Graft Copolymerization of Methyl Methacrylate onto Jute Fiber Initiated by Cerium(IV)–DMSO Redox Initiator System

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ABSTRACT: The kinetics of graft copolymerization of methyl methacrylate (MMA) onto chemically modified jute fibers initiated by the Ce(IV)–DMSO redox system was studied in the temperature range of 40–60°C. By studying the effects of the concentration of the monomer, Ce(IV), and DMSO on the rate of grafting, the optimum conditions for grafting were determined. Also, the effect of temperature, time, concentration of the acid, the amount of jute fiber, and some inorganic salts and organic solvents on the rate was investigated. A kinetic scheme was proposed on the basis of the experimental findings. Infrared spectra of chemically modified jute and grafted jute was investigated. More than 120% of grafting could be achieved with the present system. The characterization of MMA-grafted chemically modified jute by TGA and DTA studies was made. The thermal stability of the jute fibers was improved by grafting. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2569–2576, 1998

Key words: graft copolymerization; redox system

INTRODUCTION

The chemical modification of natural polymers by grafting has received considerable attention in recent years due to the wide variety of monomers available. Currently, grafting has become a potentially powerful method for producing substantial modification of the properties of natural fibers with the retention of its desirable properties.[1,2] Today, the study of grafting onto natural fibers like silk,[3] wool,[4] jute,[5] and cotton[6] is considered one of the frontier areas of research. Graft copolymerization of jute with various monomers such as methyl methacrylate (MMA), acrylonitrile (AN), and methyl acrylate (MA) using various initiator systems has gained considerable importance in recent years.[7,8] The most commonly reported initiator is Ce(IV). Trivedi and Meheta[9] first studied the kinetics of grafting of AN onto defatted and bleached jute. Majumdar and Rapson[10] studied the condition of grafting of styrene onto jute, while Ray[11] showed by X-ray studies that fiber becomes more rigid with grafting. Ceric ion-initiated grafting of jute has been reported very recently from this laboratory. Since jute is a major agricultural product of Northeastern India with many uses, we have taken up this project to incorporate desirable properties in jute by grafting. In the present context, attempts were made for the first time to graft copolymerize MMA onto jute fiber using the Ce(IV)-dimethyl sulfoxide (DMSO) redox system.

EXPERIMENTAL

The mesta variety of white jute procured from Konark Jute Mills Ltd. (Orissa, India) was sub-

jected to different chemical treatments as mentioned earlier in our research publications.[12] Except for acetylation, MMA (BDH AnalaR) was washed with 5% NaOH followed by thorough washing with conductivity water. It was then dried over anhydrous calcium chloride and stored in the refrigerator for later use. All other chemicals, that is, ceric ammonium sulfate, DMSO, H_2SO_4, etc., were of BDH or AnalaR grade and were used as such without further purification. The graft-copolymerization reactions were carried out at the desired temperature in a constant temperature bath with an accuracy of $\pm 0.1°C$. Before initiating the graft-copolymerization reaction, the jute fibers were soaked in an appropriate quantity of the monomer for about 10 min. The graft-copolymerization reactions were carried out in Pyrex vessels with $B_{24/29}$ standard joints equipped with gas inlet and outlet tubes. An appropriate quantity of the reaction mixture containing jute fiber, monomer, DMSO, H_2SO_4, and water were taken in the reaction vessel. Then, the required amount of the ammonium ceric sulfate solution was poured into the vessel containing the reaction mixture and the time was noted. The reaction was carried out at three different temperatures, that is, 40, 50, and 60°C. After specific time intervals, each reaction was arrested by quenching the vessel with ice-cold water. Then, the grafted samples were washed well with water, given a mild soaping to remove the loosely adhering polymer, washed, and air-dried to a constant weight. Finally, the fibers were extracted with acetone in a Soxhlet apparatus for 12–15 h to dissolve all the homopolymers and copolymers until a constant weight of grafted jute fiber was obtained. The percentage graft yield was calculated as follows:

