

Chemical shrinkage and diffusion-controlled reaction of an epoxy molding compound

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Abstract

A methodology for the study of cure kinetics of a highly filled epoxy molding compound is presented. An equation relating the glass transition temperature-conversion relationship was first established. The degree of conversion can then be estimated when the calorimetric method is inadequate in measuring the heat of reaction in the diffusion-controlled regime. The cure reaction is modeled as a reaction of shifting order: it first reacts autocatalytically and later switches into diffusion control. The reaction in the diffusion-controlled regime is very slow and is modeled by an n th order kinetic equation. Both the linear coefficients of thermal expansion above and below the glass transition temperature decrease linearly with degree of conversion. Based on this linear coefficient of thermal expansion-conversion relationship, it is found that chemical shrinkage is an important factor that causes interfacial stresses when the epoxy molding compound adheres to a substrate of different materials. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy molding compound; Chemical shrinkage; Cure kinetics; Diffusion control; Linear coefficient of thermal expansion

1. Introduction

Epoxy resins have relatively low volumetric shrinkage upon polymerization, good thermal and dimensional stability, excellent moisture and chemical resistance, and superior electrical and mechanical properties [1]. Epoxy molding compounds (EMCs) are often employed to encapsulate microelectronic devices. The stringent requirements for semiconductor products demand that a semiconductor packaging process has to be well designed, closely controlled, and highly reliable. Common package reliability problems related to encapsulants include package cracks, passivation film cracks, delamination, and package warpage. While the trend in semiconductor packaging is towards being smaller and thinner, both the chip size and the power consumption are becoming larger. The thermal mechanical stress in the package becomes a major issue for package reli-

ability. The prevailing surface mount technology requires the leads of a semiconductor package to be of good coplanarity, which requires the extent of warpage to be within a certain limit. The package warpage is caused by the thermal contraction mismatch of the constituent materials: silicon chip, metal frame and plastic encapsulant [2,3]. The typical values of linear coefficient of thermal expansion (LCTE) of silicon chips, Ni-Fe alloy leadframes and epoxy molding compounds are 2.3×10^{-6} , 4.3×10^{-6} and $10 \times 10^{-6} \text{ K}^{-1}$, respectively. Most researchers believe that a major part of the thermal stress arises from the LCTE mismatch. To reduce stresses resulting from thermal mismatch, EMC is highly filled with fillers of low LCTE. Also, the epoxy resins have been modified by grafting various functional polymers to reduce their LCTE or elastic moduli [4–6].

One of the sources of thermal mechanical stress that causes package warpage, which is often overlooked and less understood, is the volumetric shrinkage of plastic encapsulants upon curing (chemical shrinkage). During the polymerization of multifunctional monomers, a

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significant decrease in the specific volume results from the formation of highly crosslinked polymers. The free volume is reduced by the formation of covalent bonds at the expense of weaker van der Waals bonding. For the cure of bisphenol A dicyanate, the cure shrinkage attained a value of 12.3% [7]. The volumetric shrinkage of polydiacrylates on polymerization was between 10% and 15% [8]. In order to design a reliable semiconductor packaging process, one should be able to assess precisely the time history responses of the temperature, displacement, and stress for a package during processing [9]. The requirement for smaller package size for larger chips makes it more difficult to ensure mechanical integrity of the package. Stress analysis becomes more necessary and important in designing packages and packaging processes, and in selecting packaging materials [10]. To calculate the extent of thermal mechanical stress developed in a package, one should effectively predict the EMC property changes during a packaging process.

In an encapsulation process, thermal mechanical stresses develop while chemical reactions take place. The extent of thermal mechanical stress in the package is closely related to the extent of chemical reaction. Previous stress analysis for the packaging process seldom took chemical reaction into consideration due to a lack of understanding of the changing compound properties. In this contribution, we establish a methodology upon which one could depend to predict compound properties with known process parameters. We shall show how to construct precise cure kinetics, including both chemical kinetics and diffusion control, by establishing the relationship between T_g and degree of conversion. By controlling the extent of reaction of the EMC, the relationship between LCTE and degree of conversion can be established. The values of LCTE and extent of volumetric change (both chemical and physical shrinkage) in a packaging process can then be precisely predicted.

