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Anisotropy of Swelling of Jute

S. C. Roy

Indian Jute Mills Association Research Institute, Calcutta, India

INTRODUCTION

The most obvious method for determining the noncrystalline orientation of a fiber is that of swelling in water which is applicable primarily to amorphous chain molecules. The method is based on the assumption that the swelling agent penetrates between the chains and pushes them across their length so that the magnitude of the swelling vectors across and along the fiber axis are determined solely by their alignment relative to the axis. If B and L are measures of specific lateral and longitudinal swelling, the anisotropy of swelling $Q(= B/L)$ can be taken as an expression for the average orientation of the noncrystalline components of the fiber, and as is the case with optical and x-ray orientation factors, a swelling orientation factor, f_s (say), can be derived from Q, viz.,

$$f_s = (Q - 1)/(Q + 1/2)$$

following Hermans and Platzek.[1,2]

The chief merit of the method based upon the anisotropy of swelling is its great simplicity, as the method requires only measurements of length and breadth of the fiber. It has been observed that the anisotropy of swelling of objects similarly produced provides a certain measure of orientation, and the method leads to useful results. But the assumption on which the computation is based has been questioned on the grounds that the mechanism of swelling does not fit in with the simple representation of anisotropically swelling, independent particles, for the chain molecules are everywhere interconnected, and secondly, at least a part of the water absorption in the amorphous regions of a cellulose fiber is to be likened to that in a molecular felt structure.[2]

The restriction arising from nonindependence of the swelling particles would obviously lead to a reduction in swelling, and evidences are on record that both absorption and swelling volume are considerably reduced by crosslinking treatments of celluloses.[3,4] But there is no indication to suggest that these treatments, which are assumed to increase the degree of interlinking, affect the two swelling components in unequal proportions. On the other hand, if one is allowed to regard native (untreated) jute as a crosslinked cellulose fiber and the process of delignification as a means of reducing the degree of crosslinking, a proportionate increase in the diameter and longitudinal swelling of delignified jute, reported in our previous communication,[5] would evidently indicate that the nonindependence of the swelling units does not necessarily invalidate the principle underlying the method of swelling anisotropy.

A similar conclusion can also be drawn in regard to the other objection. It is conceivable that a felt-like structure of the type suggested would contribute increasingly to absorption and swelling with increasing vapor pressure, reaching a maximum at saturation vapor pressure or wetting. But this factor need not necessarily influence the relative values of the two swelling components. This will be evident from an analysis of Collins' data for transverse and axial swelling of cotton[6] as presented in Table I. It is seen that the value of swelling anisotropy is more or less constant throughout the entire range of relative humidity, 0–100%.

The above discussion is not meant to imply that the method should be universally applicable. The results reported by Hermans for model filaments indicate, rather, that the method might be suitable only for highly oriented fibers. Hermans[2] has given values for the swelling anisotropy of these materials from which the corresponding swelling orientation factors can be calculated and compared with the respective x-ray and optical orientation factors recorded by him. This is shown in Table II. It will be seen that as the orientation increases, the divergence between f_s and f_x or f_o, particularly the former, decreases, tending to show that there is a lower limit of orientation for the applicability of the method. In this regard one

TABLE I
Dependence of Swelling Anisotropy of Cotton on Moisture Adsorption (Calculated from Collins' data[6])

Relative humidity, %	Specific swelling (mean of absorption and desorption) Diameter B	Axial L	Swelling anisotropy Q
0	0	0	—
30	0.040	0.0019	21.1
60	0.072	0.0033	22.4
80	0.094	0.0059	15.9
90	0.128	0.0061	21.0
97	0.151	0.0075	20.1
100 (water)	0.209	0.0112[a]	18.0

[a] Absorption only.

would, however, expect that the correspondence should have been better between f_s and f_o than between f_s and f_x.

