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Studies on the Drawing of Polyamide Fibers. IV. Effect of Drawing on the Degree of Longitudinal Swelling

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Synopsis

The longitudinal dimensional change of dried nylon 6 monofilaments of various draw ratios swollen in the atmosphere of 24°C. and 100% R.H. was studied. The degree of longitudinal swelling in equilibrium changes with the conditions of drawing and the draw ratio of the sample; for the samples drawn immediately after spinning, it increases, passes through a maximum near a draw ratio of 2, and gradually decreases as the draw ratio increases; for the samples drawn many days after spinning the maximum point is at a draw ratio near 2.8, while for the samples drawn after heat-treatment the degree of longitudinal swelling does not change appreciably with the draw ratio of the sample. The rate of longitudinal swelling remains nearly constant or increases slightly in the range of draw ratios of 1–3. It then decreases with the draw ratio at draw ratios higher than 3.

Polyamide fibers change on length when they absorb water.[1–3] and the change depends on the absorption-desorption history and the degree of orientation of the sample. A freshly spun filament is extended by several per cent of its original length on the first absorption. It shrinks again when dried. A drawn filament, on the other hand, shrinks on the first absorption, and shrinks further when it is dried again. The sample, after having been subjected to such wetting and drying exhibits a reversible dimensional change in its length due to absorption and desorption of water.[3] Such behavior of polyamide fibers is shown schematically in Fig. 1.

It is known that the higher the birefringence, the more and quicker is the[4] extension of an undrawn sample due to absorption of water;[4] also, the extension rate increases with the temperature of the surrounding moisture. However, no studies have have been made on how much the drawing influences the swelling of polyamide fibers by water. In the present study we have investigated the swelling of polyamide, using monofilaments of various draw ratios.

EXPERIMENTAL

Samples

Three groups of samples were used as follows.

Group I consists of nylon 6 monofilaments drawn to various draw ratios

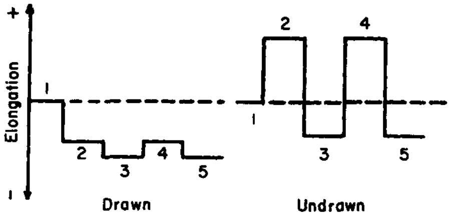

Fig. 1. Dimensional change of nylon 66 fiber due to swelling: (*1*) before wetting; (*2*), (*4*) immersed in water; (*3*), (*5*) dried in the air.

immediately after spinning; these are equivalent to the samples of group I in the previous paper.[6]

Group II consists of nylon 6 monofilaments drawn to various draw ratios several days after spinning. These are the samples of group II in the previous papers.[6]

Group III consists of nylon 6 monofilaments drawn to various draw ratios after having been heat-treated at 180°C. for 30 sec.

The undrawn monofilaments for these groups are of ca. 1300 den.

Procedure

In order to avoid the effect of absorption-desorption history of the samples on their elongation behavior on absorption, every sample was water and dried repeatedly, and then dried for more than a week in a desiccator over phosphorus pentoxide before the experiment. A sample prepared in this way was extended with a tension of 10 g. in a glass tube which was kept at 24°C. and 100% R.H., and the change in sample length during sorption of water vapor was measured with a microscope. The creep of the sample owing to the tension was negligibly small.

RESULTS AND DISCUSSION

Degree of Longitudinal Swelling in Equilibrium

The changes in the degree of longitudinal swelling S, defined by eq. (1), with sorption time are shown in Tables I–III.

$$S = 100\,(\Delta l/l_0) \tag{1}$$

Here l_0 is the initial length of dried sample and Δl is the increase in the sample length due to sorption. Several examples of sorption-elongation behavior are shown in Figure 2. All curves are S-shaped.

These data indicate that the degree of longitudinal swelling in equilibrium changes markedly with the draw ratio and the kind of samples. The equilibrium values for these groups of samples are plotted against draw ratio in Figure 3. For groups I and II, the values increase, pass through minima near draw ratios of 2.2 and 2.8, respectively, and then gradually decrease as the draw ratio increases, while the value for group III does not

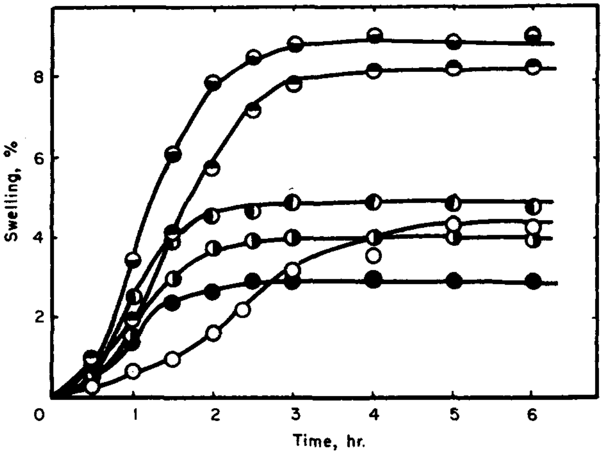

Fig. 2. Change in elongation due to swelling with time (group I) for various draw ratios: (O) 1.0; (◒) 1.6; (◓) 2.2; (◐) 2.8; (◑) 4.0; (●) 5.2.

