Dichroic Study on Polyvinylalcohol Fiber. II. Effect of the Crystallinity and Moisture Content of the Fibers on Their Deformation

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Introduction

The authors studied previously the deformation of the regenerated cellulose fiber,[1] so now the Polyvinylalcohol (PVA) fibers are being studied. The chain molecule of PVA is considered to be very flexible as compared to that of the cellulose and this difference may be expected to appear also in the deformation course. Moreover, the mechanical properties of PVA gel changes remarkably with the crystallinity and the moisture content, and the crystallinity itself can be controlled easily by the heat treatment.[2] The study of these effects of inner structure upon the deformation is considered to be very important and very interesting not only from the theoretical standpoint but also as the basic phenomena in the synthetic fiber industry, especially of Japanese vinylon.

As to the method of study of the orientation degree changed by the deformation, the X-Ray method is not necessarily effective as the crystallinity of the non-heat-treated PVA is very poor and only the dichroic method is useful for the quantitative study, because it gives the orientation of the PVA molecules by using that of a direct dye as a parameter. The dichroic data of Congo Red has already been studied by the authors[3] in the case of the cellulose fibers. PVA fibers can be dyed with direct dyes.

The double refraction and the refractive indices methods are not useful at present as their basic data of PVA fiber of ideal orientation has not been found. These data will possibly be found in the future when the orientation of PVA fiber will be determined dichroitically.

Experiment

(1) Preparation of the isotropic PVA filament.—The isotropic model filament of PVA is prepared by melt-spinning as described in the first report;[4] A sample of PVA powder containing 50% moisture was melted at 140—150°C under 4 atm. and extruded through a glass nozzle in the air of room temperature. The obtained filament has a circular cross section and a smooth surface. The diameter is about 0.17 mm and nearly equal to that of the glass nozzle.

As to the isotropy of the filament it is not perfect, but it has a slight anisotropy and the outer layer of the filament has a positive double refraction and the core a negative one as P. H. Hermans described in the case of the cellulose fiber.[5] But this anisotropy is so slight that it can be used in the following study.

(2) Crystallization of the filament.—In the two series B and C the samples were partially crystallized by heating at 140°C for one hour in the aqueous solutions of 40 and 50% ammonium sulfate respectively. The autoclave required 30 min. to be heated to 140°C from the room temperature and also to be cooled from the same temperature. The treated filaments were washed thoroughly with water and air-dried.

(3) Stretching of the isotropic filaments.—The isotropic filaments, both the non-heat-treated seires A and the heat heat-treated B and C, were dyed with Congo Red and then conditioned and stretched. The dyeing conditions are described in the next section.

The conditioning was carried out in three desiccators at 20°C for 48 hours. The desiccators contained water and the saturated solutions of Na_2SO_4 10 H_2O and $(NH_4)_2SO_4$ and the relative humidities in each desiccator are 100, 93 and 81% respectively at 20°C. It has been confirmed by a preliminary test that the 48 hours' conditioning was sufficient to get the equilibrium states.

The conditioned samples were then stretched from l_0 to l (ca. 26 cm) and then air-dried after being placed in each desiccator for 48 hours more. The degree of stretching is given by $v=l/l_0$. In this case the change of the filament volume caused by stretching was so small that the correction in the value of v was not necessary.

The middle part of the stretched filament was

(1) S. Okajima and others, *J. Soc. Chem. Ind. Japan*, **48**, 85, 86 (1945); **49**, 52, 168 (1946); S. Okajima and Y. Kobayashi, This Bulletin **24**, 85 (1951); S. Okajima and S. Hayama, ibid., **24**, 90 (1951).

(2) I. Sakurada and K. Futino, *Bull. Inst. Phys. and Chem. Research, Japan*, **21**, 1077 (1942).

(3) S. Okajima, *Japan Science Review*, **1**, No. 2, 71(1950).

(4) S. Okajima and Y. Kobayashi, *J. Soc. Chem. Ind. Japan*, **52**, 794 (1951).

(5) P. H. Hermans, Physics and Chemistry of Cellulose Fiber, Elsevier, 1949, p. 387.

placed on the deck glasses, A and B in Fig. 1, and fixed on them at the points F with celluloid solution. Cutting off the filaments at C, A and B were used as the preparates for the measurement of D.

PVA filament can be stretched at its maximum to some 6-fold under the appropriate conditions as shown below and in this case the diameter of the sample decreased and became so thin that a special device was necessary to prevent the slippage at the clamps.

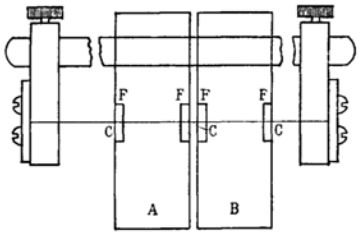

Fig. 1.