TABLE II
Comparison of Swelling (f_s), Optical (f_o), and X-Ray (f_x) Orientation Factors of Model Filaments[a]

Materials		X-ray orientation factor f_x	Optical orientation factor f_o	Swelling orientation factor f_s
X Filaments	1	0.063	0.035	—
	2	0.37	0.275	0.681
	3	0.73	0.61	0.875
	4	0.89	0.79	0.923
	5	0.90	0.905	0.93
F Filaments	1	0.085	0.035	—
	2	0.25	0.185	—
	3	0.63	0.44	0.805
	4	0.785	0.64	0.88
R Filaments	1	—	—	—
	2	0.013	0.03	—
	3	0.175	0.09	—
	4	0.425	0.225	—
	5	0.69	0.42	0.72

[a] f_x, f_o are values of Hermans;[2] f_s calculated from Q values of Hermans.[2]

In view of this and the observation that the crystalline and noncrystalline components of a highly oriented fiber, such as ramie, are in the same state of orientation,[2] it would be worthwhile to measure the swelling orientation factors of native, disoriented, and reoriented ramie and compare them with the respective x-ray or optical orientation factors as reported by Hermans for these materials. In applying the method to the study of the orientation characteristics of similar preparations of jute, one should, however, take into account that factors other than those considered for pure cellulose fibers may influence the swelling anisotropy of this fiber. For example, there is a strong indication that an extrastructural hemicellulosic contribution to diameter swelling weights the swelling anisotropy of jute, and the same is affected in varying degrees by the loss of material on treatment with alkali.[5] The alkali treatment is also known to hydrolyze certain intermolecular bonds in the structure of jute. Although this leads to an enhanced overall swelling of the fiber, we can assume that so far as its influence on the two swelling components is concerned, the effect is the same as of delignification, viz., there is a proportionate increase in transverse and longitudinal directions.[5]

EXPERIMENTAL

The starting materials for this experiment were defatted jute and purified ramie. In order to induce maximum disorientation, the fibers were allowed to swell freely in mercerizing concentration of caustic soda solution, e.g., 17% for $^1/_2$ hr. at 78 ± 2°F., and were then washed and air-dried. The reoriented samples were prepared by stretching the optimum alkali-saturated fibers to various extents, the degree of stretching being measured by the percentage of the initial length recovered. Each sample consisted of a bundle of parallel fibers mounted on a stretching frame and washed and air-dried in the stretched state. It is noted that while ramie can be restored to the original length, about 4% shrinkage has to be allowed to jute to prevent fiber breakage. The samples of progressively delignified jute and those of jute and ramie pretreated with a range of caustic-soda solutions were prepared in the same way as those described more fully in a previous report.[5]

The measurements of the diameter and longitudinal swelling of the single fiber specimens were made relative to the laboratory conditions of 65–67% R.H., the former by the microscope and the latter by the extensometric method as described earlier.[5] The x-ray photographs were taken with CuKα radiation at 30 kv. and 20 ma.

RESULTS AND DISCUSSION

Native, Disoriented, and Reoriented Ramie

The swelling orientation factors for native, disoriented, and reoriented ramie fibers as calculated from the corresponding anisotropy values are shown in Table III. The x-ray and optical orientation factors, f_x and f_o, respectively, available in the literature for these materials[2,7] are included in Table III for comparison. It will be seen that the f_s values for native and disoriented ramie are very nearly the same as the corresponding f_o or f_x values. This means that if we accept the crystalline and noncrystalline components of the fibers to be in the same state of orientation, as has been concluded by Hermans from a comparison of their optical and x-ray orientation factors, the agreement between f_s and f_o or f_x would clearly indicate that the swelling orientation factor, f_s, can be taken as correctly representing the oriented state of the noncrystalline components. It can also be used as an expression for the crystalline orientation of the fibers. Accordingly, the observation that the swelling anisotropy leads to too high an orientation factor does not seem to apply to these cases.[2]

TABLE III
Swelling (f_s), Optical (f_o), and X-Ray (f_x) Orientation Factors of Native, Disoriented, and Reoriented Ramie and Jute

Materials	Degree of restoration of original length, %	Swelling orientation factor f_s	Optical orientation factor f_o	X-ray orientation factor f_x
Native ramie	—	0.966	0.97[a]	0.97[a], 0.96[b]
Disoriented ramie	—	0.891	0.92[a]	0.90[a]
Reoriented ramie, original length restored	84	0.994	—	—
"	86	0.996	—	—
"	88	1.000	—	—
"	90	1.006	—	—
"	92	1.010	—	—
"	96	1.018	—	—
"	100	1.018	0.98[a]	0.98[a]
Native jute	—	0.996	—	0.96[b]
Disoriented jute	—	0.978	—	—
Reoriented jute, original length restored	87.0	0.989	—	—
"	89.7	0.995	—	—
"	92.0	0.997	—	—
"	96.0	1.005	—	—

