Synthesis and Swelling Behavior of Highly Porous Epoxy Polymers

Majid Sharifi, Kaustubh A. Ghorpade, Vijay I. Raman, and Giuseppe R. Palmese*

ABSTRACT: Many advantageous properties of cross-linked polymers relate to their network structures. In this study, network structures of three DGEBA-based epoxy systems at various DGEBA monomer sizes were investigated via equilibrium swelling and glass transition behavior. Each system was cured with a tetra-functional diamine, 4,4'-methylenebis(cyclohexanamine), in the presence of a nonreactive solvent, i.e., THF at a solvent-to-monomer volume fraction ranging from 0 to 92%. Experimental results revealed that the conventional swelling model (the Dušek model) accurately calculates $M_c$ values of the cured gels prepared in moderate dilute environments, up to approximately 60% by volume of THF. For gels cured in extreme dilute environments, i.e., in the presence of above 60% by volume of THF, the calculated $M_c$ values using the Dušek model were found to increase sharply as a function of the initial solvent content. The observed dramatic increase in $M_c$ values was not supported by the dry $T_g$ of the identical polymer systems. In fact, the dry $T_g$ values of the polymer systems were found to be relatively insensitive to the initial solvent content. A modification was proposed to the Dušek model that incorporates an additional term, which accounts for the probability of finding elastic chains in a polymer network. Using the modified equation, $M_c$ values were varied as expected with the molecular weight of DGEBA and insensitive to the amount of the solvent initially used during cure. Furthermore, the modified $M_c$ values were shown to be consistent with the dry $T_g$ values in view of the Fox and Loshaek model.

INTRODUCTION

Thermosets are polymeric materials that form cross-linked network structures upon curing. Among these cross-linked polymers, epoxy thermosets are one of the most widely used materials due to their relatively high mechanical strength to weight ratio, good thermal and electrical insulating properties, simple and inexpensive processing, and relatively long service life for their typical applications, particularly under humid conditions. Fundamental studies show that the physical and mechanical properties of these materials can be linked to their molecular structures and chemistry, and many of the excellent properties of epoxy materials are due to their densely cross-linked networks.

One fundamental parameter used to quantify polymer network structures is the molecular weight between cross-links ($M_c$). Among techniques used to calculate $M_c$, two well-defined methods are those based on equilibrium swelling theory and rubber-elasticity theory. Equilibrium swelling theory, which was used to characterize porous epoxy polymers in this study, was introduced by Frenkel. It was later investigated and established by Flory–Rehner and Bray–Merrill. This theory is extensively used to characterize the network structure of the hydrogels prepared in water or the systems that are free-radically crosslinked.

The equilibrium swelling theory is reliable to calculate approximate values of molecular weight between cross-links for polymer networks prepared in moderate dilute solutions. However, our experimental results showed that for gels that were cured in extreme dilutions, the calculated $M_c$ values were significantly higher.

The principal objective of this study is to employ equilibrium swelling theory to characterize and investigate the network structures of cross-linked polymers that are formed/cured in dilute environments (i.e., in the presence of excess inert solvent during cure). Experimental studies revealed that highly nanoporous structures were obtained when during-cure solvent species were removed from polymer networks via a postcure supercritical extraction/drying process.

The well-known Dušek model was used in this study to calculate $M_c$ values for polymer network systems that were cured over a range of initial solvent inclusion. The calculated $M_c$ values were compared to the glass transition temperature of the corresponding dried gels. It was observed that, at high solvent contents, $M_c$ and $T_g$ do not fit the well-known Fox and Loshaek model. The discrepancy, at high solvent contents, was resolved by adjusting the Dušek model by incorporating a...
factor that accounts for the probability of finding elastic chains in a polymer network. The modified values of molecular weight between cross-links for a series of supercritically dried epoxy polymers were determined via the modified Dušek model, and the results were then compared to the corresponding \( T_g \) values. The results revealed for gels cured in extreme dilute environments; the modified values of molecular weight were consistent with the corresponding \( T_g \) in view of the Fox and Loshahk model. This was not the case, however, when unmodified \( M_w \) values were used.

