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Electron Beam and UV Cationic Polymerization of Glycidyl Ethers PART II: Reaction of Diglycidyl Ether of Bisphenol A

Matteo Mascioni,[1] Narendra N. Ghosh,[1,2] James M. Sands,[3] Giuseppe R. Palmese[1]

[1]Department of Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania 19104
[2]Department of Chemistry, Birla Institute of Technology and Science Pilani, KK Birla Goa Campus, Zuarinagar, Goa 403726, India
[3]Materials and Manufacturing Sciences Division, US Army Research Laboratory, Aberdeen Proving Ground, Maryland 21005
Correspondence to: G. R. Palmese (E-mail: grp27@drexel.edu)

ABSTRACT: Electron-beam (e-beam) and ultraviolet (UV)-induced cationic polymerization of diglycidyl ether of bisphenol A (DGEBA) using the photo-initiator diaryliodonium hexafluoroantimonate was investigated using *in situ* NIR spectroscopy. The effect of processing parameters, such as temperature, radiation intensity, and photo-initiator concentration, on kinetics of the reaction were determined quantitatively. In contrast to the behavior of monofunctional epoxy systems reported previously, the difunctional epoxy forms a high T_g crosslinked network, so a kinetic model that takes into account diffusion limitations associated with vitrification was developed. The combined benefits of the real-time *in situ* NIR spectroscopy study and the well-defined diffusion model resulted in very accurate predictions for cure of epoxy networks by e-beam-induced polymerization. The results support the view that e-beam processing of epoxies is constrained by vitrification in the same way that UV and thermally cured epoxies are. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 487–495, 2013

INTRODUCTION

Radiation curing of polymers by ultraviolet (UV) light and electron beam (e-beam) has the potential to offer significant advantages over traditional thermal curing. Some of the advantages are shorter curing times, lower energy consumption, and reduced overall manufacturing costs as compared to typical thermally cured systems. For epoxy-based systems, despite good thermal properties and significant processing advantages, carbon-fiber composites manufactured using e-beam exhibit low compressive strength, poor interlaminar shear strength and low fracture toughness. The poor performance of the composites is linked to poor matrix and interface properties.[1–14] For such epoxies, many aspects of radiation induced cure processes and their relation to final material properties are not yet fully understood. Understanding the cure kinetics of the radiation cured epoxy systems is an important first step needed in order to design improved radiation cured epoxy systems.

In Part I, investigations of UV and e-beam-induced cationic polymerization of a mono-functional epoxy system, phenyl glycidyl ether (PGE), and development of a model for the reaction kinetics have been described.[15] The effects of processing parameters, including photo-initiator concentration, temperature, UV light intensity or e-beam dose rate, on the initiation and propagation specific rate constants (k_i and k_p, respectively) of this reaction have been reported. In the development of the PGE reaction model the cationic polymerization was treated as a living polymerization and it was not necessary to include chain transfer to hydroxyl containing moieties such as water because the epoxy was dried using molecular sieves.[15] For the radiation-induced cationic polymerization of epoxy systems the initiation reaction proceeds via a first order rate process that can be represented as:

$$I(t) = C_0[1 - \exp(-k_i \cdot t)] \tag{1}$$

where I is the concentration of cationic active centers (i.e., H^+ ions or PGE oligomer and polymer chains positively charged at one end), C_o is the initial concentration of photo-initiator and k_i is the initiation rate constant.

The propagation reaction follows a second order rate expression given by:

$$dM/dt = -k_p \cdot M \cdot I \tag{2}$$

Additional Supporting Information may be found in the online version of this article.

where M is the concentration of monomer and k_p is the propagation rate constant. From eqs. (1) and (2) the rate equation for propagation step can be derived as follows:

$$\frac{M}{M_o} = \exp\{-k_p \cdot C_o \cdot t + \frac{k_p}{k_i} \cdot C_o \cdot [1 - \exp(-k_i \cdot t)]\} \quad (3)$$

These rate equations were derived to model the radiation-induced cationic polymerization of a mono-functional epoxy system PGE,[15] which polymerizes to linear chain products with a glass transition temperature (T_g) lower than the cure temperature investigated. In such a case, diffusion limitations resulting from vitrification did not need to be considered and the study provided a detailed assessment of the intrinsic cure behavior for mono-functional epoxides. However, the epoxies used for composite fabrication are multifunctional and result in high T_g crosslinked networks. In this case low temperature curing results in severe diffusion limitations as the T_g reaches the temperature of cure at relatively low conversion. In this article an investigation of UV and e-beam-induced cationic polymerization of diglycidyl ether of bisphenol A (DGEBA) is presented and a cure model is developed that accounts for diffusion limitations in such systems starting with the intrinsic model developed for PGE.[15] This model will be referred to as the "Diffusion Limited Model".

EXPERIMENTAL

Diglycidyl ether of bisphenol A (EPON 828, Shell Chemicals USA) and a photo-initiator diaryliodonium hexafluoroantimonate salt (CD-1012, UCB Radcure, Louisville, KY) were used to create traditional multifunctional epoxy network. DGEBA was dried using 4 Å molecular sieves (Aldrich Chemical Company, USA) in order to limit the water concentration to below 0.1% in the reactant. The sieves were activated at 175°C for 12 h prior to use. Drying of DGEBA was important because it has been observed that the presence of water significantly influence radiation-induced cationic polymerization of epoxy.[11]

An *in situ* real time near infrared (NIR) spectroscopy technique was employed to monitor the reaction kinetics of UV and e-beam-induced cationic polymerization of DGEBA. The experimental apparatus consisted of a NIR spectrometer (Control Development, South Bend, IN), a temperature controller, a UV source and a custom-made sample chamber and holder.

