

Studies on Graft Copolymerization of Acrylonitrile onto Jute Fiber with Permanganate Ion Initiation System in Presence of Air

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SYNOPSIS

The graft copolymerization of acrylonitrile with jute using potassium permanganate as the initiator has been studied in the presence of air. To establish reaction conditions for the graft copolymerization of acrylonitrile (AN) onto jute, the effect of different variables such as the residual lignin content of bleached jute (after bleaching with sodium chlorite), initiator concentration, monomer concentration, time of polymerization, reaction temperature, and amount of bleached jute fiber have been studied. As evidence of polymer grafting, some instrumental analyses such as scanning electron microscopy, infrared, and thermogravimetry have been carried out. The extent of grafting of acrylonitrile depends on how much lignin is present on the jute fiber. Percent grafting and grafting efficiency have also been studied.

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INTRODUCTION

In recent years, chemical modification of jute fibers through grafting has received considerable interest. This is indeed a very fascinating field of research with unlimited future possibilities for improving the desired properties of the grafted product. Investigation of grafting by chemical means is preferred owing to their simple nature and no requirement for special equipment. To evolve a commercial process of grafting, it is necessary to choose such an initiator system which would lead to maximum grafting with minimum or no homopolymer formation in the presence of air with low initiator cost. Permanganate ion is one of the most versatile oxidizing agents because of its ability to react with almost all types of functional groups. Its use as an initiator for the graft copolymerization of vinyl monomer onto textile fibres has not been studied extensively. Use of potassium permanganate for graft copolymerization to wool, silk, nylon, and modified cotton using a permanganate ion initiation system is available.¹⁻⁹ Tripathy and co-workers reported¹⁰ kinetic studies of

the graft copolymerization of methyl methacrylate onto chemically modified jute fiber using a KMnO_4 -melonic acid redox initiator system.

It is, therefore, worthwhile to study graft copolymerization of acrylonitrile with the permanganate initiation system in a detailed way to optimize the conditions for such polymerization in the presence of air, which is a very important parameter for a commercial process, and to create polymerization in such a manner so that a minimum homopolymer is formed.

EXPERIMENTAL

Materials

Jute fiber was extracted with an alcohol-benzene mixture (1 : 2) by the Soxhlet extraction method to defat it and then it was used for experiments.

Chemicals

- (i) Potassium permanganate (AR Glaxo)
- (ii) Sodium chlorite (AR Merck)
- (iii) Acrylonitrile (Sisco Res. Lab., Bombay)
- (iv) Dimethylformamide (BDH)

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- (v) Acetyl bromide (Fluka Chemika)
- (vi) Hydroxylamine hydrochloride (S. Merck Chem)
- (vii) Potassium periodate (Merck).

Oxidation of Jute Fiber with Different Oxidizing Agents and Methods

Jute was oxidized with different oxidizing agents¹¹⁻¹³ such as sodium chlorite, potassium periodate, hydrogen peroxide, potassium permanganate, and nitric acid.

- (i) Oxidation with NaClO_2 : 5.0 g jute + 4.0 g NaClO_2 (45% av. Cl_2 , 0.7% w/v \equiv 35% on wt of fiber), acetate buffer, total volume 250 mL (liq. ratio 1 : 50), pH 4, temp 98°C, and time 2 h.
- (ii) Oxidation with KIO_4 : 5.0 g jute + 0.15 g KIO_4 , total volume 100 mL (liq. ratio 1 : 20), pH 10, temp 60°C, time 1 h.
- (iii) Oxidation with KMnO_4 : 5.0 g jute + 0.14 g KMnO_4 , total volume 100 mL (liq. ratio 1 : 20), pH 10.5, temp 60°C, time 1 h.
- (iv) Oxidation with H_2O_2 : 5.0 g jute + 100 mL borate buffer (liq. ratio 1 : 20) + 1% H_2O_2 v/v, pH 10, temp 80°C, time 1 h.¹⁴
- (v) Oxidation with HNO_3 (50%): (liq. ratio 1 : 20), at room temp (30°C), time 10 min.

Grafting

One gram bleached jute is taken for each experiment. Initially, jute is treated with 0.02 mL⁻¹ KMnO_4 (liq. ratio 1 : 150) for 10 min and the sample is washed with water thoroughly and squeezed. The permanganate-treated sample is then put into a conical flask containing 150 mL of 1% H_2SO_4 (0.0167 mL⁻¹) and 5 mL of acrylonitrile. The contents are then placed into a thermostatic water bath, the temperature of which is kept at 50°C for 2 h without any disturbance. The sample is then washed with water thoroughly and dried. The grafted jute copolymer is isolated from a mixture of copolymer and homopolymer [poly(acrylonitrile), PAN] using dimethylformamide (DMF) by Soxhlet extraction so that homopolymer PAN is dissolved out and thus separated from the grafted polymer.

