

Thermal Shrinkage of Polypropylene Fibers in Toluene by Partial Melting and Growth of Crystalline Regions

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The deformation behavior of polypropylene fibers along the fiber axis, during the cooling procedure after the heat treatment in toluene at a given temperature and during the heating procedure after the cooling, was discussed on the base of the shrinkage theory proposed in our previous paper.¹⁾ Extension along the fiber axis is interpreted by growth of crystalline regions, and the contraction along the fiber axis during the heating procedure is by partial melting of recrystallized regions.

INTRODUCTION

With respect to crystalline fibrous polymers, extension of fiber along the fiber axis is often observed during the cooling procedure after wet or dry heat treatment at a given temperature near the melting temperature as a result of growth of crystallites.

The recrystallized parts thus grown during the cooling procedure may disappear by heating after cooling, being accompanied with contraction of the fiber.

In this paper, deformation behavior of polypropylene fiber in toluene during the cooling and heating procedures is discussed on the base of the theoretical expression for thermal shrinkage of fibrous polymers in solvent derived in our previous paper.¹⁾

EXPERIMENTAL

Sample

For measurements of the thermal shrinkage, polypropylene monofilament (375 D) was used. Its birefringence Δn is $\Delta n=0.0339$ and density ρ at 23°C is $\rho=0.8845$.

The degree of polymerization x of this sample was estimated from the intrinsic viscosity $[\eta]$ in decaline at 135°C according to the equation²⁾ $[\eta]=1.10 \times 10^{-4} \times (42x)^{0.80}$. The obtained value of x was $x=4280$.

Measurement of Thermal Deformation

The thermal deformation of the samples was measured in toluene, by suspending a weight 5.751 mg/d, at a heating rate 0.435°C/min. and a cooling rate 0.5°C/min. The change of the sample length was measured by a displacement meter and recorded on an X-Y recorder.

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For polypropylene fiber used here, a value of 4% is expected for the relative shrinkage during the fiber manufacturing process.³⁾ Therefore, corrected value of S was obtained by adding 4% correction to the relative shrinkage calculated from the observed length of the original fiber at room temperature.

RESULTS AND DISCUSSION

Figures 1-5 show the relation between the reciprocal relative shrinkage $1/S$ and the reciprocal absolute temperature $1/T$ for polypropylene fibers in the course of the cooling procedure after the heat treatment in toluene at a given temperature, and of the heating procedure after cooling. The relative shrinkage has been related to the temperature by the following equation.¹⁾

$$\frac{1}{S} = \frac{xL_c}{(L_c - L_a)v_2'k} \{ (h_u - Ts_u) - (h_x - Ts_x) + f(\alpha - 1) \} \left(\frac{1}{T} \right) - \frac{xL_c}{(L_c - L_a)v_2'} \{ (1 - v_2') - \chi_1(1 - v_2')^2 \} \quad (1)$$

where,

- S : relative shrinkage
- T : absolute temperature
- h_u : heat of fusion per structural unit
- s_u : entropy of fusion per structural unit
- h_x : heat of transition per structural unit due to pseudo cross-links in amorphous regions
- s_x : entropy of transition per structural unit due to pseudo cross-links in amorphous regions
- L_c : length of sample in totally crystalline state
- L_a : length of sample in totally amorphous state
- f : force
- α : draw ratio
- x : total number of structural units in a polymer molecule
- v_2' : polymer fraction in amorphous regions
- χ_1 : interaction free energy parameter
- k : Boltzmann's constant

As seen in Figs. 1-5, each curve obtained experimentally was represented by a set of straight lines of different slopes. The straight line portions in the curves are represented by

$$\frac{1}{S} = A \frac{1}{T} - C \quad (A \text{ and } C \text{ are constants.}) \quad (2)$$

