Surface Modification of Jute Yarn by Photografting of Low-Glass Transition Temperature Monomers

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ABSTRACT: Jute yarns were grafted with three types of vinyl monomers of different functionalities such as methyl acrylate (MA), ethyl acrylate (EA), and 2-hydroxyethyl acrylate (HEA) with ultraviolet radiation. The graft copolymerization reaction between the cellulose of the jute fibers and the monomer and the chemical environment of the treated fibers were confirmed by Fourier transform infrared spectroscopy. The reduction of OH groups and increment of >C=O groups in treated jute yarns were observed. DSC studies showed that the treated jute fibers were more thermally stable compared to the untreated one. The surface topography of the yarns was analyzed by an environmental scanning electron microscope. Different parameters, such as concentration of monomers and irradiation time, were optimized with the extent of mechanical properties such as tensile strength and elongation at break of the jute yarn. MA, EA, and HEA produced enhanced tensile strengths of 87, 78, and 85%, respectively. The monomers MA, EA, and HEA showed improved elongations at break of 118, 91, and 76%, respectively. The water uptake of treated and untreated jute yarns were studied. The maximum water uptake was observed of the grafted sample compared to the untreated jute yarn. The effects of additives such as urea on mechanical properties were also studied. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 993–1000, 2003

INTRODUCTION

Jute, popularly known as the "golden fiber" of Bangladesh, is the cheapest of all natural fibers and has long been used in low-value products such as gunny bags, twine, and carpet backing. Jute fiber contains lignin (12–14%), himicellulose (21–24%), and cellulose (58–63%) along with trace ingredients such as nitrogenous matter: fats, waxes, and ash.[1] Jute is a harsh fiber due to the presence of substantial amounts of lignin and a low wax content.[2] Moreover, the presence of cellulose in a lignin matrix makes it the stiffest among the natural fibers, and this is the basic reason for its technical nonviability as a textile fiber from a spinning point of view. Despite its advantages, jute fiber bears the drawback of a nonresistance temperature and susceptibility to moisture absorption and mildew attack. The sole monomer in cellulose is D-glucose. The glucose molecules are linked successively through a glucosidic bond in the beta configuration between C-1 and C-4 adjacent units to form very long $1 \rightarrow 4$ β-glucans, which are the basic polymers of cellulose. The maximum degree of substitution for an internal D-glucose residue is 3, that is, substitution at OH-2, OH-3, and OH-6. Three hydroxyl groups in the cellulose have the opportunity to form various hydrogen bonds. Therefore, jute fibers are hydrophilic in nature, and their moisture contact can reach 3–13%.[3] The resulting high intermolecular forces plus the regular structure of the polymer result in an unusually high degree of crystallinity. The crystalline melting point of cellulose is far above its decomposition temperature. The solubility of the polymer is very low; it is doubtful that solution ever takes place unless a chemical derivative is formed.

Photo-initiated graft polymerization is one of the fastest and most efficient methods to durably modify the surface properties of synthetic and natural polymers. In the simple grafting process, some additives increase yields and reduce homopolymerization.[4] In composite formation, such as of wood–plastic composites (WPCs)[5] and jute–plastic composites (JPCs),[6] additives increase both polymer loading and mechanical properties. Studies of the accelerative effects of additives on grafting yields are of interest, as such effects can lead to lower doses of radiation being used in grafting experiments. Photografting of vinyl monomers on polyolefins,[7–8] pure cellulose,[9–11] and jute[12–14] was considerably accelerated when small amounts of polyfunctional monomers, such as tripropylene glycol diacrylate (TPGDA) and trimethylol propane triacrylate (TMPTA), were added to the grafted formula-

tions. Khan and colleagues[15] improved the mechanical properties of jute yarn with an organometallic complex using ultraviolet (UV) radiation. Similar work has been performed with additives on the grafting of different monomers onto jute to improve the physicomechanical properties. This study was based on the grafting of a low-glass-transition-temperature (low-T_g) monofunctional monomers of different chemical structures onto polar jute yarn. The effects of radiation dose and concentration of monomers on mechanical properties of grafted jute yarn were studied.

