Chemical Modification of Jute Fibers. I. Permanganate-Initiated Graft Copolymerization Methyl Methacrylate onto Jute Fibers

S. MOHARANA, S. B. MISHRA, AND S. S. TRIPATHY,*
Department of Chemistry, Ravenshaw College, Cuttack, Orissa, India

Synopsis

A study on the graft copolymerization of methyl methacrylate onto defatted jute fibers by using potassium permanganate as initiator has been made. To determine the optimum conditions for grafting, the effects of permanganate, monomer, acid, alkali treatment, time, and temperature on percentage of grafting have been studied. Kinetic studies showed that the overall reaction obeyed second order mechanism. The activation energy of the reaction has been found to be 4.34 kcal/mol. A suitable mechanism for the grafting process has been proposed. The grafted fibers have been characterized by thermogravimetric analysis (TGA, DTG, and DTA). It has been found that chemical modification of jute fiber by grafting process using permanganate as the initiator does not improve the tensile properties of the fibers.

INTRODUCTION

Synthetic graft copolymers of the cellulosic fiber (i.e., jute) with various monomers such as methyl methacrylate, acrylonitrile, and methyl acrylate using various initiator systems have gained considerably in importance in recent years.[1-5] The most commonly reported initiator is Ce(IV). The kinetics of grafting acrylonitrile onto defatted and bleached jute fibers using Ce(IV) initiator were first studied by Trivedi and Mehta.[6] These workers proved that grafting improves the extensibility and light fastness of jute fibers which are dyed with basic dyes. Huque et al.[7] studied the graft copolymerization of methyl methacrylate onto jute fibers using Ce(IV) as initiator. These workers studied the kinetics and optimum conditions of grafting. Mukhopadhyay et al.[8] studied the effect of tensile properties of jute fibers using $FeCl_3$–H_2O_2, Ce(IV), $K_2S_2O_8$ initiator systems. Majumdar and Rapson[9] studied the conditions of grafting of styrene onto jute while Ray's[10] X-ray work showed that the fiber becomes more rigid with grafting. Potassium permanganate has been reported by Tripathy et al.[11] to be powerful initiator for grafting of jute. The present article deals with studies of the optimum conditions and kinetics of grafting along with characterization of the grafted jute fibers using methyl methacrylate as the monomer and $KMnO_4$ as the initiator.

*To whom all correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 40, 345–357 (1990)
 CCC 0021-8995/90/3-40345-13$04.00

EXPERIMENTAL

The jute sample under investigation was the *Corchorus capsularis* variety (white jute) procured from Jute Corporation of India. The fibers were lightly but thoroughly combed to remove impurities and cut into small bundles of about 8–10 cm in length. The fibers were defatted by the method of Huque et al.[7] The defatted fibers were then effectively swollen in alkali solutions of different strengths, thoroughly washed with distilled water, and finally air-dried.

Methyl methacrylate was purified by the usual procedure. $KMnO_4$ solution is prepared fresh before each polymerization experiment. All chemicals used are of reagent and analytical grade.

Lignin content of jute was determined by the usual method.[12] Delignification of jute fibers by bleaching was not done, as $KMnO_4$ itself bleached the fibers to the desired extent.

Method of Grafting

The grafting procedure adopted differs from the usual method reported by earlier workers. Instead of using a sample to liquor ratio 1 : 50, a ratio of 1 : 150 was used. This has proved to be more effective than earlier methods. Before initiating graft copolymerization, the jute fibers were soaked with freshly prepared $KMnO_4$ solution (0.05M) for the desired time interval, then thoroughly washed, and dried by pressing between filter papers. The fibers were placed in pyrex flasks with $B_{24/29}$ standard joints equipped with gas inlet and outlet tubes for nitrogen passage. Appropriate quantities of sulfuric acid and conductivity water were added to the reaction vessels. Purified nitrogen gas was passed through the vessels for 5 min and the vessels were sealed by rubber tubes. The vessels were then thermostatted at the desired temperature. Required amounts of purified monomer MMA (previously thermostatted) were added to the flasks for initiating the polymerization. After the specified time interval, the reaction was arrested by quenching the vessel in ice water. The homopolymer along with the grafted jute fibers were filtered off, washed with distilled water, and dried to constant weight. Finally, the homopolymers were extracted with acetone in a soxhlet apparatus by refluxing for 12 h. The percentage of graft yield and percentage of grafting were estimated from the following equations.

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

$$\% \text{ of Grafting (G)} = \frac{\text{Dry wt of grafted fiber}}{\text{Dry wt of MMA charge}} \times 100$$

RESULTS AND DISCUSSION

The optimum conditions for the graft copolymerization of methyl methacrylate onto jute fibers were investigated by studying the effects of time; initiator, monomer, and acid concentrations; temperature, etc. on percent of graft yield and percent of grafting.

