Tensile Properties of Wet Cellulose

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ABSTRACT: Examination was made of different tensile properties of wet natural cellulose fiber (cotton) and regenerated cellulose fibers (rayon filament). Influence of the crystal region and molecular weight on tensile properties was investigated using mercerized and acid hydrolyzed cotton fibers. No influence of crystal region on tensile properties of cotton fiber was found. The effect of moisture regain on the strength and elongation of cotton decreased with decreasing molecular weight. The slope in the plot of tensile properties against moisture regain became negative, when the molecular weight of the cellulose approximated that of rayon. Changes in tensile strength and elongation with wetting may depend mainly on the number of the molecular chain ends in the amorphous region.
KEY WORDS   Cellulose / Cotton / Rayon / Tensile Properties /Moisture Regain / Molecular Weight / Molecular Chain End / Hydrolysis / Mercerization /

Generally, tensile strength and elongation of fibers decrease with wetting. In contrast, the tensile strength and elongation of natural cellulose fibers increase with wetting. These are the most unique tensile properties of natural and synthetic fibers. Nakamura et al. reported that the tensile strength of cotton cloth increases, while the relative Young's modulus decreases and the half width of X-ray diffraction peak decreases until water content of the fibers reached about 20% of which water was bound water. They concluded that the unique tensile properties of cotton fiber are caused by the formation of a stable structure and relaxation of an internal stress concentration with wetting.[1-4] However, they did not clarify why the tensile strength of regenerated cellulose does not increase with wetting.

The tensile strength of polymer material mainly depends on defects and internal stress concentration in the material, particularly on the number of chain ends in the amorphous region, rather than state of crystallites.[5,6]

This paper thus investigates the influence of molecular weight on the tensile properties of natural cellulose fiber. Molecular weight is the main difference between cotton and rayon fibers and is related to the number of the chain ends in the amorphous region.

EXPERIMENTAL

Materials

Cotton lint and yarn (Egypt cotton 80/1s) composed of cotton lint were used as natural cellulose samples. Rayon filament and yarn (viscose 150d) composed of rayon filaments were used as regenerated cellulose samples. All samples were scoured by aqueous solution before use.

To obtain samples of various molecular weights, cotton yarn was hydrolyzed for 2—120 h in 5 N HCl aqueous solution, neutralized in NH_3, washed and dried.

To prepare a sample having the crystal form of Cellulose II, the cotton yarn fixed on a frame was mercerized by immersing in 20 wt% NaOH aqueous solution for 20 min, and dried after fully washing in running water.

Cross linked fibers were prepared by cross-linking reagent (Dimethylol dihydroxy ethylenurea). The samples were squeezed by a mangle roller after immersing in a 20 wt% aqueous solution for 10 min, pre-cured at 100 °C for 10 min, cured at 140 °C for 5 min and dried after washing in distilled water. The formation of cross-links was confirmed by dissolution examination using copper oxide ammonium solutions (Schweizer reagent solution).

Measurements

Molecular Weight. Viscosities of Schweizer reagent solutions of the original cellulose fiber and hydrolyzed cellulose were measured using an Ostwald-viscometer. Molecular weight (M) was calculated using eq 1,

$$[\eta] = K_m \cdot M^\alpha \qquad (1)$$

where $[\eta]$ is intrinsic viscosity, K_m is 8.5×10^{-3} (mL g^{-1}), and α is 0.81.[7]

Moisture Regain. Moisture regain was calculated by eq 2,

$$\text{Moisture regain } (\%) = (W_w/W_d - 1) \times 100 \qquad (2)$$

where W_w and W_d are weights of water-absorbed sample obtained by keeping in a desiccator with aqueous solution of various concentrations of sulfonic acid at 20°C for 48 h and weights of dried samples obtained by vacuum drying at 100°C for 24 h.

Tensile Properties. Tensile properties were measured using an Instron (Instron Japan Co., Ltd.). The yarn sample was 30 cm long. Cotton lint and rayon filaments were taken from the yarn and both ends were placed on a length of 3 cm (cotton) or 8 cm (rayon filament) on drawing paper by a gel adhesive. Tensile speed was adjusted to minimize volatilization of absorbed water

Table I. Tensile properties of cellulose fibers

Sample	Strength/MPa				Elongation/%				Young's modulus ($\times 10^{-3}$ MPa)		
	RH9%	RH65%	RH90%	Wet/Dry	RH9%	RH65%	RH90%	Wet/Dry	RH9%	RH90%	Wet/Dry
Cotton lint	482	566	578	1.20	5.8	6.4	6.9	1.19	5.6	4.7	0.84
Cotton yarn	60	62	64	1.07	5.1	5.4	5.7	1.12	1.7	1.3	0.79
Rayon filament	197	175	154	0.78	15.9	15.4	10.6	0.67	3.4	3.0	0.91
Rayon yarn	105	103	91	0.87	19.1	18.5	17.6	0.92	3.6	2.5	0.70

during measurement. Tensile speed was 1 cm min^{-1} for the cotton yarn samples, 2 mm min^{-1} for the cotton lint, 3 cm min^{-1} for the rayon yarn samples, and 1 cm min^{-1} for the rayon filament. Measurement was done immediately after taking the samples from the desiccator. Wet samples were prepared by being kept in 100% humidity in the desiccator.

