Temperature Dependence of the Brittleness of Cellulose Fibers and of Chemically Modified Cellulose Fibers

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Synopsis

The temperature dependence of the brittleness of cellulose fibers was studied by the breaking twist angle method. The selected fibers were purified ramie cells, the same cells after fibrous acetylation to form the triacetate, annealed acetylated ramie cells, and mercerized ramie cells. Water acts as a plasticizer to reduce the brittleness of ramie and of mercerized ramie cells but does not appear to affect the brittleness of ramie cells after acetylation. The brittleness of ramie cells is reduced by similar amounts by fibrous acetylation and by mercerization. The brittleness of acetylated ramie cells is increased by annealing, which induces additional crystallization in the cells. The brittleness of ramie and acetylated ramie before and after annealing varied as the test temperature was progressively increased in the range 100–200°C. The effect of temperature on the brittleness of the fibers is interpreted in terms of the relaxation transitions previously determined on the same types of fibers, and in terms of the supramolecular structure of the fibers.

INTRODUCTION

It is important to obtain a better understanding of the temperature dependence of the physical properties of cellulose fibers so as to develop methods of improving their performance when exposed to heat. As the temperature is raised above the glass transition temperature T_g in an amorphous thermoplastic material, an inflection would be expected in the relation between such properties as stiffness, or modulus, and temperature. In a publication describing our determination of transition temperatures of cellulose using a torsion pendulum, we summarized the results of other workers.[1] Determinations made since that publication are presented in Table I, including the value of 160°C obtained by ourselves. It would appear from these data that there is general agreement that the T_g for cellulose occurs in the vicinity of 200°C, with values ranging from 160 to 240°C. Discrepancies can be ascribed to a number of factors, including the sensitivity and precision of the methods, the effective frequencies of the measurements, and the supramolecular structure of the samples. We have also measured the modulus and stress decay of cotton yarn at temperatures between 100 and 240°C and interpreted the data as showing T_g for cellulose at ca. 200°C.[4] However, it was pointed out that it would be difficult to use such measurements to obtain an accurate determination of T_g, since the mechanical properties of cotton yarn are influenced by interfiber as well as intrafiber interactions.

To explore further the effect of heat on the physical properties of cellulosic fibers and also to test our prior estimate of 160°C for the T_g of cellulose, we have now measured the effect of temperature on the brittleness of single purified ramie cells (fibers), as determined by breaking twist angle (BTA).[5] To establish the

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T, °C	Cellulose form	Method of determination	Ref.
−100 to −80[b]; 160[c]; 230[c]; 300–310[d]	Ultimate cells of ramie	Torsion pendulum	1
48[e]; 64; 80[f]; 98[f]; 190[g]; 236[h]	Cellophane	Forced vibration	2
60; 80[f]; 196[g]; 236[h]; 245	Recrystallized cellulose film	Forced vibration	2
60[i]; 145[g]; 200[h]	Amorphous cellulose film	Forced vibration	2
−93[b]; −33[j]; 177[h]	Cellophane	Forced vibration	3

[a] Assignment of the transitions by authors given in footnotes.

[b] Rotation of methylol groups.

[c] Either a double glass transition or damping peaks at 160° and 230°C due to glass transition and cellulose decomposition, respectively.

[d] Premelting transition of cellulose crystals or due to cellulose decomposition.

[e] Rupture of weak hydrogen bonds.

[f] Motion of restricted segments of main chain.

[g] Crystallization of amorphous parts of cellulose.

[h] Glass transition temperature.

[i] Formation of hydrogen bonds.

[j] Rotation of methylol water complexes.

validity of the BTA technique, determinations were made of the brittleness of other fibers on which we had also measured T_g, namely, purified ramie fibers after fibrous acetylation to form the triacetate without loss in fiber structure (ramie cellulose triacetate) and slack-mercerized ramie fibers. The BTA of ramie cellulose triacetate after annealing was also measured.

EXPERIMENTAL

Materials

Purification and preparation of the ramie, mercerized ramie, and ramie cellulose triacetate have been described previously.[1] Ramie cellulose triacetate was crystallized by heating at 210°C in silicone oil for 15 min and then allowing the sample to cool slowly over a 3-hr period. The annealed sample was washed with toluene and then alcohol. The alcohol was allowed to evaporate off at room temperature.

BTA Measurements

The apparatus and procedure used was similar to that described previously[6] except that aluminum tubing (0.051 cm OD × 0.038 cm i.d. or 0.081 cm o.d. × 0.051 cm i.d.) was used to hold the fiber instead of plastic tabs. The tubing was formed on a jig into a straight section of approximately 2.54 cm with loops of approximately 0.32-cm diameter at either end. The tubing was cut at the center of the straight section. A fiber was inserted into one of the halves and the tubing crimped onto the fiber, leaving a test length of about 3 cm. The free end of the fiber was crimped in the other half of the aluminum tubing. The looped ends of the tubing were used to mount the fiber on the instrument.

