Characterization of an Alkali-Treated Grass Fiber by Thermogravimetric and X-Ray Crystallographic Analysis

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ABSTRACT: The thermal behavior of grass fiber was characterized by means of thermogravimetric analysis and differential scanning calorimetry analysis. The results proved that the removal of water-soluble matter improved the thermal behavior of grass fiber over that of unleached fiber, and this was further enhanced by an alkali treatment of the grass fiber. The isothermal weight loss of the grass-fiber specimens was analyzed at 100, 200, and 300°C for different time periods. Accelerated aging of the grass-fiber samples was carried out to determine the effect of aging on the tensile strength. Partially delignified grass fiber showed maximum thermal stability. X-ray diffraction analysis was also performed to verify the composition and to correlate the change in the tensile strength due to the water leaching and alkali treatment. The processing of grass fiber with NaOH and NaClO$_2$ reduced the amorphous fraction in the fiber sample. This may have been a result of the loss of the amorphous noncellulosic components of the fibers and the degradation of the unordered regions of the grass fiber. However, mercerization of the grass fiber revealed an increase in the amorphous fraction after a certain time exposure, confirming the decrease in the crystallinity. The morphology of the water-leached and alkali-treated grass fiber was studied with scanning electron microscopy © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2008–2015, 2008

Key words: differential scanning calorimetry (DSC); fibers; thermogravimetric analysis (TGA)

INTRODUCTION

The properties of lignocellulosic materials are affected when they are exposed to the environment because of moisture sorption, biological degradation, ultraviolet and thermal degradation. The strength of cellulosic polymers undergoes degradation through oxidation, hydrolysis, and dehydration reactions. Lignocellulosics on outdoor exposure undergo photochemical (ultraviolet) degradation due to degradation of lignin with a characteristic color change.[1] On the heating of the lignocellulosic materials, the cell-wall polymers undergo pyrolysis reactions and produce volatile and flammable gases. The hemicellulose and cellulose polymers are degraded by heat earlier than lignin.[1] The lignin forms char, and the charred layer helps to insulate it from further thermal degradation. Works on the thermal analysis of wood, cellulose, hemicellulose, lignin, and various other lignocellulosic materials have been reviewed for investigations in different periods.[2] Ramiah[3] reported the thermal degradation of samples of cellulose, hemicellulose, and lignin, using the techniques of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) between room temperature and 600°C. The thermal behavior of different cellulosic fabrics was investigated in air and nitrogen by thermogravimetry (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA). Kinetic parameters based on weight loss for the initial and major stages of thermal degradation were determined.[4] The effects of the crystallinity, orientation, and degree of polymerization on the pyrolysis of natural and manmade celluloses were investigated by Basch and Lewin[5,6] *in vacuo* and in air using DSC and TG. Vaporization of bound water associated with cellulose fibers of natural and regenerated cellulose was investigated with DSC under both dynamic and static conditions.[7] Thermal analytical techniques and their applications in the field of fibrous cellulose have been extensively reviewed.[8–11] The thermal behavior of lignins from black liquor waste from the pulping of bagasse and cotton stalks has been investigated.[12] In this work, degradation characteristics of lignin were studied with TGA, DTA, and DTG between 20 and 1000°C.

EXPERIMENTAL

Materials

The fully grown and mature sun-dried grass stick was yellowish with a light greenish tint, and its spe-

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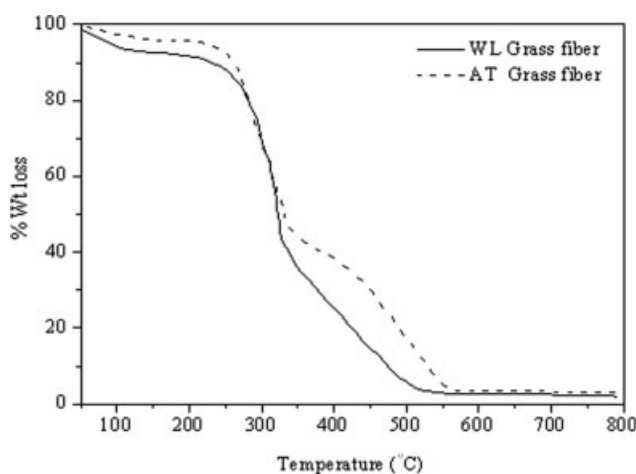
Figure 1 TGA of water-leached (WL) and alkali-treated (AT) grass fiber in air.

cific gravity was 0.64. The major constituents of the grass fiber were lignin (40%), cellulose (15%), hemicellulose (21%), water-soluble matter (22%), and ash (2%).[13] Sodium hydroxide (AR Grade; E. Merck, Mumbai, India), sodium chlorite (S.D. Fine Chemical, Bangalore, India), and sodium bisulfite (S.D. Fine Chemical) were used without further purification.

