Graft Copolymerization Reaction of Water-Emulsified Methyl Methacrylate With Preirradiated Jute Fiber

FERDOUS KHAN, S. R. AHMAD

Environmental and Chemical System Department, School of Engineering and Applied Science, Cranfield University, Royal Military College of Science (RMCS), Shrivenham, Swindon Wilts, SN6 8LA, United Kingdom

ABSTRACT: The graft copolymerization of methyl methacrylate with water-emulsified solution onto preirradiated jute fiber was studied. The jute samples were irradiated in the presence of air using a ^{60}Co source of gamma-radiation. A nonionic surfactant, commercially known as "Scintron (Triton X-114)," was used as an emulsifier. Homopolymerization was reduced by using 2-methyl-2-propene-1-sulfonic acid, sodium salt. The graft copolymerization was found to be dependent on the emulsifier concentration, radiation dose, temperature, monomer concentration, and reaction time. Maximum grafting level was achieved at temperatures in the range of 70–80°C, and the optimal reaction time for maximum grafting level was found to be between 3 and 5 h, depending on the radiation doses. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 459–468, 1997

Key words: graft copolymerization; methyl methacrylate; jute fiber; gamma-radiation; emulsifier; homopolymerization

INTRODUCTION

Graft copolymerization is a well-established technique for the modification of the physical and chemical characteristics of polymers. The nature of modification, for example, improvement in textile performances, depends on the properties of the monomer. The properties of the grafted copolymer depend not only on the type of the monomer but also on the grafting level and distribution of monomer units. For example, the grafting of hydrophilic monomers, such as acrylic acid, onto polyester and other synthetic fibers improved textile performances such as dyeability and moisture retention capability.[1,2] However, at a higher grafting level, a deterioration in tensile strength was observed.[3]

Jute fiber is a natural polymer, mainly used for manufacturing textile products, similar to those produced from synthetic fibers. Extensive research[3–14] has been carried out to accomplish efficient graft copolymerization of various monomers onto jute and cellulosic materials. Most of the early works were concerned with chemical methods of grafting. Highly efficient grafting of various monomers onto bleached and delignified jute fiber by a redox-initiation method has been achieved.[5] However, because a proportionately large quantity of chemicals is wasted in all chemical grafting methods, these are unlikely to be cost effective in industrial applications. Therefore, an alternative cost-effective method is needed, and the research presented here is aimed toward this goal.

In the past, extensive research has been carried out[15–17] on radiation-induced grafting of acrylic acid, acrylamide, methyl methacrylate (MMA), styrene, and acrylonitrile onto polyethylene, poly(vinyl chloride), and nylon. Very limited works[12,13] have so far reported on the effectiveness of this grafting technique onto lignocellulosic fiber. In the so-called simultaneous irradiation process, jute samples immersed in a solution of
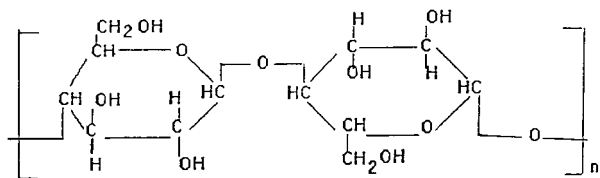
Figure 1 Cellulose chain structure showing two β-D glucopyranose units.

monomer, solvent, and other additives are irradiated. This technique has yielded a good grafting level under appropriate conditions of temperature, reaction time, and radiation doses.[11] However, the level of grafting using this technique is often limited by homopolymerization.

An alternative to the "simultaneous irradiation and grafting" method is the preirradiation method, in which samples are irradiated before being brought into contact with the reaction solution. Therefore, the reactive species are confined in the substrate. The ionizing radiation produces three types of reactive species in polymer. These are ionic, radical, and peroxide. The peroxide species are produced only when polymers are irradiated in the presence of oxygen.[18] This technique has some advantages over the "simultaneous irradiation and grafting" method, such as the formation of less homopolymer and increased depth of penetration. In addition, this method can be applied for continuous grafting in industry.

The preirradiation technique has so far been carried out with monomers in different solvents,[11,14,18] such as methanol, ethylene glycol, and others. It was reported[14] that the increase of solvent (methanol) concentration (40–90%) has a positive influence in the grafting of MMA onto jute fiber. For practical applications, the solvent will be wasted and the process is unlikely to be cost effective and environmentally friendly. In this research, the feasibility of achieving graft copolymerization of MMA onto jute fiber in water-emulsified solution is investigated. Such methods are widely used to prepare graft copolymer,[19] where emulsifier plays an important role in bringing monomers in contact with the substrate. The use of water emulsifiers has some advantages over the use of solutions. For example, in an emulsion process, reaction steps are easily controlled and graft copolymerization at low temperature (0–80°C) can be produced without the use of expensive solvent. It is therefore important to examine the feasibility of achieving effective graft copolymerization of MMA onto lignocellulosic fiber us-

ing such a medium and to evaluate optimal conditions for grafting level.

RADIOCHEMICAL PROCESSES IN CELLULOSIC FIBER

The jute fiber is a cellulosic structure with a chain of homopolysaccharide consisting of identical monomeric units of β-D-glucopyranose, as shown in Figure 1. The chains are cemented together by lignin and hemicellulose, which are present at 12–14% and 22–24%, respectively. In addition to these, the structure contains other minor constituents such as wax and fats, inorganic salts, and pigments. The lignin is a peculiar, biomolecular, three-dimensional amorphous polymer, seemingly with random distribution of stable carbon-carbon linkages between monomeric units.

