Influence of N-Acetylglycine on the Kinetics of the Ceric Ion-Initiated Graft Copolymerization of Acrylonitrile and Methyl Methacrylate onto Jute Fibers

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SYNOPSIS

The influence of N-acetylglycine on the kinetics of graft copolymerization of acrylonitrile (AN) and methyl methacrylate (MMA) onto chemically modified jute fibers was studied in the temperature range 40–60°C. The optimum conditions for grafting have been determined by studying the effects of concentrations of monomers, Ce(IV), and N-acetylglycine on the rate of grafting. Besides the effect of time, temperature, and concentration of the acid, the amount of jute fibers and some organic solvents and inorganic salts on the rate of grafting has been investigated. On the basis of experimental findings, a kinetic scheme has been proposed. Infrared spectra of chemically modified jute and grafted jute have been investigated. More than 185% graft yield could be achieved with the present system. Grafting has improved the thermal stability of jute fibers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Considerable work on graft copolymerization of natural and synthetic fibers with vinyl monomers has been reported.[1-4] Alcohols, thiols, glycols, aldehydes, and amines coupled with ceric salt in aqueous acidic solutions are highly effective redox initiator systems. Trivedi and Mehta[5] used these initiator systems to study the kinetics of grafting of acrylonitrile onto defatted and bleached jute. Methyl methacrylate (MMA) was grafted onto jute fiber by Haque et al.[6] and Tripathy et al.[7] The initiators used by the latter was potassium permanganate and H_2SO_4. Hebeish and co-workers[8,9] reported the optimum conditions of grafting of MMA onto wool using ceric ion as the initiator. Grafting of acetylated jute using the V^{+5}-cyclohexanone redox system was earlier reported from this laboratory.[10] Glycine and substituted glycines as the reducing agents in ceric ion-initiated grafting of jute has been used by us in a simple monomer system. For the first time in this laboratory, we used a mixture of two vinyl monomers

to study the kinetics of grafting onto jute fibers using the Ce(IV)–N-acetylglycine redox system.

EXPERIMENTAL

The mesta variety of white jute procured from Konark Jute Mills Ltd., Orissa, India, was subjected to different chemical treatments as mentioned earlier[10] except for acetylation. Acrylonitrile (AN) (BDH, AnalaR) was washed with 5% NaOH and 3% orthophosphoric acid, followed by thorough washing with conductivity water. It was then dried over anhydrous calcium chloride and stored in the refrigerator. MMA was also purified by a similar treatment except for the treatment with 3% orthophosphoric acid and stored in the refrigerator for use. All other chemicals used, i.e., ceric ammonium sulfate, N-acetylglycine (NAG), H_2SO_4, etc., were of BDH, AnalaR, or E. Merck grade and so needed no purification for use.

The graft copolymerization reactions were carried out at the desired temperature in a constant temperature bath with an accuracy of ±0.1°C. The chemically modified jute fibers were soaked with a requisite quantity of monomer for about 10 min before the graft copolymerization reaction started. The

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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, NAG, H_2SO_4, and water were placed in the reaction vessel, which was thermostated for 10 min to attain the temperature of the bath. Then, the requisite amount of ceric ammonium sulfate solution was added to it and the time was noted. The reaction was carried out at three different temperatures, i.e., 40, 50, and 60°C. After the specified time interval, the reaction in each vessel was arrested by quenching the vessel with ice-cold water. Then, the grafted samples were washed well with water, given a mild soaping to re-

move the loosely adhered homopolymer, washed, and air-dried to constant weight. Finally, the fibers were extracted with acetone in a Soxhlet apparatus for 12–15 h to dissolve all the homopolymers and copolymers and until a constant weight of grafted jute fiber was obtained. The percentage graft yield was calculated as follows:

% Graft yield (GY)

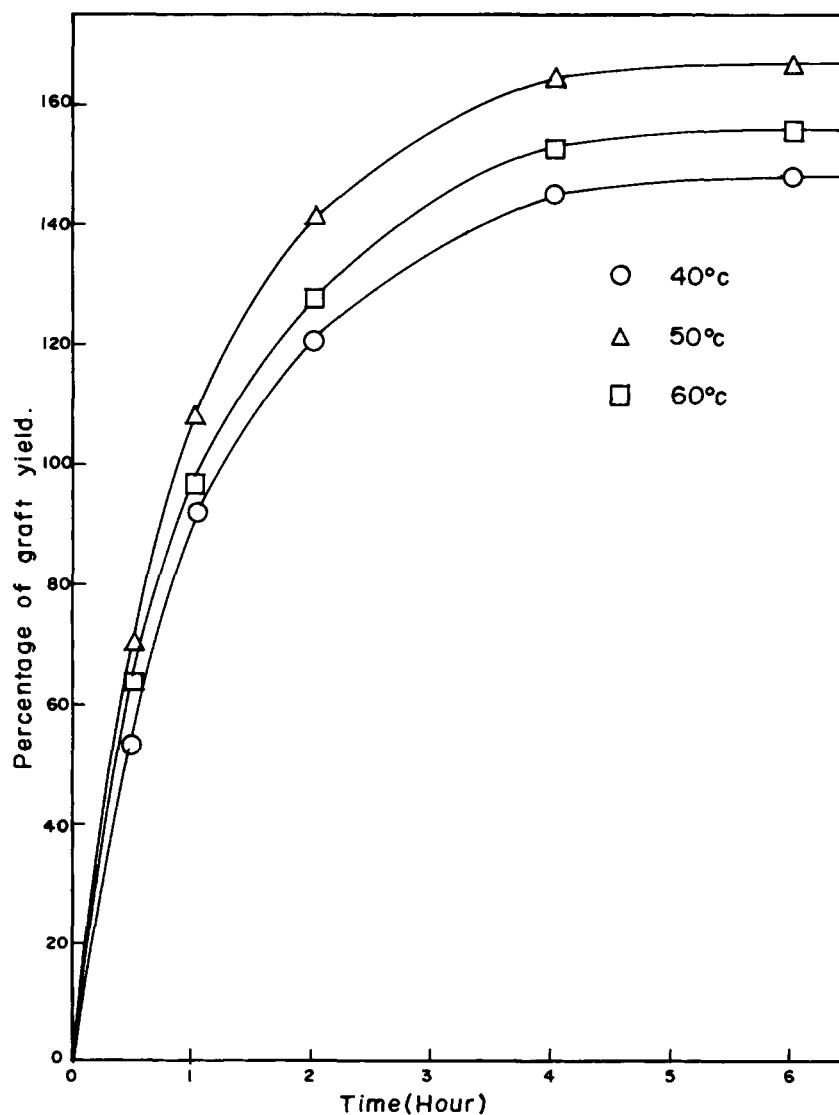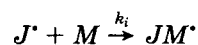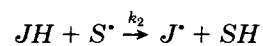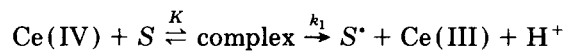$$= \frac{\text{dry wt of grafted jute-dry wt of original jute}}{\text{dry wt of original jute}} \times 100$$

