A Study on Graft Copolymerization of Methyl Methacrylate onto Jute Fiber

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Synopsis

A kinetic study of the graft copolymerization of methyl methacrylate onto jute fiber using $KMnO_4$–malonic acid redox initiator system has been made. Effects of the concentrations of malonic acid, monomer, and $KMnO_4$ on graft yield have been studied. Besides, the effects of temperature, acid, and reaction medium, some inorganic salts on graft yield have been investigated. The most remarkable features of the investigation include the proposition of a mechanism, derivation of rate expression for the grafting process, and characterization of the grafted fiber by thermogravimetric analysis.

INTRODUCTION

The synthetic graft copolymers of natural macromolecules (e.g., silk, wool, cellulosic fibers, etc.) exhibit excellent properties besides exhibiting their original properties. The literature is replete with the study of the graft copolymerization of different monomers onto the natural fibers, by using initiators, e.g. metal and non-metal ions. Very recently, Hebeish and co-workers[1-9] have made a significant contribution to the kinetic study of grafting of vinyl monomers onto cellulose and its derivatives as well as cellulosic fibers (like cotton) and their derivatives. The authors here have studied the kinetics of graft copolymerization of a monomer onto another cellulosic fiber, jute. It is expected that the properties of this fiber on modification by grafting process can improve in such wonderful ways that the modified fiber can be utilized in the manufacture of decent, fine and high grade clothings. Very recently Habibuddowla[10] has contributed a little on the study of some of the properties of grafted jute fibers. The present investigation reports a kinetic study of the permanganate–malonic acid initiated graft copolymerization of methyl methacrylate onto jute fibers.

EXPERIMENTAL

Jute fibers 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. Then 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, the

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fibers were soaked with ethylenediamine for about 30 min and washed. Again they were treated with 60% $ZnCl_2$ solution at 20°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 fibers were then ready for grafting.

Purified monomer (methyl methacrylate) $KMnO_4$, and malonic acid (AnalaR) were used for the grafting process.

Before initiating graft copolymerization, the jute fibers were soaked with appropriate quantity of monomer for 2–5 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, malonic acid solution, and conductivity water were taken in reaction vessels. The mixture and freshly prepared $KMnO_4$ solution (0.05*M*) were separately deaerated by passing nitrogen for 20 min. After the specified time interval, the reaction was arrested by quenching the vessel in the ice cold water. The homopolymer along with the grafted jute fibers were filtered off, washed with distilled water, and dried to constant weight. Finally, the fibers were extracted with acetone in soxhlet apparatus for 12 h to dissolve all the homopolymers. Percentage of grafting and rate of grafting were estimated as follows:

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

$$\text{rate of grafting } (R_G) = \frac{1000 \times W}{V \times t \times M}$$

where W = weight of the grafted fiber, V = volume of the mixture, t = time (s), M = mol. weight of the monomer (MMA).

RESULTS AND DISCUSSION

Effect of Time on Graft Yield

Figure 1 shows the effect of time on graft yield at three different malonic acid concentrations. In all these cases, the graft yield has been found to increase steadily with time, but, after 6 h, it decreases to some extent. This may be attributed to the partial dissolution of the grafted fiber on prolonged exposure to the high temperature of 50–70°C. Thus an optimum grafting efficiency is obtained within 2 h.

Effect of Monomer Concentration

The percentage of graft yield increases with increase of monomer concentration up to 0.4694 mL^{-1} and thereafter decreases. Figure 2 illustrates this fact. The enhancement of grafting by increasing the monomer concentration up to 0.4694 mL^{-1} could be associated with gel effect.

