

# Chemical Modification of Jute Fibers. II: A Study on the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ -Initiated Graft Copolymerization of Methyl Methacrylate, Acrylonitrile, and Acrylamide onto Jute Fibers

SIBENDU MOHARANA and S. S. TRIPATHY\*

Department of Chemistry, Ravenshaw College, Cuttack-753003, Orissa, India

## SYNOPSIS

The study of graft copolymerization of methyl methacrylate, acrylonitrile, and acrylamide onto both defatted and bleached jute fibers using the ferrous ammonium sulfate/ $\text{H}_2\text{O}_2$  redox initiator system has been made. To determine the optimum conditions of grafting, the effects of concentrations of ferrous ammonium sulfate, monomer,  $\text{H}_2\text{O}_2$ ; time and temperature on percentage of graft yield have been studied. Acrylamide was found to graft onto the fiber only at a fixed ferrous ammonium ion concentration ( $5 \times 10^{-4} M$ ). Kinetic studies showed that the rates of grafting follow the second-order mechanism. The activation energies of the reactions were found to be 3.351 and 2.53 kcal/mol in the methyl methacrylate and acrylonitrile systems, respectively. The grafted fibers have been characterized by thermogravimetric analysis, IR spectroscopy, and XRD studies.

## INTRODUCTION

Nowadays considerable attention has been paid to the modification of synthetic and natural textile fibers by graft copolymerization. Although a lot of work on grafting of vinyl monomers onto wool, cotton, silk, and other synthetic fibers have been reported, work on jute fibers is inadequate. The kinetics of grafting of acrylonitrile onto defatted and bleached jute fibers using  $\text{Ce(IV)}$  initiator was first studied by Trivedi and Mehta<sup>1</sup> and a similar study on grafting of MMA onto jute using the same initiator was done by Huque et al.<sup>2</sup> In our earlier communication,<sup>3</sup> we reported about the kinetics of grafting of MMA onto jute fibers using permanganate as the initiator. Ray<sup>4</sup> determined the degree of crystallinity and orientation of grafted jute fibers from X-ray diffraction studies, and the effect of grafting on the tensile properties of the fiber was studied by Mukhopadhyay et al.<sup>5</sup> The present article

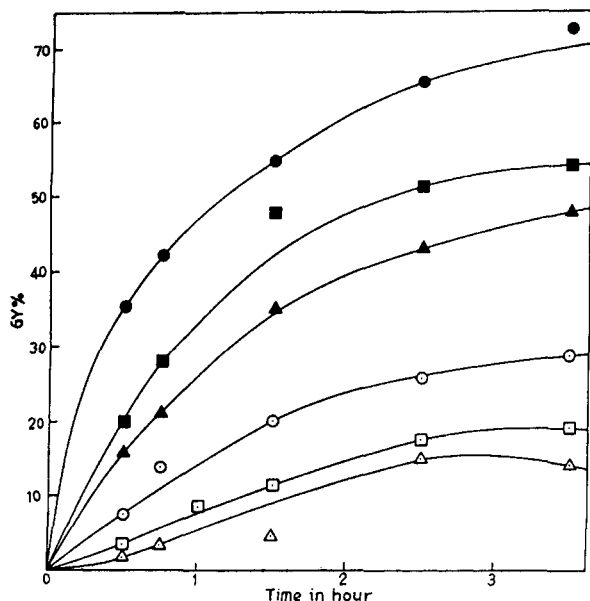
deals with the studies of the optimum conditions and kinetics of grafting along with characterization of the grafted jute fiber using methyl methacrylate, acrylonitrile, and acrylamide as monomers and  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  as the initiator.

## EXPERIMENTAL

The jute sample under investigation was the corchorus Olitorius (tossa) variety procured from the Jute Corp. of India. The fibers were lightly combed for a long time to remove the impurities and cut into small bundles of 6–8 in. in length. The fibers were then defatted with an ethanol–benzene (1 : 2 v/v) mixture in Soxhelt apparatus for 12 h. After refluxing, the fibers were washed with alcohol and air-dried. These fibers were then bleached with 0.7% sodium chlorite solution.<sup>6</sup> Methyl methacrylate (MMA), acrylonitrile (AN), and acrylamide (AA) were purified by the usual procedure.

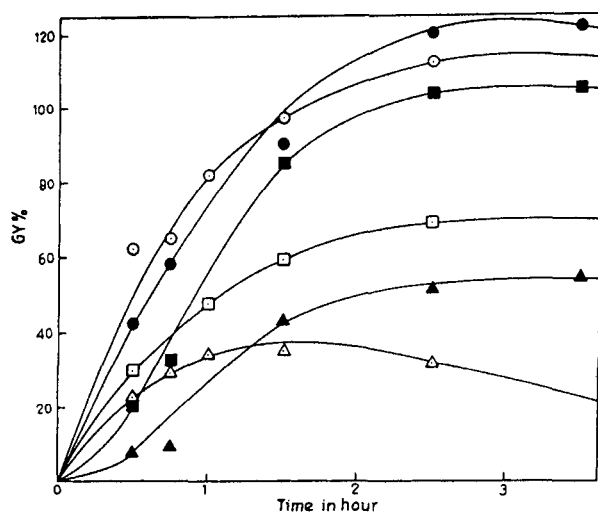
A sample to liquor ratio of 1 : 200 was used. Before initiating graft copolymerization, the jute fibers were soaked with ferrous ammonium sulfate solution for the desired time interval. Then the appropriate quantity of  $\text{H}_2\text{O}_2$  and conductivity water were taken

\* To whom correspondence should be addressed.

