UV-Radiation–Induced Preirradiation Grafting of Methyl Methacrylate onto Lignocellulose Fiber in an Aqueous Medium and Characterization

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ABSTRACT: The preirradiation method of grafting has been established by ultraviolet radiation. Methyl methacrylate (MMA) was grafted onto jute fiber in an aqueous medium. The variation of graft weight with UV-radiation time, monomer concentration, and reaction time was investigated. The conversion of monomer into homopolymer and graft copolymer was evaluated. The graft weight passes through a maximum value ($\sim$ 122%) with UV-radiation time. The optimum value of the monomer concentration was evaluated for maximum degree of grafting. Graft copolymerization of MMA onto lignocellulose fiber significantly increases the elongation at break ($\sim$ 65%) compared to that of the "as-received" sample. However, a linear decrease on breaking load was observed with the increase of graft weight. The estimation of degree of grafting was achieved using an IR technique by correlating band intensities with the degree of grafting. Considering the water-absorption property, the grafted sample showed a maximum up to 61% decrease in hydrophilicity compared to that of the as-received sample. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1667–1675, 2004

Key words: irradiation; graft copolymers; methyl methacrylate; fibers; infrared spectroscopy

INTRODUCTION

Jute is a natural biodegradable renewable lignocellulose raw material composed[1] mainly of cellulose (58–63%), hemicellulose (20–22%), and lignin (13–15%). In addition to those major constituents, jute also contains trace quantities of organic and inorganic pigments. Lignocellulose polymer is mainly used for textile products such as carpets, decorative materials, cloths, and so forth. For such applications of jute fiber a higher extensibility and low water absorption property are required. Although jute has high tensile modulus, it suffers low elongation at break compared to that of other natural cellulose fibers.

Graft copolymerization is a well-establish technique to improve the desired properties of both natural and synthetic polymers. Different methods of graft copolymerization have been developed in the last few decades and these are well reviewed.[1,2] Such methods of graft copolymerization are primarily divided into two categories: (1) chemical initiation and (2) irradiation initiation methods, which can be further subdivided into (a) high-energy irradiation and (b) UV-irradiation. Among these the ceric-ion initiation and high-energy radiation initiation are well-known methods. The high-energy radiation initiation methods also subdivided into preirradiation and "simultaneous irradiation and grafting" methods. Each method of grafting initiated by high-energy radiation has advantages and disadvantages as discussed in several published works.[3–5] It has been reported that the high-energy radiation deteriorated the mechanical properties before commencing graft copolymerization onto preirradiated jute fiber,[6] whereas the deterioration in the mechanical properties was found[1] to be negligible using UV-radiation before graft copolymerization takes place with jute fiber. This could be attributable to the fact that the UV-radiation is more selective in nature than the γ-radiation. Moreover, UV-radiation equipment is more cost effective than γ-radiation equipment.

Extensive research has been conducted[7–17] on graft copolymerization of various monomers onto natural cellulose materials by using UV-radiation. Most of the early works reported used the simultaneous irradiation and grafting method, in which the radiolysis of all components, such as parent polymer, monomer, solvent, and other additives, are factors in initiating graft

copolymer reaction. The disadvantage of this method is the substantial amount of undesirable homopolymer that forms in the system and the isolation of such product becomes difficult.

Photograft copolymerization of methyl methacrylate (MMA) was investigated by Gosh et al.[8] onto bleached jute fiber using ferric sulfate [$Fe_2(SO_4)_3$] as initiator under visible light. In this case, the light is absorbed by the chromophore formed by the cellulose–metal complex and the radicals are formed on the cellulose backbone to initiate the graft copolymer reaction. Davis et al.[9] investigated the graft copolymerization of MMA with cellulose in a nonaqueous phase using the simultaneous irradiation and grafting method and found a substantial amount of homopolymer attached onto the grafted-copolymer sample. It has been reported[12–14] that the degree of grafting of various monomers onto cellulose depends on the wavelength of light, types of photoinitiators, monomers, and the role of the various solvents in UV-radiation–induced simultaneous irradiation and grafting method. Fouassier[13] reported that a very high degree of homopolymer is formed in photoirradiation grafting of MMA using the simultaneous irradiation and grafting method. Several researchers found[16,17] that the organic solvents have a positive influence in the grafting of MMA and other monomers onto cellulose fiber by UV-radiation–induced simultaneous irradiation and grafting method. From a practical point of view, the solvent will be wasted and the technique is unlikely to be cost-effective and environmentally friendly.

An alternative to the simultaneous irradiation and grafting method is the preirradiation method, in which the cellulose polymer is exposed to radiation before being brought into contact with the grafting reaction solution. Therefore, the reactive species such as ionic, radical, and peroxide are confined into the cellulose polymer and a lesser degree of homopolymer formation is expected in the system. The peroxide species are produced only when polymers are irradiated in the presence of oxygen.[1,4] The preirradiation technique has some advantages over the simultaneous irradiation and grafting technique, such as the formation of less homopolymer in the system and increased depth of penetration. Additionally, this technique can be applied as a continuous grafting process in industry.

