

Graft-Copolymerization of Glycidyl Methacrylate onto Cotton Cellulose

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SYNOPSIS

Glycidyl methacrylate was graft-copolymerized onto cotton cellulose using both photo- and chemical-initiation techniques using different initiators. The photoinitiators used were uranyl nitrate, ceric ammonium nitrate, and benzoin ethyl ether, whereas the chemical initiators used were ceric ammonium nitrate and potassium persulfate. Optimization of various parameters of grafting, viz., time, temperature, initiator, and monomer concentrations, was carried out. Ceric ammonium nitrate gave the maximum and almost identical values of graft add-on, by both grafting techniques, at equivalent concentration of the monomer. Use of optimized conditions of ceric ammonium nitrate-photoinitiated grafting for sodium hydroxide-swollen substrate as well as for grafting baths incorporating acids enhanced the graft level. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Use of vinyl monomers is considered to be very effective in bringing about desired changes in the properties of cellulose fibers by modifying them with the help of graft-copolymerization using various techniques including photoinitiation and chemical initiation. Both the techniques have their own advantages and disadvantages. The chemical initiation has been extensively used and generally gives higher graft levels. The photoinitiation, on the other hand, is considered to be the safest way as it has the least deteriorating effect on the original fiber properties due to the lower radiation energy. Use of different photoinitiators is, therefore, very necessary to enhance grafting.

Glycidyl methacrylate (GMA) has been grafted through the chemical-initiation technique onto various substrates like nylon,¹ acrylic,² gelatin,³ polyester,⁴ and cotton fabric⁵ for improving their properties suitably. Unsensitized photoinitiated grafting of GMA onto cotton fabric has been carried out by Harris and co-workers⁶ to study the effect of the

wavelength of the incident ultraviolet light on grafting. Graft-copolymerization of GMA onto substrates like polypropylene and poly(alginic acid) has also been found useful in immobilizing trypsin, crown ethers, etc.⁷⁻⁹

The use of different swelling agents for the substrate and incorporation of mineral acids in the grafting bath has been found useful in increasing significantly the graft level of different vinyl monomers onto cellulose to suit the end use.¹⁰⁻¹³ We have found out that preswelling of cotton helps in enhancing the graft level of monomers like hydroxyethyl methacrylate,^{14,15} styrene, and acrylonitrile.¹⁶ Moreover, further improvement in grafting can be achieved by adding very small quantities of bifunctional monomers to the grafting bath.^{17,18}

In the present study, therefore, GMA was graft-copolymerized onto cotton cellulose using photoinitiation and chemical initiation techniques, making use of various organic and inorganic initiators. Optimization of parameters of grafting, viz., time and temperature of reaction as well as the concentrations of initiator and monomer, was carried out to attain the maximum graft level. The effect of adding mineral acids to the grafting bath as well as that of preswelling of the substrate on graft-copolymerization was also studied.

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EXPERIMENTAL

Materials

Substrate

The scoured and bleached 30s count cotton yarn was used as the cellulose sample after purification by the standard method.¹⁹ It had the following specifications:

Carboxyl value:	0.56 meq of COOH/ 100 g of cellulose
Copper number:	0.034
Cupra ammonium fluidity:	3.71 p ⁻¹ .

Chemicals

Glycidyl methacrylate (GMA) supplied by Merck-Schuchardt was used without further purification. Uranyl nitrate (UN), ceric ammonium nitrate (CAN), and potassium persulfate (PPS) supplied by LOBA-CHEMIE Indoastranal Co., India, and benzoin ethyl ether (BEE) supplied by Fluka were the various initiators used. UN and BEE were the photoinitiators, PPS was the chemical initiator, whereas CAN was used as both a photo- and chemical initiator. Methanol, sodium hydroxide, nitric acid, sulfuric acid, hydrochloric acid, and acetic acid used were of laboratory reagent grade. Auxipon NP, a nonionic detergent supplied by Auxichem Ltd., Bombay, was used as an emulsifier.

