

# Study on thermal diffusivity of poly(ethylene terephthalate) and poly(ethylene naphthalate)

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Thermal diffusivity ( $\alpha$ ) of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN) was measured by an AC joule heating technique as a function of temperature from the solid to the liquid state;  $\alpha$  changed drastically at the glass transition and at crystallization. In a heating run on the quenched sample, an abrupt increase of  $\alpha$  immediately after the glass transition was observed, which corresponded to cold crystallization. The relationship between glass transition temperature ( $T_g$ ) and the change ratio of  $\alpha$  at the glass transition ( $\Delta\alpha/\alpha$ ) of PET and PEN deviated from that of amorphous polymers. A biaxial stretching of PET and PEN resulted in a lowering of  $\alpha$  vertical to the stretched direction. An upward shift of  $T_g$  and a reduced drop in  $\alpha$  at the glass transition ( $\Delta\alpha$ ) was also observed. © 1997 Elsevier Science Ltd.

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## INTRODUCTION

Poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN) are crystalline polymers which show a glass transition and cold crystallization above room temperature. In the polymer industry, these transition temperatures are utilized for the processing. For example, they make it possible to form PET bottles through the blow moulding process.

Viscoelastic<sup>1</sup> and thermal<sup>2</sup> properties of polymers are important factors in controlling and simulating the moulding process<sup>3</sup>. However, some of the thermal properties, such as thermal conductivity or thermal diffusivity in the practical temperature range, have not yet been completely understood. The reasons are the difficulties in applying the measurement techniques to the transitions and the liquid state of polymers. As for the thermal diffusivity of PET, the results by flash radiometry were reported in the temperature range below 200°C<sup>4-6</sup>.

In this paper, we investigate the thermal diffusivity of PET and PEN by an AC joule heating technique<sup>7,8</sup>, which has been developed in our laboratory, in a wide temperature range including two types of transitions and the liquid state. The influence of biaxial stretching on the thermal diffusivity is also discussed.

## EXPERIMENTAL

Samples used in this study are PET, PEN and a terpolymer of PET, kindly supplied by Mitsui Petrochemical Co. The intrinsic viscosities are 0.80, 0.55 and 0.72 dl g<sup>-1</sup>, respectively.

Two types of film were prepared for the measurements; non-stretched films and stretched films. The preparations were as follows. (1) Non-stretched films: sample pellets of PET and PEN were melted at 280°C and then extruded through a film gate to a chilled roll held at 20°C, on which the samples were wound as films with a thickness of 40–50  $\mu\text{m}$ . (2) Stretched films: the injection moulded sheets of PET and PEN with a thickness of 1 mm were stretched, respectively, under the following conditions—(i) the injection moulded sheet of PET was annealed at 110°C and then stretched at a constant speed of 1.5 m min<sup>-1</sup> biaxially to a draw ratio of 3.5  $\times$  3.5; (ii) the injection moulded sheet of PEN was annealed at 150°C and stretched at a speed of 1.5 m min<sup>-1</sup> biaxially to a draw ratio of 3.8  $\times$  3.8. The thickness of the stretched films of PET and PEN was ca 40  $\mu\text{m}$ .

The sample film was cut into 1 cm  $\times$  1 cm pieces, and thin gold layers of 1 mm  $\times$  6 mm area were sputtered on both surfaces of the film. The gold layers, attached to both surfaces of the sample film, were used as a thermal wave heater operated by joule heating and as a sensor for detecting the temperature wave. The electrical resistance of the gold layer was controlled at approximately 50  $\Omega$ . Copper lead wires were attached to the surfaces of each gold layer. To avoid deformation by shrinkage or melting, samples were mounted with inorganic adhesives<sup>8</sup>.

The temperature wave diffuses across the sample in the direction of the thickness. The temperature variations caused by the temperature wave on the rear surface were detected by the gold layer sensor as a variation in the resistance which was analysed using an NF-type 5610B lock-in amplifier. The apparatus for the thermal diffusivity measurement is described in ref. 8.

