

A Study on Grafting of Methyl Methacrylate onto Jute Fiber ($S_2O_8^{2-}$ -Thiourea Redox System)

M. MISRA*, *Laboratory of Polymer Science, Post-Graduate Department of Chemistry, Ravenshaw College, Cuttack-753 003, Orissa*, and A. K. MOHANTY and B. C. SINGH†, *P. G. Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar-751004, India*

Synopsis

A study of the graft copolymerization of methyl methacrylate onto jute fiber, using $K_2S_2O_8$ -thiourea (TU) redox-initiating system has been made. The effects of concentration of monomer, $S_2O_8^{2-}$, TU on graft yield have been studied. Besides the effects of time, temperature, acid, and amount of jute fiber, some inorganic salts and organic solvents on graft yield have been investigated. The most remarkable features of the investigation include proposition of a mechanism for the grafting process and characterization of grafted fiber by infrared (IR) and thermogravimetric studies. Grafting has improved the light fastness of jute fibers dyed with basic dyes. More than 200% graft yield could be achieved in the present investigation.

INTRODUCTION

The graft copolymerization onto textile fibers is a challenging field of research having enormous future prospects.¹⁻⁴ The synthetic graft copolymers of natural macromolecules like silk, wool, cellulosic fibers, etc., exhibit excellent properties in addition to showing their original properties. Peroxydisulfate has been widely used⁵⁻⁸ as initiator for graft copolymerization of vinyl monomers onto natural fibers. Although a lot of work has been done on graft copolymerization of vinyl monomers onto cellulosic and other textile fibers, much less has been reported on grafting of vinyl monomers onto jute fiber which is an agricultural product and an important lignocellulosic fiber. Unlike cotton fiber, jute is not uniform in chemical composition which is evidenced by the multicellular structure of the fiber. Jute fiber is facing tough competition from the synthetic fibers as the latter offer certain advantages in terms of many useful properties, durability, and production economics. The survival of jute in competition with the synthetic fibers lies in the retention of jute as a preferred material in the eyes of the consumer, but it must be constantly developed and improved to retain that status. Therefore, graft copolymerization of vinyl monomers onto jute fibers has been receiving considerable

*Present address: S. B. Women's College, Cuttack-753001, Orissa, India.

†Author to whom all correspondence should be addressed.

attention in recent years. Although Ray⁹ has reported some x-ray diffraction studies of polymethyl methacrylate (PMMA) and polyacrylonitrile (PAN) -grafted holocellulose (delignified jute), not much is known about the conditions of grafting. Moreover, he has reported grafting of 30% for methyl methacrylate (MMA) and 20% for acrylonitrile (AN) using ceric-ion initiation. Grafting of AN¹⁰ and MMA¹¹ onto jute fibers using ceric-ion initiation has been reported in the last decade. Attempts have also been made to modify jute fiber by graft copolymerization of vinyl monomers using ionizing radiation.^{12,13} Agarwal and Sreenivasan^{14,15} have studied graft copolymerization of vinyl monomers, namely, MMA, AN, vinyl acetate, and styrene onto jute fibers using gamma rays. Photograft copolymerization of MMA on bleached jute fiber using ferric sulfate as initiator¹⁶ and radiation (⁶⁰Co) induced graft copolymerization of acrylamide onto jute fiber¹⁷ have also been reported. Graft copolymerization of MMA onto chemically modified jute fiber using KMnO₄-malonic acid,¹⁸ V⁵⁺-cyclohexanone¹⁹ redox systems have been reported by our research group. Redox-initiated graft copolymerization of MMA onto different modified jute fibers has also been reported by Mohanty and Singh.²⁰

The present investigation reports a kinetic study of S₂O₈²⁻-TU-initiated graft copolymerization of MMA onto chemically modified jute fibers. This system has proved to be the most effective in grafting vinyl monomers onto jute fiber.