Figure 1 Effect of reaction time: jute 0.1 g; [AN] 0.759 mol L^{-1}; [MMA] 0.467 mol L^{-1}; [Ce(IV)] 0.035 mol L^{-1}; [NAG] 0.01 mol L^{-1}; [H_2SO_4] 0.51 mol L^{-1}.

REACTION MECHANISM

With the present system, it has been proposed that the active Ce(IV) ions in sulfuric acid media interact with NAG (CH_3—CO—NH—CH_2COOH) to form a complex. Subsequently, the complex dissociates in a slower step, generating a free radical, which takes place by the abstraction of the hydrogen atom from the protonated complex.[3,11] This free radical initiates the grafting process. The reaction proceeds through the following steps:
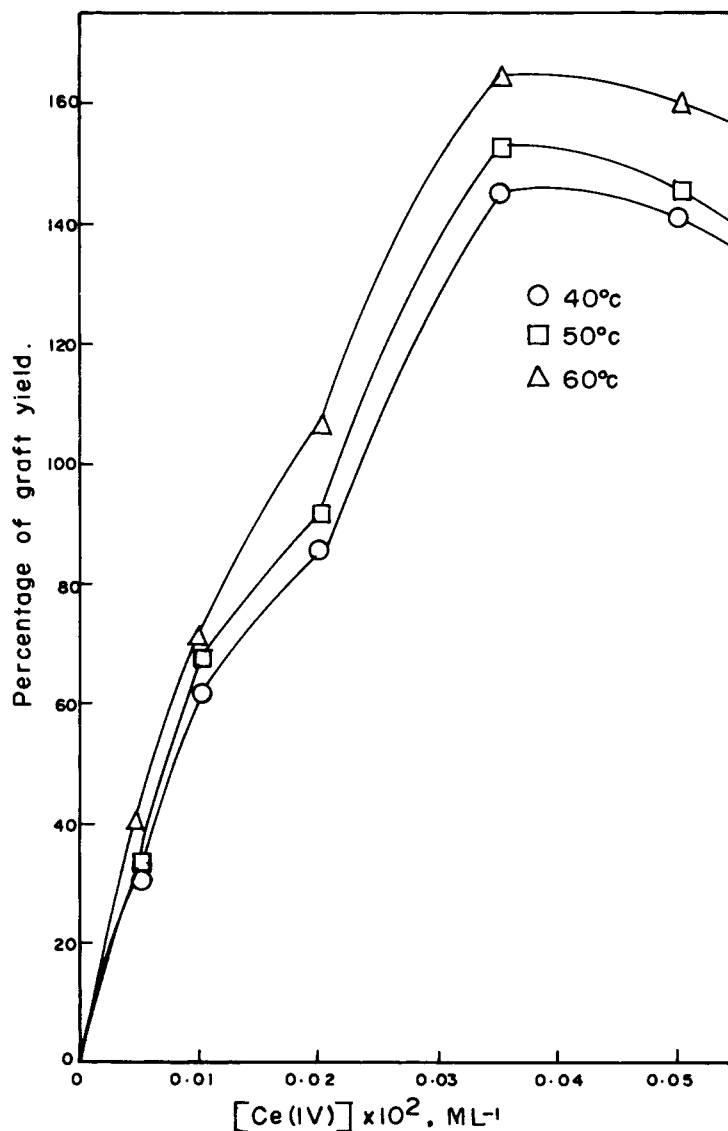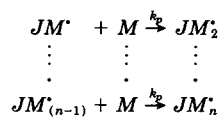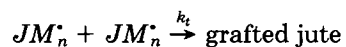
Initiation:

$$Ce(IV) + S \overset{K}{\rightleftharpoons} complex \overset{k_1}{\rightarrow} S^{\bullet} + Ce(III) + H^{+}$$

$$JH + S^{\bullet} \overset{k_2}{\rightarrow} J^{\bullet} + SH$$

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

Propagation:

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

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

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

Figure 2 Effect of metal ion concentration: jute 0.1 g; [AN] 0.759 mol L^{-1}; [MMA] 0.467 mol L^{-1}; [NAG] 0.01 mol L^{-1}; [H_2SO_4] 0.51 mol L^{-1}; time 4 h.

