

Factors Influencing the Tensile Properties of Ramie

K. E. CABRADILLA and S. H. ZERONIAN, *Division of Textiles & Clothing, University of California, Davis, California 95616*

Synopsis

Many investigators have claimed that tensile breakage of native cellulose fibers occurs primarily by rupture of covalent bonds in the cellulose molecules rather than by chain slippage resulting from rupture of such interchain bonds as hydrogen bonds. This claim has been made partly on the basis of a comparison of tensile properties of ramie fiber and of the fully esterified counterpart. This comparison indicated that the breaking load of ramie was similar to that of the fully esterified fiber. In studying the tensile properties of ramie fiber and of fully acetylated ramie fiber, we found that the degree of polymerization of the fiber was lowered during the acetylation process. Also, it was evident that both degree of polymerization and degree of crystallinity are important factors to be considered when comparing the tensile strength of native cellulose fibers and their acetylated counterparts. Although the primary cause of tensile breakage of native cellulose fibers may be due to chain scission rather than to chain slippage, it is difficult to claim supporting evidence for this theory from studies made so far on the tensile properties of esterified ramie fibers.

INTRODUCTION

The relation between fine structure and tensile properties of native cellulose fibers is not fully understood. It has been stated by some workers^{1,2} 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 is responsible for tensile failure.^{3,4,5} Important evidence cited for rupture by chain scission is the work of Sakurada.⁶ Sakurada found that the tensile strength of single ramie fibers is not changed noticeably by nitration or acetylation.

Sakurada⁶ compared the strength properties of ramie fibers before and after nitration or acetylation and found the following relation:

$$\frac{\text{strength of esterified fiber, kg/mm}^2}{\text{strength of original fiber, kg/mm}^2} = \frac{\text{cross section of fiber, mm}^2}{\text{cross section of esterified fiber, mm}^2}$$

This relation signifies that the strength of the single fibers is unchanged by substitution of the hydroxyl groups. Sakurada interpreted his results as proof that fiber rupture is due to scission of the cellulose molecules, not to chain slippage between micelles (i.e., crystallites) or cellulose chains.

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The conclusions drawn by Sakurada⁶ need to be reexamined for the following reasons. First, the amount of degradation that resulted from acetylation and nitration was not given. Thus, he must have assumed either that no degradation occurred or that degree of polymerization (D.P.) does not affect the rupture mechanism. It is unlikely that degradation was avoided by the acetylation procedure described, namely acetic anhydride, potassium acetate, and acetic acid at the boil for 49 hr.⁶ The nitration mixture consisted of nitric acid and sulfuric acid. More recent work indicates there are better procedures for nitration.⁷ Second, Sakurada did not obtain full nitration or acetylation (i.e., degree of substitution, D.S., of 3). For nitrated samples, the nitrogen content was 12.5%, which is equivalent to a D.S. of approximately 2.4.⁸ For acetylated samples, the acetic acid yield was 61.5–62.0%, which is equivalent to a D.S. of 2.93–2.96.⁸ The remaining hydroxyl groups must influence the secondary valence forces existing between the polymer chains. In addition, if all the hydroxyl groups have not been substituted, then the supramolecular structure of the product may differ from one that has been fully esterified. Hydrogen bonding could still be an important factor in interchain bonding for the nitrated fiber. In the case of the acetylated samples, hydrogen bonding would not be great and interchain hydrogen bonding would be minimal.

The importance of the work of Sakurada as a basis for theories on the tensile properties of native cellulose fibers is such that a reexamination of the tensile properties of fully esterified ramie fibers is warranted. The purpose of our study was to determine the effect of substitution of the cellulose hydroxyl groups of ramie by acetyl groups on the tensile properties of the fiber.

EXPERIMENTAL

Materials

Ramie fiber was obtained from Dr. R. V. Allison, Everglades Experiment Station, Bella Glade, Florida. The ramie had been decorticated, degummed under steam pressure of 75–80 lb in a solution of caustic soda, bleached with hydrogen peroxide, and stapled at $1\frac{1}{8}$ in.⁹ Cupriethylene-diamine hydroxide solution was obtained from Ecusta Paper Div., Olin-Matheson Chemical Corp., Pisgah Forest, North Carolina. Other chemicals were reagent grade.

Methods of Treatment

Fiber Purification. The ramie fiber was further purified by extraction in a Soxhlet for 6 hr in methylene chloride, air dried overnight, then further extracted for 6 hr in methanol, washed thoroughly in distilled water, and dried at room temperature.

