Heterogeneous Structure of Rayon. II. Orientation Degree of the Skin and Core of Rayons

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In the previous report a possibility of peeling-off the rayon fiber by a heterogeneous acetylation was recognized. So now the orientation degrees of the skin and core are measured optically, applying this method, and the effect of the conditions of acetylation upon them is discussed.

Experiment

Five samples of rayon were acetylated by using the bath A as already described in the preceding report. In some cases the other bath compositions were used, where only the diluent benzol was substituted by carbon tetrachloride or toluol. The moisture content of the sample was also controlled.

The acetylated fiber was extracted with chloroform, treated with N/5 NaOH aq. solution, washed with distilled water and air-dried. The refractive indices, $n_{\parallel}$ and $n_{\perp}$, of the peeled-off fiber were measured with the Becke's method and the observed values were corrected on the standard value of $n_{iso}=1.5356$ with the authors' method.[1] $n_{\parallel}$ and $n_{\perp}$ are the refractive indices for the plane-polarized D-line, oscillating parallel and perpendicular to the fiber axis; then the intrinsic double refraction Γ is given by $n_{\parallel}-n_{\perp}$.

The amount of the peeled-off cellulose is expressed by P_r %, which indicates the thickness of the peeled-off shell. If the sectional area and the length of the single fiber are denoted by S_0 and l, then its weight is

$$W=S_0ld,$$

and

$$L_T=(S_0-S)ld,$$

where d is the density of the original fiber and S_0 and S are the cross sectional areas before acetylation and after acetylation and extraction, followed by saponification respectively, providing, of course, that the length is very long compared to S_0, the form of the cross section remains similar during the peeling-off process, and the density is equal through the cross section. Then

$$1-L_T/W=S/S_0.$$

Therefore, $(S/S_0)^{1/2}=(1-L_T/W)^{1/2}=r/r_0,$

and $P_r=1-r/r_0=1-(1-L_T/W)^{1/2},$

where r_0 and r are the radii before and after the peeling-off.

The above assumptions are not thought to hold exactly good in the actual case, and P_r is, therefore, only an apparent representation, although it is right in the dimension.

Conditions of treatment

The results obtained are given in Figs. 1—4, from which some interesting phenomena can be seen.

(1) Effect of moisture of the sample.—The moisture content of the sample poured into the acetylation bath does not affect the orientation of peeled-off fiber according to P. H. Hermans,[2] but in our data the effect is clearly seen. Some of the examples are given in Fig. 1, where the samples V−1 and −2 were acetylated under the following conditions; the vacuum-drying was carried out at 60°C in each case.

Table 1

Conditions of Acetylation

Sample		Conditioning	Acetylation temp., °C	Diluent
V−1	(1)	Air-dried	45	Benzol
	(3)	Air-dired, acetylated after immersion into benzol overnight	60	Benzol
	(4)	Vacuum-dried	60	Benzol
	(5)	Vacuum-dried	60	Toluol
	(8)	Vacuum-dried, conditioned to the moisture content of 4.23%	60	Benzol
	(9)	Vacunm-dried, conditioned to the moisture content of 14.1%	60	Benzol
V−2	(1)	Air-dried	45	Benzol
	(2)	Air-dried	60	Benzol
	(3)	Vacuum-dried	45	Benzol

The vacuum-dried samples (4) and (5) of V−1 show the existence of the outermost layers and the cores of the completely and almost constant birefringence and the transition layers between them, while in the cases of the air-dried ones Γ decreases continuously from the surface toward the core and this tendensy is more remarkable

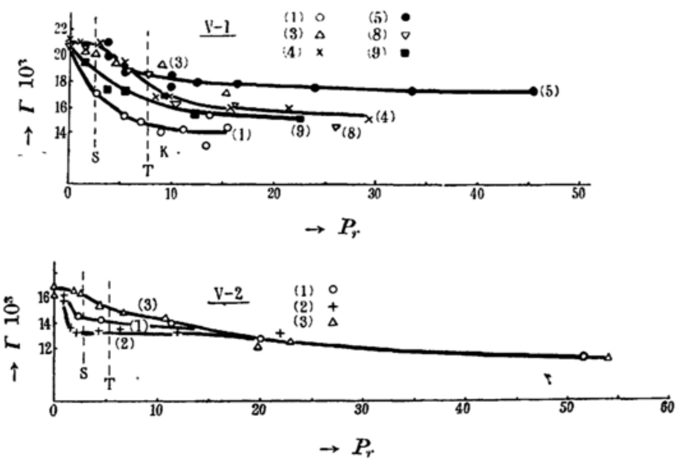

Fig. 1.