Termination:

$$JM_n^\bullet + JM_n^\bullet \xrightarrow{k_t} \text{grafted jute}$$

Oxidation:

$$S^\bullet + \text{Ce(IV)} \xrightarrow{k_0} \text{oxidation product}$$
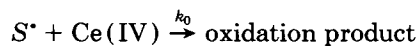
where the organic substrate, NAG, is denoted as S, and Ce(IV), JH, $J^\bullet$, M, $S^\bullet$, K, k_1, k_2, k_i, k_p, and k_t are the ceric ion, jute material, jute macroradical, monomer, organic substrate free radical, and different rate constants, respectively. Since a mixture of monomers is used, the process becomes complex and heterogeneous. Hence, rigorous kinetic analysis was not attempted.

RESULTS AND DISCUSSION

Effect of Variation of Time on Graft Yield

The percentage of graft yield vs. reaction time, studied at 40, 50, and 60°C, is depicted in Figure 1. The percentage graft yield increases steadily with time up to 4 h. This trend is contrary to the report
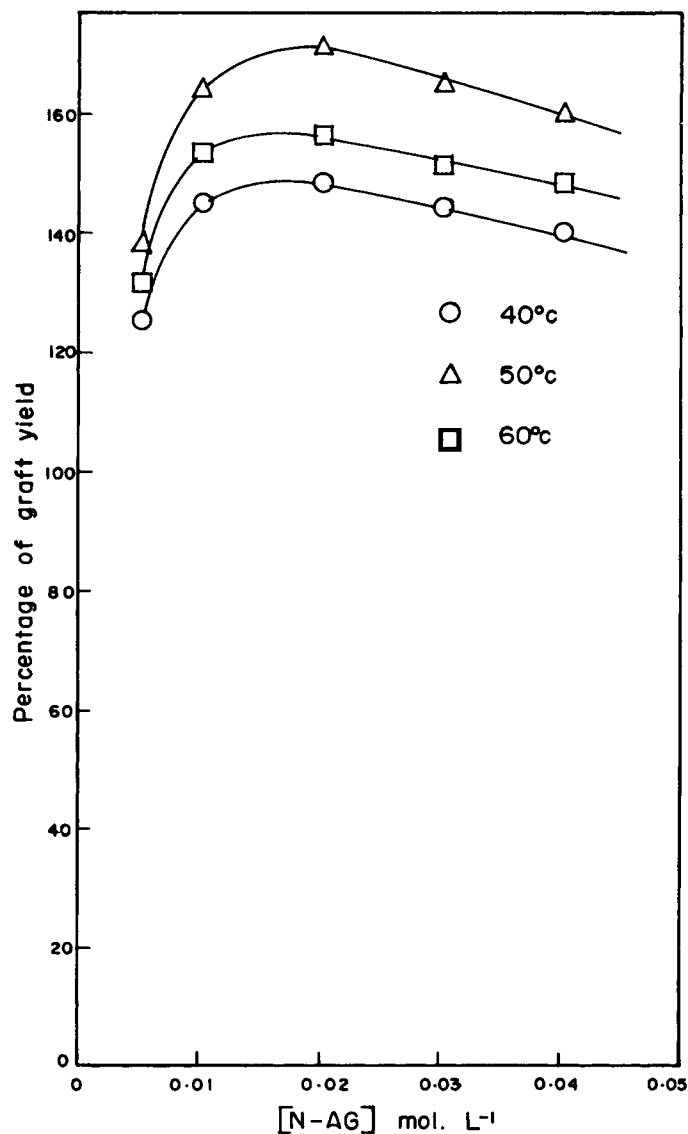

Figure 3 Effect of organic substrate concentration: jute 0.1 g; [AN] 0.759 mol L^{-1}; [MMA] 0.467 mol L^{-1}; [Ce(IV)] 0.035 mol L^{-1}; [H_2SO_4] 0.51 mol L^{-1}; time 4 h.

Table I Effect of Concentration of Acid on Graft Yield: Jute 0.1 g; [AN] 0.6072 mol L⁻¹; [MMA] 0.2335 mol L⁻¹; [NAG] 0.01 mol L⁻¹; [Ce(IV)] 0.025 mol L⁻¹; Time 4 h

No.	$[H_2SO_4]$ (mol L⁻¹)	Temp 40°C (% GY)	Temp 50°C (% GY)	Temp 60°C (% GY)
1	0.35	88.8	112.3	98.5
2	0.4	92.6	116.4	102.2
3	0.5	102.2	130.5	112.0
4	0.65	91.0	126.6	108.3
5	0.8	68.0	86.2	81.5

of Mohanty et al.,[10] but is in agreement with the reports of Haque et al.[6]

Effect of Metal Ion Concentration

We varied the metal ion concentration from 0.005 to 0.05 mL⁻¹. The graft yield increases considerably up to the concentration of 0.035 mL⁻¹ and then it falls in all the three temperatures studied. However, the fall is not steep. The significant increase in grafting percentage with increase in Ce(IV) ion concentration (Fig. 2) is attributed to the greater number of grafting sites created by the Ce(IV) ion. This 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 linear termination is probably prevelent over the other, leading to shorter grafting chains. Mutual termination is shown in the mechanism. This observation is in close agreement with the report of Santappa et al.[12] but contrary to the reports of Patnaik et al.[13] and Nayak et al.,[14] who showed that the graft yield consistently decreases with increase in Ce(IV) concentration. They proposed linear termination due to the metal ion.

Effect of N-Acetylglycine (NAG) Concentration

The effect of the organic substrate has been studied by varying the concentration of NAG over a range of 0.005 to 0.04 mL⁻¹. The percentage graft yield increases with NAG concentration up to 0.02 mL⁻¹ and then decreases (Fig. 3). This decrease in graft yield may be attributed to the formation of an increased amount of homopolymers[14] and to the rapid

rate of termination and/or formation of a radical scavenger[10,13] at higher NAG concentration.

