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Photoinduced Graft−Copolymer Synthesis and Characterization of Methacrylic Acid onto Natural Biodegradable Lignocellulose Fiber

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UV radiation induced graft copolymerization of methacrylic acid onto natural lignocellulose (jute) fiber was carried out both by "simultaneous irradiation and grafting" and by preirradiation methods using 1-hydroxycyclohexyl-phenyl ketone as a photoinitiator. In the "simultaneous irradiation and grafting" method, the variation of graft weight with UV-radiation time, monomer concentration, and the concentration of photoinitiator was investigated. In the case of the preirradiation method, the incorporation of 2-methyl-2-propene 1-sulfonic acid, sodium salt, into the grafting reaction solution played a most important role in suppressing the homopolymer/gel formation and facilitating graft copolymerization. The optimum value of the reaction parameters on the percentage of grafting was evaluated. In comparison, results showed that the method of graft−copolymer synthesis has significant influence on graft weight. The study on the mechanical and thermal properties of grafted samples was conducted. The results showed that the percentage of grafting has a significant effect on the mechanical and thermal properties in the case of grafted samples. Considering the water absorption property, the jute−poly(methacrylic acid)-grafted sample showed a maximum up to 42% increase in hydrophilicity with respect to that of the "as received" sample. Attenuated total reflection infrared studies indicate that the estimation of the degree of grafting could be achieved by correlating band intensities with the percent graft weight.

Introduction

Jute is a natural biodegradable lignocellulose polymer mainly used for textile products similar to those made from other synthetic and natural cellulose polymers. Jute differs from other natural cellulose fibers in chemical composition. The main structural element of jute fiber is cellulose (58−63%), which is held entirely within the cell units. The other major components in jute are hemicellulose (20−24%) and lignin (12−15%), which are distributed throughout the entire body of the fiber acting as a cementing material. Additionally, jute also contains trace quantities of organic and inorganic pigments. Although jute has a high tensile modulus, it suffers low elongation at break, color fastness, and so forth, compared to the other natural cellulose fibers.

Graft copolymerization is a well-known technique to impart a new property or enhance the existing properties in the parent polymer with minimum degradation of the original properties. The nature of the changes in the properties depends on the type of monomer being grafted, the percentage of grafting, the method of grafting, and the distribution of the grafted chain throughout the parent polymer.[1,2] McDowall and co-workers reported[2] that the γ-radiation-

induced preirradiation method showed higher elongation, recovery, and more uniform graft copolymer distribution throughout the cross section than the ceric ion-initiation method. In the past, research has been focused on graft copolymerization of vinyl monomers onto natural cellulose and synthetic polymers using high-energy radiation[3−7] and chemical initiation[8−12] methods.

The UV radiation initiation technique, on the other hand, is considered to be the safer technique because it results in less deterioration of the original fiber properties due to the selective nature of the radiation source. Moreover, the UV-radiation equipment is more cost effective than the high-energy (e.g., γ and electron-beam) radiation equipment. Therefore, a photoinitiator is generally used to promote the graft−copolymer reaction. Upon absorption of energy, the photoinitiator is decomposed into reactive radicals or transfers its energy to other molecules in the system, thereby facilitating the graft−copolymer reaction. In the past, research has been extensively focused[13−23] on graft copolymerization of various monomers onto other natural cellulose materials by 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 the grafting reaction. The main disadvantage of this method is the substantial amount of undesir-

Table 1. Preparation of Grafting Solutions with Different Chemical Compositions for Different Grafting Parameters

grafting parameters	chemical composition of grafting solution (mol L^{-1})				
	HCAP $\times 10^{-2}$	MAA	CH$_3$OH $\times 10^{-3}$	MPSA $\times 10^{-2}$	deionized water
Simultaneous Irradiation and Grafting					
radiation-time-dependent grafting	4.895	2.385	4.931	1.265	33.034
concentration of photoinitiator (HCAP)	0−14.68	2.385	4.931	1.265	33.034
influence of monomer concentration	4.895	0−7.074	4.931	1.265	
Preirradiation Method					
homopolymer inhibiting agent (MPSA)		2.385		0−18.97	44.44
effect of preirradiation time (0−25 min)		2.385		12.65	44.44

able homopolymer formation in the system. An alternative to the "simultaneous irradiation and grafting" method is the preirradiation one, in which the jute 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 cellulose polymer. The peroxide species are produced only when polymers are irradiated in the presence of oxygen.[1,3] The preirradiation technique has some advantages over the "simultaneous irradiation and grafting" technique, such as less homopolymer formation in the system and increased depth of penetration. Additionally, this technique can be applied as a continuous grafting process in industry.

Photografting of methyl methacrylate (MMA) was investigated by Ghosh and Paul[17] onto bleached jute fiber using ferric sulfate [Fe$_2$(SO$_4$)$_3$] 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 graft−copolymer reaction. Several authors have reported[20−23] that the graft copolymerization of various monomers onto cellulose materials depends on the type of photoinitiator and monomer and the role of various solvents in the UV-radiation-induced "simultaneous irradiation and grafting" method. The grafting of acrylamide and hydroxyethyl methacrylate onto cellulose was studied[14] using isopropyl thioxanthone as the photoinitiator. The UV-radiation-induced technique has so far not been found on the graft copolymerization of hydrophilic monomer with jute fibers. In this research, the graft copolymerization of methacrylic acid (denoted as MAA) onto jute fiber was examined using 1-hydroxycyclohexyl-phenyl ketone (denoted as HCAP) as a photoinitiator. The "simultaneous irradiation and grafting" and preirradiation methods were applied in this study. It is important to investigate the feasibility of achieving efficient grafting of MAA onto jute fiber. The MAA was selected because the hydrophilc nature of this monomer is to increase the water absorption property of the jute−PMAA-grafted fiber for applications in the geotextile industry and a variety of other uses. The graft copolymerization process is dependent on interdependent and cumulative parameters. Therefore, the present study analyzes the grafting of MAA as a function of different reaction parameters and examines how the MAA grafting influences the mechanical and thermal properties and hydrophilic nature of the grafted product with respect to those of the "as received" fiber. Samples were analyzed using attenuated total reflection infrared (ATR-IR) spectroscopy.