% Graft yield (GY) =

$$\frac{(\text{dry wt of grafted jute} - \text{dry wt of original jute})}{\text{dry wt of original jute}} \times 100$$

$$\text{Rate of grafting } (R_g) = \frac{1000 \times W}{V \times t \times M}$$

where W is the weight of the grafted jute minus the weight of the original jute; V, the volume of the reaction mixture; t, the time of the reaction in seconds; and M, the molecular weight of the monomer.
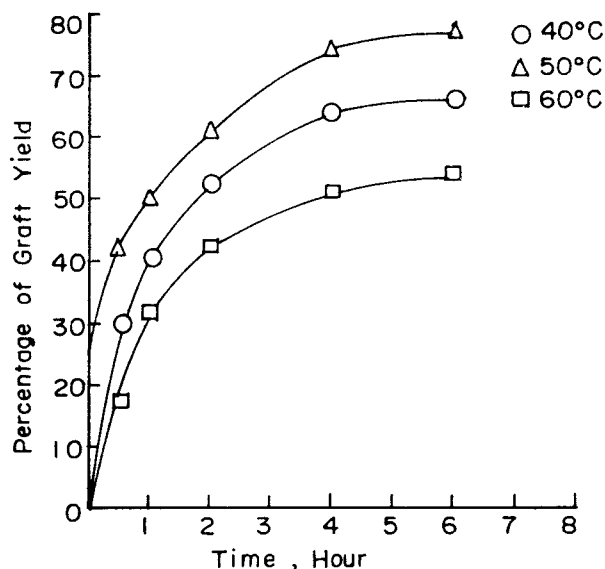

Figure 1 Time-conversion curves: jute = 0.1 g; [MMA] = 0.467 mol L^{-1}; [H_2SO_4] = 0.05 mol L^{-1}; [DMSO] = 0.25 mol L^{-1}; [Ce^{+4}] = 0.035 mol L^{-1}.

RESULTS AND DISCUSSION

The effect of the variation of the time on the graft yield as well as on the rate of grafting was investigated at three different temperatures (40, 50, and 60°C), which is depicted in Figure 1. In all the cases, the graft yield as well as the rate of grafting was found to increase steadily with increase of time up to 4 h, after which very little change was observed in the rate of grafting. For all practical purposes, the optimum time was taken at 4 h. This trend is in agreement with the reports of Haque et al.[13] and Patra and Singh.[14] This phenomenon was explained on the basis of the availability of the monomer in the swollen phase which increases with time.

