

Graft Copolymerization with a New Class of Acidic Peroxo Salts as Initiator. V. Grafting of Methyl Methacrylate onto Jute Fiber Using Potassium Monopersulfate Catalyzed by Fe(II)

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Synopsis

Graft copolymerization of methyl methacrylate (MMA) onto jute fibers was studied in an aqueous solution using a new class of acidic peroxy salt, potassium monopersulfate, as initiator, under the catalytic influence of Fe(II) under nitrogen atmosphere. The grafting reaction was influenced by the reaction time, temperature, and concentrations of monomer, initiator, and jute fibers. The grafting reactions have also been studied in the presence of various salts and solvents. The maximum grafting percent (385.4%) has been observed at 35°C for the concentration of monomer (1.4082M), initiator ($12.9 \times 10^{-3}M$), catalyst ($2.5 \times 10^{-4}M$), and solvent (acetic acid) composition of (40:60) for a reaction time of 6 h. From the experimental results a suitable mechanism for the graft initiation and termination has been put forth. The graft copolymers have been characterized, and their improved properties such as tensile strength tested.

INTRODUCTION

Chemical modification of preformed polymers both natural and synthetic through graft copolymerization provides a potential route for significantly altering their physical and mechanical properties. The grafting provides great potential for tailoring material properties to specific end use, and the modified materials find wide industrial and biomedical applications. Graft copolymerization of vinyl monomers onto cellulose, cellulose derivatives, and lignocellulosic fibers has been the subject of extensive studies since 1946.¹

Jute, a lignocellulosic fiber, is the most abundant renewable agricultural raw material and is transformed into multifarious products affecting every phase of our daily life due to its wide applications for making coarse woven fabrics such as gunny sacks and bagging, where cheapness is the prime factor. Recently efforts have been made in India and Bangladesh for commercial utilization of jute fibers^{2,3} to meet the total fabric requirements for the country as well as to minimize import of synthetic fibers. Although jute fiber possesses high dimensional stability,⁴ certain unfavorable textile properties such as high stiffness, very low elasticity, susceptibility towards sunlight, etc., have tremendously limited its use.⁵ Therefore, to minimize undesirability

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and enhance its effectiveness for intensified textile uses, graft copolymerization with jute fiber has been recently attempted in the presence of higher valency transition metal ions such as V(V), Mn(VII), and Ce(IV).⁶⁻⁸ However, no reports seem to be available on the use of potassium monopersulfate as the initiator affecting graft copolymerization onto jute fibers. Potassium monopersulfate, a new class of acidic peroxy oxidizer (oxidation potential -1.44V), is of recent origin.⁹ Samal et al. have recently exploited the chemistry of potassium monopersulfate, with regard to its mode of decomposition in solution either alone or under the catalytic influence of salts, complexing agents and salt/complexing agent couples and the versatility of the system in initiating vinyl polymerization and graft copolymerization.¹⁰⁻²³ Presently we use $\text{KHSO}_5/\text{Fe(II)}$ couple to affect graft copolymerization of MMA onto jute fibers and to screen the improved properties of the grafts.

EXPERIMENTAL

Materials. Jute fiber (*Corchorus Capsularis*) was purified by treating with hot ethanol and benzene mixture in the proportion 1:2 (v/v) in a Soxhlet apparatus. Then it was washed well with alcohol and air dried. Methyl methacrylate (MMA) (Burgoyne) was purified according to our previous method.²⁴

Potassium monopersulfate (KHSO_5) (98.9%) was a gift sample for Du Pont and was used without further purification. A stock solution of $12.9 \times 10^{-2}M$ of the initiator was used for all experiments, and the strength of the stock solution was determined by iodometry. All other reagents were of BDH (AR) grade and were used after purification by standard methods.