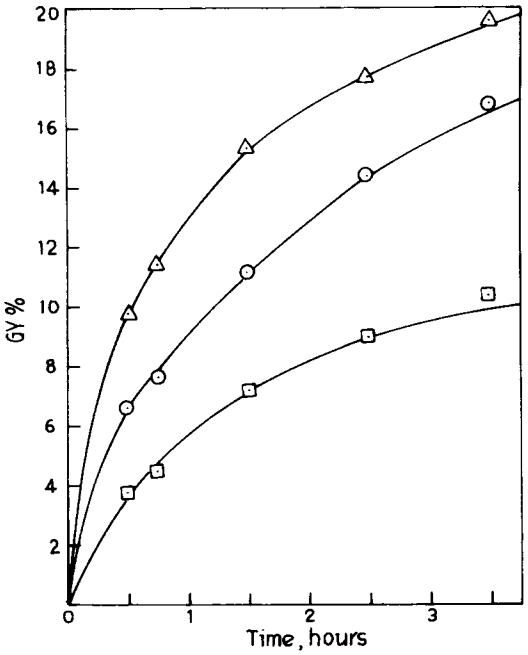


Fig. 1. Effect of reaction time and temperature on % grafting (G): (△) = 50°C, (○) 40°C, (□) 30°C. [$KMnO_4$] = 0.0033*M*, jute fiber = 0.1 g; MMA = 1 mL; [H_2SO_4] = 0.0167*M*; sample to liquor ratio, 1 : 150.

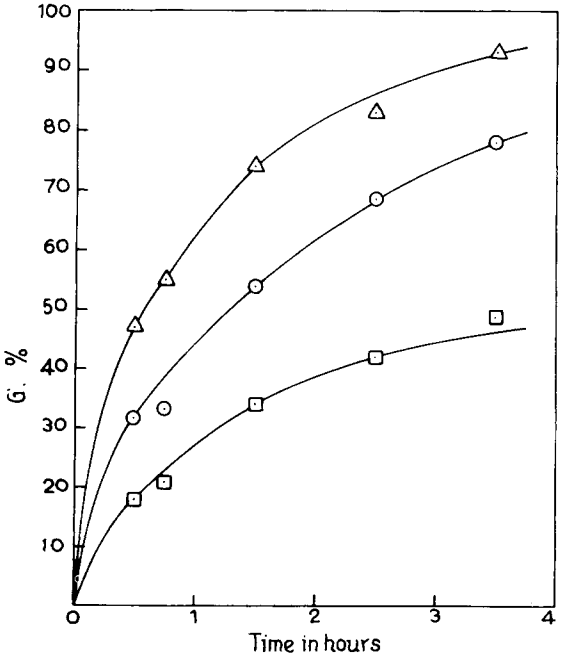


Fig. 2. Effect of time and temperature on % graft yield (GY): (△) 50°C, (○) 40°C, (□) 30°C. [$KMnO_4$] = 0.0033*M*; jute fiber = 0.1 g; MMA = 1 mL; [H_2SO_4] = 0.0167*M*; sample to liquor ratio, 1 : 150.

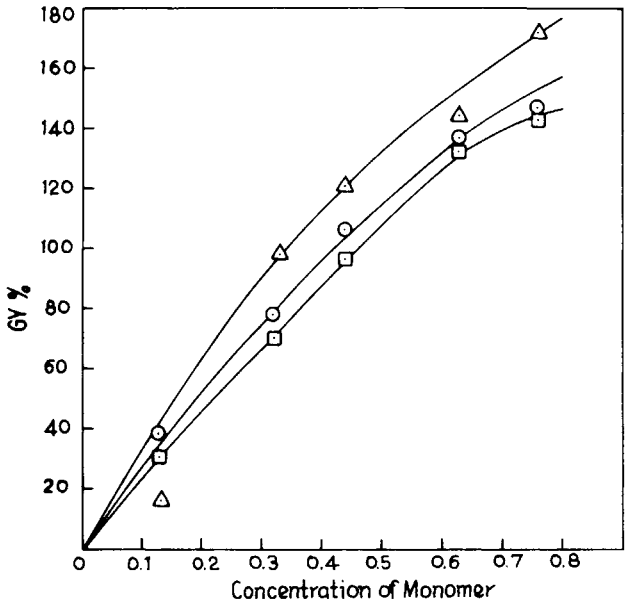


Fig. 3. Effect of concentration of monomer on % graft yield (GY): (○) = 50°C (△) 40°C, (□) 30°C. [$KMnO_4$] = 0.0033M; jute fiber = 0.1 g; [H_2SO_4] = 0.0167M; sample to liquor ratio, 1 : 150.