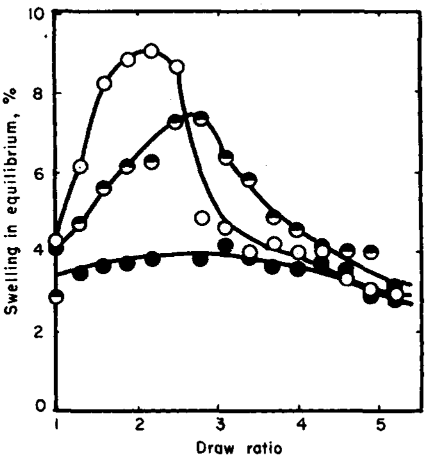

Fig. 3. Dependence of longitudinal swelling in equilibrium on draw ratio: (O) group I; (◓) group II; (●) group III.

change markedly with the draw ratio. These results are in good agreement with those of the changes in the tensile strength;[6,7] that is, the tensile strengths of groups I and II approach minima near the draw ratios of 2 and of 2.8, respectively, while the tensile strength of group III does not show a minimum value. Also, the decrease in the tensile strength at the minimum is greater for group I than for group II (see Fig. 4).

The agreement between the tensile strength and longitudinal swelling behavior is too good to consider that these are entirely independent; it may be natural to suppose that there is some common factor which controls these properties.

TABLE I
Percentage of Longitudinal Swelling of Sample Group I at 24°C. and 100%RH

Draw time ratio, min.	1.0	1.3	1.6	1.9	2.2	2.5	2.8	3.1	3.4	3.7	4.0	4.3	4.6	4.9	5.2
30	0.25	0.81	0.94	0.75	0.82	1.11	0.79	0.99	0.23	0.70	0.46	0.83	0.50	0.50	0.39
60	0.61	1.16	1.89	2.39	3.40	2.64	2.51	3.03	1.65	1.76	1.59	1.83	1.59	1.42	1.33
90	0.94	2.06	4.12	5.55	6.14	6.49	3.97	4.58	3.14	3.26	2.94	3.19	2.62	2.31	2.36
120	1.62	3.79	5.76	7.23	7.84	7.91	4.50	5.08	3.54	3.96	3.67	3.69	2.59	2.51	2.59
150	—	—	7.15	8.32	8.44	8.26	4.63	5.41	3.73	4.02	3.90	3.82	2.89	2.71	2.91
180	3.17	5.78	7.80	8.47	8.80	8.51	4.86	5.38	3.93	4.09	3.93	3.89	3.22	2.97	2.87
240	3.40	6.01	8.15	8.68	9.07	8.57	4.83	5.61	4.20	4.22	3.97	4.09	3.19	3.03	2.93
300	4.30	6.13	8.22	8.79	8.88	8.46	4.83	5.54	3.97	4.16	4.00	4.06	3.28	3.10	2.93
360	4.25	6.16	8.25	8.82	9.04	8.64	4.79	4.62	3.97	4.22	4.03	3.99	3.28	2.97	2.93
∞	4.30	6.16	8.25	8.83	9.05	8.64	4.83	4.62	3.97	4.22	4.03	4.03	3.28	3.05	2.93

TABLE II
Percentage of Longitudinal Swelling of Sample Group II
at 24°C. and 100%RH

