

Graft Copolymerization of Acrylonitrile onto Acetylated Jute Fibers

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Synopsis

Graft copolymerization of acrylonitrile (AN) onto acetylated chemically modified jute was carried out in the temperature range 40–60°C using V^{5+} -cyclohexanone redox initiator system. The effects of temperature, time, concentrations of metal ion (V^{5+}), monomer (AN), cyclohexanone, some inorganic salts, and organic solvents on percent grafting have been studied. IR spectra of acetylated chemically modified jute and grafted jute have been taken, and their characteristic bands have been identified. Grafting has improved the thermal stability and also the lightfastness rating of jute fibers dyed with basic dyes.

INTRODUCTION

The grafting of vinyl monomers onto cellulose and other cellulosic fibers has been studied extensively by various research workers.¹⁻⁵ Much less has been reported, however, regarding graft copolymerization of jute fibers. Chemically, jute is a lignocellulosic fiber. Jute fiber is facing tough competition from the synthetic fibers as the latter often offer certain advantages in terms of many physical properties, durability, and production economics. Graft copolymerization of vinyl monomers onto jute fiber has, therefore, been receiving considerable attention in recent years to incorporate the desired properties. Ceric-ion-initiated graft copolymerization of methyl methacrylate (MMA)⁶ and AN⁷ onto jute fibers have been studied. Ray⁸ has reported some X-ray diffraction studies on MMA-grafted jute fibers. Efforts have also been made to modify jute fibers by graft copolymerization of vinyl monomers using ionizing radiation.^{9,10} Agarwal and Sreenivasan¹¹ have studied graft copolymerization of vinyl monomers onto jute fibers using gamma rays. Photograft copolymerization of MMA onto bleached jute fibers using ferric sulfate as initiator in limited aqueous system has also been reported.¹² Graft copolymerization of MMA onto chemically modified jute fibers using $KMnO_4$ -malonic acid redox system has been reported by Tripathy et al.¹³ In our previous communications, we have reported the grafting of MMA onto jute fibers using redox systems consisting of V^{5+} and cyclohexanone or cyclohexanol^{14,15} and peroxydisulfate-thiourea.¹⁶ Redox-initiated graft copolymerization of MMA onto different chemically modified jute fibers like defatted jute, delignified jute, chemically modified jute, and acetylated jute has also been reported by Mohanty and Singh.¹⁷

The present investigation reports the graft copolymerization of AN onto acetylated chemically modified jute fibers using V^{5+} -cyclohexanone redox initiator system.

EXPERIMENTAL

Jute fibers (obtained from Konark Jute Mills Ltd, Orissa, India) were lightly combed for a long period to make them free from impurities and cut into small bundles of about 8×10 in. in length. The bundles were first subjected to soxhlet extraction with acetone for about 24 h, followed by washing with cold distilled water and air drying. The fibers were then extracted in a 1:2 mixture of alcohol and benzene for 14 h to dewax the sample, then treated with 17.5% NaOH for 30–45 min, and thoroughly washed with water and air-dried. After alkali treatment, fibers were soaked with ethylenediamine for about 30 min and washed. Again they were treated with 60% $ZnCl_2$ solution at $20^\circ C$ for 4 h, washed thoroughly, and air-dried. Effective swelling of the fibers could be possible by employing the last two procedures. These chemically modified jute fibers were subjected to acetylation by the method as reported by Gopal et al.¹⁸ About 2 g of chemically modified jute fibers were soaked in glacial acetic acid for 1 h at 20 – $25^\circ C$, decanted, and then soaked in 50 mL of acetic anhydride containing one drop of concentrated sulfuric acid for 5 min. The fibers were then filtered over Buchner funnel, thoroughly washed with distilled water till the fibers became free from acid, and finally the fibers were air-dried. Ten percent weight gain was possible due to partial acetylation. The partially acetylated, chemically modified jute fibers thus prepared were then kept ready for grafting.

Purified monomer (acrylonitrile), vanadium solution (prepared from ammonium meta-vanadate), and sulfuric acid (AnalaR) were used for the grafting process.

