

Molecular Weight Dependence of Tensile Properties of Ramie and Linen Fibers

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ABSTRACT

This study examines the dependence of ramie and linen tensile properties on the molecular weight of cellulose as a function of moisture absorption. The influence of the crystalline region and molecular weight on tensile properties is investigated using mercerized and acid hydrolyzed cotton fibers. No influence of the crystalline region on ramie and linen tensile properties is detected, and the effects of moisture regain on the tensile strength and elongation of ramie and linen fibers decrease with decreasing molecular weight. The slope in the plot of tensile properties versus moisture regain becomes negative when the molecular weights of ramie and linen are below about 1.22×10^5 and 0.99×10^5 , respectively. Changes in tensile strength and elongation with moisture absorption depend mainly on the number of molecular chain ends in the amorphous region.

Ramie is the vegetation of *Urticaceae* cultivated in tropical regions and linen is the vegetation of *Linaceae* cultivated in cold regions [6]. Along with cotton, these natural cellulosic fibers are interesting because their tensile strength and elongation increase with moisture absorption. However, the relationships between fine structures and tensile properties in the case of ramie or linen have been studied less than cotton. In earlier work, we studied the effect of molecular weight on tensile properties with moisture absorption using a cotton whose molecular weight was changed by acid hydrolysis [4], and we found that the high molecular weight was the reason for the increased tensile properties with moisture absorption. Therefore, we now examine the effect of molecular weight at various moisture absorption levels on ramie and linen fiber tensile properties.

Experimental

Ramie fibers, which constituted the ramie yarn (60s/1), and linen fibers, which constituted the linen yarn (40s/1), were used after scouring. To prepare a sample with the crystalline form of cellulose II, the yarn was mercerized without tension by immersion in a 20 wt % aqueous NaOH solution at 20°C for 20 minutes and dried after thoroughly washing in running water. To obtain samples with various molecular weights, yarn samples were hydrolyzed for 0.5–120 hours in a 5N HCl aqueous solution at 25°C, neutralized with 1% ammonia solution, washed, and dried.

Moisture regain in the fibers was calculated by

$$\text{Moisture regain (\%)} = (W_w/W_d - 1) \times 100 \quad (1)$$

where W_w is the weight of the sample obtained by keeping it in a desiccator with an aqueous solution of various concentrations of sulfuric acid at 20°C for 48 hours, and W_d is the weight of a dried sample obtained by vacuum drying at 100°C for 2 hours.

Tensile properties were measured with an Instron (Instron Japan Co., Ltd.). Fibers were taken from the yarn and both ends were placed on a length of 5 cm (linen) or 8 cm (ramie) of drawing paper and attached by a gel adhesive. The rate of extension (2 mm/min) was adjusted to minimize volatilization of absorbed water during the measurements. Samples were measured immediately after removal from the desiccator. Moisture-absorbed samples were prepared by equilibrating in a desiccator at 100% humidity for 48 hours. Water-absorbed samples were prepared by immersing in water at 25°C for 30 minutes.

To calculate tensile stress, the samples were cut with a microtome (HM360, Carl Zeiss inc.) after hardening with an optical-setting resin (D-800, Toa Gousei Ltd., Co.), and the cross section was measured with a digital microscope (VH6200; Keyence Co., Ltd.). Samples kept in a desiccator at 100% humidity for 48 hours were designated as moisture-absorbed samples and those immersed in water at 25°C for 30 minutes were designated as water-absorbed samples.

To determine the short axis/long axis (S/L) ratios of fiber cross sections, fiber samples were cut with a microtome after embedding in an optical-setting resin. The short and long axes were measured with a digital microscope.

X-ray diffraction intensity curves were obtained at a scanning rate of $1^\circ/\text{min}$ for 2θ from 5 to 40° with a diffractometer (Rigaku Denki Co., Ltd.) using $\text{CuK}\alpha$ radiation. Crystallinity was measured on a powdered sample [1], and the degree of crystalline orientation was measured on yarn samples.

Shrinkage was calculated by

$$\text{Shrinkage (\%)} = (1 - L_2/L_1) \times 100 \quad (2)$$

where L_1 and L_2 are the length of a dry sample and that of the shrunken sample obtained by immersing in boiling water for 30 seconds.

Viscosities of Schweizer reagent solutions of the original and hydrolyzed samples were measured with an Ostwald viscometer. Molecular weight (M) was calculated by

$$[\eta] = K_m M^\alpha \quad (3)$$

where $[\eta]$ is intrinsic viscosity, K_m is 8.5×10^{-3} (ml/g), and α is 0.81 [2].