All tests were made with fibers immersed in a silicone oil bath. Before immersion the fibers were conditioned at 65% R.H. at 21°C. The bath was brought

to the test temperature before the sample was immersed.   The BTA was measured 30 sec after fiber immersion.   All results are the mean of at least five tests at each temperature indicated.

BTA (α) was calculated as follows: By definition[5]

$$\alpha = \tan^{-1} \frac{l}{\pi d \Upsilon}$$

where l is the length of the fiber while the twist is being inserted; Υ is the number of turns imparted to one end of the fiber, the other end being fixed; and d is the diameter of the fiber.

The diameter of the fiber in centimeters was estimated from a vibroscopic determination of the linear density, μ (tex), using the relation

$$d = \left(\sqrt{\frac{4\mu}{\pi\rho}} \times 10^{-5} \right)^{1/2} \text{cm}$$

where ρ is the mass density of the fiber.

The densities of the starting ramie,[7] mercerized ramie,[7] and ramie cellulose triacetate[8] were taken as 1.55, 1.53, and 1.35 g/cm^3, respectively.   Using a density gradient column, it was determined that changes in density caused by heat treatments would be small and the effect on BTA calculations negligible.   Thus changes in density as the fiber is heated are ignored in all calculations, and the density of ramie cellulose triacetate is assumed to be the same before and after annealing.

RESULTS AND DISCUSSION

Comparison of Brittleness of Different Fibers

The BTA, and therefore the brittleness, of mercerized ramie fiber was lower than that of nonmercerized ramie fiber at 23°C (Table II).   Mercerization increases the amount of disordered material in ramie,[9] i.e., the degree of crystallinity of ramie is lowered, and also increases the moisture regain of the product at a given humidity;[9] either effect could contribute to reduced brittleness.   When the samples were tested at 100°C, the BTA of both nonmercerized and mercerized ramie fiber increased.   At this temperature, which is below the T_g of cellulose, much of the adsorbed water present in the fibers would be lost.   Thus the plasticizing effect of water would be lessened or lost, depending on the amount of water removed.   However, the BTA of nonmercerized ramie remained higher

TABLE II
Breaking Twist Angle (BTA) of Ramie and Chemically Modified Ramie at 23 and 100°C

Sample	BTA[a]	
	23°C	100°C
Starting ramie	80.9 ± 0.49	84.9 ± 0.51
Mercerized ramie	73.2 ± 1.31	78.5 ± 0.75
Ramie cellulose triacetate[b]	80.1 ± 0.63	79.4 ± 0.79
Annealed ramie cellulose triacetate	83.1 ± 0.65	83.1 ± 1.03

[a] In degrees, mean and standard error given.
[b] Formed by fibrous acetylation.

than that of mercerized ramie at 100°C. Additional experiments up to a temperature of 200°C were conducted, and the BTA of mercerized ramie was consistently less than that of the starting ramie by not less than 4°. Therefore, it can be concluded that at 23°C the decreased brittleness of mercerized ramie when compared to nonmercerized ramie is primarily caused by lower crystallinity. Plasticization by water might also be slightly greater for mercerized ramie. It will be noted that the difference in BTA between the starting ramie and mercerized ramie is greater at 23°C than at 100°C. The water plasticization effect might be greater in mercerized ramie, since the amount of moisture present in the accessible regions of this sample would be greater than in the nonmercerized sample. The orientation of the polymer chains in ramie as measured by x-ray diffraction is decreased by mercerization,[10] and this too may affect the mobility of the polymer chains in disordered regions of the fiber. However, the decrease in the amount of crystalline material is likely to have a much greater affect on brittleness than the decrease in orientation.

Within experimental error, ramie triacetate fiber has a BTA similar to the starting nonacetylated fiber at 23°C. However, it is well known that cellulose triacetate conditioned at 65% R.H. and 21°C does not adsorb as much water as nonacetylated cellulose under the same conditions.[11] Thus in the tests at 23°C there would have been less moisture present in the cellulose triacetate fiber to act as plasticizer. To determine the effect of substitution of the hydroxyl groups of cellulose by acetyl groups, comparisons need to be made when no moisture (i.e., plasticizer) is present. The BTA of the ramie cellulose triacetate is unchanged when the test temperature is increased from 23 to 100°C, indicating that the brittleness of the triacetate is not affected by adsorbed water. Since the BTA of ramie cellulose is higher than that of ramie cellulose triacetate at 100°C, it would appear that weakening of the interchain bonding by substitution of hydroxyl groups by acetyl groups has decreased fiber brittleness. However, acetylation may have reduced the crystallinity of the fiber, and this could be the primary cause of the lower BTA. Raising the degree of crystallinity increased the brittleness of ramie cellulose triacetate. This was established by determining the BTA of the triacetate fiber before and after annealing. The annealing treatment, which increases the degree of crystallinity of ramie cellulose triacetate,[1] increased the BTA of the fiber (Table II). It should be noted the decrease in brittleness due to substitution of the hydroxyl groups by acetyl groups is roughly similar to that caused by mercerization, since the BTA at 100°C is lowered 5.5° by acetylation and mercerization causes a drop of 6.4° with respect to the starting ramie cellulose.

