Dichroic Study on Polyvinylalcohol Fiber
III. Double Refraction of Polyvinylalcohol Fiber

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In the preceding paper the change of the dichroism of the model filament of polyvinylalcohol (PVA) by stretching is reported. Now the intrinsic double refraction of the same filament after stretching and heat-treatment under various conditions is given. As the dichroism and intrinsic double refraction can indicate the orientation of the molecules and it is known that the double refraction of the fiber is affected by the crystallinity, so there may be a possibility to know separately these two factors, the orientation and the crystallinity, by comparing these two measures.

In this report the double refraction of PVA filament which has previously been treated variously was observed as the preliminary experiment on the determination of the above two factors.

Experiment

(I) Preparation of the isotropic model filament and the method of stretching.—The isotropic filament of PVA was melt-spun as described in the first report of this study.[1] The stretching of the isotropic model filament was also carried out similarly as previously,[2] but now it is known that a filament is not stretched uniformly along the axis and this is not due to the irregular structure of the sample but to the stretching conditions. This is clearly shown by the following experiment: A pair of filaments, *a* and *b*, in Fig. 1, on which many small points had been marked with a special ink, were attached parallel to a stretching frame and stretched under various conditions and the degrees of stretching were observed along their axes by comparing the corresponding distances between the marks before and after stretching. Fig. 1 shows the distribution of the stretching degree (v) along the axes of a pair of filaments which had been attached to the same frame and, therefore, stretched at the same time. We can see from the figure some interesting facts, as follows:

(a) The end parts near the clamps are elongated more and the middle part is comparatively uniform. The tendency becomes remarkable as the total stretching degree grows larger.

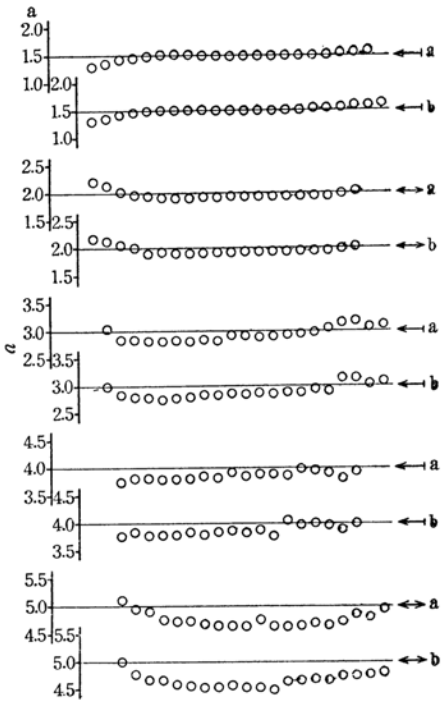

Fig. 1.

(b) The correspondence of the stretching of the two parallel filaments, *a* and *b*, is very good irrespective of the irregularity of deformation above. So the phenomenon is not caused by the irregular structure of the sample along the axis.

(c) The distribution of v along the filaments is nearly symmetrical. This is irrespective of the fact that either both ends of the filament are pulled away or only one end is pulled away, fixing the other end. These types of stretching are shown by ←→ and → in the figure.

Taking this irregularity into consideration, the test pieces used for the measurements of the intrinsic double refraction (Γ) and v were taken from the middle part of the stretched filament in the following experiments.

(II) Determination of Γ.—Some test pieces taken from the middle part of the stretched filament was comented to a frame prepared from a brass plate of 0.4 mm thickness (Fig. 2 a). A

(1) S. Okajima and Y. Kobayashi, *J. Soc. Chem. Ind. Japan*, **54**, 794 (1951).
(2) S. Okajima and Y. Kobayashi, This Bulletin, **25**, 268, (1952).

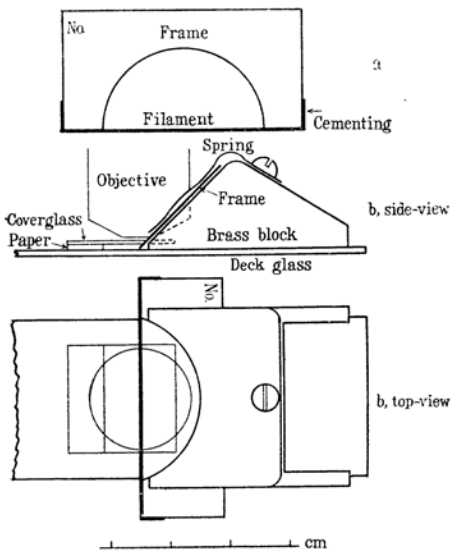

Fig. 2.

benzene-alcohol solution of benzylcellulose was used as the cementing material.

