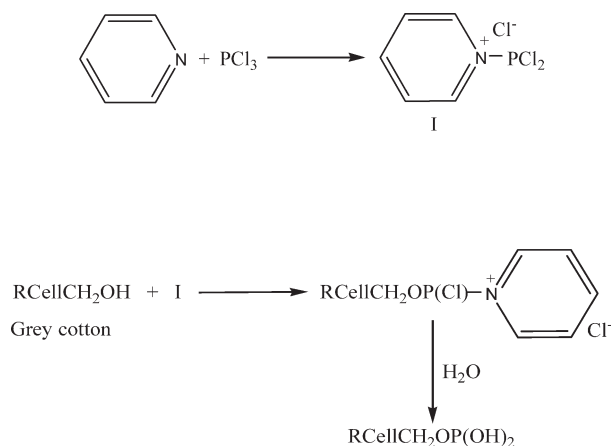
Treatment of Cotton-g-poly (4-VP-*co*-AN) with LiAlH₄. Cotton-g-poly (4-VP-*co*-AN) sample was suspended in 50 mL of tetrahydrofuran (THF) in a round bottomed flask. To it was added lithium aluminum hydride (LAH) in a catalytic amount and the mixture was stirred for at least 6h. The pendant nitrile groups in Cotton-g-poly (4-VP-*co*-AN) were reduced to primary amine groups.



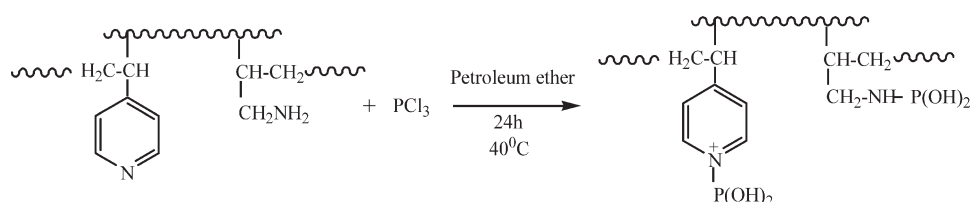
Phosphorylation Reactions. Phosphorylation was carried out by the following methods:

Phosphorylation with phosphorus trichloride. Phosphorylation of grey cotton and reduced Cotton-g-poly (4-VP-co-AN) was carried by suspending the samples in petroleum ether (200 mL) and pyridine (200 mL) in separate bi-necked flasks, respectively. Phosphorus trichloride (4 mL) was added slowly from the separating funnel to each flask and the flasks were placed in water bath maintained at 40°C. The reaction was carried out for 24 h. Thereafter, the fabrics were washed thoroughly with water to free from the solvents, dried and weighed. The samples were initially dried in air and then at 40–45°C.

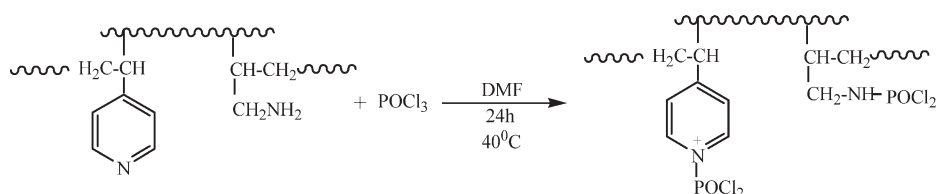
i. Grey Cotton



ii. Reduced Cotton-g-poly (4-VP-co-AN)



iii. Cotton-g-poly (4-VP-co-AN)/Reduced



Phosphorylation with phosphorus oxychloride. Phosphorylation reaction of grey Cotton and Cotton-g-poly (4-VP-co-AN) sample was carried out by refluxing the sample with phosphorus oxychloride in dimethyl formamide for 24 h. After the reaction, the fabric was washed with water and dried.

Cotton-g-poly (4-VP-co-AN)/Reduced

Flammability Test

Flammability behavior of grey, grafted and phosphorylated grafted fabrics was determined qualitatively and quantitatively.

Qualitative Determination. Qualitative determination of the flammability behavior of the fabric was carried out by burning the samples, placed vertically over the candle flame.

Quantitative Determination. Quantitative determination of flammability of all the samples was carried out on Shirley Manual Flammability Tester, which follows the relevant BS 5438: 1989 standard test.

CHARACTERIZATION

FTIR Spectroscopy

The FTIR spectra of gray cotton fabric, Cotton-g-poly (4-VP-co-AN), quaternized Cotton-g-poly (4-VP-co-AN) and phosphorylated Cotton-g-poly (4-VP-co-AN) were obtained by Thermo-5700 spectrophotometer.

SEM Analysis

The surface topology of grey Cotton fabric, Cotton-g-poly (4-VP-co-AN) and quaternized Cotton-g-poly (4-VP-co-AN) was observed by SEM using JEOL JSM-6100 scanning microscope, operating at an accelerating voltage of 10 kV. Electron micrographs of the sample were recorded at 500× and 1500× magnifications.

TGA

Thermogravimetric analysis of grey Cotton fabric, Cotton-g-poly (4-VP-co-AN) and phosphorylated Cotton-g-poly (4-VP-co-AN) was carried out on Perkin Elmer Diamond at a heating rate of 10°C min⁻¹ in air.

Physico-chemical Properties

Wettability (*W*) of grey Cotton fabric, Cotton-g-poly (4-VP-co-AN), quaternized Cotton-g-poly (4-VP-co-AN) and phosphorylated Cotton-g-poly (4-VP-co-AN) was determined by the time

taken for complete absorption of a water drop by the fabric according to BS 4554 test. The fabric is designated hydrophilic if the time taken to absorb the water drop is <200 s and hydrophobic if more than 200 s.

Moisture uptake of grey cotton fabric, Cotton-g-poly (4-VP-co-AN), quaternized Cotton-g-poly (4-VP-co-AN) and phosphorylated

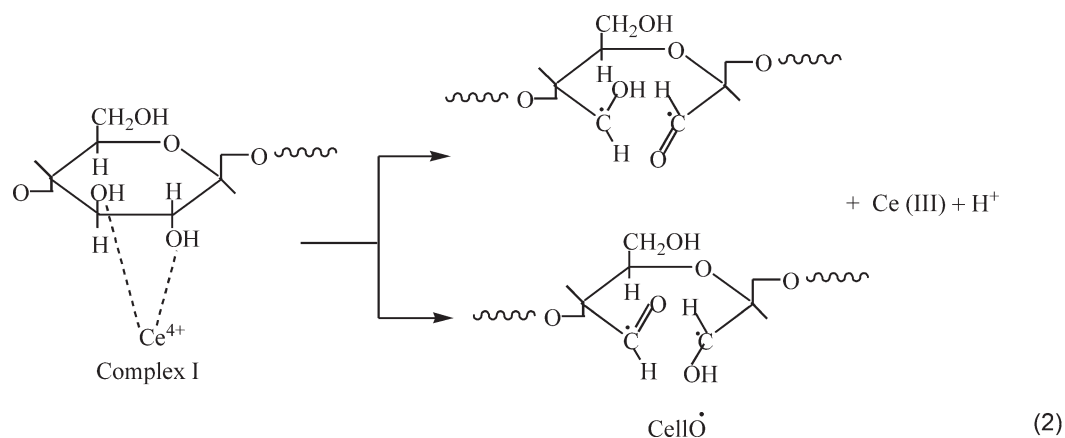
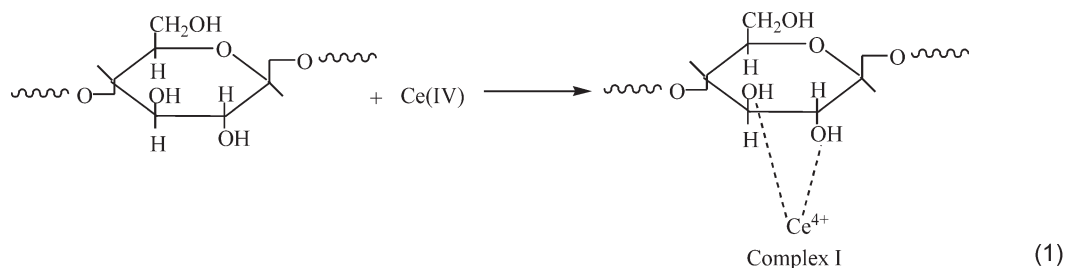
Cotton-g-poly (4-VP-co-AN) samples was studied by placing the fabric samples on the sieve placed at a height of 4" from the water level in water bath at 30°C with relative humidity 85%. The water absorption was recorded after every 1h till it became constant.

