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Steam and Heat Setting of Nylon 6 Fiber. I. Effect of Dry Heat Setting and Steam Setting on Young's Modulus and Specific Gravity of Nylon 6 Fiber*

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Synopsis

Nylon 6 fiber subjected to steam setting exhibits many differences in properties from that subjected to dry heat setting. Undrawn nylon 6 filaments were subjected, under tension or in the tensionless state, to dry heat setting at 140, 160, and 180°C. and to steam setting at 110, 120, and 130°C. Young's modulus and the bending modulus were measured, and the variation of density resulting from dry heat setting was observed with a density-gradient tube, dry *n*-butyl bromide and benzene being used as the medium. These results show that specific gravity is increased by heat-setting processes, especially by steam setting. This is considered to be caused by the increase in the degree of crystallinity. Young's modulus seems, however, to be rather decreased by steam setting; this may be attributed to the role of water molecules in loosening the molecular spacement of the fibrous structure in the case of steam setting.

1. INTRODUCTION

Many studies related to Young's modulus and density of nylon subjected to heat setting have already been reported.[1,2] We found that nylon 6 fibers subjected to steam setting exhibited very extraordinary properties. Although subsequent reports will deal with dyeability, x-ray diffraction, swelling properties, long period, and other properties of nylon 6 fiber, in the present paper we report on the state of the amorphous part (which was not previously investigated), because it seems to be due to the amorphous part that the density and crystallinity increased on steam setting, but Young's modulus increased only slightly.

We have considered especially the state of the amorphous part not previously studied.

2. EXPERIMENTAL

Samples

Samples for Measurement of Young's Modulus by Extension. Drawn monofilament (200 den.) was dried in a desiccator over $CaCl_2$. The filament was subjected to heat setting either under 1 g./den. tension or in

* This material appeared in part in *Kobunshi Kagaku*, **16**, 271 (1959).

the relaxed state (no tension). The dry heat setting involved preheating for 1 hr. (70–90 °C.), followed by dry heat setting (20 min.) at various temperatures; steam setting involved preheating for 5 min. (70–90 °C.), placing of the fiber in a vessel under vacuum, steam setting for 20 min. at various temperatures, and again being kept under negative pressure for 10 min. The sample, after being removed from the setting apparatus, was dried in a desiccator over P_2O_5 for a few days, and subsequently placed in a desiccator, conditioned at 65% R.H. with H_2SO_4 for a few weeks.

Samples for Measurement of Young's Modulus by Bending. Drawn monofilament (3300 den.) was dried under negative pressure in a desiccator over P_2O_5, after which heat setting was carried out as described above.

Samples for Measurement of Density. Drawn 1000 den. filaments (draw ratio 3) and undrawn filaments were used as samples. These filaments were subjected to dry heat setting and to steam setting as described above either under 0.1 g./den. tension (drawn filament only) or in the relaxed state. The dry-heat-set filament was further dried for more than a week under negative pressure in a desiccator over P_2O_5.

Methods

Measurement of Young's Modulus by Extension. Measurement of tension and elongation was carried out in a chamber conditioned at 20 °C. and 70% R.H. A strain meter (Toyo Sokki Co., Type US-7C) was used for measurement of tension. The cross-sectional areas were calculated from density and denier of each filament, and then stresses were calculated.

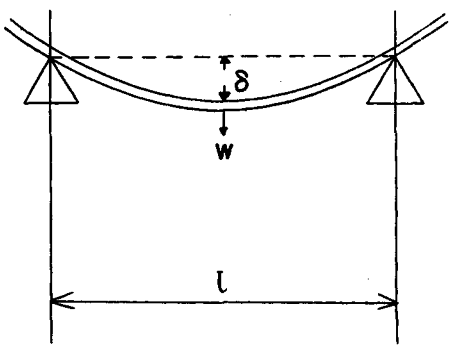

Fig. 1. Schematic diagram of bending of nylon filament.

These filaments bend by themselves, and the force required to straighten them introduces an error. Accordingly, Young's modulus by extension was calculated from stress on 0.1% elongation in the stress-strain curve.

Measurement of Young's Modulus by Bending. The filament was placed on the edges of two knives as shown in Figure 1, and the stress was measured by a strain gage in a dry nitrogen atmosphere.

Young's modulus by bending E is given by

$$E = 64Wl^3/48\pi d^4$$

where W is stress, d is denier, l is distance between the two edges, and δ is bending length.

Measurement of Density. The density-gradient tube which gave the most exact relative relation among the samples to be measured was adopted. Dry benzene and n-butyl bromide were used as the medium. Twenty mixtures of different density were prepared by mixing two liquids at a calculated ratio and densities of the mixtures were in equal steps between 1.1129 and 1.1751. The ten mixtures of low density were poured into a density-gradient tube in order from the smallest density mixture; and the ten mixtures of larger density were poured into the other tube. Then nine floats of Pylex glass were put into the tubes kept at 20°C. The density of the floats was previously measured exactly by the flotation method at 20°C. The relation between the height and the density of floats was linear. Consequently, measurement of density could be carried out exactly. The density gradient was 0.001225/cm. in both tubes, and the height of the float was measured with a cathetometer (accuracy: 1/50 mm.).