Effect of Monomer Concentration

A mixture of two monomers, AN and MMA, was taken for the present study. The concentration of one of the monomers is varied, keeping that of the other constant and vice versa. Thus, the concentration of both monomers are optimized. When the concentration of MMA is varied, keeping that of AN fixed at 0.759 mL⁻¹, the maximum graft yield is obtained with the concentration of MMA at 0.1868 mL⁻¹ in all the three temperatures studied. But when the concentration of AN is varied from 0.1518 to 1.2144 mL⁻¹, keeping that of MMA fixed at 0.2335 mL⁻¹, the graft yield is maximum with the concentration at 0.6072 mL⁻¹. Hence, the optimum monomer concentrations are 0.2335 mL⁻¹ for MMA and 0.6072 mL⁻¹ for AN. In all the cases, the graft yield decreases after the optimum concentration at all three temperatures. Figure 4(A) and (B) exhibits the maximum graft yield as 185%. In the increasing region of the plot, the percentage yield is proportional to the first power of monomer concentration. The decreasing trend in graft yield after optimum concentration may be due to the competition between homopolymerization and grafting, where the former prevails over the latter at higher monomer concentration. This is in accordance with previous reports.[13,14]

Effect of Amount of Jute Fiber

The effect of variation of the jute fiber amount also studied at three different temperatures is depicted

Table II Effect of Organic Solvents on Graft Yield: Jute 0.1 g; [MMA] 0.2335 mol L⁻¹; [AN] 0.6072 mol L⁻¹; [NAG] 0.01 mol L⁻¹; [Ce(IV)] 0.035 mol L⁻¹; [H₂SO₄] 0.51 mol L⁻¹; Time 4 h; Temp 50°C

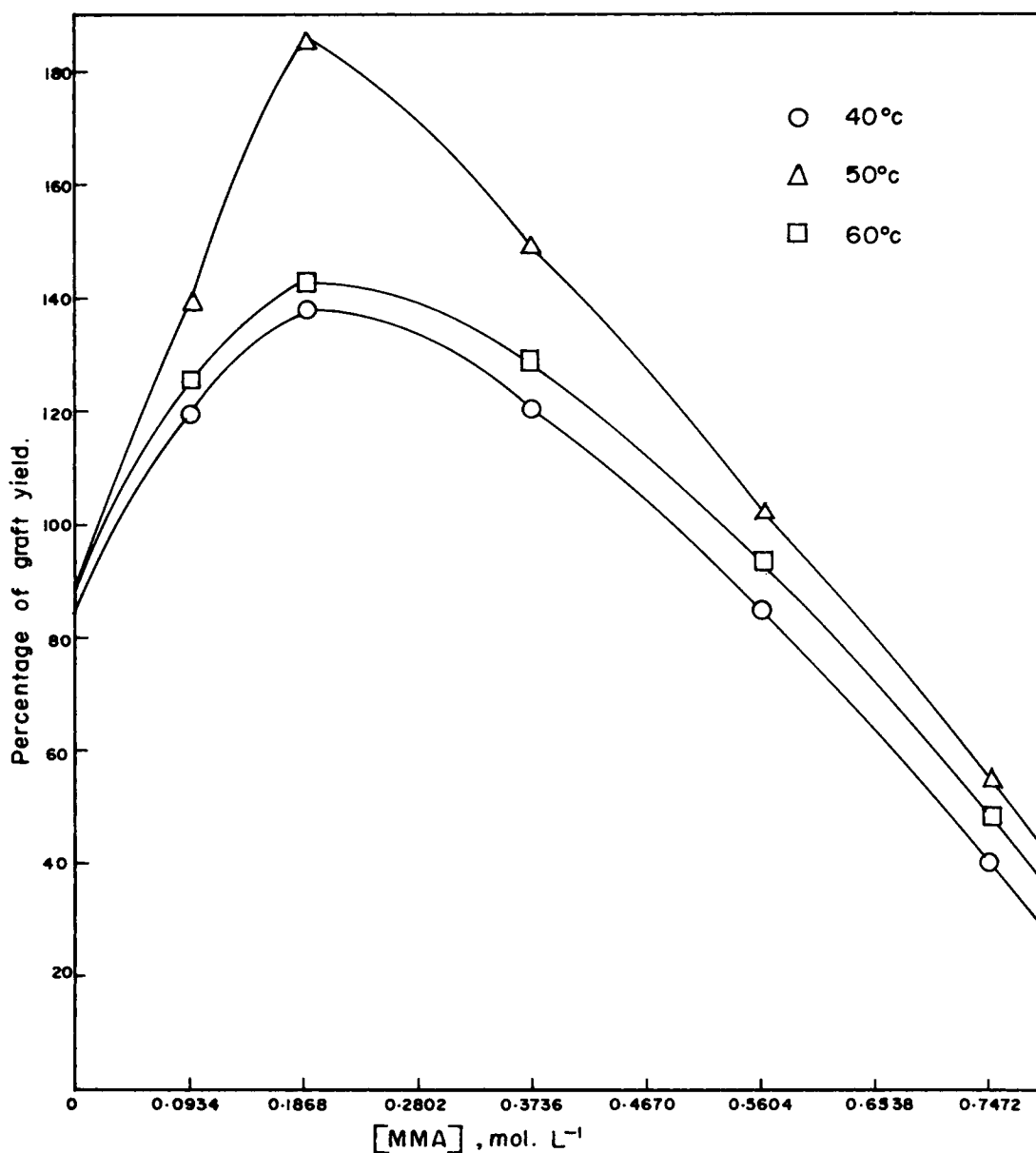| No.	Solvent (5% v/v)	% GY	[Salt] (0.01 mol L⁻¹)	% GY
1	Control	181.6	Control	181.6
2	DMF	121.0	$CuSO_4 \cdot 5H_2O$	106.5
3	Benzene	107.6	$MnCO_3$	104.0
4	Dioxane	134.3	NaCl	120.5
5	Acetone	132.6	KCl	118.4
6	Methanol	172.4	$MnSO_4 \cdot 4H_2O$	101.2

