Mechanistic Modeling of Epoxy–Amine Kinetics. 2. Comparison of Kinetics in Thermal and Microwave Fields

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ABSTRACT: An investigation was conducted to compare the rates and mechanisms of epoxy–amine reactions in thermal and microwave fields. A monofunctional model compound formulation and a multifunctional epoxy formulation were analyzed. Chromatographic, spectroscopic, and calorimetric techniques were utilized to generate data. Excellent agreement was observed between the proposed mechanistic model and experimental results. It was unequivocally found that the use of microwave energy in lieu of thermal energy had no effect on the reaction kinetics.

I. Introduction

The quest for a faster and more efficient alternative to conventional thermal energy sources has led to a considerable recent interest in the use of electromagnetic waves in the microwave frequency range to cure polymers and composites. A recent review summarizes published reports on the application of microwave energy to curing of polymers and composites and highlights the fundamental principles of microwave heating.[1]

Some advantages of microwave vis-à-vis thermal heating are attractive. For instance, unlike thermal energy, microwave energy can be supplied directly to the sample, eschewing the heat conduction through the sample and its enclosures and thus offering potential benefits in terms of increased production rates.[2] Although such process improvements are conceptually feasible, their ultimate value must be judged within the context of a comprehensive cost analysis.

From the fundamental scientific point of view an essential question regarding the use of microwaves in lieu of thermal energy is whether the microwave energy can alter the mechanism and kinetics of chemical reactions. Such capability would undoubtedly have dramatic implications in processing polymers with desired morphologies and properties. For instance, in epoxy–amine systems, an increase in the relative rate of primary amine (PA)–epoxy (E) to secondary amine (SA)–epoxy (E) reactions would favor the initial formation of a linear polymer which could be subsequently cross-linked, resulting in a network different from the one formed by random cross-linking from the onset of reactions.

Perusing the available information in the literature, one quickly learns that the hitherto reported studies have focused mainly on the global increase in heating rate with microwave energy, while treating the fundamental interactions between microwaves and polymer networks in a qualitative or, at best, semiquantitative way.[3-11] Fine effort at Michigan State University produced interesting results with emphasis on the design of equipment for processing of composites in the microwave field.[12-14]

A few years ago at Polytechnic, we initiated a comprehensive program aimed at elucidating the fundamental differences (if any!) in the chemorheology of cure in microwave and thermal fields. The results of our initial phenomenological study have been reported in the literature.[15]

The primary objective of this work, which encompasses our efforts in the past 2 years, is to develop and compare mechanistic kinetic models for epoxy–amine reactions in microwave and thermal energy fields. A model compound and a multifunctional epoxy formulation were investigated, and the results are reported herein.

II. Experimental Section

A. Materials. 1. Model Compound Formulation. The model compound formulation used in this study consisted of aniline (99.55%, Aldrich) and 1,2-epoxy-3-phenoxypropane (99%, Aldrich). The latter compound is also known as phenyl glycidyl ether (PGE) and will be referred to by its acronym.

2. Epoxy Formulation. The epoxy formulation investigated consisted of the stoichiometric amounts of the diglycidyl ether of Bisphenol A (DGEBA) epoxy resin (research grade Epon 825; courtesy of Shell Chemical Co.) and 4,4′-methylenedianiline (MDA) curing agent (Aldrich). The epoxy equivalent weight of the DGEBA resin was determined by titration to be 180.

B. Sample Preparation. 1. Model Compound Formulation. The stoichiometric amounts of aniline and PGE were mixed at room temperature and either used immediately or kept in dry ice for a maximum of 72 h.

2. Epoxy Formulation. The epoxy formulation was mixed while stirring for 7 min at 57 °C until clear. The mixture was then either processed immediately or poured into glass vials and stored in dry ice for a maximum of 72 h.

C. Processing. 1. Thermal Cure. The kinetics of cure were investigated at 90, 100, 110, and 120 °C for both model compound and epoxy formulations. About 40 mL of the model compound mixture was placed in a 100-mL three-neck bottle, immersed in an oil bath, and purged with purified grade nitrogen. A reflux condenser was fitted to prevent evaporation of aniline. An Omega CN 2010 temperature controller was employed. Small aliquots of the reaction mixture were removed and quenched at desired time intervals.