EXPERIMENTAL

Materials

Jute yarn was collected from local markets in Bangladesh. The yarn is commercially known as Tossa jute yarn and was used without further bleaching. Three monomers, methyl acrylate (MA), ethyl acrylate (EA), and 2-hydroxyethyl acrylate (HEA), stabilized with 0.005% hydroquinone monomethyl ether, were procured from Fuka Chemic Switzerland. The names, structures, and T_g's of these monomers are given in Table I. Methanol (MeOH) was used as a diluent received from Merk (Germany). The additive urea (U) was procured from Aldrich (Germany). Irgacure 651 [Benzil kital, C_6H_5—CO—$C(OCH_3)_2$—C_6H_5] from Ciba-Geigy (Switzerland) was used as the photo-initiator (PI).

Methods

The monomers were destabilized by a chromatographic column, which was packed with the absorbing material alumina (Al_2O_3). The purified monomers were then stored at a temperature of about 4–6°C. Jute yarns were cut into small pieces (25 cm long). The samples were dried in an oven at 105°C for 3 h to remove moisture and were stored in a desecrator. For each type of monomer, a series of sample solutions were prepared at different proportions of MeOH with monomer and 2% (w/v) photo-initiator in different test tubes, with each tube containing a total of 20 mL of solution. The dried yarns were immersed in test tubes having monomer and methanol solution at different proportions of monomer for 75 min. A global UV lamp (100 W), which ensured equal radiation to all the test tubes containing different samples, was used

TABLE I
Name, Structure, and T_g of Each of the Monomers Used

Sample	Monomer	Structure	T_g (°C)
1	MA	CH_2=CHCOOCH$_3$	10
2	EA	CH_2=CHCOOCH$_2$CH$_3$	−24
3	HEA	CH_2=CHCOOCH$_2$CH$_2$OH	−15

TABLE II
Composition of Different Monomer Formulations (% v/v)

Formulation	MA	EA	HEA	MeOH	PI* (% w/v)
S1	10	—	—	88	2
S2	30	—	—	68	2
S3	50	—	—	48	2
S4	70	—	—	28	2
S5	—	2	—	96	2
S6	—	5	—	93	2
S7	—	10	—	88	2
S8	—	15	—	83	2
S9	—	20	—	78	2
S10	—	—	2	96	2
S11	—	—	5	93	2
S12	—	—	10	88	2
S13	—	—	15	83	2
S14	—	—	20	78	2

* PI = photo-initiator.

to irradiate the samples. After the desired irradiation, the jute yarns were withdrawn from the test tubes and washed in hot acetone for 60 min; then, the samples were dried at 105°C for 1 h. Fourteen formulations were prepared with the three monomers in the presence of a diluent (MeOH). The compositions of these formulations are shown in Table II.

The grafting of the monomer onto jute yarns was determined from the percentage weight increased by the jute samples after extraction with hot acetone and calculated by the formula

$$\% \ Gr = [(W_t - W_o)/W_o] \times 100$$

where Gr is the percentage grafting and W_o and W_t are the weights of the virgin and extracted jute yarns, respectively.

For the MA + MeOH system, MA concentrations varied from 10 to 70% and irradiation periods varied from 10 to 75 min. For the EA + MeOH system, EA concentrations varied from 2 to 20%, and irradiation periods varied from 10 to 50 min. For the HEA + MeOH system, HEA concentrations varied from 2 to 20%, and irradiation periods varied from 5 to 20 min. Tensile properties, such as tenacity and elongation at break, (E_b) of the treated and untreated jute yarn samples were directly measured by a universal testing machine (Instron, model 1011, UK) at a crosshead speed of 0.002 m/min. To study the water-swelling behavior of both the treated and untreated samples, samples were immersed into a static water bath at 25°C. Weights of the samples were recorded after different contact times. Samples were wiped carefully to remove surface water before they were weighed. Finally, the weight gain for different samples for water treatment were determined. Water absorption was determined by the following relation:
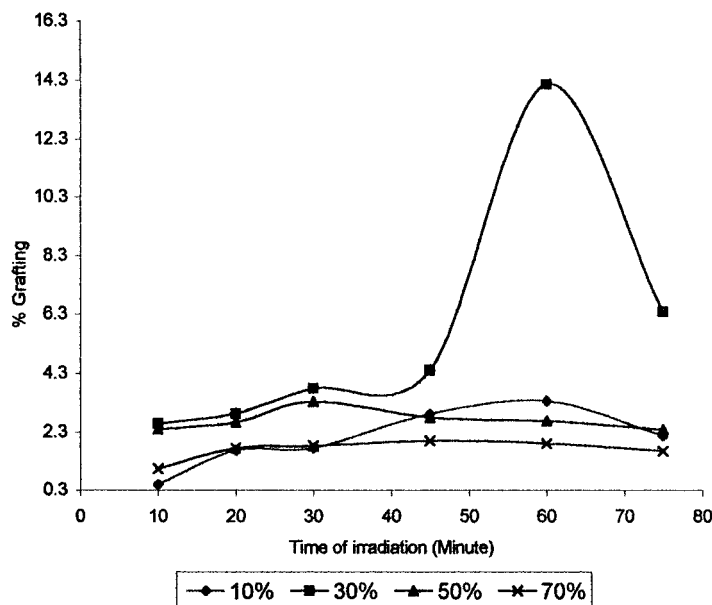
Figure 1 Grafting of MA with jute yarns at different MA concentrations against different UV irradiation periods.