Yields after mercerization and acid hydrolysis were calculated by

$$\text{Yield (\%)} = (W_2/W_1) \times 100 \quad (4)$$

where W_1 and W_2 are weights before and after mercerization or acid hydrolysis, respectively.

Retardation (R) was measured with a polarization microscope attached with a compensator (POS; Olympus Co., Ltd.), and birefringence Δn was calculated by

$$\Delta n = R/d \quad (5)$$

where d is the diameter of the fiber [7].

Results and Discussion

Table I shows the tensile strength, elongation, and Young's modulus of ramie and linen fibers under dried and moisture-absorbed conditions. The tensile strength and elongation of the samples increase with moisture absorption, though the Young's modulus decreases. These results are similar to those of cotton [4]. Nakamura

et al. [5] observed short axis/long axis (S/L) ratios of cross sections of the dried and water-absorbed cotton fibers, and they concluded that the S/L ratio changes with water absorption and as the strained cellulose molecules relax. Figure 1a shows histograms of the S/L ratios for the dried, moisture-absorbed, and water-absorbed ramie fibers. The cross sections of the dried ramie sample are shown in Figure 2a. The shape is irregular like that of cotton and does not change after moisture or water ab-

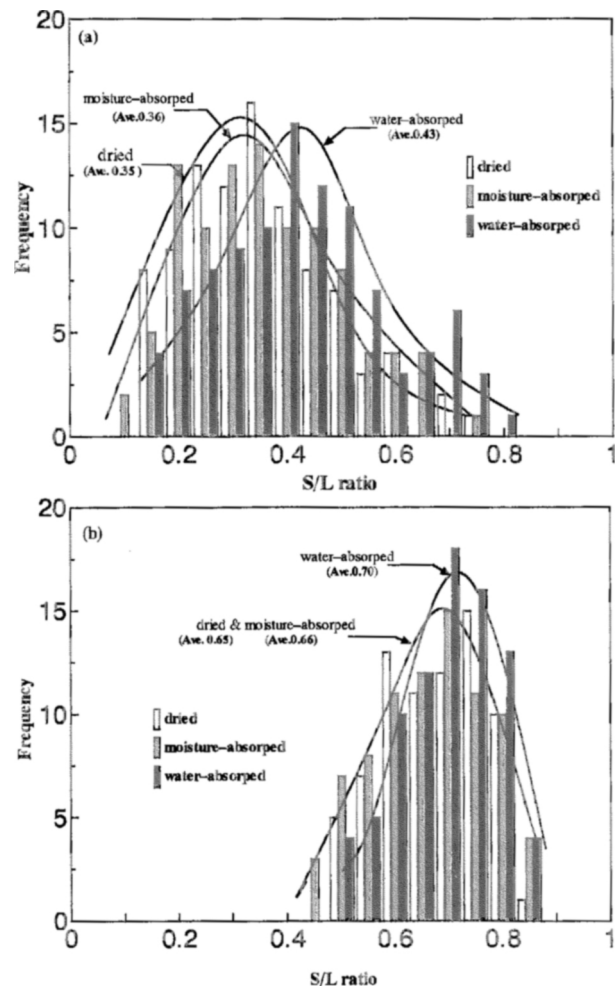


FIGURE 1. Histograms of short axis/long axis (S/L) ratios of cross sections of ramie (a) and linen (b) fibers.

TABLE I. Tensile properties of ramie and linen fibers.

Sample	Strength, MPa			Elongation, %			Young's modulus $\times 10^{-3}$ MPa		
	Dry ^a	Moisture ^b absorbed	b/a	Dry ^a	Moisture ^b absorbed	b/a	Dry ^a	Moisture ^b absorbed	b/a
Ramie fiber	745	974	1.31	2.2	2.7	1.23	14.8	12.6	0.85
Linen fiber	680	789	1.16	2.3	2.5	1.08	9.8	8.9	0.91

^a Moisture regain, ramie 2.4%, linen 2.5%.

^b Moisture regain, ramie 17.2%, linen 16.4%.

