The effect of alkyl chain length on material properties of fatty-acid-functionalized amidoamine-epoxy systems

Arun Srikanth¹, John Vergara¹, Giuseppe Palmese, Cameron F. Abrams*

Department of Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, USA

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ABSTRACT

Polyamine crosslinkers functionalized with pendant fatty acids are commercially used in epoxy coatings in part to enhance water barrier properties for corrosion prevention. However, a systematic understanding of the links between monomer molecular structure and material properties of such systems remains elusive, which limits our ability to design newer and more environmentally friendly coating systems. In this work, the effect of *n*-alkyl chain length in fatty-acid-functionalized polyamines on crosslinked epoxy-amidoamine systems is studied using a combined experimental and simulation-based approach. Both experiments and simulations show that density decreases and volume-expansion coefficients increase with increasing pendant chain length. Furthermore, it is shown that the trends in density and coefficient of volume thermal expansion with chain length obtained from simulations are consistent with an ideal mixing approximation. Interestingly, however, the glass-transition temperature T_g is found to be insensitive to chain length. Molecular simulations reveal that increasing the alkyl chain length from four to ten carbons does not introduce new flexibility mechanisms to the dense thermosets, which explains the T_g insensitivity. This work demonstrates a new way to significantly decrease the density of a thermoset polymer without compromising desirable properties such as high T_g and low coefficient of thermal expansion, and therefore may provide sounder rationale for molecular-based design of epoxy-based coatings.

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1. Introduction

Epoxy networks have a wide range of applications and are used as castings, encapsulating materials, adhesives, laminates and in coating formulations [1,2]. They can be made suitable for both high and low temperature applications ranging from $-50\text{ }^{\circ}\text{C}$ to $+120\text{ }^{\circ}\text{C}$ [3]. Epoxies are typically cured with crosslinkers to form thermosetting polymers which possess enhanced thermomechanical properties, adhesive strength, viscosity, glass transition temperature and corrosion resistance [3]. The properties of a thermosetting polymer critically depend on the type of crosslinker used and specific crosslinkers are chosen to suit specific applications [2].

Among various crosslinkers, amidoamines are preferred in applications requiring moisture resistance, and also cause less skin irritation compared to polyamines [4,5]. Amidoamines have been in use since the late 19th century [1] and are key ingredients in the commercially available formulations Ancamide 500–507 and Ancamide 2029 [6]. However, these

* Corresponding author.

E-mail addresses: ss3763@drexel.edu (A. Srikanth), john.henry.vergara@drexel.edu (J. Vergara), grp47@drexel.edu (G. Palmese), cfa22@drexel.edu (C.F. Abrams).

¹ Equal contributions.

formulations are poorly structurally characterized and consequently very little is known about their structure-property relationships. This limits our ability to design improved crosslinking agents. A key molecular feature of these formulations, however, are pendant *n*-alkyl fatty-acid chains that cap some primary amine sites that could otherwise crosslink. The effects of alkyl chain length in these crosslinkers on the properties of the polymer and on corrosion performance is not yet known and has hitherto not been investigated. In cases where alkyl chains are part of the internal structure of crosslinkers or epoxy molecules, the effect of increasing chain length has been studied. For instance, increasing the alkyl chain length in aliphatic amine crosslinkers decreases the glass transition temperature T_g and the storage modulus and increases the free volume of the epoxy thermoset [7]. It has also been shown that the glass transition temperature decreases with increase in alkyl chain length in non-epoxy based systems such as polyesters [8], polyetherimides [9], poly-*n*-alkyl methacrylates [10], *p*-alkyl styrenes, and α -olefins [11]. It is therefore worth determining whether or not increasing pendant alkyl chain length in model amidoamine crosslinkers influences basic thermomechanical properties.