The UV light source used in this study was a Novacure™ (EFOS, Mississauga, ON, Canada). It consisted of three main components: a ultra-violet lamp, a set of quartz fiber light guides and a UV light bandpass filter. The light source was equipped with a high pressure 100 W mercury vapor short arc lamp. Diffusers were used to control UV light intensity below 100 mW cm^2.[15,16]

The e-beam cure experiments were performed using a linear accelerator (LINAC) at the Boeing Radiation Effects Laboratory (Seattle, WA). The LINAC is a uniquely designed accelerator unit that has a maximum operational power of 1.0 kW. The LINAC was tuned for 10 MeV electrons. The scan rate was 0.3 Hz and the pulse repetition frequency was 15 Hz. Samples
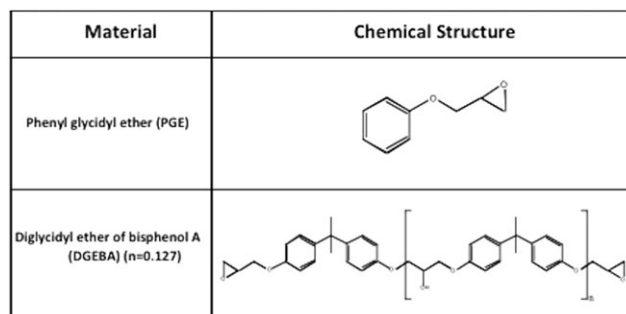

Figure 1. Chemical structures of PGE and DGEBA used in this work.

were centered within the beam scan path. Film dosimetry was used to confirm delivered doses for all configurations. For the experiments reported herein a total dose of 50 kGy was delivered to the samples without interruption. Details of the experimental setup have been described in the previous paper.[15]

To investigate the reaction kinetics numbers of experiments were conducted for UV and e-beam-induced polymerization of DGEBA by varying the process parameters (e.g., photo-initiator concentrations, UV light intensities, e-beam dose rate, and temperatures) while real time *in situ* NIR spectra were collected at selected time intervals. Reactions were performed at various temperatures ranging from 50°C to 80°C. For UV-induced polymerization, reactions were performed by varying UV light intensity from 15.9 to 58.3 mW/cm^2 with various photoinitiator concentrations ranging from 0.185 to 1.03 wt %. E-beam-induced polymerization reactions were performed with a dose rate of 7500 rad/s and 1.06 wt % photo-initiator concentration. The kinetics of the UV and e-beam-induced cationic polymerization of DGEBA was determined by monitoring the disappearance of NIR peak at 2209 nm (which is the characteristic mode of epoxy group) versus time. The detailed method of NIR data analysis has been described in our previous paper and in the Supporting Information.[15]

RESULTS AND DISCUSSION

Intrinsic Rate Parameters for DGEBA

The intrinsic rate equations developed in our previous work[15] for PGE were taken as starting point for the development of a model to describe the diffusion limited reaction behavior of radiation-induced cationic polymerization of DGEBA. PGE and DGEBA contain chemically identical glycidyl groups as shown in Figure 1. So, it was considered that for the same set of reaction conditions and in absence of diffusion limitations, the reaction kinetics of these two compounds should follow the same governing rate equations and kinetic parameters. In order to test this contention, UV-induced polymerization reaction of DGEBA was conducted and the conversion versus time data were compared with the predictions using the model developed to describe PGE polymerization for the same set of conditions as show in Figure 2.

Figure 2 shows that for UV-induced cationic polymerization reaction the kinetic parameters obtained from PGE studies can be used to describe the initial stages of the reaction of DGEBA. This result is important because it helps to develop a model
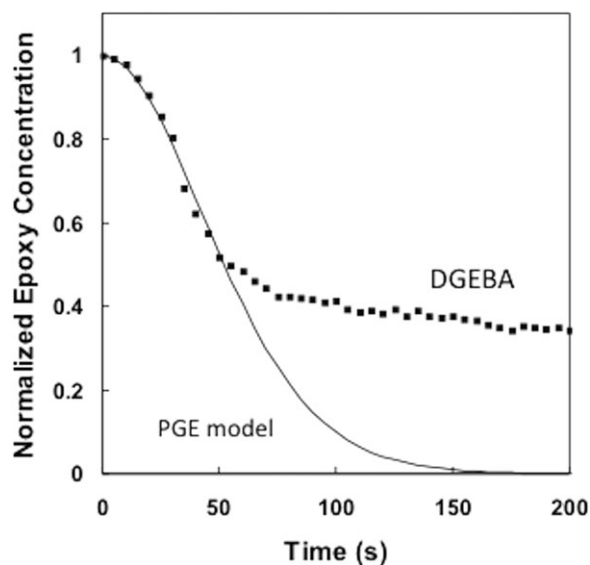
Figure 2. Comparison between experimental data for DGEBA and the kinetic model for PGE ($T = 80°C$, photo-initiator concentration $= 0.68$ wt % and UV intensity $= 58.3$ mW/cm^2). The values of k_i and k_p are 0.0069 s^{-1} and 8.14 L mol^{-1} s^{-1}, respectively.

that accounts for diffusion limitations, since it strongly suggests that the reaction parameters (k_i and k_p) can be determined independently based on the PGE model compound studies or by simply applying PGE model to the initial stages of reaction for DGEBA. For PGE it has been observed that the initiation rate constant (k_i) is dependent on UV light intensity or e-beam dose rate but independent of photo-initiator concentration and temperature. Whereas, the propagation rate constant (k_p) is dependent on temperature but independent on UV light intensity or e-beam dose rate and initiator concentration.[15]