This frame with a test piece is attached with a pair of springs to one side of a brass block which was placed on the stage of a polarization microscope (Fig. 2 b). This brass block was prepared in such a way that the above brass plate inclines by 45° to the horizontal plane. Then dropping the brass plate and reattaching it to the block, nearly the same portion of the filament can be again observed microscopically from the direction perpendicular to the first one. Then if the retardation R and width D of the same portion of the test piece are measured from the two directions perpendicular to each other, and if these two measures are R_1, D_1 and R_2, D_2, then Γ of that part is given by R_1/D_2 and R_2/D_1. The suffixed 1 and 2 mean the first and second measurements.

If the filament is not exactly circular, then D_1 differs slightly from D_2 and the above device gives a good result. Furthermore, when the section of the filament is too elliptic and the cover glass is pressed slightly, the filament against the deck glass owing to the surface tension of the mountant, the larger diameter is liable to be observed under a microscope, so now it is devised to insert a piece of paper of an appropriate thickness between the cover and deck glasses to give a sufficient space for the filament to take a free state.

The mountant was prepared by adding some cedar oil to tricresylphosphate to adjust the refractive index to that of PVA, 1.535. This mountant is vaporisable with difficulty and very suitable for our purpose.

The sample was stocked in a vacuum P_2O_5-desiccator over 15 hours and mounted in the above liquid. The magnification of the microscope was 400×.

The measurment of the retardation was carried out as usual partly by observing the diffraction colour and partly by using compensater, using D-line, as the light source.

Experimental Results

The samples were conditioned at the various humidities at 20° and 30°C. and stretched under the same conditions. They were treated as described above and the change of the double refraction by stretching were observed. The result is shown by the curve (a) in each figure below. Some of the samples were washed out with carbon tetrachloride or ether to remove the mountant and then heated in an air-oven controlled at 140 ±3°C. for various periods of time, after being conditioned in a desiccator containing the saturated solution of ammonium sulfate (81% RH at 20°C.). Some of them were washed, conditioned and heated again and again and the change of their Γ by the heat treatment were traced. The results are summarised below.

Fig. 3 shows the carried out result of experiment at 30°C. and 100% RH. The curve a is the relation of Γ versus v, which is a saturation type. The points ○ and ● are obtainde by two different observers with using two samples spun separately, but they coincide well; therefore, the reproducibility of the experiment can be said to be very good.

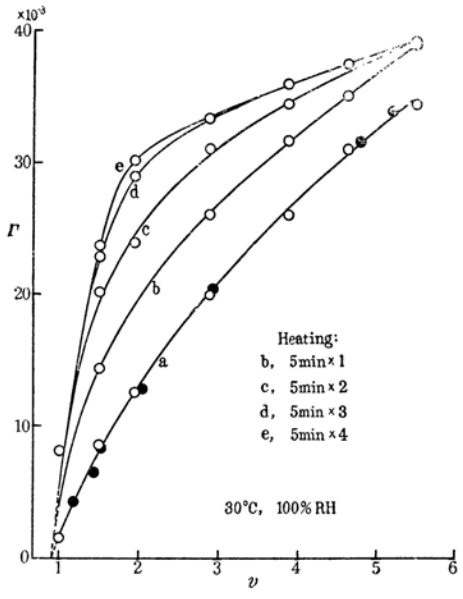

Fig. 3.

The curve b (5 min. heating ×1) is almost parallel to a and the others c~e are not parallel but their end points converge to one point and only the middle parts rise stepwise in the order c to e. Therefore the increment of Γ by heating at 140°C. is not uniform relative to v, but the change is largest at $v \fallingdotseq 2$ and the filament of the highest orientation attains the equilibrium state

after short heating, while some four heatings are required at $v \fallingdotseq 2$.

Fig. 4~7 show the similar experiments stretched at 30°C. and 93% RH, at 20°C. and 100% RH, at 20°C. and 93% RH, at 20°C. and 81% RH respectively. The character of each case is similar to that of Fig. 3. The saturated state is obtained by heating for 15~30 min. in all experiments.

