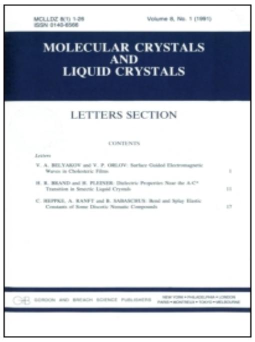

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Cure properties of alkoxysilylated epoxy resin systems with hardeners for semiconductor packaging materials

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ABSTRACT

The alkoxysilylated bisphenol A epoxy resins, dsiglycidylether of bisphenol A with 3-triethoxysilyl propyl carbamate(DGEBA-TESPC) and diglycidyl ether of bisphenol A with 3-triethoxysilyl propyl(DGEBA-TESP) are synthesized, and the effect of alkoxysilyl group on the cure properties of these resin systems with phenol novolac(PN) hardener and triphenylphosphine(TPP) catalyst are investigated. The cure kinetics of these systems were analyzed by dynamic and isothermal data from the DSC experiments, and the kinetic parameters of all systems were reported in generalized kinetic equations with diffusion effects. Thermal expansion coefficients of these epoxy systems were obtained by mean of TMA measurement. These resin systems show autocatalytic cure kinetics phenomena and the conversion reaction rate of DGEBA-TESP hybrid system with PN hardener is slightly higher than DGEBA-TESPC system. The DGEBA-TESP resin system has lower frequency factor and lower activation energy than DGEBA-TESPC resin system in k_1 reaction rate constant. However, it shows higher frequency factor and higher activation energy than that in k_2 reaction rate constant. The thermal property of glass fiber composites of DGEBA-TESPC and DGEBA-TESP is observed to be improved than DGEBA, which may arise from the facile interaction of grafted alkoxysilyl group with glass fiber.

KEYWORDS

cure kinetics; alkoxysilylated epoxy; semiconductor; packaging materials

Introduction

Epoxy resins are widely used in semiconductor packaging applications: IC substrate, epoxy molding compound for encapsulation, under fill and die bond attach, due to the good moldability as well as mechanical and electrical insulation properties [1–3]. With the advance of semiconductor packaging technology, however, the application of the current commercial epoxy resins to electronic components is often seriously limited due to the insufficient thermal properties of epoxy composites, especially in the temperature range above T_g. Therefore, the development of high heat resistant epoxy composite is desirable for the enhancement of both the physical properties and handling of thermosetting system. Many attempts have been reported to maintain good physical properties of epoxy systems even at the high temperature above T_g [4–9]. The crosslinking density of cured epoxy resin systems has been increased and the rigid structures have been introduced to the main chain of epoxy resin[4,5].

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The introduction of organic-inorganic hybrid systems was reported to attain the high Young's modulus at high temperature [6,7]. It can be found that these hybrid systems performed inorganic network formation by sol-gel reaction and general curing reaction of thermosetting epoxy resin [8]. It was also reported that a T_g-less epoxy resin could be obtained by curing bisphenol A type epoxy resin with ion-containing polymer as a catalyst [9].

This study investigated the curing properties of modified epoxy resin systems, to which alkoxysilyl side groups were introduced in order to increase heat resistance of epoxy composite at high temperature. The curing characteristics and thermal properties of these systems with phenol novolac hardener examined with DSC and TMA, respectively. The curing kinetics in the overall conversion region has been interpreted by means of the kinetic and diffusion model [10,11].

Experimental

[Materials]

The epoxy resin was diglycidyl ether of bisphenol A (DGEBA, Mn = 522), which was generously provided by Kumho P&B Corp. (Seoul, Korea). The phenol novolac with the hydroxy equivalent weight of 107 (PN; HF-1M) from Meiwa Kasei (Tokyo, Japan) and triphenyl phosphine from Aldrich Chemical Co. were used as a hardener and curing catalyst, respectively. The glass fiber fabric (E-glass, IPC spec # 2116, Nittobo) was used to prepare the epoxy glass fiber composite.

