Studies of the Drawing of Polyamide Fibers. II. The Drawing of Heat-treated Nylon Monofilaments

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In a previous paper, the present authors reported that the tensile strength of nylon 6 filament showed a minimum value at a draw ratio near 2 and that, therefore, the structure seemed to become unstable at the intermediate stage of drawing[1]. For this paper, the authors have investigated the dependences on the draw ratio of some physical properties of nylon monofilaments drawn to various draw ratios after they had been heat-treated at various temperatures from 90 to 180°C; this has been undertaken in order to investigate how the change in the structure, especially the crystallinity, of an undrawn sample influences the behavior of the drawing. Althogh the effect of the heat-treating temperature of the undrawn nylon filament on the load-elongation curve has been studied by Yumoto[2], the change in the physical properties during the drawing of heat-treated samples has not yet been studied.

Experimental

Samples.—The undrawn nlyon monofilament (about 1300 denier), prepared under the same

1) H. Hattori, Y. Takagi and T. Kawaguchi, This Bulletin, **35**, 1163 (1962).

2) H. Yumoto, ibid., **29**, 353 (1956).

conditions as that in the previous paper[1], was heat-treated, more than a week after it had been meltspun, at the temperatures of 90, 110, 114, 150, 160, 170 and 180°C, in an air-bath for 30 sec. Each heat-treated undrawn sample was drawn in water of 90°C, at the feeding speed of 5 m./min.

Measurement. — Various physical properties (strength, shrinkage in boiling water, specific gravity and birefringence) of these variously-drawn samples were measured under the same conditions as those in the previous paper[1].

Results and Discussion

Tensile Strength.—If the decrease in strength observed near the draw ratio of 2 is caused by the flow phenomenon, which is called "super drawing", the decrease in strength will stop, because heat-treatment strengthens the interaction between the polymer molecules and, therefore, it becomes more difficult for the flow during drawing to occur. The experimental results, shown in Fig. 1, indicate that

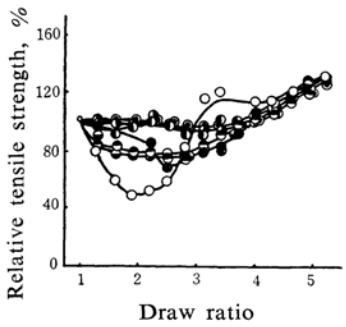

Fig. 1. Dependence of thensile strength on draw ratio.
○, Drawn immediately after spinning
●, Drawn many days after spinning
◓, Drawn after being heat-treated at 90°C
◒, Drawn after being heat-treated at 110°C
◐, Drawn after being heat-treated at 150°C
◑, Drawn after being heat-treated at 160°C
⊙, Drawn after being heat-treated at 170°C

the higher the heat-treating temperature, the less the decrease in strength at the minimum. Though a minimum point was observed near the draw ratio of 2 in the draw ratio-strength curve when the heat-treating temperature is below 110°C, no minimum point was observed when the heat-treating temperature was above 150°C. This fact suggests that the flow occurs during the drawing, and it can be one of the reasons for the minimum strength observed on the drawing of the less crystalline sample, but it seems unsatisfactory to explain this fact completely in terms of flow phenomenon, because even in case of samples which have no minimum in the draw ratio-strength curves, the strength does not increase but is kept nearly constant until it increases with the draw ratio from the ratio of 3∼3.5.

