The Effects of Various Spinning Processes on the Fine Structure of Viscose Rayon Staples (Distribution of Chain Length of Oxidizing-hydrolyzed Residue)

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The object of this paper is to study the effects of various spinning processes on the fine structure of viscose rayon staples.

In the preceding paper¹⁾, it was suggested that the distribution of crystalline size could be shown by the chain-length distribution of oxidizing-hydrolyzed residue. Determination of the average crystalline size expressed by the average degree of polymerization of acid hydrolyzed residue has been reported by many

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* This paper was partially presented at the 23rd Viscose Symposium, Takatsuki, September, 1958.

1) T. Kōshiro, K. Yagami, E. Shiratsuchi and T. Fujimura, This Bulletin, 31, 606 (1958).

authors[2]. These methods, however, except for electron-microscopy[3], give little information on the distribution of crystalline size.

The oxidizing-hydrolysis conditions employed in the preceding report were so mild that it took a long time to obtain the crystalline portion of cellulose fibers. Therefore, the modification of the oxidizing-hydrolysis conditions was studied at first and revised. Various types of rayon staples (spun in concentrated sulfuric acid, dilute sulfuric acid, high zinc per cent Müller's bath etc.) were then compared by the improved method.

Carboxyl groups of oxdizing-hydrolyzed residue were determined to clarify the cause of abnormally low iodine sorption.

The relation between the distribution of crystalline size and the lateral-order distribution by Yurugi-Maeda's method was discussed.

Experimental

Oxidizing-hydrolysis.—The samples were refluxed at 100±1°C in the mixture of 4 N sulfuric acid and 0.3 N potassium dichromate for 30 min. After the predetermined time, the residues were filtered off with a glass-filter and washed with hot water and methanol, and then dried in vacuo at 60°C for five hours and their yields were determined.

Chain-length Distribution.—The oxidizing-hydrolyzed residue was nitrated and fractionated as in the preceding report[1].

Carboxyl Group. — The carboxyl content was determined by titration with EDTA[4].

Results

Oxidizing-hydrolysis.—Since the logarithm of the yield of residues decreases inverse-proportionally to the reaction time, as shown in Fig. 1, crystallinity C is obtained by the extraporation of this time curve to zero. The crystallinity and the characteristics of crystalline portions of various rayons are given in Table I, where R_5 is the yield of residue after 5 hr.-hydrolysis, $\overline{P}$ is the average size of crystalline portion expressed by degree of polymerization, U is the uniformity of the degree of polymerization, P_m is the mode of D. P. distribution, which corresponds to the peak in the crystalline size distribution curve. The samples, which were spun in Müller's bath or in its modifications (B, Z and C) have lower crystallinity.

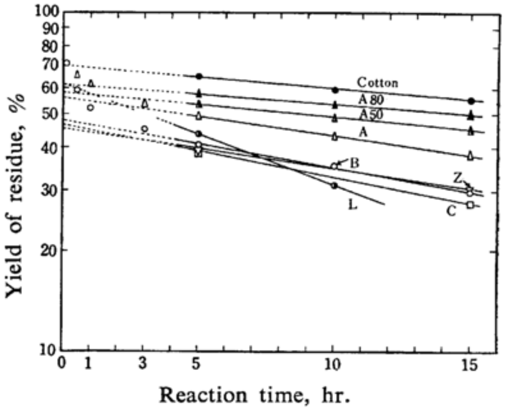

Fig. 1. Oxidizing-hydrolysis behavior of various types of rayons and cotton.

Mark	Type of rayon
B	Ordinary rayon, spun in Müller's bath.
C	Commercial tire cord,
Z	High tenacity rayon, spun in high zinc per cent Müller's bath.
L	Toramomen type, spun in dilute sulfuric acid.
A	Lilienfeldt type, spun in concentrated sulfuric acid.
A50 A, A80	treated with aqueous alkali solution, 50 and 80 g./l. of NaOH, respectively.

