Technical Section

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**DEFORMATION OF POLY(VINYL CHLORIDE), POLYPROPYLENE
AND NYLON-6 FIBERS BY RAPID HEATING***By Nobuyuki Tanaka*

(Faculty of Technology, Gunma University, Kiryu, Gunma-ken, Japan)

Abstract

The thermal deformation phenomena of PVC, PP and nylon-6 fibers heated rapidly by immersing in silicone oil of a given temperature or by irradiating with infrared ray were reported. The shrinkage rates of PP and PVC fibers were 98 and 105 mm/sec, respectively, independent of the sample initial length. The rate of nylon-6 fiber was dependent on the initial length. A damped oscillation of the sample length was found for PVC fiber upon the heating. These results suggest that necking type shrinkage takes place for PP and PVC fibers, but not for nylon-6 fibers. The oscillation of PVC fiber length may be related to the damped inertial elasticity.

Introduction

Rapid heating of polymers induces thermal deformation. The relation between the deformation and the structural change, however, has scarcely been investigated. Clarification of such relation is also important from the viewpoint of the dimensional stability of polymer products. Farrow and Simmens observed the melting behavior of nylon-6 fibers upon rapid heating in dry and in water-saturated atmospheres and found a well-defined core effect and the outbreak of internal cavitation accompanying delustering of the filament.¹

In this paper, thermal deformation was studied for poly(vinyl chloride) (PVC), polypropylene (PP) and nylon-6 fibers heated rapidly by immersing in silicone oil maintained at certain temperatures² or by irradiating with infrared ray. The mechanism of thermal shrinkage of these fibers were discussed.

Experimental**Samples**

As the samples of highly oriented fibers, the commercial monofilaments of PP (375 D) and nylon-6 (320 D), and the multifilament of PVC (66.3 d × 10 fils.) were used. No heat treatment of these fibers was performed to avoid any alteration in the structures of the original fibers. The density ρ , the crystalline orientation factor f_c , the amorphous orientation factor f_a , the birefringence Δn , the degree of crystallinity α , and the degree of polymerization x of each fiber are listed in Table 1. f_c was evaluated from the half width of the maximum X-ray reflection on the azimuthal scanning of the (1 1 0) plane for PP fibers and the (1 0 0) plane for nylon-6 fibers. f_a was calculated using the relation²

$$f_a = \frac{3}{2} \left(\frac{L_a}{L_c} \right)^2 - \frac{1}{2}$$

Table 1. ρ , f_c , f_a , Δn , α and x for PP, nylon-6 and PVC fibers

fibers	ρ g/cm ³	f_c	f_a	Δn	α %	x
PP	0.8845 (23°C)	0.90	0.759	0.0339	38.1	4280
nylon-6	1.141 (25°C)	0.94	0.764	—	30.0	90.4
PVC	1.378 (25°C)	—	—	0.01	—	—

where L_c is the length of a sample in totally crystalline state and L_a the length in totally amorphous state. The degree of crystallinity α was evaluated using the relation

$$\alpha = \left(\frac{\rho_c - \rho_a}{\rho_c - \rho_a} \right) \left(\frac{\rho_c}{\rho} \right)$$

where ρ_c is the density of the crystalline region and ρ_a the density of the amorphous region (PP: $\rho_c = 0.935 \text{ g/cm}^3$, $\rho_a = 0.856 \text{ g/cm}^3$; nylon-6: $\rho_c = 1.212 \text{ g/cm}^3$, $\rho_a = 1.113 \text{ g/cm}^3$).

Rapid Heating Methods and Thermal Deformation Measurements

Rapid heating was performed by means of two methods, one by use of the silicone oil bath thermostated at a given temperature, which can be shifted up and down by hand, and the other the Infrared Image Furnace RHL-E25 (SINKU RIKO). The length change of a sample fiber was measured by a displacement meter and recorded on an X-Y₁, Y₂ recorder, together with the temperature of the silicone oil bath or of a thermocouple set near a sample in the Infrared Image Furnace. The good pen response (maximum pen speed, above 250 mm/sec) of the recorder to catch the shrinkage rate and the damped oscillation behavior of samples was confirmed by the measurement of deformation behaviors of the same samples by use of a Transient Time Converter. During the measurement of the length change, a about 1.7 g wt. for the infrared ray method or about 4.0 g wt. for the silicone oil method were loaded on a sample unless otherwise specified. The relative shrinkage S was defined as $S = (L_0 - L)/L_0$, where L is the sample length and L_0 the initial sample length at room temperature.