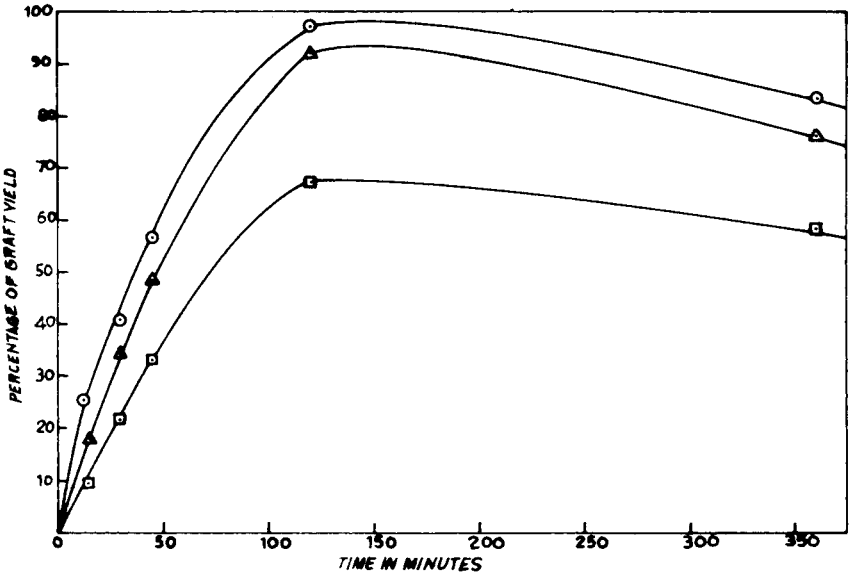

Fig. 1. *Percentage of graft yield vs. time*: $[KMnO_4]$ = 0.0175 mL^{-1}; [MMA] = 0.469 mL^{-1}, temp = 60°C. jute = 0.1 g; (○) [MA] = 0.1 mL^{-1}; (△) [MA] = 0.15 mL^{-1} (□) [MA] = 0.2 mL^{-1}.

Effect of Malonic Acid Concentration

Figure 3 represents the effect of malonic acid on graft yield at three different temperatures (50°C, 60°C, and 70°C). At all the temperatures, grafting increases steadily from 0.0125 to 0.1 mL^{-1} concentration of malonic acid up to a maximum, and thereafter decreases. This is probably due to

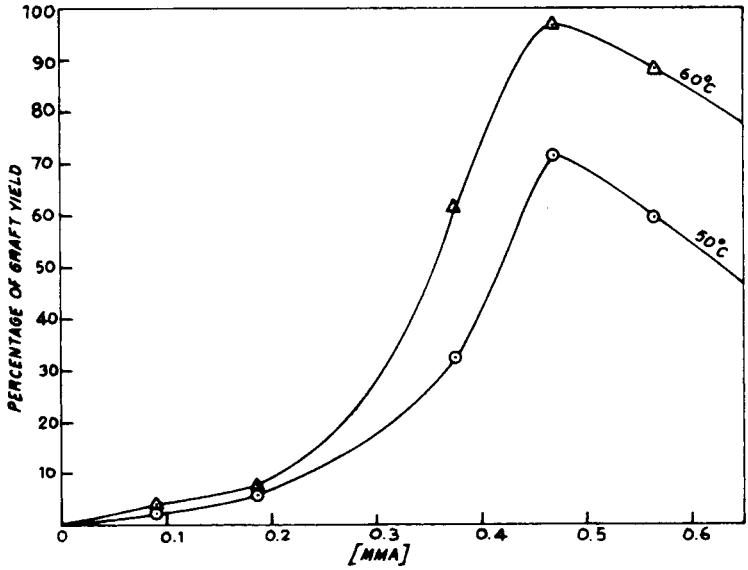

Fig. 2. Percentage of graft yield vs. monomer concentration: $[KMnO_4]$ = 0.0175 mL^{-1}, [MA] = 0.1 mL^{-1}, jute = 0.1 g, time = 4 h.