The effect of the ceric ion concentration on the percentage graft yield and rate of grafting was studied by a number of authors.[5,12,15] It has been well established that the percent of grafting increases up to a maximum with increasing ceric ion concentration. It is clear from Figure 2 that with increase of the Ce(IV) concentration from 0.005 to 0.035 mL^{-1} the rate of grafting increases rapidly at all the temperatures studied, after which there is no remarkable change. This may be attributed to the greater number of grafting sites created by the Ce(IV) ion which may be due to the predominance of mutual termination over linear termination at low concentration. But at higher concentration (above 0.035 mL^{-1}), the lin-
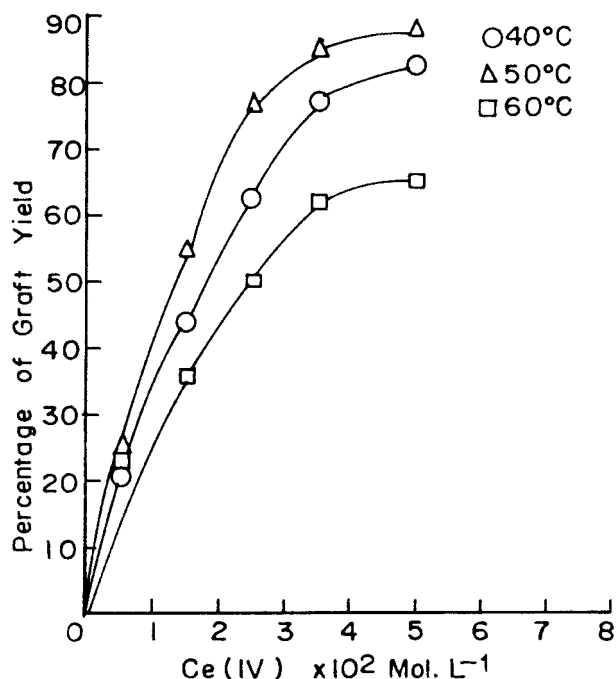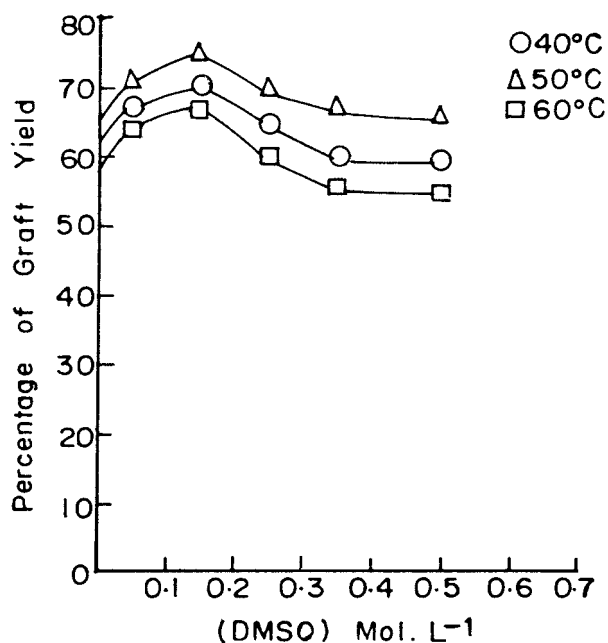
Figure 2 [Ce(IV)] versus percentage of graft yield: jute = 0.1 g; [MMA] = 0.467 mol L^{-1}; [DMSO] = 0.25 mol L^{-1}; [H_2SO_4] = 0.5 mol L^{-1}; time = 4 h.

Figure 3 [DMSO] versus percentage of graft yield: [Ce^{+4}] = 0.035 mol L^{-1}; [H_2SO_4] = 0.5 mol L^{-1}; [MMA] = 0.467 mol L^{-1}; jute = 0.1 g; time = 4 h.

ear termination probably predominates over the other types of terminations, leading to shorter grafting chains. This observation is in close agreement with the report of Santappa et al.[16] and Patra et al.[14]

The effect of the monomer on percentage graft yield and rate of grafting was also determined at 40, 50, and 60°C. The percentage of grafting increases with increase in the monomer concentration from 0.0934 to 0.3736 mL^{-1} and, thereafter, it decreases. This decreasing trend after a certain optimum concentration of MMA is probably due to competition between the homopolymerization and grafting, where the former prevails over the latter[12] at higher monomer concentration. This fact is in agreement with the grafting of MMA onto jute fiber using $KMnO_4$–malonic acid[17] and V^{5+}–cyclohexanol[18] redox initiator systems.

In the present investigation, the concentration of DMSO was varied from 0.05 to 0.50 mL^{-1}. It is seen that the percentage of grafting increases up to a critical DMSO concentration of 0.15 mL^{-1} and then decreases (Fig. 3). A similar observation was noted in the case of potassium persulfate-initiated grafting of poly-MMA onto poly(vinyl alcohol)[19] and hydroxy methacrylate onto gelatine.[20] This may be due to the rapid rate of termi-

nation and/or formation of radical scavengers at higher DMSO concentration. Similar observations were made by Mohanty et al.[15]

