

Graft Copolymerization of Acrylate Monomers onto Sulfonated Jute–Cotton Blended Fabric

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Received 12 May 2005; accepted 24 October 2005

DOI 10.1002/app.23797

Published online 8 March 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Graft copolymerization of acrylate monomers, e.g., methyl methacrylate and ethyl methacrylate, onto bleached sulfonated jute–cotton-blended fabric was carried out in an aqueous medium, using potassium persulfate as an initiator under the catalytic influence of ferrous sulfate in a nitrogen atmosphere. The parameter variables, e.g., concentrations of monomer, potassium persulfate, ferrous sulfate, reaction time, and reaction temperature, directly influenced the percent graft yield. The percent graft yield increased to a certain value in each variable, and the percent graft yield of methyl methacrylate and ethyl methacrylate was about 15.9

and 17.1%, respectively. Polymer grafting was characterized by thermogravimetric analysis, infrared spectroscopy, and X-ray diffractometry. Grafting improved the thermal stability, protected from photo-oxidative degradation, decreased the dyeability, and had positive impact on fastness characteristics. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4393–4398, 2006

Key words: graft copolymerization; jute; cotton; sulfonation; acrylate monomer

INTRODUCTION

Graft copolymerization of vinyl monomers onto cellulose, ligno-cellulose, and their derivatives has been the subject of much interest, and extensive studies since 1946. Chemical modification through graft copolymerization of preformed polymers, both natural and synthetic, provides a potential route for significantly altering the physical and mechanical properties, and the modified materials find wide industrial and biomedical applications.

Jute, a ligno-cellulosic polymer, is the most abundant renewable agricultural raw material. Although jute fiber possesses high-dimensional stability, certain unfavorable textile properties like high stiffness, very low elasticity, and susceptibility towards sunlight have tremendously limited for their use. Therefore, to minimize the undesirability and to enhance their effectiveness for intensified textile uses, graft copolymerization of vinyl monomers onto jute fibers has been attempted during the recent years, using chemical,^{1–5} photochemical,⁶ and radiation-induced^{7–10} methods of initiation where the grafted fiber shows improved tenacity, dyeability, and tensile properties. Furthermore, among the methods of initiation, chemical method of initiation of grafting involving oxidizing agents like KMnO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, $\text{K}_2\text{S}_2\text{O}_8$, and KHSO_5

are promising from the economic point of view and are quite selective in nature. Among the chemical initiators, persulfate ($\text{S}_2\text{O}_8^{2-}$) has a separate identity of its own. However, Ray¹¹ studied some X-ray diffraction studies of MMA-grafted jute fiber, but not much was known about the conditions of grafting. Graft copolymerization of MMA onto jute fiber using KMnO_4 -malonic acid¹² and V^{5+} -cyclohexanone^{13,14} redox systems, and ceric-ion initiation¹ was reported. Photograph copolymerization of MMA onto bleached jute fibers using ferric-sulfate initiation was also reported.¹⁵

The present investigation reports the graft copolymerization of acrylate monomers, such as methyl methacrylate and ethyl methacrylate onto sulfonated jute–cotton-blended fabric, by using potassium persulfate and ferrous sulfate redox initiation system in a detailed way, to optimize the conditions for such polymerization. Grafting was determined on the basis of weight increased of the fabric treated. To identify and characterize the graft on fabric, infrared spectroscopy, X-ray diffractometry, and thermogravimetric analysis (TGA) were used.

EXPERIMENTAL

Materials

As a material for investigations, loom state bleached sulfonated jute–cotton-blended (BSJCB) fabric was used. Methyl methacrylate (MMA) and ethyl methacrylate (EMA) were freed from stabilizer by washing

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with 5% sodium hydroxide solution and water. It was then dried with anhydrous sodium sulfate and distilled under reduced pressure in nitrogen before use.¹⁶ All other chemicals, e.g., $K_2S_2O_8$ (BDH), $FeSO_4$ (BDH), etc. used were of analytical reagent grade.