Graft copolymerization was carried out in a specially designed reaction vessel carrying outlet and inlet systems for deaeration. The method adopted was identical with our previous report.²⁰ Defatted jute fiber (0.2-1 g) was immersed in a mixture containing water, the required amount of methyl methacrylate (MMA), and the initiator. The reaction vessels were kept in a freezing mixture and were deaerated by passing oxygen-free nitrogen for 1 h, and were sealed airtight. The vessels were then kept in a constant temperature bath and the grafting reaction was carried out for the desired time. The homopolymers were extracted by repeated refluxing in warm acetone.

From the weight of the graft copolymer, unreacted jute, the percent grafting was calculated using the following formula:

$$\text{percent grafting} = \frac{X - Y}{Y} \times 100$$

where X = weight of the graft copolymer and Y = weight of the unreacted jute.

RESULTS AND DISCUSSION

Methyl methacrylate was graft-copolymerized with defatted jute fibers using potassium monopersulfate as initiator either alone or in the presence of a number of salts. The results of percent grafting for the individual systems are presented in Table I.

TABLE I
Results of Graft Percent in the KHSO_5 -Initiated Graft Copolymerization of Methyl Methacrylate onto Jute Fiber in the Presence of Various Salts.^a

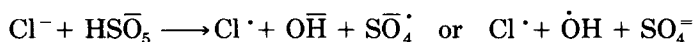
Metal salts	Graft percent
No* salt	6.2
CoSO_4	2.6
CuSO_4	0.7
$\text{Cu}(\text{OAc})_2$	7.85
FeCl_3	19.35
FeSO_4	27.1
NaBr	10.35
Na_2SO_4	5.45
$\text{Cr}_2(\text{SO}_4)_3$	11.55
ZnCl_2	2.15
MnSO_4	0.25
Ag_2SO_4	15.0
Na_2SO_3	10.5
MgSO_4	0.4
KBr	0.4
NiSO_4	2.4
CdCl_2	1.25

^aJute = 0.2 g; $[\text{MMA}] = 0.235\text{M}$; $[\text{KHSO}_5] = 12.9 \times 10^{-3}\text{M}$; temp = 35°C ; time = 2h.

From Table I, it has been observed that the presence of salts like CoSO_4 , CuSO_4 , Na_2SO_4 , ZnCl_2 , MnSO_4 , MgSO_4 , KBr , NiSO_4 , and CdCl_2 retards the percent grafting whereas the presence of salts like $\text{Cu}(\text{OAc})_2$, FeCl_3 , FeSO_4 , NaBr , $\text{Cr}_2(\text{SO}_4)_3$, Ag_2SO_4 , and Na_2SO_3 favors the percent grafting in the order $\text{FeSO}_4 > \text{FeCl}_3 > \text{Ag}_2\text{SO}_4 > \text{Cr}_2(\text{SO}_4)_3 > \text{Na}_2\text{SO}_3 > \text{NaBr} > \text{Cu}(\text{OAc})_2$.

The enhancement of graft percentage in the presence of these salts may be attributed to their effectiveness, in causing fast decomposition of KHSO_5 to massive free radicals which attack the jute and enhance the number of free-radical sites on its backbone. Chain initiation by free radical sites with monomer molecules at the immediate vicinity cause high graft yield.

The retardation of graft percentage in the presence of ZnCl_2 and CdCl_2 may be due to the following oxidation reaction:



(i) which decreases the number of initiator free radicals responsible for generating active sites on the jute backbone and so also the number of grafted chains: (ii) the chlorine radical so formed may also combine with jute-free radical preventing monomer addition and also cause premature termination of growing grafted chains. Oxidation of Cl^- to Cl^\cdot by $\dot{\text{O}}\text{H}$ radical has been noticed by Palit and Sahra.²⁵ This is in agreement with our verification of liberation of Cl_2 through dimerization of Cl^\cdot radicals. With CuSO_4 , CoSO_4 , NiSO_4 , MgSO_4 , and Na_2SO_4 the adversity may be (i) due to interference of $\text{SO}_4^{\cdot-}$ ion in the propagation step, (ii) partly due to the redox potentials of Co^{+2} , Ni^{+2} , Mn^{+2} , and Cu^{+2} backdriving the decomposition of KHSO_5 to $\dot{\text{O}}\text{H} + \text{SO}_4^{\cdot-}$ radicals, and (iii) due to premature termination of the growing grafted chains by Cu^{+2} ion. Termination of the radical end of the growing

polymer chains by Cu^{+2} ion was noticed by Bengough and Fairservice.²⁶ The reason for NaBr enhancing graft percentage and KBr decreasing has not been well understood.

