Free volume evolution in the process of epoxy curing and its effect on mechanical properties

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A B S T R A C T

We use molecular dynamics simulations to study the evolution of free volume during the process of curing of two thermoset epoxy polymers and correlate its volume fraction with the resulting thermo-mechanical properties. The simulations reveal that while the overall volume of the polymer shrinks during cure, the amount of free volume *increases*. Interestingly, this increase is due to the appearance of large voids (connected regions of free volume) while the number of small and medium-sized voids decreases during cure. We also find correlations between the location of the voids and the local chemical structure of the polymer. An analysis of the individual nanovoids shows a power-law scaling for over three orders of magnitude in volume (0.1 Å^3 to 100 Å^3) and a fractal scaling in surface with a fractal dimension ~2.37. The effect of free volume on mechanical properties is also quantified. A very small reduction in the free volume fraction (~1%) results in considerable (>10%) stiffening and strengthening.

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1. Introduction

Highly crosslinked epoxy thermoset polymers are extensively used in industries ranging from aerospace and automotive to energy and electronics because of their desirable properties for processing and thermo-mechanical performance [1]. The properties of these materials are dictated not only by their composition, but also by their processing-dependent network architecture and annealing conditions. Thus, there is significant interest in establishing chemistry, processing, structure, property relationships for these materials. This is important from an application point of view, as such knowledge would enable the effective design of optimized chemistries and processing conditions for specific applications. At the same time, the complexity of the problem makes a predictive understanding of chemistry-processing-property in polymeric materials of great interest in basic science [2—4].

Significant efforts have been devoted to understanding the relationship between network architecture in thermosets and their properties. For example, the effect of crosslink density on thermal and mechanical properties of thermosets have been characterized experimentally and via molecular simulations [5—7]. Yet, molecular architecture is not the only important microstructural feature as is

well known that different annealing procedures of the cured material can result in vastly different properties. In this paper we use large scale molecular dynamics (MD) simulations to characterize the effect of curing and annealing on the evolution of free volume in two thermosetting epoxies and how free volume affects the thermo-mechanical properties of thermoset polymers. Significant efforts have been devoted to study free volume in amorphous polymers, yet little is known about how curing affects the distribution of voids in thermosets and how these voids affect their properties.

Several techniques have been used to characterize free volume experimentally. Differential scanning calorimetry (DSC) can be used to estimate the temperature dependence of free volume change but can only give relative free volume. Positron annihilation lifetime spectroscopy (PALS) provides a more direct measure of free volume distribution in molecular materials. However, interpreting PALS data is not trivial nor without assumptions. The models used to relate lifetimes to free volume assume simple 3D void geometries and are based on simplified quantum mechanical models of the interaction of the positronium atom with the electron density surrounding the void [8]. Molecular simulations can evaluate free volume distribution with less ambiguity, see for example Ref. [9]; however the results depended on the accuracy of the models used.

Numerous studies have focused on comparing free volume predictions from PALS and molecular simulation [10—12]. Hofmann et al. compared experimental and simulation results of free volume

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distribution for various polymers, including poly(1-(trimethylsilyl)-1-propyne) and derived polymers [13] as well as polyimides [14]. They studied different possible definitions of void to analyze the molecular simulations and found qualitative, but not quantitative, agreement with experiments. More recent work compared four experimental techniques (including PALS) and molecular simulations for free volume distribution in amorphous glassy perfluoropolymers [15]. Again the authors find only quantitative agreement between the experiments and theoretical predictions. The discrepancies have multiple possible origins, including inaccuracies in the molecular models (e.g. poor equilibration of the amorphous structure) and assumptions made in the interpretation of experimental data. In PALS, ortho-positronium lifetimes are related to void volume using the lifetimes in vacuum and quantum mechanical models that assume spherical volumes and simplify the interaction between the positronium atoms and the electronic density surrounding the void [8]. To remove some of these ambiguities, Schmitz and Muller-Plathe performed quantum mechanical calculations of positronium lifetimes using actual atomistic structures obtained from MD [16]. Even in this case the predicted and observed timescales differ quite significantly.