2. Experimental

The epoxy molding compound used in this study was the commercial grade, KMC-280, supplied by Shin-Etsu Chemical Co. Ltd. The compound has a spiral flow length at 175°C of 120 cm and a density of 1.99 g cm⁻³. The variation of the T_g as a function of conversion was studied using a Perkin–Elmer differential scanning calorimeter, DSC 7. Each sample was cured isothermally for a certain amount of time, quenched, and rescanned from room temperature to 250°C at 20°C min⁻¹ to obtain the glass transition temperature and residual heat of reaction. The mid-point ($\frac{1}{2}\Delta C_p$) at the step increment in the DSC curve was taken as the T_g . For the study of chemical kinetics, a dynamic DSC scan method was used: uncured specimens were scanned from 25°C to

220°C at two different heating rates, 10°C min⁻¹ and 20°C min⁻¹, respectively. The resultant reaction heat – temperature profile was then used to fit the kinetic equations. For the study of diffusion-controlled kinetics, precured specimens were first heated at either 220°C or 240°C isothermally for different periods of time. The variation of T_g as a function of time was then recorded. The linear coefficient of linear thermal expansion was measured using a Perkin–Elmer DMA 7e in the TMA mode. Specimens of 4 mm thick were placed under a quartz probe using a contact force of 2 mN and the vertical dimension (thickness) was measured as the temperature was increased at a rate of 5°C min⁻¹.

3. Results and discussion

3.1. T_g versus conversion relationships

To determine the degree of conversion using a calorimetric method, the total heat evolved in a crosslinking reaction must be evaluated first. The most frequent experimental approach in past studies was to use the heat evolved in a dynamic DSC scan as the heat of reaction. However, a long-time post-cure procedure is recognized as a common practice for epoxy compounds to reach a full cure. This also implies that the short duration in a dynamic DSC scan is hardly enough to cure fully the compound. The experimental approach we adopted to study the effect of crosslinking on T_g was to stop the reaction at various degrees of conversion. Each sample was then re-scanned to obtain the T_g and the residual heat of reaction. The latter was used to determine the degree of conversion. The T_g for the compound cured at 240°C for 168 h, which was 148°C, was taken as the T_g for the fully cured compound. It is generally considered to be true for most thermosetting polymers that there is a one-to-one relationship between T_g and degree of conversion, regardless of their cure path [11–13]. Based on this premise, research studies on diffusion controlled kinetics usually used T_g as a measure of degree of conversion [14]. Several equations had been proposed to correlate T_g to the degree of conversion [13,15–17]. The one proposed by Fox and Loshaek using free volume arguments can be expressed as [14,15,17,18].

$$T_g = T_{g0} + \frac{\tau_1 X}{1 - \tau_2 X} = T_{g0} + \frac{\tau'_1 \Delta H}{1 - \tau'_2 \Delta H}, \quad (1)$$

where T_{g0} is the T_g of the initial reactive system, ΔH , the partial heat of reaction, τ_1 and τ_2 are adjustable parameters, and

$$\tau'_1 = \frac{\tau_1}{\Delta H_T}, \quad \tau'_2 = \frac{\tau_2}{\Delta H_T}, \quad (2)$$

where ΔH_T is the total heat of reaction of the epoxy compound. The collected experimental $\Delta H - T_g$ values were first fitted to Eq. (1) to obtain T_{g0} , τ'_1 and τ'_2 . The experimental T_g value for the fully cured compound was then substituted into Eq. (1) to calculate ΔH_T . τ_1 and τ_2 were finally calculated from Eq. (2). The variation of T_g as a function of conversion is shown in Fig. 1. The solid curve in Fig. 1 was calculated by using Eq. (1) with $T_{g0} = 288$ K, $\tau_1 = 60.5$ K and $\tau_2 = 0.545$. This equation fits the experimental data very well. This study shows that for rigid and densely crosslinked polymers, the conversion is far from complete in a dynamic DSC scan. The highest degree of conversion achievable in a dynamic DSC scan is only about 87%. As the compound reaches a high degree of conversion, the diffusion of the unreacted groups involves the movements of the highly correlated network and the reaction cannot achieve a complete conversion within a short period of time [13].