[a] Data of Hermans.[2]
[b] Data of Sen and Woods.[7]

The same results (Table III), however, show that the f_s values for the reoriented samples of ramie are much higher than the corresponding f_o or f_x values, except for the first stage of stretching at which $f_s = 0.994$ as against $f_o = f_x = 0.98$. This would suggest that the method is not suitable beyond a certain limit of orientation. As we have seen (Introduction) there is no reasonable agreement between f_s and f_o or f_x below a given degree of orientation, it follows that the applicability of the method must have been confined to a narrow range of orientation. However, in so far as the swelling orientation factor f_s is derived from the ratio of the diameter to the longitudinal swelling, it is of interest to inquire into the changes which occur in the swelling components when the native fiber is disoriented and the disoriented fiber is reoriented. These results are represented in Figure 1. It will be seen that the longitudinal swelling of both jute and ramie decreases continually with tension, eventually passing on to the negative values, i.e., shrinkage, and the effect is more pronounced in ramie than in jute. The diameter swelling, on the other hand, first rises to a maximum in either fiber and then gradually diminishes in ramie but maintains a steady value in jute. It is to be noted that the value of f_s is more critically dependent on the longitudinal than on the diameter swelling and it equals unity or exceeds it according as the longitudinal swelling is zero or negative. Since the values of $f_s \geqq 1$ have no counterparts in optical or x-ray measurements, one would imagine that after a certain stage the stretching operation does not induce any additional orientation but sets the network in a metastable state and leads to the formation of new junction points in various low order regions. The former is indicated by positive shrinkage in pure water and the latter is suggested by the continual decrease of diameter swelling. (Here the discussion is confined to ramie only, since the case of jute is more involved.) This results in an upper limit to the orientation in which the fiber must be in order that the swelling method is applicable to it. One can tentatively regard this orientation to correspond to the maximum in the diameter swelling curve, the start of decrease in diameter swelling being assumed to signal the advent of an extra-orientation factor, i.e., the formation of new junction points. This gives a value of $f_s = 0.994$ as against $f_o = f_s = 0.98$ reported for the maximum re-

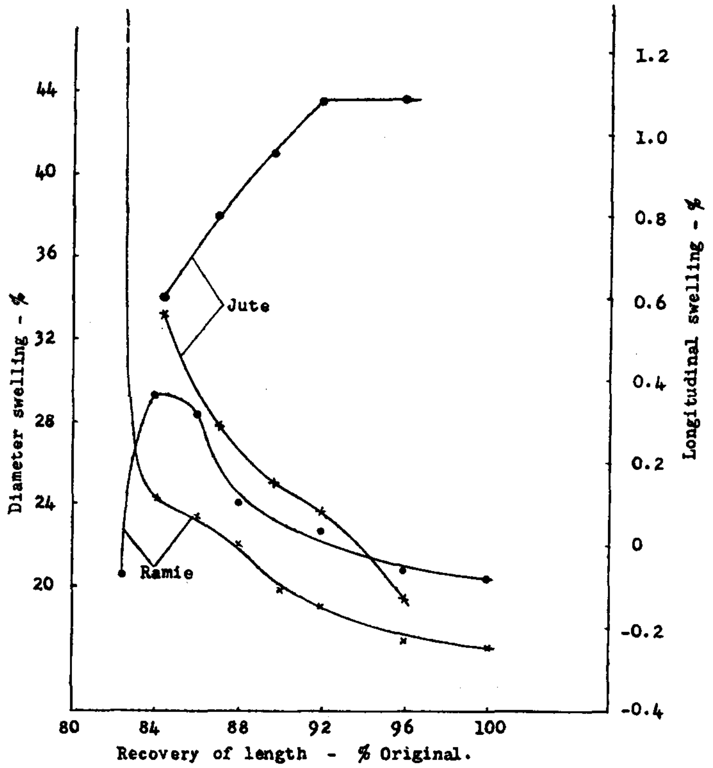


Fig. 1. Swelling of reoriented jute and ramie: (●) diameter swelling; (×) longitudinal swelling.

oriented ramie. It should be pointed out, however, that this limitation is actually associated with additional crosslinking and one would be inclined to imagine that the two limits of the range are fixed by crosslinking on the upper side and felt structure on the lower.

