

Stress Relaxation of Oriented Nylon 6 Fibers

by Toshio KUNUGI, Yukihiro ISOBE, Katsumi KIMURA,
Yoshimasa ASANUMA and Minoru HASHIMOTO

(Received August 31, 1978)

Abstract

The stress relaxation of oriented and dried nylon 6 fibers was measured at temperatures ranging from room temperature to 423°K by a simple tensile method. After the reduction for temperature and crystallinity by Takemura's procedure, the relaxation modulus curves were shifted along time axis, and the master curves were successfully obtained. The Arrhenius plots of shift factor were represented by two straight lines having a break point, the temperature of which was in agreement approximately with those of breakdown of hydrogen bonds in the amorphous region. The relation between the breakdown of hydrogen bonds and the values of apparent activation energies for relaxation was discussed. It has been found that the effects of hydrogen bonds on the relaxation behavior are similar to those of crosslinking points in crosslinked polymers. Moreover, from the constants C_1 and C_2 of the W. L. F. equation, the free volume fraction at Tg , (f_g), and the expansion coefficient of free volume at Tg , (α_f), were estimated to be 0.013 and 4.2×10^{-5} , respectively. Finally, by the use of the usual primary approximation method, the relaxation time spectra were obtained from the relaxation master curves. The obtained spectra showed two distributions of wedge-type and box-type. When the draw ratio increases, the height of distribution of the box-type becomes higher and its position shifts to longer time side, whereas those of the wedge-type remains almost unchanged.

1. Introduction

Some investigations of the stress relaxation for crystalline polymers have been carried out so far by many researchers^{1)~6)}. However, the theoretical and phenomenological analyses for the relaxation processes have not yet been performed sufficiently, because the relaxation of molecular segments in the amorphous region is affected by crystallites in complicated ways. For a more detailed analysis, therefore, it is first desired to detect high-sensitively a slight change in the relaxation behavior with time, temperature, frequency, and so on.

In the present study, the measurements of stress relaxation have been carried out by a simple tensile method using a high-sensitive strain gauge on oriented and dried nylon 6 fibers over a wide temperature range from room temperature to 423°K, which is far higher than the highest measur-

ing temperature⁶⁾, 354°K, in the previous studies published for nylon 6. Consequently, it has been found that some relaxation properties, such as the features of master relaxation curves and of relaxation time spectra and the temperature dependence of shift factor, differ from those in the previous studies^{3)~6)}.

The purposes of the present paper are to present these experimental results and to discuss the effects of crystallites and hydrogen bonds on the relaxation behavior, comparing with that of crosslinking points in crosslinked polymers.

2. Experimental

Material; The original material used in the present study is nylon 6 fiber (819.6 den/15 filaments) supplied by Toray Co. Ltd.. It has an average molecular weight of ca. 18,000. Before the measurements of stress relaxation, the original fibers

Table 1 Characteristics (at 293°K) of the specimens used for the measurements of relaxation modulus

Specimen	Crystallinity (%)	Birefringence ($\times 10^3$)	f_c	f_a
Drawn up to 3-fold	45.2	40.66	0.756	0.374
Drawn up to 4-fold	46.4	50.30	0.783	0.598

were drawn up to 3-fold or 4-fold under conditions of 23°–25°C and ca. 65% RH, and then were dried in a desiccator over phosphoric acid anhydride for two months. Characteristics of the specimens thus prepared are shown in **Table 1**. The degrees of crystallinity and the orientation factors of crystalline region (f_c) were determined in a X-ray diffraction procedure^{(7)–(9)}, the total birefringences were measured by the Berek-compensator method^{(7), (8)}, and the orientation factors of amorphous region (f_a) were calculated in the same way as described in the earlier paper⁽⁹⁾.

Measurement; The apparatus used for the measurements of relaxation moduli is a tension tensile tester, TENSILON UTM-II, SS-105-UTM (Toyo-Baldwin Co. Ltd.), equipped with an electric furnace which could be kept at a desired temperature by an automatic system. The specimens prepared in the way described above were set to the apparatus; the dimension of specimens is 50 mm in length and ca. 2×10^{-3} mm² in cross section.

After the specimens had been heated to a desired temperature at a heating rate of 4°C/min under tensionless state in a dry nitrogen gas stream, these were kept at this temperature for 5 min. Then, a small strain, which had been ascertained to satisfy a linearity of viscoelasticity in advance, was imposed upon the specimens. This strain is 1% based upon the length of the drawn specimen at this temperature. The relaxation moduli were measured at various temperatures between room temperature and 423°K for 100 min in a dry nitrogen gas stream. In this measurements, the different specimens which were prepared under the same conditions were used separately at temperatures different from each other, because the degrees of crystallinity changed with temperature.

