

Graft Copolymerization and Characterization of 2-Hydroxyethyl Methacrylate onto Jute Fiber by Photoirradiation

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Received 17 March 2005; accepted 1 October 2005

DOI 10.1002/app.23367

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: UV radiation induced graft copolymerization of 2-hydroxyethyl methacrylate onto natural lignocellulose (jute) fiber was carried out by two methods: simultaneous irradiation and grafting and preirradiation grafting. 1-Hydroxycyclohexyl-phenylketone was used as the photoinitiator in both methods. In the former method, the variation of the graft weight was measured for different values of radiation exposure time and the concentrations of both the monomer and photoinitiator. The latter method produced up to 76% graft weight compared to 45% obtained with the former method. The preirradiation method offers better control of the homopolymerization reaction compared to that afforded by the other method. The optimum value of the reaction parameters on the graft weight was evaluated. The mechanical properties of grafted samples were found to be

drastically different from those of the as-received ones and the effect was proportional to the percentage of graft weight. Differential scanning calorimetry studies showed that the percentage of graft add-on of hydroxyethyl methacrylate with jute had a significant effect on the thermal properties. IR studies indicated the degree of grafting could be estimated by correlating the band intensities with the graft weight. The jute samples grafted with poly(hydroxyethyl methacrylate) at a level of 12% graft weight exhibited a maximum 20% increase in hydrophilicity. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2898–2910, 2006

Key words: graft copolymerization; characterization; homopolymerization; UV radiation; hydroxyethyl methacrylate; jute fiber

INTRODUCTION

Jute is a biodegradable and renewable natural lignocellulose that is composed of mainly cellulose (58–63%), hemicellulose (20–24%), and lignin (12–15%). Modification of such natural polymeric materials through a graft copolymerization reaction provides an effective route to its diverse applications replacing some synthetic polymers. The nature of the modifications depends on different factors, and they are widely reported in the literature. The most important among them are the type of monomer being grafted, the percentage of graft weight, the method of graft copolymer reaction, and the distribution of the grafted chain throughout the parent polymers.^{1,2} McDowall and coworkers reported² that the γ -radiation induced preirradiation method showed higher elongation,

faster recovery, and more uniform graft copolymer distribution throughout the cross section than those achieved by the ceric-ion initiation method. The graft copolymerization of various monomers onto natural cellulose and synthetic polymers has been extensively investigated using high-energy radiation^{3–7} and chemical initiation^{8–12} methods. An alternative to those is the photoinduced graft copolymerization method initiated by UV radiation. This is considered to be a safer and cost effective technique because it results in comparatively less deterioration of the polymer due to the selective nature of the UV-induced reaction. Because the energy associated with UV radiation is comparatively lower than high-energy radiation sources (e.g., γ rays), a photoinitiator is generally needed to promote the graft copolymer reaction. UV-induced graft copolymerization of various monomers onto other natural cellulose materials has been investigated extensively.^{13–21} Grafting of methyl methacrylate onto bleached jute fiber has been investigated by Ghosh and Paul¹⁷ using ferric sulfate as an initiator under visible light. In this case the light is absorbed by the near chromophore formed by the cellulose–metal complex, and the radicals are formed on the cellulose backbone to initiate the grafting reaction. In a recent report²² we described the photoinduced graft copoly-

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Contract grant sponsor: CEC International Scientific and Technical Cooperation Scheme; contract grant number: INCO-DC.

merization of methyl methacrylate onto jute fiber in an aqueous medium. Studies have shown^{20,21} that the graft copolymer reaction of various monomers onto cellulose materials depends on the type of photoinitiator and the monomer and the role of various solvents in the UV radiation induced simultaneous irradiation and grafting technique. The grafting of acrylamide and hydroxyethyl methacrylate (HEMA) onto cellulose was studied¹⁴ using isopropyl thioxanthone as the photoinitiator. Ali et al.²³ studied a jute–vinyl monomer composite via a UV radiation *in situ* system to improve the properties of the product.

In the commonly used simultaneous irradiation and grafting technique, the concurrent homopolymer formation has been found to predominate over the graft copolymerization reaction because of the radiolysis of monomer, solvents, and other additives in the system. In an alternative preirradiation technique, the parent polymer is exposed to radiation before it is brought in contact with the reaction solution. Therefore, the reactive species such as ions, radicals, and peroxides are confined in the cellulose polymer. Several studies^{1,3,5,24} have shown that polymer peroxides are formed when irradiated in the presence of air. These are subsequently decomposed at high temperatures and in the presence of monomer, culminating in graft copolymerization. Khan et al.¹ reported that the irradiation of cellulose using a high-energy radiation source in the presence of air produces cellulose peroxides and some short-lived radicals. These are expected to contribute to the graft copolymer reaction. Similar radiation-induced chemical yields such as radicals and peroxides are expected to be formed onto the jute-cellulose backbone in the case of the photo-induced graft copolymer process. In this work the graft copolymerization of HEMA onto jute fiber was examined using 1-hydroxycyclohexyl-phenylketone (HCAP) as a photoinitiator via the simultaneous irradiation and grafting technique and preirradiation technique. We also examined how the HEMA grafting influences the mechanical, thermal, and hydrophilic properties of the grafted product with respect to the as-received fiber.

EXPERIMENTAL

Materials

Jute samples received from Amin Jute Mill Co. (Bangladesh) were stored in the dark at 20°C and about 65% relative humidity. HEMA purchased from Aldrich Chemical was stabilized with 300 ppm of hydroquinone monomethyl ether and was stored at 5°C. Methanol was used to dissolve the photoinitiator and as the solvent for homopolymer extraction in a Soxhlet apparatus. 2-Methyl-2-propene 1-sulfonic acid, sodium salt (MPSA, 98%, Aldrich Chemical) was used as

a homopolymer inhibiting agent and was stored in an oxygen-free nitrogen environment at room temperature. The sample of HCAP was kindly supplied by Ciba Geigy; it was stored in the dark at ambient conditions. Deionized water was used as a graft-copolymer reaction medium.

UV-radiation source

The UV-radiation source (Jenton STAT-I-CURE, Jenton International) consists of a compact UV oven, utilizing a 400-W mercury flood light cure source. Both the power supply and lamp are integrally mounted within the cabinet, which is connected to a shutter mechanism to prevent exposure to UV radiation when the door is open. The source produced radiant energy with about 85–90% of the light in the desired wavelength range between 300 and 400 nm.

Simultaneous irradiation and grafting method

Cleaned jute fibers, weighing about 2.0 g, were soaked in 100 mL of prepared reaction solution for 48 h to ensure the incorporation of the monomer and other additives into the jute sample. Wet samples were then exposed to UV radiation in the presence of air. The distance between samples to the center of the source was 25 cm. Following irradiation the samples were washed several times with hot deionized water to remove the traces of unreacted chemicals, which was confirmed by IR analysis. These were then dried at 40°C to a constant weight in a vacuum oven. Homopolymers were removed by extracting the grafted samples in methanol by refluxing in a Soxhlet apparatus until constant weight had been achieved. Finally, extracted samples were dried under a vacuum at 40°C and their weights were recorded. The weight percentage of grafting was calculated according to the following equation:

$$\text{graft weight (\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 are the initial weight and weight of the grafted samples, respectively. The homopolymer content in the grafted sample was calculated as follows:

$$\text{homopolymer (\%)} = \frac{W_H}{W_M} \times 100$$

where W_H is the weight difference before and after extraction of the grafted jute (the homopolymer content) and W_M is the total monomer weight used in the reaction solution.