The optimum temperature for maximum graft-
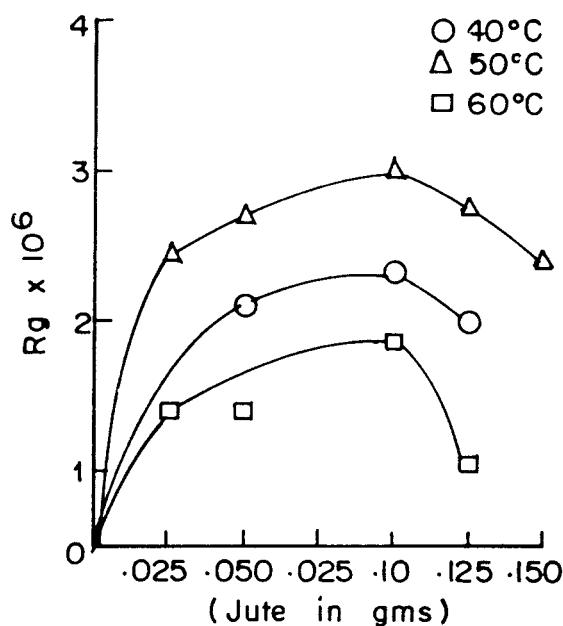
Figure 4 Effect of jute fiber versus $R_g \times 10^6$: [Ce^{+4}] = 0.035 mol L^{-1}; [H_2SO_4] = 0.5 mol L^{-1}; [MMA] = 0.467 mol L^{-1}; [DMSO] = 0.1 mol L^{-1}; time = 4 h.

Table I Effect of Acid Concentration on Graft Yield

[H₂SO₄] (mL⁻¹)	40°C		50°C		60°C	
	$R_g \times 10^6$	% GY	$R_g \times 10^6$	% GY	$R_g \times 10^6$	% GY
0.2	1.45	41.9	2.6	75.0	0.71	20.5
0.3	1.68	48.4	2.74	79.0	0.78	22.5
0.4	2.02	58.5	3.39	97.7	0.86	25.0
0.55	1.92	55.4	2.53	73.0	0.81	23.5
0.7	1.69	48.9	2.36	68.0	0.77	22.2

Jute = 0.1 g; [MMA] = 0.467 mL⁻¹; [DMSO] = 0.1 mL⁻¹; [Ce⁴⁺] = 0.02 mL⁻¹. Time = 4 h.

ing was determined by carrying out graft-copolymerization reactions at three different temperatures, namely, 40, 50, and 60°C. A perusal of the results indicates that the percentage of grafting increases up to 50°C and then decreases with increase in the reaction temperature. The increasing trend of the graft yield may be due to the swellability of jute in the substrate at higher temperature and enhancement of the rate of diffusion of the monomer with increase of the temperature.[12,14,15]

The effect of the amount of jute fiber on the R_g, also studied at three different temperatures, is depicted in Figure 4. The graft yield is found to decrease consistently with increase in the amount of the jute fiber. The maximum yield is obtained when the amount of the jute fiber is 0.10 g. This is probably due to the rate of termination becoming faster than that of initiation with increase in the jute fiber amount. This report is in agreement with those of Patra and Singh,[14] Nayak et al.,[12] and Santappa et al.[16]

Generally, the grafting reaction is more or less influenced by the reaction medium. With the variation of the acid concentration from 0.2 to 0.7 mL⁻¹, the percentage graft yield is found to increase slowly up to 0.4 mL⁻¹ and then it decreases (Table I). The decrease of the percentage of graft yield at higher acid concentration may be due to the formation of species unfavorable to grafting. This report is in agreement with earlier reports.[5,14]

The graft yield follows the following order in respect to the solvents when added in equivalent proportions (5% v/v) to the reaction medium (Table II):

Benzene > dioxane > control

> methanol > glacial acetic acid

Similarly, the effect of some inorganic salts when added to the reaction medium in equimolar concentrations follows the order

Control > NaCl > KCl > MnCO₃ > MnSO₄ · H₂O

Although the addition of most salts depress the percentage of the graft yield, MnSO₄ · H₂O depresses it considerably (Table II). The grafting process is more favored by benzene and dioxane probably due to the high swellability of jute fiber in these solvents. Glacial acetic acid was found to have the reverse effect on the graft yield due to the termination of graft radicals and jute macroradicals via chain transfer.