Acid Hydrolysis. Ramie (10 g per 500 ml of solution) was hydrolyzed in 1.0*N* hydrochloric acid in a stoppered ground glass bottle at 25°C for different lengths of time. To terminate the reaction, the ramie was washed

thoroughly with distilled water until it was acid free. The sample was then divided into two equal portions; one was air dried and the other was left in distilled water until acetylation.

Acetylation Control. Ramie (5 g) was soaked 1 hr in distilled water, after which it was washed rapidly twice with 100 ml glacial acetic acid and then soaked in 100 ml of the acid at room temperature for 10 min. This procedure was repeated twice, but the final soaking was for 40 min. The ramie was then thoroughly washed with distilled water until acid free and then air dried.

Acetylation. The procedure described below resulted in full acetylation (i.e., D.S. = 3) of the ramie fibers without dissolution of the product in the reaction solution.

Ramie (5 g) was soaked 1 hr in distilled water, filtered, and then soaked 1 hr in glacial acetic acid as described in the previous section. The ramie was filtered to remove excess acetic acid before being placed in a ground-glass stoppered bottle containing the acetylating solution. This consisted of 125 ml toluene, 67.5 ml acetic anhydride, and 0.025 ml 60% perchloric acid. Acetylation was continued for 2 hr at 25°C. The sample was then washed periodically with distilled water over an 18-hr period until it was acid free. Finally, it was air dried.

Deacetylation. Deacetylation of acetylated ramie fibers was accomplished by the method of Timell.¹⁰ Acetylated ramie (3 g) was shaken with 0.1*N* methanolic sodium methoxide at room temperature for 24 hr. The sample was then washed with anhydrous methanol, then with methanol containing 5% acetic acid, and finally with methanol again, after which it was air dried. Deacetylation by this procedure caused no degradation of the fiber.^{10,11}

Crystallization of Acetylated Ramie Fibers. Acetylated ramie fibers were crystallized in a vacuum oven at 166°C for 10 min, using a procedure similar to that of Conrad et al.¹²

Characterization of Product

Acetyl Content. The method used has been previously described.¹³ Acetyl contents were converted to D.S.

Linear Density of Fibers. A tuft of fibers was randomly selected from the sample. The individual fibers were laid parallel to each other, cut to a length of 2 cm, and weighed on a microbalance. The number of fibers (approximately 100) was then counted. Tex was calculated and reported to three significant figures.

Tensile Tests. The tensile properties of the single fibers used for measurement of linear density were measured with a table model Instron Universal Testing Machine equipped with an integrator. In a manner similar to that described by Meredith,¹⁴ a fiber was laid along the center of a paper mount and then secured at each edge by a small amount of Duco Cement. The mounted fiber was clamped between the grips of the Instron, and the sides of the mount were cut. The test length was 0.5 in. One

hundred tests were made at a constant rate of elongation of 0.05 in./min at 65% R.H. and 21°C. Breaking loads of the fibers were determined from the load-extension curves. For selected samples, the extension at break, initial modulus, yield load, and yield elongation were measured, and the rupture energy of the fibers was calculated from the integrator reading. The initial modulus is the slope of the load-extension curve at the origin (after removal of any crimp). The yield point was taken as the point where the load-extension curve ceased to be linear. Standard errors were calculated and used to determine the statistical significance of the results.¹⁴

Degree of Polymerization. Samples of nonhydrolyzed ramie, hydrolyzed ramie, and acetylated ramie after deacetylation were ground in a Wiley mill to pass a 20-mesh screen. The intrinsic viscosities in cupriethylene-diamine hydroxide were determined with Cannon-Fenske viscometers, using the procedure described in ASTM D1795-62.¹⁵ Intrinsic viscosity was converted to D.P. using the relation of Immergut et al.¹⁶:

$$\text{D.P.} = 156[\eta] \quad \text{where D.P.} > 300.$$

X-Ray Diagrams. Fiber photographs were taken with bundles of parallel fibers and nickel-filtered copper K_{α} radiation.

Width of Air-Dried Fibers. About five fibers that had been conditioned at 21°C and 65% R.H. were placed on a microscope slide, and a cover slip was placed over them. N-Heptane was used as the mountant. The prepared slide was placed on the stage of a microscope. The widest point of each of 100 fibers was measured with the aid of an eyepiece scale previously calibrated against a standard stage micrometer.