**EXPERIMENTAL SECTION**

**Materials.** Three DGEBA resins (Miller-Stephenson) with different molecular weights (Epon-828 MW = 376 g/mol, Epon-836 MW = 625 g/mol, and Epon-1001F MW = 1075 g/mol) were used as the epoxy resins. A cycloaliphatic tetra-functional diamine, 4,4’-methylenebiscyclohexanamine (PACM, Air Products), was used as the curing agent, and ultrapure tetrahydrofuran, THF (Sigma-Aldrich), was used as the inert solvent. Table 1 lists the chemical structures of the materials used in this study and their average molecular weights. Epoxies, curing agent, and solvent were used as received and without further purifications.

**Sample Preparation.** The purity of the DGEBA resins was confirmed by GPC. A stoichiometric amount of epoxy resin and the curing agent (2:1 molar ratio) were mixed with the specified amounts of the solvent (THF) in a 20 mL vial using a Thinky mixer until a clear transparent liquid was obtained. To reduce the amount of THF evaporation, the screw threads of the vials were lined with a nonadhesive Teflon tape. Sample batches were delineated by THF to epoxy-amine resin weight ratios. For instance, a “1 TEA” sample has an equal weight of solvent-to-resin monomers and so has 50% solvent by weight. Batches with TEAs of 0, 0.2, 0.5, 1, 1.5, 2, 3, 4, 6, and 8 were prepared for systems containing Epon-828 and systems containing Epon-836. Batches with TEAs of 0, 0.2, 0.5, 1, 1.5, 2, 3, and 4 were prepared for systems containing Epon-1001F.

**Curing.** The mixtures were placed at 60 ± 1 °C for sufficient time to attain close to full conversion in the presence of THF. The conversion was monitored by tracking the FTIR absorbance peak (in the near IR region) associated with oxirane bands at 4530 cm\(^{-1}\) and the peak associated with N–H bands at 5056 and 6510 cm\(^{-1}\). To ensure that fully reacted systems were obtained at the curing temperature, the samples were kept at the curing conditions for sufficient time, as listed in Table 2. FTIR spectra of the specimens after cure did not show the existence of any peaks attributed to epoxy and amine bands, suggesting complete conversion in all cases (FTIR spectra are provided in the Supporting Information). The batches containing Epon-1001F and high THF contents, i.e., 6 TEA and 8 TEA never gelled at the curing temperature of 60 °C, and thus were excluded from further analysis.

**Equilibrium Swelling Experiment.** Once fully cured gels were prepared, equilibrium swelling experiments were conducted by weighing a small cut of each gel, \( W_n \), and immersing it in a vial containing THF. The vials were capped and maintained at 60 °C for 2 days and subsequently at room temperature for 1 week. The mass uptake was recorded until an equilibrium weight was achieved.

**Supercritical Solvent Extraction.** The supercritical drying procedure was conducted using a SPI-DRY CPD supercritical fluid extraction system. This apparatus consists of a chamber where liquid CO\(_2\) can be stored. The temperature of the system was controlled by immersing the entire pressurized system in a water bath. Wet samples that were prepared in the presence of THF were immediately placed inside the chamber, and the chamber was filled with liquid CO\(_2\) until the sample was entirely immersed in liquid CO\(_2\), allowing the THF to be replaced by CO\(_2\). Samples were allowed to soak in liquid CO\(_2\) for sufficient time for the solvent exchanging process to finish. The chamber was then refilled with fresh liquid CO\(_2\). The chamber was maintained at 5–10 °C during this step. The solvent exchange process was repeated three to four times. After that, the chamber temperature was raised above the supercritical temperature of CO\(_2\) (31.1 °C), and supercritical CO\(_2\) was gradually discharged to atmosphere. Dried samples were obtained after the complete discharge of CO\(_2\).
network (PN)) was measured in the relaxed state (the state of swelling theory. Accordingly, the equilibrium volume fraction PN in a relaxed state, respectively. The quantities solvent and PN at equilibrium swollen state, presence of epoxy or primary amine moieties, implying that formation of sol fraction in the gels is reduced. At the end fraction in the mixture. This assumption is only valid if the gel, and it is assumed to be equal to the monomer weight temperature were measured from the in

\[ M_{c} = \frac{1}{\chi_{c}} \left[ \frac{n_{v}}{v_{1s}} \left( \frac{v_{2s}}{v_{2r}} \right)^{1/3} - \frac{1}{2} \left( \frac{v_{2s}}{v_{2r}} \right) \right] \]

\[ 1 \quad M_{c} = \frac{2}{M_{n}} - \frac{1}{v_{1s}} \left[ \ln(1 - v_{2s}) + v_{2s} + \chi_{c} v_{2s} \right] \]