Draw time ratio, min.	1.0	1.3	1.6	1.9	2.2	2.5	2.8	3.1	3.4	3.7	4.0	4.3	4.6	4.9	5.2
30	0.12	0.26	0.59	0.52	0.55	0.40	0.60	0.62	0.58	0.38	0.36	0.87	0.35	0.45	0.45
60	0.22	0.58	1.02	1.46	2.05	2.31	2.60	2.57	2.20	1.44	1.17	1.18	1.13	1.24	0.85
90	0.34	1.38	2.36	3.69	4.71	5.67	5.64	5.28	4.48	2.88	2.93	2.41	2.19	2.42	1.72
120	0.55	2.49	4.16	5.12	5.72	6.79	6.76	6.10	5.31	3.89	3.81	3.21	3.28	3.20	2.88
150	0.65	3.56	5.05	5.66	6.03	6.97	7.01	6.25	5.62	4.34	4.22	3.78	3.67	3.53	2.84
180	0.89	4.07	5.31	5.90	6.12	7.17	7.14	6.32	5.72	4.50	4.36	3.95	3.87	3.82	2.97
240	1.41	4.50	5.44	6.13	6.17	7.25	7.21	6.35	5.77	4.70	4.53	4.20	4.04	3.97	3.09
300	1.80	4.57	5.54	6.13	6.20	7.28	7.20	6.37	5.82	4.84	4.59	4.15	4.04	4.01	3.17
360	2.85	4.64	5.60	6.14	6.25	7.28	7.30	6.37	5.82	4.88	4.59	4.15	4.10	4.02	3.17
420	2.85	4.70	5.60	6.14	6.25	7.28	7.35	6.37	5.82	4.88	4.59	4.15	4.10	4.02	3.17
∞	2.85	4.70	5.60	6.14	6.25	7.28	7.35	6.37	5.82	4.88	4.59	4.15	4.10	4.02	3.17

TABLE III
Percentage of Longitudinal Swelling of Sample Group III
at 24°C. and 100%RH

Draw ratio, time, min.	1.0	1.3	1.6	1.9	2.2	2.5	2.8	3.1	3.4	3.7	4.0	4.6	4.9	5.2
30	0.28	0.41	0.40	0.40	0.30	0.45	0.51	0.48	0.48	0.49	0.64	0.62	0.46	0.47
60	0.44	0.61	0.85	0.94	0.88	1.20	1.50	1.86	1.34	1.80	1.75	1.59	1.46	1.84
90	0.70	1.05	1.84	2.69	2.07	2.54	3.20	2.83	2.75	2.72	2.92	2.56	2.37	2.26
120	1.16	1.64	2.97	3.25	2.94	3.36	3.79	3.45	3.39	3.26	3.25	2.95	2.67	2.50
150	1.73	2.25	3.44	3.44	3.35	3.62	4.06	3.81	3.51	3.55	3.45	3.09	2.89	2.63
180	2.62	2.59	3.61	3.56	3.55	3.86	4.14	3.76	3.58	3.54	3.50	3.22	2.87	2.71
240	3.60	3.10	3.62	3.72	3.67	3.84	4.16	3.89	3.66	3.54	3.56	3.25	2.90	2.74
300	4.04	3.20	3.67	3.70	3.83	3.80	4.14	3.86	3.65	3.67	3.70	3.59	2.97	2.74
360	4.09	3.43	3.64	3.70	3.81	3.79	4.16	3.91	3.62	3.57	3.71	3.59	2.95	2.79
420	4.09	3.45	3.64	3.70	3.81	3.79	4.16	3.91	3.62	3.57	3.71	3.59	2.95	2.79
∞	4.09	3.45	3.64	3.70	3.81	3.79	4.16	3.91	3.62	3.57	3.71	3.59	2.95	2.79

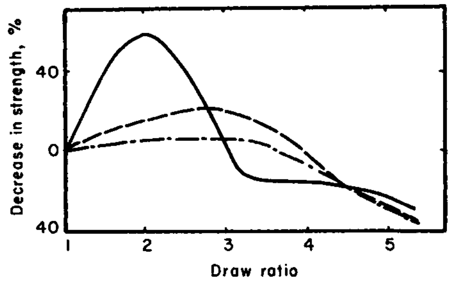

Fig. 4. Dependence of tensile strength decrease on draw ratio: (——) group I; (– –) group II; (–·–) group III.

The change in the sample length due to swelling is considered to result from the loosening of the polymer structure due to penetration of water, and subsequent deformation of the polymer to a more stable system containing sorbed water. Therefore, the weaker the interaction between the molecules, or the less stable the polymer structure, the more marked would be the change in the length of the polymer when it absorbs water. In other words, the degree of longitudinal swelling may be considered to be a measure of stability of the polymer structure, the sample that swells most in the longitudinal direction being the least stable.

