Mechanical and Thermal Properties of Glycidyl Methacrylate Grafted Cotton Cellulose

S. R. SHUKLA* and A. R. ATHALYE

Department of Chemical Technology, University of Bombay, Matunga, Bombay 400 019, India

SYNOPSIS

UV-radiation-induced graft-copolymerization of cotton cellulose was carried out with glycidyl methacrylate (GMA) using ceric ammonium nitrate (CAN) as a photoinitiator as well as a chemical initiator. With increase in the graft add-on, breaking load and moisture regain of cotton decreased, so also its thermal stability. The fiber surface changes due to grafting were ascertained by X-ray diffraction and scanning electron microscopy. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The modification of cellulose to decrease its water absorption and to prevent the resulting loss in electrical and mechanical properties has been the aim of many researchers. Although cellulose is a low-cost natural polymer with outstanding properties like thermal resistance, it is sensitive to water and its hydrophilicity has limited its applications in areas such as electrical insulation.

Since the hydroxyl groups of the cellulose molecules contribute significantly to the water sensitivity, most efforts are directed at diminishing their influence either through some normal chemical reaction or through crosslinking and graft-copolymerization of hydrophobic vinyl monomers.

In addition to the normally used chemical initiation technique, the low-energy ultraviolet (UV) radiations have been widely used for modifying fiber properties[1-5] through graft-copolymerization because of its least deteriorating effect.

Glycidyl methacrylate (GMA) has been grafted through chemical initiation technique onto various substrates[6-9] for improving their properties suitably. We have reported the UV-radiation-induced graft-copolymerization of GMA onto unswollen and preswollen cotton cellulose using both photo and chemical initiation techniques.[10]

The thermal stability of the fibers is an important aspect which is altered due to any chemical modification. Differential thermal analysis and thermogravimetric analysis efficiently determine the thermal stability of the polymers.[11] Another important characteristic from the point of view of noting the damage to textile fiber as a consequence of any chemical reaction is the breaking load, a mechanical property dependent on the type and extent of the modification of the fiber structure which has been frequently reported.[12]

In the present study, therefore, the results on cotton cellulose graft-copolymerized with GMA using ceric ammonium nitrate as an initiator both in chemical and UV-radiation-induced techniques have been reported by analyzing the grafted samples for their thermal and mechanical behavior as well as for moisture regain. The X-ray diffractograms and scanning electron micrographs were also obtained to help in illucidating the structure of grafted cotton.

EXPERIMENTAL

Materials

Substrates

The scoured and bleached 30s count cotton yarn was used as the cellulose sample.

Chemicals

Glycidyl methacrylate (GMA) supplied by Merck-Schuchardt was used without further purification. Ceric ammonium nitrate (CAN) was supplied by LOBA-CHEMIE Indoastranal Co. India. Auxipon NP, supplied by Auxichem Ltd., Bombay, was used as an emulsifier.

Graft-Copolymerization under UV Radiation

The UV-radiation-induced graft-copolymerization onto cotton cellulose was carried out as reported earlier, in the quartz flasks containing 0.20% (w/v) CAN photoinitiator and varying concentrations of GMA under the optimum conditions of time (2 h) and temperature (50°C).[10] The chemically initiated grafting was carried out in Erlenmeyer flasks kept in a thermostatically controlled water bath, the optimized conditions being 0.50% (w/v) CAN for 1 h at 80°C.[10]

After completion of grafting, each sample was taken out and extracted with methyl ethyl ketone at room temperature for one half hour to remove unreacted GMA. The homopolymer was removed by boiling the samples in hot water until constant weight and finally air-dried.[13] The graft add-on and graft yield were determined by using the standard formulas.[14]

Moisture Regain

The moisture regain of the control and grafted fibers was carried out using the standard method.[15]

Tensile Strength

The tensile strength of the cotton samples was determined in terms of the breaking load on a computerized tensile testing machine (R and D Electronics, India). Cut samples of 3 cm were used and a load of 50 g was used.

Thermal Analysis

The differential thermal analysis (DTA) and the thermogravimetric analysis (TGA) were carried out using a Stanton Redcroft Thermal Analyzer, STA 780, which records weight vs. time or temperature for TGA and temperature vs. time curves for DTA. The sample was cut to approximately 1–2 mm length and a 20 ± 5-mg sample was analyzed under nitrogen atmosphere from room temperature (30°C) to 500°C at a heating rate of 10°C/min and with a chart speed of 200 mm/h.

The differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC 7 thermal analysis controller TAC 7/DX with T graphics plotter-8. It records differential power signal, which is the power input required to maintain sample and reference at a same programmed temperature. A Cut sample of 10 ± 2 mg was taken for each analysis carried out under nitrogen atmosphere.

X-Ray Diffraction

X-Ray diffraction studies were carried out using Philips PW 1729 X-Ray generator coupled to PW 1710 diffractometer control. The plots were obtained on PM 8203A one-line recorder connected to it. It was operated at 35 kV and 20 mA. The samples were irradiated by CuK_α line while the K line was filtered out using a Ni filter. Yarn samples were powdered by cutting them finely with scissors. The powder (200 mg) was compressed under normal hand pressure in an aluminum holder having a small rectangular cavity. The scans were recorded in the range of 5° to 40° at a scanning speed of 0.02°/s.

Scanning Electron Microscopy

A Philips 515 scanning electron microscope, with an accelerating voltage up to 25 kV, was used having a resolution of 60 Å. One-centimeter sample was mounted on the stub (1.4 cm diameter) with the help of two-sided adhesive tape. Silver paste was used for contacting stubs surface and sample. Silver paste performed the dual function of bonding the specimen to the stub mechanically and electrically. The stub was then placed in a sputter coating unit and coated with gold-palladium.

RESULTS AND DISCUSSION

Effect of Grafting on Moisture Regain

The values of moisture regain of GMA-grafted cotton are given in Table I. It can be seen that as the graft add-on increases, the moisture regain decreases. This decrease in moisture regain of cotton is in proportion to the increasing hydrophobicity due to the oxirane ring in the GMA monomer.

Effect of Grafting on Breaking Load

Figure 1 indicates that the breaking load of the control and the grafted cotton samples decreased progressively as the graft add-on increased. Earlier

Table I   Effect of Photoinduced Grafting of GMA on Moisture Regain of Cotton[a]

GMA Conc (%) (w/v)	Graft Add-on (%)	Moisture Regain (%)
0.0	0.0	6.11
0.5	11.2	5.62
1.0	23.3	5.19
1.5	35.2	4.88
2.0	47.4	4.23
2.5	61.2	3.75
3.0	78.6	3.01
3.5	82.2	2.87
4.0	86.4	2.75
4.5	89.3	2.62
5.0	91.8	2.53

[a] CAN; 0.25% (w/v); time, 2 h; temperature, 50°C.

studies on grafting of styrene, acrylonitrile, and 2-hydroxyethyl methacrylate onto cotton cellulose have shown that the UV light and the grafting conditions such as time, temperature, and initiator are not instrumental in decreasing the breaking load of the substrate.[16,17] Only when the monomer is added to the grafting bath is the breaking load affected. Similar phenomena were observed in the present study also. The decrease in breaking load may be due to the fact that the grafted side chains act only as a dead load as far as the tensile properties are concerned and, hence, contribute toward the decrease in breaking load.

The breaking load values were found to be slightly lower for chemically initiated grafting than those for photoinitiated grafting at equivalent levels of graft add-on. For example, at 78% graft add-on, chemically initiated grafting gave a value of 159 g whereas photoinitiated grafting gave a value of 163 g for breaking load. This could be attributed to the somewhat severe conditions employed (temperature and initiator concentration) in the chemical initiation technique for the hydrogen abstraction from the fiber. Thus, the UV-induced grafting seems to be comparatively better in retaining the inherent mechanical properties of the backbone polymer.

Effect of Grafting on Thermal Properties

Figure 2 shows the DTA curves of natural cotton and cotton grafted under UV radiations at different levels of GMA graft add-on. In the DTA curve of control cotton, an endotherm was observed below 100°C due to moisture desorption from the sample followed by an exothermic process starting at about

290°C due to the oxidative attack at the carbonyl groups and the C — H bonds.

Below 300°C, some chain scission and loss of water molecules coming from the primary — OH groups of cotton cellulose take place. At 350°C, cotton cellulose degrades completely by the loss of — OH groups and by the breakdown of the pyranosic rings.[18] From the Figure it can be seen that both low and high GMA-grafted samples show an additional peak, representing degradation of poly-GMA. This peak shifts from 390°C for low GMA-grafted sample to 420°C for high GMA-grafted sample. In both cases the peak for cellulose degradation remains almost the same, although slightly higher in the case of low GMA-grafted cotton. The starting temperature of thermal degradation of the cotton sample shifts toward the lower side indicating loss in thermal stability on grafting. Soundarajan and Reddy[19] have reported that in the poly-GMA, the first degradation occurs at 360°C with complete degradation at 435°C.