EXPERIMENTAL

The pretreatment of jute fibers was done as mentioned earlier.¹⁸ Monomer (MMA) was purified following a standard procedure.²¹ All other chemicals (i.e., K₂S₂O₈, thiourea, sulfuric acid) were all of (BDH) AR grade and were purified where necessary.

The graft copolymerization reactions were carried out at the desired temperature, in a constant temperature bath with an accuracy of $\pm 0.1^\circ\text{C}$. Before initiating the graft copolymerization reaction, the jute fibers were soaked with an appropriate quantity of monomer for about 5–10 min. The graft copolymerizations were carried out in pyrex vessels with B_{24/29} standard joints equipped with gas inlet and outlet tubes for nitrogen. Appropriate quantity of reaction mixture containing jute fiber, monomer, TU, sulfuric acid and disulfate solution was separately deaerated by passing nitrogen for 20 min. Next, the required amount of initiator solution was poured into the vessel containing the reaction mixture. The reactions were carried out for specific times at three different temperatures, namely, 50°C, 60°C, and 70°C. After the specific time interval, each reaction was arrested by quenching the vessel in ice cold water. The homopolymer and the grafted jute fibers were filtered off, washed with conductivity water, and dried to constant weights. Finally the fibers were refluxed with acetone repeatedly for about 12 h to dissolve all the homopolymers and till a constant weight of the grafted fiber was obtained. Percentage of grafting was estimated as follows:

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

RESULTS AND DISCUSSION

Effect of Variation of Polymerization Time

The percentage of grafting of MMA onto chemically modified jute fiber as a function of grafting time is represented in Figure 1. It was observed that graft percent increases with an increase in time up to 2 h. Beyond this time, graft yield decreases to some extent. This may be attributed to the partial dissolution of the grafted fiber on prolonged exposure to heat. Thus an optimum grafting efficiency is obtained within 2 h.

Effect of Variation of Monomer Concentration

The effect of monomer (MMA) concentration on the percentage of grafting at three temperatures (50°C, 60°C, and 70°C) is demonstrated in Figure 2. The percent of grafting increases with increase of monomer concentration from 0.0940 mol/L up to 0.5645 mol/L and thereafter decreases. The decreasing trend in percent grafting after certain optimum concentration of MMA is probably due to the competition between the homopolymerization and grafting where the former prevails over the latter at higher MMA concentration.

Effect of Variation of Oxidant ($S_2O_8^{2-}$) Concentration

Effect of variation of oxidant concentration on percentage of grafting at three different temperatures i.e., 50°C, 60°C, and 70°C is presented in Figure 3. The percent of grafting increases with the increase in $S_2O_8^{2-}$ concentration up to 0.08 mol/L and beyond that the percentage of graft yield decreases. The increase of percentage graft yield with increase in oxidant concentration

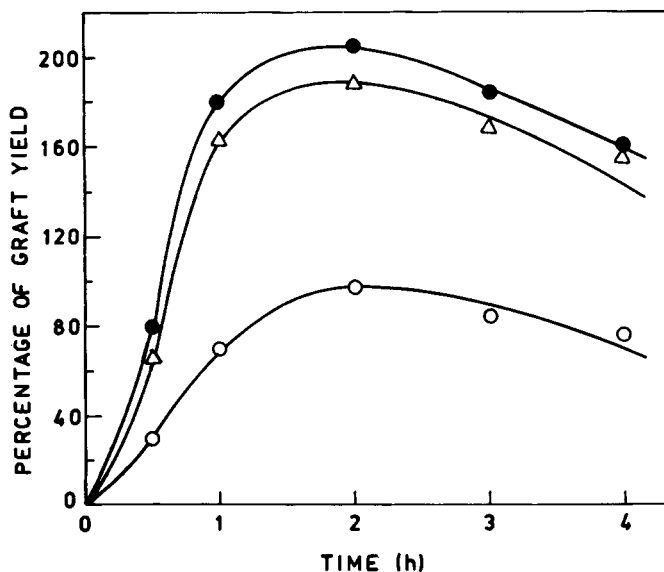


Fig. 1. Percentage of graft yield vs. time. $[S_2O_8^{2-}] = 0.05$ mol/L, $[TU] = 0.05$ mol/L, $[MMA] = 0.470$ mol/L, $[H_2SO_4] = 0.25$ mol/L, jute = 0.1 g: (○) = 50°C; (●) = 60°C; (△) = 70°C.