Production of fabric

Jute fiber was sulfonated with sodium sulfite.¹⁷ Sulfonated jute fiber was blended with 40% cotton for the production of (60 × 60) plain woven fabric. Sulfonated jute-cotton-blended fabric was bleached with hydrogen peroxide in a high pressure rapid lab deep machine.^{18,19}

Graft copolymerization

The treatment of BSJCB fabric was carried out in a 100-mL stoppered Erlenmeyer flask. Polymerization was done with 20–80% acrylate monomers, 0.2–1.2% potassium persulfate as initiator, and 0.2–1.2% ferrous sulfate as catalyst based on the weight of fabric at 30–80°C for 0.5–3.0 h in the fabric-liquor ratio of 1:30. At the end of the desired reaction period, the grafted BSJCB fabric was repeatedly washed with hot water and was dried at 60°C. It was then extracted with acetone for 10 h in a Soxhlet apparatus, to remove the loosely adhering polymer, washed, and dried.¹ Percent graft yield was calculated according to following formula:

$$\% \text{ graft yield} = \frac{B - A}{A} \times 100$$

where A and B are the weight of ungrafted and grafted BSJCB fabric, respectively.

Instrumental analysis

The thermogravimetric analysis (TGA) of fabric sample was done by Mettler TG-50 (Shimadzu, Japan). The heating rate throughout the study was 10°C/min. The measurement was made under a constant flow rate (20 mL/min) of nitrogen.²⁰

Fabric sample was mixed with KBr in the ratio 1:100, and a pellet was prepared. Then, the IR spectra of this KBr pellet were recorded with IR-470 Infrared Spectrometer (Shimadzu, Japan).

X-ray diffraction of fabric sample was measured using Phillips diffractometer. The dried isotropic sample was compressed as a pellet (diameter of 2 mm and a thickness of 1 mm) into the pore of a disk and its X-ray diagrams were made with Ni-filtered $Cu\text{-}K\alpha$ radiation at 30 kV and 20 mA. Crystallinity of the fabric sample was determined by Segal et al.²¹

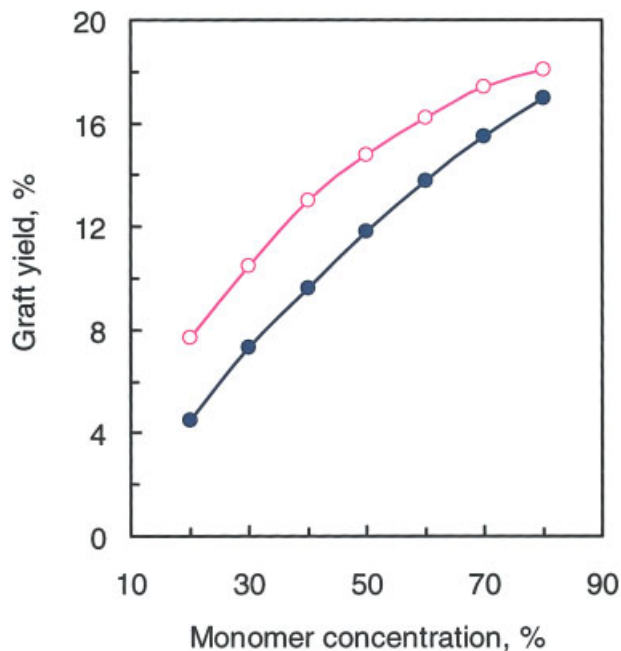


Figure 1 Effect of variation of monomer concentration on percent graft yield of acrylate monomers onto BSJCB fabric ($K_2S_2O_8$, 1.00%; $FeSO_4$, 0.60%; time, 120 min; temp, 60°C; liquor ratio, 1 : 30). (○), MMA; (●), EMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Measurement of breaking strength

The breaking strength of the fabric sample was measured by the Tensile Strength Tester (Torse's Schopper type-OS-100).²²

RESULTS AND DISCUSSION

Effect of variation of monomer concentration

The effect of variation of monomer concentration on percent graft yield is shown in Figure 1. The polymerization reaction of BSJCB fabric with MMA and EMA was carried out in the presence of $K_2S_2O_8/FeSO_4$ redox system at 2.5 h for 60°C. From Figure 1, it can be observed that the percent graft yield increased with the increase of monomer concentration within the range of monomer concentration applied, and the graft yield was 15.5 and 16.2% for 70% MMA and 60% EMA, respectively. The increase in monomer concentration in the polymerization medium increased the number of monomer reaction sites and also increased the complexation of BSJCB with MMA or EMA enhancing the reactivity owing to the formation of donor-acceptor complex. Thus, the higher availability of monomer radical sites in the vicinity of immobile cellulose macroradical increased the percent graft yield.^{5,23} From our experiment, it was observed that the percent graft efficiency decreased with the increase