When jute samples are subjected to high-energy radiation, for example, ^{60}Co γ-radiation, radicals are produced into the cellulose chain by hydrogen and hydroxyl abstraction, as explained in Figure 2(a). Gamma-radiation also ruptures some carbon-carbon bonds and produces radicals [Fig. 2(b)]. Chain scission may also take place to form other radicals [Fig. 2(c)].

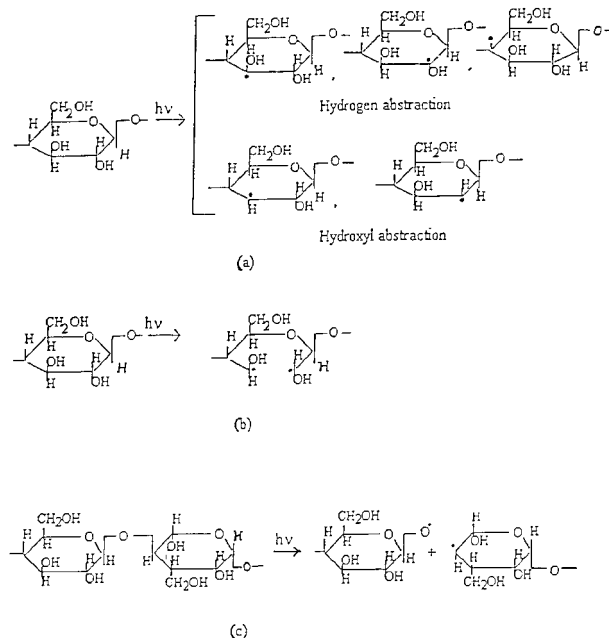In the presence of oxygen, the γ-radiation-in-

Figure 2 Modes of free radical generation into irradiated jute fiber. Radicals are formed after C—H, C—O, or C—C bond cleavages: (a) hydrogen and hydroxyl abstraction, (b) cycle opening, (c) chain scission.

duced radicals in the cellulosic material produce cellulose diperoxides (POOP) and hydroperoxides (POOH) species by a radical chain reaction process. This reaction proceeds in three steps, as follows:
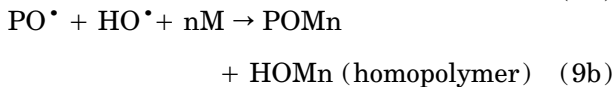
activation:
$$P \xrightarrow{\gamma\text{-ray}} P^\bullet \qquad (1)$$
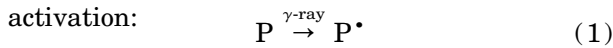
where P is the jute cellulose substrate and $P^\bullet$ corresponds to all possible radical formations according to Figure 2:

propagation:
$$P^\bullet + O_2 \rightarrow PO_2^\bullet \qquad (2)$$
$$PO_2^\bullet + P \rightarrow POOH + P^\bullet \qquad (3)$$
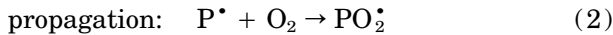
The propagation step is also in competition with the recombinant reaction
termination:
$$P^\bullet + P^\bullet \rightarrow P_2 \qquad (4)$$
$$PO_2^\bullet + P^\bullet \rightarrow POOP \qquad (5)$$
$$PO_2^\bullet + PO_2^\bullet \rightarrow POOP + O_2 \qquad (6)$$
$$PO_2^\bullet + HO_2^\bullet \rightarrow POOH + O_2 \qquad (7)$$
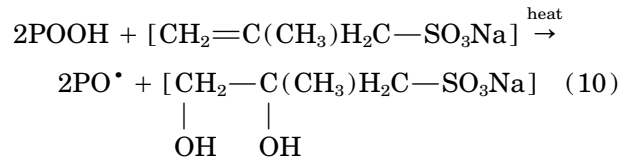
The bonds of diperoxides and hydroperoxides subsequently decompose at an elevated temperature and initiate a grafted side chain when brought into contact with the monomer. Diperoxides (POOP) are often more stable and usually do not lead to homopolymer formation. However, hydroperoxides (POOH) lead to undesirable homopolymerization in graft copolymerization, as shown below:

$$POOP \xrightarrow{heat} 2PO^\bullet \qquad (8a)$$
$$2PO^\bullet + nM \rightarrow 2POMn \,(\text{grafted jute}) \qquad (8b)$$
$$POOH \xrightarrow{heat} PO^\bullet + HO^\bullet \qquad (9a)$$
$$PO^\bullet + HO^\bullet + nM \rightarrow POMn$$
$$+ HOMn \,(\text{homopolymer}) \qquad (9b)$$

where M is the monomer [MMA: $CH_2{=}C(CH_3)$-$COOCH_3$] unit.

