

# Thermal Degradation of Flax and Jute Fibers

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**ABSTRACT:** The thermal degradation of jute and flax fibers under temperatures between 170 and 210°C for a maximum of 120 min was studied in detail. This article will analyze the effects of the thermal exposure on mechanical properties (tenacity) as well as on fiber fine structure (degree of polymerization and degree of crystallinity). It was found that temperatures below 170°C only slightly affects fiber properties, while temperatures above 170°C significantly dropped tenacity and degree of polymerization. Because of chain scissions, a slight increase in degree of crystallinity was observed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1417–1422, 2001

**Key words:** natural fibers; thermal degradation; depolymerization; crystallinity; tenacity; structure–property relations

## INTRODUCTION

Cellulose-based natural fibers combine good mechanical properties with a low density and can be used in general successfully as reinforcements for different kinds of thermosets and thermoplastics.<sup>1</sup> One of the major drawbacks seem to be the limited thermal stability of these fibers, where the first degradation occurs at temperatures above 180°C. Because of this, the typically used thermoplastics as matrix are polyvinyl chloride, polypropylene, and polyethylene, with melting temperatures below or equal to the degradation temperature.

This thermal degradation of cellulose-based fibers is greatly influenced by their structure and chemical composition,<sup>2</sup> in the following order in thermal stability (in absence of oxygen): lignin,  $\alpha$ -cellulose, hemicellulose as published by Nasser.<sup>3</sup> Contrary data were published by Ramiah<sup>4</sup> in 1970 with decomposition tempera-

tures in the order: hemicellulose < lignin <  $\alpha$ -cellulose by using the dilatometric method. However, it is well known that, when cellulose-based materials are heated in the range of 100 to 250°C some of the changes in physical properties of the fibers can be explained in terms of alterations in either physical or chemical structures<sup>5</sup> such as depolymerization, hydrolysis, oxidation, dehydration, decarboxylation<sup>6</sup> and recrystallization.<sup>5</sup>

For instance, a thermal heating of cotton fibers for 6 h at temperatures from 165°C up to 240°C leads, due to chain scission, to a decrease in the degree of polymerization (DP) from 5360 to 320, determined with viscosity measurements. The ability to crystallize could be increased by chain scission because this would permit the cellulose chains to realign themselves more easily and then crystallize (degree of crystallinity was calculated from Valentine's relation).<sup>5</sup> Zeronian stated that the crystallinity of the fiber was increased by heating. For example, the amorphous part of the cellulose,  $F_{am}$ , decreased from 0.38 to 0.30 by being heated at 240°C for 6 h. A similar behavior of DP was found in 1971 by Rusznák et al.<sup>7</sup> for untreated and alkali-treated cotton fibers at different initial moisture contents. He further found

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that an increasing moisture content of the cellulose generally reduces the decrease of degree of polymerization. From LODP data for heat-treated cotton fibers, Zeronian<sup>5</sup> stated a damage of cellulose crystallites at a temperature above 230°C.

In regard to reinforcing thermoplastics from an engineering point of view, effects of thermal exposure on the overall mechanical properties (e.g., tenacity) are of main importance, which are closely linked to the fine structure of the fibers.

For instance, heating of cotton for 20 min up to 160°C caused little loss in strength, but rapid deterioration of strength occurred above this temperature.<sup>22</sup> A similar trend was found for the modulus of cotton. The stiffness modulus remained constant between 80 and 140°C. Above 180°C it began to decrease relatively rapidly. It was commented that this decrease is an indication of the onset of thermal softening of the fiber.<sup>5</sup> In contrast, Conrad (published in ref. 5) found a gradual decrease in modulus for cotton as the temperature was raised from 100 to 233°C, while the softening temperature for cellulose ranges between 230 and 250°C, depending on the type of cellulose.

