Curing Kinetics of the No-Flow Underfill Encapsulant

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Abstract

The cure kinetics of a cycloalipatic epoxy / anhydride / Co(II) system for a no-flow underfill encapsulant, has been studied by using a differential scanning calorimetry(DSC) under isothermal and dynamic conditions over the temperature range of 160℃~220℃. The kinetic analysis was carried out by fitting dynamic/isothermal heating experimental data to the kinetic expressions to determine the reaction parameters, such as order of reaction and reaction constants. Diffusion-controlled reaction has been observed as the cure conversion increases and successfully analyzed by incorporating the diffusion control term into the rate equation. The prediction of reaction rates by the model equation corresponded well to experimental data at all temperature.

1. Introduction

Underfill encasulants as the material used as an adhesive to reinforce the physical and mechanical properties of the solder joint between the chip and the substrate in flip-chip devices.[1-2] To insert the underfill encasuant in a gap between the chip and the substrate an epoch-marking no-flcw underfilling method invented to simultaneously reflow solder bump and cure the underfill encapsulant. So this can eliminate not only the underfilling step but also the strict limitation on the viscous flux behavior underfill encapsulants to package sizes. A critical demands for underfill encapsulants used in the no-flow underfilling method is that occur their minimal cure reaction below solder bump reflow temperature and that allow a rapid cure reaction right after the completion of solder bump reflow. Beside the most underfill materials require long cure time and the final electrical, physical and mechanical properties of underfill materials depend to a large extent on the degree of curing. Based on upper requirements, the properties of the cured product are determined by the degree of cure, which depends on the curing conditions. Therefore, knowledge about the cure behavior and cure rate is essential to get optimum cure conditions for good no-flow underfill encapsulants.[3-5]

In this study, the cure kinetics of cycloalipatic epoxy/anhydride/Co(II) acetylacetonate system was studied using the DSC technique. Contribution of diffusion to the cure kinetics was also considered. This work will provide information for optimizing the cure conditions.

2. Experimantal

Materials

The epoxy resin was 3, 4- epoxy cyclohexyl-3, 4-epoxy cyclohexyl carboxylate and the hardener was hexahydro-4-methylphthalic anhydride(HMPA) which were purchased from Aldrich chemical company Inc. and used as received. Co(II) acetylacetonate was used as latent epoxy catalyst for the no-flow underfill encapsulants. The equivalent weight of epoxy resin

was 120g and HMPA was 168.2g.

Differential Scanning Calorimetry

Differential scanning calorimeter analysis data was carried out by using Perkin-Elmer Pyris 1. For dynamic heating experiments, four different heating rates were taken: 5.0, 10.0, 15.0, and 20.0℃/min from 50 to 300℃. Isothermal experiments were carried out at 160, 170, 180, 190, 200 and 210℃ in order to obtain the cure rate and the degree of conversion as a function of time.

The degree of cure a, in other words, cure conversion, was determined from the following equation;

$$\alpha = \frac{\Delta H_t}{\Delta H_\infty} \qquad (1)$$

where ΔH_i is the partial heat of reaction at time t, from isothermal scan test, and ΔH_∞ is the average total heat of reaction, and was determined from a dynamic DSC scan result at a heating rate of 5.0, 10.0, 15.0, and 20.0℃/min. The cure reaction rates can be obtained from the cure conversion data as a function of time by simply taking the derivative of α with respect to time, i.e., $\frac{d\alpha}{dt}$.

3. Results and Discussion

Cure conversion / Cure rate

To utilize Eq (1), the ΔH_∞, the total heat of reaction, was determined by the average value of reaction heats calculated from the total area under the thermogram of the DSC dynamic scans at different heating rates. Fig. 1 shows the heat flow measured by DSC during cure at different heating rates.

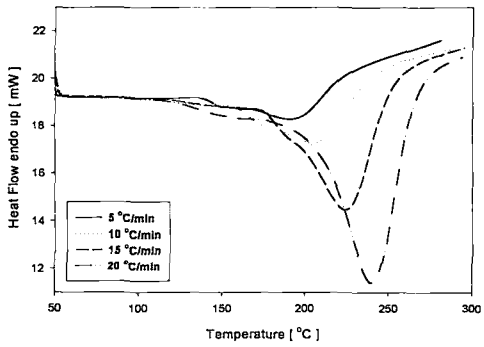

Fig. 1 DSC cure exotherm during cure at different heating rates.

The typical cure conversion (α) and the cure reaction rate ($d\alpha/dt$) curves of a series of DSC isothermal scan data for the underfill encapsulants as a function of time are shown in a Fig. 2 and a Fig. 3 respectively. A dramatic increase in conversion as time increases is observed as also can be seen in some works on cure kinetics of underfill encapsualnts, which is shown in a Fig. 2 [4]. The shape at early edges is considered as a result of the autocatalytic effect of the reaction product, which leads to high initial reaction rate. The slope is even steeper for the reactions that occur at higher temperatures since the initial reaction rate is faster at higher cure temperatures, which is shown in Fig. 3.

