

THERMAL DIFFUSIVITY MEASUREMENT OF POLYMER FILMS BY THE  
TEMPERATURE WAVE METHOD USING JOULE-HEATING

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SUMMARY

A simple method using a temperature wave method has been developed for measuring the thermal diffusivity of thin polymer films. The variation of the temperature at the rear surface was detected by sputtered gold layer as thin-film bolometers. The thermal diffusivity of four polymers, polyimide, polypropylene, polystyrene, and polyethylene terephthalate were measured by this new method over the temperature range of 20-200 °C.

INTRODUCTION

The thermal diffusivity of polymer thin films can be directly determined experimentally by some non-steady state methods such as laser-flash method (ref. 1-3) and photoacoustic method (ref.4-7). However, it is difficult to measure the thermal diffusivity of thin polymer films with molten state using these methods.

In this paper, we describe a new temperature wave method capable of measuring the sensitive thermal diffusivity of thin polymer films in wider temperature range including the melting region. This method is based on the joule-heating at the front surface of a polymer film and the observation of the temperature oscillation at the rear surface. A sputtered gold layer on both surfaces with resistance of 10-100  $\Omega$  was used as the heater and the sensor of temperature variation.

When the ac current is passed through the heater, the periodical heat flow generates and diffuses to the rear surface of the sample. It takes a short time for the heat flow to diffuse from the front surface to the rear surface, then a phase shift is produced between the heater and the detector. This phase shift depends on the thermal diffusivity and the thickness of the sample.

In order to confirm the validity of this new method, the temperature dependence of the thermal diffusivity for various polymer films were measured in the temperature range including glass transition and melting temperatures.

## EXPERIMENTAL

### Materials

The samples used were a film shaped of polyethylene terephthalate (PET, Toray), polypropylene (PP, Misui Toatsu FEL200), polystyrene (PS, Asahi-Daw Styron 666), polyimide (PI, DuPont Kapton H) and a thin microscope cover glass plate was also used as a reference material. All samples were prepared for 15mm square and 0.008-0.16 mm in thickness. Both surfaces were sputtered gold thin layer as the heating and detector layer. In order to get the desired shape of the gold layers, the samples were covered by a template of 8\*8 mm during sputtering. Thin electrical leads were attached to the end of the gold layer by using a silver paste.

### Apparatus

The block diagram of the experimental arrangement developed in our laboratory is shown in Fig.1. The copper block which maintains the temperature of the substrate is held at a constant temperature by a temperature controller.

In order to heat the front surface of sample, a frequency synthesizer (NF Electronic Industry 1920) was used as an electric source. The variation of the temperature at the rear surface was detected by the change of electrical resistance. This resistance change was converted to the change of electrical voltage. Especially, the phase shifts between the signal from sensor and the reference signal was detected with a lock-in amplifier (NF 5610B). This shift reflected the phase lag between the temperature oscillations of the front and rear surfaces.

The temperature at the surface of the sample was measured by an infrared thermometer (Nippon Avionics TVS-5000). The frequency spectrum analysis of the signal was performed by a fast Fourier transformation analyzer (Ono Sokki FFT analyzer, CF360).

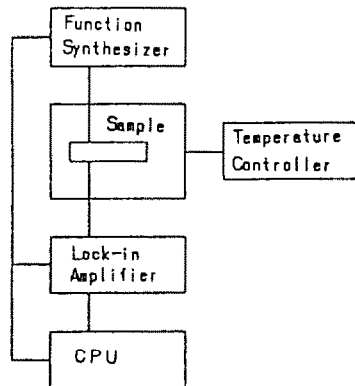


Fig.1 Schematic diagram of the experimental set up.

## RESULTS AND DISCUSSION

In this study, the sputtered gold layer was used as a resistor type thermo detector. It is needed that the detector have a large temperature coefficient of electrical resistivity. The temperature dependence of the resistance of gold layer is illustrated in Fig.2. Linear relation between temperature and resistivity with good reproducibility was observed. This figure indicated that the sputtered gold resistor detector was sufficiently sensitive and stable for this experiments.

If a voltage of frequency  $\omega/2$  is supplied to the heater having resistance  $R$ , the current passed through is written by

$$I = I_0 \cdot \cos(\omega/2) \quad (1)$$

It is noteworthy that the power dissipated in the heater is generated at frequency  $\omega$  which value corresponds to exact twice value of the applied voltage. This periodic temperature wave diffuses to the rear surface of the sample, and the temperature oscillation at the rear surface is detected by the change of the resistance of the sputtered thin gold layer.

