

Steam and Heat Setting of Nylon 6 Fiber.

VIII. Viscoelastic and Thermal Behavior of Heat-Set or γ -Irradiated Nylon 6 Fiber*

A. KOSHIMO, *Research Institute, Nippon Rayon Company, Ltd., Uji City, Kyoto, Japan*

Synopsis

Steam setting and dry heat setting was repeated alternately on nylon 6 fibers in which no further increase of crystallinity was expected, and the viscoelastic behavior of these fibers was investigated. The stress relaxation and thermal stress data indicate that steam setting weakens or breaks intermolecular bonds in the noncrystalline regions, while dry heat setting re-forms the bonds. For unset and steam-set nylon 6 fibers were γ -irradiated at doses of about 10^7 r, results of determinations of viscoelasticity, dye diffusion, and breaking in solvent show that crosslinking predominates with irradiation in vacuum and scission predominates with irradiation in air.

1. INTRODUCTION

Effects of heat setting on nylon 6 fibers have been explained on the basis of crystallization through rearrangement of intermolecular hydrogen bonds or of orientation of molecular chains in noncrystalline regions.¹⁻³

We have concluded from the previous results⁴⁻⁸ that, in steam setting, not only an increase of crystallinity, but a "loose packing state" occurs in noncrystalline regions, while in dry heat setting, a "close packing state" occurs. It was reported that, in steam setting, the water molecules accelerate the rate of breaking of intermolecular bonds and that a special lateral ordering is produced in the fiber structure.⁹ When the configurational change of the fiber structure is studied by measurement of viscoelastic properties, intermolecular junction points such as cross linkages, crystallites, pseudocrystallites, hydrogen bonds, second-order bonds, and molecular entanglements must be taken into full consideration. These points were not wholly considered in the previous reports.¹⁰ By the steam setting pretreatment of the specimen used in the present series of experiments, pseudocrystallites were transformed into crystallites and the boundary between crystalline and noncrystalline regions was made clear,⁹ so that no increase of crystallinity would occur during subsequent heat treatments. A change of viscoelastic and thermal behavior of the fibers thus treated may be expected to occur, depending on the change of con-

* This material appeared in part in *Kobunshi Kagaku*, 17, 552 (1960).

figuration of molecules in noncrystalline regions. In analyzing a stress relaxation or a force-temperature curve, it is a problem whether a crystallite is at a junction point or not. Even if such elaborately prepared specimens as the above are used, the number of weak bonds broken with increasing temperature or the number of pseudocrystallites remaining is not sure to be constant within experimental error. If variation induced by these factors is negligible, it is possible to apply here a thermodynamic equation for the elastic state¹¹ to investigate the structural change of noncrystalline regions. Actually, a linear relation between thermal force and temperature in the range 50–130°C. was found. If rubber elasticity is predominant, we can calculate the number of intermolecular bonds according to the equations of Flory.¹² Moreover, the number of bonds in noncrystalline regions was expected to be altered by γ -irradiation as well as by thermal energy. It is generally accepted¹³ that, in ionizing irradiation of nylon 6 fiber, scission of polymer chains is dominant in air and crosslinking in vacuum. In any case, crosslinking and scission may occur at the same time and, depending on the presence or the absence of O₂, either the former or the latter may predominate. This behavior was studied from thermal and viscoelastic properties of the irradiated fibers.

2. EXPERIMENTAL

Preparation of Test Specimens

Drawn nylon 6 filaments (draw ratio 3.6, 322 den.) were immersed in running water at 30 or 40°C. for 20 hr. in the relaxed state, rinsed with distilled water, and dried. They were alternatively subjected to steam setting (120°C., 30 min.) and dry heat setting (170°C., 30 min. in N₂ gas) under tension under various conditions shown in Table I. Unset and steam-set nylon 6 filaments were wound around glass rods along the longitudinal axis and held in vacuum for 3 hr. Each sample on the glass rod was then sealed in a glass tube and irradiated with γ -ray at a dose rate of 4.84×10^4 r/hr.