Before initiating graft copolymerization, the acetylated jute fibers were soaked with appropriate quantity of monomer for about 5 min. The graft copolymerization was carried out in pyrex flasks with $B_{24/29}$ standard joints equipped with gas inlet and outlet tubes for nitrogen. Appropriate quantity of reaction mixture containing jute fiber, monomer, cyclohexanone, and conductivity water were taken in the reaction vessels. The mixture and $V(V)$ solution were separately deaerated by passing nitrogen for 20 min. Then the required amount of $V(V)$ solutions were poured into the vessels containing the reaction mixture. The reactions were carried out for specific time at three temperatures 40 , 50 , and $60^\circ C$. After the specified time interval, the reaction was arrested by quenching the vessel in ice-cold water. The grafted samples were washed well by extraction with several portions of water, given a light soaping to remove the loosely adhering polymer, washed, and dried. It was also observed that, on further extraction with dimethyl formamide (DMF) for about 24 h at $30^\circ C$, the grafted samples showed a negligible weight loss. This type of observation has also been reported by Hebeish and Mehta.¹⁹ The percent grafting was calculated on dry weights, determined by storing the materials in the weighing bottles over P_2O_5 at room temperature in a vacuum desiccator until a constant weight was obtained.

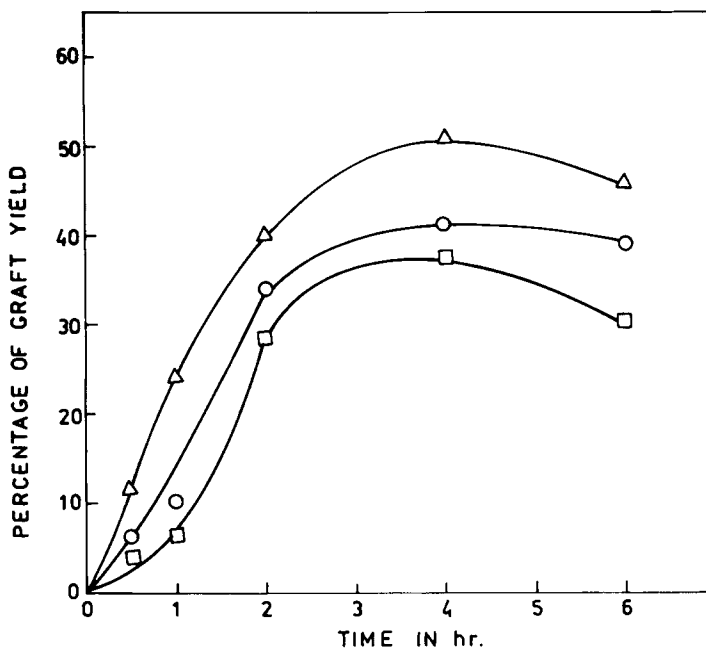


Fig. 1. Effect of reaction time: jute = 0.1 g; [AN] = 0.7513 mol L⁻¹; [V⁵⁺] = 0.05 mol L⁻¹; [cyclohexanone] = 0.241 mol L⁻¹; [H₂SO₄] = 0.20 mol L⁻¹; (O) = 40°C; (Δ) = 50°C; (□) = 60°C.

RESULTS AND DISCUSSION

Effect of Time on Graft Yield

Figure 1 shows the effect of time on graft yield at three different temperatures (40, 50, and 60°C). In all these cases, the graft yield has been found to increase steadily with time, but, after 4 h, it decreases to some extent. This may be attributed to the partial dissolution of the grafted fiber on prolonged exposure to the temperature of 40–60°C. Thus optimum graft yield is obtained within 4 h. Huque et al.,⁶ while studying the ceric-ion-initiated grafting of MMA onto jute fiber, have reported that, at each temperature range, the efficiency of grafting appears to rise with time to a certain limit and then it falls. Similar observations have also been reported by Tripathy et al.¹³ and by us^{14–17} while studying graft copolymerization of MMA onto jute fibers using different redox initiator systems.

Effect of Metal Ion Concentration

The effect of variation of V⁵⁺ concentration on percentage of graft yield is shown in Figure 2. It was observed that, under the present reaction conditions, V⁵⁺ solution does not alone initiate the graft copolymerization reaction. On coupling with a suitable substrate only the metal ion V⁵⁺ initiates the graft copolymerization reaction. Here V⁵⁺ coupled with cyclohexanone constitutes the redox initiator system.