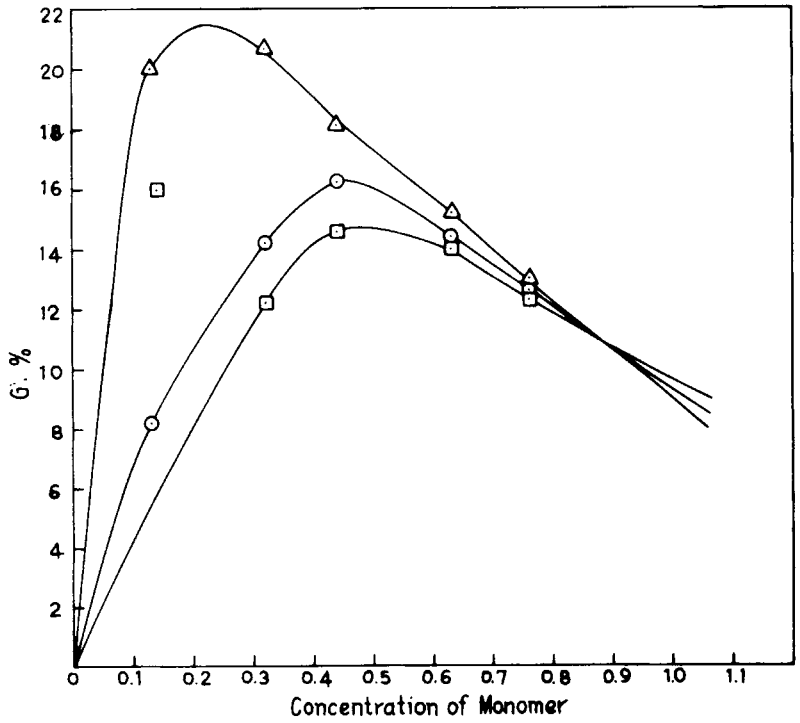


Fig. 4. Effect of concentration of monomer on % grafting (G): (○) 50°C, (△) 40°C, (□) 30°C. [$KMnO_4$] = 0.0033M, jute fiber = 0.1 g; [H_2SO_4] = 0.0167M; sample to liquor ratio, 1 : 150.

Effect of Time and Temperature

Figures 1 and 2 show the effect of time on % graft yield and % grafting, respectively, in grafting methyl methacrylate onto defatted jute fibers at three different temperatures (30, 40, and 50°C). The % grafting increases steadily with time up to 3.5 h with a maximum increase of 16.8% at 40°C; temperature increases the % grafting. Since the % grafting reaches more or less a steady value within 1 h, this value was used for all further studies.

Effect of Monomer

The effect of monomer on % GY and % G was determined at 30, 40, and 50°C by soaking the fibers in 0.01*M* concentration of $KMnO_4$. It was not possible to estimate the $KMnO_4$ concentration in the soaked and dried jute fibers in the usual method, as the $KMnO_4$ concentration was very low. Increasing monomer concentration increases the % GY. The % G increases up to 0.2M monomer concentration, and thereafter decreases as shown in Figures 3 and 4. This result is not in agreement with the result reported by Huque et al.[7] in which % G tended to increase with monomer concentration. The maximum of 20.63% G was obtained for 0.32*M* of MMA at 40°C. From this trend, the following mechanism of grafting process may be suggested. It has been proposed that MnO_4^- dissolves in the acid medium to give rise to Mn^{+3} ions via Mn^{+4}. These highly reactive Mn^{+3} ions are responsible for initiating graft copolymerization and homopolymerization.

Initiation:

$$JH + Mn(III) \longrightarrow JH - Mn(III)(Complex) \quad (1)$$

$$JH - Mn(III) \longrightarrow J^{\cdot} + Mn(II) + H^+ \quad (2)$$

$$J^{\cdot} + M \longrightarrow JM^{\cdot} \quad (3)$$

$$Mn(III) + M \longrightarrow M^{\cdot} + Mn(II) + H^+ \quad (4)$$

$$JM^{\cdot} + nM \longrightarrow JM_{n+1}^{\cdot} \quad (5)$$

$$M^{\cdot} + nM \longrightarrow M_{n+1}^{\cdot} \quad (6)$$

$$JM_{n+1}^{\cdot} + Mn(III) \longrightarrow JM_{n+1} + Mn(II) + H^+ \cdots \quad (7)$$

$$J^{\cdot} + Mn(III) \longrightarrow \text{Oxidized product} + Mn(II) \cdots \quad (8)$$

where JH and M represent jute cellulose and monomer, respectively.

