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Thermal diffusivity of thermosetting materials by temperature-wave analysis

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Abstract

Thermal diffusivity in the isothermal curing process of the thermosetting systems, including the filler highly loaded epoxy molding compound for IC packaging were examined with temperature-wave analysis based on the a.c. Joule-heating technique. The increase of the thermal diffusivity in the isothermal curing process was clearly observed as a function of time, which is related to the network formation. In the filler highly loaded thermosetting system the two step increase of thermal diffusivity was observed. The thermal diffusivity obtained at different frequency after the isothermal curing was also shown as a function of temperature.

Keywords: Curing process; Epoxy compound for IC; Epoxy resin; Temperature wave analysis ; Thermal diffusivity

1. Introduction

Thermosetting materials are widely used in many fields of industry, for example as adhesives, paints, composites, and molding compounds for IC packaging. The thermophysical properties, especially for thermal transport, are of practical importance in the molding process of the aforementioned materials.

There are, however, few available experimental results for thermal conductivity or thermal diffusivity in the curing process because of difficulty in the experimental technique, caused by the change of the physical state, and the reaction heat generated in the process. Temperature-wave analysis [1], based on the a.c. Joule-heating method [2–5], is applicable in observing the change of thermal diffusivity in the curing process. With this technique, the thermal diffusivity can be obtained under a constant-temperature scanning program in the temperature range including the solid state, liquid state and the phase-transition region, in the 10 Hz ~ 2 kHz frequency range of the temperature wave for polymers.

The temperature modulation technique in thermal analysis was reported by many authors, for example by Hatta for a.c. calorimetry [16,19–21], Reading et al. [6,7,14], Gill et al. [8], Wunderlich et al. [15], Schawe [22–24] and Van Assche et al. [17] for modulated differential scanning calorimetry (MDSC), Birge [9–11] for specific-heat spectroscopy, and Polikarpov et al. [12,13] for thermophysical properties. The advantage of the temperature-modulation technique can be described as: (1) – to observe the imaginary component of the thermophysical property due to relaxation phenomena; and (2) – to obtain the thermophysical values even under the transitions accompanying the exothermic or endothermic heat.

In this study, temperature-wave analysis is applied to the measurement of the change of thermal diffusivity in the reacting process of epoxy resins. With this technique, the phase lag and the amplitude of the

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temperature wave, passing through the sample film across its thickness, can be detected as a function of time or that of temperature [1,18]. Hence, it has become possible to detect the curing process of thermosetting systems in situ and other chemical reaction processes even under exothermic or endothermic heat conditions.

The application of temperature-wave analysis to the curing process will be proposed and the change of thermal diffusivity on the curing process in the thermosetting systems, including the filler highly loaded epoxy molding compound for IC packaging, will be reported.

2. Experimental

2.1. Samples

The samples used in this study were the commercial amine-cured epoxy resin; Araldite (Ciba Geigy), and the anhydride-cured epoxy resin; Epikote 828 (Yuka–Shell). The epoxy molding compound for IC chip encapsulation was also examined. Silica filler highly loaded epoxy and phenolic resin for molding compound for IC(TI Epoxy) was supplied by Texas Instruments (TI).

2.2. Apparatus

The schematic diagrams of the measurement system and the detail of sample cell are given in Ref. [1]. A thin gold layer was used as a temperature wave generator and another as a detecting sensor. By the passage of a sine current through the heater, the temperature wave was generated at the front surface of the sample and propagates through the sample. The amplitude of the input temperature wave was chosen by considering the sample conditions such as thickness and thermal diffusivity, α. The temperature variation at the rear surface was detected by the variation of the electrical resistance of the sensor. The a.c. component of the resistance was amplified and analyzed using a lock-in amplifier (NF-5610B). The sample film, $5 \times 10\,\mathrm{mm}^2$ in size and (10–100) μm in thickness, was inserted between two slide glass plates on which the thin gold layers were sputtered across an $1 \times 4\,\mathrm{mm}^2$ area as a sensor and a heater, respectively. The thickness of the sample was maintained by the insertion of spacers to avoid deformation during measurement.

A thermocouple was inserted into a dummy sample, which was located symmetrically to the sample on the hot stage. It was assumed that the temperature of this thermocouple was equal to that of the sample film. The temperature of the hot stage was maintained at a constant value under isothermal conditions during the curing process.

The measurement of thermal diffusivity was also performed on a cured sample under temperature scanning at constant rates of 1°C/min and 0.2°C/min.