Results and Discussion

The difficulties in forming a true cellulose triacetate are well known. It requires a catalyst such as perchloric acid.²² Preliminary work indicated considerable degradation of the ramie fiber during fibrous acetylation to a D.S. of 3, as the D.P. fell from 2150 to 525. Thus, to provide a better comparison of tensile properties of acetylated and nonacetylated fibers, a series of ramie fibers of progressively lower D.P. was prepared by acid hydrolysis (Table I). These samples were also acetylated to a D.S. of 3. The D.P. of the acetylated products was in the range of 400 to 690 (Table I). It is interesting that ramie with D.P. between 2150 and 1930 gave an acetylated product of lower D.P. than did ramie with D.P. between 1750 and 1280. In the former case, the D.P. of the acetylated products was 525-595 and in the latter case the D.P.'s ranged between 665 and 690. More highly degraded ramie (D.P. 1120-1140) gave acetylated products with D.P. of 400-440. The degradation occurring during acetylation is probably caused by acid hydrolysis.

It appears that the amount of degradation that occurs is related to the fine structure of the fiber being acetylated. Initially, acid hydrolysis occurs primarily in the amorphous regions of a fiber.¹⁷ Thus, in the prepa-

TABLE I
Degree of Polymerization (D.P.) of Hydrolyzed Ramie Fibers and of the Same Fibers
After Acetylation (Degree of Substitution = 3)

Sample no.	Time of hydrolysis, ^a hr	D.P.	
		Before acetylation	After acetylation
1	0	2150	525
2	0.25	2140	540
3	0.5	2110	595
4	1	1930	560
5	2	1750	670
6	4	1640	690
7	24	1280	665
8	36	1120	400
9	48	1140	440
10	168	835	—
11	336	635	—

^a Samples hydrolyzed with 1*N* HCl at 25°C.

ration of ramie of different D.P.'s, products with progressively degraded amorphous regions are obtained. The amount of amorphous material is also progressively reduced. Again, during the acetylation reaction, the initial substitution of the hydroxyl groups occurs primarily in the amorphous regions of the fiber. Simultaneously, acid hydrolysis is occurring in the amorphous areas also. It appears that there are optimum conditions for the state of the amorphous regions within the ramie fiber when acetylation will occur with less degradation.

Breaking Load, Initial Modulus, and Rupture Energy of Nonacetylated and Acetylated Samples

It is well known that the tensile strength of native cellulose fibers is affected by D.P.¹⁸ The breaking load initially appears to be independent of D.P. (Fig. 1, Table II). However, when acid hydrolysis reduces the D.P. below a value in the range of 1300–1600, the breaking load begins to fall rapidly.

The load–extension curves of nonhydrolyzed ramie and of the hydrolyzed ramie samples were examined in detail; and rupture energies, breaking elongations, and initial moduli were determined. Apparently, these parameters are affected by D.P. also when D.P. falls below a value of 1300–1600 (Table III).

As stated above, fibrous acetylation of nonhydrolyzed (sample 1) or hydrolyzed ramie (samples 2–9) caused a large amount of degradation. The D.P.'s of the samples were less than the critical range of 1300–1600, below which the tensile properties of hydrolyzed ramie fibers begin to fall with decreasing D.P. Thus, D.P. could be an important factor in determining the tensile failure of acetylated native cellulose fibers.

TABLE II
 Breaking Load and Tenacity of Nonhydrolyzed and Hydrolyzed Ramie Fibers Before and After Acetylation

Sample no. ^a	Before acetylation			After acetylation ^b		
	Tex	Breaking load, ^c g	Tenacity, g/tex	Tex	Breaking load, ^c g	Tenacity, g/tex
1	.598	37.4 ± 1.8	62.5	1.11	25.5 ± 1.4	23.0
2	.622	36.6 ± 1.7	58.8	1.08	25.6 ± 1.1	23.7
3	.655	37.1 ± 1.9	56.7	1.01	26.4 ± 1.3	26.1
4	.600	36.0 ± 2.0	60.1	1.15	26.0 ± 1.3	22.6
5	.666	34.2 ± 1.8	51.4	1.04	29.2 ± 1.3	28.1
6	.676	36.1 ± 1.7	53.4	1.17	28.0 ± 1.5	23.9
7	.639	32.5 ± 1.6	50.8	1.11	27.2 ± 1.2	24.5
8	.657	26.2 ± 1.3	39.9	1.06	20.6 ± 0.9	19.4
9	.615	26.8 ± 1.5	43.5	1.04	25.1 ± 1.3	24.2
10	.605	20.7 ± 1.3	34.2	—	—	—
11	.547	15.1 ± 0.9	27.7	—	—	—

^a Sample 1 nonhydrolyzed; samples 2–11 hydrolyzed; D.P.'s given in Table I.