Estimation of Residual Lignin of NaClO_2 Oxidized (Bleached) Jute Sample

The defatted jute fiber is bleached (oxidized) with a variable concentration of NaClO_2 (3.5–35% on the

weight of the fiber). The known amounts of the bleached jute samples (3–6 mg), dried and powdered, are taken in a well-stoppered tube containing 10 mL of 25% v/v acetyl bromide in acetic acid. The tube is then kept in a 70°C water bath with intermittent shaking for 30 min. The sample is then cooled to 15°C and transferred to a 100 mL volumetric flask containing 9 mL of 2N NaOH and 50 mL of glacial acetic acid. One milliliter of 7.5M hydroxylamine hydrochloride is added to it. Finally, absorbance at 280 μm is recorded.¹⁵

Analysis of Grafted Samples

As evidence of grafting, some instrumental analyses have been carried out:

- (i) Scanning by scanning electron microscope (SEM): For SEM studies, the fiber samples were first coated with a thin layer of a gold-palladium alloy using a sputter coater and then observed with the secondary mode at a beam voltage of around 5 kV using a Cambridge S250 Model.¹⁶
- (ii) The structure of acrylonitrile (AN) graft copolymerization is confirmed by infrared (IR) spectroscopy: The structures of AN graft copolymerization of bleached jute along with gray and bleached jute fibers are confirmed by IR spectroscopy using a Shimadzu FTIR-8101 Model.
- (iii) Thermogravimetric analysis (TGA): Thermogravimetric and differential scanning calorimetric (DSC) analyses were carried out using a Mettler TG 50 and DSC 25 of TA 4000 system attached to a TC-11 microprocessor. The heating rate throughout the study was 10°C min⁻¹. All the measurements were made under a constant flow rate (150 mL min⁻¹) of nitrogen. For DSC measurements, samples were placed in an alumina crucible sealed with a pierced lid. During evaluation of differential thermogravimetry (DTG), the peak temperature, weight losses at each decomposition step, and amount of char left at 650°C were measured. The figure was computer-generated on an Epson Model PCx2 attached to a TC11-4000.

Percent grafting and grafting efficiency were calculated according to the following formula:

Table I Grafting of Jute Fiber with AN After Oxidation with Different Oxidizing Agents

Oxidation of Jute Fiber with	Grafting with AN	
	% Grafting	% Grafting Efficiency
NaClO ₂	26.30	6.73
KIO ₄	Nil	Nil
KMnO ₄	Nil	Nil
H ₂ O ₃	Nil	Nil
HNO ₃	Nil	Nil

Oxidized jute 1 g; KMnO₄ concn 0.02 mL⁻¹; liq. ratio 1 : 150; H₂SO₄ concn 1%; AN 5 mL; time 2 h; temp 50°C.

$$\% \text{ Grafting} = \frac{A - B}{B} \times 100$$

$$\% \text{ Grafting efficiency} = \frac{A - B}{C} \times 100$$

where *A* is the weight of the grafted sample after extraction with DMF; *B*, the weight of original bleached fiber; and *C*, the weight of total monomer used.

RESULTS AND DISCUSSION

Effect of Lignin of Jute Fiber on Grafting

Jute is basically a lignocellulosic fiber. It contains 13–14% lignin. It is known that the lignin content is the governing factor for the rate and yield of grafting of monomer onto the lignocellulosic substrate. The extent to which lignin interferes with the grafting reaction varies from one type of cellulosic substrate to another, depending largely on its chemical nature.¹⁷ The presence of lignin generally retards the polymerization rate and gives rise to prolong inhibition periods at higher lignin levels.¹⁸ Lignin is easily oxidized by most conventional oxidants. The reaction of lignin with the oxidant gives rise to the formation of a quinonoid structure which has pronounced retarding and/or inhibiting properties.¹⁸

The oxidized jute samples are grafted with AN and the results are reported in Table I. From Table I, it is observed that as the oxidant only sodium chlorite is effective for AN grafting onto jute. Sodium chlorite removes more lignin than does hydrogen peroxide and the formal reagents have been used for the delignification of jute. In an acid medium (at pH

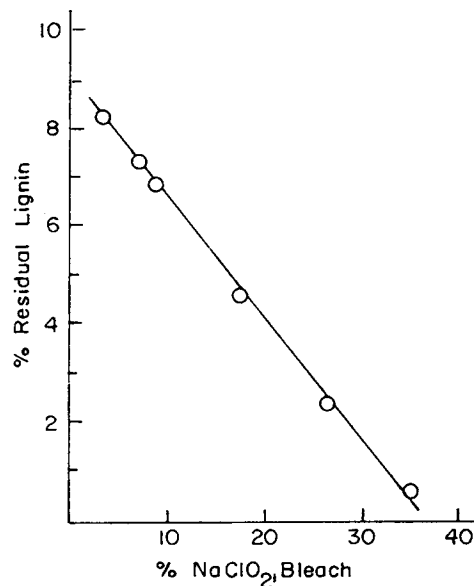


Figure 1 Residual lignin content of jute fiber after bleaching with different concentrations of sodium chlorite : liquor ratio 1 : 50; time 2 h; temperature 98°C; pH 4.