Twenty disposable glass vials, each containing 50 mg of the epoxy formulation, were placed in the oil bath. At set time intervals they were removed from the bath and quenched to arrest the progress of reactions.

2. Microwave Cure. Microwave cure was conducted in a microwave circuit assembled in our laboratory and described in detail elsewhere.[15] Microwaves at the frequency of 2.45 GHz were produced by a microwave generator. The applicator in which microwaves interacted with the sample was a rectangular waveguide, shorted at both ends and measuring 7.2 cm wide X 3.4 cm high × 41.6 cm long. The waveguide operated in the TE_{01} mode. The sample temperature was monitored by a Luxtron Model 750 fluoroptic thermometer. A Dascon 1 I/O board and an ERA 01 electromechanical relay were used to automatically maintain the constant temperature by switching the power supply

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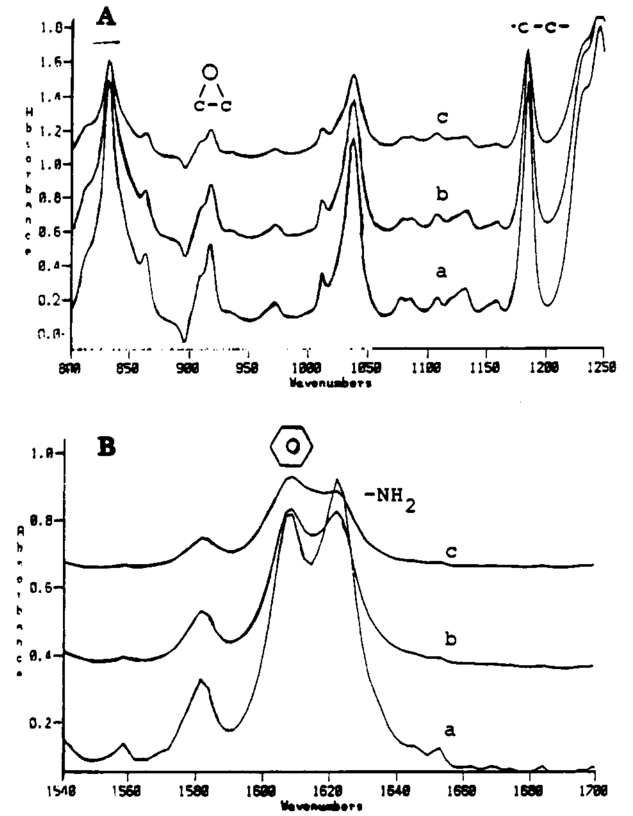

Figure 1. FTIR spectra of the multifunctional epoxy formulation cured at 100 °C for (a) 0, (b) 18, and (c) 29 min (A = wavenumbers 800–1250; B = wavenumbers 1540–1700).

on and off. The temperature variation was within ±1 °C. Purified grade nitrogen, saturated with aniline and PGE, was used during the model compound reactions to prevent oxidation and minimize evaporation. The mixture was stirred with a Teflon rod to ensure uniform temperature. At set time intervals samples were quenched and then immediately prepared for further analysis. The samples of gelled epoxy formulation were obtained from the immediate vicinity of the fluoroptic probe.

D. Techniques. 1. High-Performance Liquid Chromatography (HPLC). A Perkin-Elmer LCI-laboratory computing integrator equipped with a reverse-phase C18 column was used in the HPLC study. Details of the experimental analysis are described in part 1 of this series (preceding paper in this issue).

2. Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra were obtained on a Bio-Rad Digilab Division FTS 60 spectrometer. Each spectrum from 4000 to 650 cm^{-1} was averaged over 32 scans at 4-cm^{-1} resolution. The liquid sample spectra were obtained using NaCl pellets and a liquid cell with a path length of 0.1 mm. Methylene chloride was used as the solvent and the background spectrum. Solid samples were prepared in a mini press. Between 0.5 and 1 mg of the reaction mixture was mixed with 100 mg of dry KBr and ground into fine powder. The peak at 915 cm^{-1} was used to follow the epoxy group, while the peaks at 1630 and 3350 cm^{-1} were used to monitor the primary amine.[16-18] The aromatic C–C stretch at 1180 cm^{-1} was used as the internal standard.[18,19] The primary amine peak at 1630 cm^{-1} overlapped with the benzyl ring peak, and the two had to be deconvoluted. Figure 1 shows three spectra obtained at different degrees of cure. Digilab software was used to calculate the areas of the peaks.