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The relationship between the frequency of the generated thermal wave and the phase delay of the signal at the rear surface is expressed by<sup>7</sup>

$$\Delta\theta = \sqrt{(\pi f/\alpha)} \cdot d + \pi/4 \quad (1)$$

where  $\Delta\theta$  is the phase delay,  $\alpha$  is the thermal diffusivity,  $f$  is the frequency of temperature wave,  $d$  is the sample thickness, and  $\pi/4$  is the instrumental constant.

From the gradient in the plot of  $\Delta\theta$  and  $\sqrt{f}$ , thermal diffusivity  $\alpha$  can then be obtained if the thickness is known by another method. Since this method is based on the phase shift measurement, the influence of the backing material such as a glass plate, etc., can be neglected.

The temperature for the measurement is in the range 30–280°C. The temperature scanning speed in the heating and the cooling run is 1°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of  $\alpha$  of non-stretched PET films in the first heating and following cooling runs. In the first heating run,  $\alpha$  decreases with increasing temperature and a rapid drop is observed at 80–90°C corresponding to the glass transition. The glass transition temperature, defined as  $T_{gm}$  (the midpoint temperature during the glass transition as described in ref. 9), is 84°C. At 100°C, immediately after the glass transition, an abrupt rise in  $\alpha$  is observed, which is considered to be the cold crystallization of PET. After the cold crystallization has finished,  $\alpha$  decreases with increasing temperature again. When the temperature goes up to 250°C, another drop in  $\alpha$ , corresponding to the melting of the crystallite, is observed.

In the cooling run illustrated in Figure 1, crystallization of PET from the liquid state above the melting temperature is observed. At temperatures below 230°C,  $\alpha$  increases monotonically with decreasing temperature, and a step change is observed in the glass transition region. In this case, the glass transition temperature defined as  $T_{gm}$  is 95°C, which is 11°C higher than the  $T_{gm}$  observed in the first heating run.

Here,  $\Delta\alpha$  is introduced, which is defined as the change in  $\alpha$  at the glass transition. In the first heating run,  $\Delta\alpha$  is defined as the difference between the extrapolated lines of  $\alpha$  in the glassy state and the liquid state immediately before the occurrence of cold crystallization<sup>9</sup>. On the other hand, the cooling run,  $\Delta\alpha$  is defined as the

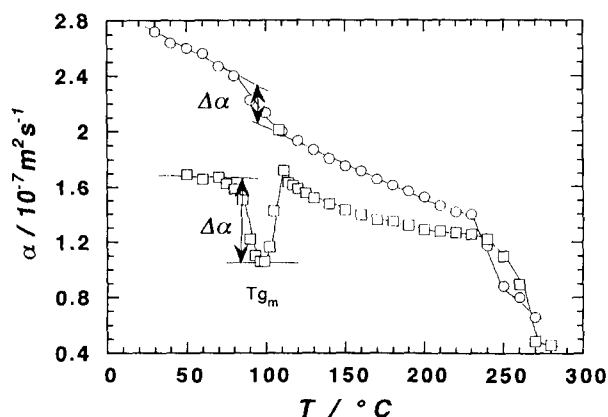


Figure 1 Temperature dependence of thermal diffusivity of PET: heating (□) and cooling (○)

difference between the glassy state and the rubbery state including the crystalline state below the crystallization temperature.  $\Delta\alpha$  decreases in the cooling run rather than in the first heating run. The cooling rate with this measurement is about 1°C min<sup>-1</sup>, much smaller than that of the film extruding process, so compared with  $\alpha$  in the first heating run, the increase in the value of  $\alpha$  and the decrease in  $\Delta\alpha$  in the cooling run are caused by the difference in crystallinity<sup>7\*</sup>.