Compared with thermoplastics less work has focused on thermosets. Early studies were stimulated by the contradictory reports on packing density, which is related with van der Waals volume, of amine-crosslinked epoxy network. Bellenger et al. [17] first studied the pack density of various epoxy-amine networks and compared it with those of linear polymers and concluded that packing density increases with crosslink density. But a more comprehensive characterization made by Gupta and Brahatheeswaran [18] found that good molecular packing for highly crosslinked epoxy networks occurs only above glassy transition temperature and polymers with higher crosslink density tend to have relatively higher free volume at glassy state because of the lacking of suitable environment for close packing at crosslink sites. Using PALS, Jean et al. [19] measured free-volume hole sizes and fractions in a series of thermosets and reported that an increase in chain length of the curing agents leads to an increase of free-volume fraction. Also using PALS, Dlubek et al. [20] investigated the free volume of poly(diethylene glycol bis(allyl carbonate)) polymer networks and found an increase in free volume with increasing crosslink density, however the crosslinking was controlled via changes in composition and, thus, the origin of the increase in free volume cannot be unambiguously determined. Further studies of Dlubek et al. [21] examined the microstructure of free volume and its temperature dependence in epoxy resin diglycidyl-ether of bisphenol A (DGEBA) but their focus was on uncured resins. In studying moisture diffusion, Wunderle et al. [22] estimated the total free volume in a bisphenol-A/diaminoethane epoxy resin based on the Bondi method [23] from atomistic models and compared with PALS measurements. Altaweel et al. [24] measured free volume by PALS in attempt to understand the effect of amine-containing poly dimethylsiloxanes (ACS) as modifier on DGEBA resin. More recently, Knorr et al. [25] compared the ballistic performance of polymeric dicyclopentadiene (pDCPD) with two DGEBA/diamine systems to get better strength-toughness trade-off encountered with conventional crosslinked polymers and suggested that void formation and growth might play an important role in the pDCPD advantages over epoxy resins. In agreement with the experiments of Dlubek et al. [20,21] our simulations show that free volume fraction indeed increases during cure and that this increase originates due to the appearance of relatively large voids caused by the strain associated with the formation of the 3D network. In addition, the simulations show that a relatively minor reduction in free volume fraction can lead to significant stiffening and strengthening.

The remainder of the paper is organized as follows. Section 2

describes the systems of interest and gives a briefs of the crosslinking procedure and the evolution of network topology. Section 3 describes the algorithm for calculating free volume and the evolution of free volume during cure. Section 4 correlated free volume with mechanical properties and discussions and conclusions are given in Section 5.

2. Simulation and materials details

We focus on two epoxy systems, diglycidyl-ether of bisphenol A (DGEBA) with 3,3′-diaminodiphenyl sulphone (33DDS) and diglycidyl-ether of bisphenol F (DGEBF) with Diethyltoluenediamine (DETDA), as shown in Fig. 1. Most results are shown for DGEBA/33DDS as in most cases DGEBF/DETDA exhibits similar trends. The simulations start from uncured resins with the desired composition (1:1 stoichiometry) and we use the MD polymerization simulation (MDPoS) method, which enables large-scale polymerization simulations using a distance-based criterion for chemical reactions with an efficient charge updating approach, to mimic the curing process [26,27]. All MD simulations are performed using open-source software package LAMMPS [28] and the Dreiding force field [29] to describe atomic interactions.

2.1. Crosslinking simulations

The crosslinking simulations are performed with perfect stoichiometries; in the case of the bifunctional epoxies with curing systems containing two amines, twice as many epoxy molecules as crosslinkers can lead, in principle, to 100% conversion. The initial model system is built packing both activated epoxy and crosslinker monomers into a simulation cell followed by a structural relaxation using MD. Both systems have approximately 65,000 atoms: 1024 DEGBA molecules combined with 512 33DDS and 1024 DEGBF with 512 DETDA. MDPoS mimics the polymerization by periodically creating bonds between pairs of reactive atoms using a distance criterion (with a cutoff equal to four times of the equilibrium N—C bond length of 1.41 Å). After the new set of bonds is fully relaxed by a 50 ps long five-step relaxation procedure, the system is thermalized for an additional 50 ps before next round bond creation. This crosslinking procedure is carried out at 600 K until either a conversion limit or a simulation time limit is reached. The crosslinked system is then cooled down to 300 K by a cooling rate 10 K/60 ps.

2.2. Chain topology

The epoxy and crosslinker monomers of interest have relatively low molecular weights. They gradually form a 3D network structure as the crosslinking chemical reactions proceed. We recently developed an algorithm to identify and classify each segment in the polymer network. Each segment is classified into three possible groups: i) crosslinked chain that start and end at crosslinks (fully reacted amine N), ii) dangling chains with only one end at a crosslink and iii) free chains [30]. At high conversion degrees, most of crosslinked, dangling and free chains consist of a single molecule and only a very small percentage of the polymer forms longer chains, consisting of multiple monomers. Fig. 2 shows the evolution of the fraction of the total molecular weight in crosslinked, dangling and free chains. We find that the number of unreacted free ends (including both free chains and dangling chains) decreases (almost linearly) with increasing conversion degree but, interestingly, even at 85% conversion over 20% of the molecular weight remain in free or dangling chains, with free chains representing just over 10%. Because only non-covalent bonds surround free ends, it has been speculated that these free ends potentially become