Cure Kinetics for the Ultraviolet Cationic Polymerization of Cycloliphatic and Diglycidyl Ether of Bisphenol-A (DGEBA) Epoxy Systems with Sulfonium Salt using an Auto Catalytic Model

M. J. M. Abadie,[1] N. K. Chia,[2] F. Boey[2]

[1]LEMP/MAO, Université Montpellier 2, S.T.L., 34095 Montpellier Cedex 05, France
[2]School of Materials Engineering, Nanyang Technological University, Singapore

ABSTRACT: This paper investigates the cure kinetics for the ultraviolet (UV) cationic polymerization for both a cycloaliphatic and diglycidyl ether of bisphenol-A (DGEBA) epoxy system, using the photoinitiator triarylsulfonium hexafluoroantimonate salt. Using an autocatalytic kinetic cure model, the reaction rate values for both cycloaliphatic and DGEBA epoxy systems were determined for different photoinitiator amount (wt %) added, and at different UV exposure temperatures. The value for the cycloaliphatic epoxy increased significantly with addition of the sulfonium salt, reaching a limiting maximum after 2%. The value for the DGEBA epoxy system also increased, to a limiting maximum after 3%. Addition of the sulfonium salt significantly lowered the activation energy for the cycloaliphatic epoxy at all levels of addition, with the reduction proportional to the amount of salt added. In contrast, the sulfonium salt did not have a major effect on the DEGBA until the addition of at least 3% of the salt. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1587–1591, 2002

Key words: radiation curing; cationic polymerization

INTRODUCTION

Ultraviolet (UV) radiation curing of polymer coatings has until recently been dominated by photoinitiated radical polymerization processes, due partly to the thermal instability of early cationic systems like aryldiazonium salts. With the advent of more stable alternatives, such as the onium salts, the cationic polymerization process has become increasingly important because of the several significant advantages it has over radical polymerization. The main advantage is its ability to allow spontaneous cure reaction in the presence of oxygen, in contrast to radical polymerization, which provides significant advantage in costs. Additionally, the cationic polymerization process also generates reactive electrophiles (acids) that helps to sustain polymerization even after the UV exposure has lapsed, giving the characteristics of what has been termed a "living" polymerization.[1] As such, the cure process require only a relatively short UV exposure, limited to just that amount of time required for photolysis of the photoinitiator. Once initiated, curing continues spontaneously long after exposure to UV radiation has been stopped. The same phenomenon has also been reported for cationic polymerization using electron beam curing.[2]

Typical onium-based epoxy systems respond throughout the UV-near visible spectral region. The mechanisms for cationic-based cure initiation and propagation have been discussed in earlier publications.[2–6]. The onium salt is initially decomposed by UV exposure into cations and a photosensitive acid, leading to liberation of an electron-deficient fragment that then becomes the polymerization initiator and then causes propagation of the polymerization. Cationic UV curing of epoxy resins has been shown to be viable in several industrial applications,[7–13] including the curing of decacarbonyl in epichlorohydrin, photosensitized epoxide coatings. Initiators used included diaryliodonium and onium salts from Groups Va and VIa for cationic polymerization,[14–19] triarylsulfonium salts,[20] and thiopyrylium salts[21]as photoinitiators for epoxide polymerization.[21]

Optimal curing for UV- induced reactions invariably requires the ability to accurately characterize the cure kinetic reactions using methods necessarily different from conventional thermal methods. Abadie[22] reported the use of differential photocalorimetry for photosensitive formulations to determine the rate and percent of conversion. Using similar approaches, Abadie and Seghier,[23] Ionescu and Abadie,[24] and Lowe[25] have been able to develop formulations of photoinitiators for cationic polymerization of various mono-

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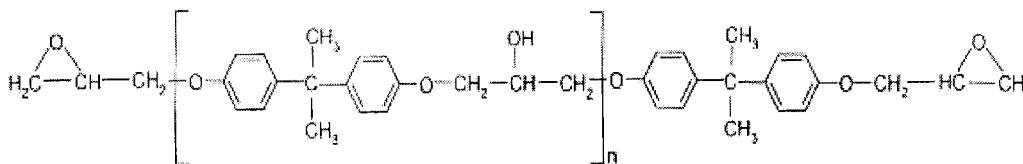*Correspondence to:* F. Boey (mycboey@ntu.edu.sg).

