Research Article

Thermal and Cure Kinetics of Epoxy Molding Compounds Cured with Thermal Latency Accelerators

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The cure kinetics and mechanisms of a biphenyl type epoxy molding compounds (EMCs) with thermal latency organophosphine accelerators were studied using differential scanning calorimetry (DSC). Although the use of triphenylphosphine-1,4-benzoquinone (TPP-BQ) and triphenylphosphine (TPP) catalysts in biphenyl type EMCs exhibited autocatalytic mechanisms, thermal latency was higher in the TPP-BQ catalyst in EMCs than in the TPP catalyst in EMCs. Analyses of thermal characteristics indicated that TPP-BQ is inactive at low temperatures. At high temperatures, however, TPP-BQ increases the curing rate of EMC in dynamic and isothermal curing experiments. The reaction of EMCs with the TPP-BQ latent catalyst also had a higher temperature sensitivity compared to the reaction of EMCs with TPP catalyst. In resin transfer molding, EMCs containing the TPP-BQ thermal latency accelerator are least active at a low temperature. Consequently, EMCs have a low melt viscosity before gelation, and the resins and filler are evenly mixed in the kneading process. Additionally, flowability is increased before the EMCs form a network structure in the molding process. The proposed kinetic model adequately describes curing behavior in EMCs cured with two different organophosphine catalysts up to the rubber state in the progress of curing.

1. Introduction

In IC design, semiconducting chips have become larger, while devices have become smaller. Highly reliable plastic-encapsulated semiconductor packages are needed for advanced electronic devices. New epoxy molding compounds (EMCs) for encapsulating microelectronic devices are needed in the near future because halogen-containing flame retardants and antimony oxide flame retardant synergists, which are widely used in present-day molding compounds, may be environmentally hazardous. In typical green molding compounds, flame retardants (e.g., phosphorus-containing compounds, nitrogen-containing compounds, metal hydrate, metal oxide, inorganic filler, and resins with high C/H ratios) have generally replaced the conventional halogen-containing flame retardants and antimony oxide flame retardants used in EMCs [1, 2]. Notably, EMC with biphenyl resins and highly loaded fillers can retard flammability and is a green material. To produce reliable packaging materials for microelectronic

devices, a highly loaded filler with specific characteristics is needed: high flame retardation, high thermal resistance, high moisture resistance, favorable mechanical properties, and a low thermal expansion coefficient of EMC [3, 4].

Catalysts are often used to accelerate curing in epoxy systems such as EMCs, epoxy prepreg, epoxy powder coating, and so forth. Choosing the appropriate type and amount of catalyst is important in epoxy formulations. In the literature [5–8], reports of catalysts for curing epoxy resin can be classified as Lewis bases and Lewis acids. Lewis bases contain an unshared pair of electrons in an outer orbit and tend to react with areas of low electron density. Their many applications include nucleophilic catalytic curing agents for epoxy homopolymerization; cocuring agents for primary amines, polyamides, and amidoamines; and catalysts for anhydrides. Tertiary amines and imidazoles are the most widely used nucleophilic catalysts. In contrast, Lewis acids, which have an empty outer orbit, tend to react with areas of high electron density. Complexation of boron trihalides with

amines enhances the curing action. Reactivity depends on the selected halide and amine. Boron trifluoride monoethylamine is a typical catalyst.