Figure 2 shows the temperature dependence of  $\alpha$  of non-stretched PEN in the first heating and the following cooling run. The thermal diffusivity of PEN has not been examined by another method, but the results by the AC joule heating technique show a tendency similar to that of PET shown in Figure 1. The glass transition temperature defined as  $T_{gm}$  is observed at 125°C and the cold crystallization is clearly observed in the temperature range 150–170°C in the heating run. In the cooling run the change of  $\alpha$  in the glass transition is unclear, but the absolute value of  $\alpha$  is higher than in the first heating run. This result also shows a tendency similar to that of PET. The upward shift of  $T_g$  and the decrease in  $\Delta\alpha$  in the cooling run indicate that the change of  $\alpha$  in the glass transition depends on the crystallinity of PET and PEN.

In Figure 3 the ratio  $\Delta\alpha/\alpha$  (at  $T_{gm}$ ) is plotted against the  $T_{gm}$  of amorphous polymers. The  $\Delta\alpha/\alpha$  of PET and PEN obtained in the first heating run of the quenched sample highly deviate from the linear relationship in the amorphous polymers. On the other hand, after the crystallization in the cooling run, the decrease in  $\Delta\alpha/\alpha$  of PET is observed from the linear relationship. These results indicate that the general relationship of  $\Delta\alpha/\alpha$  and  $T_g$  of amorphous polymers is not applicable to the glass transition of semi-crystalline polymers such as PET and PEN.

Heat conduction in polymer materials is due to the transmission of the elastic wave of phonons, which is described as equation (2) by the Debye and Eiermann model<sup>10–12</sup>:

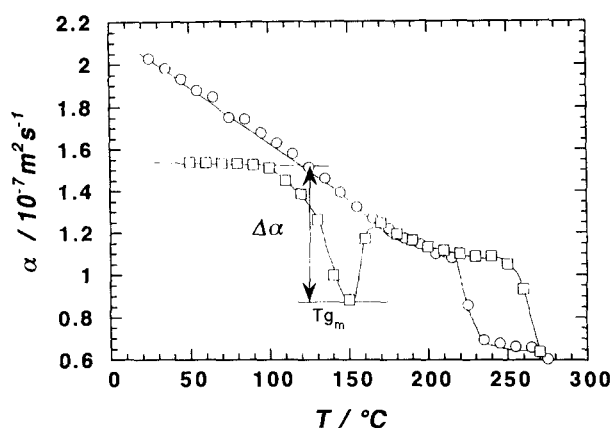
$$\lambda = (1/3) \cdot C_v \cdot \rho \cdot u \cdot l \quad (2)$$

where  $\lambda$  is the thermal conductivity,  $C_v$  is the heat capacity at constant volume,  $\rho$  is the density,  $u$  is the propagation speed of lattice vibration (sound velocity), and  $l$  is the mean free path of phonons. The relationship between thermal conductivity and thermal diffusivity ( $\lambda = \alpha \cdot C_p \cdot \rho$ ;  $C_p$  = the heat capacity at constant pressure) leads to the equation:

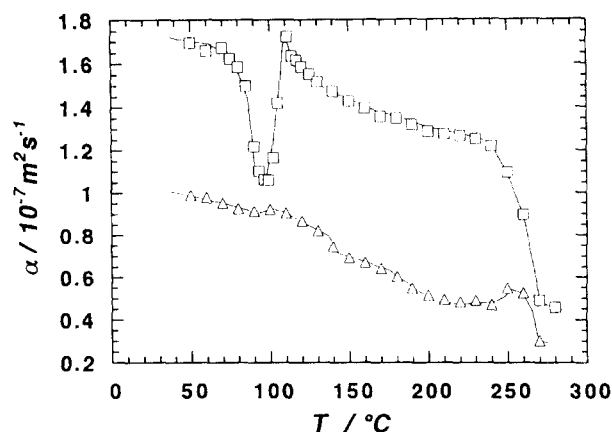
$$\alpha = (1/3)(C_v/C_p) \cdot u \cdot l \quad (3)$$

