Thermal Behavior of Vinyl Ester Resin Matrix Composites Reinforced with Alkali-Treated Jute Fibers

Dipa Ray,[1] B. K. Sarkar,[1] R. K. Basak,[2] A. K. Rana[2]

[1]Department of Materials Science, Indian Association for the Cultivation of Science, 2 A & B Raja S. C. Mallick Road, Jadavpur, Kolkata 700032, India
[2]Indian Jute Industries' Research Association, 17 Taratola Road, Kolkata 700088, India

ABSTRACT: The thermal behavior of vinyl ester resin matrix composites reinforced with jute fibers treated for 2, 4, 6, and 8 h with 5% NaOH was studied with Thermo-gravimetric analysis and differential scanning calorimetry. The moisture desorption peak shifted to a higher temperature, from 37 to 58.3°C, for all the treated-fiber composites because of improved wetting of the fibers by the resin and stronger bonding at the interface. The degradation temperature of the vinyl ester resin in the composites was lowered to 410.3°C from that of the neat resin, 418.8°C. The X-ray diffraction studies showed increased crystallinity of the treated fibers, which affected the enthalpy of the α-cellulose and hemicellulose degradation. The hemicellulose degradation temperature remained the same (299.7°C) in all the treated-fiber composites, but the enthalpy associated with the hemicellulose degradation showed an increasing trend in the treated composites with a small increase in the weight loss. This could be attributed to the increased hydrogen bonding between the more accessible —OH groups of the hemicellulose in the noncrystalline region of the jute fiber and the resin. The degradation temperature of α-cellulose was lowered from 364.2 to 356.8°C in the treated composites. The enthalpy of α-cellulose degradation showed a decreasing trend with a lowering of the weight loss. The crystalline regions of the fiber, consisting of closely packed α-cellulose chains, were bonded with the resin mainly on the surface through hydrogen bonds and became more resistant to thermal degradation; this reduced the weight loss. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 123–129, 2004

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

INTRODUCTION

The potential use of natural fibers such as jute, coir, sisal, pineapple leaf fiber (PALF), and banana as reinforcing materials in polymer matrix composites has received considerable attention recently. However, applications have been limited because these fibers are highly hydrophilic in nature and show poor wetting behavior with organic resin matrices,[1–3] which leads to a weak bond at the interface. To improve the interfacial bonding, researchers have attempted various surface treatments, such as alkali treatment,[4–7] silane treatment,[8] acetylation,[9] and cyanoethylation,[10] and different coupling agents;[11,12] among these, alkali treatment has been found to be most viable economically.

Although investigators have studied the thermal behavior of treated and untreated fibers,[13–18] the number of studies of the thermal degradation characteristics of composites has been relatively small. Varma et

al.[14] reported that the incorporation of an unsaturated polyester resin decreased the thermal stability of fibers and that fibers coated with vinyl ester resin showed a combination of the degradation characteristics of the two individual components. Recently, Saha et al.[10] reported that the initial thermal decomposition temperature of polyester composites reinforced with untreated and cyanoethylated jute shifted to a higher value, but the final decomposition temperature remained unaltered because of the cyanoethylation of the fiber. A suitable chemical pretreatment of jute fiber improved the thermal behavior of low-density polyethylene composites, as reported by Sengupta et al.[19]

Studies on the mechanical,[20] impact fatigue,[21] dynamic mechanical,[22] and fracture behavior[23] of alkali-treated-fiber-reinforced composites have revealed interesting results, as we have already discussed in our previous works. Now, an attempt has been made to study the effect of the alkali treatment on the thermal behavior of alkali-treated-fiber-reinforced composites. In this article, we examine the thermal behavior of 35 vol % alkali-treated-jute-fiber-reinforced composites with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The various changes occurring in the fibers with alkali treatment, such as an increase in the fiber fineness and a change in the

crystallinity of the fibers, which affect the wetting characteristics with the resin, producing stronger bonds at the interface, have been correlated with their thermal degradation behavior.

EXPERIMENTAL

Materials

Jute fibers (white jute, or *Corchorus capsularis*) were wrapped in black paper, kept in sealed polythene bags, and stored at 65% relative humidity and 25°C. The vinyl ester resin was grade HPR 8711 (Bakelite Hylam, Bangalope, India). Methyl ethyl ketone peroxide, cobalt naphthenate, and *N,N* dimethylaniline were used as the catalyst, accelerator, and promoter, respectively.