For instance, investigations about the effects on short thermal exposure (at maximum 12 min) to the tenacity of flax fibers were published by Bürger et al.<sup>12</sup> A general decrease of this value was observed for temperatures above 200°C, while the rate of degradation dependent on the exposition time. In this study, the decrease in mechanical properties due to exposure times shorter than 4 min were only small. Longer times (up to 4 h) reduced tenacity of ramie fibers more significantly by temperatures of 150°C,<sup>13</sup> with reinforcing this tendency by higher temperatures.

It has been stated by some workers<sup>8-11</sup> that tensile breakage of native cellulose fibers occurs by rupture of covalent bonds in the cellulose molecules. However, others believe that rupture of secondary valence bonds, primarily the hydrogen bonds, between the cellulose molecules are responsible for tensile failure.

As mentioned already, the thermal (as well as hydrolytic, photolytic, photochemical, enzymatic) degradation of cellulose fibres, which is essentially due to the scission of cellulose chains, regarded as the number of bonds being broken, correlates quite well with the decrease in tenacity.

Based on this, Testa et al.,<sup>8</sup> in his investigations on the degradation of raw cotton and raw flax fibers used an empirical relation to charac-

terize changes in physical properties by taking into account broken bonds 'B<sub>DP</sub>', eq. (1):

$$\frac{\text{Tenacity}_{\text{heat treated}}}{\text{Tenacity}_{\text{untreated}}} \propto B_{\text{DP}};$$

$$B_{\text{DP}} := \left[ \frac{1}{\overline{DP}} \right]_{\text{heat treated}} - \left[ \frac{1}{\overline{DP}} \right]_{\text{untreated}}$$

with a quite high correlation between calculated and experimental data.

As mentioned before, the resulting changes in crystallinity due to the thermal exposure are usually only slight,<sup>5,6</sup> and, because of the linear dependency between both,<sup>11</sup> it can be neglected [as in eq (1)] from a mechanical point of view.

Furthermore, the coefficient of thermal expansion of cellulose, hemicellulose, and lignin are different. At higher temperatures these differences become bigger. This causes a mismatch between various components and, consequently, creates damages such as voids or flaws affecting the overall mechanical properties.<sup>18</sup>

## EXPERIMENTAL

### Materials and Fiber Treatment

Untreated and alkali-treated tossa jute and flax fibers, both from J. Schilgen GmbH & Co., Germany, with the characteristic structural parameters according to Table I were used in this study and discussed in detail elsewhere.<sup>1</sup>

As a pretreatment, all fibers were dewaxed in methanol-benzene (1 : 1) for 24 h to remove the weaving size (potato starch and waxes). The alkali treatment was done by treating the jute and flax fibers with solutions of NaOH—concentrations of 26 and 29 wt %, respectively, for 20 min at temperatures of 20°C under isometric conditions (i.e., shrinkage = 0%) followed by washing the fibers in distilled water, neutralization with 2 wt % sulphuric acid, washing again, and drying.<sup>1</sup>

### Exposure Conditions

The fibers were thermally treated in a laboratory oven at temperatures of 170, 190, and 210°C for a maximum of 120 min at standard humidity. Thereafter, the fibers were cooled down to 23°C in a desiccator followed by a storage of 24 h at ambient temperature. The initial moisture content of

**Table I Structural Characteristics and Mechanical Properties (DIN 53834) of Untreated and Alkali Treated Jute and Flax Fibers<sup>1</sup>**

Fiber Treatment	DP	Cellulose Content (wt %)	DC (%)	$f_r^a$	$E$ (N/mm <sup>2</sup> )	$\sigma$ (N/mm <sup>2</sup> )
Jute fibers						
Untreated	403	61	68	0.943	9140	145
Alkali treated	337	74	65	0.954	17190	272
Flax fibers						
Untreated	1505	79	91	0.958	—	—
Alkali treated	1397	78	78	0.960	—	—

<sup>a</sup>  $f_r$  = value for chain orientation of crystallites in fiber axis.

