

Frequency dependent thermal diffusivity of polymers by temperature wave analysis

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Abstract

Temperature wave analysis (TWA) is an originally developed new thermal analysis that makes it possible to obtain the frequency dependent thermal diffusivity as a function of temperature. The thermal diffusivity of every materials, except for electrical conductors, can be obtained for both solid and liquid states in the frequency range from 10 Hz to 2 kHz. The technique enables studies of frequency dependent thermal diffusivity at glass transition, melting and crystallization of polymers. The experimental results for several polymers are reported in the temperature range from room temperature to above the melting point under a constant heating or cooling process. © 1997 Elsevier Science B.V.

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1. Introduction

Temperature wave analysis (TWA) is a recently developed new thermal analysis that makes it possible to obtain the frequency dependence of thermal diffusivity as a function of temperature [1]. TWA is an improved new technique which is based on the a.c. Joule-heating method developed in our laboratory [2–5]. With this technique the thermal diffusivity can be obtained under a constant heating and cooling process in the temperature range including the solid state, liquid state and the phase transition region, in the wide range of the temperature wave frequency.

The idea for applying the temperature modulation technique to thermal analysis was independently pro-

posed by Reading et al. [6,7] and Gill et al. [8], which has been developed as the modulated differential scanning calorimetry (MDSC) [14,15]. The temperature modulation technique was also reported by Birge [9–11] for specific-heat spectroscopy and Polikarpov et al. [12,13] for the thermophysical properties. The advantage of the temperature modulation technique is that the imaginary component of thermophysical properties, such as specific heat and thermal conductivity, can be obtained.

In our newly developed TWA technique, the generated temperature wave, which is directly passing through the sample in the thickness direction of the thin polymer film, can be detected as the phase delay and the decay of the amplitude as a function of temperature by the sensor directly attached to the sample. In this paper we report the results of the measurement of TWA for several polymers under a constant heating and cooling process.

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2. Theory

The heat flow through the thin films in the thickness direction, when the substrates are in contact at $x=0$ and $x=d$, is described by one dimensional heat diffusion equation as follows

$$\begin{aligned} \frac{\partial T}{\partial t} &= \alpha \frac{\partial^2 T}{\partial x^2} \quad (0 < x < d) \\ \frac{\partial T}{\partial t} &= \alpha_s \frac{\partial^2 T}{\partial x^2} \quad (x < 0 \text{ and } d < x) \end{aligned} \quad (1)$$

where T is temperature, α is thermal diffusivity of the sample and α_s is that of the substrates. It is assumed that the substrate is semi-infinite, which yields that the temperature oscillations at the infinity are given by

$$\begin{aligned} T(x \rightarrow -\infty, t) &= 0 \\ T(x \rightarrow +\infty, t) &= 0 \end{aligned} \quad (2)$$

It is assumed that the boundary conditions at $x=0$ and $x=d$ and the temperature is continuous at sample-substrate boundaries, so we have

$$\begin{aligned} T(x \rightarrow -0, t) &= T(x \rightarrow +0, t) \\ T(x \rightarrow d-0, t) &= T(x \rightarrow d+0, t) \end{aligned} \quad (3)$$

The thermal balances at the interface of polymer and substrates are

$$\begin{aligned} \kappa_s \frac{\partial T}{\partial x} \Big|_{x \rightarrow -0} - \kappa \frac{\partial T}{\partial x} \Big|_{x \rightarrow +0} &= q(t) = q_0 \exp(i\omega t) \\ \kappa \frac{\partial T}{\partial x} \Big|_{x \rightarrow d-0} - \kappa_s \frac{\partial T}{\partial x} \Big|_{x \rightarrow d+0} &= 0 \end{aligned} \quad (4)$$

where κ and κ_s are the thermal conductivities of the polymer and substrate, respectively. $q(t)$ is the exothermic heat of the resistance at $x=0$ by ac joule heating.