The UV-radiation–induced preirradiation technique has so far not been applied to the graft copolymerization of hydrophobic monomer with lignocellulose fibers in an aqueous phase. In this research, the graft copolymerization of MMA onto jute fiber in water-emulsified solution was investigated. Such an emulsion process is widely used to prepare graft copolymers,[18] where the emulsifier plays an important role in bringing the monomers in contact with the substrate. The use of water emulsifier has some advantages over the use of solution. For example, in an emulsion process, reaction steps are easily controlled and the graft copolymerization at low temperature (0–80°C) can be produced without the use of expensive solvents. It is therefore important to investigate the feasibility of achieving efficient grafting of MMA onto lignocellulose fiber using such a medium. MMA was selected because of the hydrophobic nature of this monomer is to reduce the water absorption property of the jute–PMMA-grafted fiber for applications in the carpet industry and a variety of other uses. The graft copolymerization process is dependent on interdependent and cumulative parameters. The present study analyzes the effect of preirradiation time, reaction time, and monomer concentration at a reaction temperature of 70°C, and how the MMA grafting influences the mechanical properties and hydrophobic nature of the grafted product compared to the "as-received" lignocellulose fiber. Infrared technique was used to analyze the jute–PMMA-graft copolymer.

EXPERIMENTAL

UV-radiation source

The UV-radiation source was received from Jenton International (Whitechurch, Hampshire, UK). The Jenton STAT-I-CURE contains a compact UV oven, using a 400-W Hg flood cure light source. Both power supply and lamp are integrally mounted within the cabinet, which is connected to a shutter mechanism to prevent exposure to UV when the door is open. The source produced radiant energy with about 85–90% of the light in the desired wavelength range, for example, 254, 365, or 425 nm.

Materials

Jute fibers were supplied by Amin Jute Mill Co. (Bangladesh), and on receipt the samples were stored at room temperature (~ 20°C) and about 65% relative humidity in a sealable bag in the dark. MMA was used for the graft copolymer reaction, which was inhibited with 10–100 ppm hydroquinone monomethyl ether, and after delivery it was stored at about 5°C. Methanol was used to dissolve the photoinitiator and 1,2-dichloroethane was used as the solvent for homopolymer extraction in Soxhlet apparatus. 2-Methyl-2-propene 1-sulfonic acid, sodium salt (98%) (MPSA) was used as a homopolymer-inhibiting agent and was stored at ambient conditions. These were obtained from Aldrich Chemical Co. (Gillingham, Dorset, UK). A nonionic surfactant, octylphenoxy polyethoxyethanol, used as an emulsifier throughout the grafting process, was received from BDH Chemicals (Poole, UK). Oxygen-free nitrogen (White cpst) was used. The photo-

initiator (1-hydroxy-cyclohexyl-phenyl-ketone) was supplied by Ciba Geigy (Summit, NJ) and after delivery it was stored in the dark at ambient conditions. Deionized water was used as a graft copolymer reaction medium.

Graft copolymerization

Jute fibers were gently combed thoroughly until free from bark materials and separated into small bundles. Each bundle, weighing about 2.0 g, was soaked in a solution of methanol and photoinitiator (1-HCPK; 1.0% w/v) for about 15 h to ensure the incorporation of photoinitiator into the jute substrate. Wet samples were then irradiated with UV-radiation for different lengths of time in the presence of air. The preirradiated sample was immersed into a prepared reaction solution. A reaction solution (100 mL) was prepared by dissolving the required amount of emulsifier (octylphenoxy polyethoxyethanol) and MPSA in deionized water, after which MMA was added. The solution was emulsified with the aid of a "homogenizer" at a speed of 2500 cycles/min for 2 min to break down the MMA units into fine droplets. The emulsifier contains nonpolar and polar parts in which MMA molecules and water dissolve, respectively. It is known[5] to form micelles and the MMA molecules diffuse through micelles to the jute substrate, given that water is a swelling agent for jute fiber.

The solution was confined into a 200-mL glass reaction bottle, and about 2.0 g of the preirradiated jute sample was added to the solution, after which the bottle was sealed with a rubber septum. The whole assembly was purged with N_2 gas for 2 h using inlet–outlet needles before immersing it in a thermostatic water bath with a constant agitation system. Grafting reactions commenced at a set temperature for a prefixed period. The samples were taken out from the reaction chamber, followed by washing with hot deionized water several times to remove any traces of unreacted monomer, and dried at 40°C to a constant weight in the vacuum oven.

Homopolymers were removed by extracting the grafted samples in 1,2-dichloroethane by refluxing in a soxhlet apparatus until constant weight had been achieved. Finally, extracted samples were dried in a vacuum at 40°C and their weight recorded. Weight percentage of grafting (%GW) was calculated according to the following relationship:

$$\%\text{GW} = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

where W_1 and W_2 are the initial weight and weight of the grafted jute samples, respectively.

Formation of homopolymer during grafting is undesirable because it reduces the amount of monomer available for the grafting reaction. The homopolymer content in the grafted jute was calculated as follows:

$$\%\text{Homopolymer} = \frac{W_H}{W_M} \times 100 \qquad (2)$$

where W_H is the weight difference before and after extraction of the grafted jute and is called homopolymer content and W_M is the total monomer weight used in the reaction solution. The fraction of homopolymer extracted in the solution was also collected after precipitation and measured in some cases.

Characterization

Mechanical properties

Measurement of the mechanical properties was carried out at ambient conditions by using a microprocessor-controlled material testing machine (Lloyd Instruments M 5K, Fareham, Hampshire, UK) loaded with a data analysis software package (DAPMAT 3.0). Measurements were performed using a calibrated load cell of 1 kN at a crosshead speed of 10 mm/min with an internal extensometer with automatic break detector having a constant gauge length (25 mm) throughout the tests. Samples were wrapped around the bollard before being clamped to the Grip (TG12). Parameters such as the breaking load and the corresponding elongation at which the specimen was 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 parameters were normalized with respect to the as-received sample and the results are presented.

