

Thermal Shrinkage of Polyethylene Terephthalate Fibers Swollen in Acetone-Water Mixtures

Nobuyuki TANAKA* and Akio NAKAJIMA**

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Thermal shrinkage of fibrous polymer, of which the amorphous fraction λ is constant, was investigated by assuming the presence of pseudo cross-linkages in amorphous regions. A relationship derived between the relative shrinkage and temperature based on Flory's theory on melting of cross-linked polymers was applied to polyethylene terephthalate fibers in acetone-water mixtures. Mechanism of shrinkage in the presence of cross-links and the effect of the treatment in acetone-water mixtures were discussed.

INTRODUCTION

Structural changes of fibrous polymer chains may be caused by treatment in swelling agents. Especially, in amorphous regions, the chain conformation is changed by swelling treatment¹⁾ and the chain conformation is further varied by the presence of pseudo cross-links, the change in orientation of chains, and the intermolecular forces, during the heating process after swelling treatment.

In this paper, we'll concern with the thermal shrinkage of a fibrous crystalline polymer in the temperature range in which the amorphous fraction λ is constant.

Here, we assumed the presence of pseudo cross-links in amorphous regions. For such system, a relationship was obtained between the relative shrinkage and temperature by using Flory's theory on melting of cross-linked polymers.²⁾ By applying the relation, mechanism of thermal shrinkage and effect of swelling treatment will be discussed for polyethylene terephthalate fibers treated in acetone-water mixtures.

THEORETICAL TREATMENT

On the basis of Flory's theory,²⁾ the thermal shrinkage, of pseudo cross-linked fibrous polymers with constant λ , can be theoretically understood by the following way.

The melting temperature $T_{m,i}$ of an isotropic fiber without tension is represented by

$$\frac{1}{T_{m,i}} = \frac{\Delta S + \Delta S_x + \Delta S_{el}}{\Delta H} \quad (1)$$

This equation is rewritten as

* 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.

$$\frac{\Delta g}{T_{m,i}} = \Delta S_x + \Delta S_{el} \quad (2)$$

where

$$\Delta g = \Delta H - T_{m,i} \Delta S$$

In these equations, ΔH and ΔS are, respectively the enthalpy and entropy of fusion per mole chains in the absence of cross-links, ΔS_x the entropy change per mole chains owing to the presence of pseudo cross-links, and ΔS_{el} the elastic entropy change per mole chains.

The elastic entropy change ΔS_{el} is obtained from Eq. (5) in our previous paper³⁾ when $L_a = L_i$ (isotropic length) and $\lambda = 1$, but it is negligibly small. ΔS_x is given by the equation²⁾

$$\Delta S_x = k\nu \left(\frac{1}{2} \ln Q - \frac{9}{4} + \frac{3}{4} \ln \frac{\nu}{N_s} \right) \quad (3)$$

where, Q is a dimensionless quantity of the order of unity, N_s the number of statistical segments in a network, and ν the number of pseudo cross-linked units. Eqs. (2) and (3) lead to

$$\frac{\Delta g}{T_{m,i}} = k\nu \left(\frac{1}{2} \ln Q - \frac{9}{4} + \frac{3}{4} \ln \frac{\nu}{N_s} \right) \quad (4)$$

Letting $-(9/4) + (1/2) \ln Q = A$, Eq. (4) is expressed as

$$\frac{\Delta g}{T_{m,i}} = k\nu \left(A + \frac{3}{4} \ln \frac{\nu}{N_s} \right) \quad (5)$$

Therefore, letting $T_{m,i} = T$, the number of pseudo cross-linked units is given by the equation

$$\nu = N_s B \exp \frac{4\Delta g}{3\nu kT} = N_s B \exp \frac{4N_s \Delta g}{3\nu RT} \quad (6)$$

where

$$B = \exp \left(-\frac{4}{3} A \right) = \exp \left[\frac{4}{3} \left(\frac{9}{4} - \frac{1}{2} \ln Q \right) \right]$$