The thermal diffusion equation (Eq. (1)) can be solved by these boundary conditions described in Eqs. (2)–(4). As a result, the temperature oscillation at $x=d$ is determined as [10,16]

$$T(d, t) = \frac{\{q_0 \exp(i\omega t)/(1+i)\} \exp\{-(1+i)kd\}}{[(\kappa\kappa + \kappa_s\kappa_s)^2 - (\kappa\kappa - \kappa_s\kappa_s)^2 \exp - 2(1+i)kd] / 2\kappa\kappa} \quad (5)$$

where $k = \sqrt{\frac{\omega}{2\alpha}}$ and $k_s = \sqrt{\frac{\omega}{2\alpha_s}}$. If $kd > 1$ the second term in the denominator is much smaller than the first

term and then Eq. (5) is approximated given by

$$T(d, t) = \frac{\sqrt{2}q_0\kappa k \exp(-kd)}{(\kappa\kappa + \kappa_s\kappa_s)^2} \exp\left\{i\left(\omega t - kd - \frac{\pi}{4}\right)\right\} \quad (6)$$

The condition $kd > 1$ means that the thickness of the sample is larger than the thermal diffusion length k^{-1} .

The amplitude of the signal voltage and the phase delay to the reference are determined experimentally by the lock-in amplifier. The phase shift of the temperature wave $\Delta\theta$ between two surfaces of the sample is given as

$$\Delta\theta = -\sqrt{\frac{\omega}{2\alpha}}d - \frac{\pi}{4} \quad (7)$$

using the frequency ($2\pi f = \omega$) of the temperature wave, Eq. (7) can be rewritten as follows.

$$\alpha = \pi f \left(\frac{d}{\Delta\theta + \frac{\pi}{4}} \right)^2 \quad (8)$$

According to Eq. (8), α can be determined from $\Delta\theta$ at a constant frequency. When the temperature is scanned at a constant heating or cooling rate, we can obtain the thermal diffusivity as a function of temperature.

The amplitude of the temperature wave at the rear surface can be calculated from

$$\text{Amp} = A \frac{\sqrt{2}q_0\kappa k \exp(-kd)}{(\kappa\kappa + \kappa_s\kappa_s)^2} \quad (9)$$

where A is a constant value determined from the electric resistance of the sensor and its temperature coefficient. The amplitude of temperature wave passing through the sample film in the thickness direction can then be obtained under a constant heating and cooling process.

3. Experimental

The samples used in this study were polypropylene (PP; Mitsui Petro Chemicals), poly(ethyleneterphthalate)(PET; Mitsui Petro Chemicals), poly(ethylenaphthalate) (PEN; Mitsui Petro Chemical), low density polyethylene (LDPE; Showa Denko) and polystyrene (PS; Pressure Chemical). Samples were

melt-hot-pressed into films about 10–100 μm thick. A thin synthetic sapphire plate (thickness of 200 μm) was also measured as a reference material.

Schematic diagrams of the whole TWA system and the sample cell are shown in [1]. A thin gold layer is used as a temperature wave generator and as a temperature sensor. By the passage of sine wave current supplied from a function generator through the heater, a temperature wave generates at the front surface of the sample and propagates through the sample. The amplitude of the temperature wave was chosen by considering sample conditions such as thickness and thermal diffusivity.

The temperature variation at the rear surface is detected by the variation of the electrical resistance of the sensor. The a.c. component of the resistance is amplified and analyzed using a lock-in amplifier (NF-5610B). The sample film with 5 \times 10 mm in size and 10–100 μm in thickness was inserted between two slide glass plates on which the thin gold layers were sputtered across an area 1 \times 4 mm² as a sensor and a heater respectively. The thickness of the sample is maintained by the insertion of the spacers to avoid deformation during measurement.

A thermocouple was inserted into the dummy sample, which is located symmetrically to the sample on the hot stage. It is assumed that the temperature of this thermocouple was equal to that of the sample film. The temperature of the hot stage was scanned at a constant rate in the range of 0.2 K min⁻¹–10 K min⁻¹.

4. Results and discussion

Fig. 1 shows α of sapphire as a function of temperature, which is decreasing monotonously with increasing temperature. The frequency of temperature wave was 410 Hz under the heating run of 0.2 K min⁻¹, and the cooling run of 0.2 K min⁻¹. The value of α at 25°C is in good agreement with literature values [17]. It was confirmed that the time constant of the sensor or total measurement system was short enough in the experimental frequency range up to 2 kHz.