3.2. Reaction kinetics studies

As EMC undergoes a curing reaction, the crosslinking density of the resin increases and the diffusion of the reactive functionalities becomes more correlated. After a certain stage of reaction, the rate of diffusion becomes so slow that the effective collision of reactive species decreases drastically. The crosslinking reaction can be controlled by chemical kinetics, translational diffusion or segmental diffusion [6]. There have been extensive experimental or theoretical research studies on the cure kinetics of epoxy systems [19–21]. It is certain that the intrinsic ultimate conversion of the highly crosslinked polymeric system is lower than 100% [13]. In this study, the DSC dynamic scan method was used to investigate the curing kinetics. The degree of conversion was calculated based on the obtained T_g -conversion relationship. The experimental results for the samples scanned at

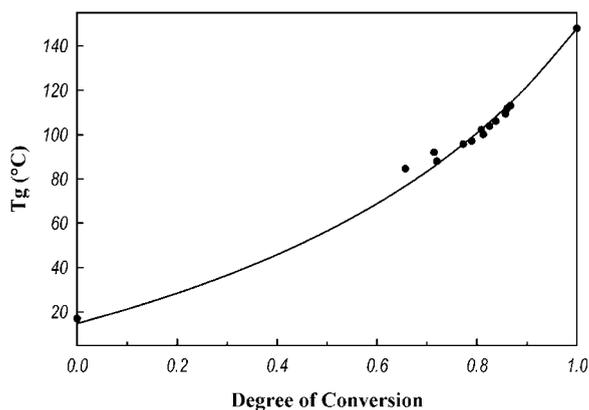


Fig. 1. T_g as a function of the degree of conversion for the EMC. The continuous line was calculated by using Eq. (1).

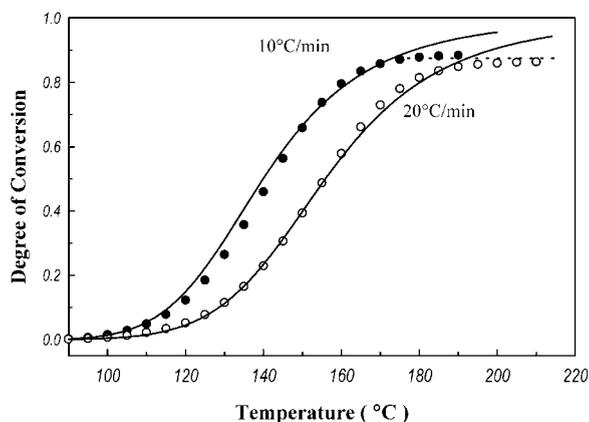


Fig. 2. Degrees of conversion of the EMC with DSC experiments at different scan rates. The symbols represent experimental data. The continuous lines were calculated using Eq. (4). The dotted lines were calculated using a combination of Eqs. (4) and (8).

two different heating rates are shown in Fig. 2. To quantify the results, the data were fitted to chemical kinetics of this form:

$$\frac{dX}{dt} = kF(X), \quad (3)$$

where k is the rate constant and X , the degree of conversion of a reactive group. $F(X)$ is a function of X and the initial composition and is given by the mechanism and orders of the reactions. It was found that a simple n th order reaction kinetic equation, $F(X) = (1 - X)^n$, did not fit the experimental data effectively. Instead, a kinetic equation of the autocatalytic type with the rate constant expressed by Arrhenius function was chosen to fit the experimental data [20]:

$$\frac{dX}{dt} = A_C \exp\left(-\frac{E_C}{RT}\right) X^m (1 - X)^n, \quad (4)$$

where A_C is the frequency factor and E_C , the activation energy. The values of fitted parameters are $A_C = 1.293 \times 10^5 \text{ s}^{-1} \text{ K}$, $E_C = 54.4 \text{ kJ mol}^{-1}$, $m = 0.49$, $n = 1.97$. The calculated degrees of conversion are also shown in Fig. 2. The autocatalytic behavior is obvious, as can be seen that the rates of reaction at the low conversion portion are quite low. As the conversion increases to some extent, the gel effect takes place and the reaction rates increase. It is also apparent that the predicted degrees of conversion deviate from the experimental ones over the final portion of conversion, and that the experimental reaction rates are much lower than those calculated by the autocatalytic kinetic equation. The reaction kinetics had switched from being chemically controlled to diffusion controlled.

