Partial Melting, Recrystallization and Thermal Shrinkage of Polypropylene Fibers

Nobuyuki Tanaka* and Akio Nakajima**

Thermal shrinkage of polypropylene fibers and those swollen in toluene was thermo-dynamically investigated. The mechanism of shrinkage was discussed by taking into account the partial melting of crystallites in connection with the effect of swelling in toluene.

INTRODUCTION

In our previous papers,[1,2] we have mentioned that the thermal shrinkage of fibrous polymers along the fiber axis could be interpreted according to Flory's theories on melting of polymer in diluent and of cross-linked polymers.

The relation between the relative shrinkage and the absolute temperature derived from these theories has been already applied to Nylon 6[1] and polyethylene terephthalate[2] fibers.

In this paper, we investigate thermal shrinkage of polypropylene fibers and those swollen in toluene. In the following, we'll discuss thermodynamically the mechanism of shrinkage and the effect of swelling in toluene for these fibers.

EXPERIMENTAL

(i) Samples

Polypropylene fibers having the degree of polymerization $x=4280$ (determined by viscosity method), density $\rho=0.8845$ at 23°C and birefringence $\Delta n=0.0339$ were used in this work.

Fibers were swollen in toluene for 15, 60 and 100 min. at 75 and 95°C. After the swelling treatment in toluene, fibers were dried at room temperature. The thermal shrinkage of these fibers was measured in the following way.

(ii) Measurement of Thermal Shrinkage

Specimens were kept for 1.5 hrs. at given constant temperatures by suspending a weight of 0.669 mg/d, and the length of the sample at that temperature was measured by a cathetometer.

For polypropylene fibers used here, a value of 4% may be expected for relative shrinkage during fiber manufacturing process.[1] Therefore, corrected value of S was obtained by adding 4% to the relative shrinkage calculated by

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* 田中　信行 : Department of Textile and Polymer Technology, Faculty of Engineering, Gunma University, Kiryu.
** 中島　章夫 : Department of Polymer Chemistry, Kyoto University, Kyoto.

using the length (observed value) of the original fibers at room temperature.

(iii) Measurement of Birefringence

A polarized microscope equiped with a Berek compensator and a Na-lamp was used to measure the birefringence of the specimens.

(iv) Measurement of Viscosity

A viscometer of Ubbelohde type was used to obtain the intrinsic viscosity $[\eta]$ of polypropylene in decalin at 135°C. The molecular weight of the sample was calculated according to the equation[3]

$$[\eta] = 1.10 \times 10^{-4} M^{0.80}$$

(v) Measurement of Degree of Orientation of Crystallites

X-ray measurements were performed with a Rigaku Denki apparatus. The degree of orientation F_c of the (110) plane of crystallite was determined from the half-width H of the maximum on the azimuthal scanning of the (110) reflection by the equation

$$F_c = \frac{180 - H}{180} \times 100 \ (\%)$$

The measurements of birefringence and orientation of crystallites, samples used were prepared by heating without tension at a heating rate of 3.0°C/min up to given temperatures where heat-treated for 1 hr. and then quenched down to room temperature.

RESULTS AND DISCUSSION

Eq. (13) in our previous paper[1] leads to the following relation between the relative shrinkage S and temperature T.

$$(1/S) = A(1/T) - C \tag{1}$$

with

$$A = -\frac{xL_c}{k(L_c - L_a)} \left\{ (h_u - Ts_u) - (h_x - Ts_x) + f(\alpha - 1) \right\} \tag{2}$$

$$C = \frac{1}{x - \zeta + 1} \left(-\frac{xL_c}{L_c - L_a} \right) \tag{3}$$

where, L_c: length of sample when totally crystalline, L_a: length of sample when totally amorphous, h_u and s_u: heat and entropy of fusion per structural unit, h_x and s_x: enthalpy and entropy changes per structural unit owing to the presence of pseudo cross-links in amorphous regions, f: force, α: drawing ratio, and ζ: length of crystallite in number of unit.