A reducing agent such as 2-methyl-2-propene-1-sulfonic acid, sodium salt (MPSA) [$CH_2{=}C(CH_3)H_2C{-}SO_3Na$] is therefore needed to reduce the homopolymerization for efficient grafting. These agents work by breaking the hydroperoxides, for example, in the case of MPSA

$$2POOH + [CH_2{=}C(CH_3)H_2C{-}SO_3Na] \xrightarrow{heat}$$
$$2PO^\bullet + [CH_2{-}C(CH_3)H_2C{-}SO_3Na] \qquad (10)$$
$$\underset{OH}{|} \quad \underset{OH}{|}$$
$$2PO^\bullet + nM \rightarrow 2POMn \,(\text{grafted jute}) \qquad (11)$$

EXPERIMENTAL

Jute fibers were received from farmers in Dhaka, Bangladesh. The precise weathering history of the samples is not known, although these were reported to have been stored at ambient conditions ($\sim$ 30°C and 78% relative humidity) for about 3 months after retting. MMA was obtained from Aldrich Chemical Co. UK for use as a monomer for grafting onto these jute samples. The choice of MMA was based on its hydrophobic property and its extensive use in the grafting of synthetic polymers and cellulosic fibers. Scintron Triton X-114 (octylphenoxy polyethoxyethanol: nonionic surfactant; BDH Chemical Ltd. UK.) as an emulsifying agent and MPSA as an inhibitor (Aldrich Chemical Co. UK.) were used without further purification. The jute fibers were combed thoroughly until free from bark materials. These were then irradiated with γ-radiation at different total doses.

In this study, samples were irradiated at room temperature ($\sim$ 20°C) in the presence of air, and then these were kept in a freezer at about -20°C immediately after the irradiation. The peroxides produced in polymers will also depend on the temperature at which samples are exposed to the ionizing radiation, on the dose rate, and on the nature of the irradiated substance. The dose rate of irradiation in most of the experiments was constant; however, in some cases, it was changed by adjusting the distance of the samples from the center of the source.

A 100-mL solution was prepared by dissolving the required amount of emulsifier (octylphenoxy polyethoxyethanol; a non-ionic surfactant) and MPSA in deionized water, and then MMA was added. The solution was confined in a 200-mL glass reaction bottle and sealed by a rubber septum. The solution was emulsified with the aid of a mechanical instrument known as a "Stuart Flask Shaker" for 30 min. About 2.0 g of the preirradiated jute samples were added into the solution; the bottle was then resealed with a rubber septum. The pure N_2 gas was passed through the

reaction solution with an inlet-outlet needle for 2 h before immersion in a water bath with a thermostated constant agitation system. Grafting reactions commenced at a set temperature for a prefixed period. The samples were taken out from the reaction chamber, washed with hot-deionized water several times, and dried until constant weight at 40°C in the vacuum is reached. The percentage of polymer loading was calculated as follows:

% Polymer Loading

$$= [(W_2 - W_1) \times 100]/W_2 \quad (12)$$

where W_1 is the initial weight of the jute sample and W_2 is the dry weight of the polymerized jute sample before extraction.

Homopolymers were removed by extracting the grafted samples in a Solvent (1,2-dichloroethane) for about 48 h in a soxhlet apparatus. These were then dried until constant weight was achieved at 40°C in a vacuum. Weight percentage of grafting is defined by the following relation:

$$\% \text{ Graft Weight} = [(W_3 - W_1) \times 100]/W_3 \quad (13)$$

where W_1 and W_3 are the initial weight and graft weight of the jute samples, respectively; the percentage of graft weight is sometimes referred to as grafting level.

In some experiments, % homopolymer was calculated with respect to the weight of MMA in solution according to the following relation:

$$\% \text{ Homopolymer} = [W_H/W_M] \times 100 \quad (14)$$

where W_H and W_M are the weights of the homopolymer formed and MMA, respectively.

RESULTS AND ANALYSIS

The emulsion graft copolymerization of MMA onto jute fibers is affected by many parameters such as emulsifier concentration, a reducing agent of homopolymerization, radiation dose, monomer concentration, temperature, and reaction time. The effects of these parameters on the level of grafting could be cumulative and interdependent. These effects are studied systematically as follows.
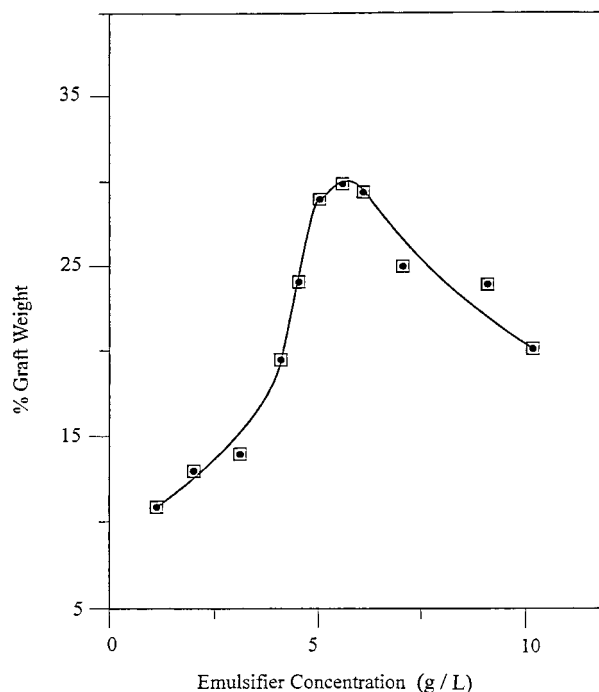

Figure 3 Influence of the emulsifier concentration on MMA grafting onto preirradiated jute fiber at 80°C. Total radiation dose = 5.0 Mrads at 0.5 Mrad/h, jute fiber ≡ 2.0 g, MMA = 10 mL, deionized water = 90 mL, reaction time = 3.0 h.

