

Effect of Alkali and Ultraviolet (UV) Radiation Pretreatment on Physical and Mechanical Properties of 1,6-Hexanediol Diacrylate-Grafted Jute Yarn by UV Radiation

Mubarak A. Khan,¹ S. Shehrzade,² M. Masudul Hassan¹

¹Radiation and Polymer Chemistry Laboratory, Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission, P.O. Box 3787, Dhaka 1000, Bangladesh

²Department of Applied Chemistry and Chemical Technology University of Dhaka, Dhaka 1000, Bangladesh

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ABSTRACT: To improve the physicochemical properties of jute yarn, grafting with 1,6-hexanediol diacrylate (HDDA) monomer was performed by a UV radiation technique. A series of HDDA solutions of various concentrations in methanol were prepared. A small quantity of photoinitiator (Darocur-1664) was also added to HDDA solutions. To optimize the conditions for grafting, the effects of monomer concentration, soaking time, and radiation doses were studied by varying the number of soaking times along with variation of monomer concentrations and UV radiation intensities. The extent of polymer loading and the mechanical properties like tensile strength (TS), elongation at break (Eb), and tensile modulus of both treated and untreated jute were investigated. The highest tensile strength, polymer loading, and modulus were achieved with 5% HDDA concentration, 5 min soaking time, and the 4th pass of UV radiation. This

set of conditions was selected as optimum and produced enhanced tensile strength (67%), modulus (108%), and polymer loading (11%) over those of virgin fiber. To further improve the mechanical properties the jute yarns were pretreated with alkali (5% NaOH) solution and after that the alkali-treated yarn were treated under UV radiation of various intensities. The pretreated samples were grafted with optimized monomer concentration (5% HDDA). Increased properties of alkali + UV-pretreated and grafted samples such as polymer loading (12%), tensile strength (103%), elongation at break (46%), and modulus (114%) were achieved over those of virgin jute yarn. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 18–24, 2004

Key words: jute yarn; photocuring; UV radiation; mercerization; polymer loading

INTRODUCTION

Cellulose is the basic polymer used to meet needs for housing, clothing, and industry. Jute is a lignocellulosic fiber. Applications of natural polymers including jute materials receded at the advent of synthetic polymers, which are quite cheap and durable compared to natural polymer materials. However, the nonbiodegradability of synthetic polymers has led to a renewed interest in jute, which has the advantages of being both renewable by agro-efforts and environmentally friendly because of its biodegradability, and attempts to improve natural polymers both genetically and chemically are ongoing. Thus, natural polymers are treated with different materials in different modes to increase their strength, durability, and sustainability while retaining their inherent degradable character to maintain an environment free of pollution. Because natural fiber is the focus of increasing worldwide attention, a number of investigators have been actively engaged in improvements of the properties of cellulose,

cellulose derivatives, and lignocellulosic fibers. As a result, different products are already available, such as natural polymer-reinforced thermoplastics¹ into plastic composites,² cellulose-reinforced thermosetting products, and so forth. Jute is a natural polymer composed mainly of cellulose, hemicellulose, and lignin.

Jute fiber contains 82–85% of holocellulose of which 58–63% is α -cellulose. The latter is composed of 55–59% glucosan, 1.8–3.0% xylan, and 0.8–1.2% polyuronide.³ It also contains trace quantities of galactan, araban, mannan, and rhammosan. Jute is a stiff fiber, lustrous in appearance, and generally has a rough texture. Jute is more susceptible to alkali, particularly NaOH, because of its hemicellulosic constituents. The action of aqueous alkali solutions on jute is generally associated with a loss in weight, attributable mainly to some loss of its hemicellulose component, and it depends on temperature, the concentration of the alkali, and the duration of treatment.⁴

Mercerization is one of the oldest methods of treating textile fibers. Mercerization is not a fiber-purification process, but it induces desirable changes in yarn and fabric properties (e.g., mechanical properties, dyeing properties, and luster). The treatment involves

Correspondence to: M. Khan (makhan@bangla.net).