Experimental Section

Materials. Jute fibers were received from Amin Jute Mill Co. (Bangladesh), and on receipt the samples were stored in the dark at 20 °C and about 65% relative humidity. MAA was used for the graft−copolymer reaction, which was stabilized with 200 ppm hydroquinone monomethyl ether, and after delivery it was stored at 5 °C. Methanol was used to dissolve the photoinitiator and 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 purchased from Aldrich Chemical Co. (Gillingham, Dorset, U.K.). Oxygen-free nitrogen (White cpst) was used. HCAP was kindly supplied by Ciba Geigy, and after delivery it was stored in the dark at ambient conditions. Deionized water was used as a graft−copolymer reaction medium.

"Simultaneous Irradiation and Grafting" Method. Cleaned jute fibers, weighing approximately 2.0 g, were soaked in 100 mL of a prepared reaction solution for 48 h to ensure the incorporation of the monomer and other additives into the jute sample. The chemical composition of the prepared reaction solution for different grafting parameters is shown in Table 1. Wet samples were then exposed to UV radiation in the presence of air. The distance between samples to the center of the source was kept constant (25 cm). Grafted samples were removed from the radiation chamber, followed by several washings with hot deionized water to remove the traces of unreacted chemicals. 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 vacuum at 40 °C and their weight was recorded. The weight percentage of grafting was calculated according to the following relationship:

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

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 and is called the homopolymer content and W_M is the total monomer weight used in the reaction solution.

Preirradiation Grafting Method. In this study, cleaned jute samples were soaked in a solution of methanol and photoinitiator (HCAP; 4.89×10^{-2} mol L^{-1}) for 48 h to ensure the incorporation of photoinitiator into the jute fiber. Wet samples were then irradiated with UV radiation for 20 min in the presence of air. The preirradiated sample was immersed into a prepared grafting solution. The chemical composition of the grafting solution is presented in Table 1. The solution was confined into a 200-mL glass reaction bottle, and about 2.0 g of the preirradiated sample was added to the solution, after which the bottle was sealed with a rubber septum. The whole assembly 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 conducted at 70 °C for 3 h. The separation procedure of unreacted monomer from the jute−PMAA-grafted sample, the homopolymer extraction procedure, and the calculation of the graft weight were same as that of the "simultaneous irradiation and grafting" method.

UV-Radiation Source. The UV-radiation source was purchased from Jenton International (Whitechurch, Hampshire, U.K.). The Jenton STAT-I-CURE contains a compact UV oven, utilizing a 400-W Hg flood cure light source. Both the power supply and the 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, for example, 254, 365, or 425 nm.

Measurement of Mechanical Properties. Tests were carried out at ambient conditions using a microprocessor-controlled material testing machine (Lloyd Instruments M 5K, Fareham, Hampshire, U.K.) 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 gage 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, 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 parameters were normalized with respect to the "as received" sample, and the results are presented.

Thermal Analysis. This was performed using a Mettler differential scanning calorimeter (DSC) at a heating rate of 10 °C min^{-1}. The DSC instrument was calibrated for temperature and energy using indium, lead, and zinc reference samples. All samples were heated for 72 h under a vacuum at 80 °C to remove moisture. DSC traces were recorded with about 5 mg of sample, in a nitrogen atmosphere.

Water Absorption Measurements. The weight of the dry samples was recorded before the samples were soaked in deionized water until an equilibrium weight was achieved at ambient conditions. 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 the sample was calculated using the following equation:

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

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, and the results are presented.

ATR-IR Spectroscopy. The IR spectra were recorded at ambient conditions using ATR spectrometers (Graseby Specac, P/N 11209) with a 10-reflection ATR unit and a solid sample holder, with a resolution of ±3 nm and a diffraction factor of 1. The maximum transmission was obtained by careful alignment of the mirrors in the spectrometer. Samples of 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.

Results and Discussion

"Simultaneous Irradiation and Grafting" Method. Upon absorption of UV radiation, the HCAP produces benzoyl and cyclohexyl radicals (denoted as P•) by α cleavage at C−C bonds (Scheme 1a).[24−26] The resultant radicals formed by the cleavage of HCAP can abstract hydrogen atoms from the jute−cellulose (Cell-H) and create active sites (Scheme 1c) for the subsequent graft−copolymer reaction (Scheme 1f). The radicals can be formed at any carbon atom (i.e., C_1-C_6) by hydrogen and hydroxyl abstraction or C−C and C−O bond cleavage in the cellulose molecules (Chart 1). The benzoyl and cyclohexyl radicals undergo the termination reaction by intermolecular hydrogen abstraction (Scheme 1b) and radical−radical coupling. Various radical species are also raised from irradiation of MAA monomer (Scheme 1d), which subsequently reacts with jute-cellulose radicals to form graft copolymerization (Scheme 1 g), and simultaneously, the monomer radicals can also initiate homopolymerization (Scheme 1h). In the reaction medium, the presence of water and CH_3OH can be utilized in different ways to promote radical formation onto jute−cellulose and MAA units through intermolecular hydrogen abstraction (Scheme 1i,j). These radicals are responsible for both graft−copolymer and homopolymer reactions. The radicals onto cellulose backbone, monomer, solvents, and other additives that are already created are also in competition with their recombination reactions.