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

(2) P. H. Hermans, *Textile Research J.*, **20**, 553 (1950).

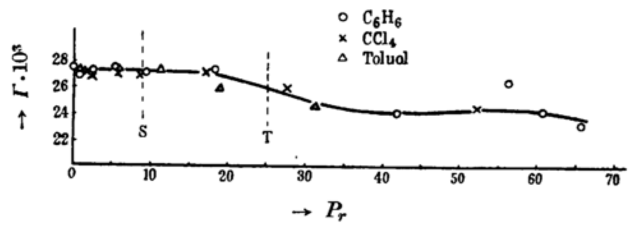

Fig. 2.—Bemberg.

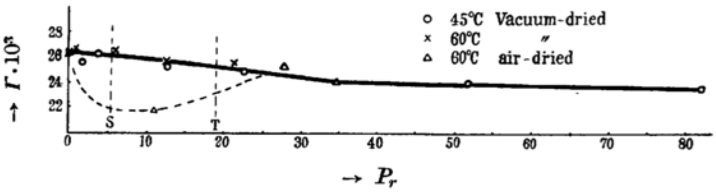

Fig. 3.—Tirecord.

the larger the moisture content of them is (rf. the samples V−1, 1, 3, 8, 9).

The cause of this phenomenon is not clear but the authors believe that the factor causing this difference is the moisture of the sample and not the vacuum-drying because the immersion of the air-dried one into benzol overnight gives the vacuum-dried type (rf. V−1, 3) and also the conditioning after the vacuum-drying gives the air-dried type again (rf. V−1, 8 and 9).

The same phenomenon can also be seen in the case of V−2, where the effect disappears as the reaction proceeds; this is because the loosely absorbed moisture is substituted by the molecules of benzol.

As the results, the moisture effect appears especially in the early stage of reaction so the vacuum-drying is thought to be necessary to recognize the existence of the outermost skin, if any, so all of the samples were vacuum-dried in the following experiments, excepting ones which were especially described.

(2) **Effect of diluent.**—Two samples of V−1 were peeled-off by acetylating in the bath C, but with using toluol and benzol as the diluent (rf, 4 and 5). Fig. 1 indicates that the curves are similar in shape but Γ of the core are more or less different.

A cuprammonium rayon was also examined by using benzol, toluol and carbon tetrachloride as the diluents. In this case the three curves coincide completely with each other as shown in Fig. 2, therefore, the effect of diluent seems to be negligible.

(3) **Effect of the acetylation temperature.**—A sample of tire cord was examined by acetylating at 45 and 60°C. Their results coincide completely as shown in Fig. 3 and, therefore, the temperature effect can be disregarded.

In the series (3) the acetylation was carried out without vacuum-drying, so the first point (P_r=10.8%) is remarkably low but the other two points are normal. The reason was already described in the section of the moisture effect.

Distribution of the orientation degree and the type of rayon

Now it is clear that the careful treatment can give the reasonable results, and observing the curves $\Gamma - P_r$ of the vacuum-dried samples, they indicate some interesting facts.

(1) **The distribution of the orientation degree and the skin structure.**—Observing the radial distribution of Γ of V−1, −2 and also −3 (Fig. 4), whose skin structures are clearly shown by the microscopical observation of the stained cross sections, the outermost skin, the core and the transition layer are recognized in each case. The orientation of the outermost skin, whose thickness is 2−4% of the total radius is constant, while that of the core decreases very faintly toward the center.

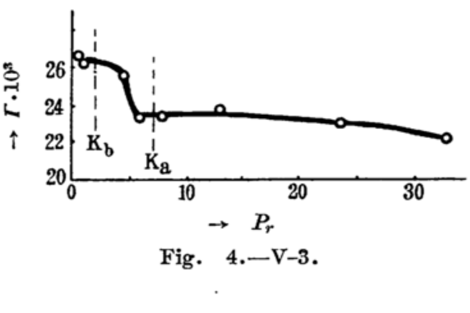

Fig. 4.—V-3.

Moreover in the case of the tire cord or the cuprammonium rayon, one of which is said to have a thickened skin and the other no skin, the similar distribution of the orientation can be seen, although the tendency is slight, as the results of the thickening of the outermost and the transition layers and also the smaller difference of orientation between the skin and core.

This difference of orientation between the skin and core is much smaller than that which was expected from the impression hitherto given by the optical observation of its cross section.

(2) **Structure of the skin.**—Some of the microstructures of the skin were tested by many authors. The density of the skin has been thought to be larger according to the methacromasic[3] observation, but the result of Hermans[2] was opposite. As to this problem a phenomenon of some importance is seen in the above data.