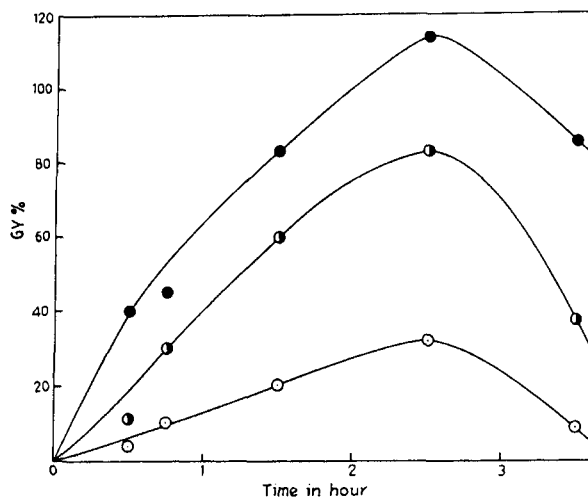


**Figure 1** Effect of reaction time and temperature on % GY: ( $\Delta$ ) 30°C; ( $\square$ ) 40°C, ( $\odot$ ) 50°C for defatted jute; ( $\blacktriangle$ ) 30°C, ( $\blacksquare$ ) 40°C, ( $\bullet$ ) 50°C for bleached jute;  $[\text{FeAmSO}_4] = 2.5 \times 10^{-4} \text{ M}$ ;  $[\text{H}_2\text{O}_2] = 2.5 \times 10^{-3} \text{ M}$ , jute fiber = 0.1 g,  $[\text{AN}] = 0.3755 \text{ M}$ , liquor ratio = 1 : 200.

in the reaction vessels. Purified nitrogen gas was then passed through the vessel for 5 min, and the vessels were sealed by rubber tubes. Required amounts of purified monomer were added to the flask for initiating the polymerization. The vessels were

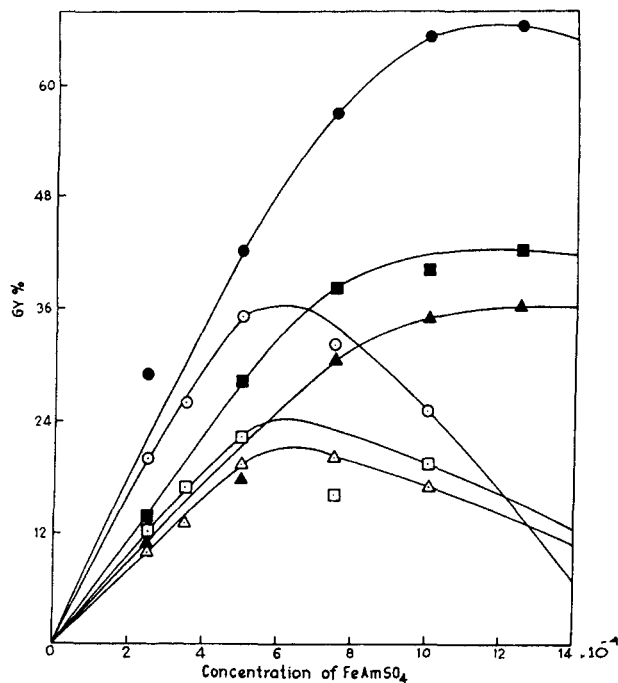


**Figure 2** Effect of reaction time and temperature on % GY: ( $\Delta$ ) 30°C, ( $\square$ ) 40°C, ( $\odot$ ) 50°C for defatted jute; ( $\blacktriangle$ ) 30°C, ( $\blacksquare$ ) 40°C, ( $\bullet$ ) 50°C for bleached jute;  $[\text{FeAmSO}_4] = 2.5 \times 10^{-4} \text{ M}$ ,  $[\text{H}_2\text{O}_2] = 2.5 \times 10^{-3} \text{ M}$ , jute fiber = 0.1 gm,  $[\text{MMA}] = 0.2372 \text{ M}$ , liquor ratio = 1 : 200.

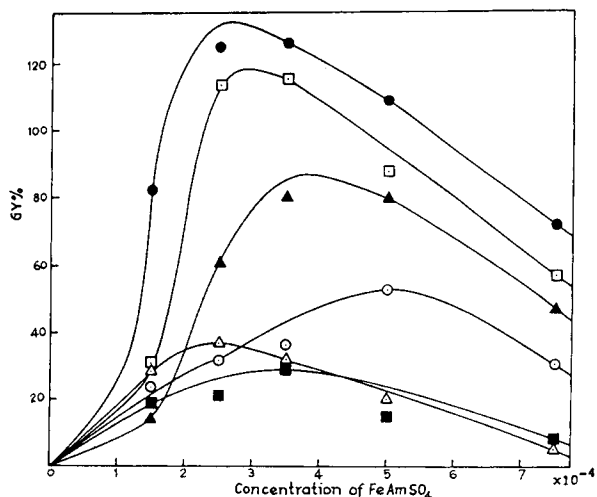


**Figure 3** Effect of reaction time and temperature on % GY: ( $\circ$ ) 30°C, ( $\odot$ ) 40°C, ( $\bullet$ ) 50°C;  $[\text{FeAmSO}_4] = 0.5 \times 10^{-3} \text{ M}$ ,  $[\text{H}_2\text{O}_2] = 1.25 \times 10^{-3} \text{ M}$ , jute fiber = 0.1 g, AA = 0.5 g, liquor ratio = 1 : 200.