Native, Disoriented, and Reoriented Jute

It is seen from Table III that the values of f_s for native, disoriented, and reoriented jute are much higher than those for the corresponding samples of ramie. This would suggest that, compared to ramie, the noncrystalline orientation of jute is quite high. This is partly true, for although the published x-ray data[7] indicate an almost equal orientation for native jute and native ramie (Table III), the microscopic evidence is in favor of a steeper fibrillar arrangement in jute,[8] and a comparison of the x-ray photographs of the samples of jute and ramie used in these experiments also suggests that the crystalline orientation of native or disoriented jute is higher than that of similar samples of ramie. (It is to be noted here that jute is not completely mercerized under normal conditions of alkali treatment,[9,10] and we have observed[11] that incomplete mercerization of jute is associated with lower shrinkage and probably also lower disorientation.) But the difference in orientation between jute and ramie may not be as much as is indicated by the difference in their f_s values, and we know that factors other than the alignment of the chain molecules may influence the diameter swelling of jute and thereby increase the value of swelling anisotropy.[5] Considering, however, that there is a measurable change in the value of f_s when native jute is disoriented and disoriented jute is reoriented, the swelling method can be usefully employed in studying the changes in orientation of this fiber.

Delignified and Alkali-Treated Jute

The variation in the swelling anisotropy Q of jute and ramie on pretreatment with a range of caustic-soda solutions is represented in Figure 2, and that of jute on progressive delignification in Figure 3. Here we use Q instead of f_s in consideration of the greater sensitivity of the former at the higher range of orientation. In order to facilitate a visual comparison of the crystalline orientation of native and dilute (5%) alkali-treated jute and those of mercerized jute and mercerized ramie, the corresponding x-ray photographs are shown in Figures 4 and 5. The following points are noted. The

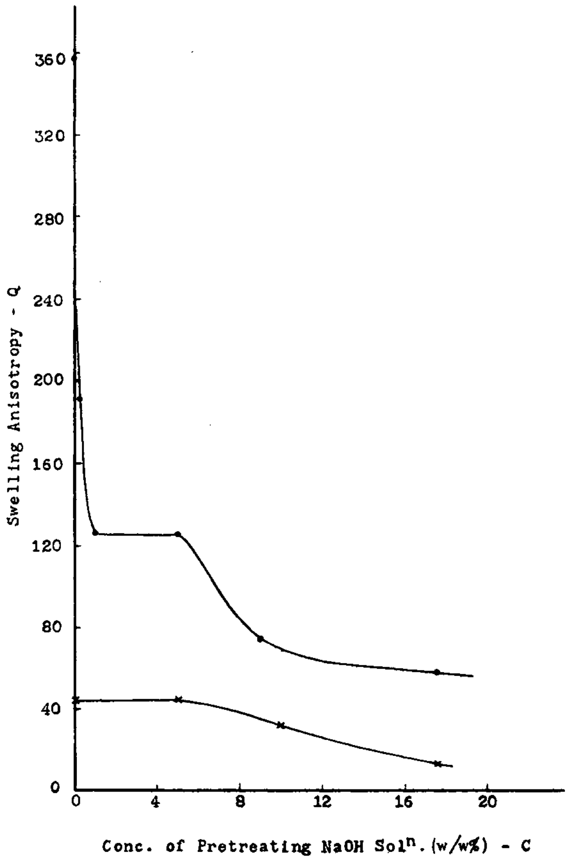


Fig. 2. Variation of Q with pretreating alkali concentration: (●) jute; (×) ramie.

swelling anisotropy of defatted jute is appreciably reduced on treatment with very dilute (0.2%) alkali, whereas that of purified ramie is not affected until the treating solution is of mercerizing concentra-

