Deformation of the Regenerated Cellulose Fibers III. Deformation and Refractive Indices of Air-Dried Filament

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This problem has already been studied by one of these authors and it was found[1] that the refractive indices of the air-dried filament change by stretching according to the first theory of Kratky or sometimes according to the second theory or along some courses between the two limits. Of course it was only in the early stage of deformation ($v_a<1.4$) that the second theory can be applied with a good conformity. The cause of this variation has not been found and here the study was continued and it was found that the deformation can be rather satisfactorily explained by the first theory of Kratky and the irregularity in the early stage is related to the drying condition of the fresh filament.

Experiment

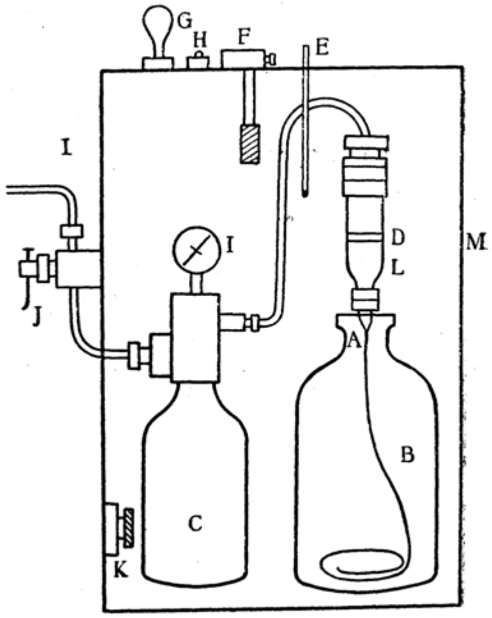
(1) **Model Filament.** A sample of commercial raw ramie was purified by extracting with ether, alcohol and then boiled in 1% NaOH solution repeatedly and bleached. The average degree of polymerization, DP, of it was about 1000.

The purified ramie was then hydrolysed with N-H_2SO_4 at 60°C for some time, followed by boiling with a 1% NaOH solution. Three samples of DP 1000, 540 and 350 were prepared by controlling the duration of hydrolysis.

These samples were dissolved in the cuprammonium solution and spun into isotropic filament of regenerated cellulose. For this purpose the cellulose was placed in a small flask having a thick wall with appropriate amounts of $Cu(OH)_2$ and NH_3-solution and its dissolution was accelerated by kneading in an atmosphere of H_2 which was supplied to the flask through a layer of conc. NH_3-solution. A glass rod (stirrer) was inserted into the flask and was connected to the flask at the mouth elastically and air-tightly by means of a rubber tube.

1) S. Okajima, *J. Soc. Chem. Ind. Japan*, **48**, 86 (1945).

The spinning apparatus was placed in a closed air thermostat as shown in Fig. 1. In the figure,



A:	Nozzle	H:	Switch
B:	Coagulating bath	I:	Manometer
C:	Air tank	J:	Valve
D:	Oil	K:	Heater
E:	Thermometer	L:	Spinning Solution
F:	Thermoregulater		
G:	Signal lamp	M:	Air thermostat

Fig. 1. Spinning Apparatus

A is a glass nozzle of 0.2∼0.3 mm diameter and B, the coagulating bath, is an aq. solution of NaOH (5%). The spinning solution, L, is kept from contact with the atmospheric oxygen by covering with a thin layer of oil D. The pressure added on L was 0.2∼0.4 atm. according to the viscosity of the spinning solution. This apparatus was also used in the experiments reported in the preceding communications on the same problem.[2]

The coagulated filament, which was deposited on the bottom of B, was taken out of B and decoppered at 25～30°C for 70 min. with a solution containing 200 g. of Na_2SO_4 and 50 g. of CH_3COOH per litre. As the regeneration is followed by a remarkable longitudinal shrinkage of the filament, it was carefully carried out under a condition that allows free shrinkage in order to keep it from the slightest tension at the regeneration.