TABLE I. CRYSTALLINITY AND THE CHARACTERISTICS IN CRYSTALLINE PORTIONS OF VARIOUS TYPES OF RAYON

Mark of fiber	R_5 %	C_0 %	$\overline{P}$	U	P_m
B	41.1	49	14.1	0.31	10~13
C	39.5	47	7.4	0.09	6~7.5
Z	39.5	46	8.3	0.25	8
L	43.9	62	11.0	0.11	9
A	49.6	56	17.5	0.27	11~15
A50	53.6	58	19.1	0.16	15 (32)
A80	56.8	62	28.2	0.66	10~20(41)

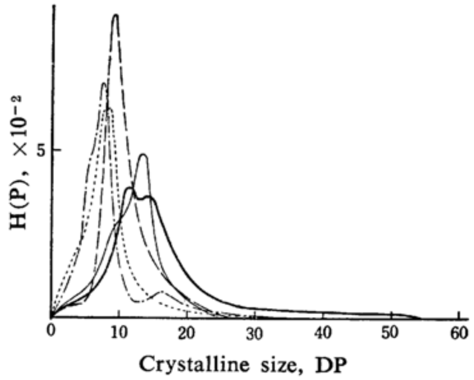

Fig. 2. Crystalline size distribution of various types of rayons.

—— B, ---- Z, —·— C, ——— L, ▬ A

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[2] See e. g., R. F. Nickerson, *Ind. Eng. Chem.*, **33**, 1022 (1941); **34**, 85, 1480 (1942); T. Yurugi, *Bull. Textile Research Inst. Japan*, No. 19 (1951); F. F. Morehead, *Textile Research J.*, **20**, 549 (1950); A. Sharples, *Trans. Faraday Soc.*, **53**, 1003 (1957); **54**, 113 (1958).

[3] B. G. Rånby and E. A. Immergut, *Ind. Eng. Chem.*, **48**, 1183 (1956).

[4] K. Ueno and Y. Yamaguchi, *J. Japan. Chem. (Kagaku-no-Ryoiki)*, **6**, 38 (1952).

Distribution of Crystalline Size.—As shown in Fig. 2, the distribution curves have only one peak. From Fig. 3, some correlations between the average size of crystallites and the peak P_m may generally be observed. It is noteworthy that by alkali treatment, P_m of Lilienfeldt-type rayon shifts to a higher D. P. showing two peaks in its distribution chart and the longer one with almost twice the length of the shorter one (Fig. 4).

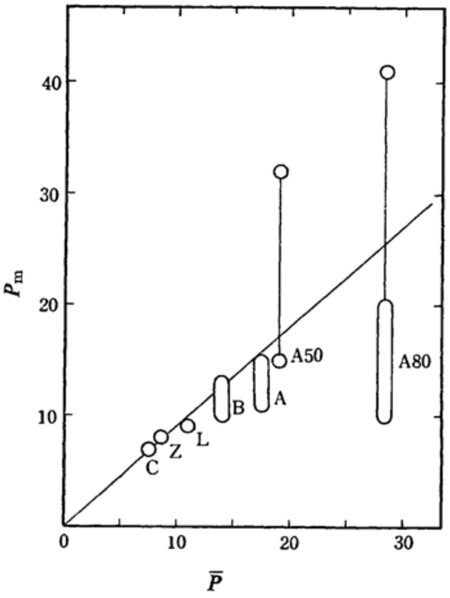

Fig. 3. Correlation between average crystalline size $\bar{P}$ and the crystalline size with maximum frequency in distribution (P_m).

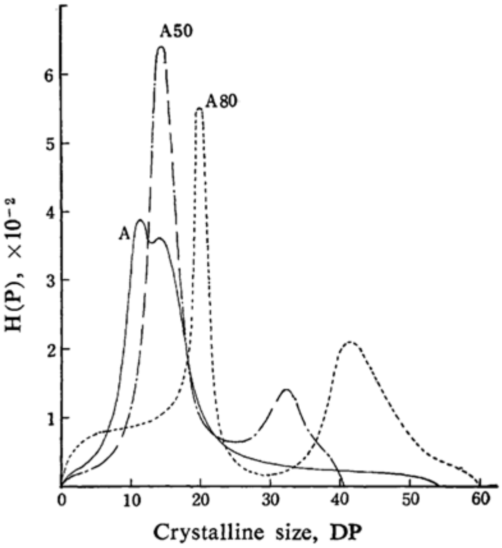

Fig. 4. Change of crystalline size distribution of Lilienfeldt-type rayon (sample A) by alkali treatment.