soaking the fibers in a dilute solution of sodium hydroxide. In the presence of less-concentrated sodium hydroxide (NaOH) solutions various ternary complexes can form between cellulose, sodium hydroxide, and water. In the complexes called soda celluloses (Na-cell) a certain number of hydrating water molecules of the sodium hydroxide hydrates are replaced by hydroxyl groups of cellulose. The formation of each type of Na-cell occurs at well-defined NaOH concentrations and temperatures.⁵

Cellulose-OH + NaOH →



Treatment with alkali increases grafting of the monomer as well as surface adhesive characteristics of the fiber by removing natural and artificial impurities, thus increasing tensile properties, elasticity, and dimensional stability.⁶ Grafting of vinyl monomer onto cellulose fiber by irradiation promises to be a potentially effective method to improve mechanical properties. When pure cellulose is irradiated with ultraviolet (UV) radiation, degradation readily occurs as a result of the direct absorption of the radiation. Intense irradiation with UV radiation results in a loss of tensile strength, a reduced degree of polymerization, and an increase in the number of carboxyl and carbonyl groups.⁷ Radiation is a very convenient method for graft initiation. Techniques involving UV are particularly attractive because UV sources are relatively cheap, flexible, and easy to install. Photoinitiation is also unique in that it allows a precise control of the duration and the rate at which initiating species are produced. UV curing technology offers the advantages of curing at ambient temperatures, faster processing, low energy consumption, greater reaction control, no emission of solvent (less pollution), improved monomer stability, high product output, reliability and safety, and cost effectiveness. However, a most important aspect of grafting with curing is that such a specific type of grafting process has both advantages and limitations.⁸ Thus, when curing of monomers onto naturally occurring macromolecules like cellulose materials, the presence of grafting during curing can lead to problems in recycling of finished product.⁹ The present investigation deals with the study of changes of physicochemical properties of alkali-treated, 1,6-hexanediol diacrylate (HDDA)-grafted, and UV-cured jute yarn. This study is therefore designed to limit polymer loading (grafting) within desired levels in the preparation of HDDA-grafted jute yarn by using UV radiation. The effect of mercerization on the grafting and mechanical properties was investigated.

EXPERIMENTAL

Materials

Jute yarn (nonbleached commercial grade Tossa Jute) was collected from the local market of Bangladesh. The difunctional monomer 1,6-hexanediol diacrylate (HDDA) and the swelling agent methanol (MeOH) were procured from Merck (Darmstadt, Germany). The free-radical initiator or the photoinitiator Darocur-1664 was also obtained from Merck.

Methods

The sample jute yarns were cut into small pieces (10–15 cm in length) and dried in an oven at 105°C for about 20 h to remove moisture and stored in a desiccator. A series of solutions (formulations) were prepared with different proportions (1–10%) of HDDA in methanol and 3% photoinitiator (Darocur-1664). The dried samples were kept immersed in each of the prepared solutions contained separately in small beakers for each of the samples and soaking time was maintained for 3, 5, 10, and 30 min for each of the required samples. The samples were then directly irradiated under a UV light of 2 kW power capacity (245–313 nm) of a minicure apparatus (Model Me-200 UV; IST Technik, Germany). The conveyor speed of the minicure was 4 m/min. The cured samples were washed in acetone for 5 min to remove the unreacted monomer from the sample surfaces. Finally, the samples were dried at 105°C for 2 h and then cooled in a desiccator. The irradiated samples after 24 h of radiation were subjected to various characterization processes. The percentage of polymer loading (PL) was determined on the basis of weight gained by the jute sample after the acetone wash treatment.

$$\text{PL (\%)} = \frac{W_t - W_0}{W_0} \times 100$$

where W_t and W_0 are the weight of the treated and untreated dry samples, respectively. Tensile properties (tensile strength, elongation at break, and modulus) of both treated and untreated samples were measured using a tensile strength testing machine (model 1011; Instron, Poole, UK). The machine was operated at a crosshead speed of 2 mm/min and a space gauge length of 30 mm.