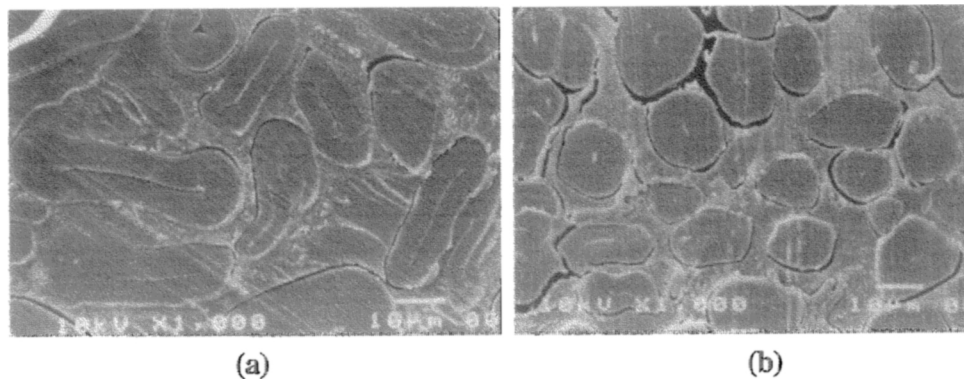


FIGURE 2. Cross sections of ramie (a) and linen (b) fibers.

sorption. The mean value of the *S/L* ratios shifts from 0.35 to 0.43 after water absorption, which is similar to the result for cotton [5]. The mean value of the *S/L* ratio of the moisture-absorbed ramie fibers, however, is similar to that of the dried one. The results for linen fibers are similar to those of ramie, as shown in Figure 1b. The cross sections of the dried linen sample are shown in Figure 2b. The shape is circular and does not change after moisture or water absorption. Nakamura *et al.* [5] speculated that the change in tensile properties is related to the dimensional change due to water absorption. However, this is wrong, because the tensile properties changed only for the moisture-absorbed samples and were not accompanied by dimensional changes.

To study the effect of the crystalline region on the tensile properties, mercerized samples were prepared under shrinkage-free conditions. The crystalline form of ramie and linen fibers transformed from cellulose I to cellulose II. The degree of crystallinity and the degree of crystal orientation decreased slightly with this process, as shown in Table II. The yields of both fibers after mercerizing were about 98%. The nonfiber materials, *i.e.*, lignin and pectin, hemicellulose, etc., remaining in the samples were probably degraded and dissolved by mercerization. The molecular weight was nearly constant before and after mercerization, as shown in Table II. Young's moduli of the dried and mercerized samples were smaller than those of the original ones, as shown in Tables I and III, because of decreases in the degrees of

TABLE II. Fine structure of ramie and linen fibers.

Sample	Original	Mercerized ^a
Ramie		
Molecular weight	5.08×10^5	4.61×10^5
Degree of crystallinity, %	79	69
Degree of orientation, %	86	80
Linen		
Molecular weight	3.71×10^5	3.59×10^5
Degree of crystallinity, %	75	63
Degree of orientation, %	87	82

^a Yield by mercerized ramie 98.1%, yield by mercerized linen 97.6%.

crystallinity and crystal orientation. The moisture-absorbed fibers had a lower Young's modulus than the dried fibers and the original fibers. Table III also shows the effects of moisture absorption on the tensile strength and elongation of mercerized ramie and linen fibers, which increase with moisture absorption, as did the original samples. Mainly, the amorphous region increases in these properties due to moisture absorption, because the tensile properties increase even if the crystalline structure changes from cellulose I to cellulose II.

Table IV shows changes in the crystallinity, crystalline orientation, or half-width of the (002) diffraction, which relates inversely to crystalline size, on the time of acid hydrolysis of ramie and linen fibers. It is clear that only the molecular weights change, and the fine structure of the crystalline region is unchanged by acid hydrolysis.

TABLE III. Tensile properties of mercerized ramie and linen fibers.

Sample	Strength, MPa			Elongation, %			Young's modulus $\times 10^{-3}$ MPa		
	Dry ^a	Moisture ^b absorbed	b/a	Dry ^a	Moisture ^b absorbed	b/a	Dry ^a	Moisture ^b absorbed	b/a
Ramie	693	851	1.23	2.9	3.5	1.21	4.4	4.2	0.95
Linen	676	811	1.20	2.8	3.3	1.18	4.0	3.4	0.84

^a Moisture regain, ramie 2.7%, linen 2.6%.

^b Moisture regain, ramie 18.4%, linen 17.2%.

