

Study of the Thermal Behavior of Alkali-Treated Jute Fibers

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ABSTRACT: Jute fibers were treated with 5% NaOH solution for 2, 4, 6, and 8 h to study the performance of the fibers as a reinforcing material in the composites. Thermal analysis of the fibers was done by the DTG and DSC technique. The moisture desorption was observed at a lower temperature in the case of all the treated fibers, which might be a result of the increased fineness of the fibers, which provides more surface area for moisture evaporation. The decrease in percentage moisture loss for the fibers treated with alkali for 6 and 8 h could be the result of the increased crystallinity of the fibers. The percentage degradation of the hemicellulose decreased considerably in all the treated fibers, conforming to the fact that the hemicellulose content was lowered on alkali treatment. The decomposition temperature for α -cellulose was lowered to 348°C from 362.2°C for all the treated fibers, and the residual char formation increased to a significant extent. The enthalpy for the thermal degradation of α -cellulose showed a decreasing trend for the fibers treated for 2 and 4 h, which could be caused by the initial loosening of the structure, followed by an increase in the enthalpy value in the case of the 6- and 8-h-alkali-treated fibers resulting from increased crystallinity, as evident from the X-ray diffraction. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2594–2599, 2002

Key words: jute fiber; chemical treatment; thermal analysis; crystallinity; enthalpy; moisture; thermal degradation

INTRODUCTION

In recent years, natural fibers like jute, coir, sisal, PALF, banana, and so forth have attracted substantial importance as reinforcing materials in polymer matrix composites, but these fibers are highly hygroscopic in nature and show poor wetting behavior when used with the organic resin matrix,^{1–3} leading to a weak bond at the interface. To improve the interfacial bonding, various surface treatments have been attempted, such as alkali treatment,^{4–7} silane treatment,⁸ acetyla-

tion,⁹ cyanoethylation,¹⁰ use of different coupling agents,^{11,12} and so forth, and among these, alkali treatment is the economically most viable one.

Thermal analysis of these untreated and treated fibers has been an important tool in visualizing the physico-chemical nature of these fibers, and it determines their commercial significance. Mahato et al.¹³ studied the thermal behavior of alkali-treated coir fibers and correlated the thermal behavior with the physico-chemical behavior of the fibers. Varma et al.¹⁴ studied the effects of different chemical treatments on the thermal behavior of jute fibers. Samal et al.¹⁵ treated PALF with 4%–16% NaOH solutions and observed the effect of alkali treatment on the thermal stability of the fibers. The thermal na-

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ture of cotton, mercerized cotton linters, and modified cotton have been studied by some workers.^{16,17} Nguyen et al.¹⁸ reviewed the thermal analysis of lignocellulosic materials. Thermal studies of jute fibers and its different constituents have been studied by Basak et al.¹⁹ in both air and a nitrogen atmosphere. Mitra et al.²⁰ carried out thermal analysis of PF-treated and CNSL-PF-treated jute fibers and reported a decrease in the thermal stability of the fibers on treatment. Thermal analysis of acetylated jute fibers was conducted by Rana et al.,⁹ and an increase in the thermal stability of the treated fibers was reported. A study on the influence of fine structure of cotton on its pyrolysis behavior was performed by Basch and Lewin.²¹

In this article, we have studied the thermal behavior of untreated and 5% NaOH-treated jute fibers (treated for 2, 4, 6, and 8 h) by TGA and DSC, and an attempt has been made to correlate the changes occurring in the fibers on alkali treatment, such as dissolution of hemicellulose, increase in fiber fineness, increase in crystallinity of the fibers, and so forth, with its thermal degradation behavior in a nitrogen atmosphere.

EXPERIMENTAL

Materials

Jute fibers (white jute, *Corchorus capsularis*) were collected from Indian Jute Industries' Research Association (IJIRA), Calcutta. The fibers were wrapped in black paper, kept in sealed polythene bags, and stored at 65% relative humidity and 25°C.