2.3. Analysis

The heat flow through the thin films across their thickness, when the substrates contact at $x = 0$ and $x = d$, is described by the one-dimensional heat diffusion equation as follows:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (0 < x < d)$$
$$\frac{\partial T}{\partial t} = \alpha_s \frac{\partial^2 T}{\partial x^2} \quad (x < 0 \,\mathrm{and}\, d < x) \tag{1}$$

where T is the temperature, α the thermal diffusivity of the sample and α_s those of the substrates. The thermal diffusion equation (Eq. (1)) can be solved with certain boundary conditions, and the temperature oscillation at $x = d$ is determined as [10,16]:

$$T(d,t) = \frac{\{q_0 \exp(i\omega t)/(1+i)\}\exp\{-(1+i)kd\}}{[(\kappa k + \kappa_s k_s)^2 - (\kappa k - \kappa_s k_s)^2 \exp\{-2(1+i)kd\}]/2\kappa k} \tag{2}$$

where $k = \sqrt{\omega/2\alpha}$ and $k_s = \sqrt{\omega/2\alpha_s}$, κ and κ_s are the thermal conductivities of the polymer and the substrate, $q(t)$ is a periodical heat flux at $x = 0$ by a.c. Joule heating. For thermally thick condition, $kd > 1$ is satisfied and $\kappa k \cong \kappa_s k_s$, Eq. (2)

reduces to

$$T(d,t) = \frac{\sqrt{2}q_0\kappa k\exp(-kd)}{(\kappa k + \kappa_s k_s)^2} \times \exp\left\{i\left(\omega t - kd - \frac{\pi}{4}\right)\right\} \qquad (3)$$

The amplitude of the signal voltage and the phase lag to the reference are determined experimentally by the lock-in amplifier. The phase shift of the temperature wave $\Delta\theta$ between the two surfaces of the sample is given as

$$\Delta\theta = -\sqrt{\frac{\omega}{2\alpha}}d - \frac{\pi}{4} \qquad (4)$$

Eq. (4) can be written using the frequency ($2\pi f = \omega$) of the temperature wave as follows:

$$\alpha = \pi f\left(\frac{d}{\Delta\theta + \frac{\pi}{4}}\right)^2 \qquad (5)$$

According to Eq. (5), α can be determined by $\Delta\theta$ at a constant frequency. When the time is developing under the isothermal condition, we can obtain α as a function of time.

On the other hand, the amplitude of the temperature wave at the rear surface can also be determined as

$$\mathrm{Amp} = A\frac{\sqrt{2}q_0\kappa k\exp(-kd)}{(\kappa k + \kappa_s k_s)^2} \qquad (6)$$

The amplitude of the temperature wave passing through the sample film across its thickness can then be obtained under isothermal conditions as a function of time.

3. Results and discussion

In Fig. 1, the thermal diffusivity α in the amine-cured thermosetting system of Araldite is shown as a function of time under the isothermal curing process at 26°C. Temperature wave is applied at 16 Hz. Thermal diffusivity moderately increases with the passage of time, going up to a value of $\alpha = 1.4 \times 10^{-7}(\mathrm{m^2\,s^{-1}})$. The increase of α in the curing process, which is related to the network formation, means that the transport of temperature becomes good with the progress of reaction. It is noteworthy that α can be clearly obtained from the curing process, in which the reaction heat is generated.

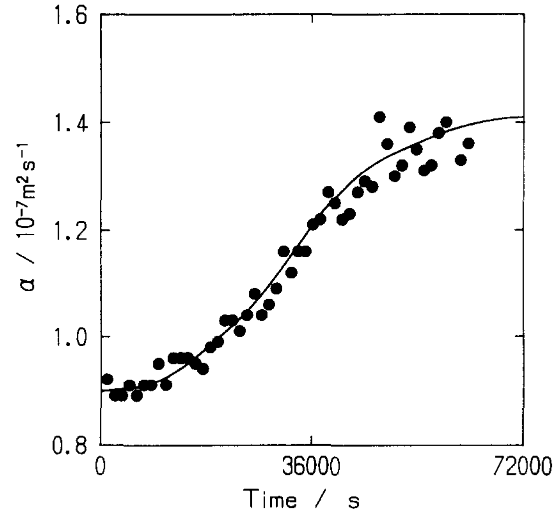

Fig. 1. Thermal diffusivity α of Araldite as a function of time under the isothermal curing process at 26°C. Temperature-wave frequency is 16 Hz.

