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

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ABSTRACT

The effects of pendant alkyl chain length n ranging from $n = 0$ to $n = 10$ in amidoamine crosslinkers on mechanical properties of epoxy thermosets are explored in this work. The glassy-state Young's modulus was estimated using non-equilibrium molecular dynamics (MD) simulations and compared with experiments. Both simulations and experiments showed that Young's modulus decreases with increase in n. Stress partitioning based on molecular interaction types showed that both Lennard-Jones and covalent bond interactions were responsible for this sensitivity, with Coulombic interactions playing no significant role. The dependence of Young's modulus on n was strain-rate dependent in the simulations, with moderate to high strain rates showing no sensitivity. A strong correlation was observed between Young's modulus from non-equilibrium MD and volume fraction of methylenes estimated from equilibrium MD. Poisson's ratios of all systems predicted from the simulations were insensitive to n, indicating a lack of anisotropy. The information revealed here on the roles of various intermolecular interactions on the mechanical properties of these thermosets could be useful for design of crosslinkers.

1. Introduction

Thermoset coatings are typically used in environments that are subject to extreme temperatures, corrosion and/or mechanical stress [1]. Mechanical failure of coatings coupled with corrosion can lead to severe degradation and loss of material [2–4]. Any coating's response to mechanical stress is critical in determining its durability and reliability [5]. Control of properties and performance of thermoset coatings by chemical modification of monomers largely relies on empirical experience [6] rather than on a deep understanding of how intermolecular interactions dictated by structure and composition give rise to these properties. Therefore, it is imperative to better understand the inherent molecular interactions involved in the deformation mechanism of coatings in order to design and overcome several limitations of contemporary coating formulations.

Amidoamine (AMAM) crosslinkers are advanageous in epoxy-based thermoset coatings for their corrosion inhibition and moisture resistance compared to polyamines [7,8]. An important aspect in the molecular structure of these crosslinkers is the presence of pendant n-alkyl chain substituents. Evidence from experiments and molecular dynamics simulations have shown that increasing the alkyl chain length decreases the density and increases the thermal expansion coefficient, but does not influence the glass transition temperature of the thermoset [9]. It has also been shown from experiments that the crosslink density and room temperature storage modulus decreases with increase in alkyl chain length [10]. However, it remains unclear whether or not chain length influences other mechanical properties such as the Young's modulus and Poisson's ratio of these thermosets. It is known that Young's modulus is related to crosslink density based on statistical theory of rubber like-elasticity [11,12]. Although commonly used by experimentalists to estimate crosslink density, these models do not take into account all the molecular interactions involved in crosslinked thermosets [13] during deformation, nor are they strictly applicable to glassy systems, and are therefore of limited value in the molecular design of such materials. Molecular dynamics simulations (MD) are useful in this regard.

MD simulations have been used in the past [14–21] to explore the effect of thermoset morphology on various mechanical properties. In particular, MD can help in the identification of key intermolecular interactions that affect the mechanical properties by enabling one to partition the total stress or energy into its components which otherwise cannot be obtained from experiments. For example, in BOF/DFDA (2,5-bis[(2-oxiranylmethoxy) methyl]-furan/5,5-methylenedifurfurylamine) and BOF/CH_3-DFDA thermosets [14], stress partitioning revealed that angle interactions influence the Young's modulus more strongly than coulombic interactions. In DCPD(dicyclopentadiene)/epoxy

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thermosets, energy partitioning helped to show that strong interactions induced by hydrogen bonds improve the modulus and yield strength [20]. MD simulations were also used to study and identify the relevant molecular interactions that influence the mechanical properties of thermoplastics such as polyethylene [22,23], polyamides [24–27] and polystyrene [28].

In the present work, the effect of pendant alkyl chain length in amidoamine crosslinkers on mechanical properties of thermosets is studied. Qualitative agreement on the effect of n on Young's modulus between MD simulations and experiments motivates a deeper investigation of the contributions to material stress at the molecular level. The correlation between equilibrium and non-equilibrium molecular-level properties extracted from the MD simulations is also considered, illustrating one way to predict non-equilibrium response based on an equilibrium state in this series of highly crosslinked thermoset materials. The experimental and simulation methodology are described first followed by analysis of simulations results.

2. Methods

2.1. Experimental

The chemical structures of the epoxy monomer, diglycidyl ether bisphenol A (DGEBA) and AMAM$_n$ crosslinkers used in this work are shown in Fig. 1, where n is the alkyl chain length. AMAM crosslinkers with chain length $n = 0$ and $n = 2$ could not be successfully synthesized. The four crosslinkers that were successfully synthesized [9] were then individually cured with stoichiometric amounts of DGEBA. Inspecting the FTIR spectra of samples indicated a complete conversion of epoxies, primary amines and secondary amines.