Dry wrinkle crease recovery angle (CRA) of grey Cotton fabric, Cotton-g-poly (4-VP-co-AN), quaternized Cotton-g-poly (4-VP-co-AN) and phosphorylated Cotton-g-poly (4-VP-co-AN) was determined according to British standard test BSEN 22313:1992, both in warp to warp (face to face) and weft to weft (end to end) directions.

Tensile strength (TS) of grey Cotton fabric, Cotton-g-poly (4-VP-co-AN), quaternized Cotton-g-poly (4-VP-co-AN) and phosphorylated Cotton-g-poly (4-VP-co-AN) was tested in the warp direction on Zwick Tensile Tester equipped with 1kN load cell

of the cellulose backbone other than the original concept of involvement of primary group of cellulose backbone. It has been shown that C₂—C₃ bond is also involved in forming complex with the transition metal ions. Thus, one cannot conclude that the free radical site, formed as a result of metal ion oxidation, would be restricted to only one site of the cellulose backbone.¹⁶ Ceric ions are also known to form complex with the monomers (M), which also dissociates activating the monomers through single electron transfer reaction. In view of this, in general, the mechanism of transition metal ion induced grafting process, where glycol groups are involved, using Ce (IV) salt, can be represented as follows:

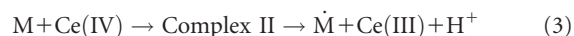
Initiation and Propagation



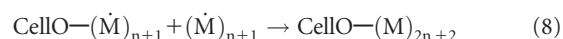
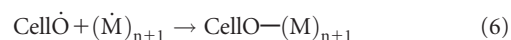
and testing was conducted at speed of 50 mm min⁻¹.

RESULTS AND DISCUSSION

Synthesis of graft copolymer of cellulose essentially involves generation of active sites on the cellulose backbone on which suitable monomer is polymerized. In the present study, CAN has been used as redox initiator for activation of grafting reaction. Ceric ions are known to form complex with various functional groups, which undergoes decomposition by one electron transfer mechanism to produce free radicals. Cotton cellulose with free hydroxyl groups enters into the complex formation with ceric ions. Thus, the proposed mechanism has been ascribed to the intermediate formation of a metal ion-cellulose complex of chelate type which is not restricted to a single site



Termination



The mechanism predicts that the ceric ions interact with cellulose to produce cellulose-ceric complex (I) and

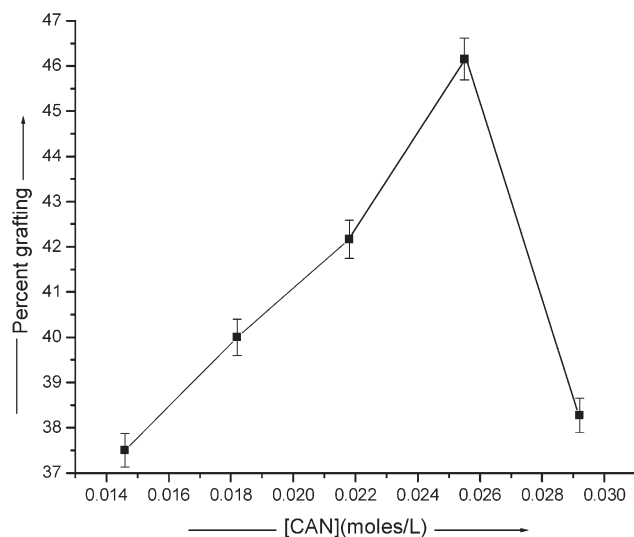


Figure 1. Effect of [CAN] on Pg of binary mixture (4-VP+AN), $[\text{HNO}_3]=0.958 \text{ mol/L}$, $[\text{AN}]=0.610 \text{ mol/L}$, $[4\text{-VP}]=0.3766 \text{ mol/L}$, Time=120min, Temperature= 50°C , Water=25mL.

monomer to give monomer-ceric complex (II), both of which dissociate to give free radicals on C_2 and C_3 of cellulose and monomer respectively with the reduction of Ce^{4+} ion. The free radicals so formed then react to produce the graft copolymer.

The effect of different reaction parameters such as concentrations of ceric ammonium nitrate, nitric acid, monomer mixture, amount of water, reaction temperature and reaction time on the percentage of grafting has been studied and the results are explained in the light of the above mechanism.

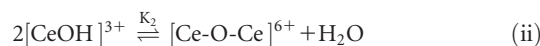
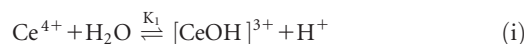
Effect of [CAN]

The generation of active sites on cotton fabric via complex formation depends upon the concentration of the initiator and in view of this, graft copolymerization of the binary monomer mixture (4-VP + AN) onto cotton fabric has been studied as a function of concentration of CAN and the results are presented in Figure 1. It is observed from the figure that percentage of grafting of the binary mixture increases with increasing [CAN], giving maximum (46.15%) at $[\text{CAN}] = 0.0255 \text{ mol L}^{-1}$. The increase in $[\text{Ce}^{4+}]$ facilitates the formation of complex (I) leading to the generation of radical sites on the polymer backbone (Step 2) and hence percentage of grafting increases. Beyond the optimum value, the excess Ce^{4+} ions increase the formation of complex (II) with monomer leading to homopolymer formation thus affecting grafting percentage. Termination of growing chains is also accelerated at higher $[\text{Ce}^{4+}]$ leading to decrease in percentage of grafting.¹²

Effect of $[\text{HNO}_3]$

Percentage of grafting of the binary mixture (4-VP+AN) was studied as a function of nitric acid concentration and the results are presented in Figure 2. It is observed that there exist an optimum concentration of nitric acid where the maximum percentage of grafting of (4-VP+AN) is obtained. Maximum grafting (46.15%) is obtained at optimum concentration (0.958 mol L^{-1}) of HNO_3 . Further increase in the concentration of HNO_3

decreases the percentage of grafting. The increase in Pg with increasing concentration of HNO_3 is due to the fact that the concentration of Ce^{4+} increases with increasing concentration of acid, which forms complete complex with the substrate i.e., cotton fabric and hence facilitates grafting.



From eq. (1)

$$[\text{CeOH}]^{3+} = \frac{k_1[\text{Ce}]^{4+}}{[\text{H}]^+}$$

The total conc. of ceric $[\text{Ce}^{4+}]_T$ is thus given by

$$[\text{Ce}]_T^{4+} = \text{Ce}^{4+} + [\text{CeOH}]^{3+} \\ = (1 + k_1/[\text{H}^+])[\text{Ce}]^{4+}$$

$$\frac{1}{[\text{Ce}]^{4+}} = \frac{1}{[\text{Ce}]_T^{4+}} + \frac{k_1}{[\text{Ce}]_T^{4+}[\text{H}]^+}$$

Decrease in percentage of grafting beyond optimum $[\text{HNO}_3]$ is attributed to the fact that with increasing $[\text{HNO}_3]$, the equilibrium (i) shifts progressively towards $[\text{Ce}]^{4+}$ formation, which is known to accelerate the termination of growing polymeric chains resulting in the decrease in percentage of grafting. Initial increase in the extent of grafting may be associated with the fact that the acid catalyzes the grafting reaction and enhances the oxidizing capacity of the initiator. The subsequent decrease in grafting may be related to the abundance of H^+ which may act as a free radical terminator.

