Alkali Treatment of Jute Fibers: Relationship Between Structure and Mechanical Properties

JOCHEN GASSAN, ANDRZEJ K. BLEDZKI

University of Kassel, Institut für Werkstofftechnik-Kunststoff- und Recyclingtechnik, Mönchebergstrasse 3, 34109 Kassel, Germany

Received 16 January 1998; accepted 13 July 1998

ABSTRACT: The mechanical properties of tossa jute fibers were improved by using NaOH treatment process to improve the mechanical properties of composites materials. Shrinkage of fibers during this process has significant effects to the fiber structure, as well as to the mechanical fiber properties, such as tensile strength and modulus. Isometric NaOH-treated jute yarns (20 min at 20°C in 25% NaOH solution) lead to an increase in yarn tensile strength and modulus of ~ 120% and 150%, respectively. These changes in mechanical properties are affected by modifying the fiber structure, basically via the crystallinity ratio, degree of polymerization, and orientation (*Hermans factor*). Structure–property relationships, developed for cellulosic man-made fibers, were used with a high correlation factor to describe the behavior of the jute fiber yarns. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 623–629, 1999

Key words: natural fibers; alkali treatment; structure-property relationships

INTRODUCTION

Although, as with most of the other vegetable fibers, cellulose forms the main structural component of jute, the noncellulosic components (e.g., lignin and hemicellulose) also play an important part in the characteristic properties of the fibers. Jute hemicellulose—which is thought to consist principally of xylan, polyuronide, and hexosanhas been shown to be very sensitive to the action of caustic soda (2 h at room temperature), which exerts only a slight effect on lignin or α -cellulose.¹ Cold caustic soda solutions in any concentration, from 0.25 up to 20%, practically dissolve no lignin from the jute fibers; but, boiling caustic soda solutions, from 0.1 to 2% in strength, dissolve \sim 20% of it.¹ The hexosans of jute fibers can be removed by dilute NaOH in the cold much more easily than other constituents of the hemicellulose. 1

A newer paper² on the alkali treatment of jute fibers reports the removal of lignin and hemicellulose that affects the tensile characteristics of the fibers. When the hemicelluloses are removed, the interfibrillar region is likely to be less dense and less rigid, and thereby makes the fibrils more capable of rearranging themselves along the direction of tensile deformation. When jute fibers are stretched, such rearrangements among the fibrils would result in better load sharing by them, hence higher stress development in the fiber.^{1,2} On the other hand, softening of the interfibrillar matrix adversely affects the stress transfer between the fibril and, thereby, the overall stress development in the fiber under tensile deformation. As lignin is removed gradually, the middle lamella joining the ultimate cells is expected to be more plastic, as well as homogeneous, due to the gradual elimination of microvoids, whereas the ultimate cells themselves are only slightly affected.²

Correspondence to: J. Gassan (kutech@hrz.uni-kassel.de). Journal of Applied Polymer Science, Vol. 71, 623–629 (1999) © 1999 John Wiley & Sons. Inc. CCC 0021-8995/99/040623-07

Furthermore, some authors $^{3-5}$ report on the $\operatorname{coir}^{3,4}$ and flax^5 fiber changes in crystallinity through alkali treatment. The increase in the percentage of crystallinity index of alkali-treated fibers occurs because of the removal on the cementing materials, which leads to a better packing of cellulose chains.³ Additionally, treatment with NaOH leads to a decrease in the spiral angle and increase in molecular orientation dependent on shrinkage state. A fair amount of randomness is introduced in the orientation of the crystallites due to the removal of noncellulosic matter.⁴ The elastic moduli of natural fibers, for instance, are expected to increase with an increasing degree of molecular orientation. Welloriented cellulosic fibers, such as flax have a much higher Young's modulus than fibers with medium orientation, such as cotton.⁶ In addition to the modification of orientation and the consolidation of weak points, other important factors with regard to the mechanical properties could be the crystallite length and degree of crystallinity, as well as the removal of fractions of cellulose of a very low degree of polymerization.⁷

The elastic properties of natural fibers may be predicted by recognizing the structural features of the cell walls in applying micromechanical theories. One of the first theories is published from Hearle,⁸ followed by some theories based on the classical lamination theory (Cave, 1968; Mark, 1972; Schniewind, 1972).⁹ These models take into account the spiral angle of the cellulose fibrils and the content of cellulose and noncrystalline regions.