Figure 4 (A) Effect of methyl methacrylate (MMA) concentration: jute 0.1 g; [AN] 0.759 mol L^{-1}; [NAG] 0.01 mol L^{-1}; [Ce(IV)] 0.035 mol L^{-1}; [H_2SO_4] 0.51 mol L^{-1}; time 4 h. (B) Effect of acrylonitrile (AN) concentration: jute 0.1 g; [MMA] 0.2335 mol L^{-1}; [NAG] 0.01 mol L^{-1}; [Ce(IV)] 0.035 mol L^{-1}; [H_2SO_4] 0.51 mol L^{-1}; time 4 h.

in Figure 5. The graft yield is found to decrease consistently with the increase of jute fiber amount. The highest yield is obtained when the same is 0.025 g. Probably, the rate of termination becomes faster than that of initiation with the increase in jute fiber amount due to abstraction of hydrogen.[15] This report is different from that previously from this laboratory[16] and is in agreement with those of Nayak et al.[14] and Santappa et al.[12]

Effect of Sulfuric Acid

The present grafting reaction is carried out in different concentrations of sulfuric acid in aqueous media. With the variation of acid concentration from 0.35 to 0.8 mL^{-1}, the % graft yield is found to increase slowly initially up to 0.5 mL^{-1} and then it decreases (Table I). The higher concentration of acid is not only unfavorable for grafting, probably
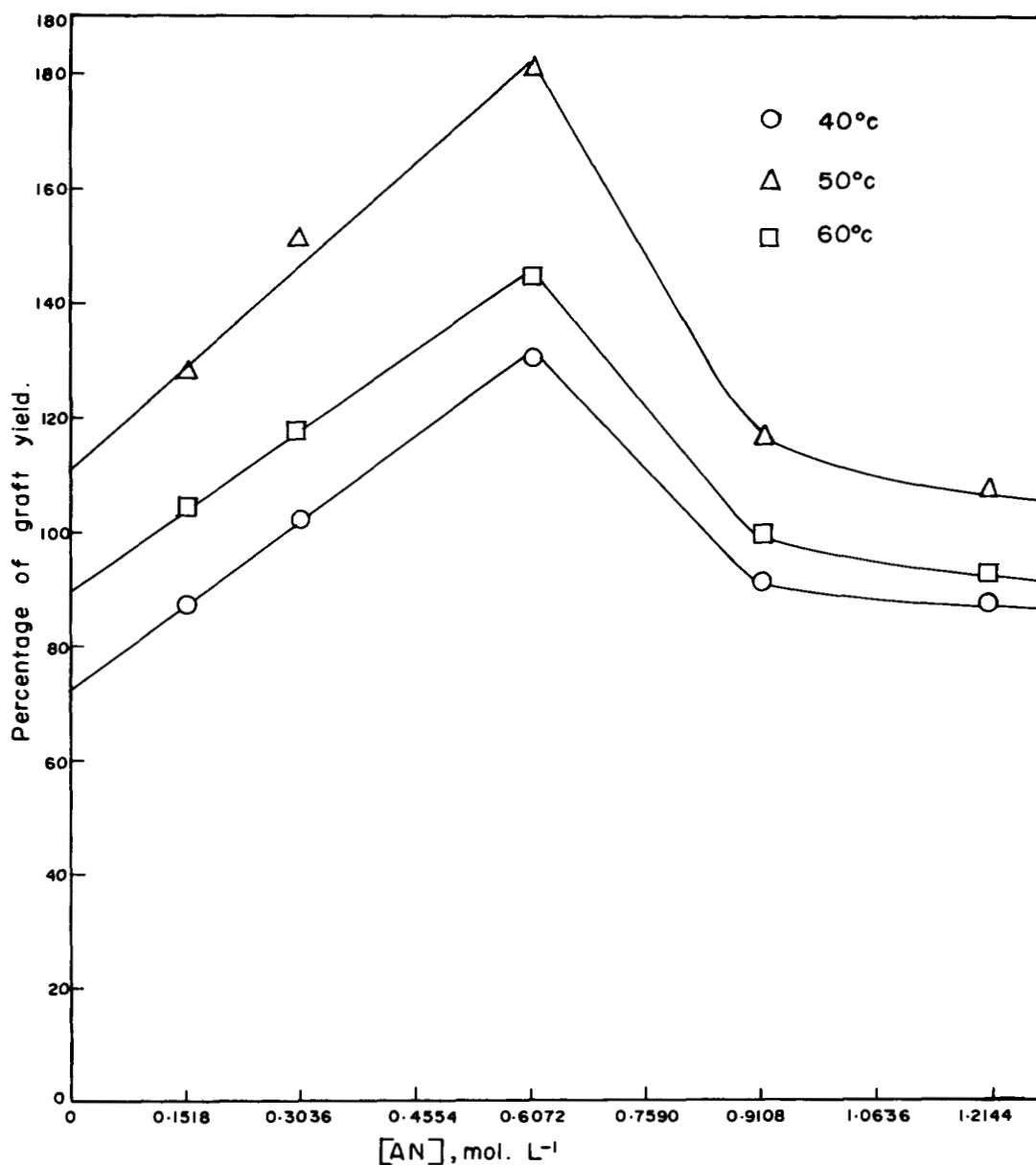
Figure 4   (*Continued from the previous page*)

due to depolymerization but it also destroys some of the useful properties of the fibers.