Swelling of Cotton Cellulose

The swollen sample of cotton was prepared by using 24% (w/w) sodium hydroxide at 20°C for 1 h, followed by water washing and drying in air. The degree of swelling of the swollen cotton fiber was measured by noting the percentage change in the diameter of the fiber on a projection microscope MP-3 PZO, Warazawa, Poland. The percent swelling was determined as reported earlier.¹⁵

Graft-Copolymerization Under UV Radiations

One gram of the cotton sample was immersed in 100 mL of the grafting bath in a quartz conical flask. The grafting bath was made up of the monomer GMA and the dissolved initiator. The initiators UN and CAN were soluble in water, whereas BEE was soluble in a methanol:water mixture containing more than 2.5% methanol. A Philips HPW 125 W

mercury vapor lamp was used as a source of UV radiation. The concentration of each initiator, UN, CAN, and BEE, was optimized by varying it between 0.10 and 0.40% (w/v). The samples in quartz flasks were irradiated for different time intervals ranging from 1 to 6 h in the temperature range of 30–60°C, controlled by using a glycerine bath. After completion of grafting, each sample was taken out and extracted with methyl ethyl ketone at room temperature for 0.5 h to remove the unreacted monomer. The homopolymer was removed by boiling the samples in hot water until constant weight and finally air-dried.^{6,20} The graft add-on and graft yield were determined by using the standard formulas.¹⁴

Graft-copolymerization Using Chemical Initiation

The procedure of graft-copolymerization using the chemical initiators CAN and PPS was similar to that used for photoinitiated grafting except that the grafting was carried out in aqueous solution using Erlenmeyer flasks kept in a thermostatically controlled water bath. The concentrations of initiators CAN and PPS were optimized by varying from 0.50 to 0.80% (w/v), whereas the time of reaction was varied from 10 min to 3 h. The temperature of reaction was varied from 50°C to boil (98°C). After completion of grafting, the sample was extracted free of homopolymer as explained above.

Infrared Spectral Analysis

The infrared spectra of the samples were recorded on Perkin-Elmer 391 infrared spectrophotometer. Two milligrams of the cut sample were mixed with 198 mg of potassium bromide and the pellet was prepared. Scanning was carried out from 4000 cm⁻¹ (2.5μ) to 400 cm⁻¹ (25.0μ) at a slow speed.

RESULTS AND DISCUSSION

The UV radiations, being weak, can dissociate only the weakest bonds in the backbone polymer; however, with the help of photoinitiators, they can generate free radicals on the surface of the backbone polymer. Thus, in the present work, three photoinitiators, namely, UN, CAN, and BEE, were used.

Although the initiators UN and CAN are soluble in water, the initiator BEE as well as the monomer GMA are soluble only in the presence of methanol in the aqueous bath. When the photoinitiated grafting was carried out in baths containing different compositions of the methanol:water mixture, it was

found that the pure methanolic grafting bath gave the least graft add-on (Fig. 1). The graft level increased with an increasing proportion of water in the bath, the maximum graft add-on being in purely aqueous medium. The literature reports the use of a 50 : 50 methanol:water bath by many researchers.^{6,21,22} The maximum level of graft add-on in the pure aqueous bath was also observed by Hebeish et al.²³ Abou-Zeid and co-workers²⁴ even tried the use of an emulsifier to get an aqueous emulsion of the hydrophobic monomer GMA.

In the present work, therefore, a pure aqueous grafting bath was used for UN and CAN, whereas for BEE-initiated grafting, a 2.5 : 97.5 methanol:water mixture was found to give the highest level of grafting. For chemical initiation using CAN and PPS also, a purely aqueous grafting bath was used. Auxipon NP, a nonionic detergent, was added to the

grafting bath to keep the monomer GMA in an emulsified condition. Fine globules of GMA were found suspended in the aqueous medium, which did not show any tendency to coalesce to form a separate layer during the course of grafting.

Effect of Initiator Concentration

To study the effect of initiator concentration on the photoinduced grafting of GMA onto cotton, the concentration of initiators, UN, CAN, and BEE, was varied from 0.10 to 0.40% (w/v) at 50°C for 3 h, keeping the GMA concentration at 2% (w/v). It can be seen from Figure 2 that up to a specific concentration in all the cases the graft add-on increased as the number of sites generated for grafting increased. Beyond these concentrations, however, the graft add-on decreased, possibly due to rapid ter-