Effect of $KMnO_4$. Figures 5 and 6 show the effect of $KMnO_4$ concentration on the % GY and % G. The % GY and % G increase up to 0.01*M* of $KMnO_4$ used for soaking the fibers, and thereafter decrease. This result may be attributed to metal ion termination at higher concentrations of $KMnO_4$.

Effect of H_2SO_4. Figures 7 and 8 show the effect of H_2SO_4 on the % GY and % G, which increase up to 0.012*M* concentration of H_2SO_4 and thereafter decrease. A plausible reason for this trend may be that depolymerization takes place at higher acid concentrations as expected from Step 7 of the proposed mechanism.

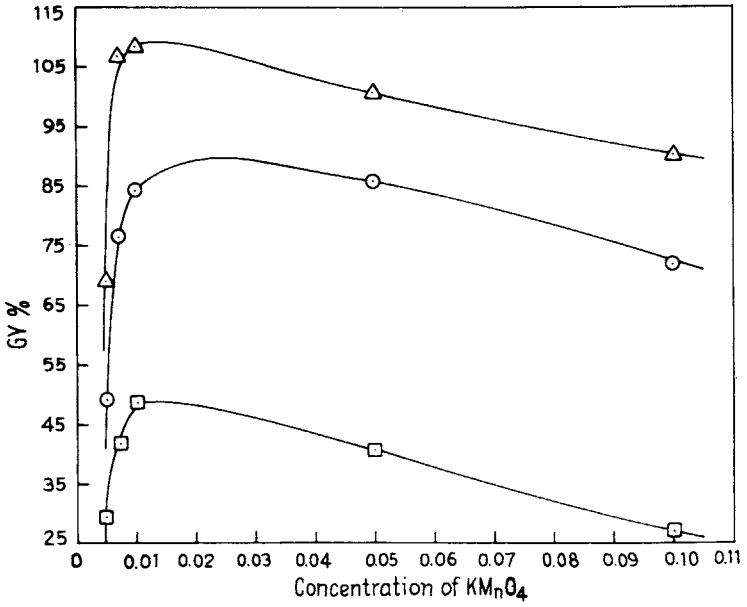


Fig. 5. Effect of $KMnO_4$ on % GY (graft yield): (△) 50°C, (○) 40°C, (□) 30°C. Jute fiber = 0.1 g; MMA = 0.5 mL; $[H_2SO_4]$ = 0.067*M*; sample to liquor ratio, 1 : 150.

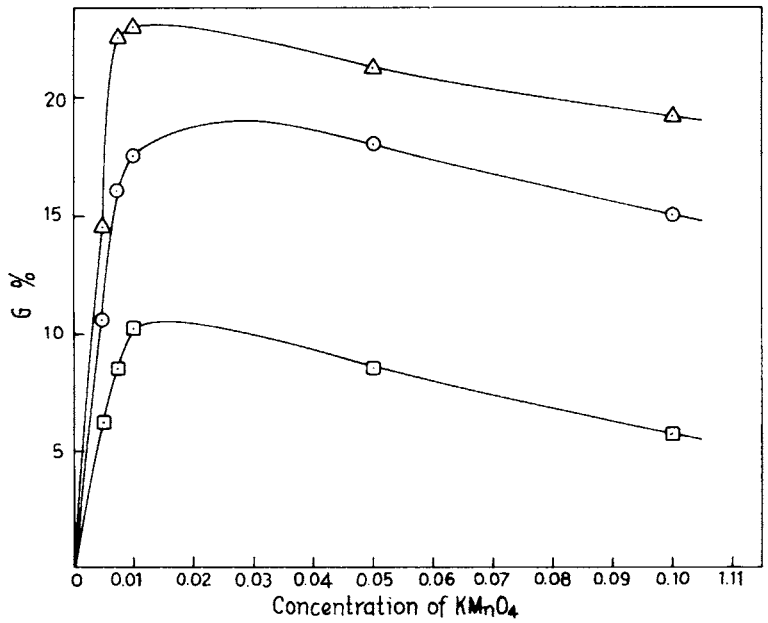


Fig. 6. Effect of $KMnO_4$ on % G: (△) 50°C, (○) 40°C, (□) 30°C. Jute fiber = 0.1 g; MMA = 0.5 mL; $[H_2SO_4]$ = 0.167*M*; sample to liquor ratio, 1 : 150.