EMCs typically include a curing accelerator (catalyst), which accelerates the curing of resin and increases the number of molding cycles for mass production. Storage stability, physical characteristics, and reliability of the encapsulated semiconductors diverge widely with the species of curing accelerator used. Capable of controlling initial polymerization, or curing, thermally latent catalysts are used in packaging. In EMCs, typical accelerators are imidazole [2, 9], amines [10–12], organophosphine [1, 10], urea derivatives [13, 14], or Lewis bases and their organic salts [15, 16]. However, most accelerators tend to reduce the pot life or moldability of molding materials, owing to their ability to initiate reactions at extremely low temperatures. Therefore, an effective hardening accelerator must have a thermal latency that promotes the rapid curing of resins when heated to a particular temperature; in contrast, latent accelerators are inert at low temperatures [1, 17]. Exactly how curing accelerators affect the physical and electrical characteristics of EMC have been thoroughly studied [16–19]. In these works, EMCs with triphenyl phosphine (TPP) have optimal physical properties and particularly good electrical properties under high humidity condition when cured, subsequently improving the reliability of the encapsulated semiconductors. However, the curing reaction of the EMC is significantly accelerated at a low temperature, in addition, a high melt viscosity during molding. EMC that contains TPP has a short pot life. Therefore, an improved organophosphine accelerator with thermally latent characteristics is urgently required for using in EMCs. Notably, the EMCs must have superior storage stability, latent reactivity, and low melting viscosity during molding.

The Lewis base catalyst, triphenylphosphine-1,4-benzoquinone (TPP-BQ), is the thermally latent catalyst used in the epoxy molding compounds, which can control initial polymerization or curing and are used in packaging [1, 20]. A previous study found that TPP-BQ accelerated the reaction of EMCs more than TPP did at high temperatures; in addition, EMCs containing TPP-BQ were relatively inert at a low temperature [20]. In the TPP-BQ complex, the resonance of BQ increases the stability of the complex and reduces the activity of lone electron pairs. Nucleophilic attack by the organophosphine accelerators appears to open the epoxide, which is suppressed in the organophosphine accelerators-cured EMC at a low temperature. The molding compounds containing TPP-BQ exhibited excellent moldability and storage stability characteristics. Moreover, they were appropriate for transfer molding, owing to their excellent latent reactivity. Additionally, molding compounds containing TPP-BQ had an extremely low melt viscosity before gelation. In low-viscosity green epoxy molding compounds, 4,4'-Diglycidyl-3,3',5,5'-tetramethyl biphenyl epoxy provides good adhesion, high toughness, and high filler loading. Because of its very low reaction rate, however, an EMC based on this biphenyl type epoxy is unsuitable for molding. This work synthesized a new organophosphine thermally latent accelerator, TPP-BQ, for use in high filler-loaded EMCs based

TABLE 1: Formulation of epoxy molding compounds.

Composition	Raw materials	Parts by weight
Epoxy	4,4'-diglycidyl-3,3',5,5'-tetramethyl biphenyl	90
Br-epoxy	Diglycidyl ether of brominated bisphenol A	10
Hardener	Phenol-aralkyl resin	88
Accelerator	Triphenylphosphine (TPP) or triphenylphosphine-1,4-benzoquinone (TPP-BQ)	3
Filler	Fused silica	1510
Coupling agent	Glycidoxypolytrimethoxysilane	7
Release agent	Ethyleneglycol ester of montanic acid	7
Colorant	Carbon black	4

on biphenyl-type epoxy. The objective of this study was to characterize the reactivity and cure behavior of EMCs cured with thermal latency catalysts, TPP-BQ, and TPP. A kinetic model was used to show how a thermal latency catalyst affects curing in an EMC.

2. Experimental

2.1. Materials and Sample Preparation. Table 1 presents the formulation of the EMC. The epoxy resins used in the experiments were 4,4'-diglycidyl-3,3',5,5'-tetramethyl biphenyl (JER Co., YX-4000H, EW = 192 g/eq) and diglycidyl ether of brominated bisphenol A (Sumitomo Co., ESB 400). The hardener was phenol-aralkyl resin (Mitsui Chemical Inc., XLC-2L, OH EW = 175 g/eq). Scheme 1 shows the chemical structure of the epoxy and the hardener.

The TPP catalyst was obtained from Hooko Co. The TPP-BQ catalyst was synthesized by the authors and was identified using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) [20]. The chemical structure of the catalysts is described in Scheme 2.