$$W_g = (W_e - W_o)100/W_o$$

where W_g is the weight gain (%) due to water uptake, W_e is the weight after water treatment, and W_o is the oven-dry weight before water treatment.

Environmental scanning electron microscopy (ESEM)

Both treated and untreated jute yarns were examined by ESEM (Electro Scan model 2020, Boston, MA). The environmental scanning electron microscope was equipped with a La B6 filament and was operated at an accelerating voltage of 20 kV with a water vapor pressure ranging form 2–3 Torr.

Fourier transform infrared spectroscopy (FTIR)

Grafted and virgin jute yarns were analyzed by FTIR (Perkin Elmer, model Spectra 2000) with the attenuated total reflectance technique.

Differential scanning calorimetry (DSC)

Thermal properties of the untreated and grafted samples were investigated with a DSC-50 from Shimadzu (Japan). The samples were investigated in the sample pan and sealed. Thereafter, they were introduced into the heating cell of the differential scanning calorimeter. Heat treatment was performed at a programmed rate of 10°C/min, and the samples were then cooled and analyzed by a computer.

RESULTS AND DISCUSSION

Grafting

The grafting values of the three monomers are shown in Figures 1, 2, and 3 for MA, EA, and HEA respectively, where grafting is plotted against the time of UV irradiation as a function of monomer concentration. The grafting values increased with increase in irradiation time, after which the grafting values decreased. The decrease in grafting at high monomer concentration and high radiation dose could have been associ-
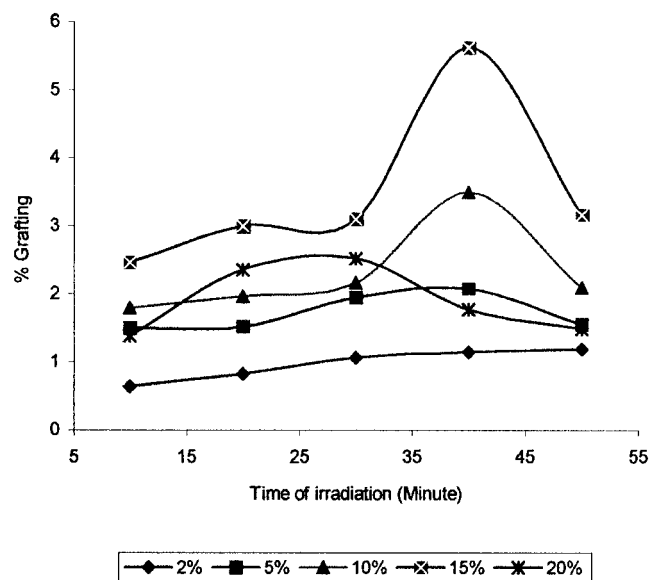

Figure 2 Grafting of EA with jute yarns at different EA concentrations against different UV irradiation periods.
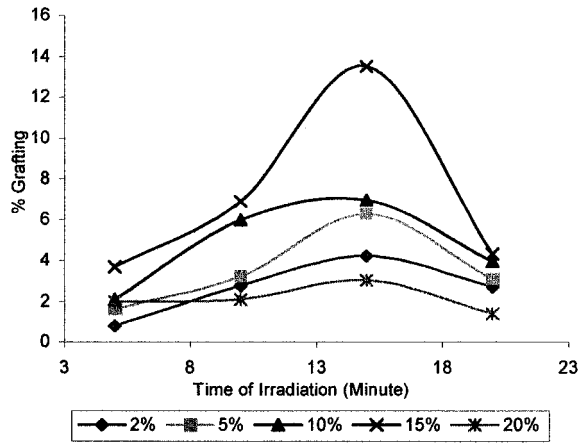
Figure 3 Grafting of HEA with jute yarns at different HEA concentrations against different UV irradiation periods.