The degree of cure was calculated from the measured values of absorbances of the internal standard and the functional group at the beginning of reaction (t_0) and after some time (t).[17,20] The degree of cure was determined in terms of the disappearance of both epoxy and primary amine.

III. Results and Discussion

Table I
Summary of Kinetic Parameters for DGEBA/MDA and PGE/Aniline Formulations

	DGEBA/MDA			PGE/aniline		
temp, °C	k_{1b}	k_{2b}	k_{2b}/k_{1b}	k_{1b}	k_{2b}	k_{2b}/k_{1b}
90	0.039	0.017	0.22	0.00304	0.0019	0.31
100	0.066	0.025	0.19	0.0055	0.0023	0.22
110	0.102	0.036	0.18	0.0073	0.0026	0.21
120	0.180	0.065	0.18	0.0085	0.0027	0.16

The development of our mechanistic kinetic model for epoxy–amine reactions is described in the first part of this series, where a reaction mechanism and rate equations for a model compound formulation were proposed and used to calculate the kinetic parameters. An excellent agreement was observed between model predictions and experimental results. The same model was then utilized for (1) the analysis of epoxy–amine reactions in the multifunctional formulation in the thermal field and (2) model compound and multifunctional reactions in the microwave field. The results are presented below. Our discussion is focused upon a direct comparison of the fundamental kinetic parameters of epoxy–amine reactions in thermal and microwave fields.

We shall begin by comparing the kinetic results obtained with the model compound (described in part 1) and the multifunctional formulation reacted in the thermal field. For that purpose, we first had to use our model to calculate the kinetic parameters of the multifunctional formulation. Since the FTIR analysis yields results in terms of epoxy and primary amine groups and our model requires as input the concentrations of reactants and products, i.e., (E), (PA), (SA), and (TA), the last two terms had to be calculated independently from mass balances. Then the corresponding kinetic parameters were calculated using the computational analysis described in part 1. The rate constants for route c of the proposed mechanism are not reported for the multifunctional formulation because we were not fully confident in the accuracy of calculations at higher degrees of cure which entailed an extrapolation between liquid and gelled samples. The rate constants for route b, however, were very accurate and are listed alongside the corresponding constants for the model compound formulation in Table I. A strong negative substitution effect is observed in both model compound and multifunctional formulations. Interestingly, the temperature dependence of the reactivity ratio is much more pronounced in the model compound than in the multifunctional formulation. The activation energies for primary amine–epoxy and secondary amine–epoxy reactions in the multifunctional formulation were found to be 14.5 and 12.5 kcal/mol, respectively. These numbers fall within the range of activation energy values reported in the literature. Since the size of the amine molecule is not thought to affect the kinetics,[21] the observed faster rate in the multifunctional formulation is attributed to the higher basicity of MDA in comparison with aniline. A similar effect was observed in an earlier study by Dobas and Eichler.[22]

Next, we shall present a direct comparison of reaction rates in thermal and microwave fields, beginning with the model compound formulation. To facilitate direct comparison of kinetic results, we shall write the following equations for the disappearance of primary amine and the production of tertiary amine:

$$-\mathrm{d(PA)_b}/\mathrm{d}t = W_2\mathrm{(PA)(E)}[k_{b1} + k_{b1}'(\mathrm{OH})^n] \qquad (1)$$

$$\mathrm{d(TA)_b}/\mathrm{d}t = W_2\mathrm{(SA)(E)}[k_{b2} + k_{b1}'(\mathrm{OH})^n] \qquad (2)$$

Equations 1 and 2 are written analogously to eqs 10 and 11 of part 1. The use of exponent n on the hydroxyl

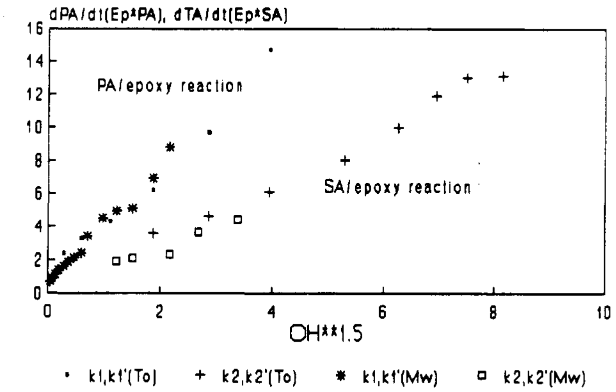

Figure 2. Reduced reaction rate as a function of hydroxyl concentration for thermal and microwave heating of the model formulation at 100 °C.