Effect of [Monomer]

Figure 3 represents the effect the concentration of the binary monomer mixture on percentage of grafting. The Pg was determined as a function of concentration of each monomer in the binary system. Keeping the concentration of 4-VP fixed at 0.376 mol L^{-1} , percentage of grafting of the binary mixture was determined as a function of [AN]. It is observed that Pg

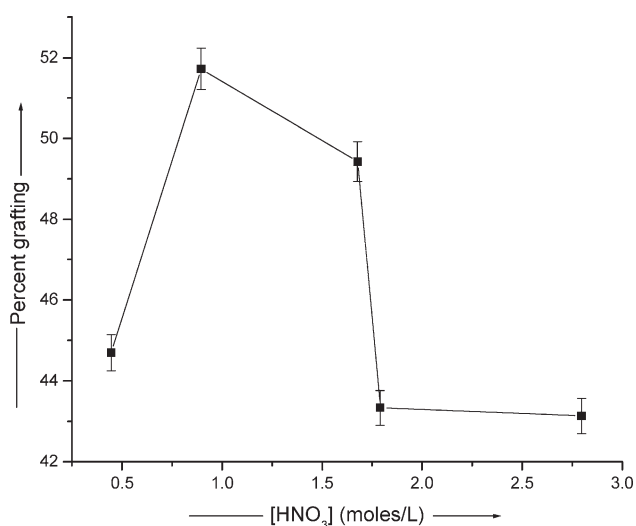


Figure 2. Effect of $[\text{HNO}_3]$ on Pg of binary mixture (4-VP+AN), $[\text{CAN}] = 0.0255 \text{ mol L}^{-1}$, $[\text{AN}] = 0.610 \text{ mol L}^{-1}$, $[4\text{-VP}] = 0.3766 \text{ mol L}^{-1}$, Time = 120 min, Temperature = 50°C , Water = 25 mL.

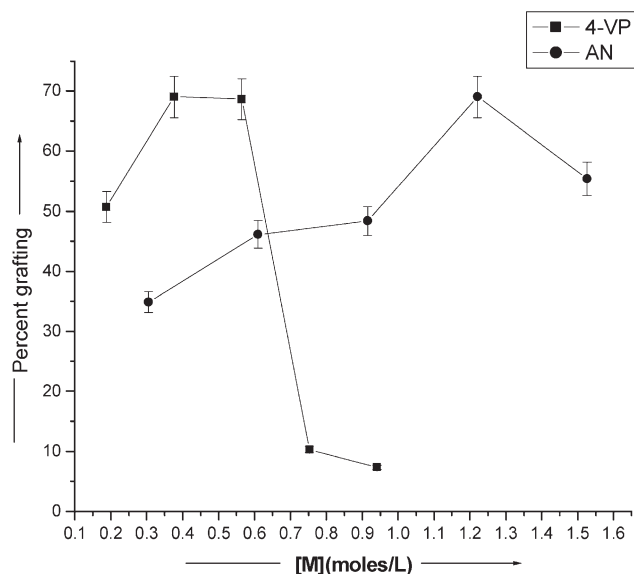


Figure 3. Effect of [Monomer] on Pg of binary mixture (4-VP+AN), [CAN] = 0.0255 mol L⁻¹, [HNO₃] = 0.958 mol L⁻¹, Time = 120 min, Temperature = 50°C, Water = 25 mL.

increases steadily with increasing [AN] giving maximum (69.05%) at [AN] = 1.22 mol L⁻¹ beyond which it decreases gradually and becomes constant. Keeping the optimum concentration of AN fixed at 1.22 mol L⁻¹, the concentration of 4-VP was varied and it was observed that percentage of grafting of binary mixture first increases and then decreases continuously with each increment in the concentration of 4-VP. Maximum percentage of grafting (69.05%) of binary mixture was obtained at 0.376 mol L⁻¹ of 4-VP.

From the results, it is thus revealed that the addition of AN to 4-VP increases the reactivity of 4-VP towards grafting. When 4-VP was grafted individually, maximum grafting (31.1%) was obtained at an optimum concentration of 0.475 mol L⁻¹.¹⁵ However, when grafting of 4-VP was carried out in a mixture with AN, maximum Pg (69.05%) was obtained at a lower concentration of 4-VP (0.376 mol L⁻¹). These observations are explained by taking into consideration of reactivity ratios of AN (r_1) and 4-VP (r_2). The r_1 of AN (0.113) and r_2 for 4-VP (0.41) reveals that the growing AN polymeric free radical chain would react preferably with 4-VP than its own monomer while the growing 4-VP chain radical would react with 4-VP than AN. This means that on increasing the concentration of 4-VP with fixed concentration of AN, percentage of grafting increases giving maximum percentage of grafting at a higher concentration with concurrent formation of homopolymer. But when concentration of AN is increased w.r.t. the fixed concentration of 4-VP, percentage of grafting increases, giving maximum grafting percentage (69.05%). But with increasing [AN] beyond the optimum value, the growing polymeric chains of AN terminate to give homopolymer because of higher k_p (32,500 L mol⁻¹ s⁻¹) and k_t (4400 × 10⁶ L mol⁻¹ s⁻¹) values. This leads to decrease in percentage of grafting.

Effect of Reaction Time

Percentage of grafting of the binary mixture onto cotton fabric was studied as a function of reaction time and the results are pre-

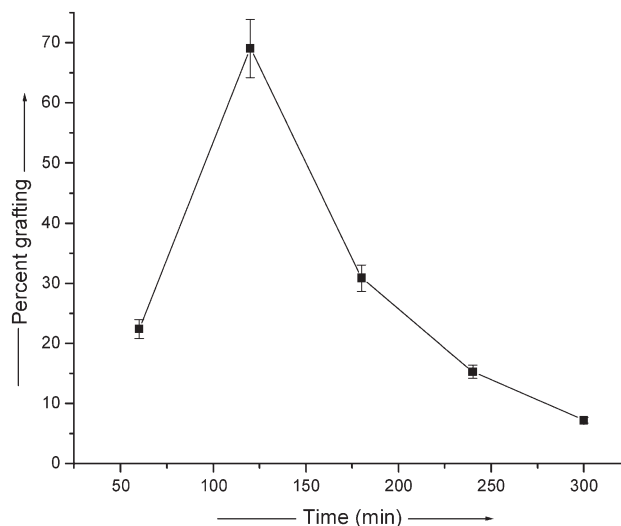
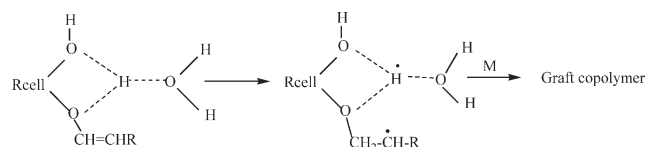


Figure 4. Effect of time on Pg of binary mixture (4-VP+AN), [CAN] = 0.0255 mol L⁻¹, [HNO₃] = 0.9585 mol L⁻¹, [AN] = 1.221 mol L⁻¹, [4-VP] = 0.3766 mol L⁻¹, Temperature = 50°C, Water = 25 mL.

sented in Figure 4. It is observed from the figure that the percentage of grafting increases with increase in time, giving maximum grafting (69.05%) in 120 min. Further increase in the time of reaction leads to backbiting of the growing grafted polymeric chains and hence decreases the percentage of grafting.¹⁷

Effect of Amount of Water

Figure 5 presents the effect of amount of water on the percentage of grafting of the binary monomer mixture and it is observed that as the amount of water increases, grafting percentage increases giving maximum (69.05%) in 25 mL of water. Cellulose being hydrophilic extensively enters into hydrogen bonding with water molecules thus exposing the sites for grafting. This also helps in the easy diffusion of monomer to these active sites leading to increase in percentage of grafting. Further increase in the amount of water results in decrease in percentage of grafting which may be due to the three component complex formed between substrate, water and the monomer (complex III), in addition to the formation of free radical site on the backbone. The complex liberates atomic hydrogen that initiates homopolymerization. In addition, with increased amount of water beyond optimum, swelling of the fabric may be to such an extent that generation of active sites becomes a slow process. Decrease in concentration of ceric ion as well as monomer takes place resulting in the decreased amount of cellulose-ceric complex and the decreased accessibility of the monomer to the active sites thereby leading to decrease in percentage of grafting.



