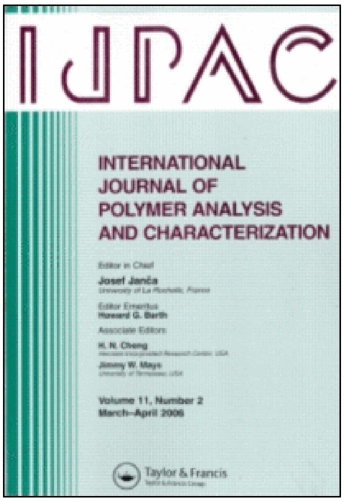

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Influence of Additives on the Performance of Photografted Jute Yarn with 3-(Trimethoxysilyl)propylmethacrylate

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Abstract: 3-(Trimethoxysilyl)propylmethacrylate (silane) solutions of different concentrations in methanol (MeOH) along with the photoinitiator Irgacure 907 were grafted onto jute yarn. Jute yarn grafted with 30% silane under UV radiation for 30 min showed the highest polymer loading (PL) value, 26.2%, with enhanced tensile strength (TS) (259%) and elongation-at-break (Eb) (337%) as compared to untreated yarn. The silanized and virgin jute yarns were characterized by X-ray photoelectron spectroscopy. To attain better performance of jute yarn, the additives (1%) urea, polyvinylpyrrolidone, urethane acrylate, and urethane diacrylate (UDAc) were used in 30% silane. Of the additives used, urea significantly influenced the PL (29%), TS (300%), and Eb (360%) values of the treated jute yarns. Water uptake and the degradation studies were also performed.

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Keywords: Natural fiber; Jute; Photocuring; UV radiation; Silane

INTRODUCTION

Global trends towards sustainable development have brought to light natural, renewable, biodegradable raw materials such as coir, flax, hemp, sisal, and jute as promising lignocellulosic fibers for different applications in textile and other industries. Among the fibers, jute contains one of the highest proportions of cellulose,[1] and cost considerations make jute an attractive fiber for the reinforcement of resin matrices. Disadvantages, however, are moisture uptake, quality variations, and thermal stability due to the presence of $-OH$ groups in β-bonded anhydroglucose units of jute cellulose.[2] Chemical modification may activate hydroxyl groups or introduce new moieties, that can effectively interlock with the matrix to improve the surface characteristics of the fiber.

Silane coupling agents are widely used to improve fiber matrix interaction. Polyalkoxysilanes exhibit excellent temperature, chemical, moisture, and environmental resistance, good electrical performance, and high ionic purity. These properties make them ideal for coating, grafting, and casting applications.[3] Hydrogen bonds as well as covalent bonding can be found in the flax silane system. Silanol, the hydrolyzed product of alkoxysilane, produces polyorganosiloxane through a condensation reaction.[4] It is reported that jute materials have improved mechanical performance and better degradation properties by using different silane coupling agents.[5,6] Incorporation of a small amount (1%) of additives containing carboamide ($>N-CO-$) groups in bulk monomer provides very significant enhancement of tensile strength with substantial increase of the composite polymer loading.[7,8] Some success has been achieved in grafting jute using different vinyl monomers under UV and gamma radiation.[9–12]

The present article deals with the grafting of jute yarn with the monomer 3-(trimethoxysilyl)propylmethacrylate in the swelling agent methanol under UV radiation and optimization of the monomer concentration and irradiation time. In addition, the effect of carboamide-containing additives on the performance of photographed jute yarn was studied.

EXPERIMENTAL

Materials

The monomer 3-(trimethoxysilyl)propylmethacrylate (silane) was procured from Fluka (Switzerland). Methanol (MeOH) was used as a swelling agent (Merck, Germany). The additives urea (U) and polyvinylpyrrolidone (PNVP) were obtained from Aldrich (Germany), and urethane acrylate M 1200 (UAc) and urethane diacrylate M 1100 (UDAc) were procured from Radcure (Belgium). Irgacure 907, [2-methyl-1-(4-methylthiophenyl)-2-morpholinopropanon-1] from Ciba-Geigy (Switzerland) was used as the photoinitiator. The substrate jute yarn was procured from Islam Jute Mills (Bangladesh).