Scheme 1. Some UV-Radiation-Induced Chemical Reactions Involved in the Synthesis of Graft Copolymerization of MAA onto Jute Fiber by the "Simultaneous Irradiation and Grafting" Method
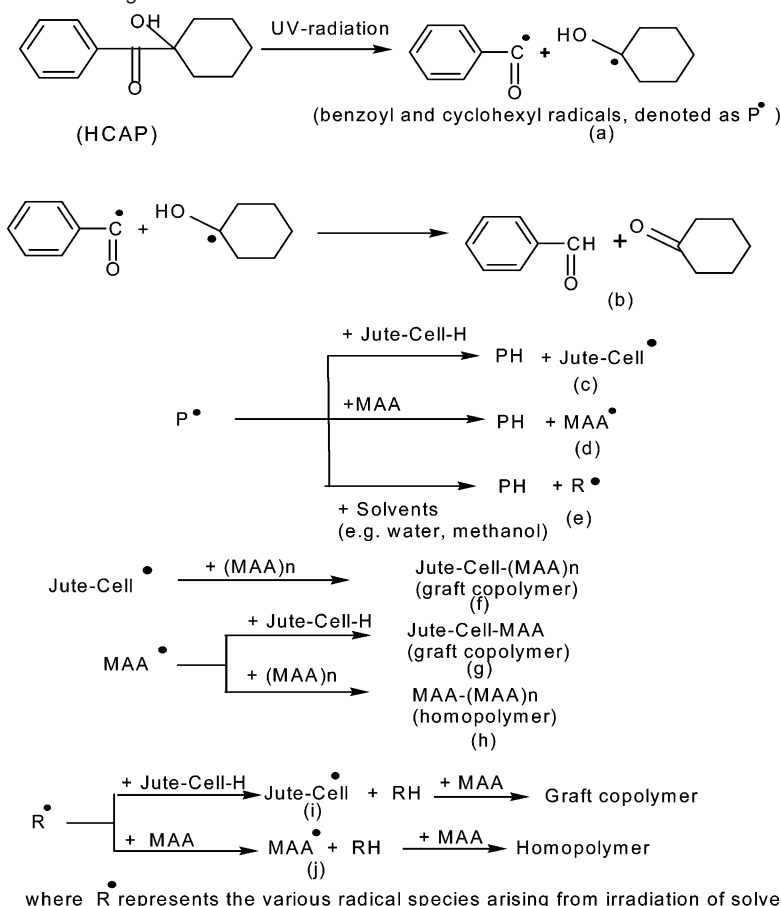
Chart 1. Cellubiose Unit
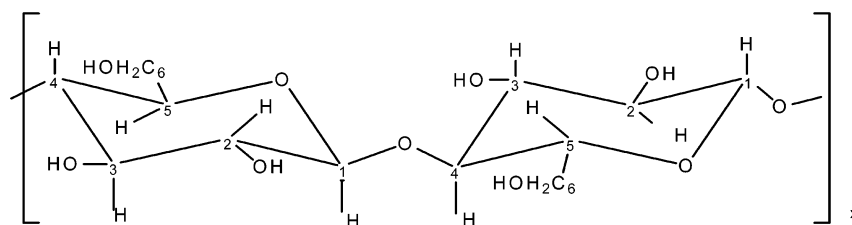
As mentioned in the Introduction, the jute contains lignin. The presence of lignin, being a polyphenolic material, will give rise to inhibition reactions.[27,28] Most likely, these will affect the overall photochemical events. Because the reaction was performed in the presence of air, the oxygen will interact in the photochemical events. The extent of grafting is very much dependent on the reaction conditions. Therefore, the grafting of MAA has been studied as a function of different reaction parameters, as discussed in the following.

Radiation-Time-Dependent Grafting. The results of the variation of the graft weight plotted as a function of the radiation time are presented in Figure 1. Results show that the graft weight increases to 47% with the increase of radiation time up to 20 min. Beyond this limit, the graft weight tends to level off. The homopolymer formation with grafted sample was found to increase linearly with radiation time as expected.

The grafting phenomenon is believed to be due to the reactions of MAA radicals with jute−cellulose radicals, which are already created by UV radiation with the aid of
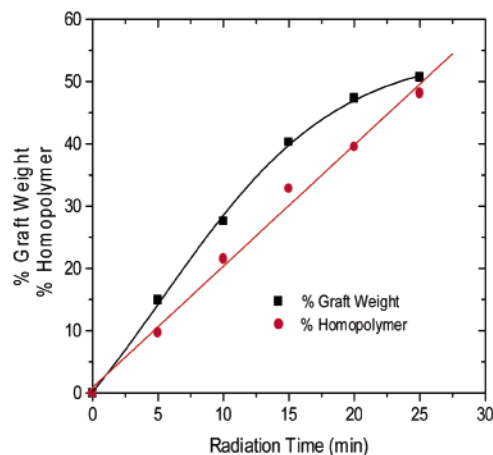
Figure 1. Influence of radiation time on the grafting of MAA onto jute fiber in the "simultaneous irradiation and grafting" method. Jute fiber = 2.0 g, HCAP = 4.895×10^{-2} mol L^{-1}, MAA = 2.385 mol L^{-1}, methanol = 4.931×10^{-3} mol L^{-1}, MPSA = 1.265×10^{-2} mol L^{-1}, and deionized water = 33.034 mol L^{-1}.

HCAP molecules. The most important factor influencing the radiochemical yield is the radiation time during grafting

reaction. The extent of grafting increased linearly with radiation time up to ~20 min. The further the increase of radiation time, the graft−copolymer formation levels off. It could be that at a lower radiation time the formation of reactive cellulose sites increases linearly, which gives rise to a copolymer reaction. However, at a higher concentration of radicals, these also undergo a termination reaction at increasing rates in proportion to their dynamic concentration, and eventually saturation of the reactive cellulose sites was achieved in the jute by MAA. A linear increase of homopolymer formation could be attributed to the fact that the number of radicals generated in the solution is higher than the concentration of the radicals in the jute−cellulose. This would then cause predominant homopolymerization in preference to grafting.

Concentration of HCAP on Grafting. The UV radiation, being weak, can dissociate only the weakest bonds in the polymer backbone, which generates few numbers of radicals for the grafting reaction. However, in the presence of HCAP as a photoinitiator a significant number of free radicals can be generated on the cellulose backbone for the graft−copolymer reaction. Therefore, the concentration of photoinitiator is the most important factor for effective graft copolymerization.

Figure 2a shows the effect of the concentration of HCAP on the graft weight. Results show that the graft weight increases to 47% with the increase of HCAP concentration of 4.89 × 10⁻² mol L⁻¹, beyond which the graft weight tends to level off. The leveling-off effect at a higher concentration of photoinitiator is, however, expected. This effect could be due to the stronger absorption of UV radiation by the photoinitiator with the increase of concentration. Consequently, the produced radicals are in competition with their termination and propagation reactions as the concentration of radicals is increased. The leveling-off effect would be the point where the propagation and termination reactions both are proportional to the HCAP concentration and the rate of radicals is independent of concentration. The MAA conversion into graft copolymer and homopolymer is plotted as a function of HCAP concentration, as shown in Figure 2b. It can be seen (Figure 2b) that the MAA conversion to homopolymer is as much as twice as that of the graft copolymer. It can be explained by the fact that at high concentrations of HCAP the increased homopolymerization is due to direct initiation of the MAA conversion in solution by benzoyl and cyclohexyl radicals resulting from the α cleavage. A similar effect has been observed in radiation-induced polymerization onto other cellulose and synthetic polymers.[15]