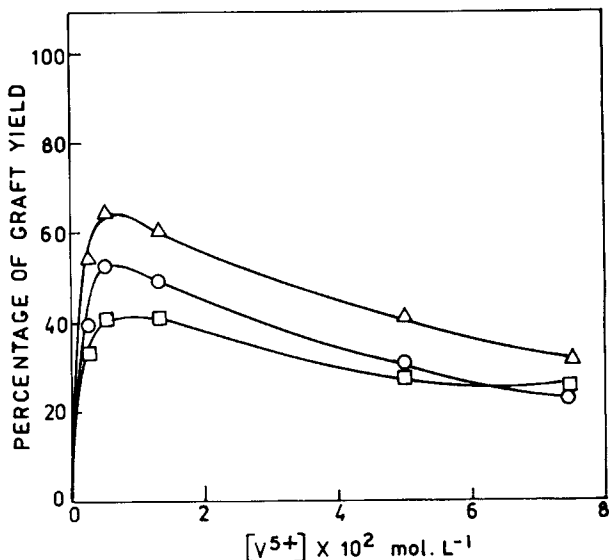


Fig. 2. Effect of metal ion concentration: jute = 0.1 g; [AN] = 0.7513 mol L⁻¹; [cyclohexanone] = 0.241 mol L⁻¹; [H₂SO₄] = 0.20 mol L⁻¹; time = 4 h; (○) = 40°C; (△) = 50°C; (□) = 60°C.

It is clear from Figure 2 that, with the increase of [V⁵⁺] from 0.004 to 0.075 mol L⁻¹, the percentage of graft yield decreases considerably. So the optimum concentration of V⁵⁺ for grafting of AN onto acetylated jute fibers was found to be 0.004 mol L⁻¹, i.e., low initiator concentration. Similar observations, i.e., maximum graft yield at low initiator concentrations (0.005–0.006 mol L⁻¹) have been made in cotton cellulose grafting.²⁰ Optimum concentration of V⁵⁺ for MMA grafting onto jute fiber as 0.005 mol L⁻¹ has also been reported by us.¹⁵

Effect of Cyclohexanone Concentration

The effect of variation of cyclohexanone concentration on percentage of grafting at three different temperatures (40, 50, and 60°C) is shown in Figure 3. It is observed that, at all the temperatures, the graft yield increases by increasing the concentration of cyclohexanone from 0.048 to 0.298 mol L⁻¹ and thereafter decreases. The decreasing trend in percent grafting after certain optimum concentration of cyclohexanone is probably due to the fast rate of termination and/or formation of radical scavenger at higher cyclohexanone concentrations. Similar observations have also been reported while studying the effect of various organic solvents on jute grafting.^{13–15}

Effect of Monomer Concentration

The effect of variation of monomer (AN) concentration on percentage of graft yield is shown in Figure 4. The percentage of graft yield increases with increase of monomer concentration from 0.30 to 1.05 mol L⁻¹. A similar type of observation has also been reported by Huque et al.⁶ and Trivedi and Mehta⁷ while reporting ceric-ion-initiated graft copolymerization of MMA and

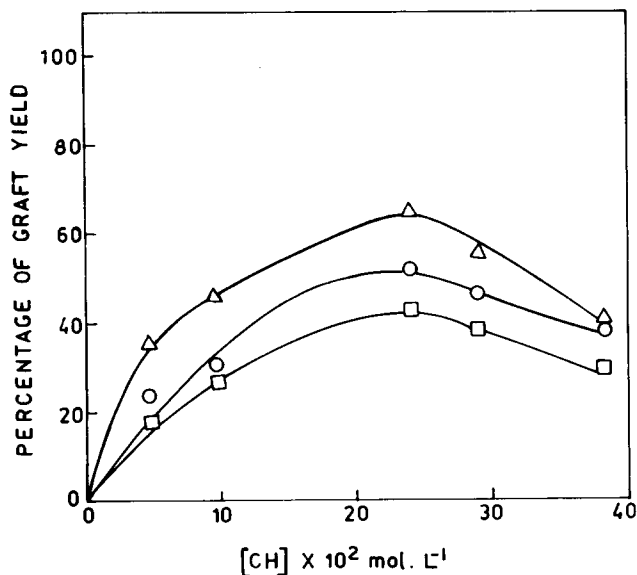


Fig. 3. Effect of cyclohexanone concentration: jute = 0.1 g; [AN] = 0.7513 mol L⁻¹; [V⁵⁺] = 0.004 mol L⁻¹; [H₂SO₄] = 0.20 mol L⁻¹; time = 4 h; (○) = 40°C; (Δ) = 50°C; (□) = 60°C.