3. Results and Discussion

As is well known, the viscoelastic properties of a hydrophilic polymer are very sensitive to the absorbed moisture or the relative humidity in the surroundings. Therefore, in order to avoid the complex effects of moisture on relaxation behavior, we measured the relaxation moduli under moisture-free conditions on the dried specimens drawn up to 3-fold and 4-fold, as described above. The obtained relaxation moduli were reduced according to Takemura's procedure⁽²⁾ which is expressed by the following equation;

$$\log Er(t)_{\text{red.}} = \log Er(t) + \log(T_0/T) - \log(A/1-A) + \log(A_0/1-A_0) \quad (1)$$

where $Er(t)_{\text{red.}}$ is the reduced relaxation modulus, $Er(t)$ is the relaxation modulus as measured, T is a measuring temperature, T_0 is the reference temperature, which in the present study is taken as the glass transition temperature of nylon 6, 323°K⁽¹⁰⁾, and A_0 and A are the crystallinities at T_0° and T° K, respectively. The curves of $\log Er(t)_{\text{red.}}$ versus $\log t$ for the specimen drawn up to 4-fold is shown in **Figure 1**. On the other hand, as shown in **Figure 2**, the degrees of crystallinity decreased from 45.2 to 38.8% in the 3-fold drawn specimen, and from 46.4 to 39.2% in the 4-fold drawn one, over a temperature range from 293° to 473°K. The value of crystallinity at each temperature was used in the calculation

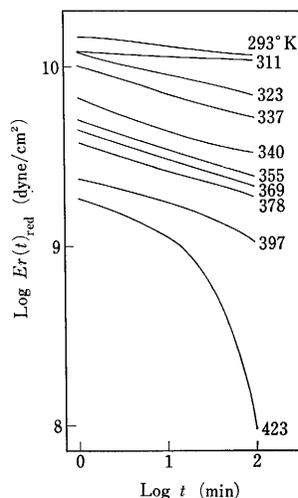


Fig. 1 Time dependence of the relaxation modulus $Er(t)_{\text{red.}}$ at the temperatures described in Figure for the nylon 6 fiber drawn up to 4-fold. The data are reduced according to Takemura's procedure.

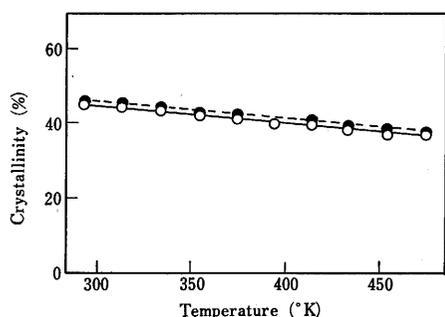


Fig. 2 Change in crystallinity of the oriented nylon 6 fibers with temperature. (○), the specimen drawn up to 3-fold; (●), the specimen drawn up to 4-fold.

by Eq. (1). The variations of crystallinity with time at a definite temperature were also checked by the same X-ray diffraction method as described previously, and were found to be negligibly small; namely the degree of crystallinity remained almost unchanged throughout the measurement of the relaxation modulus at a constant temperature.

On the basis of the assumption that the principle of time-temperature superposition is applicable to nylon 6, we tried to prepare master curves of the relaxation moduli. Consequently, the master curves shown in Figure 3 were easily obtained by shifting the reduced relaxation curves only along the time axis. In this case, the curve at 323°K was used as reference curve. In Figure 3, a fluid region can clearly be seen on the long-time side in each case of the specimens drawn up to 3-fold and 4-fold.

Moreover, Figures 4 and 5, respectively, show the relations between temperature (T) and the

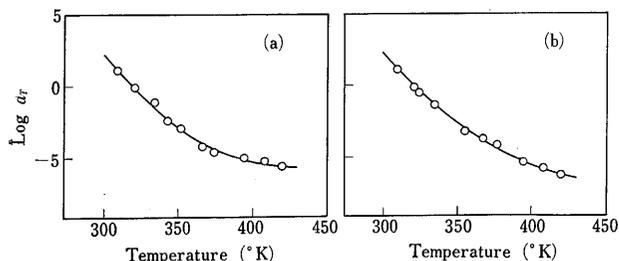


Fig. 4 Temperature dependence of logarithm of the shift factor for the oriented nylon 6 fibers. (a), the specimen drawn up to 3-fold; (b), the specimen drawn up to 4-fold.