Dyeing condition of PVA filament for the dichroic study

As already shown,[3] it is necessary to dye the fiber suitably to obtain the reasonable value of D as the over-dyeing lowers the value enormously. This condition has already been determined in the case of the cellulose fibers, but the properties of PVA are so remarkably different from that of the cellulose that the composition of the dyeing bath was newly determined as below after many trials:

Congo Red: 0.025%,

Solvent: 50% Ethanol aqueous solution.

The filament was dyed in this bath for 48 hours at room temperature. The 48 hours' dyeing was confirmed to be necessary for the complete penetration of the dye in our filament. The ethanol solution was used to prevent the swelling of the non-heat-treated PVA filament.

The sample was taken out of the dye bath and air-dried by hanging in the room air after rinsing with water.

The fixed filament on a deck glass as above was mounted in Tricresylphosphate and the two principal coefficients of absorption, $K_{\parallel}$ and $K_{\perp}$, were determined as previously described.[3] $K_{\parallel}$ and $K_{\perp}$ are the coefficients of absorption of the dyed filament for D-line, oscillating parallel and perpendicular to the fiber axis, and $D=K_{\parallel}/K_{\perp}$ is a measure of the orientation degree of the filament.

Now dyeing to various deepnesses by controlling the dye concentration in the bath and plotting the values of $K_{\parallel}$ and $K_{\perp}$ of these filaments which have been stretched by 6-fold (the maximum stretching), the points appear as shown in Fig. 2. In the figure the points are likely to belong to a linear relation (1) till $K=0.5$, but for the larger values of $K_{\parallel}$ they deviate remarkably (over-dyeing).

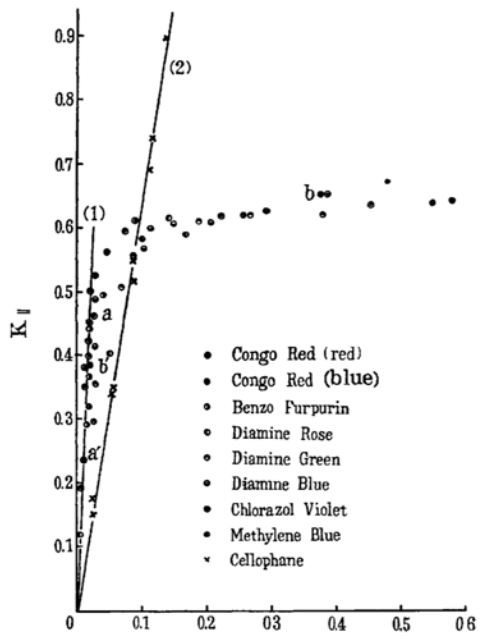

Fig. 2.

This phenomenon is the same as already shown in the case of the cellulose fibers.[3] In order to determine the value of D exactly the value of $K_{\perp}$ must be measured accurately and for this purpose it is desirable that the range of linear relationship extends sufficiently. So the similar experiments were repeated by using the following direct dyes: Diamine Rose, Diamine Green, Diamine Blue, Chlorazol violet, Benzopurpurine, and Methylen Blue. But the results are negative and the observed points begin to deviate from the same value of $K_{\parallel}$ as in the case of Congo Red. The filaments dyed with Congo Red are usually red but change to blue when they come in contact with HCl vapor and, at the same time, their coefficients of absorption increase, even when the $K_{\parallel}-K_{\perp}$ relation is kept unchanged.

A point (a) of a red filament, which has a larger $K_{\parallel}$ but is still on the line, moves to the point (b) when the filament changes to blue, but the point (a') of smaller $K_{\parallel}$ goes to (b') on the line unless $K_{\parallel}$ of (b') is smaller than 0.5. This change is reversible and the points come back to the initial points when the filaments are exposed to NH_3-gas.

The reason of this phenomenon is that the critical values of $K_{\parallel}$ and $K_{\perp}$ are the functions of the specific coefficients of absorption of the filament and not of the total absorption. The linear relationship seems to extend more in the case of the thicker filament of smaller specific absorption coefficient than the thinner filament of larger specific coefficient of absorption even though their total absorption are equall to each other.

This is proved experimentally as shown by a

line (2) in Fig. 2. In this case the values of $K_{\parallel}$ and $K_{\perp}$ were controlled by piling the strips of cellophane, which had been dyed with Congo Red and stretched. The specific coefficient of absorption of this cellophane ($K_{\parallel}$) is 0.16 and smaller than that of the above filament so the linear relationship holds good for $K_{\parallel}$ larger than 0.5. Of course the relation can be expected from the previous calculation.[3]

From these results the dyeing was carried out in this experiment so that $K_{\parallel}$ of the filament stretched to maximum did not exceed 0.5.

