

Partial Melting, Recrystallization and Thermal Shrinkage of Polyethylene Terephthalate Fibers

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Thermal shrinkage was understood theoretically by partial melting of crystalline regions on the basis of the theory of melting of polymer. Experimental results on the relation between the relative shrinkage and temperature for polyethylene terephthalate fibers were discussed according to the theoretical expression reported in our previous paper.¹⁾

INTRODUCTION

As reported in the previous papers,¹⁻³⁾ thermal shrinkage can be understood theoretically by partial melting of crystalline regions and transition due to pseudo cross-links in amorphous regions, on the basis of the theories^{4,5)} of melting of polymers. It was assumed, in our previous experimental condition,¹⁾ that the effect of recrystallization in amorphous regions during the heating process could be neglected because the heating rate was comparatively fast in the measurement of thermal shrinkage.

In this work, whereas, the thermal shrinkage of polyethylene terephthalate fibers was measured under very slow heating rate, so that the recrystallization may not be neglected. The theoretical treatment of shrinkage reported in the previous paper¹⁾ was adopted to discuss the experimental results. In connection with the thermal shrinkage data, the differential thermal analysis (DTA) data were also investigated.

EXPERIMENTAL

Sample

For measurements of thermal shrinkage and DTA, polyethylene terephthalate (PET) yarns processed by the following way were used. Undrawn yarns (278 D, 35 fils), supplied by Toyo Spinning Co. Ltd., were drawn by 4.4 times of their undrawn length at 80°C, relaxed for 10 minutes, and then cooled down to room temperature.

The degree of polymerization α of the sample was estimated, from the intrinsic viscosity $[\eta] = 0.59$ in a 6 : 4(w/w) phenol-tetrachloroethane mixture at 20°C according to the equation $[\eta] = 3.0 \times 10^{-4} M_n^{0.77}$, as $\alpha = 98.92$.

Measurement of Thermal Shrinkage

Specimens were heated, by suspending a weight of 4.56 mg/d, at a heating rate of

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0.435°/min, and the change of the sample length was detected by a displacement meter and recorded on a X-Y recorder. For the original length L_c to estimate the relative shrinkage, the length of sample drawn by 4.4 times was used. The change of the sample length in the temperature range above 250°C was measured under no tension, because the measurement of sample length under tension was impossible above 250°C.

Differential Thermal Analysis

Thermal behavior of the sample was investigated by means of a DTA apparatus manufactured by Shimadzu Seisakusho at a heating rate of 10°/min. As the standard substance, α -Al₂O₃ was used.

RESULTS AND DISCUSSION

The relation between the relative shrinkage S and the temperature for fibrous polymer derived in our previous paper¹⁾ is given by

$$\frac{1}{S} = \frac{xL_c \{ (h_u - Ts_u) - (h_x - Ts_x) + f(a-1) \}}{k(L_c - L_a)} \frac{1}{T} - \frac{1}{x - \zeta + 1} \frac{xL_c}{L_c - L_a} \quad (1)$$

L_c : length of sample in totally crystalline state.

L_a : length of sample in totally amorphous state.

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.

f : force

a : drawing ratio

ζ : length of a crystallite in number of units.

k : Boltzmann's constant.

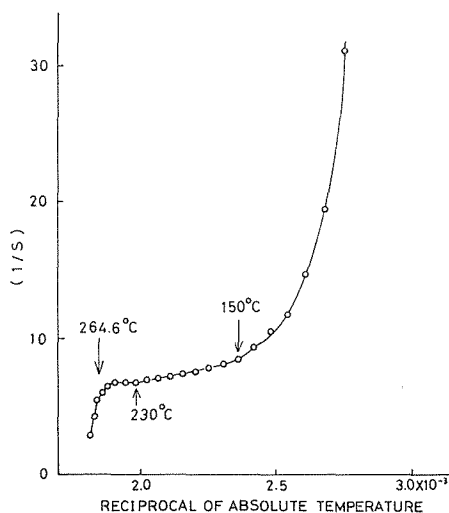


Fig. 1. Relation between the reciprocal relative shrinkage $1/S$ and the reciprocal absolute temperature $1/T$ for polyethylene terephthalate yarns.

Figure 1 shows the relation between the reciprocal relative shrinkage S and the reciprocal absolute temperature for PET sample. The curve obtained is not composed of a set of straight lines of different slopes but a smoothed curve.

In the temperature range between 150.0 and 230°C, the smooth curve may be approximated by a straight line, and the second term of the right-hand side of eq. (1) is nearly equal to -1.5 .

The temperature at which shrinkage just begins is almost equal to the drawing temperature, 80°C (see Fig. 2). In the temperature range from 80 to 150°C, it may be assumed²⁾ that the thermal shrinkage of the sample is accompanied by disappearance of pseudo cross-links in amorphous regions and, in addition, the degree of crystalline orientation, in this case, is unchanged up to 264.6°C.