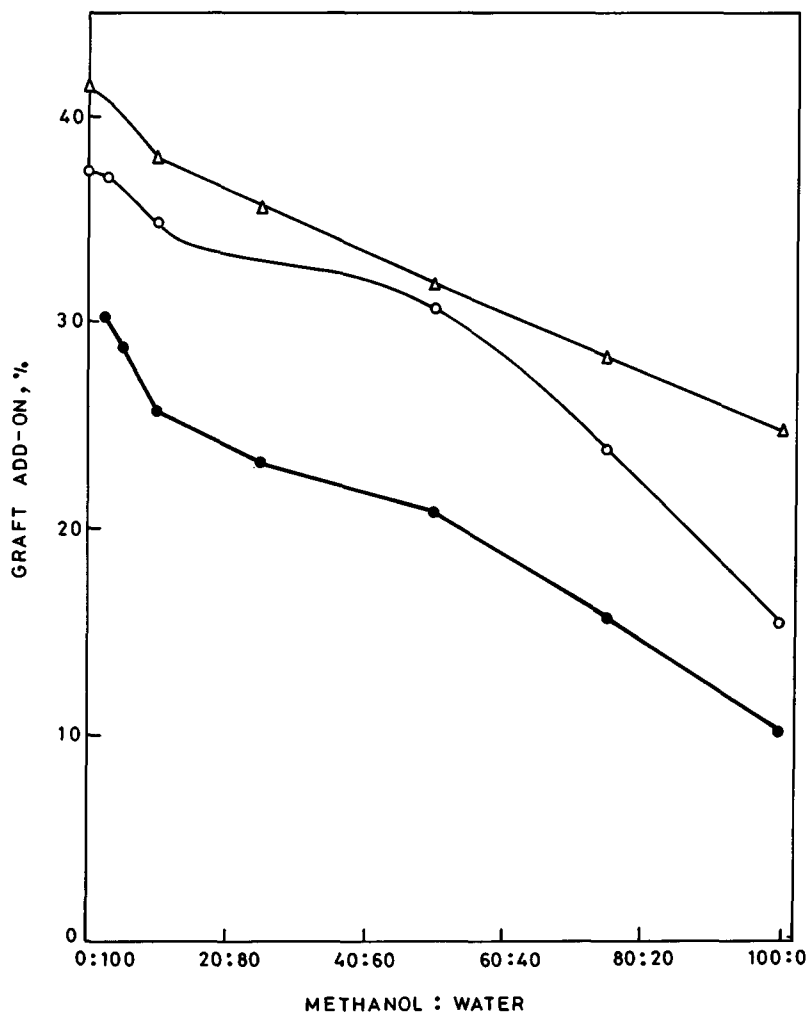


Figure 1 Effect of methanol: water composition on graft add-on: (○) UN initiator; (●) BEE initiator; (△) CAN initiator.

mination of the growing GMA side chains with increase in initiator concentration. Such an observation has been made earlier during the grafting of acrylic acid²⁵ and hydroxyethyl methacrylate^{14,15} onto cotton cellulose.

When CAN and PPS were used as chemical initiators, they were required in comparatively larger amounts. Among the three photoinitiators used, CAN gave the maximum graft add-on, whereas the graft level was the lowest in case of PPS-initiated grafting (Fig. 2).

Effect of Reaction Time

The effect of time of reaction on graft add-on is depicted in Figure 3. In the case of the photoinitiation

technique, the graft add-on increased with the time of reaction up to 2 h for all the three photoinitiators used, and beyond this time, it decreased. This tendency of graft add-on to first increase, attain a maximum value, and then decrease may be accounted for by the increasing extents of initiation and propagation of the reaction initially with time, the decrease in grafting after a particular time period being due to the detrimental effect of the UV radiations onto the grafted side chains of GMA. A similar phenomenon was also observed by Herold and Fouassier²⁶ in the case of methyl methacrylate grafting onto cotton. In case of grafting of GMA using chemical initiators, CAN and PPS, the graft add-on increased with time up to 1 h of grafting and thereafter the increase was very marginal.