Fig. 2 shows α obtained under the heating run of 10 K min⁻¹ for PP at frequency of 120 and 220 Hz, respectively. The thermal diffusivity can be obtained without the effect of the latent heat on the melting

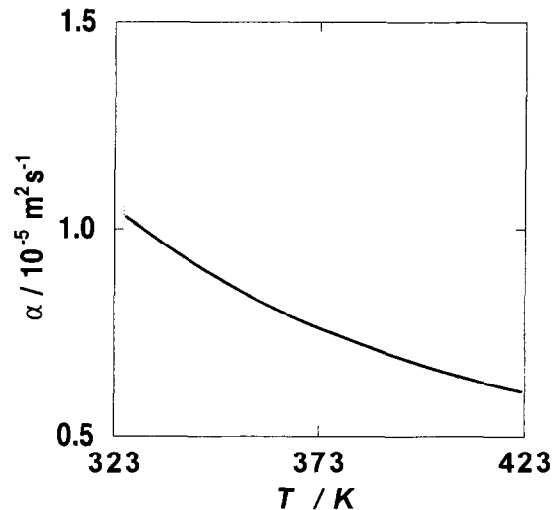


Fig. 1. Thermal diffusivity α of sapphire as a function of temperature. Temperature wave frequency is 410 Hz under a temperature scanning rate of 0.2 K min⁻¹ in heating and cooling.

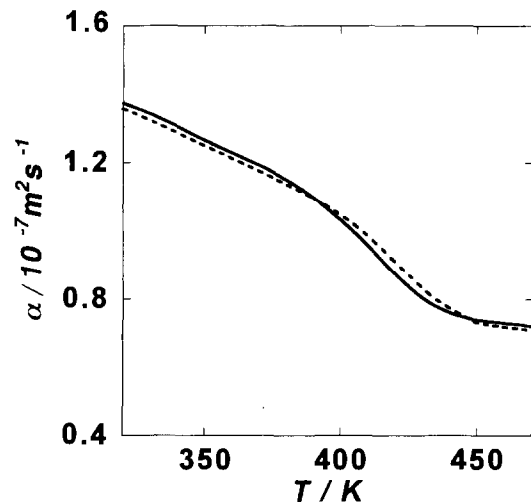


Fig. 2. Thermal diffusivity α of PP as a function of temperature under a heating rate of 10 K min⁻¹. Temperature wave frequency is (---); 120 Hz and (—); 220 Hz.

process. The frequency of TWA should be larger than the thermal diffusion length k^{-1} , so the measuring frequency was selected by sample thickness and α .

Fig. 3 shows α at frequency of 30 Hz under the heating run of 0.2 K min⁻¹ for quenched PET and PEN. The thermal diffusivity decreases with increas-