Measurements of Stress Relaxation and Thermal Force

The apparatus shown in Figure 1 with a strain gage attached was used. A specimen dried in a vacuum desiccator over P₂O₅ was straightened between two clamps under a tension of 0.033 g./den. in a bath containing silicone oil which was dehydrated at 150°C. for 5 hr. before use. The temperature was raised slowly to 130°C. A test specimen was stretched to a constant strain for 3 sec. and the resulting force was measured for 210 min. at this temperature. While temperature was changed between 50°C. and 130°C. as one cycle at a rate of 1°C./min., the thermal force was measured. The stress was calculated on the basis of the cross-sectional area of the specimen in the original unstretched state, the diameter being measured microscopically. Experimental errors were within 5%. The

TABLE I
Preparation of Test Specimens*

Sample no.	Treatment	Notation
	Original nylon 6 fiber	Unset
A	Nylon 6 fiber steam-set at 120°C. for 30 min.	Wet
A'	Sample A, dry-heat-set at 170°C. for 30 min.	Wet-dry
B	Sample A', steam-set at 120°C. for 30 min.	Wet-dry-wet
B'	Sample B, dry-heat-set at 170°C. for 30 min.	Wet-dry-wet-dry
C	Sample B', steam-set at 120°C. for 30 min.	Wet-dry-wet-dry-wet
C'	Sample C, dry-heat-set at 170°C. for 30 min	Wet-dry-wet-dry-wet-dry
D	Sample of nylon 6 fiber, γ -irradiated in air, dose 1.17×10^7	A 1 $\times 10^7$
E	Sample of nylon 6 fiber, γ -irradiated in vacuum, dose $1.17 \times 10^7 \gamma$	V 1 $\times 10^7$
F	Sample A, γ -irradiated in air, dose $1.17 \times 10^7 \gamma$	Wet + A 1 $\times 10^7$
G	Sample A, γ -irradiated in vacuum, dose $1.17 \times 10^7 \gamma$	Wet + V 1 $\times 10^7$
H	Sample of nylon 6 fiber, γ -irradiated in air, dose $3.00 \times 10^7 \gamma$	A 3 $\times 10^7$
I	Sample of nylon 6 fiber, γ -irradiated in vacuum, dose $3.00 \times 10^7 \gamma$	V 3 $\times 10^7$
J	Sample A, γ -irradiated in air, dose $3.00 \times 10^7 \gamma$	Wet + A 3 $\times 10^7$
K	Sample A, γ -irradiated in vacuum, dose $3.00 \times 10^7 \gamma$	Wet + V 3 $\times 10^7$

* Dry heat setting was carried out in nitrogen.

length of the heat-set specimen was 76.6 mm. and the extension ratio was 4.7%; for γ -irradiated specimens, the length was 70.63 mm., and the extension ratio was 4.52%.

Measurements of Density and Cross-Sectional Area

A density gradient column was made up with CCl_4 and ligroin. The density was determined from a nearly equilibrium position at about 49

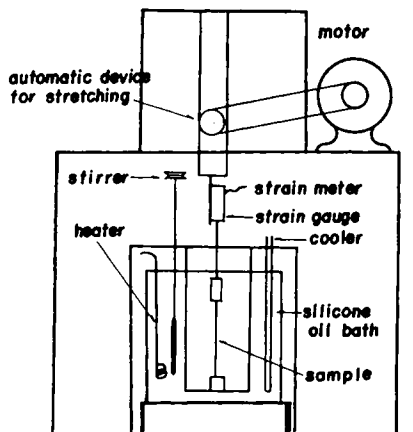


Fig. 1. Apparatus used.

min. after the test piece had been immersed in the solution at 30°C. The cross-sectional area was calculated from the diameter as measured by microscopy.

Measurements of Diffused Distance of Dye and Breaking Test in Solvent

Test specimens were dyed at pH 6.5 at 95°C. for 240 min. in an infinite bath (6 g./l.) of an acid dye (Supranol Cyanine G, C.I. Acid Blue 90, molecular weight 854). The diffused distance was measured microscopically.

