

Polymer Communication

Depression of glass transition temperature due to the chain extension in glassy state

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Abstract

The influence of the chain extension in the glassy state on the glass transition temperature was investigated for poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN) fibers. The extended samples were prepared by drawing at just above the glass transition temperature and subsequently cooling to the room temperature under a constant length condition. The glass transition temperature was measured using differential scanning calorimeter without externally applied stress to the sample. The depression of glass transition temperature with increasing the extension ratio was observed for both PET and PEN fibers. An equation for the depression of glass transition temperature is derived by modifying the DiMarzio's theory and applied to the experimental data. In lower extension for PET fiber, the equation predicts successfully the depression of glass transition temperature in accordance with the empirical result. However, for the PEN fiber and the highly stretched PET fiber, the empirical data deviates from the prediction, because of the crystallinity increment of the fiber during the drawing process. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Glass transition temperature; Chain extension; Glassy state; Entropy

1. Introduction

The glass transition of polymers is affected by various molecular and thermodynamic parameters, such as molecular weight, chain flexibility, intermolecular forces, and pressure, etc. [1]. Among these parameters, chain extension has attracted little attention, because the effect is not large. DiMarzio [2] proposed an equation for the influence of the chain extension in the rubbery state on the glass transition, and applied successfully the theory to the experimental data for cross-linked rubbers. This equation, based on the statistical theory of rubber elasticity in which the extension decreases the entropy of the chains in rubbery state, predicts the increase of glass transition temperature as a function of the extension ratio. Hence, in order to observe this phenomenon, it is necessary to apply the stress to the sample.

In general, the chain extension or orientation is developed during processing stage for fibers and extruded products, and frozen-in in the glassy state, resulting in a decrease of entropy in glassy state. Particularly, the chain conformation in fibers deviates far from the unstrained one. Therefore, in this Communication, the effect of the chain extension in the glassy state on the glass transition temperature was

investigated for poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN) fibers. In addition, the empirical data was analyzed based on the similar concept to the DiMarzio's theory [2].

2. Experimental

PET was supplied by Kolon Ind. PEN was prepared from dimethyl naphthalate and ethylene glycol by melt polycondensation, which is described in detail elsewhere [3]. The weight-average molecular weights of PET and PEN, measured by the laser light-scattering method, was 3.93×10^4 and 2.03×10^4 g/mol, respectively.

The undrawn fiber was prepared by extruding the PET and PEN melts through a capillary die mounted on a Kayeness capillary rheometer (model 8052) at 285°C. The die had a diameter of 0.38 mm and length/diameter ratio of 67. The filament was extruded in air at room temperature and collected by a take-up apparatus. The spin-draw ratio, take-up speed over extrusion speed, was 30. The fibers were drawn with several extension ratios just above the glass transition temperatures (83°C for PET fiber and 128°C for PEN fiber) to minimize plastic deformation and additional crystallization during the drawing process, subsequently

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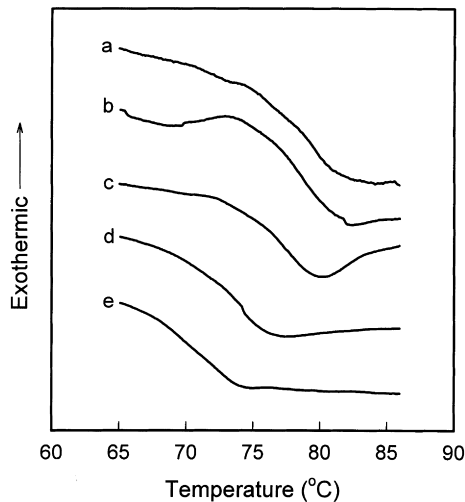


Fig. 1. DSC curves of PET in the glass transition region for: (a) chip; (b) undrawn fiber, and drawn fibers with (c) $\lambda = 2$; (d) $\lambda = 3$; and (e) $\lambda = 4$.

cooling to the room temperature under constant length condition.

