

Molecular modeling of epoxide-amine systems: Topological cure conversion limit and its influence on material properties



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ABSTRACT

The cure conversion is a key determinant of the characteristics of many thermosetting polymers. Their curing process can be monitored using experimental tools such as FTIR and DSC; however, these techniques can only provide a qualitative measure of the extent of curing reaction rather than a quantitative determination of cure conversion. In fact, the actual cure conversion in epoxy systems is not known. Many molecular simulation works assume that the cure conversion limit approaches 100% although it is unrealistic. In this work, a parametric study based on model size and a radial distribution function (RDF) of relevant functional groups reveals that a topological cure conversion limit may exist and is estimated to be about 70% for a typical epoxide-amine system based on the chosen force field and simulation conditions. Beyond this, atoms within the model may form isolated clusters and the molecular model fails to converge to an equilibrated topology with structural homogeneity. It is found that the predicted dependencies of thermal and mechanical properties on cure conversion are in concurrence with accepted norms and only show deviation when the cure conversion exceeds the limit.

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1. Introduction

Epoxide-amine epoxy is a family of thermosetting polymers characterized by complex crosslinked networks. The properties of epoxy systems are significantly determined by these irregular crosslinked networks. The nature of these networks depends on many factors such as the chemistry of resin and hardener, their stoichiometric ratio and curing conditions.

Experimental techniques such as Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) are commonly used to monitor the physical change in resin-hardener compound in terms of the extent of conversion X [1–10]. In FTIR, the changes in spectral features, such as the intensity of the epoxide group are utilized to calculate the extent of conversion using the following:

$$X = 1 - \frac{\left[\frac{A_{\text{Epoxide},t}}{A_{\text{Reference},0}} \right]}{\left[\frac{A_{\text{Epoxide},0}}{A_{\text{Reference},t}} \right]} \quad (1)$$

where $A_{\text{Reference},0}$ and $A_{\text{Reference},t}$ refer to the areas of the internal reference peak readings in the FTIR spectra chart at a reference time

and after a certain time (t) respectively. $A_{\text{Epoxide},0}$ and $A_{\text{Epoxide},t}$ are the areas of the peak readings for the epoxide groups for uncrosslinked system and the same system after a certain curing time, respectively [1–4]. Another common technique is DSC, which monitors the heat flow within a sample when subjected to a specified thermal profile. There are two ways to calculate X from DSC measurements. One way is to divide the heat released $(\Delta H)_t$ from the sample up to a time t by the total reaction heat ΔH_0 [5–7] as follows:

$$X = \frac{(\Delta H)_t}{\Delta H_0} \quad (2)$$

The other way is the DiBenedetto calorimetric method [4,8–10]. The T_g is firstly measured and then used to calculate the in-situ X in a reverse way as follows:

$$\frac{T_g - T_g(0)}{T_g(\infty) - T_g(0)} = \frac{\lambda X}{1 - (1 - \lambda)X} \quad (3)$$

Here, $T_g(0)$ is the glass transition temperature of uncured system, $T_g(\infty)$ is the glass transition temperature of the system after curing, λ is the ratio of the heat capacity step (ΔC_p) of the fully cured to that of uncured resin.

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However, a qualitative description of the curing progress by these above experimental techniques cannot provide a quantitative measure of what percentage of functional groups are involved in crosslinking reactions, i.e., a unity value for X does not mean all the reactive sites are crosslinked together. It has been reported that complete crosslinking is likely impossible to achieve due to the inherent molecular topology [4,11–14]. In this work, cure conversion α is defined as the percentage of reacted functional groups to distinct it from the extent of conversion X obtained from experimental measurements.

Taking the epoxide-amine system as an example, the cure conversion α is defined as the ratio of the number of reacted epoxide groups to the number of total epoxide groups. It has a range from 0 to 1 depending on the percentage of reacted functional groups. As mentioned, experimental techniques are unable to give an indication of the maximum attainable value of α ; yet, this value of upper topological cure conversion limit is important in the building of physically realistic models in numerical simulations.

Cure conversions over a broad range have been adopted in many molecular dynamics (MD) simulations [15–21]. For example, Yarosky and Evans [15] studied low molecular weight and water soluble epoxies with $\alpha = 50\%$, 70% and 100% . Wu and Xu [16] investigated a DGEBA + IPD system with α up to 93.7% using relatively small models. Clancy and coworkers [17] studied the effects of cure conversion, moisture content and temperature on the properties of a widely used epoxy system and the α adopted in their simulations was in the range from 38% to 86% . Vikas [18,19] did a systematic study on EPON-862 + DETDA and reported α values of as high as 95% . Holck [20] studied the interface between crosslinked epoxy and silica using α of 90% . More recently, Bandyopadhyay and Odegard studied the influence of the crosslinking distribution on the thermo-mechanical properties using models with α from 54% to 76% [21]. Although MD simulations have been extensively conducted to investigate the structure-property relationship of epoxy systems, little has been done to determine what values of cure conversions should be adopted in order to build models that represent actual physical systems. Determining a reasonable range of cure conversion for the epoxy is a prerequisite for predicting their material properties.