TABLE 1

Filament No.	Composition of the spinning solution			Temp., °C	DP of the filament
	Cellulose, %	Cu, %	NH_3, %		
S-1	13.6	5.9	18.7	25	270
S-6	11.8	5.5	21.5	30	380
S-10	8.0	3.6	12.0	20	380
S-11	8.0	3.6	12.0	30	370
S-14	12.4	4.9	10.1	30	380
S-15	9.2	3.1	6.1	25	370
S-20	3.0	1.5	8.0	20	580
S-21	8.0	3.0	10.0	25	470

The spinning conditions and some of the properties of the model filaments thus obtained are summarized in Tab. 1.

(2) **Stretching of the Model Filament.** A model filament of about 1 meter length was air-dried under a very slight tension, but being sufficient to prevent the curling up. This is designated as "isotropic filament" in this paper, although it has a small intrinsic double refraction. This slight anisotropy is of course corrected in the calculation of the final stretching degree v_d as is described later.

The air-dried isotropic fiber of known length, l_{0d}, was elongated by hanging overnight a weight W at the lower end and the residual length, l_{2d} was read after removing the weight and waiting until the equilibrium state was obtained (after 1 day). The stretching degree, v_d, was then l_{2d}/l_{0d}. Various amounts of v_d were obtained by changing

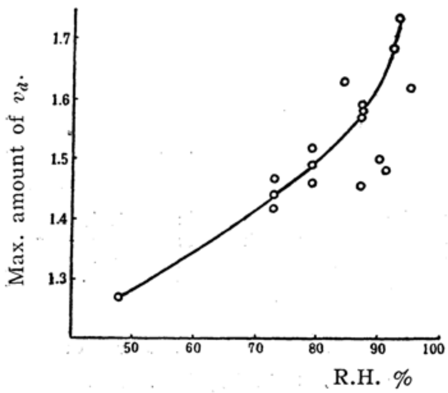


Fig. 2. Effect of the humidity upon the stretching degree.

the value of W. The maximum amount of v_d is a function of the air humidity around the filament as shown in Fig. 2. It was very difficult to carry out the stretching in the relative humidity lower than 60% in our case.

(3) **Double Refraction.** The stretched filaments were dried in vacuum at 60°C and their refractive indices $n_\parallel$ and $n_\perp$ were measured by Becke's method and corrected as already reported by the authors.[3] The intrinsic double refraction is then given by $n_\parallel - n_\perp$.

Experimental Results

(1) **Effect of the Temperature of Spinning.**—The samples S-10 and -11 were spun from the same spinning solution under the same conditions except the temperatures only, which were 20 and 30°C respectively. But the effect of this temperature difference can not be observed and the curves follow well the first theory as shown in Fig. 3.

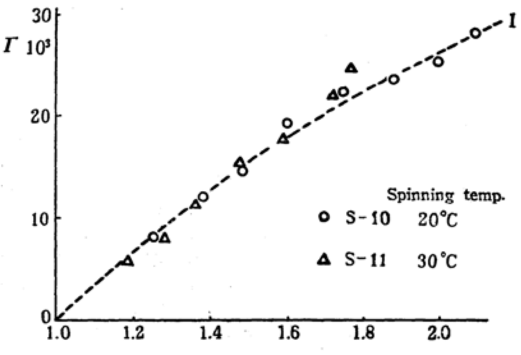


Fig. 3. Effect of the spinning temperature.

In the figure the values of v_d are corrected so as the first point of each curve is placed on the theoretical curve 1 which was calculated on the assumption of the first theory of Kratky.

(2) **Effect of the NH_3-concentration in the Spinning Solution.**—The spinning solutions of S-6, -14 and -15 are of different

2) S. Okajima, *Bull. Yamagata University*, 1950, No. 1, 21; S. Okajima and Y. Kobayashi, This Bulletin, **24**, 85 (1951); S. Okajima and S. Hayama, *ibid*, **24**, 90 (1951).