The grafting efficiency was also calculated by the ratio of the HEMA converted into graft copolymer and the total amount converted to both graft copolymer and homopolymer according to the formula

grafting efficiency (%) =

$$\frac{\text{graft weight}}{\text{graft weight} + \text{homopolymer}} \times 100$$

Preirradiation grafting method

Cleaned jute samples were soaked in a solution of methanol and HCAP photoinitiator ($4.895 \times 10^{-2} \text{ mol L}^{-1}$) for 48 h to ensure the incorporation of photoinitiator into the jute fiber. Wet samples were then irradiated with UV radiation in the presence of air. Irradiated samples were immersed in a prepared grafting reaction solution. The solution was placed in a 200-mL glass reaction bottle, 2.0 g of the preirradiated sample was added to the solution, and the bottle was sealed with a rubber septum. The bottle was purged with nitrogen gas for 2 h using inlet–outlet needles before immersing it in a thermostatic water bath with a constant agitation system. Grafting reactions were carried out at a set temperature for a prefixed period. The separation procedure of the unreacted monomer from the grafted sample, the homopolymer extraction procedure, and the calculation of the graft weight were the same as that of the simultaneous irradiation and grafting technique.

Characterization methods

The mechanical properties were studied by using a microprocessor-controlled material-testing machine (Lloyd Instruments M 5K) loaded with a data analysis software package (DAPMAT 3.0). A 1-kN calibrated load cell was used at a crosshead speed of 10 mm min^{-1} with an internal extensometer with automatic break detector having a constant gauge length of 25 mm. The parameters such as the breaking load, tensile strength, corresponding elongation, and work done at which the samples were ruptured were determined. The numerical values were calculated as an average of the 10 measurements for each type of sample. The average values of the mechanical strength were normalized with respect to the value obtained from the as-received sample.

Thermal analysis was performed using a Mettler differential scanning calorimetry (DSC) apparatus at a heating rate of $10^\circ\text{C min}^{-1}$. The DSC instrument was calibrated for temperature and energy using indium, lead, and zinc reference samples. DSC traces were recorded with about 5 mg of sample under a nitrogen flow (50 mL min^{-1}). All samples were heated for 72 h under a vacuum at 80°C to remove the moisture.

The IR spectra were recorded at ambient conditions using an attenuated total reflectance spectrometer (Graseby Specac, P/N 11209) with a 10-reflection attenuated total reflectance unit and a solid sample holder at a resolution of $\pm 3 \text{ nm}$ and a diffraction factor of 1. The maximum transmission was obtained by careful alignment of the mirrors in the spectrometer. Samples weighing $\sim 2.0 \text{ mg}$ and with a size of $< 2 \mu\text{m}$ were completely dispersed with 200 mg of dehydrated KBr using an agate mortar and pestle. The paste was then compressed into a transparent tablet by applying a pressure between 8 and 10 tons using an evacuable die.

Water absorption measurements were carried out by centrifuging the samples. The centrifuge tube had a fine mesh strainer located away from the bottom of the tube to allow excess water to drain out of the sample. The centrifuge tube was sealed to ensure 100% relative humidity to prevent absorption of water by the sample. The equilibrium water absorption capability of the samples was calculated according to the following relationship:

$$\text{equilibrium water absorption (\%)} = \frac{B - A}{C - A} \times 100$$

where A is the mass of the weighing tube, B is the mass of the weighing tube and moist sample from centrifuging, and C is the mass of the weighing tube and dry sample. The average values were calculated from five replicate measurements for each specific sample.

RESULTS AND DISCUSSION

Simultaneous irradiation and grafting method

In this method, the graft copolymerization is determined as a function of different reaction parameters such as the radiation time, HEMA concentration, and the effect of the concentration of HCAP as a photoinitiator.

Effect of irradiation time

The graft copolymerization reaction was initiated in four different chemical conditions:

Condition I: The reaction solution was prepared only with HEMA ($0.7684 \text{ mol L}^{-1}$) and deionized water (49.96 mol L^{-1}), and no other chemicals were added.

Condition II: The chemical composition of the reaction solution was monomer (e.g., HEMA, $0.7684 \text{ mol L}^{-1}$), HCAP ($4.895 \times 10^{-2} \text{ mol L}^{-1}$), CH_3OH ($4.931 \times 10^{-2} \text{ mol L}^{-1}$), and deionized water (38.85 mol L^{-1}).

Condition III: The reaction solution was prepared with HEMA ($0.7684 \text{ mol L}^{-1}$), MPSA ($2.529 \times 10^{-2} \text{ mol L}^{-1}$), and deionized water (49.96 mol L^{-1}).

Condition IV: The reaction solution contained HEMA ($0.7684 \text{ mol L}^{-1}$), HCAP ($4.895 \times 10^{-2} \text{ mol L}^{-1}$), CH_3OH ($4.931 \times 10^{-2} \text{ mol L}^{-1}$), MPSA ($2.529 \times 10^{-2} \text{ mol L}^{-1}$), and deionized water (38.85 mol L^{-1}).

The results of the variation of the graft weight with four different reaction conditions are presented in Figure 1(a). The graft weight increases exponentially with the increase of irradiation time in condition I. An increase of up to 22% for a radiation time of up to 20 min was recorded. The increase was found to be significantly higher ($\sim 39\%$) when the reaction solution contained a photoinitiator (HCAP) as in the second reaction condition. When the reaction was initiated with HEMA and the homopolymer inhibiting agent MPSA (third condition), the increase of the graft weight was approximately 25% for the 20 min of irradiation time. For the same irradiation time, the graft weight was found to be approximately 43% when the reaction was carried out using the fourth chemical condition. As expected, the homopolymer formation during the grafting reaction increased with irradiation time, depending on the condition of the reaction solution. The maximum homopolymerization was obtained when the reaction commenced without homopolymer inhibiting agent as in the case of the second condition [Fig. 1(b)]. This is attributed to the fact that the number of radicals generated in the solution is higher than the concentration of radicals in the jute cellulose. This then causes a predominant homopolymer reaction in preference to the graft copolymer reaction. When the reaction commenced in the presence of HCAP and MPSA, the graft weight was found to be significantly higher than the level of homopolymerization [Fig. 1(b)], resulting in higher grafting efficiency [Fig. 1(c)]. Although the homopolymer content is in the same range in conditions I and III, the grafting efficiency is noticeably higher in the latter case. The most important factor influencing the radiochemical yields is the irradiation time during the grafting process in the presence of photoinitiator. Upon absorption of UV radiation, the benzoyl and cyclohexyl radicals are produced by α cleavage of HCAP at C—C bonds, as shown in Scheme 1. The presence of HCAP in the system has an equal probability of increasing the radical concentration onto the jute cellulose and in the reaction solution as shown in compounds c–e in Scheme 1.