TABLE IV. Dependence of the molecular weight, crystal structure, shrinkage ratio, and birefringence on acid-hydrolysis of ramie and linen fibers.^a

Sample	Original	24 hour Hydrolyzed	120 hour Hydrolyzed
Ramie			
Molecular weight	5.08×10^5	2.01×10^5	1.22×10^5
Degree of crystallinity, %	79	74	78
Degree of orientation, %	86	82	83
Half width of (002), °	1.5	1.6	1.5
Shrinkage ratio, %	<0.5	<0.5	<0.5
Birefringence	0.058	0.061	0.057
Linen			
Molecular weight	3.71×10^5	1.67×10^5	0.99×10^5
Degree of crystallinity, %	75	76	78
Degree of orientation, %	87	86	85
Half width of (002), °	1.8	1.8	1.8
Shrinkage ratio, %	<0.5	<0.5	<0.5
Birefringence	0.061	0.066	0.063

^a Ramie yield by 24 hour hydrolyzed fibers 97.2%, 120 hour hydrolyzed fibers 96.5%. ^b Linen yield by 24 hour hydrolyzed fibers 94.6%, 120 hour hydrolyzed fibers 93.8%.

Figure 3 shows the dependence of tensile strength and elongation of ramie and linen fibers on moisture regain as a function of molecular weight. Tensile strength and

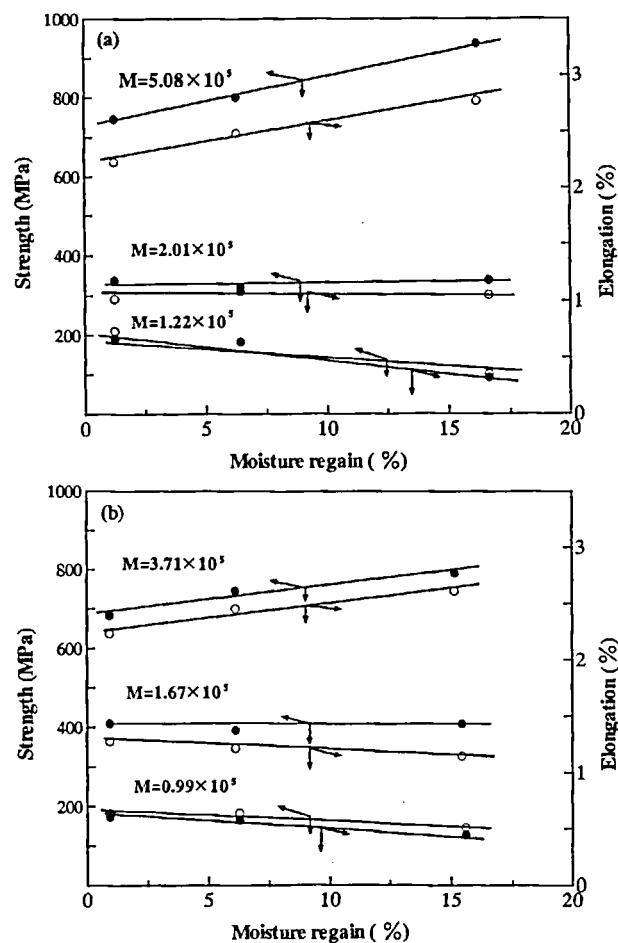


FIGURE 3. Relationship between strength, elongation, and moisture regain of ramie (a) and linen (b) fibers.

elongation for all samples regardless of moisture levels decrease with decreasing molecular weight. We believe that nonfibrous materials, which generally exist between the microfibrils, remain in the scoured ramie and linen fibers, because each yield of ramie and linen fibers after hydrolysis is 94 and 97%, respectively. Since the nonfibrous materials have lower molecular weights than that of cellulose, the change in the mean molecular weight depends on the degradation of cellulose molecules by hydrolysis. It is possible to change the tensile properties by degradation of the nonfibrous materials, but the results of Figure 3 should be explained by the increase in the molecular chain ends as defects with decreasing molecular weight. Many investigators have confirmed that fracture begins at internal stress concentration points such as chain ends in the amorphous regions and the boundary surfaces between the crystalline and amorphous regions in polymer materials, but not in the crystallite [3, 8]. Furthermore, we can see in Figure 3 that the slopes of the plots for tensile strength and elongation versus moisture regain decrease with decreasing molecular weight, and the slopes become negative below the molecular weight for ramie and linen, about 1.22×10^5 and 0.99×10^5 , respectively.