Results and discussion

Six series of stretching were carried out as shown in the next table:

Treatment	Relative humidity at the stretching at 20°C		
	100%	93%	81%
A. non-treated	A−1	A−2	A−3
B. heated in 40% $(NH_4)_2SO_4$ soln.	B−1		
C. heated in 50% $(NH_4)_2SO_4$ soln.	C−1	C−2	

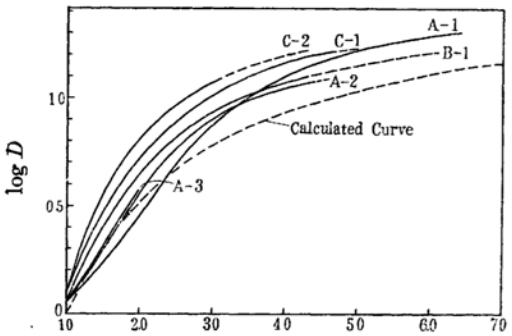

Fig. 3.

Fig. 3 shows $\log D$ as the measure of the orientation degree caused by the stretching given on the abscissa. The broken curve is the calculated one with the assumption of the first theory of O. Kratky.[6] The starting point of each curve does not coincide with the origin because of the slight anisotropy of the original filament. The curves are the mean of the several experiments.

From the figure some interesting facts can be observed as follows.

A-series. In this case the curves are slightly sigmoid but the tendency becomes slighter as the moisture content of the sample decreases, and, at the same time, the maximum degrees of stretching also decrease in the order from A−1 to A−3. The maximum stretching of A−1 is 6.4 and those of A−2 and −3 are 4.5 and 2.0 respectively, and the corresponding values of $\log D$ are 1.31, 1.09 and 0.57 respectively. The orientation degree of $\log D = 1.3$ is almost comparable to that of the ramie as reported previously[3] and, therefore, the orientation of A−1 can be said to be almost complete, while the filament of lower moisture content breaks at the lower degree of orientation.

It is well known that the moistened gel of PVA has a rubber-like elasticity but it loses the high elasticity and becomes rigid as it dries. This behaviour can be considered to be due to the decreasing microbrownian motion with the lowering of the moisture content. The above phenomena in the stretching may be due to the same cause, and therefore, generally speaking, the polymer having a more flexible chain molecule can be oriented more completely by stretching.

The authors repeatedly[7] maintained that in the case of the regenerated cellulose fiber the orientation degree at break is far from the complete orientation. This is because the chain molecule of the cellulose is too rigid to be arranged parallel in the ordinary processing. But this flexibility of the chain molecule is affected by many factors and even in the case of PVA it becomes rigid as said above because of the decaying microbrownian motion and the growing coherent force between the segments. And indeed, the deformation process of A−3 is very similar to that of the cellulose fiber. So, on the contrary, the isotropic cellulose fiber may possibly be stretched to a more highly oriented state in the properly selected conditions.

B−1. The curve is the saturation type in this case. The change is steep at first but later becomes inferior to that of A−1. The maximum value of v and $\log D$ are 6.1 and 1.21 respectively.

C-series. The curves are also the saturation type and very similar to that of B−1, and the changes of these are steeper than of the latter. But in this case the anisotropy of the original sample increased slightly by the heat-treatment, so correcting this factor, the difference between B−1 and C−1 becomes very slight although the above tendency also remains unchanged. The effect of the moisture content is also seen in this series.

Now an interesting observation will be added. It has been observed that when an isotropic fiber of regenerated cellulose is stretched higher under some conditions it appears milky due to the occurrence of a number of small lateral crackings. According to one of the authors' experiment on the cellulose fiber, this milkiness occurred in the dry stretching only and it was seen that the higher the stretching, the more anisotropic the original fiber was.

The same phenomena also appeared in the present study. The table below shows the degrees of stretching when the filaments began to appear

(6) O. Kratky, Kolloid, Z. 64, 213 (1933).

(7) S. Okajima, *J. Soc. Chem. Ind. Japan*, **49**, 168 (1946); *Bulletin of the Yamagata University, Natural Science*, No. 1, 21 (1951).

milky under their conditions, from which it is clear that even in dry stretching the phenomenon

A-1	A-2	A-3	B-1	C-1	C-2
—	4.4	—	4.3	4.7	3.1

is difficult in the moist state (A-1, not occurred) but becomes easy as the filament is demoistened (C-1, C-2) and crystallizes (C-1). The broken curves of A-2, B-1, C-1 and C-2 in Fig. 3 indicate the occurrence of this milkiness.

Conclusion

From the above results it is concluded that the relation of $\log D$ versus v of PVA filament is nearly saturation type as the first theory of Kratky requires. The demoistening and the partial crystallization of the filament does not change the tendency, but the former affects remarkably the degree of maximum stretching and the corresponding orientation, while the latter lowers the maximum stretching degree but not the degree of orientation.

Of course dichroism can indicate the orientation of the amorphous region and not the state in the crystallite. The crystallinity of the series A is very poor, so the orientation of this series may be given reasonably by $\log D$. But in the case of the filaments of higher crystallinity, the problem is not so simple because it is not yet proved whether the orientation of the amorphous part is not different from that in the crystalline region in the case of PVA. The study must await the future work. So the above results must be considered from the present stage of our knowledge.

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