Alkali Treatment

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

Thermal Analysis

TGA and DSC analyses were carried out using a Mettler TG 50 and a DSC 25 module attached to

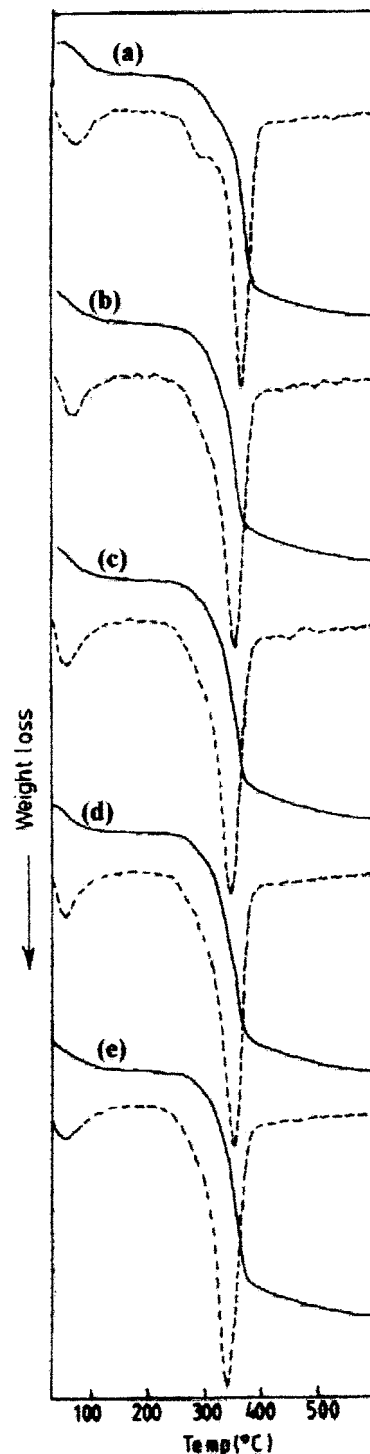


Figure 1 TG and DTG thermograms of raw and alkali treated jute fibers (a, untreated; b, 2 h; c, 4 h; d, 6 h; and e, 8 h).

a Mettler TC 11 4000 thermal analyzer (Switzerland). The thermal analyses were done in a nitrogen atmosphere under a flow rate of 100 mL/min

Table I Results of DTG Analysis of Raw and Alkali-Treated Jute Fibers

Sample	Peak Temperature °C	% Degradation	% Residue at 600 °C
Untreated jute fiber	64.7	10.604	15.977
	297.0	8.730	
	362.2	64.265	
2-h-alkali-treated jute fiber	53.3	9.208	22.095
	274.3	2.642	
	348.0	63.876	
4-h-alkali-treated jute fiber	47.7	9.318	22.826
	274.3	3.100	
	348.0	64.578	
6-h-alkali-treated jute fiber	44.8	8.719	21.422
	274.3	3.274	
	348.0	66.414	
8-h-alkali-treated jute fiber	50.5	8.104	22.365
	274.3	3.200	
	348.0	66.168	

using an alumina crucible with a pinhole. A constant heating rate of 10°C/min was maintained.

RESULTS AND DISCUSSION

The TG and DTG curves of the untreated and the alkali-treated jute fibers are shown in Figure 1 and given in Table I. In the DTG curve of the untreated jute fiber, the first peak (Table I) below 100°C was the result of evaporation of moisture. The peaks at 297° and 362.2°C were caused by hemicellulose and α -cellulose degradation, respectively.¹⁹ In the case of alkali-treated jute fibers, the moisture-loss peak shifted to a lower temperature. This tendency toward releasing moisture at a lower temperature might be caused by an increase in the surface area of the split fibers (as observed from scanning electron microscopy),²² facilitating easier evaporation of moisture at a lower temperature. The decrease in percentage moisture loss in the treated fibers could be the effect of increased crystallinity, as observed with X-ray diffraction.^{13,22} The degradation peak of the α -cellulose and the hemicellulose shifted to lower temperatures, 348°C from 362.2°C and 274.3°C from 297°C, respectively, in all the treated fibers. The percentage degradation remained almost same for the α -cellulose but decreased for hemicellulose, conforming to the observation that 41% hemicellulose was removed on alkali treatment.²² The residual char left at 600°C increased considerably from 15% to 22% in

the case of all the treated fibers (Table I). A similar observation was reported by Saha et al.,²³ who explained that mercerization reduced the hemicellulose to a considerable extent, giving rise to a lignin–cellulose complex, thereby making the product more stable than the raw sample, and this was reflected in the increased amount of residual char. An increase in residual char formation and lowering of the degradation temperature during the pyrolysis of treated cotton was also reported by Parker et al.²⁴ They explained that this might be caused by an increased rate of formation of free radicals that are stabilized by condensed carbon ring formations in the char.^{25–27} Mitra et al.²⁰ showed that the treatment of jute fiber with PF and CNSL-PF reduced the pyrolysis temperature, decreased the weight loss during pyrolysis, and enhanced the residual char formation with a lowering in the formation of the flammable volatiles, and thus concluded that the thermal stability was decreased in the case of the treated fibers. Rana et al.⁹ observed that the main decomposition temperature increased from 363°C to 373°C in acetylated jute fiber and reported a higher thermal stability of the treated fibers.