4), aqueous NaClO₂ produces mainly ClO₂ according to the equation



Chlorine dioxide is a lignin solubilizing agent and oxidizes the residual lignin and is reduced to the following equation in acid medium:

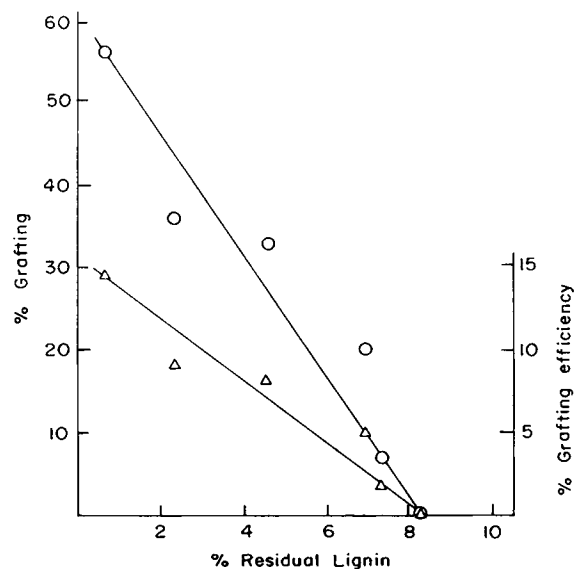
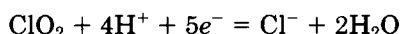


Figure 2 Relation between the lignin content of sodium chlorite bleached jute fiber and grafting: [KMnO₄] concentration 0.02 mL⁻¹; [H₂SO₄] concentration 1%; liq. ratio 1 : 150; temperature 50°C; time 2 h; AN 5 mL.

Table II Estimation of the Lignin Content of Jute Fiber After Bleaching with NaClO₂ and Polymer Grafting with AN Monomer

Bleaching with NaClO ₂ (%) (on Weight of Fiber)	Observed OD (A 280 μm)	Residual Lignin Content (%)	% Grafting	% Grafting Efficiency
3.50	54	8.26	Nil	Nil
7.00	48	7.34	6.84	1.75
8.75	45	6.88	19.97	5.08
17.50	30	4.59	32.92	8.36
26.25	15	2.29	36.30	9.26
35.00	4	0.61	57.65	14.65
Control	85	13.50	Nil	Nil

For bleaching: NaClO₂ at pH 4 with acetic acid–sodium acetate buffer; for grafting: KMnO₄ concn 0.02 mL⁻¹; liq. ratio 1 : 150; H₂SO₄ conc 1%; AN 5 mL; time 2 h; temp 50°C.



Therefore, treatment of jute with NaClO₂ yielded bleached jute through a process of oxidation whereby coloring matter and lignin are removed. At the same time, it is known that the oxidizing agent NaClO₂ is likely to bring about uncontrolled oxidation of the jute cellulose, producing mainly aldehyde groups (—CHO) on the C₂—C₃ position of the glucopyranose ring.¹⁹ In this connection, it may be mentioned that the other oxidizing agents are not at all effective to solubilize lignin for which graft copolymerization is ineffective, as reported in Table I.

Table III Relation Between KMnO₄ Concentration and Grafting

Concentration of KMnO ₄ (mL ⁻¹ × 10 ⁻⁵)	0.7% NaClO ₂ w/v Bleached Fiber	
	% Grafting	% Grafting Efficiency
31	—	—
69	—	—
95	—	—
130	0.69	0.18
160	5.69	1.40
190	6.01	1.50
220	6.78	1.70
250	17.19	4.36
500	31.12	8.00
1000	37.88	9.70
1500	38.99	10.12
2000	47.85	12.36

Bleached jute 1 g; liq. ratio 1 : 150; H₂SO₄ concn 1%; AN 5 mL; time 2 h; temp 50°C.

It is clear from the experimental evidence furnished in Figures 1 and 2 that graft copolymerization of a monomer onto jute depends on the lignin content of the jute fiber. From Figure 1 it is seen that the residual lignin content is inversely proportional to the extent of bleaching, and Figure 2 shows that the percent grafting and grafting efficiency both are inversely proportional to the residual lignin content of bleached jute fiber. It is clear from Table II that about 20% grafting can be achieved if about 50% lignin is being removed from the jute fiber by ClO₂ bleaching.

Effect of Initiator

Results showing the effect of the variation of the initiator (KMnO₄) concentration among the grafting parameters are shown in Table III and Figure 3. It is seen that percent grafting and grafting efficiency both increase gradually as the concentration of potassium permanganate is increased. During the experiment, it is observed that a considerable amount of homopolymer is formed when the initiator concentration is above 20 × 10⁻³ mL⁻¹, whereby the grafted product results in a gelled product, losing all fiber characteristics. The increased trend of percent grafting might be due to formation of a great number of grafting sites. With a further increase of permanganate concentration, the termination by Mn³⁺ ions might be prevalent, resulting in shorter grafted chains.

Effect of Temperature

Results related to the variation of temperature during grafting is shown in Figure 4. It is observed that