Complex III

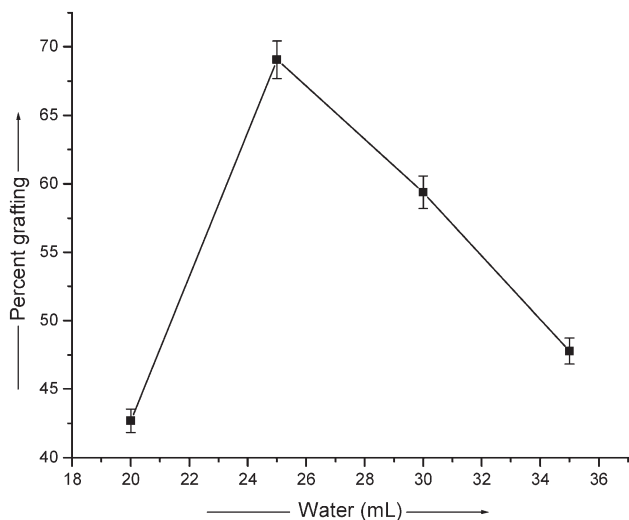


Figure 5. Effect of amount of water on Pg of binary mixture (4-VP+AN), [CAN] = 0.0255 mol L⁻¹, [HNO₃] = 0.9585 mol L⁻¹, [AN] = 1.221 mol L⁻¹, [4-VP] = 0.3766 mol L⁻¹, Time = 120 min, Temperature = 50°C.

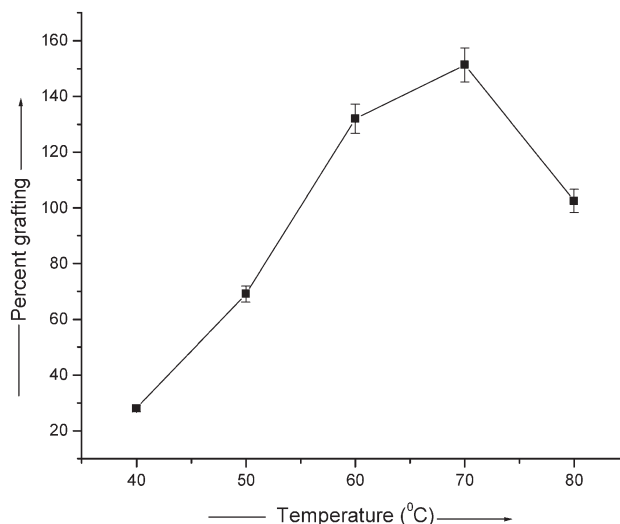


Figure 6. Effect of temperature on Pg of binary mixture (4-VP+AN), [CAN] = 0.0255 mol L⁻¹, [HNO₃] = 0.9585 mol L⁻¹, [AN] = 1.221 mol L⁻¹, [4-VP] = 0.3766 mol L⁻¹, Time = 120 min, Water = 25 mL.

Effect of Temperature

Percentage of grafting of (4-VP+AN) onto cotton fabric was studied as a function of temperature and the results are presented in Figure 6. It is observed that percentage of grafting increases with increasing temperature affording maximum grafting (151.28%) at 70°C. Increase in Pg with increasing temperature is due to the increased rate of diffusion of monomer to the active sites. Beyond the optimum temperature, decrease in Pg is attributed to the increase in various chain transfer reactions leading to termination of growing polymeric chains. Increased molecular motion with increasing temperature results in decay of the free radicals that also leads to decrease in percentage of grafting. At higher temperature, thermal polymerization is also accelerated.

Antibacterial Test

The number of colonies in the saline (bsA) solution and the colonies attached to the fabric in (bsB) saline solution with percent removal of the bacterial colonies (given in bracket) for grafted and antibacterial finished grafted fabric are presented in Table I. It is observed from the table that grafting of binary monomers on to the fabric improves the antibacterial behavior of the fabric as compared to grey cotton fabric. Antibacterial activity of the grafted cotton with respect to percent removal lies between 41 and 96%. In bsB saline solution, maximum percent removal (95.73%) is observed in Cotton-g-poly (4-VP-co-AN) (Figure 7) however, Cotton-g-poly (4-VP-co-AN)/benzoate

after quaternization completely removes (100%) both gram +ve and -ve bacteria. Thus, the quaternized Cotton-g-poly (4-VP-co-AN) with methyl 4-hydroxy benzoate behaves as an excellent antibacterial material.

Flammability Behavior

Qualitative Determination. On direct burning, grey and grafted cotton fabric burnt immediately but the propagation rate of the grafted cotton fabric was slow and a small amount of ash content was formed. The grey phosphorylated cotton samples burnt little slowly than grafted samples. The grafted phosphorylated cotton fabric, however, burnt only in the presence of the flame. The flame extinguished with the removal of the flame source. The ash content was also much higher.

Quantitative Determination. The flammability behavior of grey fabric, grafted fabric and phosphorylated grafted fabric is tabulated in Table II. The table records afterglow i.e., the time it retains the glow/burning, the total area burnt and the ash content of the sample which has been subjected to the burning flame for 12 s.

It is observed that the grey cotton burns completely with 10 s afterglow time and negligible ash content (0.02 g). In case of grafting of cotton with binary mixture of 4-VP and AN, the afterglow time increases to 18 s during which the fabric is

Table I. Number of Colonies in bsA and bsB Saline of Gram Negative and Gram Positive Bacteria with Percent Removal Given in Bracket

Sample	Gram negative bacteria (1×10^{-6})		Gram positive bacteria (1×10^{-6})	
	bsA	bsB	bsA	bsB
Cotton	387	258	212	98
Cotton-g-poly(4-VP-co-AN)	98 (74.67%)	11 (95.73%)	62 (70.75%)	57 (41.83%)
Cotton-g-poly(4-VP-co-AN)/benzoate	0 (100%)	0 (100%)	0 (100%)	0 (100%)