Effect of Alkali Treatment.—Lilienfeldt-type rayon and Müller's bath-type rayon which have clearly different fine structures, were immersed in alkaline solutions of various concentrations and then oxidizing-hydrolyzed. The results given in Fig. 5-a show that the apparent crystallinity that is, the yield of crystalline residue calculated on the basis of sample weight after alkali treatment increases in both Lilienfeldt and ordinary rayon after alkali treatment, and

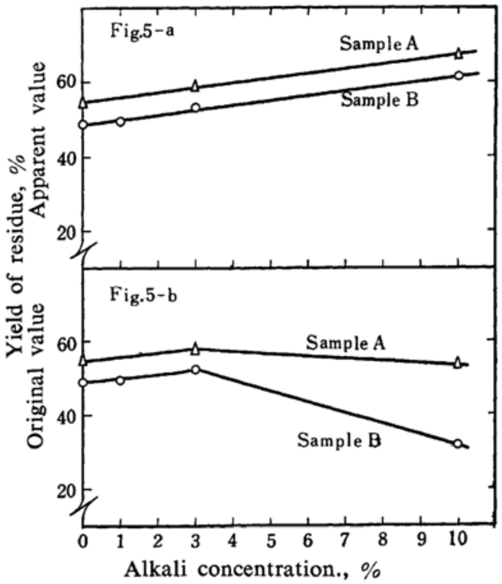

Fig. 5. Effect of alkali treatment on the yield of residue, calculated on the basis of sample weight after alkali treatment (Fig. 5-a) and untreated sample weight (Fig. 5-b).

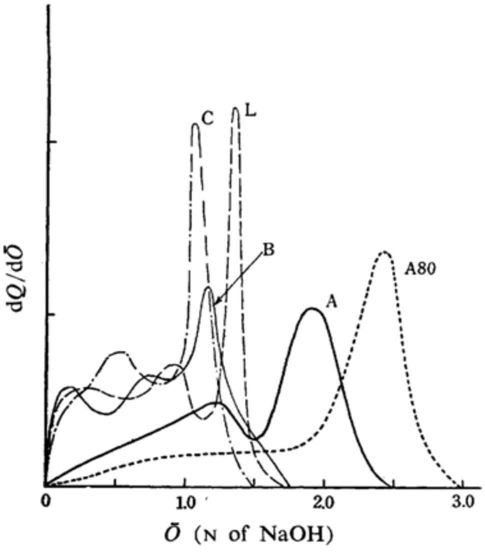

Fig. 6. Lateral-order distribution of various types of rayons by Yurugi-Maeda's method.

the tendency for recrystallization appears to be entirely the same. However, a different tendency is observed between Lilienfeldt and ordinary rayon when calculated on the basis of untreated sample weight. (Fig. 5-b)

Relation between Crystalline Size Distribution and Lateral Order Distribution by Yurugi-Maeda[5).—The lateral order distributions given in Fig. 6 are compared with the crystalline size distributions shown in Fig. 4. It is found that the modes of lateral order distribution, O_m, increase with P_m or $\overline{P}$ (Fig. 7). The higher P_m might correspond to the higher O_m.

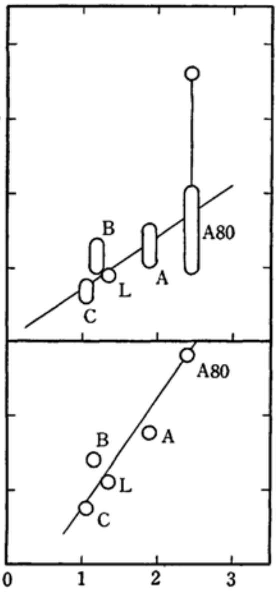

Fig. 7. The relationship between lateral-order distribution and crystalline size distribution characteristics.

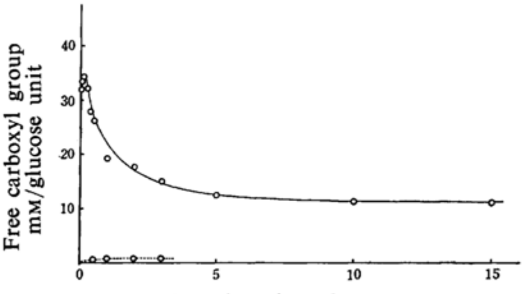

Fig. 8. Rise and fall of amount of carboxyl group during oxidizing-hydrolysis.

—— Oxidizing-hydrolysis

- - - Ordinary hydrolysis with 4 N H_2SO_4 alone.