Results and Discussion

Figure 1 shows the elapsed time dependence of the relative shrinkage S for PVC fibers heated rapidly by immersing in silicone oil of given temperatures. Over 115°C, after the initial abrupt shrinkage, damped oscillation behaviors of the deformation are observed, and then the sample length shows different behaviors; little by little decrease at 115 and 126°C, good constancy against time at 137 and 151°C, and slow increase at 169 and 181°C. At 90 and 102°C, the sample length does not oscillate but decreases gradually after the

abrupt shrinkage upon rapid heating. Figure 2 shows the shrinkage of PVC fibers during three seconds after the rapid heating by immersing in silicone oil. At 118–183°C, after the heating, the damped oscillation repeats four times. At 131–

Fig. 1 Relative shrinkage S vs. time curves during 10 minutes for PVC fibers ($L_0 = 25 \text{ mm}$) heated rapidly by immersing in silicone oil of given temperatures (a: 90°C, b: 102°C, c: 115°C, d: 126°C, e: 137°C, f: 151°C, g: 169°C and h: 181°C)

Fig. 2 Relative shrinkage S vs. time curves for PVC fibers ($L_0 = 25 \text{ mm}$) during 3 seconds after the rapid heating by immersing in silicone oil of given temperatures (---: 118°C, ----: 131°C, —: 141°C, —: 150°C, ----: 162°C, —: 172°C, ---: 183°C, ----: 195°C, ---: 207°C, and ----: 217°C)

Fig. 3 The load dependence of the thermal deformation of PVC fibers heated rapidly by immersing in silicone oil at 145°C (a: 24.0 g, b: 14.0 g, c: 8.7 g and d: 4.0 g; $L_0 = 35 \text{ mm}$)

183°C, the sample contracts to the maximum relative shrinkage $S_{\max} \approx 1.0$ at the shrinkage rate ($d\Delta L (=L_0 - L)/dt$) of 105 mm/sec. However, the unusual high values of $S_{\max}$ shown in Figures 1 and 2 must be attributed, at least in some part, to the over-run of the upper grip of the sample holder under the high shrinkage rate and the inertia. At 118°C, the shrinkage rate is a little less than those at 131–183°C. Figure 3 shows the load dependence of the deformation of PVC fibers heated rapidly by immersing in silicone oil at 145°C. With increasing the load on a sample, $S_{\max}$ decreases and the damped oscillation becomes meager. The shrinkage rate is 105 mm/sec in the cases of 4.0, 8.7 and 14.0 g loads. With 24.0 g load, the rate is a little less than 105 mm/sec. Figure 4 shows the dependence on time of the relative shrinkage S of PVC fibers heated by infrared ray. The shrinkage rate increases with increasing heating rate. The shrinkage rate at heating rates, 160.0 and 193.4 K/sec, are equally 102.4 mm/sec, which is almost equal to the shrinkage rate of 105 mm/sec obtained for the heating by immersing in silicone oil at 131–183°C. With increasing the heating rate, $S_{\max}$ is attained faster and the $S_{\max}$ value is increased. The time needed to attain $S_{\max}$ is 0.57 sec at 53.4 K/sec and 0.32 sec at 160.0 and 193.4 K/sec. The values of $S_{\max}$ at 160.0 and 193.4 K/sec are about 0.83. At 94.7–193.4 K/sec, two peaks appear in the time dependence curve of S . After the second shrinkage, the sample is elongated and then broken. At 20.0–53.4 K/sec, no peak appears in the S vs. time curves, but a shoulder, which seems to be transformed gradually to a peak with increasing the heating rate, appears at about 0.6–