ATR infrared spectroscopic analysis

The infrared spectra were taken at ambient conditions using attenuated total reflection (ATR) spectrometers (Graseby Specac, P/N 11209) with a 10-reflection ATR unit and with a solid sample holder. The maximum transmission was obtained by careful alignment of the mirrors in the spectrometer. Samples of about 2.0 mg of size less than 2 μm were completely dispersed with 200 mg of dehydrated KBr using an agate mortar and pestle. The whole was compressed into a transparent tablet by applying a pressure of 8–10 tons using an evacuable die.

Water absorption measurement

In water absorption measurements, the weight of the dry samples was recorded before samples were soaked in deionized water until an equilibrium weight

was achieved at ambient condition. Determination of the water absorption was accomplished 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 away from the sample. Also, the centrifuge tube was sealed to ensure 100% relative humidity to prevent desorption of water by the sample. The equilibrium water absorption capability of jute fiber was calculated using the following relationship:

$$\text{Equilibrium Water Absorption (\%)} = \frac{B - A}{C - A} \times 100$$

(3)

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

RESULTS AND DISCUSSION

Graft copolymerization

UV preirradiation time-dependent grafting

Samples were irradiated for different lengths of time within the range of 0–20 min in the presence of air and the distance between samples to the center of the source was maintained at 25 cm. The grafting was carried out in sealed glass reaction bottles according to the method described earlier. Immediately after irradiation the samples were immersed in the prepared reaction solution. For each experiment, the reaction solution contained 10 mL of MMA, 90 mL of deionized water, 0.5 g of emulsifier, and 0.2 g of MPSA. The grafting reaction was carried out at 70°C for 3 h with constant agitation. The jute–PMMA-grafted samples were extracted in a Soxhlet reflux system in hot 1,2-dichloroethene until constant weight was achieved. For each preirradiation time the graft weight was calculated as an average of three measurements. The results of the variation of graft weight plotted as a function of preirradiation time are presented in Figure 1. Results show that the graft weight increases to about 122% with the increase of irradiation time up to 7 min. Beyond this limit the graft weight decreases and at 20 min of irradiation time the graft weight decreased by 47% from the maximum value.

The grafting phenomenon is believed to be attributed to the subsequent reactions of reactive species (e.g., radicals and peroxides) with MMA, which were already created by UV-radiation with the aid of photoexcited molecules. The photoexcited molecules apparently abstract hydrogen atoms from the jute sub-
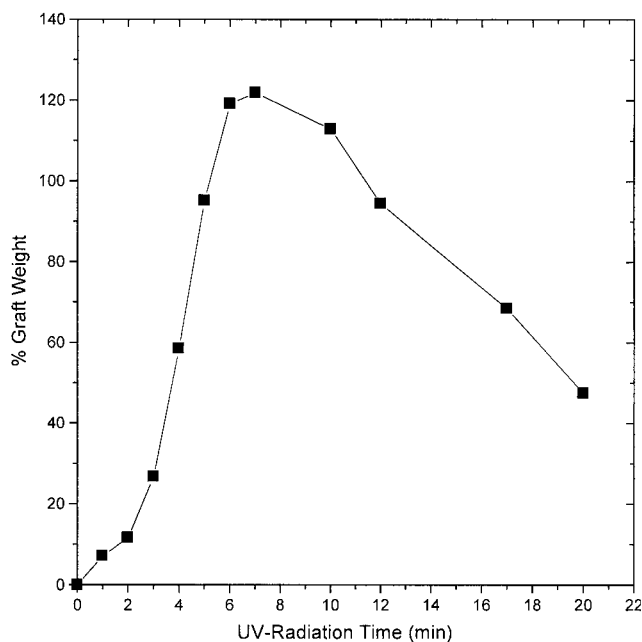
Figure 1 Variation of graft weight with UV-radiation time of MMA onto preirradiated jute fiber at 70°C. Conditions: MMA, 10 mL; jute fiber, 2.0 g; MPSA, 0.2 g; emulsifier, 0.5 g; deionized water, 90 mL; reaction time, 3.0 h.

strate and thus form macroradicals, which are capable of initiating graft copolymerization in a suitable monomer environment. The extent of grafting seems roughly proportional to irradiation time up to about 6 min, suggesting that the radical concentration increases, and that a further increase of radiation time caused radicals to be terminated by a photoinduced crosslinking reaction. During the reaction process, the MMA conversion is directly related to the concentration of reactive sites already created on the jute–cellulose backbone. Results are presented in Figure 2.

It is likely that the radicals produced in the amorphous region are mobile and migrate to neighboring sites and finally recombine with another radical; as a result the concentration of radicals decreases to an extent of radiation time and the radicals remain available for grafting. It was also noticed that during irradiation the temperature increases to 45°C and at longer radiation time the heating effect could adversely affect the radiochemical yields of jute cellulose.