Effect of Temperature

The effect of temperature on percentage grafting is shown in Figures 1–4(B). It is observed that the % grafting increases with rise of temperature up to 50°C, and at 60°C, the yield decreases. The increasing phenomenon can be attributed to the swellability of jute and the enhancement of rate of diffusion of monomer with increase of temperature.[14]

Effect of Reaction Medium

The grafting reaction is largely influenced by the reaction medium. The effect of H_2SO_4 on the grafting reaction was reported earlier.[16] The yield is depressed appreciably when some solvents are added in equal proportions (5% v/v) and follows the order
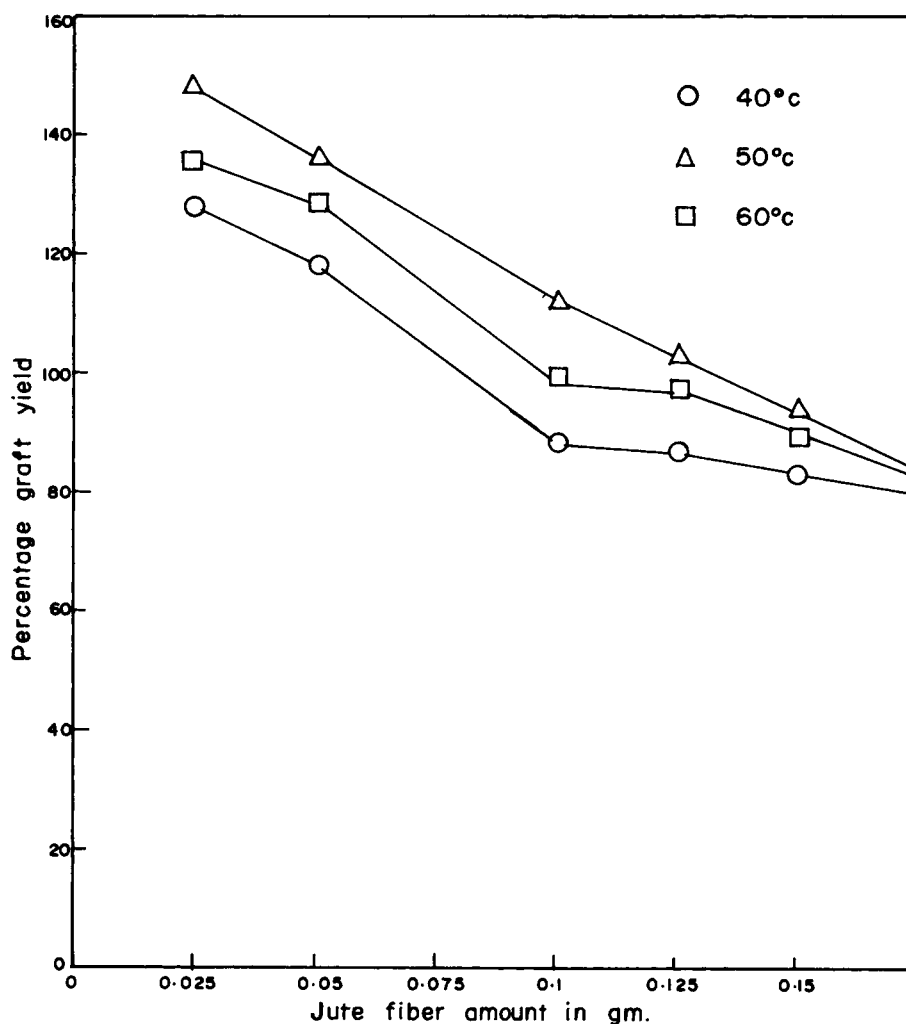
Figure 5 Effect of amount of jute fiber: [MMA] 0.2335 mol L^{-1}; [AN] 0.6072 mol L^{-1}; [NAG] 0.01 mol L^{-1}; [Ce(IV)] 0.025 mol L^{-1}; [H_2SO_4] 0.35 mol L^{-1}; time 4 h.

control > methanol > dioxane > acetone > DMF > benzene. Also, some inorganic salts, when added in equivalent molar concentration, affect the reaction rate in the order control > NaCl > KCl > $CuSO_4 \cdot 5H_2O$ > $MnCO_3$ > $MnSO_4$. Table II compares the above results.

CHARACTERIZATION

IR Spectra

IR spectra of (a) chemically modified jute and (b) AN/MMA grafted jute recorded on a Perkin-Elmer

