Graft Copolymerization of Acrylonitrile onto Jute Fibers (Studies on Ce(IV)-Hippuric Acid Redox System)

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Synopsis

Graft copolymerization of acrylonitrile (AN) onto chemically modified bleached jute fibers was studied using Ce(IV)-hippuric acid redox initiator system. The effects of time, temperature, concentration of monomer (AN), metal ion (Ce^{4+}), hippuric acid, sulfuric acid, and amount of jute fiber on graft yield have been studied. The effects of some organic solvents and inorganic salts on graft yield have also been studied. Infrared spectra of chemically modified bleached jute and grafted jute have been taken and their characteristic bands have been identified. More than 90% graft yield could be achieved with the present system.

INTRODUCTION

Although much research has been done on graft copolymerization of vinyl monomers onto cellulose and other textile fibers,[1-5] much less has been reported on grafting of vinyl monomers onto jute fiber, which is an important lignocellulosic fiber. Initiation with tetravalent cerium for graft copolymerization of vinyl monomers onto silk,[6] wool,[7] collagen,[8] and nylon[9] has gained considerable importance. Ceric ion initiated graft copolymerization of methyl methacrylate[10] and acrylonitrile[11] onto jute fibers have also been reported. Various research workers[12-14] have reported the radiation-induced grafting of vinyl monomers onto jute fibers, both by mutual irradiation and preirradiation technique. Photograft-copolymerization of methylmethacrylate onto bleached jute fibers has also been reported by Ghosh and Paul.[15] Although Ray[16] has reported some X-ray diffraction studies of polymethyl methacrylate- and polyacrylonitrile-grafted holocellulose (delignified jute), not much is known about the conditions of grafting. Graft copolymerization of methyl methacrylate onto chemically modified jute fibers[17-19] and acrylonitrile[20] onto acetylated chemically modified jute using different redox-initiating systems has been reported by our research group.

The present investigation reports a kinetic study of Ce(IV)-hippuric acid redox-initiated graft copolymerization of AN onto chemically modified bleached jute fibers. However, Trivedi and Mehta[11] have reported the ceric-ion-initiated grafting of AN onto defatted and bleached jute fibers. With bleached jute they obtained 30% grafting. Percent graft increased to a maxi-

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mum of 45% when lignin content decreased from 14% to 1.8%. In our study we have obtained around 90% graft yield.

EXPERIMENTAL

Pretreatment of jute fibers was done as mentioned earlier,[17] to obtain the chemically modified jute fibers which were then subjected to bleaching with H_2O_2 solution (1:10 liquor ratio) containing 2.5% sodium phosphate and 8% sodium silicate of jute weight. The mixture was then heated at 50–60°C for 15 min, 60–70°C, for the next 15 min, and finally from 75–80°C for the remaining 30 min. The fibers were then washed thoroughly with distilled water, kept at pH 3.5 in SO_2 water for 10 min, washed again with distilled water, and finally air dried. The chemically modified bleached jute fibers thus obtained were ready for grafting.

Purified monomer (AN), cerium (IV) solution (prepared from cerric ammonium nitrate), hippuric acid (solution was prepared in glacial acetic acid), sulfuric acid, and other reagents were of BDH, AR grade. Before initiating graft copolymerization, the jute fibers were soaked with an appropriate quantity of monomer for about 5 min. Appropriate quantities of reaction mixture containing jute fiber, monomer, sulfuric acid, hippuric acid, and cerium (IV) solution were taken in the reaction vessels. Material to liquor ratio was 1:200. The reactions were carried out for specific times at three different temperatures, 40, 50, and 60°C. After the specific time interval, the reaction was arrested by quenching the vessel in ice-cold water. Then the grafted samples were washed thoroughly by extraction with several portions of water, given a light soaping to remove the loosely adhering polymers, washed again with conductivity water, and then dried. It was observed that on further extraction with dimethyl formamide for about 24 h at 30°C, the grafted sample showed a negligible weight loss. This type of observation has also been reported by Hebeish and Mehta.[21] Hence, all the results are based on the increase in weight of the fiber after grafting followed by thorough soaping and washing. The percentage of grafting was calculated on dry weight determined by storing the materials in weighing bottles over P_2O_5 at room temperature in a vacuum desiccator till a constant weight is obtained.