Fig.3 shows the signal waveforms and the frequency spectra observed by FFT analyzer for the input voltage (35 Hz) through the heater equipped on front surface and the temperature oscillation at the rear surface for glass sample. As the input wave form oscillates at frequency  $\omega/2$ , it is

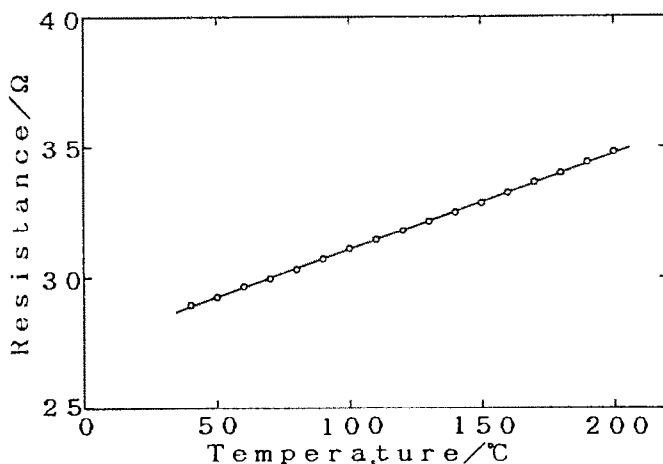


Fig.2 Electrical resistance of sputtered gold layer as a function of temperature for glass sample.

clearly demonstrated that the temperature at rear surface varied in frequency  $\omega$ . The signal observed at 50 Hz in Fig.3(b) seems to be a noise from electric source.

The heat flow described in the above is able to assume by the one-dimensional heat diffusion equation. We define  $x=0$  at the front surface of the sample and  $x=d$  at the rear surface. The periodic temperature variation at the rear surface is given by (ref.8)

$$T = T_0 \cdot \exp(-\sqrt{\omega/2\alpha} \cdot d) \cdot \cos(\omega t - \sqrt{\omega/2\alpha} \cdot d) \quad (2)$$

where  $T_0$  is the amplitude of the temperature oscillations at the heater,  $\alpha$  is the thermal diffusivity. The amplitude of the temperature oscillations is dominated by exponential behavior, and the phase shift  $\Delta \theta$  between the temperature variations at the two surfaces of the sample is dominated.

The phase shift is rewritten by

$$\Delta \theta = \sqrt{\omega/2\alpha} \cdot d + b \quad (3)$$

where  $b$  is a phase lag caused by instrumental characteristics.

When a periodic temperature wave passes through a homogeneous material, the phase lag of the heat wave is expressed by a function of both thermal diffusivity and the sample thickness. According to Eq.2, a plot of  $\Delta \theta$  versus  $\sqrt{\omega}$  is assumed to describe linear relationship. If the sample thickness is already estimated by other methods,  $\alpha$  value is able to calculate from equation(3).

Fig.4 shows the phase shifts and amplitude of the temperature wave at rear surface of glass plate of 150  $\mu\text{m}$  thickness as a function of  $\sqrt{\omega}$  for various input powers. All of the curves are linear over the frequency range from 9 to 100Hz. These results are satisfied with the relation described in Eq.2. The amplitude increases as increasing supplied powers and is exponentially damped in the whole range of frequency. In contrast, the phase shift increases with increasing frequency in same manner although they are not affected by the variation of powers. These results suggests that the amplitude is easily influenced by the condition of measurements, especially the heat loss from the specimen to its surroundings.

From the observation by the infrared thermometer, the temperature of sample increased about 1°C under the power of 33mW. Therefore, the experiment is performed under a condition that the ac temperature varies usually as small as 1°C after reaching steady state.

The thermal diffusivity of the glass plate calculated from the gradient of the line in Fig.4 is  $5.3 \cdot 10^{-7} \text{ m}^2/\text{s}$  which agreed with the value of literature.

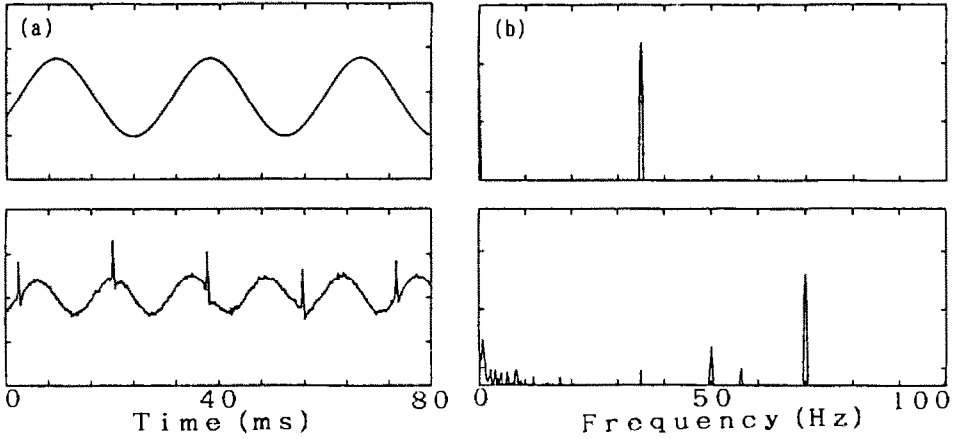


Fig.3 Wave form (a) and power spectrum(b) of applied voltage at the front surface and temperature wave signal at the rear surface.

