Heterogeneous Structure of Rayon. IV. Effect of Stretching on the Heterogeneous Structure (1)

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In the previous papers[1] the authors determined the conditions of the peeling-off of rayons by the fibre-heterogeneous acetylation and studied the properties of the skins and cores of some rayons on the market. Now the method has been applied to a series of viscose rayons prepared by a two-bath process in order to study the effect of the stretching of the rayon fiber in the second bath upon its heterogeneous structure.

Experiment

(1) Rayon samples.—The samples used were a series of viscose rayons prepared from an ordinary factory viscose by a two-bath process in the laboratory of the Teikoku Jinken Co. The spinning was carried out as shown diagramatically in Fig. 1, in which the first bath A was composed of 9.70% H_2SO_4 and 0.4% Zn besides some Na_2SO_4, its specific gravity being 1.25. The temperature was kept at 50±1°C and the immersion length was 23 cm.

The second bath B was hot water of 80°C, the immersion length being 35 cm.

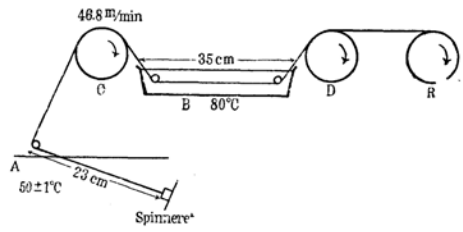


Fig. 1.

The peripheral velocity of the first godet C was fixed to 46.8 m./min. and that of the second one, D, was so controlled as to be able to stretch the yarn in the second bath to various degrees as given in Table I. The yarn collected on a bobbin R was, after being removed from R washed thoroughly, desulfured and bleached as usual. This process was carefully carried out so that the yarn was not stretched during the spinning between D and R. The details of the conditions and some of the properties of the yarns obtained are summarized in Tab. I.

TABLE I

Yarn No	Periph. speed of D, m./min.	Degree of stretch	Denier of the single filament	r	Dry stg., g./den	Dry elong., %
IIa	46.8	1.00	6.37	1.000	1.54±0.06	43.4±1.1
IIb	55.2	1.25	5.09	0.892	2.08±0.08	24.7±0.9
IIc	65.1	1.54	4.15	0.807	2.68±0.12	14.1±0.8
IId	73.0	1.87	3.41	0.753	3.26±0.11	11.1±0.3

The mechanical properties given in the above table were obtained by a test at 20°C and 65% R.H. and the values were estimated stochastically, the confidence coefficient being 95%.

The yarn was extracted with ether for several hours, washed repeatedly with hot water (60°C) and stored after air-drying. This sample was vacuum-dried immediately before use (the weight is W) and the heterogeneous acetylation was carried out for 3~300 hours at 60°C. The composition of the acetylation bath was as follows:

Acetic anhydride	5 g.	} per 0.5 g. sample.
Benzene	15 g.	
Sulfuric acid (1.84)	0.05 g.	

After acetylating the sample to the desired degree it was taken out of the acetylation bath, washed twice with benzol and further with hot water (60°C). It was then vacuum-dried and weighed (W_A). A half of it was peeled-off by pouring into chloroform and keeping over-night at 50°C, washed with water, vacuum-dried and weighed again (W'). From W, W' and W_A, L_2 and L_T are calculated as described in the previous paper.

The other half was used for the determination of the acetic acid content (A%). L_1 is then calculated from A, W and W_A.

The amount of the peeled-off cellulose is therefore $(L_1+L_2)/W$ or directly L_T/W, but the latter is smaller than the former by about 1.5% as was shown in the previous paper and also the present data show the same fact. Then the percentages of the peeled-off shell (P_r) and the layer dissolved during acetylation (P_s), are obtained from the above data as follows:

$$P_r=1-\left(1-\frac{L_T}{W}-0.015\right)^{\frac{1}{2}}=1-\left(1-\frac{L_1+L_2}{W}\right)^{\frac{1}{2}}$$

and

1) S. Okajima, S. Hayama and K. Kobayashi, This Bulletin **25**, 271, 275 (1952).

$$P_s = 1-\left(1-\frac{L_1}{W}\right)^{\frac{1}{3}}.$$

Of course P_r and P_s are given on the base of the original radius of the filament.

As to the details of the experimental methods and the notation used refer to the previous papers.

Experimental Results

The results are summarized in Figs. 2–6.