Reaction Mechanism

To explain the experimental results, the following reaction mechanism is suggested:

Initially, the active species of Ce(IV) in sulfuric acid media interact with DMSO to form a complex. Subsequently, the complex dissociates in a slow step with generation of the free-radical D⁺ by abstraction of a hydrogen atom from the pro-
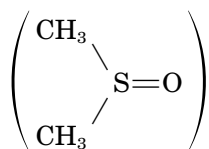
Table II Effect of Solvents and Salts on Graft Yield

Name of the Solvent	% GY	Name of Salt	% GY
Control	81.9	Control	81.7
Glacial acetic acid	74.9	NaCl	59.5
Benzene	123.6	MnSO₄H₂O	34.0
Dioxane	89.2	MnCO₃	37.2
Methanol	81.7	KCl	51.5

Jute = 0.1 g; [MMA] = 0.467 mL⁻¹; [Ce⁴⁺] = 0.35 mL⁻¹; temp = 50°C; time = 4 h; [DMSO] = 0.1 mL⁻¹; [H₂SO₄] = 0.05 mL⁻¹.

tonated complex.[14] The reaction then proceeds through the following steps (2)–(5):

1. $Ce(IV) + D \overset{K}{\rightleftharpoons} complex \overset{k_1}{\rightarrow} D^{\bullet} + Ce(III)$

2. $JH + D^{\bullet} \overset{k_2}{\rightarrow} J^{\bullet} + DH$

3. $J^{\bullet} + M \overset{k_i}{\rightarrow} JM^{\bullet}$

4. $JM^{\bullet} + M \overset{k_p}{\rightarrow} JM_2^{\bullet}$

$$\vdots \qquad \vdots \qquad \vdots$$

$JM_{(n-1)} + M \overset{k_p}{\rightarrow} JM_n^{\bullet}$

5. $JM_n^{\bullet} + JM_n^{\bullet} \overset{k_t}{\rightarrow}$ grafted jute, where DMSO

$$\begin{pmatrix} CH_3 \\ \diagdown \\ \qquad S{=}O \\ \diagup \\ CH_3 \end{pmatrix}$$

is denoted as D and $Ce(IV)$, JH, $J^{\bullet}$, M, K, k_1, k_2 k_i, k_p, and k_t are the ceric ion, jute molecule, jute macroradical, monomer, and different rate constants, respectively.

Taking into account the above reaction scheme and applying the steady-state principle to all kinds of radicals involved, the following expression for the R_g was derived:

$$\frac{d[D^{\bullet}]}{dt} = k_1 K[Ce(IV)][D] - k_2[JH][D^{\bullet}] = 0$$

or

$$k_1 K[Ce(IV)][D] = k_2[JH][D^{\bullet}]$$

or

$$[D^{\bullet}] = \frac{k_1 K[Ce(IV)][D]}{k_2[JH]} \qquad (1)$$

$$\frac{d[J^{\bullet}]}{dt} = k_2[JH][D^{\bullet}] - k_i[J^{\bullet}][M] = 0$$

$$[J^{\bullet}] = k_2[JH][D^{\bullet}]k_i[M]$$

Replacing the value of $[D^{\bullet}]$ from eq. (1),

$$[J^{\bullet}] = \left(\frac{k_1 k[Ce(IV)][D]}{k_i[M]} \right) \qquad (2)$$

$$\frac{d[JM^{\bullet}]}{dt} = k_i[J^{\bullet}][M] - k_t[JM^{\bullet}]^2 = 0$$

or

$$[JM]_n^{\bullet} = \left(\frac{k_i[J][M]}{k_t} \right)^{1/2}$$

Replacing the value of $[J^{\bullet}]$ from eq. (2),

$$[JM_n^{\bullet}] = \left(\frac{k_1 k[Ce(IV)][D]}{k_t} \right)^{1/2} \qquad (3)$$

$$Rg = k_p[JM_n^{\bullet}][M]$$

Replacing the value of $[JM^{\bullet}]$ from eq. (3),

$$R = k_p[M]\frac{k_1 k}{k_t}([Ce(IV)][D])^{1/2}$$

The experimental results are in good agreement with the proposed mechanism.