In dealing with diffusion-controlled kinetics, the released heat of reaction is hardly detectable because the reaction rate is extremely slow. Instead of using the calorimetric method, the extents of reaction were estimated by measuring the glass transition temperatures of the reacting system. The specimens were heated isothermally for certain amounts of time and their T_g were measured. The degrees of conversion were then calculated using Eq. (1). Fig. 3 shows the change of degree of conversion with time in the diffusion-controlled regime for the samples cured at two different temperatures. As can be seen, the reaction rates are very slow in contrast to those shown in Fig. 2. The mixed chemical kinetics and diffusion control in epoxy cure kinetics have been studied using the Rabinowich model [14,22,23]

$$\frac{1}{k} = \frac{1}{k_C} + \frac{1}{k_d}, \quad (5)$$

where k is the rate constant of Eq. (3), k_C , the rate constant of a chemical kinetics controlled reaction, and k_d , the rate constant for the diffusion-controlled reaction. k_d is usually described as a function of the difference between the reaction temperature and the glass transition temperature, such as [14,20,22]

$$\ln k_d = \ln k_{d,0} + \frac{\alpha_d(T - T_g)}{C_1 - (T - T_g)}, \quad (6)$$

or

$$\ln k_d = \ln k_{d,0} + B \left[1 - \frac{1}{f_g + \alpha_f(T - T_g)} \right], \quad (7)$$

where $k_{d,0}$, α_d , C_1 , B , α_f , and f_g are usually taken as empirical factors. Eq. (6) is a WLF-type equation and Eq. (7) was derived from the diffusion coefficient based on the free volume theory [14]. Both Eqs. (6) and (7) had been tried, but failed to fit the diffusion-controlled kinetics well. Instead, a simple n th order Arrhenius kinetic model fits the experimental conversion very well:

$$\frac{dX}{dt} = A_d \exp\left(-\frac{E_d}{RT}\right)(1-X)^p. \quad (8)$$

The calculated degrees of conversion are shown in Fig. 3 as solid curves. The values of the fitted parameters are $A_d = 6.0 \times 10^{15} \text{ s}^{-1}$, $E_d = 184.2 \text{ kJ mol}^{-1}$, $p = 1.45$. The inability to fit the experimental data using Eqs. (6) and (7) indicates that $T - T_g$ is not a suitable parameter to scale the rate of diffusion of the reacting species in this particular epoxy compound. Diffusion is a heat-activated process. The length of the diffusion path increases as the degree of conversion increases and is accounted for intrinsically in Eq. (8). As the reaction temperatures are well above the T_g of the reaction systems, Eq. (8) can adequately describe the average diffusion behavior in this narrow conversion range.

If the cure kinetics, including both chemical kinetics and diffusion control, could be modeled, the degree of conversion of this system could be predicted for any given temperature profile. However, the Rabinowich model failed to give satisfactory results. If one takes a close look at Fig. 2, it is clear that the levels of conversion at which the experimental degrees of conversion begin to deviate from those predicted by Eq. (4) are

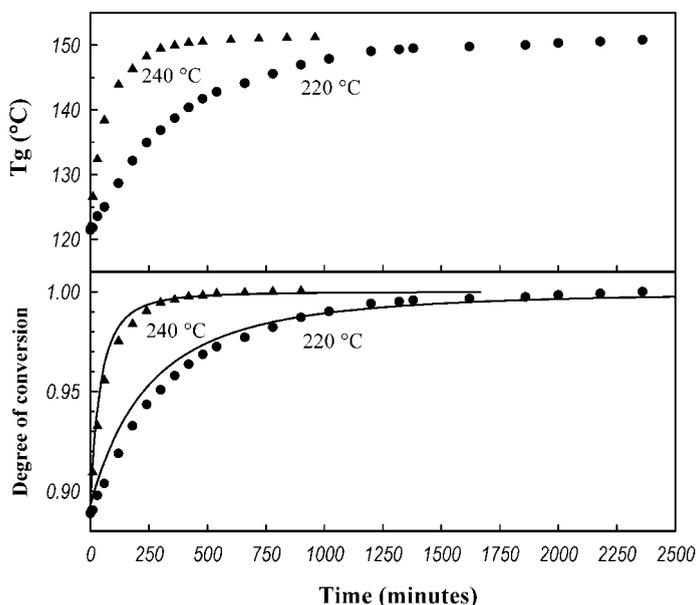


Fig. 3. Dependence of the degree of conversion on curing time at two curing temperatures. The lines are calculated using Eq. (8).

almost the same. This implies that the degree of conversion is the sole factor in defining the onset of a diffusion-controlled regime in cure kinetics. For the range of temperature of interest, temperature is not an important factor in determining the onset point. One empirical way to model the cure kinetics is to treat it as a reaction of shifting order: the reaction starts as an autocatalytic one and shifts to a diffusion-controlled one as it proceeds to a certain extent. The dotted lines in Fig. 2 were obtained by specifying that the reaction switches into diffusion control at $X = 0.875$. The quality of fit is much better using the reaction of shifting order kinetics.

