Influence of Tetrahydrofuran on Epoxy−Amine Polymerization

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ABSTRACT: The objective of this work is to understand the influence of the solvent tetrahydrofuran (THF), a hydrogen bond acceptor, on epoxy−amine polymerization reactions. The cure kinetics of the diglycidyl ether of bisphenol A (DGEBA) and 4,4′-methylenebiscyclohexanamine in the presence of THF as a solvent was monitored using Fourier transform infrared (FTIR) spectroscopy in the near-infrared (NIR) region. FTIR analysis showed that the THF remained chemically inert during the epoxy−amine reactions. A mechanistically based two-parameter catalytic model for the intrinsic kinetics was developed. This model adequately described the intrinsic kinetics of this system in the presence and absence of THF. The influence of THF on the intrinsic kinetics was investigated by varying the THF to monomers weight ratio at 60, 50, and 40 °C. Results showed that for a given cure temperature the kinetic rate constants decreased with increasing THF content up to a critical composition and remained practically constant above this composition. This retardation effect is due to the formation of a relatively more stable intermediate species caused by the dipole−dipole interaction between THF and amine moieties, where 0.3:1 THF to monomers weight ratio represents a critical composition at which all the N−H bonds are stabilized. A negative substitution effect was observed in these reaction systems, and the presence of THF enhanced this effect up to the critical composition. The kinetic parameters followed Arrhenius behavior in both the presence and absence of THF. The presence of THF reduced the diffusion limitations by increasing the free volume in the reaction medium. At 60 °C, diffusion limitations due to vitrification were not apparent for reaction mixtures having a composition greater than 0.2:1 THF to monomers weight ratio, as the intrinsic kinetic model adequately described the entire reaction.

Introduction

Epoxy−amine resins have been conventionally used to synthesize industrial thermosets for adhesive, protective coating, and composite applications. Recently, we have shown that the epoxy−amine system can be used to synthesize nanoporous thermosetting materials[1,2] that can be used as selective permeation membranes and as substrates for nanocomposites fabrication. A novel method of synthesizing nanoporous polymer networks was reported which involves reacting the step-growth cross-linking system of epoxy−amine in the presence of a solvent (THF) to high conversions without micro/macroscopic phase separation. In this technique, the pore and network structures are basically formed by the polymerization mechanism where the presence of chemically inert and miscible solvent affects the way the monomers react to form pore walls and subsequently how the pore walls encapsulate the solvent to form pore structures. Thus, depending on the solvent content, polymer networks with different pore sizes/structures could be obtained by this technique. The polymerization mechanism in general depends on the reaction chemistry, intrinsic kinetics, and transport or diffusion limitations in the reaction mixture. The objective of this work is to determine how the presence of a solvent influences the aforementioned chemical and physical phenomena that govern the mechanism that is responsible for the formation of pore and network structures in the reactive encapsulation of solvent (RES) technique. Such an effort would be the first step toward understanding the relationship between the pore structure and the process which could potentially be useful in designing materials with tailored porosity and pore sizes using this technique. A fundamental investigation was carried out where (i) a NIR technique was used to monitor the cure kinetics of epoxy−amine system in the presence of tetrahydrofuran (THF), (ii) a kinetic model that adequately describes the intrinsic kinetics of this system in the presence and absence of THF was developed and was used to analyze the intrinsic kinetics of epoxy−amine and the influence of THF in the system, and (iii) the influence of THF on the vitrification behavior of the epoxy−amine-THF system was examined in an effort to understand how THF influences the diffusion limitations of the reacting mixture.

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Experimental Section

Materials. The materials used in this work are shown in Figure 1. The difunctional epoxy resin was diglycidyl ether of bisphenol A (DGEBA)−EPON 828 ($n = 0.13$), purchased from Miller-Stephenson Chemical Co. The purity of EPON 828 was analyzed using HPLC and epoxide titration techniques. The chromatograms did not show peaks that could be attributed to impurities, and the epoxy equivalent weight determined by the titration was in the expected range of 180−192 g/equiv, suggesting that epoxy used is relatively free from impurities (>99%) and of the correct number-average molecular weight and functionality. The tetrafunctional amine was 4,4′-methylenebiscyclohexanamine (PACM) obtained from Air Products and Chemicals. THF was purchased from Sigma-Aldrich. PACM and THF were >99% pure. Cure kinetics were monitored for reaction mixtures containing stoichiometric quantities of epoxy and amine (2:1 mole ratio of monomers) with varying amounts of THF. Reaction mixtures with composition ranging from 0:1 to 2:1 THF to monomers weight ratio were investigated.