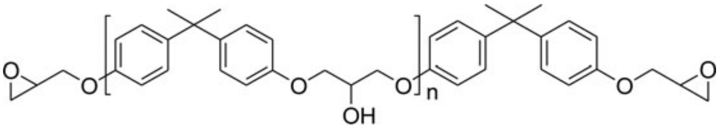
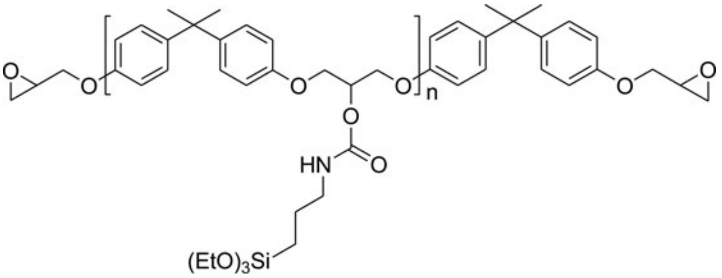
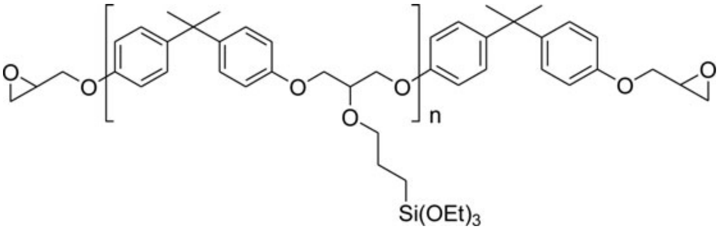
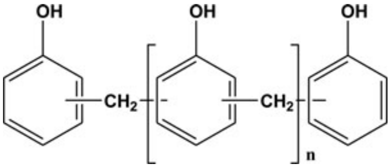
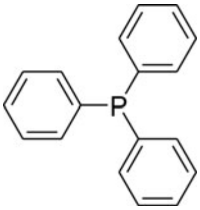
For the synthesis of two modified-DGEBA resins, 3-(triethoxysilyl)propyl isocyanate, triethoxysilane triethylamine, allyl bromide, anhydrous potassium carbonate, and platinum oxide were purchased from Aldrich Chemical Co. and all reagents used were analytical grade. Reactions were generally carried under dry argon. Anhydrous solvents or reaction mixtures were transferred via oven-dried syringe or cannula. ^{1}H NMR spectra were recorded on a BRUKER AVANCE III 400 MHz spectrometer. Detailed descriptions of the chemicals used in this study are summarized in Table 1.

[Synthesis of DGEBA with 3-(triethoxysilyl)propyl)carbamate) (DGEBA-TESPC, 1a)]

((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(3-(4-(2-(4-(oxiran-2-ylmethoxy)phenyl)propan-2-yl)phenoxy)propane-1,2-diyl)bis((3-(triethoxysilyl)propyl)carbamate)

A mixture of DGEBA(48.24 g, 92.41 mmol), 3-(triethoxysilyl)propyl isocyanate (45.77 ml, 184.83 mmol), triethylamine (32.20 ml, 231.03 mmol) were refluxed in anhydrous methylene chloride (300 mL) on an oil bath for 1 h. After the completion of the reaction, the mixture was cooled, and the solvent was removed. The residual mass was subjected to column chromatography over silica gel to afford the pure products **1a** (57.64 g, 93%). ^{1}H NMR (400MHz, $CDCl_3$) : $\delta = 0.63–0.65$ (m, 4H), 1.13–1.24 (m, 18H), 1.61–1.67 (m, 26H), 2.75 (q, $J = 2.5$ Hz, 2H), 2.91 (t, $J = 4.5$ Hz, 2H), 3.18–3.21 (m, 2H), 3.25–3.27 (m, 3H), 3.34–3.36 (m, 2H), 3.70–3.84 (m, 18H), 3.92–3.95 (m, 2H), 4.12–4.25 (m, 10H), 5.33–5.39 (m, 2H), 6.81–6.82 (m, 13H), 7.11–7.13 (m, 13H), 8.59 (br, 2H).

Table 1. Description of chemicals used in this study.