Influence of MAA Concentration on Grafting. The monomer addition to the reactive cellulose sites is the basis of the grafting reaction. The monomer concentration in the grafting process is one of the most important chemical parameters regardless of the method of graft copolymerization reaction. It influences the graft copolymerization by adjoining the required number of MAA units onto the polymer branch during the reaction. Figure 3 shows that the graft weight increases to ~47% with the increase of MAA concentration up to 2.358 mol L⁻¹. Beyond this limit, the
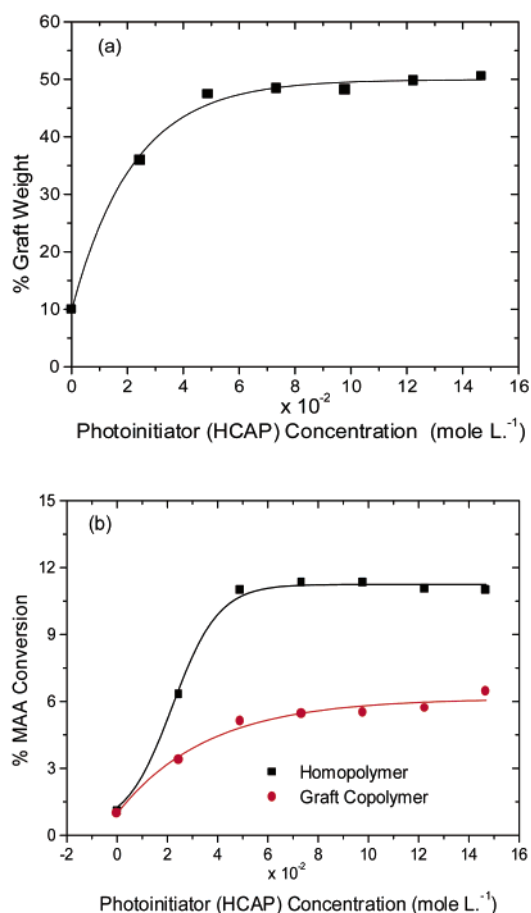

Figure 2. Effect of the concentration of photoinitiator (HCAP) on grafting of MAA onto jute fiber in the "simultaneous irradiation and grafting" method: (a) HCAP concentration versus % graft weight and (b) HCAP concentration versus % MAA conversion. Radiation time = 20 min, jute fiber = 2.0 g, MAA = 2.385 mol L⁻¹, methanol = 4.931 ×10⁻³ mol L⁻¹, MPSA = 1.265 × 10⁻² mol L⁻¹, and deionized water = 33.034 mol L⁻¹.
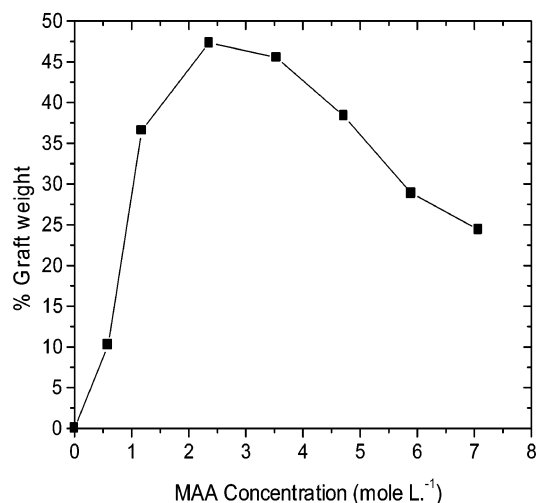

Figure 3. Influence of monomer concentration on grafting of MAA onto jute fiber in the "simultaneous irradiation and grafting" method. Radiation time = 20 min, jute fiber = 2.0 g, HCAP = 4.895 ×10⁻² mol L⁻¹, methanol = 4.931 ×10⁻³ mol L⁻¹, and MPSA = 1.265 × 10⁻² mol L⁻¹.

graft weight decreases and at 7.074 mol L⁻¹ of MAA concentration the graft weight dropped to 24%. This could be attributed to the higher radical concentration of MAA in the reaction solution directly initiated by the benzoyl and

Scheme 2. Some UV-Radiation-Induced Chemical Reactions Involved in the Synthesis of Graft Copolymerization of MAA onto Jute Fiber by the Preirradiation Method
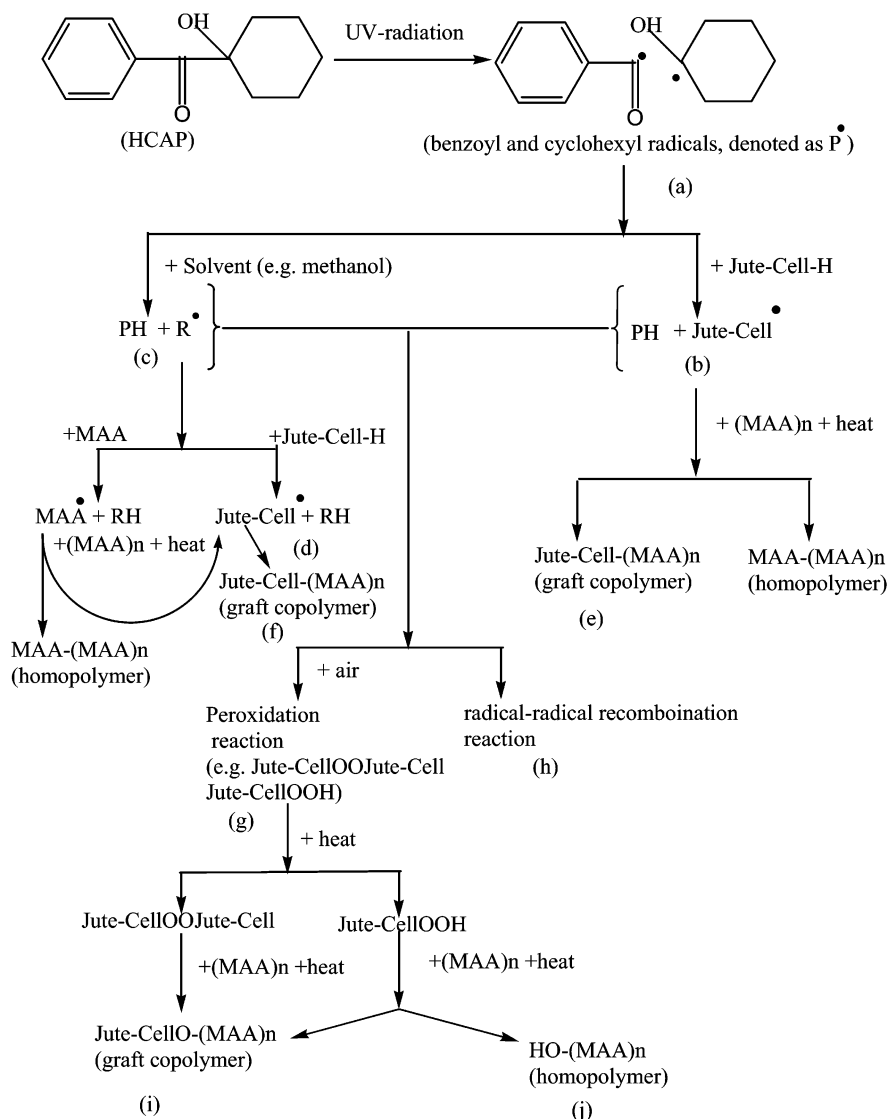
cyclohexyl radicals resulting from the cleavage of HCAP compared to the jute−cellulose radicals. This resulted in a rapid homopolymer formation as the concentration of MAA was increased, which consequently decreased the graft copolymerization.

