Study of Methyl-Methacrylate-Viscose Fiber Graft Copolymerization and the Effect of Grafting on Thermal Properties

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ABSTRACT: The graft copolymerization of methyl-methacrylate onto viscose fibers was studied under photoactive conditions with visible light using Ce^{4+}/Ti^{3+} combination as redox initiator in a limited aqueous medium. Polymerization conducted in the presence of light at $30 \pm 1^{\circ}C$ produced significant grafting, compared with that conducted in the dark under the same conditions. The % grafting, % total conversion, and % grafting efficiency were studied by varying time, monomer concentration, initiator concentration, and pH of the medium. The mechanism of polymerization and graft copolymer formation have been discussed. Characterization of the grafted fibers was done by Fourier transform infrared spectroscopy and scanning electron microscopy. The effect of % grafting on thermal properties was studied by thermogravimetric analysis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 135–140, 1999

Key words: graft copolymerization; redox initiator; limited aqueous medium; viscose fiber; thermogravimetry

INTRODUCTION

Modification of fiber properties by grafting has evoked considerable interest in recent years. Grafting of vinyl monomers onto viscose fiber has improved various properties.^{1,2} Different methods of initiation (such as high-energy radiation,^{2–5} redox systems,⁶⁻¹⁰ etc.) have been used for this purpose. The use of ceric salts and persulfate have also been reported.^{11,12} However, graft copolymerization of vinyl monomers onto viscose fiber under visible light has not been investigated so much, and further scope for investigations in this area are still open. The present work has been undertaken to investigate the grafting of methylmethacrylate (MMA) onto a viscose fiber using a combination of Ce^{4+}/Ti^{3+} as a redox initiator system in limited aqueous medium.

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EXPERIMENTAL

Processed viscose staple fibers $(1.5 \times 51 \text{ mm}; \text{gray} \text{staple, bright-bleached, Nagda})$ were supplied by Jayasree Textiles (Rishra, Hooghly, West Bengal, India). Ceric ammonium sulfate and titanium(III) chloride (15% solution in 10% HCl) from E. Merck, Germany, were used directly. MMA was obtained from a local market and purified by a standard procedure.^{13,14}

Grafting Procedure

A weighed amount of viscose fiber was taken in a borosilicate glass ampoule fitted with a standard joint and was soaked with an aqueous solution of ceric ammonium sulfate of known volume and concentration. A known volume of MMA was then added, followed by soaking with a known volume and concentration of Ti^{3+} solution under a nitrogen atmosphere. The ampoule was then tightly

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		Formation of PMMA ^b		
Initiator System	Conditions of Polymerization	Free	Grafted	
Ce ⁴⁺ /Ti ³⁺	Dark, $30 \pm 1^{\circ}$ C, $2h$	+	+	
Ce^{4+}	Dark, $30 \pm 1^{\circ}$ C, $2h$	+	—	
Ti^{3+}	Dark, $30 \pm 1^{\circ}$ C, $2h$	_	—	
Ce^{4+}/Ti^{3+}	Photo, $30 \pm 1^{\circ}C$, $2h$	+	++	
Ce^{4+}	Photo, $30 \pm 1^{\circ}$ C, $2h$	+	+	
Ti ³⁺	Photo,30 \pm 1°C,2h	—	_	

Table IGraft Copolymerization of MMA onViscose Fiber^a

^a Initiator system: [Ce⁴⁺] 0.01×10^{-2} *M*/L; 0.97×10^{-2} *M*/L; [MMA] 2.19×10^{-2} *M*/L; pH 3.0.

^b +, low; ++, high; -, nil.

stoppered. The polymerization experiment was conducted by placing the ampoules at the middle of the space between two parallel placed and illuminated fluorescent tube lamps (40 W) apart by 10 cm for specified time periods.