Alkali treatment

Jute fibers, 50 cm long, were soaked in a 5% NaOH solution at 30°C with a liquor ratio of 15:1. The fibers were kept immersed in the alkali solution for 2, 4, 6, or 8 h. The fibers were then washed several times with fresh water to remove any NaOH sticking to the fiber surface, were neutralized with dilute acetic acid, and were finally washed again with distilled water. A final pH of 7 was maintained. The fibers were then dried at room temperature for 48 h, and this was followed by oven drying at 100°C for 6 h.

Fabrication of the composites

Jute/vinyl ester composites containing raw and alkali-treated jute fibers were fabricated in the form of cylindrical rods 6 mm in diameter. Hollow, cylindrical glass tubes with a 6-mm internal diameter were used as molds. The resin was mixed with the accelerator, promoter, and catalyst (1% each). The jute fibers were dried in an oven at 100°C for 4 h before use and were soaked in the mixed resin; the wetted fibers were pulled through the glass tubes by hand.

The samples within the glass tubes were cured at room temperature for 24 h and then postcured in an oven at 80°C for 4 h. The glass tubes were then cleanly broken to release the composite rods. Composites with 35 vol % untreated and treated jute fibers were prepared for investigation. In this case, the volume percentage was equal to the weight percentage because the densities of the jute fiber and the vinyl ester resin were both equal to 1.3 g/cm^3.

Thermal analysis

TGA and DSC were performed with a Mettler TG 50 and a DSC 25 module attached to a Mettler TC 11 4000 thermal analyzer. The thermal analyses were done in a

TABLE I
DTG Analysis of the Unreinforced Vinyl Ester Resin and the Untreated Jute Fiber

Sample	Peak temperature (°C)	Degradation (%)	Residue at 600°C (%)
Vinyl ester resin	418.8	93.040	7.2307
Untreated jute fiber	64.7	10.604	15.977
	297.0	8.730	
	362.2	64.265	

nitrogen atmosphere at a flow rate of 100 mL/min with an alumina crucible with a pin hole. A constant heating rate of 10°C/min was maintained.

RESULTS AND DISCUSSION

There were significant changes in the linear density, chemical composition, mechanical properties, and crystallinity of the jute fibers upon alkali treatment.[24] A weight loss was observed after the alkali treatment of the fibers, with a 41% reduction of the hemicellulose content. The fibers were somewhat leached, with a decrease in the linear density from 3.67 tex to 1.62 tex after 8 h of treatment. X-ray diffraction showed that the I_{002} (intensity of the X-ray diffraction on 002 plane) peak height for 8-h-treated fibers increased by 23.4% over that of untreated fibers, and this was indicative of the increased crystallinity of the fibers. The effect of the alkali treatment on the thermal properties of the fibers has been discussed elsewhere.[25]

TGA and DSC analysis

Untreated jute fibers

In the differential thermogravimetry (DTG) curve of the untreated jute fiber [Table I and Fig. 1(a)], the first peak (64.7°C) below 100°C was due to the evaporation of the moisture. The small hump at 297°C and the strong sharp peak at 362.2°C were due to the decomposition of the hemicellulose and α-cellulose, respectively.[18]

In the DSC curve of the untreated jute fiber, a strong and sharp endothermic peak (83.1°C) was observed below 100°C that was due to moisture desorption [Table II and Fig. 2(a)].[18] The small and broad exothermic hump at 289.9°C and the sharp endothermic peak at 365.7°C were due to the hemicellulose and α-cellulose degradation, respectively.[18]