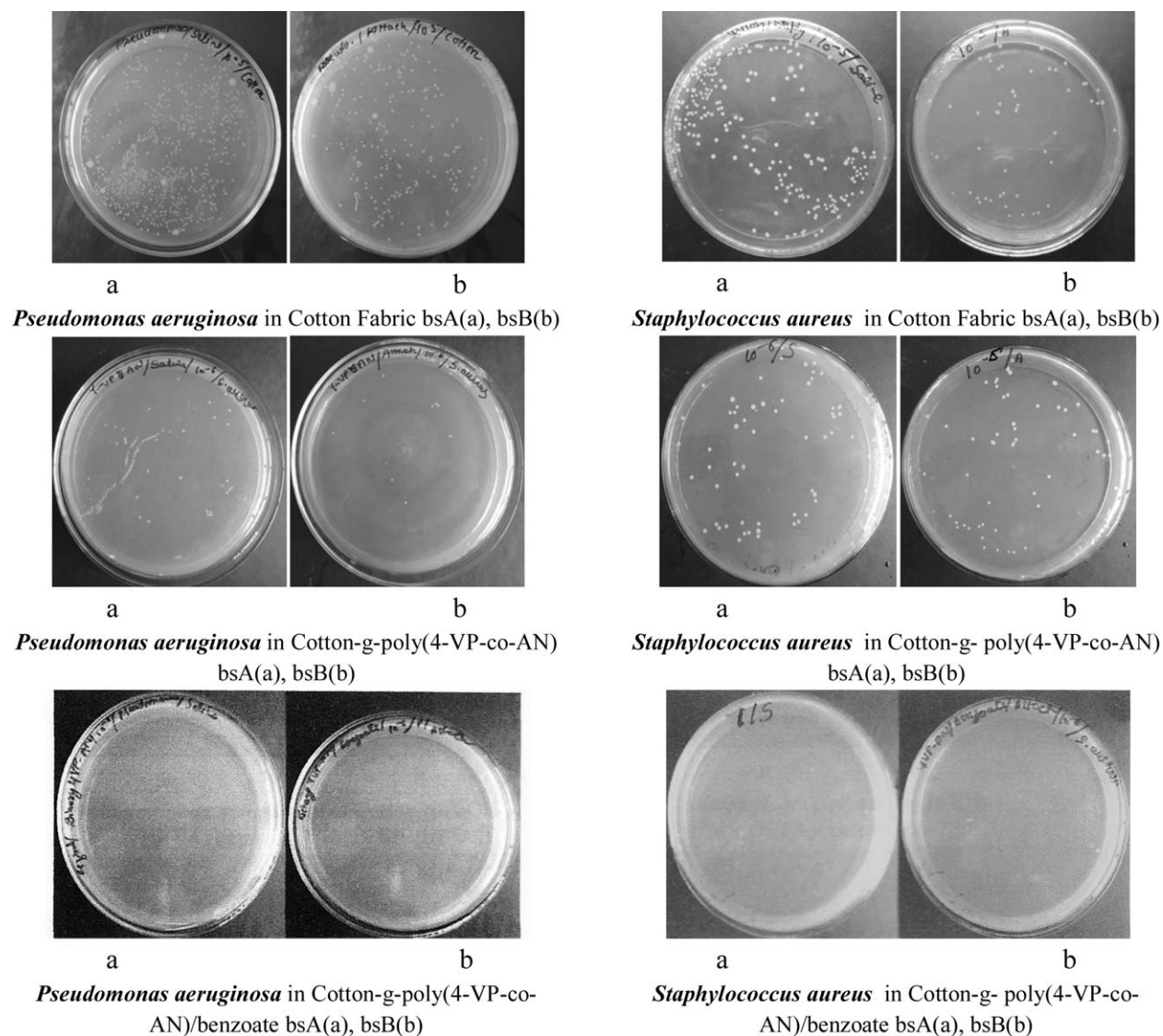


Figure 7. Number of colonies of bacteria in bsA and bsB Saline in grey, grafted and quaternized cotton fabric.

completely destroyed. The ash content is also higher as compared to cotton fabric. This indicates that the grafting of cotton has improved upon the flammability behavior to the extent that the time taken for complete burning has increased i.e., the propagation of the flame is reduced.

Introduction of phosphorus to the fabric improves flammability behavior. The afterglow comes to zero meaning that as soon as the flame is withdrawn, the burning stops. This is indicative of only small areas of the fabric, which are exposed to the flame. Higher ash content is formed than that of grey fabric.

Table II. Vertical Flammability Tests for Grey, Grafted, Quaternized, and Phosphorylated Grafted Cotton Samples

Type of sample	Time of flame (s)	After glow (s)	Area burnt of total area (160 cm ²)	Flame duration (s)	Ash content (g)
Untreated cotton	12	10	Completely burnt	2	0.02
Cotton-g-poly(4-VP-co-AN)	12	18	Completely burnt	41	0.83
Cotton-g-poly(4-VP-co-AN)/Quat/PCl ₃	12	0	1.66	-	0.20
Cotton-g-poly(4-VP-co-AN)/POCl ₃	12	0	3.00	-	0.22

Time of flame (in seconds) is the time for which flame is applied.

After glow is the glowing combustion in a material after cessation of the flame.

Flame duration of the time up to which the cotton keep burning after the removal of flame.

Ash content is the wt. of ash in grams of the burnt area.

Table III. Rate of Flame Propagation for Grey, Grafted, Quaternized, and Phosphorylated Cotton Samples

Samples	Rate of flame propagation (mm s^{-1})
Untreated cotton	16.66
Cotton-g-poly(4-VP-co-AN)	3.27
Cotton-g-poly(4-VP-co-AN)/Quat/ PCl_3	1.02
Cotton-g-poly(4-VP-co-AN)/ POCl_3	1.75

On comparison of the rate of flame propagation (Table III), it is observed that in the grey and grafted samples, the cotton fabric is completely burnt. On the other hand, in case of the grafted phosphorylated sample, the flame extinguishes immediately after the removal of burning flame. The rate of propagation is very slow and only that area is burnt to which the flame is applied, with higher char formation.

Thus, from the above results, it is evident that grafting with monomers containing nitrogen as one of the elements and introduction of phosphorus upon phosphorylation reaction improves the flammability behavior of the fabric because of the synergistic effect of these elements.

CHARACTERIZATION

FTIR Analysis

IR spectra of cotton fabric, Cotton-g-poly (4-VP-co-AN), quaternized and phosphorylated Cotton-g-poly (4-VP-co-AN) respectively are presented in Figure 8. IR spectra of cotton fabric exhibits a broad peak at 3376 cm^{-1} (bonded $-\text{OH}$ groups) and peaks at 2921 , 1454 , and 1059 cm^{-1} arising from ν_{CH_2} , $\nu_{\text{C}-\text{C}}$ and $\nu_{\text{C}-\text{O}-\text{C}}$ stretching respectively are observed. Cotton grafted with binary mixture of 4-VP and AN shows a peak at 2244 cm^{-1} ($\nu_{\text{C}\equiv\text{N}}$ str.) and peaks at 1374 , 1508 , 1639 , and cm^{-1} due to $\nu_{\text{C}-\text{N}}$ and $\nu_{\text{C}=\text{N}}$ str., respectively of the pyridine ring. These additional bands confirm the formation of the graft copolymer of cotton fabric with binary mixture of 4-VP and AN.

In the FTIR spectrum of methyl 4-hydroxy benzoate treated Cotton-g-poly (4-VP-co-AN), the medium peak at 1580 cm^{-1} due to conjugated $\text{C}=\text{N}$ of pyridine ring becomes stronger with high intensity upon quarterization where as the peak due to the nitrile group appears with lower intensity which may be due to bulky counter ion, methyl 4-hydroxybenzoate phenolate ion. Additional peak at 1508 cm^{-1} ($\nu_{\text{C}=\text{N}}$ def.) is also observed.

FTIR spectra of the phosphorylated sample shows that in case of PCl_3 treated Cotton-g-poly (4-VP-co-AN), in addition to the regular peaks, peaks at 1508 cm^{-1} ($\nu_{\text{C}=\text{N}}$ str.), 3417 cm^{-1} ($\nu_{\text{N}-\text{H}}$ str.) and 723 cm^{-1} ($\nu_{\text{P}-\text{Cl}}$ str.) are observed while POCl_3 treated grafted sample of Cotton-g-poly(4-VP-co-AN) showed peaks at 3348 cm^{-1} ($\nu_{\text{N}-\text{H}}$ str.), 1163 cm^{-1} ($\nu_{\text{P}=\text{O}}$ str.), and 1033 cm^{-1} ($\nu_{\text{P}-\text{O}-\text{C}}$ str.). Additional peaks due to the presence of phosphorus in the phosphorylated samples give an evidence of the post grafting phosphorylation reactions and introduction of phosphorus in the grafted cotton fabric samples.

SEM Analysis

Figure 9 represents the SEMs of grey cotton fabric, Cotton-g-poly (4-VP-co-AN) and quaternized Cotton-g-poly (4-VP-co-

AN) respectively, at different magnifications ($500\times$ and $1500\times$). The comparison of the SEMs of the grafted sample with that of ungrafted sample gives a clear indication of change in the topology of the grafted sample. It is evident from figures that after graft copolymerization the thin cellulosic fibers lying apart started forming thick bundles due to incorporation of grafted chains onto the back bone affecting morphological distinction between grey and grafted sample. In the grey cellulose, the fiber surface is even, while in the grafted cellulose, the fibers have deposition of polymer, thus presenting an uneven surface.