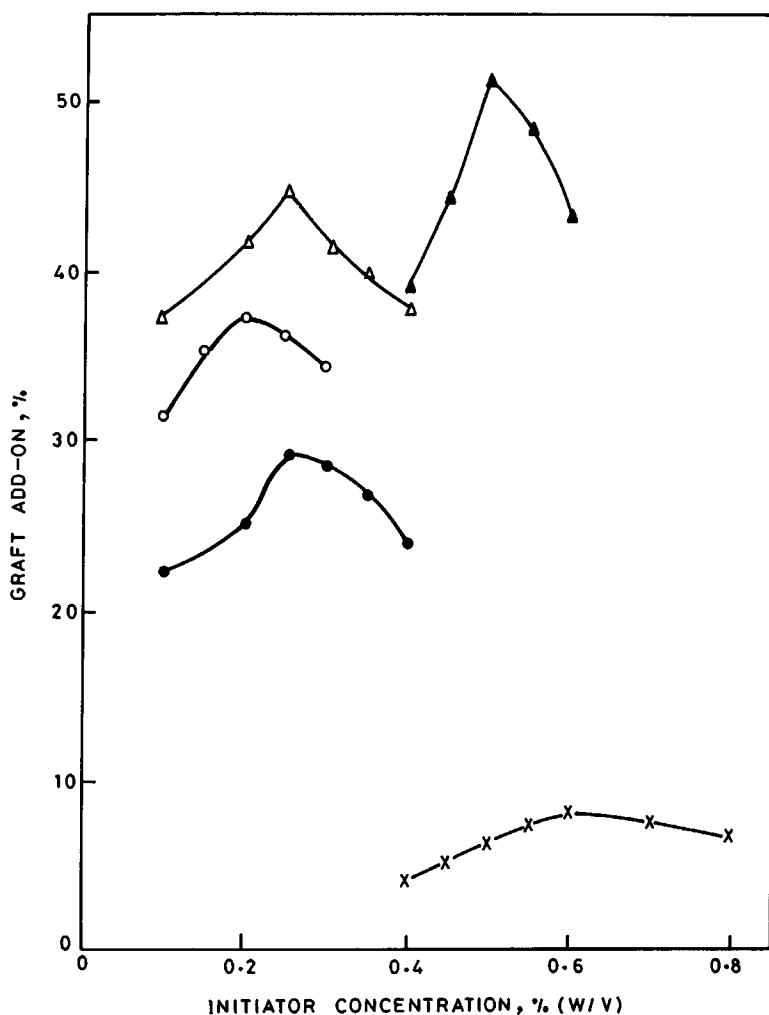


Figure 2 Effect of initiator concentration on graft add-on: (○) UN photoinitiator, 3 h, 50°C, and 2% (w/v) GMA; (●) BEE photoinitiator, 3 h, 50°C, and 2% (w/v) GMA; (△) CAN photoinitiator, 3 h, 50°C, and 2% (w/v) GMA; (▲) CAN chemical initiator, 3 h, 70°C, and 2% (w/v) GMA; (X) PPS chemical initiator, 1 h, 75°C, and 1% (w/v) GMA.

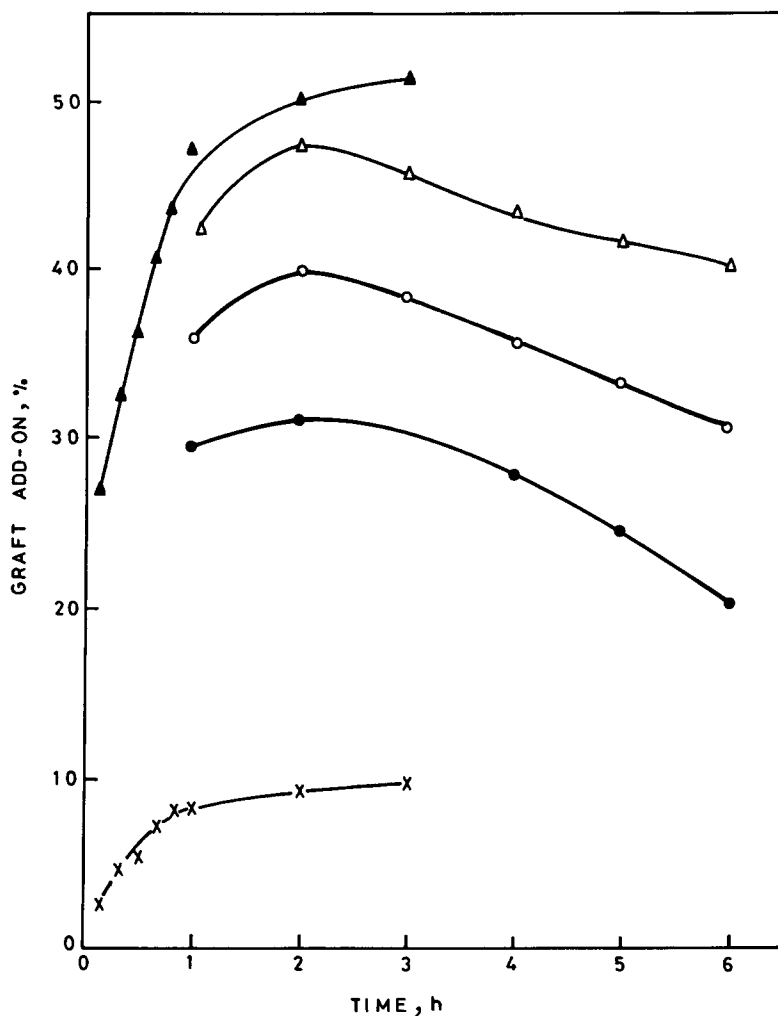


Figure 3 Effect of time of reaction on graft add-on: (○) UN photoinitiator 0.20% (w/v), 50°C, and 2% (w/v) GMA; (●) BEE photoinitiator 0.25% (w/v), 50°C, and 2% (w/v) GMA; (△) CAN photoinitiator 0.25% (w/v), 50°C, and 2% (w/v) GMA; (▲) CAN chemical initiator 0.50% (w/v), 70°C, and 2% (w/v) GMA; (X) PPS chemical initiator 0.60% (w/v), 75°C, and 1% (w/v) GMA.