This technique was also applied to the thermosetting system of Epoxy for IC chip encapsulation. The time development of $\Delta\theta$ (phase shift) and Amp (amplitude) are shown in Fig. 2. on the isothermal curing process at 80°C under the temperature wave of

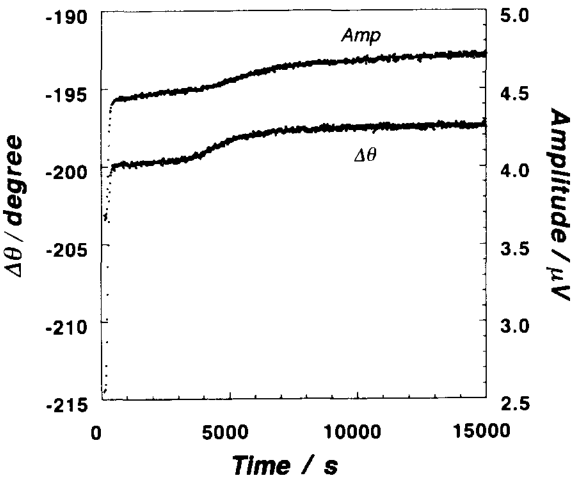

Fig. 2. $\Delta\theta$ (phase shift), and Amp (amplitude) of Epoxy for IC as a function of time under the isothermal curing process at 80°C. Temperature-wave frequency is 16 Hz.

16 Hz. Immediately after the beginning of isothermal curing, a rapid increase of $\Delta\theta$ and Amp are both observed. After this rapid increase, $\Delta\theta$ and Amp keep a constant value for some time, and then increase moderately again.

It is not our purpose here to analyze the chemical process precisely, but the two-step changing of thermal diffusivity is suggestive of the curing mechanism of this thermosetting system. In order to consider the relation between the curing and the molding times, we assume the classical expression for the kinetics:

$$\mathrm{d}x/\mathrm{d}t = k(1-x)^n \tag{7}$$

where x is the fraction of species consumed after time, t, n the reaction order parameter, and k the specific rate constant. It is assumed that the time scale for curing process corresponds to the practical molding time. Here, the process of step change is defined as Stage I (the first increase) and Stage II (the second increase). $\Delta\theta$ and Amp increase in both stages, and in Stage II the increase of Amp shows a retardation from the increase of $\Delta\theta$. Amp includes the term of thermal conductivity, so it suggests that the network formation in the curing process also affects the heat conduction.

In Fig. 3. the α of Epoxy for IC as a function of time under the isothermal curing process at 80°C is calculated with $\Delta\theta$. The two-step increase of α in the curing process is clearly observed. A larger change of α is observed in Stage I than in Stage II.

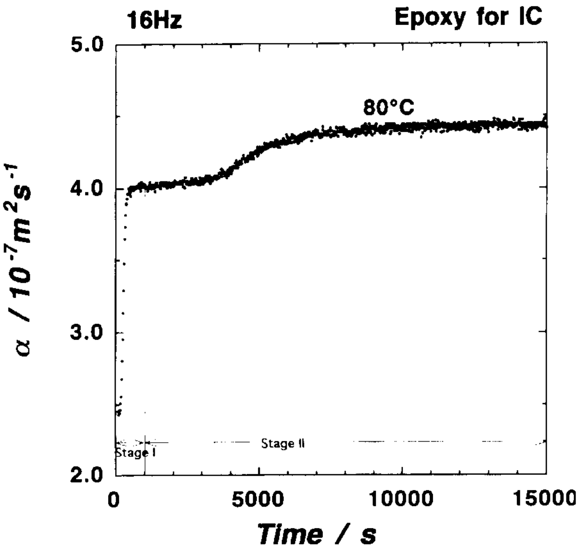

Fig. 3. Thermal diffusivity α of Epoxy for IC as a function of time under the isothermal curing process at 180°C. Temperature-wave frequency is 16 Hz.

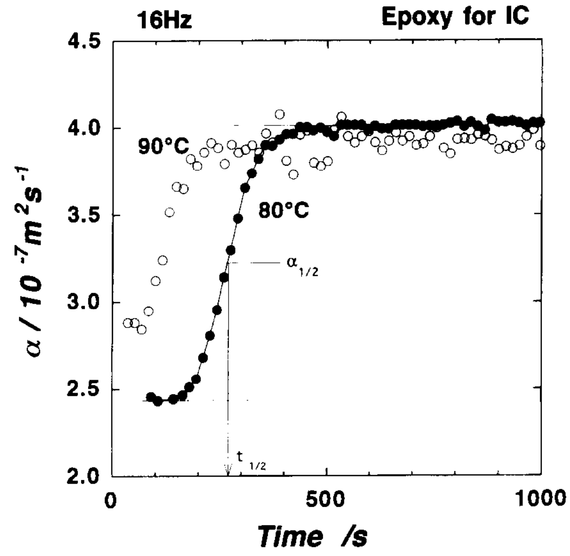

Fig. 4. Thermal diffusivity α of Epoxy for IC in the early stage (Stage I) of the curing process at 80°C and 90°C. Temperature-wave frequency is 16 Hz. The half time $(t_{1/2})$ of Stage I is indicated by an arrow in this figure ($\alpha_{1/2}$ is the half the value of the difference between the α before and after the curing). In Stage II, $t_{1/2}$ is also defined in the same way.