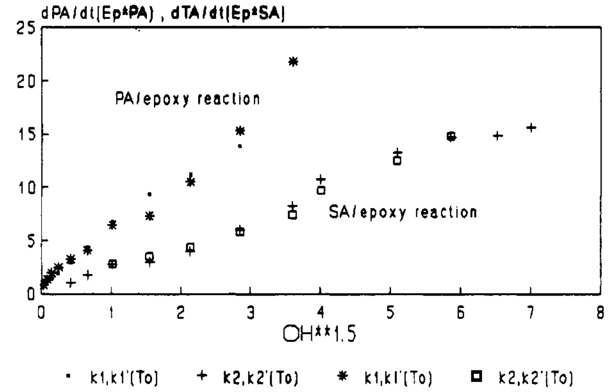

Figure 3. Reduced reaction rate as a function of hydroxyl concentration for thermal and microwave heating of the model formulation at 110 °C.

concentration term renders eqs 1 and 2 useful over a wide range of conversion. Next, eqs 1 and 2 are rewritten as

$$-\frac{\mathrm{d(PA)_b}/\mathrm{d}t}{W_2\mathrm{(PA)(E)}} = k_{\mathrm{b1}} + k_{\mathrm{b1}}'(\mathrm{OH})^n \qquad (3)$$

and

$$\frac{\mathrm{d(TA)_b}/\mathrm{d}t}{W_2\mathrm{(SA)(E)}} = k_{\mathrm{b2}} + k_{\mathrm{b2}}'(\mathrm{OH})^n \qquad (4)$$

Plots of the reduced reaction rate (the left-hand side of eqs 3 and 4) as a function of hydroxyl concentration, with a best-fit value of $n = 1.5$, should yield straight-line fits of data over the entire course of reaction and, more importantly, provide an immediate telling comparison of reaction kinetics in thermal and microwave fields. In Figures 2–4, reduced reaction rates are plotted as a function of hydroxyl concentration for the model formulation at 100, 110, and 120 °C. It is quite clearly seen in these figures that the kinetics of aniline/PGE reactions in thermal and microwave fields do not differ.

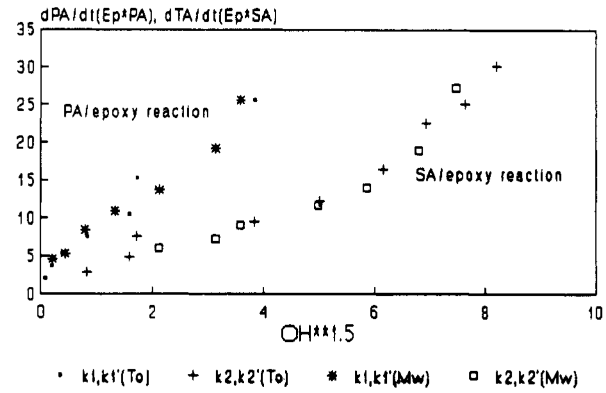

Figure 4. Reduced reaction rate as a function of hydroxyl concentration for thermal and microwave heating of the model formulation at 120 °C.

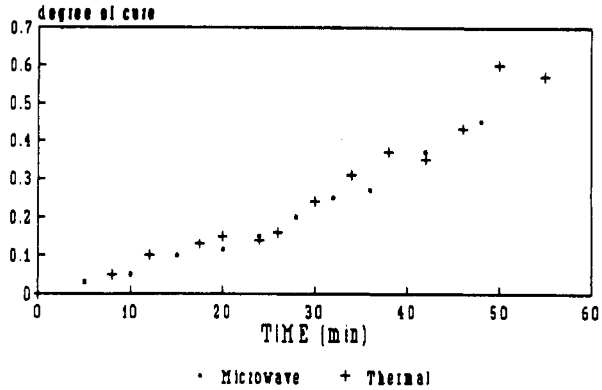

Figure 5. Degree of cure as a function of time for thermal and microwave cure of the multifunctional formulation at 90 °C.