Effect of Reaction Temperature

Figure 4 shows the effect of reaction temperature on graft add-on. In the case of the photoinitiation system, the graft add-on increased with increasing temperature up to 50°C and decreased thereafter for UN and CAN as well as for the BEE photoinitiator. The chemical initiation method using CAN and PPS initiators gave increased graft add-on with increasing temperature up to 80°C and then decreased. This could be attributed to the fact that with increase in temperature more and more free radicals are formed, which increase the grafting. However, the increase in temperature beyond a spe-

cific limit causes an increased extent of radical termination, thereby reducing the graft level.

Effect of Monomer Concentration

The effect of increasing the GMA concentration from 1.0 to 6.0% (w/v) on the graft add-on and the graft yield is shown in Figures 5 and 6, respectively. Figure 5 shows that the graft add-on increased with increase in GMA concentration, in all cases. The chemical initiation, using PPS, gave the lowest graft add-on levels. Comparing the role of CAN as a photoinitiator and as a chemical initiator, it was ob-

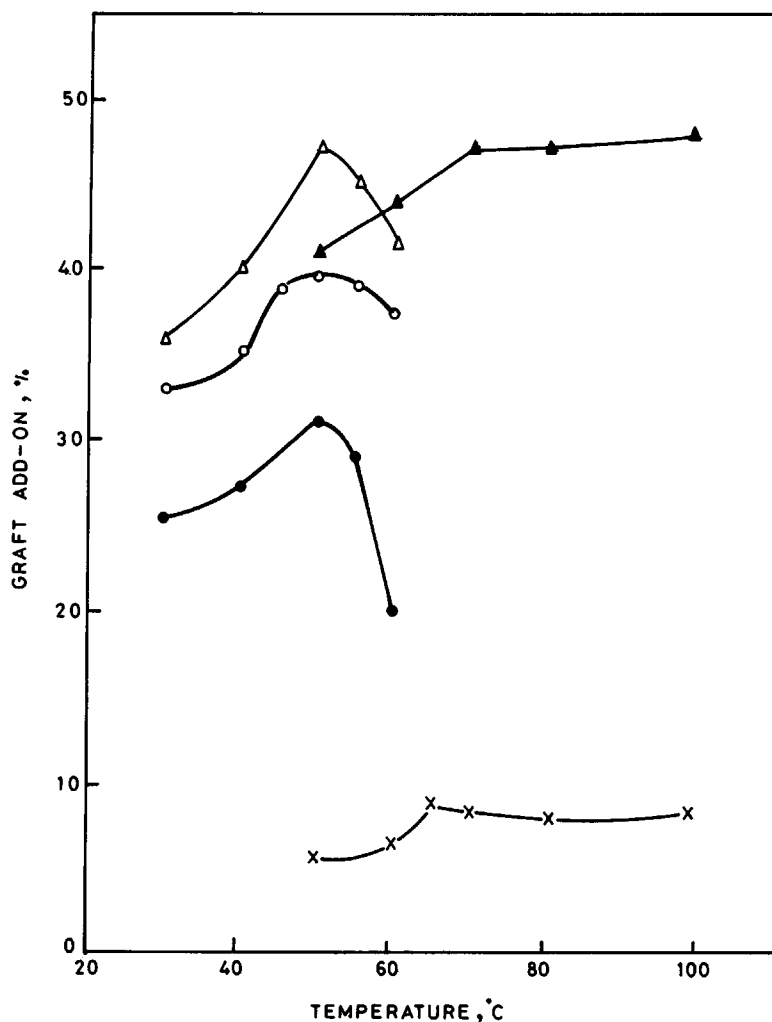


Figure 4 Effect of temperature of reaction on graft add-on: (○) UN photoinitiator 0.20% (w/v), 2 h, 2% (w/v) GMA; (●) BEE photoinitiator 0.25% (w/v), 2 h, 2% (w/v) GMA; (△) CAN photoinitiator 0.25% (w/v), 2 h, 2% (w/v) GMA; (▲) CAN chemical initiator 0.50% (w/v), 1 h, 2% (w/v) GMA; (X) PPS chemical initiator 0.60% (w/v), 1 h, 1% (w/v) GMA.

served that in both techniques of grafting the graft add-on levels were almost similar. Moreover, the optimum concentration of CAN as a chemical initiator (0.50% [w/v]) is higher than that as a photoinitiator (0.25% [w/v]).