Influence of Emulsifier Concentration

The choice of the emulsifier is based on the criterion that it must produce a stable emulsion between the monomer and water phases. Eleven samples were tested in a series of experiments (results are shown in Fig. 3) to achieve grafting at the same irradiation and chemical conditions, but with different amounts of the emulsifier (0.1–1.0 g) added into the solution. In these experiments, the reaction time was maintained at 3.0 h and the temperature was kept at 80°C.

In the first test, 0.11 g of the emulsifier was added into the solution and the grafting was found to be about 10%, with approximately 0.4% homopolymer extracted from grafted jute fiber. In the second test, at the same grafting conditions but with 0.2 g of the emulsifier, the grafting level was found to be ∼ 13% and about 2% homopolymer was extracted. Further tests with increasing amounts of the emulsifier up to 0.6 g into the grafting solution showed a sharp increase of the percentage of grafting up to about 30%. Above this level of the emulsifier, the percentage of grafting was found to decrease, as shown in Figure 3.

It was observed that the amount of homopoly-

Table I   The Contribution of MPSA at Different Concentrations in the Emulsion Graft Copolymerization Process of MMA onto Jute Fiber

MPSA Concentration (g/L)	MMA Homopolymerized onto Jute (%)	MMA Homopolymerized into Solution (%)	MMA Grafted onto Jute (%)	MMA Unchanged in the Emulsion (%)
0	3.8	1.4	12.3	82.5
1	3.7	0.4	14.6	81.3
2	3	0.1	13.8	83.1
3	4.1	0.2	11.2	84.5
4	5	0.4	10.2	84.4
8	5.1	2.7	9.5	82.7

merization increased when a large amount of emulsifier was added to the grafting solution. A systematic study on this was not undertaken because a homopolymerization inhibitor was subsequently used to minimize the homopolymerization while maintaining an optimal level of grafting (vide afro).

The existence of an optimal emulsifier concentration for maximum grafting under any grafting condition can be explained by invoking the concept of the critical micelle concentration. At a certain concentration of emulsifier, the aggregation of emulsifier molecules gives rise to a minimum in the surface energy. At this level, the graft copolymerization takes place most probably in an emulsifier layer, in a zone close to the surface of the polymer molecules. A further increase in the emulsifier concentration will progressively inhibit the copolymerization of the monomer onto jute and at the same time will encourage polymerization of the emulsifier, thus decreasing the grafting level. From this study, the emulsifier at 5.0 g/L is chosen for subsequent grafting of MMA onto jute fibers.

Reducing Agent of Homopolymerization

Homopolymerization of the monomer is inevitable during a grafting reaction. The homopolymers are normally removed from the grafted material by repeated washing. Since it requires one or more chemical operation to reduce the homopolymers to an acceptable level, it is advantageous to reduce homopolymerization by incorporating some inhibiting agents into the grafting solution. The chemical, MPSA, is known[20] to prevent the homopolymerization and therefore was chosen for this study.

A series of experiment was done with different concentrations (grams per liter) of MPSA into the grafting solution. The effectiveness of MPSA at different concentrations in the reaction medium is shown in Table I. Six samples weighing about 2 g each were tested at the same irradiation conditions. The solution was composed of 10 mL of MMA, 90 mL of deionized water, and 0.5 g of emulsifier (nonionic surfactant).

In the first test, a 36.5% grafting level was achieved where the solution contained no inhibitor and about 3.8% of MMA was transformed into homopolymer onto jute fiber. The latter were mostly removed during the extraction in the soxhlet apparatus. It was also found that the postreaction solution contained about 1.4% homopolymers, which was collected after precipitation.

The second sample went through the same treatment with 1 g/L of MPSA in the emulsion solution. In this case, the grafting level was found to be ~ 40% and ~ 3.74% MMA transformed into homopolymer on jute fiber; however, the postreaction solution contained only ~ 0.4% homopolymers. Similarly, the third sample was tested with 2 g/L of MPSA into emulsion solution; the corresponding graft weight was found to be ~ 39%, which is slightly less than that obtained in the second test, but the homopolymerization on jute fiber and also in the emulsion solution was minimal, as shown in Table I.

Subsequently, several more tests were done with increasing the concentration of MPSA up to 8 g/L of emulsion solution. The graft weight was found to decrease from the maximum 39% down to 32% at 4 g/L of MPSA, although the concentration of homopolymers was found to have increased proportionately. The decrease in grafting level at the concentration of MPSA above 4 g/L was considerably slower, but the homopolymer concentration in the postreaction solution increased almost
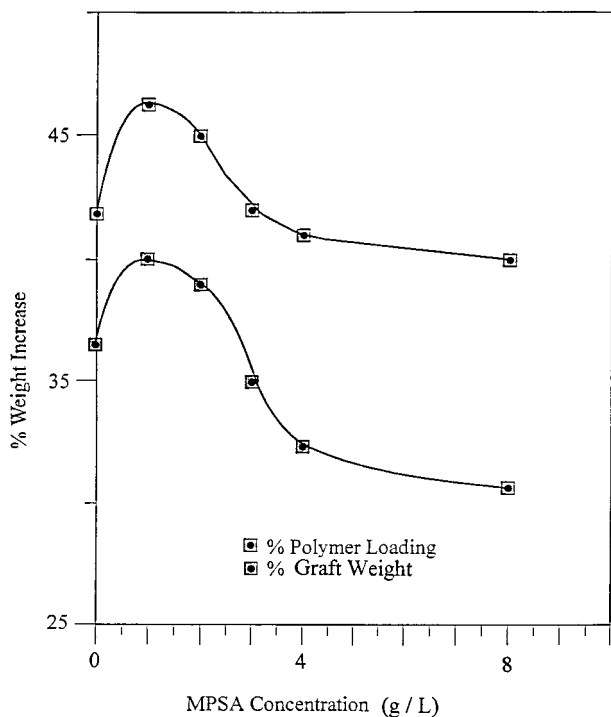
Figure 4 Effect of different concentrations of homopolymer reducing agent (MPSA) on MMA grafting onto preirradiated jute fiber at 80°C. Total radiation dose = 5.0 Mrads at 0.3 Mrad/h, jute fiber ≡ 2.0 g, emulsifier ≡ 0.5 g, MMA = 10 mL, deionized water = 90 mL, reaction time = 3.0 h.