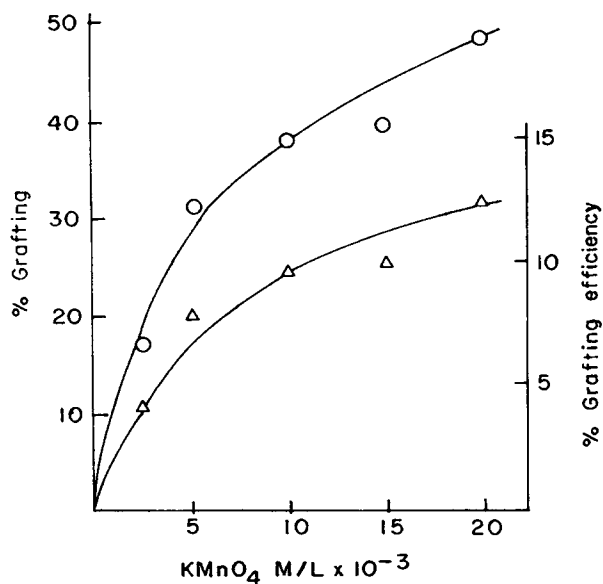


Figure 3 Optimum concentration of potassium permanganate as initiator for graft copolymerization of jute (0.7% w/v or 35% o.w.f. NaClO₂ bleached) with AN: liq. ratio 1 : 150; [H₂SO₄] concentration 1%; temperature 50°C; time 2 h; AN 5 mL.

the percent grafting and grafting efficiency both increase up to 50°C, and beyond that, both decrease sharply. It was reported earlier¹⁰ in work done on grafting with the KMnO₄-malonic acid system that grafting was not possible below 50°C. The grafting yield is being reduced.

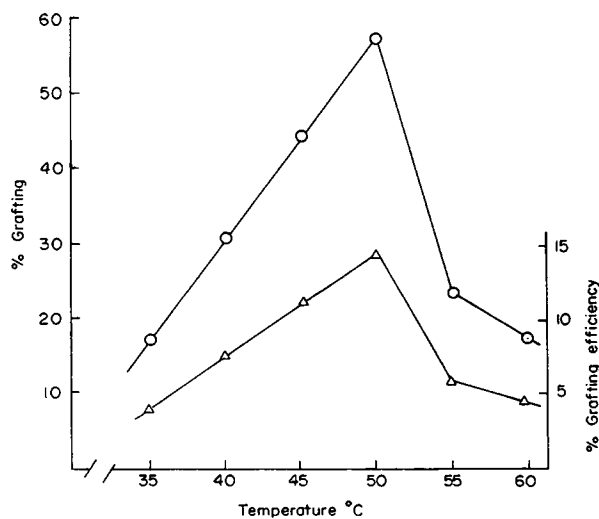


Figure 4 Optimum temperature for graft copolymerization of jute (0.7% w/v or 35% o.w.f. NaClO₂ bleached) with AN: [KMnO₄] concentration 0.02 mL⁻¹; [H₂SO₄] concentration 1%; liq. ratio 1 : 150; time 2 h; AN 5 mL.

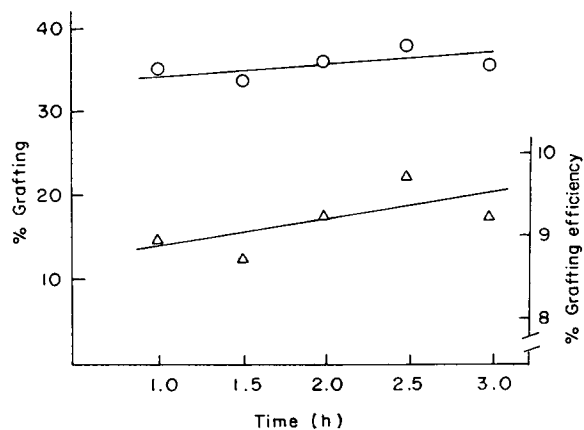


Figure 5 Optimum time of reaction for graft copolymerization of jute (0.7% w/v or 35% o.w.f. NaClO₂ bleached) with AN: [KMnO₄] concentration 0.02 mL⁻¹; [H₂SO₄] concentration 1%; liq. ratio 1 : 150; temperature 50°C; AN 5 mL.

Effect of Time

Variation of reaction time during grafting is reported in Figure 5. It appears from the figure that the dependence of percent grafting and grafting efficiency both are more or less equal for time span between 1 and 3 h.

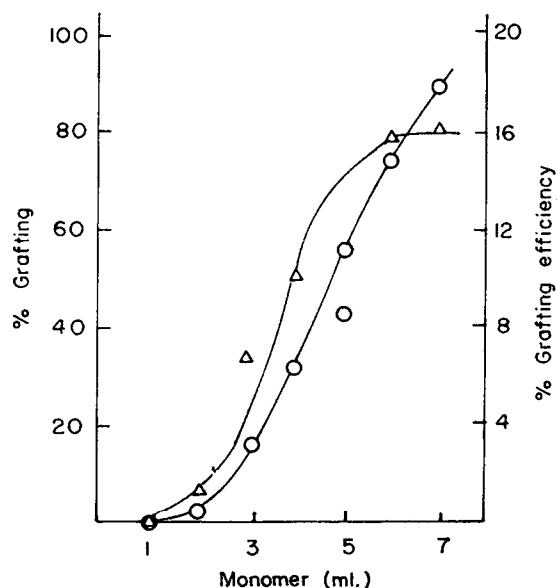


Figure 6 Variation of monomer concentration (AN) with respect to grafting of jute (0.7% w/v or 35% o.w.f. NaClO₂ bleached), [KMnO₄] concentration 0.02 mL⁻¹; [H₂SO₄] concentration 1%; liq. ratio 1 : 150; time 2 h; temp 50°C.