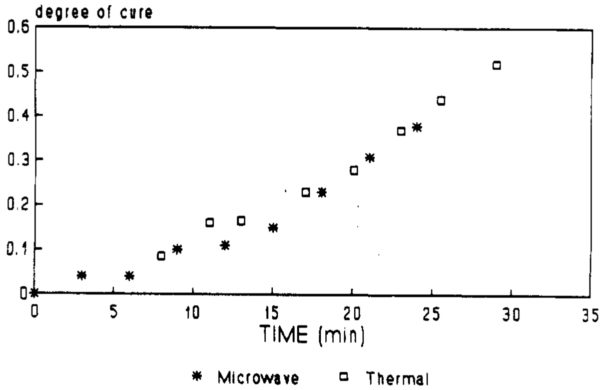

Figure 6. Degree of cure as a function of time for thermal and microwave cure of the multifunctional formulation at 100 °C.

We then proceeded to compare the kinetics of cure of the multifunctional formulation. The results of that analysis are shown in Figures 5–7, where degree of cure calculated from the FTIR data is plotted as a function of time for three different temperatures. The trend emerging from these figures reveals sharply that the cure kinetics of the multifunctional epoxy formulation are also identical in microwave and thermal fields. The kind of comparative analysis presented here, based on fundamental kinetic models, has not been reported in the literature. In our earlier study of a DGEBA/DDS formulation we actually observed a slightly slower reaction rate in the microwave field.[15] DeLong et al.,[23] however, studied a DGEBA/MDA formulation and reported a slightly faster rate in the microwave field. A careful examination of both reports reveals that the observed differences were indeed quite small and could be ascribed to experimental variations, thus essentially agreeing with the conclusions reached herein. In sharp contrast to our findings, however, are those of Lewis et al.[9] and Hedrick et al.,[10] who studied a series of systems, including epoxy resins, poly(ether ketone) (PEK), and poly(amic acid), and found an astonishing increase in kinetics, anywhere from 8- to 34-fold, depending on the system. It is instructive to emphasize that we are not talking about an observed increase in production rates (which is feasible), but kinetic rates (which is unlikely)! Their claim that, for instance, an epoxy–amine system will react several times faster at the same temperature in the microwave than thermal field is quite curious but, unfortunately, an explanation of that statement has not

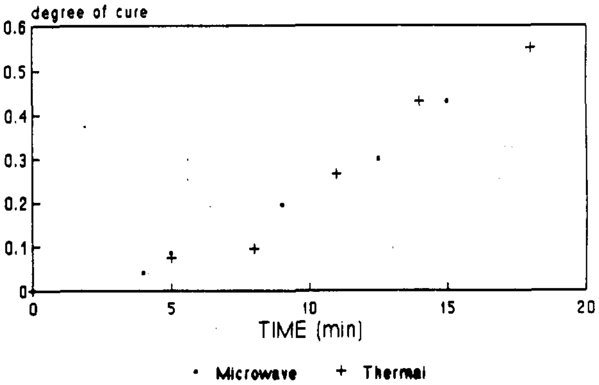

Figure 7. Degree of cure as a function of time for thermal and microwave cure of the multifunctional formulation at 110 °C.

been put forward. It is not intuitively clear why that should happen, and there is nothing in our work to support their tenet. The equivalence of fundamental kinetic parameters further implies that network morphologies and their physical/mechanical properties should not differ for a given formulation as a function of the source of energy for cure. The unaffected kinetics notwithstanding, there are still other aspects of microwave cure of polymers and composites that may warrant further attention, such as selectivity with respect to chemical composition, reduction of cure exotherm, etc.

IV. Conclusions

We have completed a comprehensive investigation in which we compared the fundamental kinetics of epoxy–amine reactions in thermal and microwave fields. A model compound formulation and a multifunctional formulation were studied. Chromatographic and spectroscopic techniques were utilized and a mechanistic model was used to calculate the kinetic parameters. It was decisively shown for both formulations that the kinetics of reaction in thermal and microwave fields did not differ. By implication then, morphologies and properties of cured networks are not expected to vary as a function of the type of energy source.

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