Preliminary

Fine Structure and Tensile Properties of Ramie Fibers in the Crystalline Form of Cellulose I, II, and III_I*[1]

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Intrnduction

Physical and mechanical properties of cellulose fibers will reflect their framework, crystalline and noncrystalline structural substances. Our first challenge is to bring tensile properties of natural/converted ramie fibers and their crystal morphology in focus.

Experimental

Sample Preparation Starting form of the sample is highly oriented cellulose I of purified ramie fibers. Cellulose II was prepared by immersing the fibers in 3.5 N NaOH solution for 2 hours followed by washing with cold water and dried in an ambient condition. Cellulose III_I was obtained by soaking fibers in 75%(w/w) ethylenediamine for 1 hour followed by rinsing with 99% methanol. Each procedure was repeated until respective fibers gave the typical X-ray diagrams.

Crystallinity Index, Crystallite Size and Crystal Lattice Strain X-ray measurement was carried with a bundle of 100 ramie fibers attached to an X-ray sample holder equipped with a load cell. Crystallinity index was evaluated from the equatorial diffraction curve as a ratio of the sum of integrated intensities of $1\bar{1}0$, 110, and 200 reflections to the total integrated intensity. Crystallite size was calculated from Sherrer's equation. Crystal lattice strain ε_c, originated by tensile force P applied on the bundle, was evaluated from the shift $\Delta\theta$ of diffraction angle 2θ of (004) plane by the following equation.

$$\varepsilon_c = \Delta d/d = -\cot\theta\Delta\theta$$

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From ε_c and P, Young's modulus of cellulose crystal was estimated on the assumption that the density of respective fibers is equivalent to that of each crystal. Namely,

$$Ec = 100 l \rho P / w_0 \varepsilon_c$$

where w_0, l and ρ are oven dried weight, length and density of the fibers, respectively.

Tensile Test of a Single Fiber The tensile test of a single fiber of 11mm in the span-length was performed up to the total number of fifty. Subsequently cross-sectional area of the fiber was measured with the light-microscopical photograph.

Hygroscopic Isotherm Internal surfaces of the fibers in the respective crystalline forms were evaluated from the hygroscopic isotherm using B.E.T. theory.

Results and Discussion

Crystalline Morphology of Cellulose I, II, and III_I All the experimental results were shown in Table 1. The crystallinity index of ramie cellulose decreased and the internal surface increased, while crystallite width did not change by the treatment of sample preparation. These results suggest that microfibrils of cellulose II and III_I have less ordered region than that of cellulose I in the longitudinal direction.

Tensile Properties of Fibers Young's modulus of cellulose I was similar to the previously

Table 1. Properties of ramie cellulose I, II, III_I.

	CrI (%)	Crystallite width (nm)	*Ec* (GPa)	*Ef* (GPa)	Failure Strain ($\times 10^{-2}$)	Strength (MPa)	IS (m^2/g)
Cellulose I	64	4.9	122	19	3.2	554	123
Cellulose II	53	4.9	48	21	5.0	798	207
Cellulose III_I	38	5.1	63	11	5.8	560	161

CrI: Crystallinity Index; *Ec*: crysyal lattice modulus; *Ef*: fiber elastic modulus; IS: internal surface.

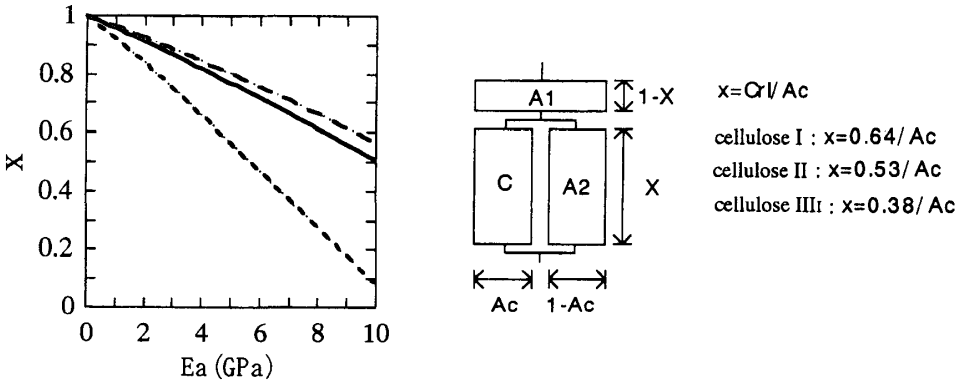

Fig. 1. Relationship of X and amorphous Young's modulus. cellulose I : ——; cellulose II : — — —; cellulose III_I: - - - -; A1, A2: amorphous component; C: crystalline component.

reported value[1)], while cellulose II was rather small. It is remarkable that Young's modulus, tensile strength and ultimate strain of the fibers became large by the conversion from cellulose I to II, while Young's modulus of cellulose III_I became small.

Mechanical Model Interpretation The crystal and fiber strains were not consistent at any given applied force for each sample. Hence a series-parallel model (Fig. 1) consists of one crystal (c) and two amorphous (A1, A2) components is suitable for each sample. Substituting Young's modulus of the crystal and crystallinity index into the model, the relationship between Young's modulus of the amorphous region and a fraction x of the crystal in the model is as in Fig. 1. Assuming that *Ea* was kept constant through the sample preparation we could estimate the amorphous fraction in series.

Conclusion

Ramie fibers in the three modified crystal forms did not show significant change in appearance but exhibited different tensile behavior caused by alternation in the fine structure.

Reference

1) K. Tashiro : *Prog. Polym. Sci.*, Vol. 18, 377–435 (1993).