$$\% \text{ Graft yield} = \frac{\text{dry wt of grafted jute} - \text{dry wt of original jute}}{\text{dry wt of original jute}} \times 100$$

RESULTS AND DISCUSSION

Effect of Reaction Time on Graft yield

Figure 1 shows the effect of reaction time on percentage of graft yield at three different temperatures (40, 50, and 60°C). In all these cases, graft yield has been found to increase steadily with increase of reaction time up to 3–4 h and then assumes steady value. Thus an optimum graft yield is obtained within 4 h. This type of observation is similar to that observed by Huque et al.[10] while reporting ceric ion-initiated grafting of methyl methacrylate onto jute fibers.

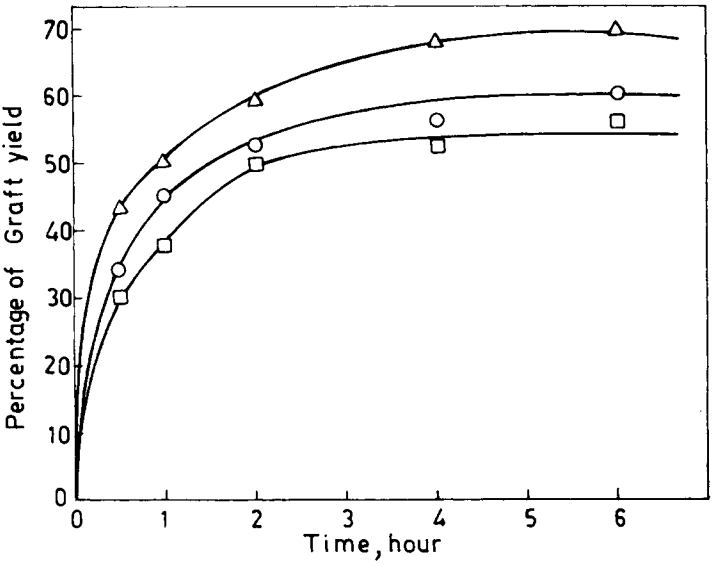

Fig. 1. Effect of reaction time on graft yield. Jute = 0.1 g, [AN] = 0.7585 mol · L^{-1}, [Ce(IV)] = 0.04 mol · L^{-1}, [hippuric acid] = 0.00125 mol · L^{-1}, [H_2SO_4] = 0.8 mol · L^{-1}. (○) = 40°C, (△) = 50°C, (□) = 60°C. 2.5% v/v acetic acid.