3.3. Chemical shrinkage studies

For a crosslinked polymer, most previous theoretical models relate their molar thermal expansivities to the crosslink density [17]. As the crosslink density of a highly crosslinked polymer system like epoxies cannot be effectively measured, it will be much more practical to derive an equation to relate the linear coefficient of thermal expansion to the degree of conversion. We have derived a simple relation by applying the Simha and Boyer concepts for thermal expansion [7,24–26]:

$$\beta_g = \beta_{g,1} - \beta_{g,2}X, \quad (9a)$$

$$\beta_\ell = \beta_{\ell,1} - \beta_{\ell,2}X, \quad (9b)$$

where β_g and β_ℓ are the linear coefficients of thermal expansion below and above T_g , respectively, and $\beta_{g,1}$, $\beta_{g,2}$, $\beta_{\ell,1}$ and $\beta_{\ell,2}$ are constants. In a microelectronic packaging process, the epoxy molding compounds are transferred from a low-temperature transfer pot to high-temperature mold cavities wherein the crosslinking reaction takes place. Since the linear coefficients of thermal expansion of polymeric materials are much larger than those of either silicon chips or leadframes, one of the requirements for the packaging molding compounds is that their processing shrinkage should be as low as possible. During the transfer molding process, the EMC experiences chemical shrinkage upon crosslinking and physical shrinkage upon cooling from mold temperature to room temperature. Fig. 4 shows the change of linear thermal strain with temperature for the EMC of different T_g values. One notices that there are two distinct slopes (LCTE) in each of these curves, and that the slopes decrease as T_g increases. The two slopes correspond to the LCTE below and above T_g . Upon heating from 50°C to 240°C, the EMC of the lower T_g experiences a larger thermal expansion. For example, the linear thermal strain for the EMC of a T_g of 103°C ($X = 0.81$) is 1.85 times that for the EMC of a T_g of 148°C ($X = 1$). A part of the difference in thermal strains comes from the difference in T_g (since the LCTE above T_g is much larger than that below T_g), and the other part

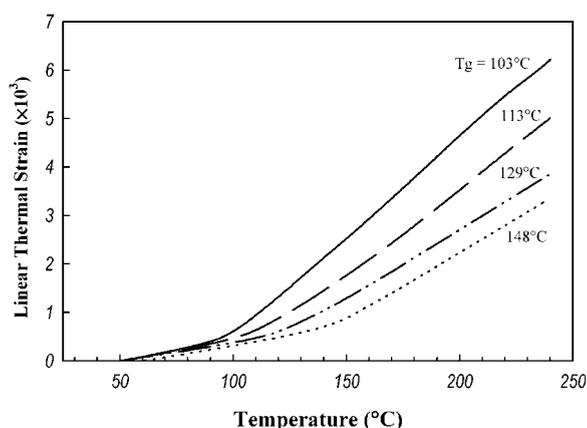


Fig. 4. Variation of experimental linear thermal strain upon temperature for the EMC with different T_g values.

comes from decreasing LCTE with increasing T_g . A plot of LCTE versus the degree of conversion should be linear if Eqs. (9a) and (9b) were to hold. Such a graph is displayed in Fig. 5. The degree of conversion was calculated from T_g by using Eq. (1). The two linear lines indicate that Eqs. (9a) and (9b) are adequate in relating LCTE to the degree of conversion. The obtained values of the parameters are $\beta_{g,1} = 9.57 \times 10^{-6} \text{ K}^{-1}$, $\beta_{g,2} = 1.83 \times 10^{-6} \text{ K}^{-1}$, $\beta_{\ell,1} = 8.64 \times 10^{-5} \text{ K}^{-1}$ and $\beta_{\ell,2} = 6.02 \times 10^{-5} \text{ K}^{-1}$.