In the case of Fig. 6 the sample b' was heated for 15 min. immediately after vacuum drying and had not been conditioned, and the curve b' is somewhat lower than the corresponding curve b, which was heated after the ordinary conditioning. The curves b and b' shift to c and c' respectively by the secondary heating of 15 min. after ordinary conditioning, where c' is also below the corresponding c. Therefore some amount of moisture in the filament seems to have a good effect upon the raising of Γ, although the moisture in the filament vaporises rapidly in such an open heating. The phenomenon is not the problem of the rate of change and it remains after reaching the equilibrium state.

The stretching at 20°C. and 81% RH is very poor as shown in Fig. 7; this fact has been pointed out already in the previous paper with using dichroism.

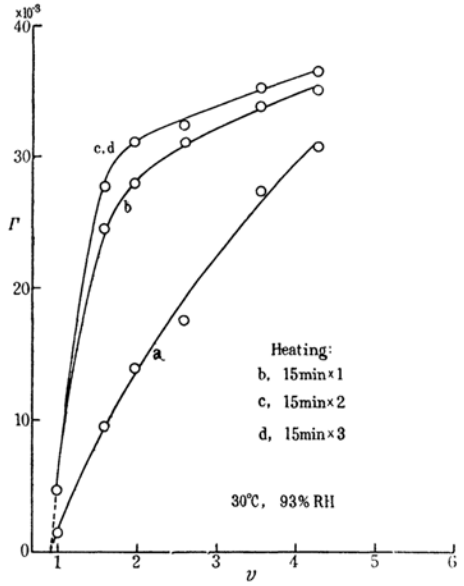

Fig. 4.

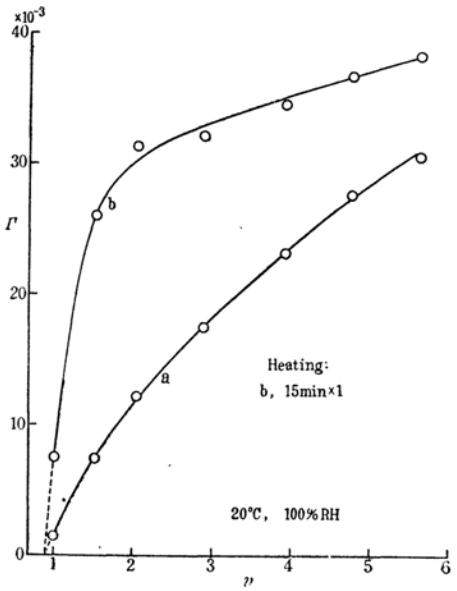

Fig. 5.

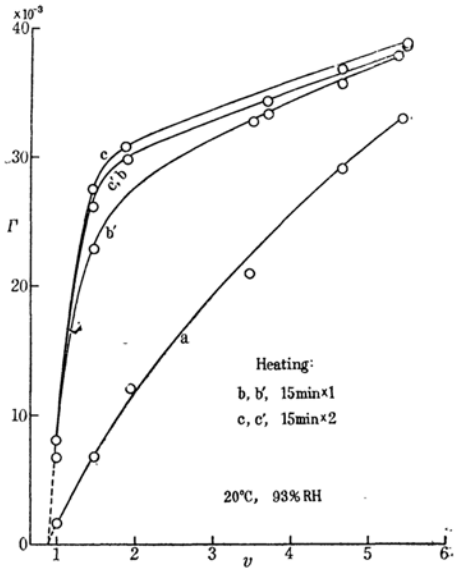

Fig. 6.

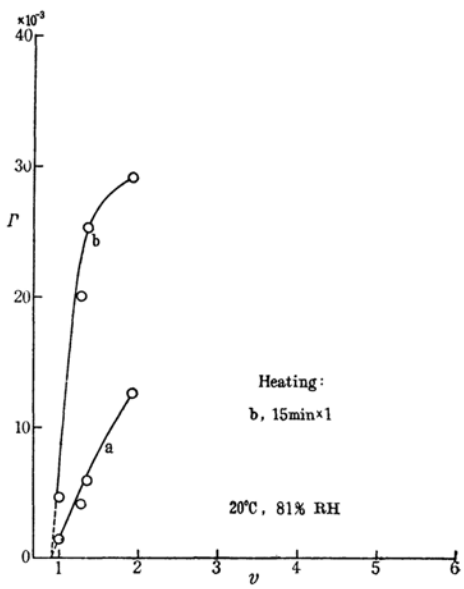

Fig. 7.