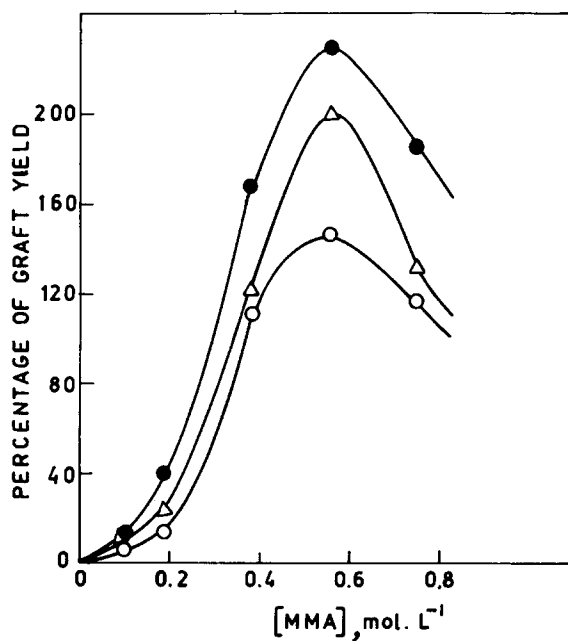


Fig. 2. Percentage of graft yield vs. monomer concentration. $[S_2O_8^{2-}] = 0.08$ mol/L, $[TU] = 0.05$ mol/L, $[H_2SO_4] = 0.25$ mol/L, jute = 0.1 g, time = 2 h: (○) = 50°C; (●) = 60°C; (Δ) = 70°C.

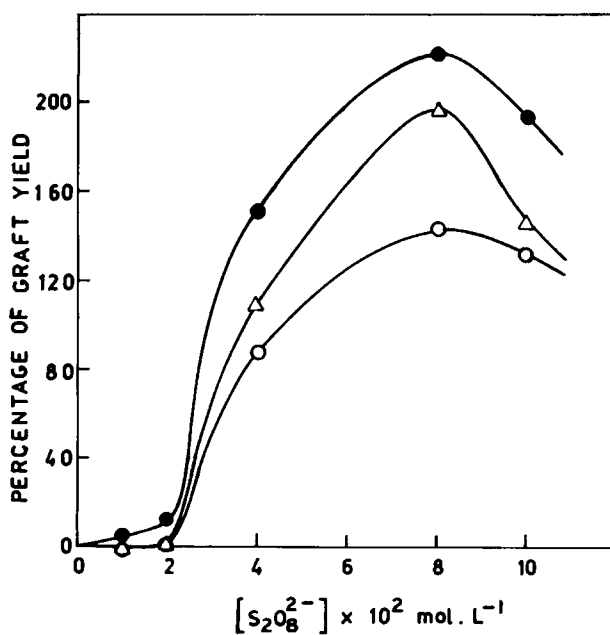


Fig. 3. Percentage of graft yield vs. peroxy disulfate ($S_2O_8^{2-}$) concentration. $[TU] = 0.05$ mol/L, $[MMA] = 0.470$ mol/L, $[H_2SO_4] = 0.25$ mol/L, jute = 0.1 g, time = 2 h: (○) = 50°C; (●) = 60°C; (Δ) = 70°C.

