Studies of the Drawing of Polyamide Fibers. I. Dependence of Some Physical Properties on the Draw Ratio

By Hiroshi HATTORI, Yasuo TAKAGI and Tatsuro KAWAGUCHI

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It is well-known that an oriented fiber is obtained from synthetic linear high polymer by drawing it to several hundred per cents of its original length, and that various properties of the fiber are changed by this drawing.

The relation between the draw ratio and some physical properties of nylon 6 monofilament—especially the tensile strength and the shrinkage in boiling water—has been studied in order to elucidate the process of the change in polymer structure during the course of the drawing.

A curious relation was discovered between the draw ratio and the tensile strength; that is, the tensile strength becomes the smallest at a draw ratio near two.

Experimental

Samples.—*Group I.*—An undrawn monofilament of nylon 6 (1300 denier), which had been meltspun and quenched in water, was drawn immediately after spinning in hot water at 90°C to various draw ratios, from 1 to 5.2, at intervals of 0.3. The feeding speed of the undrawn sample at the drawing was 26 m./min.

Group II.—The same undrawn monofilament as that in group I was drawn 53 days after it had been meltspun. The feeding speed of the undrawn sample at the drawing was 5 m./min., and the temperature of the water bath was 95°C.

Measurement.—Tensile tests of these samples were carried out with an Instron tensile tester at 20°C and at 65% RH. From the load-elongation curves thus obtained, the tensile strength and Young's modulus were measured. The shrinkage was measured by treating the samples in boiling water for 30 min. without tension. Birefringence was measured as follows: The sample was cut obliquely, and its wedge-shaped end was laid between crossed Nichol's prisms of a polarization microscope. From the number of the interference fringes which were observed on the wedge portion of the sample when the monochromatic light of a sodium lamp was used as the light source, the birefringence was determined according to the following equation:

$$\Delta n = N\lambda/d \qquad (1)$$

where Δn is the birefringence, N, the number of interference fringes, λ, the wevelength of the light, and d, the diameter of the sample.

Results

Change of Tensile Strength by Drawing.—In many kinds of fibers made from synthetic linear high polymers, the tensile strength of a filament changes with the draw ratio[1-4]. Generally, the strength of a filament from such

1) T. Yoshida, *J. Soc. Textile and Cellulose Ind. Japan*, **11**, 230 (1955).
2) J. Furukawa, K. Muramatsu and S. Ohya, *J. Japan Soc. Testing Materials*, **8**, 320 (1959).
3) R. Suda, *J. Soc. Textile and Cellulose Ind. Japan*, **8**, 272 (1952).
4) A. R. Urquart, *J. Appl. Chem.*, **4**, 195 (1954).

a polymer, whose crystallinity increases with orientation, tends to increase with the draw ratio. Polyamide filaments also become stronger as the degree of orientation increases, when the draw ratio is high enough.

The present authors investigated the change in tensile strength of nylon 6 monofilaments over a wide range of draw ratios. Figure 1 is the plot of the tensile strength against the draw ratio. This figure shows that the strength decreases, reaches a minimum and then increases again as the draw ratio increases, though the draw ratio and the decrease in strength at the minimum point differ between group I and group II. In group I, a 90%-drawn sample is 60% weaker than the undrawn sample, but in group II a 150%-drawn sample (the weakest one) is 35% weaker than the undrawn sample.

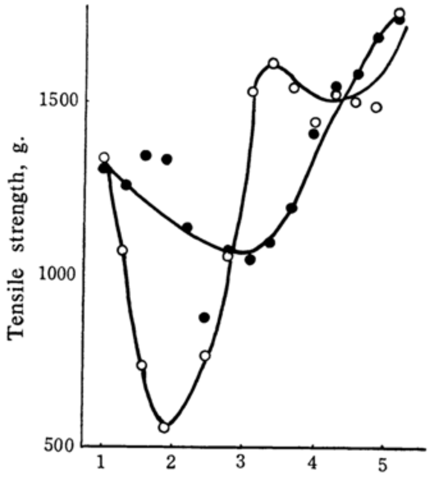

Fig. 1. Dependence of tensile strength on the draw ratio. ○, Group I ●, Group II

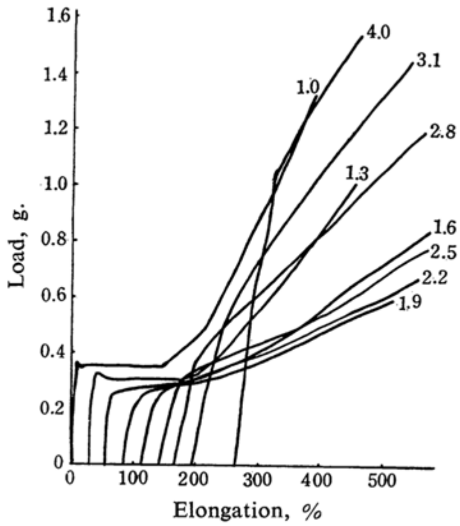

Fig. 2. Load-elongation curves for group I.