In the "simultaneous irradiation and grafting" method, solvents such as methanol and water are capable of swelling the trunk lignocellulose polymer and as well as those being solvents for MAA and HCAP, which leads to appreciable grafting. For the grafting reaction, interaction of hydrogen atom abstraction and energy transfer are predominant. In the MAA−methanol−cellulose grafting system, intermolecular hydrogen abstraction can be utilized in different ways to promote the grafting reaction. With liquid methanol, the methoxy radical ($CH_3O^\bullet$) is the principal species formed whereas with aqueous methanol $^\bullet CH_2OH$ predominates.[21] The homopolymerization could be initiated by the direct radiolysis of MAA or by reaction of MAA with the radiolysis products of water, that is, the hydrogen atom ($H^\bullet$), the hydroxyl radical ($OH^\bullet$), and HCAP.

Preirradiation Grafting Method. The photochemical reactions involved in the preirradiation method follow a similar pathway as the "simultaneous irradiation and grafting" method, as shown in Scheme 2. In this case, the radiation was carried out in the methanol−HCAP−jute system; therefore, the intermolecular hydrogen abstraction from cellulose molecules can occur in different ways, which leads to radical formation onto the cellulose backbone (Scheme 2b,d). In the presence of air, the UV-radiation-induced radicals probably react with oxygen to produce peroxides that can initiate polymerization (Scheme 2g). Also, radicals on the jute not reacted with oxygen can initiate the copolymer reaction when the MAA is introduced into the system (Scheme 2e,f). At an elevated temperature, cellulose diperoxides (Cell−OO−Cell) and hydroperoxides (Cell−OOH) are decomposed to give peroxy radicals, which are capable of initiating the grafting reaction in contact with monomer (Scheme 2i) discussed elsewhere.[1,3]

The propagation step is also in competition with the recombinant reaction (Scheme 2h). As mentioned earlier, the lignin present in jute most likely acts as a radical scavenger.
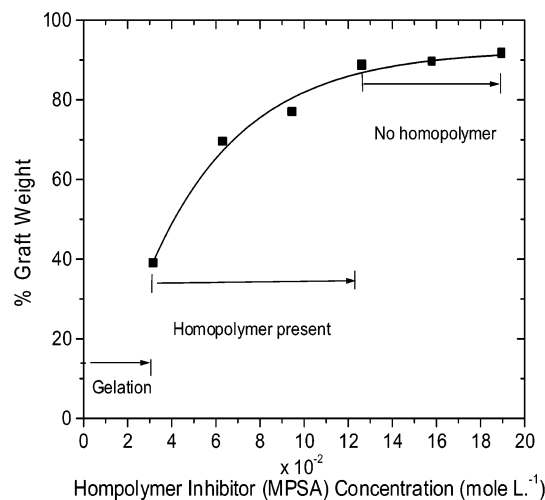
Figure 4. Effect of the concentration of MPSA on grafting of MAA onto jute fiber in the preirradiation method. Radiation time = 20 min, jute fiber = 2.0 g, reaction temperature = 70 °C, and reaction time = 3.0 h. The grafting reaction solution contained MAA = 2.385 mol L^{-1} and deionized water = 44.44 mol L^{-1}.
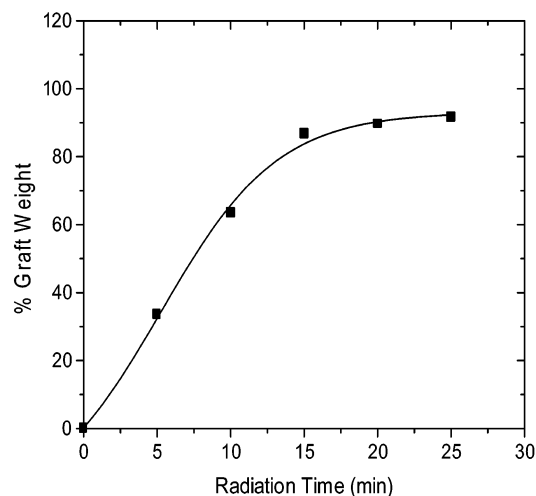

Figure 5. Variation of graft weight with UV radiation time of MAA onto preirradiated jute fiber. Jute fiber = 2.0 g, reaction temperature = 70 °C, and reaction time = 3.0 h. Grafting solution contained MPSA = 12.65 × 10^{-2} mol L^{-1}, MAA = 2.385 mol L^{-1}, and deionized water = 44.44 mol L^{-1}.

The cellulose radicals may also terminate by abstracting hydrogen atoms from methanol molecules and also with other radicals. The hydroxyl radical ($^\bullet$OH) formed by the decomposition of Cell−OOH is capable of initiating homopolymerization [HO−(MAA)n; Scheme 2j]. A reducing agent such as MPSA is, therefore, added to reduce the homopolymer formation for an efficient graft−copolymer reaction. This agent works by decomposing the hydroperoxides.[3]

Effect of Homopolymer Inhibiting Agent (MPSA) on Grafting. An undesirable homopolymer side reaction (i.e., homopolymerization of the monomer) during the grafting reaction is inevitable. It is well-known[29,30] that the addition of certain metal salts to the reaction mixture can suppress the formation of homopolymer, thus leaving the monomer free to take part in the grafting reaction and facilitating the isolation of the graft−copolymer product. The MPSA is known[3,30] to prevent the homopolymerization and enhance the grafting reaction. Therefore, MPSA was chosen for this study. The results of the variation of graft weight as a function of MPSA concentrations are presented in Figure 4. At MPSA concentrations below 3.16 × 10^{-2} mol L^{-1}, no grafting was observed, but a gel was formed in the reaction medium showing very high homopolymerization, which prevented the graft−copolymer reaction. With increasing the MPSA concentration above 3.16 × 10^{-2} mol L^{-1}, no gel formation was observed in the reaction medium, which allows the MAA to be grafted with jute. As the concentration of MPSA increased up to 12.65 × 10^{-2} mol L^{-1}, the graft weight increased to 89%, beyond which no homopolymer was observed and the graft weight reaches a saturation level (Figure 4). From this study, the MPSA = 12.65 × 10^{-2} mol L^{-1} was chosen as a homopolymer inhibiting agent for subsequent grafting of MAA onto jute fibers.

