Plastic Deformation of the Regenerated Cellulose Fibers. II. Deformation of Freshly Prepared Fibers from the Standpoint of Refractive Indices

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I. Introduction

In the report already presented by one of the authors[1] about the same problem, the refractive indices $n_{\parallel}$ and $n_{\perp}$ were plotted against the stretching degree v_{2w}, in the swollen state, for the author believed that the orientation degree of the regenerated fiber remained unchanged even when it was air-dried or reswollen, as its dichroic constant had been found unchanged by these treatments.[2] It was concluded from the result that the deformation conformed to the second theory of Kratky[3] till $v_{2w}=1.4$, but to the first theory[4] thereafter. In this conclusion the volume change during stretching was neglected, so taking this factor into consideration, the authors studied the problem from the standpoint of dichroism and some different conclusions were obtained in the previous paper.

Now to ascertain this result from other points of view the same study was repeated again by tracing the change of the refractive indices during stretching.

(1) S. Okajima, *J. Soc. Chem. Ind. Japan*, **49**, 167 (1946).
(2) S. Okajima, T. Nakayama and F. Adachi, *J. Soc. Chem. Ind. Japan*, **49**, 128 (1946).
(3) O. Kratky, *Kolloid-Z.*, **84**, 149 (1938).
(4) O. Kratky, *Kolloid-Z.*, **64**, 213 (1933).

II. Experiment

(1) Sample.—Two samples were used. They were prepared by the cuprammonium method already described in a previous report,[5] but in the present study the more viscous solution of cellulose was used. The conditions of preparation were summarized in Table 1; the sample No. 20 was the same as that used in the previous paper.

Table 1

Sample No.		S-1	S-20
Spinning solution	Cellulose (%)	13.6	3
	Cu (%)	5.9	1.5
	NH_3 (%)	18.7	8
Spinning temp. (°C.)		25	20
DP		270	580
Swelling degree, q_0[6]		6.56	13.9

(2) Stretching.—The swollen isotropic fiber of 30∼95 cm. (l_{0w}) was stretched slowly in water to l_{1w} and the length was kept unchanged overnight. After that tension was released for one day, the residual length, l_{2w} was measured. During the operation the fiber was kept always in water; the temperature were 22.5° and 14° in the cases of S-1 and S-20 respectively. The stretched fibers were air-dried and their refractive indices were measured.

(3) Intrinsic Double Refraction.—The specimens were dried under vacuum at 60° and $n_{\parallel}$ and $n_{\perp}$ were measured by the Becke's method. The immersion liquids were prepared by mixing appropriate amounts of two or three among monochlorbenzol, *o*-dichlorbenzol, iodbenzol and tricresylphosphate. Observed data were corrected on the standard base of $n_{iso}=1.5356$, as it has already been precisely reported.[7] The intrinsic double refraction Γ is given by $n_{\parallel}-n_{\perp}$.

In the above notations $n_{\parallel}$ and $n_{\perp}$ are the refractive indices of fiber for the plane-polarized D-line, oscillating parallel and perpendicular to the fiber axis, while n_{iso} is that of the isotropic one.

(4) Swelling Degree.—The volumes of the fiber swollen in water during streching, V_{0w}, V_{1w}, V_{2w} and the volumes after drying $V_{(d}$, V_{2d}, were measured microscopically as described previously. From these results the swelling degrees, q_0 and q_2 were calculated. The detail of the method has been given in the preceding paper. The suffixes *w* and *d* mean the wet and dry states. 0 and 1 the states before and immediately after stretching and 2 the residual one.

III. Experimental Results

(1) **S-1.**—Fig. 1 shows the relation $R_{2w}\sim v_{2w}$ and $v_{1w}\sim v_{2w}$. The knick point G can not be observed clearly in this case. Correcting the effect of the small intrinsic double refraction of the original sample and plotting Γ against v_{2w}, a similar curve (1) is obtained to that shown in the previous paper (Fig. 2).

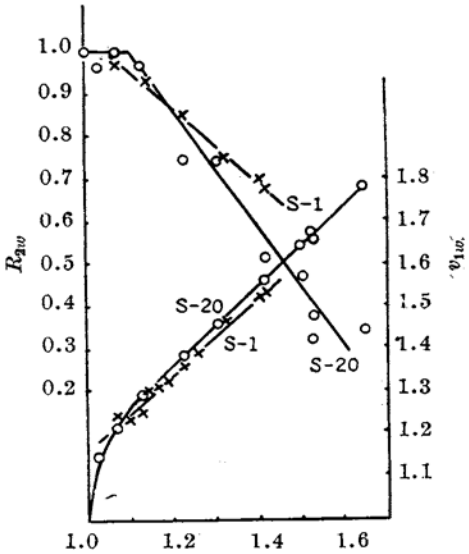

Fig. 1.