The filler was fused silica with a mean particle size (D_{50}) of 20 μm (Tatsumori Co.). The coupling agent was glycidoxypolytrimethoxysilane (Shin-Etsu Chemical Co.). The release agent was ethylene glycol ester of montanic acid (Hoechst Co.). The colorant was carbon black (Cabot Co., CM 800).

The materials were weighed out in the ratios given in Table 1 and thoroughly kneaded using a two-roll mill with the cold roller operated at 15°C and the hot roller operated at 120°C. After mixing, EMC was cooled and pulverized. Each sample was then stored in a refrigerator at 4°C.

2.2. Instruments. Calorimetric measurements were made using a differential scanning calorimeter (DSC) (Perkin-Elmer DSC-7) equipped with an intracooler. Isothermal and dynamic-heating experiments were performed at a 50 mL/min nitrogen flow. In dynamic curing, the sample was

SCHEME 1: The chemical structure of the (a) 4,4'-diglycidyloxy-3,3',5,5'-tetramethyl biphenyl epoxy and (b) phenol-aralkyl resin.

SCHEME 2: The chemical structure of the (a) TPP and (b) TPP-BQ.

heated at a rate of 10°C/min from 0°C to 250°C. The isothermal curing reaction was performed at five temperatures (130, 150, 165, 175, and 185°C). The reaction was considered complete when the isothermal DSC thermogram stabilized at the baseline level, which generally required approximately 1 h. At the end of the reaction, the total area under the exotherm calculated according to the extrapolated baseline was used to calculate the isothermal heat of curing, ΔH_{I_0} (Jg⁻¹). After the curing reaction was completed in the calorimeter, the sample was cooled to 40°C. After curing, the samples were scanned at 10°C/min from 40°C to 250°C to measure residual heat from the reaction, ΔH_R (Jg⁻¹). The total heat of curing (ΔH_T) was calculated by summing the isothermal heat (ΔH_{I_0}) and the residual heat (ΔH_R) from the reactions. The isothermal conversion at time t was defined as $\alpha_I(t) = \Delta H_I(t)/\Delta H_T$. The obtained T_g values were taken as the temperatures of the onset of glass transition (at which the specific heat changed) in the DSC thermograms.

Morphology studies of the cured epoxy molding compounds were performed by scanning electron microscope (Hitachi S-4800 field-emission SEM). The fracture samples were polished and coated with gold by vapor deposition using a vacuum sputter.

2.3. Kinetic Analysis. A general equation for the autocatalytic cure reactions of many epoxy systems is as follows [21–25]:

$$r = \frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n, \quad (1)$$

where α is the extent of conversion, r is the rate of the reaction, k_1 and k_2 are the apparent rate constants, and m and n are the kinetic exponents of the reactions. The kinetic constants k_1 and k_2 are assumed to be in Arrhenius form [22–24, 26]:

$$k_i = A_i \exp\left(-\frac{E_{ai}}{RT}\right), \quad (2)$$

where A_i is the preexponential constant, E_{ai} is the activation energy, R is the gas constant, and T is the absolute temperature. The $\ln k_i$ can be plotted versus $1/T$, and the activation energies are obtained in the equation. Equation (1) reveals that constant k_1 can be calculated from an initial reaction rate in which α approximates 0. Additionally, (1) provides an initial estimate of the reaction order n by performing the following modification:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(k_1 + k_2\alpha^m) + n \ln(1 - \alpha). \quad (3)$$

Except for the initial region, a plot of $\ln(d\alpha/dt)$ versus $\ln(1 - \alpha)$ is expected to be linear and to have a slope of n . Further rearrangement of (1) gives

$$\ln\left[\frac{d\alpha/dt}{(1 - \alpha)^n} - k_1\right] = \ln k_2 + m \ln \alpha. \quad (4)$$

