Heterogeneous Structure of Rayon. I. Some Observations of the Heterogeneous Acetylation of Rayon

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It has long been known that the viscose rayons have the skins whose microstructures differ from those of the cores, but until recently there was no attempt to clear up these differences by studying the microstructures of the skin and core separately, excepting a short report by Nakayama,[1] who studied separately their orientation degrees by preparing a longitudinal section of rayon.

But this method requires extreme skill, so the authors studied the same problem since 1950 with a completely different method and have gained some interesting results. Recently the authors learned that some papers referring to the same problem have already appeared since 1946 by Elöd,[2] Preston,[3] and Hermans,[4] among which we could read the original papers by Preston and Hermans, according to which the similar experiments seem to be carried out by Elöd to get some similar results. But some discrepancies are thought to exist between the results of these authors, including the authors of this present paper, so our data are also reported here.

Consideration about the heterogeneous acetylation suitable for peeling-off the rayons

A method can easily be considered to trace radially the heterogeneous structure by peeling-off the rayon from the surface toward the center. And the authors also tried this chemically by acetylating the outer layers of the filament to the various depths by acid-catalyzed heterogeneous

(1) T. Nakayama, *Textile Review, Japan*, **40**, 60 (1949).
(2) E. Elöd & H. G. Fröhlich, *Melliand Textilb.*, **27**, 103 (1946); *Textile Research J.*, **18**, 487 (1948).
(3) J. M. Preston, *J. Textile Inst.*, **39**, T 211 (1948); **40**, T 327 (1949).
(4) P. H. Hermans, *Textile Research J.*, **20**, 553, (1950).

reaction by keeping the fibrous state and subsequent dissolution of the acetylated shell. The topochemical acetylation of the cellulose fiber was precisely studied by I. Sakurada,[5] who concluded that the acetylation is also a micelle-heterogeneous reaction and the fiber must be swollen for the sake of the rapid and smooth acetylation.

But for our present purpose, it is desirable that the penetration velocities of the acetylation reagents through the inter-micellar region be as equal as possible to that through the micell itself, although then the acetylation velocity may necessarily be very much smaller. So the heterogeneous acetylation of rayons was tried under the deswollen states in the following experiments.

Nitration, which is more speedy than acetylation, may also be used instead of acetylation for the above purpose, on which the study is now in progress.

Experiment

(1) **Sample.**—Five rayons were used as samples:

V-1: a viscose rayon on the market, 120/25 denier.

V-2: a viscose rayon, manufactured some 15 years ago, 120/25 denier.

V-3: an old viscose rayon, manufactured on trial some 40 years ago by Prof. Hata, who was one of the famous pioneers of the Japanese rayon industry.

T: a viscose tire cord.

C-1: a cuprammonium rayon on the market.

These samples were extracted with ether for 10 hours, washed with hot distilled water (60°C) repeatedly. The purified samples were vacuum-dried and acetylated; in some experiments the air-dried samples were also used. The effect of the moisture content of the sample will be discussed in the following paper.

(2) **Acetylation.**—1 gm. of a sample was poured into an acetylating bath, contained in an ordinary test tube stoppered lightly by a cork stopper and acetylated at the constant temperature. Four bath compositions shown in Table 1 were tried, among which the bath A is the most suitable and was used successfully for the most experiments at 40 ~60°C. At 100°C the integration of the fiber was too remarkable for bath A to be used.

Table 1

Bath composition	A	B	C	D
Benzol	30 g.	30 g.	30 g.	
Acetic anhydride	10 g.	10 g.	10 g.	40 g.
Sulfuric acid (1.84)	0.05cc.	0.025cc.	0.10 cc.	
Potassium acetate				12 g.
Glacial acetic acid				10 g.

The bath C contains too much sulfuric acid and disintegrated the fiber considerably, although the reaction proceeds rapidly in this case; when B is used, on the contrary, the reaction is too slow due to the too small content of the catalyst. These two baths are, therefore, not suitable. In the bath D, the fiber form was retained completely even when it was used at 100°C, but the acetylated product did not dissolve in any usual solvents and this was abandoned.

When the samples had been acetylated for the desired time (0.5~1160 hours), they were taken out, washed with benzol, and with hot distilled water (60°C) repeatedly and air-dried at room temperature.