Differential Scanning Calorimetry. A Perkin Elmer Differential Scanning Calorimeter model DSC-7 was used to measure the glass transition temperature of the supercritically dried gels. All samples were tested through a heat/cool/heat protocol for three cycles, at a temperature range of 30–200 °C with a scanning rate of 10 °C/min. Values of glass transition temperature were measured from the inflection point that appeared in the third cycle (see the Supporting Information).

\[ \chi_{c} = \frac{1}{v_{1s}} \left[ \ln(1 - v_{2s}) + v_{2s} + \chi_{c} v_{2s} \right] \]

\[ \Delta H_{f} = \frac{1}{v_{1s}} \left[ \ln(1 - v_{2s}) + v_{2s} + \chi_{c} v_{2s} \right] \]

Table 3. Average Values of \( v_{1s}, v_{2s}, v_{1r}, \) and \( v_{2s} \) for Each Epoxy System

| THF: epoxy-amine wt. ratio (TEA) | vol. fraction of THF in the relaxed gel, \( v_{2r} \) | vol. fraction of PN in the relaxed gel, \( v_{2r} \) | vol. fraction of THF in the swollen gel, \( v_{2s} \) | vol. fraction of PN in the swollen gel, \( v_{2s} \) |
|---------------------------------|-------------|-------------|-------------|-------------|
| 0                              | 0           | 1           | 0.383       | 0.383       |
| 0.2                            | 0.221       | 0.779       | 0.449       | 0.449       |
| 0.5                            | 0.415       | 0.585       | 0.552       | 0.552       |
| 1                              | 0.586       | 0.414       | 0.65        | 0.65        |
| 1.5                            | 0.68        | 0.32        | 0.699       | 0.699       |
| 2                              | 0.739       | 0.261       | 0.741       | 0.741       |
| 3                              | 0.81        | 0.19        | 0.787       | 0.787       |
| 4                              | 0.85        | 0.15        | 0.836       | 0.836       |
| 6                              | 0.895       | 0.105       | 0.887       | 0.887       |
| 8                              | 0.919       | 0.081       | 0.915       | 0.915       |

At least three attempts were conducted for each system, and the average values of \( v_{1s}, v_{2s}, v_{1r}, \) and \( v_{2s} \) are reported in Table 3. Molecular Weight between Cross-Links. The classic equilibrium swelling theory was used to calculate the values of molecular weight between cross-links, \( M_{c} \), for the resulting epoxy systems. Accordingly, the average molecular weight between cross-links for a gel that forms in the presence of an inert solvent is quantified by

\[ 1 \quad M_{c} = \frac{1}{\chi_{c}} \left[ \ln(1 - v_{2s}) + v_{2s} + \chi_{c} v_{2s} \right] \]

Here, \( M_{n} \) is the number average molecular weight of the primary chains, \( M_{c} \) is the average molecular weight between cross-links, \( v_{1s} \) is the molar volume of the solvent phase, and \( v_{2s} \) is the specific volume of the polymer phase. \( \chi_{c} \) is the only material-specific parameter that characterizes the interaction energy between the solute (PN) and the solvent (THF).

The fraction, \( \frac{1}{M_{c}} \), generally approaches to zero due to the relatively large \( M_{n} \) values in cross-linked polymer systems. Therefore, eq 5 can be rewritten as

\[ 1 \quad M_{c} = \frac{1}{\chi_{c}} \left[ \ln(1 - v_{2s}) + v_{2s} + \chi_{c} v_{2s} \right] \]

The Flory–Huggins interaction parameter, \( \chi_{c} \), was estimated using the Hansen solubility parameter calculations in view of the group contribution method. According to the chemical structures of the PN repeating units and THF, this quantity was found to be approximately 0.424 at room temperature for the epoxy systems in this study (calculation details are provided in the Supporting Information).

