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Measurement of the Thermal Diffusivity of Thin Films by an AC Joule-Heating Method[1]

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A new thermal analysis named TWA (Temperature Wave Analysis) is proposed. This technique is based on the AC joule-heating method developed in our laboratory, and makes it possible to obtain thermal diffusivity precisely as a function of temperature at a constant frequency. The theoretical background and the calculation procedure for this technique are reported. This technique was applied to the study of the first order transition of high density polyethylene and the glass transition of glycerin.

KEY WORDS: glass transition; glycerin; high-density polyethylene; melting; polyimide; temperature wave analysis; thermal diffusivity.

1. INTRODUCTION

The AC Joule-heating method, which has been developed in our laboratory, is able to measure the thermal diffusivity α of thin films in both, the solid and the liquid states. It is possible to measure over a wide temperature range including phase transitions. We have measured α for numerous polymers and related materials and reported its variation in the phase transition region with a high accuracy [1–6].

In this method, thin gold layers are attached on both surfaces of the film-like sample as a heater and a sensor. A temperature wave is generated at the front surface of the sample when AC current passes through the heater. This temperature wave diffuses to the rear surface and its phase shifts. The phase shift is related to the thermal diffusivity, the temperature

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wave frequency and the distance from the front surface. Temperature variation at the rear surface is detected by the resistance variation of the sensor.

In the present study, we improved this AC Joule-heating method into a new thermal analysis based on the thermal diffusivity measurement. That is, we made it possible to measure the thermal diffusivity continuously under a constant heating or cooling rate. In this new method, the phase shift $\Delta\theta$ and the amplitude of the temperature wave are observed as a function of temperature.

2. EXPERIMENTAL PROCEDURE

Samples used in this study were polyimide film (duPont Kapton), high-density polyethylene film (Showa-Denko Sholex F7150), and glycerin (Tokyo-Kasei Co.). Samples were shaped into 10 × 10mm in size and 10–200 μm in thickness.

Thin gold layers 3 × 6 mm in size were sputtered on both surfaces of the thin polymer film. One of these two layers is used as a heater and the other as a sensor. The electrical resistance of both thin gold layers was controlled to approximately 50 Ω. Copper lead wires with a small diameter (0.15 mm) were attached to both layers with silver paste. Samples were enveloped by epoxy adhesive to avoid deformation upon melting [3]. In the case of the liquid sample, glycerin, it was infused into the interspace of two glass plates with spacer films. On each of these glass plates, a thin gold layer as a resistance and a thick gold layer as a lead were sputtered. The sample was set in the heating block and its temperature was controlled under a constant scanning rate.

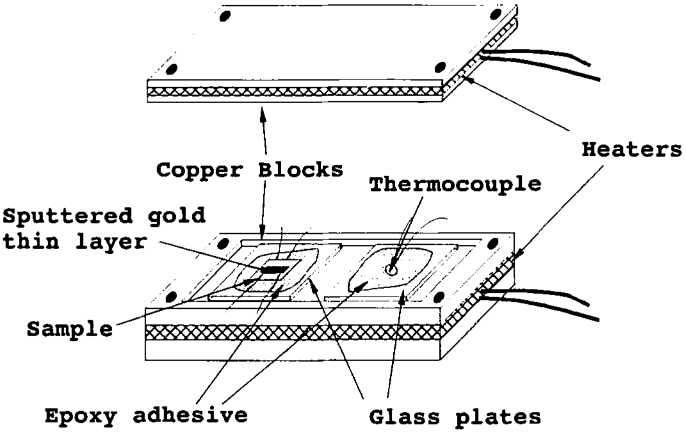

Fig. 1. Schematic diagram of the sample and its surroundings.

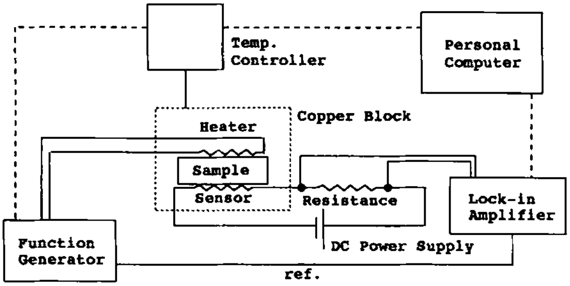

Fig. 2. Schematic diagram of the experimental arrangement.