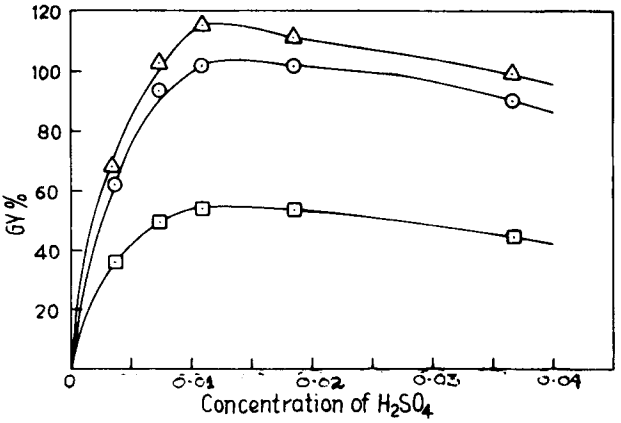


Fig. 7. Effect of H_2SO_4 on % GY: (△) 50°C, (○) 40°C, (□) 30°C. Jute fiber = 0.1 g; MMA = 0.5 mL; $[KMnO_4]$ = 0.0033*M*; sample : liquor = 1 : 150.

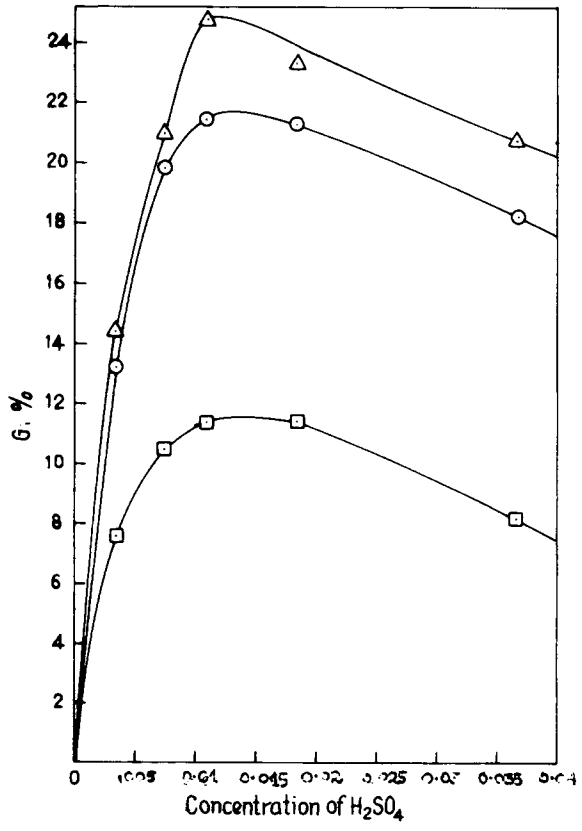


Fig. 8. Effect of H_2SO_4 on % G: (△) 50°C, (○) 40°C, (□) 30°C. Jute fiber = 0.1 g; MMA = 0.5 mL, $[KMnO_4]$ = 0.0033*M*, sample to liquor ratio, 1 : 150.

TABLE I
Effect of Alkali Swelling Period[a]

Temperature (°C)	Time period of alkali swelling (min)	GY (%)	G (%)
50	1	71.4	15.03
	4	89.1	18.76
	10	88.0	18.53
	20	71.4	15.03
	40	68.5	14.42
40	1	75.0	15.79
	4	65.0	13.68
	10	86.5	18.21
	20	97.2	20.46
	40	62.5	13.16
30	1	60.5	12.74
	4	51.5	10.84
	10	76.0	16.00
	20	68.5	14.42
	40	64.3	13.35

[a]Jute fiber = 0.1 g; $[KMnO_4] = 0.0033M^-$, MMA = 0.5 mL; $[H_2SO_4] = 0.0167M$; sample to liquor ratio, 1:150.

TABLE II
Effect of Concentration of Alkali[a]

Temperature (°C)	Conc. of alkali (%)	GY (%)	G (%)
45	5	127.2	26.78
	10	132.4	27.87
	15	71.5	15.05
	20	107.4	22.61
	25	94.6	19.92
40	5	47.0	9.89
	10	49.4	10.4
	15	68.3	14.38
	20	54.0	11.37
	25	33.3	7.00
35	5	58.5	12.32
	10	48.7	10.25
	15	45.0	9.47
	20	63.3	13.33
	25	57.5	12.11

[a]Jute fiber = 0.1 g; $[KMnO_4] = 0.0033M$; MMA = 0.5 mL; $[H_2SO_4] = 0.0167M$; sample to liquor ratio, 1:150.

Effect of Alkali Swelling Period

The effect of swelling of fibers by alkali (30%) for different time intervals on the % GY and % G is shown in Table I. With the increase in the swelling period, both % GY and % G increase to an optimum value and thereafter decrease. The probable reasons for this are the hydrolysis of the oxide linkage in the cellulose units and excessive delignification which are unfavorable for the grafting process.