Carboxyl Group of Oxidizing-Hydrolyzed Residue.—As shown in Fig. 8, the carboxyl group in oxidizing-hydrolyzed residue of Müller's bath-type rayon increased rapidly to a maximum value in the initial five minutes and decreased gradually to a levelling-off value after 5~8 hr.

Discussion

The chief reason why the crystalline size in our experiment was smaller than the measured values by small angle X-ray scattering, electron microscope or viscosity of cuprammonium solution of the hydrolysis residue, may be due to the fact that the Staudinger's K_m constant used for calculation was not appropriate, but it is justifiable for the purpose of comparing sizes. According to this experiment, not only the mean size of crystallites but also their distribution is indicated with rayons produced by different methods—particularly, spun in various kind of spinning baths. High tenacity rayon of high percentage zinc bath is generally composed of uniform and small crystallites but the size of crystallites of the Lilienfeldt-type rayon is large and also the distribution is not perfectly uniform indicating two distribution peaks, large and small. It is well known that when viscose rayon is treated with aqueous alkali solution of appropriate concentration, generally, the orientation of crystallites is disturbed, the strength is reduced and the elongation is improved, and it has also been confirmed by electron microscopy, X-ray and acid hydrolysis that the mean length of crystallites increases[6).

However, when seen from the viewpoint of distribution of length of crystallites, the entire distribution tends to increase in length of crystallites when Lilienfeldt-type rayon is treated with alkali and also, other peaks in the vicinity of about twice the peak of short particles become higher. This probably indicates the possibility that within the crystalline region of Lilienfeldt-type rayon, there is originally a defective part in short crystals which swells and relaxes by alkali treatment, next it deswells and recrystallizes during drying and fuses into one crystal. Of course, this manner of assumption is ideological and it is natural to assume that the distribution of crystallite length is not necessarily the fusion of two crystallites which recrystallize but growth occurs at the terminating part of the crystallites.

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5) H. Maeda, *J. Soc. Textile Cellulose Ind., Japan* (*Sen-i Gakkai-shi*), **12**, 6 (1956), etc.

6) See e. g., P. H. Hermans and A. Weidinger, *Nature*, **165**, 238 (1950); *J. Polymer Sci.*, **6**, 533 (1951); K. Katō and K. Yamada, *High Polymer Chemistry* (*Kôbunshi Kagaku*), **16**, 627 (1959); *Textile Research J.*, **29**, 368 (1959).

Crystalline Size Distribution and Lateral Order Distribution. — There are many low lateral order parts in fibers with many small crystallites and many high lateral order parts in fibers with large crystallites. Also, as the mode of lateral order distribution of Lilienfeldt-type rayon will shift to the high order side when its crystalline size moves to the larger side by alkali treatment, it can be assumed that lateral order distribution is affected by distribution of length of crystallites, in addition to hydrogen bond density. The small difference between both distributions may be due to the difference in the degree of depolymerization.

Accessibility of Oxidizing-hydrolysis Residue. —In view of the fact that, at first, carboxyl group increases rapidly and then reduces to its levelling-off value, it seemed reasonable to assume that, at first, the amorphous part is rapidly oxidized, then the oxidized amorphous part is removed by hydrolysis and finally a part of the carboxyl radicals remain on the surface of the crystallites. Therefore, it is possible that the iodine absorption accessibility of the residue is much lower than that for the residue of ordinary hydrolyzed residue due to the repulsion of iodine anion by carboxyl radicals.

Summary

The fractionation of oxidizing-hydrolyzed residue was applied to study the fine structure of various types of rayons.

It was assured that tirecord, high-tenacity rayon spun in high zinc percent Müller's bath, Toramomen and ordinary rayon have one sharp peak in each crystalline size distribution curve and smaller crystallites than Lilienfeldt-type rayon which shows two peaks in the crystalline size distribution curve.

The alkali-treatment of Lilienfeldt-type rayon increases not only its crystallinity but also the crystalline size, probably owing to the fusion of two adjacent crystallities.

There can be a correlation between the crystalline size distribution by oxidizing-hydrolysis and the lateral-order distribution; namely, the higher lateral-order portion may consist of the longer crystallite.

The carboxyl group in the oxidizing-hydrolyzed residue increases rapidly in the initial stage of hydrolysis and then decreases to an equilibrium value. The apparently lower accessibility by iodine sorption may be due to the negative carboxyl group remaining.

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