Effect of reaction time

For this study, samples were exposed to a UV-radiation source for 5.0 min with the same other irradiation and chemical conditions as before. Preirradiated samples were immersed in the reaction solution where the chemical compositions of the emulsion solution contained 5 g/L of emulsifier, 2 g/L of MPSA, 10% (v/v)
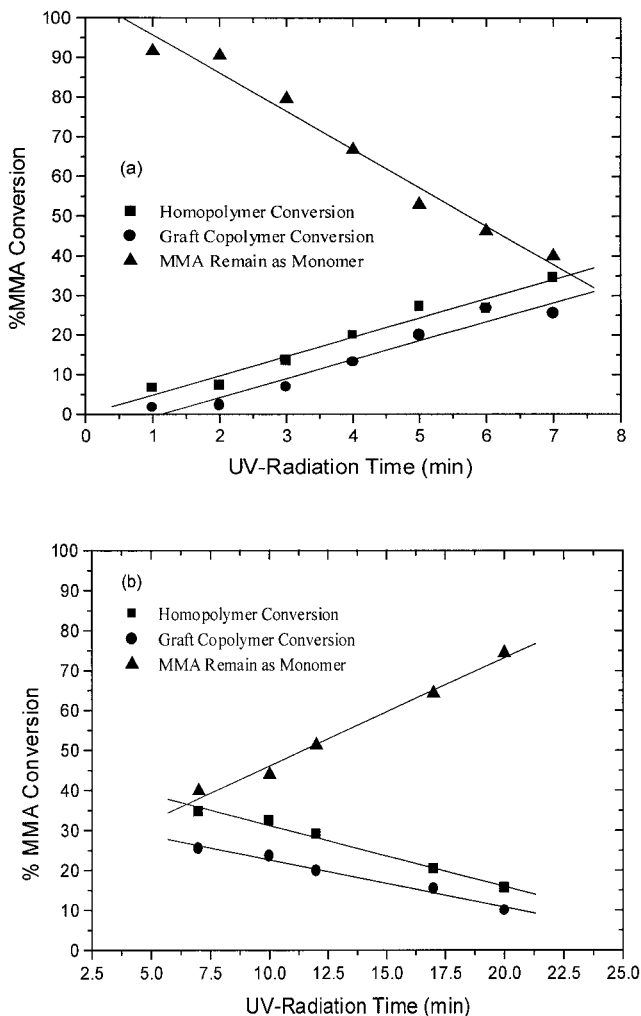
Figure 2 Percentage MMA conversion with radiation time in the UV-radiation–induced preirradiation grafting process.

of MMA, and 90% (v/v) of deionized water. The reaction temperature was found[5] to play a significant role in the graft copolymerization process. Under the above chemical compositions for an arbitrarily chosen reaction time of 3 h, 70°C temperature was found to give significant degree of grafting in the previous tests. Therefore, the experiments on the reaction time were carried out at this temperature. The results of the variation of graft weight as a function of the reaction time are presented in Figure 3. Results show that the graft weight increases sharply up to 95% with the prolonged reaction time up to 3 h. The increase of graft weight for a particular irradiation time is expected with the increase in reaction time until all the radiation-induced reactive species are depleted.

Influence of MMA concentration on grafting

Monomer concentration is the most effective chemical parameter in the graft copolymerization reaction re-

gardless of the method of grafting reaction. The monomer concentration in the reaction solution influences the degree of grafting by chemical reaction with the cellulose radicals because it controls the monomer diffusion. In these tests, samples were irradiated under the UV-radiation source for 5.0 min with the radiation conditions the same as for the reaction time–dependent grafting. For each experiment, the reaction was conducted at a set temperature of 70°C for 3 h. The reaction solutions were prepared with different amounts of MMA and deionized water with the other chemical compositions the same as before.

The results in Figure 4 show that the grafting level increases to about 94% with the increase of MMA concentration of 10% (v/v), beyond which the degree of grafting level tends to level off. It was also observed that there was some unemulsified MMA, floating on the surface of the solution, for grafting conducted at 15% (v/v) MMA concentration. The emulsifier with the aid of homogenizer under constant mechanical agitation breaks down the MMA monomer into fine droplets and stabilizes them into the water phase. Because jute is a highly water absorbent material, the MMA units are distributed onto the surface of the jute substrate. An increase in the amount of MMA in the water phase resulted in the formation of larger particles. The number of particles formed was dependent on the emulsifier concentration in the aqueous phase and the number of micelles originally present. The increased number of MMA droplets obtained by in-
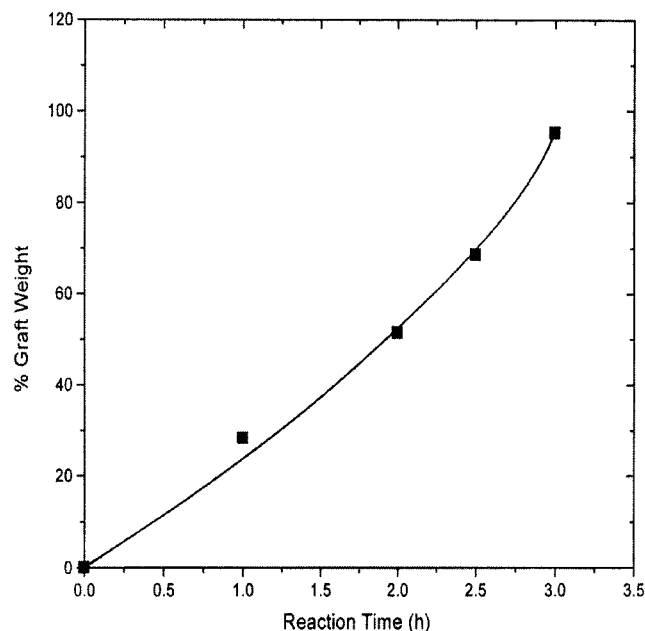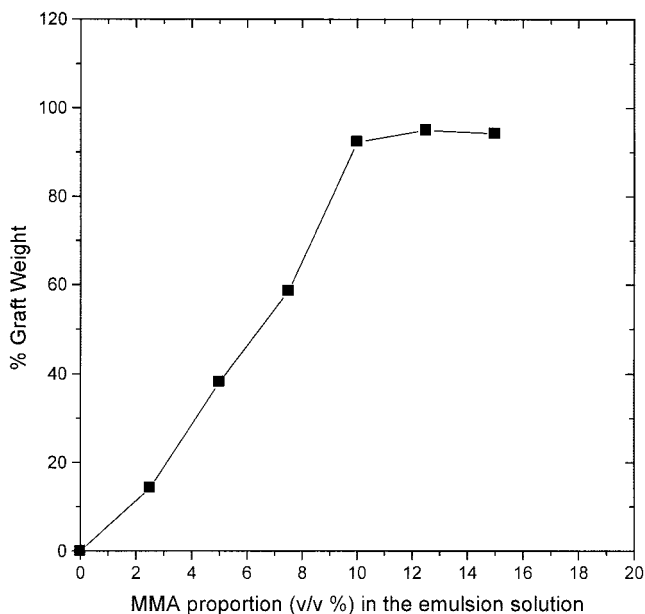