Characterization

IR spectra of the chemically modified jute and MMA-grafted chemically modified jute were recorded on a Perkin–Elmer 843 Model infrared spectrophotometer in the form of potassium bromide pellets and are shown in Figures 5 and 6, respectively. It is observed that both spectra show a characteristic broad absorption band of the hydroxyl group around 3400 cm^{-1}. A similar type of observation in the IR spectra was also reported by Trivedi and Meheta[9] and Singh et al.[12] However, the spectra of MMA-grafted chemically modified jute shows an additional peak of an ester group at 1731 cm^{-1}. This indicates the presence of the MMA unit in the grafted jute and provides strong evidence of grafting. The slightly reduced intensity of the —OH peak as a result of grafting, as observed in this case, is due to the large concentration of —OH groups in jute. It is a probable site for grafting. The sharp peak of 1731 cm^{-1} is characteristic of the carboxylate end group in the grafted polymer and this also confirms the mechanism of the grafting suggested.

The thermal behavior of chemically modified jute and MMA-grafted jute fibers are examined through TGA curves, which were recorded on a General U22A Model DuPont 9900 thermal analyzer within a temperature range 0–650°C and with a heating rate of 20°C per minute in an atmosphere of nitrogen and are shown in Figures 7 and 8. In the case
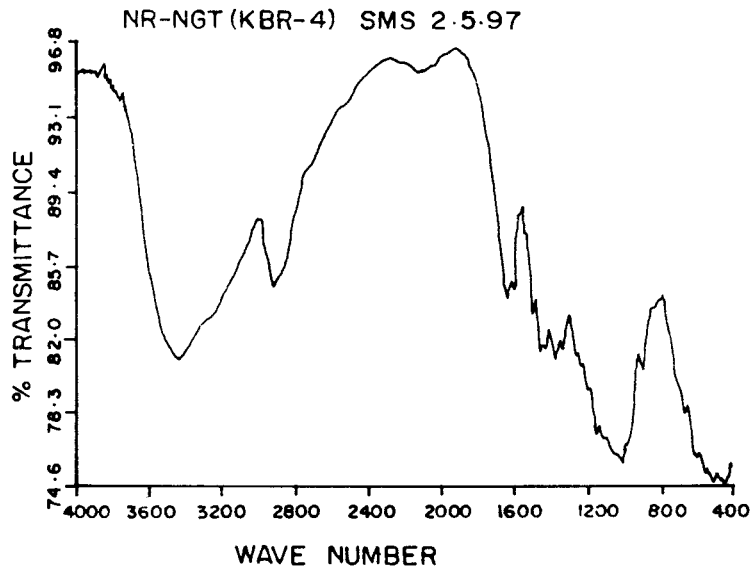
Figure 5 IR spectra of chemically modified jute fibers.

of ungrafted jute, the maximum decomposition temperature was 401°C, but with grafted jute of a 71, 96, 109 and 113% gross yield, the maximum decomposition temperatures of 430, 450, 458, and 462°C were noted. It is evident from this analysis that the thermal stability of grafted jute is more than that of the nongrafted one and also that the thermal stability of grafted jute increases slowly with increase in the percentage of grafting. Figure 7 is the continuous weight loss curve for thermal degradation of 12.924 mg of nongrafted jute from 20 to 650°C. Decomposition was observed to begin at 40°C and become very rapid at 300°C and the maximum

weight loss occurred at 401°C. Figure 8 shows the thermal degradation of 11.618 mg of the MMA-grafted jute sample from 30 to 650°C. Decomposition begins slowly at 40°C and becomes rapid at 250°C. The reaction was complete at 462°C and resulted in the maximum weight loss. The curves of Figures 7 and 8 contain the information necessary to evaluate the kinetics of degradation by Broido's method[21] based on the expression