The thermograms of control and grafted cotton are shown in Figure 3. Shapes of thermograms of control cotton and grafted cotton do not differ from
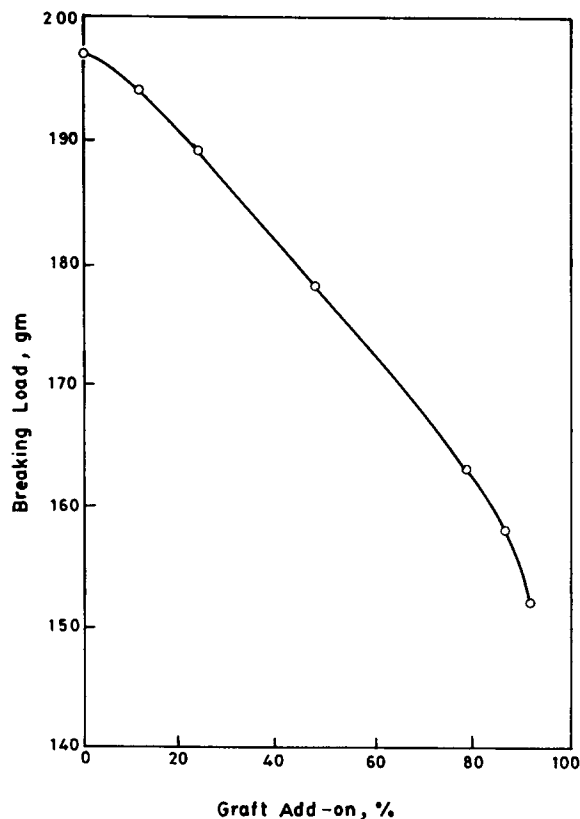

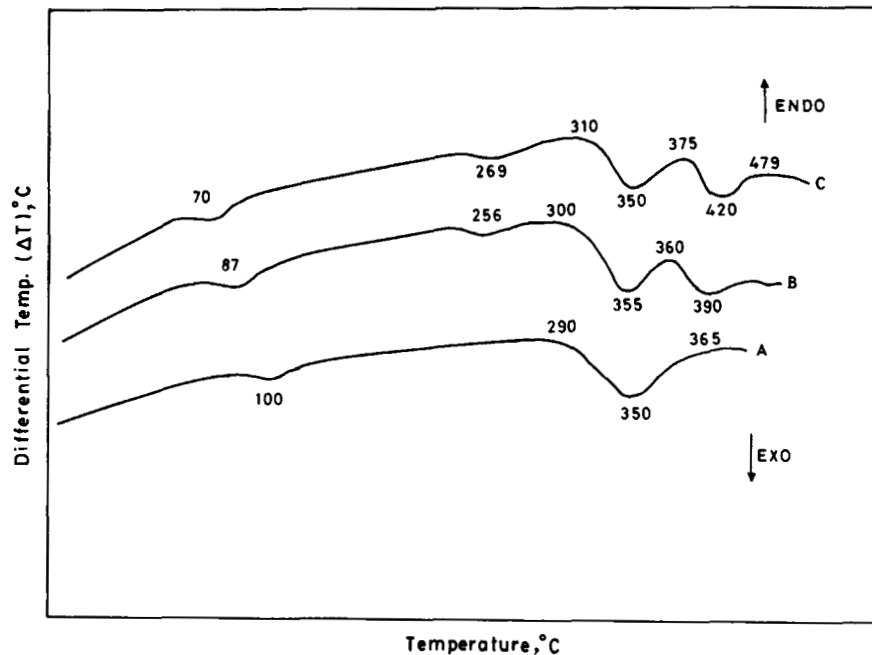**Figure 1**   Effect of GMA-graft add-on on breaking load of cotton cellulose.