The graft yield, as seen from Figure 6, increased with increase in monomer concentration initially up to 3% (w/v) GMA in the case of the photoinitiation technique, whereas it increased up to only 2% (w/v) GMA in the case of the chemical initiation technique of grafting. Beyond these monomer concentrations, the graft yield decreased. The decrease was found to be sharp, using the CAN initiator in both the grafting techniques as compared to other initiators. This suggests that even though the graft

add-on increased beyond specific GMA concentration, the homopolymerization also increased, which is reflected in the lowering of the graft yield.

The various optimized conditions of GMA graft-copolymerization onto cotton cellulose are given in Table I. Among the two grafting techniques used with different initiators, it was observed that CAN as a photoinitiator gave a maximum graft add-on of 78.60% at the highest possible graft yield of 26.20% using a 3% GMA concentration. Using 2.0% (w/v) GMA, the graft add-on value was 47.40%.

Grafting onto Swollen Substrate

When a similar graft-copolymerization reaction was carried out on the NaOH-swollen cotton sample,

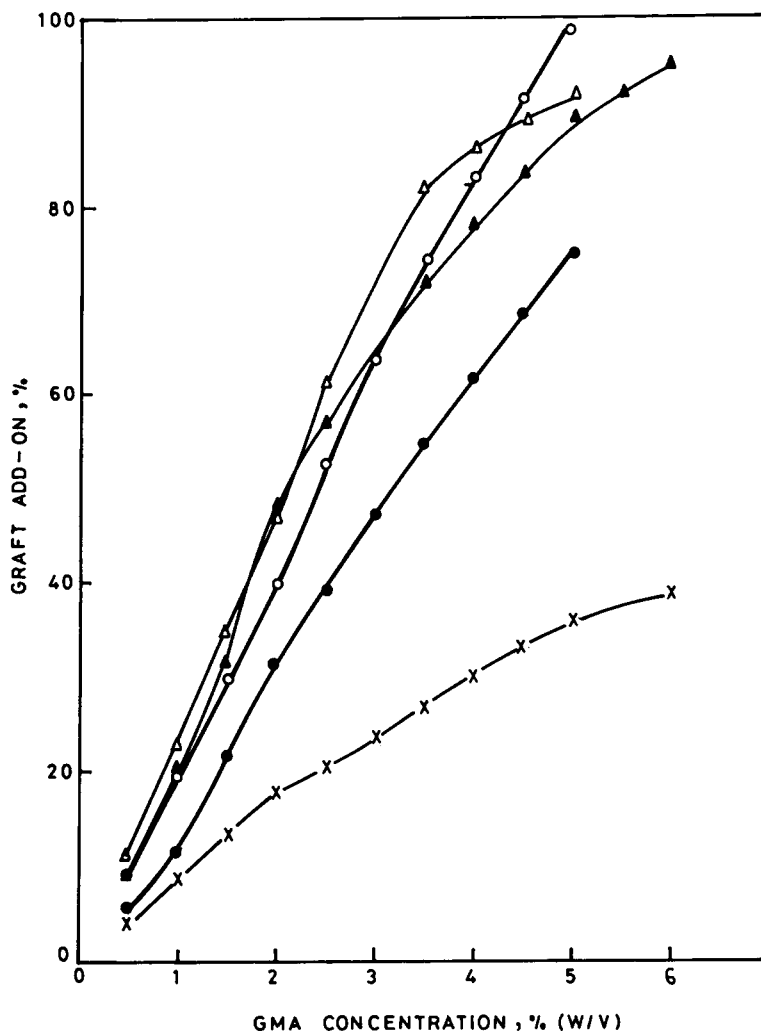


Figure 5 Effect of GMA concentration on graft add-on: (○) UN photoinitiator; (●) BEE photoinitiator; (△) CAN photoinitiator; (▲) CAN chemical initiator; (X) PPS chemical initiator.

under the given optimized conditions of initiator concentration, time, and temperature for CAN photoinitiation using 2% (w/v) GMA, it was found that the swollen sample gave an increased graft level as compared to that on the unswollen one. This is obviously attributable to the comparatively higher accessibility and greater reactivity of the swollen substrate.