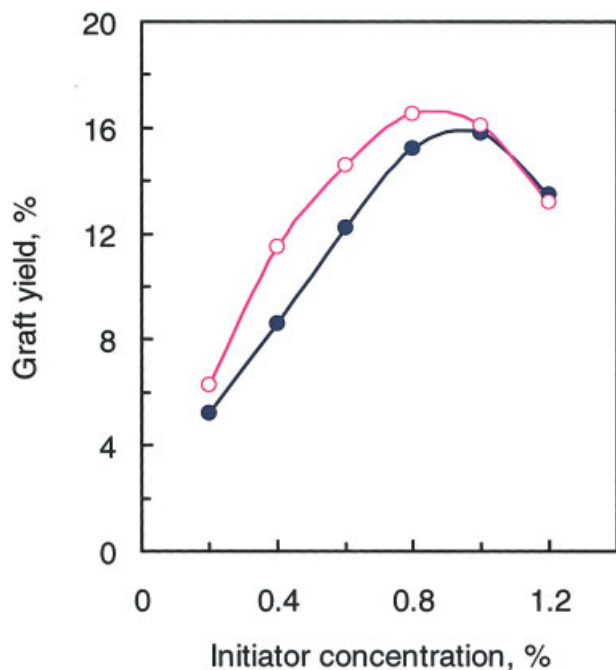


Figure 2 Effect of variation of initiator ($K_2S_2O_8$) concentration on percent graft yield of acrylate monomers onto BSJCB fabric (monomer, 60%; $FeSO_4$, 0.60%; time, 120 min; temp, 60°C; liquor ratio, 1:30). (○), MMA; (●), EMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of monomer concentration, as more monomer radical prevails to form homopolymer over grafting.

Effect of variation of initiator concentration

The effect of increase of potassium persulfate ($K_2S_2O_8$) as initiator on the percent graft yield of BSJCB fabric is shown in Figure 2. The percent graft yield increased with the increase of initiator concentration up to 1.0% for MMA and 0.8% for EMA, and thereafter it decreased. At 1.0% $K_2S_2O_8$ for MMA and 0.8% $K_2S_2O_8$ for EMA, the percent graft yield was 15.8 and 16.5%, respectively. The increase in initiator concentration increased the number of primary radicals,²⁴ which caused the number of active sites on the backbone of BSJCB and monomer radicals to increase; as a result, the percent graft yield increased. The retarding effect of $K_2S_2O_8$ at above 1.0% for MMA and 0.8% for EMA on percent graft yield might be because of the predominancy of homopolymerization over grafting, the termination of growing grafted chain by primary radicals, and the production of excess Fe(III) ions, which interacted with the growing grafted chains, leading to the cease of their growth.

Effect of variation of reaction time

The effect of increase of reaction time on percent graft yield of BSJCB is shown in Figure 3. From Figure 3, it

can be seen that the percent graft yield increased with the increase of reaction time up to 2 h for MMA and up to 1.5 h for EMA, and beyond which it decreased. The maximum percent graft yield obtained at these reaction times was 15.6 and 16.7%, respectively. At longer reaction time, monomer sometimes causes degradation of the graft on the BSJCB; as a result, percent graft yield decreased.

Effect of variation of reaction temperature

The effect of rise of temperature on percent graft yield of BSJCB fabric is shown in Figure 4. It can be seen from Figure 4 that the percent graft yield increased with the increase of temperature up to 70°C for MMA and 60°C for EMA, and beyond this temperature the percent graft yield decreased. The percent graft yield at these temperatures was 15.9 and 17.1%, respectively. Increase in reaction temperatures increased the rate of production of active primary radicals, which increased the number of grafting sites at a higher rate and also increased the rate of monomer diffusion into the fiber matrix where grafting was also initiated by complexed monomer. The decrease in percent graft yield above 70 and 60°C for MMA and EMA, respectively, might be due to the formation of homopolymer