proportionately. The difference in the corresponding values of grafting and polymer loading is a measure of the extractable homopolymers from the grafted jute fibers, as shown in Figure 4.

The existence of an optimal MPSA concentration for minimum homopolymerization under any grafting conditions can be explained by the fact that MPSA contains an unsaturated, allylic-type, inhibiting functional group [$H_2C{=}C(CH_3)CH_2{-}$] acting as a free radical transferring agent. However, at high concentrations, this inhibitor enters the grafted layer and blocks the propagation of the grafting reaction. Consequently, premature chain termination of the grafted side chain occurs. From this investigation, 2 g/L of MPSA into the solution was considered to be an optimal concentration of homopolymerization inhibitor for the grafting of MMA onto jute fiber.

The Effect of Radiation Dose on Grafting

Results on the effect of the total irradiation dose on the grafting level are shown in Figure 5. Experiments were carried out for five different irradia-

tion doses between 1.0 and 5.0 Mrads at the same intensity of irradiation, and the grafting solutions were prepared at the same chemical conditions for each sample. Samples were grafted at a temperature of 80°C for 3 h. The results show that the grafting level increases almost linearly with the radiation dose up to about 3.0 Mrads. Above this limit, the grafting level tends to saturate and the increase with the further increase of irradiation dose up to about 5.0 Mrads is negligible.

The saturation of grafting at high irradiation doses is, however, expected. At low irradiation doses, the formation of peroxides increases linearly, which subsequently gives rise to grafting when brought in contact with monomer units. However, at a higher concentration of peroxides, these also undergo radiation-induced decomposition at increasing rates in proportion to their dynamic concentration. This is expected to slow down and eventually level off the rate of peroxides available for grafting. Similar results have been reported[21] for the grafting of acrylonitrile onto polyethylene film. It is to be noted that grafting level will also depend on the monomer concentration, reaction temperature, and reaction time.
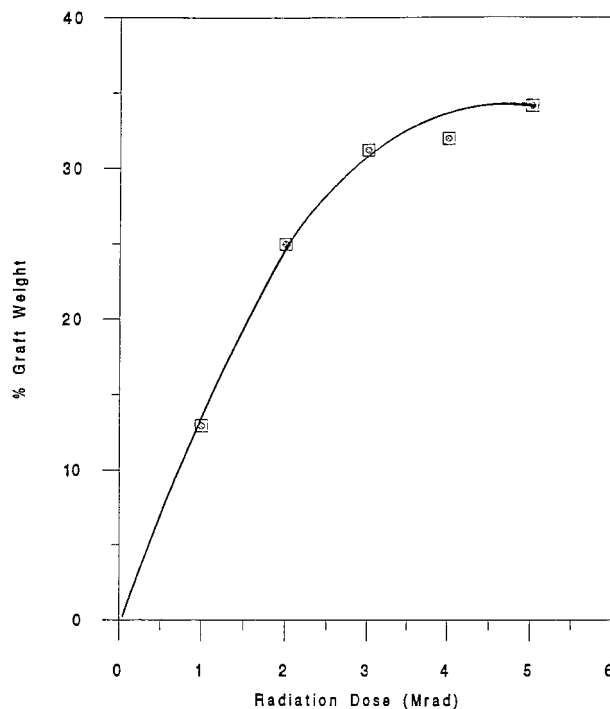

Figure 5 Effect of preirradiation dose on MMA graft copolymerization onto jute fiber at 80°C. Dose rate = 0.5 Mrad/h, jute fiber ≡ 2.0 g, MMA = 10 mL, emulsifier ≡ 0.5 g, MPSA = 0.2 g, deionized water = 90 mL, reaction time = 3.0 h.
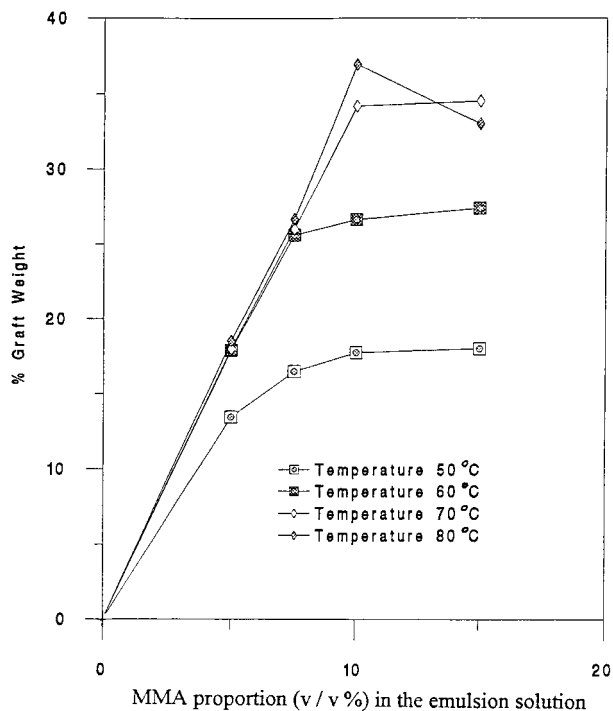
Figure 6 Influence of the volumic percentage of MMA in the MMA/deionized water emulsion on the grafting level onto preirradiated jute fiber at different temperatures. Total radiation dose = 5.0 Mrads at 0.5 Mrad/h, jute fiber ≡ 2.0 g, emulsifier ≡ 0.5 g, MPSA = 0.2 g, total solution = 100 mL, reaction time = 3.0 h.