After polymerization, the contents were washed, dried, weighed, and transferred into a soxhlet unit. The free poly(MMA) (PMMA) (homopolymer) was extracted from the gross product by refluxing with benzene as the solvent. The residue containing a mixture of viscose fiber-PMMA graft copolymers and unreacted silk fibers was treated with a petroleum ether-methanol mixture to collapse the swollen structure; it was then dried in vacuum dryer at 40°C and weighed. The dried residue was termed apparent graft copolymer. The % grafting, % total conversion, and % grafting efficiency were calculated in the following way after correction was made for the loss in weight on treatment without MMA solution.

% Grafting

$$= \frac{\text{PMMA in the apparent graft copolymer (g)}}{\text{Viscose sample taken (g)}} \times 100 \quad (1)$$
% Total conversion=
$$\frac{\text{Total PMMA formed (g)}}{\text{MMA taken (g)}} \times 100 \quad (2)$$

% Grafting efficiency

$$= \frac{PMMA \text{ in the apparent graft copolymer (g)}}{Total PMMA \text{ formed (g)}} \\ \times 100. \quad (3)$$

Measurements

The Fourier Transform Infrared Spectroscopy (FTIR) spectra have been recorded on a Perkin–Elmer (Model FTIR-1600) instrument. The morphological structure was investigated by a scanning electron microscope (model no. S-415A, Hitachi, Japan). Thermal behavior was examined on a Perkin–Elmer Delta Series TGA-7 instrument under a nitrogen atmosphere at a heating rate of 20° C min⁻¹.

RESULTS AND DISCUSSION

Preliminary investigations indicated (Table I) that the rate of polymerization, when done in the presence of light at $30 \pm 1^{\circ}$ C was much faster than when done in the dark under the same conditions. Thus, all experiments were conducted under photoactive conditions.

The results showing the effect of variation of time, monomer concentration, initiator concentration, and pH of medium on % grafting, % total conversion, and % grafting efficiency are presented in Figures 1–5.

Effect of Variation of Polymerization Time

The results are shown in Figure 1. Both % grafting and % total conversion increases over the time period studied (1–5 h). The % grafting efficiency first increases up to 4 h and then declines. The observations are in accordance with Bendak and Habeish¹⁵ and Shukla and colleagues.¹⁶ The decrease in % grafting efficiency after 4 h may be



Figure 1 Variation of time with % grafting (\bigcirc), % total conversion (\triangle), and % grafting efficiency (\bigcirc).



Figure 2 Variation of monomer concentration with % grafting (\bigcirc) , % total conversion (\triangle) , and % grafting efficiency (\bullet) .

attributed to the retardation of diffusion of monomer due to titanium ion deposition on the fiber surface and also as a result of the increased viscosity of the medium.

Effect of Variation of Monomer Concentration

Results are shown in Figure 2. The % grafting and % total conversion increased expectedly over the range of monomer concentration studied. Grafting efficiency, however, showed a gradual decreasing trend. The increasing trend may be due to the formation of complex between viscose and monomer or gel effect.

Effect of Variation of Ce⁴⁺ Ion Concentration

The related results are shown in Figure 3. All three properties (i.e., % grafting, % total conver-



Figure 3 Variation of Ce⁴⁺ ion concentration with % grafting (\bigcirc), % total conversion (\triangle), and % grafting efficiency (\bigcirc).



Figure 4 Variation of Ti^{3+} content with % grafting (O), % total conversion (\triangle), and % grafting efficiency (\bigcirc).

sion, and % grafting efficiency) show a decreasing trend with increasing Ce^{4+} ion concentration homopolymerization that prevails over grafting.¹⁷

Effect of Variation of Ti³⁺ Ion Concentration

The related results are shown Figure 4. Both % grafting and % total conversion show an increasing trend up to Ti³⁺ content of 1.2 mL; after that, both decrease. Grafting efficiency shows a decreasing trend throughout the range of concentration studied.



Figure 5 Variation of pH with % grafting (\bigcirc) , % total conversion (\triangle) , and % grafting efficiency (\bullet) .



Figure 6 FTIR spectra of MMA polymer (curve a), ungrafted viscose fiber (curve b), and grafted viscose fiber (curve c).

At higher Ti^{3+} concentration, the rate of termination prevails over initiation and propagation, which results in the decreasing rate of % grafting and % total conversion after 1.2 mL Ti^{3+} content (as observed from Fig. 4).