In view of eq 6, values of \( M_{c} \) for the three DGEBA systems, Epon828-PACM, Epon836-PACM, and Epon1001F-PACM, were calculated and plotted vs initial solvent content (\( v_{1s} \)), as shown in Figure 1. The results indicated that the average values of molecular weight between cross-links substantially deviate from those of the dense systems (epoxy systems cured in the absence of an inert solvent). The deviation was slight and negligible until 20% volume fraction of the solvent is reached. This deviation slightly increased in more dilute environments, up to 60% volume fraction of the solvent. For epoxy systems in extreme dilutions, above 60% volume fraction...
of the solvent, $M_c$ values dramatically increased. The fact that $M_c$ increased with increasing dilution was comprehensively investigated in the work of Rolfs et al.\textsuperscript{22} and Haeusler et al.\textsuperscript{23} It is well understood that the presence of a solvent during cure attributes to increased network defects in the form of free chain ends and cycles, thus leading to elastically ineffective cross-links. As a result, cross-linked systems cured in dilute environments are generally capable of swelling more than identical cross-linked systems cured in less dilution, due to the formation of relatively less elastic chains. However, the dramatic increase of $M_c$ values above 60% volume fraction of solvent, as shown in Figure 1, could be due to two probable factors: (1) a significant number of network defects in the form of free chain ends and chain cycles in this case resulted in a substantial change in molecular structures such that the number of effective elastic chains that oppose swelling are few. (2) The model may not be adequate to predict the behavior of swelling when polymer networks are formed in extreme dilute environments.

An investigation was conducted to understand the influence of the initial solvent content on dry density and $T_g$ to determine whether polymer networks with substantially larger $M_c$ values were truly formed.

In our earlier research work, we presented the formation of porous aerogels upon supercritical extraction of a sacrificial solvent that was present during epoxy-amine polyaddition reactions.\textsuperscript{18} Drying under supercritical conditions eliminates capillary forces. Because of the relatively low temperatures and limited relaxation of elastic chains, pore structures were created during carbon dioxide evaporation. It should be noted that the supercritical extraction process was not completely free from shrinkage of a polymer network, since the solubility mismatch between the polymer network and the liquid carbon dioxide causes pore structures to slightly shrink or collapse.

To verify, the densities of selected samples were measured using the water displacement method in view of ASTM D792. Accordingly, the densities of supercritically dried aerogels were increased upon thermal annealing as the pores collapsed. For example, the density of Epon828-PACM (8 TEA) increased from approximately 0.3 to around 1.2 gr/cc upon thermal annealing. It was observed that the density values of the aerogels after thermal annealing were comparable to those of the dense polymer networks (0 TEA, Epon828-PACM).

The increase in density upon thermal annealing suggests that pore structures, which were formed upon CO\textsubscript{2} evaporation during supercritical extraction, collapse to a great extent. We have shown, in another publication, that these thermally annealed fully cured polymer networks comprise molecular structures with altered topologies.\textsuperscript{24,25} In view of the cited literature, the presence of an inert solvent during polycondensation cure, in fact, changes the directionality of covalent bond formations. Extracting the solvent in a postcure thermal step provides a polymer network with an identical density and $T_g$ to that of the dense structures. However, the altered molecular topology was found to provide unique mechanical characteristics, particularly large-strain mechanical performance, to the resulting polymer systems. The whole concept is schematically represented in Figure 2.

**Thermal Analysis.** Values of glass transition temperature for supercritically dried samples, or aerogels, were measured using a DSC. The average $T_g$ values and their associated error bars (from at least three replicates) for each system are shown in Figure 3.

Results shown in Figure 3 suggest that the dry $T_g$ for each polymer system is not significantly affected by the solvent content during the cure. In highly cross-linked polymers, $T_g$ is a measure of segmental mobility of polymer chains and thus can be related to $M_c$ and/or cross-linking density. However, $T_g$ cannot elucidate the difference between porous and dense structures.

For aerogels (TEA > 0), a slight deviation in $T_g$ values from the dense systems (TEA = 0) was observed. The difference in glass transition temperature between the dense systems and the aerogels is primarily due to the plasticization of elastic chains by the presence of residual solvent molecules that were permanently trapped (and were never removed in supercritical
The glass transition temperature values for supercritically dried samples. X-axis is the volume fraction of the solvent in the gels prior to supercritical extraction/drying.

According to the Fox and Loshaek model, a given cross-linked polymer system with a comparatively larger molecular size between cross-links would have a comparatively lower value of $T_g$ at a given cross-linking density. In accordance with the Fox and Loshaek model, thermosets made from resins with larger molecular weights typically form domains in the systems at $v_1$, above 0.6. This increase in $T_g$ is apparent in Figure 3.

There is a clear difference in the average $T_g$ values of each system due to the molecular size of the resins. In accordance with the Fox and Loshaek model, thermostses made from resins with larger molecular weights typically form domains with lower cross-linking densities. Under such conditions, local mobility of elastic chains tends to be higher at a given temperature, thus leading to overall lower $T_g$ values compared with thermosets having higher cross-linking densities. In accordance with the Fox and Loshaek model, thermosets made from resins with larger molecular weights typically form domains in the systems at $v_1$, above 0.6. This increase in $T_g$ is apparent in Figure 3.