Grafting in Presence of Acids

Use of acids in the grafting bath has been shown to improve the graft level of vinyl monomers onto cellulosic substrates.^{27,28} Different acids were, therefore, used to determine their effect on the graft add-on

in the CAN-photoinitiated system using 2.0% (w/v) GMA. The results are shown in Table II. Use of 0.1*N* sulfuric acid and nitric acid showed significant improvement in the graft add-on. Hydrochloric acid was found to be only slightly effective, whereas acetic acid was ineffective in enhancing the graft add-on. However, when the concentration of the acid in the bath was increased from 2 to 10% (v/v), it was observed that the graft add-on continued decreasing. Addition of 0.1*N* acetic acid to the grafting bath did not change the graft level even up to 10% (v/v). This suggests that the mere use of acidic pH of the grafting bath does not help in improving the graft level. Thus, the effectiveness of the acids used is in the decreasing order $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HCl}$,

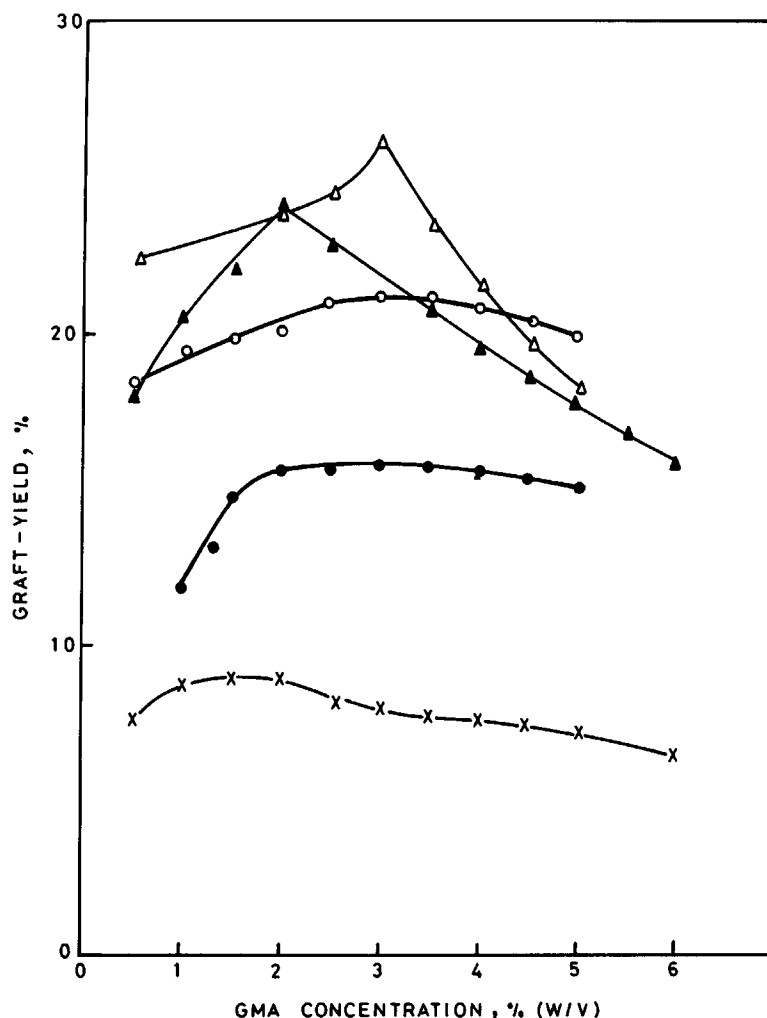


Figure 6 Effect of GMA concentration on graft yield: (○) UN photoinitiator; (●) BEE photoinitiator; (△) CAN photoinitiator; (▲) CAN chemical initiator; (X) PPS chemical initiator.

acetic acid being totally ineffective. Similar results were obtained by Hebeish and co-workers^{29,30} in the case of methyl methacrylate and acrylonitrile grafting of cotton cellulose using manganese (IV). Thus,

the amount of reduced ceric ion in the reaction system increased in the above order.

Garnett et al.³¹ suggested that use of mineral acids in the cellulose grafting bath assists in the enhance-

Table I Optimized Conditions of GMA-Grafting onto Unswollen Cotton Cellulose

Grafting Parameter	Photoinitiation			Chemical Initiation	
	UN	CAN	BEE	CAN	PP
Initiator concentration (% [w/v])	0.20	0.25	0.25	0.50	0.60
Time (h)	2	2	2	1	1
Temperature (°C)	50	50	50	80	70
GMA concentration (% [w/v])	3.0	3.0	3.0	2.0	2.0
Maximum graft add on (%)	63.60	78.60	47.30	48.28	17.90
Maximum graft yield (%)	21.20	26.20	15.76	24.13	8.95