Since the absorbed water can penetrate only into the amorphous regions of the polymer,[8] and as crystalline regions are considered to play the role of junction points in a network structure,[9] the elongation of the polymer sample due to swelling should be more marked as the amorphous structure becomes easier to loosen by the absorbed water. On the other hand, the change in the equilibrium water regain of the polymer with the degree of orientation or with the crystallinity is too small to explain the change in the longitudinal swelling with the draw ratio (the maximum value of longitudinal swelling is 9% and the minimum 3%).[10,11] Therefore, it is considered that such a large difference in the degree of longitudinal swelling is observed because the polymer is anisotropic with respect to the swelling, and it deforms itself more in the direction along which secondary bonds in the amorphous region are weaker than it does in another direction, even if the water content in the polymer is equal. In other words, the more the degree of longitudinal swelling of a sample, the weaker the secondary bonds in the amorphous region of the sample along the fiber axis.

This concept can also explain the analogy between the decrease in tensile strength decrease and that in logitudinal swelling. The difference in the draw ratio dependence of longitudinal swelling at equilibrium among the three groups of samples (I, II, and III) seems to show the effect of the crystallinity of the undrawn polymer on the structure of drawn polymer, though no exact explanation can be given. A further study will be made in other reports in this series.

We have also noticed a discrepancy between the dependence of shrinkage in boiling water and that of longitudinal swelling on the draw ratio.

The peculiarity of the former property observed in the intermediate stage of drawing is most marked in the samples of group III, while that of the latter property is pronounced in the samples of group I. This discrepancy might be due to the fact that the shrinkage in boiling water is an irreversible deformation under more severe conditions (boiling for 30 min.), while the latter is a reversible elongation under mild conditions (soaking in water at room temperature).

Rate of Swelling

The plot of dimensional change of nylon 6 filament soaked in water versus time makes an S-shaped curve with a gentle initial slope, as shown in Figure 2. This small initial slope is said[5] to be due to viscoelastic relaxation in the initial stage of absorption. Since the purpose of this paper is to investigate the effect of drawing on the rate of elongation by the absorption (rate of longitudinal swelling), we have chosen, as an index related to this rate the value* $\bar{t} = t_{1/2}/D$, where $t_{1/2}$ is the time needed for a sample to swell by half the elongation at equilibrium and D is the thickness of sample (denier); $\bar{t}$ is inversely proportional to the rate of longitudinal swelling. The values of $t_{1/2}$, D, and $\bar{t}$ are listed in Table IV. A plot of $\bar{t}$ versus draw ratio is shown in Figure 5.

TABLE IV
$t_{1/2}$, D, and $\bar{t}$

	Group I			Group II			Group III		
Draw Ratio	$t_{1/2}$, min.	D, d.	$\bar{t}$, min./d.	$t_{1/2}$, min.	D, d.	$\bar{t}$, min./d.	$t_{1/2}$, min.	D, d.	$\bar{t}$, min./d.
1.0	140	1428	0.098	246	1476	0.167	162	1406	0.115
1.3	108	1112	0.097	117	1176	0.100	125	1208	0.104
1.6	91	916	0.099	98	978	0.100	90	1020	0.088
1.9	80	768	0.104	84	837	0.100	77	845	0.091
2.2	72	656	0.110	75	729	0.103	87	714	0.122
2.5	78	579	0.135	74	646	0.115	78	624	0.125
2.8	59	523	0.113	74	575	0.129	70	558	0.123
3.1	57	480	0.119	69	522	0.132	62	507	0.122
3.4	60	444	0.135	69	476	0.146	70	469	0.149
3.7	66	419	0.158	81	438	0.185	60	437	0.137
4.0	70	397	0.176	80	407	0.197	64	410	0.156
4.3	64	378	0.169	86	380	0.226	—	—	—
4.6	62	364	0.170	87	359	0.242	66	366	0.180
4.9	63	352	0.179	81	340	0.238	60	345	0.174
5.2	66	345	0.191	86	325	0.265	50	328	0.153

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* According to Kunzman,[5] $t_{1/2}$ is proportional to the square of sample diameter or to the thickness of sample (D). Supposing that this relation holds in the present case, we can consider $t_{1/2}/D$ to be related only to the internal structure of sample, but not to the sample thickness.

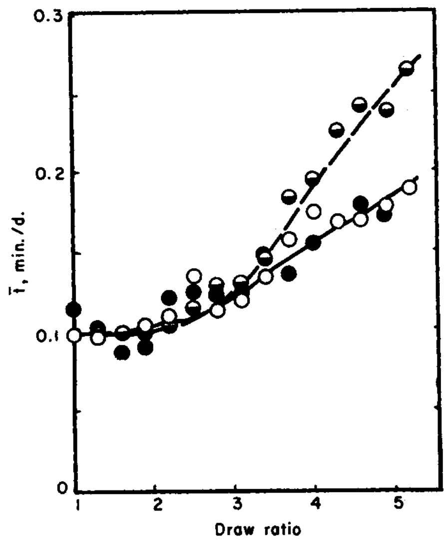

Fig. 5. Relation between $\bar{t}$ and draw ratio: (O) group I; (⊖) group II; (●) group III.