For e-beam-induced polymerization of DGEBA, k_i and k_p were determined by performing the polymerization reaction with photo-initiator of 1.06 wt % and a dose rate of 7500 rad/s and varying the system temperature between 50°C and 80°C. The data for these experiments are given in Figure 3. Fits to the initial portions of the concentration versus time plots obtained by using the intrinsic model developed for PGE are also shown in Figure 3. The model fits show very close agreement to the initial reaction behavior of DGEBA. The values for k_i and k_p obtained from these fits are given in Table I. For comparison Table I also lists k_i and k_p for UV-induced polymerization of PGE at the same temperatures.[15] These results show that (i) k_i is found to be generally independent of temperature but temperature strongly influences k_p (ii) at a given temperature, UV and e-beam-induced cationic polymerizations can be described by the same propagation rate constants k_p. Furthermore, the temperature dependence of k_p can be expressed by an Arrhenius relationship, as shown in Figure 4. The activation energy for the propagation reaction of the e-beam-induced polymerization of DGEBA was found to be 71.3 kJ/mole, which is in good agreement with the value calculated for UV curing of PGE (70.152 kJ/mole).

Relationship Between T_g and Conversion

The results given in Figure 3 not only show that the rate of epoxy reaction increases with increasing temperature as expected but also that full conversion is not achieved in all cases. The results also show that final conversions are consistently higher as the isothermal temperature of cure is increased. In order to be able to describe such diffusion limited behavior mathematically the relationship between conversion and T_g is needed. For step growth polymerizations of epoxies with amines a direct relationship exists between glass transition temperature (T_g) and conversion of that is independent of the reaction path used to achieve that conversion.[4,17] It was not clear whether a
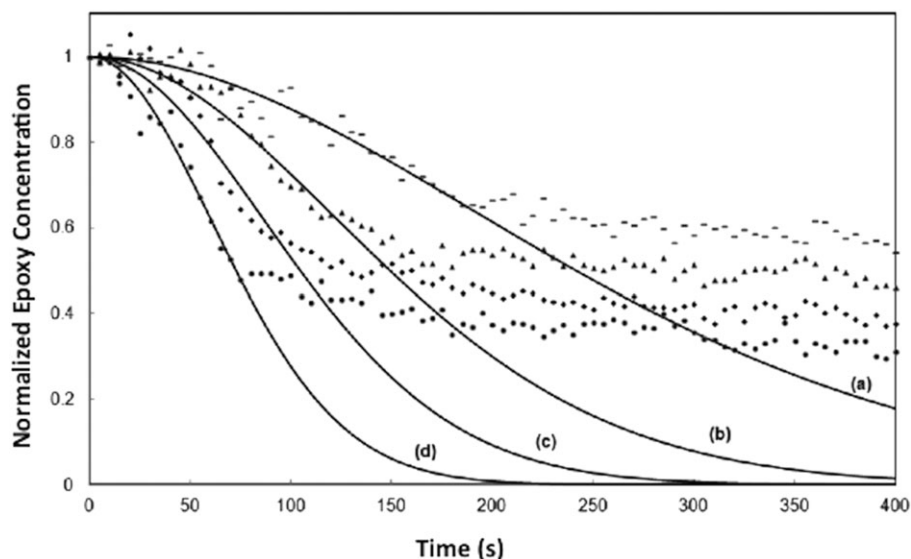

Figure 3. Comparison of change of epoxy conversion with time during e-beam-induced polymerization of DGEBA at different temperatures. Experimental data at 50°C (−), 60°C (°), 70°C (◆) and 80°C (●) and prediction by PGE model at (a) 50°C, (b) 60°C, (c) 70°C, and (d) 80°C. (dose rate $= 7500$ rad/s and photo-initiator concentration $= 1.06$ wt %).

Table I. Effect of Temperature on k_i and k_p for UV and e-Beam-Induced Polymerization of DGEBA and PGE

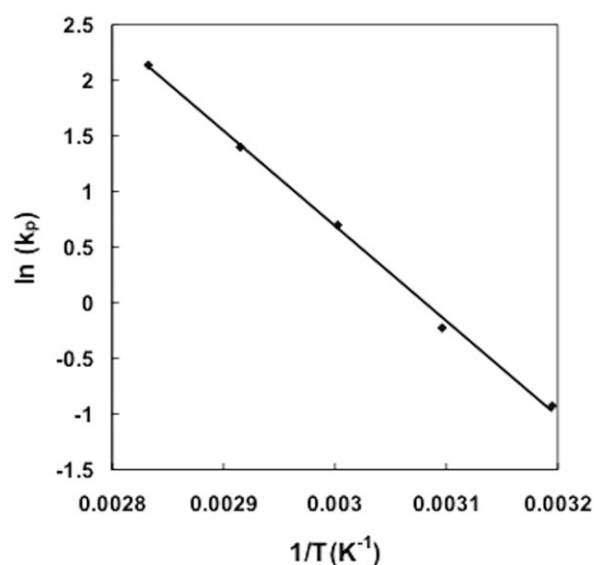| Temperature (°C)	k_i (e-beam[a], DGEBA) (s^{-1})	k_p (e-beam[a], DGEBA) (L mol^{-1} s^{-1})	k_i (UV[b], PGE) (s^{-1})	k_p (UV[b], PGE) (L mol^{-1} s^{-1})
50	0.0021	0.802	0.00159	0.80
60	0.00205	2.025	0.00165	2.11
70	0.00201	4.078	0.00182	4.11
80	0.00195	8.497	0.0018	8.14

[a] e-beam dose rate = 7500 Rad/s and photo-initiator concentration = 1.06 wt %.
[b] UV intensity = 15.9 mW/cm^2 and photo-initiator concentration = 0.44 wt %.

one-to-one relationship exists for chain polymerization of di-functional epoxies, so a number of experiments were performed at a given temperature but varying either the UV light intensity or photo-initiator concentration. The results obtained by varying UV light intensity are shown in Figure 5.