Because MPSA at higher concentrations is known²² to prevent homopolymerization, it was added to the solution for an efficient graft copolymer reaction. The results in Figure 1(c) show the addition of MPSA

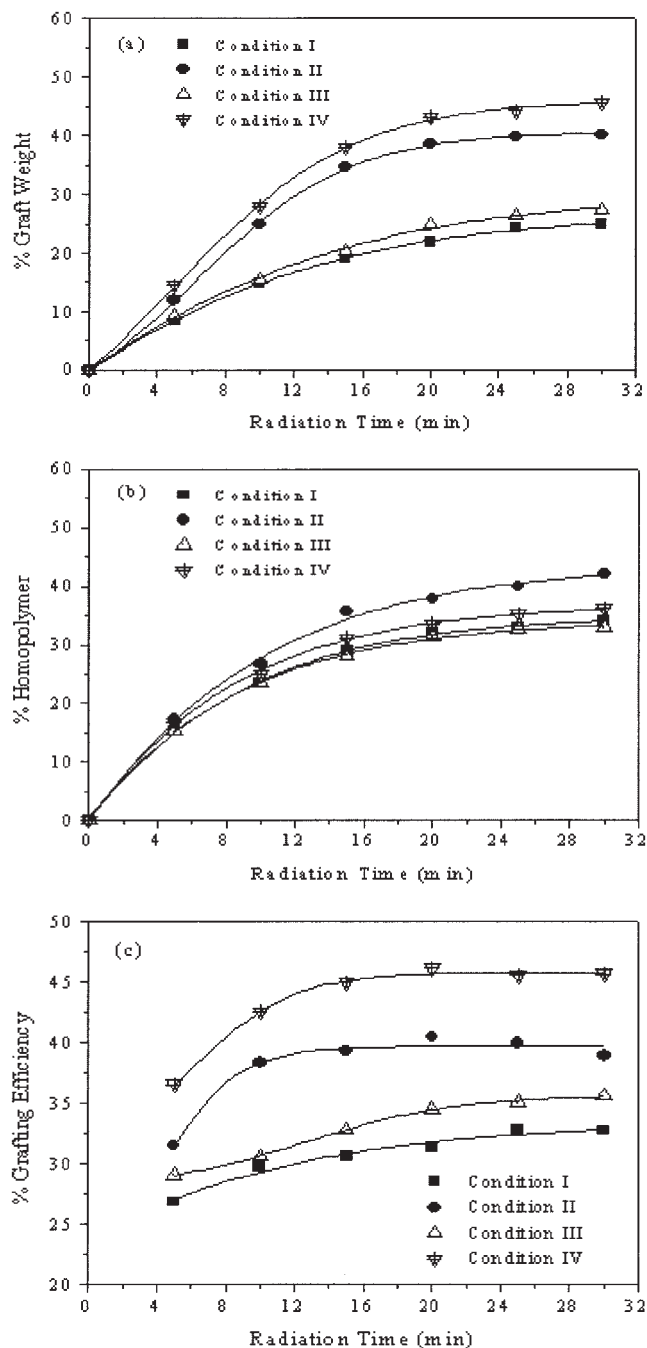
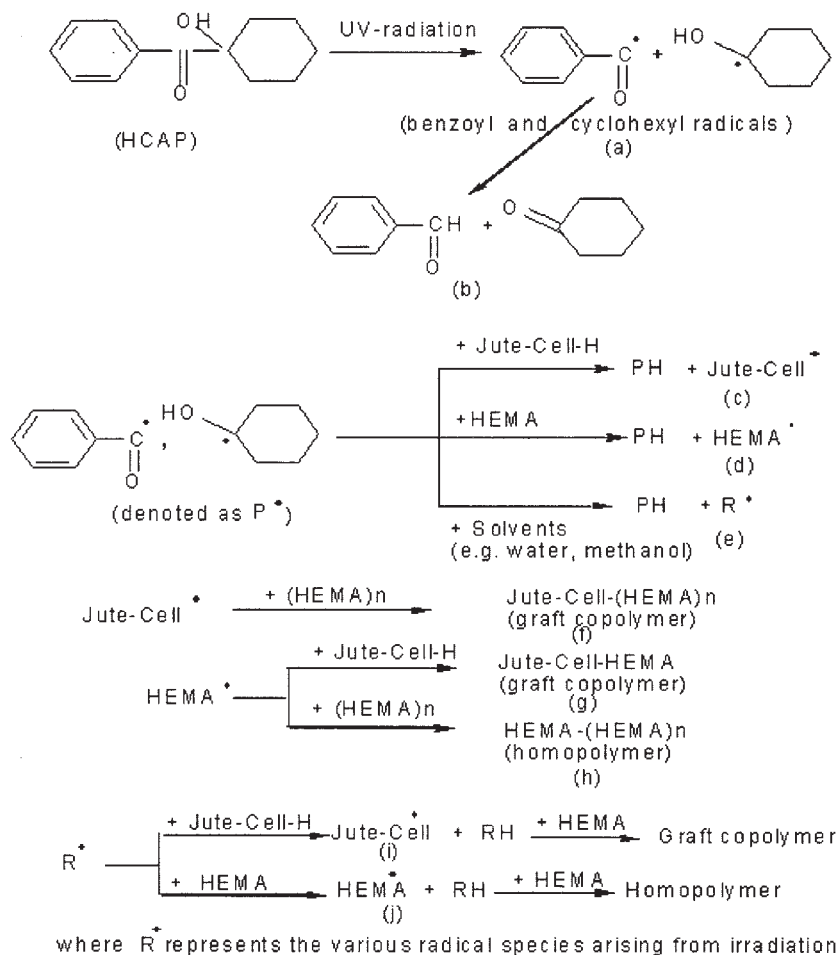


Figure 1 The effect of the radiation time on the graft weight of HEMA onto jute fiber (2.0 g) using the simultaneous irradiation and grafting technique under four different conditions. (a) The percentage of graft weight, (b) the percentage of homopolymer, and (c) the percentage of grafting efficiency versus the radiation time. Condition I: $0.7684 \text{ mol L}^{-1}$ HEMA and 49.96 mol L^{-1} deionized water; condition II: $0.7684 \text{ mol L}^{-1}$ HEMA, $4.895 \times 10^{-2} \text{ mol L}^{-1}$ HCAP, $4.931 \times 10^{-2} \text{ mol L}^{-1}$ CH_3OH , and 38.85 mol L^{-1} deionized water; condition III: $0.7684 \text{ mol L}^{-1}$ HEMA, $2.529 \times 10^{-2} \text{ mol L}^{-1}$ MPSA, and 49.96 mol L^{-1} deionized water; condition IV: $0.7684 \text{ mol L}^{-1}$ HEMA, $4.895 \times 10^{-2} \text{ mol L}^{-1}$ HCAP, $4.931 \times 10^{-2} \text{ mol L}^{-1}$ CH_3OH , $2.529 \times 10^{-2} \text{ mol L}^{-1}$ MPSA, and 38.85 mol L^{-1} deionized water.



Scheme 1 The chemical reactions involved in the UV radiation induced graft copolymer reaction of HEMA onto jute fiber by the simultaneous irradiation and grafting method.

($2.529 \times 10^{-2} \text{ mol L}^{-1}$) in the reaction solution caused the efficiency of grafting to increase from 31% in condition I to 35% in condition III. About 6% higher grafting efficiency was obtained in condition IV compared to that of condition II maximum graft weight. The saturation of grafting levels (percentage of grafting) at higher irradiation times ($> \sim 20 \text{ min}$) is attributed to the fact that at lower irradiation times the formation of reactive cellulose sites increases linearly to give a proportional increase in homopolymers. However, as the concentration of radicals increases, the efficiency of the termination reaction rises proportionately and becomes comparable to the homopolymerization reaction, giving rise to the observed saturation effects.