Methods

Water leaching of the grass fiber

To remove the water-soluble matter from the grass fiber, the samples were kept immersed in distilled water for 24 h at 25°C. The grass-fiber sample to water ratio was 1 : 300 (w/w). During 24 h of immersion, the water was renewed every 8 h to maintain a concentration gradient of soluble matter between the sample and water.

Alkali treatment of the grass fiber

The grass-fiber samples were treated with aqueous sodium hydroxide solutions of various concentrations for different time periods at room temperature (25°C) to assess the influence of alkali on the strength and durability of the grass fiber.

Delignification of the grass fiber

The delignification of the grass fiber was carried out by the treatment of the sample with boiling sodium chlorite solutions of various concentrations for different time periods. After the sodium chlorite treatment, the samples were treated with a 2.5% sodium bisulfite solution at 50°C for 30 min to bleach the yellow color of the samples, and this was followed by washing with distilled water.

DSC and TGA

DSC was carried out for the dry grass-fiber powder sample with a Mettler TA 4000 thermal analyzer (New Castle, DE). TGA of the same kind of sample was carried out with a Mettler–Toledo TGA 850 thermal analyzer in a nitrogen atmosphere (flow rate = 50 mL/min), whereas TGA in air was carried out with a Mettler TA 4000 thermal analyzer in static air. All these experiments were carried out at a heating rate of 10°C/min.

Isothermal stability of the grass fiber

The isothermal weight loss was measured by the heating of the grass-fiber specimens in a tubular oven in the presence of air at 100, 200, and 300°C for different time periods. After the specified time, the difference in weight was measured to obtain the weight loss due to heating at a constant temperature. Accelerated aging of the grass-fiber samples in air was determined by the placement of the samples in an air-aging oven at 70°C for 24 and 48 h. After the heating of the samples at this temperature in the presence of air for specified time periods, the tensile strengths of the aged and unaged sample were measured.

X-ray diffraction (XRD) analysis

XRD of dry and split grass fiber was carried out with a Philips PW 1729 (USA) X-ray generator with a Co target (λ = 0.179 nm) at a scanning speed of 3°/min, and the data were recorded every 0.02° (2θ) for the angular range of 2θ = 10–50°.

TABLE I
Degradation Temperatures and Weight-Loss Characteristics of Water-Leached and Alkali-Treated
Grass-Fiber Samples from TGA in an Air Atmosphere

Grass fiber	First degradation				Second degradation				Third degradation				Residue (%)
	Start (°C)	Peak (°C)	End (°C)	Weight loss (%)	Start (°C)	Peak (°C)	End (°C)	Weight loss (%)	Start (°C)	Peak (°C)	End (°C)	Weight loss (%)	
WL	28.3	61.7	148.3	7.13	148.3	318.3	360.0	59.9	360	440	541	30.9	2.00
AT	25.0	71.7	161.7	5.18	181.7	295.0	381.7	54.1	381	508	568	37.7	2.14

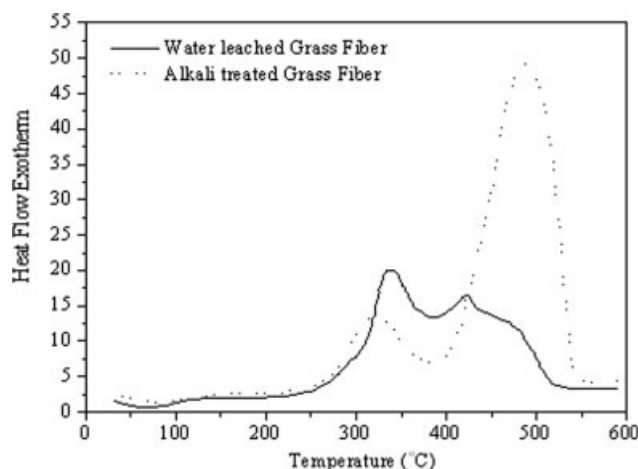AT = alkali-treated (5%, 1.0h); WL = water-leached.

