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Steam and Heat Setting of Nylon 6 Fiber. IV. Relationship between Heat Setting and Swelling*

M. TSURUTA, A. KOSHIMO, and T. TAGAWA,
Research Institute, Nippon Rayon Company, Ltd., Uji City, Kyoto, Japan

Synopsis

The swelling and dissolution of heat-set nylon 6 fiber in aqueous sulfuric acid were examined. Steam-set fiber having good dyeability swells with much more difficulty than the dry-heat-set and unset fibers. Similar phenomena are seen in the examination of density of nylon 6 fiber subjected to heat setting, and it is found that the resistance to swelling depends on the crystalline region rather than on the amorphous region.

1. INTRODUCTION

Schwertarsek[1] has reported on the swelling and dissolution of nylon 6; however, a decrease of swelling tendency as a result of heat setting was not reported. Kurokawa and Kawagishi[2] examined the swelling of nylon 6 in sulfuric acid solution and reported that there was no distinct difference between heat set and unset fibers.

Nylon 6 fiber shows a greater increase of density on steam setting than on dry heat setting.[3] In spite of our expectation that nylon 6 fiber subjected to steam setting has a very compact structure and decreased dyeability, there was increased dyeability, as described in a previous report.[4]

In this paper, the influence of sulfuric acid solution as a swelling agent and solvent on the heat-set fiber is examined. Usually unset nylon 6 fiber dissolves at room temperature in 27–30% sulfuric acid solution; consequently, for the examination of dissolved states the above concentration range is suitable, while an acid concentration below 27% is desirable for observation of the swelled states of the fiber.

Filament and bristle of nylon 6 previously subjected to heat setting were used. The swelling behavior and solubility in 27 and 30% sulfuric acid solutions were qualitatively observed, and the effects of heat setting were further examined by the quantitative measurement of swelling in 20, 23, and 26% sulfuric acid solutions with increasing of fiber cross-sectional area.

2. EXPERIMENTAL

Materials

Filament. Monofilament (100 den./24 filaments) was used. The conditions and procedure of heat setting were the same as those in previous papers.[3,4]

* This material appeared in part in *Kobunshi Kagaku*, **16**, 333 (1959).

Bristle. Undrawn bristle (10,000 den.) was drawn to a draw ratio of 3× and was heat-set under the same conditions as described previously.[3]

Preliminary Experiment

Monofilament samples cut to 2–3 mm. length were mounted on glass microscope slides, and the swelling produced by drops of 27% sulfuric acid solution was observed. The change of diameter R (in per cent) of the monofilament was used as a measure of swelling:

$$R, \% = 100(l - l_0)/l_0 \qquad (1)$$

where l_0 and l are the filament diameters before and after swelling, respectively.

For the experiment with the bristle, 30% sulfuric acid solution was used; this was near the critical concentration at which there was a transition from swelling to dissolving. Each sample was cut to a length of 2 mm. and mounted on a slide glass with vinyl acetate as adhesive agent as shown in Figure 1, caution being taken not to stain the other upper side of the samples. After being dried at room temperature in vacuum, the samples were swelled in 30% sulfuric acid solution for 10, 15, or 45 min. at room temperature, then taken out, rinsed quickly with water, and dyed in a bath containing 1% of a direct dyestuff (Remastrol Blue F3GL) for 1 hr. at 60°C. The swelled, the corroded, and the dissolved state of the surface of the bristle and its dyeability were observed by a microscope at low magnification.

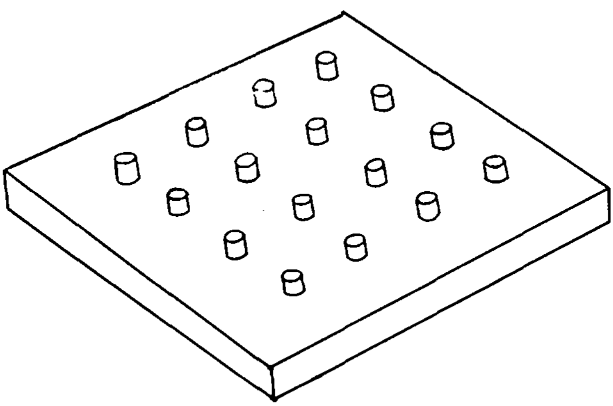

Fig. 1. Preparation of the sample for swelling of nylon bristle.