Effect of HEMA concentration

The effect of the HEMA concentration ($0\text{--}1.153 \text{ mol L}^{-1}$) as a function of the percentage graft weight is plotted in Figure 2. This shows that the graft weight increases nonlinearly with the HEMA concentration

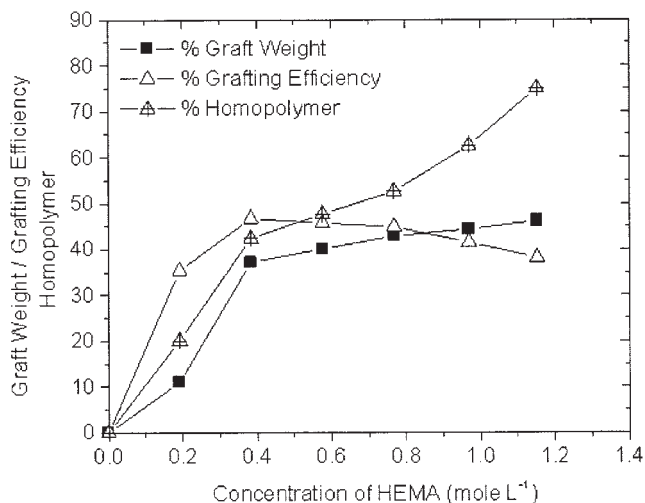


Figure 2 The influence of the HEMA concentration on the grafting in the simultaneous irradiation and grafting method with a 20-min radiation time, 2.0 g of jute fiber, $4.895 \times 10^{-2} \text{ mol L}^{-1}$ HCAP, $4.931 \times 10^{-3} \text{ mol L}^{-1}$ CH_3OH , and $2.529 \times 10^{-2} \text{ mol L}^{-1}$ MPSA.

and an increase of $\sim 46\%$ is obtained at a concentration of $1.1526 \text{ mol L}^{-1}$. Above a $0.3846 \text{ mol L}^{-1}$ concentration of HEMA the rate of grafting is significantly slow. This is attributed to the higher radical concentration of HEMA in the reaction solution directly initiated by the benzoyl and cyclohexyl radicals (Scheme 1, compound d), which results from the cleavage of HCAP, compared to the jute-cellulose radical formation (Scheme 1, compound c). Therefore, homopolymer was rapidly formed as the concentration of HEMA was increased, which consequently decreased the grafting efficiency (Fig. 2).

In the simultaneous irradiation and grafting method, CH_3OH and H_2O solvents are capable of swelling the lignocellulose polymer, as well as being solvents for HEMA and HCAP, which leads to appreciable grafting. For the grafting reaction, the interaction of hydrogen atom abstraction and energy transfer is predominant. During irradiation the presence of CH_3OH and H_2O in the grafting system can be utilized to promote the grafting reaction through intermolecular hydrogen abstraction. With liquid methanol the methoxy radical ($\text{CH}_3\text{O}^\cdot$) is the principal species formed whereas with aqueous methanol the formation of $^\cdot\text{CH}_2\text{OH}$ predominates. The homopolymerization could be initiated by the direct radiolysis of the HEMA or by reaction of the HEMA with the hydrogen atom (H^\cdot) and the hydroxyl radical (OH^\cdot), and benzoyl and cyclohexyl radicals.

Effect of HCAP concentration

The reaction solution was prepared with HCAP [$(0-14.68) \times 10^{-2} \text{ mol L}^{-1}$], HEMA (0.3842 and $0.7684 \text{ mol L}^{-1}$), CH_3OH ($4.931 \times 10^{-3} \text{ mol L}^{-1}$), and deionized water (38.85 mol L^{-1}) in the absence and presence of MPSA ($2.529 \times 10^{-2} \text{ mol L}^{-1}$). The graft weight obtained was plotted against the concentrations of HCAP for two different concentrations of HEMA in the presence and absence of homopolymer inhibiting agent (MPSA), as shown in Figure 3(a). The fitted data showed a first-order exponential for both the copolymer and the homopolymer with the concentration of HCAP. The presence of MPSA in the reaction medium gave a higher percentage of grafting compared to those without MPSA (Fig. 3).

The saturation effect demonstrated by the nonexponential fit at a higher concentration of HCAP is attributed to stronger absorption of UV radiation by HCAP molecules. The progressing predominance of the termination reaction with the higher levels of radicals similar to the case in the irradiation effect is attributed to the saturation effect in this case as well. The leveling-off point in the graph in Figure 3(a) is where the propagation and termination reactions are both proportional to the HCAP concentration and the rate of radical formation is independent of its concentration.

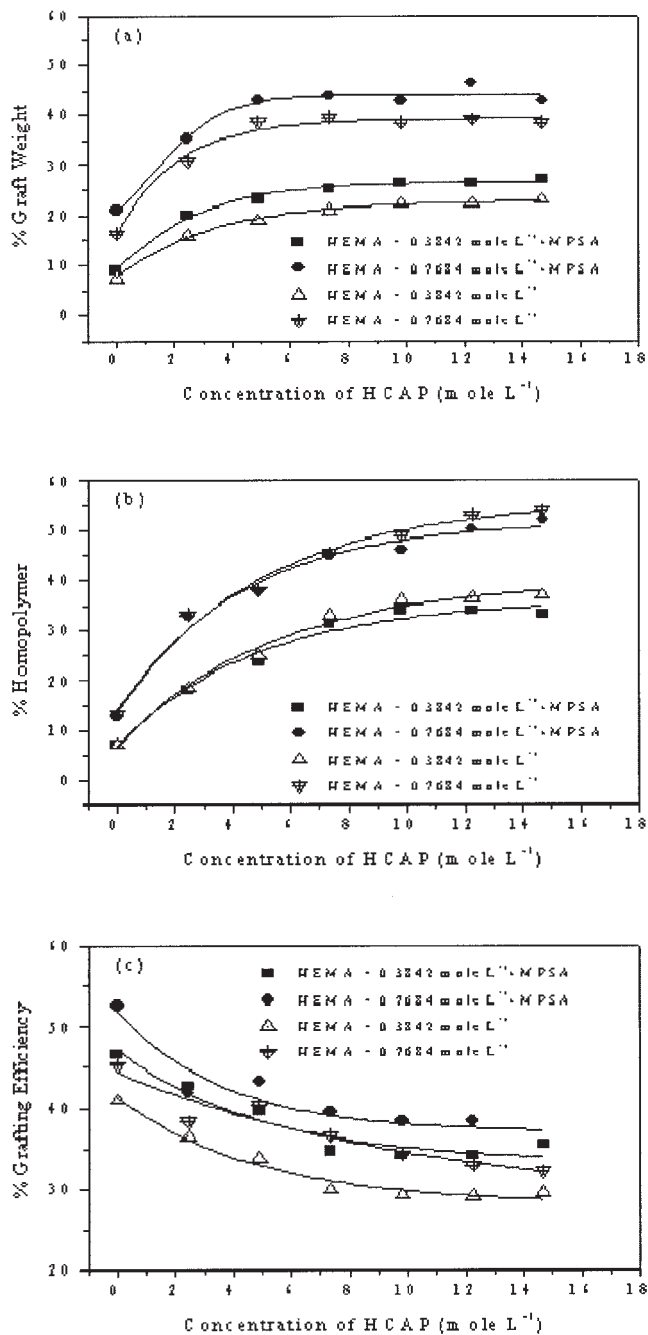


Figure 3 The effect of the concentration of HCAP in the simultaneous irradiation and grafting method with a 20-min radiation time, 2.0 g of jute fiber, $4.931 \times 10^{-3} \text{ mol L}^{-1}$ CH_3OH , and 0.3842 and $0.7684 \text{ mol L}^{-1}$ HEMA in the absence and presence of $2.529 \times 10^{-2} \text{ mol L}^{-1}$ MPSA; (a) the percentage of graft weight, (b) the percentage of homopolymer, and (c) the percentage of grafting efficiency versus the concentration of HCAP.

