Journal of Thermal Analysis, Vol. 40 (1993) 721-726

THERMAL DIFFUSIVITY MEASUREMENT OF POLYETHYLENE MELT BY A NEW TEMPERATURE WAVE METHOD

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Thermal diffusivity of high density polyethylene (PE) has been measured by a new a. c. Joule-heating method. The diffusivity was determined at various temperatures between room temperature and above melting point in heating and cooling processes. This method is based on the phase shift of temperature waves across film sample, so that it offers several advantages, e.g., easy measuring in polymer melts.

Keywords: high density polyethylene, temperature wave method

Introduction

Thermal diffusivity is generally used to measure than thermal conductivity in measurement period and simplicity of instruments. Some non-steady state methods have been suggested for measuring thermal diffusivity. We propose a new simple method for thermal diffusivity measurement which is based on the ac Joule heating at the front surface of polymer thin film and the observation of the temperature oscillation at the rear surface [1].

In this report, temperature dependence of thermal diffusivities for high density polyethylene was measured in the temperature range from room temperature to above melting point under stepwise heating and cooling process. Furthermore, the influence of crystallinity was also investigated.

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Experimental

A commercial high density polyethylene, Showa-denko Sholex F7150, was used as sample for this measurement. Film-shaped samples were prepared from the pellets by melt hot press, and then quenched in cool water. A 50 μm thick film of sample was cut into 10 mm·10 mm and gold thin layers were sputtered on both surfaces across an area 3 mm·6 mm as shown in Fig. 1.

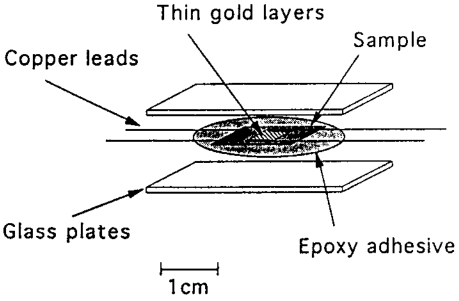

Fig. 1 Sample-heater-sensor geometry

These layers on the front and the rear surfaces were used for a heater occurring thermal wave by Joule heating and a sensor detecting the temperature wave, respectively. Electrical resistance of the gold layers was controlled at approximately 50 Ohm. Copper lead wires were attached to both faces of the each gold layers. To avoid the deformation of shrinkage or melting, samples were mounted between two thin glass plates which were bonded in place by an epoxide resin.

The frequency of the temperature wave varies twice higher than that of applied voltage. Thermal wave was diffusing across the sample for vertical direction to the rear surface. The temperature variations on the rear surface were detected by the gold layer sensor as resistance variation which was analyzed using a NF type 5620 lock-in amplifier.

The relationship between thermal wave frequency and the phase shift of the signal at rear surface is expressed by Eq. (2)

$$\Delta\theta = \sqrt{\pi f/\alpha}\, d + \beta \tag{1}$$

Where $\Delta\theta$ is phase shift, α is thermal diffusivity, f is frequency of thermal modification, d is sample thickness and β is instrumental constant.

Figure 2 shows typical data on relationship between the square root of f and the phase shift at 30° and 180°C, which correspond to solid and melt state of polyethylene. The gradient and thermal diffusivity can then be obtained from Eq. (1) Since this method is based on the phase shift measurement, the influence of the backing material such as glass plate etc. can be neglected.

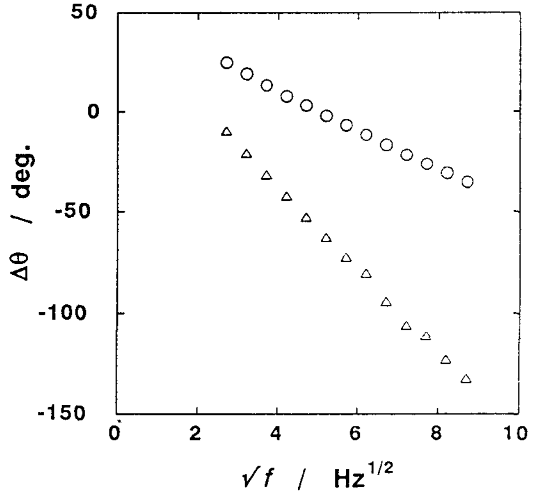

Fig. 2 Phase shift *vs.* square root of frequency for polyethylene obtained at 30°C (o) and 180°C (Δ)

Results and discussion

Thermal diffusivity of high density polyethylene is shown in Fig. 3 as a function of temperature under several heating and cooling runs. The value decreases with increasing temperature, and a rapid fall off was observed at around 130°C, which corresponded to the melting temperature of this sample identified by differential scanning calorimeter (DSC). In the solid state, the thermal diffusivities of polyethylene are different on repeated runs. However, reproducible data were obtained in high temperature melt region. The values and temperature dependence of the melts are in good agreement with that of the reported in the literature [3, 4].