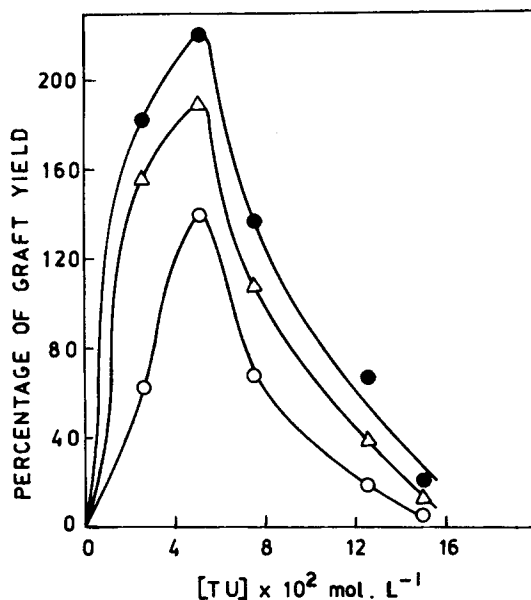


Fig. 4. Percentage of graft yield vs. thio-urea (TU) concentration. $[S_2O_8^{2-}] = 0.08$ mol/L, $[MMA] = 0.470$ mol/L, $[H_2SO_4] = 0.25$ mol/L, jute = 0.1 g, time = 2 h: (○) = 50°C; (●) = 60°C; (△) = 70°C.

indicates that termination by combination is more preferable than termination by disproportionation.

Effect of Variation of Thiourea Concentration

The effect of TU concentration on percent of grafting at three different temperatures (50°C, 60°C, and 70°C) is represented in Figure 4. At all the temperatures, the percentage of graft yields increase by increasing the concentration of TU from 0.025 mol/L to 0.05 mol/L and thereafter decrease consistently. This decrease is probably due to the fast rate of termination and/or formation of radical scavenger at higher TU concentration.

Effect of Variation of Amount of Jute Fiber

The effect of variation of amount of jute fiber on the percent of graft yield is depicted in Figure 5. It is observed that within the range studied, the percentage of graft yield increases by increasing the amount of jute fibers in the polymerization system. This suggests that the integrated surface area of fiber greatly affects the diffusion of monomer and free radical species. It is rather possible that the reducing properties of jute contribute toward activation of $S_2O_8^{2-}$ -TU redox system thereby giving rise to higher grafting.

Effect of Variation of Temperature

The graft copolymerization of MMA onto jute fibers was studied at three different temperatures (50°C, 60°C, and 70°C) keeping the concentrations of all other reagents fixed. It was also found that grafting onto jute fibers became hardly possible below 50°C, unlike grafting of other natural fibers like

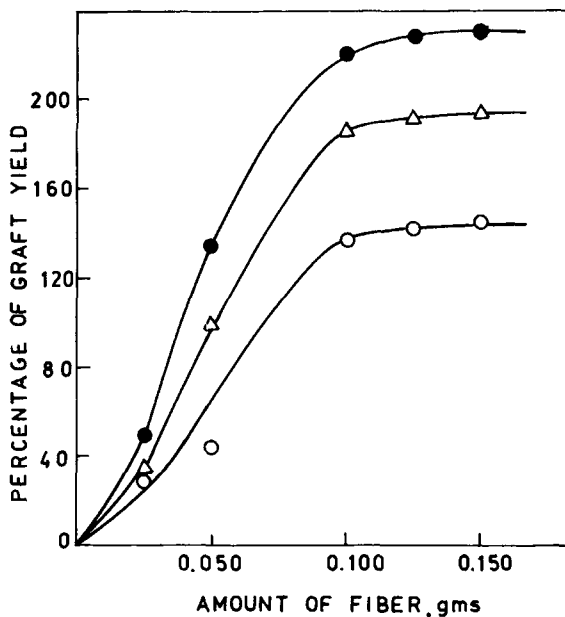


Fig. 5. Percentage of graft yield vs. amount of jute fiber. $[S_2O_8^{2-}] = 0.08$ mol/L, $[TU] = 0.05$ mol/L, $[MMA] = 0.470$ mol/L, $[H_2SO_4] = 0.25$ mol/L, time = 2 h: (○) = 50°C; (●) = 60°C, (Δ) = 70°C.

silk.²¹ This may be due to the rigidity of the cellulosic structure of jute as compared with other fibers. The effects of temperature on percent grafting are depicted in Figures 1–5. Under the present reaction conditions the percent of grafting is maximum at 60°C within 2 h. However, the percentage of graft yield decreases with an increase of temperature to 70°C. In all the experiments similar type of results were observed. Again, it is also observed that in each temperature range, the percentage of grafting appears to rise with time to certain limit and then it falls.