Methods

Surface Treatment

A series of solutions were prepared at different silane concentrations (5–50 wt%) in methanol along with 2% (w/v) photoinitiator in different Pyrex test tubes, each tube containing a total of 20 mL solution. Jute yarns (20 cm long) were dried at 105°C for 3 h to remove moisture and stored in a desiccator. The dried yarns were immersed in test tubes having monomer and methanol solution at different proportions of monomer for 30 min. These tubes were placed in a rotary rack, which moved around a global UV lamp of 100 W (300–400 nm). During irradiation, the test tubes spanned their own axes while rotating around the lamp, which was hung in the middle, to ensure equal radiation to all samples. The irradiation period varied from 15 to 300 min. After the desired irradiation the jute yarns were withdrawn and washed with distilled water for 60 min, then dried at 105°C for 3 h. Polymer loading was determined on the basis of weight gained by the jute sample after the entire treatment process. After optimization of the bulk monomer (silane) concentration and irradiation time, five different formulations were prepared at a fixed amount of silane (30%), different additive (1%), and photoinitiator (2%) in methanol and subjected to grafting.

Mechanical Tests

Tensile strength (TS) and elongation-at-break (Eb) of the jute yarn samples were directly measured with a Universal Testing machine (Instron, model 1011, UK) at a cross head speed of 2 mm/min and gauge length of 30 mm. The change in tensile properties was expressed by tensile strength factor (T_f) and elongation at break factor (E_f).

Water Uptake

The water uptake of treated and untreated samples was monitored in a static water bath, at 25°C, in which samples were completely immersed.

Weights of the samples were recorded after different contact times and samples were carefully wiped to remove surface water before weighing.

X-Ray Photoelectron Spectroscopy (XPS)

The XPS spectra of the untreated (VJY) and grafted samples (SJY) were recorded with a Physical Electronics instrument (PHI 5400 ESCA). All spectral data were collected using a Mg anode operated at a power of 300 W with an analyzer pass energy of 33 eV. Changes in the surface-treated samples were elucidated by curve fitting the carbon 1*s* (C_{1s}) and oxygen 1*s* (O_{1s}). The spectra were fitted with a Lorentzian-Gaussian mix Voigt profile function using a nonlinear least-squares curve-fitting program.

Simulated Weathering Test

The grafted and virgin samples were treated by using a simulated weathering tester from Q-Panel Co. (USA; model Q.U.V.). The weathering test was performed in alternating cycles of sunshine over 4 h (65° ± 2°C) and dew and condensation for 2 h (45° ± 2°C). This treatment was carried out for a period of about 600 h.

Soil Degradation Study

Cellulose degrades when buried in soil having at least 25% moisture. To test this property, the grafted sample and untreated samples were weighed individually and buried in soil for 72 days. After this period, samples were withdrawn carefully, washed with distilled water, dried at 105°C for 20 min, and kept at room for 24 h, then weighed to determine weight loss.

RESULTS AND DISCUSSION

Optimization of Monomer Concentration

Polymer loading (PL) of the silane-treated jute yarns was determined at different monomer concentrations, that were UV irradiated. The PL values tabulated in Table I(a), show that the PL values initially increase quite sharply with irradiation time, after which they decrease with further increase of irradiation time and monomer concentration. The highest PL value (32%) was obtained at 120 min and 50% silane concentration. At low silane concentration, the PL value is less because the vinyl monomer promotes rapid free radical propagation with help from the photoinitiator, leading to a network polymer structure through graft polymerization via

Table I.

	Monomer concentration (%)				
Irradiation time (min)	5	10	20	30	50
(a) Polymer loading (PL) of treated jute yarns					
15	7.67	7.81	8.48	9.84	8.96
30	8.86	10.06	11.56	26.21	14.32
60	9.13	17.89	13.98	23.97	16.52
120	9.23	11.63	18.65	17.46	31.92
180	10.23	9.49	12.5	13.49	19.87
300	8.52	8.73	11.61	7.54	12.45
(b) Tensile factor (T_f) of treated jute yarns					
15	1.02	1.46	1.28	1.56	1.29
30	1.24	1.67	1.32	2.59	1.39
60	1.71	1.98	1.74	2.11	1.83
120	1.87	1.82	1.58	1.91	1.91
180	1.52	1.71	1.48	1.61	1.61
300	1.45	1.3	1.39	1.42	1.41
(c) Elongation factor (E_f) of treated jute yarns					
15	1.05	1.22	1.14	1.97	1.86
30	1.66	1.88	2.61	3.37	2.26
60	1.83	2.42	2.36	2.93	2.83
120	2.27	2.79	2.21	2.27	2.21
180	1.99	2.63	1.81	1.71	1.91
300	1.87	1.85	1.61	1.48	1.64

their double bonds.[13] As the silane concentration increases, the amount of residual unsaturation also increases with the consequence of faster rate of formation of a three-dimensional network structure causing restricted

Table II. Atomic concentration of elements of untreated jute (VJY) and silane-grafted jute (SJY)

	Concentrations (%)	
Elements	VJY	SJY
C_{1S}	55.04	36.82
O_{1S}	39.38	50.68
Ca_{2p}	0.87	1.37
N_{1S}	4.71	2.02
Si_{2p}	None	9.11

mobility. The decrease in PL values after the attainment of the maximum PL values could be caused by radiation degradation at higher UV doses.[14] The decrease in PL values at higher monomer concentration could be associated with the fact that the homopolymerization reaction between monomer and monomer radicals is more dominant than that between the monomer and jute cellulose reaction.