The purpose of this article is to report results of a combined experimental and molecular-simulations based approach to understanding the role of pendant alkyl chain length on thermomechanical properties of thermoset polymers comprising conventional epoxy networks and model amidoamine crosslinkers. Molecular dynamics (MD) simulations have proven to be useful in estimating properties of thermoset polymers and providing molecular-level rationales for structure-property relations [12–20]. The aim here is to systematically investigate this single molecular-level feature using newly synthesized pure amidoamine (AMAM) crosslinkers of varying alkyl chain lengths. These crosslinkers are cured with the diepoxy diglycidyl ether of bisphenol A (DGEBA) and the effect of alkyl chain length on the properties of the resulting thermosets are investigated. The main properties that are addressed here are density ρ , glass transition temperature T_g , and coefficient of volume thermal expansion α . It is shown that an ideal-mixing approximation is sufficient to explain trends in ρ and α with chain length. The T_g was found to be insensitive to *n* and molecular simulations provide detailed explanations for this behavior.

2. Methods

2.1. Experimental

The epoxy monomer considered here is diglycidyl ether bisphenol A (DGEBA). The crosslinkers considered are amidoamines (AMAM), derived from diethylenetriamine (DETA) via attachment of one fatty acid chain to a single primary amine site. The AMAM series considered here vary in alkyl chain length *n* from 0 to 10, and we denote a particular AMAM with a subscript indicating the number of methylenes in the amide moiety. DGEBA and AMAM structures are shown in Fig. 1. DGEBA was acquired from Miller-Stephenson chemicals. DETA, fatty methyl esters (methyl hexanoate, methyl octanoate, methyl decanoate, methyl dodecanoate), and chloroform were acquired from Sigma Aldrich, while magnesium sulfate was acquired from BDH. Polyvinyl fluoride, PVF (Tedlar) was used as release film for making thick epoxy/amine films and was acquired from DuPont. All chemicals were used as received.

2.1.1. Synthesis of AMAM crosslinkers

In order to synthesize AMAM crosslinkers of specified chain length, an appropriate fatty methyl ester was reacted with DETA. The synthetic scheme is shown in Fig. 2. Diethylenetriamine (0.467 mol, 48.26 g) was heated to 90 °C and mixed in a two-neck round-bottom flask for 30 min. The ester was then added dropwise to the hot DETA at a 1:10 equivalent ratio

Fig. 1. Chemical structures of (a) DGEBA and (b) AMAM_n.

Fig. 2. Synthetic Scheme for the production of AMAM crosslinkers.

Table 1

Amine hydrogen equivalent weight (AHEW) and the molecular weight (MW) for AMAM_n systems.

Alkyl chain length (n)	AHEW	MW (g/mol)
4	67.1	201.2
6	76.5	229.4
8	85.8	257.4
10	95.2	285.5

(10 mol of DETA:1 mol of methyl ester) and allowed to react for 12 h. The reaction products were diluted in 150 mL of chloroform and washed with 100 mL of water twice to remove unreacted DETA. The chloroform phase was dried with MgSO₄ and roto-evaporated to isolate the desired mono-amidoamines shown in Fig. 2.

¹H NMR (Varian Unity Inova NMR, 500 MHz) was used to confirm the AMAM_n chemical structures with a spectral window of ±2000 Hz and 32 scans at 25 °C. ¹H NMR spectra are presented in the supporting information. The purity of the AMAM_n structures was found to be about 98–99%. AMAM₀ and AMAM₂ could not be successfully synthesized due to cyclization of the monoamide to an imidazoline. The AMAM_n crosslinkers that were successfully synthesized (n = 4, 6, 8, and 10) were used in curing. The amine hydrogen equivalent weight (AHEW) and the molecular weight for the AMAM_n systems is shown in Table 1.