(3) **Measurement of the acetic acid content.**—0.5 g. of the acetylated product was poured into a 20 cc. of N/2 NaOH aq. solution in a tightly closed flask and saponified for 48 hours at the room temperature, after which the consumed alkali was titrated and acetic acid content was calculated as usual. The saponification was ascertained to be enough and it needed to be continued for 48 hours under the present conditions.

The observation of the acetylation process

(1) **Partial dissolution of the fiber during the acetylation.**—If W g. of a sample is acetylated under an ideal condition and if we obtain W_A g. of the partially acetylated product, whose degree of acetylation is x mole. per glucose residue and the acetic acid content is 100 A%, then

$$A = 60x/(162+42x) \qquad (1)$$

and therefore,

$$x = 162\,A/(60-42\,A), \qquad (2)$$

and

$$W_A = \frac{W}{162}(162+42x) = \frac{W}{1-0.7A}. \qquad (3)$$

But the observed value of W_A was always smaller than that calculated from the relation (3), and this decrease in weight became larger and larger as the acetylation time elongated and A also grew larger. This is thought to be due to the partial dissolution of the acetylated part of the rayon.

Now this partially dissolved cellulose, actually dissolving as triacetylcellulose, is assumed to be L_1 g, them

$$W_A = (W-L_1)/(1-0.7\,A). \qquad (4)$$

So L_1 can be calculated from W_A, W and A.

Fig. 1 shows the relations of L_1 and A of the samples V-1 and V-3, acetylated under various conditions (see the next report), according to which L_1 grows linearly but slowly with A, (α-range), and beyond a certain point K the curve is very steep (β-range). Similar phenomena are also seen in the cases of the other samples as shown in

(5) I. Sakurada, *J. Soc. Chem. Ind. Japan*, **35**, 123 B, 283 B, (1932); **36**, 280 B, 299 B, (1933); **37**, 53 B, 599 B, (1934).

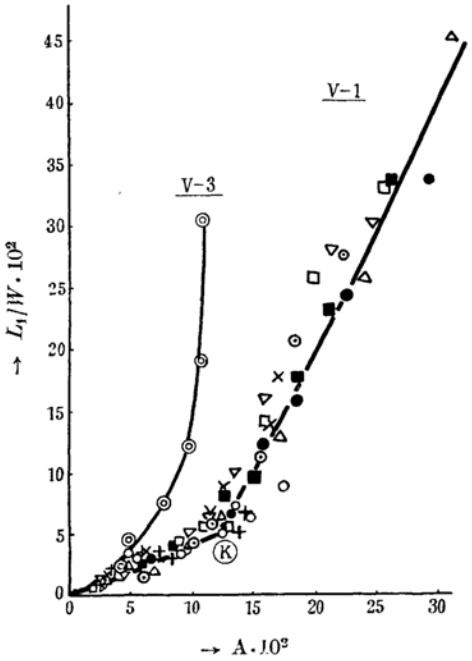

Fig. 1.

Fig. 2. In the α-range the fluctuation of the points is comparatively small, and its slope is independent upon the type of the rayon, while they are dispersed in the β-range and the slopes also vary from sample to sample. The position of K and the slopes of the curves in the β-range are characteristic to each sample, but not remarkably affected by the acetylating conditions. The characteristic of the curve will be described in the following paper. Because of these facts, acetyl content A did not obey the diffusion formula as suggested by I. Sakurada,[5] but after a certain time of reaction, the acetylation velocity increased again.

(2) Microscopic observation of the acetylated fibers.—As well known, many stripes running parallel to the fiber axis can be seen under a microscope on the surface of our viscose samples (Fig. 3 A), but as the acetylation proceeds the surface of the fiber becomes very rugged and many small cracks which cover the stripes appear on them (Fig. 4). But when the yarn is poured

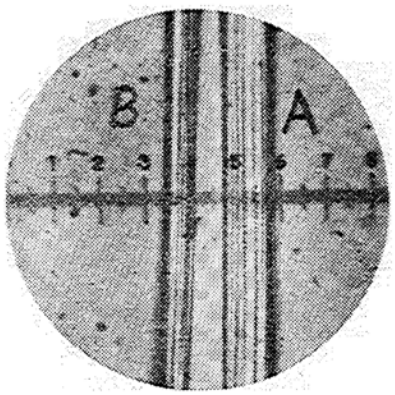

Fig. 3.