In this work, an iterative crosslinking algorithm was employed to build randomly crosslinked networks of an epoxide-amine system of various cure conversions up to 100% . A parametric study on model size and a radial distribution function (RDF) analysis are used to demonstrate the existence of a topological cure conversion limit. The thermal and mechanical properties of the epoxide-amine system are calculated for models over a large range of cure conversion to show the dependence of material properties on cure conversion.

2. Models and simulation details

The resin is diglycidyl ether of bisphenolA (DGEBA) and the hardener is diethylenetoluenediamine (DETDA). The molecular

models are shown in Fig. 1. Only the reactions between the epoxide and amine groups are considered following previous works [16,18,19]. The primary amine in the hardener may become a secondary or tertiary amine depending on the number of hydrogens replaced by other groups. The primary and secondary amines are assumed to have equal reactivity with epoxide groups. Periodic cells of resin and hardener mixture are built using the Amorphous module and the crosslinking process is carried out using the Perl program, an embedded scripting language in Materials Studio 4.3 [22].

In the course of crosslinking, results are stored at intervals of $\alpha = 0.1$ for analyses. The simulations are carried out using LAMMPS [23]. All the models with various α are equilibrated under NVT for 2 ns and further relaxed under NPT for 5 ns using a time step of 1 fs. The MD simulations of the epoxy system are performed using the Consistent Valence Force Field (CVFF) [24]. The suitability of CVFF for epoxy has established by previous simulation works [18,19,25,26]. The temperature and pressure are controlled using the Nose-Hoover thermostat and barostat, respectively. The cutoff distance for van der Waals and electrostatic forces is set at 10 \AA . Long range Columbic forces are treated by the particle-particle-particle-mesh (PPPM) technique.

3. Crosslinking process

The framework for building crosslinked networks based on updating the covalent bonds involved in the chemical reactions between the functional groups has been demonstrated in earlier works [15–21]. Initially, a certain number of resin and hardeners molecules are randomly placed inside a periodic cell and the system is equilibrated to eliminate any unphysical topology generated during the placing process. The epoxide and amine groups are identified as reactive sites and their positions are recorded. Each epoxy and amine group is defined as a reactive pair and the distance between these two groups is defined as the reaction distance. All the reaction distances are compared and the reactive pair with minimum reaction distance is targeted for the crosslinking reaction, i.e., the formation of corresponding chemical bonds, after which the molecular topology is updated. The system is subjected to energy minimization to relax the newly formed topology before proceeding to next reaction iteration.

There are two common strategies for building models to achieve a pre-determined cure conversion. Either a target α [15] or a maximum reaction distance [16–18,27–29] for them to form bonds is specified. In the first approach, the crosslinking procedure continues until the target α is attained. While simple to implement, the target α is usually arbitrarily assigned as actual values are unknown. The second option is based on a termination criterion of the reaction distance between potential reactive sites of the epoxide group and amine group. The distances of all potential reactive pairs are calculated every iteration. If they are larger than the specified termination reaction distance, the crosslinking process is stopped.

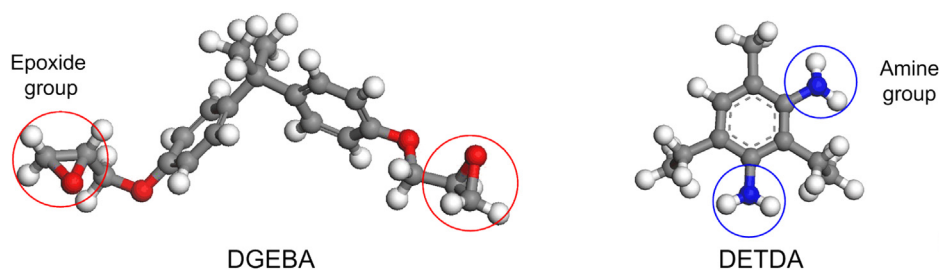


Fig. 1. Molecular structures of epoxy resin (DGEBA) and curing agent (DETDA). Atoms: Gray(C), White (H), Red (O), Blue (N). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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