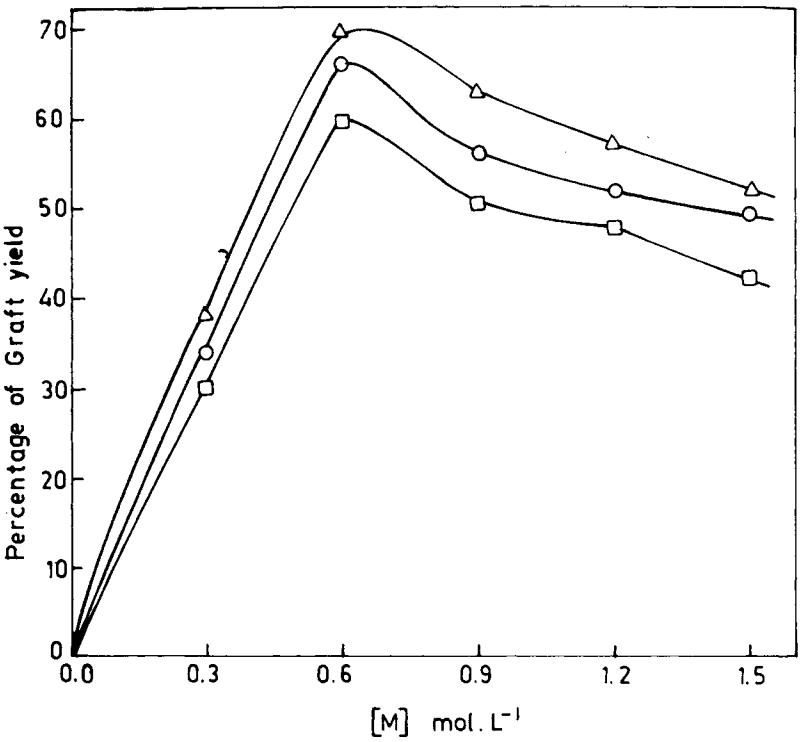

Fig. 2. Effect of monomer on graft yield. Jute = 0.1 g, [Ce(IV)] = 0.04 mol · L^{-1}, [hippuric acid] = 0.00125 mol · L^{-1}, [H_2SO_4] = 0.8 mol · L^{-1}, time = 3 h. (○) = 40°C, (△) = 50°C, (□) = 60°C. 2.5% v/v acetic acid.

Effect of Monomer on Graft Yield

The effect of variation of monomer (AN) concentration on graft yield is shown in Figure 2. It is observed that the percentage of graft yield increases with increase of monomer concentration from 0.303 mol. L^{-1} to 0.606 mol. L^{-1} and further increase of monomer concentration results in decreased graft yield. Similar observations have also been reported in the case of grafting of methyl methacrylate onto jute fibers using different redox systems.[17-19] The decreasing trend of graft yield after certain optimum concentrations of monomer could be ascribed to the competition between homopolymerization and grafting, where the former prevails over the latter at higher monomer concentration. Trivedi and Mehta[11] have reported that percent graft is doubled when the amount of monomer is increased four times while reporting ceric ion-initiated grafting of AN onto jute fibers. This difference in observation might be due to the different type of initiator used as well as to the experimental conditions used in each case.

Effect of Metal Ion (Ce^{4+}) on Graft Yield

In the present investigation Ce(IV) coupled with hippuric acid forms the redox-initiating system. The effect of variation of Ce(IV) concentration, keeping the concentrations of all other reagents fixed at three different tempera-

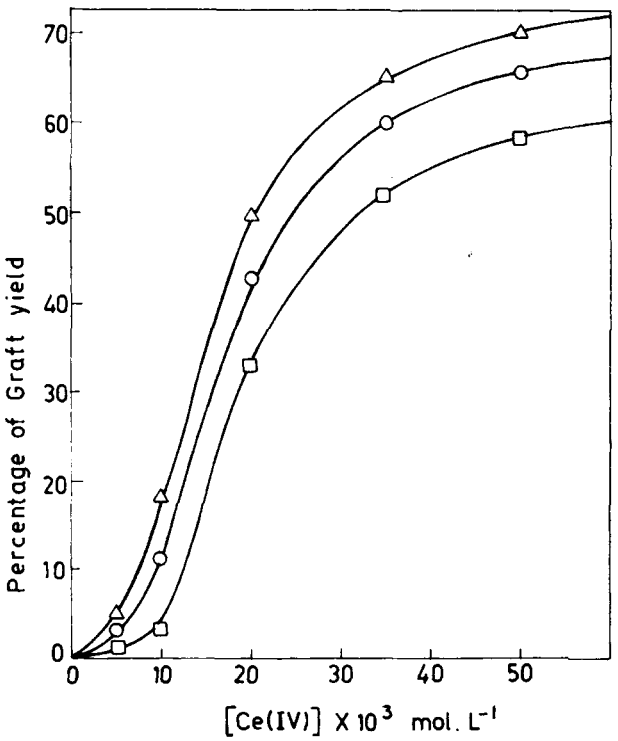

Fig. 3. Effect of metal ion (Ce^{4+}) on graft yield. Jute = 0.1 g, [AN] = 0.7585 mol · L^{-1}, [hippuric acid] = 0.00125 mol · L^{-1}, [H_2SO_4] = 1.0 mol · L^{-1}, time = 3 h. (○) = 40°C, (△) = 50°C, (□) = 60°C. 2.5% v/v acetic acid.