To calculate tensile stress, the samples were cut with a microtome (HM360 ; Carl Zwiss Inc.) after hardening with optical-setting resin (D-800; Toa Gousei Co., Ltd.) and cross sections were measured using an digital microscope (VH6200 ; KEYENCE Co., Ltd.).

X-Ray Diffraction. X-Ray diffraction intensity curves were obtained at a scanning rate of 1° min^{-1} and scanning region of 5—40° with a diffractometer (Rigaku Denki Co., Ltd.) using Cu-K_α radiation. Crystallinity was measured using a powdered sample. The degree of crystal orientation was measured using yarn samples.

Shrinkage. Shrinkage was calculated by eq 3,

$$\text{Shrinkage }(\%) = (1 - L_2/L_1) \times 100 \quad\quad (3)$$

where L_1 and L_2 are the length of dry sample and length of the shrunk sample obtained by immersing in boiling water for 30 s.

RESULTS AND DISCUSSION

Influence of Wetting on Tensile Properties

Table I shows tensile strength, elongation and Young's modulus of cotton and rayon samples at various levels of moisture regain. There are differences in strength for the lint (filament) and yarn samples. A cross section of yarn which contains spaces between lints composed of the yarn is larger than the total cross section of the lints, and strength is calculated using the cross section. The results of cotton and rayon yarns are consistent tensile properties of cotton lint and rayon filament. Tensile properties of yarns may thus depend directly on lint and filaments.

Influence of Crystal Region on Tensile Properties

The crystal form, Cell-I, of natural cellulose is transformed to Cell-II by mercerization, which is the same crystal form as that of rayon.[8,9] The degree of orientation in crystal region and half width from X-ray diffraction patterns of cotton fiber are changed by this process as shown in Table II. The molecular weight of the mercerized cotton did not change from that of the original cotton. This means that we can investigate the effects of the crystal region on tensile strength and elongation in the wet state using the original cotton and the mercerized cotton only. Figures 1a and 1b show the

Table II. Fine structure of cellulose

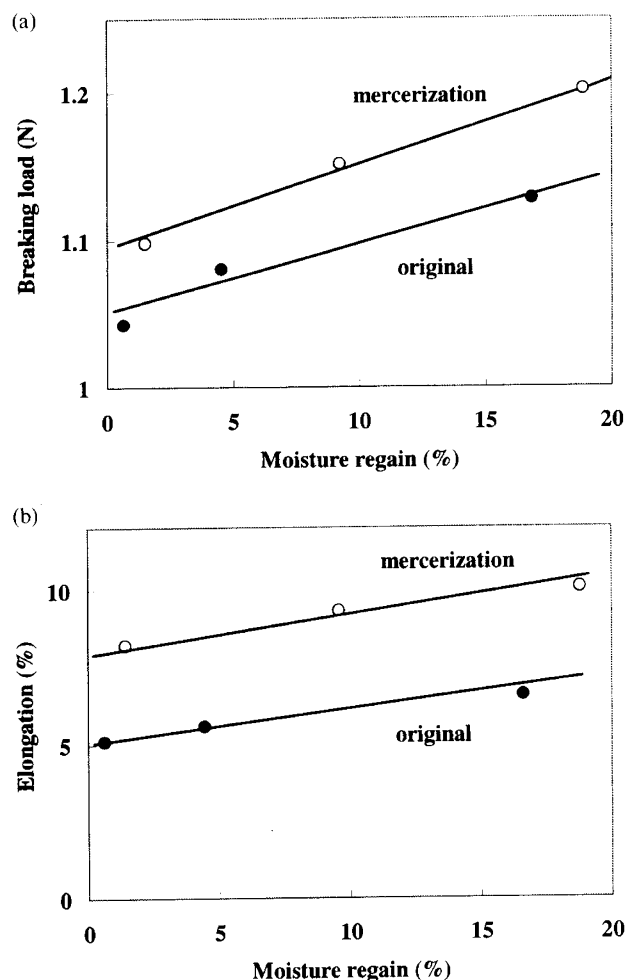| Sample	Cotton	Marcerized cotton	Rayon
Degree of crystallinity/%	72	69	50
Degree of orientation/%	74	78	69
Half width (X-ray diffraction patterns)/°	1.8	2.7	—