In Fig. 1, the relative shrinkage S was plotted against reciprocal of the absolute temperature T for polypropylene fibers treated in different ways together with untreated sample.

Each curve obtained may be represented by a set of straight lines of different slopes. This means that, in definite temperature ranges, the relation given by
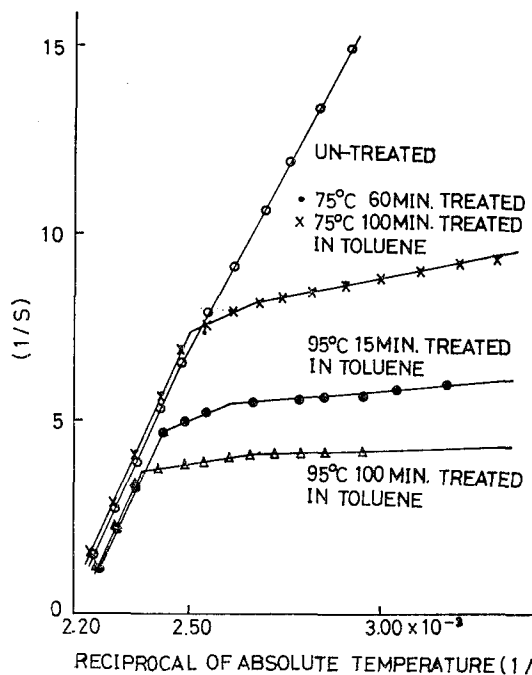
Fig. 1. Relation between the reciprocal relative shrinkage $1/S$ and the reciprocal temperature $1/T$ for polypropylene fibers treated in toluene.
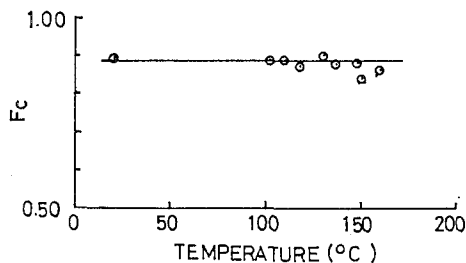

Fig. 2. Relation between the degree of orientation, F_c, of crystallites and the temperature of heat-treatment for polypropylene fibers.

Eq. (1) is expected to hold. As shown in Fig. 2, the degree F_c of orientation of crystallites is constant in the whole temperature range investigated here. Therefore, slope of each straight line portion may be explained by Eq. (2).

If $\zeta \ll x$ and ζ is almost constant, then L_a becomes approximately constant in definite temperature range, from Eq. (3). Thus, the difference in Gibbs free energies of amorphous and crystalline regions, $\{(h_u - Ts_u) - (h_x - Ts_x) + f(\alpha - 1)\}$, is also regarded as to be constant.

In Fig. 3, the slope A is plotted against T. As obvious from Fig. 3, the slope A changes stepwise, and is smaller in lower temperature range. The quantity C for swollen samples is always negative at temperature range below 105°C. Since the right-hand side of Eq. (3) is always positive, explanation of thermal shrinkage by Eq. (1) seems difficult. Alternative explanation for this experimental result
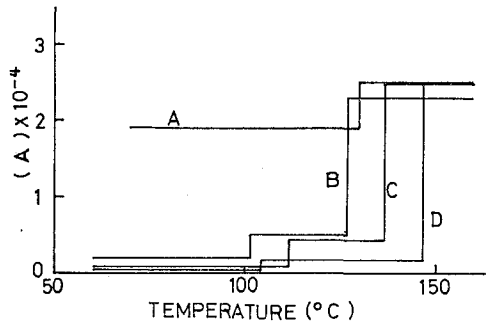
Fig. 3. Slope A of straight line portion of curves in Fig. 1 plotted against temperature.
  A: untreated.
  B: treated in toluene at 75°C for 100 min.
  C: treated in toluene at 95°C for 15 min.
  D: treated in toluene at 95°C for 100 min.

may be either that Eq. (1) is modified by adding a correction term independent of equilibrium system, or that the thermal shrinkage in this temperature range may occur in terms of decrease in numbers of pseudo cross-links in amorphous regions, because the crystallinity is almost unchanged within this temperature range.