3. RESULTS AND DISCUSSION

Young's Modulus

By Extension. Figures 2 and 3 show stress–strain curves of filaments subjected to heat setting with and without tension, respectively.

When filaments were subjected to heat setting in the relaxed state, the stress of the dry-heat-set filament increased as compared with that of the unset one. On the other hand, stress of the steam-set filament was decreased as compared with that of the unset one, except for the filament subjected to steam setting at 110°C. When filaments were subjected to heat setting under tension, stress between dry-heat-set and steam-set fila-

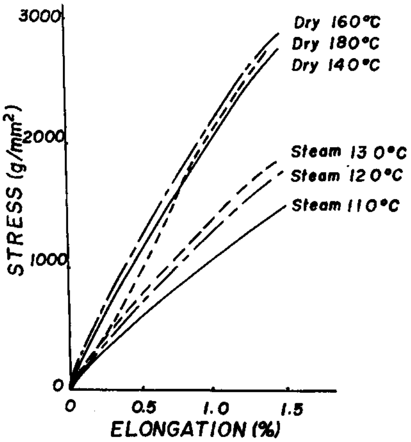

Fig. 2. Stress–strain curves for nylon 6 fibers subjected to various heat setting treatments under 1 g./den. tension.

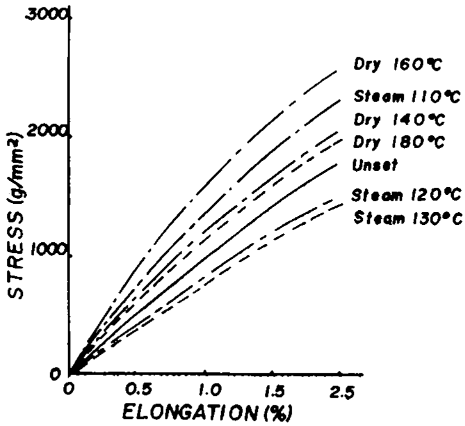

Fig. 3. Stress-strain curves for nylon 6 fibers subjected to various heat setting treatments without tension.

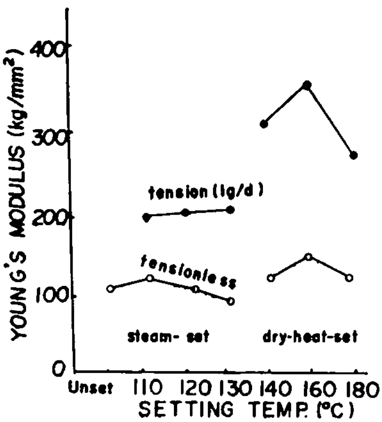

Fig. 4. Relation between various conditions of heat setting and Young's modulus.

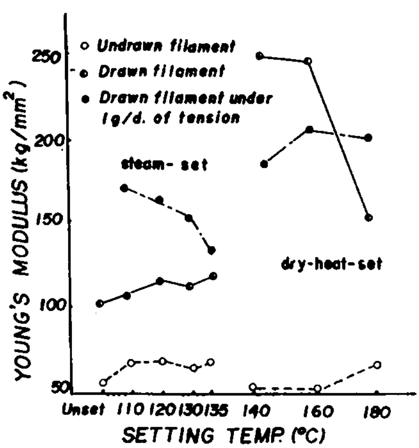

Fig. 5. Relation between various conditions of heat setting and bending modulus.

ments showed more apparent relation as described above. Figure 4 shows Young's modulus by tension calculated from stress for 0.1% elongation in the above figures. This figure agrees with the results described above.

By Bending. Figure 5 shows Young's modulus by bending for each type of filament. There is a distinct difference in the Young's modulus by bending between dry-heat-set and steam-set filaments. In general, Young's modulus by bending increases in proportion to the increase of tension as well as Young's modulus by extension. In only the case of a filament subjected to steam setting under tension, Young's modulus decreases in proportion to the increase in setting temperature. We have observed an extraordinary phenomenon, i.e., that the degree of heat setting of the steam-set filament is larger than that of the dry-heat-set one, but Young's modulus by bending the dry-heat-set filament is larger than that of the steam-set filament.

Density

The density of the steam-set filament was larger than that of the dry-heat-set one, whether drawn or undrawn filaments were subjected to the heat setting, and whether the setting was carried out with or without tension. This is shown in Figure 6. This means that there is a distinct increase of the degree of crystallinity, which agrees with the results of x-ray and infrared spectral studies. If the degree of crystallinity increases, Young's modulus or tensile strength will increase. This phenomenon is recognized for dry-heat-set filament. However, as described above, the degree of crystallinity of steam-set filament increases more than that of the dry-heat-set one, and Young's modulus and tensile strength show no large increase. For these reasons, we could not dismiss the changes occurring in the amorphous parts.