Tensile Properties

The tensile factor (T_f) is the ratio of the tensile strength of the treated jute sample (TS_t) to that of the untreated sample (TS_o). Similarly, the elongation factor (E_f) is the ratio of the elongation-at-break of the treated jute sample (Eb_t) to that of the untreated virgin sample (Eb_o). The results of T_f values of silane-treated samples are given in Table I(b). The tensile strength increases with irradiation time up to 30 min and then decreases as the irradiation time is increased. The highest tensile factor (2.6) was

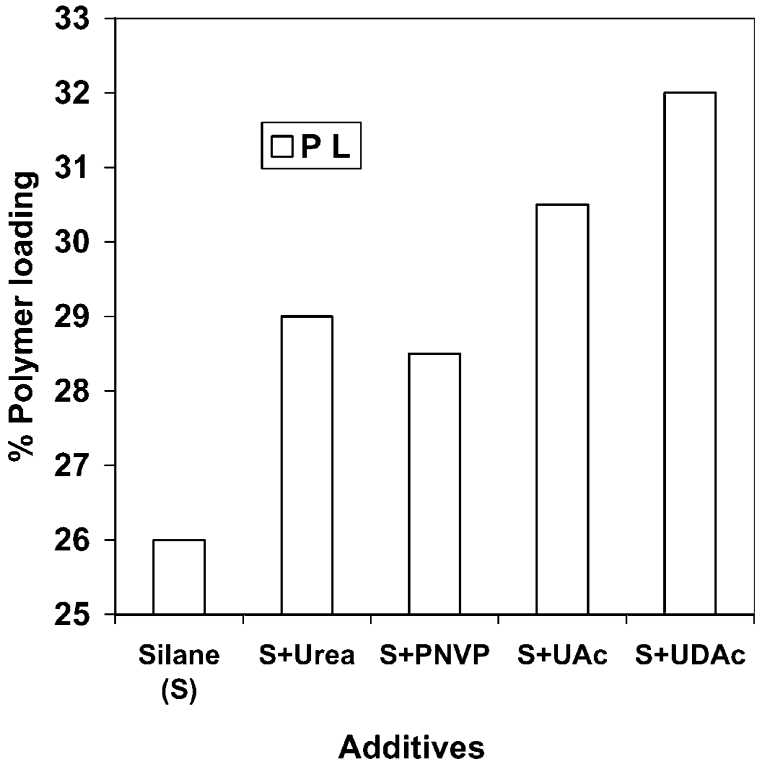

Figure 1. Effect of additives on polymer loading (PL).

obtained at 30 min irradiation and 30% silane concentration. The highest T_f value was obtained for the samples with the PL value of 26.2%, but for the highest PL value (32%), the Tf value was 1.9. The decrease of the T_f value with PL increase may be due to the formation of excess cross-linked polysiloxane, which forms a brittle polymer product. The enhancement in elongation-at-break of the silane-treated jute yarns, in Table I(c), shows that the highest elongation factor (3.4) is attained by the sample treated with 30% silane concentration at 30 min irradiation.

It appears that the highest T_f and E_f values are attained by the silane-grafted sample (SJY) at 30 min irradiation with 30% silane concentration, considered to be an optimized system. Henceforward, all subsequent experiments were carried out with this sample.

Evaluation By XPS

X-ray photoelectron spectra for the untreated (VJY) and silanized jute fibers (SJY) show two distinct O_{1S} and C_{1S} peaks at 533 and 285 eV,