Figure 1. (a) Relationship between breaking load of cotton yarn and moisture regain. (b) Relationship between elongation of cotton yarn and moisture regain.

effects of moisture regain on the tensile strength and the elongation of the mercerized cotton, as well as original cotton, increases with wetting. The tensile properties are thus not affected by change of the crystal region, and differences of the tensile properties of cotton and rayon exist in the amorphous region.
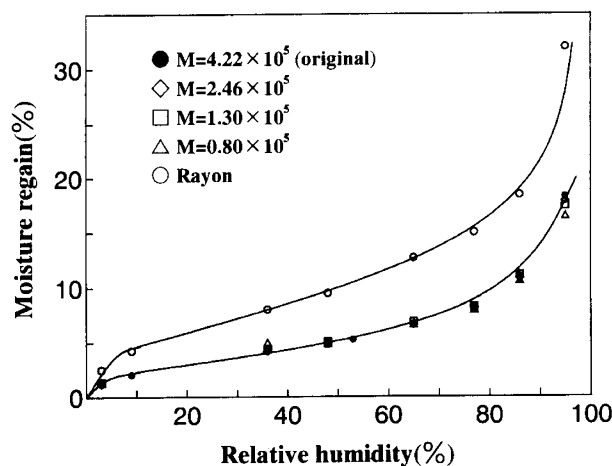
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Figure 2. Isothermal sorption diagrams of various molecular weights of cotton and rayon.

Effects of Molecular Weight on Moisture Regain and Tensile Properties

There are differences of M (*i.e.*, molecular weight) in the cotton and the rayon, and the number of chain ends in the amorphous region depends on M. M of natural cotton fiber is 2×10^5—5×10^5 and rayon is about several ten thousand. Therefore, it is important to study the effects of M, which changes by acid hydrolysis, on the physical properties of the wet and dry samples.

The isothermal sorption diagram of the cotton and rayon samples of M is shown in Figure 2. The diagram shows an inverse-sigmoid type curve. The diagram of the rayon filament shows larger than that of the cotton fibers over the whole range of relative humidity. This means that the rayon filament has a larger number of adsorption sites than the cotton fiber.

There is no difference in isothermal sorption curves for hydrolyzed cotton samples. This indicates that the cellulose molecules show hardly any conformational change in the amorphous region by acid hydrolysis, although the number of chain ends increases with the formation of short length molecules since the degree of crystallinity for the original cotton (about 72%) did not change by acid hydrolysis and the main absorption sites will exist in the amorphous region.

Figures 3a and 3b show the dependence of the breaking load and elongation of the cotton lint on moisture regain as a function of molecular weight (M) which changes in acid hydrolysis. In the cases of $M = 4.22 \times 10^5$ (original cotton) and $M = 2.46 \times 10^5$, the breaking load and elongation increase with moisture regain. However in the case of $M = 0.80 \times 10^5$, which approximates that of rayon, the breaking load and elongation decrease with increasing moisture regain. These results support the proposal that changes in tensile properties with wetting mainly depend on M, or with increase in the number of the molecular chain ends in the amorphous region as speculated above. The crystallinity of the cotton fiber is very high. Mobility of the amorphous cellulose chain is very low because shrinkage is very low ($<0.1\%$). Therefore, the amorphous cellulose chains are easily cut by the stress concentration points around each rigid crystallite in the dry cotton, even at short elongation. If wet cotton is strained, the probability of fracture at the molecular
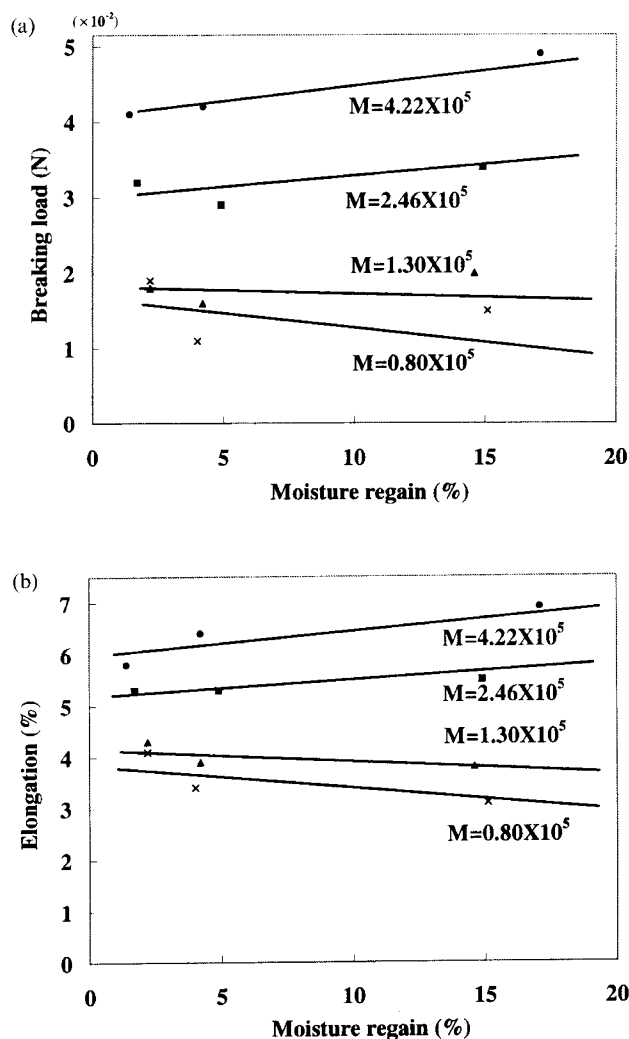
Figure 3. (a) Relationship between breaking load of cotton lint and moisture regain. (b) Relationship between elongation of cotton lint and moisture regain.