$$\ln\left(\frac{1-y}{y}\right) = -\frac{E^*}{R}\frac{1}{T} + \text{constant} \qquad (1)$$
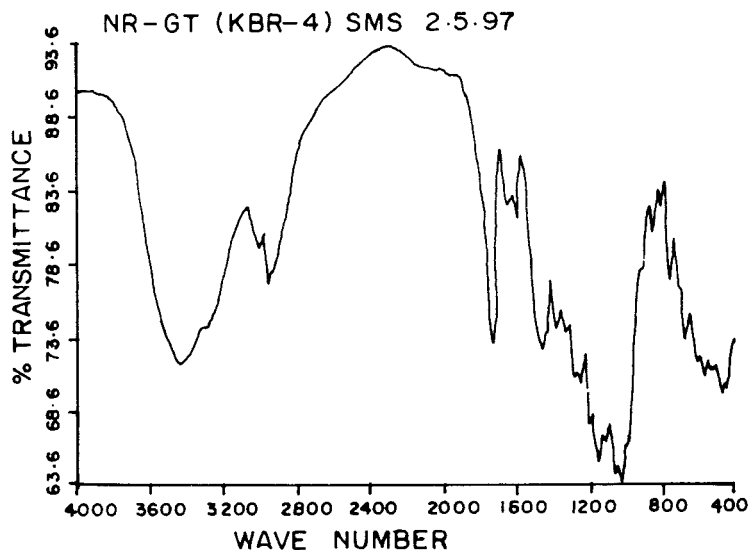

Figure 6 IR spectra of chemically modified jute fiber grafted with MMA.
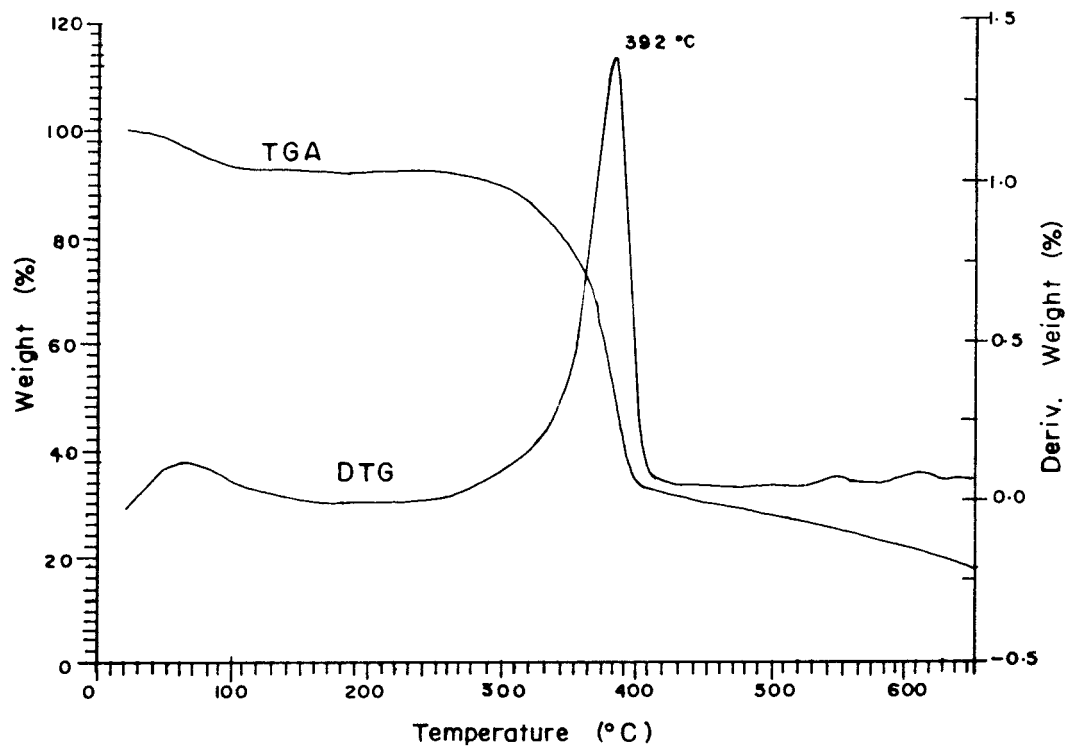
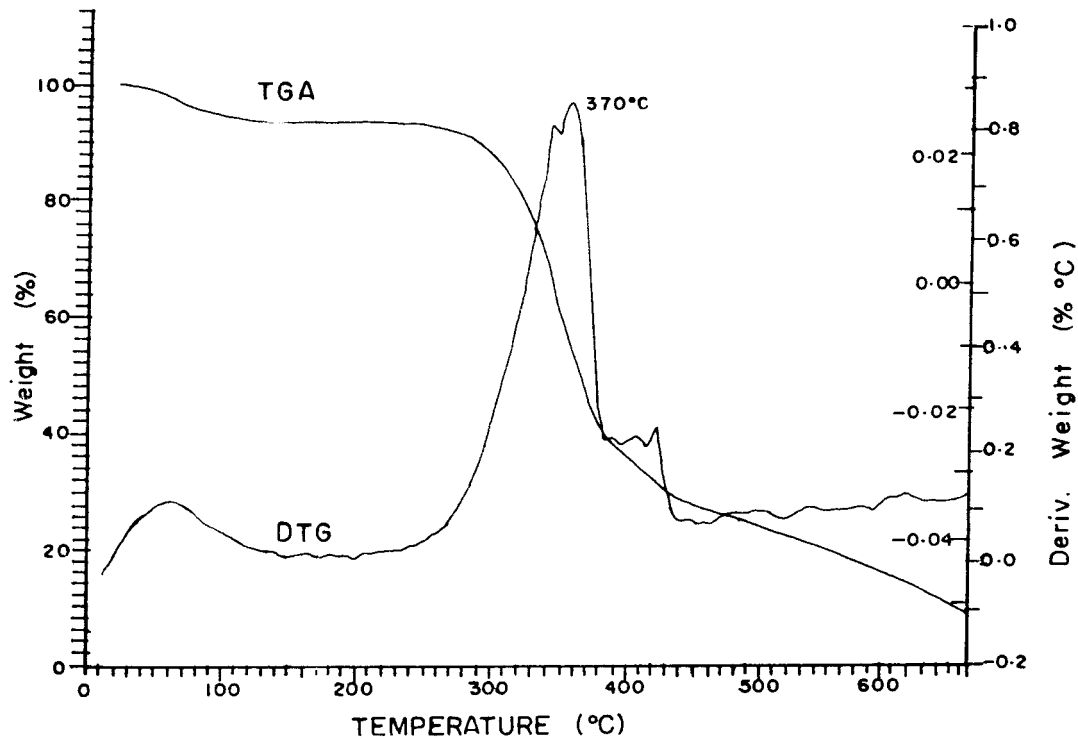**Figure 7**   TGA and DTG curves of nongrafted jute.