AN onto jute fibers, respectively. However, in the case of grafting of MMA onto jute fibers using KMnO₄-malonic acid¹³ and V⁵⁺-cyclohexanol¹⁵ redox initiator systems, the percentage of graft yield was found to increase with increase of monomer concentration up to an optimum value beyond which it decreased.

Effect of Temperature

The effect of temperature on percentage of graft yield is shown in Figures 1-4. It is observed that the percentage of graft yield increases with rise of temperature from 40 to 50°C and then falls with further increase of temperature to 60°C. Again it is observed from Figure 1 that, within each temperature range studied, the percentage of graft yield appears to rise with time up to 4 h and then it falls. Thus, under the present reaction conditions, the maximum percentage of graft yield could be achieved at 50°C within 4 h.

Effect of Reaction Medium

The reaction medium plays an important role in the graft copolymerization reaction. All the graft copolymerization reactions have been carried out in aqueous sulfuric acid medium at the desired temperature. The graft yield almost remains constant with the variation of sulfuric acid concentration from 0.04 to 0.40 mol L⁻¹. The graft yield follows the following order with the solvents when added in equal proportions (5% v/v): control > acetone > DMF > methanol > dioxane. It is observed that all the solvents depress the graft yield. Similarly the effect of some inorganic salts when added in equivalent molar concentrations follows the order: control > NaCl > MnSO₄ > K₂SO₄ > CuSO₄. All the salts depress the percentage of graft yield and

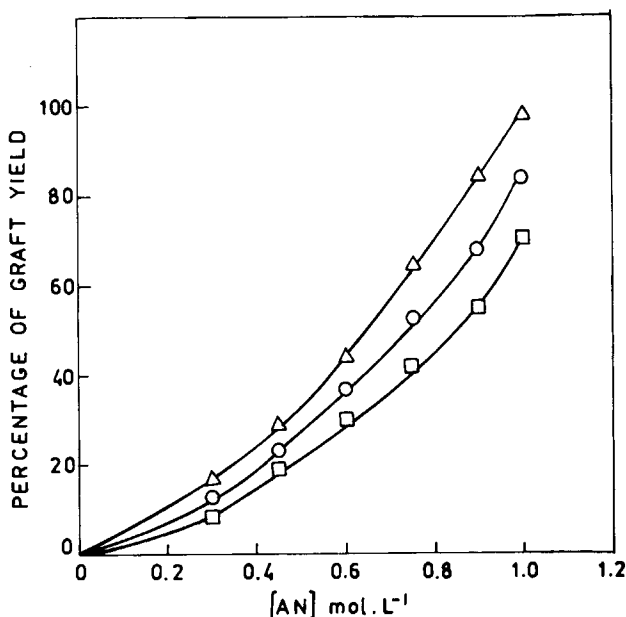


Fig. 4. Effect of monomer concentration: jute = 0.1 g; $[V^{5+}] = 0.004 \text{ mol L}^{-1}$; [cyclohexanone] = 0.241 mol L⁻¹; $[H_2SO_4] = 0.20 \text{ mol L}^{-1}$; time = 4 h; (○) = 40°C; (△) = 50°C; (□) = 60°C.

TABLE I^a

| Solvent 5% (v/v) | Effect of salt and solvent | | | Effect of sulfuric acid | |
|---------------------|----------------------------|-------------------------------------|---------------|---------------------------------------|---------------|
| | % Grafting | [Salt] = 0.1 mol L ⁻¹ | % Grafting | $[H_2SO_4]$ (mol L ⁻¹) | % Grafting |
| Control | 65.1 | Control | 65.1 | 0.40 | 60.3 |
| Acetone | 60.3 | NaCl | 59.8 | 0.10 | 63.2 |
| DMF | 55.7 | CuSO ₄ | 10.2 | 0.20 | 64.6 |
| Methanol | 45.5 | MnSO ₄ | 42.7 | 0.30 | 62.8 |
| Dioxane | 29.9 | K ₂ SO ₄ | 31.4 | 0.40 | 61.7 |

^a Jute = 0.1 g; $[AN] = 0.7513 \text{ mol L}^{-1}$; $[V^{5+}] = 0.004 \text{ mol L}^{-1}$; [cyclohexanone] = 0.241 mol L⁻¹; $[H_2SO_4] = 0.20 \text{ mol L}^{-1}$; time = 4 h; temp = 50°C.