FTIR Spectroscopy. Different techniques have been used over the years to monitor the cure kinetics of the epoxy−amine systems. These include chemical assays such as epoxide

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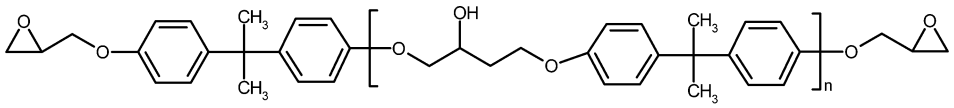
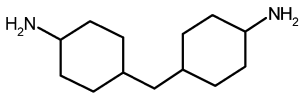


Diglycidyl ether of bisphenol A (DGEBA), EPON 828, n=0.13



4,4'-Methylenebiscyclohexanamine, PACM

Tetrahydrofuran (THF)

Figure 1. Epoxy−amine monomers and solvent (THF) used in this work.

titration,[3] size exclusion chromatography (SEC),[3,4] differential scanning calorimetry (DSC),[5−8] FTIR, and nuclear magnetic resonance (NMR)[9] spectroscopy. FTIR spectroscopy in the near-infrared (NIR) region is widely used for this purpose. The salient features in using FTIR-NIR for monitoring the epoxy−amine reactions are summarized by Xu et al.[10] and Mijovic et al.[11] This technique is used in this work to monitor the cure kinetics of the epoxy−amine system in the presence and absence of THF. A Nexus 670/870 FTIR spectrometer (Thermo Nicolet Corp.) with CaF_2 beam splitter was used to record the NIR spectra (4000−7000 cm^{-1}) of reaction mixtures at regular intervals. Each spectrum was an average of 32 individual scans at 8 cm^{-1} resolution. Investigation of epoxy−amine cure kinetics and influence of THF on this cure kinetics required monitoring the concentration of various functional groups involved in the reaction. FTIR scans and mass balance equations were used for this purpose. The functional groups of interest are the epoxy [EP], primary amine [PA], secondary amine [SA], and tertiary amine [TA].

Epoxy. The two epoxy peaks at 4530 and 6065 cm^{-1} are usually used to monitor the epoxy functional groups. St. John et al.[12] used the epoxy peak at 6065 cm^{-1}. This peak overlaps with the aromatic peak at 5960 $cm^{-1}$and therefore needs to be self-deconvoluted to obtain quantitative information.[9] The peak used to monitor the epoxy groups in this work and many others[10,13,14] is the one at 4530 cm^{-1}. This peak does not overlap with other peaks and provides a direct means for monitoring the epoxy concentration.

Primary Amine. The primary amine peak at 4925 cm^{-1} is well resolved and was used to monitor the primary amine functional groups in the reaction mixture. This peak position was found to shift in the presence of THF. Such effects were due to dipole−dipole interactions between THF and amines, which will be discussed later in detail. Concentrations of other functional groups of interest such as secondary and tertiary amines were calculated using mass balances and measured values of [EP] and [PA] concentrations.

Experimental Setup. The solvent used in this work, THF, was relatively volatile (boiling point, 65 °C). Therefore, sealed glass tubes (i.d. = 1.6 ± 0.05 mm) had to be used as sample holders. These were prepared by filling a glass tube sealed from one end with the reaction mixture to about $^3/_4$ its length and subsequently sealing the other end using a burner. The glass tube thus prepared was positioned in the path of the infrared beam using an aluminum block maintaining a constant path length for the IR beam passing through the reaction mixture for the entire cure time. A temperature controller precisely controlled (±0.5 °C) the temperature of the aluminum block throughout the period of data collection. Weighing the glass tubes with the reaction mixture before and after the reaction showed no weight loss, confirming that no material was being lost due to evaporation during these experiments. Background scans were taken before each experiment using an empty glass tube.

Model Fitting Procedure. The experimental concentrations of epoxy and primary amine were fitted to a two-parameter catalytic model using a least-squares approach. A computer routine 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. The MATLAB program solved the differential equations of the model to obtain the computed concentrations. These concentrations were compared to the experimental measurements, and the kinetic parameters were accordingly adjusted to minimize the error function.

Dynamic Mechanical Analysis (DMA). The glass transition temperature (T_g) of the gels prepared from reaction mixtures of composition ranging from 0:1 to 1:1 THF to monomers weight ratio was evaluated using a TA Instruments 2980 dynamic mechanical analyzer (DMA). Temperature scans with a frequency of oscillation of 1 Hz and amplitude of 15 μm were performed at a rate of 10 °C/min. A liquid nitrogen cooling accessory was used as needed. Typical sample dimensions were 25 mm in length, 8 mm in width, and 3 mm in thickness. T_g was taken to be the peak of the loss modulus curve. Each experiment was carried out by heating and cooling the sample, and an average of T_g from these ramps is reported.

Results and Discussion

The objective of this work is to elucidate the reaction chemistry, intrinsic kinetics, and diffusion limitations of the epoxy−amine−THF system in order to gain a better understanding of how cure conditions influence the resulting polymer network and pore structures. The following discussion is divided into: (i) Reaction chemistry—the reactions that are relevant for the epoxy−amine system and the influence of THF on these reaction steps, i.e., reactivity of THF is discussed based on literature and FTIR analysis. (ii) Intrinsic kinetics—an intrinsic kinetics model that accurately describes the reacting system is developed which is subsequently used to analyze and discuss the influence of THF on the intrinsic kinetics of the epoxy−amine reaction. In addition, the substitution effects and Arrhenius behavior of the system and the influence of THF on these are also discussed. (iii) Diffusion limitation—diffusion limitations due to vitrification and the plasticization effect of THF are discussed. In this section, the influence of THF content on the conversion at which the reaction medium vitrifies and the glass transition temperature (T_g) of the fully cured polymer networks are discussed. Additionally, critical THF concentrations and reaction conditions are determined for which vitrification does not occur during the entire reaction and related diffusion limitations may be neglected.