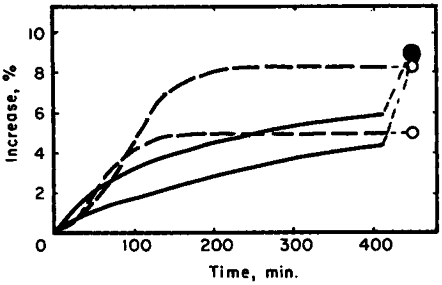

Fig. 6. Comparison of weight increase with length increase: (——) weight increase; (– –) length increase.

Although these points are considerably scattered, they fall about a curve which is flat in the range of low draw ratio and then becomes steep above a draw ratio of about 3. In the other words, the rate of swelling in the axial direction does not change much in the range of low draw ratio, but it decreases sharply with draw ratio at draw ratios above 3. This fact also suggests that the polymer structure becomes unstable in the initial stage of drawing and, after this stage, it begins to be more and more stable above a draw ratio of about 3.

Relation between Longitudinal Swelling and Increase of Water Content

The elongation of samples due to swelling is, of course, caused by the increase in the water content of sample. There is a time-lag between the water sorption and elongation, as is already known.[4] We measured the increase in the water content of a sample using a spring balance under the same conditions as those used to measure the degree of elongation by swelling. Typical results are shown in Figure 6. The longitudinal dimensional change reaches a limiting value much faster than the sample weight increases to an equilibrium value.

From this result it is suggested that the water absorbed in the initial stage of swelling chiefly causes the longitudinal swelling of sample, while the water absorbed afterward contributes to the increase in the diameter of sample. A further study of this will be reported in a subsequent paper in this series.

CONCLUSIONS

We have investigated the dependence of longitudinal dimension change of nylon 6 monofilament on the draw ratio and discovered that fibers of intermediate draw ratio are most sensitive to water. This is an additional support for our assertion that the polymer structure becomes most unstable in the intermediate stage of drawing.

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Résumé

Les auteurs ont étudié le changement de dimension longitudinale pour différents rapports d'étirement de monofilaments de nylon 6 séchés lorsqu'on les fait gonfler à une température de 24° et à 100% RH. On a obtenu les résultats suivants: le degré de gonflement longitudinal à l'équilibre change avec les conditions et le rapport d'étirement de l'échantillon; pour les échantillons étirés immédiatement après filage il augmente, passe par un maximum pour un rapport d'étirement 2, et diminue progressivement avec l'augmentation du rapport d'étirement; pour les échantillons étirés plusieurs jours après filage le point maximum se situe aux environs du rapport d'étirage égal à 2,8 tandis que pour les échantillons étirés après traitement à chaud, le degré de gonflement longitudinal ne change pratiquement pas avec le rapport d'étirement de l'échantillon. La vitesse de gonflement longitudinal demeure presque constante ou bien augmente légèrement pour les rapports d'étirement situés entre 1 et 3. Elle diminue alors pour des rapports d'étirement supérieurs à 3.

Zusammenfassung

Die Autoren haben die Änderung der Längsdimension von getrocknetem Nylon-6-Einzelfäden von verschiedenem Dehnungsverhältnis bei der Quellung in einer Atmosphäre von 24°C und 100% RF untersucht. Folgende Ergebnisse wurden erhalten: Der

Grad der Gleichwichtslängsquellung hängt von der Dehnungsbedingung und dem Dehnungsverhältnis der Probe ab; bei unmittelbar nach dem Spinnen gedehnten Proben nimmt er zu, geht in der Nähe des Dehnungsverhältnisses 2 durch ein Maximum und nimmt bei steigendem Dehnungsverhältnis langsam ab. Bei Proben, die viele Tage nach dem Spinnen gedehnt wurden, liegt das Maximum in der Nähe des Dehnungsverhältnisses 2,8, während bei Proben, die nach einer Hitzebehandlung gedehnt wurden, der Längsquellungsgrad nicht merklich vom Dehnungsverhältnis der Probe abhängt. Die Geschwindigkeit der Längsquellung bleibt im Bereich des Dehnungsverhältnisses von 1 bis etwa 3 nahezu konstant oder nimmt schwach zu. Dann findet im Bereich eines Dehnungsverhältnisses höher als 3 eine Abnahme mit dem Dehnungsverhältnis statt.

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