Effect of Reaction Medium

The reaction medium plays an important role in graft copolymerization reactions. The effect of sulfuric acid concentration on percentage of graft yield has been studied. At all three temperatures (50°C, 60°C, and 70°C) the increase of acid concentration from 0.05 mol/L to 0.40 mol/L increase the percent of graft yield (Table I). However, further increase of acid concentration was found to destroy some of the useful properties of fiber. The proof of this fact in terms of characterization will be communicated in our subsequent papers.

The graft yield follows the order with the solvents when added in equal proportions (5% v/v): acetic acid = control > dioxane > methyl alcohol > acetone. The important feature in this trend is that, excepting acetic acid, all other solvents depress the percent of grafting. Similarly the effect of neutral salts when added in equal molar concentrations follows the order: control > $MnSO_4$ > $CuSO_4$ > KBr > NaCl. The above results are shown in Table II.

TABLE I

Effect of Acid Concentration: Jute = 0.1 g [MMA] = 0.470 mol/L, $[S_2O_8^{2-}] = 0.05$ mol/L
 [TU] = 0.05 mol/L, Time = 2 h

[H ₂ SO ₄] mol/L	% Graft yield		
	50°C	60°C	70°C
0.05	50.0	58.0	77.5
0.10	75.1	138.0	112.1
0.20	91.5	185.0	167.0
0.30	103.0	208.5	192.0
0.40	132.0	223.0	199.0

TABLE II

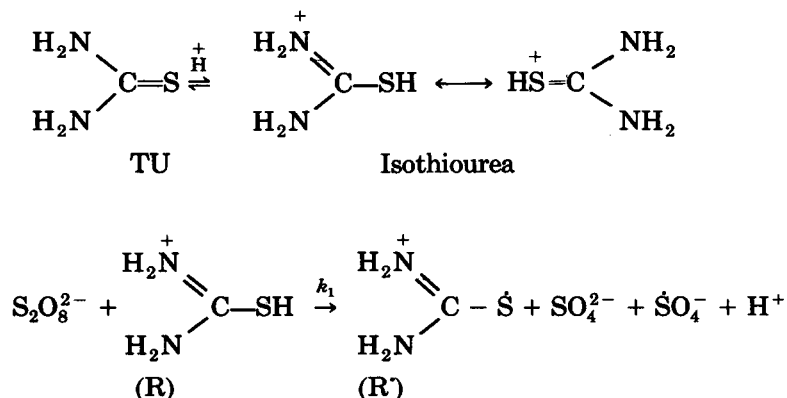
Effect of Solvents and Inorganic Salts: Jute = 0.1 g [MMA] = 0.470 mol/L, $[S_2O_8^{2-}] = 0.08$ mol/L, [H₂SO₄] = 0.25 mol/L, [TU] = 0.075 mol/L, Temp = 60°C Time = 2 h

Solvent (5% v/v)	%GY	[Salt] 0.01 mol/L	%GY
Control	128.0	Control	128.0
Acetone	59.0	CuSO ₄	105.2
Dioxane	74.5	KBr	87.3
Acetic acid	128.2	MnSO ₄	107.1
Methyl alcohol	65.0	NaCl	74.8

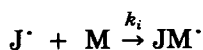
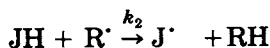
Reaction Mechanism

In a system containing peroxydisulfate, methyl methacrylate (M), thiourea (R), and jute fibers (JH), isothiurea (existing in a tautomeric equilibrium with TU) may interact with $S_2O_8^{2-}$ to form a primary free radical (R'). This radical abstracts hydrogen from jute molecule, yielding a macroradical (J'). The following is an outline of the reaction mechanism.