Effect of Alkali Concentration Used for Swelling

The effect of alkali concentration used for swelling the jute samples for a given time (5 min) on the % GY and % G is shown in Table II. When alkali concentration is increased from 5 to 25%, there is no measurable increase in either the % GY or % G, nor has any specific trend been found.

Effect of Weak Acids

The effect of weak acids such as oxalic, malonic, citric, tartaric, and succinic acids on the % GY and % G has been determined. The % GY and % G were greatest for succinic acid (81.3, 17.12 at 40°C, respectively).

Kinetics of Grafting

A gravimetric method was used for determining the rate constants. These were determined from the slope of straight lines obtained in the plot of $(MMA)^{-1}$ versus time according to method of Trivedi and Mehta[6] (Fig. 9). This suggests a second-order rate process with respect to monomer concentration. The activation energy was determined from the slope of the straight line obtained from the plot of log k versus $1/T$ according to the Arrhenius expression $k = Ae^{-E/RT}$. The activation energy of the grafting process was found to be 4.34 kcal/mol from Figure 10.

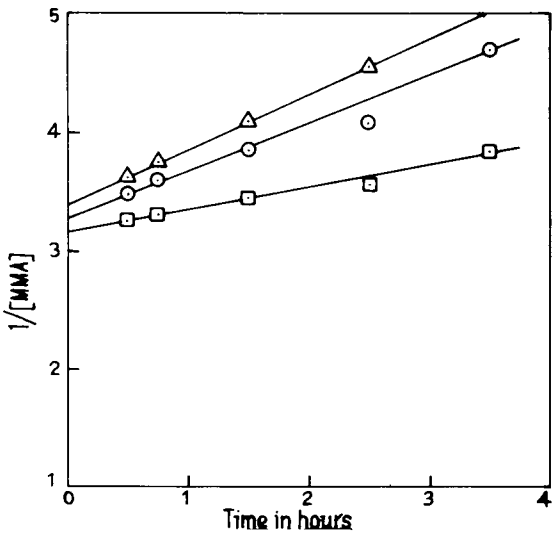


Fig. 9. Defatted Jute = 0.1 g, $[KMnO_4] = 0.0033M$, $[H_2SO_4] = 0.0167$.

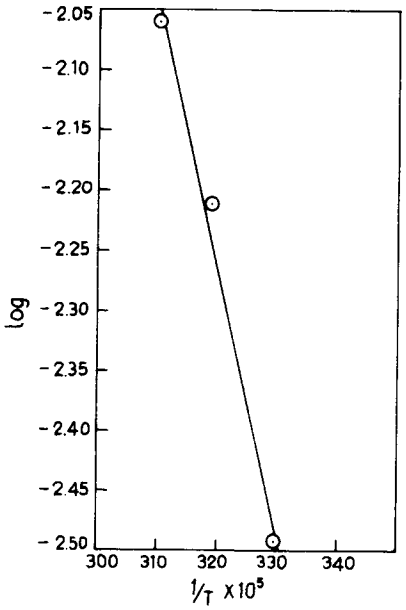


Fig. 10. Plot of log K vs. $1/T$. [$KMnO_4$] = 0.0033M; [H_2SO_4] = 0.0167M.

CHARACTERIZATION

Thermal Analysis

The TG, DTG, and DTA curves for the defatted and grafted jute samples are shown in Figure 11. In the defatted sample, the weight loss began with a 10% loss in weight at 100°C, with the maximum weight loss taking place at the decomposition temperature (T_D) 300°C. At this temperature, the DTA showed an endothermic curve indicating a physical change, most likely melting, and, at 300°C (i.e., at T_D) showed an exothermic curve showing chemical change, most likely degradation. In the case of the grafted jute fiber (120% GY), the weight loss is much less (10%) (up to 300°C) with significant decomposition taking place at 340°C. This suggests that the grafted sample is thermally more stable than the ungrafted one and decomposition is very limited in the former case.

Tensile Strength

The results found on the tensile properties of grafted jute fibers relative to ungrafted fibers were contradictory to the results published by earlier workers. Majumdar et al.[9] reported that the tenacity of the control jute fiber increases on grafting from 23.7 to 36.6% G, but a further increase in add-on has no significant effect. We have found that at any % G, the fiber becomes weak and tenacity decreases. This may be due to the degradation of cellulose molecules on prolonged treatment with water at high temperature, but primarily it is due to the presence of an oxidizing initiator. We believe there is little chance of enhancing the tensile strength of jute fibers by chemical grafting. These results are in agreement with x-ray diffraction studies in