As shown in Figs. 1 and 2 of Report I, there is a knick point K on each curve of L_1/W versus A. The curve indicate the ratio of the rate of acetylation of the fiber and the rate of dispersion of the acetylated layer in the bath, so the appearance of a knick point means the occurence of the abrupt change of this ratio, which may probably be caused by the dissolving away of the skin, providing, of course, that the resistance of the skin toward the penetration of the acetylating agents and dispersing away in the bath is larger than that of the core. The behaviour is the same in the case of the air-dried sample and this seems to indicate a priori existence of the outermost skin in the original fiber.

This presumption is supported by the following consideration. If the amount of cellulose which was lost in the acetylating bath (actually as triacetylcellulose) up to the knick point K is L'_K per 100 part of the original sample and the acetic acid content at K is $10^2.A$ %, then the weight of the partially acetylated sample, W_K, is given by the formula (1) of Report I as follows,

$$W_K=(100-L'_K)/(1-0.7\,A) \qquad (1)$$

If the corresponding value of L_2 at K is denoted by L''_K, then

$$100-L'_K-L''_K+1.778\,L''_K=W_K \qquad (2)$$

$$L''_K=\frac{0.7A(100-L'_K)}{(1-0.7A)\times 0.778} \qquad (3)$$

The value of L_T/W is smaller than $(L'_K+L''_K)/W$ by some 1.5 according to Fig. 7 in the preceding report, therefore in this case

$$L_T=L'_K+L''_K-1.5 \qquad (4)$$

This gives the corresponding value of P_r.

The table below contains these values at the knick point, where the values of L'_K and A of each sample are obtained on each curve in Figs. 1 and 2 of the preceding paper. In the case of $V-3$, the curve is too steep to obtain the correct value of K, so K_a and K_b are used as the limiting values as shown in Fig. 5; the acutal value must be between them.

Table 2

Sample	$V-1$	$V-2$	$V-3$ (a)	$V-3$ (b)	T	C
A (%)	12	11	8.5	4	25	31
L'_K/W	5.3	6	8	1.8	12	15
L_T/W	15.0	10.5	14.1	3.9	34.5	43.8
P_r (%)	7.8	5.4	7.3	2.0	19.1	25.0

(3) K. Ohara, *Scientific Paper. I. P. C. R.*, **25**, 154 (1934).

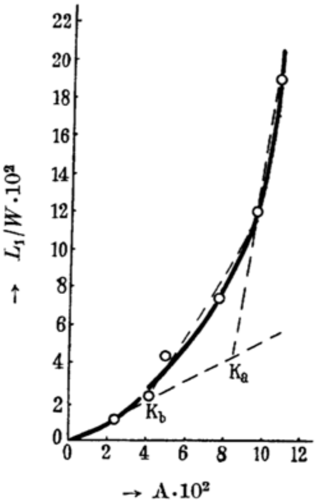

Fig. 5.—V-3.

The calculated value of P_r is indicated by a broken line (T) on each curve of $\Gamma-P_r$; then all of them seem to be in the transition layer of each sample. And in the case of $V-3$ also the transition layer is held between the above two limiting lines.

The same behaviour is also seen in the tire cord or the cuprammonium rayon. This fact is thought to support the existence of the skin structure as described above even in a case, where the existence of the skin has been denied. Of course the skin structure of these rayons are not so remarkable and correspondingly the knick points are less distinct.

These results allow us to venture to calculate the thickness of the outermost skin. If we suppose that the knick point K appears when the outermost skin of the least porosity has dispersed away in the bath liquor and the resistance for the acetylation and the dispersion have decreased abruptly, then L_1 indicates the amount of the outermost skin, which is easily calculated from the $L_1/W-A$ curve.

As shown in Figs. 1—3, in which the calculated value is indicated by a broken line (S), the above supposition is proved to be nearly true in the cases of $V-1$ and -2 and the tire cord. But the value of the cuprammonium rayon which is obtained is too thin. This is probably because the microstructure of the cuprammonium rayon is more or less different from that of the viscose rayon due to the different nature of the spinning reaction.

As to $V-3$ it is very difficult to obtain exactly as already described, so it was omitted from the present discussion.

Furthermore, it is worthy to note that the slope of curve $L_1/W-A$ between the origin and K is constant but thereafter it varies according to the type of rayon, which may indicate that the microstructures of the skin of the various rayons are nearly equal to each other but not of the core.

Conclusion

A peeling-off method by the heterogeneous acetylation can give reasonably the radial distribution of the degree of orientation when it is carried out under the appropriate conditions. The skin structure is shown by this method in the cases of the tire cord and even the cuprammonium rayon. And the resistance of the skin against penetration and dispersion seems larger than that of the core.

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