Figure 1 (a) Structure of DGEBA epoxy; (b) structure of cycloaliphatic epoxy; (c) structure of triarylsulfonium hexafluoro-antimonate salt.

mers. This paper attempts to characterize the effect of the photoinitiator on the cure kinetics of a UV-cured cycloaliphatic epoxy and a DGEBA epoxy system, using a triarylsulfonium hexaflouroantimonate salt as the photoinitiator, by using constitutive kinetic modeling equations. For thermal curing, these constitutive kinetic equations fall under two general categories: n^{th}-order and autocatalytic. Thermally cured epoxy systems have been adequately modeled by either of the two models,[32–39] though in more complicated systems such as bismaleimide (BMI), which involves multiple cure,[33] a combination of both systems could be required.[34] The model could then represent an overall process if these chemical reactions occur simultaneously. Alternatively, for reactions that occur sequentially, two separate models could be used sequentially.[35]

Previous UV curing work has shown the autocatalytic model fits the radiation cure reaction and, as such, is used for this work. An auto-catalyzed reaction assumes that at least one of the reaction products is also involved in the propagating reaction, and is thus characterized by an accelerating isothermal conversion rate, with its maximum occurring well after conversion initiation. This result is because the reactants can be converted via alternative paths. To take into account these autocatalytic characteristics, a generalized expression as follows can be used:[32]

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \qquad (1)$$

where α is the degree of conversion, n is the reaction order, and the rate constant k (T) is the temperature-dependent rate constant given by the Arrhenius relationship

$$k = A\exp(-E/RT) \qquad (2)$$

where E is the activation energy, R is the gas constant, T is the absolute temperature, and A is the pre-exponential or frequency factor. Accurate calculation of the activation energy is necessary because then the rate constant would be more precisely known. This is done by curing the sample isothermally and plotting the resulting conversion rate values against cure time.[40–44] The activation energy is then obtained from the Arrhenius plot in eq. 2 of $\ln(d\alpha/dt)_{\alpha i}$ versus T^{-1},

where the $(d\alpha/dt)_{\alpha i}$ is the conversion rate associated with a fixed conversion α_I.

EXPERIMENTAL

The epoxy resins used in this study were a difunctional cycloaliphatic epoxide monomer, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate from Union Carbide Company (identified as ERL 4221E) and diglycidyl ether of bisphenol-A (DGEBA) from Shell Chemical (identified as Epikote 828). The photoinitiator used was the salt triarylsulfonium hexafluoroantimonate (UVI 6974) from Union Carbide Corp. The amount of photoinitiator used ranged between 0.5 and 5 wt %. The structures for the two epoxies and the photoinitiator are shown in Figure 1.

The respective epoxy and the appropriate amount of photoinitiator were stirred together until a homogenous phase was formed at room temperature and subsequently cured as a coating of ~50 μm thickness on a glass slide. All experiments were carried out using the DSC 910 photocalorimeter from TA Instruments with a 930 DPC mercury vapor lamp as the radiation source. The double measuring head DSC 912 was capable of analyzing two samples simultaneously. The 200 W lamp yielded an intensity measuring 2.5 mW/cm². Precise control of the homogeneity of the luminous flux between the reference cell and the sample cells was done with a double measuring head with the aid of a calibrated radiometer. A flux of
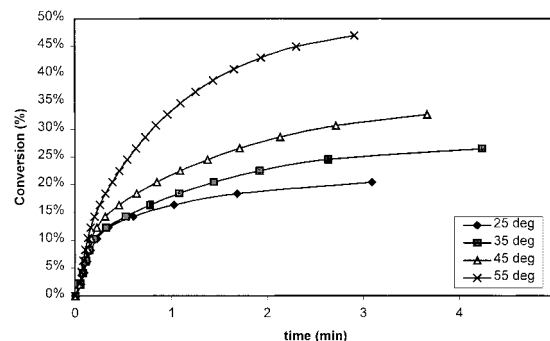

Figure 2 Time–conversion relationship of cycloaliphatic epoxy and 5 wt % sulfonium salt at four isothermal temperatures.
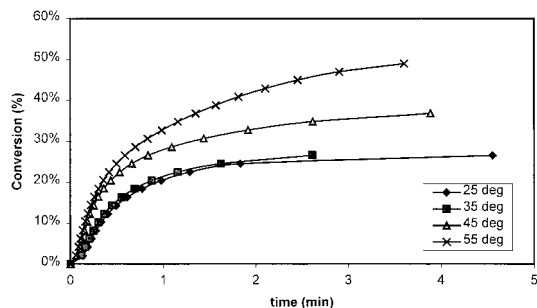
Figure 3 Time–conversion relationship of DGEBA epoxy and 5 wt % sulfonium salt at four isothermal temperatures.

nitrogen gas at 5–20cm^3/min was used to purge the cell prior to any run.

All experiments were carried out at four different isothermal temperatures, at 25, 35, 45, and 55 °C, respectively. The samples were heated to the respective isothermal temperature and then exposed to ultraviolet (UV) irradiation for a period of 5 min. To obtain a more consistent baseline, the reference pan used consisted of 1 mg of the epoxy mixture to be studied that have already been exposed to UV irradiation for 15–20 min.