Quantitative Experiment

The degree of swelling is usually estimated by the quantity of solvent absorbed by a polymer. This method involves some difficulties, such as removal of solvent adhering to the surface of the fiber when sulfuric acid is used; also considerable error would be introduced in weighing. Furthermore when there is difference in the crystallinity or in the packing state of the amorphous region, as is the case with the samples used in this experiment, there will not be a rational relationship between swelled volume and quantity of solvent absorbed.

Bristle samples heat-set under various conditions were fixed on a slide glass as in the qualitative experiment and treated with 20, 23, or 26% sulfuric acid solution at 20°C. for a certain time. The diameters of these samples were measured two times for each before and after the treatment. From the measurement of diametric changes, the coefficient of increase of area S, defined as the degree of swelling shown in eq. (2):

$$S = (r_t^2 - r_0^2)/r_0^2 \tag{2}$$

where r_0 and r_t are the diameter before and after t hours swelling.

Four pieces from the same sample were measured, and S was calculated as a mean value from the eq. (2).

3. RESULTS AND DISCUSSION

Qualitative Experiment

Depending on the conditions of heat setting, swelled appearances are grouped as shown in Figure 2. Figure 2*A* shows no swelling and Figure 2*B* shows the highest swelling, where the filament swells instantly around the surface just after contact with the sulfuric acid solution.

The part corroded shows foaming and bubbles along the surface which

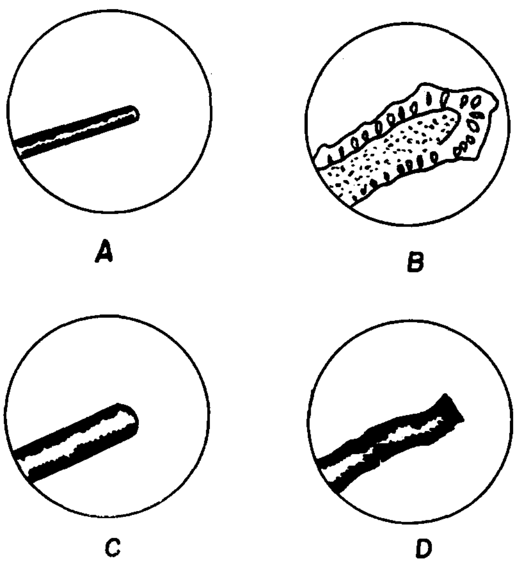

Fig. 2. Swelled state of the nylon filaments subjected to various heat setting treatments and swelled with sulfuric acid solution.

become bigger as the time passes. At last the surface is broken and the filament loses its shape and is dissolved away gradually. In Figure 2*C*, the filament swells gradually with retention of the original shape; such swelling is different from that shown in Figure 2*B*. The filament shown in Figure 2*D* swells very slowly by the degradation of the cut end or at the site of a defect of the surface of the filament.

The shape in swelling is classified into the following three groups according to conditions of heat setting. (*1*) Conditions producing swelling of the

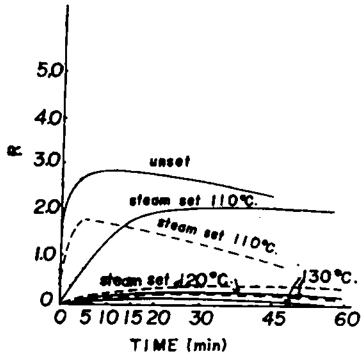

Fig. 3. Change of the diameter of steam-set nylon filament in swelling: (——) steam setting without tension; (--) steam setting under 1 g./den. tension.

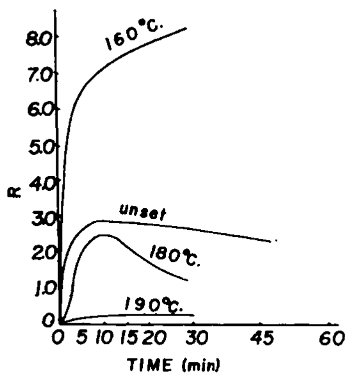

Fig. 4. Change of the diameter of dry-heat-set nylon filament under 1 g./den. tension in swelling.

type shown in Figure 2*B* are: no treatment, steam setting at 110°C., and dry heat setting at 160 or 180°C. (*2*) Swelling of the type shown in Figure 2*C* is produced by steam setting at 120°C. (*3*) Swelling of the type shown in Figure 2*D* is produced by steam setting at 130 or 140°C. and dry heat setting at 190°C.