Further, the relation between the relative shrinkage S and the number of pseudo cross-links ν is represented by

$$S = \left(1 - \frac{L_a}{L_c} \right) \lambda = \left(1 - \sqrt{\frac{\nu m}{V}} \sqrt{\nu} \right) \lambda = (1 - C\sqrt{\nu}) \lambda \quad (7)$$

where

$$C = \sqrt{\frac{\nu m}{V}} \quad (8)$$

ν is the specific volume of amorphous regions, m the weight of a segment, and V the total volume of amorphous regions. Eq. (7) leads to

$$\left(1 - \frac{S}{\lambda} \right)^2 = C^2 \nu. \quad (8)$$

Accordingly, the relation between S and T is given by

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$$\ln\left(1 - \frac{S}{\lambda}\right) \ln\left(\frac{L_a}{L_c}\right) = \frac{1}{2} \ln(C^2BN_s) + \frac{2N_A \Delta g}{3\nu RT} \quad (9)$$

Eq. (9) is further rewritten as

$$S = \lambda \left\{ 1 - D \exp\left(\frac{2N_A \Delta g}{3\nu RT}\right) \right\} \quad (10)$$

where

$$D = \exp\left\{\frac{1}{2} \ln(C^2BN_s)\right\}$$

EXPERIMENTAL

(i) Samples

The sample used here is polyethylene terephthalate fiber of 150 denier. This sample is just the same as that used in our previous paper.²⁾ The degree of polymerization, x , of this sample was estimated as $x=1520$, from intrinsic viscosity value in a 1:1 (w/w) phenol-*m*-cresol mixture at 20°C according to the equation: $[\eta] = 1.7 \times 10^{-6} M_n + 0.006$, in which M_n denotes the number average molecular weight. The sample is drawn fiber and its density ρ at 25°C is $\rho=1.3890$.

This sample was swollen in acetone-water mixtures for 24 hr. at 20°C, and then the thermal shrinkage was measured for thus swollen samples. The acetone concentrations in acetone-water mixtures are 0, 25, 50, 75, and 100%. The sample treated in water (0% acetone) was used as a reference. The length of sample treated in an acetone-water mixture for 24 hr. was almost equal to that treated for 7 days in the same solution at 20°C.

For measurements of orientation of crystallites, density, and birefringence, samples, heated without tension at a heating rate of 3.0°C/min up to given temperatures and kept 1 hr. at these temperatures then quenched down to room temperature, were used.

(ii) Measurement of Thermal Shrinkage

Samples were kept for 1.5 hr. at given constant temperatures by suspending a weight of 2.0 mg/d, and the length of the sample at that temperature was measured by a cathetometer.

Since 2% relative shrinkage is expected at room temperature for original fiber, the corrected value of S was obtained³⁾ by adding 2% to the relative shrinkage calculated by using the observed length of the fiber at room temperature.

(iii) Measurement of Orientation of Crystallites

X-ray measurements were performed with a Rigaku Denki apparatus. The degree of orientation F_c of the (100) plane of crystallite was determined from the half-width H of the intensity curve on the azimuthal scanning of the (100) reflection according to the equation:

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

(iv) Measurement of Birefringence

A polarized microscope equipped with a Berek compensator and a Na-lamp was used to investigate the birefringence of samples.

RESULTS AND DISCUSSION

The crystallinity of a sample treated in an acetone-water mixture was almost equal to that of the sample treated in a dry oven at temperatures up to 140°C. The amorphous fraction λ of these samples was about 0.53 at 25°C (see Fig. 1). Therefore, it may be assumed that the thermal shrinkage up to 140°C is caused mainly by the change of fine structure of amorphous regions. Thus Eq. (9) is applied to samples heat-treated below 140°C. From Figs. 2 and 3, it is also pointed out that the orientation of crystallites and the birefringence of unswollen fiber were almost constant in the temperature range up to 140°C.

Figure 4 shows the relation between $\ln\{1-(S/\lambda)\}$ and $1/T$. Each curve obtained may be represented by a set of straight lines of different slopes. Slopes of straight lines after the refraction points (low temperature range) for samples treated in 25, 50, 75, and 100%-acetone mixtures were almost the same and slightly lower than that for sample treated in water (0%-acetone). Before refraction points (high temperature range), slopes of straight lines were almost the same for all the samples used here; *i.e.*, for both unswollen and swollen samples.

The temperature corresponding to refraction point of the curve, and Gibbs free energy, $4gN_A/\nu$, per mole of cross-linked units, for temperature ranges before and after the refraction point calculated from the slopes of straight lines, were listed in Table 1.