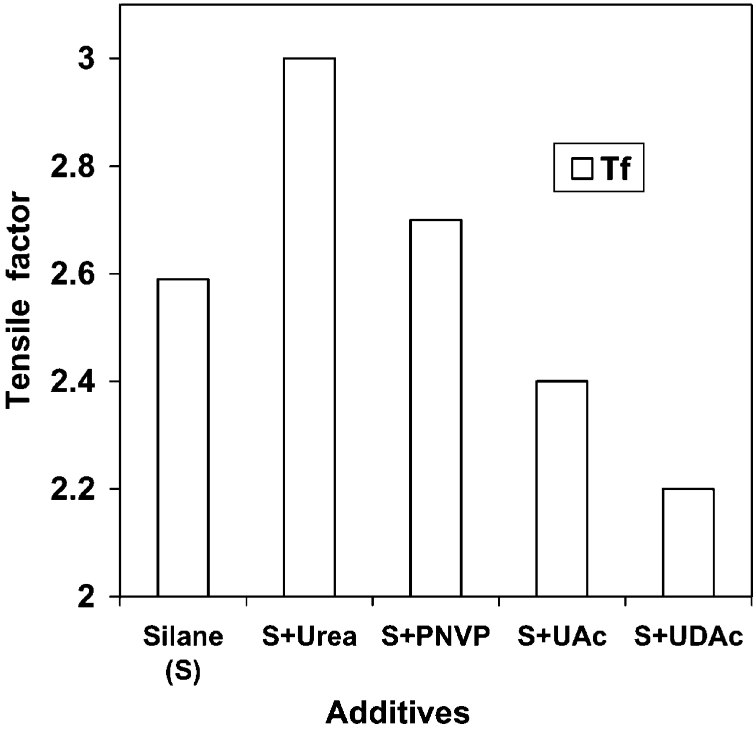

Figure 2. Effect of additives on tensile factor (T_f) of an optimized grafted sample.

respectively. All the silanized jute fibers show characteristic emission peaks at energies ranging from 150 to 155 eV for 2*s* electron of Si (Si_{2S}) and 99 to 140 eV for 2*p* electron of Si (Si_{2P}).[15,16] The atomic concentration of elements in VJY and SJY are presented in Table II, which shows the presence of Si in SJY.

Effect of Additives

To study the effect of additives on the polymer loading (PL), tensile strength, and elongation-at-break values of the jute yarn, a minute amount of additive (1%) was incorporated in the optimized formulations (30% silane in methanol) at 30 min UV irradiation. The PL values are graphically represented in Figure 1. PL increases in the presence of additive in the order UDAc > UAc > U > PNVP > silane. UDAc imparts the highest PL (32%) values among these additives, because it

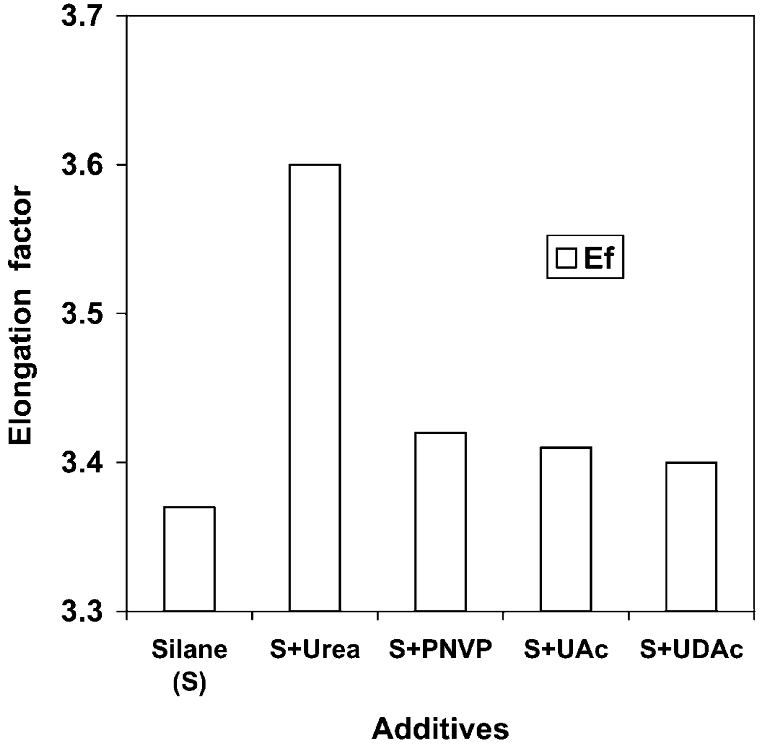

Figure 3. Effect of additives on elongation factor (E_f) of an optimized grafted sample.