Effect of Monomer/Polymer Ratio

The graft copolymerization of methyl methacrylate onto jute fiber has been studied in a series of monomer concentrations ranging from 0.12 to 1.9M at five initiator concentrations (3.23×10^{-3} – $25.8 \times 10^{-3}M$) at a fixed concentration of FeSO_4 ($2.5 \times 10^{-4}M$) and fixed weight of jute fibre (0.2 g). It has been observed that the percent grafting increases on increasing the m/p ratio up to 28.2, beyond which it decreases (Fig. 1). The enhancement of percent grafting here may be interpreted in terms of MMA concentration and its reactivity. Increase of m/p ratio increases monomer (MMA) concentration at close proximity of the fiber backbone, where some of the MMA molecules form a donor-acceptor complex, through interaction of their ester functions with OH groups on the jute backbone. Out of the uncomplex monomers, those which are at the immediate vicinity of reaction sites become acceptors of the jute radicals, resulting in chain initiation, and thereafter themselves become free-radical donors predominantly for the complexed monomers converted to strong acceptors and neighbors to them rather than the remaining uncomplexed ones a little far away. These factors result in an increase in the

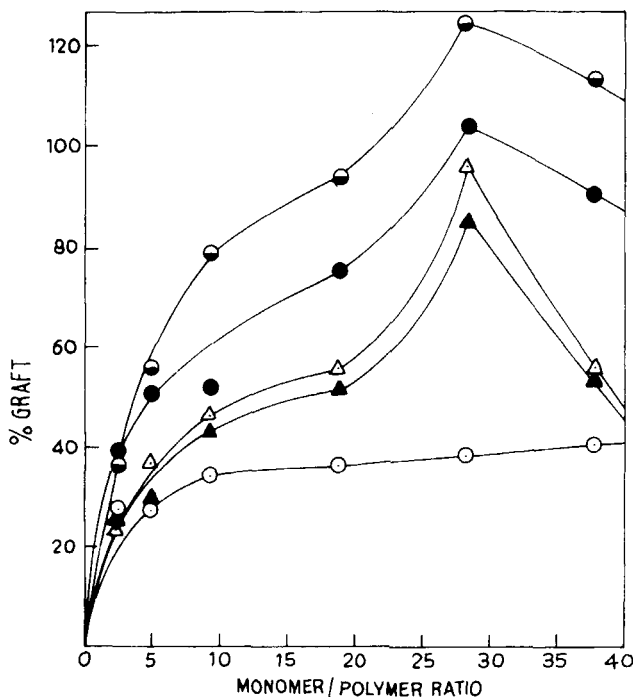


Fig. 1. Variation of graft percent at a fixed time; effect of monomer/polymer ratio at various $[\text{KHSO}_5]$ initiators: jute = 0.2 g; $[\text{FeSO}_4] = 2.5 \times 10^{-4}M$; temperature = 35°C ; time = 6 h. $[\text{KHSO}_5]$: (○) $3.22 \times 10^{-3}M$; (●) $6.45 \times 10^{-3}M$; (◐) $12.9 \times 10^{-3}M$; (△) $19.35 \times 10^{-3}M$; (▲) $25.8 \times 10^{-3}M$.

reactivity of the monomers, thereby enhancing percent grafting. A similar explanation for enhancement of percent grafting has been suggested by Gaylord²⁷ and Hebeish et al.²⁸

The decrease of percentage grafting beyond the cited m/p ratio may be attributed to the fact that at much higher monomer concentration probably (i) agglomeration of the fiber as well as PMMA homopolymer results in the formation of lumps, thereby decreasing the number of free radical surface sites available for monomer addition,²⁹ and (ii) swelling and to some extent solubility of grafted PMMA chains and PMMA homopolymer probably form a layer over the fiber backbone and shield the generated free radical sites, thereby preventing monomer addition. That MMA is a solvent for PMMA which swells it and makes it soluble has been reported by Fox et al.³⁰ The K and α values in the Mark-Houwink equation $[\eta] = KM^\alpha$ are 6.75×10^{-3} and 0.72 respectively at 30°C in MMA as a solvent for PMMA.