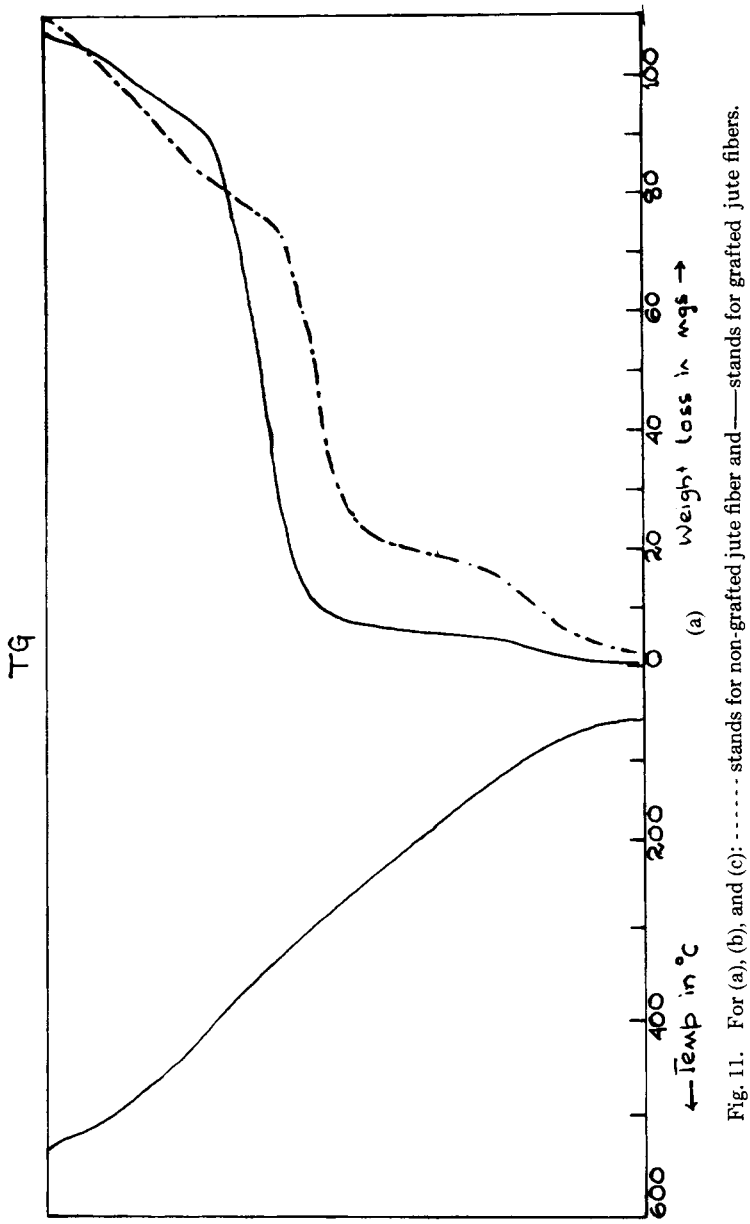
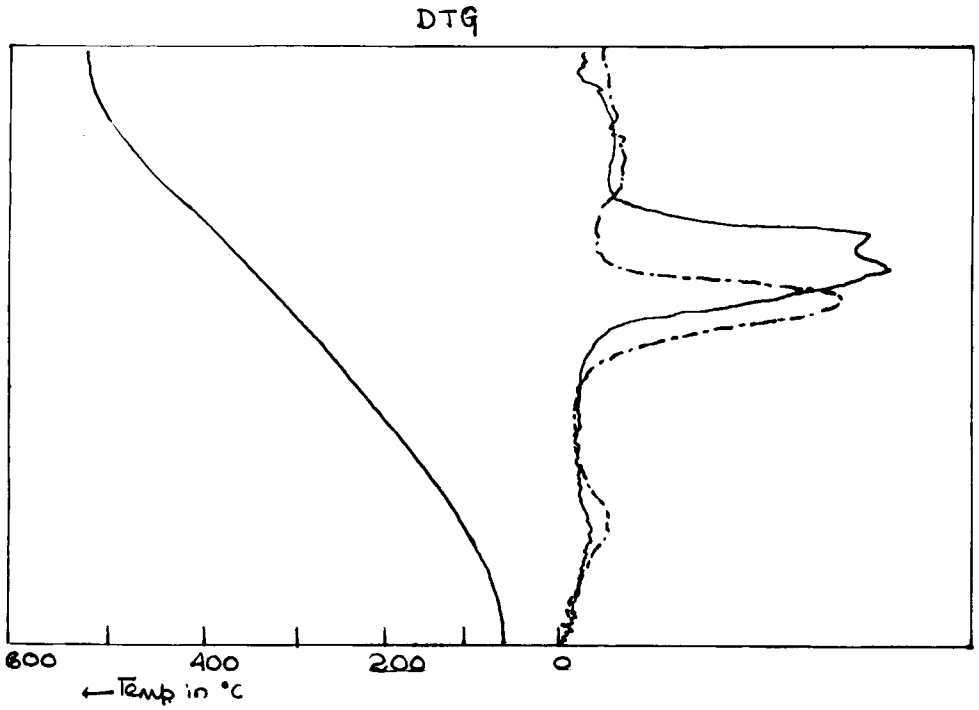
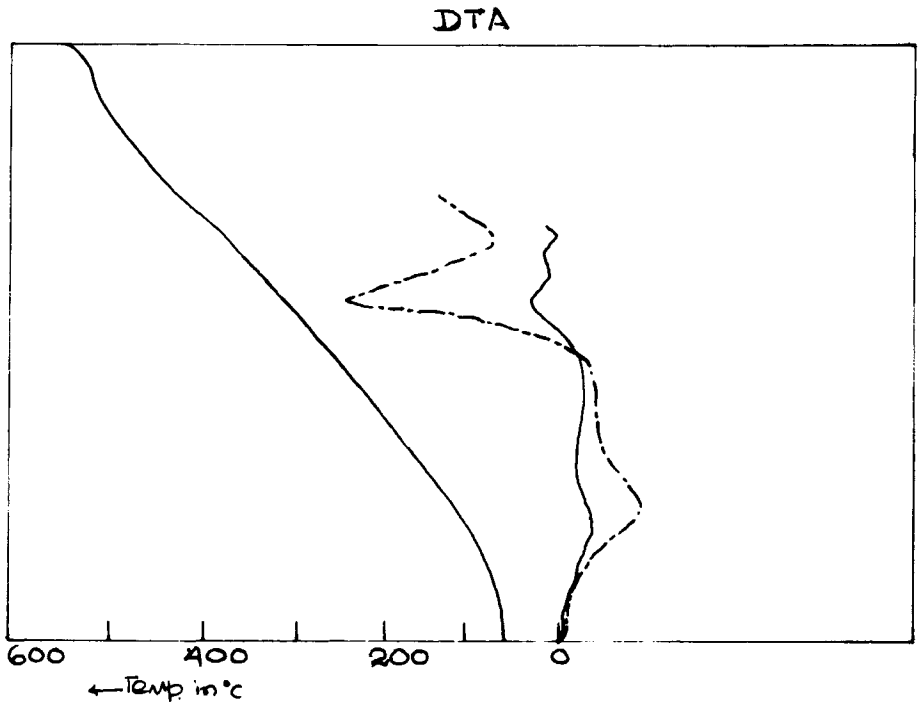