The constants, A and C , are given by Eqs.(3) and (4), respectively.¹⁾

$$A = \frac{xL_c}{(L_c - L_a)v_2'k} \{ (h_u - Ts_u) - (h_x - Ts_x) + f(\alpha - 1) \} \quad (3)$$

$$C = \frac{xL_c}{(L_c - L_a)v_2'} \{ (1 - v_2') - \chi_1(1 - v_2')^2 \} \quad (4)$$

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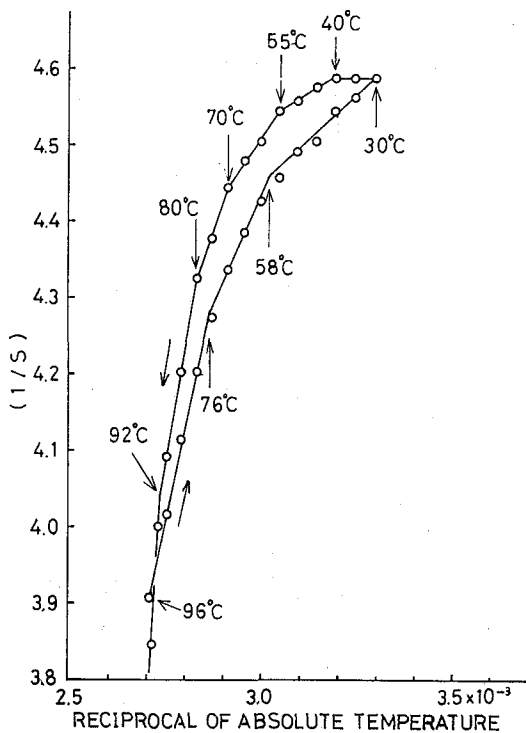


Fig. 1. Relation between the reciprocal relative shrinkage and the reciprocal absolute temperature for polypropylene fiber in the cooling procedure after the heat-treatment in toluene at 96°C and in the heating procedure after cooling.

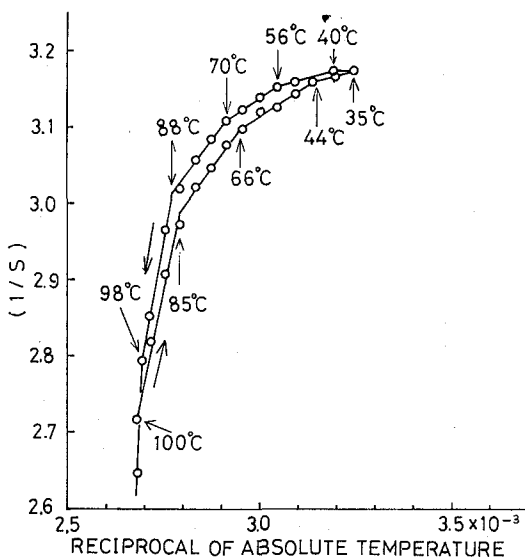


Fig. 2. Relation between the reciprocal relative shrinkage and the reciprocal absolute temperature for polypropylene fiber in the cooling procedure after the heat-treatment in toluene at 100°C and in the heating procedure after cooling.

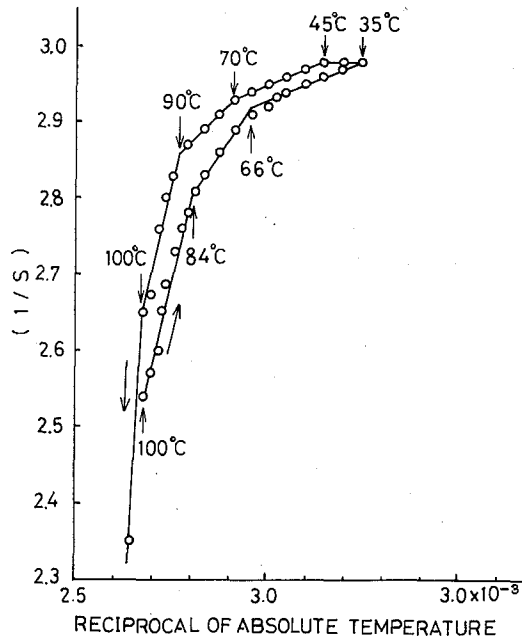


Fig. 3. Relation between the reciprocal relative shrinkage and the reciprocal absolute temperature for polypropylene fiber in the cooling procedure after the heat-treatment in toluene at 100°C and in the heating procedure after cooling.