DP = degree of polymerization; DC = degree of crystallinity;  $f_r$  = Herman's orientation factor;  $E$  = yarn Young's modulus;  $\sigma$  = yarn tensile strength.

both types of fibers were approximately 8 wt % measured by Carl Fischer titration.<sup>1</sup>

### Degree of Polymerization

DP was calculated from results of viscosity measurements in Cuoxam solution with a Ubbelohde viscometer (No. 0 and 1) by using eq. (2):

$$DP = \frac{\eta_{sp}}{1 + 0.28\eta_{sp}} \frac{200}{c}$$

with:  $\eta_{sp} = \frac{t}{t_0} - 1$   
for:  $0.1 < \eta_{sp} < 0.2$

where  $\eta_{sp}$  is the specific viscosity,  $c$  [g/100 mL] the concentration of jute or flax fibers,  $t$  [s] the time of flow of the fiber-cuoxam solution, and  $t_0$  [s] the time of flow of the cuoxam solution alone. The given DP values in this article are average values out of two samples with a standard deviation lower than 7%.<sup>23</sup>

### Degree of Crystallinity (DC)

DC was measured by using the iodine absorption method.<sup>15</sup> For this method, the fibers were added to iodine (5 g J<sub>2</sub>, 40 g KI, 50 mL distilled water) and Na<sub>2</sub>SO<sub>4</sub> solution and stored and stirred for several hours in darkness. The used amount of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution for the following titration procedure for the iodine-Na<sub>2</sub>SO<sub>4</sub> solution with and without fibers were used to calculate the degree of crystallinity "DC" with eq. (3):

$$DC = 100 - \frac{37.925}{m} \left[ 1 - \frac{V_{\text{sample}}}{v_{\text{control}}} \right]$$

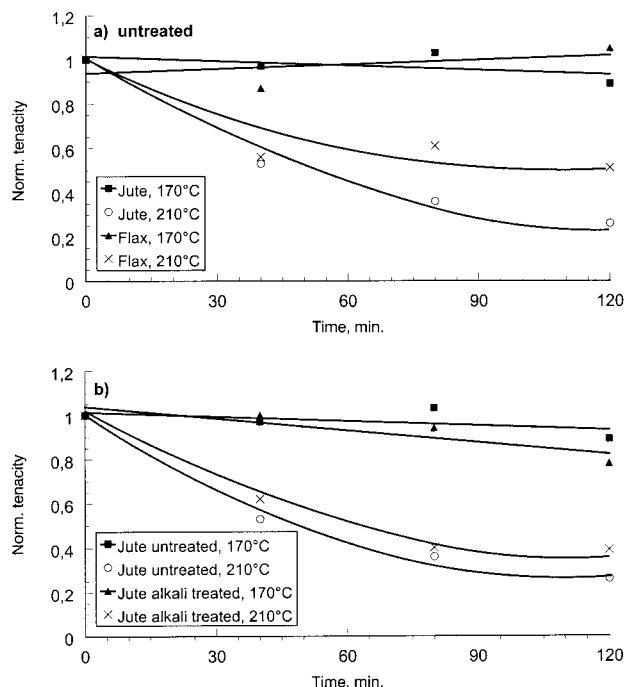
with  $m$  [g] as mass of the sample,  $V_{\text{sample}}$  [mL] and  $V_{\text{control}}$  [mL] as the used amount of a Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> titration solution for the iodine-Na<sub>2</sub>SO<sub>4</sub> solution with and without fibers. Three samples were investigated in each case, the standard deviation was at maximum 1%.

### Tensile Test

A DIN 53 834 yarn tensile test with a free span length of 500 mm and a test speed of 2 mm/min was used to measure the strength and tenacity of the yarns at ambient temperature. Ten samples were investigated, and in each case with a standard deviation below 15%.