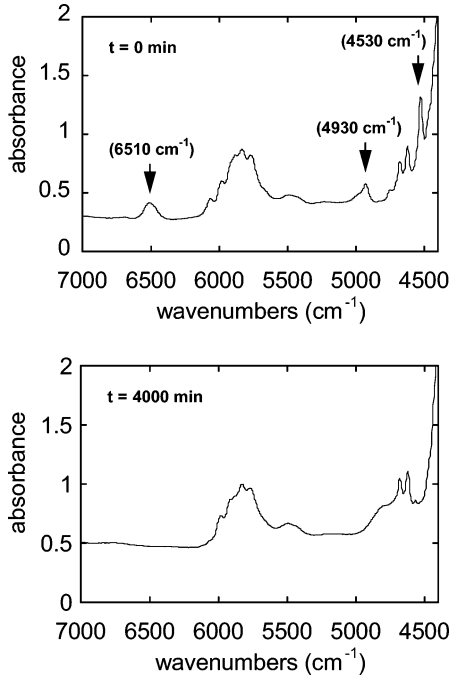


Figure 2. NIR spectra of the reaction mixture with 0.5:1 THF to monomers weight ratio at 60 °C at time = 0 (top) and 4000 min (bottom), showing that the reaction of stoichiometric quantities of epoxy and amine goes practically to completion in the presence of THF as seen by the disappearance of the epoxy peak at 4530 cm^{-1}, primary amine peak at 4930 cm^{-1}, and primary and secondary amines peak at 6510 cm^{-1}.

Reaction Chemistry. The primary amine−epoxy addition, secondary amine−epoxy addition, hydroxyl−epoxy etherification, and epoxy−epoxy etherification are some of the reaction steps reported for the epoxy−amine system.[10,12,15] Occurrence and extent of these reactions in a system depend on the cure temperature, ratio of monomers, and the presence of chemically reactive solvent or impurities. Synthesis of nanoporous polymer networks by the RES technique entails reacting stoichiometric quantities of epoxy and amines in the presence of a chemically inert solvent by primary amine−epoxy and secondary amine−epoxy additions below the boiling point of the solvent (THF, boiling point 65 °C). Thus, any other reaction steps are considered undesirable because it can then lead to inhomogeneous polymer networks by influencing the molecular weights between cross-links.[1,2] For the cure temperatures and ratio of monomers used in this work the undesirable hydroxyl−epoxy etherification and epoxy−epoxy etherification can be neglected.[12,15] However, the presence of solvent or impurities in the system could still influence the chemistry by reacting with the epoxy or amine functional group, thereby causing undesirable reaction paths that will lead to inhomogeneity in the resulting polymer network. Therefore, the solvent used in this system for synthesizing nanoporous polymer networks should remain chemically inert. The issue of the reactivity of THF is discussed below on the basis of FTIR analysis of these systems.

FTIR was used to monitor the cross-linking reactions in order to ensure that THF does not react with the epoxy and amine functional groups. Figure 2 shows the spectra at time t = 0 and 4000 min for the reaction mixture with 0.5:1 THF to monomers weight ratio at 60 °C. The fact that all epoxy, primary amine, and secondary amine moieties react practically to completion, as shown by the disappearance of the epoxy peak at 4530 cm^{-1}, primary amine peak at 4930 cm^{-1}, and primary and secondary amines peak at 6510 cm^{-1}, indicates that the reaction taking place is the desired reaction, and THF does not react with epoxy or amine functional groups since such reaction of THF would result in incomplete reaction of epoxy or amine. FTIR analysis demonstrates that starting with stoichiometric quantities of epoxy and amine the reaction goes to completion at temperatures below the boiling point of THF and that THF is chemically inert and does not initiate undesirable reaction pathways. Thus, for the cure temperatures used in this study, the polymer networks are predominantly formed by the desirable primary amine−epoxy addition and secondary amine−epoxy addition. Although THF does not react in the system, it could influence the intrinsic kinetics by inhibiting these addition reactions as discussed in the following section.

Intrinsic Kinetics. The hydroxyl groups are known to catalyze the epoxy−amine addition reactions.[3,10,12] To understand the intrinsic kinetics of these systems, it would be useful to know the concentration of epoxy [EP], primary amine [PA], secondary amine [SA], tertiary amine [TA], and hydroxyl [OH] moieties as a function of reaction conditions and compositions. The epoxy and primary amine groups are monitored using FTIR, and the concentrations of other functional groups of interest are calculated using mass balance relations as follows. In the absence of undesirable reaction pathways, eqs 1 and 2 represent epoxy and primary amine mass balances, respectively.

$$[EP]_0 = [EP] + [SA] + 2[TA] \quad (1)$$

$$[PA]_0 = [PA] + [SA] + [TA] \quad (2)$$

where $[EP]_0$ and $[PA]_0$ are concentrations of epoxy and primary amine at time $t = 0$ and [EP], [PA], [SA], and [TA] are the concentrations of epoxy, primary amine, secondary amine, and tertiary amine, respectively, present in the system at time t. The concentrations of these groups are expressed in mol/L. Combining eqs 1 and 2 results in expressions for secondary and tertiary amine concentrations given by eqs 3 and 4, respectively.