ated with the fact that the homopolymerization reaction between the monomer and monomer radicals is dominant in the monomer and jute cellulose reaction.[10] However, for the MA system, the highest grafting value (14.1%) was achieved within 60 min of irradiation time and with a 30% MA solution. For the EA system, the highest grafting value (5.6%) was achieved

within 40 min of irradiation time and with a 15% EA solution. For the HEA system, the highest grafting value (13.5%) was achieved within 15 min of irradiation time and with a 15% HEA solution. The grafting efficiency of monomers onto the backbone of cellulose of jute depended on their chemical structure and size and on their T_g's.[6] MA produced the highest grafting value because it had the smallest molecular structure size of the monomers. It was easily diffused into the jute.

Tensile properties

Tensile properties, tensile strength (TS) and elongation at break (E_b), of the treated yarns were determined and compared with those of the untreated yarns. The tensile properties of the jute yarns could be expressed by factors, namely, the tenacity strength factor (T_f) and elongation factor (E_f). T_f is the ratio of the TS of the treated sample (T_{S_t}) to that of the untreated sample (T_{S_0}), that is $T_f = T_{S_t}/T_{S_0}$. Similarly, E_f is the ratio of the E_b of the treated sample (E_{b_t}) to that of the untreated sample (E_{b_0}), that is, $E_f = E_{b_t}/E_{b_0}$. The tensile properties (T_f and E_f) of the treated jute yarns are given in Table III versus the time of irradiation with respect to mono-

TABLE III
Grafting, T_f, and E_f of Each of the Treated Samples with Respect to Irradiation Time in Minutes

| Sample concentration | Irradiation time (min) | | | | | | | | | | | | | | | | | |
| | 10 | | | 20 | | | 30 | | | 45 | | | 60 | | | 75 | | |
	Gr	T_f	E_f	Gr	T_f	E_f	Gr	T_f	E_f	Gr	T_f	E_f	Gr	T_f	E_f	Gr	T_f	E_f
MA																		
10	0.49	1.01	1.02	1.66	1.08	1.09	2.91	1.15	1.45	2.17	1.19	1.21	1.66	1.49	1.67	3.35	1.19	1.25
30	2.58	1.26	1.37	2.94	1.43	1.58	3.77	1.57	1.68	4.40	1.64	1.74	14.2	1.87	2.18	6.39	1.77	1.91
50	2.94	1.23	1.34	2.62	1.27	1.42	3.33	1.47	1.61	2.78	1.36	1.48	2.67	1.32	1.45	2.37	1.18	1.30
70	1.04	1.03	1.05	1.75	1.09	1.11	1.82	1.11	1.12	2.0	1.18	1.10	1.91	1.14	1.13	1.65	1.05	1.08

| Sample concentration | Irradiation time (min) | | | | | | | | | | | | | | |
| | 10 | | | 20 | | | 30 | | | 40 | | | 50 | | |
	Gr	T_f	E_f	Gr	T_f	E_f	Gr	T_f	E_f	Gr	T_f	E_f	Gr	T_f	E_f
EA															
2	0.63	1.03	1.04	0.82	1.05	1.08	1.06	1.09	1.10	1.14	1.12	1.14	1.18	1.14	1.17
5	1.50	1.15	1.26	1.52	1.17	1.27	1.94	1.23	1.45	2.07	1.25	1.48	1.55	1.18	1.33
10	1.79	1.22	1.40	1.96	1.25	1.59	2.16	1.27	1.62	13.48	1.49	1.82	2.08	1.24	1.61
15	2.46	1.29	1.65	2.99	1.33	1.74	3.09	1.38	1.78	5.62	1.64	1.91	3.15	1.41	1.79
20	1.38	1.17	1.21	2.35	1.28	1.63	2.52	1.30	1.67	1.77	1.16	1.37	1.48	1.09	1.24

| Sample concentration | Irradiation time (min) | | | | | | | | | | | |
| | 5 | | | 10 | | | 15 | | | 20 | | |
	Gr	T_f	E_f	Gr	T_f	E_f	Gr	T_f	E_f	Gr	T_f	E_f
HEA												
2	0.79	1.06	1.03	2.76	1.36	1.18	4.20	1.59	1.31	2.69	1.37	1.53
5	1.61	1.17	1.09	3.20	1.48	1.21	6.25	1.79	1.45	3.07	1.18	1.20
10	2.09	1.31	1.15	5.95	1.67	1.42	6.95	1.82	1.66	3.95	1.54	1.24
15	3.67	1.51	1.23	6.89	1.74	1.66	13.5	1.85	1.76	4.33	1.64	1.36
20	1.98	1.19	1.13	2.09	1.27	1.24	3.02	1.47	1.20	1.40	1.10	1.09