tures (40, 50, and 60°C) is shown in Figure 3. It is observed that percentage of graft yield is increased by increasing the concentration of Ce(IV) from 0.005 mol. L^{-1} to 0.05 mol. L^{-1}. This trend of increased graft yield percentage may be due to the creation of a greater number of reaction sites caused by the increased Ce(IV) concentration in the grafting reaction. Similar types of observation, namely increase of percent grafting with the increase of Ce(IV) concentration have also been reported by Trivedi and Mehta.[11]

Effect of Hippuric Acid on Graft Yield

The effect of variation of hippuric acid concentration on percentage of graft yield is shown in Figure 4. It is seen that within all the temperature scales studied, the percent graft yield is increased by increasing the concentration of hippuric acid from 0.0005 mol. L^{-1} to 0.002 mol. L^{-1} and thereafter decreases. At zero hippuric acid concentration, graft yields were found to be 20%, 23%, and 18% at 40°C, 50°C, and 60°C, respectively. This trend of decreasing percent grafting after certain optimum concentration of hippuric acid is probably due to the rapid rate of termination and/or formation of radical scavenger at higher hippuric acid concentration. Similar observations have been reported while studying the effect of various organic substrates on jute grafting.[17-19]

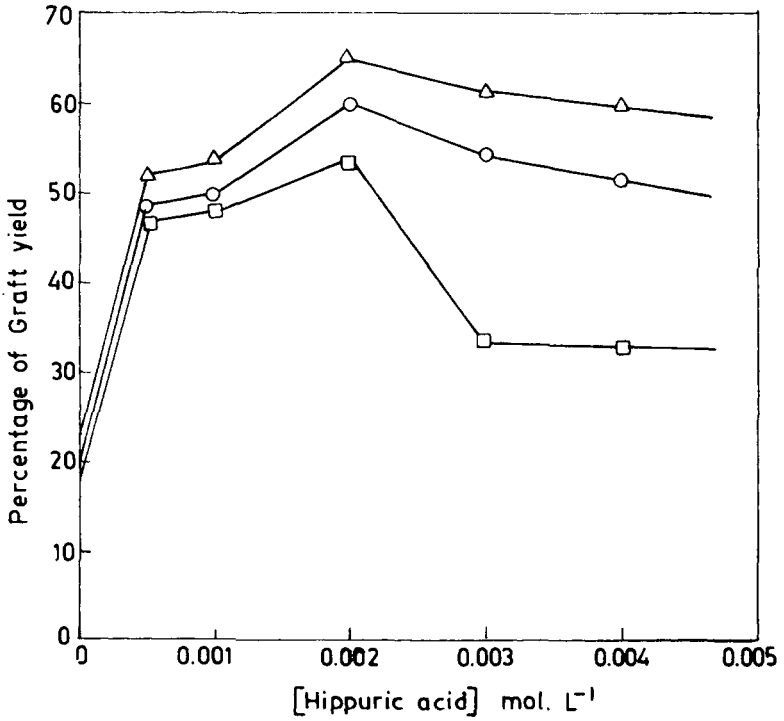

Fig. 4. Effect of hippuric acid on graft yield. Jute = 0.1 g, [AN] = 0.7585 mol · L^{-1}, [Ce(IV)] = 0.05 mol · L^{-1}, [H_2SO_4] = 1.0 mol · L^{-1}, time = 3 h. (○) = 40°C, (△) = 50°C, (□) = 60°C. 8% v/v acetic acid.

