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NEW TECHNIQUE FOR FOURIER TRANSFORM THERMAL ANALYSIS

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Abstract

A new technique for the simultaneous measurement of higher order harmonic of temperature wave under temperature scan was proposed. The mathematical rule for the propagation of harmonies in the film shaped specimen was examined and the principle of Fourier transform thermal analysis was theoretically and experimentally justified. This principle applied to a technique called 'Fourier transform thermal analysis', makes it possible to determine simultaneously thermal diffusivity, heat capacity per unit volume and thermal conductivity as a function of frequency and temperature. The results on thermoplastics were shown and the glass transition and the crystallization were discussed.

Keywords: Fourier transform, harmonic, temperature wave, thermal diffusivity

Introduction

A new thermal analytic method which detects the propagation of temperature wave in the thickness direction of the film shaped specimen under temperature scan is proposed. This technique is classified into a transient method and the first stage has been originally developed in our laboratory [1–12] in the last decade. The main features are as follows. (1) using thin high-sensitive sensor with negligible heat capacity; (2) the temperature wave propagating in the thickness direction of the specimen is directly observed as the phase delay and the amplitude decay detected on a sensor, which is located at a distance *d* from a heater position, by using a two-phase lock-in amplifier; and (3) the thermal properties of thin film specimens can be determined non-destructively without any pre-treatment such as a blackening.

In addition to the above description the advantage of this a.c. technique is to detect the thermal properties even under the phase transitions with latent heat because the specified locked frequency is used to detect the propagation of temperature wave. This method is applicable to thermal analysis of various materials, thermoplastics [4, 5], thermosetting materials [9], porous materials [11], composites [12], fabrics and ceramics during heating or cooling process.

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Furthermore, at this stage a linear response of harmonic of temperature wave was successfully observed by inputting a square pulse train [13]. The principle described below was applied to a technique called ‘Fourier transform thermal analysis, (FT-TWA)’ which makes it possible to determine simultaneously thermal diffusivity, heat capacity per unit volume, and thermal conductivity in only one time temperature scan.

In this article the capability of wide application of FT-TWA to various material such as polymer, organic material, solution, ceramics, metal, and bio-material was examined. The phase transitions are discussed with the analysis of thermal diffusivity under temperature scanning. The experimental proofs of the mathematical rules at a constant temperature, and the mathematical procedures of the simultaneous measurements of thermal property were reported as previously [13, 14].

Principle

To analyze the propagation of temperature wave in the experimental system, a one-dimensional heat conduction model is assumed. A film specimen with thickness d is located between substrates that have known thermal properties and semi-infinite thickness. When a temperature wave is generated on the front surface ($x=0$), it propagates in the thickness direction to be detected on the rear surface ($x=d$). The waveform is selected as a sinusoidal wave, a square pulse train with a variable duty factor, a triangular wave, combinations, etc. The sinusoidal wave is very simple and suitable for calculating the precise thermal property as a function of temperature. When a square pulse train with constant angular frequency ω and pulse height V_0 is input on the heater, temperature wave consisted of multiple frequency is generated by a.c. Joule heating. The Fourier transform of input voltage $V(t)$ is derived as follows.

$$V(t)=V_0\left\{a+\sum_{\substack{n=-\infty\\(n\neq 0)}}^{\infty}\left|\frac{\sin(an\pi)}{n\pi}\right|\exp[(\mathrm{i}(n\omega t-an\pi)]\right\} \tag{1}$$

where a ($0<a<1$) is a duty factor and n is an integer. If the temperature wave decays to zero at an infinite position in substrates, temperature oscillation at rear surface $T(d,t)$ detected by a sensor is obtained by solving the one-dimensional thermal diffusion equation [15, 16] for each nth order, assuming a linear combination of the temperature wave, if $kd>>1$ or $k\lambda-k_s\lambda_s\cong 0$

$$T(d,t)=\frac{2c\sqrt{\alpha}}{(c\sqrt{\alpha}+c_s\sqrt{\alpha_s})^2}j_0\sum_{\substack{n=-\infty\\(n\neq 0)}}^{\infty}\left|\frac{\sin(an\pi)}{n\pi}\right|\sqrt{\frac{1}{|n|\omega}}\exp\left(-\sqrt{\frac{|n|\omega}{2\alpha}}d\right)\exp\left\{\mathrm{i}\left(n\omega t-\sqrt{\frac{|n|\omega}{2\alpha}}d-\frac{\pi}{4}-an\pi\right)\right\} \tag{2}$$