The glass transition temperature was measured by using Du Pont 910 differential scanning calorimeter (DSC) and heating scan was conducted at 10°C/min. The crystallinity of the fiber was calculated by:

$$\text{crystallinity(\%)} = \frac{\Delta H_f - \Delta H_c}{\Delta H_f^0} \times 100, \quad (1)$$

where ΔH_f is the heat of fusion and ΔH_c the heat of cold-crystallization, obtained from the DSC scan curve of the fiber sample. ΔH_f^0 is the heat of fusion for 100% crystalline phase: 140 J/g for PET and 103 J/g for PEN [4].

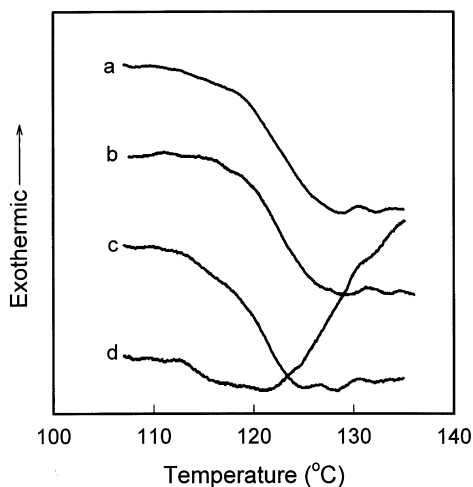


Fig. 2. DSC curves of PEN in the glass transition region for: (a) chip; (b) undrawn fiber, and drawn fibers with (c) $\lambda = 2$; and (d) $\lambda = 3$.

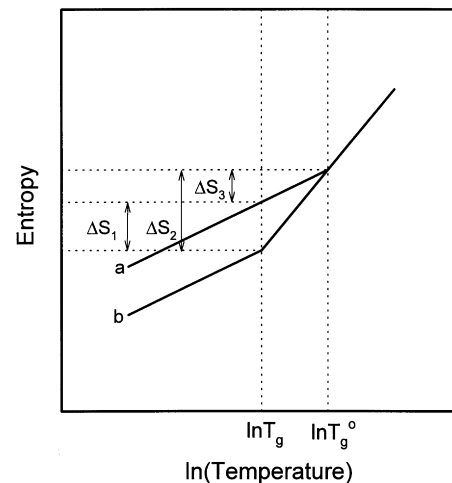


Fig. 3. Schematic illustration of the temperature dependence of entropy: (a) before extending; (b) after extending.

3. Results and discussion

Fig. 1 shows the DSC curves in the glass transition region for the PET chip, undrawn fiber, and drawn fibers. The glass transition temperature of the chip is almost equal to that of the undrawn fiber. This means that the chain extension may not be effectively developed during the spinning process in this study. Hence, the extension ratio of the undrawn fiber is considered to be unity. For the drawn fibers, the glass transition temperature tends to decrease with the increasing extension ratio. The glass transition temperature of the drawn fiber with $\lambda = 4$ is depressed by ca. 9°C with respect to the undrawn fiber. Fig. 2 shows the DSC curves in the glass transition region for the PEN chip, undrawn fiber, and drawn fibers. The glass transition temperature of the chip is almost equal to that of the undrawn fiber and the glass transition temperature of drawn fiber decreases with increasing the extension ratio, similar to the result for PET. The exothermic heat generated from 122°C in the fiber sample with $\lambda = 3$ is due to the cold-crystallization of PEN. The depression of glass transition temperature with the extension ratio can be explained as follows. The entropy-driven stress of the extended chains in rubbery state is stored in glassy state during the cooling process under a constant length condition. This residual stress in glassy state is exerted in the glass transition region during the DSC heating scan, which results in the depression of glass transition temperature. After passing through the glass transition region on DSC heating scan, the extended chains in glassy state are converted into the relaxed conformations, because there is no externally applied stress.