3) S. Okajima and Y. Kobayashi, *J. Soc. Chem. Ind. Japan*, 1943, **46**, 941; S. Okajima, *Bull. Yamagata University*, 1950, No. 1, 21.

NH_3-concentration, while their DP are equal to each other. The solutions of the latter two were evacuated for some time after preparing by the ordinary recipes and the NH_3-concentration was lowered to 10.1 and 6.1% form the original concentrations of 18 and 10% respectively.

The deformations of these filaments are also similar to that of the highest concentration, S-6, and all three coincide with curve 1. (rf. Fig. 4).

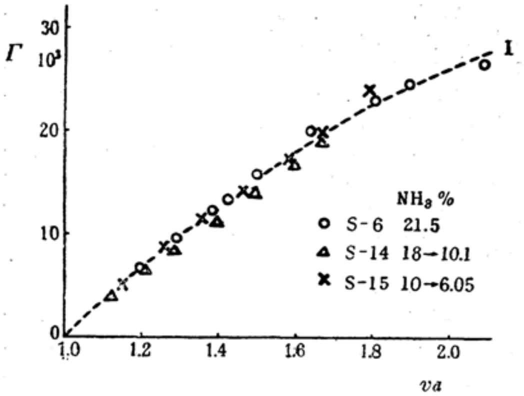


Fig. 4. Effect of NH_3-concentration.

(3) **Effect of the Cellulose Concentration of the Spinning Solution.**—A series of filaments were prepared from the spinning solution of varying cellulose concentration from 3.0 to 13.6%. Of course DP of the cellulose in the solution was higher in the case of the lower concentration and vice versa for the sake of keeping the viscosity of the solution within comparatively narrow limits, which was necessary for the smooth spinning.

It is seen from Fig. 5 that all the curves are in the vicinity of the theoretical curve

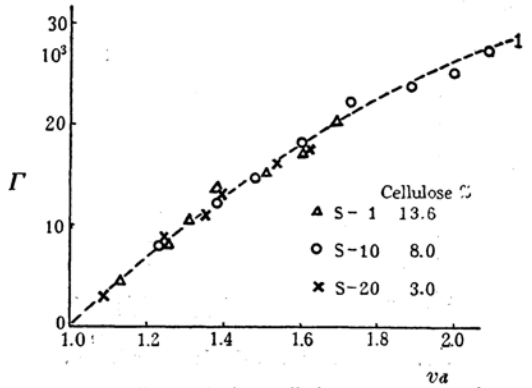


Fig. 5. Effect of the cellulose concentration

1. The effect of the concentration appears remarkably in the swelling degree of the regenerated filaments[4], but in the dry state it nearly disappears and the double refraction changes along the same course.

(4) **Effect of the Drying Condition.**—As is well known the drying of the freshly prepared fibre affects some properties of the fibre irreversibly and so now the effect of the air humidity in drying is observed.

For this purpose each of the two samples (S-20 and S-21) were divided into three parts and dried in the air of 30, 60 and 80% R.H. (S-20-1∼-3 and S-21-1∼-3). Each of S-21 series was further divided into two parts (S-21-1∼-3 and S-21-1′∼-3′) and the former were stored in a room controlled 70% R.H., while the latters in a desiccator of 90% R.H. They were stretched in the as me surroundings to observe the effect of the drying conditions. These air conditions are summarized in Tab. 2.

TABLE 2

Filament No.	S-20			S-21			S-21		
	1	2	3	1	2	3	1′	2′	3′
Drying: T, °C	34	34	9.5	33	18	16	33	18	16
R.H., %	30	60	80	30	60	78	30	60	78
l_{0a}/l_{0w}: before aging	0.656	0.678	0.692	0.666	0.675	0.687	0.666	0.675	0.687
after aging	—	—	—	0.666	0.675	0.687	0.693	0.688	0.697
Aging: T, °C					19			20	
R.H., %					70			80	
Stretching: T, °C		11–13			18–22			18–22	
R.H., %		74–79			73			87–88	

Figs. 6∼8 indicate that in the first two series the influence of different drying conditions is apparent: the filament dried at lowes R.H. has a steeper initial change while that dried at 80% R.H. shows an ordinary change. But this difference does not exist between S-21-1′∼-3′ and three curves coincide with each other and also with the curve 1.