where, t is time, i is $(-1)^{1/2}$, λ is thermal conductivity, α is thermal diffusivity, c is heat capacity per volume, k is $(\omega/2\alpha)^{1/2}$, n is integer, j_0 is heat flux, and subscript s means the substrate. Phase delay ($\Delta\theta_n$) and amplitude decay (A_n) of each nth order harmonic are derived as,

$$\Delta\theta_n = -\sqrt{\frac{|n|\omega}{2\alpha}}d - \frac{\pi}{4} - an\pi \tag{3}$$

and

$$A_n = B\frac{2c\sqrt{\alpha}}{(c\sqrt{\alpha}+c_s\sqrt{\alpha_s})^2}\left|\frac{\sin(an\pi)}{n\pi}\right|\sqrt{\frac{1}{|n|\omega}}\exp\left(-\sqrt{\frac{|n|\omega}{2\alpha}}d\right) \tag{4}$$

where B is an instrumental constant determined by the heater resistance, applied pulse voltage, the heater area, and the sensor sensitivity. As a consequence, α, c and $\lambda=\alpha c$ are simultaneously obtained by analyzing $\Delta\theta_n$ and A_n of each n^{th} harmonic because other parameters are given as experimental conditions.

Experimental

The measurement system consists of function synthesizer (NF Electronic Instruments, NF1946), digital lock-in amplifier (Stanford Research, SR830), d.c. source for sensor, temperature controller (ULVAC HPC7000), specimen holder on hot stage, and personal computer (Fig. 1). The square pulse train with a frequency f=0.1 Hz~100 kHz, and a duty factor a=0.05~0.5 is applicable as an inputting pulse train. The frequency range for the measurement is selected considering the thermal diffusion length, $kd\geq1$. The sinusoidal wave was also examined to compare with the square wave and to check the accuracy of the absolute value. The generated temperature wave is selected less than 0.1 K on the front surface, and at that time less than

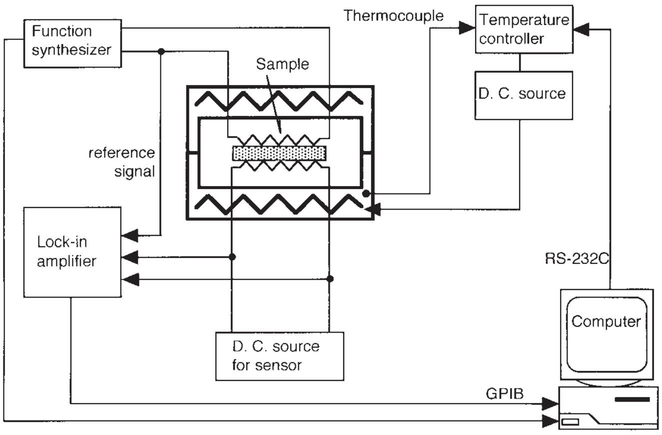

Fig. 1 Schematic diagram of measurement system

10 mK on the rear surface. A rate of heating or cooling is 0.2 K min^{-1} in order to minimize the temperature distribution in the specimen. The Fourier spectrum of temperature wave at rear surface was also observed by fast Fourier transform (FFT) analyzer.

Table 1 Thermal diffusivity of various material calculated by TWA technique

Specimen	Thickness d/μm	Thermal diffusivity $\alpha \cdot 10^{-7}$/m^2 s^{-1} (at r.t.)
Si wafer	575	950
Sapphire	126	150
Bi/Te/Sb	765	7.9
Quartz	417	7.4
Borosilicate glass	78	5.5
Polyethylene	92	3
Polyimide	26	1.5
Polystyrene	28	1.2
Silicon rubber	311	0.9
Cellulose paper	70	0.6
Epidermis of onion	84	2
Dried epidermis of onion	59	4.5
Pure water	51	1.4
Toluene	38	0.88

The film specimens used for the measurement are listed in Table 1. Polymer films, water, solvent, *n*-alkane, paper, rubber, quartz, and borosilicate glass were examined. The electric conductive materials such as Si wafer and the thermoelectric materials were also examined by a new technique [20] using a special heater coated with the insulator layer less than 0.1 μm.