Based on the same framework of DiMarzio's theory [2], the equation for the depression of glass transition temperature is derived as follows. The temperature dependence of entropy for an amorphous polymer in the glass transition region follows a schematic diagram shown in Fig. 3 (curve a). The glass, transition temperature is defined as an

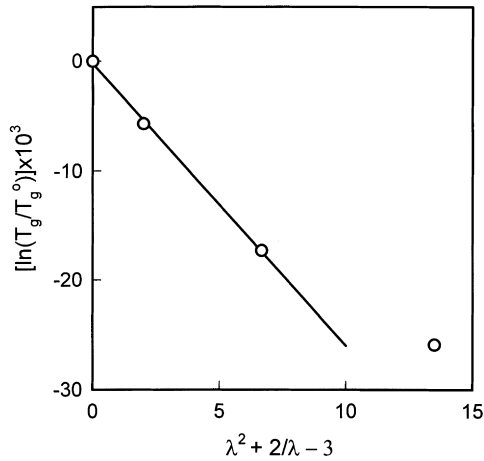


Fig. 4. Plot of $\ln(T_g/T_g^0)$ versus $(\lambda^2 + 2/\lambda - 3)$ for PET fiber.

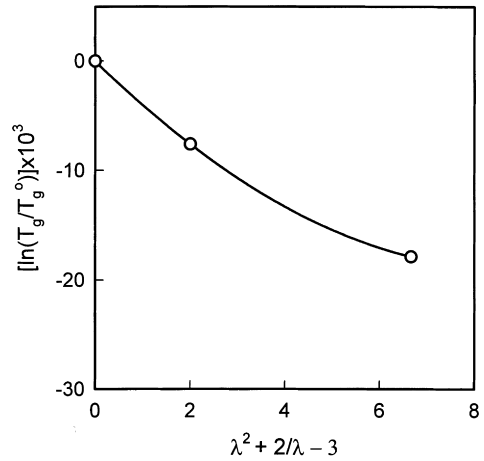


Fig. 6. Plot of $\ln(T_g/T_g^0)$ versus $(\lambda^2 + 2/\lambda - 3)$ for PEN fiber.

intersecting point of two distinct curves, which have different tangential slopes of C_p^G and C_p^R . Here C_p^G and C_p^R are the heat capacities in the glassy and rubbery states, respectively. The chain extension in the rubbery state decreases the entropy of the chains, and this entropy decrement may be stored in the glassy state after cooling the stretched sample below the glass transition temperature. On DSC heating scan, the entropy of the extended chains follows the curve b in Fig. 3. After passing through the glass transition region, the curve b coincides with the curve a, because the extended chains are relaxed. According to the statistical theory of rubber elasticity, the entropy change per mole of chains between cross-links is given by [5]:

$$\Delta S_1 = -\frac{R}{2} \left(\lambda^2 + \frac{2}{\lambda} - 3 \right), \quad (2)$$

where R is gas constant and λ the extension ratio. This expression is found on the Gaussian statistics of the chains, affine deformation, and incompressibility on deformation. The entropy decrement stored in the glassy state results in a depression of the glass transition temperature, as shown in

Fig. 3 (curve b). The glass transition temperatures, before and after extending, are denoted as T_g^0 and T_g , respectively. The entropy difference of the chains in the rubbery state between T_g^0 and T_g is expressed as:

$$\Delta S_2 = \frac{\bar{M}_c}{M_u} \int_{T_g^0}^{T_g} C_p^R d \ln T, \quad (3)$$

where \bar{M}_c is the number-average molecular weight between cross-links and M_u is the molecular weight of repeating unit. Similarly, for the chains in the glassy state:

$$\Delta S_3 = \frac{\bar{M}_c}{M_u} \int_{T_g^0}^{T_g} C_p^G d \ln T. \quad (4)$$

The relation $\Delta S_1 = \Delta S_2 - \Delta S_3$ yields:

$$T_g = T_g^0 \exp \left[-\frac{R}{2\Delta C_p} \frac{M_u}{\bar{M}_c} \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \right] \quad (5)$$

where $\Delta C_p = C_p^R - C_p^G$. It should be noted that in these expressions the heat capacities represent the values per mole of repeating units and are assumed to be independent

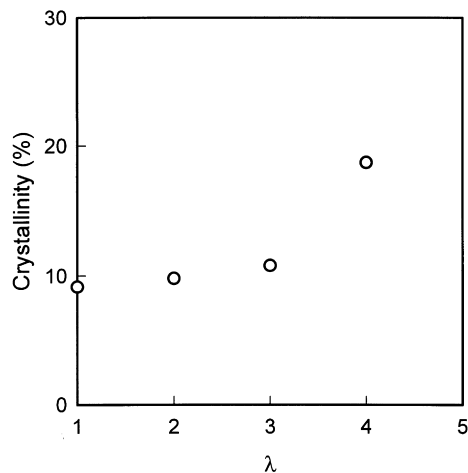


Fig. 5. Crystallinity change with the extension ratio for PET fiber.