The coefficient of diametric increase *R* shown in Figures 3 and 4 reveals that the fibers subjected to steam setting at 120, 130, or 140°C. or to dry heat setting at 190°C. swells hardly at all.

In an experiment involving the swelling of bristle for 15 min. in a 30% sulfuric acid solution, the unset bristle, and that steam-set at 110°C., swelling takes place at first around the circumference of the section the bristle assuming a mushroom-like shape. Bristles steam-set at 120 and 135°C., however, are quite different, and retain their original shape even after 45 min. swelling. Bristles subjected to dry heat setting at 140 or 160°C. also swell to a mushroom-like shape after 10 min. swelling, but the shape of bristles heat-set at 180°C. is stable.

These steam and dry heat settings described above were carried out without tension in all cases. When the fiber is heat-set under a tension of 1 g./den. no perceptible differences were noted.

The dyeability is the same as that described previously, i.e., the harder to swell the steam-set fiber is, the better the absorption of dyestuff. Dry-heat-set fiber decreases in dyeability with increasing temperature up to a temperature of 160°C. On the contrary, increased dyeability is observed for the fiber dry-heat-set at 180°C. The relation of the dyeability and resistance to swelling of the dry-heat-set fiber is similar to that in steam-set fiber; it is presumed that a decrease in orientation is involved in this phenomenon.

Quantitative Experiment

The results of quantitative swelling experiments with bristle by 20, 23, and 26% sulfuric acid solutions are shown in Figures 5–7.

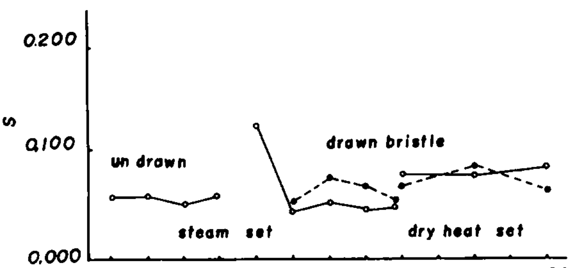

Fig. 5. Change of the cross-sectional area of nylon bristle subjected to various heat-setting treatments and swelled in a 20% aqueous sulfuric acid solution for 22 hr.: (——) heat setting without tension; (--) heat setting under 1 g./den. tension.

For 20–22 hr. swelling it is found that distinct differences of swelling observed for the samples heat set under various conditions with the increase of sulfuric acid concentration. For example, in Figure 7, swelling is more difficult for the steam-set sample compared with the corresponding dry-heat-set bristle. This is in accord with the results of the qualitative experiments.

An increase of swelling resistance with the increase of heat-setting temperature, expecially in the case of dry heat setting, is apparent. There is a tendency for undrawn bristle to swell more easily with increasing steam-setting temperature, but this cannot be explained fully. Further, there is a slight increase in swelling of the dry-heat-set bristle under tension compared with the bristle set without tension.

The explanation for this is believed to be as follows on the basis of comparison between un-set drawn bristle and drawn bristle with respect to swelling tendency. The former swells easily. In the drawn bristle the polymer molecules are aligned along the direction of the fiber axis; how

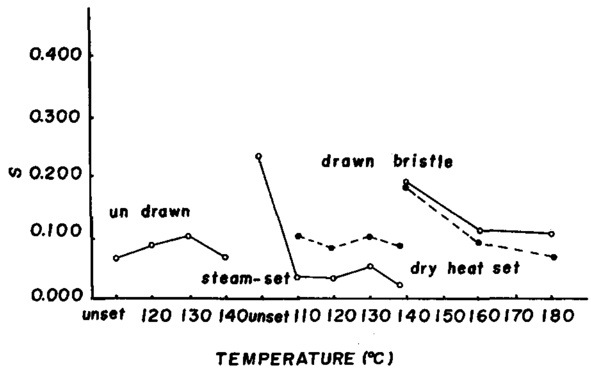

Fig. 6. Change of the cross-sectional area of nylon bristle subjected to various heat-setting treatments and swelled in a 23% aqueous sulfuric solution for 22 hr.: (——) heat setting without tension; (--) heat setting under 1 g./den. tension.