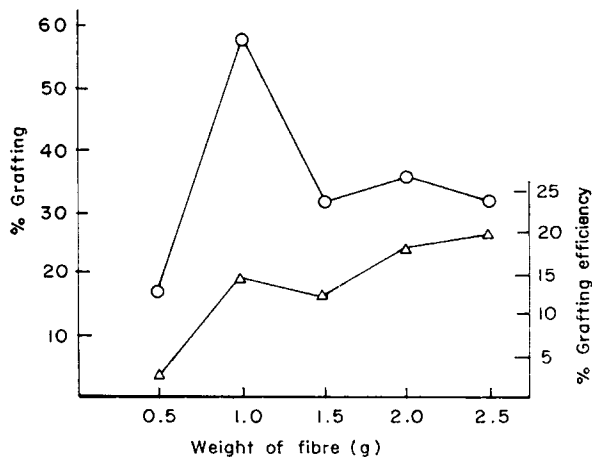


Figure 7 Relation between the variation of fiber weight and grafting: $[KMnO_4]$ concentration 0.02 mL^{-1} ; $[H_2SO_4]$ concentration 1%; liq. ratio 1 : 150; time 2 h; temp 50°C ; AN 5 mL.

Effect of Monomer

Results related to the variable amount of monomer used in the grafting reaction are shown in Figure 6. It is seen that percent grafting and grafting efficiency both increase steadily with increase of the amount of the monomer. It was also found during the experiment that a high amount of homopolymer is formed with a higher amount of monomer used. The increasing trend of percent graft yield with increase

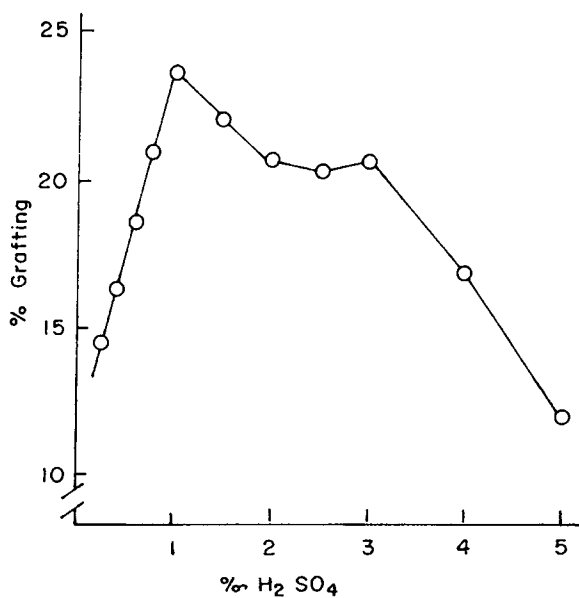


Figure 8 Effect of sulfuric acid concentration on grafting: $[KMnO_4]$ concentration 0.02 mL^{-1} ; liq. ratio 1 : 150; time 2 h; temp 50°C ; AN 5 mL.

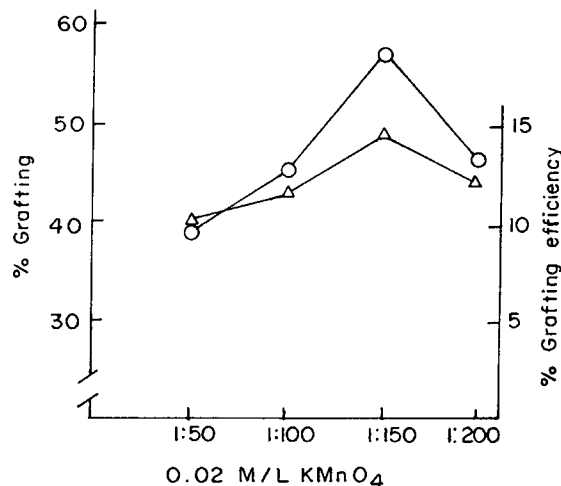


Figure 9 Optimization of liquor ratio (fiber : liq.) of initiator $KMnO_4$ for grafting: $[KMnO_4]$ concentration 0.02 mL^{-1} ; $[H_2SO_4]$ concentration 1%; time 2 h; temp 50°C ; AN 5 mL.

of monomer concentration could be associated with the gel effect.

Effect of Variable Amount of Jute

The results are shown in Figure 7. The experiments were conducted using 0.5–2.5 g of bleached jute. It is observed that percent grafting and grafting efficiency both appear optimum for 1.0 g of jute, and beyond that, the same are lower identically.

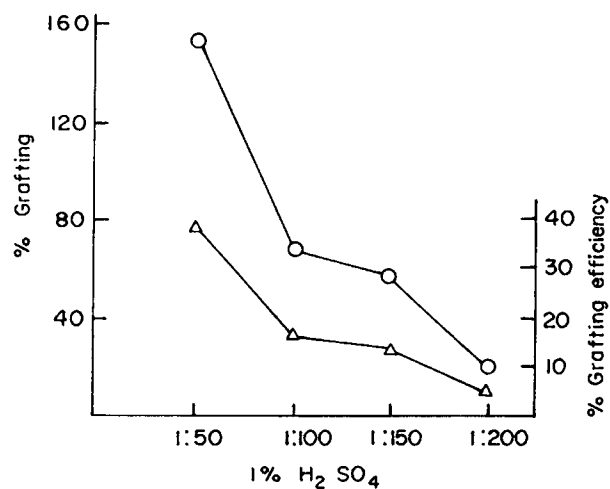


Figure 10 Optimization of liquor ratio (fiber : liq.) of H_2SO_4 for grafting: $[KMnO_4]$ concentration 0.02 mL^{-1} ; $[H_2SO_4]$ concentration 1%; time 2 h; temp 50°C ; AN 5 mL.