Alkali-treated jute fibers

In the DTG curves of the alkali-treated fibers (treated for 2, 4, 6, or 8 h), the moisture desorption peak shifted to a lower temperature because of the increased fine-
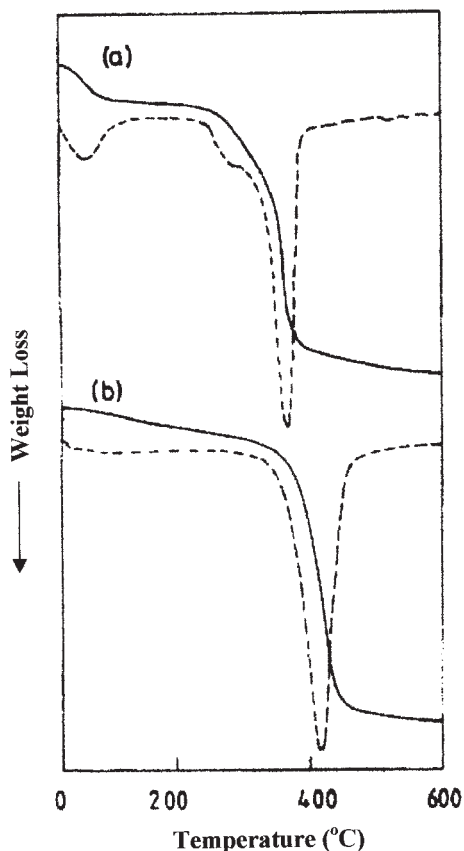
Figure 1 (—) TG and (- - -) DTG curves of (a) untreated jute fiber and (b) vinyl ester resin.

Figure 2 DSC curves of (a) untreated jute fiber and (b) vinyl ester resin.

ness of the fibers, which provided more surface area for moisture evaporation. The hemicellulose degradation peak shifted to a lower temperature (274.3°C), and the degradation percentage of hemicellulose decreased considerably; this conformed to the fact that a significant amount of hemicellulose was removed during the alkali treatment. The α-cellulose degradation temperature was lowered from 364.2 to 348°C, and the residual char formation increased to a significant extent (from 15.9 to 22%).[25]

Like the DTG curves, the DSC curves of the alkali-treated fibers also showed a reduction of the moisture desorption peak to a lower temperature. However, the

hemicellulose and α-cellulose degradation temperatures remained almost unaltered, and there was a significant change in the enthalpy of degradation. We discussed these results in detail in a previous work.[25]

Vinyl ester resin

The main decomposition peak in the DTG curve of the vinyl ester resin [Fig. 1(b)] was observed at 418.8°C, with a 7.23% residual char at 600°C (Table I). No significant moisture loss peak was observed in the DTG curve of the vinyl ester resin, and this indicated the low moisture content of the resin.

The DSC curve of the neat vinyl ester resin showed an endothermic peak at 419.3°C with an enthalpy of 239.64 J/gm. The moisture desorption peak below 100°C was small and, therefore, was neglected [Table II and Fig. 2(b)].

Jute/vinyl ester composites

The overall thermal degradation pattern of the vinyl ester resin matrix composites reinforced with untreated and alkali-treated jute fibers was an additive contribution by the individual thermal degradation features of the two components: the matrix and the fibers. The TGA and DSC results of the composites are given in Tables III and IV, respectively. The thermogravimetry (TG)/DTG and DSC curves of the composites are shown in Figures 3 and 4, respectively.

With untreated fibers. In the DTG curve of the composites reinforced with untreated jute fibers, the first peak at 37°C [Table III and Fig. 3(a)] was due to the evaporation of moisture.[18] The small, broad hump ob-

TABLE II
DSC Analysis of the Vinyl Ester Resin and the Untreated Jute Fiber

| Sample	Peak temperature (°C)	Nature of the peak	Enthalpy of degradation ΔH (J/g)
Vinyl ester resin	419.3	Endo	239.64
Untreated jute fiber	83.1	Endo	228.65
	289.9	Exo	31.984
	365.7	Endo	46.886

TABLE III
DTG Analysis of 35 vol % Raw and Alkali-Treated-Jute-Fiber-Reinforced Composites

Sample	Peak temperature (°C)	Degradation (%)	Residue at 600°C (%)
Raw jute/vinyl ester composite	37.0	3.3174	8.8628
	299.7	4.0642	
	364.2	25.560	
	416.0	57.7058	
2-h-alkali-treated-jute-fiber/vinyl ester composite	41.8	3.8372	10.135
	299.7	3.6302	
	358.7	25.448	
	413.2	56.7058	
4-h-alkali-treated-jute-fiber/vinyl ester composite	44.8	3.4303	10.135
	299.7	3.4487	
	360.5	25.8033	
	410.3	56.982	
6-h-alkali-treated-jute-fiber/vinyl ester composite	44.8	3.9312	10.403
	299.7	4.1082	
	356.8	24.7378	
	410.3	56.504	
8-h-alkali-treated-jute-fiber/vinyl ester composite	58.3	4.6838	10.598
	299.7	4.2393	
	356.8	21.9597	
	410.3	58.4732	

served at 299.7°C and the small, sharp peak at 364.2°C were due to the decomposition of the hemicellulose and α-cellulose, respectively,[18] in the fiber part of the composites. The degradation peak of the resin part of the composites was observed at 416°C, which was very close to the degradation peak of the unreinforced resin (see Table I). As the resin content of the compos-