A schematic diagram of the sample and the heating block is shown in Fig. 1. The sample temperature is controlled by two heaters attached to the upper and the lower side of the block, to avoid the development of a temperature gradient in the thickness direction. The sample on the glass plate with epoxy adhesive, is located on one side of the heating block. On the other side, a thermocouple on the glass plate with epoxy adhesive is located symmetrically to the sample. We assumed that the temperature of this thermocouple was equal to that of the sample.

Figure 2 shows the schematic diagram of the experimental arrangement. The passage of AC current through the heater generates a temperature wave at the front surface of the sample which diffuses to the rear surface. The AC part of the temperature at the rear surface is detected by the variation of the electrical resistance of the sensor. This variation of the resistance is converted into the variation of the voltage and amplified by a lock-in amplifier. All instruments are controlled by a personal computer.

3. COMPUTATIONAL PROCEDURE

In our measuring system, samples are placed between sufficiently thick backing materials, such as glass or epoxy resin, so that the thickness of that can be considered infinite. On the other hand, thin gold layers attached on both surfaces are sufficiently thinner than the sample thickness. Thus, the influence of this thin gold layer can be neglected.

From the above, the measuring system of our method can be described by the one-dimensional thermal diffusion equation [7–8]. Figure 3 shows the boundary conditions of this equation. Periodical heat flux J is applied to the front surface of the sample. This periodical heat flux is expressed as

$$J = J_0 \exp(i\omega t) \tag{1}$$

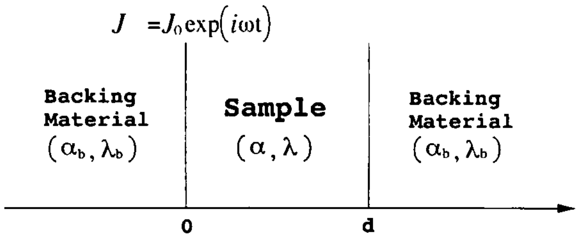

Fig. 3. Schematic diagram of the measuring principle.

where ω is the angular frequency of the temperature wave, t is time, and i is $(-1)^{1/2}$.

As the solution of the thermal diffusion equation the AC component of temperature at the rear surface of the sample T_{ac} is given as

$$T_{ac} = \frac{\{2J_0\lambda k \exp(i\omega t)/(1+i)\}\ \exp\{-(1+i)\,kd\}}{(\lambda k + \lambda_b k_b)^2 - (\lambda k - \lambda_b k_b)^2 \exp\{-2(1+i)\,kd\}} \tag{2}$$

where

$$k = \sqrt{\frac{\pi f}{\alpha}}, \qquad k_b = \sqrt{\frac{\pi f}{\alpha_b}}$$

The parameters in the above equations are defined as follows: f is the frequency of the temperature wave and equals $\omega/2\pi$, d the sample thickness, α the thermal diffusivity of the sample, α_b the thermal diffusivity of the backing material, λ the thermal conductivity of the sample, and λ_b the thermal Conductivity of the backing material [9].

If the thermally thick condition,

$$kd = \sqrt{\frac{\pi f}{\alpha}}, \qquad d > 1 \tag{3}$$

is satisfied, Eq. (2) reduces to

$$T_{ac} = \frac{\sqrt{2}\,\lambda k J_0 \exp(-kd)}{(\lambda k + \lambda_b k_b)^2} \exp\left\{i\left(\omega t - kd - \frac{\pi}{4}\right)\right\} \tag{4}$$

The phase shift of the temperature wave $\Delta\theta$ between two surfaces of the sample is given as

$$\Delta\theta = -\sqrt{\frac{\pi f}{\alpha}}, \qquad d - \frac{\pi}{4} \tag{5}$$

By means of Eq. (5), α is determined from the relationship between $\Delta\theta$ and $f^{1/2}$.