From the results shown in Figure 5, it is clear that the UV light intensity used to cure the epoxy resin did not affect the final conversion at a given isothermal temperature of cure suggesting that the T_g reached was the same for all conditions. Similar results were obtained by varying photo-initiator concentration. Based on these findings, a direct relationship between T_g and conversion is also found in the cationic polymerization of DGEBA at least for the range of experimental conditions investigated in this work. In order to obtain the specific correlation between degree of conversion and T_g, dry samples of DGEBA cured up to a specified conversion (i.e., reacted until the final limiting conversion was achieved) were tested using DSC to measure T_g. The relationship between T_g and conversion of epoxy groups was modeled using the Di Benedetto equation.[17]

$$\frac{(T_g - T_{go})}{T_{go}} = \frac{(E - F) \cdot \alpha}{1 - (1 - F) \cdot \alpha} \quad (4)$$

where E and F are two fitting parameters, α is the conversion of epoxy groups (or in general the extent of cure) and T_{go} is the glass transition temperature of the unreacted resin which was measured to be 263.4 K. The values of E and F were calculated by fitting the experimental data to the eq. (4) and the values for E and F were found to be of 0.58 and 0.32, respectively. The parameters E and F have also a direct physical meaning. E is defined as the ratio between the segmental mobilities of cross-ilnked and uncrosslinked monomers and F is the ratio of the respective lattice energies. The comparison between experimental data and equation prediction is provided in Figure 6.

Diffusion Limited Model
As pointed out earlier, the main feature that distinguishes the radiation-induced cationic polymerization of DGEBA from that of PGE in the range of temperatures considered is the fact that when T_g of the system reaches the isothermal cure temperature, vitrification quenches the reaction. Several approaches have been reported to model this dependence mathematically, both for free radical crosslinking reactions and for epoxy-amine curing systems.[4,18,19]

Figure 4. Arrhenius dependence of k_p on temperature for e-beam curing of DGEBA.
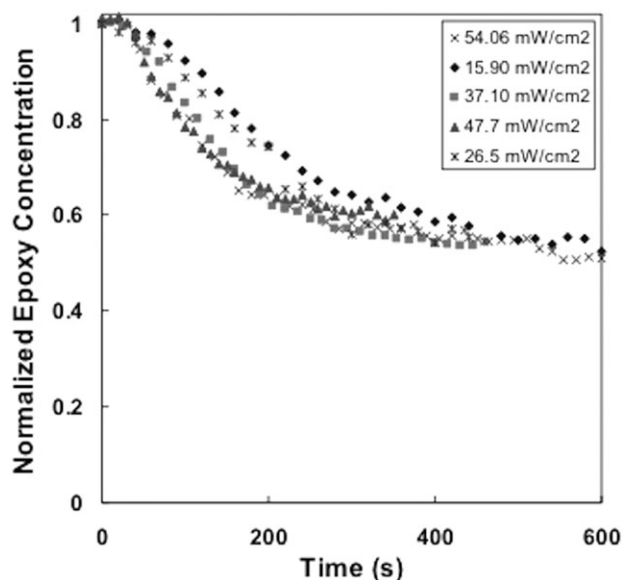
Figure 5. Effect of UV light intensity on the final conversion of epoxy groups of DGEBA ($T = 60°C$ and concentration of photo-initiator = 0.185 wt %).
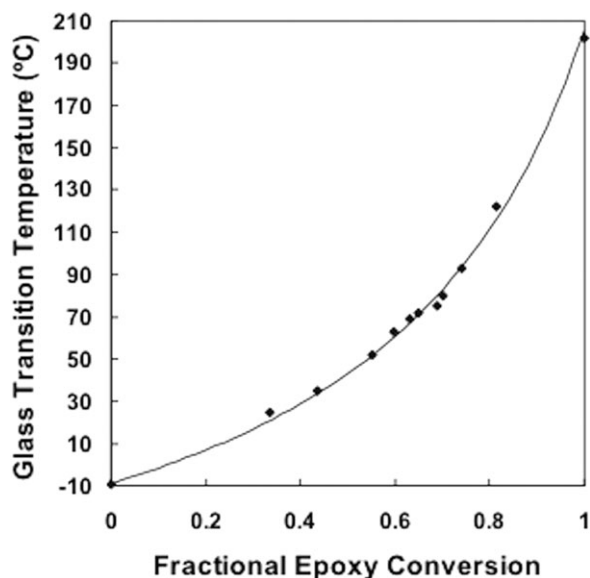
Figure 6. Plot of glass transition temperature versus degree of cure and predictions of the DiBenedetto equation.

Free volume theory is one of the important approaches that has been used for modeling diffusion limitations in epoxy polymerization. The basic assumption of this theory is that molecular transport occurs by means of a redistribution of the free volume in the system. This leads to a mathematical expression for the diffusivity in the system.[20,21]

$$D = D_o \cdot \exp\left[B \cdot \left(1 - \frac{1}{f}\right)\right] \quad (5)$$

where D_o is temperature dependent Arrhenius diffusivity, B is a constant which depends on a critical void size for motion, and f is the fractional free volume available for reaction at any given time. This expression for the diffusivity as a function of the free volume has been used in modeling the dependence of the propagation rate constant on conversion for a polymer-forming system.[4,18,19] In general, for a system in which the disappearance of monomer is due to both chemical reaction and diffusion of the reactant in the surrounding medium, the propagation rate constant can be expressed as the product of propagation rate constant in absence of diffusion limitation and an effectiveness factor η,