Table IV Grafting in Presence of Solvents

Solvents	Concentration % v/v	% Grafting	% Grafting Efficiency
DMF	3	15.13	3.87
H · CO · N(CH ₃) ₂	6	9.84	2.50
	9	4.61	1.18
Ethyl alcohol	3	6.48	1.60
C ₂ H ₅ OH	6	1.82	0.45
	9	—	—

Bleached jute 1 g; KMnO₄ concn 0.02 mL⁻¹; liq. ratio 1 : 150; H₂SO₄ concn. 1%; AN 5 mL; time 2 h; temp 50°C.

Effect of Sulfuric Acid Concentration on Grafting

Results are presented in Figure 8 showing the effect of sulfuric acid concentration on grafting. It is observed that the percent grafting is found optimum at 1% acid concentration and then it is decreased gradually as the acid concentration is increased.

Effect of Liquor Ratio (Fiber : Liquor) of Initiator KMnO₄ and H₂SO₄

The results are shown in Figures 9 and 10. It is observed from Figure 9 that percent grafting and grafting efficiency both gradually increase with increase of the liquor ratio (fiber : liquor) of the initiator solution (20×10^{-3} mL⁻¹ KMnO₄) and 1 : 150 is found optimum, beyond which both decrease.

Table V Grafting in Presence of Metal Ions

Metal Salts	Concentration (mML ⁻¹)	% Grafting	% Grafting Efficiency
CuSO ₄	2.5	12.66	3.24
	5.0	12.26	3.13
	7.5	10.37	2.64
	10.0	8.72	2.22
FeCl ₃	2.5	14.36	3.67
	5.0	14.13	3.61
	7.5	14.61	3.73
	10.0	12.18	3.11
LiOH	2.5	14.19	3.62
	5.0	16.06	4.09
	7.5	16.38	4.19
	10.0	16.38	4.19
Control	—	14.26	3.64

Bleached jute 1 g; KMnO₄ concn 0.02 mL⁻¹; liq. ratio 1 : 150; H₂SO₄ concn 1%; AN 5 mL; time 2 h; temp 50°C.

Similarly, Figure 10 shows that percent grafting and grafting efficiency both decrease with increase of the liquor ratio (1 : 50 to 1 : 200) of 0.0167 mL⁻¹ H₂SO₄ (= 1%). In the case of the lower liquor ratio (1 : 50) of H₂SO₄, it was observed that a high amount of homopolymer is formed and that the percent grafting and grafting efficiency both are too high.

Effect of Solvents and Metal Salts on Grafting

The graft yield was solvent-dependent. Two solvents were taken, one dimethylformamide (DMF), which

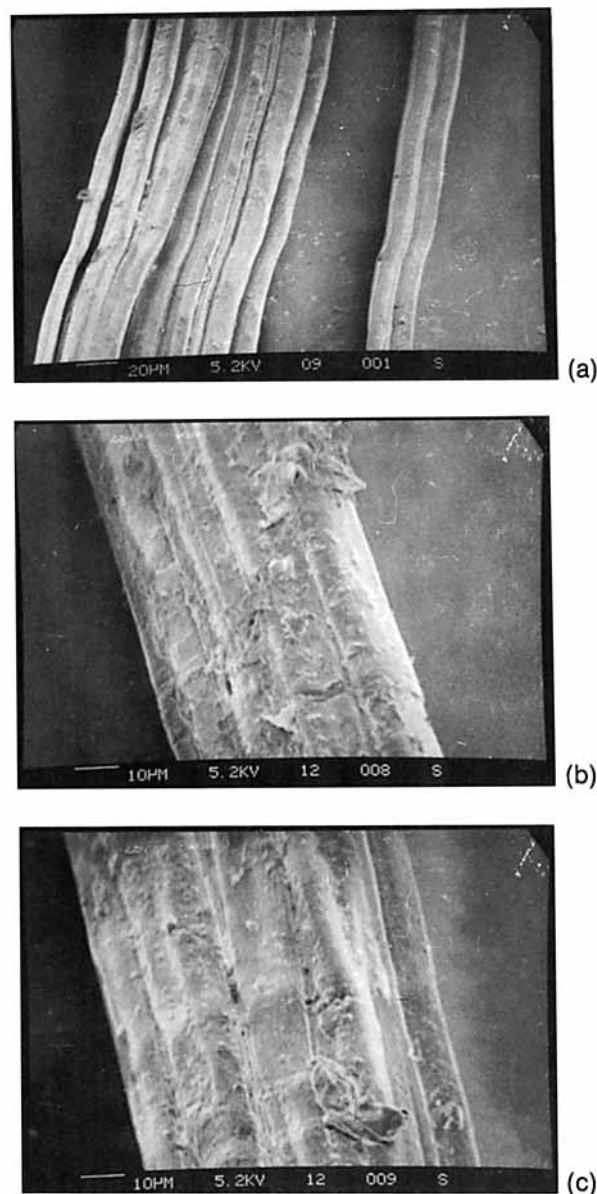


Figure 11 Scanning electron micrographs of bleached jute and grafted jute fiber grafted with AN monomer.