$$[SA] = [2([PA]_0 - [PA])] - ([EP]_0 - [EP]) \quad (3)$$

$$[TA] = ([EP]_0 - [EP]) - ([PA]_0 - [PA]) \quad (4)$$

These equations relate [SA] and [TA] to directly measured and known quantities. Thus, the variation of secondary and tertiary amine concentrations with time was calculated from these equations using the experimentally monitored epoxy and primary amine concentrations. It is also important to know the concentration of hydroxyl groups during the reaction in order to account for the catalytic epoxy−amine reactions. The concentration of hydroxyl groups present in the system was calculated from mass balance as follows:

$$[OH] = [OH]_{auto} + [OH]_{initial} \quad (5)$$

where [OH] is the concentration of the hydroxyl groups present in the system at time t, $[OH]_{auto}$ is the concentration of hydroxyl groups formed due to the epoxy−amine reaction, and $[OH]_{initial}$ is the concentration of hydroxyl groups initially present in the system. Each

epoxy−amine addition results in a hydroxyl group. The concentration of hydroxyl groups formed due to these reactions, $[OH]_{auto}$, is therefore given by eq 6.

$$[OH]_{auto} = [SA] + 2[TA] \quad (6)$$

The $[OH]_{initial}$ could be due to the hydroxyl groups present in the reactant molecules and impurities. It is assumed that the reacting system is relatively free from hydroxyl-containing impurities and that the hydroxyl groups initially present are due to the OH groups in EPON 828, $n = 0.13$, so that eq 7 can be used to calculate initial hydroxyl concentration.

$$[OH]_{initial} = 0.13\frac{[EP]_0}{2} \quad (7)$$

The variation of hydroxyl group concentration with time was calculated by substituting eqs 3, 4, 6, and 7 into eq 5 and using the values of [EP] and [PA] determined experimentally.

The well-known noncatalytic and catalytic pathways of epoxy−amine reactions are given by

$$[PA] + [EP] \xrightarrow{k_1'} [SA] + [OH] \quad (8)$$

$$[PA] + [EP] + [OH] \xrightarrow{k_1} [SA] + 2[OH] \quad (9)$$

$$[SA] + [EP] \xrightarrow{k_2'} [TA] + [OH] \quad (10)$$

$$[SA] + [EP] + [OH] \xrightarrow{k_2} [TA] + 2[OH] \quad (11)$$

where k_1' and k_1 are the noncatalytic and catalytic kinetic parameters of primary amine−epoxy addition and k_2' and k_2 are the noncatalytic and catalytic kinetic parameters of secondary amine−epoxy addition, respectively. Efforts have been made to model the epoxy−amine kinetics in the absence of any solvent.[10,12,16−20] Xu et al.[10] used a three-parameter model by assuming that the secondary amine−epoxy addition takes place only through the catalytic path. Paz-Aubin et al.[16] used a four-parameter model based on cure kinetics and free volume theory. Mijovic et al.[17] developed a four-parameter model based on different hydrogen-bonded species present in the system. In our study, we reduced the number of parameters to two by asserting that the OH group concentration initially present in the system is high enough to allow us to neglect the noncatalytic reaction terms. In fact, the epoxy monomer used, EPON 828, possesses a significant concentration of OH. Thus, neglecting the noncatalytic reaction terms and assuming the reaction to be first order with respect to all the groups involved, the rate expressions for primary amine, epoxy, secondary amine, and tertiary amine are given by the following set of equations.

$$\frac{d[PA]}{dt} = -k_1[PA][EP]([OH]_{auto} + [OH]_{initial}) \quad (12)$$

$$\frac{d[EP]}{dt} = -k_1[PA][EP]([OH]_{auto} + [OH]_{initial}) - k_2[EP][SA]([OH]_{auto} + [OH]_{initial}) \quad (13)$$

$$\frac{d[SA]}{dt} = k_1[PA][EP]([OH]_{auto} + [OH]_{initial}) - k_2[EP][SA]([OH]_{auto} + [OH]_{initial}) \quad (14)$$

$$\frac{d[TA]}{dt} = k_2[EP][SA]([OH]_{auto} + [OH]_{initial}) \quad (15)$$

Equations 12−15 represent a two-parameter catalytic model that we have used to fit the experimental data. Since THF is chemically inert, this model can be applied to the epoxy−amine reacting systems in its neat form or in the presence of THF by simply considering initial concentration differences due to dilution by THF. A more interesting effect that the presence of THF could have is to influence intrinsic kinetics by interacting with the reactive functional groups forming intermediate species. In fact, THF being a hydrogen-bond acceptor is expected to inhibit the reaction by interacting with the amine groups.[21] This model allows us to probe such behavior.

Influence of THF on the Intrinsic Kinetics. A systematic approach was undertaken to determine the effect of THF on epoxy−amine intrinsic kinetic parameters. The cure behavior of the epoxy−amine system with and without THF was monitored using FTIR and appropriate mass balance equations as previously discussed. The two-parameter catalytic model (eqs 12−15) was used to fit the experimental concentration measurements by the procedure described in the Experimental Section. All of the kinetic parameters reported in this section were obtained by fitting the initial part of the cure, up to a point where the primary amine reaction is complete. Generally, the diffusion limitations are insignificant during the initial stages of the cure. In Figure 3, results are shown for a reaction carried out at 60 °C and in the absence of THF. Similarly, Figure 4 shows the models fits for a reacting system at 60 °C with a THF to monomers ratio of 0.3:1 by weight. These figures demonstrate that the two-parameter model fits the experimental data adequately for the epoxy−amine system in the absence and presence of THF during the initial stages of cure.