mer concentration. The TS values increased with time of irradiation and with monomer concentration and attained maxima. After the maxima, the TS values decreased, which may have been due to the degradation of grafted bonds as a result of excess radiation doses.[9] Among the formulations of the three monomers, the highest T_f was obtained by 15% HEA, which was followed by 30% MA. The highest E_b was obtained by MA, which was followed 15% EA. Tensile properties of the treated samples are shown in bars in Figure 4 against different monomers. Vinyl unsaturated monomers were used to graft onto the cellulose backbone to increase physicomechanical properties and thermal stability and to reduce moisture uptake. This reactivity is governed by various factors such as the number of double bonds, shape, size, and T_g. It allows monomers of small size to diffuse more readily into the cellulose backbone and to react with active sites, which enhances grafting yields.[16] The chemical properties of the grafted samples increased with T_g. A monomer promotes rapid free-radical-induced propagation reactions, leading to polymer network (crosslinked) polymer structures through grafting via their double bonds.[17] A mobilizer increases the radical–radical terminations and decreases the extent of scission reactions and oxidation.[18] When the mechanical properties, TS (T_f), and E_b (E_f) were plotted (Fig. 5) against T_g of the monomers, the results clearly demonstrated that the T_f and E_f of the grafted jute increased with T_g values of the respective monomers.

Characterization of surface topography

Both treated and treated jute surfaces were characterized by ESEM to study surface topography and mor-
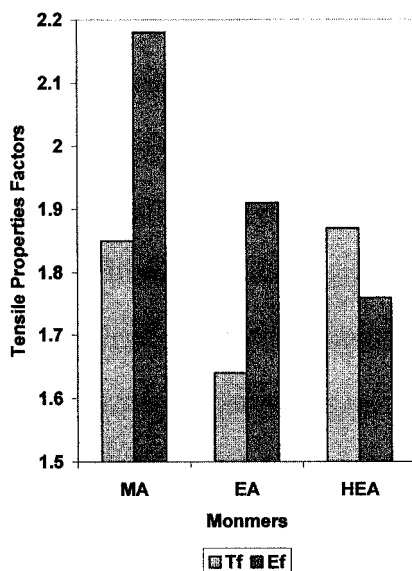

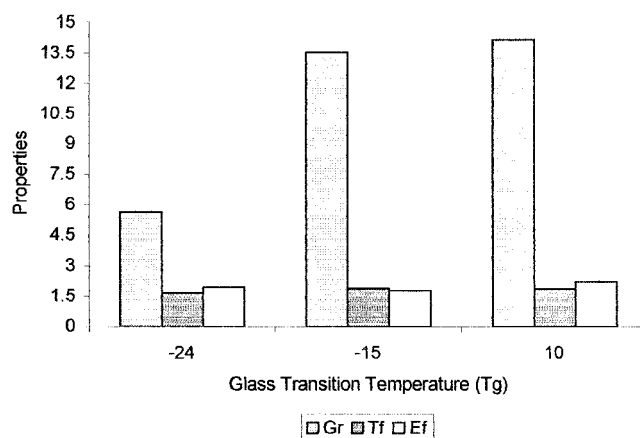**Figure 4** Tensile properties of the treated samples against different monomers.

Figure 5 Grafting values and tensile properties against T_g of the monomers.

phology. The ESEM pictures of untreated and treated jute yearn are shown in Figures 6(a) and 6(b,c,d), respectively. As shown in Figure 6(a), the surface of untreated fiber was smooth and showed its maticular nature. The fibrillate structure and porosity of the individual was related on the fiber surface. As shown in Figure 6(b), where the yarns were grafted, rough surface topography and morphology of the fiber surface were observed. A significant change in morphology and various etching was observed in grafted jute.