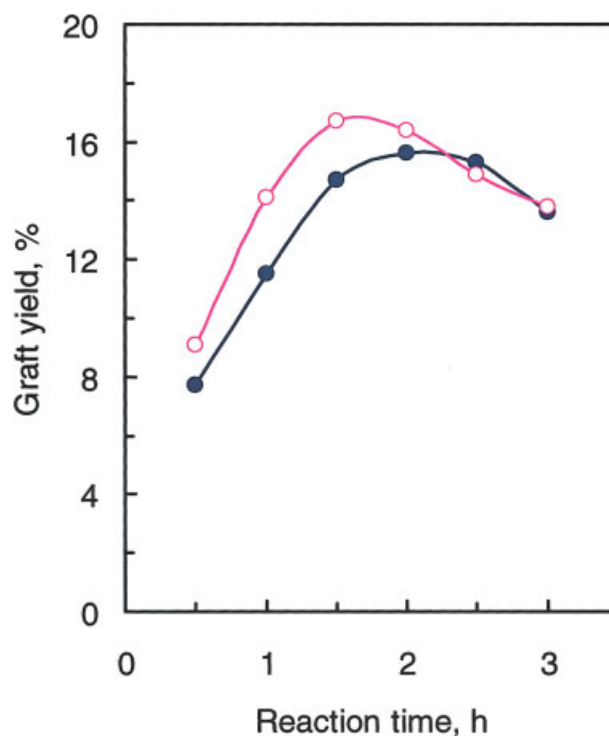


Figure 3 Effect of variation of reaction time on percent graft yield of acrylate monomers onto BSJCB fabric (monomer, 60%; $K_2S_2O_8$, 1.00%; $FeSO_4$, 0.60%; temp, 60°C; liquor ratio, 1:30). (○), MMA; (●), EMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

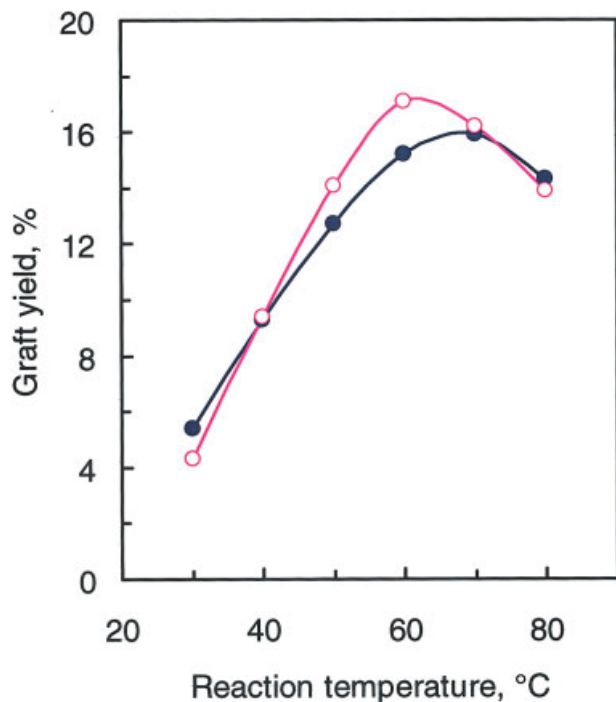


Figure 4 Effect of variation of reaction temperature on percent graft yield of acrylate monomers onto BSJCB fabric (monomer, 60%; $K_2S_2O_8$, 1.00%; $FeSO_4$, 0.60%; time, 120 min; liquor ratio, 1 : 30). (○), MMA; (●), EMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

over grafting, and the premature termination of growing grafted chains by excess Fe(III) ions produced on oxidation of Fe(II) ions.²⁴

Effect of variation of catalyst concentration

The effect of ferrous sulfate ($FeSO_4$) concentration as catalyst on the percent graft yield of BSJCB fabric is shown in Figure 5. The percent graft yield increased with the increase of the catalyst concentration up to maximum value, and then it decreased. The effective maximum catalyst concentration for MMA and EMA was 0.6 and 0.8%, respectively, and the corresponding percent graft yields were 15.7 and 16.9%. Ferrous sulfate might increase the swellability of the fabric substrate and also affected the hydrolysis of BSJCB cellulose, leading to uncoiling of the cellulose chains and enhancing the monomer accessibility.^{25,26} The excess Fe(III) ions produced on oxidation of Fe(II) ions and the homopolymer formation over grafting were the cause of retarding the percent graft yield.