## RESULTS AND DISCUSSION

It is known<sup>16</sup> that amorphous cellulose, as one part of natural fibers, form hydrogen bonds at 60°C and recrystallize at 150°C. Furthermore, differences in the thermal expansion coefficient of  $\alpha$ -cellulose, hemicellulose, and lignin can cause nonreversible damages and voids that can affect the physical properties of such fibers.<sup>17,18</sup> For exposure temperatures up to 170°C, both, recrystallization and the differences in thermal expansion coefficient seem not to be significant enough to have a markable influence on the tenacity of the investigated untreated jute and flax fibers [Fig. 1(a)]. Tenacity at 170°C measured for flax fibers was independent from the exposure time, while tenacity of jute fibers decreases at maximum 15% after an exposure of 120 min. Like jute fibers, the same trend was found by Hermann et al.<sup>13</sup> for ramie fibers with a drop of fiber strength of ap-



**Figure 1** Influence of exposure time and temperature on the normalized tenacity of (a) untreated jute and flax fibers, (b) untreated and alkali-treated jute fibers.

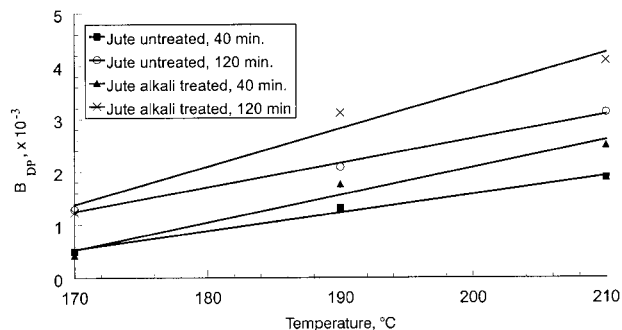
proximately 30% after an exposure of 2 h at 175°C.

For higher temperatures (above 170°C), a significant decrease in tenacity was measured for both types of fiber. Moreover, this decrease was higher for untreated jute than for untreated flax fibers, perhaps due to the greatly higher DP, cellulose content, and slightly higher crystallinity ratio of the flax fibers (Table I). It is well known that the fine structure affects the pyrolysis and other thermal characteristics of cellulose<sup>19</sup> and cellulose-based materials, i.e., the thermal stability increases with an increase in molecular weight<sup>20</sup> and crystallinity.<sup>6</sup>

Starting from a higher tenacity (Table I), the drop of the values measured by increasing time or temperature of alkali-treated jute fibers is similar to the results measured for the untreated ones [Fig. 1(b)]. Confirmed with the published data for linen fibers,<sup>21</sup> a slightly improved thermal stability of jute and linen fibers can be reached due to alkali treatment.

As mentioned before, a thermal exposure leads to chain scissions and depolymerization,<sup>5</sup> respectively, until DP is leveled off to one characteristic DP value for the exposure conditions used.<sup>7</sup>

In our case for the chosen exposure conditions, the degradation process regarding DP for both



**Figure 2** Influence of exposure time and temperature on broken bonds “ $B_{DP}$ ” for untreated and alkali-treated jute fibers.

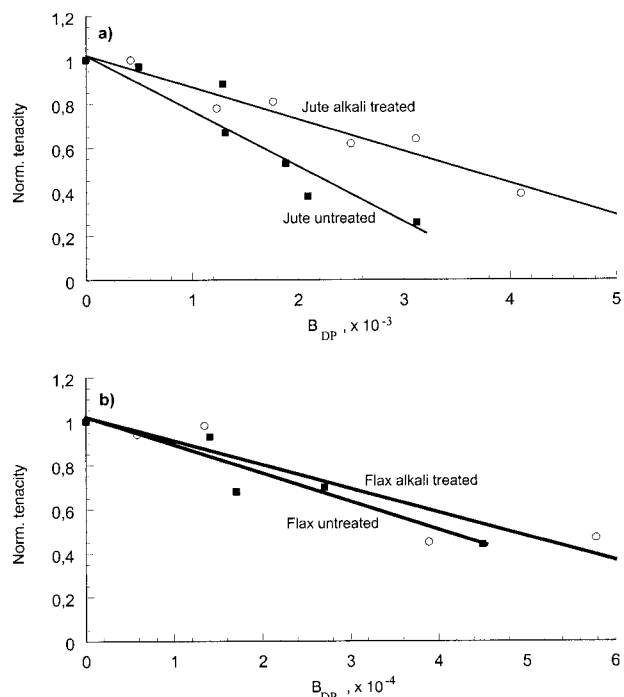
fibers was not complete after 120 min either at 170 or at 210°C.