(1) Structural Difference between the Skin and the Core.—In the previous paper it was described that the acetylated shell of the fiber so degradated that it partly dispersed into the acetylation bath and that this rate of dispersion of the skin part was smaller than that of the core. This is true also in the present case (ref. Fig. 2). The

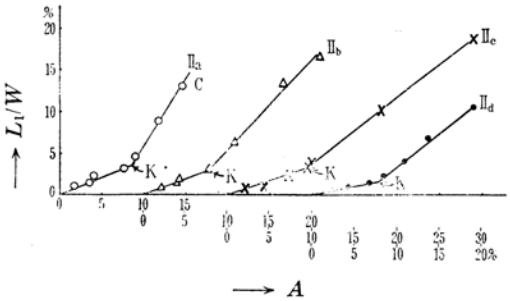


Fig. 2.

relation between the amount of this loss (L_1/W) and the acetic acid content (A) of the acetylated yarn is given by a broken line OKC. The amount of L_1/W corresponding to the inflection point $K-L_K/W$ in Table II—indicates the weight percentage of the outermost skin. These values and the thicknesses estimated from them are given in the second and third lines of the table.

Table II

Sample		IIa	IIb	IIc	IId
L_K/W, %		3.3	2.5	2.0	1.7
P_r % calculated from	Fig. 2	1.7	1.5	1.5	0.8
	Fig. 3	1.9	1.4	1.4	0.7

As the slopes of the lines OK and KC decrease in the order from IIa to IId, the rate of acetylation relative to the rate of dispersion of the acetylated portion increases with the growth of the stretching degree both in the skin and in the core. But the absolute rates do not necessarily change similarly.

In Figs. 3 and 4 rP_r and $r(P_r-P_s)$ are plotted against the acetylation time t, where r is the relative mean radius of each filament calculated from the denier, taking the denier of IIa as unity, so that the rate of the dispersion and the apparent rate of acetylation of IIa—IId can be compared directly, irrespective of the difference of their deniers.

As seen from Figs. 3–4, an inflection point appears on each curve, which tells that the

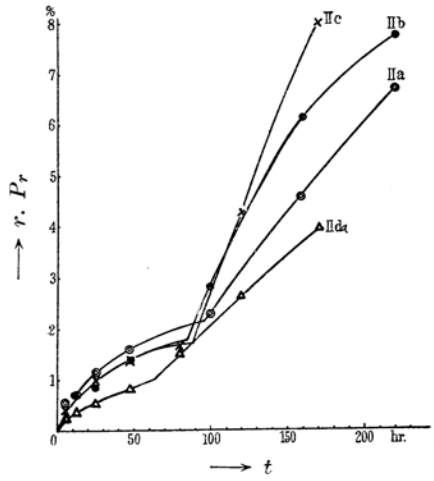


Fig. 3.

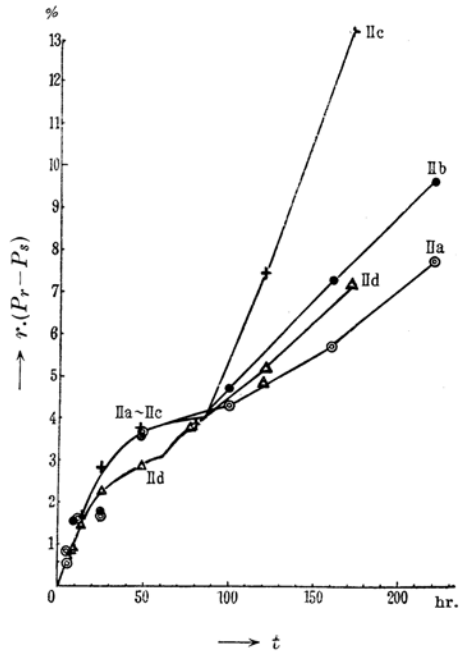


Fig. 4.

outermost skin exists and that the rates of the dispersion and the acetylation increase abruptly when the skin disappears from the filament. This is because the structure of the outermost skin is remarkably dense compared with that of the core or of the transition layer. Then the thickness of the skin layer is estimated also from the curve in Fig. 3 as shown in the fourth line of Table II. A good comformity between the corresponding values in the third and fourth lines

supports this view.

Among IIa—IId the outermost skin becomes thinner in the order from IIa to IId.

As to the effect of the stretching of a rayon fiber on its microstructure, the skin becomes slightly denser while the core becomes looser as the stretching increases, with an exception of IId, the structure of which is extraordinarily denser.

An electronmicrograph taken by Hermans[2] shows that a number of small pores exist within the outermost skin. These pores may be caused by the gasses evolved by the decomposition of viscose. Then we can suppose from the above two figures that the porosity within the outermost skin becomes the larger as the yarn is stretched the higher.

But this generalization can not be applied to the case of the yarn IId, the core of which is thought to have rather greater density and smaller porosity than that of IIb. To this point the authors shall return later.