Birefringence.—It is thought that the degree of molecular orientation due to the drawing will be lower when the flow occurs during the drawing than when it does not occur. Therefore, the degree of flow can be roughly estimated by comparing the draw ratio-birefringence curves. In the previous paper. the authors noticed the difference observed between the draw ratio-birefringence curve of samples drawn immediately after spinning (I) and that of samples drawn many days after spinning (II). For this paper, we have also compared the curves of samples drawn after the heat-treatment at various temperatures. The results are shown in Fig. 2. All curves,

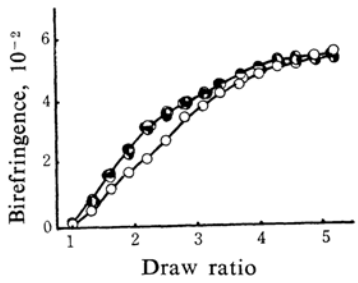

Fig. 2. Dependence of birefringence on draw ratio.
○, Drawn immediately after spinning
●, Drawn many days after spinning
◓, Drawn after being heat-treated at 90°C
◒, Drawn after being heat-treated at 150°C
◐, Drawn after being heat-treated at 160°C
◑, Drawn after being heat-treated at 170°C

except the curve for the samples of group I quite overlap with each other, regardless of whether the minimum strength was observed or not. In consideration of the fact, it is obvious that the phenomenon of minimum strength observed in certain samples is due not only to the flow but also to some other reasons. It is thought that, even if the apparent degree of orientation is equal, the change in internal structure depends on the structure of the undrawn sample and that the difference in the change among heat-treated samples appears most remarkably at the draw ratio near 2, where the polymer structure becomes most unstable.

Shrinkage in Boiling Water.—In the previous part of this paper, the authors chiefly discussed the influence of the heat-treatment of an undrawn sample on the change of strength with the draw ratio, but it is thought that strength data are not precise or reliable

enough to be discussed in detail. From this point of view, the data of shrinkage in boiling water seem to be better as the basis for a discussion of the change of structure during drawing.

The shrinkage in boiling water of heat-treated samples, shown in Fig. 3, changed very peculiarly with the heat-treating temperature and draw ratio. In the case of samples drawn after heat-treatment, the degree of shrinkage rapidly increased in the initial stage of drawing, passed a maximum, and then decreased as the draw ratio increased. At the extreme draw ratio, the degree of shrinkage for all the

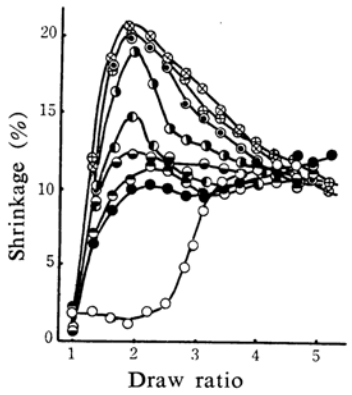

Fig 3. Dependence of shrinkage in boiling water on draw ratio.
○, Drawn immediately after spinning
●, Drawn many days after apinning
◓, Drawn after being heat-treated at 90°C
◒, Drawn after being heat-treated at 110°C
◐, Drawn after being heat-treated at 114°C
◑, Drawn after being heat-treated at 150°C
⊙, Drawn after being heat-treated at 160°C
⊗, Drawn after being heat-treated at 170°C
⊕, Drawn after being heat-treated at 180°C

samples seems to converge to the same value, regardless of the heat-treating condition. The maximum value always appeared near the draw ratio of 2 and increased as the heat-treating temperature of the undrawn sample was raised. It seems very important that the maximum point always appears at a draw ratio near 2. This implies that the internal structure of a nearly 100% drawn sample becomes most unstable and that some unknown change in the drawing mechanism occurs at a draw ratio near 2.

It is known that polyethylene terephthalate fiber also shows a maximum of heat-shrinkage near this draw ratio, but the mechanism seems quite different in polyethylene terephthalate and in nylon; in the former case[3], the undrawn polymer is almost perfectly amorphous and becomes partially crystalline when it is drawn, while in the latter case the higher the crystallinity of the undrawn polymer, the more remarkable the maximum of heat-shrinkage and the decrease of crystallinity due to drawing.

Though some possible reasons will be considered later in further detail, it is natural to think that the polymer structure becomes most unstable when the shrinkage is at its maximum.