then thermostatted at the desired temperature. After the specified time interval, the reaction was arrested by quenching the vessel in ice-cold water. The homopolymer along with the grafted jute fibers were filtered off, washed with water, and dried to constant



**Figure 4** Effect of  $\text{FeAmSO}_4$  on % GY: ( $\Delta$ ) 30°C, ( $\square$ ) 40°C, ( $\odot$ ) 50°C for defatted jute; ( $\blacktriangle$ ) 30°C, ( $\blacksquare$ ) 40°C, ( $\bullet$ ) 50°C for bleached jute; AN = 1 mL (0.797 g),  $[\text{H}_2\text{O}_2] = 1.0 \times 10^{-3} \text{ M}$ , liquor ratio = 1 : 200, jute fiber = 0.1 g.

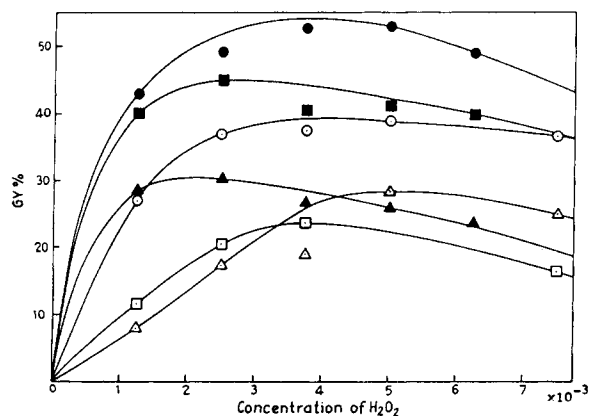


**Figure 5** Effect of  $\text{FeAmSO}_4$  on % GY: ( $\Delta$ ) 30°C, ( $\blacksquare$ ) 40°C, ( $\odot$ ) 50°C for defatted jute; ( $\blacktriangle$ ) 30°C, ( $\square$ ) 40°C, ( $\bullet$ ) 50°C for bleached jute;  $[\text{MMA}] = 0.2372 \text{ M}$ ,  $[\text{H}_2\text{O}_2] = 2.5 \times 10^{-3} \text{ M}$ , liquor ratio = 1 : 200, jute fiber = 0.1 g.

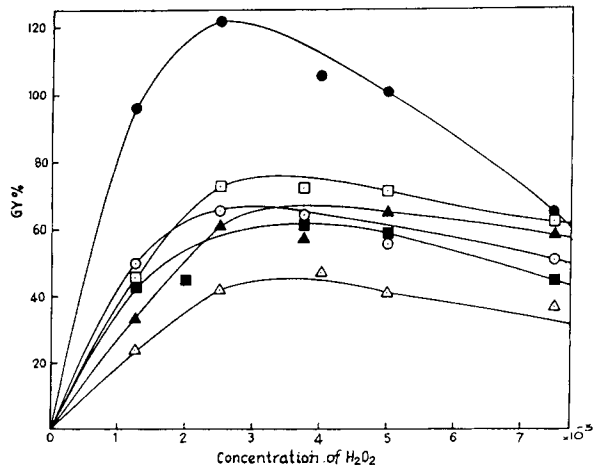
weight at 60–70°C. The homopolymers of MMA and AA were then extracted with acetone and water in Soxhelt apparatus, respectively. In the case of AN-grafted fibers, the solvent extraction was not done as there is no weight loss due to extraction with DMF.

The percentage of graft yield was estimated from the following equation.

$$\% \text{ of graft yield (GY)} = \frac{\text{dry wt grafted fiber} - \text{dry wt original fiber}}{\text{dry wt original fiber}} \times 100$$



**Figure 6** Effect of  $\text{H}_2\text{O}_2$  on % GY: ( $\Delta$ ) 30°C, ( $\square$ ) 40°C, ( $\odot$ ) 50°C for defatted jute; ( $\blacktriangle$ ) 30°C, ( $\blacksquare$ ) 40°C, ( $\bullet$ ) 50°C for bleached jute;  $[\text{AN}] = 1 \text{ mL (0.797 g)}$ ,  $[\text{FeAmSO}_4] = 2.5 \times 10^{-4} \text{ M}$ , liquor ratio = 1 : 200, jute fiber = 0.1 g.