On the other hand, properties such as fiber strength are significantly influenced by crystallinity of the fibers, length of their crystallites, and the orientation of crystallites with respect to the fiber axis and others.^{10,11} Krässig¹² used this fact to develop empirically based structure-property relationships for man-made cellulosic fibers, such as different rayon fiber types and cotton, as well as to discuss the strength degradation of raw flax fibers due to an acid hydrolysis.¹³ Furthermore, the strength of other cellulose-based natural fibers, such as ramie^{14,15} or banana fibers,¹⁶ was similarly affected by these structural features and was successfully correlated by taking into account the average fiber degree of polymerization^{14,15} or Hermans factor and cellulose content.¹⁶

EXPERIMENTAL

Used Materials and Fiber Treatment

Tossa jute fiber yarns from J. Schilgen GmbH & Co., with a fineness of ~ 280 tex and a tenacity of 13.5 cN/tex, were used for this study.

With pretreatment, the fibers were dewaxed in methanol-benzene (1:1) for 24 h to remove the weaving size (potato starch and waxes). Alkali treatment was conducted by treating the fiber samples with different solutions with NaOH concentrations up to 28 wt % for maximum 30 min at two different temperatures (20°C and 50°C, respectively), followed by washing the fibers in distilled water, neutralization with 2 wt % sulfuric acid, washing again, and drying.¹⁷

Used Methods

A yarn tensile test (according to DIN 53 834), with a free span length of 500 mm and a test speed of 2 mm min⁻¹, was used to measure the modulus and strength of the untreated and alkali-treated jute fiber yarns at ambient temperature. Ten samples were investigated; in each case, the standard deviation was at a maximum of 15%.

The crystallinity ratio, CrR, was investigated according to the method of Ant-Wuorinen and Visapää, which is described in detail elsewhere.^{12,18} By this method, the crystallinity is calculated by the ratio between the crystalline scatter of the (002) reflection, Crh, with the height of the "amorphous reflection," Amh [eq. (1)].

$$CrR = 1 - \frac{Amh}{Crh} \tag{1}$$

The average *degree of polymerization* of the whole fiber, as a typically used value to characterize cellulose-based natural fibers,^{13,15} was determined by the Ubbelohde viscometric method¹⁷ with a standard Cuoxam solution. The *DP* was calculated with eq. (2):

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

with $\eta_{sp} = \frac{t}{t_0} - 1$
for $0.1 < \eta_{sp} < 0.2$ (2)



Figure 1 Influence of treatment time and temperature on the shrinkage of jute fiber yarns due to NaOH treatment (28 wt % NaOH solution).

where $\eta_{\rm sp}$ is the specific viscosity, *c* is the concentration, *t* is the time of flow of the jute-cuoxam solution, and t_0 is the time of flow of the neat cuoxam solution itself.

X-ray investigations were done¹⁹ by using a Siemens-Diffraktometer D5000 in symmetrical transmission. The Hermans factor, as a value for the chain orientation of the crystallites with respect to fiber axis, was estimated from the (004) interference of oriented fiber bundles.

Scanning electron microscopic investigations were performed compare the fracture behavior of untreated and alkali-treated fibers.

RESULTS AND DISCUSSION

Physical Properties

The influence of NaOH treatment time on the shrinkage of jute fiber yarns at different temperatures is shown in Figure 1. It was observed that the rate of the reaction for both temperatures is very fast, within $\sim 5-7$ min. The major portion of the reaction seems to be completed after a maximum of 15 min. MacMillan and colleagues²⁰ also observed comparable results for jute fibers for the loss in weight as a function of the treatment time for different treatment temperatures (22°C up to boil) and concentrations (1 up to 10 wt % NaOH). They discussed that, during the rapid initial period of reaction, acetyl groups—together with a small portion of the hemicellulose—are attacked and removed.

Treatments with strong concentrated alkali solutions, as in Figure 1 with 28 wt % NaOH, are more drastic than in the case of the investigations from MacMillan and colleagues.²⁰ Therefore, additionally, effects like breakages of bonds along with a pronounced disorientation effect are typical.²¹

The NaOH treatment leads to further changes in mechanical properties of the fibers, such as tensile modulus and tensile strength (Fig. 2 for jute) independent of shrinkage during alkali treatment and other treatment parameters. According to Roy²¹ and Zeronian,²² for jute and cotton fibers, respectively, these changes are possible due to interacting factors such as:

- 1. rupture of alkali-sensitive bonds existing between the different components of the fiber as a result of swelling and partial removal of the hemicellulose; the fiber becomes more homogeneous through microvoid elimination (e.g., the stress transfer between ultimate cells improves)^{2,21,22}
- 2. formation of new hydrogen bonds between certain cellulose chains due to the removal of hemicellulose, which normally separates the cellulose chains; this may also occur as a result of the release of initial strains and subsequent readjustments to the chains after intracrystalline swelling action, thus resulting in a probable change in the orientation of noncrystalline cellulose^{21,22}
- 3. change in the parts of crystalline cellulose^{21,22}
- 4. changes in the orientation of molecular chains.^{21,22}

It is well-known from results of mercerized cotton fibers,⁶ for instance, that Young's modulus or tensile strength in the direction of the fiber axis



Figure 2 Influence of shrinkage during the alkalization process on the modulus and strength of jute fiber yarns (25 wt % NaOH, treatment time = 20 min, treatment temperature = 20° C).



(a)



(b)

Figure 3 Influence of fiber shrinkage during NaOH treatment on the fracture behavior of jute fiber yarns (26 wt % NaOH, treatment time = 20 min, treatment temperature = 20° C). (a) Slack conditions. (b) Isometric conditions.

increases with increasing mercerizing stretch, because of a reduction of interfiber differences in mechanical properties due to reducing interfiber differences in orientation.⁶ A comparable behavior, as was discussed for these cotton fibers, was found for NaOH-treated jute fiber yarns (as shown in Fig. 2).

In comparison with untreated fibers, this distinctly improved yarn modulus (150%) and strength (120%) in the case of isometric NaOHtreated yarns was based on the above factor of 1 to 4, as well as on the change in geometric shape and dimensions of the fiber (reduced in diameter to $\sim 28\%$), which is typical² of these treatment conditions. Furthermore, these changes in fiber structure because of NaOH treatment under different shrinkage states lead to alternated fracture behavior (as shown in Fig. 3). For the NaOH-treated yarns under slack conditions [Fig. 3(a)], longer pull-outs of cellulose microfibrils from the hemicellulose/lignin matrix, as is the case for isometric conditions, are characteristic.

Fiber Structure

Depending on the applied tension on the fiber during NaOH treatment, various effects—such as changes in the crystalline modification of cellulose (I to II), changes in geometric shape and dimensions, changes in degree of crystallinity and degree of polymerization, as well as changes in fibrillar orientation—are possible.

Many authors^{3-6,21,22} reported changes in crystallinity through alkali treatment for coir,^{3,4} flax,⁵ jute,²¹ and cotton^{6,22} fibers. An increase in the crystallinity ratio CrR, from 81% for the untreated fibers to CrR = 85% (Fig. 4), occurs (according to Varma and colleagues³) because of the removal of the cementing material (lignin and hemicellulose), which probably leads to a better packing of cellulose chains. In earlier published results,¹⁷ the removal of hemicellulose (from 28 wt % to 17 wt % and for lignin from 11 wt % to a value of 4 wt %) was given for the same jute fibers under the same treatment conditions.

The tension applied to the cellulosic material, whether stretching or limiting the possibilities of shrinkage, plays a fundamental role with regard to the transformation of crystalline structure. Further, if tension is applied during treatment process, swelling of the cellulose structure is impaired, and the conversion of the crystal lattic to



Figure 4 Influence of shrinkage during the alkalization process on the crystallinity ratio CrR of jute fiber yarns (25 wt % NaOH, treatment time = 20 min, treatment temperature = 20° C).



Figure 5 Influence of shrinkage during the alkalization process on the degree of polymerization and *Hermans factor* f_r of jute fiber yarns (25% NaOH, treatment time = 20 min, treatment temperature = 20°C).

cellulose II is incomplete.²³ The ratio of conversion of cellulose I to cellulose II, for cotton⁷ and in general²⁴ for investigated jute¹⁷ fibers, is more pronounced when the applied tension is lower. The investigated slack and isometric NaOH-treated jute fibers showed¹⁷ a cellulose I : cellulose II ratio of 87 : 13 and 97 : 3, respectively.