Effect of Variation of pH

Results are shown in Figure 5. The % grafting increases up to pH 2.2, after which it decreases. The % total conversion, however, follows a steadily increasing trend throughout the range of pH studied (0.5–3.0). Thus, as expected, grafting efficiency shows an increasing trend up to pH 2.2 and then decreases. The results may be explained by the fact that, at higher pH values, Ti hydroly-

ses and precipitation of ${\rm Ti}^{3+}$ take place on the fiber, which prevents grafting.

FTIR Studies

The FTIR spectra of the PMMA (curve a), ungrafted fiber (curve b), and grafted fiber (curve c) are shown in Figure 6. In the spectra of MMA polymer initiated by the Ce⁴⁺/Ti³⁺ initiator system and the grafted fiber, the absorption band in the range of 1733-1734 cm⁻¹ is due to the presence of the ester group. The absorption band in ungrafted viscose fiber and in grafted viscose fiber in the range of 3446-3448 cm⁻¹ is due to the presence of a hydroxyl group. As expected, the absorption band within the range of 3446-3448 cm⁻¹ characteristic of hydroxyl group should change with the amount of grafting. But, this is not reflected because viscose contains a large number of -OH groups in its structure, as evident from curve b.

Thermal Decomposition Studies

Thermogravimetric analysis (TGA) and differential TGA studies on viscose fiber, PMMA homopolymer, MMA grafted viscose fibers, with varying degree of grafting area, are shown in Table II. From these studies, it may be concluded that the grafting of MMA on viscose fiber improves the thermal stability of the fiber. This may be due to the fact that the grafted MMA polymers get entangled and form a crosslinked type network, which when heated forms a insulative carbonaceous char barrier on the surface, thus inhibiting degradation.

Sample Particulars	Inception ^a Temperature (°C)	Peak Pyrolysis Temperature (°C)		$\begin{array}{l} \mbox{Temperature of Decomposition } (T_D) \\ \mbox{ in °C at Weight Loss } (\%) \end{array}$						
		1st Peak	2nd Peak	20	30	40	50	60	70	Residual Wt. (%)
Viscose Fiber	230	375	_	324	347	359	368	376	388	24.19
MMA homopolymer MMA-grafted viscose fiber	271	—	420	382	393	400	407	412	—	Negligible
68.15% grafting	263	376	409	345	350	372	380	395	402	9.12
80.5% grafting	270	379	412	360 265	372	386 200	397 200	400	410	7.35
110.45% gratting	282	3//	423	305	387	390	399	406	419	4.05

Table II Analysis of TGA and Differential TGA Curves

^a Starting degradation temperature derived from the derivative curve.





Figure 7 Scanning electron micrographs of: (a) ungrafted viscose fiber, (b) 68% PMMA grafted viscose fiber, (c) 80.5% PMMA grafted viscose fiber, and (d) 100% PMMA grafted viscose fiber.

Morphological Structure

The morphological structures are shown in Figure 7. The surface of the ungrafted fiber is smooth. The presence of nodules or lumps on the surface of the grafted fibers may be due to the PMMA, which is chemically bonded to the surface of the fiber.

Mechanism

From the literature survey, it has been found that very limited reports are available on photograft copolymerization of MMA on viscose fiber using Ce^{4+}/Ti^{3+} initiator system in limited aqueous medium. However, the radical generating process is complicated due to a multiplicity of factors. The probable mechanism may be due to redox reaction of the Ce^{4+}/Ti^{3+} combination. Considering the previous works of redox-induced graft copolymerization of MMA on cellulose fibers, the radical generation may be written as

CONCLUSIONS

The initiator system Ce⁴⁺/Ti³⁺ for graft copolymerization of MMA on viscose fiber has been found to be much more effective in the presence of light than in the dark. Characterization of the grafted fiber by FTIR, TGA, and scanning electron microscopy indicates evidence of grafting on the fiber backbone. Thermal stability of the fiber has also increased by grafting as indicated in TGA.

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