The degree of conversion (α) was calculated from a ratio of the reaction enthalpy and the theoretical enthalpy, the latter being represented as

$$\Delta H_{th} = \frac{f \Delta H_{epoxy}}{M} \qquad (3)$$

TABLE I
Regression Analysis Results for Cycloaliphatic Epoxy with Sulfonium Salt

Sulfonium salt; wt %	Temperature, °C	m	k, min
0.5	25	0.48	2.358
	35	0.53	2.540
	45	0.56	2.949
	55	0.41	3.139
1.0	25	0.53	4.91
	35	0.51	5.92
	45	0.50	6.09
	55	0.51	5.97
2.0	25	0.54	5.76
	35	0.53	7.33
	45	0.54	7.15
	55	0.52	6.83
3.0	25	0.55	6.11
	35	0.56	7.70
	45	0.57	6.89
	55	0.53	6.90
5.0	25	0.57	6.96
	35	0.54	6.82
	45	0.54	7.03
	55	0.52	7.06

TABLE II
Regression Analysis Results for DGEBA Epoxy with Sulfonium Salt

Sulfonium salt, wt %	Temperature, °C	m	k, min^{-1}
0.5	25	0.46	0.645
	35	0.46	0.855
	45	0.44	1.436
	55	0.52	2.406
1.0	25	0.45	0.647
	35	0.45	0.853
	45	0.46	1.467
	55	0.51	2.545
2.0	25	0.48	1.068
	35	0.47	1.347
	45	0.48	1.929
	55	0.53	3.641
3.0	25	0.54	2.389
	35	0.50	2.815
	45	0.50	3.605
	55	0.56	4.860
5.0	25	0.54	2.839
	35	0.55	3.423
	45	0.51	4.392
	55	0.50	4.875

where ΔH_{th} is the theoretical enthalpy, f is the functionality of the monomer, ΔH_{epoxy} is the enthalpy of polymerization of the epoxy monomer (22,000 cal/mol), and M is the molecular weight of the epoxy monomer.

RESULTS AND DISCUSSION

The results obtained for the degree of conversion, α, of the cycloaliphatic epoxy/5% sulfonium salt system are plotted against the UV exposure time (min) at the respective isothermal temperatures of 25, 35, 45, and 55 °C in Figure 2. Similar results obtained for the DGEBA/5% sulfonium salt system are plotted in Figure 3. Evidently, for both cases, the conversion increased with the temperature of UV exposure. The maximum percentage conversion achieved by both systems was <50%, approaching a plateau in each case. We believe that because a gel point was reached
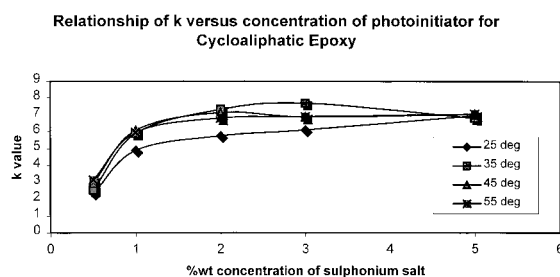

Figure 4 Effect of concentration of photoinitiator with UV-cured cycloaliphatic epoxy.
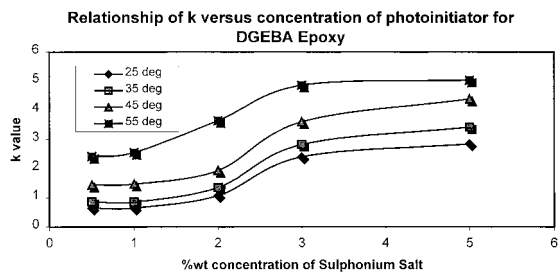
Figure 5 Effect of concentration of photoinitiator with UV-cured DGEBA epoxy.

at this stage, consumption of the epoxy was subsequently inhibited.

Previous work[24] has indicated that the auto-catalytic kinetic model was more appropriate for the UV curing of similar systems. Thus, by using an auto-catalytic model represented by eq.1, all the plots for Figures 2 and 3 were modeled using a regression analysis approach. The results of the regression analysis performed for both the cycloaliphatic and DGEBA systems, for varying wt % of sulfonium salt content, have been tabulated in Tables I and II, for the values of k, n, and m, respectively.

To enable comparisons with more complex systems and to make the comparison meaningful, the order of reaction, n, was assumed to be similar in value for the different cure temperatures, and was set at 1.5 based on previous works.[45, 46] This approximation is realistic to the extent that the formulation of the reactants did not change, and the range of temperature considered varied only from 25 to 55 °C. The values of k (T) were thus determined measured. The obtained value of k, the rate constant, was then used to calculate the activation energy of the reaction.