Grade Name	Structure	Remarks
DGEBA		[1]EEW = 250
DGEBA-TESPC		[1]EEW = 350
DGEBA-TESP		[1]EEW = 356
HF-1M		[2]HEW = 107
TPP		

[1] EEW : Epoxy Equivalent Weight(g/equiv.),
[2] HEW : Hydroxy Equivalent Weight(g/equiv.).

[Synthesis of DGEBA with 3-(triethoxysilyl)propyl group) (DGEBA-TESP, 2a)]

(((((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(3-(4-(2-(4-(oxiran-2-ylmethoxy)phenyl)propan-2-yl)phenoxy)propane-1,2-diyl))bis(oxy))bis(propane-3,1-diyl))bis(triethoxysilane)

[Allylated DGEBA-TESP1 (2a-1)]

A mixture of the **DGEBA**(38.0 g, 72.80 mmol), allyl bromide (7.60 ml, 87.36 mmol), and anhydrous potassium carbonate (60.41 g, 436.8 mmol) were refluxed in anhydrous acetone (300 mL) on an oil bath for 18 h. After the completion of the reaction, the mixture was cooled, filtered, and the solvent was removed. The residual mass was extracted with ethyl acetate (2 × 250 mL) and dried (Mg_2SO_4). After removal of ethyl acetate, the residual mass was subjected to column chromatography over silica gel to afford the pure products **2a** (38.50g, 97%). ^{1}H NMR (400MHz, $CDCl_3$) : $\delta = 1.62$ (s, 30H), 2.72–2.74 (m, 6H), 2.87–2.89 (m, 6H), 3.31–3.34 (m, 6H), 3.92 (dd, $J = 4.8$ Hz, 6H), 4.06–4.19 (m, 18H), 4.23–4.24 (m, 4H), 5.18 (dd, $J = 0.8$Hz, 2H), 5.30 (dd, $J = 1.2$ Hz, 2H), 5.90–5.97 (m, 2H), 6.80–6.82 (m, 20H), 7.11–7.14 (m, 20H).

[DGEBA-TESP (2a)]

A mixture of the compound **2a-1** (23.20 g, 42.44 mmol), triethoxysilane (7.84 ml, 42.44 mmol), and Platinum oxide (97 mg, 0.424 mmol) were heated to 85°C in anhydrous toluene (50 mL) on an oil bath for 24 h under argon. After cooling to room temperature, the crude is filtered through activated charcoal with anhydrous ethyl acetate. The filtrate is concentrated, dried under reduced pressure, and purified by vacuum distillation to give a yellow oil (26.0 g, 92%). ^{1}H NMR (400MHz, $CDCl_3$) : $\delta = 0.64$–0.68 (m, 1H), 0.87–0.90 (m, 1H), 1.19–1.30 (m, 6H), 1.55–1.74 (m, 12H), 2.73 (q, $J = 2.4$Hz, 2H), 2.88 (t, $J = 4.4$Hz, 2H), 3.31–3.35 (m, 2H), 3.65 (t, $J = 7.0$Hz, 1H), 3.79–3.85 (m, 3H), 3.92–4.00 (m, 3H), 4.06–4.19 (m, 5H), 6.80–6.82 (m, 6H), 7.10–7.14 (m, 6H).

[The sample preparation for reaction kinetics]