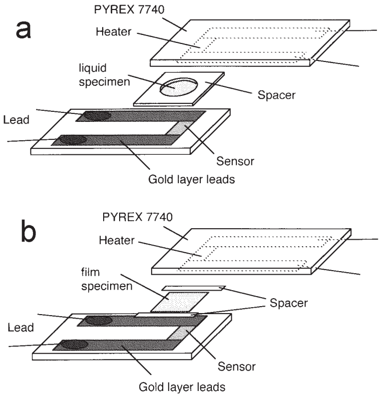

Fig. 2 An example of measurement cell; a – liquid specimen; b – film specimen

That is, there is no limitation for selecting the materials for TWA measurement, as long as the film shaped specimen. Basically a gold thin resistor controlled at about 50 Ω with rectangular area of 1×4 mm was sputtered on each surfaces of the substrate, pyrex 7740, one as a heater and the other as a sensor. The specimen film was inserted between the substrates, with a spacer to maintain a constant thickness (Fig. 2). When the specimen is liquid it is encapsulated in a sealed cell.

When the thickness *d* is known, thermal diffusivity is both calculated with the slope of the linear plot of $\Delta\theta$ *vs.* $\omega^{1/2}$ in Eq. (3), and by directly calculating with Eq. (5) which is rewritten from Eq. (3)

$$\alpha = \frac{n\omega d^2}{2\left(\Delta\theta_n + \frac{\pi}{4} + an\pi\right)^2} \tag{5}$$

By using Eqs (4) and (5) temperature dependent thermal property can be obtained in the temperature scanning.

Results and discussion

Figure 3 shows a relationship between $\Delta\theta$ and $\omega^{1/2}$ of various materials at r.t. The specimens were synthetic sapphire, pyrex 7740, Si wafer, thermoelectric materials, cellulose paper, high density polyethylene, ultra pure water, the inside epidermal

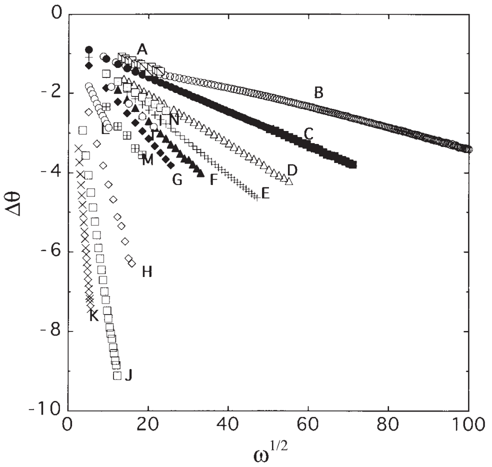

Fig. 3 Phase delay $\Delta\theta$ plotted *vs.* square root of angular frequency $\omega^{1/2}$ of temperature wave propagating in the thickness direction in film specimen of various materials. A – silicon wafer 575 μm; B – sapphire 126 μm; C – polyimide 26 μm; D – polystyrene 28 μm; E – borosilicate glass 78 μm; F – pure water 51 μm; G – polyethylene 92 μm; H – quartz 417 μm; I – toluene 38 μm; J – silicon rubber 311 μm; K – Bi/Te/Sb 765 μm; L – cellulose paper 70 μm; M – epidermis membrane of onion 84 μm and N – dried membrane of onion 59 μm

membrane of onion, and toluene. As predicted by Eq. (3) a linear relationship between $\Delta\theta$ and $\omega^{1/2}$ in the condition $kd\geq1$, was observed, with the intercept $-\pi/4$. The thermal diffusivity obtained by the slopes in Fig. 3 are shown in Table 1.

In Table 1 thermal diffusivity was directly calculated from the slope in Fig. 3 without any reference material or calibration. The values are almost consistent with the literature value. As well known, the thermal property of solid specimen depends on the physical state and anisotropy, so it is not easy to obtain a fixed value as a standard material. On the other hand, pure water shows high accordance with the literature value and can be selected as a standard material in this measurement. The thermal diffusivity of paper, which is considered as a composite of air and the cellulose fiber, is to be taken as an apparent value. The precision of thermal diffusivity, which depends on the measurement of thickness and its distribution of the specimen, can be controlled less than 2%. It is also possible to determine thermal conductivity, and heat capacity per unit volume by TWA method [21] and the results are shown in Table 2. In this article the measurement of thermal diffusivity on the phase transition is mainly discussed in the following.

Table 2 Thermal conductivity, thermal diffusivity, and heat capacity per unit volume at r.t. calculated by TWA technique

Sample	Thermal diffusivity	Heat capacity per volume	Thermal conductivity λ/W m^{-1} K^{-1}	
	$\alpha\cdot10^{-7}$/m^2 s^{-1}	$c\cdot10^6$/J m^{-3} K^{-1}	measured	literature
Toluene (l)	0.88	1.5	0.13	0.13
$C_{12}H_{26}$ (l)	0.75	1.6	0.12	0.14
Pure water (l)	1.4	4.4	0.63	0.59
PE (s)	3.5	1.5	0.53	0.46~0.53
PI (s)	1.7	1.5	0.26	0.29

Figure 4 shows the thermal diffusivity of PS under heating and cooling on the glass transition detected by the sinusoidal wave with the frequencies 64, 80, 120, 214 and 320 Hz. In the measurement with sinusoidal wave, the frequency of temperature wave is fixed, so in order to examine the frequency dependence of thermal diffusivity on the glass transition, repeated measurements are needed.