The model fitting procedure was carried out for systems with increasing THF content at 60, 50, and 40 °C. Tables 1 and 2 summarize the primary and secondary amine−epoxy addition kinetic parameters k_1 and k_2, respectively, for all the reaction conditions. These kinetic parameters are plotted against THF content in Figures 5 and 6, respectively, for the three cure temperatures investigated. The error bar in these figures represents the standard deviation for conditions where multiple experiments were conducted. Figure 5 shows that initially the primary amine−epoxy rate constant (k_1) decreases sharply with increasing THF content and then remains constant. Thus, it appears that above a particular THF composition the solvent content does not significantly influence k_1. Figure 6 shows that same trends occur for the value of secondary amine−epoxy rate constant (k_2) with respect to initial THF content. Thus, addition of THF increasingly inhibits the epoxy−amine reaction up to some critical value of THF composition as shown by the dependence of kinetic rate constants on THF content. This effect is consistent throughout the cure temperature range investigated.

The left-hand side of Figure 7 depicts the dipole−dipole interaction between the hydrogen-bond donor

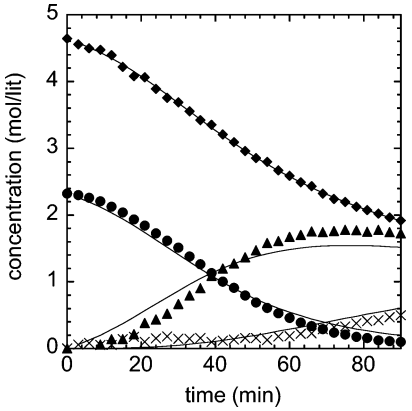


Figure 3. Representative model fits to the experimental data; cure kinetics of epoxy and amines without THF (0:1) at 60 °C. ◆, ●, ▲, and × represent the experimental concentrations of epoxy, primary amine, secondary amine, and tertiary amine, respectively, and the corresponding lines represent the model prediction of these concentrations for the optimum kinetic parameters k_1 = 0.00566 L²/(mol² min) and k_2 = 0.00113 L²/(mol² min).

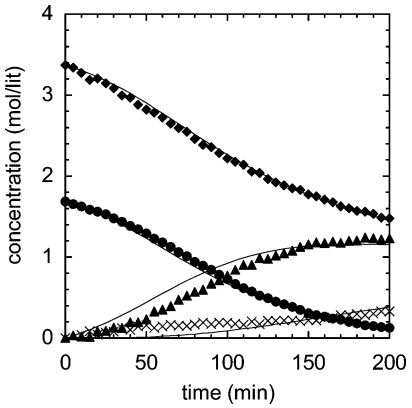


Figure 4. Representative model fits to the experimental data; cure kinetics of epoxy and amines with THF (0.3:1) at 60 °C. ◆, ●, ▲, and × represent the experimental concentrations of epoxy, primary, secondary, and tertiary amines, respectively, and the corresponding lines represent the model prediction of these concentrations for the optimum kinetic parameters k_1 = 0.00475 L²/(mol² min) and k_2 = 0.00085 L²/(mol² min).

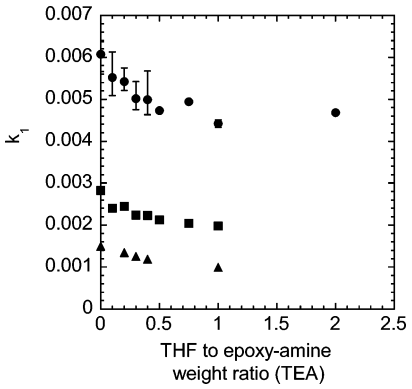


Figure 5. Influence of THF content on the primary amine−epoxy addition kinetic parameter (k_1 in L²/(mol² min)) at (●) 60, (■) 50, and (▲) 40 °C, showing that there exists a critical composition above which THF content does not significantly influence the value of k_1.

(amine) and acceptor (THF) present in the reaction mixture. These interactions influence the N−H bond vibration and cause the primary amine peak to shift to higher wavenumber in the NIR spectra. The right-hand side of Figure 7 shows the primary amine peak position for the initial reaction mixtures as a function of THF content. As shown in this figure, the primary amine peak shifts to a higher wavenumber up to a value between 0.3:1 and 0.4:1 THF to monomers ratio by weight and stops shifting for reaction mixture above this composition. A reaction mixture containing equal number of dipoles due to N−H bonds and dipoles due to THF would have a composition of 0.3:1 THF to monomers weight ratio. In such a mixture, ideally all the N−H bonds would be stabilized due to the dipole−dipole interactions. The results shown in Figures 5−7 are consistent with this explanation since they show that the decrease in the values of kinetic parameters k_1 and k_2 ceases at roughly the 0.3:1 ratio. This suggests that the formation of stable N−H bonds from the dipole−dipole interaction between THF and amine results in an inhibiting effect that is proportional to the number of interactions. Above 0.3:1, there would be no free N−H bonds for excess THF molecule to interact with, and increasing the THF content above this composition does not affect the rate constants.