Pretreatment of the samples by alkali and UV radiation

Virgin fibers were initially treated with 5% alkali for 1.5 h. The fibers of the alkali-treated samples were then smoothly washed with distilled water to a pH of 7, which was confirmed by use of litmus paper. Then

the alkali-treated samples were dried and their tensile strength was measured.

Some dry alkali-treated samples were treated with monomer and passed under two, four, six, and eight UV passes. The irradiated samples were washed with normal acetone after 24 h. The different weights of the samples before irradiation and after acetone wash determined the extent of polymer loading. The tensile properties of the treated samples were measured.

Other dry alkali-treated samples were irradiated with five, 10, 15, 30, and 50 UV passes and their tensile properties were measured again.

Again, dry alkali- and UV-pretreated (with five, 10, 15, 30, and 50 passes) samples were soaked in monomer and irradiated and washed with acetone in the same manner. Tensile properties of these samples were also determined.

RESULTS AND DISCUSSION

In the present investigation the physicochemical properties of jute yarns were improved by UV radiation through graft copolymerization using a single impregnating monomer (HDDA) and its solution in methanol (MeOH). The bulk monomer HDDA was mixed with MeOH to swell the cellulose backbone for better impregnation of HDDA solution. To obtain enhanced physicochemical properties the surfaces of jute yarns were pretreated with alkali and ionizing UV radiation and grafted with the same monomer. Most of the data presented in this report are average values of at least five samples, and the results obtained are within $\pm 3\%$.

Optimization of monomer concentration

The samples were soaked in different solutions containing different monomer concentrations (1, 2, 3, 5, and 10%) for 5 min to optimize a definite HDDA monomer for grafting of jute yarns. After soaking, these samples were cured under UV radiation at different intensities (2, 4, 6, and 8) expressed by the number of passes. After 24 h of radiation the samples were subjected to different characterization tests to find an optimum concentration of monomer: 5% HDDA demonstrated the best performance.¹⁰

Optimization of soaking time and radiation doses

To optimize the soaking time into the monomer solutions the washed and dried fibers were soaked in 5% HDDA for 3, 5, 10, and 30 min and then irradiated under UV radiation with different numbers of passes (two, four, six, and eight). To remove the unreacted monomer from the samples the yarns were washed with acetone after 24 h of irradiation polymer loading and tensile properties were investigated.

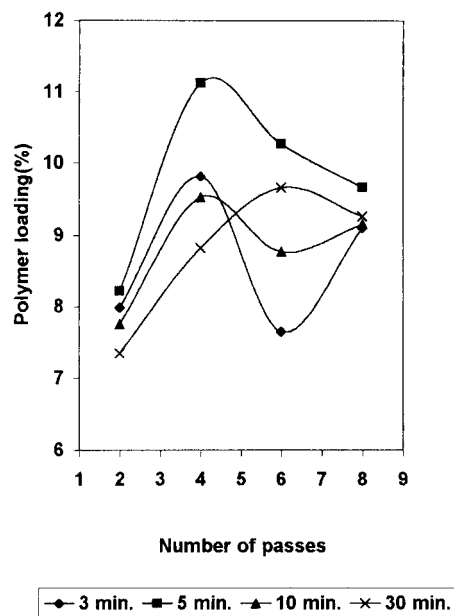


Figure 1 Polymer loading (PL) of treated jute yarn versus UV radiation intensities as a function of soaking time.

Polymer loading (PL)

The results are graphically represented in Figure 1, where PL values are plotted against UV intensity (number of passes) as a function of soaking time for 5% HDDA. It may be observed from the graph that PL increases with soaking time up to 5 min; above 5 min soaking time PL values decrease with increasing soaking time. The PL values increase with initial radiation doses, attain the maximum values, and then decrease as the radiation doses (number of passes) increase. The radiation-induced graft copolymerization reaction of vinyl monomers onto the cellulose backbone is effected by the diffusion of monomer into the fiber, the swelling of trunk polymer, and the Trommsdorff effect of solvent on graft polymer radicals.^{11,12} Swelling increases the cross-sectional area of the fiber at the same time the fiber surface becomes lustrous. As a result the monomer can easily diffuse in the fiber and react with cellulose at a low swelling time. At longer swelling times, the fiber becomes twisted, shrinks, and changes its outer fibrillar layers. The decrease in PL values after the attainment of the maximum PL values could be caused by the radiation degradation at higher UV doses, which was established in previous works by different detection techniques. However, the highest PL value was achieved at 5 min soaking time by the sample treated with 5% HDDA; after that the PL values decrease with increasing soaking time. The maximum PL values (11.3%) were attained with the fourth pass, except for 30-min soaking time, which yielded the maximum PL value at the sixth pass.