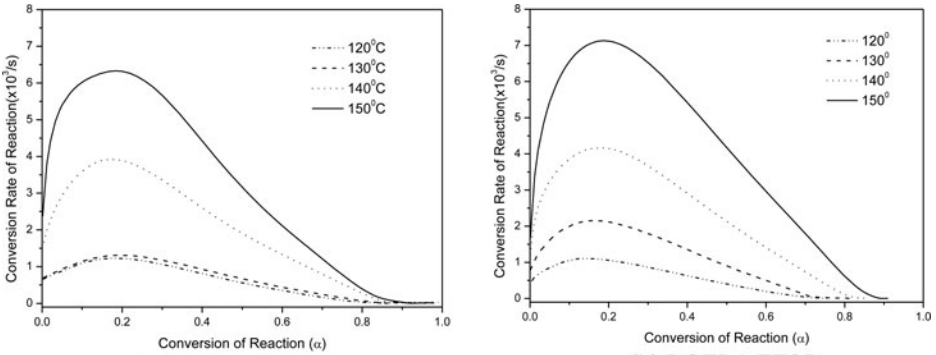
All the epoxy resin compositions in this study were composed of the same equivalent weight ratio (1:1) of epoxy and hydroxyl groups, and a catalyst (triphenyl phosphine) was added to these composition with 1 phr (per hundred resin) unit. All the components in each composition were mixed well by Thinky Mixer (Thinky Co., Tokyo, Japan) in Methyl Ethyl Ketone (MEK) solvent at room temperature until a homogeneous solution was obtained. After vacuum evaporation of MEK was done and fully dried in order to remove the solvent, each sample was immediately quenched and stored in a refrigerator at 4°C to prevent the cure reaction.

[The preparation of glass fiber composite]

The homogeneous mixture solution described in the above paragraph was used as a matrix system and the E-glass fiber fabric was used to fabricate a glass fiber reinforced composite. That is, the homogeneous mixture was poured in an aluminum mold with a sheet of glass fiber fabric. Then the solvent within the impregnated glass sheet was removed under the reduced pressure at 100°C. The degassed composite sheet was placed in a hot press and cured at 120°C for 2 h and subsequently post-cured at 180°C for 2 h and 230°C for 2h. The thickness and resin content of the cured composite film was 100μm and 40 wt. %, respectively.

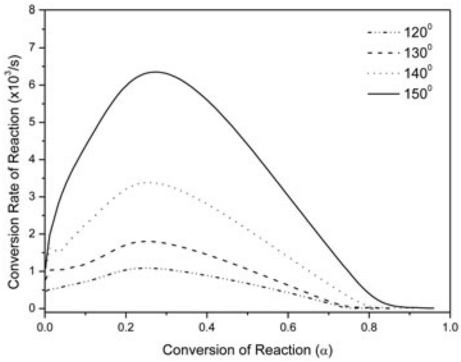
[Measurement]

Calorimetric measurements were performed using a TA-2020 differential scanning calorimeter (TA Instruments, New Castle, DE). This was calibrated in the range of -40 to 450°C. Isothermal and dynamic-heating experiments were conducted under a nitrogen flow of 60 mL/min. For a dynamic cure, the sample was heated at a rate of 5°C/min from -10 to 300°C, beyond which decomposition was observed. A set of isothermal cure curves was obtained to evaluate the kinetic parameter for the curing reactions. To measure the thermal expansion coefficient and glass transition temperature of these systems, each sample specimen was prepared in a mold with a hot press. The thermal properties of epoxy systems were



(a) DGEBA-TESPC

(b) DGEBA-TESP



(c) DGEBA

Figure 1. Isothermal conversion rate as a function of the conversion of the epoxy resin systems: (a) DGEBA-TESPC, (b) DGEBA-TESP, (c) DGEBA.

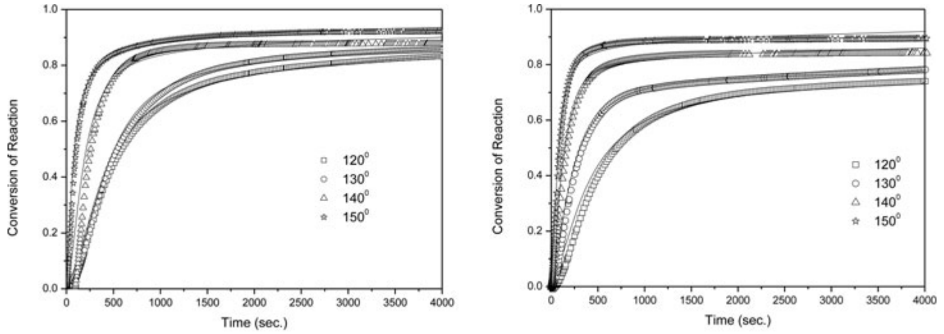
measured using a thermomechanical analyzer (TMA Q400, TA Instruments). The dimension of specimen was 16 mm long, 4 mm wide and 0.1 mm thick and applied force was 0.1N. The temperature was varied from room temperature to 250°C at a heating rate of 5°C/min. The CTE (α_1) in the glassy state was taken from the slope in the temperature range of 60°C to 100°C and the onset temperature where the slope of TMA expansion curve is changed was taken as the glass transition temperature (T_g).