^b Degree of substitution of acetylated samples = 3.

^c Mean and standard error given.

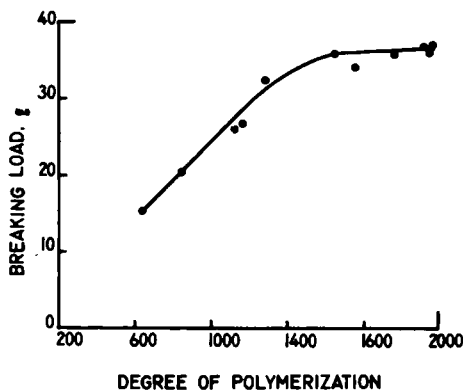


Fig. 1. Relation between breaking load and degree of polymerization of hydrolyzed ramie fibers.

The breaking loads of the acetylated products fall into groups (Table II). For example, samples of D.P. higher than 600 had a higher breaking load (27.2–29.2 g) than did samples of D.P. between 440 and 600 (25.1–26.4 g). Thus, there appears to be a correlation between D.P. and breaking load. However, the ranges of D.P.'s and of breaking loads for the acetylated samples are relatively small, as is the range of rupture energies (Table IV). Therefore, in the remainder of this discussion, there will be no differentiation between acetylated nonhydrolyzed ramie and hydrolyzed and acetylated ramie. They will both be referred to simply as acetylated ramie samples. It should be noted that there were large differences between the breaking elongations and initial moduli of the acetylated samples (Table

TABLE III
Tensile Properties of Selected Ramie Samples Before Acetylation

Sample no. ^a	Breaking load, ^b g	Rupture energy ^b , g-cm	Breaking elongation, ^b %	Initial modulus, ^b g
1	37.4 ± 1.8	.981 ± .064	3.95 ± .12	1060 ± 46
2	36.6 ± 1.7	.941 ± .061	3.91 ± .11	1050 ± 51
7	32.5 ± 1.6	.776 ± .050	3.80 ± .10	834 ± 41
9	26.8 ± 1.5	.608 ± .043	3.45 ± .10	791 ± 37
10	20.7 ± 1.3	.420 ± .034	2.92 ± .10	740 ± 35
11	15.1 ± 0.9	.238 ± .018	2.25 ± .06	765 ± 29

^a Sample 1 nonhydrolyzed ramie fibers, remaining samples hydrolyzed; D.P.'s given in Table I.

^b Mean and standard error given.

TABLE IV
Tensile Properties of Selected Ramie Samples After Acetylation^a

Sample no.	Breaking load, ^b g	Rupture energy, ^b g-cm	Breaking elongation, ^b %	Initial modulus, ^b g
1	25.5 ± 1.4	1.06 ± .07	5.42 ± .16	618 ± 25
2	25.6 ± 1.1	1.12 ± .06	5.72 ± .16	675 ± 22
7	27.2 ± 1.2	1.25 ± .09	5.62 ± .18	784 ± 29
9	25.1 ± 1.3	0.95 ± .07	4.39 ± .16	838 ± 33

^a Tensile properties of samples before acetylation given in Table III; D.P.'s given in Table I.

^b Mean and standard error given.

IV). However, any comparisons made below between breaking elongations or initial moduli of nonacetylated ramie samples and those of the acetylated ramie samples could be made also between the nonacetylated ramie samples and individual acetylated ramie samples.

There were significant differences in the tensile properties of the non-acetylated ramie control (sample 1) and the acetylated ramie samples, with the exception of rupture energies. The tensile strength and initial modulus of the ramie control were significantly higher than those of the acetylated ramie samples (Tables III and IV), and the breaking elongation of the ramie control was significantly lower than that of the acetylated ramie samples. This comparison does not take into consideration the difference in D.P. between the ramie and the acetylated ramie samples.