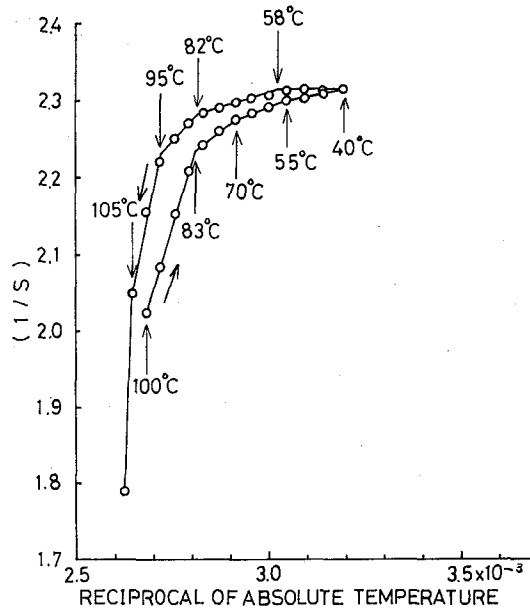


Fig. 4. Relation between the reciprocal relative shrinkage and the reciprocal absolute temperature for polypropylene fiber in the cooling procedure after the heat-treatment in toluene at 100°C and in the heating procedure after cooling.

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Temperatures corresponding to the break points of the curves in Figs. 1, 2, 3, 4 and 5 are characteristic of the partial melting and of the recrystallization in crystalline regions, respectively, in heating and cooling procedure.

The relation between the relative shrinkage and temperature in its cooling and heating procedures exhibits hysteresis (Fig. 6). With respect to curves A and B, the relative shrinkage during the cooling procedure is somewhat larger than that during the heating procedure. Further, the extension during cooling procedure after heat-treatment was remarkable for samples heat-treated at a given temperature above 90°C (A, B, C and D in Fig. 6). In particular, with respect to samples heat-treated at a given temperature in between 90°C and 100°C (B, C and D in Fig. 6), it may be pointed out that the larger the relative shrinkage resulted by the heat-treatment is, the larger the degree of extension during cooling procedure after heat-treatment becomes. However, for sample (A) heat-treated at 102°C, the degree of extension was slightly less than that of sample (B) heat-treated at 100°C. Also, for all samples, the increment of relative shrinkage against temperature was largest in the highest temperature range in the course of the heating procedure.

For samples shown in Figs. 4 and 5, it seems that the recrystallized parts appear during the cooling procedure from 100°C or from 102°C are partially melted during the heating procedure up to 105°C. But, for samples heat-treated at 96°C and 100°C shown in Figs. 1, 2 and 3, this tendency was negligibly small. Therefore, it seems that the amorphous regions are considerably recrystallized during the cooling procedure down from 100°C or 102°C for samples shown in Fig. 4 and Fig. 5.

The polymer fraction v'_2 in amorphous regions, and the Gibbs free energy difference $N_A \Delta G [= N_A \{ (h_u - Ts_u) - (h_x - Ts_x) + f(a-1) \}]$ between crystalline regions and amorphous regions were calculated from Eqs. (5), (6) and (7) derived by rearranging Eqs. (3) and (4).