Effect of Initiator Concentration

Graft copolymerization was studied at various initiator concentration (3.23×10^{-3} – $25.8 \times 10^{-3}M$) with a series of m/p ratios (2.35–37.6) and at a fixed concentration of FeSO_4 ($2.5 \times 10^{-4}M$) at 35°C (Fig. 2). It has been observed that the percent grafting increases on increasing the initiator concentration up to $12.9 \times 10^{-3}M$, beyond which it decreases. The increase of

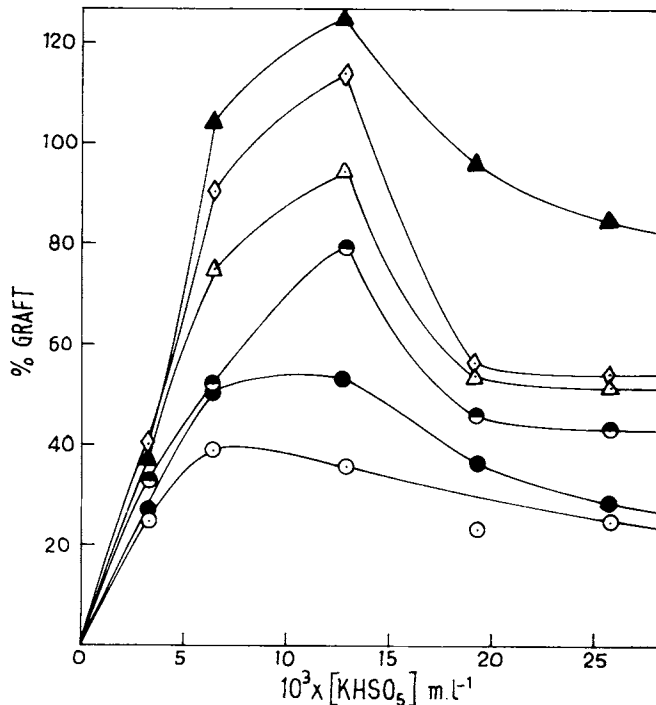


Fig. 2. Variation of graft percent at fixed time; effect of initiator (KHSO_5) concentration at various monomer/polymer ratios: jute = 0.2 g; $[\text{FeSO}_4] = 2.5 \times 10^{-4}M$; temperature = 35°C ; time = 6 h. m/p : (\circ) 2.35; (\bullet) 4.7; (\ominus) 9.4; (\blacktriangle) 18.8; (\blacktriangle) 28.2; (\diamond) 37.6.

percent grafting with increasing initiator concentration may be ascribed to the increase of active sites on the backbone of the jute fiber arising from the attack of diffused KHSO_5 on the polymer matrix.

The retarding effect of percent grafting with initiator concentration beyond $12.9 \times 10^{-3}M$ may be due to (i) predominancy of homopolymerization over grafting, (ii) termination of growing grafted chains by excess of primary radicals formed from the initiator, (iii) premature termination of polymer chains by Fe(III) ions produced during the disproportionation of the $\text{Fe(II)}/\text{KHSO}_5$ redox pair [Fe(III) ion has proved to be an ideal retarder of radical polymerization],³¹ (iv) a decrease in molecular weight (M_w) of the grafted PMMA chains from 10^5 to 10^4 orders has been noticed, and (v) overall oxidation of the jute fibers, retarding monomer addition, onto them.