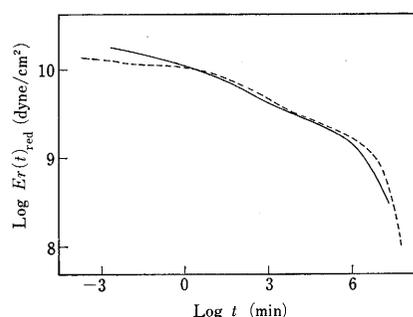


Fig. 3 Master curves of the relaxation modulus $Er(t)_{red}$ for the oriented nylon 6 fibers. —, the specimen drawn up to 3-fold; ---, the specimen drawn up to 4-fold. The reference temperature is 323°K for both specimens.

logarithm of shift factor ($\log a_T$), and between the reciprocal of temperature ($1/T$) and $\log a_T$. As is evident from Figure 5, each curve of $\log a_T$ versus $1/T$ can be represented by two straight lines intersecting at one point. This fact indicates that there are two relaxation-mechanisms with different apparent activation energies in the temperature ranges below and above the break point. The temperatures of these break points agreed approximately with those¹¹⁾ (350°–385°K) of α -transi-

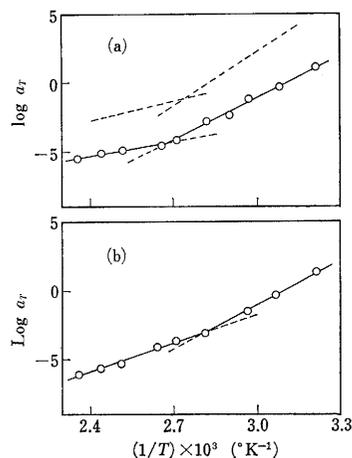


Fig. 5 Plots of logarithm of the shift factor against the reciprocal of absolute temperature for the oriented nylon 6 fibers. (a), the specimen drawn up to 3-fold; (b), the specimen drawn up to 4-fold. The broken line shows the data by Hoashi and Andrews¹²⁾.

Table 2 Apparent activation energies (ΔHa) and the temperatures of the break points in Arrhenius plots

Specimen	ΔHa (Kcal/mole)	Temp. of break point in Arrhenius plot (°K)
Drawn up to 3-fold	17 (High temp.)	371
	47 (Low temp.)	
Drawn up to 4-fold	33 (High temp.)	350
	49 (Low temp.)	
Data by Hoashi and Andrews ¹²⁾ (Annealed at 433°K)	34 (High temp.)	380
	60 (Low temp.)	

tion caused by the breakdown of hydrogen bonds in the amorphous region.

Similar relations between $\log a_T$ and $1/T$, which are composed of two straight lines, have been also reported for nylon 6 by Hoashi and Andrews¹²⁾, for polyethylene by Takayanagi¹³⁾, and for unsaturated polyester by Kitoh *et al.*¹⁴⁾. In Figure 5 are also shown the data according to Hoashi and Andrews, which were obtained from a measurement of dynamic viscoelastic property. In spite of the difference between the experimental methods, the Arrhenius plot has a feature similar to those obtained by the authors. Recently, it has also been found by Kodama¹⁵⁾ that the relation between $\log a_T$ and $1/T$ for a reinforced epoxy resin is represented by three straight lines and three values of ΔHa calculated from each line become smaller, in the order of lower, medium, higher temperature ranges.

In Table 2, the values of the apparent activation energy for the relaxation (ΔHa) are summarised together with the temperatures of the break points. The values of ΔHa were calculated from a slope of each straight line in Figure 5 by Eq. (2);

$$\Delta Ha = R d \ln a_T / d(1/T) \quad (2)$$

where R is the gas constant. It is evident from Table 2 that the value of ΔHa in the high-temperature range above the break point is smaller than that in the low-temperature range below the point. It seems most reasonable to interpret this fact on the basis of an idea that a value of ΔHa for relaxation is regarded as a measure of the difficulty of the movement of molecular segments.

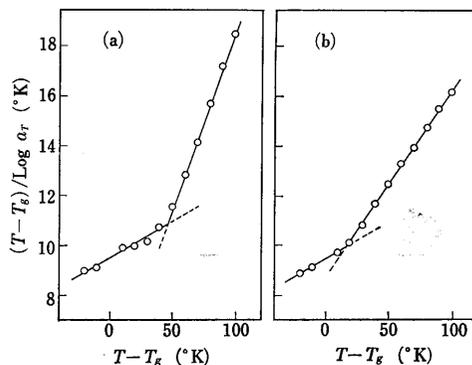


Fig. 6 Relation between $(T-T_g)/\log a_T$ and $(T-T_g)$ for the oriented nylon 6 fibers. (a), the specimen drawn up to 3-fold; (b), the specimen drawn up to 4-fold.