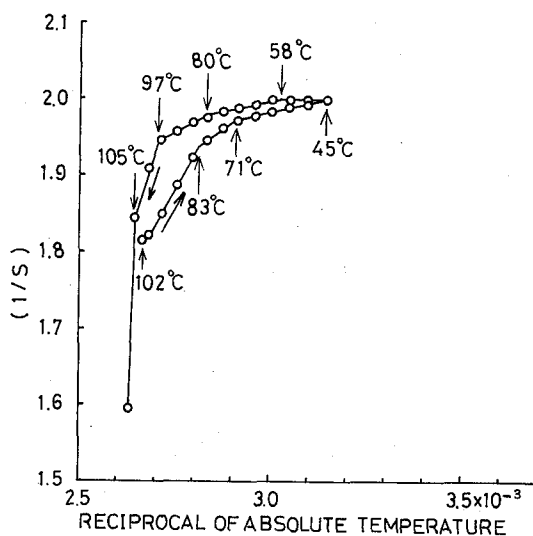


Fig. 5. Relation between the reciprocal relative shrinkage and the reciprocal absolute temperature for polypropylene fiber in the cooling procedure after the heat-treatment in toluene at 102°C and in the heating procedure after cooling.

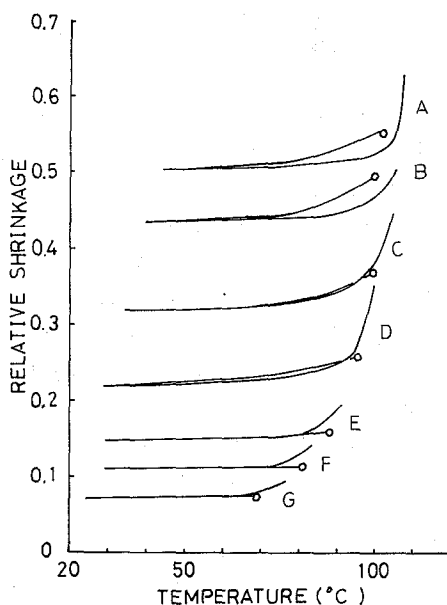


Fig. 6. Relation between the relative shrinkage and the temperature for polypropylene fiber in the cooling procedure after the heat-treatment in toluene at a given temperature (o) (A: 102°C, B: 100°C, C: 100°C, D: 96°C, E: 89°C, F: 82°C and G: 70°C), and in the heating procedure after cooling.

$$v_2' = 1 - \frac{\left\{1 + \frac{C(L_c - L_a)}{xL_c}\right\} - \sqrt{\left\{1 + \frac{C(L_c - L_a)}{xL_c}\right\}^2 - \frac{4\chi_1 C(L_c - L_a)}{xL_c}}}{2\chi_1} \quad \text{for } \chi_1 \neq 0 \quad (5)$$

$$v_2' = \frac{xL_c}{xL_c + (L_c - L_a)C} \quad \text{for } \chi_1 = 0 \quad (6)$$

$$N_A \Delta G = A \left(\frac{L_c - L_a}{xL_c} \right) R v_2' \quad (7)$$

The calculated values of v_2' and $N_A \Delta G$ were summarized in Table I.

Numerical values of v_2' in the highest temperature ranges in the cooling and heating procedures were considerably large comparing with v_2' prior to cooling. v_2' in the highest temperature range in the cooling procedure was slightly larger than that in the heating procedure. Therefore, in the initial stage of the cooling procedure, presumably, the solvent in the amorphous regions is excluded from amorphous regions and thus resulting in the crystallization of amorphous regions.

With increasing relative shrinkage which resulted from the heat-treatment at a temperature above 100°C, v_2' in the highest temperature ranges in both the cooling procedure and heating procedure increased and $N_A \Delta G$ decreased.

For sample 1 (D in Fig. 6) which heat-treated at 96°C, v_2' in the highest temperature ranges in both cooling and heating procedure was slightly larger than that of sample 2 (C in Fig. 6) which heat-treated at 100°C. On the other hand, $N_A \Delta G$ of sample 1 in the cooling

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 Table I-A. v_2' and $N_A \Delta G$ in the Cooling and Heating Procedures for Polypropylene Fiber in Toluene