CuSO₄ depresses the graft yield considerably. Table I reveals the above results. Lowering of graft yield due to the addition of some organic solvents may be due to the termination of grafted radical of jute via chain transfer. The lower percentage of graft yield than the control condition due to the addition of some salts may be attributed to the ionic dissociation of the added electrolyte which interferes with the usual polymerization reaction, resulting in the premature termination of the growing chains.

CHARACTERIZATION OF THE GRAFTED FIBERS

Infrared Spectra

IR spectra of the acetylated chemically modified jute and AN-grafted acetylated chemically modified jute have been recorded on a Perkin-Elmer 337

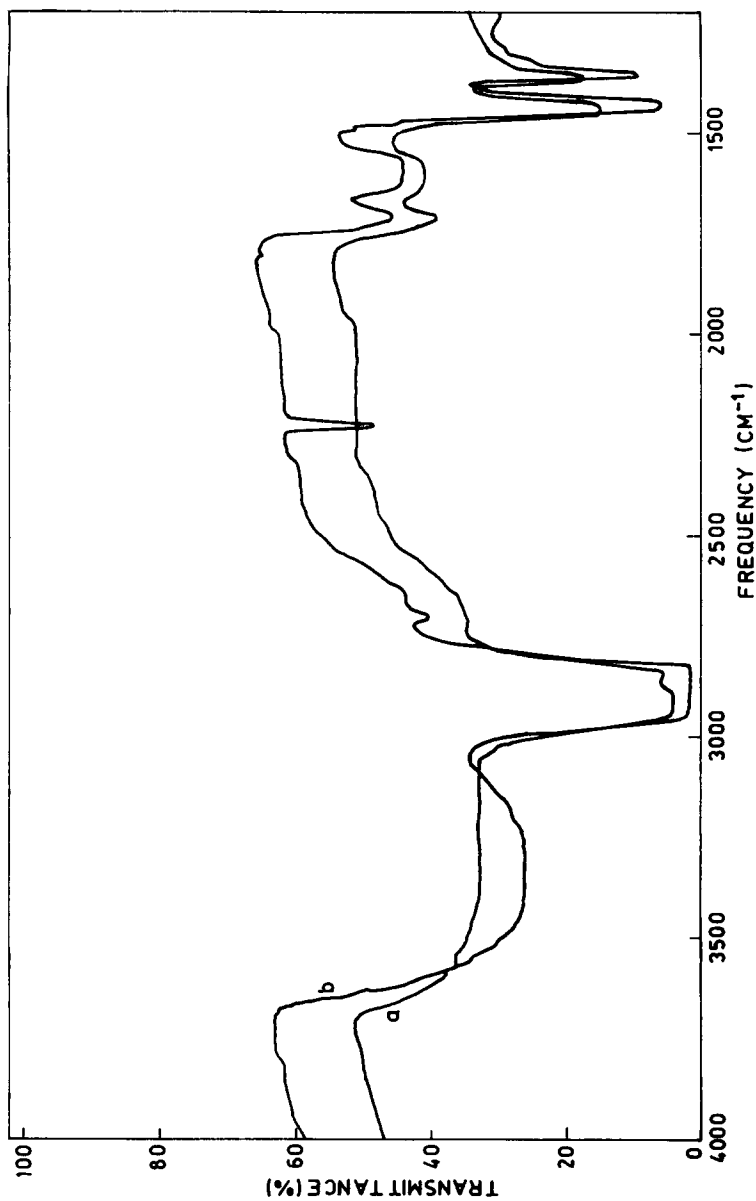


Fig. 5. (a) IR spectra of acetylated jute fibers (in nujol); (b) IR spectra of AN-grafted acetylated jute fibers (in nujol).