Figure 3 Effect of reaction time on the degree of MMA grafting onto preirradiated jute fiber. Conditions: radiation time, 5 min; reaction temperature, 70°C; MMA, 10 mL; jute fiber, 2.0 g; MPSA, 0.2 g; emulsifier, 0.5 g; deionized water, 90 mL.

Figure 4 Influence of the volumic percentage of MMA in the MMA/deionized water emulsion on the degree of grafting onto preirradiated jute fiber. Conditions: radiation time, 5 min; reaction temperature, 70°C; jute fiber, 2.0 g; MPSA, 0.2 g; emulsifier, 0.5 g; reaction time, 3.0 h.

creasing the amount of MMA requires more emulsifier at the water–MMA interface, so that somewhat less emulsifier is available for micelle formation.

## Characterization

Mechanical properties

From the load versus extension curves, the maximum load at which the samples break down and the corresponding elongation at break were measured. The load versus extension plots followed a similar pattern for both grafted and as-received samples. The mechanical parameters for samples having different graft weight by the UV-radiation induced preirradiation method were evaluated and normalized by the value obtained for the as-received sample and defined as the relative breaking load and elongation. The relative values were plotted as a function of the percentage graft weight (%GW) and the results are presented in Figure 5. The breaking load decreases up to 38% with the increasing graft weight up to 67% of MMA. The relative breaking load is found to decrease linearly with the increase in graft weight. The decrease in breaking load with %GW is termed the constant of deterioration ($K_d = -0.00937/\%GW$) and is represented as

$$F_{rb} = 1 + K_d(\%GW) \qquad (4)$$

where F_{rb} is the relative breaking load, which is the ratio of the breaking load of the grafted to that of as-received samples, and K_d is the constant of deterioration determined from the slope of the straight line. However, the percentage of elongation showed an increase of up to 65% and reached a steady level with the increase of graft weight to 67%. The data points were fitted to a first-order exponential equation of the following form:

$$E1_{re} = E1_0 + A_1\exp[-(\%GW)/t_1] \qquad (5)$$

where El_{re} represents the relative elongation at break (i.e., normalized with respect to the values for the as-received sample). The coefficients were estimated to be $El_0 = 1.6302 \pm 0.0255$, $A_1 = -0.61786 \pm 0.04427$, and $t_1 = 6.27 \pm 1.12$. The results (Fig. 5) show that grafting of jute causes a decrease in the breaking load. This could be attributable to the dead weight of graft chains attached to the lignocellulose backbone. Further, the fiber may have interchain PMMA-graft links that make the fibers rigid. Consequently, there is a decrease in the binding strength despite a reinforcement by the graft copolymerization of MMA onto jute fiber. 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 copolymer with MMA. This reduces the hydrogen bonding or the degree of chain entanglements. The increase in elongation suggests that the degree of molecular chain mobility becomes
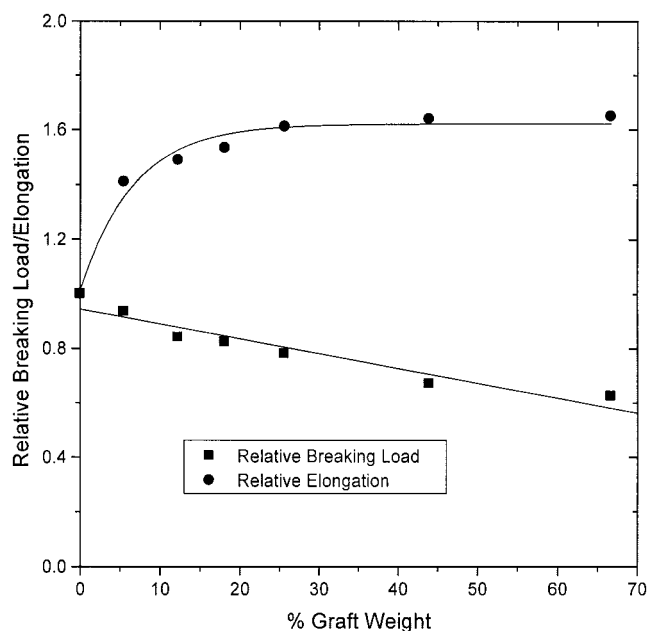
Figure 5 Variation of the relative breaking load and elongation with the degree of MMA grafting onto jute fiber by UV-radiation–induced preirradiation method.
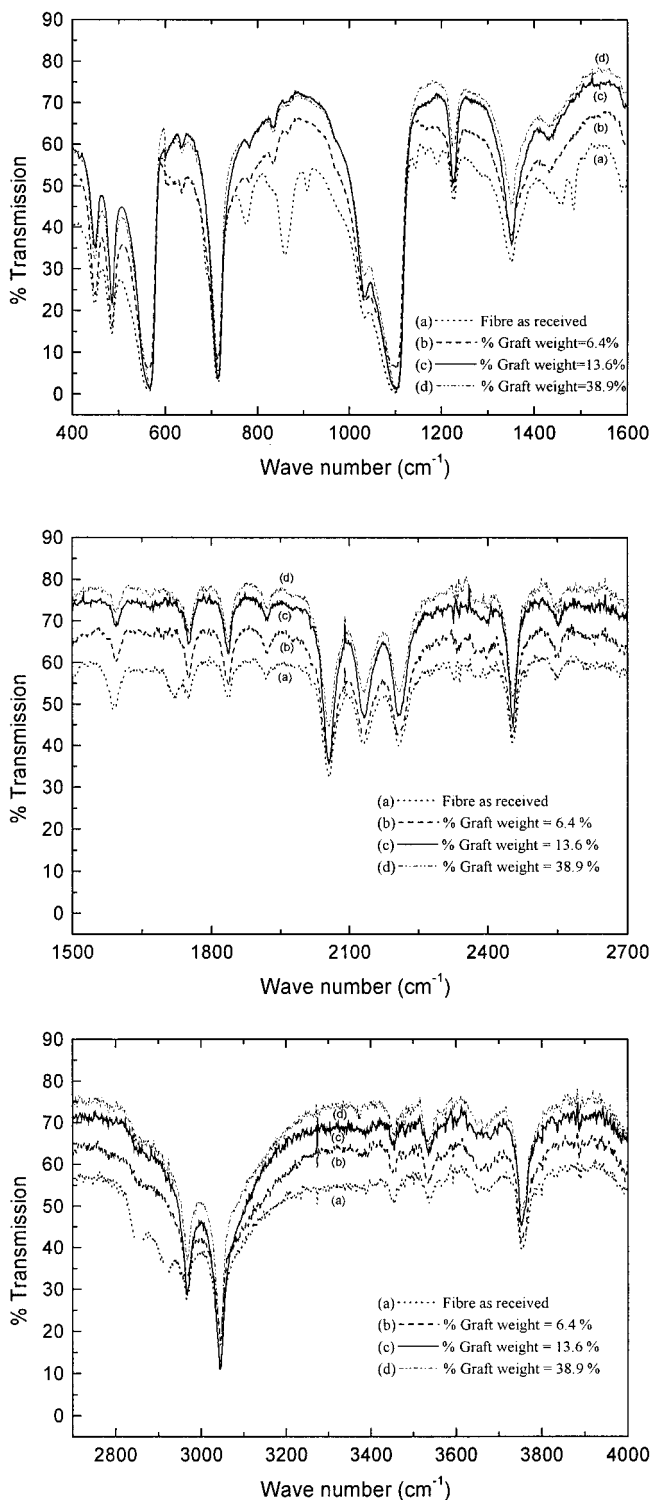
**Figure 6** Infrared absorption spectra of "as-received" and MMA-grafted jute fiber.

higher by graft copolymer reaction of the jute substrate with MMA monomer.

ATR infrared spectroscopic analysis

Infrared spectra were recorded over the range of wavenumbers from 400 to 4000 cm^{-1} with a resolution

of ± 3 nm and a diffraction factor of 1, according to the procedure described in the experimental section. The spectral signatures of the as-received and jute–PMMA-grafted samples are presented in Figure 6. The vibrational modes correspond to the absorption bands 3800–3600 cm^{-1} attributed to O—H stretching vibration of free OH groups, 3500–3400 cm^{-1} attributed to O—H stretching frequencies of intermolecular bonds, and 3300–2500 cm^{-1} attributed to chelated intramolecular bonds of O—H and C—H stretching vibrations. The absorption bands 2500–2000 cm^{-1} are attributed to hydrogen-bonded O—H stretching vibrations; and bands 2000–1650 cm^{-1} to aromatic overtones, C—H out-of-plane bend, and C=O stretching vibrations of ester ketonic groups. The bands at 1596 and 1431 cm^{-1} are attributed to C—H deformation of –CH$_2$–, 1350 and 1225 cm^{-1} to O—H deformation of phenolic hydroxyl group, and 1150–1040 cm^{-1} to O—H deformation and C—O stretching. The bands in the range of 1000–650 cm^{-1} appear to be attributable to out-of-plane C—H deformation vibrations and, in this range, the absorption bands at 858, 775, and 908 cm^{-1} are affected on grafting reaction of MMA onto jute fibers. The absorption bands in the range 650–400 cm^{-1} are attributed to aromatic substitution of benzene rings.