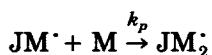
Radical formation:



Initiation:

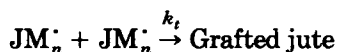


Propagation:



$$\vdots$$


Termination:



Oxidation:



where $S_2O_8^{2-}$, R^{\cdot} , JH , J^{\cdot} , M , k_1 , k_2 , k_i , k_p , k_t , and k_0 are peroxydisulfate ion, free radical, jute molecule, jute macroradical, monomer, and different rate constants, respectively.

Characterization of the Grafted Jute Fiber

Infrared Spectra. Infrared spectra (A) of natural jute (chemically modified) and of (B) MMA-grafted jute samples in the form of KBr pellets are shown in Figure 6. It is seen that natural jute (chemically modified) shows the characteristic broad absorption peak at about 3400 cm^{-1} where as the spectrum of MMA-grafted jute shows an additional peak of ester group at about 1715 cm^{-1} . One would have expected the intensity of $-\text{OH}$ peak to be reduced as a result of grafting, since it is the probable site for grafting. However, this is not observed. Probably due to the large concentration of $-\text{OH}$ groups in jute the small differences in its concentration as a result of grafting are not distinguished.

Thermal Property

The thermal behavior of natural jute (chemically modified) and MMA grafted jute was examined through thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG). TGA and DTG curves of chemically modified jute (Fig. 7a) and of MMA-grafted jute (Fig. 7b) were recorded through DT 30 Shimadzu (Japan) model thermal analyzer. As it was difficult to exactly pinpoint the deviation from base line in case of TGA curves, we

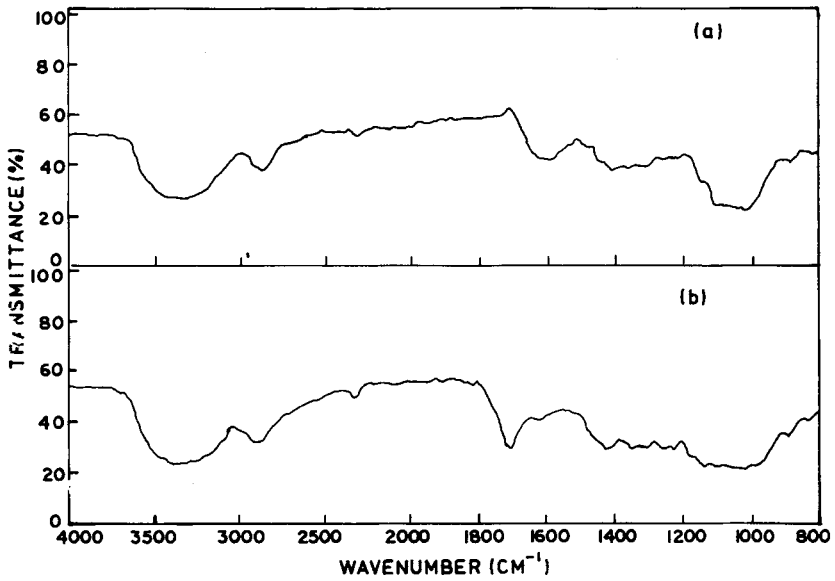


Fig. 6. IR Spectra. a → Chemically modified jute; b → MMA-grafted jute.