A more valid comparison of the effect of acetylation on the tensile strength of native cellulose fibers is that between the acetylated ramie samples and hydrolyzed ramie of similar D.P. The ramie hydrolyzed 336 hr (sample 11) had a D.P. of 635, close to the average D.P. of the acetylated ramie samples (555). The breaking load, rupture energy, and breaking elongation of acetylated ramie samples were markedly higher than those of the hydrolyzed ramie (Tables III and IV). They were also significantly

TABLE V
Yield Load and Yield Elongation of Selected Ramie Samples

Sample no.	Before acetylation		After acetylation	
	Yield load, ^a g	Yield elongation, ^a %	Yield load, ^a g	Yield elongation, ^a %
1	5.4 ± .4	.51 ± .02	8.2 ± .4	1.37 ± .06
2	5.1 ± .3	.52 ± .03	7.2 ± .2	1.08 ± .03
7	4.7 ± .2	.61 ± .03	7.8 ± .4	1.00 ± .03
9	4.7 ± .3	.65 ± .03	7.8 ± .3	.94 ± .03
10	3.9 ± .3	.53 ± .03	—	—
11	4.1 ± .2	.58 ± .03	—	—

^a Mean and standard error given.

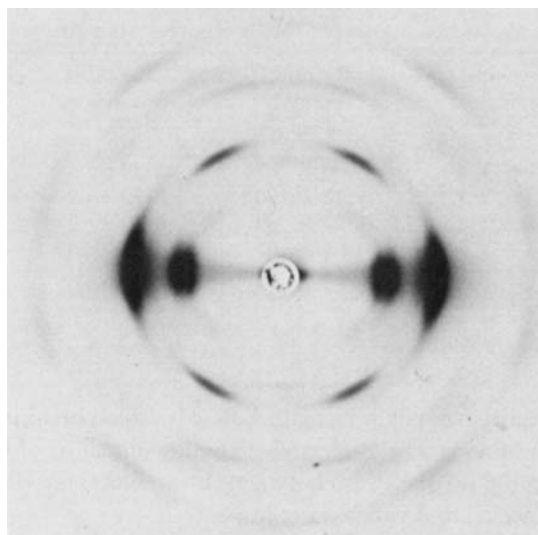


Fig. 2. X-Ray diagram of ramie.

higher than those of hydrolyzed ramie sample 10, which had a D.P. of 835. Thus, it appears that D.P. is not the only factor which influences the tensile properties of native cellulose fibers and of acetylated fibers.

Acetylation of ramie eliminates interchain hydrogen bonding, and only secondary valence forces, such as van der Waals' forces, are present between acetylated cellulose chains. The effect of secondary valence forces on the tensile properties is complex, as becomes more apparent by consideration of the yield points of hydrolyzed ramie and of acetylated ramie samples. Beyond the yield point, a fiber no longer approximates to being elastic, and the secondary valence bonds, including hydrogen bonds, begin to rupture. Below the yield point, interchain bonds would be stretched; but rupture of these bonds would be minimal. The yield load, but not the yield

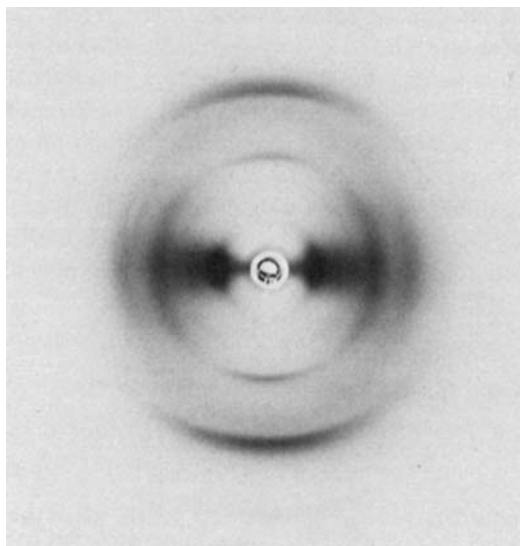


Fig. 3. X-Ray diagram of acetylated ramie.

elongation, of hydrolyzed ramie decreases as the D.P. of the hydrolyzed ramie decreases (Table V). The yield point for acetylated ramie samples occurs at significantly higher yield load and yield elongation than for either the ramie control (sample 1) or the hydrolyzed ramie fiber with a D.P. in the same range as in the acetylated samples (sample 11). These results indicate that the type of interchain secondary valence bonds has a marked influence on the load-extension curves, at least on their initial portions, of native cellulose fibers and of esterified native cellulose fibers. Because van der Waals' forces are weaker than hydrogen bonds, and because ramie has a higher crystallinity than its acetylated counterpart, it is difficult to understand why the acetylated samples should have a higher yield point than the nonacetylated samples. The high crystallinity of ramie is well established,¹⁹ and other workers have found that a loss in crystallinity of cellulose occurs on acetylation (see, for example, ref. 20). X-Ray photographs were taken in our study. The x-ray diagram of ramie (Fig. 2) is similar to that published by other workers such as Hermans.¹ The x-ray diagram of acetylated ramie fibers (Fig. 3) is indicative of low crystallinity since the photograph has a diffuse background and the x-ray reflections are broad. In addition, many of the x-ray reflections are weak.