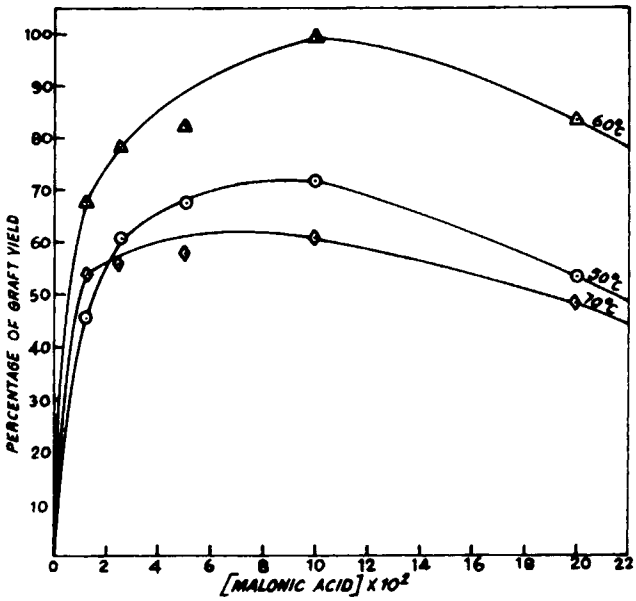

Fig. 3. Percentage of graft yield vs. malonic acid concentration: $[KMnO_4] = 0.0175\ mL^{-1}$, [MMA] = 0.469 mL^{-1}, jute = 0.1 g, time = 4 h.

fast rate of termination and/or formation of radical scavenger at higher malonic acid concentration.

Effect of Temperature

The graft copolymerization of methyl methacrylate onto jute fibers was studied at three different temperatures ranging from 50°C to 70°C, keeping the concentrations of all other reagents fixed. The percentage of graft yield increases initially with the rise of temperature from 50°C to 60°C, and then falls with further increase of temperature (Fig. 4). It has also been found that grafting onto jute fibers becomes hardly possible below 50°C, unlike the grafting of other natural fibers like silk, wool, etc. This may be due to the rigidity of the cellulosic structure of jute compared with other fibers.

Effect of Permanganate

The effect of concentration of permanganate on the percentage of graft yield is shown in Figure 4. The percentage of graft yield increases with the increase of permanganate concentration up to 0.0175 mL^{-1}, and, beyond this, the percentage of graft yield decreases. The obvious reason of the above trend is that a greater number of grafting sites are created by increase in permanganate concentration. At the same time the termination by Mn^{+3} ions may be prevalent at these high concentrations, resulting in shorter grafted chains.

Effect of Reaction Medium

The reaction medium plays an important role in the graft copolymerization reaction. The graft yield follows the order when added in equal

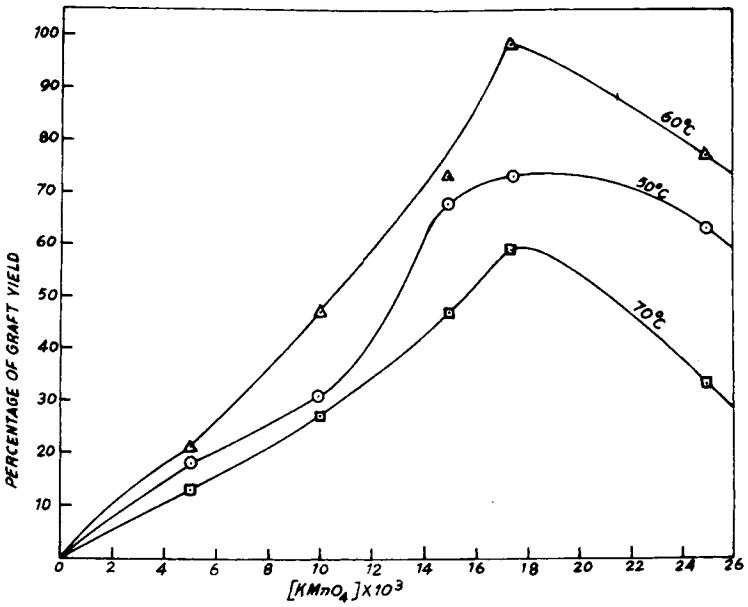

Fig. 4. Percentage of graft yield vs. permanganate concentration: [MMA] = 0.469 mL^{-1}, jute = 0.1 g, [MA] = 0.1 mL^{-1}, time = 4 h.

proportion (5% v/v): DMF > control > EtOH > acetone > dioxane and depicted in Table I: The important feature in this trend is that, excepting DMF, all other solvents depress the percentage of graft yield.