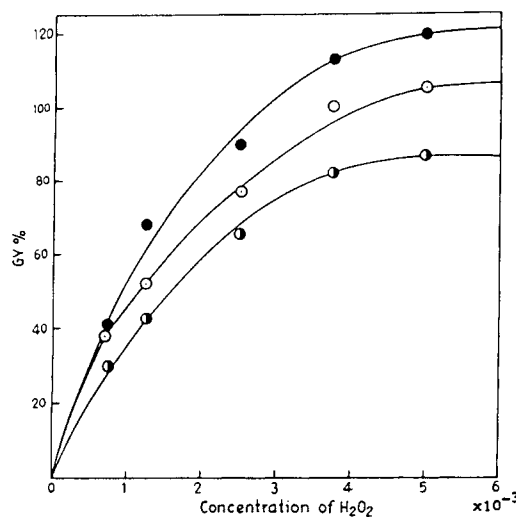
**Figure 7** Effect of  $\text{H}_2\text{O}_2$  on % GY: ( $\Delta$ ) 30°C, ( $\blacksquare$ ) 40°C, ( $\odot$ ) 50°C for defatted jute; ( $\blacktriangle$ ) 30°C, ( $\square$ ) 40°C, ( $\bullet$ ) 50°C for bleached jute;  $[\text{MMA}] = 0.2372 \text{ M}$ ,  $[\text{FeAmSO}_4] = 2.5 \times 10^{-4} \text{ M}$ , liquor ratio = 1 : 200, jute fiber = 0.1 g.

**RESULTS AND DISCUSSION**

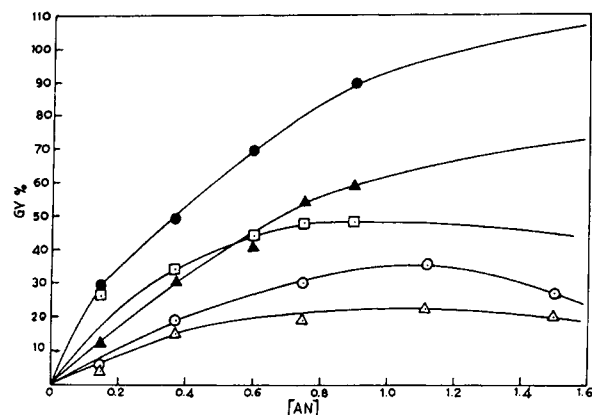
The optimum conditions for graft copolymerization of vinyl monomers onto jute fibers were investigated by studying the effects of time, initiator, monomer, and temperature, etc. on % graft yield (% GY).

**Effect of Time and Temperature**

The graft copolymerization onto jute fibers was studied at three different temperatures, i.e., 30, 40,



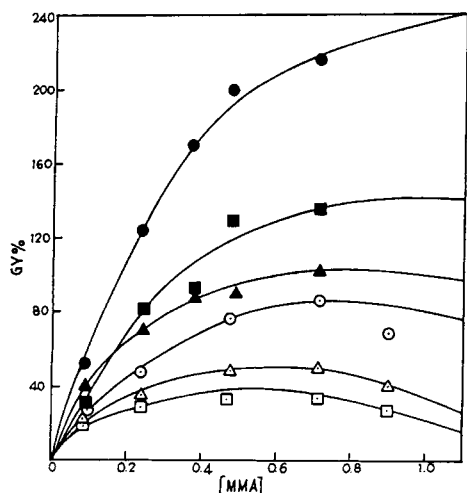
**Figure 8** Effect of  $\text{H}_2\text{O}_2$  on % GY: ( $\bullet$ ) 30°C, ( $\odot$ ) 40°C, ( $\bullet$ ) 50°C;  $[\text{AA}] = 0.5 \text{ g}$ ,  $[\text{FeAmSO}_4] = 0.5 \times 10^{-3} \text{ M}$ , liquor ratio = 1 : 200, jute fiber = 0.1 g.



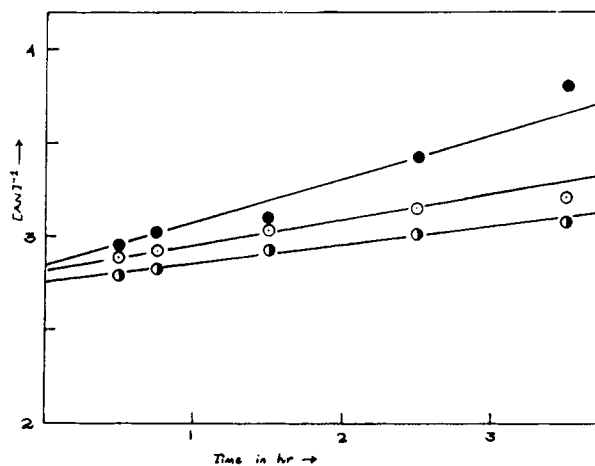
**Figure 9** Effect of AN on % GY: ( $\Delta$ ) 30°C, ( $\circ$ ) 50°C for defatted jute; ( $\blacktriangle$ ) 30°C, ( $\square$ ) 40°C, ( $\bullet$ ) 50°C for bleached jute;  $[\text{FeAmSO}_4] = 12.5 \times 10^{-4} M$ ,  $[\text{H}_2\text{O}_2] = 1 \times 10^{-3} M$ , liquor ratio = 1 : 200, jute fiber = 0.1 g.

and 50°C, keeping the concentrations of all other reagents constant. The percentage of graft yield in both bleached and defatted jute increases with rise in temperature as illustrated in Figures 1, 2, and 3. A low value of % GY at 30°C may be attributed to the rigidity of the structure of the cellulose and lignin in jute fiber.

The % GY is generally higher in the case of bleached jute than in the case of defatted jute alone. This may be due to the fact that upon delignification (accompanied by bleaching) the hydroxy methyl group in the cellulose skeleton gets oxidized and becomes more susceptible to form radical.