Figure 2 DSC analysis of water-leached and alkali-treated grass fiber.

Scanning electron microscopy (SEM)

The surface and inner morphology of the water-leached and alkali-treated grass-fiber samples was evaluated by SEM with a JEOL (USA) JSM 5800.

RESULTS AND DISCUSSION

TGA and DSC analysis of the grass fiber

To determine the stability at elevated temperatures, the grass-fiber samples were analyzed by TGA in air and by DSC analysis in air at a heating rate of 10°C/min. Such thermal stability studies were carried out for water-leached and alkali-treated grass-fiber samples. The results of TGA in air are shown in Figure 1, and the values are presented in Table I.

First degradation

Weight loss in the first step occurs because of absorbed moisture in the sample. The peak temperature of first degradation indicates that the removal of moisture from the water-leached sample is easier than that from the alkali-treated sample. It is also observed that the moisture content of the alkali-treated sample is less than that of the water-leached sample. The decrease in the moisture absorption capacity of the alkali-treated sample is due to the decrease in the hemicellulose content (Table I).

Second degradation

Weight loss in the second step occurs because of the degradation of cellulose and hemicellulose. In the water-leached sample, the second degradation peak temperature is 318.3°C, whereas in the case of the alkali-treated sample, the second degradation peak temperature is 295°C. This lower peak temperature in the alkali-treated sample is due to the partial removal of hemicellulose from the natural fiber. In the alkali-treated sample, because of the removal of hemicellulose, some bond breaking occurs, and this leads to the lower degradation temperature compared to that of the water-leached sample. The weight-loss percentage in the second degradation step in the case of the water-leached sample is higher than that of the alkali-treated sample (Table I).

Third degradation

In the third step, lignin present in the grass fiber degrades. In the case of the alkali-treated sample, the peak temperature is 508°C, and the weight loss is 37.7%. This weight loss is very close to the amount of lignin present in the grass fiber. In the case of the water-leached sample, the third degradation temperature is 440°C, and the weight loss is 30.9%. From this weight-loss pattern, we can say that the alkali-treated samples are more stable than the water-leached samples. The residues in the water-leached and alkali-treated samples are almost equal (Table I).

DSC of the water-leached grass fiber in an air atmosphere

The results of DSC analysis of water-leached and alkali-treated samples are shown in Figure 2, and the values are presented in Table II. The DSC run for

TABLE II
DSC Thermal Transition Data (in Air) of Water-Leached and Alkali-Treated Grass-Fiber Samples

DSC peak	Start (°C)		Peak (°C)		End (°C)		ΔH (J/g)	
	WL	AT	WL	AT	WL	AT	WL	AT
First endotherm	30	30	72	80	160	190	234	270
Second exotherm	200	200	342	318	390	380	2400	1369
Third endotherm	—	—	390	380	—	—	—	—
Fourth exotherm	390	380	428	489	540	540	1754	3285

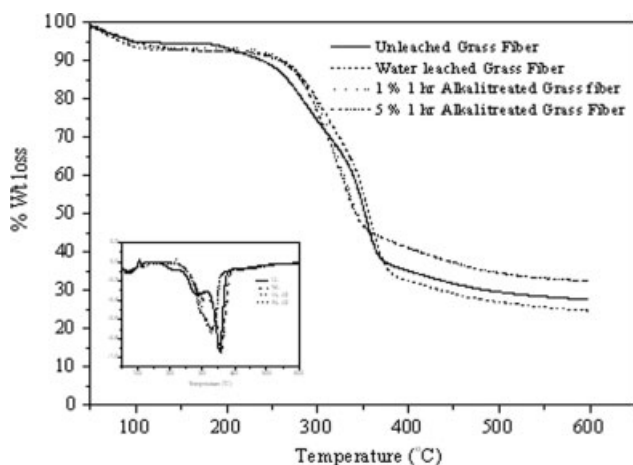AT = alkali-treated (5%, 1h); WL = water-leached.