Dependence of Grafting on Monomer Concentration

Monomer concentration in the solution is one of the reaction parameters for grafting. It influences the graft copolymerization by adjoining the required number of monomer units onto the polymer branch during the reaction. The dependence of grafting level on the concentration of monomer was studied at four different reaction temperatures in the range of 50–80°C. In these tests, samples were irradiated with a 5.0-Mrad dose at the same dose rate of 0.5 Mrad/h and the reaction time was maintained at 3.0 h. The reaction solutions contained 5 g/L of the emulsifier and 2 g/ L of MPSA, with various proportions of MMA in deionized water.

The results (Fig. 6) show that the grafting level tends to saturate above 7.5% (v/v) MMA concentration at 50°C reaction temperature. A similar trend was found at 60°C; the saturation level is also reached at about 7.5% MMA concentration, but the grafting level was increased from 17 to 27%. At the reaction temperature of 70°C, the

grafting level was found to increase linearly up to a maximum of 35% at the concentration of 10% MMA, whereas at 80°C, the maximum grafting level of ~ 37% was obtained at the same MMA concentration. It was also observed that there was some unemulsified monomer, floating on the surface of the solution after the reaction was conducted at 15% (v/v) MMA concentration. From this study, 10% (v/v) MMA into the reaction solution was found to give the maximum grafting level in the temperature range of the tests presented here.

Temperature Effect on MMA Grafting

The speed of the reaction and the number of monomer units added onto the growing polymer branch are also influenced by temperature. The preirradiation conditions of the samples and the chemical composition of the solutions were fixed for all samples.

Results in Figure 7 show that the graft copolymerization reaction did not take place at reaction temperatures below 40°C. It is however expected, since peroxides, being the grafting initiators, are
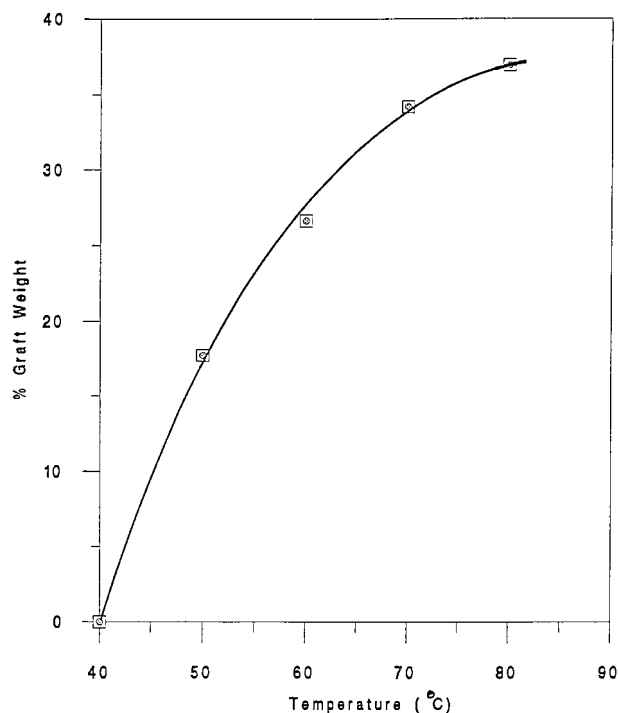

Figure 7 Effect of temperature on MMA grafting onto preirradiated jute fiber. Total radiation dose = 5.0 Mrads at 0.5 Mrad/h, jute fiber ≡ 2.0 g, emulsifier ≡ 0.5 g, MPSA = 0.2 g, MMA = 10 mL, deionized water = 90 mL, reaction time = 3.0 h.
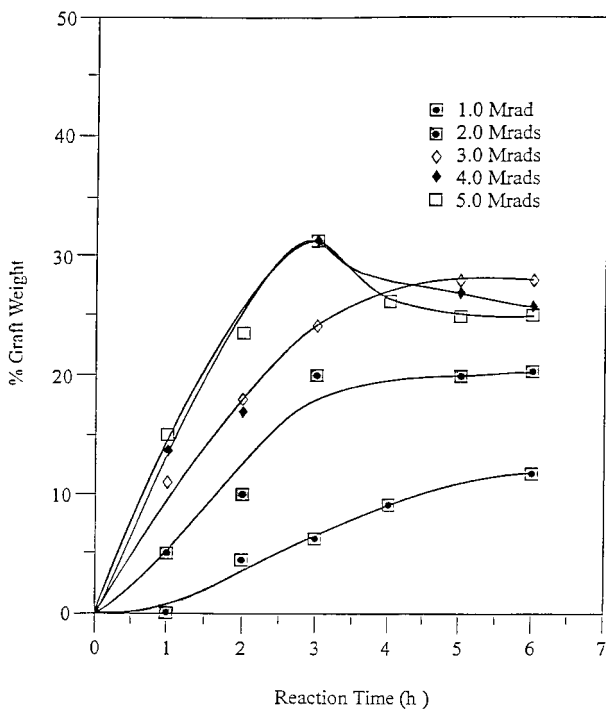
Figure 8 Effect of reaction time on MMA grafting onto jute fiber at 70°C. Samples are irradiated at different total doses with same dose rate 0.5 Mrad/h. Jute fiber ≡ 2.0 g, emulsifier ≡ 0.5 g, MPSA = 0.2 g, MMA = 10 mL, deionized water = 90 mL.