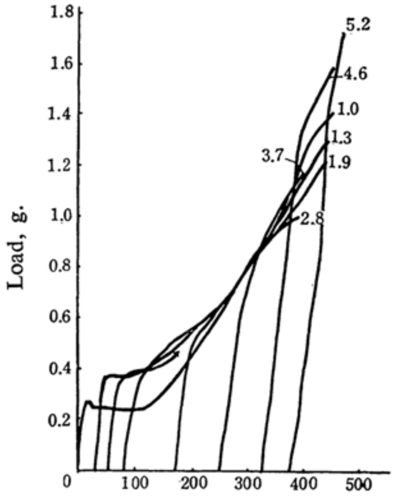

Fig. 3. Load-elongation curves for Group II.

These differences may result from some change in the structure of the undrawn filament during the lapse after spinning.

The load-elongation curves of these samples were shown in Figs. 2 and 3.

There is a contrast between the groups of curves of these two groups. In the case of group I, the yield value and the slope at the higher elongation of the load-elongation curve become smaller and reach a minimum at a draw ratio near 2 ; then the yield value increases, and the slope becomes steeper as the draw ratio increases.

The curves of group II do not show such tendencies, but they nearly overlap one another in the range of high elongation percentages.

Young's modulus obtained from the initial slope of the load-elongation curve was plotted against the draw ratio of the sample in Fig. 4. Young's modulus is nearly constant in the range of draw ratio from 1 to ca. 2, and then it increases with the draw ratio. This behavior suggests that the mechanism of drawing in the

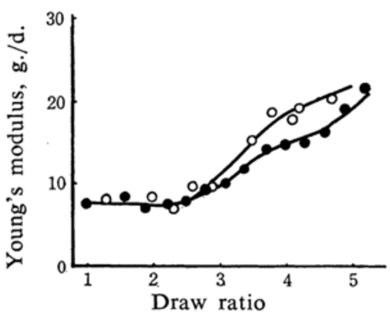

Fig. 4. Plot of Young's modulus against draw ratio. ○, Group I ●, Group II

range of lower draw ratio differs from that in the higher draw ratio.

Other polyamides (nylon 66, 69 and 610) exhibited behavior similar to that of nylon 6.

Shrinkage in Boiling Water.—The shrinkage of group I in boiling water, as shown in Fig. 5, is kept nearly constant in the range of draw ratio lower than ca. 2, increases rapidly in the range of draw ratio from ca. 2 to ca. 3.5, and gradually approaches to a saturation point as the draw ratio increases.

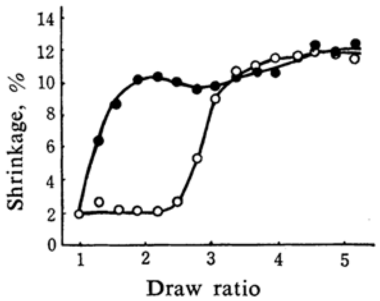

Fig. 5. Relation between draw ratio and shrinkage in boiling water.
○, Group I ●, Group II

Such behavior seems to be related to the existence of a minimum strength point near draw ratio 2, but, as is shown in Fig. 5, the dependence of the shrinkage of group II on the draw ratio differs from that of group I. In this case, the shrinkage increases quite rapidly in the first stage of drawing and then nearly saturates near the draw ratio of 2.

This difference between I and II seems to be a proof that the difference in the inner structure of the undrawn samples influences the mechanism of drawing.

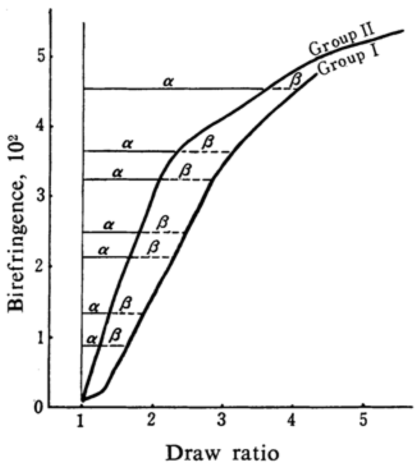

Fig. 6. Change of birefringence with draw ratio.

Birefringence.—Figure 6, a plot of the birefringence against the draw ratio, also shows a difference between groups I and II.

The rate of increace in birefringence at a low draw ratio is less in group I than in group II. This means that the degree of orientation does not always correspond to the draw ratio, but depends on the history of the undrawn sample.