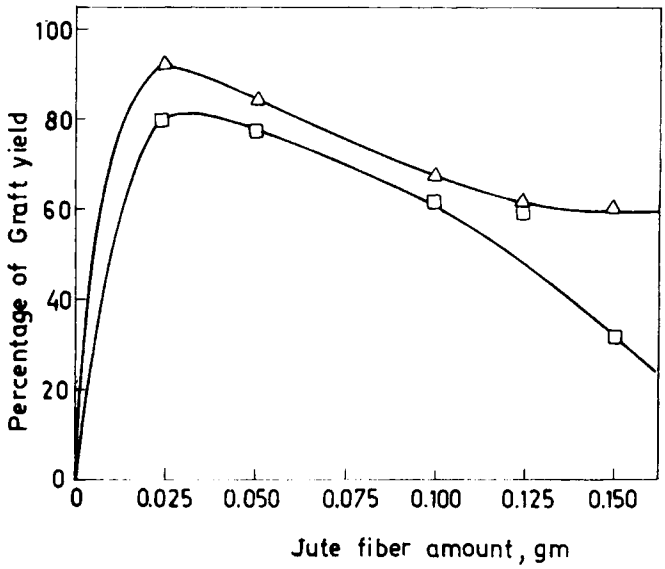

Fig. 5. Effect of jute fiber amount on graft yield. [AN] = 0.7585 mol · L^{-1}, [Ce(IV)] = 0.05 mol · L^{-1}, [hippuric acid] = 0.002 mol · L^{-1}, [H_2SO_4] = 1.0 mol · L^{-1}, time = 3 h. 4% v/v acetic acid. (△) = 50°C, (□) = 60°C.

Effect of Jute Fiber Amount on Graft Yield

The effect of variation in the amount of jute fibers on percentage of graft yield at two different temperatures (50 and 60°C) is shown in Figure 5. It is seen that, within the range studied, the graft yield decreases by increasing the amount of jute fibers in the polymerization system. This type of observation is quite contrary to our previous observation that the graft yield increases by increasing the amount of jute fiber in the polymerization system.[18, 19]

Effect of Temperature

The graft copolymerization of acrylonitrile onto jute fibers has been studied at three different temperatures ranging from 40 to 60°C, keeping the concentrations of all other reagents fixed. It is observed that the percentage of graft yield increases with the rise of temperature from 40 to 50°C and then falls with further increase of temperature to 60°C. The effects of temperature on percentage of graft yield have been shown in Figures 1 to 5. Again, it has been found that grafting onto jute is seldom possible below 40°C, unlike the grafting of other natural fibers such as silk.[6] This might be due to the rigidity of the cellulosic structure of jute as compared with other natural fibers. From Figure 1 it is observed that within each temperature range, the percentage of graft yield appears to rise with time up to 4 h and then falls. Thus, the maximum percentage of graft yield lies at 50°C within 4 h.

Effect of Reaction Medium

The reaction medium plays an important role in graft copolymerization reaction. The percentage of graft yield decreases with an increase of sulfuric

acid concentration. The increase in concentration of acid is not only unfavorable to grafting, but also it destroys some of the useful properties of the fibers. Proof of this in terms of measurement of thermal stability data will be reported in our subsequent communication.

The graft yield follows the following order when the solvents are added in equal proportions (5% v/v):

$$\text{Dioxane} > \text{control} \simeq CH_3OH > \text{DMF} > \text{acetone}$$

Similarly, the effect of some neutral salts when added in equivalent molar concentration follows the order:

$$NaCl > MnSO_4 > CuSO_4 > K_2SO_4 > \text{control}$$

Table I summarizes the above results.

Reaction Mechanism

In a system containing ceric ammonium nitrate, acrylonitrile, hippuric acid, and jute fibers, Ce^{4+} may interact with hippuric acid to form a complex which dissociates to give a free radical. This radical abstracts hydrogen from the jute molecule (JH) yielding a macroradical ($J^{\cdot}$). The following is an outline of reaction mechanism.

Initiation:

$$Ce^{4+} + \text{Hippuric acid} \overset{K}{\rightleftharpoons} \text{complex}$$

$$\text{Complex} \overset{k_1}{\rightarrow} R^{\cdot} + Ce^{3+} + H^+$$

$$JH + R^{\cdot} \overset{k_2}{\rightarrow} J^{\cdot} + RH$$

$$J^{\cdot} + M \overset{k_3}{\rightarrow} JM^{\cdot}$$

Propagation:

$$JM^{\cdot} + M \overset{k_p}{\rightarrow} JM_2^{\cdot}$$

$$\vdots$$

$$JM_{n-1}^{\cdot} + M \overset{k_p}{\rightarrow} JM_n^{\cdot}$$

TABLE I[a]