The first term in (4) can be determined from the previously estimated values for k_1 and n . A plot of the left-hand term in (4) versus $\ln(\alpha)$ is expected to yield a straight line. The slope and intercept can then be used to estimate the reaction order m and the autocatalytic kinetic constant k_2 , respectively. The described procedure is applicable for obtaining the preliminary kinetic parameters from the first trial. However, an iterative procedure is required to yield more values. Equation (4) can also be reformulated as

$$\ln\left(\frac{d\alpha}{dt}\right) - \ln(k_1 + k_2\alpha^m) = n \ln(1 - \alpha), \quad (5)$$

where k_2 , m , and n are estimated according to the stated procedures; the left-hand terms in (5) can be plotted against $\ln(1 - \alpha)$; and a new value of the reaction order n is checked against the one obtained earlier. The same iterative procedure can be repeated until the values of m and n converge to within a deviation of 1%.

3. Result and Discussion

3.1. Analyzing Curing kinetics for EMCs with Thermal Latency Catalyst. After the EMCs with TPP and TPP-BQ catalysts were cured at isothermal temperatures of 130, 150, 165, 175, and 185°C, the above models were used for kinetic analysis. Figures 1 and 2 plot the curing rate curves for EMCs catalyzed by TPP-BQ and TPP, respectively, at five isothermal temperatures. Figure 1 shows that the curves are distinctly autocatalytic with the maximum rates occurring 3.0, 1.9, 1.2, 1.0, and 0.8 min after the start of the reaction at isothermal reaction temperatures of 130, 150, 165, 175,

FIGURE 1: Plots of the reaction rate versus time for TPP-BQ-cured EMCs at isothermal temperatures.

FIGURE 2: Plots of the reaction rate versus time for TPP-cured EMCs at isothermal temperatures.

and 185°C, respectively. Figure 2 clearly shows that these rate curves are autocatalytic. The maximum rates were observed at 3.0, 2.2, 1.9, 1.8, and 1.7 min after the start of the reaction at isothermal reaction temperatures of 130, 150, 165, 175, and 185°C, respectively. The result shown in these figures demonstrates that the mechanism of the TPP-BQ-cured EMCs and that of TPP-cured EMCs has the same autocatalytic nature. However, the reaction rate of the TPP-BQ-cured EMC is clearly enhanced at high temperature and restrained at low temperature since the maximum rate increases with reaction temperature in the molding compounds. The epoxy reaction rate revealed a similar effect in the epoxy molding compounds with TPP catalyst. Figures 3(a) and 3(b) show the times of the maximum rate and curing time, respectively, in the epoxy molding compounds cured with organophosphine accelerators. In the epoxy molding compounds cured with catalysis with organophosphine accelerators, the times of the maximum rate and curing time depended on both the reaction temperature and the organophosphine accelerator type. Figure 3(a) indicates that EMCs catalyzed by TPP had a shorter time of the maximum rate than that of EMCs catalyzed by TPP-BQ at a low temperature (130°C). Conversely, EMCs catalyzed by TPP-BQ had a shorter time of the maximum rate than that of EMCs catalyzed by TPP at high temperatures (150, 165, 175, and 185°C). The same change was also observed in the curing time in EMCs catalyzed by organophosphine accelerators (Figure 3(b)). At low temperature (130°C), the curing rate of EMCs containing TPP exceeded that of EMCs containing TPP-BQ; at high temperatures (150, 165, 175, and 185°C), however, EMCs

containing TPP-BQ are cured at a higher rate compared to EMCs containing TPP. The EMCs catalyzed by TPP-BQ accelerator also had a rapid rate of curing at the molding temperatures used specifically for IC encapsulation ($T = 175\text{--}185^\circ\text{C}$). These findings indicate that TPP is better than TPP-BQ as a catalyst for curing EMCs at low temperatures. At high temperatures, however, the acceleration in reaction time was larger in EMCs cured with TPP-BQ than in EMCs cured with TPP, and EMCs containing TPP-BQ were relatively inert at a low temperature. Notably, the general biphenyl EMC transfer molding temperatures used for IC encapsulation range from 175 to 185°C. During molding, EMCs containing TPP-BQ are least active before the temperature reaches the molding temperature. The experimental results indicate that TPP-BQ is superior to TPP as a latency accelerator in biphenyl type EMCs.