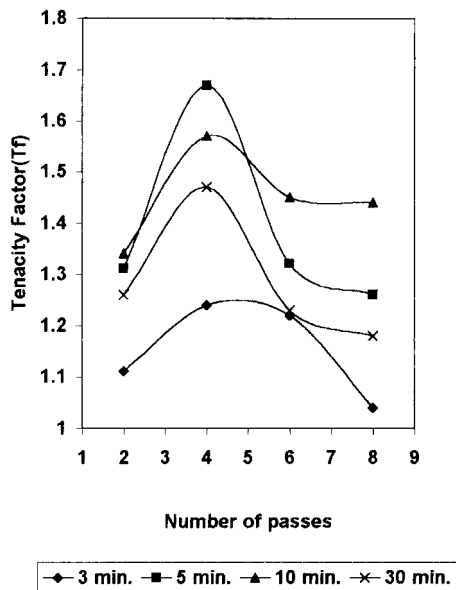


Figure 2 Tenacity strength factor (T_f) of treated jute yarn versus UV radiation intensities as a function of soaking time.

Tensile properties

The results are represented in Figure 2, where tensile strength factors (T_f) are plotted against the number of passes of UV radiation with respect to soaking time. Tensile strength in terms of tensile strength factor (T_f) shows that T_f increases with soaking time because increased swelling led to increased diffusion of monomer into the reaction sites and a greater amount of grafting; hence tensile strength (TS) values are increased. The highest T_f value (1.67) was imparted by the sample soaked for 5 min soaking time and four passes of radiation followed by 10 min soaking time and the same UV doses.

The elongation factor (E_f) is shown plotted against UV radiation intensities (number of passes) with respect to soaking time in Figure 3. The highest enhancement of elongation ($E_f = 1.2$) was obtained at 10 min soaking time and four passes of radiation.

Modulus factors are graphically represented in Figure 4, where M_f values are plotted against number of passes (UV radiation intensity). The highest modulus ($M_f = 2.08$) was observed with 5 min soaking time and at the fourth pass of radiation where tensile strength is also maximum. Modulus factors, like the T_f value, also increased with increasing UV doses up to four passes until it reached 5 min; above this soaking time the value decreased. It can thus be concluded from the above discussion that a soaking time of 5 min is optimum for the modification of the jute yarn surface and the optimized UV radiation dose is four passes under the UV lamp used in this study. After analyzing all the data, it was determined that 5% HDDA, 5 min soaking time, and four UV passes yield the maximum T_f , M_f ,

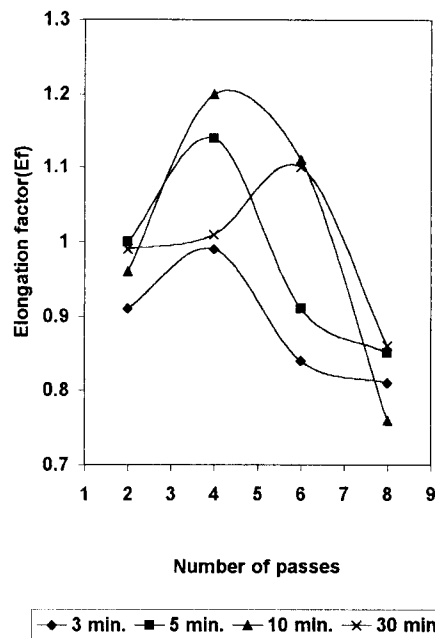


Figure 3 Elongation factor (E_f) of treated jute yarn versus UV radiation intensities as a function of soaking time.

and PL values. So, this set of conditions was thus established as the optimum.