As discussed, the aerogels cured in more dilute solutions form polymer network structures with higher porosity. The increased porosity facilitates the residual solvent species leaving the system in the first DSC heating cycle. This might be the reason for the apparent increase in $T_g$ values for all of the systems at $v_1$, above 0.6. This increase in $T_g$ is apparent in Figure 3.

There is a clear difference in the average $T_g$ values of each system due to the molecular size of the resins. In accordance with the Fox and Loshaek model, thermostses made from resins with larger molecular weights typically form domains with lower cross-linking densities. Under such conditions, local mobility of elastic chains tends to be higher at a given temperature, thus leading to overall lower $T_g$ values compared with thermostses having higher cross-linking densities.

Generally, in a cross-linked polymer, the glass transition temperature is related to the molecular size entrapped between cross-links as expressed by the Fox and Loshaek model:

$$T_g = T_{g\infty} + \frac{\xi}{M_c}$$

Here, $T_{g\infty}$ is the glass transition temperature of the elastic chain backbone at infinite molecular weight, and $\xi$ is proportional to the molecular weight of the monomer resins and the molar ratio of the epoxy resin to the curing agent.

According to the Fox and Loshaek model, a given cross-linked polymer system with a comparatively larger molecular size between cross-links would have a comparatively lower $T_g$.

Values of $\xi$ and $T_{g\infty}$ were calculated from experimental $T_g$, and $M_c$ of the dense systems (TEA = 0) using linear regression with the assumption that $\xi$ and $T_{g\infty}$ share the same values for all of the DGEBA/PACM epoxy systems. Accordingly, $\xi$ was approximately 41,702 (g/mol) and $T_{g\infty}$ was around 272.78 K ($\sim 0$ °C). The value of $T_{g\infty}$ suggests that in the limit of $M_c$ going to infinity, $T_g$ of a polymer should reach to a value of approximately $0$ °C. In other words, if $M_c$ values of aerogels (TEA > 0) increase as predicted by the Dušek model (shown in Figure 1), aerogel $T_g$ values would be expected to dramatically drop to a limit of approximately $0$ °C.

Aerogel $T_g$ values were calculated at $M_c$ predicted by the Dušek model with the above $\xi$ and $T_{g\infty}$ (results are provided in Figure S5 in the Supporting Information). Contrary to the calculated $T_g$, measured $T_g$ values of the aerogels did not exhibit the dramatic drop predicted by the Fox and Loshaek model in combination with the Dušek model. Figure 4 shows the average $T_g$ vs $M_c$ values calculated from the Dušek model. The results indicate that, for the three systems under study, $T_g$ values did not substantially decrease (as predicted) with the dramatic increase of $M_c$ for samples formed at very high dilutions. This discrepancy suggests that the Dušek model (eq 6) may be inadequate for calculating $M_c$ values in cross-linked systems that are formed in very high dilutions.

**Modification to the Dušek Model.** Dušek described polymer network structures based on Flory’s description of cross-linked systems. Flory visualized polymer networks as meshes that are characterized by their number of elastic chains ($\nu$) in systems formed in the absence of a sacrificial solvent or in moderate solvent dilutions. However, in systems formed in very high dilutions, elastic chains cannot be found everywhere. In other words, the elastic and swelling behavior of porous structures that contain significant pore volume previously occupied by solvent species is different than the elastic and swelling behavior of dense structures. Therefore, a factor was introduced to the Dušek model that accounts for the probability of finding an elastic chain in the entire volume of the gel ($PN + solvent$). Since all elastic chains are part of the polymer phase, this probability is at least equal to the probability of finding $PN$ in the gel. This probability term is defined in the equation below.

$$P_n = \frac{\text{vol-PN}(V_{PN})}{\text{vol-PN}(V_{PN}) + \text{vol-sol}(V_f) + \text{free\ vol}(V_f)}$$
The free volume in a gel is generally expected to be much lower than the volume of the gel \( (V_f \ll V_{PN} + V_s) \); hence, neglecting the \( V_f \) term, the simplified expression is equal to the volume fraction of PN in the relaxed gel.