Figure 2 DTA curves of cotton cellulose: (A) control cotton, (B) low GMA-grafted cotton, and (C) high GMA-grafted cotton.

each other significantly. It may be observed that the low grafted (11.2%) cotton needed slightly higher temperature of decomposition for any weight loss throughout the temperature range, whereas for the higher GMA-grafted (63.2%) cotton, upto 50%

weight loss, a somewhat lower temperature was needed for decomposition, which then increased at higher weight loss. At around 400°C, the weight loss was maximum in the case of higher GMA-grafted cotton. The GMA grafting, thus, decreased the
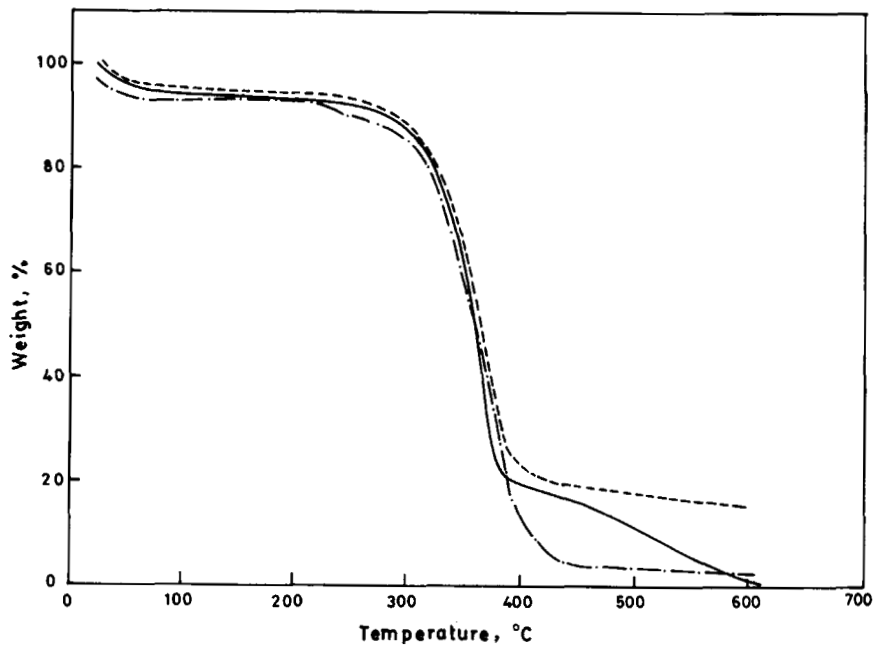

Figure 3 TGA curves of cotton cellulose: (———) control cotton, (– – – – –) low GMA-grafted cotton, and (– — – — –) high GMA-grafted cotton.
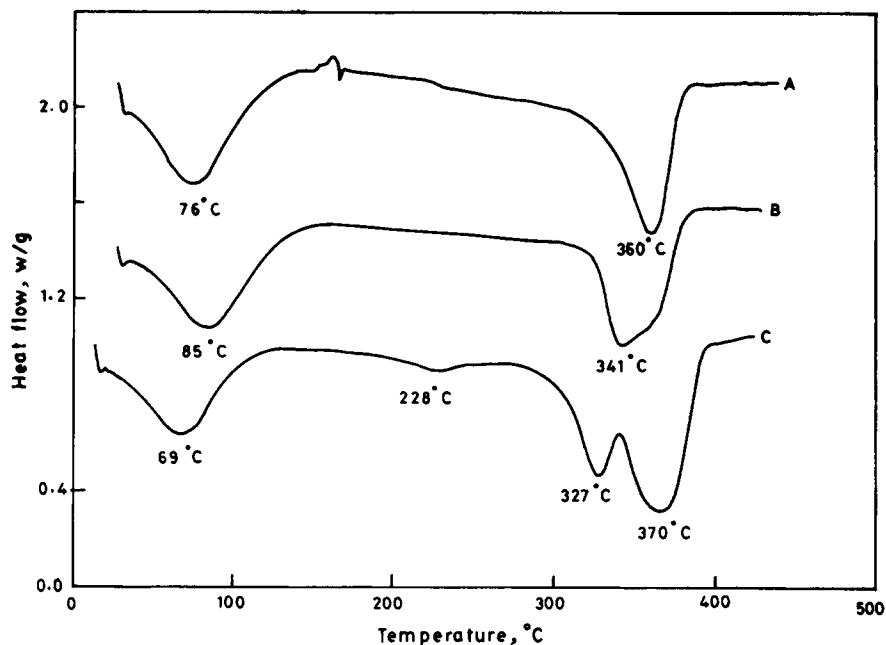
Figure 4   DSC curves of cotton cellulose: (A) control cotton, (B) low GMA-grafted cotton, and (C) high GMA-grafted cotton.

thermal stability of cotton particularly at the higher graft add-on level.