With the sample swollen in toluene for 100 min. at 95°C (sample D), the value of C is nearly zero in the temperature range of 104.4~146.3°C. Thermal shrinkage in this temperature range may be governed by both the recrystallization during cooling process after swelling treatment at 95°C, and the partial melting during subsequent heating process. The recrystallization and partial melting is almost reversible and, at the same time, the thermal deformation of the sample during the cooling-heating cycle in this temperature range is also approximately reversible as well. Such behavior for sample D, in this temperature range, was also recognized for samples B and C.

If the recrystallization-partial melting process and the thermal deformation during heating-cooling cycle in this temperature range are perfectly reversible, then the following relation must be held for an equilibrium system:[4]

$$G_a - fL_a = G_c - fL_c \tag{4}$$

Since G_c and G_a are written as $G_c = N_A(h_u - Ts_u)$, and $G_a = N_A(h_x - Ts_x)$, Eq. (4) is rewritten as

$$L_c - L_a = (1/f)(G_c - G_a) = (N_A/f)\{(h_u - Ts_u) - (h_x - Ts_x)\} \tag{5}$$

Combining Eq. (2) with Eq. (5), we obtain

$$(N_A/f)\{(h_u - Ts_u) - (h_x - Ts_x)\} = (xL_c/kA)\{(h_u - Ts_u) - (h_x - Ts_x)$$
$$+ f(\alpha - 1)\} \tag{6}$$

When $\alpha \cong 1$ under a constant force f, $f(\alpha - 1)$ is negligibly small, and Eq. (6) is written as
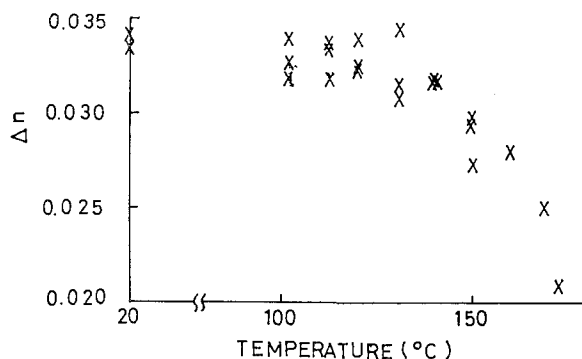
$$\frac{N_A}{f} = \frac{xL_c}{kA} \tag{7}$$

Fig. 4. Birefringence Δn plotted against temperature of heat-treatment.

where N_A is Avogadro's number.

Now let us estimate the degree of polymerization, x, from Eq. (7) and compare it with that ($x=4280$) determined from intrinsic viscosity data. For this purpose, we shall use the slope in the temperature rang 104.4~146.3°C for sample D. Let the length of sample at room temperature be 10 cm, then 4 % should be corrected from the reason mentioned above to obtain L_c. Thus we obtain $10/(1-0.04)=10.42$ cm. On the other hand, the weight of fiber (375 denier) for 10 cm length is 0.00417 g, which corresponds to 9.92×10^{-5} mole. So we can calculate the length L_c for 1 mole fiber as $L_c=105040$ cm. Further, applied force f is 0.251 g-wt (0.669 g-wt/d) and this leads to $f=245.98$ dyn. Accordingly, we obtain

$$x = \frac{1.987 \times 1700}{245.98 \times 105040 \times 2.39 \times 10^{-8}} = 5470$$

by using the slope $A=1700°K$, $R=1.987$ cal/°K·mole, and 1 erg$=2.39 \times 10^{-8}$ cal. Thus the degree of polymerization, x, estimated from Eq. (7) is 1.28 times that ($x=4280$) determined from intrinsic viscosity in decalin at 135°C. Taking into consideration assumptions used here, we can say that the model developed above acquired quite sufficient support.