The time required to break a test specimen under a tension of 0.039 g/den. at 80°C. in sulfuric acid solution (29.8%) was also measured.

3. RESULTS AND DISCUSSION

The values of density and diameter obtained are shown in Table II. After the first steam-setting, the density varies from 1.1343 to 1.1423 and remains constant thereafter. Therefore, the change of viscoelastic behavior of nylon 6 specimens caused by the variation of crystallinity may be negligible within experimental error. For the γ -irradiated specimens, the densities of unset and steam-set samples are little changed by γ -irradiation in vacuum but increased by that in the air. In the latter case, production of oxides or peroxides, or increase of crystallinity are supposed. In all cases, the diameter of the fiber does not change.

TABLE II
Diameter and Density

Sample	Diameter, mm.	Density, (d_{20}^0)
Unset	0.2028	1.1343
Wet	0.2021	1.1423
Wet-dry	0.2043	1.1428
Wet-dry-wet	0.2002	1.1431
Wet-dry-wet-dry	0.2004	1.1430
Wet-dry-wet-dry-wet	0.1976	1.1433
Wet-dry-wet-dry-wet-dry	0.1998	1.1431
Wet	0.2033	1.1444
A 1×10^7	0.1986	1.1367
V 1×10^7	0.1986	1.1329
Wet + A 1×10^7	0.1978	1.1577
Wet + V 1×10^7	0.2050	1.1452
A 3×10^7	0.2003	1.1366
V 3×10^7	0.1966	1.1335
Wet + A 3×10^7	0.2018	1.1505
Wet + V 3×10^7	0.2011	1.1450

Figure 2 shows the stress-relaxation curves for the specimens subjected repeatedly to steam, and dry heat setting. The ratio of final to initial stress, f/f_0 , was plotted against the logarithm of time as shown in Figure 3.

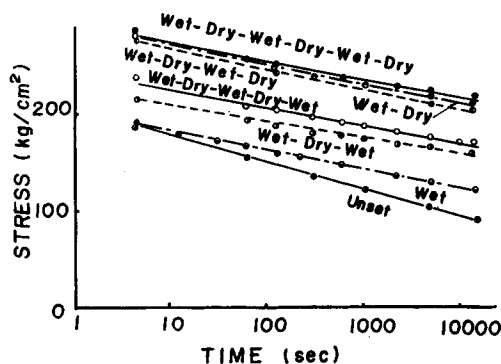


Fig. 2. Stress-relaxation curves for heat-set fibers.

A linear relation is found between f/f_0 and $\log t$. The values of initial and final (at 210 min.) stresses for steam-set specimens are smaller than those for dry-heat-set ones and for the series in which the initial treatment was steam setting ("wet") are lower than that for which the initial treatment was dry heat setting. Whenever heat setting was repeated in such a way as to go a final "wet" treatment to a "dry" one, from "wet" to "dry," from "wet-dry" to "wet-dry-wet," and so on, each the stress relaxation curve changed in relative position in a nearly reversible manner. Comparison of the slopes of $f/f_0 - \log t$ curves shows that those of dry-heat-set specimens are more gentle than those of steam-set ones. In Figure 3, there is also observed a kind of reversible behavior in the change of slope. The following equations were derived experimentally from the above results.

$$f = f_0 - A \log t \quad (1)$$

$$f/f_0 = 1 - (A/f_0) \log t \quad (2)$$

where f is stress, f_0 is initial stress, t is time, and A is a constant.

Equations (1) and (2) may be modified to the following:

$$df/dt = - \log e (A/t) \quad (3)$$

$$d(f/f_0)/dt = - (A/f_0)t \log e \quad (4)$$

where A and A/f_0 are the slopes in Figures 2 and 3, respectively, and are associated with the rate of stress-relaxation. The values thus obtained are listed in Table III. These values show that the rate of stress relaxation for steam-set specimens is higher than that for dry-set fibers. Figure 4 shows thermal stress as a function of temperature. A linear relation is observed between stress f and temperature T . Before going on to the discussion, it is assumed that the elastic force due to the change of enthalpy in the crystalline regions is negligible in comparison with that due to entropy in noncrystalline regions. This assumption is supported by other reports¹⁴ as well as by the fact that the temperature coefficients of