Figure 8   TGA and DTG curves of MMA grafted jute fibers (% GY, 113).

where y is the fraction of the number of initial molecules not yet decomposed. E^* is the energy of activation; R, the gas constant; and T, the temperature in the Kelvin scale.

The energy of activation was evaluated from eq. (1) by plotting $\ln[(1-y)/y]$ versus $1/T$. The order of the reaction was found from the slope of the curve and E^* was evaluated from the intercept. The values of E^* for nongrafted jute was found to be 6.828 kcal/mol, and for 113% MMA-grafted jute, 18.523 kcal/mol.

The energy of activation was also evaluated by the Anderson and Freeman[22] method utilizing the expression

$$\ln \frac{dw}{dt} = \ln - \left(\frac{E}{R}\right)\frac{1}{T}$$

where w is the weight of remaining sample; n, the order of the reaction; dw/dt, the reaction rate; E, the energy of activation; R, the gas constant; and T, the temperature in the Kelvin scale.

When $(\ln\,dw/dt)/(1/T)$ was plotted against $(\ln\,w)/(1/T)$, the intercept at the ordinate gave the value of E/R and the slope gave the value of n. The value of E for nongrafted jute was found to be 8.955 kcal/mol, whereas for 113% MMA-grafted jute, it was 15.124 kcal/mol.

CONCLUSION

The spectroscopic data confirm that the grafting of jute has occurred at the hydroxyl group and it also confirms the mechanism suggested for grafting. The thermal analysis data show that the grafted jute sample is more thermally stable than is the nongrafted one, considering both the maximum decomposition temperature and energy of activation. The increase in the maximum decomposition temperature as well as the energy of activation with grafting may be ascribed to additional chemical bonds introduced into the molecule during the grafting process.

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