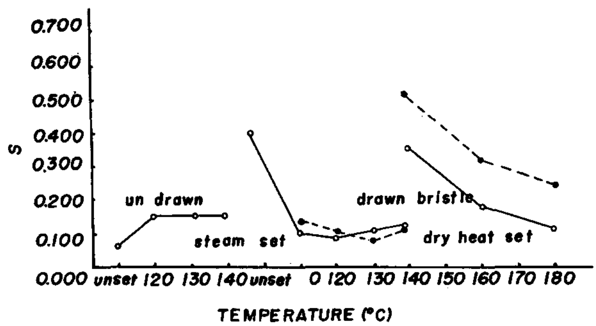

Fig. 7. Change of the cross-sectional area of nylon bristle subjected to various heat-setting treatments and swelled in a 26% aqueous sulfuric acid solution for 20 hr.: (——) heat setting without tension; (--) heat setting under 1 g./den. tension.

ever, when these intermolecular attachments are broken by the swelling agent, the polymer molecules are easily released and may lie at angles to the fiber axis. Each molecule of such fiber which shows the anisotropic phenomenon is in a low state of entropy. In the case of heat setting under tension, a further decrease of entropy occurs. And as soon as these intermolecular attachments forces are broken by the swelling, the entropy will increase.

Considering the swelling tendency of dry-heat-set fiber in connection with the variation of the density described in Part I,[3] it is seen that there is a close relationship, namely, the fiber having the higher density shows a higher resistance to swelling.

In general, when a solid material is dissolved in a solvent, the relative magnitude of cohesive energy and solvation energy of the material is always a problem. The high polymers due to the size of the molecules involved, generally have very large cohesive energies; polyamide, a crystalline high polymer, has an especially strong lattice energy in the crystalline regions.

In the initial step of swelling the swelling agent penetrates into the amorphous region by breaking intermolecular bonds and produces some swelling. If the concentration of the swelling agent is low and the solvation energy is small, no further swelling occurs. An increase in the solvation energy as a result of an increase in concentration of the swelling agent or heating causes more intermolecular bonds of the polymer to be broken, and then the swelling proceeds. When the solvation energy is not sufficient to break down the crystalline lattice, however, the swelling remains within the "limited" stage.

Naturally, as the crystalline region remains unchanged, the x-ray pattern does not show any change.

If the solvation energy which would break down the lattice is attained, finally the crystalline part will disintegrate, and an absolute solution having the highest entropy can be obtained.[5]

Thus, the results obtained by the measurement of swelling suggests the occurrence of structural changes among heat-set nylon samples in connection with such properties as crystallinity and dyeability.

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Résumé

On a examiné les effets de gonflement et de dissolution de solutions d'acide sulfurique sur des fibres de nylon 6 chauffées. Une fibre chauffé à la vapeur, ayant un bon pouvoide coloration, est caractérisée par une grande résistance aux gonflements, si on la compare avec des fibres chauffées à sec ou pas chauffées du tout. Des phénomènes anaelogues sont observés lorsqu'on examine la densité des fibres de nylon 6 soumises à un chauffage, comme décrit plus haut, en on a trouvé que la résistance au gonflement dépend plutôt de la région cristalline que de la région amorphe.

Zusammenfassung

Die Quellungs- und Lösungswirkung von Schwefelsäurelösung auf hitzebehandelte Nylon-6-Fasern werden untersucht. Dampfbehandelte Fasern mit guter Anfärbbarkeit quellen im Vergleich mit mit Trockenhitze und ohne Hitze behandelten Fasern sehr schwer. Ähnliche Erscheinungen können bei der Untersuchung der Dichte von unter Hitzebehandlung stehender Nylon-6-Faser beobachtet werden, und man findet, dass die schwere Quellbarkeit eher vom kristallinen als vom amorphen Bereicht abhängt.

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