Figure 3 TGA of unleached, water-leached, and alkali-treated grass fiber in a nitrogen atmosphere.

these samples was performed in air at a heating rate of 10°C/min. The DSC run of water-leached grass-fiber sample in air shows a broad endothermic peak around 72°C. This type of endothermic peak is due to the absorbed moisture/water present in the grass fiber. ΔH (enthalpy change during transition) of this endotherm is very low (234 J/G). In addition to this endotherm, two exothermic peaks appeared at 342 and 428°C that correspond to the thermal decomposition of hemicellulose and lignin constituents of the grass fiber, respectively. Others[14] have reported similar degradation temperatures of hemicellulose and lignin. The second exotherm corresponds to the degradation of hemicellulose, and the fourth exotherm corresponds to the degradation of lignin. The degradation exotherm of hemicellulose is higher than that of lignin, although lignin is thermally more stable than hemicellulose. The third endothermic peak around 390°C corresponds to the thermal decomposition of cellulose.

DSC of the alkali-treated grass fiber in an air atmosphere

DSC curves of the alkali-treated sample show a small endothermic peak around 80°C (Table II). This type of endothermic peak occurs because of the absorbed moisture in the alkali-treated grass fiber. ΔH of this endotherm is low but higher than that of the water-leached sample. From this information, we can say that the removal of moisture from the alkali-treated sample requires more energy than that from the water-leached sample.

The second and fourth exothermic peaks at 318 and 489°C correspond to the thermal decomposition of hemicellulose and lignin constituents of the alkali-treated grass fiber, respectively. The peak temperature for hemicellulose degradation in the alkali-treated sample is lower than that in the control sample. This indicates that in the presence of alkali, some degradation of hemicellulose occurs. ΔH of the exotherm of hemicellulose degradation in the alkali-treated sample is also lower than that of the control sample (Table II).

The fourth exothermic peak temperature for lignin in the alkali-treated sample is very high compared to that of the control sample. This indicates that after the alkali treatment, lignin is transformed into the alkali salt, which is thermally more stable than the naturally occurring lignin. ΔH of alkali lignin is also much higher than that of the control sample (Table II).

The third endothermic peak around 380°C (Table II) corresponds to the thermal decomposition of cellulose. From the aforementioned thermal data, we can say that overall thermal stability of the grass fiber increases after the alkali treatment.

TGA of unleached, water-leached, and alkali-treated samples in N$_2$

TGA of unleached, water-leached, and alkali-treated grass-fiber samples was also carried out in a nitrogen atmosphere; the results are shown in Figure 3, and the values are presented in Table III. In each case, three-stage degradation has been observed. In the first stage, although the 5% alkali-treated sample shows degradation at a higher temperature, the weight loss is more or less the same in each case. In the second stage although the unleached and water-leached samples degrade in a higher temperature

TABLE III
TGA of Unleached, Water-Leached, and Alkali-Treated Samples in an N$_2$ Atmosphere

Grass fiber	First degradation				Second degradation				Third degradation				Residue (%)
	Start (°C)	Peak (°C)	End (°C)	Weight loss (%)	Start (°C)	Peak (°C)	End (°C)	Weight loss (%)	Start (°C)	Peak (°C)	End (°C)	Weight loss (%)	
UL	30.0	65.6	107.2	5.05	231.9	353.5	389.1	58.98	389.1	462.0	536.0	8.37	27.6
WL	28.5	70.1	145.8	7.25	227.0	329.8	387.7	58.92	387.7	458.9	568.8	8.37	24.6
AT-5	28.5	74.5	162.2	7.24	217.1	329.8	374.3	48.73	374.3	463.4	561.3	10.5	32.4
AT-1	28.5	68.9	130.9	6.47	217.0	328.2	374.3	49.75	374.3	454.5	562.0	10.4	32.5

AT-5: 5%, 1h; AT-1: 1%, 1h.
AT = alkali-treated; UL = unleached; WL = water-leached.

TABLE IV
Thermogravimetric Degradation of Hemicellulose in Unleached, Water-Leached, and 5%, 1-h Alkali-Treated Grass-Fiber Samples in Nitrogen

Sample	Hemicellulose degradation temperature (°C)			Weight loss (%)
	Start	Peak	End	
UL	231.9	282.2	311.9	20.1
WL	227.0	295.0	310.0	16.8
AT	217.1	295.7	298.0	13.3

AT = alkali-treated; UL = unleached; WL = water-leached.

Figure 4 TGA of cellulose, hemicellulose, and delignified grass fiber in a nitrogen atmosphere.

range, their weight loss is higher compared to that of the alkali-treated samples. After the third stage of degradation beyond 560°C, the alkali-treated samples show higher char residue than the unleached and water-leached samples.