	Effect of solvent and salt			Effect of sulfuric acid	
Solvent 5% v/v	% Grafting	[Salt] 0.01 mol. L^{-1}	% Grafting	[H_2SO_4] mol. L^{-1}	% Grafting
Control	63.0	Control	63.0	1.4	59.0
CH_3OH	62.9	$CuSO_4$	70.0	1.6	52.3
Dioxane	64.1	NaCl	79.0	1.8	49.8
Acetone	15.0	K_2SO_4	64.5	—	—
DMF	57.2	$MnSO_4$	71.5	—	—

[a]Jute = 0.1 g, [AN] = 0.7585 mol · L^{-1}, [Ce(IV)] = 0.05 mol · L^{-1} [hippuric acid] = 0.002 mol · L^{-1}, [H_2SO_4] = 1.0 mol · L^{-1}, temp = 50°C, time = 3 h. 4% v/v acetic acid.

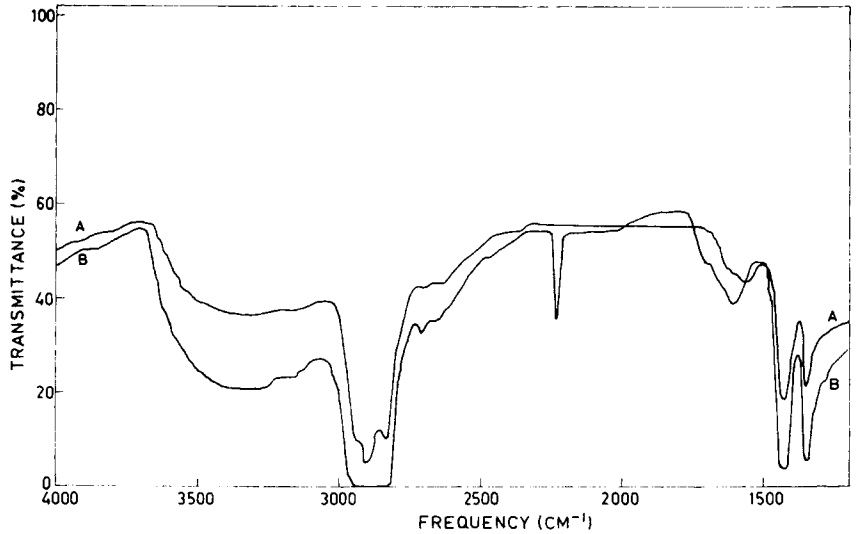

Fig. 6. IR spectra. (A) Chemically modified bleached jute. (B) AN-grafted chemically modified bleached jute.

Termination:

$$JM_n^{\cdot} + Ce^{4+} \xrightarrow{k_t} JM_n + Ce^{3+} + H^+$$

Oxidation:

$$J^{\cdot} + Ce^{4+} \xrightarrow{k_o} \text{oxidation product}$$

where Ce^{4+}, $R^{\cdot}$, JH, $J^{\cdot}$, M, K, k_1, k_2, k_3, k_p, k_t, and k_o are ceric ion, free radical, reactive jute molecule, jute macroradical, monomer, and different rate constants, respectively.

IR Spectra

Infrared (IR) spectra of (A) chemically modified bleached jute and of (B) AN-grafted chemically modified jute in nujol were recorded on a Perkin-Elmer 337 (IR) spectrophotometer and are shown in Figure 6. It is observed that the original ungrafted jute (A) shows the characteristic broad absorption band of hydroxyl group around 3100–3500 cm^{-1}. However, the spectrum of AN-grafted jute (B) shows an additional peak of nitrile group at about 2240 cm^{-1}, thereby confirming the occurrence of grafting. One would have expected the intensity of —OH peaks to be reduced as a result of grafting, since it is a probable site for grafting. This, however, is not observed. Possibly, due to large concentrations of —OH groups of jute, the small differences in its concentration as a result of grafting are not detected.

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