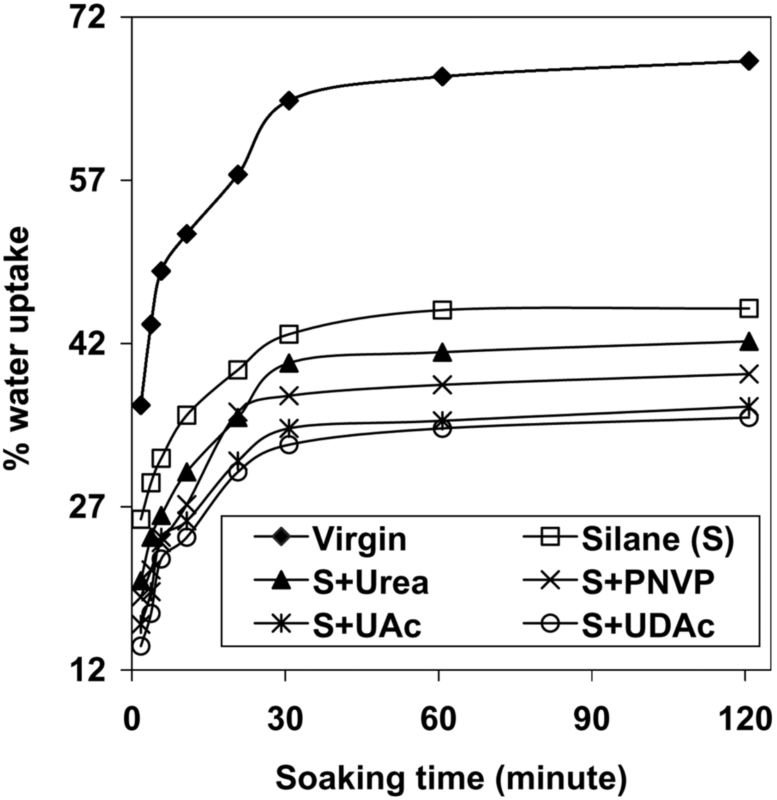

Figure 4. Water uptake of the virgin and grafted samples with and without additives.

has difunctional acrylate groups that can form cross-links with cellulose.[17] Similarly, the second PL highest value (30.5%) was achieved by UAc due to the presence of one effective site at on the acrylate group for reaction with cellulose. The molecular structures of PNVP and urea are different but both have a carboamide (>N—CO–) group, which is capable of augmenting grafting of bulk monomer with the substrate.[8] Urea has lower MW than PNVP and thus can more rapidly diffuse into the cellulose matrix. Thus, urea achieved more grafting than PNVP. Urea as an additive has been used in radiation grafting of wood[8] and jute[11] plastic composites and has been shown to increase grafting yield and mechanical properties.

The change of T_f in the presence of additives shows the following trend: U > PNVP > UDAc > UAc > silane (Figure 2). Urea and PNVP possess >C=O groups adjacent to a nitrogen atom having a long pair of

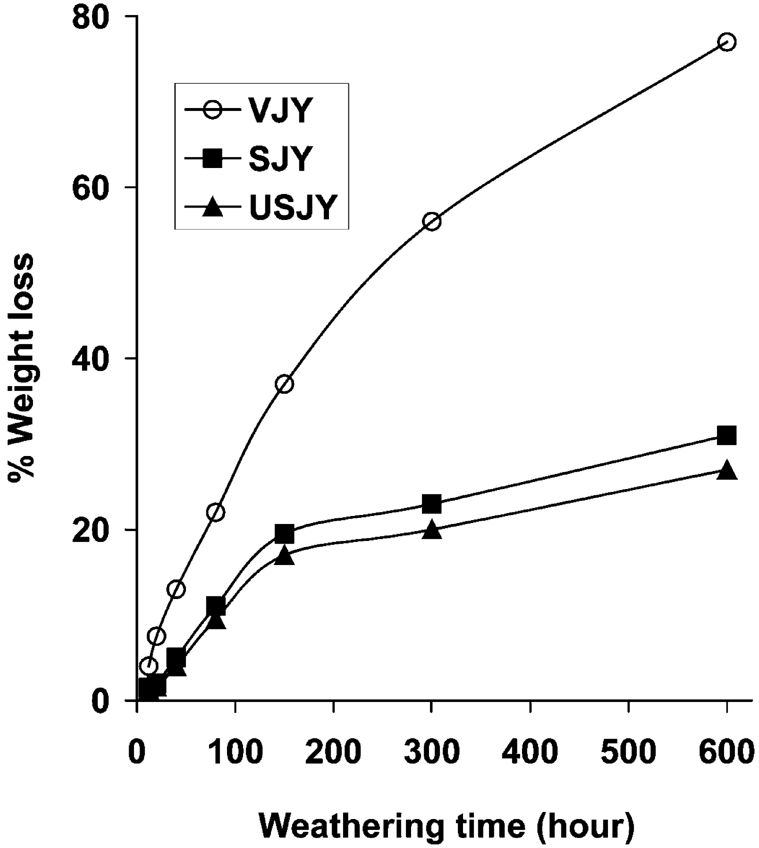

Figure 5. Weight loss of the virgin (VJY) and grafted samples (SJY and USJY) from weathering testing.

electrons, which may help bridge the monomer and cellulose. Oxygen in >C=O is more electronegative, thus promoting H-bonding with the monomer and cellulose backbone.[18] Hence, urea is an inclusion compound complexing with silane monomer, leading to an increase in the monomer concentration at a grafting site and enhancing reactivity at that site.[19] Thus, the enhancement of tensile strength factor (3.0) as well as the elongation factor could be caused by the augmentation process of the carbamide group (>N−CO−) present in urea and PNVP. However, in the case of UAc and UDAc, the lower T_f values may be caused by the brittle character possessed by the yarns at high grafting.