2.1.2. Curing

DGEBA was individually cured with each of the four AMAM_n (n = 4, 6, 8, and 10) crosslinkers to produce crosslinked polymer systems. The mechanism of epoxy-amine curing is shown in Fig. 3. DGEBA and crosslinker were mixed at stoichiometric ratio (one epoxy ring to one amine hydrogen) and drawn down with a 4 mil bird applicator on a PVF wrapped steel panel. The drawn film was then cured at 80 °C for three hours and post cured at 160 °C for one and a half hours. The resulting films were on average 100 μm in thickness and were easily peeled off the PVF-wrapped panels and stored in a desiccator to prevent moisture uptake. Polymer bars were made using a homemade rectangular silicon molds where the desired polymer composition was cured at 80 °C for three hours and post cured at 160 °C for one and a half hours. Three samples of each system were prepared. These samples were then polished down to dimensions of 17.5 mm in length, 10–12 mm in width, and approximately 2 mm in thickness. These bars were then core drilled with a drill bit of 4.4 mm OD and the resulting cylinders were used for Thermal Mechanical Analysis (TMA). The FTIR spectra of samples shown in Fig. 4 indicate that 100% conversion of epoxies, primary amines and secondary amines was achieved. The samples were then used for measurement of polymeric properties.

2.1.3. Measurement of *T_g*, CVTE's and density

Properties were measured for the five cured polymer compositions over three samples each. Differential scanning calorimetry (DSC; TA Q2000) was used for measuring *T_g*. Heat/cool scans were recorded between 40 °C to 100 °C. *T_g* was measured for the polymer systems and was taken to be the inflection of the thermograms during the second heating. The second heat scan was chosen for determining *T_g* because the first heat scan exhibited noise due to the relaxation of residual stresses in the polymer systems due to open curing. Thermomechanical analysis (TMA) with a temperature ramp rate of 2 °C/min was used for calculating the coefficient of linear thermal expansion β, and subsequently α, defined as

$$\beta = \frac{1}{l} \frac{\partial l}{\partial T} = \frac{1}{3} \alpha \quad (1)$$

Fig. 3. Schematic of curing mechanism.

Fig. 4. N-IR Spectra of cured samples.

where the second equality holds for isotropic materials. Dimension change with temperature was measured using TA 2940 over a temperature range of 20–180 °C. The slope $\frac{\Delta l}{\Delta T}$ in the rubbery and glassy region was then calculated. β for both glassy and rubbery regimes was then calculated using the length of the sample at 20° and 180 °C, respectively.

Density was measured using a density gradient column as described in ASTM D1505. All samples were thin films with an average thickness of 100 μm ; these films were immersed in DI water at 23 °C for about 10 min prior to exposure to the density gradient to ensure no air bubbles would form.

2.2. Simulation

MD simulations were performed on crosslinked DGEBA/AMAM_n systems for chain lengths n between 0 and 10. A total of six polymer systems each consisting of 192 DGEBA molecules and 128 crosslinkers molecules of were simulated. Five independent replicas of each system composition were generated and simulated.

2.2.1. Crosslinking protocol

The first step in simulating a polymer system was to generate a molecular model for the epoxy and a crosslinker molecule (Fig. 1). A hydrogenated DGEBA with pre-opened epoxy rings was used in this work. The molecular models were built using avogadro [21]. After this, atom types were assigned to atoms corresponding to Generalized Amber Force Field (GAFF) [22,23]. Partial charges were assigned to the atoms using AM1-BCC method [24,25]. The force-field parameters for the topology were obtained from GAFF based on the assigned atom types. This was carried out using the antechamber suite [26]. After this step, a system or a replica of a system was created by randomly placing epoxy monomers and crosslinker molecules in a simulation cell using packmol [27].