Figure 5a shows the waveform of the signal detected on the sensor, which is observed as a voltage oscillation. The signals were preamplified (gain=100) prior to the input in the oscilloscope. Triangular-like waveforms are observed when a square pulse train with frequency 70 Hz and duty factor a=0.2 is inputted. The signals in Fig. 5b were taken from the fast Fourier transform of the time signals in Fig. 5a. The line spectra are observed at frequencies of 70, 140, 210, 280 Hz, corresponding to the fundamental frequency, and the 2nd, 3rd, and 4th order harmonic, respectively. According to Eq. (4), no signals can be observed when $\sin(an\pi)$ is zero. In Fig. 5b, $\sin(0.2n\pi)$ becomes zero when n is a multiple of 5.

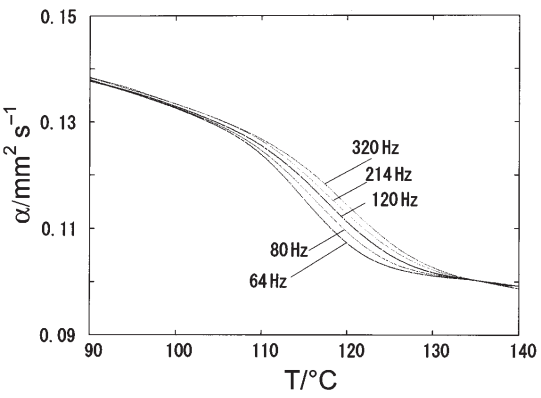

Fig. 4 Thermal diffusivity of polystyrene calculated from the phase delay of sinusoidal temperature wave. The frequency of temperature wave is as follows; *f*=64, 80, 120, 214, 320 Hz, thickness *d*=28 μm, and the temperature scan rate is 0.2°C min^{-1} on heating and cooling

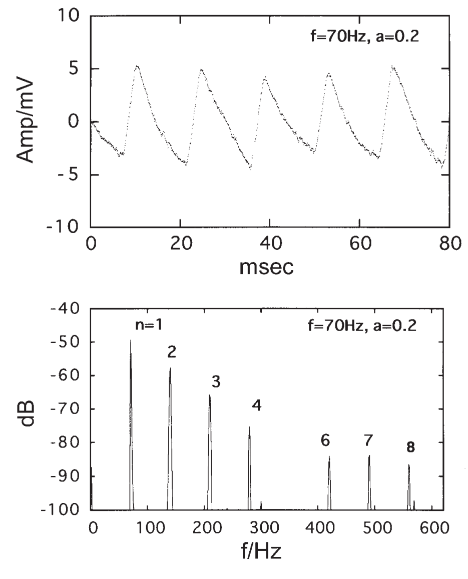

Fig. 5 Waveform (a) and FFT spectrum (b) of temperature wave detected on a sensor in polystyrene film with thickness *d*=28 μm. The fundamental frequency is *f*=70 Hz, and duty factor *a*=0.2

The advantage of Fourier transform thermal analysis is the simultaneous measurements of multiple frequencies in only one time temperature scan. Figure 6 shows the temperature dependent α of PS, calculated from $\Delta\theta_n$ of the 1st to the 4th harmonic with a fundamental frequency of 70 Hz and a duty factor *a* of 0.2 at a heating and a cooling rate of 0.2°C min^{-1}. The glass transition was clearly observed as a change of

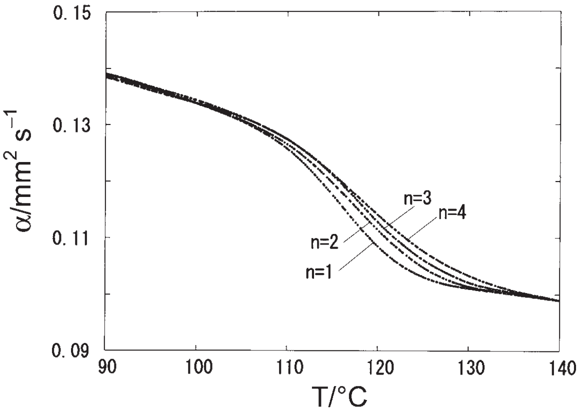

Fig. 6 Thermal diffusivity α of polystyrene calculated from $\Delta\theta_n$. Fundamental frequency f=70 Hz, duty factor a=0.2, the harmonic order n=1st to 4th, thickness d=28 μm, and the temperature scan rate is 0.2°C min^{-1} in heating and cooling

thermal diffusivity dependent on the frequency of temperature wave. The higher the frequency, the higher the transition temperature was observed. Above and below the glass transition temperatures, no frequency dependence was observed. In comparison with Fig. 4, the harmonic leads to the same frequency dependence of thermal diffusivity, with the identical values in molten state and in solid state.