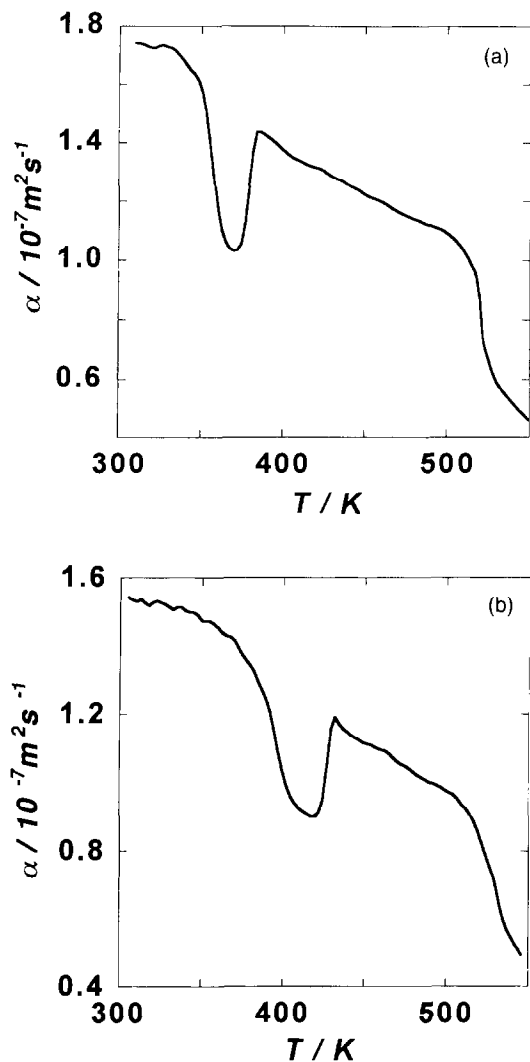


Fig. 3. Thermal diffusivity α as a function of temperature under a heating rate of 0.2 K min^{-1} . (a) PET and (b) PEN. Temperature wave frequency is 30 Hz.

ing temperature and an abrupt decrease in α is observed at $80\text{--}90^\circ\text{C}$ for PET and $100\text{--}110^\circ\text{C}$ for PEN, corresponding to the glass transition. Immediately after the glass transition, an abrupt increase in α is observed at 100°C for PET and 150°C for PEN, which is considered to be the cold crystallization. After the cold crystallization has finished, α decreases

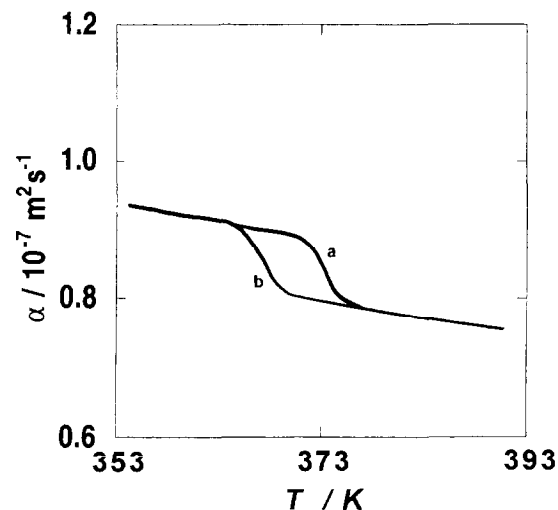


Fig. 4. Thermal diffusivity α of LDPE as a function of temperature. a; under a heating rate of 0.2 K min^{-1} , b; under a cooling rate of 0.2 K min^{-1} . Temperature wave frequency is 18 Hz.

with increasing temperature again. When temperature goes up to 250°C , another drop down of α , corresponding to the melting of the crystallite, is observed.

By the way, α in the cooling process changed drastically at the crystallization temperature which is several degrees lower than melting temperature. Typical curves observed in LDPE are illustrated in Fig. 4. The frequency of temperature wave was 18 Hz under the heating run of 0.2 K min^{-1} , and the cooling run of 0.2 K min^{-1} .

The results in Figs. 2–4 show that TWA enables us to obtain the change of thermal diffusivity at the melting and crystallization process of polymers.

Fig. 5 shows the phase shift and the amplitude of temperature wave at frequency of 80, 120 and 210 Hz (respectively) under the heating run of 1 K min^{-1} for PS. The amplitude decays and the phase shift decreases with increasing frequency as expected by Eq. (7) and Eq. (9). In both cases the glass transition is clearly observed as the change of the slope.

With the phase shift data and Eq. (8), the thermal diffusivity (α) can be obtained as a function of temperature. The α thus obtained for PS is shown in Fig. 6. The frequency dependent α is clearly observed on the glass transition region. A frequency dependence of α means that α consists of a real part and an imaginary part. The result of an imaginary component