TABLE IV
DSC Analysis of 35 vol % Raw and Alkali-Treated-Jute-Fiber-Reinforced Composites

| Sample	Peak temperature (°C)	Nature of peak	Enthalpy of degradation ΔH (J/gm)
Raw jute/vinyl ester composite	63.5	Endo	96.463
	307.8	Exo	11.499
	365.0	Endo	18.468
	412.7	Endo	252.88
2-h-alkali-treated-jute-fiber/vinyl ester composite	67.5	Endo	92.00
	305.2	Exo	18.244
	363.1	Endo	11.995
	412.8	Endo	224.90
4-h-alkali-treated-jute-fiber/vinyl ester composite	64.4	Endo	91.703
	307.8	Exo	18.272
	365.0	Endo	13.834
	413.3	Endo	181.09
6-h-alkali-treated-jute-fiber/vinyl ester composite	65.4	Endo	98.077
	305.2	Exo	20.327
	363.1	Endo	10.218
	413.4	Endo	162.00
8-h-alkali-treated-jute-fiber/vinyl ester composite	65.4	Endo	95.926
	308.2	Exo	23.312
	413.4	Endo	183.87
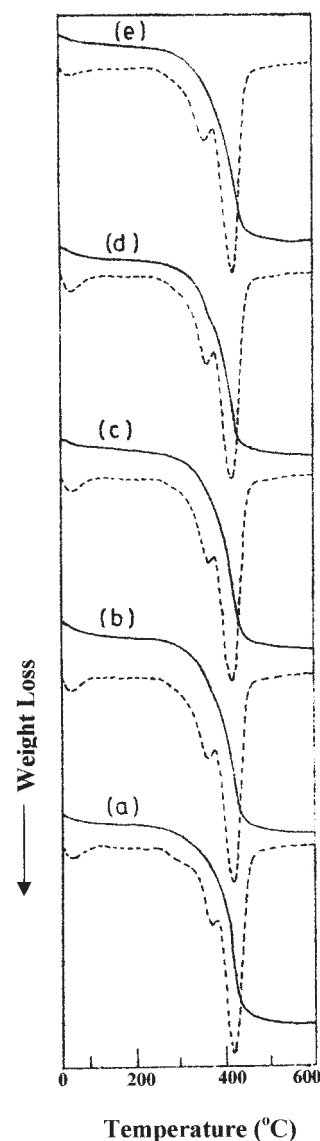
Figure 3 (—) TG and (- - -) DTG curves of composites reinforced with (a) untreated jute fiber and (b–e) alkali-treated jute-fiber. The treatment times were (b) 2, (c) 4, (d) 6, and (e) 8 h.

ites was higher (65%) than the fiber content (35%), the resin degradation peak was more prominent than the fiber degradation peak, as shown in Figure 3.

An endothermic moisture desorption peak (83.1°C) was observed below 100°C in the DSC curve of the composites reinforced with untreated jute fibers [Table IV and Fig. 4(a)]. The small, broad hump (exothermic) observed at 307.8°C and the small, sharp endothermic peak observed at 365°C were due to the degradation of the hemicellulose and α-cellulose, respectively.[18] The strong, sharp endothermic peak at 412.7°C was due to the degradation of the resin part in the composites.