TABLE III
 A , A/f_0 , and N

Sample	A , kg.-cm. ⁻² (log sec.) ⁻¹	A/f_0 , (log sec.) ⁻¹	$N \times 10^{-11}$ cm. ⁻²
Unset	28.0	0.147	5.0
Wet	19.4	0.103	1.3
Wet-dry	16.2	0.090	2.4
Wet-dry-wet	16.4	0.075	1.7
Wet-dry-wet-dry	19.7	0.071	2.1
Wet-dry-wet-dry-wet	18.3	0.075	1.7
Wet-dry-wet-dry-wet-dry	16.6	0.059	2.0

thermal stress observed in this experiment were all positive. As shown in Figure 4, the values of both thermal stress and slope of the curves for steam-set specimens are smaller than those for dry-heat-set samples. The slope for the "wet" sample changed to a larger value for the "wet-dry"

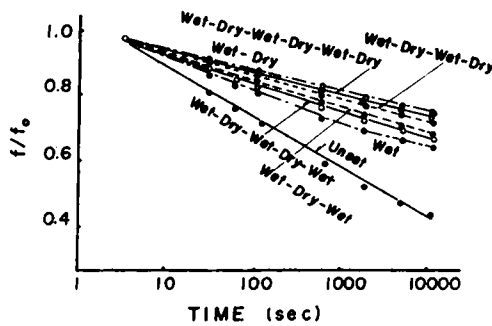


Fig. 3. Plot of f/f_0 against time t .

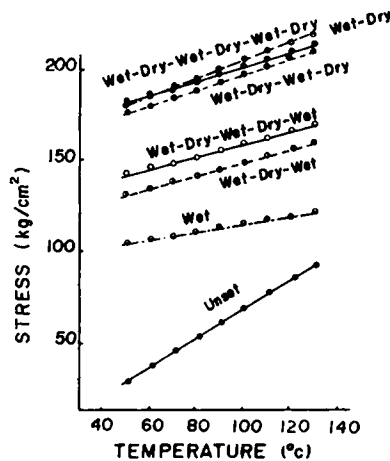


Fig. 4. Force-temperature curves for heat-set fibers.

sample, and so on. There was also found a nearly reversible behavior like the one mentioned above. The elastic force of crystallites is believed to remain unchanged, for density is nearly constant at this range of temperature. Therefore, the nature of rubber elasticity due to the change of entropy must be changed in a nearly reversible way by steam and dry heat setting. As the ratio of extension is below 5% and the change of volume is negligible, it is possible to calculate the number of effective network chains according to Flory's theory¹² by using the following equation:

$$T(\partial f/\partial T)_{v,L} = NKT[\alpha - (1/\alpha^2)] \quad (5)$$

where $(\partial f/\partial T)_{v,L}$ is the slope of the curve in Figure 4, T is absolute temperature, K is the Boltzmann constant, α is strain, and N is the number of effective network chains in a unit volume. The N values calculated are shown in the third column of Table III. As is clearly seen here, the degree of intermolecular cross-linking changes with each treatment. The reason why a reversible change of the number of cross linkages takes place can be attributed only to the fact that a constant number of intermolecular bonds in noncrystalline regions undergoes repeated scission or linking in accordance with steam setting or dry heat setting, respectively. Hydrogen bonds or other intermolecular bonds in noncrystalline regions are partly broken by steam setting, and molecular chains become more mobile. Therefore, an increased rate of stress relaxation, decreased stress at 1.26×10^4 sec. and a decreased temperature coefficient of thermal force in rubber elasticity are expected naturally. In dry heat setting, the situation is perhaps reversed. This explanation is considered to be reasonable and the facts may support the previously proposed theory⁵ of loose packing and close packing with respect to the structural changes of noncrystalline regions.