The existence of MPSA in the grafting medium can be explained by the fact that it contains an unsaturated allylic-type inhibiting functional group [H$_2$C = C(CH$_3$) CH$_2$$^-$] which acts as a free radical transferring agent. This inhibitor compound has a higher diffusion capacity through grafting medium than the parent polymer.[30] The differences in the

performance can be attributed to different radical transfer rates between MPSA and each homopolymer radical of poly-(methacrylic acid) (PMAA).

Effect of Preirradiation Time on Grafting. The effect of the radiation time on the graft weight is shown in Figure 5. Results show that the graft weight increases up to 87% with the increase in radiation time until 15 min. Above this limit, the increase of the graft weight is negligible. It is most likely that for a lower irradiation time the formation of reactive species (e.g., radicals, peroxides) increases linearly, which subsequently gives rise to grafting in contact with MAA monomer units. For a higher radiation time, the leveling-off effect (Figure 5) is due to the increased radical−radical coupling or disproportionation reaction. Similar results have been reported[1,3] for the grafting of MMA onto preirradiated jute fiber initiated by high-energy irradiation.

Mechanical Property. The maximum load, tensile strength, percent elongation, and work done at which the samples break down were evaluated from the load versus extension curves. The load versus extension curves followed a similar pattern for both "as received" and grafted samples. The results of the relative mechanical parameters were plotted as a function of the percent graft weight as shown in Figure 6. The breaking load decreases up to 47% and the tensile strength up to 73% with the increase of graft weight up to 48% of MAA. The decrease in breaking load and tensile strength as a function of the graft weight followed a first-order exponential function, represented in 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 estimated to be $Y_{BL_0} = 0.50$, $K' = 0.51$, and $D_c = 0.062$, and for the tensile strength, $Y_{TS_0} = 0.25$, $K' = 0.78$, and $D_c = 0.092$. However, the percentage of elongation was found
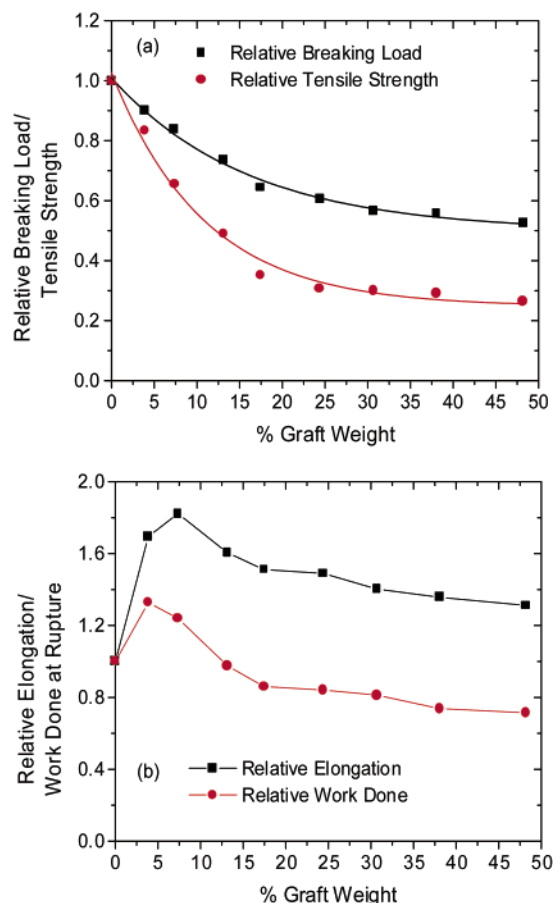
Figure 6. Variation of the mechanical properties with the percentage of MAA grafting onto jute fiber by the UV-radiation-induced "simultaneous irradiation and grafting" method.

Figure 7. DSC thermograms of samples: (a) "as received" fiber, (b) graft weight = 13.13%, and (c) graft weight = 47.34%.

to increase up to ∼80% with increasing graft weight ∼ 8%. As the graft weight increased up to 48%, the elongation decreased to 31% with respect to the "as received" fiber (Figure 6b). For a graft weight of 8%, the work done at rupture was found to increase 24% with respect to the "as received" fiber. For further increase of the graft weight (up to 48%), the work done decreased significantly.

The results (Figure 6) have shown that the grafting of MAA with jute causes a decrease in the breaking load and tensile strength. This could be attributed to the dead weight of the graft chains attached to the cellulose backbone. Further, the fiber may have interchain PMAA−graft links making the fibers rigid. Consequently, there is a decrease in the binding strength despite reinforcement by the graft copolymerization of MAA 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 MAA. 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 PMAA−graft copolymer add-on with the jute sample.