Effect on Brittleness of Increasing Sample Temperatures Above 100°C

As the test temperature of ramie cellulose triacetate increased above 100°C, an inflection occurred in the relation between BTA and temperature at about 115°C and then the BTA passed through a maximum (Fig. 1). It is suggested the occurrence of this maximum signifies that physical changes are taking place immediately before the maximum, which may be associated with the changes following the second-order transition found by dilatometry to occur between 105 and 120°C.[12-15] In our earlier paper[1] we referred to this transition as T_3. The brittleness of the ramie cellulose triacetate fiber began to decrease at about
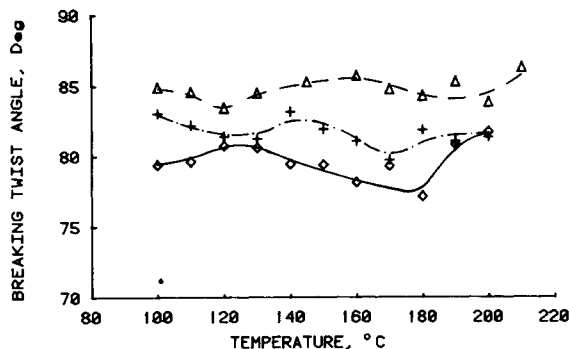
Fig. 1. Effect of temperature on the breaking twist angle of fibers: (△) starting ramie; (+) ramie cellulose triacetate after annealing; (◊) ramie cellulose triacetate before annealing.

130°C, passed through a minimum, and increased sharply at 190°C. In our earlier study we found T_g for this sample was about 140°C. The brittleness of a polymeric material would be expected to decrease above its T_g. Thus the minimum in the BTA–temperature relation occurring between 140 and 190°C for ramie triacetate would appear to support the finding that T_g for this sample is ca. 140°C. The increase in BTA above 180°C is probably caused by the occurrence of additional crystallization of the triacetate. It will be noted from Figure 1 that the BTA of the nonannealed ramie cellulose triacetate at 190–200°C is similar to that of triacetate annealed at 210°C. Also, using differential thermal analysis we have found an exotherm for ramie cellulose triacetate beginning at ca. 173°C and peaking at 188°C, and evidence has been presented which indicates that this exotherm is caused by crystallization.[1] Data obtained by the torsion pendulum technique indicated that small amounts of crystallization can occur in ramie cellulose triacetate at temperatures lower than 170°C. It is possible that the minimum found between 140 and 190°C in the BTA–temperature plot would have been deeper if such crystallization had not occurred.

When ramie cellulose triacetate was annealed at 210°C before testing, two minima were present in the relation between BTA and temperature (Fig. 1). Since the sample had been crystallized at 210°C, additional crystallization would not be expected to have occurred while BTA measurements were being made. If a comparison is made between the BTA–temperature curves for annealed cellulose triacetate and the nonannealed sample in the temperature range 100–190°C, it will be seen that for a given temperature, the BTA of the annealed sample remains consistently higher due to its higher degree of crystallinity. The annealed sample passes through a minimum with its nadir at 125°C. It is suggested that this minimum is caused by the same changes that terminated with a rise in BTA for nonannealed ramie cellulose triacetate at 120°C and was related to changes following second-order transition T_3. Transition T_3 may be a relaxation process associated with the elimination of water from the polymer. It is speculated that the temperature of T_3 for the annealed sample is higher than that for the nonannealed sample because of the additional crystallinity caused by annealing, which could arise by growth of existing crystallites and the formation of new crystals in amorphous regions. The restriction placed on molecular mobility in the amorphous regions by the additional crystallization may be the cause of the shift in T_3 to a higher temperature.

It will also be observed that both curves pass through minima with their nadirs between 160 and 180°C. The minimum occurred in the BTA–temperature curve for the annealed sample at 170°C. The T_g for this sample had been determined previously as 190°C. Thus it appears that in this highly crystalline material, loss in brittleness occurred below its T_g. The increase in BTA that occurs at temperatures above 170°C is probably due to the increased order of the polymer chains in the amorphous regions.

Two minima are also present in the relation between BTA and temperature for the nonacetylated starting ramie (Fig. 1). The nadirs are at 120 and 180 or 200°C. The minimum at 120°C may be related to a relaxation process associated with the removal of all adsorbed water by the heat. The second minimum may be associated with physical changes occurring after the T_g has been reached. The T_g for this sample was found at ca. 160°C by the torsion pendulum technique. From the BTA–temperature curve, the T_g can be estimated as occurring at 165°C. There could be several reasons why the minimum at 180 or 200°C is relatively shallow. For example, ramie is a highly crystalline fiber. Depending on the interpretation of x-ray data, the degree of crystallinity ranges from 70 to 95%.[1] Additionally, it is claimed that heating cellulose at elevated temperatures induces intermolecular linkages.[16,17] These crosslinks would tend to increase the brittleness of cellulose fibers and thus increase the BTA of the ramie cellulose.

Runs with mercerized ramie were discontinued after preliminary data obtained on the BTA of mercerized ramie indicated that it would behave similarly to nonmercerized ramie at high temperatures.

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