\[
P_r = \frac{\text{vol-PN}(V_{PN})}{\text{vol-PN}(V_{PN}) + \text{vol-solvent}(V_s)} = \nu_{1r}
\]

In the limit of low solvent dilutions, the volume of the solvent is much smaller than the volume of PN \( (V_s \ll V_{PN}) \); thus, the probability factor, \( P_r \), becomes unity, and the effect of porosity can be neglected. This is consistent with our observations of \( \nu_{1r} < 0.2 \) in Figure 1. After incorporating the probability factor \( (P_r) \) into the Dus\'ek model, eq 10 is derived (see the Supporting Information for the mathematical derivation of eq 10).

\[
M_c = -\frac{\nu_{1r}^2}{\nu_{1r}} \left[ \ln(1 - \nu_{2s}) + \nu_{2s} + \xi(\nu_{2s})^2 \right]
\]

For each of the aerogels, \( M_c \) values were calculated in view of the modified Dus\'ek model (eq 10), and results were plotted vs solvent content in a relaxed state, \( \nu_{1r} \), as shown in Figure 5. In this case, \( M_c \) values were relatively constant for each polymer system. The \( M_c \) values calculated from the modified Dus\'ek model supports the contention that the true molecular weight between nodular cross-links in a polymer network was not changed due to the presence of the inert solvent, but rather that the changes that occur pertain primarily to the directionality of covalent bond formations.

In Figure 6, the dry \( T_g \) for each of the gels was plotted vs the modified \( M_c \) values. The results indicate that the effect of the initial solvent content on the dry \( T_g \) and \( M_c \) is minimal. In addition, the modified \( M_c \) values of the systems cured in extreme dilutions were consistent with the dry \( T_g \) values via the Fox and Loshaek model. This observation suggests that the modified Dus\'ek model (eq 10) successfully predicted the approximate \( M_c \) values of the systems prepared in extreme dilute environments.

**Effect of Network Structure on Equilibrium Swelling.**

According to Flory’s theory of mixing for cross-linked polymers\(^{12}\), the favorable interaction between polymer chains and fluid molecules allows a spontaneous mixing/swelling to occur. However, as the mixing process continues, a retractive force develops from the elastic nature of polymer chains that opposes the swelling process. A state of equilibrium is reached when configurational entropy, associated with elastic retractive forces, and favorable interactions between a solvent and a polymer provide a minimum free energy for the system. Figure 7 shows the equilibrium volume fraction of THF in the swollen state vs the corresponding quantity in the relaxed state (as prepared). The increasing trend of an equilibrium volume fraction in the swollen state \( (\nu_{1s}) \) implies that gels that are cured in more dilute solutions have a higher swelling capacity due to a greater number of network defects in the form of free chain ends and chain cycles.

In the dense structures \( (\nu_{1r} = 0) \), it was also observed that the equilibrium volume fraction of solvents in the swollen state \( (\nu_{1s}) \) is in the following order: Epon1001-PACM > Epon836-PACM > Epon828-PACM. This observation can be explained by the cross-linking density and \( M_c \) values. As shown in Table...
1, the epoxy resin molecular weight is in the following order: Epon1001F > Epon836 > Epon828. Therefore, “Epon1001F creates polymer networks with larger \( M_c \) values in cured form, supported by the results shown in Figure 5. Larger cross-linkers give rise to reduced elastic retractive forces in Epon1001F-PACM systems relative to the other two systems, thus leading to more solvent swelling capacity.

Additionally, it was observed that the difference between equilibrium solvent uptake in the swollen state in each of the three systems gradually decreased as the curing-cure solvent content, \( v_{\text{sol}} \), increased. This difference is negligible for the gels prepared in very dilute environments, such as the ones at \( v_{\text{sol}} > 0.8 \). The results in Figure 7 suggest that equilibrium solvent uptake for thermosets that were cured in highly dilute environments (\( v_{\text{sol}} > 0.8 \)) may be determined by a nodular distance rather than molecular weight between cross-links because the opposing elastic retractive forces appear to be relatively comparable regardless of the resin type. In a separate research work, Sharifi et al.\(^{(2)}\) proposed that the elastic property of polymer networks cured in the presence of excess inert solvent may be determined by a quantity called "topological distance." They proposed that in dense polymer network structures, this quantity is similar to the size of cross-linkers; however, for polymer networks that are cured in the presence of excess inert solvents, this quantity is generally larger than the size of cross-linkers. The proposed quantity "topological distance" may explain as to why the difference between the equilibrium solvent uptake in the swollen state is gradually decreasing with the increase of \( v_{\text{sol}} \). In the case of curing in excess dilutions, elastic retractive forces may be dominantly determined by the "topological distance" rather than \( M_c \), which is annotated in Figure 7.