Results and discussion

The cure reaction of alkoxysilylated epoxy resin systems with PN hardener followed an autocatalytic cure reaction, as shown in Figure 1(a,b), which is a typical characteristic of an epoxy resin system with phenol novolac hardener [12]. Being compared with that of epoxy resin system without alkoxysilylation, the isothermal conversion rates of DGEBA/PN system are plotted as a function of reaction conversion (α) in Figure 1(c). The generalized autocatalytic kinetic equation with respect to the diffusion effect can be written as follows: [3].

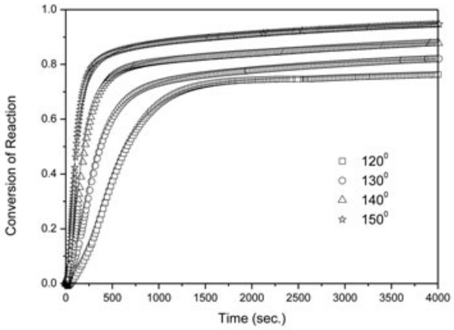
$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \frac{1}{1+\exp[C(\alpha-\alpha_c)]} \tag{1}$$

where m and n are the reaction order of the system, k_1 and k_2 are kinetic rate constants of the system, C is a constant and α_c is the critical conversion. All kinetic constants in this



(a) DGEBA-TESPC

(b) DGEBA-TESP



(c) DGEBA

Figure 2. Comparisons between the experimental values of α and theoretical values obtained from the generalized autocatalytic kinetic model for the epoxy resin systems: (a) DGEBA-TESPC, (b) DGEBA-TESP, (c) DGEBA.

equation for each resin system were obtained with a previous method [2,3]. Since conversion rates are that enthalpy change rate with time is divided into total reaction enthalpy, the enthalpy change rates with time were obtained by measuring isothermal experiments and the total reaction enthalpy was measured by dynamic-heating experiments using DSC [13]. To compute the kinetic parameters in eq.(1) without any constraints on the parameters, they were calculated by fitting the experimental data to eq.(1).

Figure 2(a,b) shows the comparisons between the experimental values of reaction conversion and the values calculated using generalized autocatalytic model for alkoxysilylated epoxy/PN systems. Those for DGEBA/PN system were represented in Figure 2(c). Good agreements were found over the whole curing temperature range for this system. The kinetic parameters are reported in Table 2 and Table 3 for these systems that followed the autocatalytic curing reaction. As shown in Figure 1, the conversion rate of DGEBA-TESP system with PN as hardener is higher than that of other epoxy resin systems. We postulated that the lower reaction rate of DGEBA/PN system was attributed to the higher reaction order as shown in Table 2, and the increase in the reaction conversion rate of DGEBA-TESP/PN system was the result of its lower activation energy of k_1 reaction rate constant and higher pre-exponential factor of k_2 rate constant, being compared with that of DGEBA-TESPC/PN system, as shown in Table 2.

Kinetics of the condensation reaction of epoxide with phenol showed the linear chain growth and branching reaction, and it can be seen that k_1 and k_2 are related to linear chain growth reaction rate constant with *n*th-order characteristics and branching reaction rate constant with autocatalytic reaction due to the generation of catalytic hydroxyl group by

Table 2. Kinetic parameters of epoxy resin systems according to the epoxy resin change.