Effect of Catalyst Concentration

Graft copolymerization has been studied at various FeSO_4 concentrations (0.25×10^{-4} – $30.0 \times 10^{-4}M$) at fixed concentrations of monomer ($1.4M$) and initiator ($12.9 \times 10^{-3}M$). It has been observed that the percent grafting increases with increase of FeSO_4 concentration up to $2.5 \times 10^{-4}M$, beyond which it decreases (Fig. 3). The enhancement of percent grafting may be attributed to increase in the concentration of $\text{Fe(II)}-\text{KHSO}_5$ transient adduct, which undergoes forced decomposition at the fiber surface, resulting in the production of jute radicals at a faster rate. The decrease of percent grafting at higher concentrations ($> 2.5 \times 10^{-4}M$) of Fe(II) may be ascribed to the detrimental factor of excess of Fe(III) ions produced upon the oxidation of Fe(II) . The premature termination of the growing grafted chain by excess of

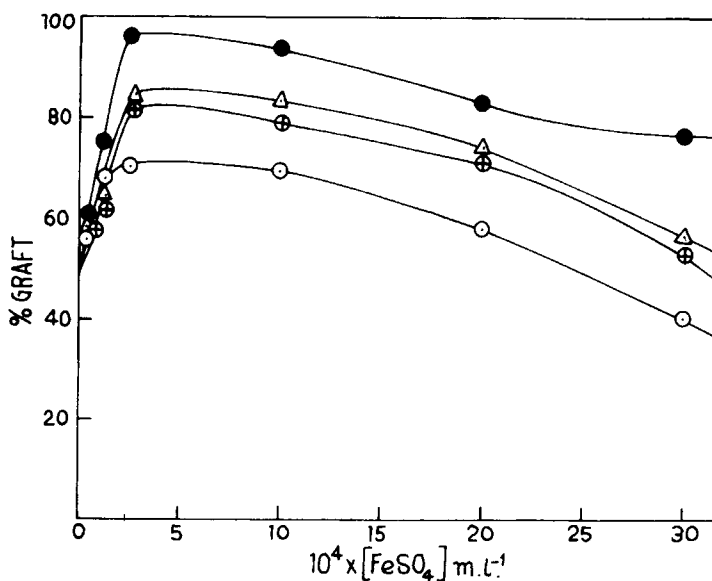


Fig. 3. Variation of graft percent at fixed time; effect of $[\text{FeSO}_4]$ at various temperatures: jute = 0.2 g; $[\text{MMA}] = 1.4082M$; $[\text{KHSO}_5] = 12.9 \times 10^{-3}M$; time = 6 h. Temperature ($^{\circ}\text{C}$): (\odot) 30; (\bullet) 35; (\triangle) 40; (\oplus) 45.

Fe(III) ions has been observed by Morin and Rogovin³² and Mishra et al.³³ in $\text{H}_2\text{O}_2/\text{Fe(II)}$ -system-initiated graft copolymerization.

Effect of Temperature

The effect of reaction temperature on percent grafting is shown in Figure 4. It has been observed that the percent grafting increases up to 35°C and then decreases. The increase in the percent grafting may be ascribed to (i) increase in the production rate of active free radicals, which increase the number of grafting sites at a greater rate, thereby, increasing the rate of graft initiation by radical and (ii) increase of temperature increasing the rate of diffusion of methyl methacrylate onto the fiber matrix, where grafting is also initiated at the complexed monomers. Samal et al.^{20,34,35} have a similar explanation for grafting of acrylamide onto nylon 6, silk fiber, and cellulose.