Characterization of grafted jute yearn by yearn FTIR

The chemical reaction behavior between monomers and cellulose jute was studied by FTIR. Untreated jute yearn was used a reference. In Figure 7, the IR spectra of grafted jute (grafted yarn) and untreated (virgin yarn) are shown for 4000–700 cm^{-1} and for 1800–700 cm^{-1}, respectively. The characteristic feature of the spectrum of jute is due to its lignin and hemicellulose components, which exist in the jute. With the MA treatment, the carbonyl ($=C=O$) band again appeared at 1740 cm^{-1} in the curve of grafted yarn due to the presence of an ester group in MA. A new sharp band was observed at 1539 cm^{-1}, which could be attributed to the C=C stretching of MA.[19] Another new peak at 1396 cm^{-1} was observed, corresponding to the CH$_3$ deformation of MA.[20] The reduction of OH groups and increase in $=C=O$ peak intensity in grafted jute were higher than those of untreated yarn. The absorption bands of the previous peaks were indicative of the existence of MA deposited on jute fiber, and MA might have reacted with the cellulose backbone of cellulose through the graft copolymerization reaction.

Characterization of grafted jute yearn by yarn DSC

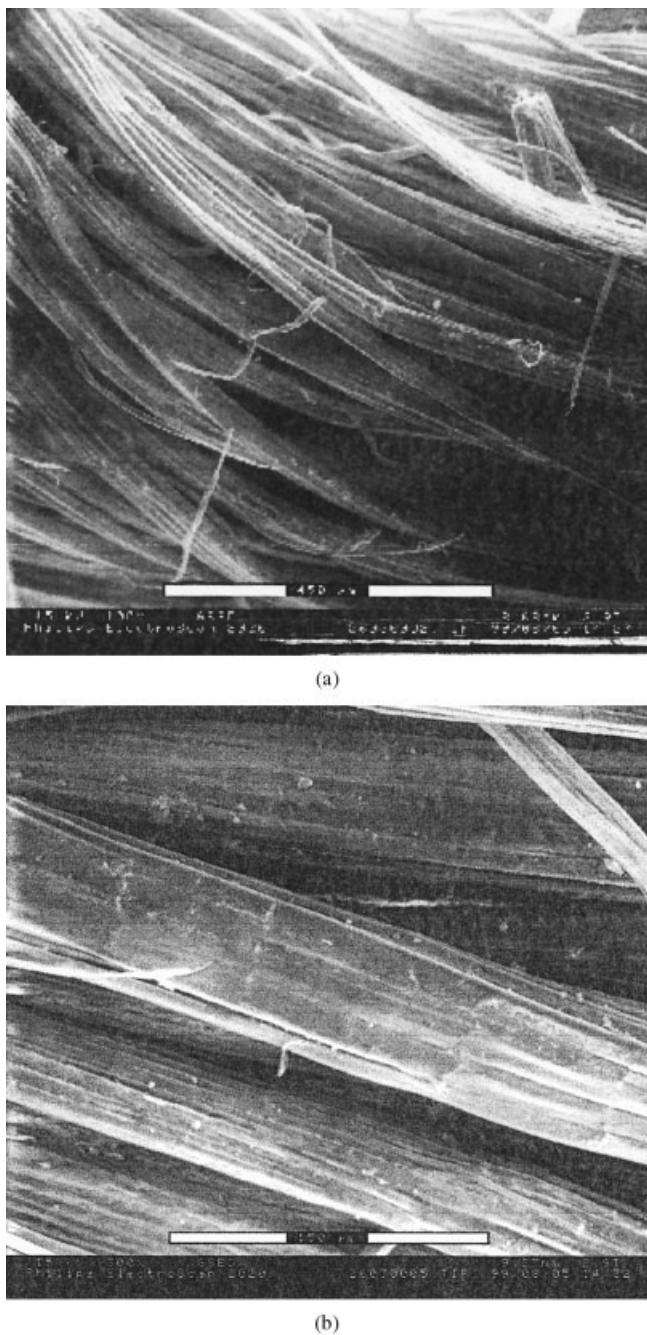DSC thermograms obtained from the untreated and grafted jute yarns exhibited both endothermic and

Figure 6 ESEM for jute yarns: (a) untreated and (b) treated.