Epoxy Resin	Temperature(°C)	k_1 (s^{-1})	k_2 (s^{-1})	m	n	Temperature dependency of the rate constant	m + n (Avg.)
DGEBA-TESPC	120	0.47×10^{-3}	0.83×10^{-2}	1.0	2.8	$k_1 = 8.53\times10^4$	3.3
	130	0.50×10^{-3}	0.84×10^{-2}	1.1	2.2	$\exp(-6.29\times10^4/RT)$	
	140	0.62×10^{-3}	1.41×10^{-2}	0.8	2.3	$k_2 = 7.31\times10^3$	
	150	2.03×10^{-3}	2.10×10^{-2}	0.6	2.3	$\exp(-4.51\times10^4/RT)$	
DGEBA-TESP	120	0.43×10^{-3}	0.76×10^{-2}	0.8	3.6	$k_1 = 3.42\times10^3$	3.7
	130	0.79×10^{-3}	1.55×10^{-2}	0.9	3.4	$\exp(-5.16\times10^4/RT)$	
	140	1.19×10^{-3}	1.74×10^{-2}	0.7	2.6	$k_2 = 4.00\times10^4$	
	150	1.26×10^{-3}	2.45×10^{-2}	0.6	2.2	$\exp(-5.01\times10^4/RT)$	
DGEBA	120	0.40×10^{-3}	2.40×10^{-2}	1.6	3.7	$k_1 = 5.78\times10^4$	5.0
	130	0.97×10^{-3}	5.46×10^{-2}	1.8	4.0	$\exp(-6.08\times10^4/RT)$	
	140	1.31×10^{-3}	5.55×10^{-2}	1.5	3.3	$k_2 = 2.45\times10^3$	
	150	1.55×10^{-3}	5.75×10^{-2}	1.1	3.0	$\exp(-3.69\times10^4/RT)$	

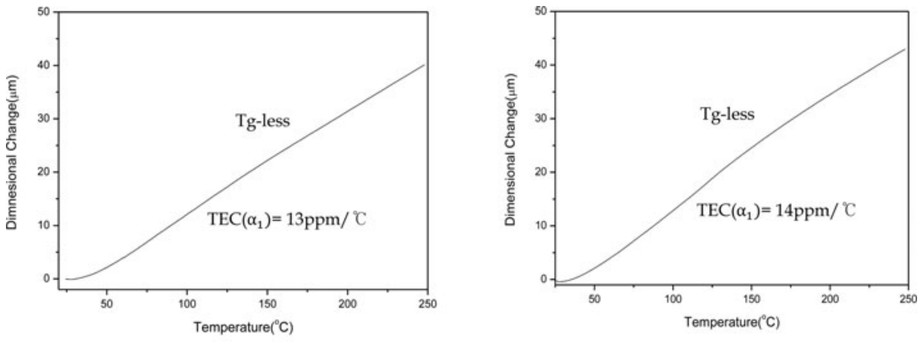
phenol-epoxide addition, respectively [12,14]. Therefore, it can be assumed that the reaction conversion rates of DGEBA-TESPC/PN showed the orientation-dominant effect, and those of DGEBA-TESP manifested the activation energy-dominant effect, being compared with DGEBA/PN in respect to k_1 reaction rate constant. In case of k_2 reaction rate constant, the orientation-dominant effect was manifested with frequency factor increases in alkoxysilylated epoxy resin system, being compared with DGEBA/PN system. The critical and final cure reaction conversions of each epoxy resin systems used in this experiment according to the change in temperature are summarized in Table 3. A shown in Table 3, the DGEBA-TESP system with highest reaction conversion rate showed lowest the critical and final cure reaction conversion. It can be postulated that the epoxy resin system with early branching reaction decreased the cure reaction conversion and crosslinking density.

The thermal property of glass composite was determined using TMA and the results are summarized in Figure 3. For the coefficient of thermal expansion (CTE), DGEBA-TESPC and DGEBA-TESP composite systems show the slightly lower CTE than the unmodified DGEBA composite. But, if we consider that, in the case of unfilled resin systems, the modified resin show the similar CTE to DGEBA resin, the reductions of CTE due to the formation of fiber composite seems to be more efficient in the alkoxysilylated epoxy systems than DGEBA system.