Examination of Sakurada's Relation

Sakurada⁶ suggested that the tensile strength of ramie is not affected by acetylation or nitration, and, consequently, tensile failure in native cellulose fibers is controlled by covalent bonds, not by secondary valence bonds. To test this hypothesis, the following assumption, also implicit in the work of Sakurada, was made. Hydrogen bonding between the cellulose chains is

eliminated in the acetylated ramie as D.S. is 3. Thus, the only possible interaction between acetylated cellulose chains is due to weaker secondary valence forces, such as van der Waal's forces. Consequently, if chain slippage does not occur at tensile failure, then the tensile strength of acetylated ramie should be the same as that of the nonacetylated ramie fibers.

In his work, Sakurada⁶ based his conclusions on the assumption that esterification expands the cross-sectional area of the fiber due to the substitution of the hydroxyl groups, and thus the number of cellulose chains per fiber cross section remains unchanged. He stated the following relation exists:

$$\frac{\text{strength of esterified fiber, kg/mm}^2}{\text{strength of original fiber, kg/mm}^2} = \frac{\text{cross section of the fiber, mm}^2}{\text{cross section of esterified fiber, mm}^2}$$

Although we cannot directly compare our work with that of Sakurada, owing to a difference in acetylation techniques, this relation can be evaluated.

In the present study, there was little fiber shrinkage during acetylation. Calculation of the tex of acetylated ramie in terms of the amount of cellulose in the fiber gave a value of 0.65, which is roughly similar to the tex of the nonhydrolyzed or hydrolyzed ramie (Table II). Therefore, it may be assumed that the increase in fiber weight upon acetylation is largely due to the addition of the acetyl groups. Acetylation mainly appears to expand the cross-sectional area of the fiber. It was determined microscopically that the width of ramie control fibers increased from 0.0388 mm to 0.0602 mm on acetylation, an increase of 55%. Also, the width of hydrolyzed ramie fibers increased by about a similar amount on acetylation. Consequently, it is again assumed that the number of polymer chains per fiber cross section is not changed by acetylation. The ultimate tensile stress of the fibers was calculated from the cross-sectional area and breaking load. The cross-sectional area of the fibers was calculated from the tex and density of the fiber using the relation

$$\text{cross-sectional area} = \frac{\text{tex}}{\text{density}} \times 10^{-3} \text{ mm}^2.$$

The density of ramie cellulose²¹ was taken as 1.51 g/cm³, and the density of acetylated ramie cellulose was assumed to be similar to that of acetylated cotton cellulose,¹² which is 1.35 g/cm³.

Comparison of the ratios obtained for the ultimate tensile stress and cross-sectional area of the control ramie and acetylated control ramie (sample 1, Table VI) indicates that the ratios are not similar. However, if the ratios for the hydrolyzed ramies and for the hydrolyzed and acetylated ramies are compared (Table VI), it can be seen that the ratios for sample 9 are roughly similar; and thus Sakurada's relation may be valid in this one

TABLE VI
Cross-Sectional Area and Ultimate Tensile Stress of Nonhydrolyzed and Hydrolyzed Ramie Fibers Before and After Acetylation

Sample no. ^a	Before acetylation		After acetylation		Ratios	
	Cross-sectional area, mm ²	Ultimate tensile stress, kg/mm ²	Cross-sectional area, mm ²	Ultimate tensile stress, kg/mm ²	Cross-sectional area ^b	Ultimate tensile stress ^c
1	.396	94.4	.882	31.0	.48	.33
2	.412	88.8	.800	32.0	.52	.36
3	.434	85.5	.748	35.3	.58	.41
4	.397	90.7	.852	30.5	.47	.34
5	.441	77.6	.770	37.9	.57	.49
6	.448	80.6	.867	32.3	.52	.40
7	.423	76.8	.822	33.1	.51	.43
8	.435	60.2	.785	26.2	.55	.44
9	.407	65.8	.770	32.6	.53	.50

^a Sample 1 nonhydrolyzed; samples 2-9 hydrolyzed; D.P.'s given in Table I.

^b (Cross-sectional area of fiber before esterification)/(cross-sectional area of esterified fiber).