The DSC curves of control cotton and the cotton grafted with GMA are shown in Figure 4. The samples exhibited an endothermic peak below 100°C corresponding to moisture desorption. The major endothermic peak in the control cotton at 360°C can be attributed to the decomposition of cellulose by oxidation of volatile and charred products.[20] In the case of low GMA-grafted cotton, the cellulose decomposition peak was shifted to the lower temperature of 341°C and appeared as a broad endotherm which indicated the almost simultaneous decomposition of grafted polymer chains and the decomposition of cellulose. The two distinct endothermic peaks at 327 and 370°C appeared in the case of high GMA-grafted sample and could be attributed to the early decomposition of cellulose at 327°C followed by decomposition of grafted polymeric GMA chains at 370°C. Thus, the DSC studies also confirm the decrease in the thermal stability of cotton due to GMA grafting.

X-Ray Diffractogram

From Figure 5, it can be seen that the crystallinity of the control cotton and the low graft add-on sample is almost equivalent. The crystallinity of the high grafted sample is, however, low as indicated by the lower peak height at around Channel No. 900. Thus,

high GMA graft levels decrease the crystallinity of cotton, which have an impact on the mechanical and thermal properties.

Scanning Electron Micrographs

The scanning electron micrographs of the low and high GMA-grafted cotton are shown in Figure 6. The fiber surface became increasingly rough with small clusters of the GMA polymer attached to it due to graft-copolymerization.
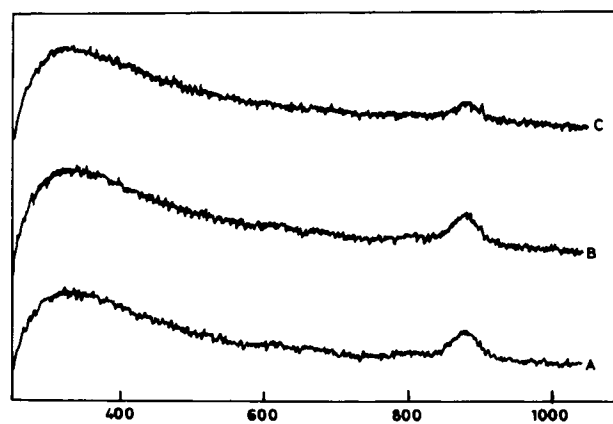

Figure 5   X-ray diffractograms of cotton cellulose: (A) control cotton, (B) low GMA-grafted cotton, and (C) high GMA-grafted cotton.
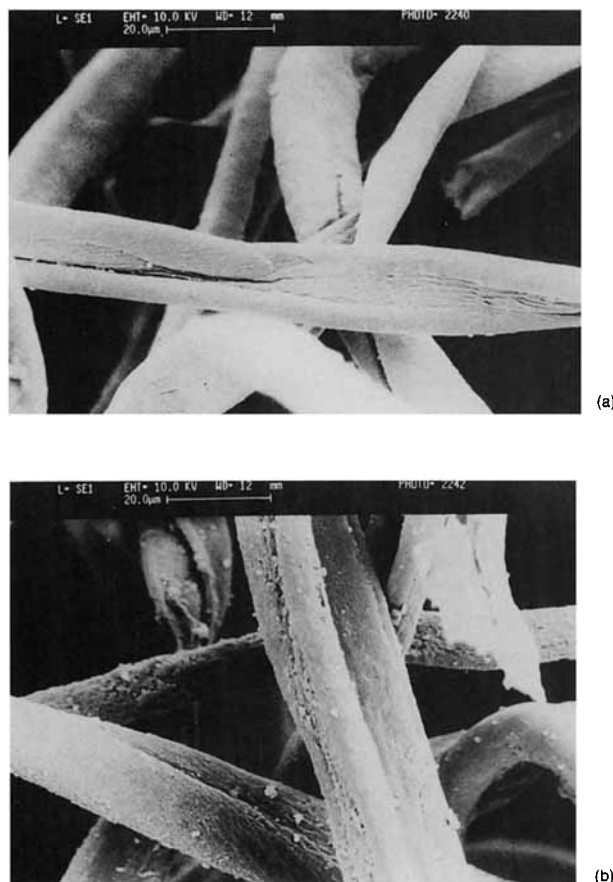
Figure 6   SEM photographs of cotton cellulose: (A) low GMA-grafted cotton and (B) high GMA-grafted cotton.

CONCLUSION

It may be concluded that the grafting of the hydrophobic monomer GMA decreases both the breaking load and the thermal stability of cotton cellulose significantly. Improved hydrophobicity leads to better hydrophobic-hydrophilic balance of the cotton substrate, which may be useful in immobilizing enzymes successfully. These studies are being conducted.

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