Table 2 presents the mean residual heat of reaction (ΔH_R), isothermal heat of reaction (ΔH_{I0}), total heat of curing (ΔH_T), and isothermal conversion (α_I). Note that the heat from reactions in the EMCs was calculated based on the net weight of the biphenyl/phenol-aralkyl resin in the molding compounds without considering the weight of fillers in the EMCs. In this work, the total heats of curing ($\Delta H_{I0} + \Delta H_R$) were independent of the organophosphine accelerator type. The mean value was 184 Jg^{-1} . At a 130°C curing temperature, the table also shows that the isothermal conversions (α_I) were 92.9 and 93.4% for EMCs containing TPP and TPP-BQ, respectively, which indicated that the reactions were incomplete at a low temperature. However, the isothermal conversions (α_I) were 100% when the EMCs were completely

TABLE 2: Heats of reaction of epoxy molding compounds catalyst by TPP and TPP-BQ.

Accelerators	T ($^{\circ}\text{C}$)	ΔH_{I_0} (J g^{-1})	ΔH_R (J g^{-1})	ΔH_T (J g^{-1})	α_1 (%)
TPP-BQ	130	170	12	182	93.4
	150	184	0	184	100
	165	183	0	183	100
	175	185	0	185	100
	185	186	0	186	100
TPP	130	171	13	184	92.9
	150	183	0	183	100
	165	184	0	184	100
	175	183	0	183	100
	185	185	0	185	100

cured at high temperatures (150–185 $^{\circ}\text{C}$). The table also shows that the ultimate conversion (α_1) for EMCs catalyzed by organophosphine accelerators increased from 93 to 100%, as cure temperature increased from 130 to 185 $^{\circ}\text{C}$, which indicate that the reactions would be expected to reach diffusion control (rubber state) regions at progressively higher conversions, as reaction temperatures increase. Furthermore, EMCs containing TPP and TPP-BQ accelerators not only had similar reaction rate curves, but they also had similar ΔH and α_1 , which suggests EMCs containing TPP and TPP-BQ accelerators have a similar reaction mechanism.

3.2. Autocatalytic Model Analysis. The molding compound data were then analyzed using the proposed autocatalytic mechanism. The kinetic parameters were determined using the above procedures. For the kinetic constants k_1 and k_2 , two activation energies, ΔE_1 and ΔE_2 , could be obtained by plotting $\ln k_1$ and $\ln k_2$, respectively, versus $1/T$. Figure 4 shows the plots for $\ln k_1$ and $\ln k_2$ versus $1/T$, from which the activation energies were determined for the EMCs. Table 3 lists the rate constants obtained after considerable iteration and graphic procedures. Reaction orders m and n approximated 0.5 and 1.4, respectively, and did not substantially vary among EMCs with different organophosphine accelerators. For the TPP-BQ-catalysis EMCs, the E_{a1} and E_{a2} values obtained in this study were 15.2 and 11.6 kJ mol^{-1} , respectively. In contrast, the E_{a1} and E_{a2} values obtained for the TPP-catalysis EMCs were 11.4 and 9.6 kJ mol^{-1} , respectively. As activation energy increased, the temperature sensitivity of the reaction increased. Restated, for a large activation energy, a temperature increase of only a few degrees significantly increased k , subsequently increasing the reaction rate. In comparison to TPP catalyst-cured EMCs, TPP-BQ catalyst-cured EMCs had higher activation energies. Further, since the difference in ΔE_{a1} (3.8 kJ mol^{-1}) between TPP-BQ catalyst-cured EMCs and TPP catalyst-cured EMCs was larger than the difference in ΔE_{a2} (2 kJ mol^{-1}) between TPP-BQ catalyst-cured EMCs and TPP catalyst-cured EMCs, the increased reaction rate might be associated with k_1 . Since k_1 governs the early stage-autocatalytic reaction and since k_2 affects

FIGURE 3: Curing times of organophosphine accelerators-cured EMCs at isothermal temperatures: (a) times of the maximum rate and (b) curing times.

the reaction after the initial autocatalytic stage, the rate of increase at high temperatures in EMCs with TPP-BQ catalyst should be expected to accelerate in the initial stage of the reaction [26].