The elongation factors of treated jute yarns in the presence and absence of additives are shown in Figure 3. The highest E_f (3.6) was achieved with urea (USJY) and slightly increased for the other yarns,

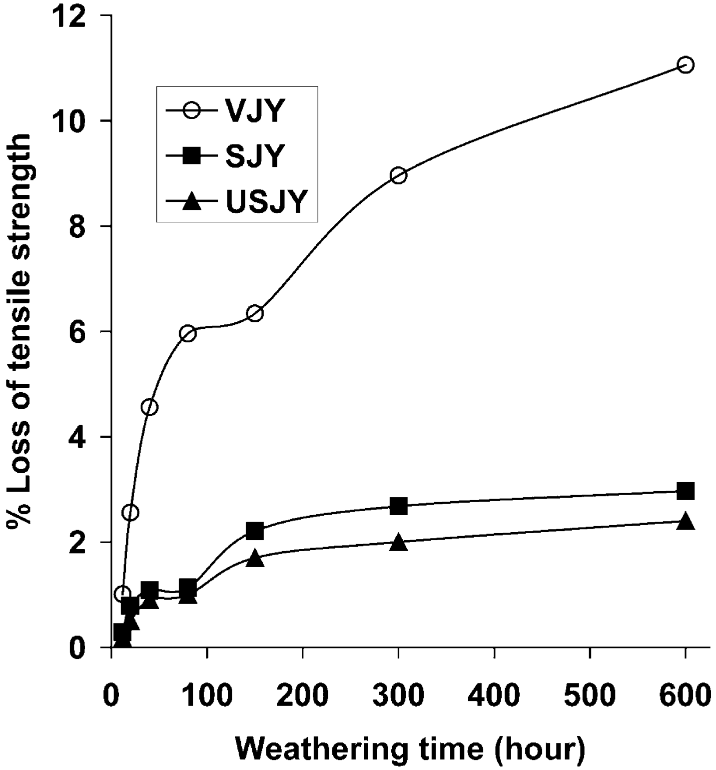

Figure 6. Loss of tensile strength of the virgin (VJY) and grafted samples (SJY and USJY) from weathering testing.

indicating that they are stretchable even at high grafting.[9] Thus, urea is a unique additive that provides higher stretchability/elongation and tensile strength of grafted jute yarn.

Water Uptake

Virgin and grafted jute yarns were immersed in water contained in a static bath at 25°C for about 120 min, and the amount water of taken up was periodically monitored. The results are shown in Figure 4, in which water uptake is plotted against soaking time. Almost all the samples attained the maximum water uptake within the initial 30 min. As expected, the untreated yarn absorbs the highest amount of water (67%) as compared to the treated yarns (35–45%), depending on grafting values. Lower uptake of water by the sample treated with urea suggests that a denser