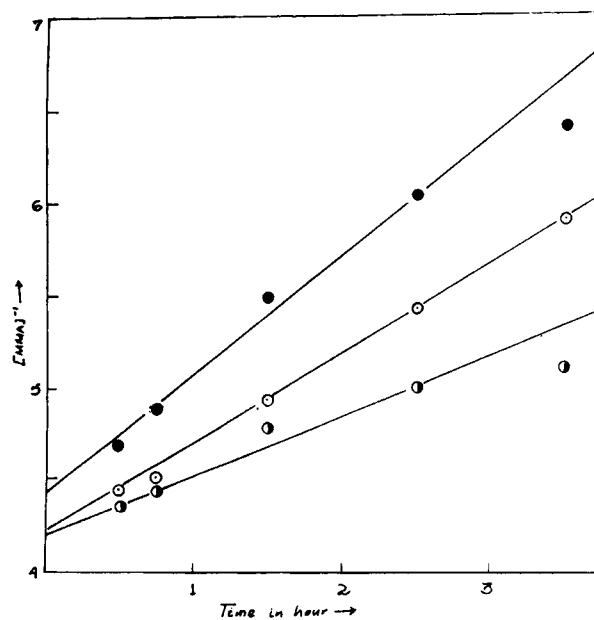


**Figure 10** Effect of MMA on % GY: ( $\Delta$ ) 30°C, ( $\square$ ) 40°C, ( $\circ$ ) 50°C for defatted jute; ( $\blacktriangle$ ) 30°C, ( $\blacksquare$ ) 40°C, ( $\bullet$ ) 50°C for bleached jute;  $[\text{FeAmSO}_4] = 2.5 \times 10^{-4} M$ ,  $[\text{H}_2\text{O}_2] = 2.5 \times 10^{-3} M$ , liquor ratio = 1 : 200, jute fiber = 0.1 g.

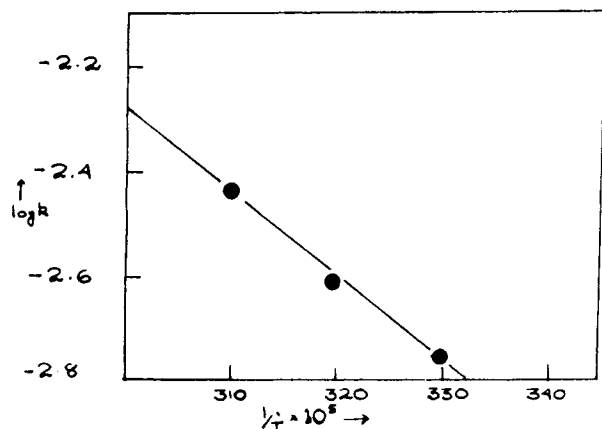


**Figure 11** Reciprocal of concentration of AN vs. time, bleached jute.  $[\text{FeAmSO}_4] = 7.5 \times 10^{-4} M$ ,  $[\text{H}_2\text{O}_2] = 2.5 \times 10^{-3} M$ ; ( $\circ$ ) 30°C, ( $\square$ ) 40°C, ( $\bullet$ ) 50°C.

It is also found that the % GY in both bleached and defatted jute increases at the beginning and subsequently assumes steady values. In case of MMA grafting onto bleached jute fibers, the % GY (125%) is the maximum at 50°C in 2.5 h; in the case of grafting of AN and AA onto bleached jute fibers the corresponding values of % GY and time at 50°C are 72.5%, 3 h and 114%, 2.5 h, respectively. The unusual trend of decrease in % GY in AA grafting after 2.5 h might possibly be due to the depolymerization of the growing graft chains at 50°C as



**Figure 12** Reciprocal of concentration of MMA vs. time, bleached jute.  $[\text{FeAmSO}_4] = 2.5 \times 10^{-4} M$ ,  $[\text{H}_2\text{O}_2] = 2.5 \times 10^{-3} M$ ; ( $\circ$ ) 30°C, ( $\square$ ) 40°C, ( $\bullet$ ) 50°C.



**Figure 13** Plot of  $\log k$  vs.  $1/T$ ; bleached jute;  $[AN] = 0.3755 M$ ,  $[FeAmSO_4] = 7.5 \times 10^{-3} M$ ,  $[H_2O_2] = 2.5 \times 10^{-3} M$ .

a result of a longer reaction period. Similar trends have also been found in defatted fibers, but % GY is relatively lower than the bleached fibers. Grafting of AA onto defatted jute fibers could not be possible by any means.

#### Effect of Ferrous Ammonium Sulfate ( $FeAmSO_4$ )

The effect of the concentration of ferrous ammonium sulfate on % GY is shown in Figures 4 and 5. The % GY increases with increase in the concentration of  $FeAmSO_4$  up to  $0.25 \times 10^{-2} M$  in the case of grafting of MMA onto defatted and bleached jute, and, beyond this, % GY decreases. In the case of grafting of AN onto defatted jute, % GY increases up to  $0.6 \times 10^{-2} M$  and in bleached jute rapidly up to  $1.2 \times 10^{-2} M$  and then assumes steady values. The possible reason of the above trend is the formation of a greater number of active sites by the increase in ferrous ammonium sulfate concentration up to a limiting value. Beyond this value, possibly the concentration of initiating free radicals is depleted due to mutual combination. An unusual behavior has been found in the case of grafting AA onto the fiber. Grafting was found only in one specified concentration of  $FeAmSO_4$  ( $5 \times 10^{-4} M$ ). Therefore, this value has been taken for the study of all other effects. The reason for such behavior is difficult to suggest at this stage.