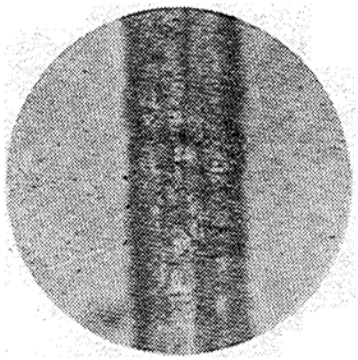

Fig. 4.

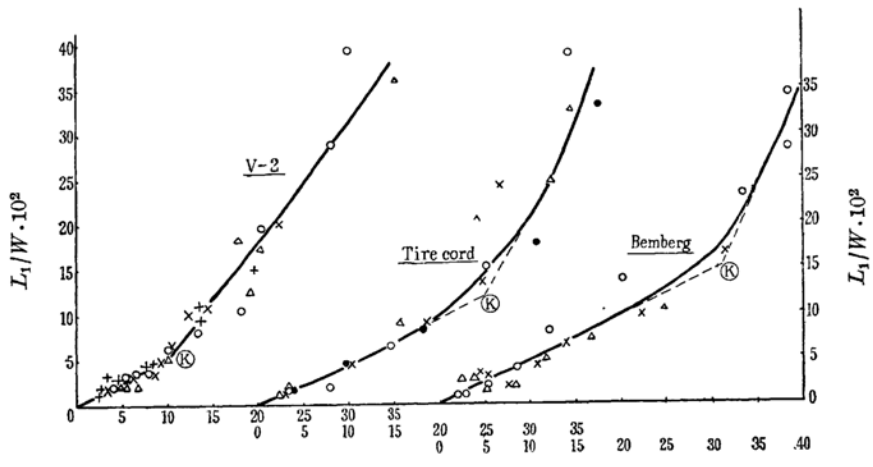

Fig. 2.

into chloroform and warmed at 60°C for 3—4 hours, the stripes reappear again and at the same time the fiber becomes transparent and the external appearance recovers, excepting that its diameter becomes slender (Fig. 3 B). This observation can be clearly explained by considering that the outer layer of a certain thickness, corresponding to the acetylation time, changed to triacetyl cellulose. These acetylated layer depolymerized considerably during the acetylation, so it is partly soluble in the acetylation bath and also its mechanical strength is also very poor and it cracks as the result of the mechanical shocks. This layer can be removed by treating with chloroform. If the acetylation proceeds fiber-heterogeneously the dissolution by chloroform occurs concentrically and, again, the stripes can be seen on the new surface of the rayon, and of course, then, the fiber becomes slender.

The fiber shown in Fig. 5 is an example of the partially acetylated yarn stretched a little, where a part of the peeled layer is seen, and in Fig. 6 the outer shell is more clearly shown.

The degrees of polymerisation of the acetylated shell and the non-acetylated core are separately measured in Table 2, in which DP of the acetylated part was measured viscometrically by dissolving in chloroform and that of the core in cuprammonium solution. The extremely low degree of polymerisation of the acetylated layer allows us to consider its poor mechanical property. As shown in Figs. 1—2 the larger dispersion of the points in the β-range may partly be due to the mechanical removing during the treatment as well as the extraction with the solvent. On the contrary the core is thought not to be degraded to some extent. This is very important when we discuss the mechanical properties of the skin and core separately by such a peeling-off method. But this problem requires further precise study.

Table 2

Sample	Degree of Peeling-off, %	Degree of Polymerization		
		Original rayon	Acetylated shell	Core
V-1	18.8	250	—	270
	19.3	240	60	230
	11.8	240	55	220
V-2	10.0	270	75	250

(3) Solubility of the acetylated product.—If the acetylation proceeds from the outer layer concentrically as considered above, the amount of cellulose, L_2, which changed to triacetylcellulose and remained undissolved during the reaction and the corresponding weight of triacetylcellulose, L_A, can be calculated from the value of A as follows:

$$L_A = \frac{291}{162} L_2 = 1.778\, L_2 \qquad (5)$$

And the value of L_1+L_2 can be also obtained directly by measuring the difference between W and the residue after extracting the acetylated shell with chloroform followed by saponification

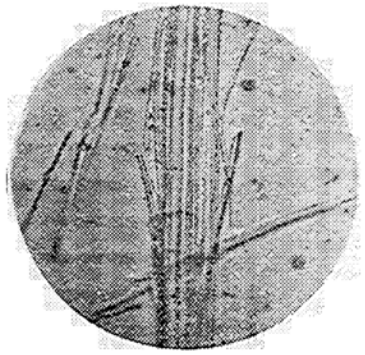

Fig. 5.