These results indicate that sufficiently high molecular weight is the most important factor in increasing tensile strength with moisture absorption, or a small number of the molecular chain ends in the amorphous region. Shrinkage ratios and birefringence values are also given in Table IV. Shrinkage ratios are very low for every hydrolyzed sample. Birefringence values of the original and all hydrated samples are 0.057–0.066, which is extremely high in comparison with the birefringence (0.041) of highly oriented viscose fibers. This indicates that amorphous cellulose chains and fibrils, which are constructed in series by the crystalline and amorphous regions, orient highly without depending on the molec-

ular weight. The isothermal absorption curves do not change with decreasing molecular weight, as shown in Figure 4. These results indicate that the number of main absorption sites existing in the amorphous region are not changed by acid hydrolysis, and support the theory of amorphous cellulose chain orienting highly in these fibers. Since cellulose molecules probably form the intermolecular hydrogen bonds between many side groups (OH group), the internal rotation of the amorphous cellulose chains is very difficult. Therefore the amorphous cellulose chains and fibrils will slip by each other through elongation, and the slippage distance at the fracture corresponds to the tensile elongation. The moisture-absorbed samples, which have a small number of internal stress concentration points, show longer slippage distances than the dried sample by weakening the intermolecular hydrogen bonding force. Consequently, tensile strength increases. The decrease of the slope with decreasing molecular weight can be explained as follows: The intermolecular and interfibril slippage becomes shorter with decreasing molecular weight because of the many defect points. Consequently, fracture easily occurs in the acid hydrolyzed sample with a lower molecular weight.

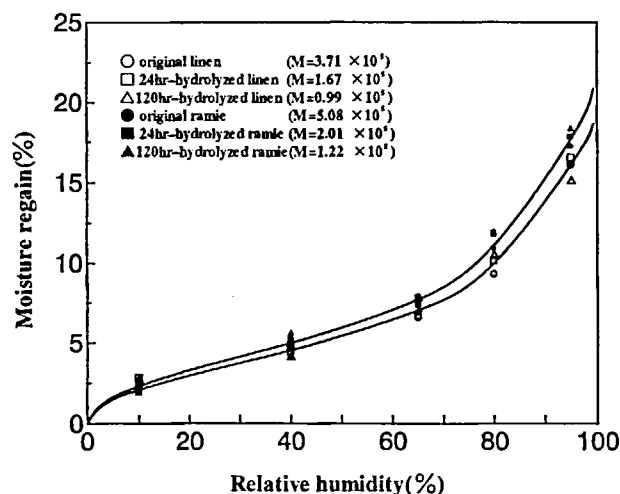


FIGURE 4. Isothermal sorption diagrams of ramie and linen fibers.

Conclusions

We have examined the dependence of tensile properties on the molecular weight of cellulose as a function of moisture absorption using ramie and linen of various

molecular weights. The tensile properties of the fibers change even when samples are kept at various humidity levels where moisture regain is below 15 wt %. Dimensional changes in the cross sections of the fibers with wetting do not occur for samples at 100% humidity, while they do occur only in the sample immersed in water. These mean that the tensile properties are mainly changed by moisture absorption rather than water absorption accompanied by dimensional changes.

The tensile strength and elongation increase with increasing moisture regain for the original samples, and the effect of moisture absorption on the tensile properties of the samples decreases with decreasing molecular weight. Dependence of tensile strength and elongation on moisture regain decreases with decreasing molecular weight, and the slope becomes minus when the molecular weights of ramie and linen are below about 1.22×10^5 and 0.99×10^5 , respectively. These results mean that the tensile properties of ramie and linen change with moisture absorption depending mainly on the number of molecular chain ends in the amorphous region.

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Literature Cited

- Alexander, L. E., "X-ray Diffraction Method in Polymer Science," John Wiley & Sons, NY, 1969, pp. 137-140.
- Brandrup, J., and Immergut, E. H., "Polymer Handbook," 3rd ed., John Wiley & Sons, NY, 1989, p. IV-31.
- Kausch, H. H., and De Vries, K. L., Molecular Aspects of High Polymer Fracture as Investigated by ESR Technique, *Int. J. Fract.* **11**, 727-759 (1975).
- Miyake, H., Gotoh, Y., Ohkoshi, Y., and Nagura, M., Tensile Properties of Wet Cellulose, *Polym. J.* **32**, 29-32 (2000).
- Nakamura, K., Hatakeyama, T., and Hatakeyama, H., Effect of Bound Water on Tensile Properties of Native Cellulose, *Textile Res. J.* **53**, 682-688 (1983).
- Ott, E., "Cellulose and Cellulose Derivatives," Interscience Publishers Inc., NY, 1943, pp. 16-17.
- Tsuboi, S., "Polarization Microscope," Iwanami-shoten, Tokyo, 1959, p. 169.
- Vettegren, V. I., Novak, I. I., and Friedland, K., Overstressed Interatomic Bonds in Stressed Polymers, *Int. J. Fract.* **11**, 789-801 (1975).

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