Specific Gravity.—The change in specific gravity with the draw ratio is shown in Fig. 4. The specific gravity of a untreated sample or of a sample which had beed heat-treated at a lower temperature increased with the draw ratio, while that of a sample which had been heat-treated at a higher temperature decreased with the draw ratio. This fact indicates that when the crystallinity of an undrawn sample is low, it is increased by orientation, but when it is rather high, the orientation-induced crystallization is exceeded by the decrease of crystallinity due to the rupture of crystallites during drawing.

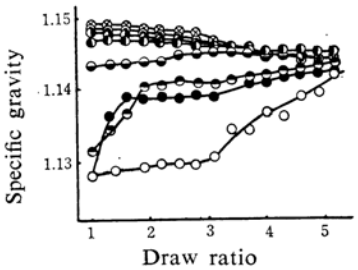

Fig. 4. Dependence of specific gravity on draw ratio.
○, Drawn immediately after spinnirg
●, Drawn many days after spinning
◓, Drawn after being heat-treated at 90°C
◒, Drawn after being heat-treated at 110°C
◐, Drawn after being heat-treated at 150°C
◑, Drawn after being heat-treated at 160°C
⊙, Drawn after being heat-treated at 170°C
⊗, Drawn after being heat-treated at 180°C

Similarly to such properties as strength and shrinkage in boiling water, specific gravity seems to converge to the same value at the extreme draw ratio, regardless of the kind of sample.

Therefore, we can deduce that the structure of highly-oriented nylon filaments is same, whether the crystallinity of an undrawn sample is low or high.

Further Discussion of the Change of Structure with the Drawing.—From the results mentioned above, especially of the shrinkage in boiling water, we believe that there is a certain difference between the mechanism of drawing

3) T. Kawaguchi, unpublished.

in the initial stage (of a lower draw ratio) and that in the later stage of drawing (of a higher draw ratio); in the former, the unstabilization of the polymer structure is predominant, while in the latter a stable structure of drawn polymer is constructed. In other words, a mechanism of drawing is proposed that consists of the unstabilization and stabilization of the polymer by orientation. The former is predominant in the initial stage of drawing, while the latter is predominant in the later stage of drawing.

Therefore, let us further discuss the results of shrinkage in boiling water, because the effect of heat-treatment is most pronounced in these results. It is considered that heat-shrinkage occurs because molecules become more labile upon a rise in the temperature and move in such a direction that the latent strain in the polymer is eliminated; the shrinkage is, then, a measure of the internal strain of polymer. Therefore, it is thought that the internal structure becomes most unstable when the heat-shrinkage becomes greatest.

In the case of ployethylene terephthalate fiber[3], the plot of heat-shrinkage against specific gravity falls on a single curve, in which the shrinkage decreases as the crystallinity increases, regardless of the condition of drawing. This fact implies that the orientation is fixed by the crystallization which occurred during the drawing. In case of nylon, however, this is not true, because the curve of shrinkage in boiling water against specific gravity, as shown in Fig. 5, depends on the heat-treating temperature of the undrawn sample. These facts indicate that, in addition to the degree of orientation and the crystallinity, some unknown factors contribute to the appearance of a maximum near the draw ratio of 2 in the draw ratio-shrinkage curve.

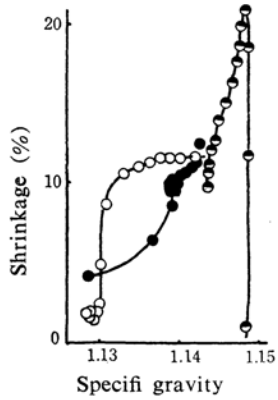

Fig. 5. Relation between specific gravity and shrinkage in boiling water.
○, Drawn immediately after spinning
●, Drawn many days after spinning
◓, Drawn after being heat-treated at 170°C

The curve of shrinkage against the heat-treating temperature of undrawm sample shown in Fig. 6 has an inflection near the temperature of 120°C. According to Yumoto[2], this temperature is a kind of transition, because inflection points are observed near this temperature in the curves of both specific gravity and yield load in the load-extension curve against the heat-treating temperature of undrawn nylon 6 filament. The heat-treating of undrawn nylon filament at a temperature above 120°C seems to tighten its structure much more than treating below this temperature. Therefore, the maximum value of shrinkage in boiling water is thought to be qualitatively proportional to the tightness of the structure of an undrawn filament.