DSC Analysis. The thermal behavior of jute is considered to represent a summation of the individual behaviors of its
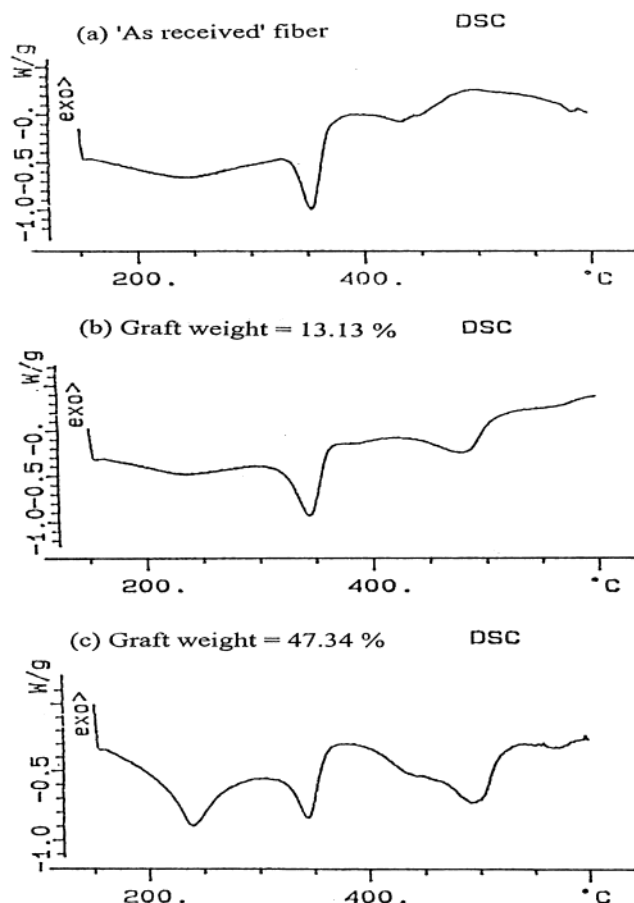
components[31,32] (e.g., cellulose, hemicellulose, lignin, etc.). Figure 7 shows a comparison of DSC thermograms of "as received" jute fiber and jute−PMAA graft−copolymer samples. The DSC thermogram of the "as received" jute fiber (Figure 7a) showed an endothermic tendency from 162 up to 243 °C, which is attributed to partial dehydration of the −OH primary groups and decomposition of minor constituents in jute. On further rise of the temperature up to 328 °C, an exothermic reaction was observed which is attributed to the decomposition of hemicellulose. The degradation was significantly higher above 300 °C. A large endotherm in the region between 328 and 375 °C having a peak maximum at 355 °C represents the complete loss of −OH groups of the monomer units of cellulose and depolymerization and volatilization of cellulose, followed by exothermic decomposition of degraded products.[31,32] The large but broad exothermic peak in the region 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 13% graft weight, we found a broad endothermic peak between 308 and 366 °C having a peak maximum at 342 °C (Figure 7b). This is assigned to the depolymerization of cellulose−graft−PMAA. For higher graft weight (e.g., 47% graft weight), the endothermic peak became broader, a shoulder peak appeared at 395 °C, and the exothermic peak disappeared in the region between 431 and 585 °C as a result of the PMAA-grafted chain addition with jute fiber as shown in Figure 7c. The results represent
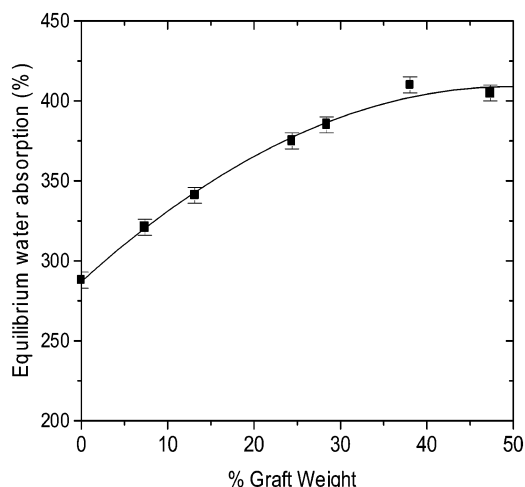
Figure 8. Equilibrium water absorption versus % graft weight of MAA onto jute fiber.

the degradation process of both the lignocellulose and the grafted PMAA chain.

Equilibrium Water Absorption. Figure 8 shows the equilibrium water content as a function of the percent graft weight. For the "as received" jute sample, the equilibrium water content was found to be ∼288%. With the increase of the graft weight up to ∼38%, the equilibrium water content increased to 410%, beyond which it remained unaltered. The results of the equilibrium water content for jute−PMAA samples suggest that the pendant PMAA chains admixed molecularly throughout the lignocellulose matrix, thus increasing the hydrophilic backbone. The extremely hydrophilic MAA monomer swells significantly within the lignocellulose matrix, altering the mobility of the cellulose moieties remarkably. Several factors may account for this, such as varying combination of the graft distribution, hydrogen bonding, and cross-linking, all of which will affect the ability of the graft−copolymer structure to imbibe the free, nonbound condensation water. For example, the less rigid structure will allow higher equilibrium water contents. It was observed that above a certain graft weight (e.g., >38%), the samples became rigid, which could decrease the mobility of the cellulose chain structure, and, therefore, the equilibrium water content becomes restricted.

ATR-IR Spectroscopic Analysis. The spectral signatures of the "as received" and jute−PMAA-grafted samples are presented in Figure 9. The detailed assignments of the bands and corresponding possible modes are given in Table 2. The absorption bands at 858, 775, and 908 cm^{-1} are affected because of MAA grafting. It is also noted (Figure 9) that for the grafted samples the peaks at 1457, 1484, and 1723 cm^{-1} have disappeared. The most noticeable difference between the IR spectra of the "as received" and jute−PMAA-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 61.77 μm), respectively, and the plotted results of the peak height versus graft weight are shown in Figure 10. 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
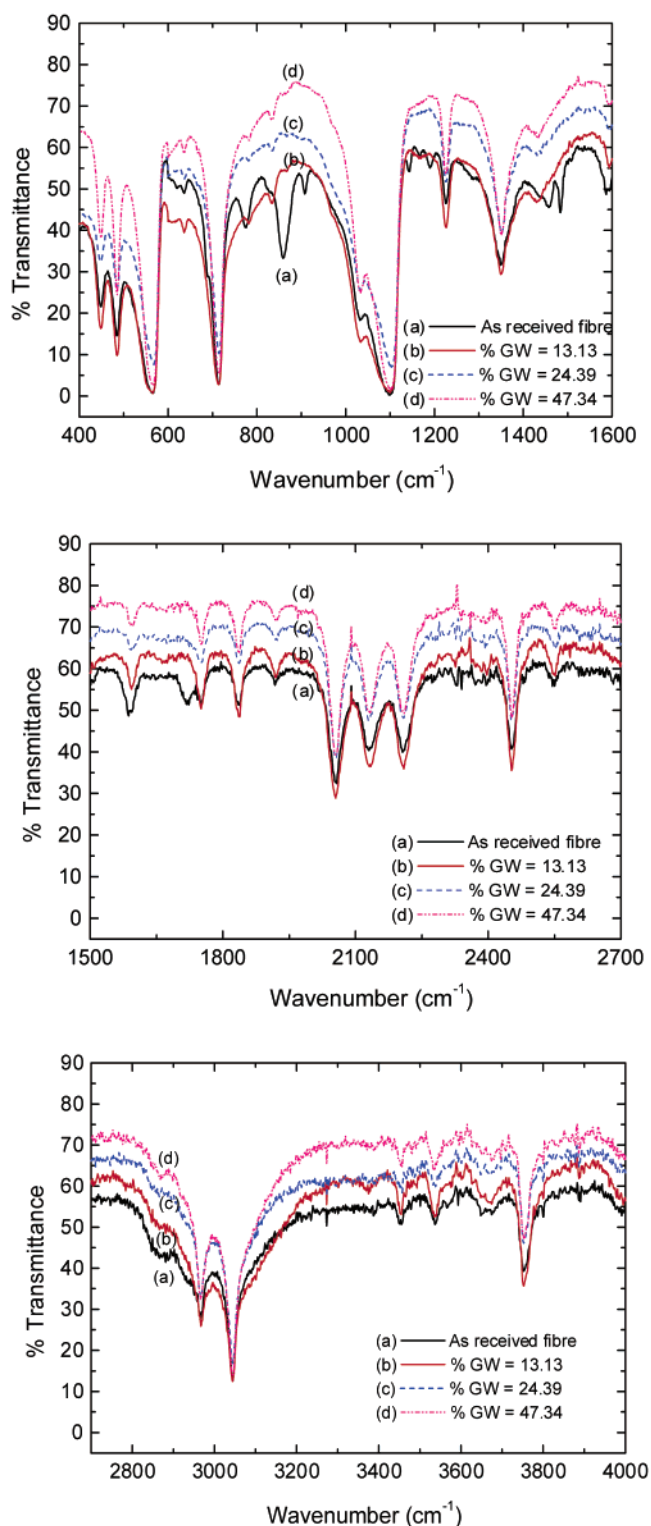