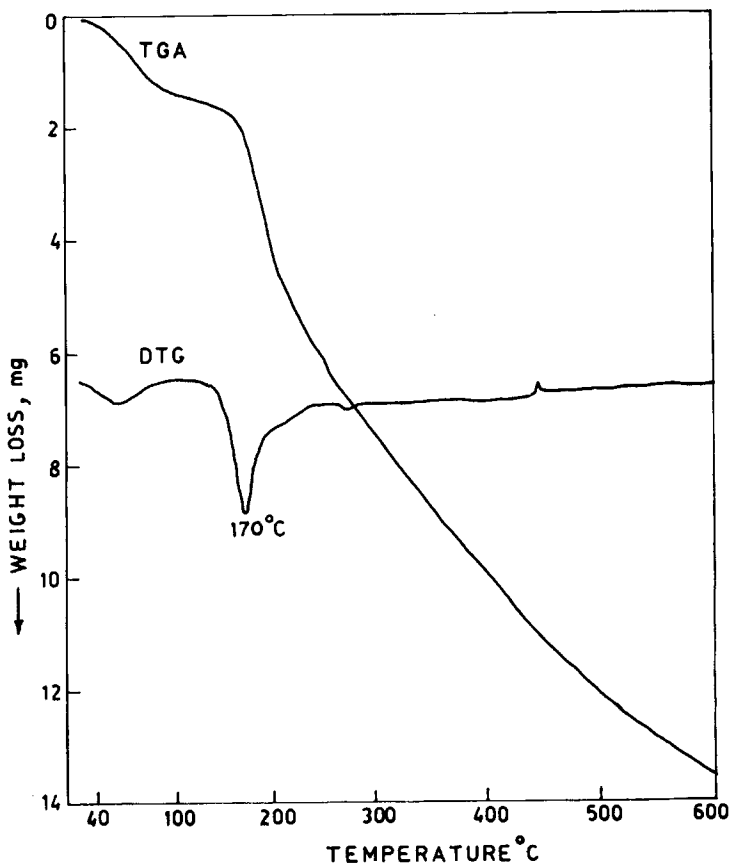


Fig. 6. TGA and DTG curves of acetylated chemically modified jute fibers.

spectrophotometer and are shown in Figures 5(a) and 5(b), respectively. From Figure 5(a) it is observed that the ungrafted acetylated jute shows the characteristic broad absorption band of hydroxyl around 3400 cm^{-1} and of ester group (due to partial acetylation) at about 1730 cm^{-1} . However, the spectrum of AN-grafted acetylated jute shows an additional peak of nitrile group at about 2240 cm^{-1} , thereby confirming the occurrence of grafting. Similar observations in IR spectra have also been reported by Trivedi and Mehta⁷ in grafting AN onto jute fibers.

Thermal Decomposition Studies

The thermal behavior of acetylated chemically modified jute and AN-grafted acetylated jute fibers are examined through TGA and DTG curves which were recorded on DT30 Shimadzu (Japan) thermal analyzer. The TGA and DTG curves of ungrafted jute, i.e., acetylated chemically modified jute, and AN-grafted acetylated jute fibers (GY = 30.5 and 65.1%) are shown in Figures 6–8. In case of ungrafted acetylated jute the maximum decomposition temperature (T_D) was found out to be 170°C . As a result of grafting, the thermal stability of jute was found to be enhanced considerably. In the case of AN-grafted