Above 230°C, there is a temperature region at which $1/S$ is constant against $1/T$. If L_c , L_a , and ζ are assumed to be constant in this temperature range, then the right-hand side of the following equation, derived by rearranging eq.(1), should be constant.

$$\frac{(h_u - Ts_u) - (h_x - Ts_x) + f(\alpha - 1)}{T} = k \left\{ \frac{(L_c - L_a)}{xL_c} \frac{1}{S} + \frac{1}{x - \zeta + 1} \right\} \quad (2)$$

$$= k C = \text{constant} \quad (2')$$

This means that the Gibbs free energy term $[(h_u - Ts_u) - (h_x - Ts_x) + f(\alpha - 1)]$ is proportional to the absolute temperature.

Further, if $f=0$ or $\alpha=1$, and let the ratio of $(h_u - h_x)$ to $(s_u - s_x)$ be T_m^* :

$$(h_u - h_x)/(s_u - s_x) = T_m^* \quad (3)$$

then,

$$\frac{1}{T} - \frac{1}{T_m^*} = \frac{R}{N_A(h_u - h_x)} \left\{ \frac{(L_c - L_a)}{xL_c} \frac{1}{S} + \frac{1}{x - \zeta + 1} \right\} = \frac{R}{N_A(h_u - h_x)} C \quad (4)$$

According to Fig. 1, above 264.6°C, $1/S$ decreased abruptly against $1/T$, though the

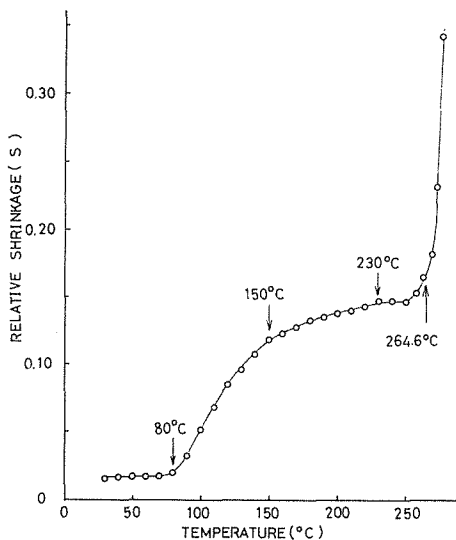


Fig. 2. Relation between the relative shrinkage S and the absolute temperature T for polyethylene terephthalate yarns.

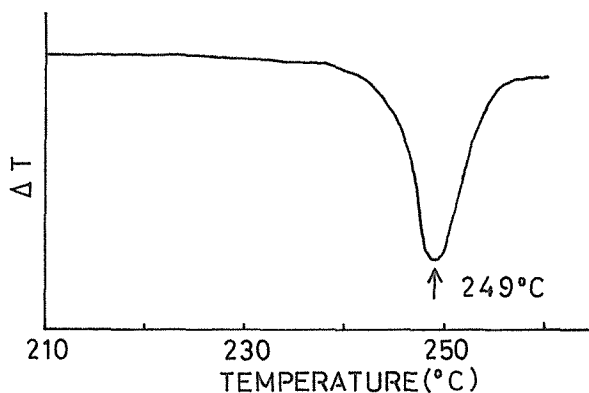


Fig. 3. Differential thermal analysis curve for polyethylene terephthalate.

melting temperature estimated by means of DTA at a heating rate of $10^\circ/\text{min}$ was 248.8°C (see Fig. 3). This difference in melting temperature may be attributed to the difference in heating rate for both measurements, because the heating rate in shrinkage measurement was very slow compared with that in DTA measurement. Thus, recrystallization in amorphous regions might not be neglected during the measurement of shrinkage. According to eq. (4), the melting temperature T_m^* may be increased with increasing temperature for shrinkage measurement, if $(h_u - h_x)$ is regarded as constant. The temperature (264.6°C) at which $1/S$ decreased abruptly is approximately equal to the melting temperature (267°C) cited in the literature.⁶⁾

If we assume that $\lambda=1$ at $T=267.0^\circ\text{C}$, then the relative shrinkage is written as

$$S = (L_c - L_a) / L_c \quad (5)$$

Substitution of eq. (5) in eq. (4) leads to the following equations.

$$\frac{1}{T} - \frac{1}{T_m^*} = \frac{R}{N_A(h_u - h_x)} \left(\frac{1}{x} + \frac{1}{x - \zeta + 1} \right) \cong \frac{2R}{N_A(h_u - h_x)x} \quad (6)$$

$$N_A(h_u - h_x) = \frac{2R}{x} \frac{T T_m^*}{(T_m^* - T)} \quad (7)$$

Finally, $N_A(h_u - h_x)$ is calculated from eq. (7) by assigning that $T=540.0^\circ\text{K}$ and $T_m^*=554.0^\circ\text{K}$, as

$$N_A(h_u - h_x) = 858.54 \text{ cal/mole}$$

In this calculation, the equilibrium melting temperature 554.0°K obtained by Ikeda and Mitsubishi⁷⁾ was used for T_m^* .

Since the heat of fusion, $N_A h_u$, of polyethylene terephthalate is known⁹⁾ as 5500 cal/mole, $N_A h_x$ is also estimated.

$$N_A h_x = 5500 - 858.54 = 4641.46 \text{ cal/mole}$$

The value of $N_A h_x$ may be dependent on both the intermolecular forces in the amorphous regions and the degree of orientation of amorphous chains.

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