With respect to crystallinity, the tension through treatment also plays an important role in the case of the tested jute fibers, which is in contrast to the observations for cotton fibers.⁷ Shrinkage during NaOH treating process affects the crystallinity ratio CrR, with ~ 20% between the minimum and maximum CrR value. For cotton fibers,⁷ with a distinctly higher transformation ratio, the crystallinity of cellulose I with increasing fiber length variation increases; the total crystallinity decreases in comparison. For the used jute fibers with only their small transformation ratios, it is perhaps dominated by the behavior of cellulose I, which is responsible for the decrease in crystallinity ratio CrR with higher shrinkage degrees (Fig. 4). The average degree of polymerization DP of the jute fibers seemed to decrease, compared with $DP \approx 400$ for untreated fibers, more or less slightly in the dependence on shrinkage when alkalized (Fig. 5) what is already known from (slack and tension) mercerization of cotton fibers.²³ In contrast to the observations by alkali treatment of cotton fibers with a cellulose content for untreated ones up to 94 wt %⁶, degradation of the degree of polymerization of jute fibers due to alkali action is combined with distinctly redamptions of low molecular weight products, such as hemicellulose.

Additionally, dependent on shrinkage state, a change in orientation (*Hermans factor*) was ob-

served for jute fibers (Fig. 5). Isometric and slack conditions lead to changes of *Hermans factor*, from 0.943 for the untreated fibers to 0.954 and 0.937, respectively. Sreenivasan and colleagues⁴ and Shelat and colleagues⁶ published similar general tendencies for coir and cotton fibers, respectively. Sreenivasan and colleagues⁴ discussed their observations with the influence of the removal of intracellular inclusions (e.g., the noncellulosic hemicellulose) due to the alkali attack.

Correlation Between Fiber Structure and Properties

For cellulosic man-made,^{12,25} cotton,^{6,26} ramie,^{14,15} banana,¹⁶ and jute⁶ fibers, respectively, many authors^{6,12,14–17,25,26} showed that changes in mechanical properties can be attributed almost exclusively to changes in crystallite orientation^{6,12,16,17,25,26} (*Hermans factor*), the average fiber degree of polymerization,^{14,15} and cellulose content.¹⁶ An obvious flaw was found in correlating mechanical properties, such as static Young's modulus with a crystallite orientation factor.^{6,12,16,17,25,26} Tripp and colleagues²⁷ reported that the strength of the cotton fibers was related to a number of supermolecular structural factors, especially to the average fiber molecular chain length and crystallite orientation.

With respect to more general relations between mechanical properties and structure of cellulosebased fibers, Krässig¹² published cellulosic manmade fiber coherences [eq. (3)] for tensile strength by taking into account the crystallinity ratio CrRand Hermans factor f_r .

$$\sigma \propto CrRf_r^i \tag{3}$$

In the case of dry rayon fibers, the exponent i was given by 2, and in the case of wet fibers by



Figure 6 Correlation between the crystallinity ratio CrR and *Hermans factor* f_r and the tenacity of NaOH-treated jute fiber yarns.



Figure 7 Correlation between degree of polymerization DP, LODP, crystallinity ratio CrR, and *Hermans factor* f_r , and the tenacity of NaOH-treated jute fiber yarns.

2.5. Using eq. (3) to formulate the materials behavior of treated jute fiber yarns, a good agreement with experimental data (correlation factor of 87%) was found (Fig. 6). Krässig¹² further described the tensile behavior of various man-made fibers by eq. (4).

$$\sigma \propto \left[\frac{1}{DP} - \frac{1}{LODP}\right] CrRf_r^{2.5}$$
(4)

This equation explains that strength is dependent on the length of the fiber-forming (cellulose) molecules (DP) in relation to the length of the elementary crystallites (LODP) forms the structure network of the fiber, on the perfection of lateral order CrR and on the degree of orientation f_r .

Similar to published results of cellulosic manmade fibers, the tenacity of the NaOH-treated jute fiber yarns increases with increasing product of the structural parameters according to eq. (4) (Fig. 7). The correlation factor with 66% is not as good as the data fitting by eq. (3). Thus, the additional structural feature, the degree of polymerization, has no effect with regard to the correlation effectivity.

CONCLUSIONS

The mechanical properties of tossa jute fibers were influenced by using the NaOH treatment process. Shrinkage of fibers during this treatment had significant influences on the fiber structure (crystallinity ratio, degree of polymerization, and *Hermans factor*), as well as on the mechanical fiber properties, such as tensile strength and modulus. Isometric NaOH-treated jute yarns (20 min at 20°C in 25 wt % NaOH solution) lead to an increase in yarn tensile strength and a modulus of $\sim 120\%$ and 150%, respectively. Under slack conditions, the mechanical properties are up to 10% of the values of untreated yarns.

These changes in mechanical properties are affected by modifying the fiber structure basically *via* the crystallinity ratio, degree of polymerization, and orientation (*Hermans factor*).