Pretreatment of the samples with alkali and UV radiation

Tensile properties

Jute samples were chemically treated with 5% NaOH and their tensile properties were measured. These al-

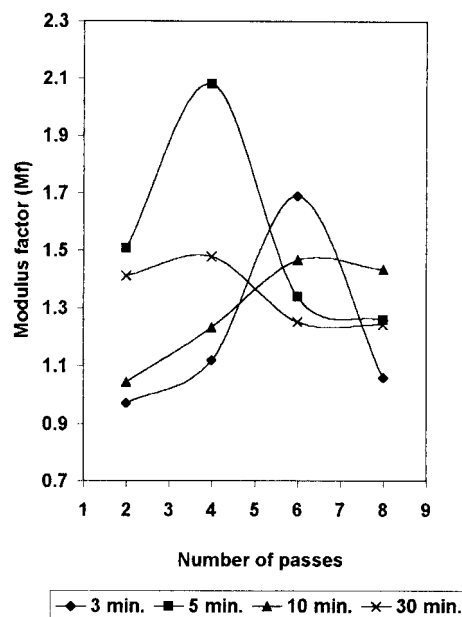


Figure 4 Modulus factor (M_f) of treated jute yarn versus UV radiation intensities as a function of soaking time.

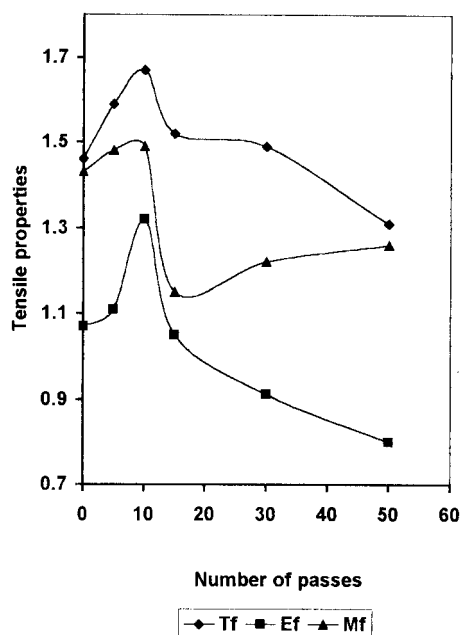


Figure 5 Tensile properties of alkali and UV pretreated jute yarn (without monomer soaking) versus different doses of UV radiation (5% HDDA).

kali-treated jute samples were pretreated with different numbers of UV passes (5, 10, 15, 30, and 50) and their tensile properties were measured. The results are shown in Figure 5, where tensile properties are plotted against the number of UV passes of pretreatment. When samples were alkali treated and these alkali-treated samples were irradiated with different numbers of UV passes, then *Ef*, *Tf*, and *Mf* values increased with preirradiation pass but after attaining the maxima these values decrease with increasing number of UV pretreatment passes. The *Tf* value of the only alkali-treated sample (0 pass) was 1.46 but the alkali + UV-pretreated samples showed higher tensile strength (1.67). Similarly, *Ef* and *Mf* values of these samples also exhibited properties enhanced over those of only alkali-treated samples. All the maximum values of *Tf*, *Mf*, and *Ef* values were obtained at the 10th pass.

Grafting of the alkali + UV-pretreated samples by optimized monomer concentration

After alkali treatment some jute samples were treated with monomer and then irradiated with two, four, six, and eight UV passes. Some alkali-treated samples were pretreated with different numbers of UV passes (5, 10, 15, 30, and 50) and then again treated with monomer. The preirradiated samples were always soaked in the optimized monomer concentration (5%) for the optimized soaking time (5 min).