Discussion

These curious relations between the draw ratio and some physical properties of polyamide filament seem to be due to one cause, that is, the process of the change of polymer structure during the drawing changes near the draw ratio of 2.

At first, the flow phenomenon during drawing was considered to be the cause. This phenomenon is known to occur when an amorphous undrawn polymer, such as polyethylene terephthalate, is drawn under a controlling condition; it is called "super drawing"[5]. In an extreme case of flow, orientation does not occur at all and the fiber becomes weaker. In the case of polyamide monofilament, it is probable that the flow phenomenon occurs because the polyamide melt was quenched in water, with the result that the crystallinity of the undrawn filament is low (the crystallinity of the undrawn sample of group I is less than 10%, and that of group II is 14%).

The fact that the decrease in strength at the minimum is more striking in the case of group I (lower crystallinity) than in the case of group II (higher crystallinity) also suggests the possibility of the flow.

In order to give a more quantitative explanation of this, the authors assume, as the first approximation, (a) that during the process of the drawing of group II, no flow phenomenon occurs at all, and (b) that unless flow occurs when group I is drawn, its birefringence is quite the same as that of group II at a same draw ratio.

According to these assumptions, α in Fig. 6 corresponds to an effective drawing accompanying real orientation, and β is a deformation due to the flow. Figure 7 is the drawing of a model in which α and β are shematically distinguished from each other. Now we suppose that an undrawn filament of a unit length is "effectively" drawn $(1+\alpha)$ times and then elongated further $(1+\gamma)$ times by flow deformation, where $\gamma=\beta/(1+\alpha)$, the final length being $(1+\alpha+\beta)$. So, $(1+\gamma)$ or $((1+\alpha+\beta)/(1+\alpha))$ is the draw ratio due to the flow only.

5) A. B. Thompson, *J. Polymer Sci.*, **34**, 741 (1959).

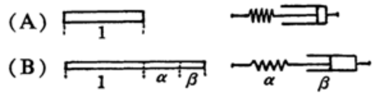

Fig. 7. Model of deformation.
(A) undrawn sample; (B) drawn sample

The values of α, β and $(1+\gamma)$ are listed in Table I.

If the monofilament did not become thinner because of the flow, the strength would be equal to the measured strength multiplied by the factor $(1+\gamma)$. The right column of Table II is the result of this multiplication. Although the magnitude of strength-decrease becomes smaller by this correction, the value is still the smallest at the draw ratio of 1.82 and becomes extraordinarily large near the draw ratio 3.

TABLE I. CALCULATION OF THE RATIO OF FLOW DEFORMATION

Draw ratio[a]	α	β	$1+\alpha$	$\frac{1+\alpha+\beta}{1+\alpha}$
1.00	0.00	0.00	1.00	1.00
1.28	0.03	0.25	1.03	1.24
1.54	0.21	0.33	1.21	1.27
1.82	0.35	0.47	1.35	1.35
2.09	0.58	0.51	1.58	1.32
2.38	0.71	0.67	1.71	1.39
2.66	0.99	0.67	1.99	1.34
2.94	1.20	0.74	2.20	1.34
3.78	2.36	0.42	3.36	1.12

[a]Actual draw ratio: (denier on undrawn filament) ÷ (denier of drawn filament)

TABLE II. CORRECTED TENSILE STRENGTH

Draw ratio	Measured strength s, g.	Corrected strength $s\times\frac{1+\alpha+\beta}{1+\alpha}$, g.
1.00	1340	1340
1.28	1063	1320
1.54	735	933
1.82	558	754
2.09	765	1010
2.38	1050	1390
2.66	1538	2060
2.94	1620	2170
3.78	1450	1620

Therefore, we cannot give a satisfactory explanation of the phenomenon of minimum strength by considering only the flow as the cause, though this seems to contribute partly to the phenomenon, because the assumptions mentioned above are not always correct.

Another possible cause of the phenomenon is a change in the mechanism of drawing in the intermediate stage of drawing. It is known that the crystal form of nylon 6 changes from α form to β form when it is drawn about 150%[6]. Therefore, it may be reasonable to consider that the phenomenon of minimum strength is related to the transition of crystal form. However, as the crystallinity of the undrawn samples is rather low and as the strength of a sample seems to depend chiefly on the state of the amorphous part and not on the crystal form, the transition of the crystal form itself has no direct influence on the change in strength. Therefore, it is more natural to consider that on the intermediate stage of drawing, where the transition of crystal form can occur, the structure of the polymer becomes most unstable, as the result of which the strength reaches a minimum, though the authors are not sure how or why the structure becomes most unstable.