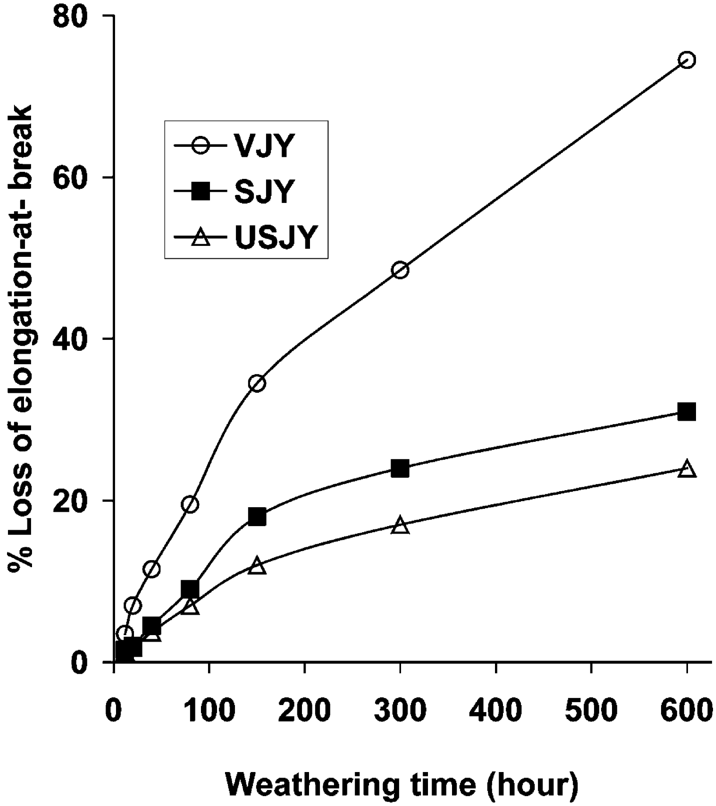

Figure 7. Loss of elongation-at-break of the virgin (VJY) and grafted samples (SJY and USJY) from weathering testing.

integrated network structure is formed,[20] which reduces the hydrophilic nature of the grafted jute yarn.

Simulated Weathering Testing

Virgin jute yarn (VJY), silane-grafted jute yarn (SJY), and additive urea-treated silane-grafted jute yarn (USJY) were subjected to simulated weathering testing with alternating cycles of sunshine (4 h) and condensation (2 h), over a period of about 600 h. The weight loss and the loss of TS and Eb were determined periodically, as shown in Figures 5–7 respectively. The initial rate of losses due to weathering follows more or less the same trend for all the cases. The higher TS loss of VJY is about 12% at 600 h, with a minimum value of 2.4% for USJY. Similarly, the

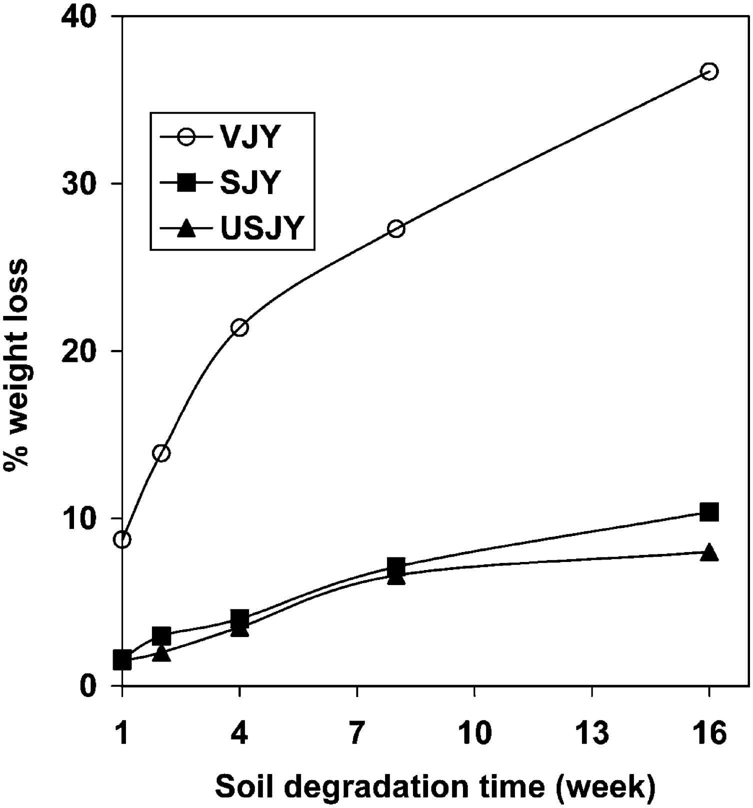

Figure 8. Weight loss of the virgin (VJY) and grafted samples (SJY and USJY) due to soil degradation.

higher Eb loss is 74% for VJY, with a minimum value of Eb loss of 24% for USJY.

Soil Degradation

Samples VJY, SJY, and USJY were buried in soil (25% water) for a period of 16 weeks in order to study the effect of environmental conditions on the degradability of the sample. The weight loss and the loss of TS and Eb were periodically measured and the results are represented in Figures 8–10 respectively. The initial rate (up to 21 days) of change due to weathering is more or less the same for all properties tested. The weight loss of the sample treated with urea was minimal (8%) as compared to the silanized sample (10.4%). The maximum degradation rate of the