Thermogravimetric analysis

The thermal behavior of BSJCB, MMA- and EMA-grafted fabrics was examined by their TGA thermograms, and the results are listed in Table I. From the

Table, it can be observed that the moisture and volatile matters loss of grafted BSJCB fabrics up to 295°C was 2.9–3.2% lower than that of ungrafted BSJCB fabric. On the other hand, the char residues at 600°C of the grafted fabrics were 1.3–4.3% higher. The lower moisture content and the higher char residue of the grafted fabric, than those of ungrafted fabric, were related to the monomer pertained to the grafting. The actual pyrolysis of the grafted fabrics was ended at 391–395°C, which was slightly higher than BSJCB fabric, and the corresponding weight loss at the end of pyrolysis of the grafted fabrics was lower. This TGA of fabric samples suggest that the thermal stability of MMA- and EMA-grafted fabrics is higher than that of ungrafted fabrics.

FTIR spectroscopy

The infrared spectra of the BSJCB, MMA- and EMA-grafted BSJCB fabrics are shown in Figure 6. From Figure 6, it can be observed that the characteristic broad absorption bands of hydroxyl groups were at around 3315–3455 cm^{-1} . However, the spectra of MMA- and EMA-grafted BSJCB fabrics showed an additional peak of ester groups at 1710–1720 cm^{-1} . This ultimately proved that the BSJCB fabric was be-

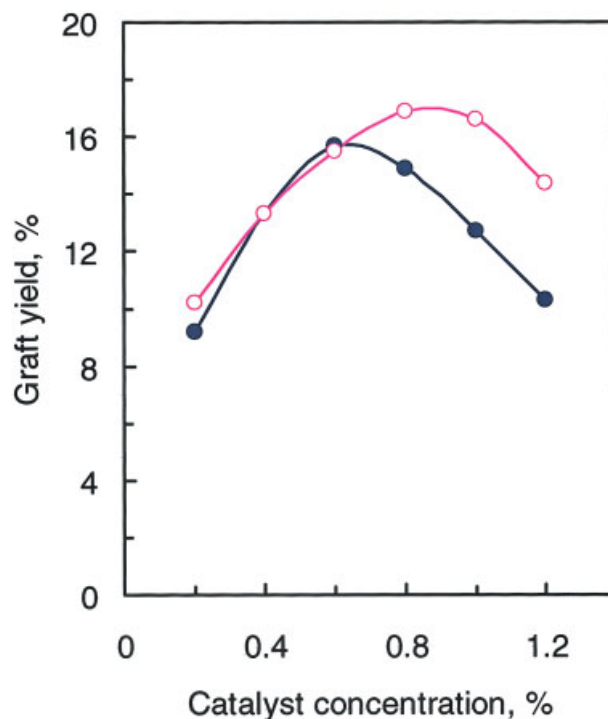


Figure 5 Effect of variation of catalyst ($FeSO_4$) concentration on percent graft yield of acrylate monomers onto BSJCB fabric (monomer, 60%; $K_2S_2O_8$, 1.00%; time, 120 min; temp, 60°C; liquor ratio, 1 : 30). (○), MMA; (●), EMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
TGA of Ungrafted, MMA- and EMA-Grafted BSJCB Fabrics

Fabric sample	Initial weight loss region (°C)	Weight loss (%)	Actual pyrolysis region (°C)	Weight loss at the end of pyrolysis (%)	Residual char at 600°C (%)
Blended	25–289	10.4	289–384	64.6	13.8
MMA	25–286	7.5	286–395	65.6	15.1
EMA	25–289	7.2	289–391	62.2	18.1

ing grafted with MMA and EMA. As the probable sites for grafting of BSJCB fabric was —OH group, it was expected that the intensity of —OH peak to be reduced as a result of grafting. However, this was not observed. Probably because of the large concentration of —OH group in BSJCB fabric, the small differences in its concentration as a result of grafting were not distinguished.