Polymer loading (PL)

PL values are plotted against the number of UV passes in Figure 6. PL values increase sharply with increasing UV pretreatment passes. The maximum PL value (12) was achieved with the alkali + UV (15th pass) + monomer-treated sample. Alkali + UV + monomer-treated jute yarns show a slightly higher PL value than that of the alkali + monomer-treated jute sample (11.5). During alkali + UV + monomer treatment, PL values increased because more monomer may be introduced into the cellulose backbone as a result of mercerization and application of a UV radiation-induced modified surface. Mercerized fibers yielded higher PL values than those of unmercerized fibers. Alkali treatment increased the amorphous region as a result of dissolution and leaching out of fatty acids and some other lignin components from jute yarns. As a consequence the surface became rough, thus increasing monomer uptake as well as crosslinking.¹³

Tensile properties

Figure 7 shows that the alkali-treated sample when treated with UV does not show major improvement in tensile strength, elongation at break, and modulus. If the alkali + UV-pretreated samples are grafted with monomer, however, then the tensile strength and modulus increase substantially (Fig. 7). The reason is that the mercerization treatment improves the fiber surface adhesive characteristics by removing natural and artificial impurities, thereby producing a rough surface topography. It changes the form of the cellulose crystallites, increasing the amount of amorphous cellulose at the expense of crystalline cellulose. Mercerization breaks down the composite fiber bundle

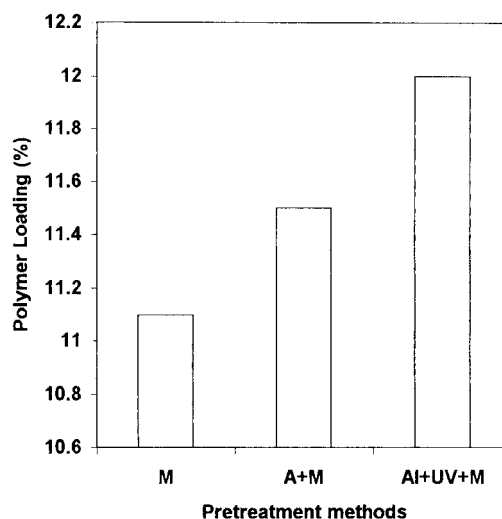


Figure 6 Tensile properties of alkali and UV pretreated and grafted jute yarn (with monomer soaking) versus different doses of UV radiation (5% HDDA).

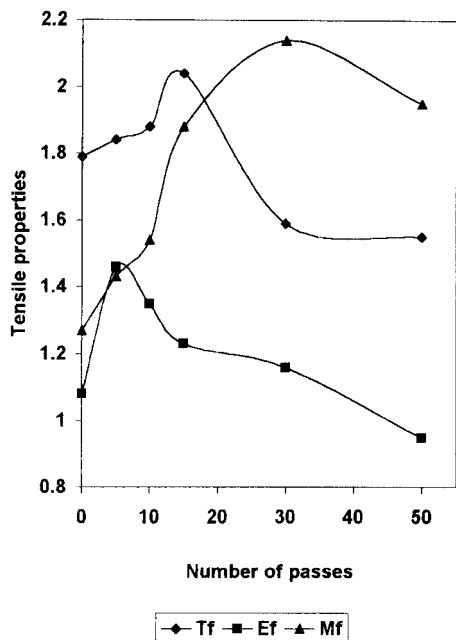


Figure 7 Comparison of tensile properties of different alkali and UV pretreatment methods.

into smaller fibers, increasing the effective surface area available for contact with a wet matrix.¹⁴ Thus alkali treatment improves the tensile properties.

After alkali + UV + monomer treatment, values of *Tf*, *Ef*, and *Mf* increased with the increasing number of passes but, after attaining maximum value, these values decreased. The tensile properties increased with the number of UV passes of pretreatment up to a certain limit, after which they decreased. Two oppos-

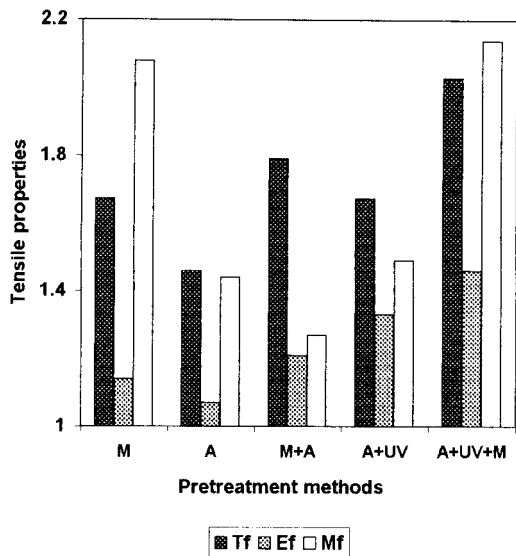


Figure 8 Tensile properties of alkali and UV pretreated and grafted jute yarn (with monomer soaking) versus different doses of UV radiation (5% HDDA).