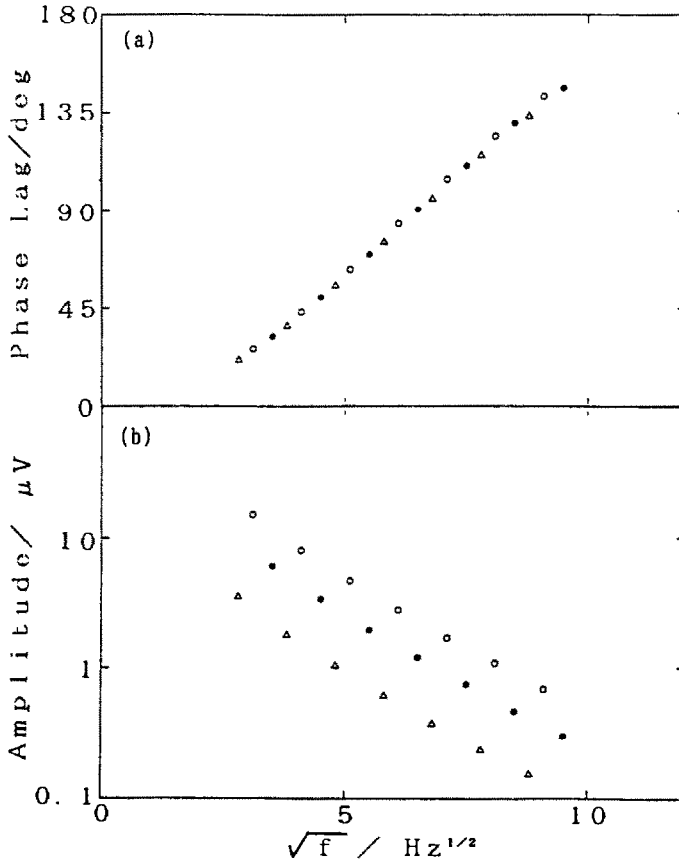


Fig.4 Plots of phase lag(a) and amplitude (b) versus the square root of the modulation frequency for glass sample. The electric power applied to heater are 65(O),33 (●) and 12 mW( $\Delta$ ), respectively.

The measured thermal diffusivity of polypropylene, polyimide, polystyrene and polyethylene terephthalate at room temperature are plotted in Fig.5 as a function of the sample thickness. In the case of same polymer, these values of all samples with different thicknesses are in good agreement with each other to better than 5 %. This discrepancy probably arises from the noise in the sensor and the accuracy in the measurement of sample thickness. The results determined here for all samples are agreed well with those reported previously.

Fig.6 shows the temperature dependences of the thermal diffusivities obtained for several polymers as the temperature rises from 20 to 200 °C. Each polymer indicates a characteristic curve in this temperature region.

The temperature dependence of thermal diffusivity for polyimide and polyethylene terephthalate exhibits same trends, with monotonously decreasing with increasing temperature.

By contrast, the thermal diffusivity of polystyrene shows an obviously peak observed at 110 °C and rapid fall-off at around 120 °C with increasing temperature. This peak temperature corresponds to the glass transition temperature measured by differential scanning calorimeter. The temperature dependence of thermal diffusivity for polystyrene shows a good reproducibility of results except for the value at the peak.

In the case of polypropylene sample, there are two temperature regions where the thermal diffusivity shows a relatively large drop with increasing temperature. The temperature of these drops corresponds to the temperatures of the an intrinsic molecular motion of polypropylene. The former drop attributes to the crystalline dispersion temperature and the latter to melting region.

Though a definite conclusion cannot be made at this stage, Fig.5 suggests that molecular motions which can be described in terms of melting or glass transition take place the complex behavior of thermal diffusion. Furthermore, morphological changes in polymers should considerably affect the thermal diffusivity. To elucidate the relationship between the thermal diffusivity and the molecular motion associated with structural transitions, further investigations are required.