$$k = k_p \cdot \eta \quad (6)$$

where k is the time dependent propagation rate constant for the reaction of epoxy groups, η is the effectiveness factor and is a quantitative indication of the extent to which diffusion limitations are significant in the system and k_p is the intrinsic (i.e., diffusion limitation free) propagation rate constant. The limiting values for η are 0 when $T = T_g$ and 1 when diffusion limitations are negligible. η can also be expressed as a function of the dimensionless Damkoehler number (Da), which physically represents the relative importance of reaction and diffusion phenomena in the system:

$$\eta = \frac{1}{1 + Da} \quad (7)$$

$$Da = k_p \frac{1}{4 \cdot \pi \cdot d_{AB} \cdot D \cdot L} \quad (8)$$

where L is the Avogadro number, D is the diffusivity and d_{AB} is the collision diameter in the specific system. By lumping these parameters together and combining with eq. (5), the Damkoehler number can be expressed as:

$$Da = \frac{k_p}{k_{do} \cdot \exp\left[B \cdot \left(1 - \frac{1}{f}\right)\right]} \quad (9)$$

$$k_{do} = 4 \cdot \pi \cdot L \cdot d_{AB} \cdot D_o \quad (10)$$

where k_{do} is the diffusion rate constant given by eq. (10). From physical point of view, the Damkoehler number can be thought as the ratio between the rate of the reaction that controls the disappearance of monomer and the rate at which reacting pair come together to a distance lower than the collision diameter d_{AB}.

According to the free volume theory, the fractional free volume available for reaction, f, is essentially a linear function of the departure of the system temperature from the conversion-dependent glass transition temperature. In mathematical terms,

$$f = f_o + \beta \cdot (T - T_g) \quad (11)$$

where f_o is the fractional free volume at the glass transition state and has been reported for epoxy-amine systems as 0.025;[22] β is the thermal expansion coefficient, which for DGEBA-type resins is found to be equal to $4.84 \cdot 10^{-4}$ K^{-1} (Ref. 22) and T_g is the glass transition temperature, which has been considered a function only of conversion (or degree of cure) in our case given by eq. (4). The significance of the free volume can be understood by considering that the crosslinking reaction always occurs through holes and voids present in the forming network. The fractional free volume is a quantitative indication of the availability of such voids in the system. The driving force for the diffusion controlled monomer depletion is given by $T - T_g$.

On the basis of all these considerations, the effective propagation rate constant k can be expressed as:

$$k = k_p \cdot \frac{1}{1 + Da} = k_p \cdot \frac{\frac{1}{k_p}}{1 + \frac{k_p}{k_{do} \cdot \exp\left[B \cdot \left(1 - \frac{1}{0.025 + 4.84 \cdot 10^{-4} \cdot (T - T_g)}\right)\right]}} \quad (12)$$

and the rate expression can be expressed as:

$$-\frac{d\alpha}{dt} = k \cdot (1 - \alpha) \cdot I = \frac{-k_p}{1 + \frac{k_p}{k_{do} \cdot \exp\left[B \cdot \left(1 - \frac{1}{0.025 + 4.84 \cdot 10^{-4} \cdot (T - T_g)}\right)\right]}} \cdot (1 - \alpha) \cdot I \quad (13)$$

where $I = C_o \cdot (1 - \exp(-k_i \cdot t))$ (eq. 1) so that;

Table II. Effect of Temperature on the Diffusion Rate Constant ($k_{d\,o}$) and B for e-Beam-Induced Polymerization of DGEBA

Temperature (°C)	$k_{d\,o}$ (L mol^{-1} s^{-1})	B
50	460,817	0.5553
60	993,748	0.5569
70	1,753,125	0.5431
80	2,801,249	0.5638

E-beam dose rate= 7500 Rad/s and photo-initiator concentration = 1.06 wt %.

$$\frac{d\alpha}{dt} = \frac{-k_p}{1 + \frac{k_p}{k_{do} \cdot \exp\left[B \cdot \left(1 - \frac{1}{0.025 + 4.84 \cdot 10^{-4} \cdot (T - T_g)}\right)\right]}} \cdot (1 - \alpha) \cdot C_o[1 - \exp(-k_i \cdot t)]$$

(14)

where α is the fractional conversion of epoxy groups, and k_{do} and B are the fitting parameters.

For our system the relationship between T_g and conversion is given by eq. (4) and the intrinsic parameters k_i and k_p are obtained from PGE studies and model results[15] or by fitting the initial stages of the reaction with the intrinsic model as described earlier. Thus expression above can be used to model the system behavior as a function of two fitting parameters k_{do} and B. It has been reported that for epoxy-amine systems and some free-radical systems B is usually a constant, independent on temperature or other reaction conditions.[4,19,23] For DGEBA-amine networks, the value of B is 0.9−1.1[4,18,19] and for the free radical chain polymerization of N-vinylformamide the value of B is 0.4.[23] Since cationic polymerizations follow a chain mechanism and epoxy amine reactions follow a step mechanism, it is reasonable for the system investigated in this work to expect a value of B closer to 0.4 than to 1.