Each system replica was then equilibrated using constant-energy MD for 50 ps followed by pressure- and temperature-controlled MD for 1.5 ns. During the equilibration period, the temperature and pressure were maintained at 300 K and 1 atm, respectively. After equilibration, the system was crosslinked according to the reaction mechanism shown in Fig. 3 by creating bonds between bonding partners. The bonding partners (reactive atoms) were the end carbon atoms in the epoxy and nitrogen atoms in the primary and the secondary amines in the crosslinkers. Now, with the positions of the reactive atoms as the center, the search radius R was iteratively increased in steps of 2 Å (Δr). At each iteration, potential bonding partners were identified and new bonds were created after which the hydrogen atoms were deleted. An equal reactivity assumption was employed during bond search; i.e., no distinction was made between a primary amine and a secondary amine. After each round of bond formation, atom types of the hydrogens bonded to the reactive carbon atoms were changed, the partial charges (within three bonds of the crosslinking atoms) were updated and force-field parameters were re-assigned to the newly formed topology. The system was then relaxed by employing a two stage-potential energy minimization: first, by using a Hessian-free truncated Newton algorithm followed by conjugate gradient algorithm [28] which ensured that the bond lengths of the created bonds were close to the equilibrium length. Iterations continued until the desired conversion limit was met (100%). The crosslinking procedure described above is shown in the form a flow chart in Fig. 5.

Fig. 5. Crosslinking algorithm.

The minimizations were not always successful in relaxing the bonds to the equilibrium length. In the case of an unsuccessful minimization, the replica was discarded and a new replica was prepared and subjected to equilibration and crosslinking. This process of creating a new replica of the system and subjecting it to equilibration and crosslinking was repeated until five replicas of each system were obtained for which minimizations were successful. A 100% conversion was achieved for the all crosslinked systems. For 100% conversion, our algorithm yields about 40% successfully crosslinked systems. Unsuccessful minimizations arose from particular bonding arrangements that resulted in topological restraints that prevented new bonds from shrinking to their proper lengths. These were treated as random events and were discarded. A possible way to enhance the success rate of the algorithm is to restrict the number of bonds created at each iteration, which in essence constitutes uniformly distributing the bond energy such that change in bond energy is almost kept constant at each iteration. However, because generation of crosslinked trials using this algorithm is very fast, the relatively high failure rate observed here did not limit the overall simulation throughput.

2.2.2. Estimation of T_g

To observe the glass-transition phenomenon, the crosslinked systems were subjected to a temperature ramp, i.e., they were held at a high temperature for about 6 ns and then slowly cooled down in steps of 15 K by carrying out an NPT simulation for 2 ns at each temperature which corresponds to a cooling rate of 7.5×10^9 K/s. The pressure was maintained at 1 atm throughout the temperature ramp. The six DGEBA/AMAM_n systems were subjected to a temperature ramp starting from 500 K and decreasing to 200 K. The specific volume of the five replicas of a system was calculated every 5 ps, at each temperature. The second ns at each temperature was used to compute ensemble averages.

This average specific volume as a function of temperature for the polymer systems is shown in Fig. 6. Once the average specific volume as a function of temperature was obtained, two linear fits to this data, one fit to the glassy region and another

Fig. 6. Specific volume as a function of temperature. Linear fits to the rubbery and glassy region are shown for a representative system (DGEBA/AMAM₀).

fit to the rubbery region, were constructed. For all systems, specific volume data in the temperature range of 425–500 K was used for the linear fit in the rubbery region and the specific volume data in the temperature range of 200–275 K was used for the linear fit in the glassy region. An ordinary least squares procedure was used to construct the linear fits and T_g is then interpreted as the intersection of the two linear fits. MATLAB [29] was used to construct the linear fits. This method of estimating T_g is illustrated in Fig. 6. Uncertainties in T_g were also estimated [30].