4. RESULTS AND DISCUSSION

4.1. Polyimide

Figure 4 shows the relationship between $\Delta\theta$ and $f^{1/2}$ for 26 μm-thick polyimide film at 40 and 160°C. In this measurement, the temperature is kept constant and the temperature wave frequency is scanned in a step-like manner. From Eq. (5), $\Delta\theta$ is proportional to the square root of the frequency $f^{1/2}$, therefore α is determined from the slope of this linear relationship. In Fig. 4, a good linear relationship is observed in the frequency region above approximately 10 $\mathrm{Hz}^{1/2}$, a thermally thick region, at each temperature. In this frequency region, a is determined to be $1.50 \times 10^{-7}\ \mathrm{m}^2 \cdot \mathrm{s}^{-1}$ at 40°C and $1.19 \times 10^{-7}\ \mathrm{m}^2 \cdot \mathrm{s}^{-1}$ at 160°C. This technique, frequency scanning type, is conventionally used in our laboratory for the precise determination of α.

In our new method, TWA, in contrast, the frequency of the temperature wave is fixed and the sample temperature is scanned. As a result, $\Delta\theta$ and the amplitude of T_{ac} are obtained as a function of temperature. We can determine the thermal diffusivity by applying the phase shift data directly to Eq. (5). In other words, it is calculated from the slope of the

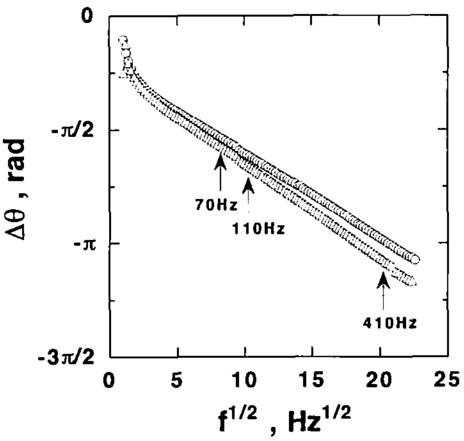

Fig. 4. Phase shift $\Delta\theta$ vs. $f^{1/2}$ for polyimide film at 40°C (○) and 160°C (△). Sample thickness is 26 μm.

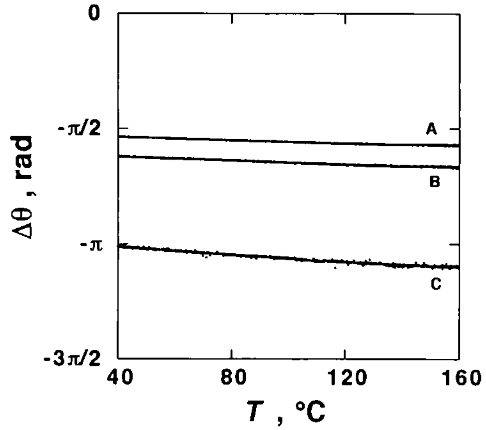

Fig. 5. Phase shift $\Delta\theta$ for polyimide film as a function of temperature. Sample thickness is 26 μm. Temperature wave frequencies are 70 Hz (A), 110 Hz (B), and 410 Hz (C). Scanning rate is 0.2°C · min^{-1} heating.

linear function that relates $-\pi/4(f^{1/2}=0)$ and $\Delta\theta$ (square root of the measuring frequency) in Fig. 4.

Figure 5 shows the TWA for $\Delta\theta$ at constant frequencies of 70, 110, and 410 Hz (shown by arrows in Fig. 4). The temperature is controlled from 40 to 160°C under a constant scanning rate of 0.2°C · min^{-1} in heating. $\Delta\theta$ decreases with increasing temperature at each frequency. As expected from Eq. (4), the amplitude of T_{ac} decreases with increasing frequency. Thus, TWA at 410 Hz shows a little wide dispersion because the signal intensity is relatively weak.

Figure 6 illustrates the temperature dependence of α for polyamide, calculated from $\Delta\theta$ in Fig. 5. There is a small deviation in the absolute value of α at each frequency. We consider this deviation to be due to the experimental apparatus, such as a zero deviation of the lock-in amplifier, therefore it can be easily corrected by comparing with the α determined by the conventional frequency scanning type method. This can be done since in the conventional method, a is not related to the absolute value of $\Delta\theta$ but is related to the slope of the linear relationship between $\Delta\theta$ and $f^{1/2}$.