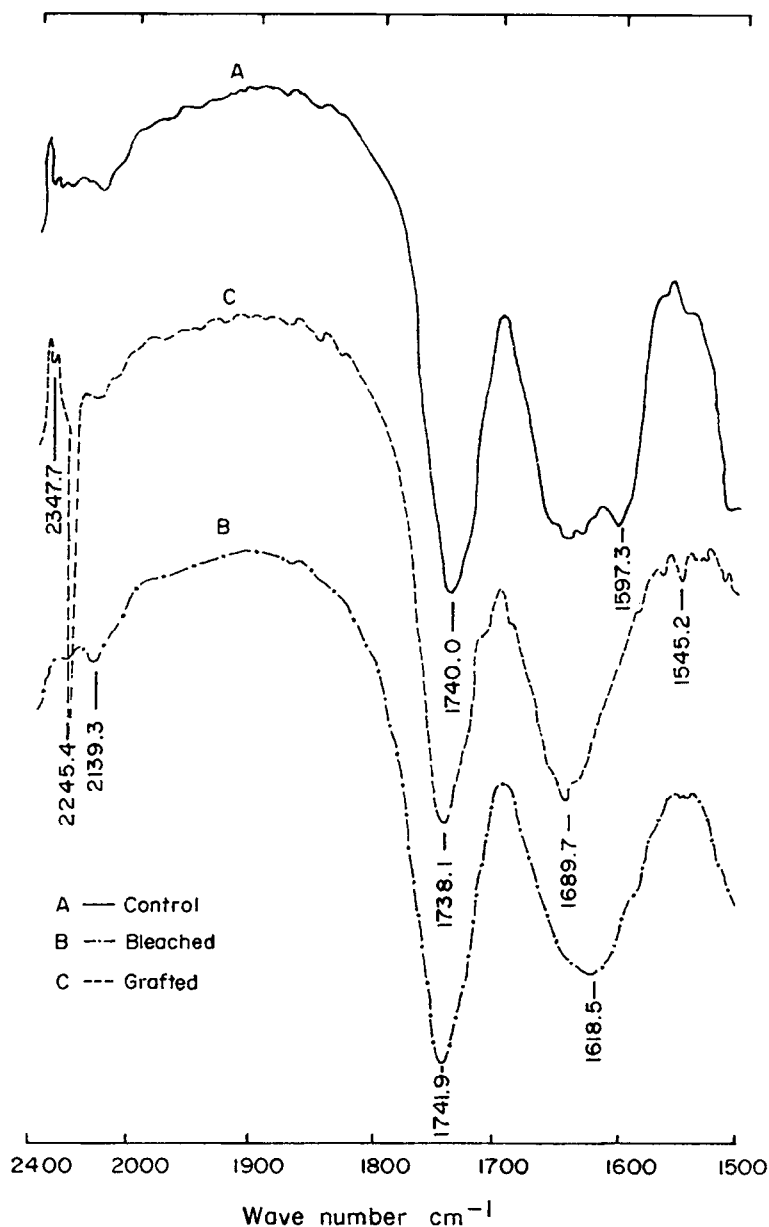


Figure 12 FTIR spectrophotographs of (A) control jute, (B) bleached jute, and (C) grafted jute fiber grafted with AN monomer.

is a solvent for the homopolymer, and the other, ethanol, a nonsolvent for the homopolymer. The results are shown in Table IV. It is observed that DMF > control > ethanol. Again, with increase in concentration of the solvent, the grafted yield decreased considerably in both cases. The effect of neutral salts on grafting is presented in Table V. It is seen that the addition of an equal concentration of the neutral salts in the grafting reaction followed the order LiOH > FeCl₃ > control > CuSO₄.

Evidence of Grafting

SEM Studies

Comparison of scanning electron micrographs of the vinyl monomer-treated (grafted) and -untreated samples are shown in Figure 11. It is seen that the deposition of polymer onto the jute fiber is clear compared to the untreated fiber. The deposition of the polymer onto the fiber makes a film and it fills