A detailed analysis for α in the early stage (Stage I) of Epoxy for IC is shown in Fig. 4. The rapid increase of α can be clearly observed as a function of time immediately after the beginning of the curing process at 80°C and 90°C, respectively. α increases rapidly up to the value $\alpha - 4.0 \times 10^{-7}$ (m^{2}s^{-1}), thereafter α remains constant until the beginning of the Stage II. The half time $(t_{1/2})$ of each step of the curing process is defined in Fig. 4.

In Fig. 5, the half time $t_{1/2}$, plotted against 1/T for the different thermosetting systems: Araldite, and Epoxy for IC (stage I and stage II). As a first-order approximation, $n = 1$ in Eq. (7) is assumed. A linear relation between the $\log t_{1/2}$ and 1/T is observed in both systems, and both in Stage I and Stage II. The slope in Stage I is three times larger than the slope in Stage II, and the slopes in Stage II and Araldite are almost identical. The activation energy assuming the Arrhenius type is 27.8 kJ/mol for Araldite, 25.5 kJ/mol for Stage II and 73.9 kJ/mol for Stage I.

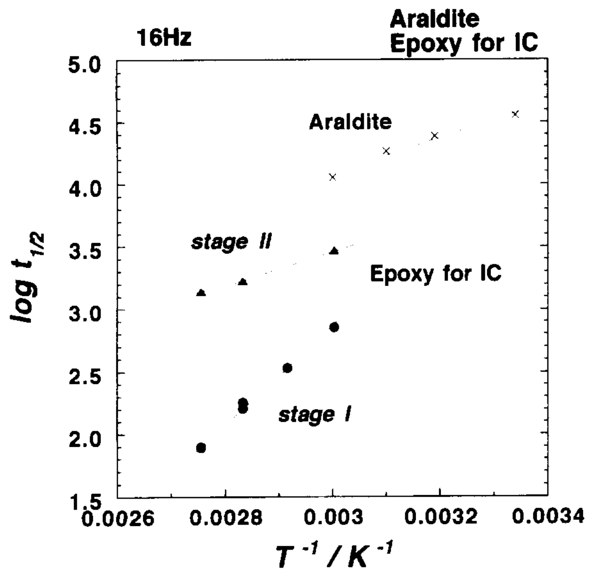

Fig. 5. The half time $t_{1/2}$, defined by an arrow in Fig. 4, is plotted against 1/T for the different thermosetting systems; Araldite, and Epoxy for IC (Stages I and II).

From a practical viewpoint, the time scale in Stage I corresponds to the injection molding time at the molding temperature. The time scale of the exothermic heat in the reaction process detected by DSC also corresponds to Stage I [25]. The physical meaning of Stage II is not clear at the present stage. It can only be assumed that Stage II concerns with the enhancement of the three-dimensional network or a kind of degradation. It should be reported in future, considering the relation between the change of thermal diffusivity and the reaction heat.

Temperature wave analysis of completely cured (at 90°C) Epoxy for IC is shown in Fig. 6. $\Delta\theta$ is shown as a function of temperature under a heating and a cooling run of ± 1.0°C/min. Temperature-wave frequency is 6, 20, and 60 Hz, respectively. The almost linear change in $\Delta\theta$ is observed both in the heating and the cooling runs.

Fig. 7 shows thermal diffusivity α of cured Epoxy for IC calculated with $\Delta\theta$ in Fig. 6 as a function of temperature. The α calculated from each frequency of temperature wave is in good accordance under the heating and cooling run of ± 1.0°C/min.