The data in Table IV have been obtained from the critical analysis of the TGA thermograms of unleached, water-leached, and alkali-treated grass fiber in a nitrogen atmosphere in the temperature ranges mentioned. The weight-loss data correspond to the hemicellulose content in the three different samples. It has also been reported by others[15] that hemicellulose degrades in the temperature range of 225–310°C. Table IV shows that the hemicellulose degradation is higher for the unleached sample than for the water-leached sample. This is due to the removal of some water-soluble sugars during water leaching. The weight-loss percentage in the case of the alkali-treated sample is still lower than that of the water-leached sample because of the progressive removal of hemicellulose. Higher peak temperatures for water-leached and alkali-treated samples indicate that both are thermally more stable than the unleached sample.

TGA for cellulose, hemicellulose, and partially delignified grass fiber in nitrogen is shown in Figure 4. The data in Table V have been obtained from TGA thermograms of isolated cellulose, hemicellulose from grass fiber, and partially delignified grass fiber. Table V shows that the degradation of cellulose and hemicellulose occurs up to 381°C, whereas the degradation of partially delignified material occurs up
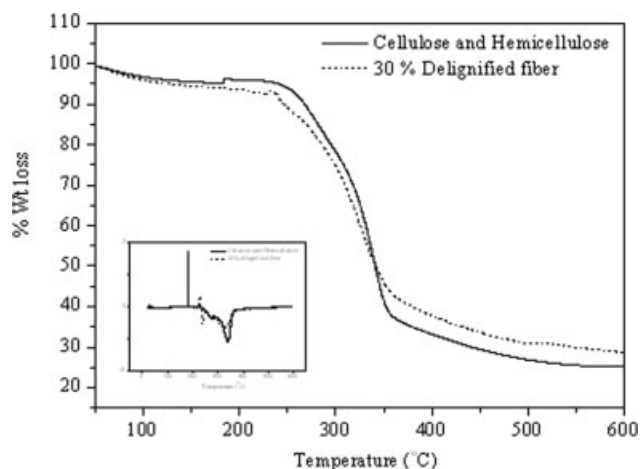
to 568°C. From this observation, it is evident that the lignin is responsible for the thermal stability of the grass fiber.

XRD analysis of the grass fiber

In the XRD study, the crystallinity (%) and crystallinity ratio (%) increased in the case of the alkali-treated sample compared to the control sample (Figs. 5 and 6). However, the crystallinity (%) and crystallinity ratio (%) of the grass fiber became maximum when it was treated with a particular alkali concentration for a specific time period, after which the crystallinity of the fiber decreased. From the experimental data, it was observed that the maximum crystallinity and tensile strength were achieved in the case of the 5%, 15-min alkali-treated sample. In the XRD pattern of the grass fiber, there are three sharp peaks other than the characteristic peak for cellulosic material. This type of sharp peak in the XRD pattern of the fiber may be due to the presence of some metal in the grass matrix. There are some reports of changes in the crystallinity by an alkali treatment of coir[16] and flax[17] fibers. The increase in the crystallinity of the alkali-treated fibers is due to the removal of interfibrillar cementing materials, which leads to better packing of cellulose chains.[18]

TABLE V
TGA of Isolated Cellulose, Hemicellulose, and Partially Delignified Grass-Fiber Samples in a Nitrogen Atmosphere

Sample	First degradation				Second degradation				Third degradation				Residue (%)
	Start (°C)	Peak (°C)	End (°C)	Weight loss (%)	Start (°C)	Peak (°C)	End (°C)	Weight loss (%)	Start (°C)	Peak (°C)	End (°C)	Weight loss (%)	
CH	28.4	64.1	209.6	4.11	209.6	279.4	298.6	17.7	298.6	340.2	381.7	43.9	25.2
DL	28.4	70.1	148.7	5.57	202.1	323.9	386.3	54.3	386.3	—	568.8	9.82	28.7

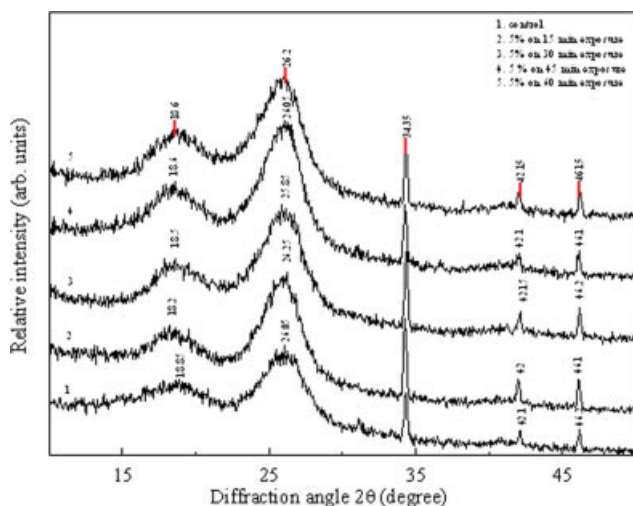CH, isolated cellulose and hemicellulose; DL, partially delignified grass fiber.