Effects similar to those of dry heat setting were expected to be obtained by γ -irradiation, so γ -irradiation of nylon 6 fiber was carried out. Figures 5 and 6 show stress relaxation and force-temperature curves, respectively, for γ -irradiated specimens. As is clear in Figure 5, when unset and steam-set nylon 6 fibers are irradiated by γ -ray in vacuum, the initial or final stress at 1.26×10^4 sec. increases as a function of γ -ray dose. On the other hand, greater values of initial stress and smaller values of final stress at 1.26×10^4 sec. are observed for specimens γ -irradiated in air. Figure 6 shows the force-temperature curves, and here a linear relation is seen. The temperature coefficient for unset nylon specimens γ -irradiated in vacuum with a dose of 3×10^7 increases slightly. This is attributed to the formation of crosslinkages. The temperature coefficient for unset nylon γ -irradiated in air with a dose of 3×10^7 r decreases, and this fact indicates main chain scission. However, only slight changes are seen with an irradiation dose of 1×10^7 r either in air or in vacuum. For the specimens steam-set and γ -irradiated, the temperature coefficients of thermal stress are smaller than those observed in Figure 4. This may be attributed to the predominant effect of steam setting, as shown in Table II, and to the fact that the effects

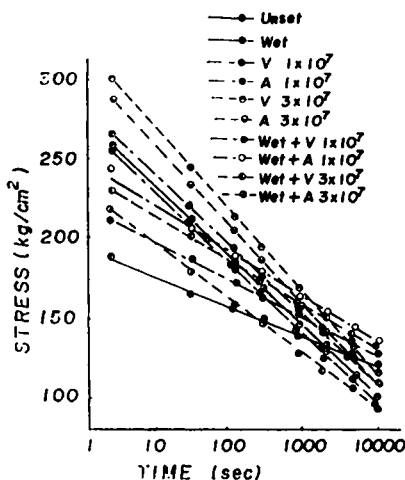


Fig. 5. Stress-relaxation curves for γ -irradiated fibers.

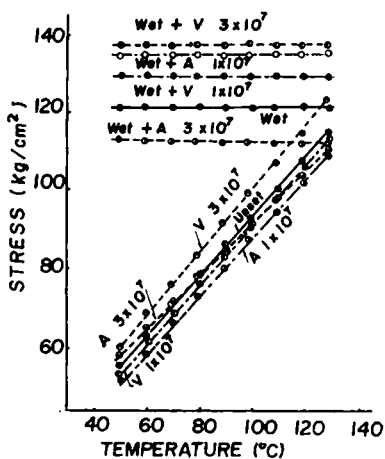


Fig. 6. Force-temperature curves for γ -irradiated fibers.

of irradiation are comparatively small. The changes of stress relaxation and force-temperature curves indicate that γ -irradiation of steam-set nylon 6 fibers in vacuum produces intermolecular bonds just as in the case of dry heat setting. However further investigation is necessary to confirm this.

Distances of diffusion of dye from the surface of a specimen and times for breaking of the fiber in solution are shown in Table IV. The rate of diffusion of dye depends on the closeness of packing of noncrystalline regions. Thus, the facts that the diffused distances of dye for the specimens γ -irradiated in vacuum are smaller than those for unirradiated specimens and that those for the specimens irradiated in air are larger than any other, may suggest that in the fibers irradiated in vacuum formation of cross

TABLE IV
Diffused Distance of Dye and Time of Breaking in Solvent (H_2SO_4)^a

Specimen	Diffused distance (95°C., 240 min.), μ	Time to breaking in H_2SO_4 soln. (80°C., 30%), sec.
Unset	20.2	14.5
Wet	45.0	55.3
A 1 \times 10 ⁷	23.8	37.5
Wet + A 1 \times 10 ⁷	44.0	44.6
V 1 \times 10 ⁷	19.0	39.4
Wet + V 1 \times 10 ⁷	38.8	47.4
A 3 \times 10 ⁷	24.3	30.4
Wet + A 3 \times 10 ⁷	43.0	32.0
V 3 \times 10 ⁷	19.0	25.5
Wet + V 3 \times 10 ⁷	42.0	49.6

^a The dye used was Supranine Cyanine G (C.I. Acid Blue 90).

linkages in noncrystalline regions occurs, while, in the fibers irradiated in air, scission of main chains takes place.