Sample	T_h (°C)	T_m (°C)	$1/S$ at T_h	$1/S$ at T_m	Procedure	Temp. Range (°C)	χ_1	v_2'	$N_A \Delta G$ (cal/mol)
1	96	104	3.906	1.773	Cooling	96- 76	0	0.9997	0.628
							0.5	0.9997	0.628
							1.0	0.9997	0.628
					Heating	80- 92	0	0.9995	0.785
							0.5	0.9995	0.785
							1.0	0.9995	0.785
2	100	105	2.716	1.701	Cooling	100- 85	0	0.9994	0.693
							0.5	0.9994	0.693
							1.0	0.9994	0.693
					Heating	88- 98	0	0.9993	0.764
							0.5	0.9993	0.764
							1.0	0.9993	0.764
3	100	107	2.540	1.810	Cooling	100- 84	0	0.9996	0.564
							0.5	0.9996	0.564
							1.0	0.9996	0.564
					Heating	90-100	0	0.9995	0.641
							0.5	0.9995	0.641
							1.0	0.9995	0.641
4	100	108	2.024	1.789	Cooling	100- 83	0	0.9997	0.433
							0.5	0.9997	0.433
							1.0	0.9997	0.433
					Heating	95-105	0	0.9994	0.638
							0.5	0.9994	0.638
							1.0	0.9994	0.638
5	102	107	1.815	1.596	Cooling	102- 83	0	0.9999	0.270
							0.5	0.9999	0.270
							1.0	0.9999	0.270
					Heating	97-105	0	0.9996	0.494
							0.5	0.9996	0.494
							1.0	0.9996	0.494

T_h : temperature of heat-treatment, T_m : melting temperature in toluene

procedure is slightly smaller and v_2' in the heating procedure is slightly larger than that of the sample 2 (C in Fig. 6).

In lower temperature range, however, v_2' and $N_A \Delta G$ could not be estimated because C became negative value. C should be always a positive constant. If C is a negative constant, then Eqs. (3) and (4) can not be applied to the relation between $1/S$ and $1/T'$ (straight line portions).

Table I-B. v'_2 and $N_A\Delta G$ in the Heating Procedure Prior to Cooling for Polypropylene Fiber in Toluene

$1/S$ at T_m	Procedure	Temp. Range (°C)	χ_1	v'_2	$N_A\Delta G$ (cal/mol)
1.650	Heating	75 - 105*	0	0.9755	18.488
			0.5	0.9752	18.482
			1.0	0.9749	18.477

* $T_m=105^\circ\text{C}$

However, even in the case that C is a negative constant, if Eq. (8), derived by separating the Gibbs free energy difference $N_A\Delta G$ in Eq. (1) into enthalpy and entropy terms and by rearranging Eq. (1), is applied to these straight line portions, then the shrinkage behaviors in the lower temperature range indicating straight line portions may be taken into account theoretically.

$$\frac{1}{S} = \frac{xL_c}{(L_c - L_a)v'_2 k} \{ (h_u - h_x) + f(\alpha - 1) \} \left(\frac{1}{T} \right) - \frac{xL_c}{(L_c - L_a)v'_2} \left\{ \frac{(s_u - s_x)}{k} + (1 - v'_2) - \chi_1(1 - v'_2)^2 \right\} \quad (8)$$

In such case, A and C are, respectively, represented by the following equations.

$$A = \frac{xL_c}{(L_c - L_a)v'_2 k} \{ (h_u - h_x) + f(\alpha - 1) \} \quad (9)$$

$$C = \frac{xL_c}{(L_c - L_a)v'_2} \left\{ \frac{(s_u - s_x)}{k} + (1 - v'_2) - \chi_1(1 - v'_2)^2 \right\} \quad (10)$$

Therefore, if C is a negative constant, then, $\{ (h_u - h_x) + f(\alpha - 1) \}$ and, further, $[-(s_u - s_x) - k\{(1 - v'_2) - \chi_1(1 - v'_2)^2\}]$ may become positive constants.

Thus, in the low temperature range, special deformation due to the disappearance and appearance of the pseudo cross-links in amorphous regions should be further take into consideration in addition to the deformation by the partial melting and recrystallization of crystalline regions.

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