Figure 5 XRD of alkali-treated grass fiber. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Isothermal stability of the grass fiber

Isothermal weight loss of the unleached and water-leached grass fiber

The isothermal weight loss of both the water-leached and unleached samples at 100°C shows that there is no considerable amount of weight loss at 100°C up to 34 h, whereas at 200 and 300°C, it is unstable. Figures 7 and 8 show the isothermal weight loss versus time. However, in the isothermal experiment, it was observed that the weight-loss percentage of the unleached sample was higher than that of the leached sample in a particular time interval at a fixed temperature. This observation also supports the accelerated-aging behavior of both unleached and water-leached samples.
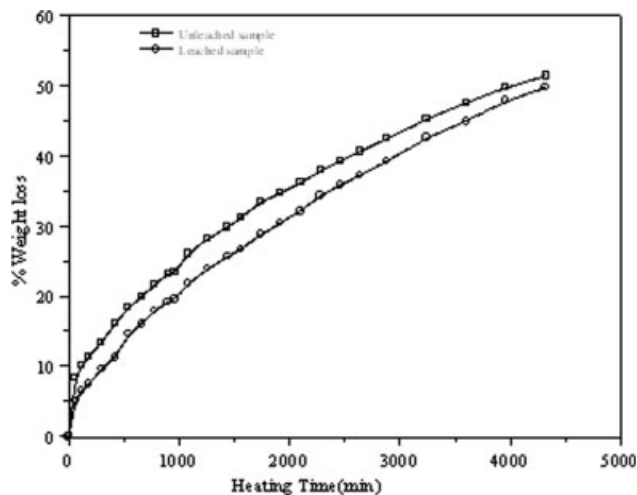

Figure 7 Isothermal weight loss of unleached and water-leached grass fiber in air at 200°C.

Accelerated-aging behaviors of both the unleached and water-leached grass fiber at 70 ± 2°C

The performance stability of the grass-fiber samples was evaluated by a simulated test using an accelerated-aging oven in the laboratory. Both the water-leached and unleached and dried samples were put in a constant-temperature air-aging oven at 70 ± 2°C for various durations. After the samples were kept in the aging oven for a specified period, they were taken out and cooled to room temperature in a desiccator. Then, the weights of the oven-aged samples were measured, and negligible weight loss of the samples occurred during aging at the oven temperature. Next, the aged samples were subjected to tensile strength measurements.

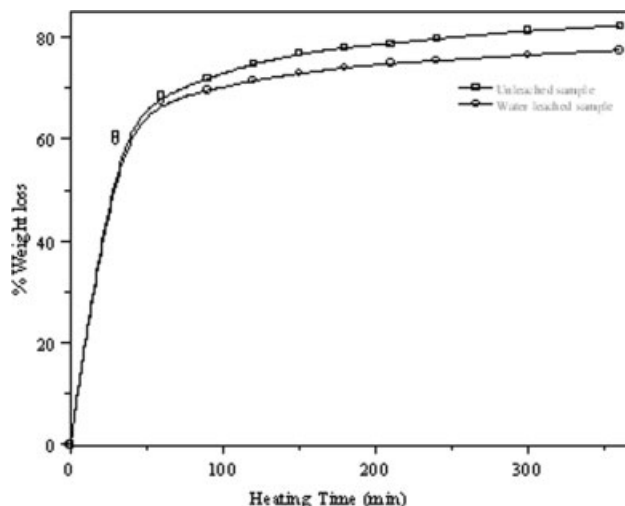The tensile strengths of the unleached unaged and leached unaged grass-fiber samples are almost com-

Figure 6 Crystallinity (%) and crystallinity ratio (%) of alkali-treated grass fiber.