The results also show [Fig. 3(b)] that the degree of homopolymerization is higher than that of the graft copolymerization, which causes a decrease in the grafting efficiency [Fig. 3(c)]. The possibility of direct initiation of the homopolymerization in solution by benzoyl and cyclohexyl radicals resulting from α

cleavage may explain this observation. A similar effect has been observed in radiation-induced grafting of other cellulose polymers.¹⁵ The presence of H₂O and CH₃OH in the reaction medium can also promote radical formation onto jute-cellulose and HEMA molecules through intermolecular hydrogen abstraction. These radicals are responsible for both copolymer and homopolymer reactions.

Preirradiation graft copolymerization

In this study jute fibers were irradiated in the presence of methanol and HCAP. Following irradiation, the graft copolymer reaction commenced at 70°C for 3 h with two different chemical compositions. In the first case, the solution was prepared with HEMA (0.1921 mol L⁻¹) and MPSA (2.529 × 10⁻² mol L⁻¹) in deionized water (49.96 mol L⁻¹); in the second case, no MPSA was used. The percentages of graft weight, homopolymer, and grafting efficiency were measured for irradiation times between 0 and 25 min and the results are presented in Figure 4. As in the case of the simultaneous irradiation and grafting process, the results show that the graft weight increases exponentially and saturates above an irradiation time of ~20 min. At this time, the graft weight was calculated to be ~70% when the reaction solution contained MPSA. It is most likely that at lower irradiation times the formation of reactive species (e.g., radicals, peroxides) increases linearly, which subsequently gives rise to a graft copolymer reaction in contact with HEMA molecules. For a higher radiation time, the saturation effect may be attributed to increased radical-radical coupling or disproportionate reaction rates. The results of homopolymer formation in the system [Fig. 4(a)] show a trend similar to that of the graft copolymer reaction. A similar trend was observed when the grafting reaction commenced in the absence of MPSA, as shown in Figure 4(b). In this case the maximum graft weight achieved was ~54% compared to 74% in the presence of MPSA.

The results confirm that the preirradiation method gives rise to less homopolymer and produces a significantly higher graft weight and grafting efficiency (Fig. 4) than those obtained by the simultaneous irradiation and grafting method (Fig. 1). The photochemical reactions involved in the preirradiation method are shown in Scheme 2. In this case, the irradiation was performed in the methanol-HCAP-lignocellulose system in the presence of air. Therefore, the intermolecular hydrogen abstraction from jute-cellulose molecules can occur in different ways, which leads to the formation of reactive sites on the jute-cellulose backbone (Scheme 2, compounds b, d, g). The monomer (HEMA) itself is never exposed to UV radiation, so there is little chance of homopolymer formation in the system

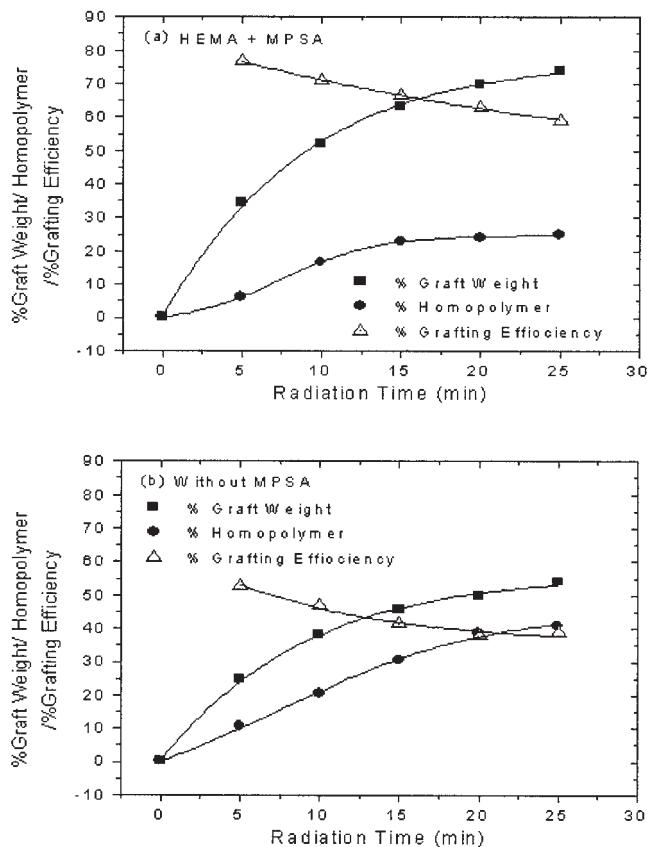
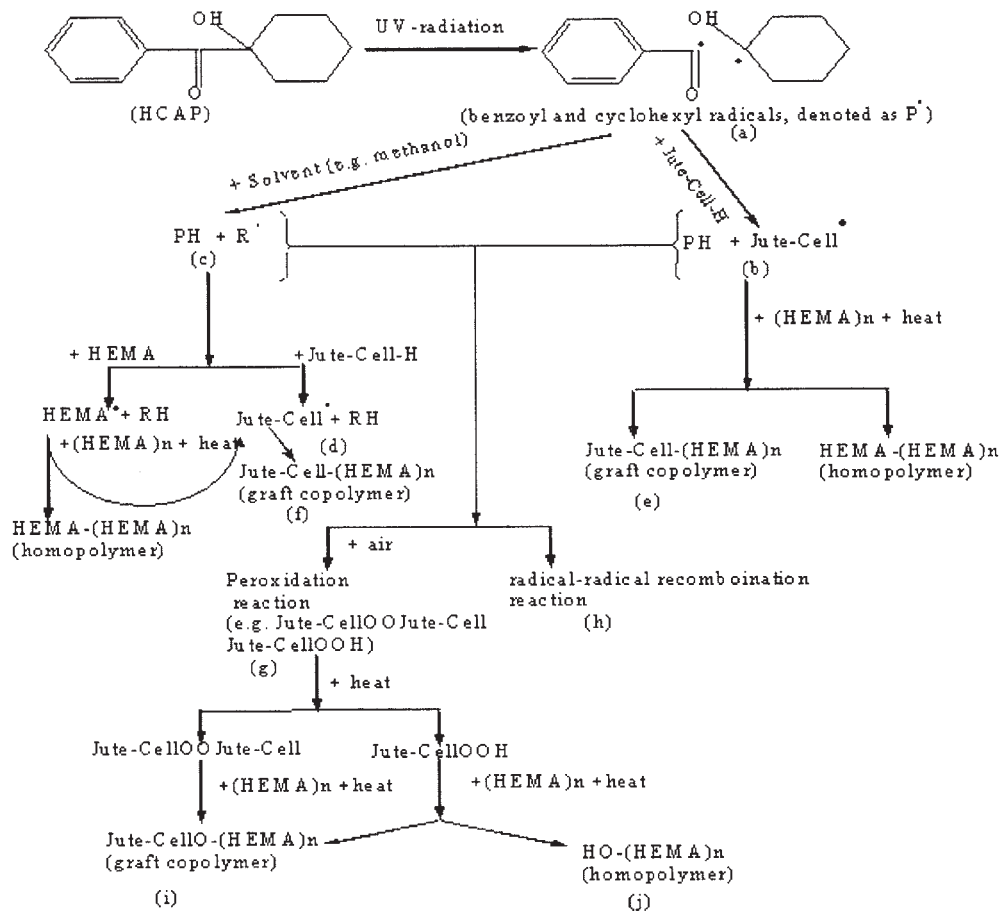


Figure 4 The variation of the graft weight with UV radiation time of HEMA onto preirradiated jute fiber; 2.0 g jute fiber, 70°C reaction temperature, 3.0-h reaction time. The grafting solution contained (a) 2.529 × 10⁻² mol L⁻¹ MPSA, 0.1921 mol L⁻¹ HEMA, and 44.44 mol L⁻¹ deionized water or (b) 0.1921 mol L⁻¹ HEMA and 44.44 mol L⁻¹ deionized water.

unlike the simultaneous irradiation and grafting one. Because the irradiation was performed in air, at least some of the radicals reacted with oxygen to produce cellulose diperoxide (Cell-OO-Cell) and hydroperoxide (Cell-O-OH, Scheme 2, compound g). The radicals on the jute, which did not react with atmospheric oxygen, can initiate a graft copolymer reaction when HEMA is introduced into the system (Scheme 2, compounds e, f). At higher temperatures the cellulose diperoxide is decomposed to give peroxy radicals (2CellO[·]), which are capable of initiating a copolymer reaction in contact with HEMA molecules (Scheme 2, compound i). We envision that the cellulose hydroperoxide may be transformed into both peroxy (CellO[·]) and hydroxyl ([·]OH), which are capable of initiating copolymer and homopolymer reactions (Scheme 2, compounds i, j), respectively. In addition, the lignin in jute, which is a polyphenolic material, is likely to affect the overall photochemical event^{25,26} in the graft copolymer reaction.