Here, above room temperature, the difference between  $C_v$  and  $C_p$  is negligible, so  $l$  and  $u$  are the dominant modes for the thermal diffusion.  $l$  and  $u$  are related to the distance between the polymer chain (intermolecular distance)  $d_w$ <sup>10</sup>, which is more sensitive to the physical state such as pressure–volume–temperature than the intramolecular distance  $d_h$ . The physical properties of polymers such as thermal expansivity, isothermal compressibility and heat capacity at constant pressure changed discontinuously at the glass transition<sup>13–18</sup>. In

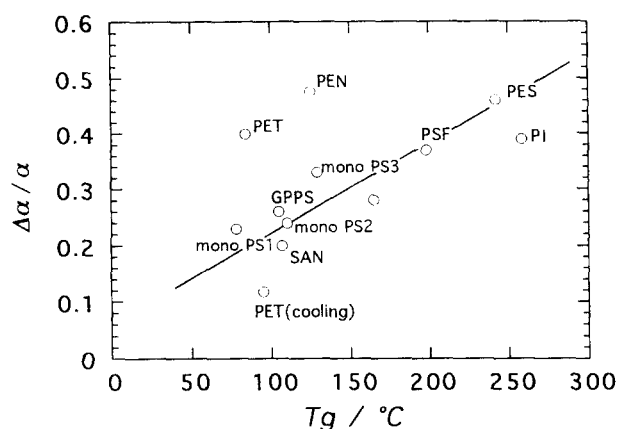
\*  $\Delta H$  (heat of fusion)  $\approx 0 \text{ J g}^{-1}$  for the quenched PET used in the first heating run;  $\Delta H = 48 \text{ J g}^{-1}$  for the slowly cooled PET in the second cooling run.



**Figure 2** Temperature dependence of thermal diffusivity of PEN: heating ( $\square$ ) and cooling ( $\circ$ )



**Figure 4** Temperature dependence of thermal diffusivity of stretched PET ( $\Delta$ ) and non-stretched and quenched PET ( $\square$ ) under heating run

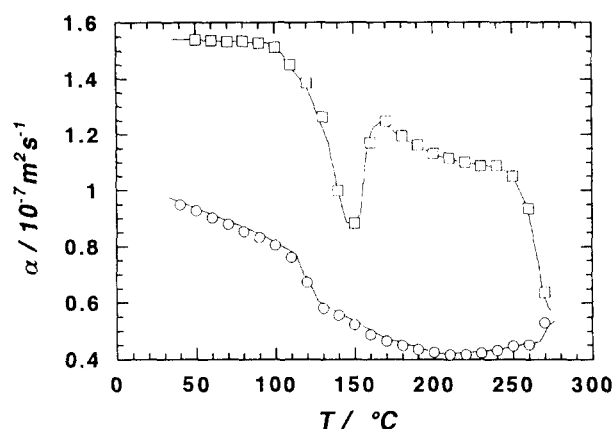


**Figure 3** Relationships between  $\Delta\alpha/\alpha$  and  $T_g$  of amorphous polymers compared with those of PET and PEN. GPPS: polystyrene (Topolex 55051); SAN: poly(styrene-co-acrylonitrile) (Laitac A 180PC), PES: poly(ether sulfone) (Vitrex 4800); PSF: poly(arylether-aryl sulfone) (Udel); PI: polyimide (Larc); mono.PS1: monodispersed polystyrene ( $M_w = 2200$ ); mono.PS2: monodispersed polystyrene ( $M_w = 10\,000$ ); mono.PS3: monodispersed polystyrene ( $M_w = 200\,000$ ); PET (quenched sample), PEN (quenched sample); PET (cooling) (cooling rate  $1^\circ\text{C min}^{-1}$ )

the case of thermal diffusivity, it is considered that the change of  $d_w$  in the glass transition results in a change of  $l$  and  $u$ , and then  $\alpha$  changes as observed in  $\Delta\alpha$ .  $\Delta\alpha/\alpha$  means a change ratio of  $\alpha$  on the glass transition of each polymer. The deviations of PET and PEN from the linear relationship of  $T_g$  and  $\Delta\alpha/\alpha$  in spite of the subsequent cold crystallization suggest the characteristic in the cohesive state of amorphous PET and PEN.