With alkali-treated fibers. In the alkali-treated-jute/vinyl ester composites, the moisture loss peak shifted to
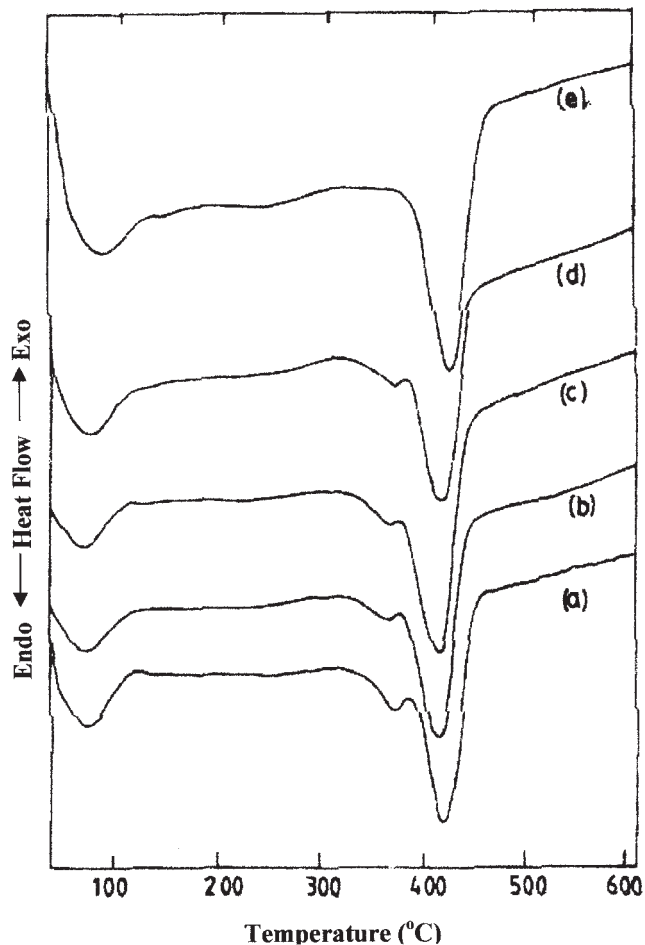
Figure 4 DSC curves of composites reinforced with (a) untreated jute fiber and (b–e) alkali-treated jute-fiber. The treatment times were (b) 2, (c) 4, (d) 6, and (e) 8 h.

higher temperatures, from 37°C for the untreated-fiber-reinforced composites to 58.3°C for the 8-h-treated-fiber-reinforced composites [Table III and Fig. 3(b–e)]. This tendency of releasing moisture at a higher temperature in the treated composites could be due to the improved wetting of the finely separated fibers by the resin; this produced a stronger bond at the interface and reduced the available surface area required for moisture desorption through a delay in the moisture evaporation. The hemicellulose degradation temperature in the fiber part of the composites remained the same in all the composites reinforced with the treated fibers (299.7°C), with a slight increase in the weight-loss percentage for the 6- and 8-h-treated-fiber-reinforced composites (Table III). The α-cellulose degradation temperature in the fiber part of the composites decreased in the treated-fiber-reinforced composites (from 364.2°C for the untreated composites to 356.8°C for the 8-h-treated-fiber composites) with a reduction of the weight-loss percentage for the 6- and 8-h-treated-fiber composites. The main degradation temperature of the resin part in the composites de-

creased from 416°C for the composites reinforced with the untreated fibers to 410°C for the 8-h-treated-fiber-reinforced composites, with nearly the same weight loss (56–58%) in all the composites (Table III).

In the DSC curves of the composites reinforced with the alkali-treated jute fibers, a significant change was observed in the α-cellulose degradation peak. The small, sharp peak in the untreated-fiber-reinforced composites gradually became smaller in the 2-, 4-, and 6-h-treated-fiber-reinforced composites and finally disappeared in the 8-h-treated-fiber-reinforced composites [Table IV and Fig. 4(b–e)].
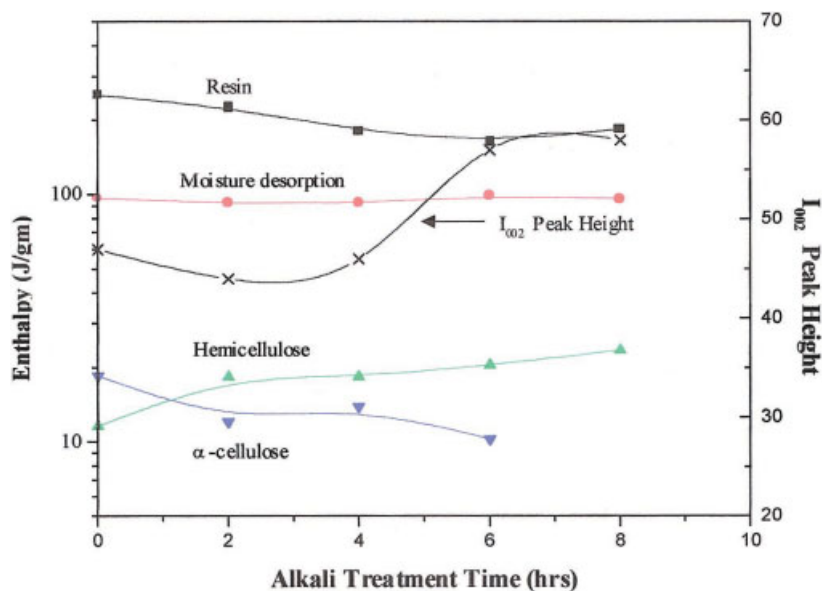
Correlation between the enthalpy of degradation and the crystallinity of the fibers