Similarly, the effect of neutral salts, when added in equal concentrations, on graft yield follows the order: $MnSO_4$ > NaCl > control > K_2SO_4 > $CuSO_4$ and is depicted in Table II.

Reaction Mechanism

The mechanism of graft copolymerization which fits the results may be represented as follows: It has been proposed that MnO_4^- dissolves in the reaction medium to give rise to Mn^{+3} ions via Mn^{+4}. These highly reactive Mn^{+3} ions are responsible for initiating graft copolymerizations. The scheme of reaction may be proposed as follows:

Initiation:

$$Mn^{+3} + RH \underset{}{\overset{K}{\rightleftharpoons}} \text{complex} \xrightarrow{k_1} R\cdot + Mn^{+2} + H^+$$

(where RH=malonic acid)

TABLE I[a]

Solvent	% of graft yield
DMF	136.3
Dioxan	47.3
Acetone	78.3
EtOH	93.7
Control	98.4

[a] [$KMnO_4$] = 0.0175 mL^{-1}, [MMA] = 0.469 mL^{-1}, jute = 0.1 g, temp = 60°C, time = 4 h.

TABLE II[a]

Salt	% of graft yield
NaCl	103.4
$CuSO_4$	67.8
$MnSO_4$	117.3
K_2SO_4	87.3
Control	98.3

[a] General conditions are the same as those in Table I; [salt] = 0.01*M*.

$$JH + R\cdot \xrightarrow{k_2} J\cdot + RH$$

$$J\cdot + M \xrightarrow{k_i} JM\cdot$$

Propagation:

$$JM\cdot + M \xrightarrow{k_p} JM_2$$

$$\bullet$$

$$\bullet$$

$$\bullet$$

$$JM_{n-1}\cdot + M \xrightarrow{k_p} JMn$$

Termination:

$$JM_n\cdot + Mn^{+3} \xrightarrow{k_t} JM_n + Mn^{+2} + H^+$$

Oxidation:

$$J\cdot + Mn^{+3} \xrightarrow{k_o} \text{oxidation products} + Mn^{+2}$$

Making use of the steady state principle, the expression for the rate of grafting may be put forth as follows:

$$R_G = \frac{k_p k_i k_1 K\,[RH]\,[M]^2}{k_t(k_i[M] + k_0[Mn^{+3}])}$$

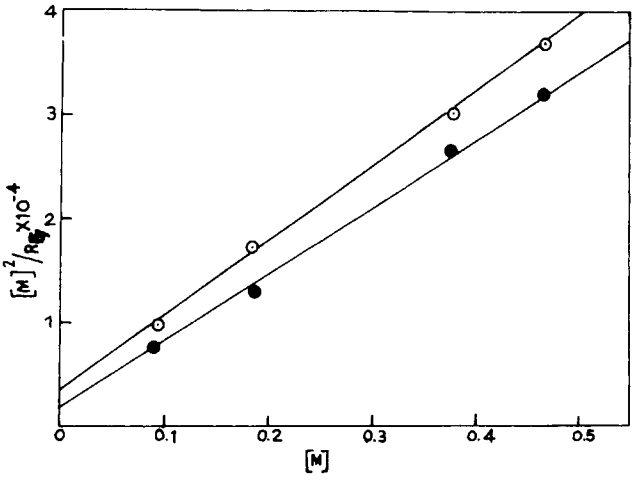

Fig. 5. $[M]^2/R_G$ vs. [M] plot: (○) temp = 50°C; (●) temp = 60°C.