(2) Orientation Degrees of the Skin and of the Core.—The relation between Γ and P_r is similar to these of the commercial viscose rayons already described in the second report. Three parts of the structure, i.e., the outermost skin, the transition layer and the core are clearly distinguished also here (rf. Fig. 5). The thickness of the outermost

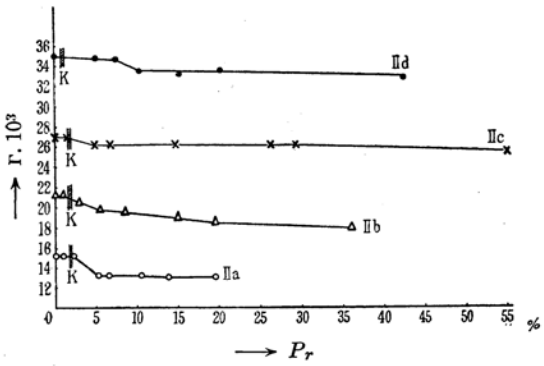


Fig. 5.

skin calculated from the inflection point (Figs. 2—3) coincides well with that found on the corresponding curve as indicated by K with an exception of IId, whose outermost skin is abnormally thick.

As to the orientation degree, both Γ of the skin and of the core grow almost linearly with the stretching degree or the difference between that of the skin and that of the core is kept nearly constant irrespective of the stretching (rf. Fig. 6). So if a fibre of nearly

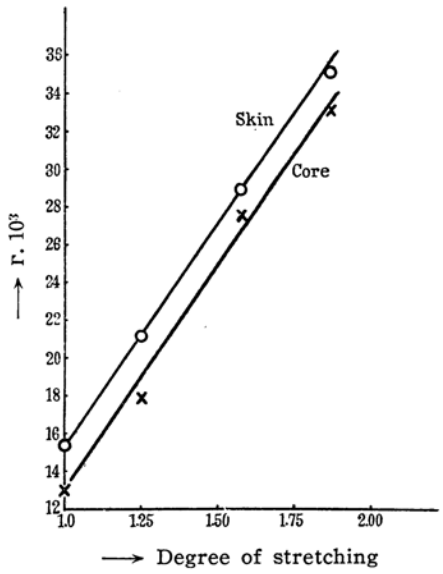


Fig. 6.

isotropic core is prepared by extructing a viscose slowly into a coagulating bath and not drafted[3] or stretched, its skin seems to be of low orientation. That it is truly the case is experimentaly proved. Then the orientation of xanthate molecules due to the high velocity gradient near the spinneret wall is considered to be feasible, if any, or the orientation seems not to be fixed in the hydrate cellulose fibre, even when the high orientation may occur in the viscose.

(3) Abnormality of IId.—As described above some properties of the filaments change systematically in the order from IIa to IId according to the degree of stretching, but IId often deviates from this order.

Many studies have been carried out on the mechanism of the viscose spinning process. They are however fragmentary and the results obtained are not yet conclusive. In order to explain the above results, attempt is made here to consider also this mechanism from author's view point. It is however partly a conjecture for which we hope future experiments will prove.

The first change of a viscose stream extruded from a spinneret orifice into the bath solution is the production of the Zn-xanthate layer on its surface and not the direct regeneration of the Na-xanthate. This layer is assumed to be hydrophobic compared with the ordinary Na-xanthate and cross-linked by Zn. Because of this the cellulose layer

2) P. H. Hermans, *Textile Research J.*, **20**, 105 (1950).

3) "Drafting" and "Stretching" are used as the same thing as "Verzug" and "Verstreckung" of Kauch and Harms; cf. Herbert Brandenberger; Melliand Textilber., **34**, 823 (1953).

regenerated from this Zn-xanthate has also a denser structure. This is the outermost skin considered in this study. It is well known that the addition of $ZnSO_4$ to the spinning bath retards the regeneration to follow. This is considered to be due to the stability of the Zn-xanthate, the retarded penetration of the sulfuric acid (inward) and the enhanced osmotic dehydration of viscose and xanthate (outward), because of the denser structures of the Zn-xanthate and of the hydrate cellulose layers derived from it.

The viscose stream is drafted by the first godet to attenuate the filament so that the orientation occurs during the osmotic dehydration. As the yarn of IIa—IId are drafted equally and the stretching in the second bath is supposed to attenuate the cross section uniformly, the percentage occupied by the outermost skin of each filament must be equal to each other. But the observed thickness of the outermost skin of the yarn is thinner the higher it is stretched. This may be due to the slippage of the yarn on the first godet, the actual drafting not being kept constant as expected.