#### Effect of $H_2O_2$

Figures 6, 7, and 8 represent the effect of  $H_2O_2$  concentration on % GY at three different temperatures for AN, MMA, and AA, respectively. In case of AN and MMA, % GY increases steadily up to  $2.5 \times 10^{-3}$

$M$  concentration of  $H_2O_2$  and thereafter assumes nearly constant values. This may be due to the enhanced rate of termination, which balances the rate of propagation. In the case of AA, the grafting increases steadily up to  $5 \times 10^{-3} M$  and then remains constant.

#### Effect of Monomer

The % GY increases with increase of monomer concentration as shown in Figures 9 and 10 for grafting of AN and MMA, respectively. But, in the case of grafting AA, no systematic trend has been observed. The enhancement of grafting by increasing the monomer concentration could be associated with gel effect.

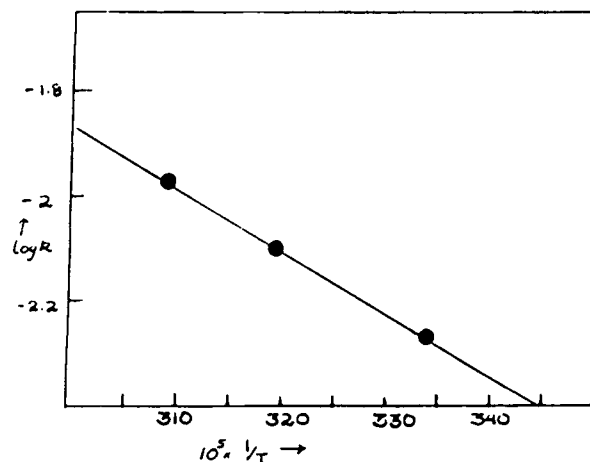
#### Kinetic Studies

Gravimetric method was used for determining the rate constants. These were determined from the slopes of straight lines obtained from the plot of  $(AN)^{-1}$  versus  $t$  and  $(MMA)^{-1}$  versus  $t$  as illustrated by Figures 11 and 12, respectively. These suggest that the grafting process is second order with respect to monomer concentration. The activation energy was determined from the slope of the straight lines obtained from the plot of  $\log k$  versus  $1/T$ . The activation energies were found to be 3.351 and 2.53 kcal/mol for grafting of AN and MMA onto bleached jute fibers, respectively (Figs. 13 and 14).

#### Characterization of the Grafted Jute Fibers

##### Thermal Analysis

The thermal behavior of grafted jute fibers were examined by the study of their primary thermograms.



**Figure 14** Plot of  $\log k$  vs.  $1/T$ ; bleached jute.  $[MMA] = 0.2372 M$ .

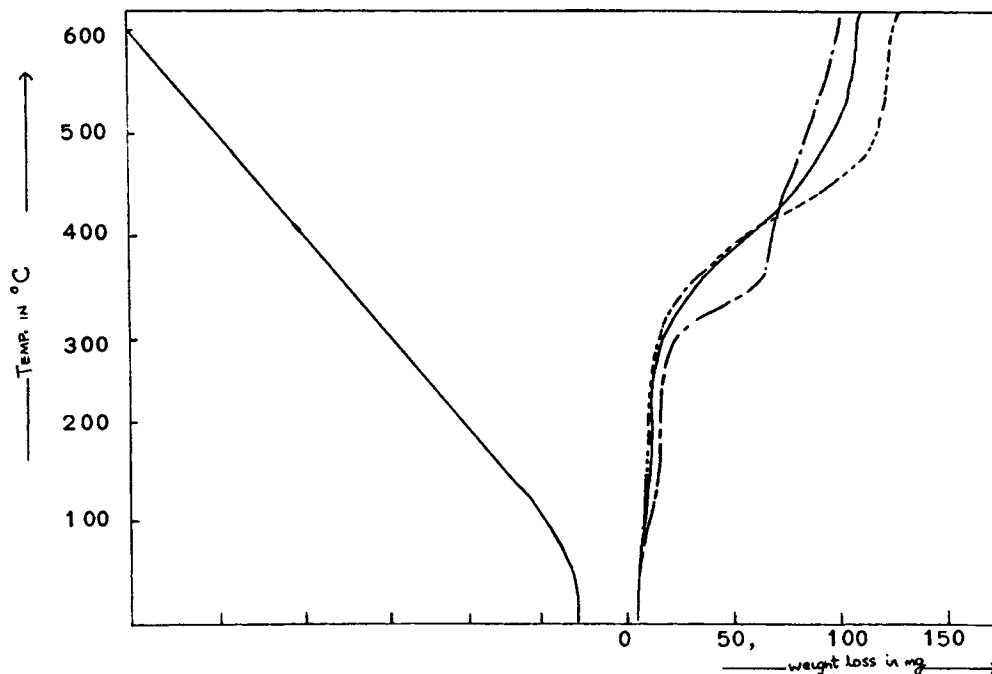


Figure 15 (···) MMA grafted bleached jute; (—) MMA grafted defatted jute; (-·-·-) nongrafted bleached jute.