The above phenomena may be explained by a concept that difference in drying

4) P. H. Hermans, "Physics and Chemistry of Cellulose Fibre", 1949.

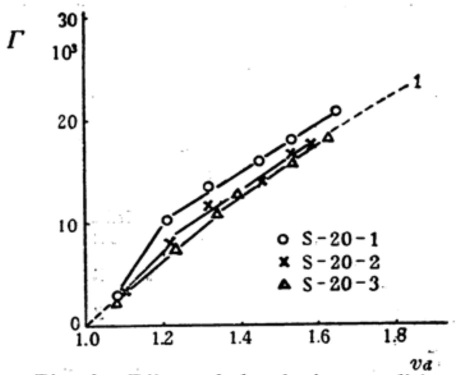


Fig. 6. Effect of the drying condition.

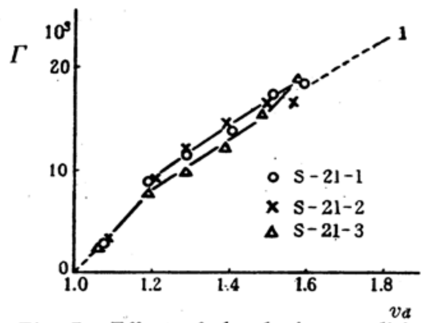


Fig. 7. Effect of the drying condition.

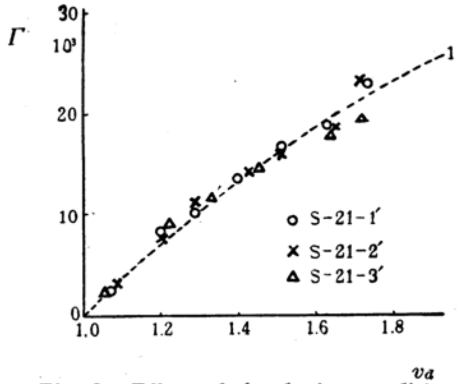


Fig. 8. Effect of the drying condition.

condition brings about some structural difference which disappears while being aged in such humid air as 90% R.H. but does not disappear in the low humidity. This concept is supported by the data in Tab. 2, according to which the dry length of the isotropic filament relative to the wet increases appreciably as the air becomes humid, and this difference disappears while the filaments are aged in 90% R.H. although it remains in the low humidity. These behaviors will have some connection with the change in weak junctions of cellulose molecules which will become less cohesive in the higher moisture content of the filament.

Summary and Discussion

Deformation of the dried filament can be expressed in the term of the first theory of Kratky on the whole as in the case of swollen filament(2). And this behavior is not affected by the slight change of the spinning conditions of the filament such as the temperature and the composition of the cellulose solution. But in the case of the fila ment dried in the less humid air the orientation occurs more prominently in the early stage of the stretching but soon follows the above deformation mechanism.

This drying effect will illustrate the variation seen in the previous paper.(1) Of course it is noteworthy that the value of l_{0a} changes a few percent with the variation of the air humidity during measuring and, therefore, this factor must be taken into consideration when l_{0a} and l_{2a} are read under the different air conditions. Some of our older data are thought to contain small fuctuations due to this fact.

One of the authors has also reported[5] that a filament stretched in water to some degree seems to have the same molecular orientation pattern as that given by stretching in the dry state to the corresponding anisotropy and this anisotropic filament deforms further by restretching in the dry state according to the same mechanism which is shown by the isotropic filament in the dry deformation. This seemedto be a very curious and interesting fact but now becomes clear as the deformation mechanisms of the fresh (swollen) and driedfilaments are similar to each other.

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5) S. Okajima, *J. Soc. Chem. Ind. Japan*, **48**, 87, (1949); **49**, 52, (1944.).