Scheme 2 UV radiation induced chemical reactions involved in the graft copolymerization of HEMA onto jute fiber by the preirradiation method.

Characteristic properties

The maximum load, tensile strength, percentage of elongation, and work done at which the samples break down were evaluated from the load versus extension curves. The parameters (relative to their values for ungrafted samples) were plotted as a function of the percentage of graft weight as provided in Figure 5(a,b). The decrease in breaking load and tensile strength plotted as a function of graft weight (GW) follows a first-order exponential function [Fig. 5(a)], represented by the following form:

$$Y_{rBL,rTS} = Y_{BL_0,TS_0} + K' \exp[-D_c(\% GW)]$$

where Y_{rBL} and Y_{rTS} are the relative breaking load and tensile strength, respectively; the parameters Y_{BL_0} and Y_{TS_0} are the corresponding intercepts; K' is the coefficient of the exponential function; and D_c is defined as a deterioration constant. For the breaking load the values of these parameters were calculated to be $Y_{BL_0} = 0.26$, $K' = 0.75$, and $D_c = 0.014$; for the tensile strength they were $Y_{TS_0} = 0.18$, $K' = 0.81$, and $D_c = 0.046$. Figure 5(b) shows the dependence of the per-

centage of elongation and work done at rupture with increasing graft weight. The percentage of elongation showed an initial increase up to ~88% and work done at rupture up to 24% with an increasing graft weight of ~63%. Beyond this graft weight, both the elongation and work done at rupture showed a sharp decrease [Fig. 5(b)]. The fitted data points showed a second-order polynomial function of the following form:

$$E_{re}/W_{rw} = 1 + K_1 \times (\% GW) + K_2(\% GW)^2$$

where E_{re} represents the relative elongation at break, which is normalized with respect to the values for the as-received sample. The coefficients were calculated to be $K_1 = 0.036$ and $K_2 = -3.62 \times 10^{-4}$. In addition, W_{rw} represents the relative value of work at rupture, which also follows a trend similar to that for the elongation [Fig. 5(b)], and the coefficients were calculated to be $K_1 = 0.018$ and $K_2 = -2.47 \times 10^{-4}$.

The results (Fig. 5) have shown that the grafting of HEMA with jute causes a decrease in breaking load and tensile strength. This could be attributed to the

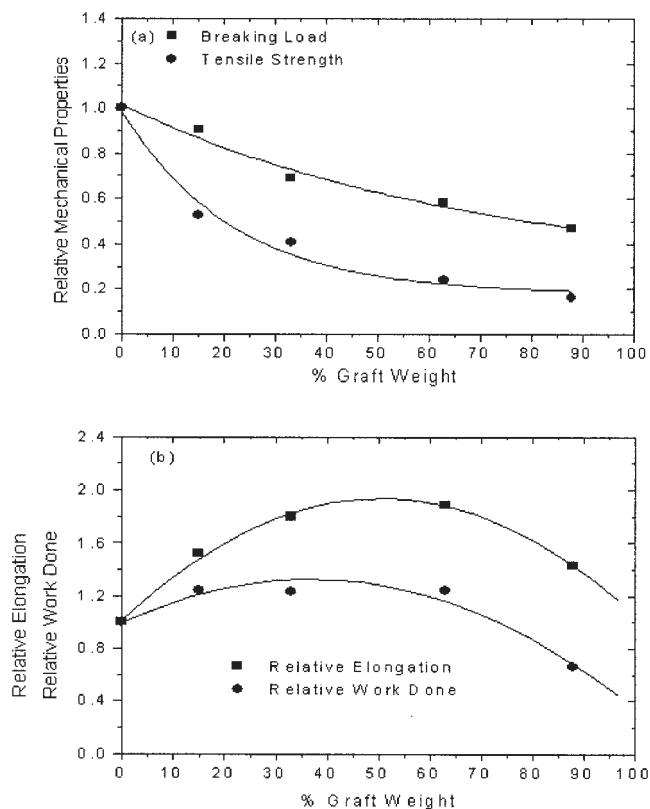


Figure 5 The variation of the mechanical properties with the percentage of HEMA grafting onto jute fiber by the UV-induced preirradiation method.

dead weight of graft chains attached to the cellulose backbone. Further, the fiber may have interchain poly-(HEMA) (PHEMA) graft links, making the fibers rigid. Consequently, there is a decrease in the binding strength despite reinforcement by the graft copolymerization. It is likely that a greater disruption of the strong hydrogen bonds in the jute-cellulose main structure cannot compensate for the relatively weaker bonds produced by the graft copolymerization. This is brought about by the difference in the position of the grafted chain with the lignocellulose backbone relative to the equivalent jute substrate based copolymer, thus reducing the hydrogen bonding or the degree of chain entanglements. The increase in elongation suggests that the degree of molecular chain mobility becomes higher by the PHEMA-graft copolymer add-on with lignocellulose fiber.

Figure 6 shows a comparison of DSC thermograms of as-received jute fiber and jute-graft-PHEMA copolymer samples. The DSC thermogram of the as-received jute fiber [Fig. 6(a)] shows an endothermic tendency from 162 to 243°C, which is attributed to partial dehydration of the —OOH primary groups and decomposition of minor constituents in the jute. While increasing the temperature to 328°C, an exothermic reaction was observed that was attributed to

the decomposition of hemicellulose. The degradation was significantly higher above 300°C. A large endotherm between 328 and 375°C with a peak minimum at 355°C corresponds to the complete loss of —OH groups of the monomer units of cellulose and depolymerization and volatilization of cellulose, followed by exothermic decomposition of degraded prod-