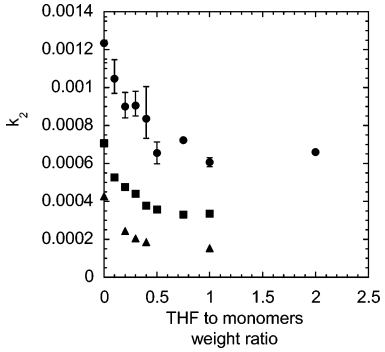


Figure 6. Influence of THF content on the secondary amine−epoxy addition kinetic parameter (k_2 in L²/(mol² min)) at (●) 60, (■) 50, and (▲) 40 °C, showing that there exists a critical composition above which THF content does not significantly influence the value of k_2.

Substitution Effects. The epoxy addition to a primary amine could influence the reactivity of secondary amine through steric hindrance and change in the basicity of amino group. These effects are usually referred to as substitution effects. The reactivity ratio (k_2/k_1) of secondary to primary amine addition kinetic parameters gives a measure of the substitution effects present in these systems. The substitution effects present in the epoxy−amine system could influence the structure and properties of the final polymer network. Thus, the reactivity ratio (k_2/k_1) is a key parameter in predicting the resulting polymer network structure and the influence of cure conditions such as temperature and solvent content on these structures. A reactivity ratio of 0.5 would mean that there are no substitution effects, i.e., equal reactivity of primary and secondary amines, as two hydrogen atoms are attached to the nitrogen atom in a primary amine. Usually, negative substitution effects are expected in epoxy−amine systems, i.e., $k_2/k_1 < 0.5$. Under these conditions, primary amine addition occurs faster than the secondary amine addition resulting in longer linear chains before cross-links appear which could influence the network structure. Substitution effects depend on the nature of the substituents attached to primary amine and the solvent present in the system.[10] There is significant discussion in the literature over the reactivity ratio for the epoxy−amine systems. Some of the discussed issues include the

Table 1. Summary of the Catalytic Primary Amine−Epoxy Addition Kinetic Parameter (k_1) for the Set of Experiments Carried out at 60, 50, and 40 °C

	k_1 (L²/(mol² min)) at 60 °C			k_1 (L²/(mol² min)) at 50 °C	k_1 (L²/(mol² min)) at 40 °C
THF-to-monomers weight ratio	expt 1	expt 2	expt 3	expt 1	expt 1
0:1	0.006 38	0.006 18	0.005 66	0.002 83	0.001 5
0.1:1	0.006 13	0.005 36	0.005 08	0.002 41	
0.2:1	0.005 75	0.005 32	0.005 21	0.002 45	0.001 34
0.3:1	0.005 42	0.004 87	0.004 75	0.002 24	0.001 26
0.4:1	0.005 67	0.004 65	0.004 63	0.002 23	0.001 19
0.5:1	0.004 77	0.004 69		0.002 12	
0.75:1	0.004 94			0.002 05	
1:1	0.004 51	0.004 33		0.001 98	0.000 99
2:1	0.004 69				

Table 2. Summary of the Catalytic Secondary Amine−Epoxy Addition Kinetic Parameter (k_2) for the Set of Experiments Carried out at 60, 50, and 40 °C

	k_2 (L²/(mol² min)) at 60 °C			k_2 (L²/(mol² min)) at 50 °C	k_2 (L²/(mol² min)) at 40 °C
THF-to-monomers weight ratio	expt 1	expt 2	expt 3	expt 1	expt 1
0:1	0.001 37	0.0012	0.001 13	0.000 71	0.000 43
0.1:1	0.001 15	0.000 97	0.001 02	0.000 53	
0.2:1	0.000 98	0.000 89	0.000 84	0.000 48	0.000 24
0.3:1	0.000 98	0.000 88	0.000 85	0.000 44	0.000 21
0.4:1	0.001 00	0.000 73	0.000 77	0.000 38	0.000 19
0.5:1	0.000 60	0.000 71		0.000 36	
0.75:1	0.000 72			0.000 33	
1:1	0.000 63	0.000 58		0.000 34	0.000 15
2:1	0.000 66				

presence of substitution effects,[3] discrepancies in the ratios reported,[3] and temperature dependence of the ratio.[18] In this work, we determine the influence of THF on the substitution effects.

Our measured values of reactivity ratio for the DGEBA−PACM systems without THF is in the range of 0.2−0.285 for the range of cure temperatures investigated, confirming the presence of a negative substitution effect due to the nature of the attached substituent group. The influence of THF on the substitution effects is given in Figure 8, which shows how the reactivity ratio is affected by THF content for reactions at different cure temperatures. The presence of THF enhances the substitution effects, as shown by the decrease in reactivity ratio, up to the critical THF to monomers ratio of 0.3:1 discussed earlier.

Arrhenius Behavior. The catalytic primary and secondary amine−epoxy addition kinetic parameters were analyzed for their Arrhenius behavior, and the influence of THF on this behavior was determined. Linear relationships were observed (Arrhenius plot) for the kinetic parameter k_1 for the systems without and with THF (0.3:1), suggesting that the primary amine−epoxy reaction follows Arrhenius relationship in the absence and presence of the solvent. The activation energies were about 60 kJ mol^{-1} under these conditions. Similar results were obtained for the secondary amine−epoxy addition kinetic parameter k_2. The k_2 activation energies were 46 and 64 kJ mol^{-1} for systems without and with THF (0.3:1), respectively.

