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Micro-scale thermal diffusivity measurements of banded spherulites of poly-(L-lactic acid) using a thermo-electric micro sensor

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ABSTRACT

We have succeeded in developing a thermo-electric micro sensor designed with a three-dimensional electric wiring to measure the thermal diffusivity in micro scale. Temperature wave in the area of 12.5 μm in diameter is observed as a periodical change of thermo electromotive force. The phase shift of temperature wave is measured by means of a lock-in method and the thermal diffusivity of polymer film is determined with a standard deviation less than 2%. The micro-scale distribution of thermal diffusivity in the banded structures of spherulites of poly-L-lactic acid (PLLA) is demonstrated.

1. Introduction

Thermal analysis in the localized small area has become important in needs of research and development for highly integrated electric devices. For example, polymeric low-*k* material is a candidate of next generation electric insulator, however, several problems still remain in thermal properties. The molecular orientation [1,2] of polymeric materials causes the anisotropic thermal conductivity, and in order to increase the thermal conductivity of polymers nano/micro fillers are compounded as a practical procedure [3,4]. Modulated thermo reflectance microscopy is a method to evaluate the thermal conductivity of thin films [5] by scanning a laser beam spot of 100 μm in diameter [5,6]. In order to measure the absolute value of thermal diffusivity in the localized area, 10–30 μm in diameter in the through thickness direction of films, a contact type thermoelectric thermal probe is developed in this study.

The newly developed micro-sensor is applied to measure the micro-scale distribution of thermal diffusivity in the banded and non-banded structures of polymeric spherulites of poly-L-lactic acid (PLLA) [7] that is known as a biodegradable polymer. It is commonly accepted that the formation of banded spherulites is attributable to the lamellar twisting along the direction of radial growth [8,9]. The correlation of the localized thermal diffusivity with the anisotropic structure of lamellar is examined.

2. Experimental

2.1. Micro TWA measurement method

Temperature wave analysis (TWA) method is one of the standard method [10–13] to measure thermal diffusivity of the film-shaped specimen in the through thickness direction. In order to measure the thermal diffusivity in a micro scale, we propose a modified TWA method by using a micro scale thermo-electric sensor designed with a three-dimensional electric wiring.

Instead of using a pair of resistive sensor and heater that was prepared with a sputtered platinum/gold [10,11] layer, a pair of indium tin oxide (ITO) (as a resistive thin film heater) and a thermoelectric micro-sensor was chosen for the micro-scale measurement of temperature wave. The transparent ITO heater is usable for a fine positioning of the specimen under an optical microscope, and the thermoelectric sensor is free from the heat generation via the bias electric current. These are advantageous for the micro-scale measurement, because a resistance-type temperature sensor generates an inevitable heat when it is applied to the localized small area.

The setup for the measurement is shown in Fig. 1. The specimen is put between a thin ITO resistive heater and a thermoelectric micro sensor. Sinusoidal waveform voltage is applied to ITO film heater from a function synthesizer (NF Corporation, 1920A) that generates a periodic heat flow and the thermoelectric micro sensor measures a periodical temperature change in the micro-scale. The phase delay between the heater and sensor can be measured with a two-phase lock-in amplifier (NF Corporation, 5610B) over several frequencies. The thermal diffusivity α is calculated with a relationship between the phase delay $\Delta\theta$ [rad] and the frequency f [Hz]

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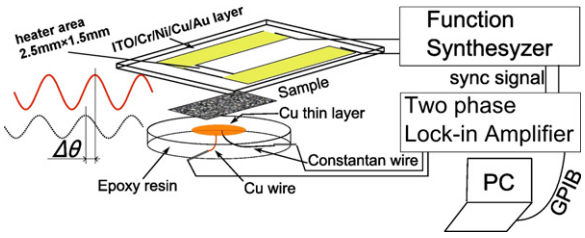

Fig. 1. Schematic diagram of the measuring instrument of TWA with a thermoelectric micro sensor buried in a disk of epoxy resin. The ITO resistive heater on the glass substrate is used as a heater to generate a temperature wave.

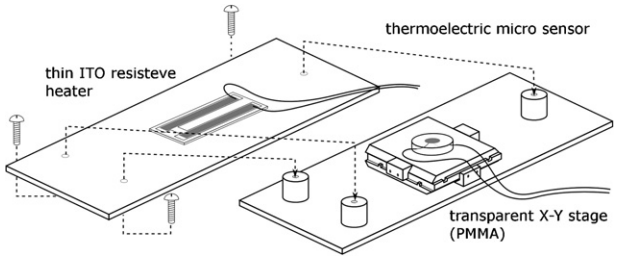

Fig. 2. The schematic view of the *X–Y* stage made of PMMA with a screw mechanism to fix the specimen in the fine position to achieve a good thermal contact. A Newton's ring is used to check the thermal contact.