Application of Diffusion Limited Model to e-Beam-Induced Polymerization of DGEBA

The values of k_i and k_p for e-beam-induced polymerization of DGEBA were obtained by fitting the initial portion of the time-dependent concentration profiles for DGEBA given in Figure 3 as described earlier. The resulting values are given Table I. Using these values, the full range of conversions (α) versus time data for DGEBA was then fit to the diffusion limited model by a least squares approach. A computer routine developed in MATLAB® was used to minimize an objective function equal to the sum of the squares of the difference between each data point and the model prediction. For each guess value of the two parameters, the program solves the differential equation (eq. 14) and accordingly adjusts the values of the fitting parameters so that the error function is minimized. The values of k_{do} and B obtained for e-beam-induced polymerization of DGEBA are listed in Table II. The value of B has been found to be roughly constant and independent of temperature. The average value of B was found to be as 0.55. The value of k_{do} increases with increasing temperature and follows Arrhenius behavior as shown in Figure 7. Figure 8 shows the comparison between the experimental conversion versus time plots and the one predicted

by the model. An excellent agreement was observed between the experimentally obtained data and the predictions by the diffusion limited model for e-beam-induced polymerization of DGEBA at various temperatures.

Application of Diffusion Limited Model to UV-Induced Polymerization of DGEBA

In the case of UV-induced polymerization of DGEBA it was also found that the data predicted by diffusion limited model fit the experimentally obtained data well. For this set of experiments intrinsic k_i and k_p values were obtained from experiments using PGE. Figure 9 shows a representative plot demonstrating the characteristically good fit between experimental data and model predications. The values of k_{do} and B for UV-induced polymerization of DGEBA obtained by varying process parameters (temperature, UV light intensity, and photo-initiator concentration) are listed in Tables III and IV. Table IV shows the influence of temperature for a fixed photo-initiator concentration (0.68 wt %) and a UV light intensity (42.4 mW/cm^2) and Table IV provides the values of k_{do} and B obtained for experiments conducted at a fixed temperature (70°C) but for varying photo-initiator concentration and UV light intensity.

The following observations have been made when fitting the model to the experimentally obtained data:

1. In this case also the value of B has been found to be roughly constant and independent of temperature, UV light intensity or photo-initiator concentration. The average value of B was found to be as 0.55 ± 0.06—the same as was found for e-beam experiments but with a greater variance.

2. The effective diffusion rate constant k_{do} was found to depend both on light intensity and photo-initiator concentration. It was observed that a linear relationship exists relating the product of light intensity and photo-initiator concentration to the effective diffusion rate constant k_{do} as
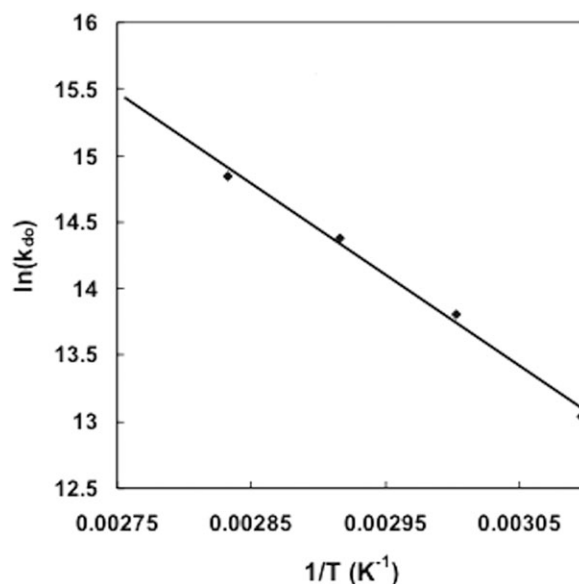
Figure 7. Arrhenius temperature dependence for k_{do} for e-beam-induced polymerization of DGEBA (dose rate = 7500 rad/s and photo-initiator concentration = 1.06 wt %).
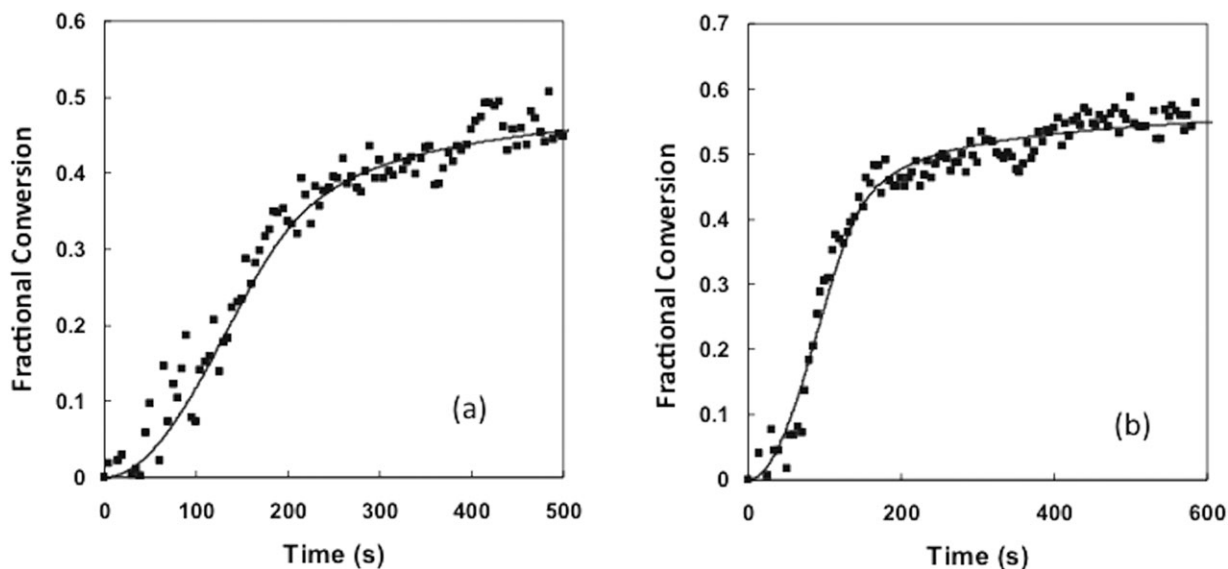
Figure 8. Conversion versus time experimental data and model predictions for e-beam-induced polymerization of DGEBA at different conditions (a) e-beam dose rate = 7500 rad/s, temperature = 50°C, and photo-initiator concentration = 1.06 wt % and (b) e-beam dose rate = 7500 rad/s, temperature = 60°C and photo-initiator concentration = 1.06 wt %.

shown in Figure 10. The dependence of k_{do} on UV light intensity and photo-initiator concentration can be qualitatively explained based on the fact that if the number of active centers increases (i.e., if C_o or the UV light intensity increase), then the average distance between active center and monomer molecules decreases, thus increasing the value of k_{do}. This point is discussed in greater detail in the following section.