Diffusion Limitations. The diffusion limitations present in the reacting system could influence the final polymer network structure by decreasing the reaction rate, disrupting the network connectivity, and limiting the conversion. Therefore, an understanding of the diffusion limitations in the reaction medium is necessary for designing nanoporous polymer networks. For a given reaction mixture, the diffusion characteristics depend on the amount of free volume present in the system,[22] which depends on the cure temperature, the degree of conversion, and the amount of solvent. The presence of solvent increases the free volume of the system and reduces the diffusion limitations as the solvent molecules increase the mobility of the reaction medium. On the other hand, with increasing monomer conversion, the free volume of the system decreases and the diffusion limitations increase as the resulting polymer networks reduce the mobility of the reaction medium. Thus, a system vitrifies when the free volume of the reaction medium reduces below a critical value, representing the onset of a diffusion-controlled regime known as vitrification. An experimental study was carried out to determine the influence of THF on the vitrification and T_g of the epoxy−amine systems. The influence of THF content on T_g of the final polymer gels and the conversion at which the system vitrifies were used to determine the critical composition of THF, above which diffusion limitations due to vitrification can be neglected. Furthermore, fits of the two-parameter model over the full conversion range were carried out to investigate whether the model is capable of describing the reaction behavior to full conversion in the absence of vitrification.

Influence of THF on Diffusion Limitations. The onset of the diffusion-controlled regime due to vitrification becomes apparent when the reaction mixture passes from a rubbery to glassy state. There is a significant decrease in the mobility of the reaction medium as it vitrifies that is accompanied by a drastic reduction of the reaction rate. The influence of THF on vitrification can be understood by fixing the cure temperature and determining the effect of THF content on the conversion at which vitrification occurs. Figure 9 shows the effect of THF content on the diffusion limitation due to vitrification at a cure temperature of 60 °C. From this plot, the epoxy conversion at which this system vitrifies, as seen by no apparent change in the normalized epoxy concentration, was determined. By

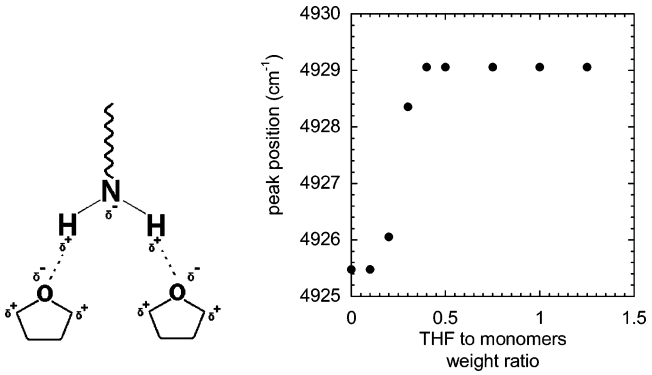


Figure 7. Left-hand side: schematic showing the dipole−dipole interaction between amine and THF present in the reaction mixture. Right-hand side: primary amine peak shift (in wavenumbers, cm^{-1}) due to dipole−dipole interaction plotted against THF content in the initial reaction mixture, showing that the peak shifts to a higher wavenumber up to a value between 0.3:1 and 0.4:1 THF to monomers ratio by weight and stops shifting for reaction mixture above this composition.

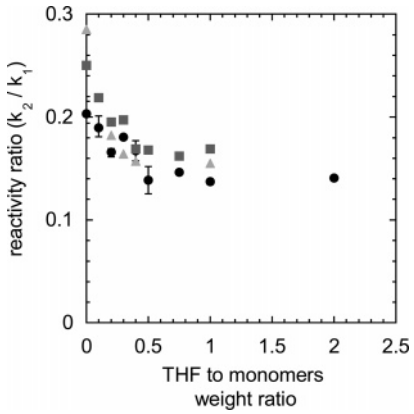


Figure 8. Plot of the reactivity ratio (k_2/k_1) vs THF content at (●) 60, (■) 50, and (▲) 40 °C, showing the negative substitution effects present in this reaction system and that the presence of THF enhances this effect up to the critical composition.

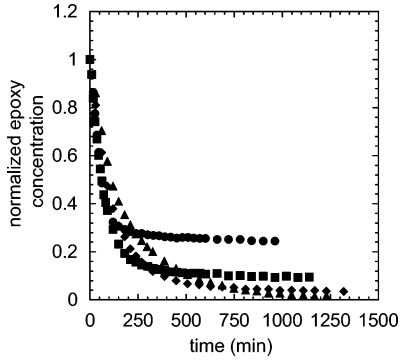


Figure 9. Plot of the normalized epoxy concentrations for reaction mixtures with increasing THF content (●) 0:1, (■) 0.05:1, (◆) 0.1:1, and (■) 0.2:1 at 60 °C, showing that the conversion at which system vitrifies increases with THF content.

this standard, the reaction mixtures with 0:1, 0.05:1, and 0.1:1 composition vitrify at 75, 91, and 96% conversion, respectively. Whereas, the reaction mixture with composition 0.2:1 does not vitrify as the system reacts practically to completion. Thus, the presence of THF increases the conversion at which the system vitrifies presumably by creating additional free volume in the

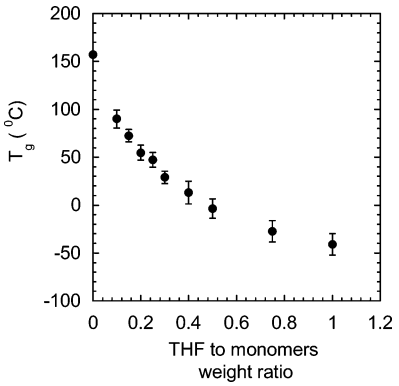


Figure 10. Plot of the glass transition temperature (T_g) of epoxy−amine gels synthesized with increasing THF content, showing the plasticization effect of THF on the final polymer network.

reaction medium and thereby requiring a higher conversion for vitrification. At 60 °C, the composition 0.2:1 THF to monomers weight ratio represents a critical composition of the reaction mixture, above which the system does not exhibit diffusion limitations due to vitrification.