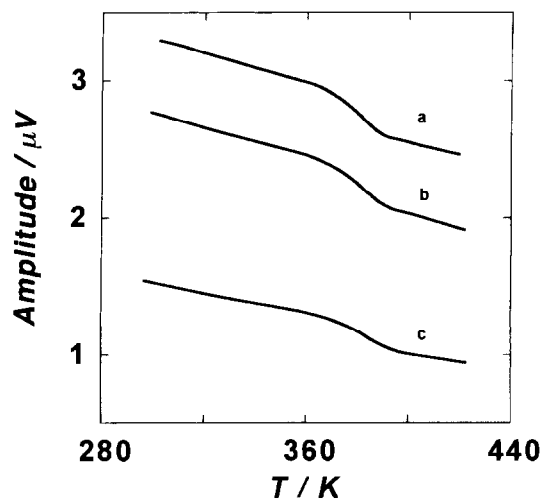
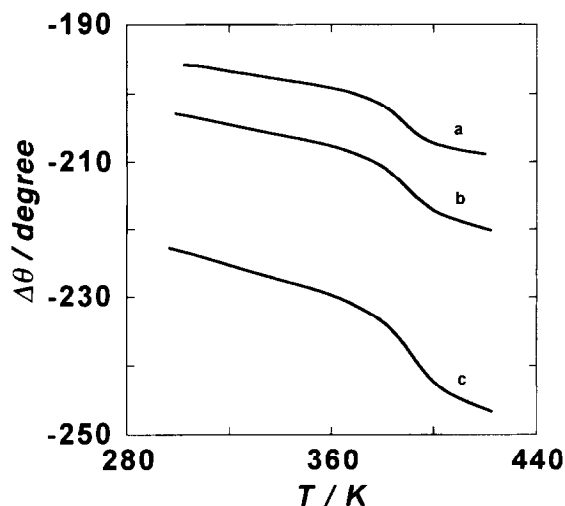


Fig. 5. (a) Phase shift $\Delta\theta$, and (b) amplitude of PS as a function of temperature under a heating rate of 1 K min^{-1} . Temperature wave frequency is a; 80 Hz, b; 120 Hz and c; 210 Hz.

in thermophysical properties was shown using the temperature wave technique, for example to measure $C_p\kappa$ [9–13], where C_p is specific heat at constant pressure. The computational procedure of imaginary component of α will be reported in future.

Here we assume that the thermal diffusivity α can be separated into a real part α' and an imaginary part α'' , where the latter has a non-zero value in the glass transition region. With this assumption, α is

$$\alpha(\omega) = \alpha'(\omega) + i\alpha''(\omega) \quad (10)$$

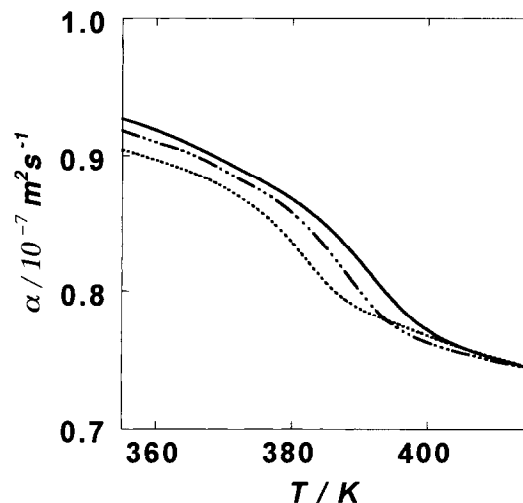


Fig. 6. Thermal diffusivity α of PS as a function of temperature calculated from $\Delta\theta$ in Fig. 5(a) under a heating rate of 1 K min^{-1} . Temperature wave frequency is (· · ·); 8 Hz, (— · — · —); 120 Hz and (—); 210 Hz.

TWA determines both phase delay ($\Delta\theta$) and amplitude (Amp.), so Eq. (7) and Eq. (9) give rise to two simultaneous equations in α' and α'' .

TWA is thus a new technique which enables us to obtain the frequency dependent thermal diffusivity of polymers.

5. Conclusion

The frequency dependent thermal diffusivity of PS, PP, LDPE, PET and PEN were examined by TWA as a function of temperature. The processes of melting, crystallization, cold crystallization, and glass transition were clearly detected as a change of thermal diffusivity. The thermal diffusivity was strongly dependent on the temperature wave frequency at the glass transition. TWA is a technique not only for determining the thermal diffusivity but also for getting new information about transition phenomena, such as a frequency dependence of the thermal diffusivity.

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