Fig. 11. For (a), (b), and (c): ------ stands for non-grafted jute fiber and——stands for grafted jute fibers.



(b)



(c)

Fig. 11. (*Continued from the previous page.*)

which the degree of crystallinity decreases on grafting. The details of x-ray diffraction and infrared (IR) spectral studies and their correlation with tensile properties will be reported in a future communication.

We gratefully acknowledge the help rendered by CSIR, New Delhi in providing financial assistance to one of the authors (SM) and RRL, Bhubaneswar for taking TGA, DTA, and DTG of samples.

References

1. G. N. Richards, *J. Appl. Polym. Sci.*, **5**, 539 (1962).
2. S. Kaizerman, G. Mino, and F. Meinhold, *Text. Res. J.*, **32**, 136 (1962).
3. Y. Iwakura, T. Kurosaki, K. Uno, and Y. Imai, *J. Polym. Sci.*, **4**, 673 (1964).
4. N. M. Berghein, O. Ellegson, K. Kringsted, and P. Kroken, *Nor. Skogind*, **17**, 347 (1963).
5. H. Nåvita, N. Uduino, and S. Maduida, *Sen'i Gakkaishi*, **19**, 225 (1963).
6. I. M. Trivedi and P. C. Mehta, *Cell. Chem. Technol.*, **7**, 401–416 (1973).
7. M. M. Huque, H. Mahmood, and A. J. Mian, *J. Polym. Sci.*, **18**, 1447 (1980).
8. A. K. Mukhopadhyay, B. K. Sarkar, and A. S. Dutt, *J. Appl. Polym. Sci.*, **27**, 4525 (1982).
9. S. K. Majundar and W. H. Rapson, *Text. Res. J.*, **34**, 1007–1015, 1015–1021 (1964).
10. P. K. Ray, *J. Appl. Polym. Sci.*, **12**, (7), 1787–1791 (1968).
11. S. S. Tripathy, S. Jena, S. B. Mishra, N. P. Padhi, and B. C. Singh, *J. Appl. Polym. Sci.*, **30**, 1399–1406 (1985).
12. P. Klason, *Cell. Chem.*, **4**, 81(1923), **12**, 36 (1931).

Received October 22, 1988
Accepted September 26, 1989