An alternate method for understanding the influence of THF on vitrification is by fixing the conversion and evaluating the effect of THF content on the glass transition temperature of the final network, i.e., investigating the plasticization effect of THF on the epoxy−amine system. In this study, fully cured networks of DGEBA and PACM were synthesized with increasing THF content at 60 °C. The gels synthesized with less than 0.2:1 THF to monomers ratio were postcured in sealed vials at elevated temperatures to obtain complete conversion. Thus, the conversion of all the materials used was 100% for all practical purposes. This was validated by taking FTIR scans of the samples after cure. The T_g of these samples was measured using a DMA as described in the Experimental Section. Figure 10 illustrates the effect of THF content on the T_g of these gels. The reduction in T_g of the gels indicates that THF plasticizes the epoxy−amine network. This plot corroborates the conclusion drawn from Figure 9 that, at a cure temperature of 60 °C, the systems with THF content 0.2:1 and above ($T_g \leq 50$ °C) do not pass through T_g and therefore would not exhibit diffusion limitations associated with vitrification. Furthermore, this plot can be used to understand the vitrification behavior of the reaction at other cure temperatures. For example, at 40 °C, there would be no diffusion limitations due to vitrification for reaction mixture with THF content 0.3:1 and above.

Full Conversion Fits. It is clear that there are no diffusion limitations due to vitrification for a reaction mixture with THF content 0.2:1 and above at 60 °C. In the absence of diffusion limitations, the intrinsic kinetics model based on initial conversion data should describe the entire range of the reaction. This assertion was tested by comparing the model predictions to the experimental data extended to almost full conversion. As a representative experiment, Figure 11 shows the fit of the epoxy concentration for a reaction mixture with 1:1 THF to monomers weight ratio at 60 °C using the two-parameter model. The kinetic parameters used were those obtained by fitting the initial stages of the reaction where the diffusion limitations are presumed to be insignificant (as reported in Tables 1 and 2). From

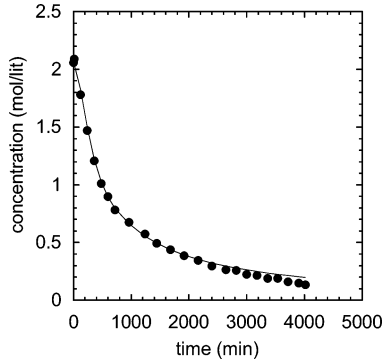


Figure 11. Plot showing the experimental data fit for the two-parameter model for a reaction mixture with composition 1:1 at 60 °C, showing that there are no diffusion limitations as the two-parameter model describes the cure kinetics to nearly full conversion. ● represents the experimental concentration of epoxy, and the line represents the model prediction for $k_1 = 0.00451$ L²/(mol² min) and $k_2 = 0.00063$ L²/(mol² min).

Figure 11, it can be concluded that the two-parameter model adequately describes the cure kinetics to nearly full conversion. This suggests that there are no significant diffusional constraints during polymerization in this system and that the two-parameter model adequately describes the entire cure kinetics in the absence of vitrification.

Conclusions

The cure kinetics of the EPON 828−PACM system in the presence and absence of THF was monitored using FTIR-NIR. FTIR analysis was used to ensure that THF remained chemically inert during this reaction. A two-parameter catalytic model that adequately describes the intrinsic reaction kinetics of these systems in the presence and absence of THF was developed. The influence of THF on the intrinsic kinetics of the system was investigated by quantifying the effect of THF content on the kinetic rate constants at three cure temperatures: 60, 50, and 40 °C. For a given cure temperature, it was found that increasing THF content decreased both the primary amine−epoxy addition (k_1) and secondary amine−epoxy addition (k_2) rate constant up to a critical THF composition and that above this composition increasing the THF content did not have a significant effect on the rate constants. This inhibiting effect was explained by the formation of stable intermediate species due to the dipole−dipole interaction between THF and amine where 0.3:1 THF to monomers weight ratio is a critical composition at which all the N−H bonds are stabilized by such interactions. The epoxy−amine reaction system showed negative substitution effects in the absence and the presence of THF. The presence of THF increased the negative substitution effects up to the critical THF composition. The reactivity ratios (k_2/k_1) of these systems were in the range of 0.285−0.14 for the THF compositions and cure temperatures investigated. The kinetic parameters obtained from the two-parameter model followed Arrhenius behavior for the conditions investigated.

The presence of THF in the reaction mixture reduces the diffusion limitations by creating additional free volume. For fully cured system at 60 °C, the composition of 0.2:1 represent a critical composition of the reaction mixture, above which the system does not vitrify. Generally, the two-parameter model was found to capture the cure kinetics of epoxy−amine system for almost the entire conversion range in the absence of vitrification.

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