Fig. 4 Relative shrinkage S vs. time curves for PVC fibers ($L_0 = 25$ mm) during 3 seconds after the rapid heating by irradiating infrared ray at several heating rates (a: 20.0 K/sec, b: 26.7 K/sec, c: 40.0 K/sec, d: 53.4 K/sec, e: 94.7 K/sec, f: 100.1 K/sec, g: 160.0 K/sec and h: 193.4 K/sec)

0.8 seconds after the rapid heating. Figures 5a–5e and 6 show the dependence of the deformation of PVC fibers on the initial sample length L_0 . For the rapid heating by immersing in silicone oil at a temperature 130–210°C and infrared ray at heating rates 160.0, 177.4 and 181.6 K/sec, as seen in Figures 5 and 6, the shrinkage rates are almost constant independent of L_0 . These results suggest that in the rapid heating procedure the sample length decreases within a short time, probably by the necking. A similar result was

Fig. 5a The initial length dependence of the contraction length ΔL vs. time curves for PVC fibers heated rapidly by immersing in silicone oil at 102°C (a: $L_0 = 10$ mm, b: $L_0 = 25$ mm, and c: $L_0 = 35$ mm)

Fig. 5b The initial length dependence of the contraction length ΔL vs. time curves for PVC fibers heated rapidly by immersing in silicone oil at 119°C (a: $L_0 = 10$ mm, b: $L_0 = 25$ mm, and c: $L_0 = 35$ mm)

Fig. 5c The initial length dependence of the contraction length ΔL vs. time curves for PVC fibers heated rapidly by immersing in silicone oil at 131°C (a: $L_0 = 10$ mm, b: $L_0 = 25$ mm, and c: $L_0 = 35$ mm)

Fig. 5d The initial length dependence of the contraction length ΔL vs. time curves for PVC fibers heated rapidly by immersing in silicone oil at 144°C (a: $L_0 = 10$ mm, b: $L_0 = 25$ mm, and c: $L_0 = 35$ mm)

Fig. 5e The initial length dependence of the contraction length ΔL vs. time curves for PVC fibers heated rapidly by immersing in silicone oil at 155°C (a: $L_0 = 10$ mm, b: $L_0 = 25$ mm, and c: $L_0 = 35$ mm)

Fig. 6 The initial length dependence of the thermal deformation of PVC fibers heated rapidly by irradiating infrared ray (a: 160.0 K/sec, $L_0 = 25$ mm; b: 177.4 K/sec, $L_0 = 35$ mm; c: 181.6 K/sec, $L_0 = 50$ mm)

observed for PP fibers. The L_0 dependence of the shrinkage rate of PP fibers heated rapidly was investigated. The thermal deformation of PP fibers heated rapidly by irradiating infrared ray are shown in Figure 7. The shrinkage rate is 98.1 mm/sec independent of L_0 . Figure 8a shows the thermal deformation of PP fibers heated rapidly by immersing in silicone oil at 188°C, which is higher than T_m of PP. The shrinkage rate is 98.5 mm/sec independent of L_0 . At silicone oil temperature of 160°C, below T_m , as seen in Figure 8b, the shrinkage rate changes dependently on L_0 . The results shown in Figures 7 and 8a suggest that the rapid heating procedure causes the necking of PP fiber within a short period, resulting in the contraction of the sample. Figure 9 shows the thermal deformation of nylon-6 fibers heated rapidly by immersing in silicone oil at given temperatures. The shrinkage rate and S_{max} increases with increasing the silicone oil temperature. At 163–192°C, the shoulder appears at 0.3–0.6 seconds after the rapid heating. This part seems to be transformed to a peak, with increasing the temperature of silicone oil. At 163–192°C, S_{max} appears at about ten seconds after rapid heating. Figures 10a, b and c show the L_0 dependence of the thermal deformation of nylon-6 fibers heated rapidly by immersing in silicone oil at 214, 227 and 245°C. As seen in Figure 10, the shrinkage rate varies with L_0 . The value of S_{max} is almost constant irrespective of L_0 . Figure 11 shows the