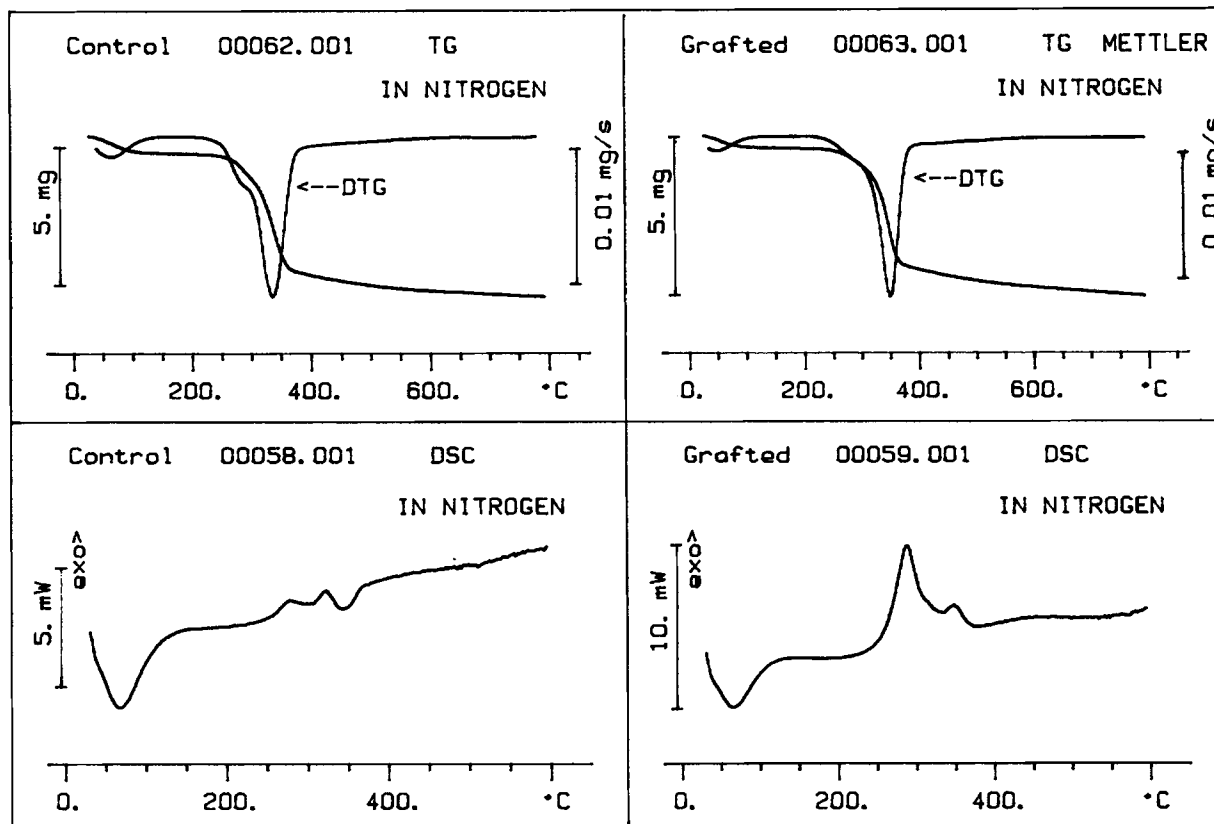


Figure 13 TG, DTG, and DSC curves of control (bleached) and grafted jute fiber in nitrogen atmosphere.

the gaps between the fibrils. So, the difference of fiber surface structure is prominent.

IR Spectroscopy

The infrared (IR) spectra of the three samples of jute, (i) dewaxed, (ii) dewaxed and oxidized with NaClO_2 , and (iii) dewaxed, oxidized, and grafted jute, are shown in Figure 12. As expected, the spectra for

the first two cases, i.e., defatted and bleached, are more or less similar in nature. They show characteristic absorption bands of hydroxyls and carboxyls around $3 \mu\text{m}$ (3334 cm^{-1}) and $5.5\text{--}6.5 \mu\text{m}$ ($1690\text{--}1750 \text{ cm}^{-1}$), respectively, whereas for the IR spectra for grafted jute, an additional peak at $2240\text{--}2250 \text{ cm}^{-1}$ ($4.1\text{--}4.2 \mu\text{m}$) is visible which is characteristic for the nitrile group corresponding to AN grafted onto jute. In the case of grafted jute, the removal of

Table VI Results of TGA of Control (Bleached) Jute and Grafted Jute in Nitrogen

Sample	Degradation Temperature (°C)	Weight Loss (%)	Residual at 650°C (%)
Control (bleached) jute	64.0	9.08	
	295.7	10.25	18.82
	337.0	60.14	
Grafted jute	52.0	6.81	
	299.7	7.17	31.19
	346.0	53.95	

Table VII Results of DSC of Control (Bleached) and Grafted Jute in Nitrogen

Sample	Peak Temperature (°C)	Nature of Peak
Control (bleached) jute	68.4	endo
	278.7	exo
	322.8	exo
Grafted jute	64.4	endo
	287.2	exo
	352.2	exo

the carboxyl peak indicated the possible site for grafting. This eventually proves that the jute is being grafted with AN.

Thermogravimetric Analysis: Characterization

The TG, DTG, and DSC curves for control (bleached) and grafted jute fiber are shown in Figure 13 and the results are summarized in Tables VI and VII. The DTG curve of control (bleached) jute fiber shows an initial weight loss (9.08%) at 64°C due to moisture loss (Fig. 13 and Table VI). In the pyrolysis temperature range, the first peak (shoulder) at 295.7°C is due to hemicellulose decomposition and the second peak at 337°C is due to α -cellulose decomposition. Maximum decomposition occurs at the second pyrolysis step (60.14%). In the case of grafted jute fiber, the maximum decomposition occurs at higher temperature (346°C) with less weight loss (53.95%) than that of the control jute fiber. Residue left at 650°C for grafted jute fiber is higher than that of control jute. DSC curves of control and grafted jute fiber show one endothermic and two exothermic peaks (Fig. 13 and Table VII). In the case of grafted jute fiber, both exothermic peak temperatures are higher than that of control jute. All these experimental results suggested that the grafted jute fiber is thermally more stable than is the control (bleached) jute fiber.

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