In the temperature range above 146.3°C, L_a for swollen samples is almost constant, so shrinkage may be assumed to depend on the decrease in crystallinity by partial melting. This may be confirmed by the decrease in birefringence in this temperature range. Since L_a is constant, the shrinkage may be caused by the decrease in crystallinity without being accompanied by the decrease in orientation of amorphous chains.

The decrease in birefringence is remarkable at temperature above 135°C, which is very close to the refraction point (130°C) of unswollen sample (sample A). The birefringence is generally represented by

$$\Delta n = \Delta n_c(1-\lambda) + \Delta n_a \lambda + \Delta n_f \qquad (8)$$

where, Δn is the total birefringence of sample, Δn_c the birefringence of crystalline regions, Δn_a the birefringence of amorphous regions, Δn_f the form birefringence, and λ the amorphous fraction. Neglecting the form birefringence, we obtain the amorphous fraction λ.
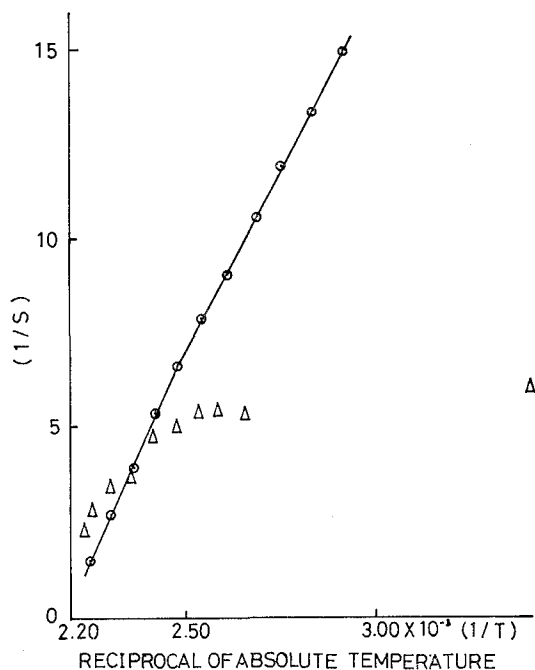
Fig. 5. Relation between $1/S$ and $1/T$, obtained from measurements of sample length ($\bigcirc$) and estimated from Eq. (10) ($\triangle$).

$$\lambda = \left(\frac{\Delta n_c}{\Delta n_c - \Delta n_a}\right) - \left(\frac{\Delta n}{\Delta n_c - \Delta n_a}\right) \tag{9}$$

If both Δn_c and Δn_a are constant, then λ should be proportional to Δn.

On the other hand, the relative shrinkage $S[=(L_c-L_a)\lambda/L_c]$ is represented by

$$S = \left(\frac{\Delta n_c - \Delta n}{\Delta n_c - \Delta n_a}\right)\frac{L_c - L_a}{L_c} \tag{10}$$

Therefore, S is estimated from Eq. (10) using[5] $\Delta n_c = 41.5 \times 10^{-3}$, $\Delta n_a = 0$, and $L_a = 0.091 \, L_c$ (see below). In Fig. 5, the value of $1/S$ calculated from Eq. (10) was plotted against $1/T$. In the temperature range above 130°C, the value of $1/S$ estimated from Eq. (10) is nearly equal to that obtained from the measurements of sample length. On the basis of these experimental results, it is assumed that the thermal shrinkage above 130°C is related to the partial melting of the crystallites.

Refraction points appeared in curves of Fig. 1 were listed in Table 1. The lower refraction point of each sample may correspond to the temperature at which crystallization stops or becomes very slow during the cooling process after the swelling treatment at 75 or 95°C. With respect to the heating process after cooling to room temperature, this temperature may correspond to the temperature at which partial melting takes place rapidly. The refraction point 130°C of the untreated sample is nearly equal to the refraction points 131°C and 127°C for samples treated, in toluence at 75°C, for 60 and 100 min., respectively. At

Table 1. Refraction Points (°C) of Polypropylene Fibers with and without Swelling Ttreatment.