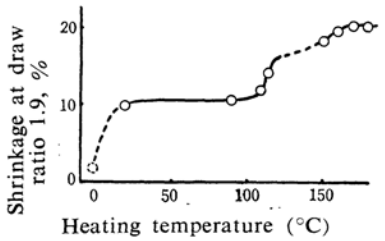

Fig. 6. Relation between heat-treating temperature and the shrinkage at the draw ratio of 1.9.

Now we will discuss the change in shrinkage in connection with that of specific gravity. When the crystallinity of an undrawn sample is low, its specific gravity increases with the draw ratio, but when the crystallinity of an undrawn sample is high, its specific gravity decreases as the draw ratio increases and a maximum of shrinkage is observed. Therefore, it is suggested that a transition from crystalline parts to amorphous parts occurs because of the destruction of crystallites during drawing as well as of a reverse transition owing to strain-induced crystallization, and that the higher the crystallinity of an undrawn sample, the more the destruction of crystallites and the acccumulation of internal strain, as a result of which the shrinkage in boiling water shows a maximum near the draw ratio of 2, where the structure becomes most unstable, though the authors cannot completely explain why it becomes most unstable.

In the case of isotactic polypropylene monofilaments which had been quenched and drawn to various draw ratios, a similar relationship to that of heat-treated and drawn nylon monofilament was also observed between the draw

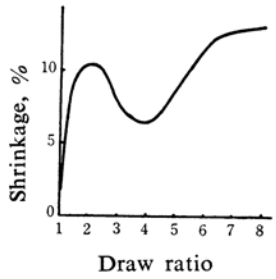

Fig. 7. Change of shrinkage in boiling water of polypropylene monofilament with draw ratio.

ratio and shrinkage in boiling water; that is, a maximum of shrinkage appeared at a draw ratio near 2 (Fig. 7). This phenomenon to seems to be due to the same reason as that for nylon 6, because the crystallinity of undrawn polypropyrene is thought to be rather high even when it is quenched.

Conclusion

Some physical properties have been measured on nylon monofilaments which had been drawn to various draw ratios after the heat-treatment of undrawn samples at various temperatures. The authors found that the shrinkage of a sample in boiling water changes very peculiarly with the draw ratio, showing a maximum, and suggested that the polymer structure becomes, unstable in the intermediate stage of drawing, though no satisfactory explanation of the unstabilization effect has been given. Further effort will be made to make sure of the "unstabilization" during drawing and to elucidate the mechanism of the drawing.

Summary

In order to investigate the influence of the structure of an undrawn sample on the change in physical properties upon drawing, undrawn nylon monofilaments were drawn to various draw ratios after having been heat-treated at several temperatures; some properties, such as tensile strength, shrinkage in boiling water and specific gravity, were then measured on these drawn samples. Although the minimum of tensile strength observed at the draw ratio near 2 had a tendency to disappear upon the heat-treatment of an undrawn sample, the strength did not increase in the range of a low draw ratio. When an undrawn sample was heat-treated above 150°C, a maximum appeared at a draw ratio near 2 in the plot of shrinkage in boiling water against the draw ratio. The higher the heat-treating temperature of an undrawn sample, the greater the maximum of shrinkage. The specific gravity decreased during drawing when the undrawn sample was of a rather high crystallinity, but it increased when the undrawn sample was of a low crystallinity. These results have been discussed, and it has been suggested that the polymer structure becomes most unstable at the intermediate stage of drawing.

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