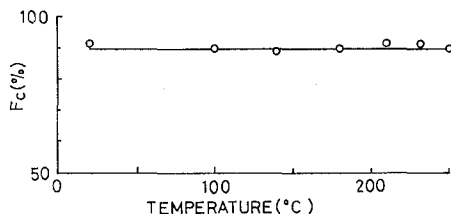


Fig. 1. Density of heat-treated sample *vs.* temperature of heat-treatment for polyethylene terephthalate fibers.

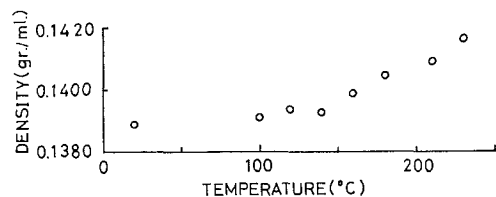


Fig. 2. Degree F_c of orientation of crystallites *vs.* temperature of heat-treatment for polyethylene terephthalate fibers.

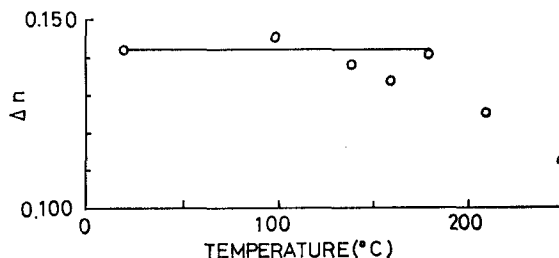


Fig. 3. Birefringence *vs.* temperature of heat-treatment for polyethylene terephthalate fibers.

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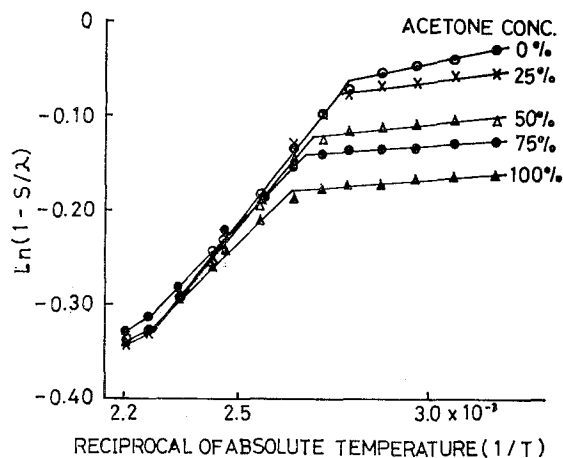


Fig. 4. Relation between $\ln[1 - (S/\lambda)]$ and reciprocal temperature $1/T$ for polyethylene terephthalate fibers treated in acetone-water systems.

Table 1. Refraction Point ($^{\circ}\text{C}$), and Gibbs Free Energy $\Delta gN_A/\nu$ for Polyethylene Terephthalate Fibers.

Acetone % in acet.- water mixture	Refraction point ($^{\circ}\text{C}$)	$\Delta gN_A/\nu$ (cal/mole)	
		High temp. range	Low temp. range
0	85.7	1550.0	298.0
25	89.3	1550.0	163.9
50	98.8	1490.4	119.2
75	100.6	1251.9	104.3
100	105.8	1192.3	119.2

These refraction point ($^{\circ}\text{C}$) may correspond to the glass transition temperatures of polyethylene terephthalate in these systems. If we regard that $\Delta gN_A/\nu$ is constant independent of acetone concentration of the mixture, then Δg should be proportional to the number, ν , of pseudo cross-linked units. As obvious from Table 1, the refraction point shifted to higher temperature with increasing acetone concentration. Further, above refraction temperature (high temperature range), the relative shrinkages of swollen samples were almost the same as that of unswollen (0%-acetone) sample. These results may suggest that pseudo cross-links in amorphous regions of swollen samples which disappear by heat-treatment above refraction temperature may be already affected by the treatment in acetone-water mixture at 20°C . Therefore, the thermal shrinkage, in the temperature range where λ is constant, seems to be caused by the decrease in the number of pseudo cross-links in amorphous regions, because the birefringence and the degree of orientation of crystallites are almost invariant in this temperature range.

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