^c (Ultimate tensile stress of esterified fiber)/(ultimate tensile stress of fiber before esterification).

case. It is interesting that the ultimate tensile stress of the ramie Sakurada used for acetylation (65.4 kg/mm²) was similar to that of the hydrolyzed ramie (sample 9). The relation of Sakurada appears to be valid only for specific cases involving ramie fibers of low strength. It should be noted also that the value of this relation is questionable, as it can be simplified to

$$\frac{\text{breaking load of esterified fiber}}{\text{breaking load of starting fiber}} = 1.$$

Effect of Crystallinity and Orientation on Tensile Strength of Fibers

As noted above, we found that the breaking load of acetylated ramie fibers was higher than that of nonacetylated ramie that had been hydrolyzed to roughly the same D.P. One possible explanation for this is that supra-molecular structure of the fibers is markedly affecting their breaking load. Degree of crystallinity and the orientation of chain molecules within the fiber have been considered important factors influencing the tensile behavior of cellulose fibers.¹⁸

Ramie is a fiber of high crystallinity and high orientation¹; and it is assumed that, on acid hydrolysis, the fiber retains the same, or slightly higher, crystallinity and orientation. Supporting evidence is that hydrolysis of another native cellulose fiber of similar crystallinity, namely, cotton, results in only a slight increase in degree of crystallinity and degree of orientation.¹⁸ With respect to acetylated ramie, it is speculated that orientation would probably decrease, rather than increase, during the

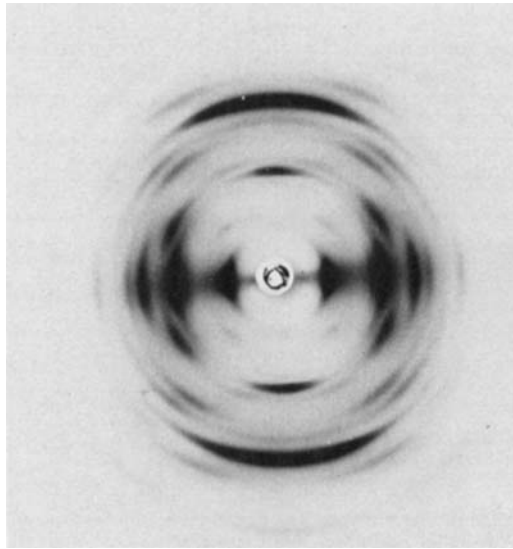


Fig. 4. X-Ray diagram of acetylated ramie that has been crystallized.

acetylation, as it is possible for the polymer chains to take up a more random configuration if interchain bonding is sufficiently weakened during the acetylation process. Thus, the tensile strength of acetylated ramie samples would be expected to decrease, rather than increase, as a result of any changes in chain orientation that occurred during acetylation. It appears, therefore, that change in chain orientation cannot explain the higher breaking load of acetylated ramie fibers in comparison with that of non-acetylated fibers of similar D.P.

As noted earlier, x-ray photographs (Fig. 3) indicated that the degree of crystallinity of acetylated ramie samples was low, and it appeared that there was a loss in crystallinity during acetylation. The higher breaking load of acetylated ramie samples in comparison to nonacetylated ramie of similar D.P. could be explained, at least in part, on the lower crystallinity of the acetylated products. We suggest that, in fibers of low crystallinity, the chain molecules in the amorphous regions of the fiber are able to straighten more easily and that the lengths of the chains between crystalline regions are more nearly uniform. Thus, as a tensile force is applied to a fiber of low crystallinity, the chains are more evenly strained than in a fiber of high crystallinity, and a greater proportion of the chains have to tauten and rupture simultaneously in order for the low crystallinity fiber to break. Consequently, the tensile strength of the low crystallinity fiber is higher than that of the high crystallinity fiber.

The effect of crystallinity on the tensile properties of acetylated ramie was studied to obtain supporting evidence for the above thesis. Crystallization of acetylated ramie fibers was induced by heat treatment. Comparison of x-ray photographs of the samples before (Fig. 3) and after (Fig. 4)

TABLE VII
Tensile Properties of Selected Acetylated Ramie Fibers Before and After Crystallization