The DSC curves of the untreated and alkali-treated jute fibers are shown in Figure 2, and the corresponding values are given in Table II. An endothermic peak below 100°C was observed, resulting from moisture loss. The exothermic peak at 289.9°C and the endothermic peak at 365.7°C were caused by the hemicellulose and α -cellulose decomposition, respectively.^{21–24} In case of the

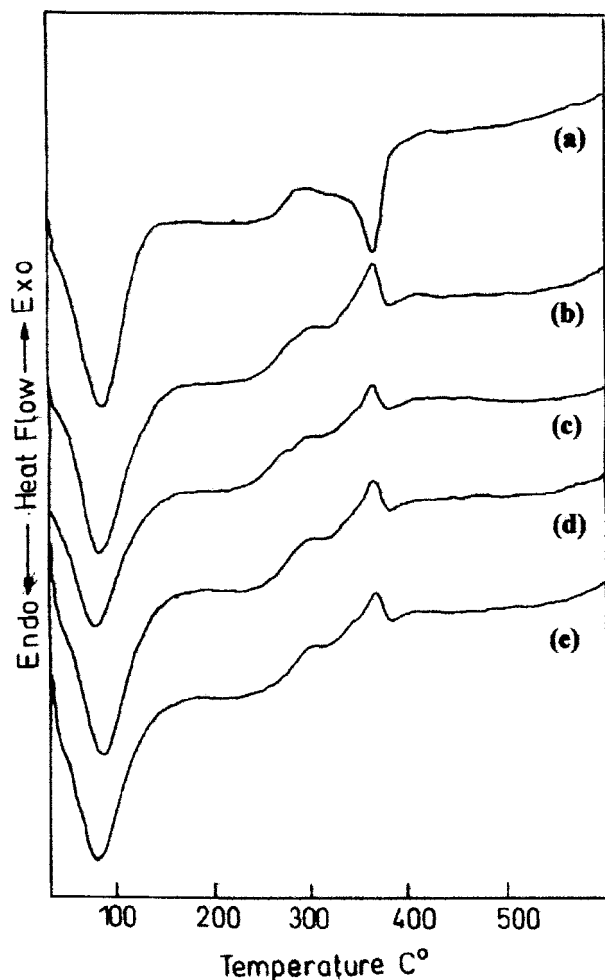


Figure 2 DSC curves of raw and alkali treated jute fibers. (a, untreated; b, 2 h; c, 4 h; d, 6 h; e, 8 h).

treated fibers, the α -cellulose decomposition peak changed from endothermic to exothermic. Similar inversion was reported by Mitra et al.²⁰ in the case of PF and CNSL-PF treated fibers and by Sikdar et al.²⁸ for the bleached jute fibers, but no such inversion was observed for acetylated⁹ or cyanoethylated¹⁰ jute fibers. It is, therefore, apparent that the removal of the noncellulosic constituents, such as hemicellulose during alkali treatment and lignin during NaClO_2 treatment, leading to the destruction of the chemical linkages between the constituents might have some influence in inverting the α -cellulose degradation peak from endothermic to exothermic. In the case of acetylation or cyanoethylation, where only the hydroxyl groups took part in the chemical reaction, no such inversion was observed.

The enthalpy associated with moisture desorption, α -cellulose, and hemicellulose decomposition showed a decreasing trend up to 4 h of treatment but increased again in the case of 6- and 8-h-treated fibers (given in Table II and shown in Fig. 3). This initial lowering in the enthalpy might be caused by the loosening of the chain structure on alkali treatment, facilitating easier decomposition, whereas the increase in enthalpy for 6- and 8-h-treated fibers could be caused by the closer packing of the cellulose chains, resulting in increased crystallinity of the fibers, as observed from X-ray diffraction.²² The increased H-bonding between the closely packed cellulose chains tends to stabilize the structure and increase the enthalpy values. Basch and Lewin²¹ reported a

Table II Results of Differential Screening Calorimetry Analysis of Raw and Alkali-Treated Jute Fibers