known to be stable at low temperatures. The percentage of grafting was found to increase rapidly with the increase in reaction temperature from 50 to 70°C, reaching a saturation level at 35% graft weight.

At elevated temperatures, peroxides decompose into radicals. Monomer (MMA) units diffuse through the polymer to these peroxide radicals to allow graft copolymerization reaction to take place. However, at higher temperatures, the rate of decomposition of the few remaining peroxides is expected to slow down due to the progressive depletion of peroxides and eventually levels off with a further increase in temperature.

The Effect of the Reaction Time

Preirradiated samples of jute were immersed into the reaction solution where the chemical compositions of the solution contained 5 g/L of emulsifier, 2 g/L of MPSA, and 10% (v/v) MMA, which were found to provide the optimal grafting level in our earlier experiments. Reaction temperature was also found to play a significant role in the graft copolymerization process. Under the above condi-

tions and an arbitrarily chosen reaction time of 3 h, 70°C was found to give an adequate grafting level in the previous tests. Tests on the reaction time were therefore carried out at this temperature. Samples irradiated at 0.5 Mrad/h, for five different total doses, were studied.

The results on the variation of the percentage of grafting as a function of the reaction time are shown in Figure 8. Graft weight was found to be linearly increased for reaction times up to about 3.0 h for all samples, irrespective of total irradiation doses. Figure 9 shows the variation in grafting rate, that is, the slope of the percentage of grafting versus reaction time plot in Figure 8, with their corresponding irradiation doses. The rate of grafting was found to be $2.95 \pm 0.03\%$/h for a 1.0-Mrad irradiation dose. This increases significantly up to $9.8 \pm 0.07\%$/h when irradiated up to a dose of 4.0 Mrads. The rate of grafting remains constant with a further increase of irradiation doses due to the leveling off of the peroxides.

For reaction times longer than 3.0 h, there does not appear to be any significant increase in the grafting level (Fig. 8). The increase of graft weight for a particular irradiation dose is expected to be linear with the increase in reaction time until all of the radiation-induced peroxides
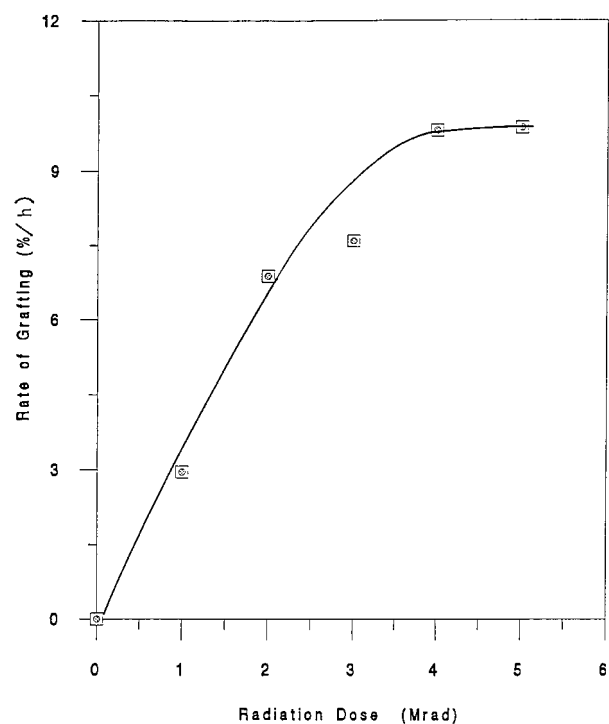

Figure 9 Variation of the percentage of rate of grafting with radiation doses.

are depleted. However, for high radiation doses (4.0 and 5.0 Mrads), graft weight was found to reach a maximum at about the same reaction time and to decrease with a subsequent increase in reaction time. Similar results have been reported[6,7,15] in the grafting of MMA onto jute fiber and polyethylene film. It may be possible that the grafted polymer becomes partially soluble in the MMA-emulsified solution on prolonged exposure to higher temperature in the solution.

DISCUSSION

The findings of these experiments have shown that effective graft copolymerization of MMA onto jute fiber could be achieved in a water-emulsified solution. This has removed the restriction of finding a solvent for the monomer and other additives normally needed for such a grafting process.

The monomer units need to penetrate the jute fiber and come in contact with the reactive species already created by ionizing radiation for a grafting reaction to take place. The emulsifier under a constant mechanical agitation breaks down the monomer phase into fine droplets and disperses and stabilizes them into the solution; therefore, these are uniformly distributed onto the surfaces of the jute substrates. However, at high concentrations of the emulsifier, the progressively higher rate of homopolymerization competes with the grafting reaction and reduces its efficiency. In any emulsion polymerization process, it is therefore important to optimize the concentration of emulsifier, although for maximum grafting level, the optimal concentration will depend on their type and chemical characteristics.