4.2. High-Density Polyethylene

Figure 7 shows the TWA for 111-μm-thick high-density polyethylene film. This is repeatedly measured in the temperature range from 50 to

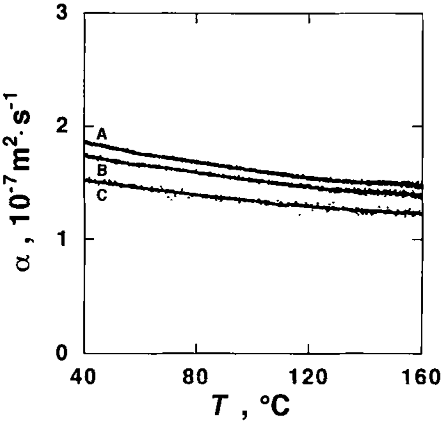

Fig. 6. Thermal diffusivity α of polyimide film as a function of temperature. Sample thickness is 26 μm. Temperature wave frequencies are 70 Hz (A), 110 Hz (B), and 410 Hz (C). Temperature scanning rate is 0.2°C · min^{-1} heating.

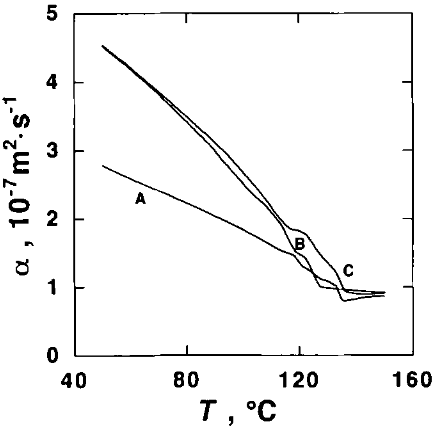

Fig. 7. Thermal diffusivity α of high density polyethylene as a function of temperature: A, first heating; B, cooling; C, second heating. Sample thickness is 111 μm, temperature wave frequency is 9 Hz, and scanning rate is 0.2°C min^{-1} in both heating and cooling.

150°C, including the melting region. The temperature wave frequency is 9 Hz and the scanning rate is 0.2°C · min $^{-1}$ in both heating and cooling.

Obvious changes of α are observed around first-order transition temperatures, such as melting or crystallization. There is no influence of the enthalpy change on α. At this stage, the enthalpy change can be considered as a DC signal, hence it does not affect the AC component [10].

4.3. Glycerin

Glycerin is a typical low molecular compound for the study of the glass transition behavior, which has been widely studied by various techniques. Some authors have reported that the heat capacity depends on the measuring frequency in the glass transition region [11–13].

Figure 8 shows α determined from the TWA for 120-μm-thick glycerin. Temperature is controlled from -100 to -40°C under a constant heating rate of 0.4°C min $^{-1}$. Temperature wave frequencies were 4, 9, 18, and 36 Hz. The frequency dependence of a is clearly observed in the glass transition temperature region. It can be concluded that the thermal diffusivity depends on the measuring frequency as well as the heat capacity in the glass transition region of glycerin.

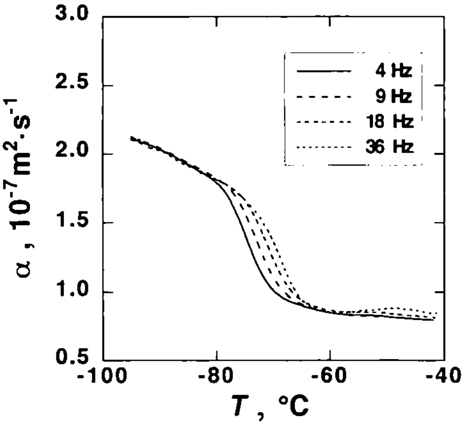

Fig. 8. Thermal diffusivity α of glycerin as a function of temperature. Sample thickness is 120 μm. Temperature wave frequencies are 4, 9, 18, and 36 Hz. Temperature scanning rate is 0.4°C · min $^{-1}$ heating.

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