The decrease in the percent grafting beyond 35°C may be attributed to (i) activation of jute backbone and initiator leading to overall oxidation of the former, (ii) increase in the rate of production of homopolymers, and (iii) premature termination of the growing grafted chains by Fe(III) ions produced upon oxidation of Fe(II) ions. Premature termination by higher valency transition metal ions has been observed by Bamford et al.³¹ and Samal et al.³⁶

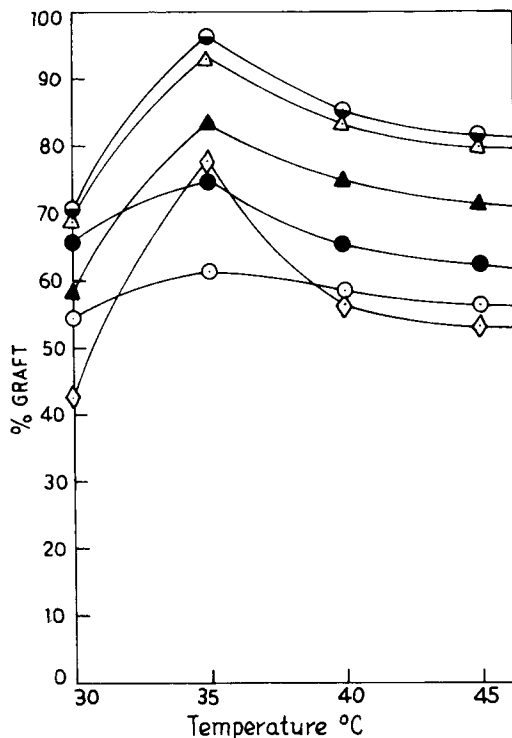


Fig. 4. Variation of graft percent at fixed time; effect of temperature at various FeSO_4 concentrations: jute = 0.2 g; $[\text{MMA}] = 1.4082 M$; $[\text{KHSO}_5] = 12.9 \times 10^{-3} M$; time = 6 h. $[\text{FeSO}_4]$ (○) $0.25 \times 10^{-4} M$; (●) $1.25 \times 10^{-4} M$; (◐) $2.5 \times 10^{-4} M$; (▲) $10 \times 10^{-4} M$; (▲) $20 \times 10^{-4} M$; (◇) $30 \times 10^{-4} M$.

This is similar to what has been put forward in the case of the effect of initiator concentration.

Effect of Organic Solvents

The effect of organic solvents on the graft percent has been studied. Solvents like pyridine, acetone, methyl alcohol, formic acid, and acetic acid of various compositions from 5 : 95 to 50 : 50 (v/v) at 35°C and at fixed concentrations of MMA (1.41M), KHSO_5 ($12.9 \times 10^{-3}M$), FeSO_4 ($2.5 \times 10^{-4}M$), and jute (0.2 g) (Fig. 5). The effect of graft percentage with pyridine may be due to the retarding effect of pyridine-*N*-oxide formed on oxidation of pyridine with KHSO_5 . The oxidation of pyridine to pyridine-*N*-oxide is known,⁹ and the retardation of radical polymerization by *N*-oxides has been recognized by Miura et al.³⁷ The experimental data with acetone and methyl alcohol may be due to the increase in the rate of production of primary radicals, which under the existing experimental conditions render the termination rate relatively fast as compared to the rate of growth of the grafted chains. This is in agreement with the view of Schulz et al.³⁸ and Konar and Palit.³⁹ Further, the