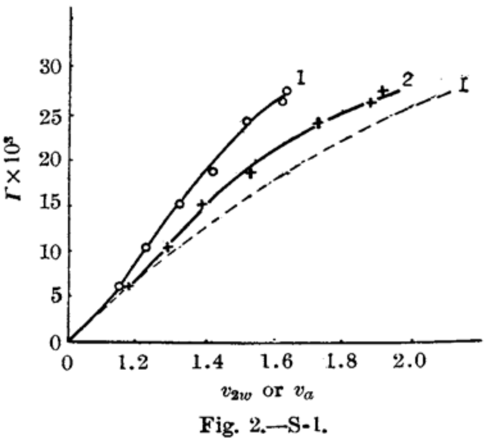

Fig. 2.—S-1.

But when the correction of the volume decrease is added further to the above v_{2w} and it is denoted as v_a the curve (2) is obtained. Both curves are qualitatively similar and it may be concluded that comparing with the theoretical curve (I), they deviate upward at the beginning but afterwards go parallel to the theoretical curve, which has already been calculated[8] on

(5) S. Okajima and other. *J. Soc. Chem. Ind. Japan*, **43**, 355 (1940); etc.

(6) About the notations used in this report, see the preceding paper.

(7) S. Okajima and Y. Kobayashi, *J. Soc. Chem. Ind. Japan*, **46**, 941 (1943).

(8) S. Okajima, *J. Soc. Chem. Ind. Japan*, **40**, 793, 795 (1937).

the assumption of Kratky's first theory.

(2) **S-20.**—In this case too similar phenomena can be seen. (Figs. 1 and 3). A knick point G is clearly seen in this case. The relation $\Gamma \sim v_{2w}$ is also the same as that of S-1 but corrected curve against v_a satisfies the theory from the first and deviates for $v_a > 1.6$.

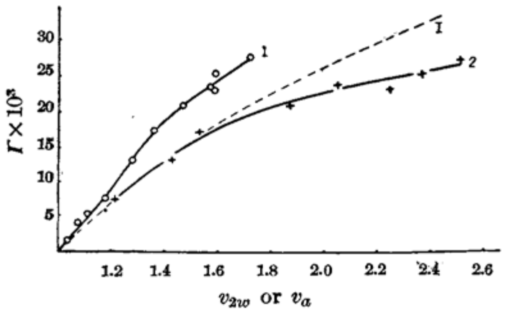

Fig. 3.—S-20.

The swelling degrees of S-1 and S-20 are 6.56 and 13.9 respectively. The deformation curve of the former, which is prepared from the solution of the higher cellulose concentration and has a smaller swelling degree, deviates remarkably upward from the theoretical curve, while the latter prepared from the solution of the more dilute cellulose concentration and highly swollen satisfies the theory. This tendency coincides with that gained dichroitically in the preceding study.

IV. Comparison with the Data by P. H. Hermans and Others

P. H. Hermans, J. J. Hermans, D. Vermaas and A. Weidinger(9) studied the orientation of the viscose and the regenerated fibers using x-ray and retardation methods and obtained very interesting results, among which the case of the regenerated fibers is very akin to our study, so their data are picked up in Table 2 in order to compare them with ours. The notations are changed according to the present authors' rule.

In Table 2 Γ is calculated as $f_0 \cdot \Gamma_\infty$, where f_0 is the orientation factor and Γ_∞ is the intrinsic double refraction at the complete orientation and 0.043 according to Hermans. v_a is also corrected in such a way that the first point of each curve comes on the theoretical one.