**CONCLUSIONS**

Equilibrium swelling and glass transition temperature were used to characterize epoxy polymer networks cured in the presence of an inert solvent. Three epoxy resins with different molecular weights were cured with a curing agent, PACM. Calculated \( M_c \) values from equilibrium solvent uptake suggested that gels with a dramatic increase in cross-link size formed in extreme dilution, \( v_{\text{sol}} > 0.8 \). Considering the Fox and Loshaek model, dry \( T_g \) values were not in accordance with the calculated \( M_c \) values of the corresponding samples. The discrepancy suggested that the conventional model may be inadequate to predict \( M_c \) values of the cross-linked polymers cured in excess dilutions. The model was modified by incorporating a probabilistic factor, \( P_o \), based on the probability of finding an elastic chain in a porous structure. Using the modified model, the \( T_g \) values were predicted by the modified \( M_c \) values via the Fox and Loshaek model. Results implied that the values of molecular weight between cross-links were relatively insensitive to the amount of the solvent initially present during cure. Curing a cross-linked polymer in a highly dilute solution creates defects in the form of free chain ends and cycles, thus leading to elastically ineffective cross-links, resulting in higher swelling capacity, and without substantial influence on \( M_c \).

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04035.

Mathematical derivation of the modified Dušek equation (Equations 1–8); solubility parameter calculations for epoxy-amine systems and tetrahydrofuran (Equations 9–13); structural groups in the PN repeat unit and tetrahydrofuran used to calculate the solubility parameters (Figure S1); structural group contributions to the cohesive energy combination parameter and the van der Waals volume (Table S1); solubility parameters and molar volumes of the PN repeat unit and THF (Table S2); calculation of the interaction parameter \( \chi \) using Hildebrand’s regular solution theory (Equations 14 and 15); FTIR scans of epoxy-amine-THF for the Epon828-PACM systems (Figure S2); DSC third heating scans on supercritically dried gels (aerogels) for 0, 0.5, 1, and 3 TEA samples (Epon828-PACM) (Figure S3); \( T_g \) vs 1/\( M_c \) of the dense systems (TEA = 0) for all of the DGEBA/PACM systems (Figure S4); calculated \( T_g \) values of epoxy systems based on \( M_c \) values calculated via the Dušek model (Table S3); calculated \( T_g \) values of epoxy systems based on \( M_c \) values calculated via the Dušek model, assuming \( \xi \) and \( T_{\infty} \) share the same values in all of the DGEBA/PACM epoxy systems (Figure S5) (PDF)

**AUTHOR INFORMATION**

*Corresponding Author*

Giuseppe R. Palmese – Chemical and Biological Engineering Department, Drexel University, Philadelphia, Pennsylvania 19104, United States; orcid.org/0000-0002-0063-2425; Email: palmese@coe.drexel.edu

*Authors*

Majid Sharifi – Chemical and Biological Engineering Department, Drexel University, Philadelphia, Pennsylvania 19104, United States

Kaustubh A. Ghorpade – Chemical and Biological Engineering Department, Drexel University, Philadelphia, Pennsylvania 19104, United States

Vijay I. Raman – Chemical and Biological Engineering Department, Drexel University, Philadelphia, Pennsylvania 19104, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04035

*Notes*

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The research was sponsored by the Army Research Laboratory and was accomplished in part under Cooperative Agreement Number W911NF-12-2-0002. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Laboratory or the U.S. Government.

**REFERENCES**

(1) Askeland, D. R. *The Science and Engineering of Materials*, 3rd ed.; Chapman & Hall, 1996; p 256.

(2) Pascualt, J.-P.; Williams, R. J. J. *Epoxy Polymers: New Materials and Innovations*; Wiley-VCH Verlag GmbH & Co. KGaA, 2010; p 367.
(3) Sue, H. J.; Puckett, P. M.; Bertram, J. L.; Walker, L. L.; Garcia-Mein, E. I. Structure and property relationships in model diglycidyl ether of bisphenol-A and diglycidyl ether of tetramethyl bisphenol-A epoxy systems. I. Mechanical property characterizations. J. Polym. Sci., Part C: Polym. Symp. 1999, 37, 2137−2149.