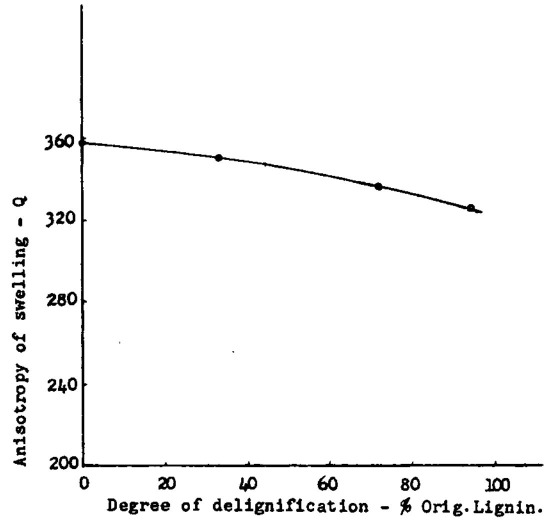
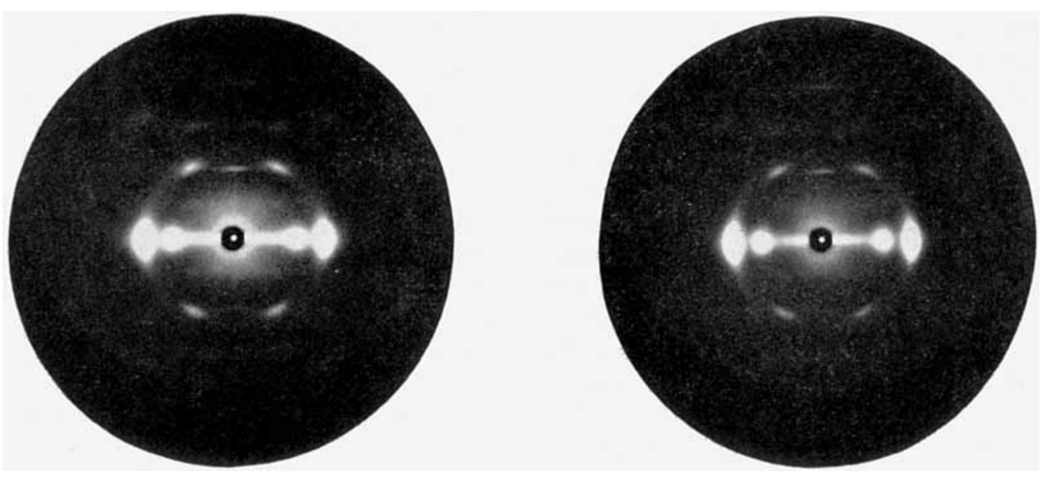


Fig. 3. Variation of Q with delignification.

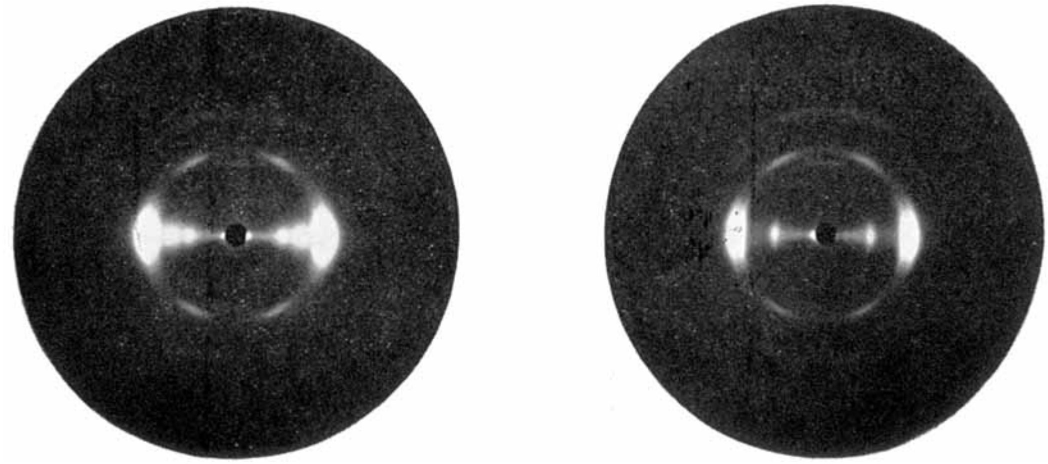
tion (Fig. 2). The dilute alkali treatment also leads to a certain disorientation of the crystallites of jute (Fig. 4). On the other hand, compared to ramie, both noncrystalline and crystalline orientations are higher in mercerized jute (Table III and Figs. 2 and 5). Figure 3 shows that delignification has no marked effect on either crystalline or noncrystalline orientation of jute. A reference to our earlier communication[5] will show that the delignified jute has enhanced swelling in both transverse and longitudinal directions, but the increases in the two components are in equal proportions.