It was observed that the thermal stability of the grafted jute is higher than that of the original jute. In the case of defatted jute, the decomposition tem-

perature ( $T_D$ ) is approximately 300°C and, in the case of bleached jute, 310°C. In the case of MMA-grafted jute,  $T_D$  is 315°C when the original jute fiber

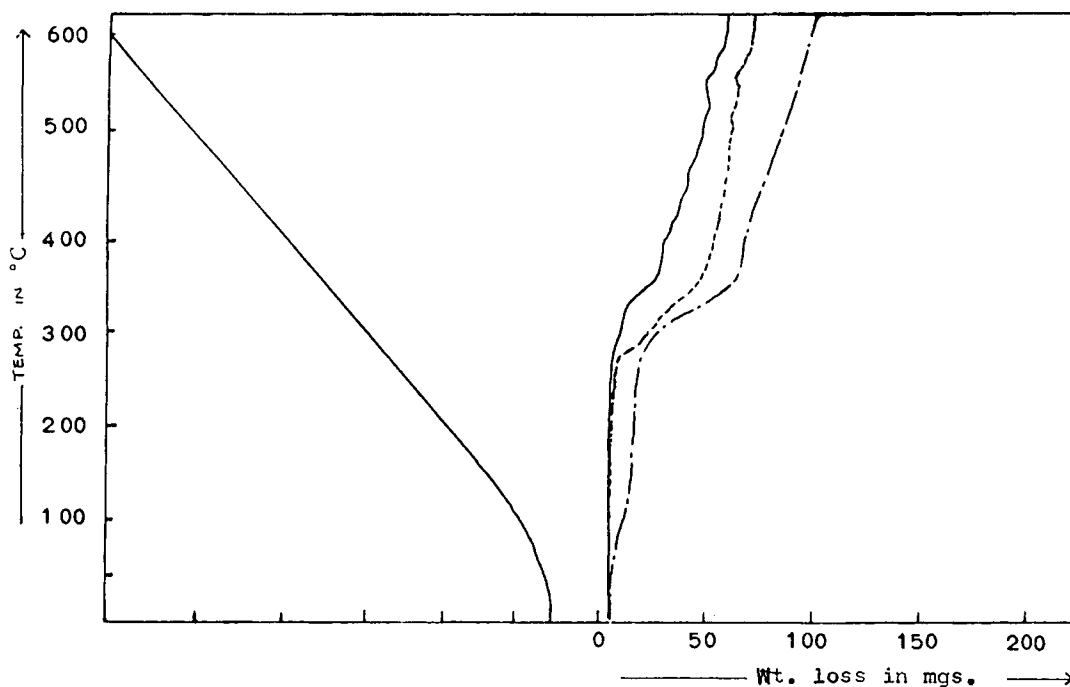


Figure 16 (···) AN-grafted defatted jute; (—) AN-grafted bleached jute; (-·-·-) nongrafted bleached jute.

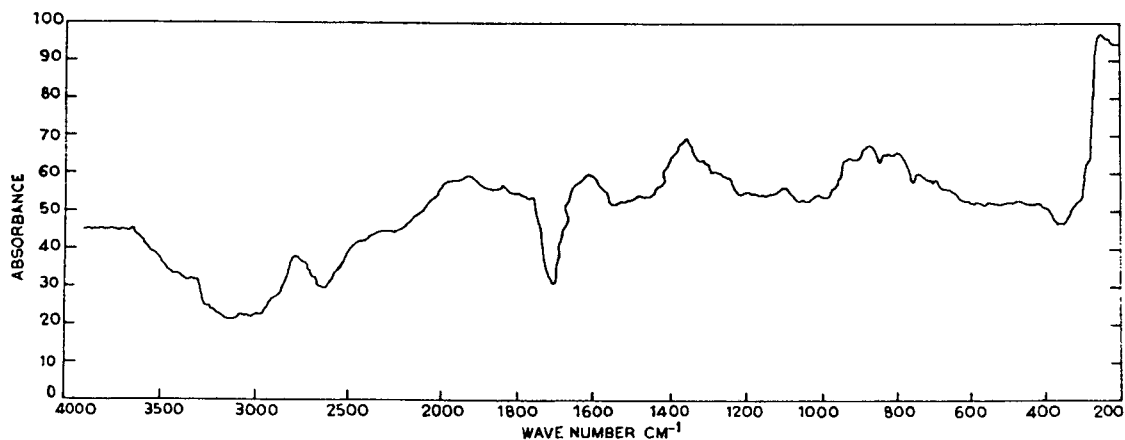


Figure 17 IR spectra of MMA-grafted jute.

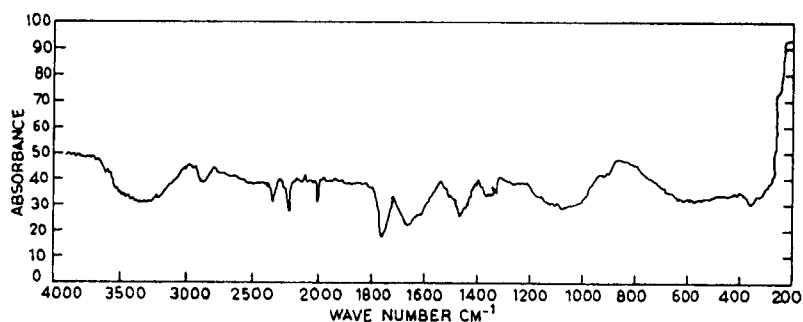


Figure 18 IR spectra of AN-grafted jute.