In Figure 2, the experimental data are plotted in terms of percentage of the number of bonds that have been broken “ $B_{DP}$ ” vs. temperature of exposure for 40 and 120 min. This figure illustrates for both types of fiber and treatments a linear increase of “ $B_{DP}$ ” with increasing temperature. Similar to results on cotton fibers,<sup>6</sup> the rate of depolymerization of jute fibers is greater for the alkali treatment fibers.

These increased chain scissions due to thermal exposition typically lead to a higher crystallinity. This crystallization may result from an increase in the size of preexisting crystallites, by, for example, the realignment of cellulose chains on crystallite surface, or at their ends. It is also possible that the crystallization occurs by the formation of completely new crystallites within the amorphous areas. As assumption for this mechanism, the DP has to be smaller than a critical value, which was given for cotton about the DP = 460.<sup>5</sup>

**Table II** Influence of Exposure Time and Temperature on the Degree of Crystallinity DC (%) of Untreated and Alkali-Treated Jute Fibers

Treatment Conditions	Temperature (°C)	DC Time = 40 min	DC Time = 120 min
Untreated	23	68	68
	170	70	70
	190	66	72
	210	81	71
Alkali treated	23	65	65
	170	67	64
	190	68	71
	210	70	70



**Figure 3** Influence of broken bond “ $B_{DP}$ ” on the normalized tenacity of (a) untreated and alkali-treated jute fibers, (b) untreated and alkali-treated flax fibers.

By taking into account the DP of the untreated and alkali-treated jute fibers before exposition with 403 and 337, respectively, this mechanism discussed above could be the reason for the measured general increase of the DC (Table II).

From mechanical point of view, these higher DC values (up to 20%) have no remarkable effect on the mechanical properties of the fibers, as known from the structure–property relations published by Krässig for man-made cellulose fibers.<sup>11</sup> In contrast to this, the changes in DP have significant effects on the tenacity, as shown in Figure 3 for untreated and alkali-treated jute and flax fibers. As known from thermal aged cotton and photolyzed raw flax fibers,<sup>8</sup> the decrease of tenacity with increasing  $B_{DP}$  is typically linear over a wide range, similar to our results. Figure 3 further illustrates a good correlation between the changes in DP and the mechanical property by using eq. (3).

## CONCLUSION

A series of experiments has been conducted to determine the thermal degradation of untreated and alkali-treated jute and flax fibers. For these

investigations, the fibers were exposed to temperatures between 170 and 210°C for a maximum of 120 min. The exposed fibers have been mechanically tested in a yarn tensile test to measure the influence on tenacity. The effects on fiber fine structure were fixed by using degree of polymerization “DP” and degree of crystallinity “DC.”

In all cases both fibers showed none or only a slight decrease in tenacity and DP at temperatures below to 170°C. For temperatures above 170°C the tenacity as well as the DP decrease rapidly, and was depending on both exposure time and temperature. In general, a higher temperature or longer time of exposure led to an increase in level of depolymerization and to a drop in tenacity. For maximum exposure conditions used with a temperature of 210°C for 120 min, this drop in tenacity was found to be roughly 70%.

Because of chain scission due to this thermal treatment, an increase in DC with a maximum of 20% was found, but can be more or less neglected from a mechanical point of view as previously shown by Krässig for man-made cellulose fibers. In contrast, changes in DP were found to be very sensitive to the tenacity of the fibers. The broken bond empirical relation according to Testa et al. successfully fitted the observed changes in yarn tenacity by taking the broken bonds “ $B_{DP}$ ” into account.

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