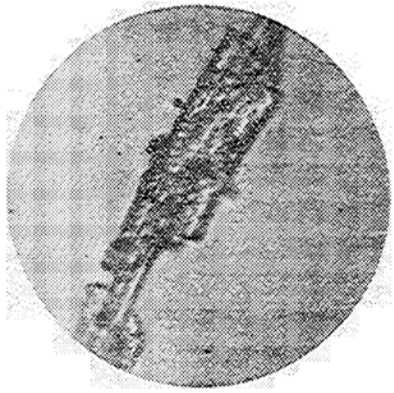

Fig. 6.

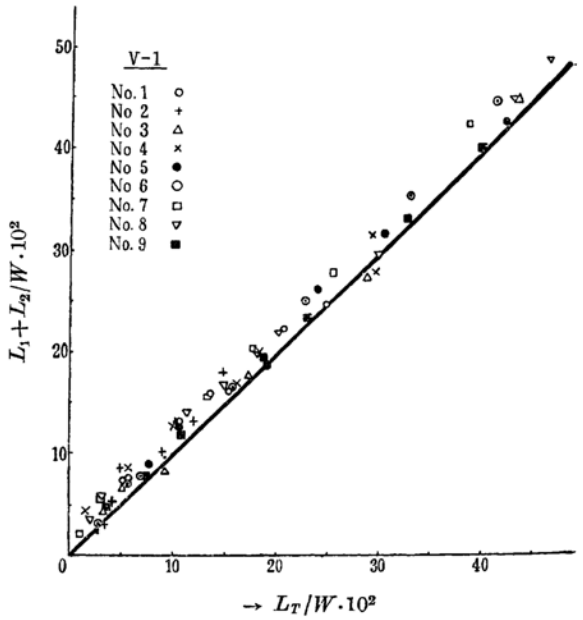

Fig. 7.

with N/5 NaOH aq. solution. If this is denoted by L_T, it must be equal to L_1+L_2, provided that the fiber is acetylated completely heterogeneously. And indeed this is nearly true as shown in Fig. 7. In the figure $(L_1+L_2)/W$ is plotted against L_T/W, where a nearly theoretical relation can be seen (a line in the figure is bisecting between the coordinates), although there is a tendency that the former values are slightly (1—2%) larger than the latter ones, which may probably be due to the incomplete extraction. There is necessarily a continuous distribution of the acetyl groups between the outer layer of triacetylcellulose and the completely unchanged core, and therefore, the smaller part of the acetyl groups remain unextracted.

The Fig. 7 shows the case of V-1 as an example; in the other cases the same relation holds good, excepting values larger than 50%, where the relation is inverse and L_T/W is larger than $(L_1+L_2)/W$, which may perhaps be due to the disintegration of the sample and the loss during the treatments, as the fiber becomes too slender.

Observing th fibers, which were extracted with only chloroform and not treated with dilute alkali, the refractive indices, $n_{\parallel}$ and $n_{\perp}$, are equal to these of the extracted one followed by saponification, in spite of the fact that the remarkable difference of the refractivity has been known between the cellulose and triacetylcellulose. So the surface layer of the core containing acetyl group is considered to be very thin in other words, the acetylated layer can be removed almost quantitatively. In order to ascertain this point the next experiment was carried out.

Two samples of V-1 were acetylated at 60°C for 6 (P) and 15 (Q) hours. Their respective acetyl contents are 3.06 and 6.14% and the thickness of the acetylated layers are estimated to be nearly 0.8 and 2.9% of their radius respectively (see the next paper). The denier of the single filament in this case is 5.04 and its mean diameter is nearly 10 micron. Therefore the thickness of the acetylated layers are 900 and 3000 A. respectively.

Observing the sample Q under a microscope existence of a thin layer of different refractivity can be clearly recognized on the surface of the fiber by the appearance of the two Becke's lines. But in the case of P, a single Becke's line appears ordinarily and the outer layer can not be recognized. Therefore, it is thought that the unextracted acetyl content of some 1—2% does not cover the refractivity of cellulose itself. This observation can support the above consideration. The critical thickness of this diffuse layer may be the order of the wave length.

Conclusion

The acetylation type of the not-swollen rayon is fiber-heterogeneous and it proceeds concentrically from the outer surface and the acetylated layer can be removed nearly quantitatively by chloroform. This reaction may be suitable for the peeling-off the rayons.

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