Due to the alkali action under isometric conditions, the crystallinity ratio slightly increases from 81% to 85%. Higher shrinkage rates reduce the crystallinity ratio to values of 60% in the slack state. The degree of polymerization decreased, compared with untreated values more or less slightly dependent on the shrinkage state. The isometric and slack alkalization of the jute fibers led to further changes of *Hermans factor*, from 0.943 for untreated fibers to 0.954 and 0.937, respectively. *Hermans factor* correlated linearly with fiber shrinkage, whereas higher shrinkage conditions resulted in a lower orientation.

Structure-property relationships, developed for cellulosic man-made fibers, were used with a high correlation factor to describe the behavior of jute fiber yarns. Correlations, with a correlation factor of 87%, were reached by using eq. (3).

The authors wish to express their gratitude to Dr. H.-P. Fink at the Fraunhofer-Institut für Angewandte Polymerforschung, Teltow (Germany) for X-ray investigations. We also thank J. Schilgen GmbH & Co. for providing the jute fibers.

REFERENCES

- Sarkar, P. B.; Mazumdar, A. K.; Pal, K. B. J Text Inst 1948, 39, T44.
- Mukherjee, A.; Ganguly, P. K.; Sur, D. J Text Inst 1993, 84, 348.
- Varma, D. S.; Varma, M.; Varma, I. K. Text Res Inst 1984, 54, 349.
- Sreenivasan, S.; Bahama Iyer, P.; Krishna Iyer, K. R. J Mater Sci 1996, 31, 721.
- Sharma, H. S. S.; Fraser, T. W.; McCall, D.; Lyons, G. J Text Inst 1995, 86, 539.
- Shelat, B. R.; Radhakrishnan, T.; Iyer, B. V. Text Res J 1960, 33, 836.
- Freytag, R.; Donzé, J.-J. in Handbook of Fiber Science and Technology, M. Lewin, Ed., Marcel Dekker, Inc., New York, 1983.
- 8. Hearle, J. W. S. J Appl Polym Sci 1963, 7, 1635.

- Salmén, L.; de Ruvo, A. Wood Fiber Sci 1985, 17, 336.
- Zeronian, S. H.; Kawabata, H.; Alger, K. W. Text Res J 1990, 60, 179.
- Fink, H.-P.; Ganster, J.; Fraatz, J.; Nywlt, M. in Proceedings of the Akzo-Nobel Viscose Chemistry Seminar Challenge in Cellulosic Man-made Fibres, Stockholm, May 30–June 3, 1994.
- Krässig, H. A. Cellulose—Structure, Accessibility and Reactivity, Gordon and Breach Science Publishers, Yverdon, 1993.
- Testa, G.; Sardella, A.; Rossi, E.; Bozzi, C.; Seves, A. Acta Polym 1994, 45, 47.
- 14. Meredith, R. The Mechanical Properties of Textile Fibers, North-Holland Publishing Company, Amsterdam, 1956.
- Cabradilla, K. E.; Zeronian, S. H. J Appl Polym Sci 1975, 19, 503.
- 16. Bhama Iyer, P.; Vivekanandan, M. V.; Sreenivasan, S.; Krishna Iyer, K. R. Indian Text J 1995, 42.

- Gassan, J. Dissertation at the Institute of Materials Engineering, University of Kassel, Kassel, Germany, 1997.
- Richter, U.; Krause, T.; Schempp, W. Die Angewandte Makromolekulare Chemie, 1991, 185/186, 155.
- 19. Fink, H.-P.; Walenta, E. Das Papier, 1994, 48, 739.
- MacMillan, W. G.; Sen Gupta, A. B.; Majumdar, S. K. J Text Inst 1954, 45, T703.
- 21. Roy, M. M. J Text Inst 1953, 44, T44.
- Zeronian, S. H. in Cellulose Chemistry and Its Applications, T. P. Nevell and S. H. Zeronian, Eds., Ellis Horwood Limited, Chichester, 1985.
- Zeronian, S. H. J Appl Polym Sci Appl Polym Sym 1991, 47, 445.
- 24. Barkakaty, B. C. J Appl Polym Sci 1976, 20, 2921.
- Lenz, J.; Schurz, J.; Wrentschur, E. Colloid Polym Sci 1993, 271, 460.
- 26. Rebefeld, L. Text Res J 1958, 28, 462.
- Tripp, V. W.; Orr, R. S.; Ziifle, H. M.; Conrad, C. M. Text Res J 1958, 28, 404.