The Young's modulus of each post-cured DGEBA/AMAM$_n$ system was then measured by conducting tensile tests in accordance with ASTM D-638 standard test method [29] using a universal testing machine (UTM, Instron 8832). Tensile tests were performed on dumbbell-shaped samples (type IV) of all the samples of DGEBA/AMAM$_n$ systems. Samples were tested at ambient conditions using an extensiometer to measure strain with a constant cross-head speed of 1 mm/min and a gauge length of 45 mm. For each formulation, at least six specimens were tested and analyzed.

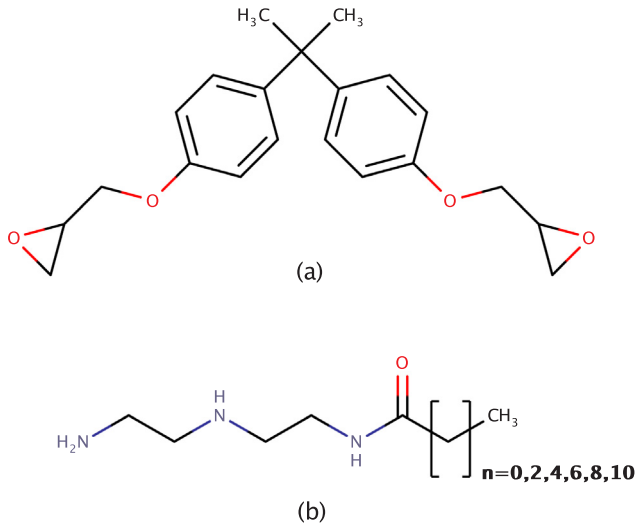

Fig. 1. Chemical structures of (a) DGEBA and (b) AMAM$_n$,n is the alkyl chain length.

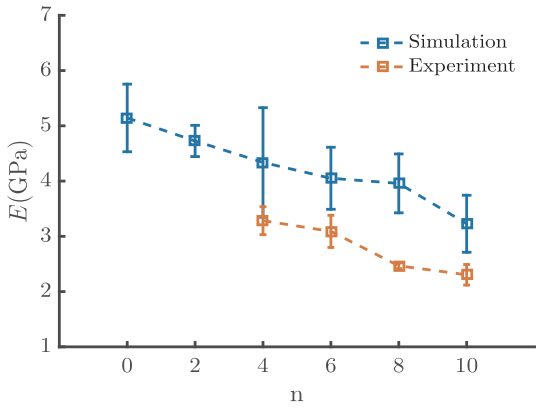

Fig. 2. Young's modulus vs. n from simulation and experiment.

2.2. Simulation

2.2.1. System description

A total of six crosslinked DGEBA/AMAM$_n$ system compositions were considered in this study. Five independent replicas of each system composition with 100% conversion were generated using the incremental capture radius crosslinking algorithm [9]. Each replica consisted of 192 DGEBA molecules and 128 crosslinker molecules of a particular chain length before crosslinking. The DGEBA/AMAM$_n$ systems were heated to 500 K and annealed to 300 K at a rate of 7.5×10^9 K/s. The annealed systems at 300 K were subsequently used in non-equilibrium MD (NEMD) simulations to estimate mechanical properties. To estimate the Young's modulus E and Poisson's ratio ν, each replica was subjected to three independent uniaxial tensile deformation in x, y and z directions by imposing a constant engineering strain rate ($\dot{\epsilon}$) of 10^7 s^{-1}. The dimension L along the deformation direction was calculated as

$$L(t) = L_O(1 + \dot{\epsilon}\, dt) \tag{1}$$

where L_O,dt represent the original length before deformation and the timestep respectively. A thermostat was used and zero pressure was maintained in the transverse directions. It is important to point out that particle positions were not scaled to enforce the strain; only the box dimension is changed.

2.2.2. Estimation of mechanical properties

The Young's modulus E is given by

$$E = \frac{d\sigma}{d\,\epsilon}|_{\epsilon=0} = \frac{\Delta\sigma}{\Delta\,\epsilon} \tag{2}$$

where σ ,ϵ is the normal stress and the normal strain in the direction of deformation. The normal stress can be partitioned into components based on molecular interactions,

$$\sigma = \sum_i \sigma_i \text{ and } i = \{\text{LJ,C,cov,ke}\}. \tag{3}$$

where σ_{LJ},σ_C,σ_{cov},σ_{ke} are the normal stress due to Lennard-Jones (LJ), Coulombic, covalent and kinetic energy interaction types, respectively. The covalent interactions include the bond, angle and dihedral interactions.

Therefore,

$$E = \sum_i E_i = \sum_i \frac{\Delta\sigma_i}{\Delta\,\epsilon} \tag{4}$$

where E_i is the ith component of E and signifies the contribution due to a specific interaction type. These components can be viewed as an estimate of the load-bearing capacity of each interaction type. For example, stretch in hydrogen bonds (if present in the system) during deformation would be reflected in high values of E_C. Any conformational changes