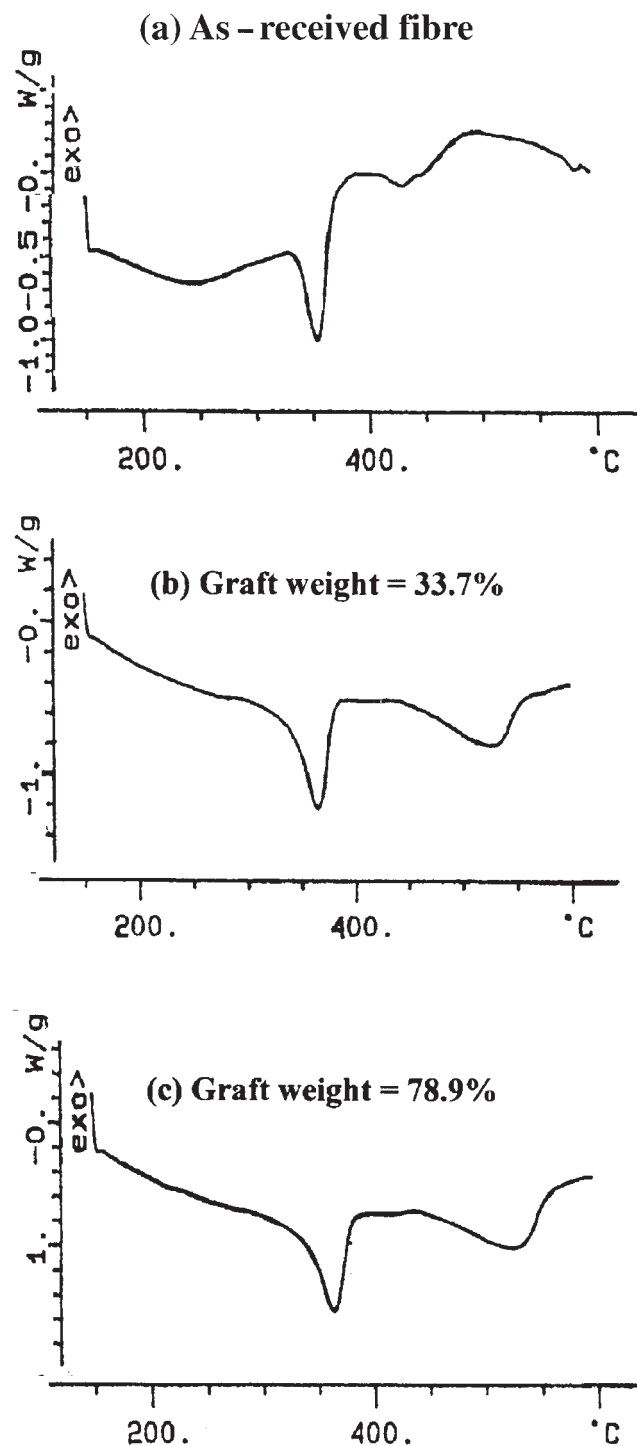


Figure 6 DSC thermograms of samples of (a) as-received fiber, (b) 33.7% graft weight, and (c) 78.9% graft weight.

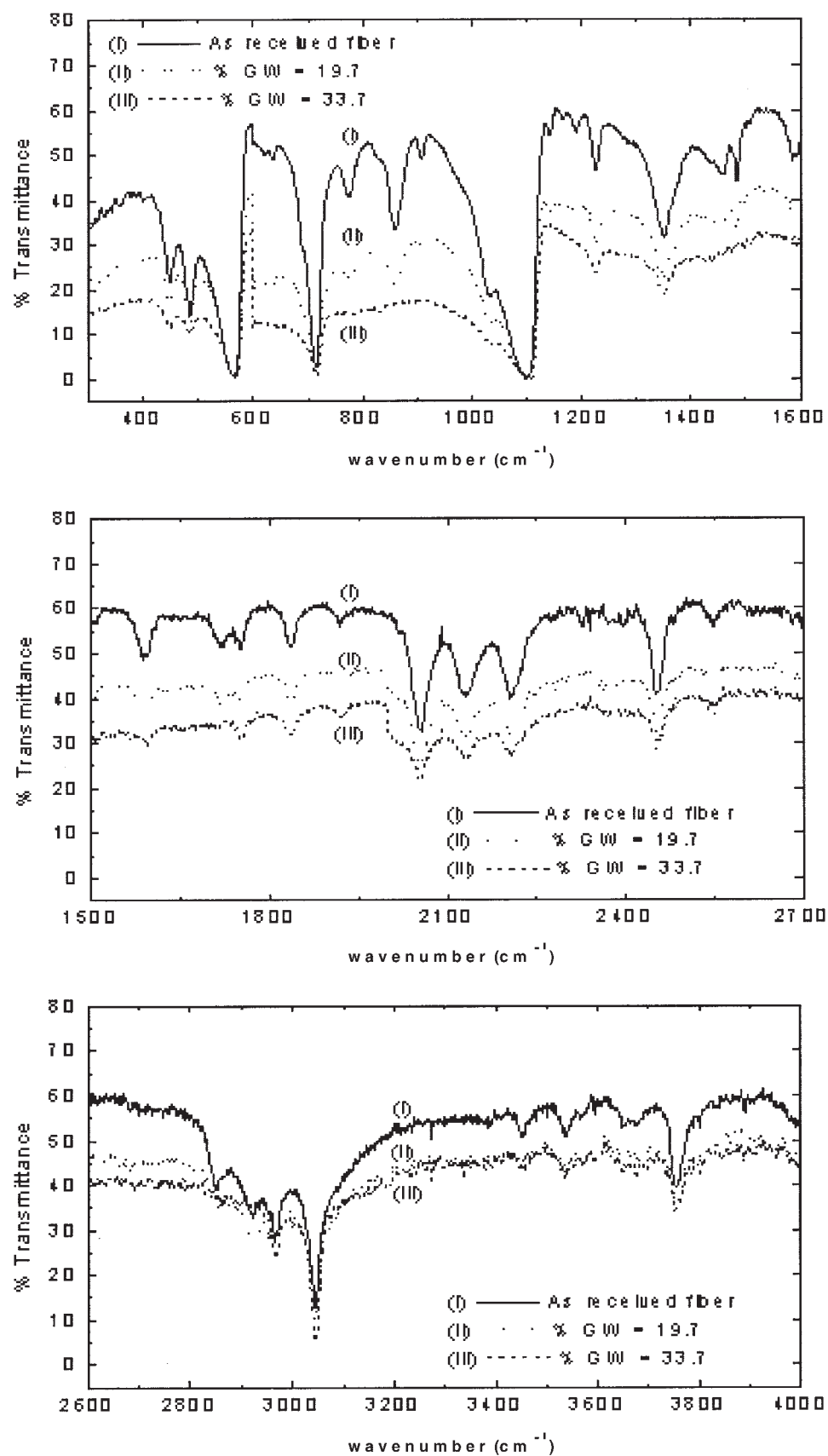


Figure 7 IR spectra of as-received fiber and jute-PHEMA grafted samples with various percentages of graft weight (% GW).

ucts.^{27–29} The large but broad exothermic peak between 431 and 585°C with a maximum at 494.7°C is attributed to the decomposition of lignin. In the case of grafted jute with 33.7% graft weight, we found a broad endothermic peak between 264 and 390°C with a peak minimum at 364°C [Fig. 6(b)] that is assigned to the depolymerization of cellulose-graft-PHEMA. For 78.9% graft weight, the endothermic peak became broader by 10°C with a peak minimum at 366°C, a shoulder peak appeared at 395°C, and an exothermic peak became weaker in the region between 431 and 585°C because of the PHEMA-grafted chain addition with jute [Fig. 6(b,c)]. The results represent the degradation process of both the lignocellulose and grafted-PHEMA chain.

The spectral signatures of the as-received and jute-PHEMA grafted samples are presented in Figure 7. The vibration modes corresponding to the absorption bands at 3800–3600 cm^{-1} are responsible for the O—H stretching vibration of free OH groups, those at 3500–3400 cm^{-1} are responsible for the O—H stretching frequencies of intermolecular bonds, and those at 3300–2500 cm^{-1} are responsible for chelated intramolecular bonds of O—H and C—H stretching vibrations. The absorption bands at 2500–2000 and 2000–1650 cm^{-1} appear for hydrogen bonded O—H stretching vibrations and aromatic overtone C—H out of plane bending and C=O stretching vibrations of ester ketonic groups, respectively. The bands at 1596 and 1431 cm^{-1} are for C—H deformation of $-\text{CH}_2-$, at 1350 and 1225 cm^{-1} are for O—H deformation of the phenolic hydroxyl group, and at 1150–1040 cm^{-1} are for O—H deformation and C—O stretching. The bands in the range of 1000–650 cm^{-1} appear to be due to out of plane C—H deformation vibrations that affect the grafting reaction of HEMA onto jute fibers.