## CONCLUSION

For a new technique of thermal diffusivity measurements on polymer thin film, a sputtered gold layer was coated on both surfaces as the heater and sensor, respectively. Since the gold layer has a much higher thermal diffusivity than the polymer and its thickness is much smaller, no significant influence on the measurements was recognized. The simple mathematical

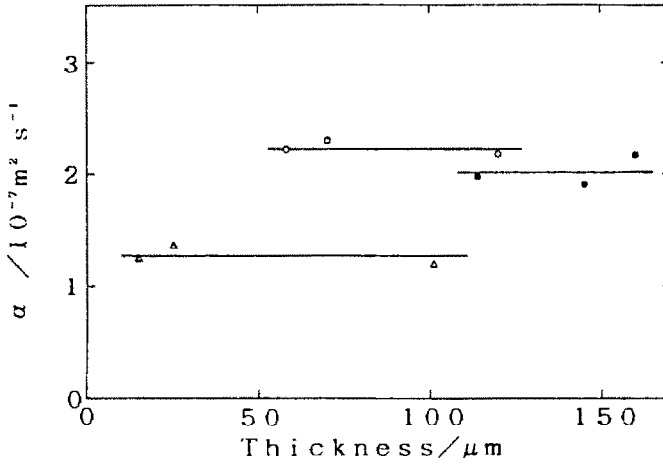


Fig. 5 Experimental value of thermal diffusivity as a function of sample thickness. Measurements were carried out at 20°C for polypropylene( $\circ$ ), polystyrene( $\bullet$ ) and polyethylene-terephthalate( $\Delta$ ).

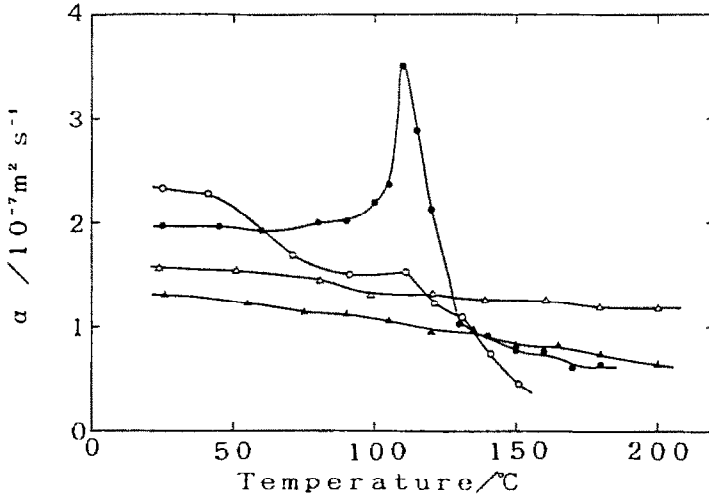


Fig. 6 Temperature dependence on thermal diffusivity for Polypropylene( $\circ$ ), polystyrene( $\bullet$ ), polyimide( $\Delta$ ), and polyethylene-terephthalate( $\blacktriangle$ ).

relationship between the phase shift of the temperature wave and the input frequency appears to fit very well the experimental conditions employed.

It is founded from the measurements for polymer films with thickness below 150  $\mu\text{m}$  that thermal diffusivity of thin films can be quantitatively determined by developed in this investigation. This measuring method is applicable for a variety of polymeric materials in a wide range of temperature including melting region.

#### REFERENCES

- 1 C.L.Choy, W.H.Luk and F.C.Chen, Thermal conductivity of highly oriented polyethylene, *Polymer*, 19, (1978) 155-162.
- 2 C.L.Choy, F.C.Chen and W.H.Luk, Thermal conductivity of oriented crystalline polymers, *J. Polym. Sci. Polym. Phys. Ed.*, 18, (1980) 1187-1207.
- 3 C.L.Choy, W.P.Leung and Y.K.NG, Thermal diffusivity of polymer films by the flash radiometry method, *J. Polym. Sci.* 25, (1987) 1779-1799.
- 4 M.J.Adams and G.F.Kirkbright, Thermal diffusivity and thickness measurements for solid samples utilising the photoacoustic effect, *Analyst*, 102 (1977) 678-682.
- 5 T.Hashimoto, K.Okuno, M.Kineshita and A.Takaku, Photoacoustic measurements of thermal diffusivity of pyrolyzed poly( $\alpha$ -chloroacrylonitrile) films, *Koubunshi Ronbunshu*, 44(6) (1987) 445-449.
- 6 T.Hashimoto, J.Cao and A.Takaku, Thermal diffusivity measurements for thin films by the photoacoustic effect, *Thermochim.Acta*, 120 (1987) 191-201.
- 7 N.F.Leite, N.Cella, H.Vargas and L.C.M.Miranda, Photoacoustic measurement of thermal diffusivity of polymer foils, *J. Appl. Phys.*, 61(8) (1987) 3025-3027.
- 8 H.S.Carslaw and J.C.Jaeger, *Conduction of Heat in Solids*, Oxford University Press, New York, 1959, pp.64-70.