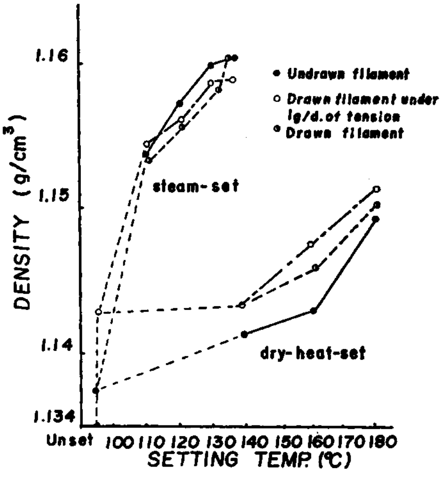

Fig. 6. Relation between conditions of heat setting and density.

4. CONCLUSION

It is expected that the density and degree of crystallinity of nylon 6 fiber subjected to steam setting increase very markedly. However, the increase of Young's modulus is not so large as that of fiber subjected to dry heat setting. This is an apparently incompatible result. A similar phenomenon was observed in tensile strength of nylon 6 fiber subjected to heat setting under tension or in the relaxed state.

The tensile strength of the fiber subjected to dry heat setting at 160–170 °C. increases slightly as compared with that of unset fiber, and the degree of increase grows larger with increasing tension.

On the other hand, the tensile strength of this fiber subjected to steam setting decreases compared to that of the unset fiber, and the degree of decrease becomes larger with decreasing tension or rising temperature, and this fiber melts at 163 °C. in saturated steam.

From these phenomena, we have supposed changes in the fibrous structure of nylon 6 fiber as follows: (*1*) a decrease in the crystalline orientation; (*2*) hydrolysis of polymer molecules in the amorphous part or the decrease of hydrogen bonding among polymer molecules. The first assumption is based on the fact that Young's modulus of both dry-heat-set and steam-set fibers does not increase as much as expected in the tensionless state. The phenomenon described above occurs also on hydrolysis or on decreases in hydrogen bonding. In the former, however, it is difficult to explain the increase of density and crystallinity under conditions sufficiently severe to cause hydrolysis, and preferably, the phenomena can be explained by the decrease in hydrogen bonding.

The hydrogen bonds among polymer molecules are due to the existence of water molecules at high temperature, and as the intermolecular spaces increase, there is permeation of water molecules among the polymer molecules. When nylon 6 fiber is cooled again, the amorphous part shows the state of so-called loose packing, because the rebonding is prevented by the existence of water molecules. Consequently, as the amorphous parts between crystalline sections are soft, even if the degree of crystallinity increases, it is expected that the increase of Young's modulus and tensile strength are not so large as that of crystallinity.

The packing of the amorphous part becomes a little more dense with steam setting under tension compared to the tensionless state, because the disorder of crystalline orientation and the swelling of the amorphous part do not occur under tension, and the force of the component vertical to the fiber axis acts to draw neighboring molecules closer together.

In subsequent papers, we will study such factors as x-ray diffraction, dyeability, swelling, intrinsic viscosity, and amino and carboxyl endgroup contents.

References

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Résumé

On a trouvé que la fibre de nylon 6 soumise au bain de vapeur a des propriétés différentes de celle soumise à un bain chaud it sec. On a soumis des filaments de nylon 6 non étirés sous tension ou sans tension, à des bains chauds et secs de 140 à 180°C. et à des bains de vapeur de 110 à 130°C. On a mesuré les modules de Young, les modules de courbure et les densités. De ces résultats on a remarqué que si la densité augmente avec le traitement au bain sec et spécialement avec le traitement au bain de vapeur, le module de Young et le module de courbure sont plus petits dans le traitement à la vapeur que dans le traitement au bain sec. Ceci peut être attribué au rôle des molécules d'eau par relâchement de la partie amorphe par traitement au bain de vapeur.

Zusammenfassung

Eine Nylon-6 Faser unterscheidet sich nach Dampfbehandlung in vielen Eigenschaften von einer trocken hitzebehandelten. Nicht gereckte Nylon-6-Fäden wurden mit und ohne Dehnung einer Behandlung mit trockener Hitze bei 140 bis 180°C. und einer Dampfbehandlung bei 110 bis 130°C. unterzogen. Es wurden der Young-Modul, der Biegemodul und die Dichte gemessen. Aus diesen Ergebnissen wird gefolgert, dass zwar die Dichte bei der Hitzebehandlung, besonders bei Dampfbehandlung, zunimmt, jedoch der Young-Modul und der Biegemodul bei Dampfbehandlung kleiner sind als bei Trockenhitzebehandlung. Das wird auf die auflockernde Wirkung vou Wassermolekülen auf die amorphen Teile bei Dampfbehandlung zurückgeführt.

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