Figure 4 shows the temperature dependence of  $\alpha$  in a biaxially stretched PET film in comparison with the results of the non-stretched one.  $\alpha$  of the stretched film is lower than that of the non-stretched film below the melting temperature, and the effect of  $\Delta\alpha$  on the glass transition and the cold crystallization is unclear in the stretched film.

Figure 5 shows the temperature dependence of  $\alpha$  in the heating run of the stretched PEN film. A biaxial stretching results in the lowering of  $\alpha$ , and the glass transition temperature shifts to the higher temperature. Clear cold crystallization cannot be observed, but a slight increase of  $\alpha$  with increasing temperature above  $200^\circ\text{C}$  is observed.



**Figure 5** Temperature dependence of thermal diffusivity of stretched PEN ( $\circ$ ) and non-stretched and quenched PEN ( $\square$ ) under heating run

The results illustrated in Figures 4 and 5 show the temperature dependence of anisotropy of thermal diffusivity and its influence on the transitions. The anisotropy of thermal conductivity of polymers in the solid state has been studied by several researchers<sup>19-29</sup>. The AC joule heating technique allows the observation of change in anisotropy of thermal diffusivity on the glass transition and the cold crystallization in the temperature run from the solid to the liquid state. Qualitatively,  $\alpha$  changes with the change of  $u$  and  $l$  in equation (2), which are related to  $d_w$ , and under the anisotropy by stretching,  $\alpha$  depends on the anisotropy of  $d_w$  in the direction of stretching and the vertical direction. The quantitative problem needs further refinement and subsequent discussion.

Figure 6 shows the temperature dependence of  $\alpha$  in the first heating run of the terpolymer of PET. A rapid drop in  $\alpha$ , corresponding to the glass transition, is observed at  $50\text{--}80^\circ\text{C}$ . After the glass transition,  $\alpha$  increases with increasing temperature, but the rate of cold crystallization is slower than that of PET observed in Figure 1. This phenomenon is due to the deceleration of cold crystallization by the copolymerization. Around  $230^\circ\text{C}$  a drop in  $\alpha$  is observed, which corresponds to the melting of the crystallite.

Empirically, the blowing temperature of a PET bottle in the blow moulding process corresponds to the temperature at which  $\alpha$  shows a minimum value between

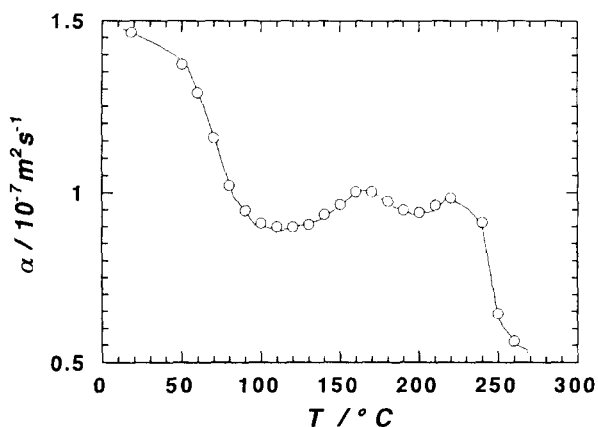


Figure 6 Temperature dependence of thermal diffusivity in the terpolymer of PET (O) under heating run