Table II Effect of Fiber Preswelling and Addition of Acids on Grafting of GMA onto Cotton Cellulose: CAN, 0.25% (w/v); GMA, 2% (w/v); Time, 2 h; Temperature, 50°C

Grafting Condition	Concn of Acid (%)	Graft Add-on (%)
Control cotton		47.40
Preswollen cotton		53.90
Nitric acid in bath	2	52.10
	4	51.80
	10	47.30
Sulfuric acid in bath	2	51.85
	4	51.10
	10	50.60
Hydrochloric acid in bath	2	48.00
	4	48.00
	10	47.90
Acetic acid in bath	2	47.20
	4	47.35
	10	47.25

ment in grafting, both by causing inter- and intracrystalline swelling of the substrate and also by acting as a catalyst in the hydrolysis of cellulose, leading to uncoiling of the chains and improving the monomer accessibility. Further, they showed that homopolymerization also is enhanced in the presence of acids. A higher concentration of acids, however, may cause degradation of the backbone cellulose as well as of the graft chains.

Infrared Spectra of the Grafted Fibers

The infrared spectra of the control and grafted fibers are shown in Figure 7. It can be seen from the graph that for the cotton-*g*-GMA sample additional peaks are obtained at 1720 cm^{-1} , confirming the introduction of ester carbonyl group and peaks at 1000, 900, and 850 cm^{-1} for the presence of an epoxy oxirane link in the grafted fibers.^{32,33} Also, with increase in the graft level, the intensities of these characteristic peaks corresponding to those of GMA increased.

The physical and mechanical properties of the GMA-grafted cotton are being evaluated from the point of view of its end uses.

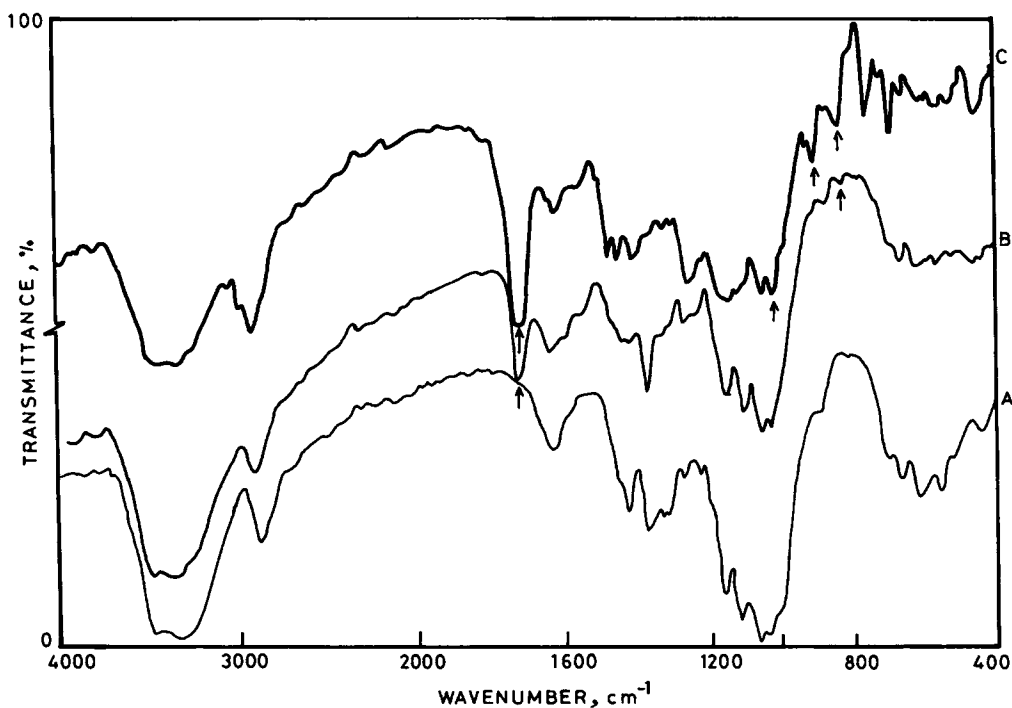


Figure 7 Infrared spectra of cotton samples: (A) ungrafted cotton; (B) 9.2% GMA-grafted cotton; (C) 63.6% GMA-grafted cotton.

CONCLUSION

It may be concluded that the graft add-on level greatly depends on the nature of initiator used. Although the UV radiations provide weak energy, with the help of a suitable initiator like CAN, they can give very high graft add-on values on optimizing the grafting parameters. Further, the concentrations of photoinitiators required are also substantially low. Preswelling the substrate enhances grafting due to more openness of the fiber structure. Use of a specific acid capable of reducing ceric ion to form more free radicals enhanced GMA grafting.

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