The disorientation in both crystalline as well as noncrystalline regions of jute on dilute alkali treatment appears to be an interesting result. It indicates a difference in structure of the fiber from



(a) (b)

Fig. 4. X-ray photographs of (*a*) native jute; (*b*) jute treated with 5% NaOH.



(a) (b)

Fig. 5. X-ray photographs of (*a*) mercerized jute; (*b*) mercerized ramie.

that of ramie. While no permanent effect is observed in ramie unless the crystalline regions are disturbed by treatment with mercerizing concentration of alkali, treatments usually supposed to be confined to the noncrystalline regions only influence the crystalline orientation of jute. We have seen elsewhere that ramie undergoes a positive shrinkage in premercerizing alkali,[11] but it is not known if the same is associated with any disorientation. If, however, a certain disorientation is presumed, it must be completely reversible on washing out of the alkali. On the other hand, it may be mentioned in this connection that the crystalline orientation of ramie can be markedly influenced, being improved if the fiber, while swollen in dilute alkali, is stretched and subsequently washed and air-dried in the stretched state; a similar though less marked effect is also observed in pure water. The corresponding effects are less marked in jute.

A lower maximum disorientation of crystalline and noncrystalline components of jute on mercerization is another feature which distinguishes it from ramie, and together with the previous result reveals a dual character of the fiber, viz., a greater susceptibility and a lower ultimate reactivity. We have noticed elsewhere[11] that the shrinkage and probably also disorientation produced in mercerizing alkali solution does not wholly stay in jute as in ramie, but is partially restored on washing and drying. This reminds one of the partial reversion of soda cellulose I to cellulose I in jute, and is presumably to be traced to some sort of restrictive influence operative in the structure of the fiber.

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Synopsis

The use of swelling anisotropy as a means of determining the orientation of cellulose fibers has been critically reviewed, and it has been shown that the method should be suitable for highly oriented fibers within a certain range of orientation. The application of the method to untreated and variously treated jute fibers reveals certain structural differences with ramie, of which the following are noteworthy. Both noncrystalline and crystalline orientations of jute are influenced by treatments which can be regarded as being confined to the intercrystalline regions only and which do not affect ramie. As compared with ramie, the ultimate maximum disorientation, produced on mercerization treatment is markedly less in jute, and this holds for both

the crystalline as well as the noncrystalline components of the fiber.

Résumé

L'emploi de l'anisotropie de gonflement comme mode de détermination de l'orientation des fibres de cellulose a été revu de façon critique, et on a montré que cette méthode pouvait être adaptée pour des fibres de degré d'orientation élevé dans une certaine région d'orientation. L'application de cette méthode à des fibres de jute non traitées d'une part et d'autre part traitées de différentes façons a révélé certaines différences de structure dans le cas de la ramie; parmi celles-ci les suivantes sont assez remarquables: (*1*) Les orientations cristallines et non-cristallines du jute sont influencées par des traitement qui peuvent être considérés comme étant limités aux régions intercristallines seulement et qui n'affecte pas la ramie. (*2*) Comparé à la ramie la désorientation maximum finale, produite par mercérisation est manifestement moindre dans le cas du jute et ceci vaut et pour les composants cristallins de la fibre et pour les composants non-cristallins.

Zusammenfassung

Ein kritischer Überblick über die Verwendung der Quellungsanisotropie zur Bestimmung der Orientierung in Cellulosefasern wurde gegeben und es wurde gezeigt, dass die Methode für hochorientierte Fasern innerhalf eines bestimmten Orientierungsbereiches verwendbar ist. Die Anwendung der Methode auf unbehandelte und verschieden behandelte Jutefasern lässt gewisse strukturelle Unterschiede gegenüber Ramie erkennen, von denen die folgenden bemerkenswert sind: (*1*) Sowohl die nichtkirstalline als auch kristalline Orientierung von Jute wird durch eine Behandlung beeinflusst, die als auf die interkristallinen Bereiche beschränkt angesehen werden kann und die Ramie nicht beeinfluss. (*2*) Im Vergleich mit Ramie ist das Grenzmaximum der Desorientierung, das durch Mercerisierung erzeugt wird, bei Jute wesentlich geringer; das gilt in gleicher Weise für die kristallinen und nichtkristallinen Faserkomponenten.

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