Effect of U as an additive

U has previously been used as an additive in radiation grafting for the preparation of WPC[21] and JPC[9] and has been shown to increase the grafting yield and mechanical properties. U is an inclusion compound whose properties assist partitioning by complexing with monomer. This can lead to an increase in the monomer concentration at the grafting site and, thus, to enhanced reactivity at that site.[22] In the UV system, long irradiation time are necessary to achieve grafting, thus indicating that U acts as a poor reactive initiator in UV reactions. To study the effects of additives on
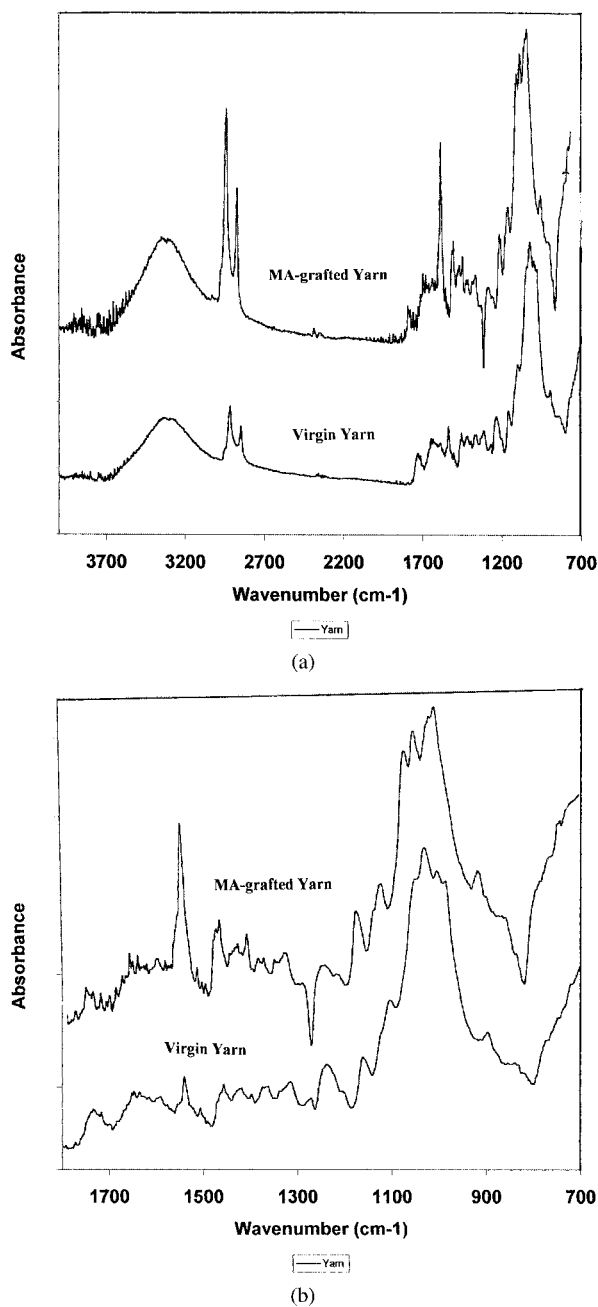

Figure 7 IR spectra of MA-grafted jute yarn.

exothermic transitions, as shown in Figure 8, where the peak temperature appeared differently with respect to the sample conditions. The exothermic transition (upward peak) or melting temperature for virgin yarn was 324°C, whereas that of the grafted yarn shifted to a higher temperature. The appearance of both endothermic and exothermic peaks could be related to the morphological changes that possibly occurred by the decomposition of hemicellulose and cellulose, respectively.
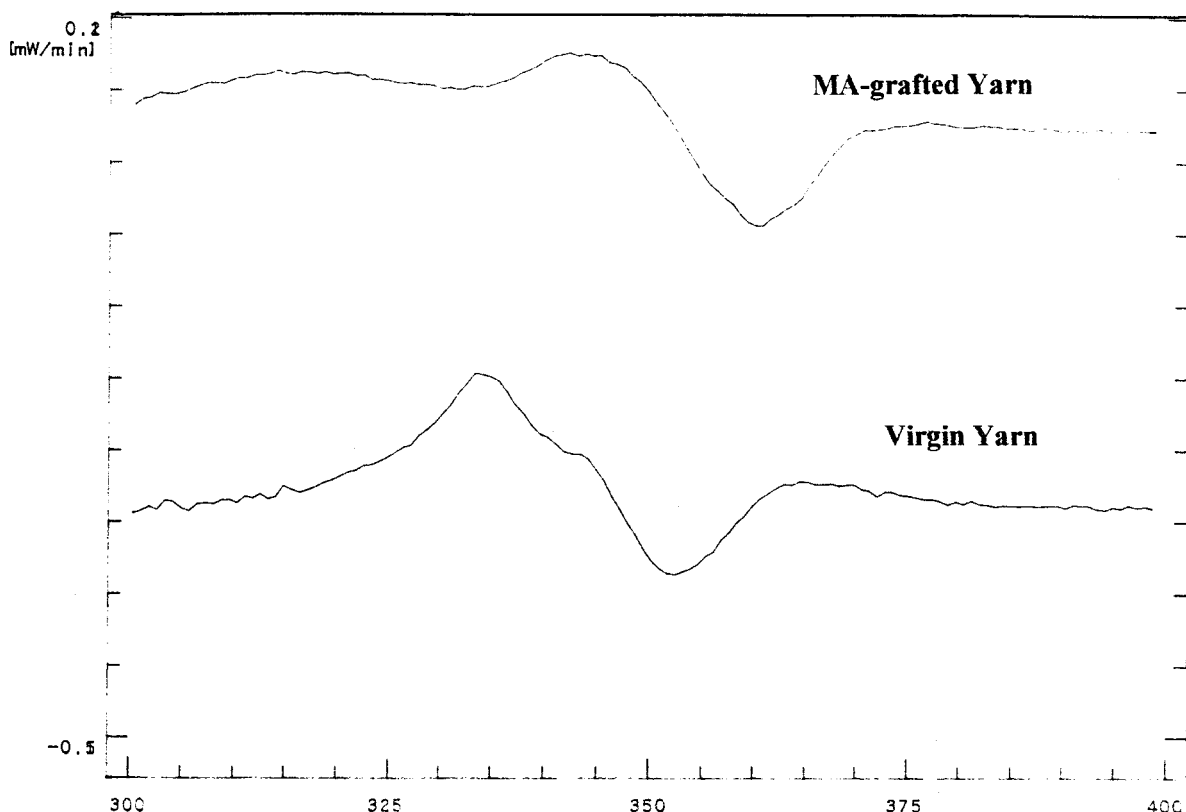
Figure 8 DSC for treated and untreated jute yarn.