The most noticeable difference between the IR spectra of the as-received and jute-graft-PHEMA samples are found in the bandshapes. A bandshape analysis was carried out on the intensity for the bands at 714, 1100, and 3045 cm^{-1} and the plotted results of the peak height versus graft weight are shown in Figure 8. Such bands follow a first-order approximation, so that the intensity (I) is proportional to the population of the energy state in which the vibrating molecules exist. If these molecules exist in an energy level E_1 , they can migrate to higher energy level E_2 by overcoming a potential barrier $\Delta E = E_2 - E_1$. The results (Fig. 8) showed that the HEMA grafted with jute decreased the band intensity (i.e., 714, 1100, and 3045 cm^{-1}) in a nonlinear fashion. The intensity of bands depends only on the population of the vibrational energy states, which corresponds to the concentration of the vibrating group in the matrix.³⁰ The nonlinear decrease in the intensity with the graft weight could be

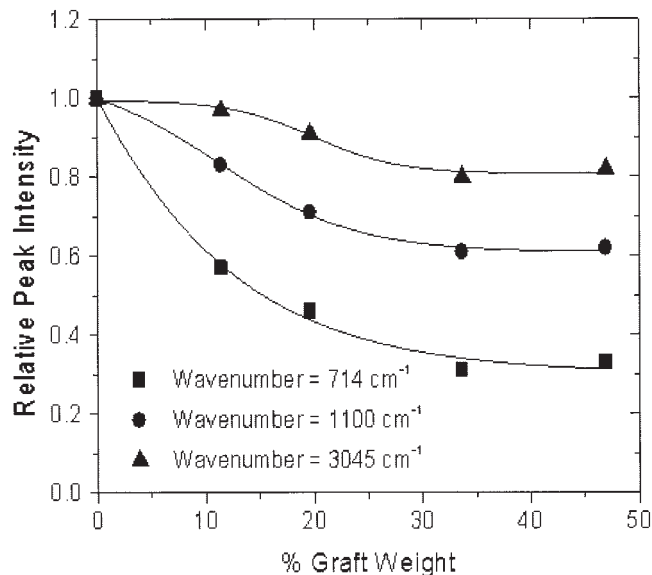


Figure 8 The change of the intensity with the graft weight at wavenumbers of 714, 1100, and 3045 cm^{-1} .

attributed to the increasing ΔE with the concentration of HEMA molecules in the jute-cellulose matrix. This could be related to the constancy of the ΔE , and the changes in bandshape could be attributed to altering the molecular chain orientations.³⁰

Water is a polar liquid whereas the polarity of jute fiber depends on the relative proportion of the polar linkages in the cellulose chain. The graft copolymerization of HEMA in jute is expected to increase the proportion of such polar groups along the cellulose chain. Figure 9 shows the equilibrium water content as a function of the percentage of graft weight. The equilibrium water content was found to increase with grafting, reaching values from 288 to 347% for a graft weight of $\sim 12\%$. The factors such as varying combinations of graft distribution, hydrogen bonding, and crosslinking may affect the ability of the graft copolymer structure to imbibe the free, nonbound condensation water. For example, the higher rigid structure will allow lower equilibrium water contents. We observed that above 12% graft weight, the copolymerized samples appeared in a rigid structural form. As a result, the mobility of the cellulose chain structure became restricted, which could decrease the equilibrium water content. It is known³¹ that fibers hold water in their lumens and capillaries, as well as on the surface. At a higher graft weight, it is likely to block the capillaries and reduce the equilibrium water absorption property.

CONCLUSION

UV radiation induced graft copolymerization of HEMA onto lignocellulose (jute) fiber was achieved

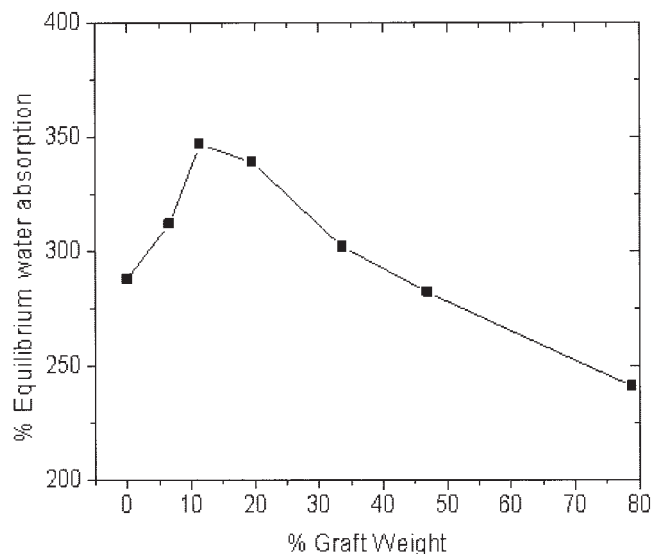


Figure 9 The equilibrium water absorption versus the percentage of graft weight of HEMA onto the jute fiber.

by applying both the simultaneous irradiation and grafting method and the preirradiation method. The graft copolymerization process was affected by many reaction parameters, which were cumulative and interdependent. When all other parameters were constant, the concentration of reactive species (e.g., radicals and peroxides) was parameterized by the percentage of grafting in the case of the variation of the irradiation time in both methods. On this basis, the reactive sites were proportional to the total irradiation time, although it appeared that the number of such sites tended to saturate above a certain irradiation time that was dependent on the conditions of the reaction. The maximum graft weight ($\sim 74\%$) was achieved in the case of the preirradiation method (Fig. 4), which was significantly higher than the maximum graft weight ($\sim 45\%$) obtained in the simultaneous irradiation and grafting method (Fig. 1). The higher degree of homopolymerization affected the graft copolymer reaction in the latter case. MPSA played a significant role in enhancing the grafting efficiency in both methods of grafting. In the preirradiation method the homopolymer reaction was largely reduced. The concentration of HCAP was an important factor to generate radiation-induced chemical yields for the subsequent graft copolymer reaction. However, above $4.895 \times 10^{-2} \text{ mol L}^{-1}$ of HCAP, the graft weight tended to saturate. The graft weight increased significantly as the concentration of HEMA increased to $0.7684 \text{ mol L}^{-1}$; above this concentration the increase of graft weight was not significant.

The mechanical properties of grafted samples showed a decreasing trend for the breaking load and

tensile strength, suggesting disruption to the stronger bonds and PHEMA-graft add-on produces relatively weaker bonds. The elongation and work done at rupture increased significantly up to a certain level of graft weight, beyond which the changes were decreased. DSC analysis demonstrated that the thermal stability of jute-graft-PHEMA copolymer samples was lower than the ungrafted fiber. IR showed that the decrease in band intensity with graft-copolymer add-on seemed to be additive for the backbone or side chain. The equilibrium water absorption provided evidence that the PHEMA-graft add-on with jute increased the water content up to a certain level of graft weight ($\sim 12\%$). This was attributed to the hydrophilic nature of the PHEMA-grafted chain. Beyond 12% graft weight, the hydrophilic nature of copolymerized samples was reduced.

The author extends special thanks to Dr. E. Kronfli for valuable discussions. This research is partly funded by the CEC under an International Scientific and Technical Cooperation scheme.

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