Figure 8 Isothermal weight loss of unleached and water-leached grass fiber in air at 300°C.
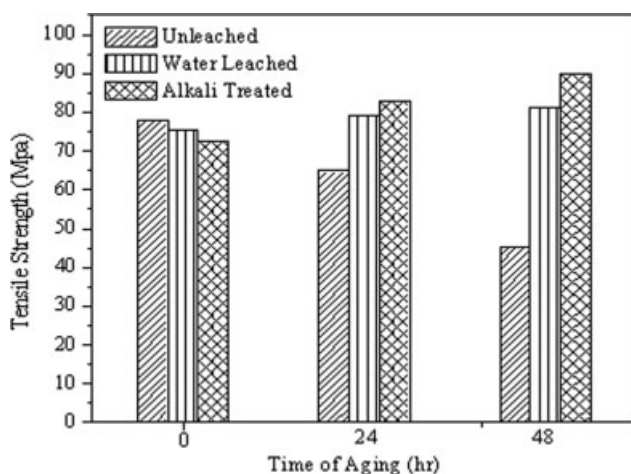
Figure 9 Effect of the tensile strength on the time of aging of unleached, water-leached, and alkali-treated grass-fiber samples.

parable. However, the leached samples show better mechanical strength after 24 and 48 h of aging at 70 ± 2°C than the original value (tensile strength of the unaged and leached sample; Fig. 9). However, in the case of the unleached sample, there is a large decrease in the tensile strength with the increase in the aging time (Fig. 9). The tensile strength increases because of alkali treatment on aging. Therefore, the thermal aging behaviors of the two samples (leached and unleached) are opposite in nature.

This type of aging behavior can be explained as follows. The removal of water-soluble materials leads to the creation of some void spaces inside the bulk of the grass fiber. Therefore, upon the applica-

tion of tensile stress, some alignment of fibers occurs in the bulk of the sample along its length in comparison with that effect in the unleached sample, as a result of which the leached sample shows better or almost comparable tensile properties. From the results of the accelerated-aging test of the samples, it is apparent that the water-soluble materials remaining in the grass fiber have some definite action on the aging process. The presence of water-soluble material has shown a pronounced influence on faster degradation of the unleached grass fiber. Therefore, the aging property of the unleached sample is poor, whereas in the leached sample, the absence of such materials increases the thermal stability, which further increases because of the alkali treatment of the grass fiber (Fig. 9).

SEM analysis of the grass fiber

SEM pictures of the grass-fiber samples were taken to study the surface features and inner morphology. Both the water-leached and alkali-treated samples (lengthwise and cross section) were viewed under SEM. A large difference between the SEM pictures of water-leached and alkali-treated samples [Fig. 10(a,b)] can be observed. In the water-leached grass-fiber sample, a meshlike structure can be seen on the outer surface of the grass fiber. However, the removal of hemicellulose (cementing material) in the alkali treatment leads to the destruction of the mesh structure and splitting of the fibers into finer filaments. After the alkali treatment, there is a reduction in the fiber diameter due to the removal of cemented material. This fiber fibrillation, which breaks down the composite fiber bundle into smaller ones,
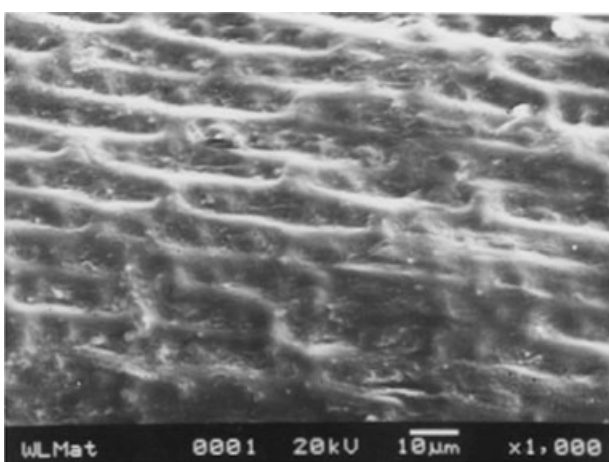
(a)
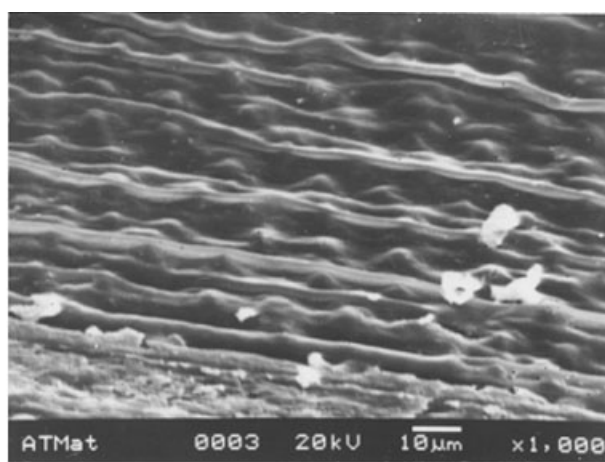
(b)

Figure 10 SEM photographs of (a) a water-leached but untreated (control) grass-fiber surface in the longitudinal direction at 1000× and (b) a water-leached but 5% alkali-treated (15 min) grass-fiber surface in the longitudinal direction at 1000×.