this UV grafting process, a minute amount (1%) of additive such as U was incorporated into 30% MA, 15% EA, and 15% HEA solutions. The values of Gr, T_f, and E_f are shown in Figure 9. Incorporation of U into the MA + MeOH and HEA + MeOH systems substantially enhances the Gr values as well as tensile properties. Therefore, in these particular cases of UV radiation with MA and HEA, this additive did not enhance any properties of the treated jute yarns. However, for the EA + MeOH system, when U was used as an additive, T_f increased. This enhancement could have

been caused by the augmentation process rendered by the carboamide group ($=$N—CO—) present in U.

Water uptake

Water uptake by the treated and untreated samples was monitored at 25°C. The equilibrium water uptakes of the highest grafted samples of the three monomers are shown in Figure 10. Almost all the samples attained the maximum water uptake within the initial 5 min; then, the soaking rate decreased in the treated
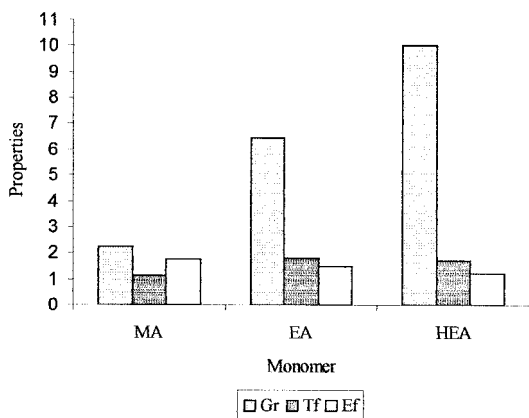

Figure 9 Effect of U on grafting values and tensile properties.
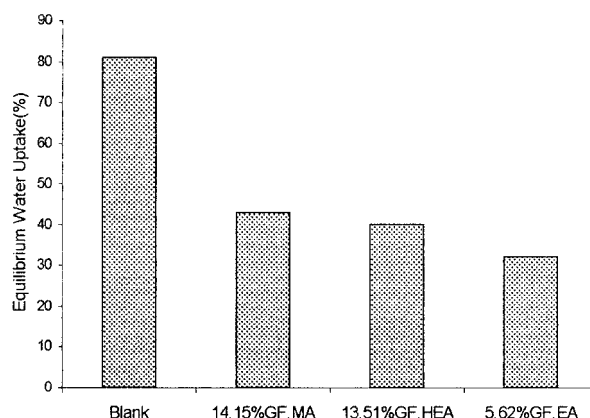

Figure 10 Equilibrium water uptake of the treated and untreated jute yarns.

samples, whereas the untreated samples still continued to soak very slowly in the water. The untreated sample gained water up to about 61%, whereas the treated samples gained about 40 to 46% depending on grafting values. From these results it was clear that water sorption capacity decreased with increasing grafting values for the treated jute yarns.

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