The SEM photograph of cotton fabric before quaternization or antimicrobial treatment of all the samples shows that the diameter of the grafted fabric is larger than the untreated cotton fabric leading to decrease in space between the fibers. After quaternization of grafted fabric with methyl 4-hydroxy benzoate, the fabric shows rough surface and presence of some granular material indicating that the finishing agent is attached to the surface of fabric. The change in the topology of the antibacterial cotton fabric in comparison to that of the grafted cotton fabric evinces the occurrence of reaction on the surface.

TGA Analysis

The primary thermograms of cotton fabric, Cotton-g-poly (4-VP-co-AN) and phosphorylated Cotton-g-poly (4-VP-co-AN) are presented in Figure 10. The initial decomposition temperature (IDT), final decomposition temperature (FDT), the temperatures of the DTA peaks and decomposition temperature (DT) at every 10% weight loss for each sample are tabulated in Table IV.

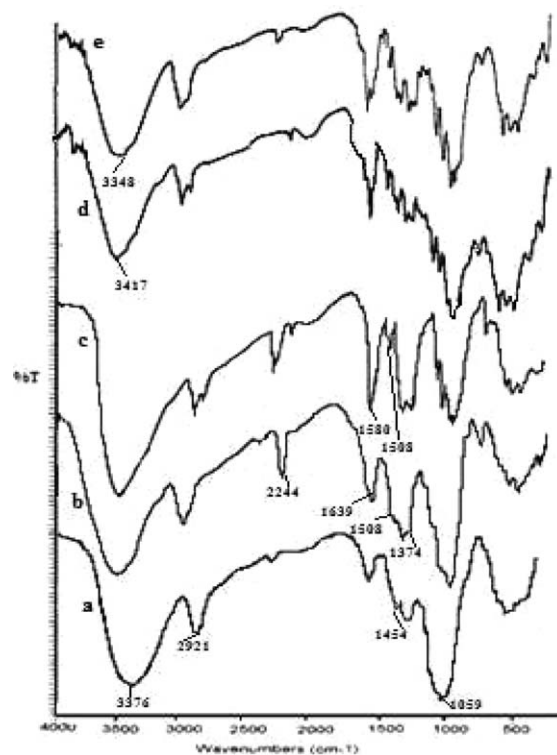


Figure 8. FTIR of (a) Cotton Fiber (b) Cotton-g-poly(4-VP-co-AN) (c) Cotton-g-poly(4-VP-co-AN)/Benzoate (d) Cotton-g-poly(4-VP-co-AN)/ PCl_3 (e) Cotton-g-poly(4-VP-co-AN)/ POCl_3 .

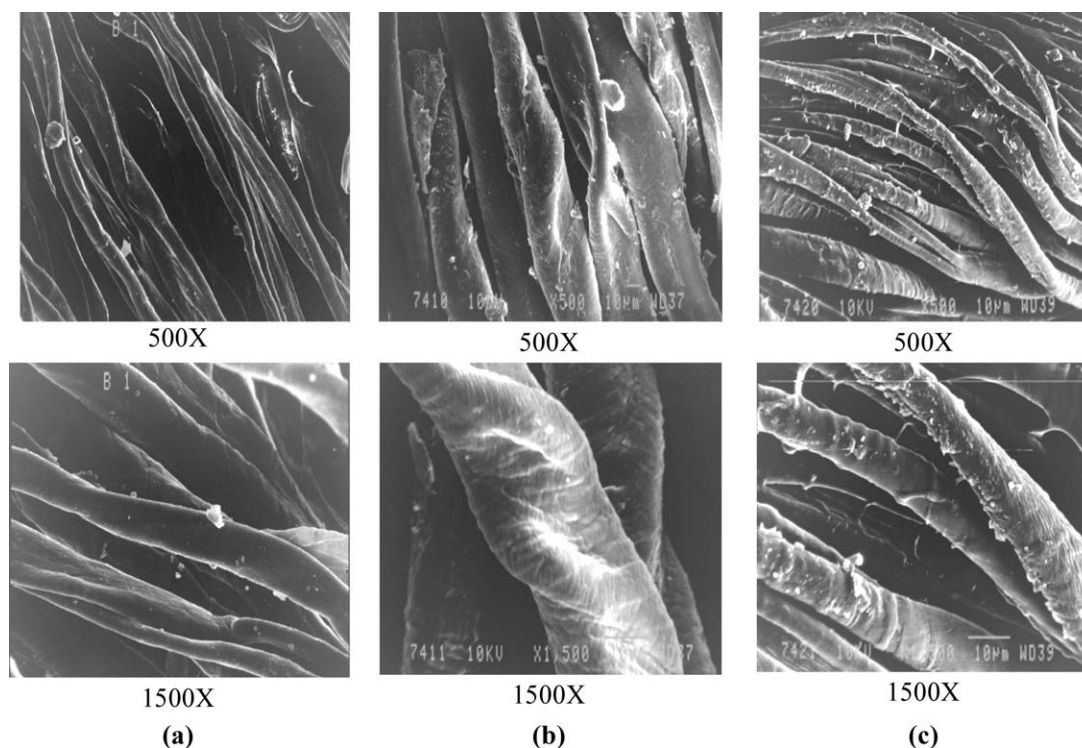


Figure 9. SEM of (a) Grey, (b) cotton-g-poly(4-VP-co-AN) and (c) Cotton-g-poly(4-VP-co-AN)/Benzoate at 500 \times and 1500 \times magnifications.

It is observed from the thermograms that grey cotton is stable up to 325 $^{\circ}$ C from where begins the initial decomposition. Further rise in temperature degrades the fabric at a faster rate which is indicated from a very small difference in the temperature between each 10% weight loss from 10 to 70% weight loss. The temperature difference between 70 and 80% weight loss is quite high (49.55 $^{\circ}$ C). Formation of stable glycosan has been reported on thermal degradation of cellulose. Final decomposition begins at 490 $^{\circ}$ C with 100% weight loss.

On perusal of the thermogram of Cotton-g-poly (4-VP-co-AN) and Table IV, it is observed that IDT values (215 $^{\circ}$ C with 1.99 wt % loss) is lower than the grey cotton fabric but the final decomposition temperature (FDT) is higher. The decomposition temperatures at every 10 wt % loss are lower up to 50 wt % loss beyond which it increases with increase in temperature difference between the decomposition temperatures at every 10 wt % loss indicating better thermal stability than that of grey cotton. Also, the percentage of residue left in case of Cotton-g-poly (4-VP-co-AN) is higher (7.5%).

The primary thermograms of PCl_3 and POCl_3 treated Cotton-g-poly (4-VP-co-AN) show double stage of decomposition with initial decomposition temperatures (IDT) (259.4 $^{\circ}$ C and 263.63 $^{\circ}$ C, respectively) lower than the IDT of pristine cotton fabric (325 $^{\circ}$ C), however, the FDT of PCl_3 and POCl_3 treated grafted fabric (685 and 584.5 $^{\circ}$ C, respectively) is higher than the pristine (490 $^{\circ}$ C) and the binary mixture grafted cotton fabric (600 $^{\circ}$ C). The DT values at every 10% weight loss for the phosphorylated grafted fabric is lower than the untreated cotton-g-poly(4-VP-co-AN) grafted fabric, but the temperature difference

between each 10 wt % loss is much higher and the temperature difference between 30 and 40% shoots to a difference of 182.33 and 145.0 $^{\circ}$ C in PCl_3 and POCl_3 treated grafted fabric respectively. The phosphorylated samples have much higher percent residue of 28.22%, 25.29% in PCl_3 and POCl_3 treated fabric as compared to untreated cotton-g-poly (4-VP-co-AN) with no residue.