The preirradiation grafting process has the advantage over "simultaneous irradiation and grafting" in that the monomer and other additives (if necessary) are not subject to exposure to ionizing radiation. The preirradiation processes are also more viable for commercialization. However, in this process, the reactive species must be present in the substrate before the commencement of the graft copolymerization reaction. This is achieved by irradiating the samples before placing them into the reactor system.

The MPSA used in these experiments has been found to reduce homopolymerization, although not to a significant extent. However, in jute substrate, the effectiveness of this inhibitor was not as good as it is in other polymers.[20] It is therefore necessary to locate other more efficient and less expensive inhibitors for the MMA grafting onto jute fibers.

Results on the effect of reaction temperature on grafting suggest that the reactive species remain inactive at temperatures below 40°C. Above this temperature, these species become very sensitive and produce free radicals. At higher temperatures, swelling of the substrate increases and therefore allows the monomer to diffuse more rapidly to the substrate, consequently improving the grafting level. However, at very high temperatures, for example, above 80°C, homopolymerization efficiency becomes significant and interferes with the grafting reaction, thus reducing its efficiency. Also, at high temperatures, a pressure buildup inside the reaction bottles takes place, which may adversely affect the grafting process.

CONCLUSIONS

The graft copolymerization of hydrophobic monomer (MMA) onto preirradiated jute fiber in water-emulsified solution has been achieved. The criteria for such a grafting method will apply to free radical peroxidation graft copolymerization of natural fibers, irrespective of the mode of initiation of the reaction. The following conclusions have been made from the results obtained in this work.

- There is an optimal concentration of emulsifier for maximum grafting in heterogeneous-phase graft copolymerization process.
- Although MPSA at lower concentration (1.0–2.0 g/L) enhances the grafting level to some extent, it is not an efficient inhibitor for the grafting process presented here.
- The total irradiation dose determines the number of grafting sites, although these sites do not increase significantly above a certain irradiation dose.
- The increase in grafting level is linearly dependent on the monomer concentration until the active radicals are completely depleted.
- Grafting reaction does not commence below 40°C up to 3 h reaction time, and the efficiency rises with the reaction temperature up to about 80°C.
- Grafting level increases linearly with the increase in reaction time until all of the radicals are depleted.

REFERENCES

1. K. Kaji, *Ind. Eng. Chem. Prod. Res. Dev.,* **24,** 95 (1985).
2. M. H. Rao and K. N. Rao, *Radiat. Phys. Chem.,* **26** (6), 669 (1985).
3. S. Moharana, S. B. Mishra, and S. S. Tripathy, *J. Appl. Polym. Sci.,* **40,** 345 (1990).
4. S. Moharana and S. S. Tripathy, *J. Appl. Polym. Sci.,* **42,** 1001 (1991).
5. A. K. Mohanty and B. C. Singh, *J. Appl. Polym. Sci.,* **34,** 1325 (1987).
6. S. S. Tripathy, S. Jena, S. B. Misra, N. P. Padhi, and B. C. Singh, *J. Appl. Polym. Sci.,* **30,** 1399 (1985).
7. S. R. Shukla and A. R. Athalye, *J. Appl. Polym. Sci.,* **54,** 279 (1994).
8. A. K. Mohanty, S. Patnaik, and B. C. Singh, *J. Appl. Polym. Sci.,* **37,** 1171 (1989).
9. R. K. Samal, H. S. Samantaray, and R. N. Samal, *J. Appl. Polym. Sci.,* **37,** 3085 (1989).
10. R. K. Samal, R. N. Samal, Sabyasachi Dash, and H. S. Samantaray, *Indian J. Text. Res.,* **14,** 187 (1989).
11. N. A. Ghanem, N. I. El-Awady, K. Singer, and M. I. Aly, *Eur. Polym. J.,* **15,** 1007 (1979).
12. P. Ghosh, A. R. Bandyopadhyay, and S. Das, *J. Macromol. Sci. Chem.,* **A19,** 1165 (1983).
13. S. K. Majumdar and W. H. Rapson, *Text. Res. J.,* **34,** 1015 (1964).
14. F. R. Al-Siddique, A. U. Khan, and R. A. Sheikh, *J. Bangladesh Acad. Sci.,* **7,** 87 (1983).
15. A. Chapiro, *J. Polym. Sci.,* Prague Symposium, **29,** 321 (1958).
16. V. T. Stannett, *Radiat. Phys. Chem.,* **35**(1–3), 82 (1990).
17. I. M. Trivedi, P. C. Mehta, K. N. Rao, and M. H. Rao, *J. Appl. Polym. Sci.,* **19,** 1 (1975).
18. A. Chapiro, *J. Polym. Sci.* Symposium No. 50, 181 (1975).
19. J. I. Kroschwitz (Exec. Ed.), *Encyclopedia of Polymer Science and Engineering,* 2nd Ed., Wiley-Interscience Publ., New York, 1986.
20. R. Chatelin and L. Gavet, U.S. Pat. 5,266,632 (1993).
21. A. Chapiro, in *Irradiation of Polymers,* Advances in Chemistry Series 66, *American Chemical Society,* 1967, Chap. 2.