It is also noted (Fig. 6) that for the samples grafted with MMA the peaks at 1457, 1484, and 1723 cm^{-1} have disappeared. The most noticeable difference between the IR spectra of as-received and jute–PMMA-grafted samples are found to be in band shapes. A band shape analysis was carried out for the intensity for the bands at 1100 and 3045 cm^{-1} (i.e., 22.314 and
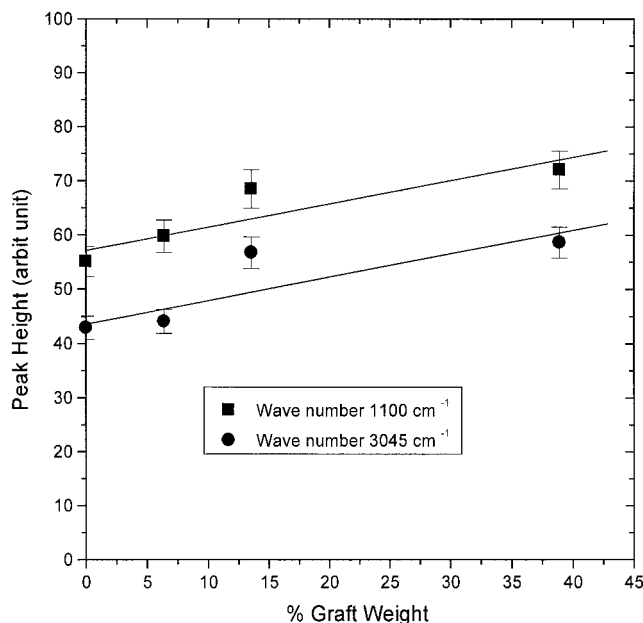
Figure 7 Change of intensity with degree of grafting at wavenumbers 1100 and 3045 cm^{-1}.

61.77 μm), respectively, and the plotted results of the peak height versus graft weight are shown in Figure 7. 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 $\Delta E = E_1 - E_2$. The population of the vibrational energy state N is then given by Boltzmann distribution law:

$$N = N_0 \exp(-\Delta E / kT) \tag{6}$$

By replacing the population of the energy state by the integral intensity, this can be expressed as

$$I = I_0 \exp(-\Delta E / kT) \tag{7}$$

where I_0 is a constant quantity, T is the temperature, and k is the Boltzmann's constant.

The results (Fig. 7) showed that the samples grafted with MMA increased the band intensity (i.e., 1100 and 3045 cm^{-1}). The intensity of such bands depends only on the population of the vibrational energy states, which corresponds to the concentration of the vibrating group in the matrix.[20] The increase in the intensity with degree of grafting could be attributed to the decreasing energy barrier (ΔE) with the concentration of MMA units in the jute–cellulose matrix. The linear relationship suggests that the concentration of vibrating groups increases for the grafting reaction of MMA with jute fibers. This could be related to the constancy of the energy barrier ΔE and the changes in band shape could be attributed to altering the molecular chain orientations.[19]

Equilibrium water absorption

The water absorption at equilibrium in samples of as-received jute fiber and in jute–PMMA-grafted copolymer was examined according to the procedure described in the experimental section. The plotted results for the equilibrium water absorption versus the percentage graft weight are presented in Figure 8. For the jute–PMMA-grafted sample the equilibrium water content decreases by 61% with increasing graft weight of up to about 18%, and beyond this grafting level it remains unaltered (Fig. 8). The results of equilibrium water content for jute–PMMA-grafted fiber suggest that the pendant polymethyl methacrylate (PMMA) chains admixed molecularly throughout the lignocellulose matrix, thus hindering sites on hydrophilic backbone. It is known[20] that fibers hold water, in their lumens and capillary as well as on the surface. A higher level of grafting is likely to block the capillaries and reduce the equilibrium water content.
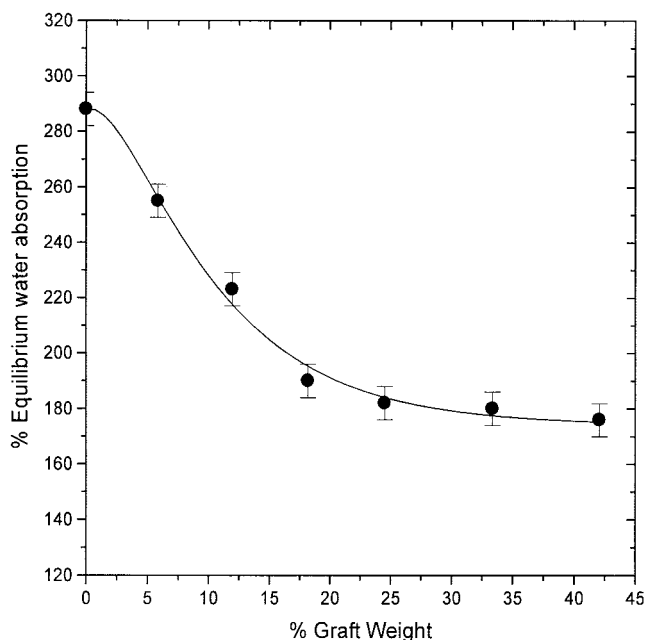
Figure 8 Equilibrium water absorption for different degrees of grafting of MMA onto jute fiber.