The cooling process, indicated as closed circles in the figure, the gradient of thermal diffusivity curve changes drastically at a temperature 5°C below the melting temperature. This point corresponded to the crystallizing temperature of polyethylene sample under this cooling conditions. It was observed that the measured values under cooling were smaller than that of the values obtained for heating processes between the melt temperature and 90°C. This method required small sample size specimens, low temperature gradient across the sample thickness, so that the properties can be measured with high resolution for temperature.

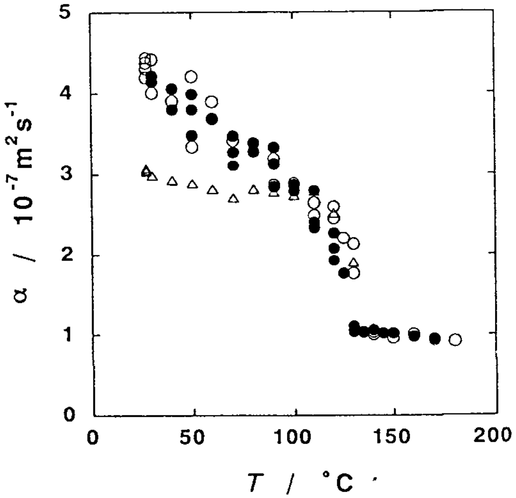

Fig. 3 Temperature dependence of thermal diffusivity for polyethylene; (Δ) first heating run, (o) second heating run and (•) cooling runs

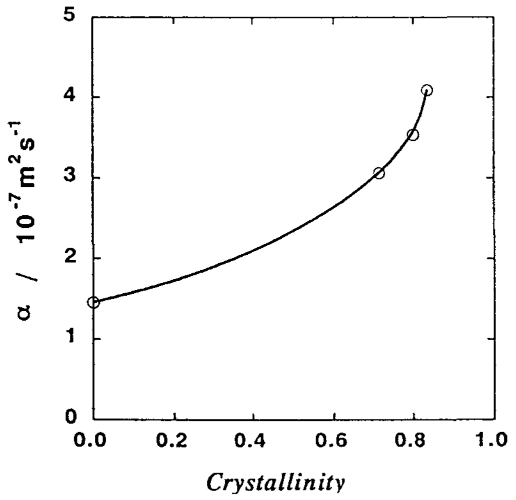

Fig. 4 Effect of crystallinity on thermal diffusivity of polyethylene at 23°C. Crystallinity was determined by density of samples which were crystallized at various temperature

The difference of first and second heating samples shown in Fig. 3 are different in crystallization conditions. The first heating sample had relatively low crystallinity due to the process pretreatment (corresponds to cooling of a few hundred degrees per minute). By contrast, the second and third heating sample had higher crystallinity resulting from a constant slow cooling cycle of about 0.2 deg$\cdot$min^{-1}. How the difference of cooling rate may effect the high order structures of polyethylene e.g., crystallinity is well documented.

The values of solid state varied from sample to sample, being sensitive to structure. Samples were prepared under various crystallization conditions and crystallinities were calculated from density measurement. The relationship between crystallinity and thermal diffusivities at 23°C is shown in Fig. 4. The thermal diffusivity at zero crystallinity is obtained by extrapolation to room temperature from the values at melting region. This figure indicates that thermal diffusivity increased with increasing crystallinity which conferred previous literature observations [5, 6].

Polymer structures are separated into two regions namely crystalline and amorphous, the thermal diffusivity in crystalline region is much larger than that of amorphous region. In the high temperature region, around the melting region, the gradient of thermal diffusivity curves became more severe as the temperature was increased. This may be effected by rapid structure modifications of crystallite by melting or crystallizing. Since the melts or amorphous part in solid was the state of having much imperfection than crystallite, its small thermal diffusivity was reasonable.

Conclusion

Thermal diffusivity of high density polyethylene was measured by a new a. c. Joule heating method developed in our laboratory. Thermal diffusivities changed drastically at melting and crystallizing point at which obvious structural changes occurred.

It was concluded that the main advantage of this method was described as follows: 1) small temperature gradient across the sample, 2) wide temperature range including melt state, 3) small sample size, 4) short measurement period, 5) high resolution for temperature.

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Zusammenfassung — Mittels einer neuen Methode wurde die Temperaturleitfähigkeit von hochdichtem Polyethylen (PE) vermessen. Die Leitfähigkeit wurde bei verschiedenen Temperaturen zwischen Raumtemperatur und Temperaturen oberhalb des Schmelzpunktes, sowohl beim Erhitzen als auch beim Abkühlen bestimmt. Diese Methode basiert auf der Phasenverschiebung von Temperaturwellen durch eine Filmprobe hindurch, was verschiedene Vorteile bietet, wie z.B. leichte Messung in Polymerschmelzen.