chain ends is very low, because the cotton has high M, namely very few chain ends. The elongation of the wet cotton fiber is accompanied by rearrangement (or orientation) of the amorphous chain until a large scale elongation without fracture, because the amorphous cellulose chains are more mobile than the dry ones due to bonded water. Consequently, wet cotton fiber shows higher strength than dry cotton fiber.

The orientation of the amorphous cellulose chain in dry rayon is mobile because shrinkage is very high (7.1%) and crystallinity is very low, as shown in Table II. Therefore, the amorphous cellulose chains are packed loosely and elongate easily in dry rayon. Rayon has low M, *i.e.*, many chain ends. If wet rayon is strained, the probability of fracture at the chain-ends is high. This is the most important reason why the tensile strength of the wet rayon is lower than that of dry rayon.

Cellulose molecule has many side groups (OH group) and thus intermolecular hydrogen bonding force in addition to the number of chain ends in the amorphous region may affect tensile properties.

Influence of Cross-Linking on Tensile Properties

Tensile strength and elongation of the rayon which has a short molecular chain should increase by

Table III. Tensile properties of cross-linking rayon filaments

Sample	Strength/MPa			Elongation/%			Young's modulus ($\times 10^{-3}$ MPa)		
	Dry	Wet	Wet/Dry	Dry	Wet	Wet/Dry	Dry	Wet	Wet/Dry
Original	197	154	0.78	15.9	10.6	0.67	3.4	3.0	0.91
Cross link	235	171	0.73	10.0	10.9	1.09	4.3	3.2	0.74
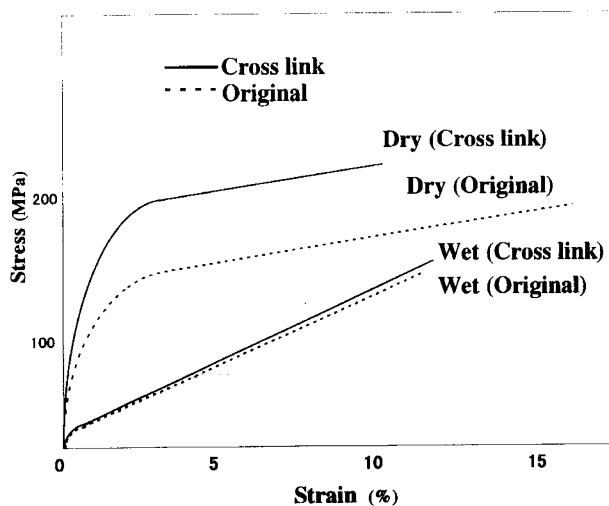
Figure 4. Stress–strain diagram of rayon filament.

cross-linking because of the formation of a long molecular chain, namely decrease of chain ends. Table III and Figure 4 show cross-linking effects on the tensile strength, elongation and Young's modulus of rayon filaments. Tensile strength and Young's modulus of the dry rayon filament increase with cross-linking, but tensile elongation decreases. These effects result from restriction of mobility of amorphous chains by cross-linking.

The elongation of wet cross-linked rayon filaments is larger than that of dry cross-linked rayon filaments as with cotton fiber samples. The tensile strength of cross-linked rayon is lower than dry cross-linked rayon. This means probably that the mobility of the amorphous molecular chain decreases by three-dimensional cross-linking, and intramolecular cross-linkings are formed and many chain ends remain even after cross-linking, although it is difficult to analysis quantatively intramolecular cross-linking.

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