Several factors may account for the observations including a combination of the degree of crystallinity, graft distribution, and crosslinking, all of which will affect the ability of the graft copolymer structure to imbibe the free, nonbound condensation water. For example, the tighter the structure, the lower the equilibrium water absorption. It was observed that above a certain level of grafting, the samples become rigid, which could decrease the mobility of the cellulose chain structure, and therefore the equilibrium water content becomes restricted.

CONCLUSIONS

Experimental studies of graft copolymerization have shown that the effective graft copolymerization of the hydrophobic monomer MMA onto jute fibers could be achieved by applying the UV-radiation–induced preirradiation technique in an aqueous phase. Throughout this study, the radiation was conducted in the presence of air, and therefore, the reaction of oxygen with cellulose radicals will produce cellulose peroxides for initiation of the subsequent grafting reaction. At shorter radiation times, the exposure of the samples under UV-radiation was not long enough for oxygen diffusion, and thus the influence of oxygen on the radiochemical yields of jute will be less compared to that at longer exposure times. In the graft copolymerization process, the parameters are interdependent and the results of the study are summarized as follows:

- Because all other parameters are constant, the concentration of radicals will be reflected by the degree of grafting with variation of the UV-exposure time. In this study, the maximum graft weight (~ 122%) was obtained on exposure to the UV-radiation source for 7.0 min. On a further increase of the exposure time, a decreasing trend suggesting a progressive radical decay by their recombination reaction was observed. The grafting level increases almost linearly with the increase in reaction time until all the radicals are depleted. The percentage graft weight increased linearly with the monomer concentration until the active radicals are completely depleted and then a leveling-off effect was observed above 10% (v/v) of MMA concentration in the reaction solution.

- The mechanical properties of the jute–PMMA-grafted copolymer showed a linear decreasing trend for the breaking load, whereas the elongation increases with an increase of the graft weight up to 26%, beyond which the change was found to be negligible.

- In the IR spectra the peaks at 1457, 1484, and 1723 cm^{-1} were not observed for the jute–PMMA-grafted sample. The infrared spectral absorption measurements showed that the results of a band shape analysis could be correlated with the degree of grafting. The infrared spectra for the bands, such as at 1100 and 3045 cm^{-1}, seem to be additive for the backbone or side chain.

- The equilibrium water absorption shows that the jute–PMMA-graft reduces the water content up to certain level of graft weight, which is about 18% GW. This was attributed to the hydrophobic nature of the PMMA-grafted chain, which causes heavy restrictions on swelling.

References

1. Ferdous Khan. Ph.D. Thesis, RMCS, Cranfield University, UK, 1999.
2. Hebeish, A.; Guthrie, J. T. The Chemistry and Technology of Cellulosic Copolymers; Springer-Verlag: Berlin/Heidelberg/New York, 1981; Chapter 3.
3. McDowall, D. J.; Gupta, B. S.; Stannett, V. T. Polym J 1987, 19, 643.
4. Ferdous Khan; Ahmad, S. R.; Kronfli, E. Adv Polym Technol 2002, 21, 1.
5. Ferdous Khan; Ahmad, S. R. J Appl Polym Sci 1997, 65, 459.
6. Ferdous Khan; Ahmad, S. R.; E. Kronfli, Polym Degrad Stab 1999, 63, 79.
7. Mohanty, A. K.; Singh, B. C. Polym Plast Technol Eng 1988, 27, 435.
8. Ghosh, P.; Paul, S. K. J Macromol Sci Chem 1983, A20, 169.
9. Davis, N. P.; Garnett, J. L.; Urquhart, R. G. J Polym Sci Symp 1976, 55, 287.
10. Da Silva, M. A.; Helena Gil, M.; Lapa, E. J Appl Polym Sci 1987, 34, 871.
11. Harris, J. A.; Arthur, J. C., Jr.; Carra, J. H. J Appl Polym Sci 1978, 22, 905.
12. Hon, D. N.-S.; Chan, H.-C. In: Graft Copolymerization of Lignocellulosic Fibers; Hon, D. N.-S., Ed.; ACS Symposium Series 187; American Chemical Society: Washington, DC, 1982; p. 101.
13. Fouassier, J. P. In: Graft Copolymerization of Lignocellulosic Fibers; Hon, D. N.-S., Ed.; ACS Symposium Series 187; American Chemical Society: Washington, DC, 1982; p. 83.
14. Shukla, S. R.; Athaly, A. R. J Appl Polym Sci 1994, 54, 279.
15. Tripathy, S. S.; Jena, S.; Mishra, S. B.; Padhi, N. P.; Singh, B. C. J Appl Polym Sci 1985, 30, 1399.
16. Kubota, H.; Murata, Y.; Ogiwara, Y. J Polym Sci Polym Chem Ed 1973, 11, 485.
17. Davis, N. P.; Garnett, J. L.; Urquhart, R. G. Polym Lett Ed 1976, 14, 537.
18. Kroschwitz, J. I., Ed. Encyclopedia of Polymer Science and Engineering, 2nd ed.; Wiley–Interscience: New York, 1986.
19. Dessouki, A. M.; Badr, Y.; Zahran. A. H.; Mousa, A.; Abo-Zeid. Radiat Phys Chem 1986, 27, 347.
20. Zeronian, S. H. In: Cellulose Chemistry and Its Applications; Nevell, T. P.; Zeronian, S. H., Eds.; Ellis Horwood: Chichester, UK, 1985; Chapter 5.