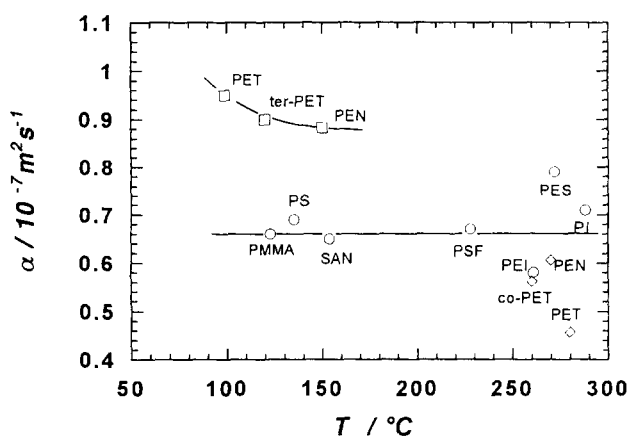


Figure 7 The comparison of  $\alpha$  in the melt state (at  $T_g + 30^\circ\text{C}$ ) of amorphous polymers (O) with  $\alpha$  between the glass transition and the cold crystallization of quenched PET, PEN and the terpolymer of PET (square) under heating run.  $\alpha$  at  $T_m + 20^\circ\text{C}$  of PET, PEN and the terpolymer of PET is also shown as ( $\diamond$ ). PS: polystyrene (Topolex 55051); SAN: poly(styrene-co-acrylonitrile) (Laitac A 180PC); PMMA: poly(methyl methacrylate) (Parapet GF); PES: (polyether sulfone) (Victrex 4800); PSF: poly(arylether-aryl sulfone) (Udel); PI: polyimide (Larc); PEI: poly(ether imide) (Ultem); PET; PEN; ter-PET (terpolymer of PET)

the glass transition and the cold crystallization. For a further consideration,  $\alpha$  of amorphous polymers at  $T_g + 30^\circ\text{C}$  is shown in Figure 7. The amorphous polymer exhibits an almost constant value of  $\alpha$  at  $T_g + 30^\circ\text{C}$ . The value of  $\alpha$  at  $T_m + 20^\circ\text{C}$  of PET and PEN groups is also shown in Figure 7. The minimum value of  $\alpha$  between the glass transition and the cold crystallization of PET and PEN groups shows a higher value than  $\alpha$  of amorphous polymers in the liquid state above the melting temperatures. The minimum value of  $\alpha$  in PET and PEN groups also shows the temperature dependence. These results also suggest the characteristic of the glassy state of PET and PEN.

It is to be noted that the AC joule heating technique is sufficiently sensitive to observe the change in the physical state of PET and PEN through the change in  $\alpha$  on the glass transition and the subsequent cold crystallization.

## CONCLUSIONS

The thermal diffusivity of PET and PEN were measured by the AC joule heating technique as a function of temperature from the solid to the liquid state. The drastic changes of  $\alpha$  in the glass transition and the crystallization were clearly observed, which is due to the change in the heat conduction mode of polymers such as the intermolecular distance, or the configurational mode of  $\alpha$ . The cold crystallization of amorphous samples was also observed as an increase of  $\alpha$ , and its deceleration was observed in the terpolymer of PET.

A biaxial stretching of PET and PEN resulted in a lowering of  $\alpha$  vertical to the stretched direction. The upward shift of  $T_g$  and the reduced drop in  $\alpha$  on the glass transition ( $\Delta\alpha$ ) indicated that the exerted constraints on the amorphous regions impeded the molecular motions vertical to the stretched direction.

The characteristic behaviour of  $\alpha$  in the glass transition of PET and PEN was observed. The relationship between  $T_g$  and  $\Delta\alpha/\alpha$  of PET and PEN deviates from the linear relationships observed generally in amorphous polymers.

The AC joule heating technique for thermal diffusivity measurement is applicable to investigation of the physical state of polymers, which is concerned with the chemical structures and the thermal history in processing.

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