as described in Eq. (1) [10,11]. The sample thickness d [m] and β are the constant values. Measurement parameters are determined so that thermal diffusion length of temperature wave is enough shorter than the thickness of specimen.

$$\Delta\theta = -\sqrt{\frac{\pi f}{\alpha}}d + \beta \quad (1)$$

2.2. Thin ITO resistive heater

Tightly focused UV pulse laser beam was used to ablate the ITO layer on the glass substrate (Geomatec Corporation, ITO layer thickness: 80–90 nm) in order to cut a heater area in rectangular shape. Unnecessary ITO layer was isolated in this laser ablation process. Bonding layers (Cr, Ni, and Cu) and a conductive gold layer were deposited on the lead area of the heater. Cr and Ni were sputtered by a magnetron sputtering method. Cu layer was deposited by a vapor deposition and Au layer was deposited by an ionic sputtering. The heater resistance of ITO was controlled within 40–60 Ω. If a solution casting procedure on the ITO heater was required, the copper wires were attached with a gold paste and an epoxy glue after polishing the surface of the specimen.

2.3. Thermoelectric micro sensor

The whole part of thermoelectric micro-sensor consists of a disk of epoxy resin matrix (Epicote828, cure condition: triethylenetetramine 13 wt%, 60 °C, 4 h), a constantan and copper thin wires buried in the matrix, and a deposited thin Cu layer. After polishing the top surface (Ra < 100 nm, with 0.3 μm polishing compound slurry) of the disk to make a slightly convex surface, a thin Cu layer (conductive and semi transparent) was deposited on the top surface with PVD to form a micro-scale hot junction at a tip of the constantan wire 12.5 μm in diameter.

2.4. Repeatability test

To confirm the repeatability of the measurement with the micro-scale TWA method, thermal diffusivities of polymer films were measured at each ten times. Poly-(methyl methacrylate) (PMMA) film (Sumitomo Chemical Co. Ltd., SUMIPEX, 77 μm), polystyrene film (Asahi Kasei Corporation, 50 μm), polyimide (PI) film (Du Pont-Toray Co. Ltd., Kapton H, 25 μm) were chosen for this test because of the flat surface and the uniformity in thickness.

2.5. Thermal diffusivity mapping in polymer spherulites

PLLA (Sigma Aldrich, Mw 100,000–150,000) 5 wt% chloroform solution was casting on the ITO thin resistive heater and dried for over 24 h in the atmospheric condition. PLLA cast film (20–30 μm in thickness) was molten at 190 °C, 5 min, then cooled down at a rate of 10 °C/min to the temperature 125 °C or 130 °C and isothermally crystallized until spherulites grew up to several 100 μm in diameter, and then quenched (at a rate of about 20 °C/s) to the room temperature. The thermal treatment was conducted in the hot stage system (FP82 HT, Metler-Toledo). The surface of the semi-crystallized film were slowly polished by using a polishing plate with a polishing compound (1 μm) slurry. The surface roughness on the specimen was controlled under 100 nm (Ra). The polished surface of the specimen and the sensor were softly contacted with a fine positioning under optical microscope using a transparent guide as shown in Fig. 2.

In order to avoid an air flow and an electric noise, the measurement system was placed in the steel container during the measurement. The micro-scale measurement of thermal diffusivity of PLLA spherulites was repeatedly done with changing the sensor position monitored under optical microscope. This procedure enables to visualize the thermal diffusivity mapping.

3. Results and discussion

3.1. Repeatability test

The averaged values of thermal diffusivity of PMMA, PS, and PI films of each ten times measurements are shown in Table 1. The standard deviation is less than 2%. It suggests that a good thermal contact was kept over whole experiments with a mechanical clamping system that is shown in Fig. 2. The zero-order bright fringe of Newton's rings observed under bright field microscope is used to confirm a good thermal contact between the sensor and the sample. By changing the torque applied to a three screw anchors in Fig. 2, the position of zero-order bright fringe of Newton's rings moves over a hot junction. Simultaneously, the center bright area size of Newton's rings corresponds to a contact pressure. The position and the area size of the zero-order fringe pattern were precisely controlled in order to achieve a good thermal contact on the same conditions. The thermal grease was not used in order to observe Newton's rings.

3.2. Thermal diffusivity mapping in PLLA spherulites

Fig. 3 shows the plot of the phase delay $\Delta\theta$ and the square root of frequency of temperature wave measured with a micro-sensor located at a different positions of (a), (b), and (c) as depicted in Fig. 4(B). The frequency was chosen so that the thermal diffusion legth of temperature wave is sufficiently shorter than the thickness

Table 1
Thermal diffusivity of polymer films, PMMA, PS, and PI, measured with a micro sensor.

Sample	Thermal diffusivity/10^{-7} m^2 s^{-1}
PMMA	1.09 ± 0.007
PS	1.06 ± 0.014
PI	1.06 ± 0.011