The higher FDT of PCl_3 and POCl_3 treated grafted fabric with high percent residue indicates thermal stability and hence flame retardancy is imparted to the fabric. It is well known that the flame retardant polymers decrease the beginning temperature of the thermal degradation. This phenomenon is associated with their endothermic decomposition and as the consequence, the pyrolysis rate decreases. The acidity associated with certain phosphorous analogues and its electrophilic nature lowers the activation energy for dehydrating cellulose. Additionally, phosphorous promotes char formation. It is thought that nitrogen reacts with phosphorous to form polymeric species containing P–N bonds. Nitrogen enhances the electrophilicity of phosphorous thereby making it a stronger Lewis acid and also promoting the phosphorylation reactions. Thus, the synergistic effect of nitrogen and phosphorus elements in the polymer has an enhanced impact on the flame retarding properties of the cotton fabric.

Physicochemical Properties

Crease Recovery Angle. The crease recovery angle (CRA) across the length both face to face (weft) and end to end (warp) of grey cotton, Cotton-g-poly (4-VP-co-AN), quaternized and

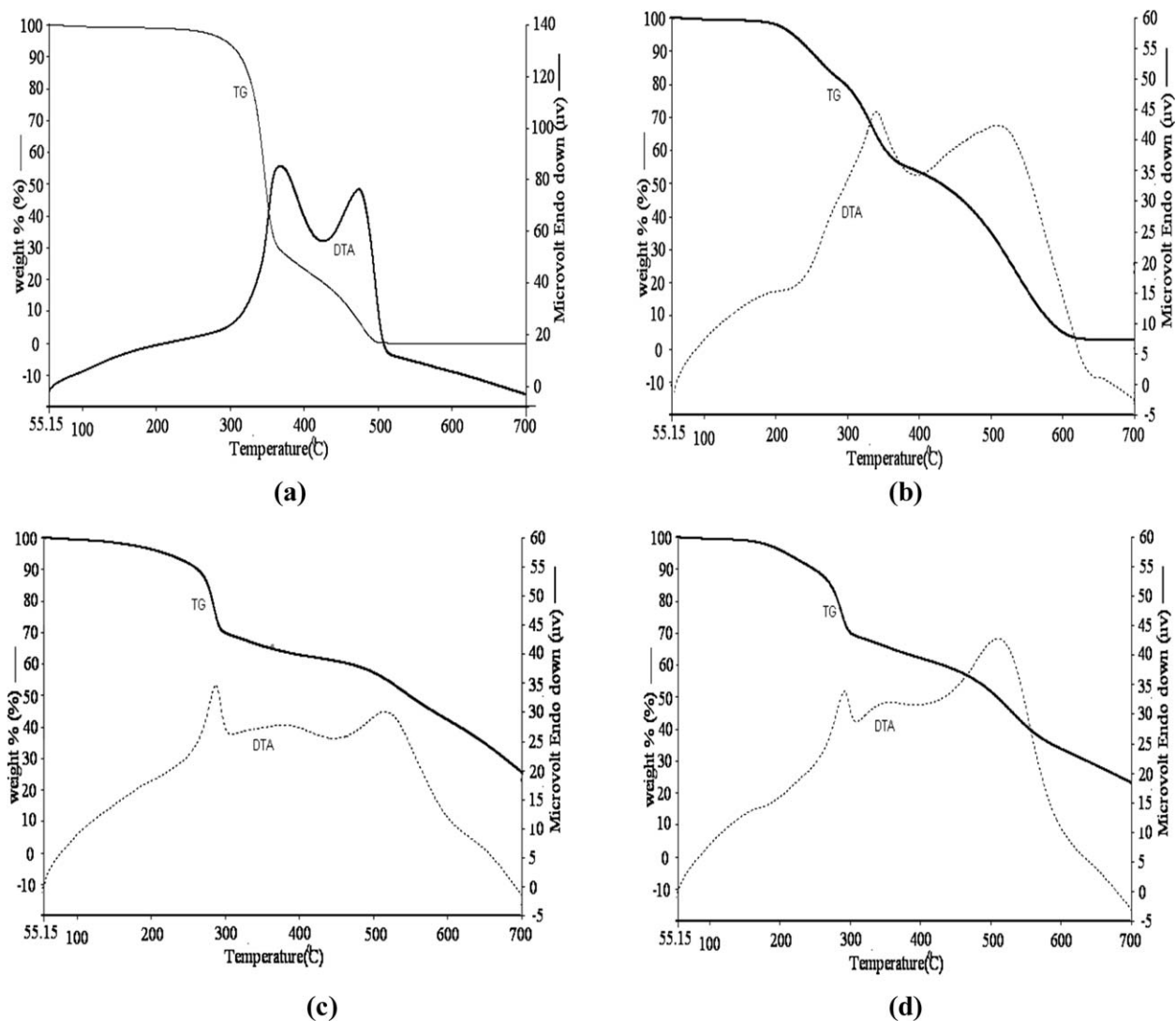


Figure 10. TGA of (a) grey Cotton fabric (b) Cotton-g-poly(4-VP-co-AN) (c) Cotton-g-poly(4-VP-co-AN)/PCl₃ (d) Cotton-g-poly(4-VP-co-AN)/POCl₃.

phosphorylated Cotton-g-poly (4-VP-co-AN) were measured and the results are presented in Table V.

It is observed from the table that the crease recovery angle of the grafted fabric increases in comparison to the values obtained for the grey cotton fabric both in warp to warp and weft to weft directions. These results reveal that the wrinkle freeness or crease recovery angle has increased i.e. the crease resistance improves upon grafting in the fabric.

The increase in the crease recovery angle of the grafted sample is explained on the basis that in the unmodified cotton fabric, the H-bonds formed between the hydroxyl of the folded samples do not easily break upon removal of the load and/or form H-bond with the adsorbed moisture thus forming the crease. However, in case of the grafted sample the H-bonds are formed between the nitrogen groups of the grafted sample which are less stable than the H-bonds between two hydroxyl groups and hence persists for shorter duration and recover from the crease.

It is also observed that the phosphorylated sample shows lower crease recovery angle than that of the grafted fabric but higher than that of cotton fabric. The crease recovery angle higher than cotton fabric reveals that the flame retardant fabric has crease resistant or wrinkle free properties. The decrease in crease recovery angle of the phosphorylated grafted samples as compared to grafted one is due to the generation of charge on the nitrogen of phosphorylated samples and presence of hydroxyl groups in case of PCl₃ treated samples which are capable of hydrogen bonding.

In case of the quaternized sample, the crease recovery angle is higher than cotton fabric but lower than their respective grafted samples.

Wettability of Fabric. The results for the time taken to absorb a drop of water by cotton fabric after every 1h are given in Table VI.

Because the time taken for complete absorption of water drop by the grey and grafted cotton fabric is <200 s, both the

Table IV. Thermal Data Obtained from TGA and DTA of Grey, Grafted, Quaternized, and Phosphorylated Sample of Cotton Fabric

Sample	TGA		DT at every 10 wt % loss										Exothermic DTA peaks (°C)	
	IDT (°C)	FDT (°C)	10%	20%	30%	40%	50%	60%	70%	80%	90%	% residue	1st peak	2nd peak
Grey cotton	215.0	600.0	245.0	295.0	325.0	360.0	440.0	490.0	510.0	540.0	585.0	-	350 (84 μ V)	481.8 (79 μ V)
Cotton-g-poly (4-VP-co-AN)	259.4	685.0	266.3	282.5	293.4	475.8	552.5	640.0	685.9	-	-	28.2	282 (33 μ V)	516 (29 μ V)
Cotton-g-poly (4-VP-co-AN)/Quat/PCl ₃	263.6	584.5	262.5	285.0	305.0	450.0	512.5	570.0	670.0	-	-	22.9	289 (33.1 μ V)	505 (43.5 μ V)

IDT—initial decomposition temperature, FDT—final decomposition temperature, DTA—differential thermal analysis, DT—decomposition temperature.