The autocatalytic kinetic model and the rate constants obtained (listed in Table 3) were used to calculate empirical curves of conversion versus time for the organophosphine accelerator-cured EMCs at all five isothermal cure temperatures. Figures 5 and 6 show that the empirical conversion

TABLE 3: Kinetic parameters for epoxy molding compounds catalyst by TPP and TPP-BQ.

Accelerator	T ($^{\circ}\text{C}$)	m	n	k_1 (min^{-1})	k_2 (min^{-1})	E_{a1} (kJ mol^{-1})	E_{a2} (kJ mol^{-1})	$\ln A_1$	$\ln A_2$
TPP-BQ	130	0.4	1.3	6.6	12.8	18.3	11.6	16.5	13.3
	150	0.4	1.4	6.5	61.7				
	165	0.5	1.0	20.2	129.4				
	175	0.6	1.0	39.8	200.5				
	185	1.3	1.1	114.8	330.8				
TPP	130	0.5	1.3	12.6	31.6	12.6	9.6	12.9	12.3
	150	0.5	1.3	16.5	102.9				
	165	0.6	1.4	45.5	189.3				
	175	0.6	1.5	73.1	291.0				
	185	0.5	1.5	110.9	476.9

FIGURE 4: Kinetic analysis for organophosphine accelerators-cured EMCs in an autocatalysed reaction: (a) plots of $\ln k_1$ against $1/T$ and (b) plots of $\ln k_2$ against $1/T$, respectively.

curves fit the experimental data quite well until the cure reactions progress to the rubber state for TPP-BQ-cured EMCs and TPP-cured EMCs. Epoxy resins are thermosets whose individual chains have been chemically linked by covalent bonds during isothermal reaction. Once formed, these cross-linked networks resist heat softening and creep. Generally, a rubber-like state may be defined as an amorphous and cross-linked polymer above its glass transition temperature (T_g). Following cross linking, flow of one molecule past another is suppressed in organophosphine accelerator-cured EMCs in the rubber state. In the work, a similar T_g value (120°C) was obtained in fully cured TPP-BQ-cured EMCs and TPP-cured EMCs. Apparently, the model satisfactorily describes the kinetic well. However, diffusion control in the rubber state

affects the predictive accuracy of the model. This indicates that the cure kinetics for organophosphine accelerator-cured EMCs in the later stage are indeed subject to diffusion control in the rubber state. In the organophosphine accelerator-cured EMCs, the predictability of the model at high cure temperatures is better than that at low cure temperatures.

3.3. Comparison of TPP-BQ-Cured EMCs with TPP-Cured EMCs. Figures 7 and 8 show the rate versus conversion curves for organophosphine accelerator-cured EMCs at five isothermal cure temperatures (130, 150, 165, 175, and 185°C). Figure 7 shows the similar trends in cure reaction rates observed in TPP-BQ-cured EMCs at five cure temperatures. The maximum rates approximated 33% and 17% of the

FIGURE 5: Comparison between the autocatalytic model and data for TPP-BQ-cured EMCs at isothermal temperatures.