The plots for the values of k against the concentration of photoinitiators for the two epoxy systems are shown in Figures 4 and 5. The k value for the cycloaliphatic epoxy increased significantly with the initial increase in the sulfonium salt amount up to 2%, after which further addition of the salt gave only marginal increases at the lower temperature (see Fig-
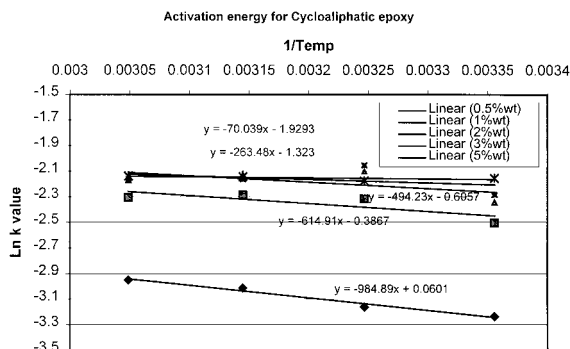

Figure 6 Plot of ln k against $1/T$ for cycloaliphatic epoxy for various concentrations of sulfonium salt.
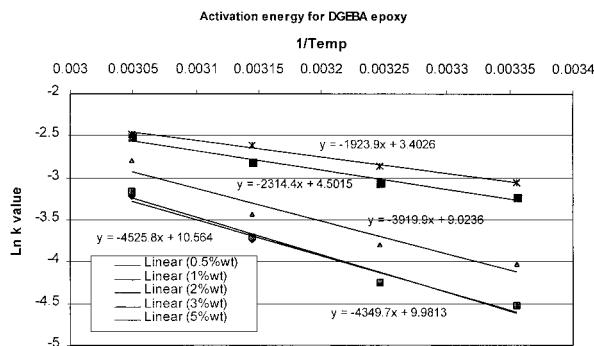

Figure 7 Plot of ln k against $1/T$ for DGEBA epoxy for various concentrations of sulfonium salt.

ure 4). The reaction rate also did not increase at higher temperatures. The plots for the values of k against the concentration of the sulfonium salt added for the DGEBA epoxy system are shown in Figure 5. The change in temperature in this case appeared to significantly affect the values of k obtained, with the highest temperatures giving the highest k values. Also, the amount of sulfonium salt added increased the k value up to 3, after which further increase in the salt content did not significantly increase the k values.

The effect of the sulfonium salt added on the value of the activation energy can be more clearly seen in Figures 6 and 7, for the cycloaliphatic and DGEBA systems, respectively. The ln (k) versus $1/T$ data were plotted for the different temperatures at which the material was cured. The slope of the linear graphs thus obtained provides the means to determine the activation energy as the salt content increased. The values of the activation energy so obtained were then tabulated against the wt % of salt added, as shown in Table III and Table IV, for the cycloalipathic epoxy and DGEBA system, respectively. The results clearly show that the addition of the sulfonium salt significantly lowered the activation energy for the cycloaliphatic epoxy at all levels of addition, with the reduction proportional to the amount of salt added. In contrast, the sulfonium salt did not have any effect on the DEGBA until the addition of at least 3% of the salt.

Finally, a note on the ln A values: ln A in the Arrhenius equation is the pre-exponential factor or collision factor. Normally, an increase in the speed of

TABLE III
Kinetic Parameters of Cycloaliphatic Epoxy with Various Concentrations of Sulfonium Salt as photoinitiator

Concentration of PI (%)	E_a (kJ/mol)	ln A (l/s)
0.5	8.19	4349.7
1	5.11	4525.8
2	4.11	3919.9
3	2.19	2314.4
5	0.58	1923.9

TABLE IV
Kinetic Parameters of DGEBA Epoxy with Various
Concentration of Sulfonium Salt as Photoinitiator

Concentration of PI (%)	E_a (kJ/mol)	ln A (1/s)
0.5	36.16	984.89
1	37.62	614.91
2	32.59	494.23
3	19.24	263.48
5	15.99	70.039

the reaction should be reflected in the increase in the collision factor as well. Our observation is in contrast with what should be expected. This resultcan probably be explained by the fact that the onset of the gel point sets in early because of the faster reaction (which in turn affects the collision factor). We also observe that the collision factor is higher for the cycloaliphatic epoxy than DGEBA, a confirmation of the fact that reactivity of former is much greater than that of the latter.

CONCLUSION

Using an autocatalytic kinetic cure model, the reaction rate values for both cycloaliphatic and DGEBA epoxy systems were determined for different photoinitiator wt % added and at different UV exposure temperatures. The value for the cycloaliphatic epoxy increased significantly with addition of the sulfonium salt reaching a limiting maximum after 2 %. The value for the DGEBA epoxy system also increased to a limiting maximum after 3%. Addition of the sulfonium salt significantly lowered the activation energy for the cycloaliphatic epoxy at all levels of addition, with the reduction proportional to the amount of salt added. In contrast, the sulfonium salt did not have any effect on the DEGBA until the addition of at least 3 % of the salt.

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