2.2.3. Estimation of CVTE

The CVTE (α) is generally defined as,

$$\alpha = \frac{1}{v(T)} \left(\frac{\partial v}{\partial T} \right)_p \quad (2)$$

The CVTE in the rubbery (α_r) and glassy (α_g) states of each of the DGEBA/AMAM systems were calculated using the above expression. For calculating α_r , the slope of linear fit to the rubbery region was used for $(\frac{\partial v}{\partial T})_p$ and specific volume at the highest temperature (500 K) to which the systems were subjected, was used for $v(T)$ in Eq. (2). Similarly, for calculating α_g , the slope of the linear fit to the glassy region was used for $(\frac{\partial v}{\partial T})_p$ and specific volume at the lowest temperature (200 K) to which the systems were subjected, was used for $v(T)$ in Eq. (2). The uncertainties in α_g and α_r were calculated using standard rules of error propagation [31].

2.2.4. Simulation methods

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator [32]) was used as the MD engine for equilibration, crosslinking, and for the temperature ramps with the following specifications. A cutoff distance of 9 Å for the non-bonded interactions (electrostatics and Lennard-Jones) was used and tail corrections were used [33]. Periodic boundary conditions were used. Long range electrostatic interactions were computed using the particle-particle particle-mesh algorithm. The PPPM algorithm uses damped particle-particle interactions in real space (less than 9 Å) and particle-mesh interactions at long and short range in reciprocal space [34]. The temperature was maintained using a Nosé hoover thermostat [35,36] and pressure was maintained using a Parrinello-Rahman barostat [37]. The velocity-Verlet scheme was used for integrating the equations of motion and a timestep of 1 fs was used. Some tools in Visual Molecular Dynamics (VMD [38]) were used for analysis of LAMMPS trajectories and visualization.

3. Results and discussion

In the present section the focus is on analyzing the effect of chain length in the crosslinkers on ρ , T_g , and $\alpha_{r,g}$ of crosslinked DGEBA/AMAM_n systems obtained from the experiments and simulations.

3.1. Effect of chain length on density

The mass density of DGEBA/AMAM_n systems obtained from simulations and experiments as a function of alkyl chain length n at room temperature (300 K) is shown in Fig. 7. Although quantitatively higher by a few percent (as has been observed in other simulation-experimental studies on epoxy based polymer systems [12,17,18,14]), mass densities predicted by simulations agree qualitatively with those from experiments in that density decreases with the addition of methylene

Fig. 7. Density of DGEBA/AMAM_n systems as a function of alkyl chain length at 300 K, 1 atm.

units in the AMAM crosslinker. This decrease follows a linear relation with respect to the effective volume fraction of methylene units Φ_m , consistent with an ideal mixing approximation. That is, if one considers methylene units as solute and the rest of the polymer as solvent, then the mass density ρ of the DGEBA/AMAM_n system, according to ideal mixing, is given by,

$$\rho(\Phi_m) = \rho_0 + \Phi_m(\rho_m - \rho_0) \quad (3)$$

where ρ_0 and ρ_m represent the density of methylene-free polymer “solvent” and the density of methylene “solute” respectively. For a given DGEBA/AMAM_n system, the volume fraction $\Phi_m = \frac{V_n - V_0}{V_n}$, where V_0 is the system volume of DGEBA/AMAM₀ and V_n is the system volume of DGEBA/AMAM_n.

A fit of Eq. (3) to the densities from simulation is shown in Fig. 8. From this fit, the pure-component density of methylene units was estimated to be 0.85 g/cc. Unsurprisingly, the density of methylene units is substantially lower than that of methylene-free polymer (DGEBA/AMAM₀), and Eq. (3) therefore dictates that the density must decrease as Φ_m increases. It is to be noted that 0.85 g/cc is in the density range of low density polymers such as PEE (polyethylethylene) and PVE (polyvinylethylene) [39] whose chemical structures are primarily composed of repeating methylenes.

3.2. Effect of chain length on T_g

The T_g of crosslinked DGEBA/AMAM_n systems obtained from MD simulation and experiments is shown in Fig. 9. Both simulations and experiments show that increase in alkyl chain length have no influence on T_g in the crosslinked DGEBA/AMAM_n systems. The T_g obtained from simulations is higher compared to experiments due to high cooling rate employed in simulations. This can be corrected by subtracting a shift factor from the T_g obtained from simulations which is about 33–55 K [40]. The T_g obtained from simulations is then in good agreement with experiments after applying this correction.