3. A dependency of k_{do} on temperature according to an Arrhenius functional form exists (Figure 11). The calculated activation energies for UV and e-beam-induced

polymerization for k_{do} were found to be 60 and 57 kJ/mole, respectively. The values for both cases are closely matching. This activation energy can be physically thought as the energy required producing the diffusive motion of one mole of monomer in the reaction medium.

Observed Dependence of k_{do} on UV Light Intensity and Photo-Initiator Concentration

Martin and Hamielec[24] assessed the diffusivity of a reacting pair of polymers or of oligomers in terms of their molecular weight and the viscosity of the surrounding reaction medium. The key result was that D_o and therefore k_{do} should be inversely proportional to the average molecular weight of the reacting molecules raised to a power n. However; we, and others, have assumed k_{do} to be a constant. Furthermore, based on the fitting results presented in earlier sections, a constant value of k_{do} allows an accurate representation of the experimental data in the entire range of conversions and for the range of processing conditions investigated. This can be explained based on the fact that the only stage in the reaction in which k_{do} plays an important role is the transition period between the reaction-controlled kinetics and the post-vitrification stage. At early stages of reaction, the system is reaction controlled, and the system can be accurately
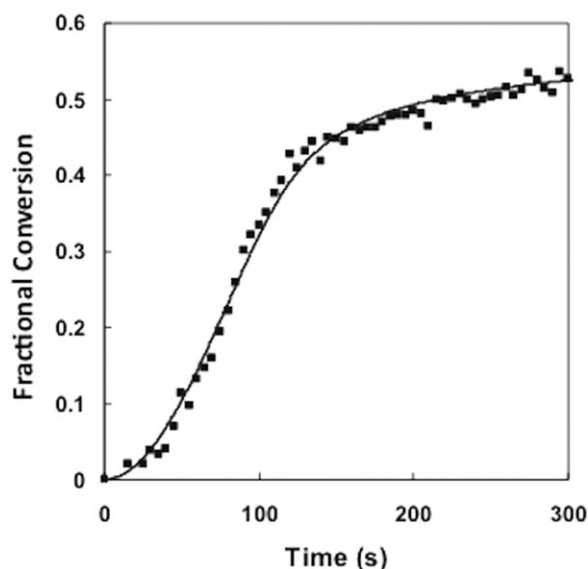

Figure 9. Representative comparison of experimental data and model prediction for DGEBA (UV intensity = 42.4 mW/cm², temperature = 60°C and photo-initiator concentration = 0.68 wt %).

Table III. Effect of Temperature on the Diffusion Rate Constant (k_{do}) and B for UV-Induced Polymerization of DGEBA

| Temperature (°C)	k_{do} (L mol^{-1} s^{-1})	B
50	163,972	0.5821
60	367,206	0.5311
70	594,241	0.4794
80	1,152,330	0.5552

UV intensity = 42.4 mW/cm² and photo-initiator concentration = 0.68 wt %.

Table IV. Effect of UV Light Intensity and Initiator Concentration on the Diffusion Rate Constant k_{do} and B for UV-Induced Polymerization of DGEBA

Photo-initiator concentration (wt%)	UV intensity (mW/cm^2)	k_{do} (liter mol^{-1}s^{-1})	B
0.185	15.9	230037	0.5792
0.185	26.5	265043	0.5911
0.185	37.1	319497	0.58811
0.185	47.7	235518	0.6204
0.185	54.06	319921	0.6175
0.3	15.9	281098	0.4972
0.3	50.88	431562	0.5138
0.4	58.3	591074	0.49439
0.68	15.9	373539	0.5017
0.68	26.5	433679	0.5039
0.68	42.4	594301	0.4893
0.68	47.7	620829	0.51133
0.68	58.3	753274	0.5231
1.03	15.9	440127	0.5047
1.03	26.5	556459	0.6970
1.03	37.1	842964	0.5751

Experiments were performed at 70°C.