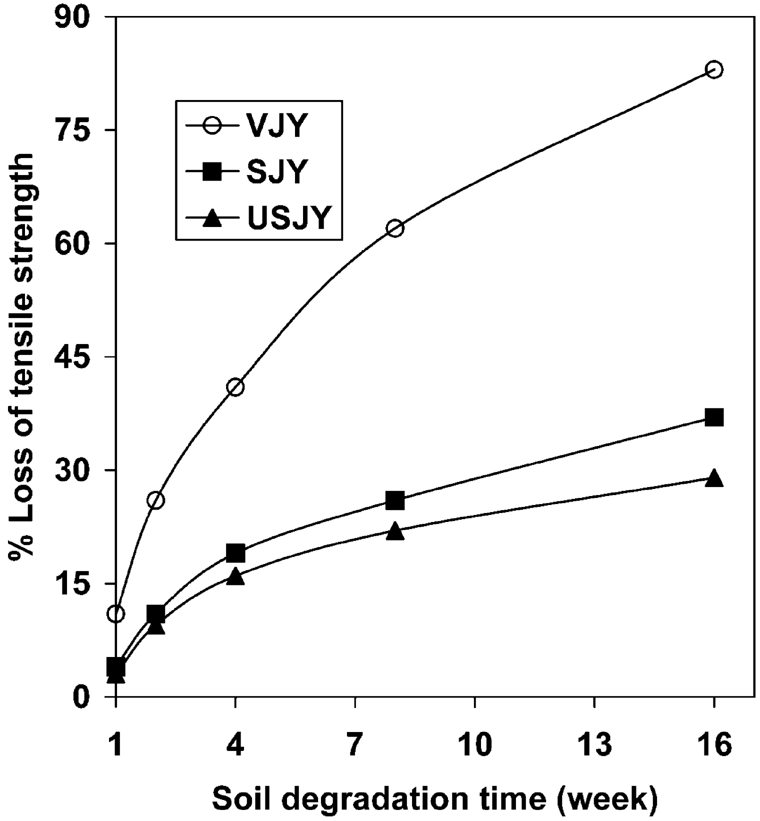

Figure 9. Loss of tensile strength of the virgin (VJY) and grafted samples (SJY and USJY) due to soil degradation.

untreated sample reached more than 36% weight loss within 16 weeks. The loss of tensile strength (29%) and elongation-at-break (35%) due to soil degradation were minimal for the sample treated urea after 16 weeks, which may be due to the presence of urea in the jute fiber.[6]

CONCLUSION

Improved mechanical and degradative performance of jute yarn, treated with different concentrations of silane in methanol with UV radiation, was attained at 30 min irradiation with 30% silane. This sample had a tensile strength of 2.59% and elongation-at-break of 3.37%. For further improvement, the urea-treated silanated sample (USJY) performed better in terms of enhanced tensile properties. Incorporation of additives with

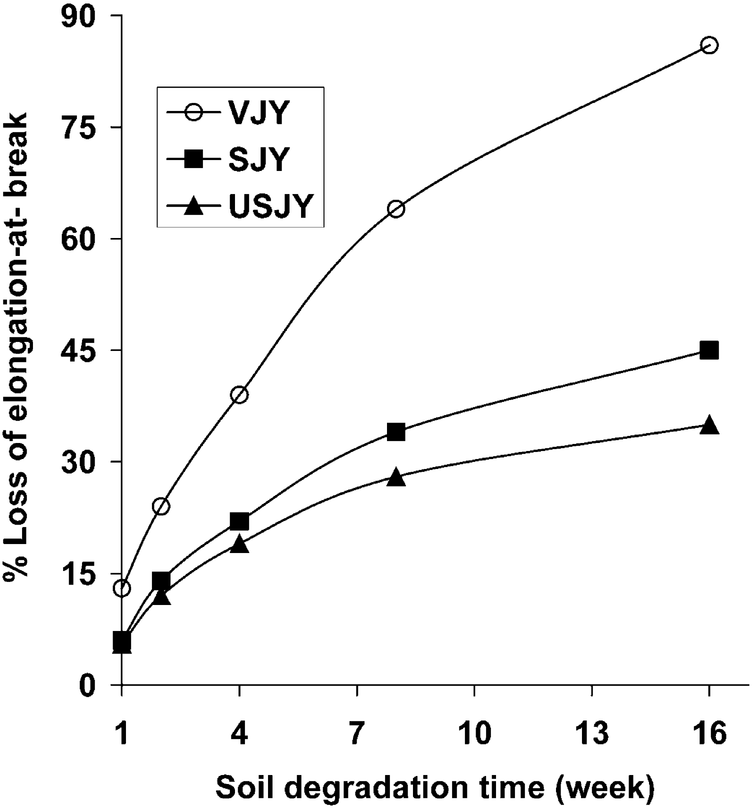

Figure 10. Loss of elongation-at-break of the virgin (VJY) and grafted samples (SJY and USJY) due to soil degradation.

silane treatment reduced the water absorption capacity, in which the lowest water uptake (35%) was achieved by USJY. USJY showed the best weathering durability over the other treated samples. Soil degradation studies demonstrated that the treated samples decomposed. This treatment may tend to suggest diverse applications of jute yarns.

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