Table 2

Cellulose conc., %		q_0	q_{2w}	v	v_a	q_2/q_0	$\Gamma\times10^3$
(i) Freshly regenerated fiber.							
F_3	4.0	8.1	7.85	1.04	1.04	0.97	1.5
		7.7	7.35	1.19	1.20	0.96	5.6
		7.6	6.3	1.45	1.545	0.83	15.3
F_5	6.0	5.95	5.8	1.03	1.04	0.98	1.5
		5.95	5.4	1.20	1.24	0.91	8.0
		5.95	4.7	1.49	1.60	0.79	18.9
		5.95	3.5	1.79	2.09	0.59	29.5
F_9	10.5	4.7	4.7	1.05	1.04	1.00	1.7
		4.7	4.3	1.24	1.26	0.92	10.5
		4.5	3.16	1.56	1.73	0.70	23.4
		4.75	3.16	1.65	1.86	0.665	25.8
(ii) Reswollen fiber							
R_3	4.0	2.34	2.45	1.25	1.06	1.05	2.4
		2.09	2.26	1.39	1.17	1.08	7.1
		2.10	2.18	1.62	1.38	1.04	12.0
		2.15	2.02	1.99	1.76	0.94	17.6
R_5	6.0	2.34	2.73	1.22	1.03	1.15	1.2
		2.30	2.84	1.41	1.17	1.23	4.1
		2.36	2.95	1.64	1.35	1.25	10.1
		2.20	2.52	1.92	1.65	1.14	18.1
R_9	15.5	2.31	2.60	1.23	1.05	1.13	1.9
		2.29	2.75	1.43	1.19	1.20	6.45
		2.33	2.35	1.73	1.585	1.00	18.9
		2.31	2.26	1.96	1.83	0.98	24.1

According to these data the volume of the fiber decreases from the first in the freshly regenerated one, but a remarkable increase can be seen in the case of the reswollen fiber. Our data also confirm this, and even the freshly prepared sample also showed a slight increase of the volume as described in Part I.

The relation between Γ and v_a is shown in Fig. 4; all the samples have the similar behaviors and they satisfy the first theory on the whole. But on precise observation, the curves of F_9 and F_3 deviate up and down respectively from the theoretical curve (1), although F_5 coincides with it completely. At the swelling degrees of F_3, F_5 and F_9 are 8.1,

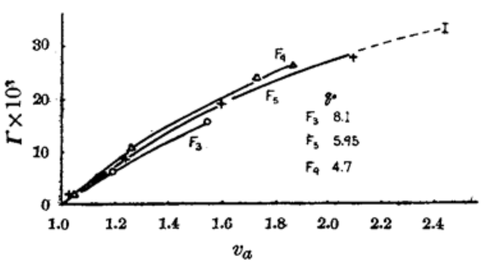

Fig. 4.

(9) P. H. Hermans, J. J. Hermans, D. Vermaas and A. Weidinger, *J. polymer Science*, **3**, 1 (1948).

5.95 and 4.7 respectively, it may be said that the higher the swelling degree of the fiber is, the more effective the orientation is. This tendency is the same as already pointed out repeatedly by the authors.

As to the case of the reswollen fiber it will be treated fully in the following papers.

V. Comparison with the Affined Deformation Theory

Affined deformation formula proposed for the rubber-like polymers has been extended by J. J. Hermans[10] as below for the case where the volume is changed during the deformation

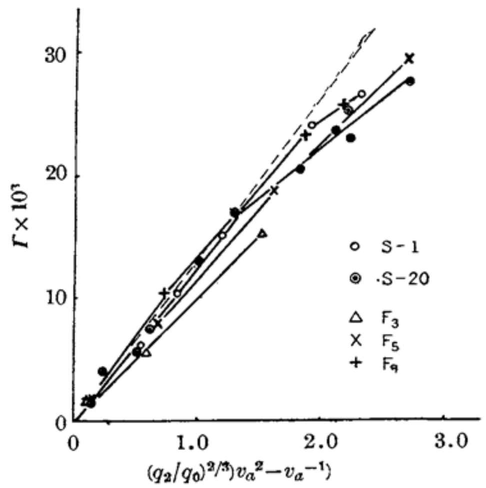

Fig. 5.

(10) J. J. Hermans, *Trans. Faraday Soc.*, **43**, 591 (1947).

$$\Gamma = k(q_2/q_0)^{2/3}(v_a^2 - v_a^{-1}).$$

This has also been discussed by our dichroic data and its approximate conformity has been recognized in the preceding paper.

In Fig. 5 our values of Γ and Hermans' data in Table 2 are plotted against $(q_2/q_0)^{2/3}$ $(v_a^2 - v_a^{-1})$. The broken line in the figure is a theoretical relation which is required by the line shown in Fig. 8 in Part I. Of course the inclination of this line is calculated from that of the $\log D$-line by using the relation.

$$\log D = 20\,\Gamma.$$

Now all the points are on each line for the smaller degree of stretching and the inclinations of the lines are nearly coincide with that of the theoretical one, excepting the cases F_3 and F_5. But for the abscissa larger than 1.3 the points deviate downward. So the conformity between the experiment and theory is limited within a narrow range and can not be said to be perfect.

VI. Conclusion

The results obtained by using the double refraction are similar to that already described in the first report.

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