Figure 9. IR spectra of "as received" fiber and jute−PMAA-grafted samples with various percent graft weight (%GW).

E_1, they can migrate to a higher energy level E_2 by overcoming a potential barrier $\Delta E = E_1 - E_2$.

The results (Figure 10) showed that the MAA grafted with jute 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.[33] The increase in the intensity with the graft weight could be attributed to the decreasing energy barrier (ΔE) with the
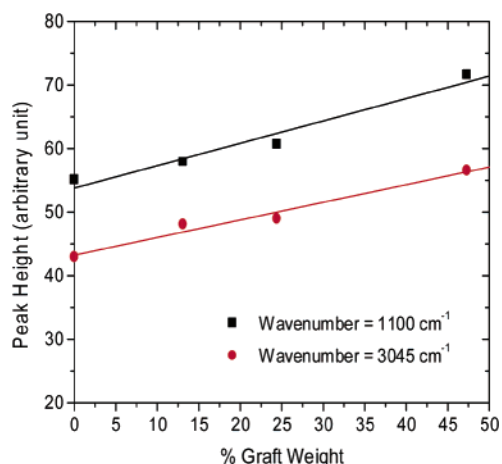
Figure 10. Change of intensity with graft weight at wavenumbers 1100 and 3045 cm^{-1}.

Table 2. Characteristic Modes of the ATR-IR Spectra of Jute Fibers

frequency (cm^{-1}) bands	characteristics modes
3800−3600	O−H stretching vibration of free OH groups
3500−3400	O−H stretching frequencies of intermolecular bonds
3300−2500	chelated intramolecular bonds of O−H and C−H stretching vibrations
2500−2000	hydrogen bonded O−H stretching vibrations
2000−1650	aromatic overtones, C−H out-of-plane bend, and C=O stretching vibrations of ester ketonic groups
1596 and 1431	C−H deformation of −CH$_2$−
1350 and 1225	O−H deformation of phenolic hydroxyl group
1150−1040	O−H deformation and C−O stretching
1000−650	out-of-plane C−H deformation vibrations
650−400	aromatic substitution of benzene rings

concentration of MAA units in the jute−cellulose matrix. The linear relationship suggests that the concentration of vibrating groups increases for the grafting reaction of MAA 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.[33]

Conclusion

The graft copolymerization of MAA with jute fiber was achieved by applying both "simultaneous irradiation and grafting" and preirradiation methods. In the graft copolymerization process, the reaction parameters are interdependent. Because all other parameters are constant, the concentration of the radicals will be reflected by the percentage of grafting with variation of the UV-exposure time in both methods. The total radiation time determines the number of grafting sites, although these sites do not increase significantly above a certain irradiation time. In both cases, the graft weight increases almost linearly with the increase in radiation time up to about 15 min. On a further increase of the radiation time, the graft weight tends to saturate. The percentage of graft weight is significantly higher in the case of the preirradiation method (Figure 5) than that obtained in the "simultaneous irradiation and grafting" method (Figure 1). The concentration of HCAP is an important factor to generate radiochemical yields for the subsequent graft−copolymer reaction. However, above 4.895×10^{-2} mol L^{-1} of concentration of HCAP the percentage of grafting tends

to level off. The increase in graft weight is linearly dependent on the MAA concentration up to about 20% (v/v), and for further increase of monomer concentration [up to 60% (v/v)], the graft weight is decreased. In the case of the preirradiation method, it was impossible to conduct the graft−copolymer reaction in the absence of MPSA because of homopolymer/gel formation in the reaction medium. A very high graft weight was achieved in this method by incorporating MPSA between 3.16×10^{-2} and 18.97×10^{-2} mol L^{-1} in the reaction solution.

The mechanical properties of the jute−PMAA-grafted samples showed a decreasing trend for the breaking load and tensile strength, suggesting disruption to the stronger bonds, and the PMAA−graft add-on produces relatively weaker bonds. The elongation and work done at rupture increases significantly up to a certain graft weight, beyond which the changes were found to be decreased. Results of DSC indicate that the thermal stability of jute fiber "as received" sample is greater than that of the jute−PMAA-grafted samples. The equilibrium water absorption shows that the PMAA−graft add-on with jute increases the water content up to a certain level of graft weight (which is ∼38% graft weight). This was attributed to the hydrophilic nature of the PMAA-grafted chain. In the IR spectra, the peaks at 1457, 1484, and 1723 cm^{-1} were not found for jute−PMAA-grafted samples. IR spectral measurements have shown that the results of band shape analysis could be correlated with grafting. The IR spectra for the bands, such as at 1100 and 3045 cm^{-1}, seem to be additive for the backbone or side chain.

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