As to the difference in the changes of some properties between groups I and II, the authors have considered the influence of the history of the sample from spinning to drawing. The decrease in tensile strength of group II is less than that of group I, and the shrinkage of group II increases more rapidly in the first stage of drawing than that of group I.

Therefore, we suppose (1) that sufficient time is necessary for a network structure in the polymer to be completed, and (2) that, if a structure is once completed, it does not completly disappear but partly remains after the sample has been deformed.

Thus, when a sample is drawn immediately after spinning (before the structure of the undrawn filament is formed), it becomes either stronger or weaker, depending on the draw ratio, becoming the weakest near the draw ratio of 2. On the contrary, when the sample is drawn after the structure of undrawn filament is completed (group II), the structure of the undrawn sample remains in the drawn one, and, as a result, the strength decrease at the minimum becomes less than that of group I.

The difference in birefringence-shrinkage relationship, shown in Fig. 8, between groups I and II can be explained to some extent by these assumptions. The sample drawn before the structure of the undrawn filament is formed retains less residual internal stress than the sample in which the structure of undrawn filament has not disappeared; therefore, the shrinkage of group II increases rapidly with the draw ratio from the first stage of drawing, while that of group I does not.

As the phenomenon of minimum strength near the draw ratio of 2 is observed not only in the case of monofilaments drawn in hot

6) K. Fuchino and A. Okada, *Sci. Rep. Toyo Rayon Co.*, 4, 163 (1949).

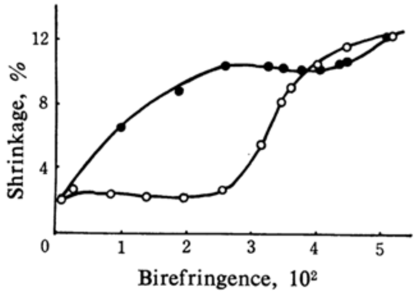

Fig. 8. Relation between birefringence and shrinkage in boiling water.
○, Group I ●, Group II.

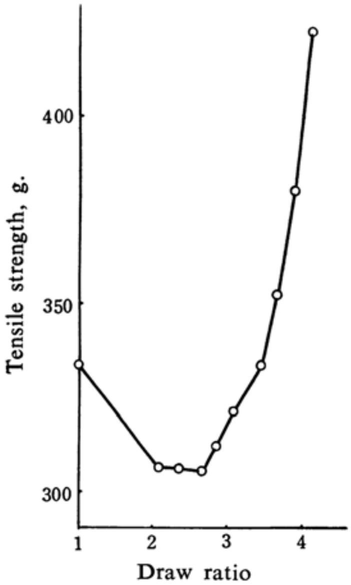

Fig. 9. Change of tensile strength of nylon filament yarn with draw ratio.

water, but also in the case of multifilament yarns cold-drawn with an ordinary draw-twister (Fig. 9), this phenomenon seems to be peculiar to polyamide fibers, irrespective of the way of drawing.

Further efforts will be made in order to explain the change in physical properties by drawing more systematically and quantitatively in the experiments to be described in later papers of this series.

Conclusion

From some peculiar behaviors of nylon 6 monofilament concerning the change in physical properties with the change in draw ratio, the authors have discussed the change in the molecular structure of the polymer during drawing.

Although no definite conclusions were obtained, the following assumptions seem to fit the observed phenomena:

(a) The flow of the polymer occurs during drawing to some extent.

(b) The structure of polyamide filament becomes most unstable near the draw ratio of 2.

(c) Sufficient time is necessary for a network structure in the polymer to be completed.

(d) If a structure is once completed, it does not completely disappear but partly remains even after the polymer has been deformed.

Summary

The relation between the draw ratio and some physical properties of nylon 6 fibers was investigated, using monofilament drawn in hot water to various draw ratios. The tensile strength decreases, passes through a minimum at a draw ratio near 2, and then increases as the draw ratio becomes higher. The decrease in strength at the minimum in the sample drawn immediately after spinning amounts to 60% of the strength of the undrawn sample. The shrinkage in boiling water of the sample drawn immediately after spinning is nearly zero in the range of a low draw ratio, increases in the range of the ratio from ca. 2 to ca. 3.5, and gradually approaches a saturating value, but that of the samples drawn many days after spinning increases most rapidly in the range of the ratio from 1 to ca. 2 and then gradually approaches to a saturating value with the draw ratio. On the first stage of drawing, the rate of increase in birefringence with the draw ratio of the sample drawn immediately after spinning is smaller than that of the sample drawn many days after spinning. On the basis of these results, the authors discussed the mechanism of the drawing of polyamide filaments.

Nagoya Laboratory
Research Department
Toyo Rayon Co., Ltd.
Minato-ku, Nagoya