Fig. 8. Density of the DGEBA/AMAM_n systems as a function of volume fraction of methylene units at 300 K, 1 atm. Line is a fit of Eq. (3) to the simulation data.

Fig. 9. Glass transition temperature T_g of the DGEBA/AMAM $_n$ systems as a function of alkyl chain length n .

Segmental relaxation is characterized using the autocorrelation function of the end-to-end vector of the AMAM $_n$ crosslinker molecules, defined by

$$c(t) = \frac{\langle \vec{R}_{ee}(t_0) \cdot \vec{R}_{ee}(t_0 + t) \rangle}{\langle R_{ee}^2 \rangle} \quad (4)$$

where $\vec{R}_{ee}$ is the distance vector joining the two ends of any AMAM $_n$. The function $c(t)$ was calculated for each of the DGEBA/AMAM $_n$ systems at 500 K ($\approx T_g + 100$ K), and results appear in Fig. 10. It can be observed that there is no significant difference in the segmental relaxation regardless of chain length. This is likely because the additional rotatable C–C bonds introduced by lengthening an AMAM $_n$ chain are not topologically inside the crosslinked network, and therefore lengthening them does nothing to reduced steric constraints on the crosslinks. It should be further remarked that if T_g were to decrease with increasing n it would result in increased segmental relaxation as observed in other epoxy [7] and non-epoxy based thermosets [10].

This lack of increased segmental flexibility in the face of increasing chain lengths could arise because the alkyl chains are isolated from each other and essentially pinned inside the dense thermoset. From the MD simulations of the crosslinked systems, *intermonomer* methylene-methylene radial distribution functions (RDF's) were computed; these are shown in Fig. 11. These data clearly show that there is no correlation in the arrangement of intermonomer methylenes, and that they are not forming microphase separated domains. This is consistent with the ideal mixing approximation already demonstrated and provides some additional molecular-level rationale for the T_g insensitivity.

Fig. 10. Autocorrelation of the end-end vector in the crosslinker molecule in the simulated DGEBA/AMAM $_n$ systems at $T_g + 100$ K, 1 atm. Uncertainties over samples are shown for $n = 0$ and $n = 10$.

Fig. 11. Intermolecular methylene-methylene radial distribution functions in each simulated DGEBA/AMAM_n systems at 300 K, 1 atm.

Fig. 12. Rubbery-state coefficient of volume thermal expansion α_r vs. alkyl chain length n in DGEBA/AMAM_n systems at 1 atm.

3.3. Effect of chain length on CVTE

The coefficients of thermal expansion of the rubbery state (α_r) and glassy state (α_g) of DGEBA/AMAM_n systems measured experimentally and computed from simulations are shown in Figs. 12 and 13, respectively, and all data are reported in Table 2. Both experiments and simulations agree that $\alpha_r > \alpha_g$ at each alkyl chain length n . Experiments do not show a clear trend and the simulations show only a weakly increasing α_r with n , with only a 25% increase from DGEBA/AMAM₄ compared to DGEBA/AMAM₁₀ (Fig. 12). Experiments and simulations both show weak increases in α_g with n (Fig. 13). As the number of $-\text{CH}_2-$ groups increases with alkyl chain length, it may result in increased sub- T_g motions that are associated with secondary relaxation (β -relaxation) process [41]. This might provide a possible reason for the increase in α_g with n . Simulations systematically underpredict both α_r and α_g . This may be due to the high cooling rate used in simulations or due to network imperfections in experimental polymer samples [42,43] which are otherwise absent in simulated polymer systems. It is worth mentioning that CVTEs obtained from MD simulations are mostly lower [12,17,18,14] but sometimes in close agreement [44,45] or even higher [46] compared to experiments.