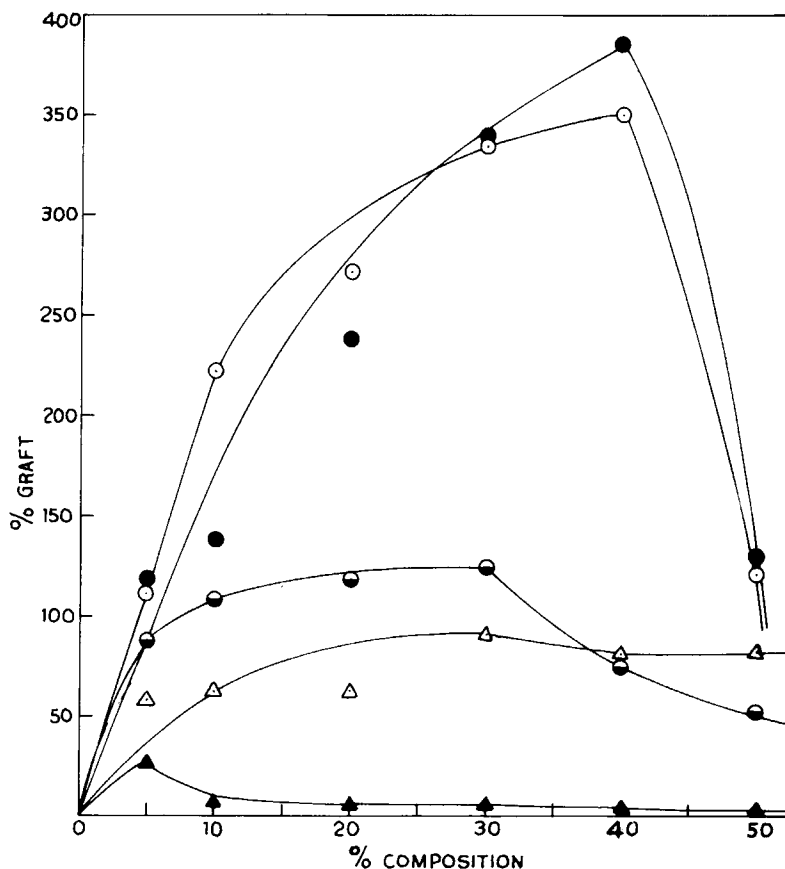


Fig. 5. Variation of graft percent at fixed time; effect of solvent composition: jute = 0.2 g; $[\text{MMA}] = 1.4082M$; $[\text{KHSO}_5] = 12.9 \times 10^{-3}M$; $[\text{FeSO}_4] = 2.5 \times 10^{-4}M$; temperature = 35°C; time = 6 h. (○) HCOOH ; (●) CH_3COOH ; (◐) CH_3OH ; (△) CH_3COCH_3 ; (▲) pyridine.

interchain hydrogen bonding, in this case interlocking the polymer chain, is not rigid, so that the rate of mutual combination of the growing grafted chains increases.

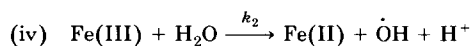
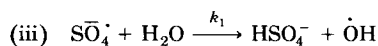
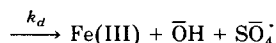
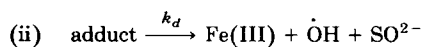
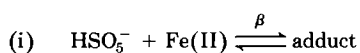
Radical enhancement of graft percentage in the presence of formic acid may probably be attributed to (i) swellability of the jute fibers leading to creation of free-radical sites in the interior of the fiber matrix where the penetrated monomers are grafted and (ii) high reducing activity of formic acid generating free radicals through facile redox reaction on the fiber surface leading to surface grafting.

With acetic acid, $\dot{\text{C}}\text{H}_2-\text{COOH}$ radicals formed from acetic acid attack the jute backbone in addition to the attack by $\dot{\text{O}}\text{H}$ and $\text{S}\dot{\text{O}}_4^-$ radicals from the initiator. This combining attack is responsible for creating more free radical sites on the jute backbone and hence the high graft yield. This seems to be reasonable as acetic acid has been proved to undergo oxidation to glycollic acid via the formation of $\dot{\text{C}}\text{H}_2-\text{COOH}$.⁹

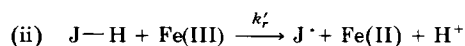
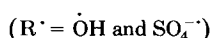
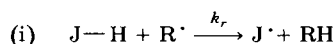
MECHANISM

The mechanism of graft copolymerization reactions may be pictured as involving generation of macrojute radicals resulting from the attack of the free radical species ($\dot{\text{O}}\text{H}$, $\text{S}\dot{\text{O}}_4^-$) obtained by facile decomposition of KHSO_5 in the presence of Fe(II) as catalyst. To some extent, macrojute radicals may also be produced from the attack of Fe(III) ions onto jute Fe(III) ions, and free-radical species are produced from the redox reaction of KHSO_5 and Fe(II) . The macroradicals so generated subsequently, attack the monomer, leading to chain initiation in vinyl polymerization and graft copolymerization. The termination of the graft copolymerization is due to the interaction with Fe(III) ions and mutual combination of the grafted chains on different backbones.