Namely, it is considered that, when the hydrogen bonds are broken down at temperature near the break points, the mobility of segments increases and the values of ΔHa consequently decrease. This idea is also supported by another fact that the value of ΔHa for the specimen drawn up to 4-fold is larger than that for the specimen drawn up to 3-fold in the temperature range above the break point. When the orientation and crystallinity increase by elongation, the motion of molecular segments in the amorphous region must be inhibited.

On the other hand, Kitoh *et al.*¹⁶⁾ and Shibayama *et al.*¹⁷⁾ reported for unsaturated polyester and crosslinked epoxy resin, respectively, that the values of ΔHa for relaxation increase with an increase in the crosslinking density in temperature ranges above T_g . If the hydrogen bonds in nylon 6 would act as crosslinking points in crosslinked polymers, an interpretation similar to that mentioned in their papers could be offered for the difference between two values of ΔHa in the temperature ranges above and below the break point.

Williams, Landel and Ferry¹⁸⁾ introduced a relation between a_T and temperature (T) for almost nonpolar amorphous polymers; the relation is expressed by Eq. (3),

$$\log a_T = -\frac{C_1(T-T_g)}{C_2+T-T_g} \quad (3)$$

where T_g is the glass transition temperature, and

Table 3 Values of C_1 , C_2 , f_g and α_f for drawn nylon 6 fiber, unoriented poly(ethylene terephthalate) fiber^{a)}, and amorphous polymer

Polymer	C_1	C_2	f_g	α_f (deg ⁻¹)
Drawn nylon 6 fiber	32.9	311.3	0.013	4.2×10^{-5}
Unoriented poly(ethylene terephthalate fiber)	31.25	109.3	0.014	1.27×10^{-4}
Amorphous polymer	17.44	51.6	0.025	4.8×10^{-4}

a) From the report by Takayanagi *et al.*²¹⁾

C_1 and C_2 are constants. In order to check the applicability of this equation to nylon 6 which is one of semicrystalline polymers, the relation between $(T-Tg)/\log a_T$ and $(T-Tg)$ in the following equation, derived from Eq. (3), was plotted.

$$\frac{T-Tg}{\log a_T} = -\frac{C_2}{C_1} - \frac{T-Tg}{C_1} \quad (4)$$

The obtained curves were also composed of two straight lines, as shown in Figure 6. From the slope and the intercept of the straight line in the lower-temperature range containing Tg , the C_1 and C_2 for the specimen drawn up to 3-fold were determined to be 33 and 311, respectively. The values of C_1 and C_2 obtained for the specimen drawn up to 4-fold are nearly equal to the above values, 33 and 311.

The C_1 and C_2 can be related to the free volume fraction at Tg (f_g) and the expansion coefficient of free volume at Tg (α_f) by means of Eqs. (5) and (6), respectively;

$$C_1 = \frac{B}{2.303 f_g} \quad (5)$$

$$C_2 = \frac{f_g}{\alpha_f} \quad (6)$$

where the B is a constant and taken usually as unity. By the use of Eqs. (5) and (6), f_g and α_f were calculated to be 1.3×10^{-2} and 4.2×10^{-5} , respectively.

In Table 3, the values of C_1 , C_2 , f_g , and α_f thus obtained are compared with those for typical amorphous polymers and poly(ethylene terephthalate). The values of f_g and α_f for nylon 6 are smaller than those for amorphous polymers. However, the value of f_g , being one-half of 0.025 for amorphous polymers, was in good agreement with one for poly(ethylene terephthalate), which was calculated from Thompson-Wood's data²⁰⁾ by Taka-

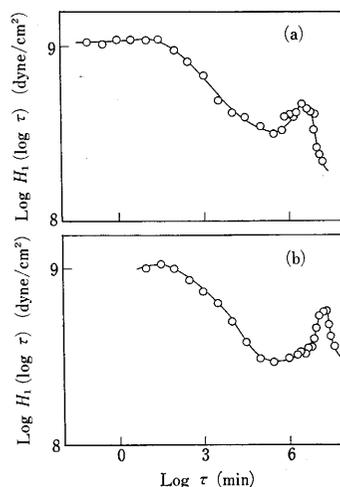


Fig. 7 Relaxation time spectra for the oriented nylon 6 fibers. (a), the specimen drawn up to 3-fold; (b), the specimen drawn up to 4-fold.

yanagi *et al.*²¹⁾, who mentioned that this value seems to be a reasonable one as f_g for a partial crystalline polymer, having a crystallinity of 48%. On the other hand, Shibayama *et al.*¹⁷⁾ and Kitoh *et al.*²²⁾ reported for unsaturated polyester and for epoxy resin, respectively, that the values of f_g and α_f regularly decrease with increase in the crosslinking density. Now, it is possible to assume that the effect of crystallites in crystalline polymers on the f_g and α_f is similar to that of crosslinking points in crosslinked polymers. The crystallites, as well as crosslinking points, seem to prevent the segmental motion of amorphous chains, and to restrict the thermal expansion of free volume. In the case of nylon 6, as compared with poly(ethylene terephthalate), the effect of hydrogen bonds must be overlapped on that of crystallites.