The relationship between CVTEs (α_r, α_g) and n obtained from simulations is consistent with the ideal mixing rule defined by

$$\alpha_{r,g} = \alpha_{0r,g} + \Phi_m(\alpha_{mr,g} - \alpha_{0r,g}) \quad (5)$$

where $\alpha, \alpha_0, \alpha_m, \Phi_m$ represents the thermal expansion coefficient of DGEBA/AMAM_n system, thermal expansion coefficient of the methylene-free polymer, the thermal expansion coefficient of the methylene and the volume fraction of the methylenes

Fig. 13. Glassy-state coefficient of volume thermal expansion α_g vs. alkyl chain length n in DGEBA/AMAM $_n$ systems at 1 atm.

Table 2

Coefficients of volume thermal expansion in the rubbery state (α_r) and the glassy state (α_g) of crosslinked DGEBA/AMAM $_n$ systems at 1 atm.

n	$\alpha_r \times 10^{-4} \text{ (1/K)}$		$\alpha_g \times 10^{-4} \text{ (1/K)}$	
	Simulation	Experiment	Simulation	Experiment
0	3.184 ± 0.188	–	1.437 ± 0.025	–
2	3.317 ± 0.157	–	1.647 ± 0.025	–
4	3.376 ± 0.138	6.00 ± 0.096	1.708 ± 0.018	2.25 ± 0.18
6	3.702 ± 0.182	6.27 ± 0.408	1.746 ± 0.038	2.37 ± 0.075
8	3.910 ± 0.075	6.60 ± 0.624	1.986 ± 0.052	2.79 ± 0.10
10	4.220 ± 0.134	6.12 ± 0.099	2.076 ± 0.040	2.64 ± 0.015

in the polymer system respectively. The fit of Eq. (5) to the simulation data is shown in Fig. 14. The value of α_{mr} and α_{mg} were estimated to be $7.4 \times 10^{-4} \text{ 1/K}$ and $4.15 \times 10^{-4} \text{ 1/K}$ respectively. The thermal expansion coefficients of methylenes is significantly higher compared to the thermal expansion coefficients of DGEBA/AMAM $_0$. This is expected as low molecular weight additives tend to have high thermal expansion coefficients [11] and therefore Eq. (5) stipulates that α must increase as Φ_m increases, however, the increase is not significant as observed here. Both α_r and α_g are in good agreement with the ideal-mixing approximation. This agreement is a consequence of methylene units being well dispersed and the absence of correlation among the methylene units in the polymer system (Fig. 11).

Fig. 14. Coefficient of volume thermal expansion of DGEBA/AMAM $_n$ systems as a function of volume fraction of methylene units at 1 atm. Line is a fit of Eq. (5) to the simulation data.

4. Conclusions

Amidoamine (AMAM_n) crosslinkers with pendant alkyl chains of four different lengths ($n = 4, 6, 8$, and 10) were synthesized and cured with DGEBA to generate novel crosslinked thermosets. In addition, MD simulations were used to study model DGEBA/AMAM_n systems for $n = 0, 2, 4, 6, 8$, and 10 . Satisfactory agreement between simulations and experiments was observed for densities, glass transition temperatures, and coefficients of volume thermal expansion. The trend in density and CVTE with n followed an ideal-mixing approximation based on partitioning into solvent polymer and solute alkyl chains fairly robustly, which was further corroborated by the lack of methylene-methylene correlations seen in radial distribution functions. However, it was found that T_g was largely insensitive to n . This indicates that although the pendant alkyl chains affect density and CVTE, they do not plasticize these thermosets. This observation was further corroborated by end-to-end autocorrelation functions of the AMAM_n monomers from MD which indicated no increase in segmental flexibility with n . These findings are relevant for the design of novel crosslinking molecules in thermosets where alkylation is anticipated to both lower density and potentially improve moisture barrier properties without compromising T_g or α , and suggests that pendant alkylation is a desirable approach.

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