Sample	Treatment in Toluene	Refraction Point (°C)	
A	untreated	—	130.0
B'	75°C, 60 min. treated	107.0	131.0
B	75°C, 100 min. treated	101.5	127.0
C	95°C, 15 min. treated	111.6	136.8
D	95°C, 100 min. treated	104.4	146.3

75°C, the refraction point was almost constant independent of time of treatment. Therefore, it is assumed that 75°C is the critical swelling temperature for the present fibers in toluene. Above 130°C, $1/S$ of the sample treated in toluene at 75°C for 60 and 100 min. was almost identical with that of the untreated sample.

Whereas, for samples swollen at 95°C for 15 and 100 min., the refraction point shifted toward higher temperature with increasing time, i. e., from 136.8 to 146.3°C. This tendency will be ascribable to the solubility effect of polypropylene fibers in toluene. The melting temperature of polypropylene in toluene is near 105°C and the cohesive energy densities[6] of polypropylene and toluene are, respectively, 8.20 and 8.902 $(cal/cm^3)^{1/2}$. Accordingly, toluene is a good solvent for polypropylene. The temperature, at which $1/S$ of swollen samples is almost equal to that of unswollen sample, may be shifted to higher temperature with increasing treatment temperature in toluene.

Above 130°C, the slope A of all these treated fibers was equal to that of the unswollen sample, though $1/S$ was slightly less than that of the unswollen sample. This lowering of $1/S$ may result from the decrease in orientation of crystallites, i. e., the degree of orientation of crystallites for untreated sample, and for both
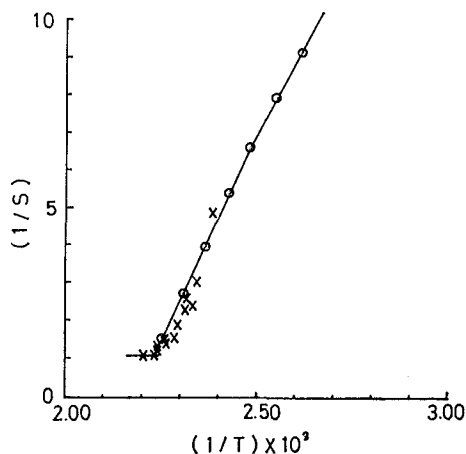
Fig. 6. Relation between $1/S$ and $1/T$ near melting temperature.
  ○: obtained from measurements of sample length at given temperatures.
  ×: obtained from measurements of length of samples quenched down to room temperature after the heat-treatment at given temperatures near the melting temperature.

samples treated for 15 and 100 min. at 95°C are 0.90 and 0.80, respectively. But it was assumed that, in the dry heating process preceded by the swelling in toluene, the degree of orientation of crystallites was almost invariant.

Since it was difficult to measure the value of S near the melting temperature under a constant load, we measured the length of each sample that was heated without tension at a heating rate of 3.0°C/min to a given temperature near the melting temperature and then quenched down to room temperature. $1/S$ obtained by such measurement was plotted against $1/T$ in Fig. 6. The melting temperature obtained from the curve is 173.0°C. At 173.0°C, $\lambda=1$ and $1/S=1.10$. Accordingly, $L_a=0.0909\,L_c$. This relation, $L_a=0.0909\,L_c$, was used to calculate $1/S$ from Eq. (10).

REFERENCES

(1) N. Tanaka and A. Nakajima, *Bull. Inst. Chem. Res., Kyoto Univ.*, **48**, 236 (1970).
(2) N. Tanaka and A. Nakajima, *ibid.*, **49**, 377 (1971).
(3) B. Kinsinger and R. E. Hughes, *J. Phys. Chem.*, **63**, 2002 (1959).
(4) L. Mandelkern, "Crystallization of Polymers", McGraw-Hill, New York (1964).
(5) N. Yamada, N. Kishi and Z. Orido, Abstract of 13 th Symposium on Macromolecules, Soc. Polymer Sci., Japan, 654 (1964).
(6) A. S. Michaels, W. R. Vieth and H. H. Alcalay, *J. Appl. Polymer Sci.*, **12**, 1621 (1968).