337 IR and Shimadzu IR 408 spectrophotometers in the form of KBr pellets and nujol paste, respectively, are shown in Figure 6(A) and (B). Both the spectra of grafted and chemically modified jute show a characteristic broad absorption band around 3450–3200 cm^{-1}. However, the spectrum of grafted jute shows additional peaks at 2260 cm^{-1}, thereby indicating the occurrence of AN grafting, and another absorption band around 1720 cm^{-1}, indicating an ester group and, hence, MMA grafting. The intensity of the —OH peak is expected to be reduced as a result of grafting since it is the probable site for grafting. This is not observed possibly due to the large concentration of the —OH groups of jute. The small difference in its concentration as a result of grafting
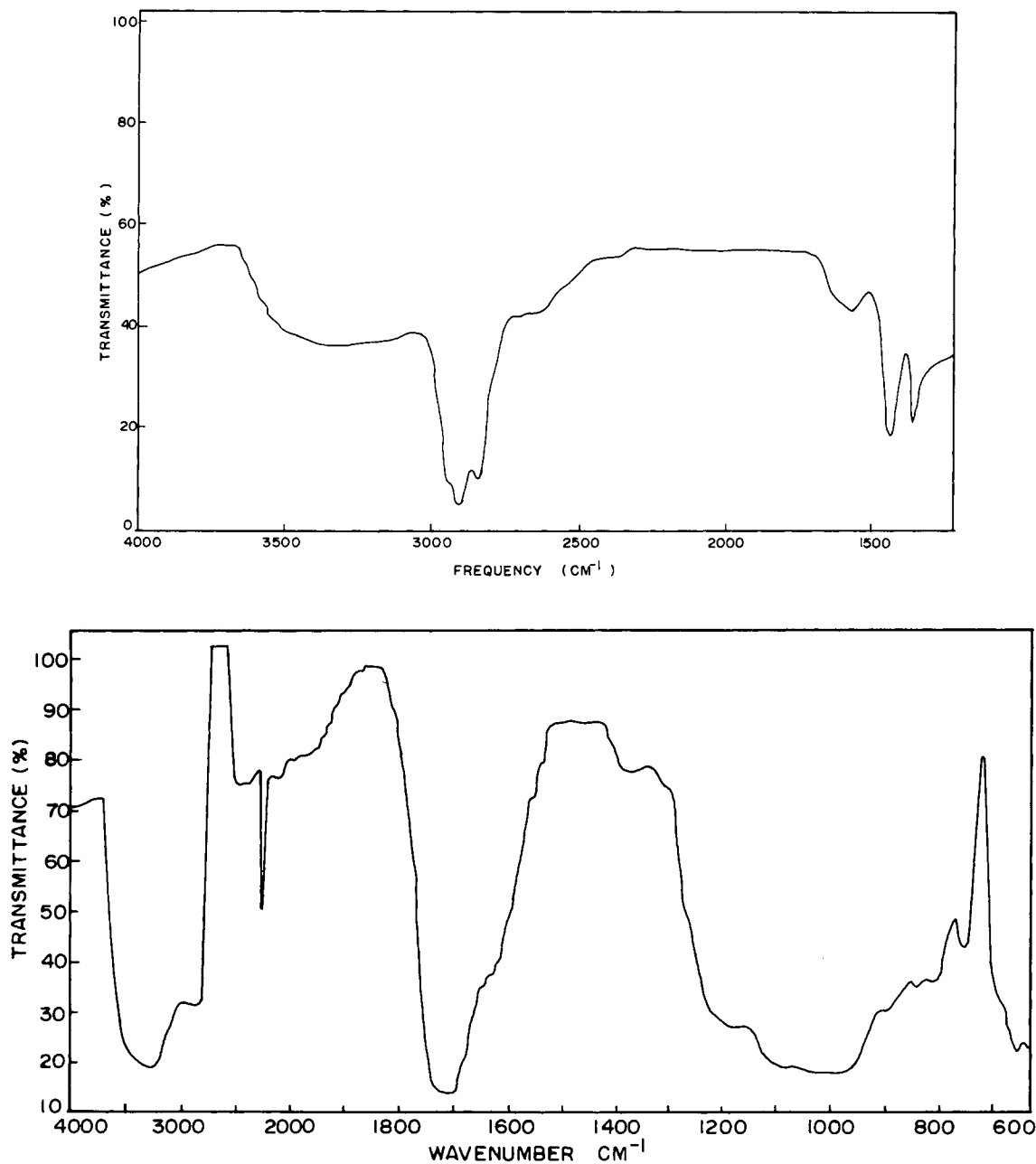
Figure 6   (A) IR spectra of chemically modified jute fiber. (B) IR spectra of chemically modified jute fiber with AN/MMA mixture.

is not detected. Similar reports have been given by other workers.[5,10,12,14]

Thermogravimetric Analysis

The TGA and DTA curves of chemically modified jute and AN/MMA-grafted jute recorded on Shimadzu DT 48 thermal analyzer are shown in Figure 7(A) and (B). In the case of ungrafted jute, the maximum decomposition temperature was 302°C. But with grafted jute of graft yields of 162% and 184%, the maximum decomposition temperatures are at 332 and 340°C, respectively. Therefore, the increase of graft yield from 162 to 184% enhances the maximum decomposition temperature by 8°C.
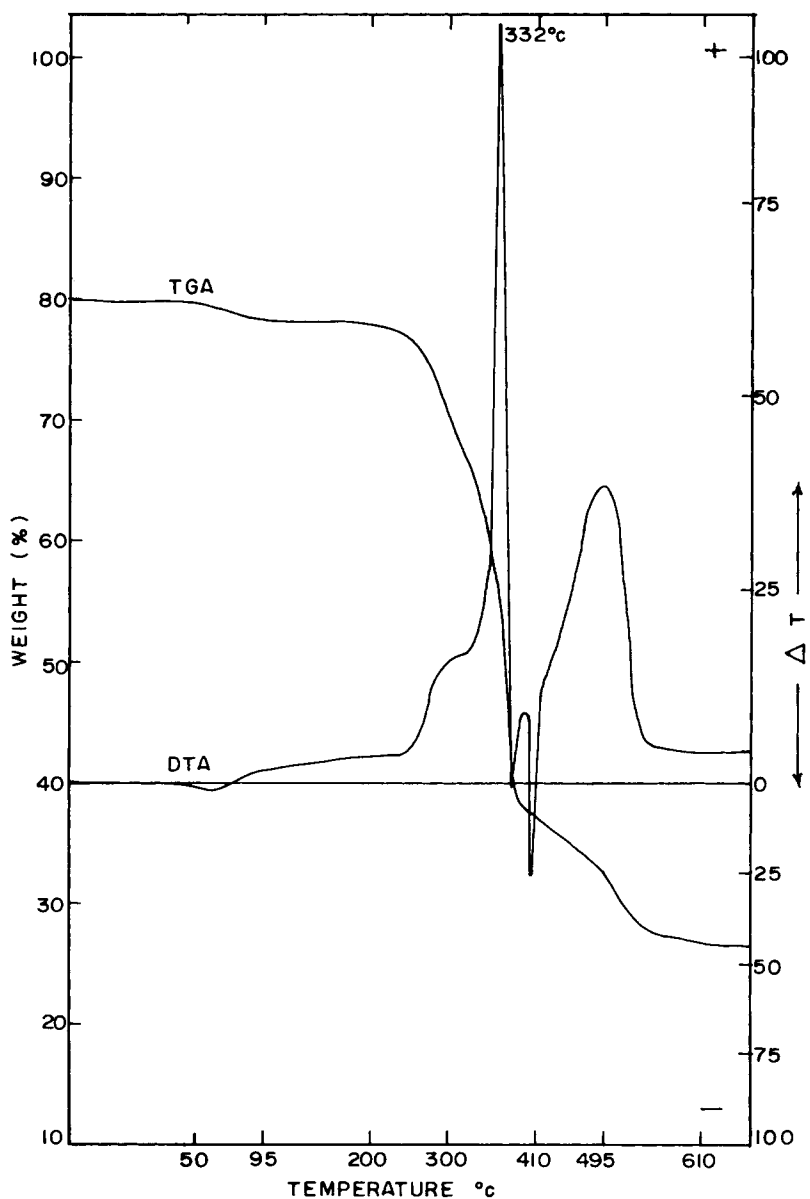
Figure 7   TGA and DTA curves of AN/MMA grafted jute fibers. (A) GY = 162%; (B) GY = 184%.