Fig. 7 The initial length dependence of the thermal deformation of the PP fibers heated rapidly by irradiating infrared ray (L_0 and heating rate; a: 25 mm, 220.1 K/sec, b: 35 mm, 220.1 K/sec, c: 50 mm, 181.4 K/sec)

Fig. 8a The initial length dependence of the contraction length ΔL vs. time curves for PP fibers heated rapidly by immersing in silicone oil of 188°C (a: $L_0 = 25$ mm, b: $L_0 = 35$ mm)

Fig. 8b The initial length dependence of the contraction length ΔL vs. time curves for PP fibers heated rapidly by immersing in silicone oil of 160°C (a: $L_0 = 25$ mm, b: $L_0 = 35$ mm and c: $L_0 = 50$ mm)

Fig. 9 Relative shrinkage S vs. time curves for nylon-6 fibers ($L_0 = 50$ mm) heated rapidly by immersing in silicone oil of given temperatures (a: 163°C, b: 178°C, c: 192°C, d: 203°C, e: 207°C, f: 208°C, g: 210°C, h: 227°C, i: 233°C and j: 244°C)

L_0 dependence of the thermal deformation of nylon-6 fibers heated rapidly by irradiating infrared ray at a heating rate of 199.4 K/sec. The shrinkage rate increases with increasing L_0 , although the

Fig. 10a The initial length dependence of the contraction length ΔL vs. time curves for nylon-6 fibers heated rapidly by immersing in silicone oil at 214°C (a: $L_0 = 25$ mm and b: $L_0 = 50$ mm)

Fig. 10b The initial length dependence of the contraction length ΔL vs. time curves for nylon-6 fibers heated rapidly by immersing in silicone oil at 227°C (a: $L_0 = 25$ mm and b: $L_0 = 50$ mm)

Fig. 10c The initial length dependence of the contraction length ΔL vs. time curves for nylon-6 fibers heated rapidly by immersing in silicone oil of 244°C (a: $L_0 = 25$ mm and b: $L_0 = 50$ mm)

value of $S_{\max}$ is almost constant independent of L_0 . Figure 12 shows the load dependence of the thermal deformation of nylon-6 fibers heated rapidly by irradiating infrared ray at a heating rate of 199.4 K/sec. The shrinkage rate, the value of $S_{\max}$ and the time to attain $S_{\max}$ depend on

Fig. 11 The initial length dependence of the contraction length ΔL vs. time curves for nylon-6 fibers heated rapidly by irradiating infrared ray at the heating rate of 199 K/sec (a: $L_0 = 25$ mm and b: $L_0 = 35$ mm)

---: Temperature of a thermocouple set in the furnace.

Fig. 12 The load dependence of the thermal deformation of nylon-6 fibers heated rapidly by irradiating infrared ray at the heating rate of 199 K/sec (a: 11.7 g, b: 6.4 g and c: 1.7 g; $L_0 = 35$ mm)

the load.

Prevorsek and Tobolsky reported^{3,4} the microscope observation that in the heating at a relatively slow heating rate the necking type shrinkage occurs at near T_m for PP, polyethylene (PE) and nylon-66 fibers, but not for nylon-6 fibers, indicating nylon-6 fiber contracts homogeneously. These facts suggest that a study on the melting phenomena of fibrous polymers must accompany

a morphological examination. Iida and Sakami reported⁵ that in the drawing of an undrawn PP fiber the necking appears, but not for nylon-6 fibers. In view of the results of Prevorsek and Iida and their coworkers, it may be concluded that for PP and PVC fibers heated rapidly by irradiating infrared ray at a high heating rate and by immersing in silicone oil at temperatures, in the range 130–210°C for PVC fibers and over T_m for PP fibers, the shrinkage of necking type occurs within a very short time duration. This doesn't happen for nylon-6 fibers under any rapid heating condition.

The damped oscillation behavior of thermal deformation observed distinctly for PVC fibers heated rapidly may be related to the damped inertial elasticity, which is expressed by the following equation⁶.

$$m \frac{d^2 \gamma}{dt^2} + \eta \frac{d\gamma}{dt} + G\gamma = S$$

where m is the sample weight, γ the strain, S the constant stress, η the coefficient of viscosity and G the Young's modulus.

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