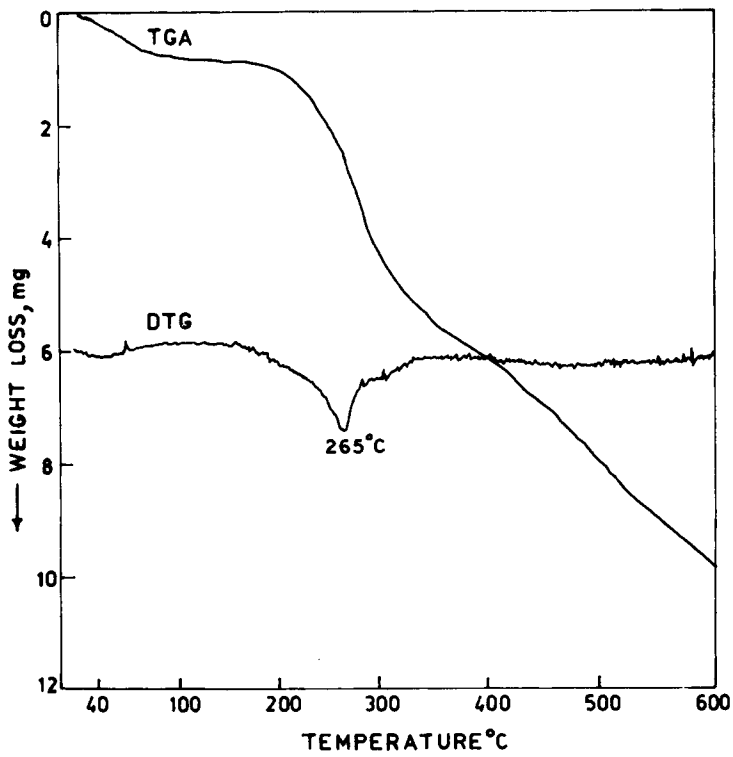


Fig. 7. TGA and DTG curves of AN grafted acetylated jute fibers (GY = 30.5%).

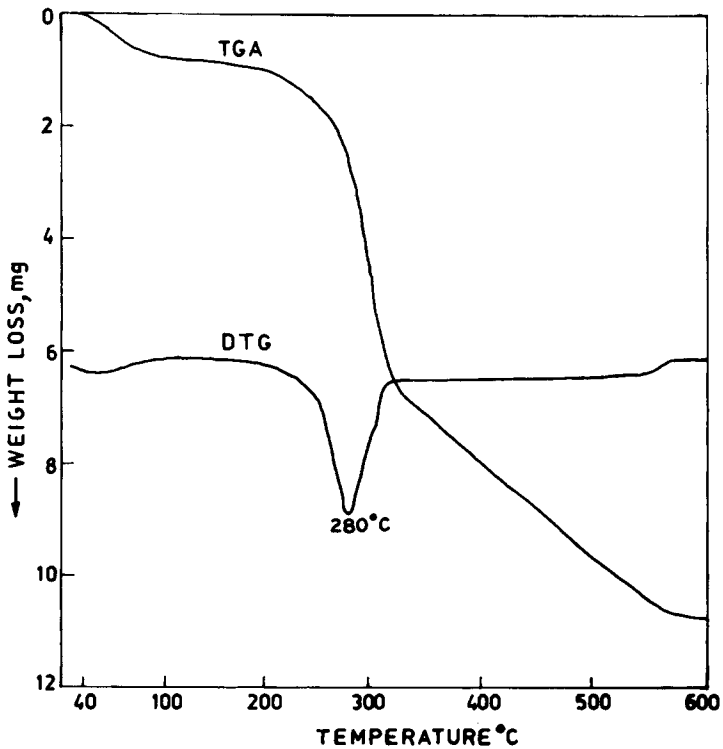


Fig. 8. TGA and DTG curves of AN grafted acetylated jute fibers (GY = 65.1%).

TABLE II
Light Fastness Data of Jute Dyed with Rhodamine B

| Sample particulars | Fastness to light (rating) |
|---|----------------------------|
| Chemically modified jute | 3 |
| Acetylated chemically modified jute | 2 |
| AN grafted acetylated chemically modified jute fibers | 4-5 |

acetylated chemically modified jute (GY = 30.5%), the maximum decomposition temperature was found out to be 265°C. Again it is observed that the thermal stability of AN-grafted acetylated chemically modified jute increases as the percentage of graft yield increases. From Figure 8, it is observed that AN-grafted jute (GY = 65.1%) shows the maximum decomposition temperature (T_D) at about 280°C.

Dyeability Property of Grafted Jute Fibers

The dyeing of the fibers has been carried out with a basic dye Rhodamine B, by a standard method of jute dyeing. The results are shown in Table II.

It is observed that the light fastness rating of dyed AN grafted acetylated jute is higher by about 3 units from that of ungrafted acetylated jute. Again by acetylation of the chemically modified jute the light fastness rating of the fiber decreases by one unit. The dye uptake might be reduced after acetylation because of the protection of free hydroxyl groups of jute.¹⁸ Increase in light fastness rating as a result of grafting of AN⁷ and MMA¹⁵ onto jute has also been reported earlier.

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