FIGURE 6: Comparison between the autocatalytic model and data for TPP-cured EMCs at isothermal temperatures.

conversion at high temperatures (165, 175, and 185 °C) and at low temperatures (130 and 150 °C), respectively. In contrast, the trends in cure reaction rates of TPP-cured EMCs are similar at five cure temperatures, and the maximum rate approximated 20% and 10% of the conversion at high temperatures (165, 175, and 185 °C) and at low temperatures (130

FIGURE 7: Plots of the reaction rate versus conversion for TPP-BQ-cured EMCs at isothermal temperatures.

and 150 °C), respectively (Figure 8). In TPP-BQ accelerator-cured biphenyl EMCs, the reaction of the biphenyl/phenol-aralkyl resin at higher conversions still maintained a high rate of progress in the cure reaction. In contrast, the reaction rate of TPP accelerator-cured EMCs was high in the early stage and low in the later stage. After 70% conversion, TPP-BQ-cured EMCs had a higher rate than TPP accelerator-cured EMCs did at the five cure temperatures shown in the figures. In resin transfer molding, EMC flowed through the molding part until the compound was transformed into gel. If the curing rate of EMC was too fast, the melting EMC would have increased the viscosity and decreased the flowability in the mold. Both viscosity and flowability are generally related to the degree of reaction of EMC during molding. In microelectronic packaging, the acceleration of the reaction of EMC containing TPP-BQ is weak at low temperatures but strong at high temperatures during thermal latency curing. The experimental results suggest that the TPP-BQ accelerator is an ideal thermal latency accelerator for curing EMCs.

3.4. Morphology of EMCs with High Filler Content. The EMCs with high filler contents are accelerated by organophosphine accelerators, TPP-BQ and TPP, which provide excellent flowability in the molding process. In the molding process, melting EMCs with high flowability easily fill the whole mould before hardening. Figures 9(a) and 9(b) show the morphology of the fractured surface of EMCs with 88 wt% content of silica accelerated by TPP-BQ and TPP accelerator, respectively, and cured at 175 °C. In Figure 9(a), the spherulic silica of varying sizes is well distributed and packed closely

FIGURE 8: Plots of the reaction rate versus conversion for TPP-cured EMCs at isothermal temperatures.

on the fractured surface of the EMC in the cured sample. Because TPP-BQ-cured EMCs have a low melt viscosity before gelation as well as least active at low temperatures, the organic matrixes and filler are easily and well mixed in the kneading process; in addition, the flowability of EMC is increased in the molding process. In contrast, the silica is less evenly distributed and is loosely packed in the fractured surface of the TPP-cured EMC shown in Figure 9(b). The silica is not well mixed in the TPP-cured EMC because the EMC had a high reaction rate and a high viscosity in the kneading process.

4. Conclusions

In isothermal curing, TPP is a more rapid catalyst compared to TPP-BQ for curing EMCs at low temperatures. However, TPP-BQ accelerated the reaction of EMCs more than TPP did at high temperatures, and EMCs containing TPP-BQ were relatively inert at a low temperature. An autocatalytic mechanism was observed for organophosphine accelerator-cured EMCs. Kinetic parameters for the EMCs with TPP-BQ and TPP accelerator were obtained, and the proposed kinetic model accurately described the cure behavior of organophosphine accelerator-cured EMCs up to the rubber state. Although the reaction mechanism for both TPP-BQ-cured EMCs and TPP-cured EMCs was similar, thermal latency was superior in the TPP-BQ-cured EMCs. The model showed that the increased temperature sensitivity resulted from the larger activation energy in EMCs with TPP-BQ accelerator. Based on the observations in this study, the rate increase at high temperatures in EMCs with TPP-BQ catalyst

FIGURE 9: Morphology of organophosphine accelerators-cured epoxy molding compounds: (a) TPP-BQ-cured EMC and (b) TPP-cured EMC, respectively.

should be pronounced in the initial stage of the reaction. Furthermore, in TPP-BQ accelerator-cured biphenyl EMCs, the reaction of the EMC at high conversions remained high as the cure reaction progressed during the EMC transfer molding process. In microelectronic packaging, the acceleration of the reaction of EMC containing thermal latency TPP-BQ accelerator correlates positively with temperature. This suggests that the TPP-BQ accelerator is an ideal thermal latency accelerator for curing EMCs.

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