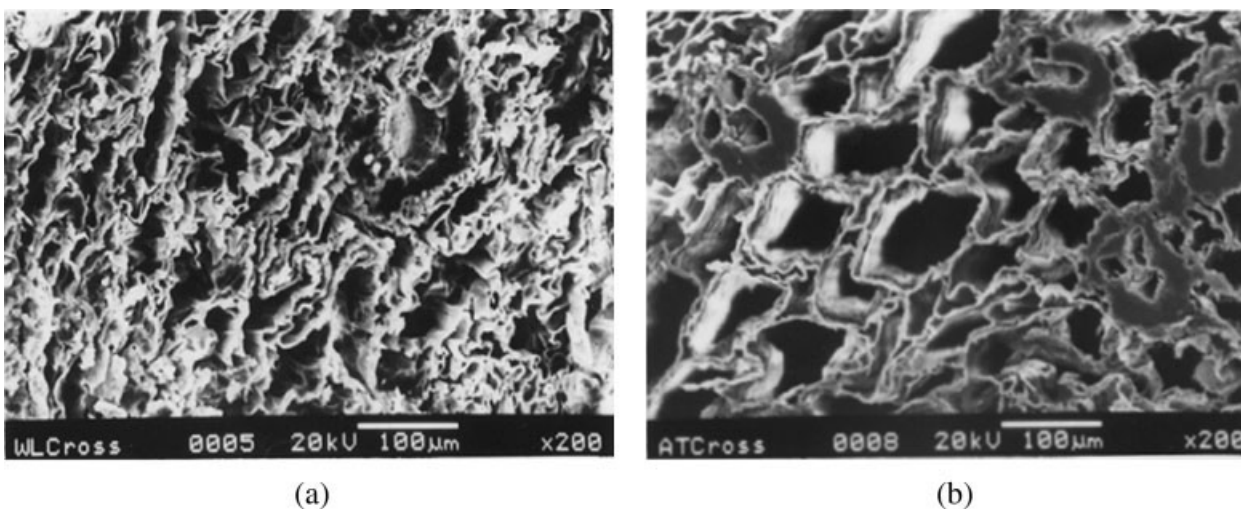**Figure 11** SEM photographs of (a) a water-leached but untreated (control) grass-fiber cross section at 200× and (b) a water-leached and 5% alkali-treated (15 min) grass-fiber cross section at 200×.

increases the effective surface area available for wetting by the resin in composite applications, if any. The SEM photographs of the surfaces of untreated and alkali-treated grass-fiber samples are shown in Figure 10(a,b), respectively. The treated fiber has a rough surface topography. In addition, the alkali treatment leads to fiber fibrillation, that is, breaking down of the composite fiber bundle into smaller fibers. This increases the effective surface area available for contact with the matrix. In other words, the alkali treatment reduces the fiber diameter and thereby increases the aspect ratio. Therefore, the development of a rough surface topography and the enhancement of the aspect ratio offer better fiber–matrix interface adhesion and an increase in the mechanical properties. From a cross-sectional view of both water-leached and alkali-treated grass fiber, it can be seen that the pore size increases because of the removal of hemicellulose [Fig. 11(a,b)].

CONCLUSIONS

On the basis of these studies, the following conclusion can be drawn:

- The treatment of grass fiber with alkali leads to a modification of its thermal stability. A higher char yield was obtained in grass fiber at 508°C.
- XRD analysis revealed that the alkali treatment of grass fiber reduced the content of the amorphous fraction in the fiber sample.
- An isothermal weight-loss study of unleached and water-leached grass-fiber samples revealed that the weight-loss percentage of the unleached sample was higher than that of the leached sample

at a particular time interval at a fixed temperature.
- The aging property of the water-leached grass-fiber sample was better than that of the unleached grass-fiber sample.

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