Coupled with reaction kinetic Eqs. (9a) and (9b) enable one to evaluate the thermal strain with known time-temperature processing profiles. Here, we use a virtual process to depict the growth of the interfacial strain. In this process, the virgin EMC at 25°C ($X = 0$ and $T_g = 15^\circ\text{C}$) is heated instantaneously to 180°C. The compound expands immediately, then crosslinks and shrinks. After the compound achieves a full cure ($T_g = 148^\circ\text{C}$), it is cooled down back to 25°C. The

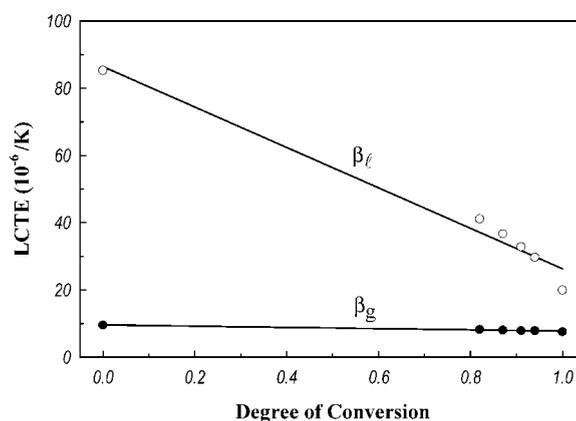


Fig. 5. LCTE as a function of the degree of conversion for the EMC. β_g and β_ℓ represent the LCTE below and above T_g , respectively.

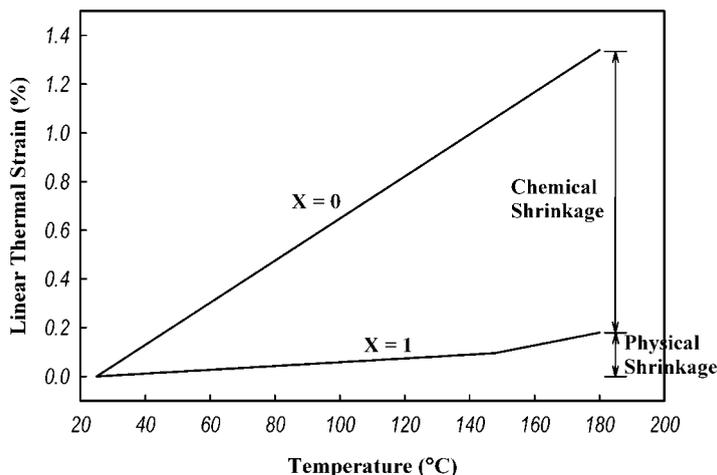


Fig. 6. A schematic representation of the chemical and physical shrinkages in a process where the virgin EMC at 25°C is heated immediately to 180°C. After the EMC cures completely, it is cooled down to 25°C.

compound is assumed to attach to a substrate which has a much smaller LCTE and is also heated to 180°C. At 180°C and $X = 0$, there is no stress at the interface as the resin adheres to the substrate. This is because the compound is in the liquid state and is free to move to relax any stress imposed upon it. As the EMC reacts, gels and shrinks, the interfacial stress builds up. The interfacial stress grows further upon cooling down to 25°C as each material shrinks to a different extent. As one can see from Fig. 6, the amount of linear strain contributed by chemical shrinkage is 1.18%, whereas that contributed by physical shrinkage is only 0.18%. We demonstrate here that even for a compound of low volumetric shrinkage, the shrinkage resulted from chemical reaction is considerably larger than that from thermal contraction. The extent of reaction is thus an important factor that affects the stress and strain state of a polymeric material in a reactive process, in addition to process parameters such as temperature and pressure.

4. Conclusions

The relationship between T_g and the degree of conversion of a commercial epoxy molding compound was successfully constructed by controlling the extent of reaction and measuring the residual heat of reaction. Eq. (1) is used to describe this relationship and fits the experimental data very well. The reaction of this particular epoxy molding compound can be modeled as a reaction of shifting order: it first reacts autocatalytically and later switches into diffusion control. The switch point is at the degree of reaction of 0.875. The reaction in the diffusion-controlled regime can be modeled by a simple n th order kinetic equation with its rate constant described by an

Arrhenius equation. The experimental linear coefficients of thermal expansion, both above and below T_g , decrease approximately linearly with increasing degree of conversion. Chemical shrinkage due to crosslinking reaction is found to be an important factor on dimensional change for reaction-processed polymers.

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