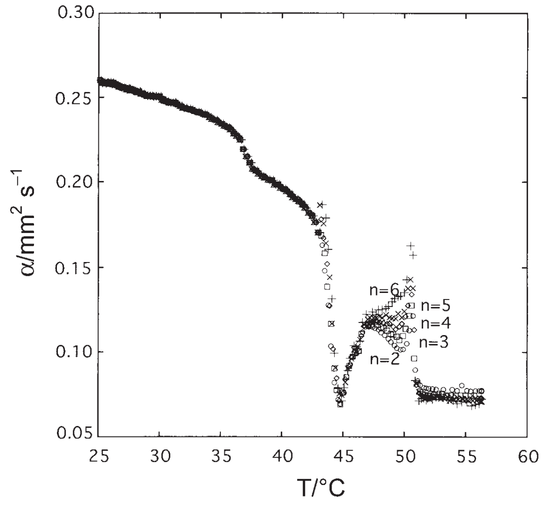

Fig. 7 Thermal diffusivity α of n-$C_{25}H_{52}$ calculated from $\Delta\theta_n$ in cooling from the liquid state. Fundamental frequency f=15 Hz, duty factor a=0.125, the harmonic order n=2nd to 6th, thickness d=53 μm, and the cooling rate is 0.2°C min^{-1}. (o): n=2 (30 Hz), (□): n=3 (45 Hz), (◊):n = 4 (60 Hz), (×): n=5 (75 Hz), (+): n=6 (90 Hz)

Figure 7 shows the thermal diffusivity of *n*-pentacosane calculated from $\Delta\theta_n$ of the 2nd to the 6th harmonic with a fundamental frequency of 15 Hz and a duty factor *a* of 0.125 at a cooling rate of 0.2°C min^{-1} from the liquid state. The liquid to solid phase transition was observed at 51°C as a steep increase of α. In this process no frequency dependence was observed. Compared with the previous studies of DSC [17, 18], a steep increase of α at 45°C corresponds to the transition of hexagonal to orthorhombic. In addition, a delta transition [19] was also observed at 37°C. The frequency dependence of α was observed after crystallization and in the transition process in the rotational phase. This phenomenon is quite new with significant meanings. The first point is that only by the a. c. technique can these phenomena be detected without any influence of the latent heat. The second point is that Fourier transform thermal analysis makes possible the simultaneous measurement at thermal diffusivity at multiple frequencies.

During the phase transition it takes time to reorganize the molecules, and, as a result, frequency dependence was observed. On the other hand, in the liquid state at higher temperature, for example, the molecular motion corresponds to the experimental frequency range, so the frequency dependence was not observed.

Conclusions

A new thermal analysis is proposed in which the propagation of temperature wave is detected under temperature scan. The measurement procedure is simple and a small quantity of specimen is needed without any special pre-treatment. The thermal diffusivities of various materials were shown, for example, the solid and liquid states of polymer and *n*-alkane, pure water and solvent, inorganic materials, and electric conducting materials such as Si wafer and thermoelectric material. The phase transitions of polystyrene and *n*-alkane were examined and the frequency dependence was found out by one time temperature scan. The thickness range for the measurement is from sub-micron to 1 mm, the frequency range is up to 100 kHz.

This technique is unique that the input and the output signals are separately detected, therefore, at least two absolute values are obtained. Both phase delay and amplitude decay are experimentally detected. Once the measurement system was calibrated with a standard material with a known thermal property, such as water, toluene, thermal conductivity or heat capacity per unit volume can be determined.

The simple and the unique measurement system made it possible to observe the propagation of harmonic in the thickness direction. By inputting a square pulse train with a various duty factor, thermal property at plural frequencies can be simultaneously detected under temperature scan. It means that the frequencies dependence can be precisely examined in only one time scan.

This technique was named as FT-TWA (Fourier transform temperature wave analysis) and the unique measurement results especially observed in the phase transitions, which could not be seen in the conventional thermal analysis, were shown.

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