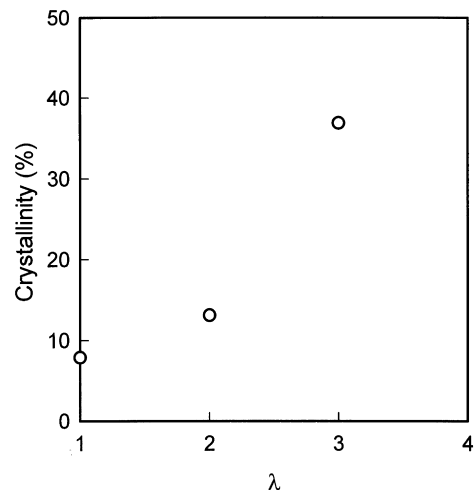


Fig. 7. Crystallinity change with the extension ratio for PEN fiber.

of temperature. Eq. (5) predicts the glass transition temperature as a function of extension ratio and can be also used to determine \overline{M}_c values for both physically and chemically cross-linked polymers. Eq. (5) is identical with the Eq. (21) in Ref. [2], excepting that a sign in the argument of the exponent in different. However, a major difference between the two equations is that Eq. (5) of this article expresses the depression of glass transition temperature due to the chain extension in glassy state, while Eq. (21) in Ref. [2] explains the increment of glass transition caused by the chain extension in rubbery state. The measurements of the increase of glass transition are exceedingly difficult, as an external stress must be applied to a sample to maintain stretched state of a sample. However, it is easy to measure the depression of glass transition temperature, because the method of sample preparation is simple and an external stress is unnecessary on measuring the glass transition temperature.

Eq. (5) can be rearranged as:

$$\ln\left(\frac{T_g}{T_g^0}\right) = -\frac{R}{2\Delta C_p} \frac{M_u}{\overline{M}_c} \left(\lambda^2 + \frac{2}{\lambda} - 3\right). \quad (6)$$

Assuming that ΔC_p remains constant during deformation, a plot of $\ln(T_g/T_g^0)$ against $(\lambda^2 + 2/\lambda - 3)$ must satisfies a linear relation. As shown in Fig. 4, in which the midpoints of the heat capacity changes in Fig. 1 are used as the T_g values, the linear relationship between $\ln(T_g/T_g^0)$ and $(\lambda^2 + 2/\lambda - 3)$ is satisfied for up to $\lambda = 3$. However, the data of $\lambda = 4$ deviates from the straight line. Fig. 5 shows the crystallinity change with the extension ratio for PET fiber. The crystallinity change up to $\lambda = 3$ is negligible, while the crystallinity of the fiber with $\lambda = 4$ is abruptly high. In linear crystalline polymers, chain entanglements and

crystals act as junction points of chains. Therefore, the increase of crystallinity induces the changes of both T_g^0 and \overline{M}_c , which might be the reason for the deviation from the linear relation. The \overline{M}_c value can be determined from the slope of the straight line in a plot of $\ln(T_g/T_g^0)$ against $(\lambda^2 + 2/\lambda - 3)$. Estimating from the line slope up to $\lambda = 3$ with $\Delta C_p = 77.8 \text{ J/mol/K}$ [4] and $M_u = 192.17 \text{ g/mol}$ leads to $\overline{M}_c = 3.99 \times 10^3 \text{ g/mol}$. In the present system, the \overline{M}_c means the number-average molecular weight between physical cross-links, such as chain entanglements and small crystallites formed during the spinning process. For the PEN samples, a linear relation is not satisfied (Fig. 6) and also the crystallinity depends strongly on the extension ratio (Fig. 7). Hence, it is inadequate to apply the theory to the systems, where additional crystallization occurs during the drawing process.

Acknowledgements

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