The relaxation time spectra, finally, were determined from the master curves of $Er(t)_{red.}$ by the use of the usual primary approximation method;

$$H_1(\log \tau) = -Er(t)_{red.} \frac{d \log Er(t)_{red.}}{d \log t} \quad (7)$$

The obtained spectra are shown in Figure 7. Although it is generally known that⁴⁾ the relaxation spectra of textile fibers can be approximated

well only by box-type distribution, the spectra obtained here have clearly shown both distributions of wedge-type and box-type, similar to those of typical amorphous polymers. The wedge-type distribution, however, is flatter and higher than those of amorphous polymers; the slopes are about $-1/5$ and are significantly smaller than the theoretical slope of $-1/2$ according to Rouse²³. When the draw ratio increases from 3-fold to 4-fold, the box-type distribution becomes higher and its position shifts to longer time side, whereas the wedge-type one remains almost unchanged. This fact suggests that the distribution of the box-type is influenced more sensitively by the increases in orientation and crystallinity caused by elongation than that of the wedge-type. Although the box-type distribution seems to be related to the structural changes in crystalline region, the details of the reason is not clear at present.

Acknowledgement

This research was supported in part by a grant from Yamanashi Kogyo-Kai.

References

- 1) E. Catsiff, J. Offenbach, and A. V. Tobolsky, *J. Colloid Sci.*, **11**, 48 (1956).
- 2) K. Nagamatsu, T. Takemura, T. Yoshitomi, and T. Takemoto, *J. Polym. Sci.*, **33**, 515 (1958).
- 3) S. Onogi, K. Sasaguri, and T. Adachi, *J. Polym. Sci.*, **58**, 1 (1962).
- 4) K. Fujino, H. Kawai, T. Horino, and K. Miyamoto, *Textile Res. J.*, **26**, 852 (1956).
- 5) T. Yoshitomi and K. Nagamatsu, *J. Polym. Sci.*, **27**, 355 (1958).
- 6) N. Tokita, *J. Polym. Sci.*, **20**, 515 (1956).
- 7) M. Hashimoto and T. Kunugi, *Kogyo Kagaku Zasshi*, **73**, 1499 (1970).
- 8) M. Hashimoto, T. Kunugi, N. Otagiri, and S. Shindo, *Kogyo Kagaku Zasshi*, **74**, 1431 (1971).
- 9) M. Hashimoto, T. Kunugi, N. Otagiri, and K. Amemiya, *Nippon Kagaku Kaishi*, **1972**, 454.
- 10) H. A. Stuart, "Die Physik der Hoch Polymern," **4**, p. 6380 Sprinle (1953).
- 11) T. Kunugi, K. Amemiya, and M. Hashimoto, *Nippon Kagaku Kaishi*, **1973**, 1010.
- 12) K. Hoashi and R. D. Andrews, *J. Polym. Sci., Part C*, **38**, 387 (1972).
- 13) M. Takayanagi, "Proceedings of the Fourth International Congress on Rheology", Part 1, 161, Interscience Publishers, New York (1965).
- 14) M. Kitoh, Y. Miyano, and K. Suzuki, *Kobunshi Ronbunshu*, **32**, 55 (1975).
- 15) M. Kodama, *Kobunshi Ronbunshu*, **32**, 13(1975).
- 16) M. Kitoh and K. Suzuki, *Kobunshi Ronbunshu*, **32**, 147 (1975).
- 17) K. Shibayama and Y. Suzuki, *J. Polym. Sci., Part A*, **3**, 2637 (1965).
- 18) M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
- 19) J. D. Ferry, "Viscoelastic Properties of Polymers", John Wiley & Sons, Inc., New York, N. Y. (1970) p. 318.
- 20) A. B. Thompson and D. W. Woods, *Trans. Faraday Soc.*, **52**, 1383 (1956).
- 21) M. Takayanagi, M. Yoshino, and Y. Saeki, *Zairyo Shiken*, **8**, 308 (1959).
- 22) M. Kitoh and K. Suzuki, *Kobunshi Ronbunshu*, **33**, 19 (1976).
- 23) P. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1953).