described using the diffusion-limitation free kinetic model. After vitrification occurs the reaction rate is equal to zero for all practical purposes. The fact that experimental data can be fitted using a value of k_{do} independent of molecular weight (i.e., conversion) suggests that during the transition between the reaction controlled and the diffusion controlled states the dependence of the diffusion coefficient on molecular weight can be considered negligible for practical purposes.
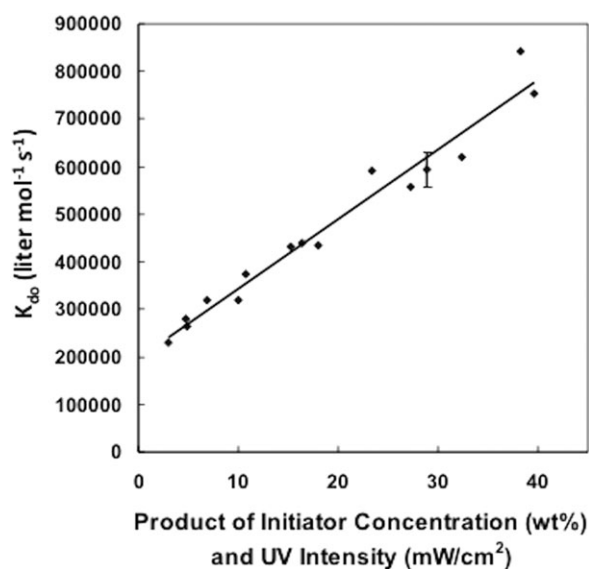
Figure 10. Plot of glass transition temperature versus degree of cure and predictions of the DiBenedetto equation.
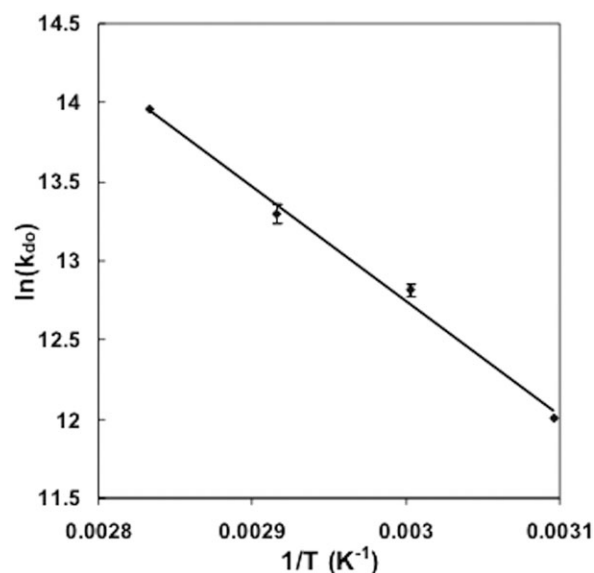
Figure 11. Effect of temperature on the diffusion parameter k_{do} for DGEBA. UV intensity was 42.4 mW/cm^2 and photo-initiator concentration 0.68 wt %.

A linear dependence was empirically found to exist between k_{do} and the product of photo-initiator concentration and light intensity. Since D_o was considered to be constant, the dependence of k_{do} on these processing parameters can be explained only by questioning the role of d_{AB} in this analysis.

In the traditional Rabinowich approach, on which our model is based, a molecule A is surrounded by B molecules. The rate of reaction between the two species A and B is considered to depend on two factors: the average diffusion-dependent duration of the encounters between A and B molecules (equal to the average time that A spends within a distance d_{AB} from B) and the characteristic time for reaction.

The duration of the encounters is given by eq. (15).

$$\tau = d_{AB}^2/D \qquad (15)$$

This assumes that the characteristic time for diffusion is equal to the time that a molecule of A spends within one coordination sphere of B, neglecting the time required for A to approach B due to bulk diffusion. This is equivalent to considering a system consisting of a B molecule completely surrounded by A molecules located at a distance d_{AB} from B. The case considered in this work is different than the one considered by Rabinowich, in that each active center can be surrounded not only by monomer molecules, but also by crosslinked polymer or free volume. This suggests that the time required for a monomer molecule to reach the first coordination sphere of an active center due to bulk diffusion cannot be considered negligible, but has to depend on the relative amounts of monomer and active center molecules at the moment in which diffusion limitations start to control the rate of reaction.

This consideration suggests that the characteristic time for diffusion τ_D can be expressed as a function of a characteristic

length l, related to the average distance between a monomer molecule and a cationic active center:

$$\tau_D = \frac{l^2}{D} \qquad (16)$$

Based on the traditional theory, the characteristic time for reaction is defined by eq. (16).

$$\tau_R = \frac{L \cdot d_{AB}^3}{k_p} \qquad (17)$$

In this equation L is the Avogadro number, d_{AB} the collision diameter as defined in the Rabinowich theory and k_p the intrinsic propagation constant. The Damkoehler number, defined as the ratio between the diffusion and reaction characteristic times, can be expressed as:

$$Da = \frac{\tau_D}{\tau_R} = \frac{k_p}{d_{AB}^3 \cdot \frac{L}{l^2} \cdot D_o \cdot \exp[B \cdot (1 - \frac{1}{f})]} \qquad (18)$$

and, by comparison with eq. (9), k_{do} can then be taken as:

$$k_{do} = \frac{d_{AB}^3 \cdot L \cdot D_o}{l^2} \qquad (19)$$

Therefore, the dependence of k_{do} on UV light intensity and initiator concentration can be qualitatively explained based on the fact that if the number of active centers at the vitrification point increases (i.e., if C_o or the UV light intensity increase), then the average distance l between active center and monomer molecules decreases, thus leading to the observed increase in k_{do}.

CONCLUSIONS

Real-time *in situ* NIR was used to characterize the polymerization of DGEBA initiated with CD-1012 by both UV and e-beam. The resulting conversion profiles were fitted to a model for cure of di-functional epoxy DGEBA under continuous irradiation that was developed to account for diffusion limitations associated with vitrification. The effect of cure temperature, radiation intensity, and initiator concentration were evaluated quantitatively. To account for diffusion limitations in the cross-linked systems, a free volume-based parametric model was used to relate diffusion parameters to measurable quantities. The predictions of this diffusion limited model match the results obtained experimentally and parameters obtained from the fit equation ware consistent with comparable reactions reported in literature. The diffusion limited model was shown to predict the behavior of the radiation-induced cationic polymerization of epoxy systems for a broad range of conditions (e.g., radiation intensities, photoinitiator concentration, and temperature) while conducting a very limited number of experiments. In principle the model can be extended to different radiation-induced cationically cured epoxy systems. This work provides strong evidence that vitrification has a rate limiting effect on e-beam cured epoxies similar to that observed for thermally cured systems.

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