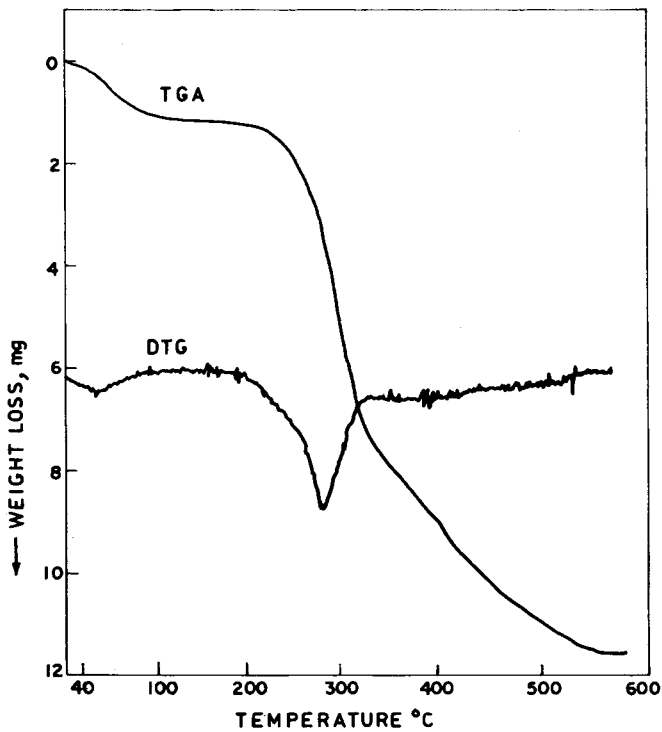


Fig. 7a. TGA and DTG curves of natural jute (chemically modified). Rate of heating = 10°C/min.

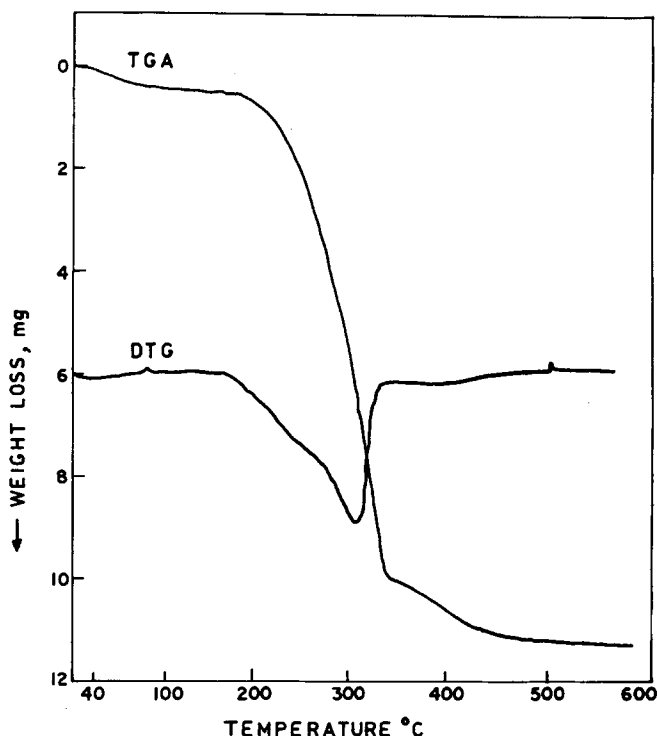


Fig. 7b. TGA and DTG curves of MMA grafted jute. Rate of heating = 10°C/min.

have taken DTG peak temperatures to represent the thermal stability of jute fibers. The thermal stability of the grafted jute was found to be higher than that of natural jute (chemically modified). In case of natural jute (chemically modified) the maximum decomposition temperature (T_D) was found to be 280°C but in case of grafted jute maximum T_D was found to be 315°C. However, the details regarding the effect of increase of percent grafting upon thermal stability will be reported in a subsequent communication.

Dyeability Property of Grafted Jute Fibers

The dyeability property of grafted jute fibers has been studied. As the jute fibers possess moderate affinity towards basic dyes, the dyeing of the fibers has been carried out with a basic dye, Rhodamine B, by a standard method for jute dyeing.²² the results of light fastness rating of dewaxed or defatted

TABLE III
Light Fastness Data of Jute Dyed with Rhodamine B

Sample particulars	Fastness to light (rating)
Defatted natural jute	3
Natural jute (chemically modified)	3
MMA grafted jute fibers	5-6

natural jute, chemically modified natural jute and MMA grafted jute fibers are represented in Table III.

It is observed from the table that light fastness rating of dyed grafted jute is higher by about 3 units from that of natural jute. Again, it is clear from the table that the chemical modification of fibers: the removal of lignin has no effect on the fastness of dyeing.

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