(4) Marks, M. J.; Verghese, N. E.; Hrovat, K. J.; Laboy-Bollinger, A.; Buck, J. C.; Rabon, J. A., Jr.; O’Connell, C. L.; Allen, L. The effects of monophenol chain terminators on the structure-property relationships of controlled epoxy networks. J. Polym. Sci., Part B: Polym. Phys. 2008, 46, 1632−1640.

(5) Lin, C. J.; Bell, J. P. The effect of polymer network structure upon the bond strength of epoxy–aluminum joints. J. Appl. Polym. Sci. 1972, 16, 1721−1733.

(6) Crawford, E.; Lesser, A. J. The effect of network architecture on the thermal and mechanical behavior of epoxy resins. J. Polym. Sci., Part B: Polym. Phys. 1998, 36, 1371−1382.

(7) Flory, P. J. Statistical mechanics of swelling of network structures. J. Chem. Phys. 1950, 18, 108−111.

(8) Flory, P. J.; Erman, B. Theory of elasticity of polymer networks. 3. Macromolecules 1982, 15, 800−806.

(9) Flory, P. J.; Rehner, J., Jr. Statistical mechanics of cross-linked polymer networks. I. Rubberlike elasticity. J. Chem. Phys. 1943, 11, 512−520.

(10) Frenkel, J. A theory of elasticity, viscosity and swelling in polymeric rubber-like substances. Rubber Chem. Technol. 1940, 13, 264−274.

(11) Flory, P. J.; Rehner, J., Jr. Statistical Mechanics of Cross-Linked Polymer Networks II. Swelling. J. Chem. Phys. 1943, 11, 521.

(12) Flory, P. J. Principles of Polymer Chemistry, Cornell University Press, 1953; p 672.

(13) Dušek, K. Phase separation during the formation of three-dimensional polymers. J. Polym. Sci., Part B: Polym. Lett. 1965, 3, 209−212.

(14) Dušek, K. Phase separation during the formation of three-dimensional polymers. J. Polym. Sci., Part C: Polym. Symp. 1967, 1289−1299.

(15) Bray, J. C.; Merrill, E. W. Poly(vinyl alcohol) hydrogels. Formation by electron beam irradiation of aqueous solutions and subsequent crystallization. J. Appl. Polym. Sci. 1973, 17, 3781−3796.

(16) Peppas, N. A.; Hilt, J. Z.; Khademhosseini, A.; Langer, R. Hydrogels in biology and medicine: from molecular principles to biomanufacturing. Adv. Mater. 2006, 18, 1345−1360.

(17) Langer, R.; Peppas, N. A. Advances in biomaterials, drug delivery, and biomanufacturing. AICHE J. 2003, 49, 2990−3006.

(18) Raman, V. I.; Palmese, G. R. Design and characterization of nanoporous polymeric materials via reactive encapsulation of a chemically inert solvent. Colloids Surf., A 2004, 241, 119−125.

(19) Mijovic, J.; Andjelic, S. A study of reaction kinetics by near-infrared spectroscopy. I. Comprehensive analysis of a model epoxy/amine system. Macromolecules 1995, 28, 2787−2796.

(20) Raman, V. I.; Palmese, G. R. Influence of Tetrahydrofuran on Epoxy-Amine Polymerization. Macromolecules 2005, 38, 6923−6930.

(21) Hansen, C. M. Hansen Solubility Parameters: A User’s Handbook; CRC Press, 2007.

(22) Rolfes, H.; Stepto, R. F. T. Network formation and properties: rate theory description of effects of ring formation on elastic shear modulus of RA2 + RB3 networks. Makromol. Chem., Macromol. Symp. 1990, 40, 61−79.

(23) Haeusler, K. G.; Stepto, R. F. T.; Armbrust, J.; Bischof, G. J. Characterization of crosslinked polymers by means of the evaporation analysis. VI. Effect of network imperfections. Plaste Kautsch. 1987, 34, 128−130.

(24) Jang, C.; Sharifi, M.; Palmese, G. R.; Abrams, C. F. Crosslink network rearrangement via reactive encapsulation of solvent in epoxy curing: A combined molecular simulation and experimental study. Polymer 2014, 55, 3859−3868.

(25) Sharifi, M.; Jang, C.; Abrams, C. F.; Palmese, G. R. Toughened epoxy polymers via rearrangement of network topology. J. Mater. Chem. A 2014, 2, 16071−16082.