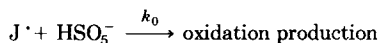
1. Primary radical and Fe(III) production:



2. Formation of macrojute radicals:

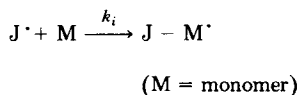


3. Oxidation

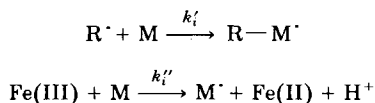


4. Initiation:

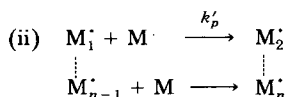
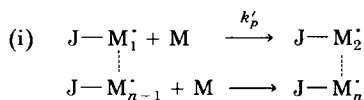
(i) graft copolymerization,



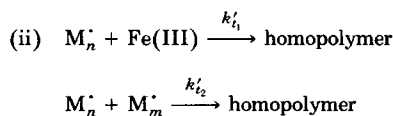
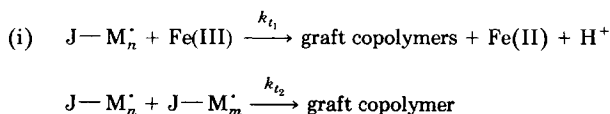
(ii) homopolymerization,



5. Propagation:



6. Termination:



7. Dimerization:

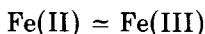
Two macrojute radicals might coupled to yield a dimerized product:



Applying the steady state conditions and considering the graft copolymerization predominating over homopolymerization oxidation and dimerization of jute radicals, the rate of graft copolymerization (R_p) has been evaluated to be

$$8. \quad R_p = \frac{\beta k_d k_r i_i k_p [\text{Fe(II)}] [\text{HSO}_5^-] [J] [M]^2}{k_{t_1} [\text{Fe(III)}] (k_i [M] + k_0 [\text{HSO}_5^-])}$$

If the reaction exhibits massive oxidation of Fe(II) to Fe(III), i.e.,



and

$$k_0[\text{HSO}_5^-] \gg k_i[\text{M}]$$

then eq. 8 can take the form

$$9. \quad R_p = \frac{\beta k_d k_r k_i k_p}{k_0 k_t} [\text{J}][\text{M}]^2$$

which indicates that the rate of graft copolymerization R_p is directly proportional to the square of the monomer concentration.

PROPERTIES OF THE GRAFTS

Methyl methacrylate-grafted jute fibers had the following properties: (a) The absorption of water and water vapor abruptly decreased, (b) the increase in luster of the fiber was not so significant, (c) resistance towards attack of mineral acids and alkalis greatly enhanced, (d) tensile properties: The tensile properties of the grafted jute fibers were determined through determination of tenacity and stiffness following the method of Huque and Habibuddin.⁴⁰ The tenacity was expressed as g/den. After conditioning the jute samples, they were combed the fiber aggregates of uniform length were taken and weighed, and the length was determined.

The tensile strength was determined by a Zeueigles strength tester. The stiffness or tensile modulus at break was determined from the value of tenacity and elongation at break using the relation

$$\text{stiffness at break} = \frac{\text{tenacity at break}}{\text{elongation at break}}$$

The results of the tensile properties are recorded in Table II where it is understood that grafting of methyl methacrylate onto jute fibers enhances their tensile strength, which increases with graft percent.

TABLE II
Effect of Graft Percent on Tensile Properties of Methyl Methacrylate-Grafted Jute Fibers

Grafted sample	Grafting (%)	Elongation at break [(BL)%]	Tenacity (g/den)	Tensile modulus at break
Jute-g-PMMA	36.70	1.40	2.42	172.80
	51.00	1.52	2.76	181.50
	104.10	1.76	3.45	196.00

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