The drafting brings about the higher orientation of the outermost skin compared with that of the core, because the dehydration of the latter is not sufficiently high to be orientated effectively by this drafting.

Now in the second bath the yarn is stretched to various degrees and at the same time a sudden decomposition occurs because of the high temperature.

The orientation degrees of the outermost skin and of the core are raised further by this stretching and fixed as seen in Fig. 5.

The stretching also accelerates the dehydration of the core by the squeezing action, but at the same time the increase of the density of the outermost skin due to higher stretching retards the penetration of the liquids as shown in Fig. 7. As the result,

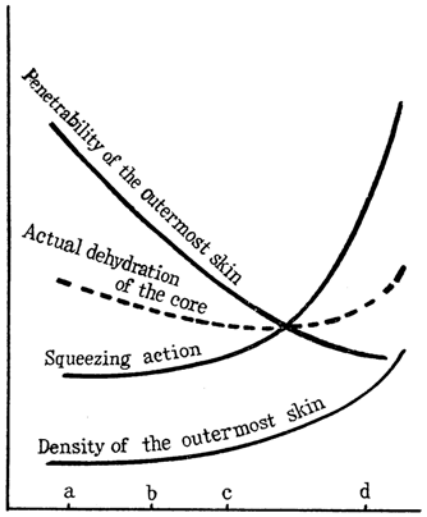
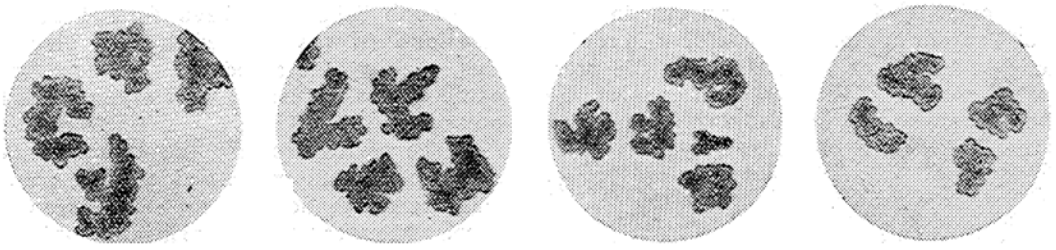


Fig. 7.

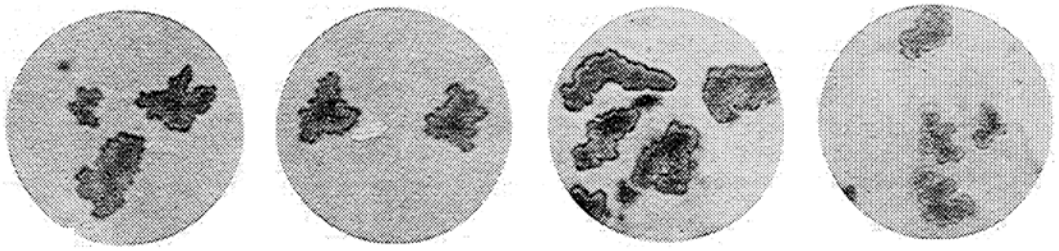
the actual dehydration goes through a minimum point with stretching.

Fig. 8.

(a) Dyed with Oxamine pure blue B



(b) Dyed with Oxamine blue 4R



The sudden decomposition of viscose or xanthate evolves gasses and brings about a porous structure. But the more the viscose or xanthate core is dehydrated, the less is the destruction of the structure and the denser is it. So the outermost skin becomes denser in the order from IIa to IId, but the density of the core goes through a minimum (IIc).

In the case of IId the dehydration of the core proceeds and it approaches so near to the state of the outermost skin, that the orientation of that part is fixed effectively similarly to that of the outermost skin and the apparent outermost skin becomes extraordinarily thick. The origin of this outermost skin is thus dual and it can be distinguished only by the acetylation as shown in Fig. 5.

The relation between the outermost skin and the ordinary skin is as follows. The skin layer of an ordinary viscose filament has hitherto been recognized by metachromasis. The thickness of this skin seems to be larger than the authors' outermost skin. According to P.H. Hermans a number of tiny pores exist within an outermost layer (this seems to correspond to the authors' outermost skin), the pores being observed to grow larger toward the centre. Metachromasis is based on the distribution of the pore size so that the skin hitherto observed is thick and its thickness is dependent upon the state of the polydispersity of the dyes used.

Fig. 8 indicates the skins of IIa—IId dyed with Oxamine pure blue B and Oxamine blue 4R. These skins are thicker than our outermost skin and the latter dye seems to give a thicker skin than the former.

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