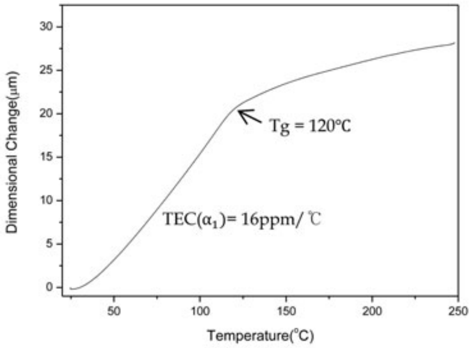
In contrast, the effect of modification moiety on T_g is much more significant than CTE. As depicted in Figure 3, the alkoxysilylated DGEBA composite systems do not show any thermal

Table 3. Values of the constant C, critical cure reaction conversion(α_c, and final cure reaction conversion(α_∞) at different temperature of the epoxy resin systems.

Epoxy Resin	Temperature(°C)	C	α_c	α_∞
DGEBA-TESPC	120	6.56	0.77	0.83
	130	15.42	0.79	0.86
	140	25.53	0.82	0.88
	150	13.33	0.85	0.92
DGEBA-TESP	120	24.49	0.68	0.74
	130	37.46	0.71	0.78
	140	52.06	0.79	0.84
	150	26.91	0.81	0.90
DGEBA	120	64.07	0.73	0.76
	130	21.14	0.77	0.82
	140	20.58	0.81	0.88
	150	17.92	0.94	0.95