Now summing up the curve *a* and the one heated to equilibrium in each experiment, it is indicated as shown in Fig. 8, that the rise of Γ by stretching becomes sharper as the stretching is carried out at lower humidity and higher temperature, while the difference disappears when these samples are heated to equilibrium and the original curves converge nearly to one relation, where the maximum value of Γ amounts to $38\sim 39\times10^{-3}$.

Now an experiment was made, in which the filament stretched at 20°C. and 100% RH were heated at 140°C. for 25 min., when one half of it (*b*) was treated as before but immediately after vacuum drying, while the other half (*c*) was heated at the same temperature after conditioning at 20°C. and 81% RH and at the higher humidity by supplying the water vapor. As shown in Fig. 9 the moisture effect is clearly recognized here also, but the effect is not similar to the case of Fig. 6 and it is in the reverse direction and, therefore, the optimum moisture content seems to exist for the raising of Γ. The difference here is also considered, not to be caused by the different rate of change as the effect remains in the equilibrium state, which is attained by repeating the heat-treatment for 60 min.

In this experiment also a filament (●) was stretched very slowly (8 hours were required for the total stretching) as compared to the experiment hitherto described, in which the stretching was carried out within 10 seconds. According to the figure the slower stretching is more effective to raise Γ but the maximum value does not change so much.

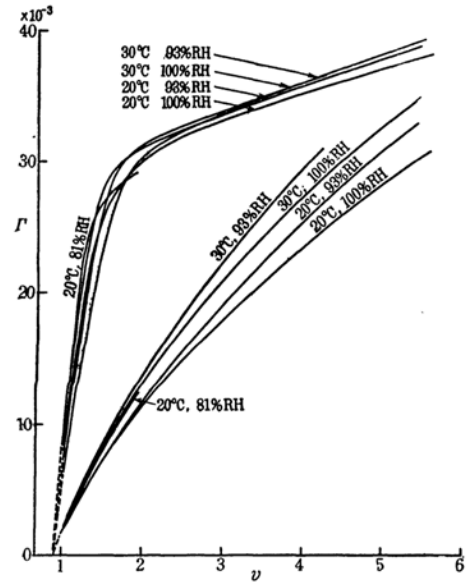

Fig. 8.

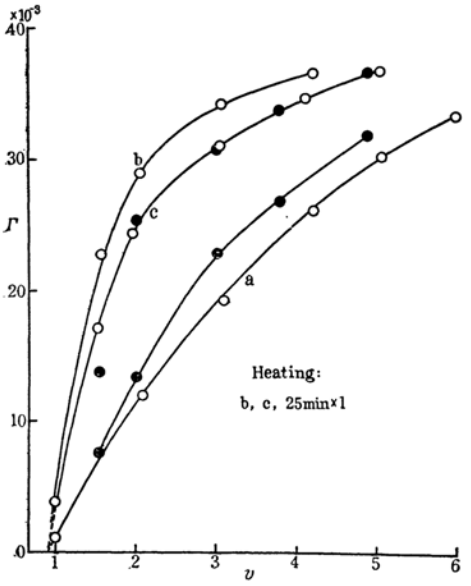

Fig. 9.

Discussion

A similar stretching experiment has been carried out and the change of the dichroism by stretching has been reported in the preceding paper. Now comparing the experimental results obtained under the similar conditions in the preceding paper to these in the present study, the similar trends are seen. In both cases the change of the measures becomes less sharp as the moisture content increases. But there are small discrepancies in detail; for example, the dichroic curve of a filament of higher moisture is sigmoid but the birefringence curves are all saturation type as shown above.

This is certainly because the dichroic data indicate principally only the orientation of PVA molecules independently on the crystallinity, while Γ relates also to the crystallinity. According to K. H. Meyer[3] PVA partly crystallize by stretching only and then the orientation curves indicated by the dichroism and the double refraction may be different. But quantitative study on the crystallization of PVA is not yet reported and this is an important problem for the vinylon industry of Japan. The detailed comparison of the two orientation curves will be given in the following paper.

The authors are indebted to Dr. Yazawa for the sample of PVA used, for which their thanks are due.

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(3) K.H. Meyer, "Natural and synthetic high polymers."