The time to break in H_2SO_4 solution for steam-set fibers having a high degree of crystallinity is longer than that for unset fibers. This is perhaps attributable to increased crystallinity or increased size of crystallite in the former; this result corresponds with that reported by the author previously.¹⁵ The fact that the time to break for unset specimens is lengthened by irradiation and the time for steam-set ones is shortened, may be explained as follows in consideration of different effects of irradiation on crystalline and noncrystalline regions. Namely, the ease of breaking is considered to depend on the relative amounts of crystalline and noncrystalline regions as well as on the state of intermolecular bonding in both regions. The rate of breaking of a single molecular chain in γ -irradiation is same in both crystalline and noncrystalline regions; however, crystalline regions have greater probability per unit area of breaking with irradiation because of their closer packing. Because the packing of noncrystalline regions of unset nylon 6 fiber is comparatively close, crosslinking may occur easily in unset samples the instant a molecular chain is broken. Due to the lower degree of crystallinity, unset, γ -irradiated specimens may predominate over steam-set, γ -irradiated ones in the effect that cross-linkages in noncrystalline regions retard the rate of breaking more strongly than crystallites. The molecular configuration of noncrystalline regions in steam-set specimens is in a more released state, and crosslinking occurs with greater difficulty. As mentioned above, the effects of increased crystallinity due to steam setting on the rate of breaking is greater than that of γ -irradiation. Then, for the steam-set specimens, effects of γ -ray on crystalline regions are considered to affect markedly the rate of breaking. When molecular chains are broken in crystalline regions, the radicals formed may be longer

lived than in noncrystalline regions.^{16,17} Even if some degree of oxidation occurs when test specimens are exposed to an oxidizing atmosphere (air, O₂) before the time to breaking is measured, the oxidation proceeds to a smaller extent than that in noncrystalline regions. The possibility of cross-linking is also slight; because molecular mobility is depressed in the crystal lattice. Therefore, steam-set nylon 6 fibers will become easy to break in solvent by γ -irradiation. In comparison of γ -irradiation in air with that in vacuum, it is easy to infer that, in air, not only crosslinking but also scission occurs at the same time, and specimens γ -irradiated in air are more easily broken than those irradiated in vacuum.

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Résumé

Un traitement par chauffage de la vapeur et par chauffage à sec a été appliqué alternativement sur des fibres de nylon 6, pour lesquelles on s'attendait à ne plus avoir d'augmentation de cristallinité; on en a étudié le comportement viscoélastique. A partir du comportement des forces de relaxation et des forces thermiques, on voit que par chauffage à la vapeur les liens intermoléculaires sont affaiblis ou cassés dans les régions noncristallines, tandis que par chauffage à sec les liens se refont. Lorsque les fibres de nylon 6 non-chauffées et chauffées à la vapeur sont irradiées par des rayons- γ d'environ 10⁷ röntgen, les propriétés telles que la viscolélasticité, la diffusion de la couleur, et la cassure dans un solvant, montrent que sous vide le pontage est prédominant alors qu'en présence d'air c'est la rupture qui est la plus importante.

Zusammenfassung

Dampfbehandlung und Trockenhitzebehandlung werden abwechselnd an Nylon-6-Fasern, bei welchen keine Zunahme der Kristallinität mehr erwartet wird, durchgeführt

und ihr viskoelastisches Verhalten untersucht. Das Spannung-Relaxations- und thermische Spannungsverhalten zeigt, dass die Hitzebehandlung die intermolekularen Bindungen in den nicht-kristallinen Bereichen schwächt oder zerstört und die Trockenhitzebehandlung die Bindungen wieder herstellt. Bei Bestrahlung von nicht hitzebehandelten und von dampfbehandelten Nylon-6-Fasern mit Gammastrahlen von etwa 10^7 Röntgen zeigt das viskoelastische Verhalten, die Farbstoffdiffusion und der Abbau im Lösungsmittel, dass im Vakuum Vernetzung vorherrscht und in Luft Abbau.

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