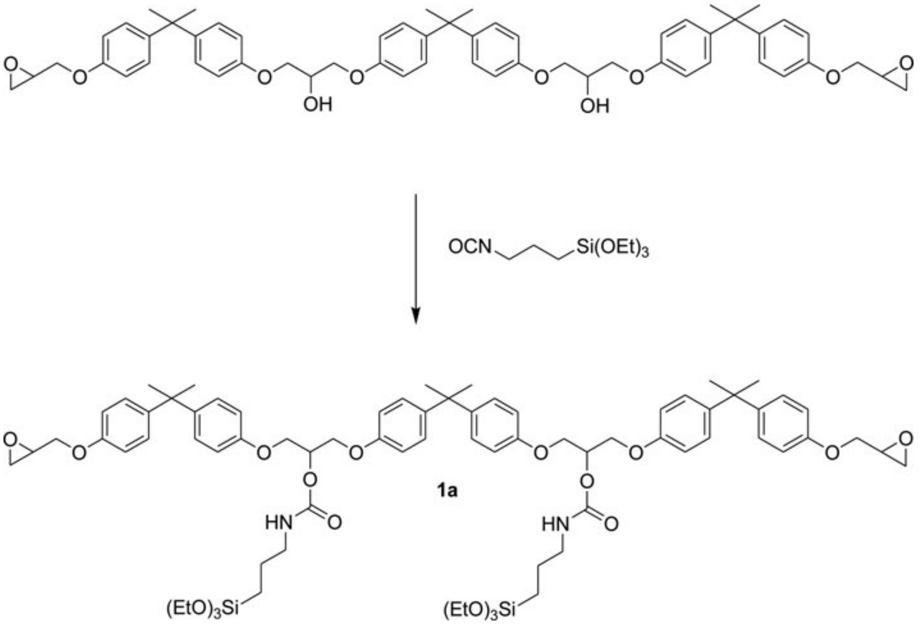


(a) DGEBA-TESPC (b) DGEBA-TESP

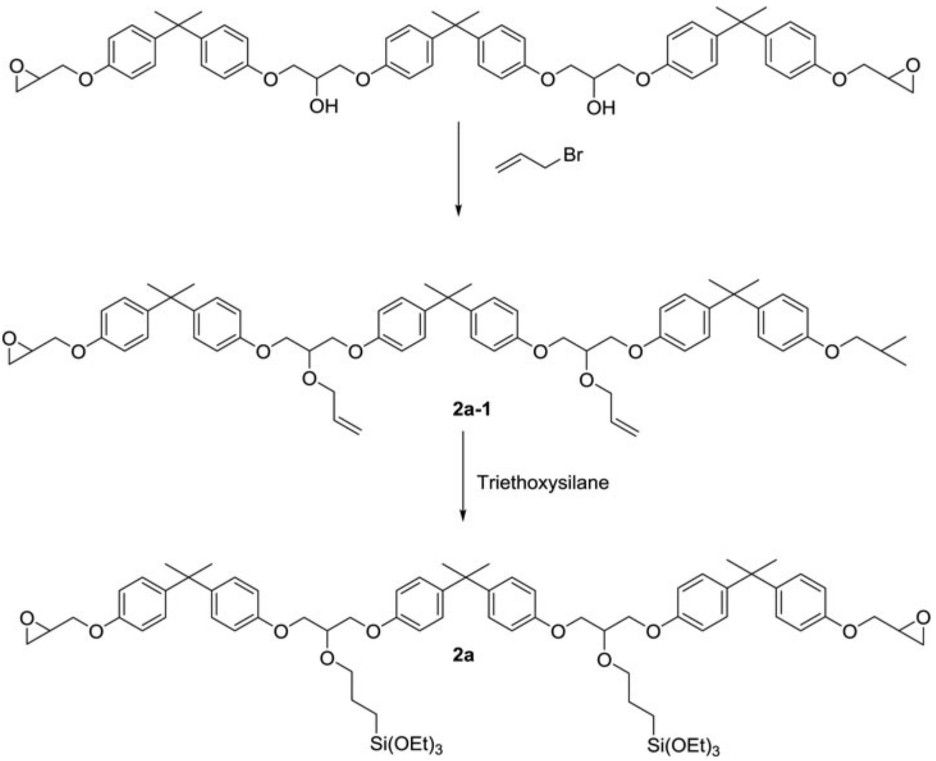


(c) DGEBA

Figure 3. Thermal expansion graph of epoxy composites with the filler content of 40wt. %: (a) DGEBA-TESPC, (b) DGEBA-TESP, (c) DGEBA.



Scheme 1. Reaction process and structure of DGEBA-TESPC.



Scheme 2. Reaction process and structure of DGEBA-TESP.

transition (i.e. T_g-less) within the measured temperature range, whereas the DGEBA composite shows the glass transition temperature of 120°C. The disappearance of T_g in alkoxysilylated epoxy system upon forming the glass fiber composite is very unique and interesting observation. This observation of the modified DGEBA is speculated to result from the chemical bonding with the glass fiber surface and the alkoxysilyl group: The formation of the interfacial bonding due to the alkoxysilyl group may restrict the segmental motion of epoxy network seriously, which leads to the better thermal properties of epoxy composite.

Conclusions

The alkoxysilylated epoxy resins were synthesized and their curing reactions with PN hardener were investigated by the thermal analysis method. The curing reactions in all systems proceeded through an autocatalytic kinetic mechanism, irrespective of epoxy resins employed. The experimental values of the reaction conversion were compared with the values calculated using a generalized autocatalytic model including a diffusion term, and good agreements were found over the whole curing temperature range for all resin systems. The reaction conversion rate of DGEBA-TESP epoxy resin system with PN hardener increased when compared with other epoxy resin systems. These increases in DGEBA-TESP resin systems with PN hardener are caused by the lower activation energy of k_1 reaction rate constant and higher collision frequency factor of k_2 reaction rate constant, which results from the orientation effect with respect to autocatalytic cure reaction conversion kinetic data. However, DGEBA-TESP resin system showed lowest the critical and final cure reaction conversion, which was attributed to the higher cure reaction conversion rate. The characteristics of

T_g-less composites can be shown in alkoxysilylated epoxy resin systems with glass fiber as filler according to the miscibility increase with glass fiber. It can be postulated that the lower thermal expansion coefficient of the DGEBA-TESPC epoxy resin system with glass fiber is represented by the improvement of crosslinking density due to the cure reaction increase. The glass transition temperatures of DGEBA-TESPC and DGEBA-TESP composite are significantly improved than that of DGEBA, probably due to the facile interaction of grafted alkoxysilyl group with glass fiber fabric.

Acknowledgments

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