The enthalpy associated with the hemicellulose degradation in the fiber part of the composites showed an increasing trend in the treated-fiber-reinforced composites (Fig. 5). The enthalpy value increased by 58% for 2- and 4-h-treated-fiber-reinforced composites, by 76.7% for the 6-h-treated-fiber-reinforced composites, and by 99% for the 8-h-treated-fiber-reinforced composites. On the contrary, the enthalpy for the α-cellulose degradation in the fiber part of the composites showed a decreasing trend in the treated-fiber-reinforced composites (Fig. 5).

Jute, a lignocellulosic fiber consisting of α-cellulose, hemicellulose, and lignin, has a semicrystalline structure. The α-cellulose predominantly forms the crystalline region, whereas the lignin and hemicellulose form the amorphous region. The hydroxyl groups of the hemicellulose are more accessible and so actively take part in the hydrogen bonding with the resin. As the fibers become finer with the alkali treatment, more and more —OH groups become available for hydrogen bonding with the resin. The increased hydrogen bonding between the hemicellulose and the resin tends to stabilize the structure, and the enthalpy values increase with a slight increase in the weight-loss percentage. On the other hand, α-cellulose being crystalline, only the —OH groups present on the surface of the crystalline region take part in hydrogen bonding with the resin. In the 6- and 8-h-treated composites, the crystalline regions, consisting of closely packed α-cellulose chains, were bonded with the resin mostly on the surface and, therefore, suffered less degradation; the enthalpy values were also lowered. The 8-h-treated fibers being most crystalline, the peak due to α-cellulose degradation almost disappeared in the DSC curve of the 8-h-treated-fiber-reinforced composites.

CONCLUSIONS

The thermal degradation behavior of vinyl ester resin matrix composites reinforced with 5% NaOH-treated

Figure 5 Variation of the enthalpy of degradation of the resin and jute-fiber constituents (α-cellulose and hemicellulose) in the composites and the crystallinity of the fibers with the alkali treatment time.

jute fiber (treated for 2, 4, 6, or 8 h) was investigated with TGA and DSC techniques in a nitrogen atmosphere. The changes occurring in the fibers due to the alkali treatment, such as the splitting of the fibers into finer filaments, the increase in the crystallinity of the fibers, and the improved bonding between the fiber and the resin, had a considerable effect on the thermal degradation behavior of the composites. The moisture release temperature increased from 37 to 58.3°C in the treated composites because of improved wetting and stronger bonding at the interface. The degradation temperature of the resin part of the composites was lowered from 416°C for the composites with untreated fibers to 410.3°C for the 8-h-treated-fiber-reinforced composites, and this was indicative of the reduced thermal stability of the resin in combination with alkali-treated jute fibers. The hemicellulose degradation temperature (299.7°C) remained the same in the untreated and treated composites, but the increased hydrogen bonding between the highly accessible —OH groups of the hemicellulose in the noncrystalline region of the jute fiber and the resin in the treated composites tended to stabilize the structure and increase the enthalpy value with a small increase in the weight loss. The closely packed α-cellulose chains in the crystalline regions of the fibers were bonded with the resin only on the surface. As the 6- and 8-h-treated fibers were most crystalline, the resin-covered crystalline regions were more resistant to thermal degradation and suffered lower weight loss. In the DSC curve of the 8-h-treated composites, the peak due to α-cellulose degradation almost disappeared, and this indicated that the closely packed α-cellulose chains were highly resistant to thermal degradation in combination with the resin. This was also reflected in the increased amount of residual char formation at 600°C. However, the main degradation temperatures of the resin and the fiber (α-cellulose mainly) were lowered in the treated composites, and this was indicative of the lower thermal stability of the treated composites.

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