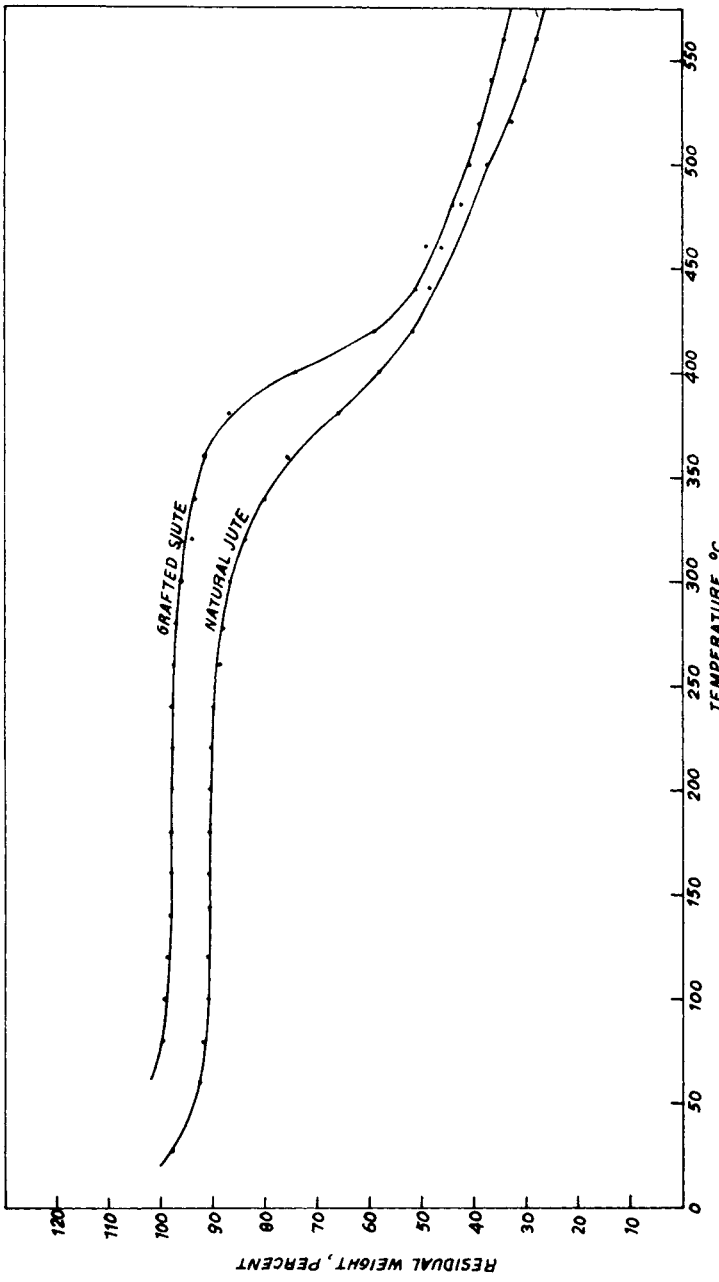

Fig. 6. Primary thermograms of natural and grafted jute fibers: initial weight of the grafted sample = 150 mg.

By rearranging the above equation, the following equation can be obtained:

$$\frac{[M]^2}{R_G} = \frac{k_t[M]}{k_p k_1 K[RH]} + \frac{k_t k_0[Mn^{+3}]}{k_p k_i k_1 K[RH]}$$

From Figure 5, it can be seen that the plots of $[M]^2/R_G$ vs. [M] give reasonable straight lines for different temperatures.

Characterization of the Grafted Jute Fiber

Besides the kinetic study of grafting, the confirmation of the occurrence of grafting has been done through the thermogravimetric analysis (TGA). The thermal behavior of natural jute grafted with methyl methacrylate was examined by a study of their primary thermograms. Figure 6 represents the primary thermograms of natural jute (chemically modified) and jute grafted with MMA. Although the two curves are very much different, their shapes do not differ very much from each other (sigmoidal). The study of the two thermograms shows that the thermal stability of the grafted jute has been found to be higher than that of natural jute (chemically modified). In natural jute (chemically modified) decomposition temperature T_D is approximately 310°C but in the grafted jute T_D is approximately 375°C. In natural jute, the main weight loss occurs between 300°C and 400°C, whereas in grafted jute the main weight loss occurs between 360°C and 400°C. Hence the effect of grafting MMA onto jute is to make it more thermally stable up to about 400°C and this effect becomes more predominant as the percent graft-on increases. After about 400°C, the grafted jute fibers lose weight more rapidly than normal jute.

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