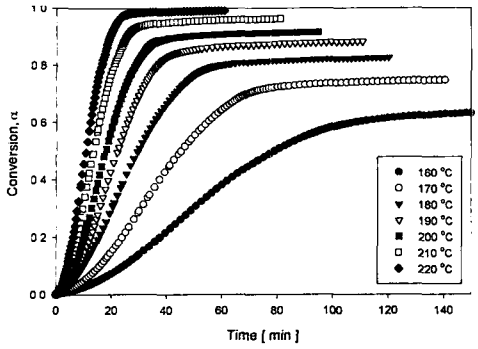

Fig.1 Time-conversion relationships at several cure temperature by isothermal method.

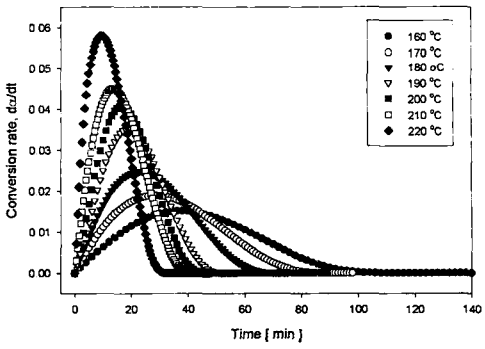

Fig. 2 Time-conversion rate relationships at several cure temperature by isothermal method.

Isothermal kinetics: autocatalytic model with diffusion control factor

The autocatalytic model is a general equation based on a phenomenological approach to analyzing the cure kinetics of amine-cured epoxy system and is as follows;

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \qquad (2)$$

where α is the conversion, k_1 and k_2 are the rate constants, m and n are the kinetic exponents of the reactions, and m+n is the overall reaction order. In the present study, the autocatalytic model has been used to determine the cure kinetics of anhydride-cured epoxy system. Isothermal DSC data at several temperatures were obtained to adjust the experimental results with the kinetic equation, and finally the reaction orders and the rate constants were calculated simultaneously by using the nonlinear regression method.

A rate equation with diffusion control factor is a semiempirical equation based on a free-volume considerations, and has been proposed to explain the retardation of cure reaction in the later stage of the reaction, virtually subjected to diffusion control as a result of vitrification. The final rate equation can be written;

$$\frac{d\alpha}{dt} = \frac{(k_1 + k_2\alpha^m)(1-\alpha)^n}{1+\exp[C(\alpha-\alpha_c)]} \qquad (3)$$

where C is α parameter of diffusion control, and αc is a critical value of cure conversion. As a reaches to αc, cure reaction becomes to be controlled by diffusion.

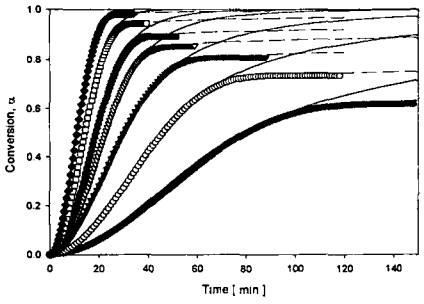

Fig. 3 Time-conversion relationships at several cure temperature by isothermal method: experimental data(symbols) and calculated data(lines)

Table I Kinetic parameters for the no-flow underfill encapsulant obtained from each isothermal test

T [℃]	m	n	m+n	$1000 \times k_2$ [min^{-1}]	$1000 \times k_1$ [min^{-1}]
160	0.9243	2.6161	3.5404	1.775	58.34
170	0.8801	1.9256	2.8056	2.570	78.78
180	0.8392	1.5693	2.4085	4.860	92.93
190	0.7644	1.2882	2.0527	3.905	115.33
200	0.7536	1.1758	1.9294	4.617	136.95
210	0.6802	0.9378	1.6180	6.286	145.80
220	0.5411	0.7772	1.3183	1.763	160.03

In the present study, conversion versus reaction time at 160, 170, 180, 190, 200, 210 and 220℃ of underfill encapsulants are shown in Fig. 3, the calculated lines were obtained from the Eq. (3), with and without diffusion control factor, and with the experimental data. And all parameters in Eq. (3) can be obtained simultaneously by applying nonlinear regression method and the calculated results are listed in Table 1.

Autocatalytic nature, characterized by the maximum cure rate at the early stage of the reaction, is clearly shown from the start of the cure reaction. As cure conversion approaches to the final conversion, differences between model predictions without diffusion control factor and experimental data became pronounced, which indicates that at the later stage of reaction diffusion controlled factor in the rate expression should be considered as shown in Eq. (3). The autocatalytic model, predicted using the calculated parameters, can fit only the initial stage of the reaction because of vitrification, and this fact suggests that diffusion effect should be considered in the vitrification-occurring region.

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