	Before crystallization		After crystallization	
Sample no.	5	6	5	6
D.P.	670	690	610	570
Tex	1.04	1.17	.998	1.08
Breaking load, ^a g	29.2 ± 1.3	28.0 ± 1.5	22.1 ± 1.1	18.8 ± 1.1
Tenacity, g/tex	28.1	23.9	22.1	17.4
Rupture energy, ^a g-cm	1.31 ± .08	1.29 ± .09	.807 ± .051	.689 ± .057
Breaking elongation, ^a %	6.04 ± .15	5.87 ± .16	4.74 ± .14	4.60 ± .15
Initial modulus, ^a g	773 ± 32	692 ± 30	683 ± 29	606 ± 31
Yield load, ^a g	7.3 ± .3	7.8 ± .4	7.1 ± .3	6.6 ± .4
Yield elongation, ^a %	0.97 ± .03	1.10 ± .04	1.07 ± .03	1.15 ± .05

^a Mean and standard error given.

the treatment indicated that crystallization had occurred, as the x-ray reflections of the latter samples were markedly stronger and sharper. The breaking load of acetylated ramie fiber which had been crystallized was significantly lower than that of the uncrystallized acetylated ramie (Table VII). These results support our contention that a high degree of crystallinity in a fiber can result, in some instances, in the fiber having a lower tensile strength than that of a fiber of the same chemical constitution but with a lower degree of crystallinity. Additionally, there was a significant drop in rupture energy and breaking elongation upon crystallization, but the yield point was not affected. Although the small decrease in D.P. which occurred during the crystallization treatment may have caused part of the loss in strength, it was not large enough to account for the total loss.

When comparisons are being made of the tensile strength of fibers which have failed by a mechanism including both chain slippage and chain scission, the strength should be considered either as tenacity or ultimate tensile stress rather than as breaking load. The ultimate tensile stress of the control nonacetylated ramie fiber (94.4 kg/mm²) was higher than that of the acetylated ramie samples before crystallization (Table VI). The ultimate tensile stress of hydrolyzed ramie (sample 11), which had a D.P. similar to that of the acetylated samples, was 41.7 kg/mm², which again was higher than that of any of the noncrystallized acetylated samples or those of acetylated samples 5 and 6 after crystallization (29.9 and 23.5 kg/mm², respectively). In contrast, the tenacity of nonacetylated sample 11 was 27.7 g/tex, similar to that of the acetylated ramie samples before crystallization (Table VII). However, even if for a given D.P. the ultimate tensile stress or the tenacity of nonacetylated hydrolyzed ramie fibers was similar to that of the acetylated ramie samples, it would not necessarily mean that tensile breakage occurred by similar processes in these samples.

The breaking elongation of the acetylated ramie samples both before (Table IV) and after (Table VII) crystallization was greater than that of

the nonhydrolyzed or hydrolyzed ramie samples (Table III). Thus, it appears that during the application of tensile stress, considerably more interchain or intercrystallite slippage occurred within the acetylated ramie fibers than in either nonhydrolyzed or hydrolyzed ramie fibers. As discussed earlier, acetylation apparently caused little shrinkage of the fibers. However, a reduction in fiber length of about 2% as a result of the polymer chains assuming a more random configuration during acetylation would account for the increased extension at break of the acetylated samples. Our methods are not precise enough to detect such small reductions in fiber length. Thus, the greater extension at break of the acetylated samples does not necessarily imply that more chain slippage occurred at fiber breakage in the acetylated samples than in the nonacetylated ones. The increased extensibility of the acetylated fibers could be due, at least in part, to the cellulose triacetate chains straightening as the tensile force was applied.

It should be noted that the yield points of both crystallized and non-crystallized acetylated ramie fibers (Tables V and VII) were higher than that of the nonhydrolyzed or hydrolyzed ramie fibers (Table V). This indicates that substitution of the cellulose hydroxyl groups by acetyl groups markedly influenced the tensile properties of fibers on application of a small tensile stress.

CONCLUSIONS

The primary cause of tensile breakage of native cellulose fibers may be due to chain scission rather than to chain slippage, but it is difficult to claim supporting evidence for this theory from studies made so far on the tensile properties of esterified ramie fibers. Our results indicate that, in any comparison of the tensile properties of native cellulose fibers with those of the same fibers after chemical modification, the D.P. and degree of crystallinity of the samples have to be considered. Also the degree of orientation of the fibers is important. Thus both degree of orientation and degree of crystallinity need to be systematically varied and quantitatively measured in future studies to obtain a better understanding of the mechanical properties of native cellulose fibers. Studies of the tensile properties and supramolecular structure of chemically modified native cellulose fibers remain of value for obtaining basic information concerning the tensile properties of native cellulose fibers, as it is easier to vary the degree of crystallinity and orientation of many cellulose derivatives as compared to native cellulose. Also, the polarity of the side groups and the type of interchain bonding can be varied widely.

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