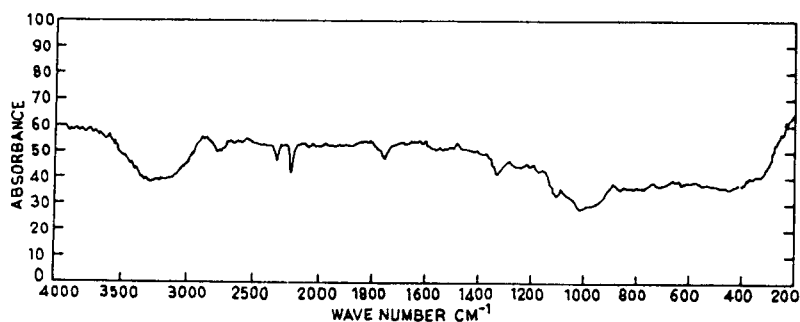


Figure 19 IR spectra of AA-grafted jute.

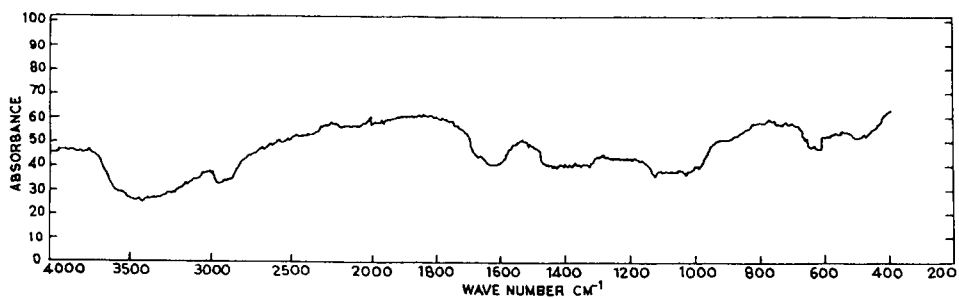


Figure 20 IR spectra of bleached jute.

is defatted and 380°C when the original fiber is bleached. On the other hand, in the case of AN-grafted fiber,  $T_D$  values are 360 and 380°C when defatted and bleached, respectively. In the case of AA-grafted fiber, the decomposition temperature is 360°C. The TG data are shown in Figures 15 and 16.

### Infrared Spectroscopic Studies

Both natural and grafted jute show a broad absorption peak at about 3400  $\text{cm}^{-1}$ , indicative of the —OH group. MMA-grafted jute shows a peak at about 1755  $\text{cm}^{-1}$  for  $\text{>C=O}$  group and at 1100  $\text{cm}^{-1}$  for C—O stretching vibration. In AN-grafted jute, IR spectrum shows a weak peak at 2350  $\text{cm}^{-1}$  indicative of —C≡N group and an unusual peak at about 1760  $\text{cm}^{-1}$  indicative of a  $\text{>C=O}$  group. The probable reason for the appearance of the latter peak may be the formation of carbonyl function during the grafting process. In the case of AA-grafted jute, the IR spectrum shows a very weak absorption peak at about 1750  $\text{cm}^{-1}$  due to  $\text{>C=O}$  group. The weakness may be attributed to the amido-imidol tautomerism existing in the amide linkage. The IR data for AN-grafted jute fibers as reported by Trivedi and Mehta<sup>1</sup> in  $\text{Ce}^{4+}$  ion initiation method are not agreeable with the data found out in this investigation. The possible site of grafting of the monomer may not be the carbonyl function as reported by them. Hence it is difficult to suggest the true mechanism as to whether the cases are true or pseudo grafting. But the occurrence of true grafting can be partly evident from the increasing broadness of all the peaks in MMA-grafted jute samples compared to

the corresponding peaks of homopolymer and physical mixture (jute and PMMA) samples. IR data are depicted in Figures 17–20.

### XRD Studies

The degree of crystallinity of fibers were determined by comparing the areas between (002) plane and the composite (001) + (00 $\bar{1}$ ) plane peaks and the background line of wide-angle X-ray diffractograms. It was found that the degree of crystallinity decreases with increase in the percentage of grafting resulting in the loss of tensile strength of grafted fibers (results to be published elsewhere).

We gratefully acknowledge the help rendered by CSIR, New Delhi for providing financial assistance to one of the authors (S.M.); RRL, Bhubaneswar for taking TGA and X-ray studies and RSIC, IIT, Bombay for taking IR spectra of the samples.

### REFERENCES

1. I. M. Trivedi and P. C. Mehta, *Cell. Chem. Technol.*, **7**, 401–416 (1973).
2. M. M. Hugue, Md. Habibuddin, A. J. Mahmood, and A. J. Mian, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 1447–1458 (1980).
3. S. S. Tripathy, S. Jena, S. B. Misra, N. P. Badhi, and B. C. Singh, *J. Appl. Polym. Sci.*, **30**, 1399–1406 (1985).
4. P. K. Ray, *J. Appl. Polym. Sci.*, **12**(7), 1787–1791 (1968).
5. A. K. Mukhopadhyay, B. K. Sarkar, and A. S. Dutt, *J. Appl. Polym. Sci.*, **27**, 4525–4527 (1982).
6. M. H. Rahman, M. M. Houque, and Pak, *J. Sci. Ind. Res.*, **13**, 303 (1970).

Accepted March 21, 1990