ing phenomena, such as photocrosslinking and photodegradation, occur simultaneously under UV radiation. At lower doses, free radicals are stabilized by combination reactions and, as a result, photocrosslinking occurs. The higher the number of active sites generated on the polymeric substrate, the greater the grafting efficiency. At higher radiation, however, the main chain may be broken and the polymer may degrade into fragments. As a result tensile properties decrease with increasingly higher UV doses. Intense irradiation with UV radiation results in a loss of tensile strength, a reduced degree of polymerization, and an increase in the number of carboxyl and carbonyl groups.

The highest *Tf*, *Ef*, and *Mf* values were achieved with 15, 5, and 30 UV passes, respectively. From Figure 8, it may be observed that when alkali-treated samples are treated with monomer, they show better tensile properties (*Tf* and *Ef* values) than those of only alkali-treated or only grafted samples. The *Mf* value of only alkali-treated samples decreased when the alkali-treated samples were treated with monomer. These samples also attained a lower *Mf* value than that of only monomer-treated samples, although in the case of alkali + UV- and alkali +UV + monomer-treated samples, *Mf* values increased substantially. However, the highest *Tf*, *Ef*, and *Mf* values of the alkali + UV + monomer-treated sample are higher than those obtained from the alkali + monomer and alkali + UV-treated sample. Among all the treatments, the alkali +UV + monomer-treated sample exhibited the most enhanced tensile properties. Both mercerization and pretreatment with UV radiation modify the jute surface so that more monomer may penetrate into the cellulose backbone, and their overall effect may increase the tensile properties.

CONCLUSIONS

Jute yarns were grafted with 1,6-hexanediol diacrylate (HDDA) monomer and its solution in methanol (MeOH). Solutions containing different HDDA concentrations were prepared in methanol along with photoinitiator. The concentration of monomer, soaking time in the monomer solutions, and intensity of UV radiation were optimized with the extent of mechanical properties. Optimum conditions to carry out further treatment were established as 5% HDDA concentration, 5 min soaking time, and the 4th pass of UV radiation. Enhanced tensile strength (67%), elongation at break (14%), modulus (108%), and polymer loading (11%) were achieved after treating the jute yarns with HDDA + MeOH and curing under UV radiation. To further improve the tensile properties the surface of jute yarns was pretreated by alkali along with nonionizing UV radiation. Alkali and UV pretreatment promoted more enhancements in tensile properties than

did the simple alkali treatment. The best performance was achieved with alkali and UV-pretreated and HDDA-grafted jute samples, enhancing tensile strength (103%), elongation at break (46%), and modulus (114%).

This is significant and impressive information for diverse application of jute and its products. From earlier experiments, it was found that tensile properties could be increased by simple mercerization, although the present investigation reveals that if the mercerized samples are UV pretreated and grafted with monomer, the tensile properties increase significantly; however, the enhancement in polymer loading was not satisfactory. The main aim of this experiment was to upgrade properties by maintaining the inherent degradable nature of jute and at the same time by keeping polymer loading at a minimum level. Therefore, the amount of impregnating monomer can be reduced and the production cost can be minimized while substantially enhancing the tensile properties. Because mercerization is one of the effective methods of treating fibers and because radiation is a very convenient method for graft initiation, which can induce desirable changes in fibers, the sum of these two effects can produce an outstanding result. Techniques involving UV radiation are particularly attractive, given that UV sources are relatively cheap, flexible, and easy to install. Because natural fiber (jute) is more sensible and environmentally friendly, this treatment

may promote innovative and diverse applications of jute and jute products.

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