Table V. Crease Recovery Studies of Grey, Grafted, Quaternized, and Phosphorylated Cotton Fabric

Sample	Face to face (weft) crease recovery angle (°)	End to end (warp) crease recovery angle (°)
Cotton fabric	50.0	45.0
Cotton-g-poly(4-VP-co-AN)	150.0	148.0
Cotton-g-poly(4-VP-co-AN)/benzoate	95.0	83.0
Cotton-g-poly(4-VP-co-AN)/PCl ₃	84.0	52.0
Cotton-g-poly(4-VP-co-AN)/R/PCl ₃	85.0	79.0

samples are hydrophilic. However, in case of grafted cotton fabric, the time of water drop absorption approaches to 200 s (112 s) therefore it has some hydrophobic character also. In the cotton fabric, the absorption of water drop takes place due to hydrogen bond formation between the hydroxyl groups on the fabric. The swelling index (water retention) has a strong linear relationship with the total nitrogen content in the fabric. The higher the nitrogen content, the lower is the swelling index (water retention). High nitrogen content or low swelling index reduces the water absorption rate of the fabric and increases the contact angle when the water drop is in initial contact of the fabric.

The time of absorption of water drop decreases from the observed time of the grafted samples on phosphorylation indicating that phosphorylation increases hydrophilicity. The results corroborate with those of CRA studies, where phosphorylation/addition of hydroxyl group and electron deficient nitrogen are responsible for decrease in CRA.

Wettability of quaternized fabric depicts that the absorption of drop of water by changing the post treatment reactions gets changed and the samples show hydrophilic nature.

Moisture Regain. Percent moisture absorption studies of grey cotton, Cotton-g-poly (4-VP-co-AN), quaternized and phosphorylated Cotton-g-poly (4-VP-co-AN) were undertaken at 30°C at relative humidity levels (RH) of 85%. The results for moisture uptake by cotton fabric after every 1h are presented in Table VII.

It is observed from table that the percent moisture content of gray fabric increases with time. It absorbs 10.25% of moisture

Table VI. Wettability of Grey, Grafted, Quaternized, and Phosphorylated Cotton Fabric

Types of samples	Time taken (s)
Cotton fabric	5.0
Cotton-g-poly(4-VP-co-AN)	112.0
Cotton-g-poly(4-VP-co-AN)/benzoate	69.0
Cotton-g-poly(4-VP-co-AN)/POCl ₃ , Py	8.0
Cotton-g-poly(4-VP-co-AN)/Quat/PCl ₃	5.0

Table VII. Moisture Regain of Grey, Grafted, Quaternized, and Phosphorylated Cotton Fabric

Types of samples	Moisture gain (%) after							
	1 h	2 h	3 h	4 h	5 h	6 h	7 h	24 h
Cotton fabric	10.25	14.10	14.10	15.30	15.30	15.30	16.66	16.66
Cotton-g-poly(4-VP-co-AN)	5.71	9.09	9.09	10.60	10.60	10.60	12.10	18.10
Cotton-g-poly(4-VP-co-AN)/benzoate	7.45	9.26	11.21	11.21	14.57	16.23	16.23	21.02
Cotton-g-poly(4-VP-co-AN)/POCl ₃	6.95	9.57	11.08	13.21	16.21	19.21	19.21	27.25
Cotton-g-poly(4-VP-co-AN)/quat/PCl ₃	5.03	9.37	12.72	12.72	16.36	18.36	21.36	33.76

in first 1h that increases to 15.3% in 4 h and remains constant till 6 h then increases to 16.66% in 7 h and remains constant till 24 h. In case of Cotton-g-poly (4-VP-co-AN), percent regain is lower in the first 1 h (5.71%) which increases with time up to 4 h reaching a value (10.60%) that remains constant till 6 h as in grey fabric but increases thereafter giving maximum percent moisture gain in 24 h (18.10%). The moisture regain shows that binary mixture grafted cotton fabric has little affinity for the water as compared to grey cotton fabric. Incorporation of poly (vinyl) chains by replacing the free hydroxyl groups through grafting affects the moisture uptake. The percentage uptake by the grafted cotton fabric is lower than the cotton fabric corroborating the wettability results.

The phosphorylation reactions show increase in moisture regain than that of the grafted samples. The percent moisture regain respectively of PCl₃ and POCl₃ treated binary mixture (21.36%, 10.54%) is higher as compared to the grafted sample (9.41%). These high values are attributed to the solubilization of the cationic end of the polymer and hydroxyl groups in aqueous media resulting in the easy approach of water moieties to the inner region of cellulose backbone. It may, thus, be concluded that phosphorylation imparts better hydrophilic character as compared to their respective grafted samples.

Quaternization shows different effect on value of moisture regain depending upon the nature of monomer grafted. There is an increase in the water-uptake property of the graft copolymer, resulting from the generation of charged groups on grafted monomer moieties. The moisture regain of quaternized samples of the binary mixture (21.02%) after 24 h is found to be higher as compared to the grafted samples (9.41%). This high value is attributed to the solubilization of the cationic end of the polymer in aqueous media resulting in the easy approach of water moieties to the inner region of cellulose backbone.

Table VIII. Mechanical Strength of Grey, Grafted, Quaternized and Phosphorylated Cotton Fabric

Types of samples	R_m (N mm ⁻²)	ϵR_m (%)	R_b (N mm ⁻²)	ϵ Break (%)
Cotton fabric	120.31	16.30	23.99	22.21
Cotton-g-poly(4-VP-co-AN)	36.25	11.36	12.95	15.22
Cotton-g-poly(4-VP-co-AN)/POCl ₃ /Py	7.92	8.22	2.47	16.15
Cotton-g-poly(4-VP-co-AN)/benzoate	56.37	27.58	30.52	30.45
Cotton-g-poly(4-VP-co-AN)/Ouat/PCl ₃	10.03	8.21	7.33	12.12

R_m (N mm⁻²) = maximum tensile stress, ϵR_m = strain observed at maximum tensile stress.
 R_b (N mm⁻²) = stress at breaking point, ϵ Break = strain observed at the breaking point.

Mechanical Strength. The maximum strain on fabric v/s stress of grey cotton, Cotton-g-poly (4-VP-co-AN), quaternized and phosphorylated Cotton-g-poly (4-VP-co-AN) at maximum load are presented in Table VIII.

Graft copolymerization although is known to impart additional properties to the preformed polymer backbones but it disturbs the crystalline properties of the polymer. When grafting of cotton fabric was carried out with (4-VP+AN) mixture, it is observed that the tensile or tear strength of the fabric decreases. The fabric tear strength is highly correlated with the total nitrogen content. High nitrogen content which results from the wrinkle-free treatment, causes low tear strength and modifies the porous structure of the material that decreases tensile strength.

It is observed from the table that the least strength is shown by Cotton-g-poly (4-VP-co-AN)/POCl₃/Py. The fabric tear strength is highly correlated with the total nitrogen and phosphorus content. High nitrogen and phosphorus content causes low tear strength. Flame retardant application can generally reduce the tear strength and the dynamic water absorption rate. The former is a property important to fabric durability and the latter is a property important to clothing comfort. However, controlling the grafting percentage, a balance between the two can be achieved to utilize the modified fabric with its overall improved properties.

CONCLUSION

Successful grafting of binary mixture of AN and 4-VP onto cotton fabric using CAN as redox initiator has been achieved. The physico-chemical properties of grey, grafted, phosphorylated and quaternized cotton fabric reveals that the grafted fabric show better crease resistant properties and hydrophobic nature in comparison to the grey cotton fabric while phosphorylation

and quaternization of grafted fabric shows increase in moisture regain.

Grafting of AN and 4-VP and quaternization of grafted fabric improves the antibacterial behavior of the fabric with complete removal of both gram +ve and -ve bacteria making it as an excellent anti-bacterial material as compared to grey fabric. Grafting with monomers containing nitrogen as one of the elements and introduction of phosphorous upon phosphorylation reactions improves the flammability behavior of the fabric because of the synergistic effect of these elements. The modified fabric burns only upon introduction of the flame that too with slow propagation of the flame and as the flame is removed burning of the fabric stops.

Thus, grafting of AN and 4-VP as a mixture on to cotton fabric provides a materials with both antibacterial and flame retarding properties together with improved physico-chemical properties.

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