Thermal diffusivity α of cured Epikote 828 is shown in Fig. 8 as a function of temperature under a cooling program of -0.2°C/min. The curing was performed at 150°C for 90 min. The glass transition is clearly observed as an increase of α at ca. 140°C. Temperature-wave analysis is effective for the measurement of thermal diffusivity in the complicated systems such as a thermosetting material for IC chip

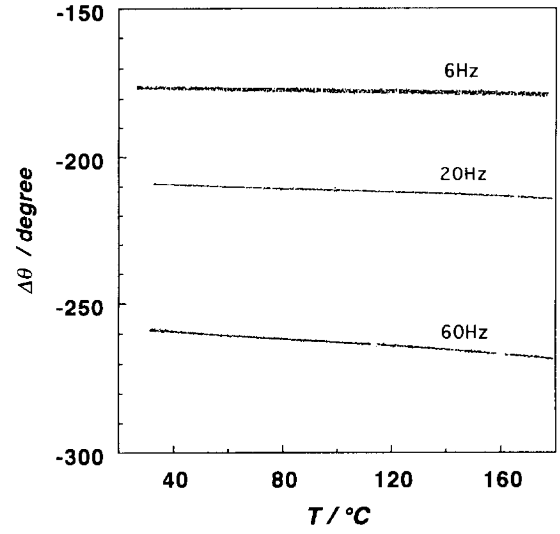

Fig. 6. Temperature-wave analysis of cured (at 90°C) Epoxy for IC. $\Delta\theta$ as a function of temperature under a heating run with $+1.0$°C/min. Temperature-wave frequency is 6, 20, and 60 Hz.

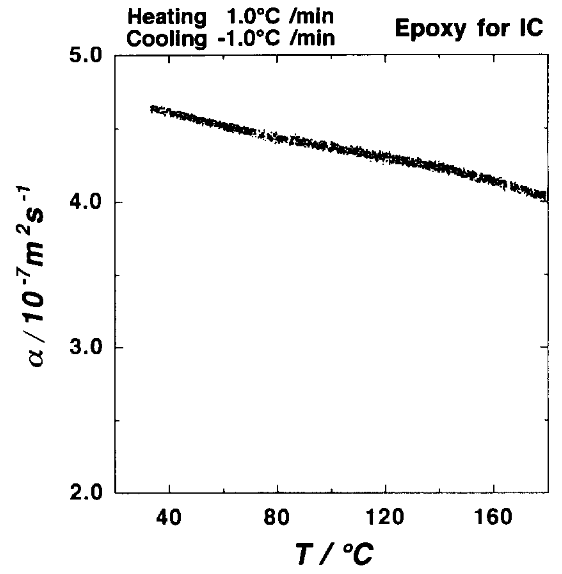

Fig. 7. Thermal diffusivity α of cured Epoxy for IC as a function of temperature under a heating run with $+1.0$°C/min, and a cooling run with -1.0°C/min.

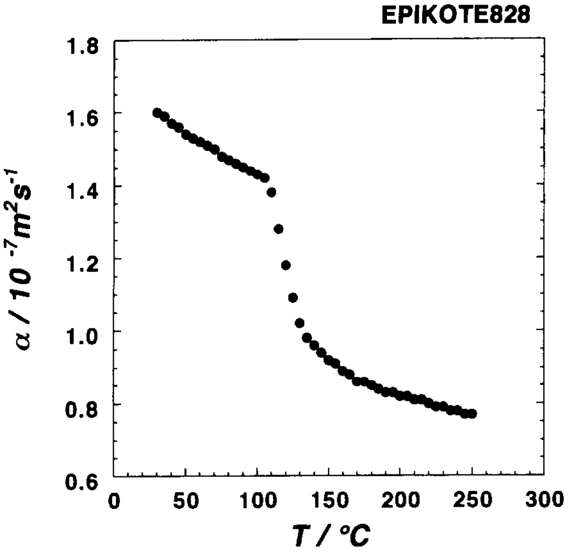

Fig. 8. Thermal diffusivity α of cured Epikote 828 as a function of temperature. The curing condition is at 150°C for 90 min.

encapsulation, and is sensitive to the change of the fine structure in the curing process and in the glass transition.

4. Conclusion

The change of thermal diffusivity on the curing process was successfully examined by temperature-wave analysis in the thermosetting systems of amine-cured epoxy resins, and silica filler highly loaded epoxy for molding compound for IC. The two step increase of thermal diffusivity on the curing process, Stages I and II were observed in the Epoxy for IC systems. The time scale in Stage I calculated at the molding temperature corresponds to the time scale in the practical molding process. As for the completely cured epoxy, a clear glass transition was observed in the anhydrite-cured epoxy, but not clear in silica filler highly loaded epoxy compound in the measurement of thermal diffusivity as a function of temperature.

Temperature-wave analysis is effective for the measurement of thermal diffusivity in the complicated systems such as a thermosetting material for IC chip encapsulation, and is sensitive to the change of the fine structure in the curing process and in glass transition.

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