Sample	Peak Temperature °C	Nature of Peak	ΔH (J/gm)
Untreated jute fiber	83.1	Endo	228.65
	289.9	Exo	31.984
	365.7	Endo	46.886
2-h-alkali-treated jute fiber	83.9	Endo	210.25
	294.0	Exo	20.086
	362.9	Exo	31.689
4-h-alkali-treated jute fiber	77.4	Endo	187.13
	291.3	Exo	18.335
	366.8	Exo	22.151
6-h-alkali-treated jute fiber	80.6	Endo	216.49
	290.7	Exo	22.787
	364.2	Exo	27.551
8-h-alkali-treated jute fiber	79.0	Endo	227.01
	292.7	Exo	22.966
	364.2	Exo	27.905

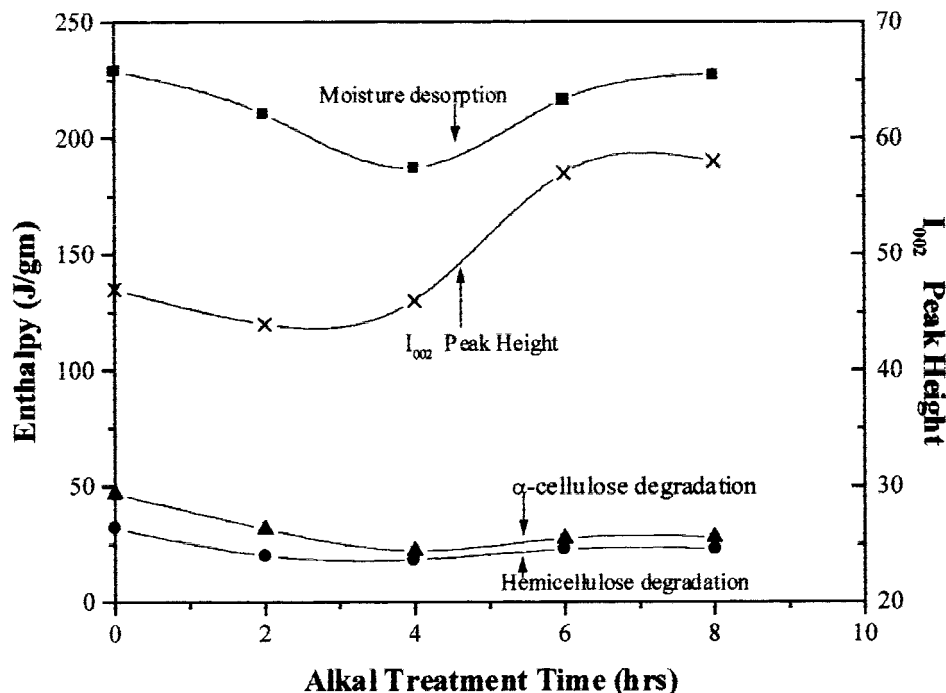


Figure 3 The variation of the enthalpy and crystallinity of the fibers with alkali treatment time.

similar observation in the case of cotton fiber. They also concluded that a correlation might exist between the DSC peak areas and the percentage crystallinity of the fibers. They observed that the fine structure of cellulose had considerable influence on its pyrolytic behavior and that the stabilizing effect of crystallinity was clearly evident in the DSC behavior of the fibers.

CONCLUSION

The thermal degradation behavior of 5% NaOH treated jute fibers (for 2, 4, 6, and 8 h) was investigated with the help of TGA and DSC. The changes occurring in the fibers as a result of alkali treatment, such as dissolution of hemicellulose, splitting of the fibers into finer filaments, increase in crystallinity of the fibers, and so forth, were found to have considerable influence on the degradation behavior of the fibers. The increase in fiber fineness facilitated moisture evaporation at a lower temperature in the case of the treated fibers, and the increase in crystallinity reduced the percentage moisture loss for 6- and 8-h-alkali-treated fibers. The α -cellulose and hemicellulose decomposition temperatures were lowered and

the residual char formation was enhanced in the treated fibers, lowering the formation flammable volatiles, thus reducing the thermal stability of the alkali-treated fibers. In DSC, the enthalpy associated with the moisture desorption, α -cellulose, and hemicellulose decomposition showed a decreasing trend up to 4 h of treatment, after that, there was an increase in enthalpy that might be attributed to the increase in the crystallinity of the fibers, as observed from X-ray diffraction.

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