Hence, grafting makes the jute thermally more stable and this effect becomes more predominant as the percent grafting increases. Similar observations have been reported earlier.[7,10,14]

CONCLUDING REMARKS

From the results, it should be concluded that Ce(IV)-NAG is an effective redox system. It is not possible to carry out grafting onto jute fibers using most redox couples comprising Ce(IV) and any organic substrate, because of the competition between homopolymerization and grafting. It is only possible in the case of an effective redox pair to modify fiber properties by grafting. Though AN and MMA are successfully grafted individually onto jute fibers using various redox systems from this laboratory, the mixture has been found to be relatively more effective. From our results, the mechanism of grafting is established. The optimum conditions for an effective grafting reaction has been worked out as follows:
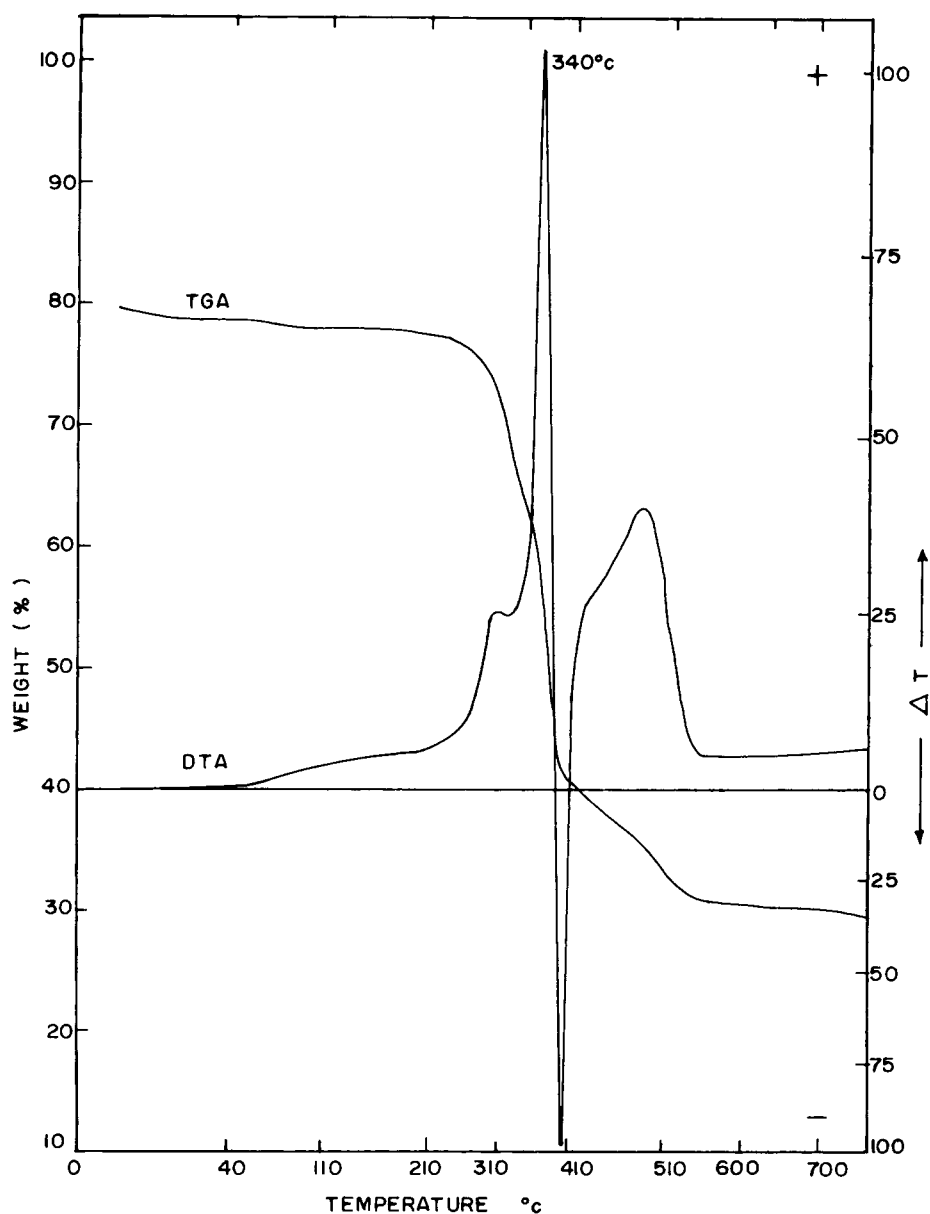
Figure 7 (*Continued from the previous page*)

Jute 0.025 g;   [AN] 0.6072 mL^{-1};

[MMA] 0.2335 mL^{-1};   [Ce(IV)] 0.035 mL^{-1};

[NAG] 0.02 mL^{-1};   [H$_2$SO$_4$] 0.5 mL^{-1}

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