X-ray diffractometry

The crystalline structure of BSJCB, MMA- and EMA-grafted fabrics was examined by a study of their X-ray diffractograms. The degree of crystallinity of BSJCB

fabric, MMA- and EMA-grafted fabrics was measured 73.9, 61.7, and 55.2%, respectively. The lower crystallinity of MMA- and EMA-grafted fabrics was due to the incorporation of the amorphous monomers to BSJCB fabric by graft copolymerizations. This indicates that the monomer may chemically bind the cellulosic chains, confirming additional strength to the BSJCB fabric.

Physical characteristics

The breaking strength of grafted BSJCB fabric was higher than that of ungrafted fabric. Again, the loss in breaking strength of grafted BSJCB fabric on exposure to sunlight in air for 300 h was around 7.0% lower than that of BSJCB fabric. This means that grafting of BSJCB fabric with MMA and EMA decreased the loss in breaking strength by photo-oxidative degradation. The incorporation of monomer through grafting increased the breaking strength as well as decreased the photo-oxidation degradation occurred by sunlight.

The BSJCB and their modified fabrics were dyed (2.0% dye) with Direct Yellow 29 and Direct Red 31 at 100°C for 60 min in the fabric-liquor ratio of 1:30. The dye absorption of the grafted fabric was around 9.0% lower than that of the ungrafted fabric, which means that grafting increased the hydrophobicity of the grafted fabric. Experiments showed that the grafting had a positive impact on color fastness to sunlight in air, on wash fastness to soap medium up to 100°C, and on color fastness to some common acids and alkalis.

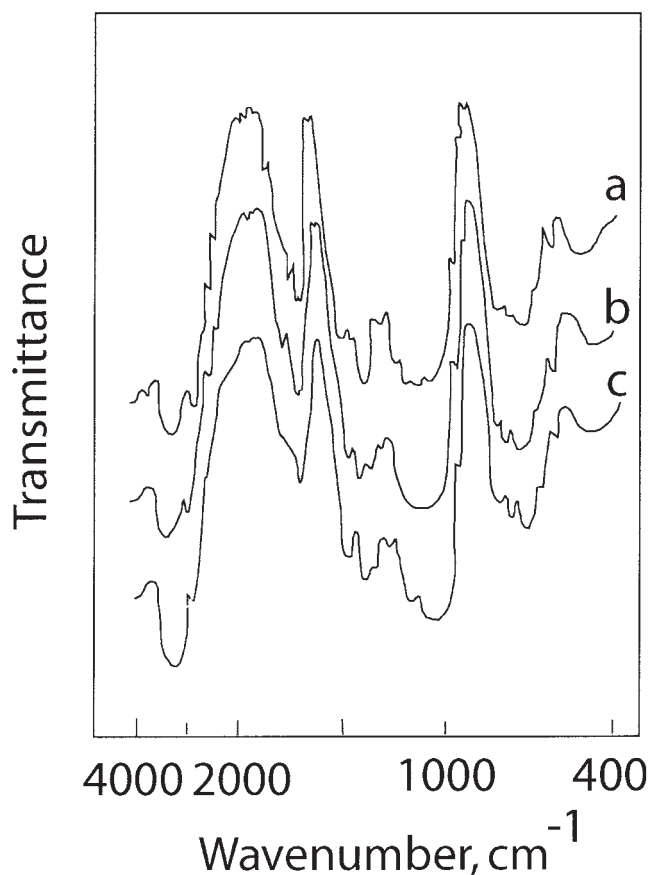


Figure 6 FTIR spectra of ungrafted and grafted BSJCB fabrics. (a) BSJCB fabric; (b) MMA-grafted BSJCB fabric; and (c) EMA-grafted BSJCB fabric.

CONCLUSIONS

Grafting of acrylate monomers onto BSJCB fabric increased the weight of base polymer, hydrophobic nature, and improved the textile performance by providing additional properties. The increase or decrease of percent graft yield depended on the number of both cellulose-macroradicals and monomer radicals whose production also depended on the initiator, catalyst, and other parameter variables. Excess of monomer radicals or primary radicals had detrimental effect. Thus, proper choice of initiator, catalyst, and parameter variables would give better yield.

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