



Coarse-grained molecular dynamics modeling of reaction-induced phase separation

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ARTICLE INFO

Article history:

Received 14 March 2018

Received in revised form

18 June 2018

Accepted 23 June 2018

Available online 26 June 2018

Keywords:

Phase separation

Chemical reaction

Coarse-grained

Correlation function

ABSTRACT

We develop a model to describe reaction-induced phase separation in thermoplastic-toughened thermoset polymers at molecular scales. To achieve the temporal and spatial scales required for phase separation we use coarse-grained molecular dynamics where beads represent bi-functional epoxy, a diamine crosslinker and monomers in the thermoplastic. The model describes the curing of the thermoset using a distance criterion to identify chemical reactions on the fly during a molecular dynamics simulation. We characterize how composition, curing temperature and conversion degree affect the onset of phase separation and domain growth. The onset of phase separation in terms of degree of cure depends on cure temperature and the subsequent growth of domain size during cure can be described with two power laws. Interestingly, the domain size vs. time following quenching after cure also follows power-law behavior but with exponent of approximately $\frac{1}{4}$, lower than those observed in simple binary mixtures and linear chain polymers.

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1. Introduction

Epoxy resins are widely used as matrix in composites for structural applications. They have many advantages over other polymers, such as high stiffness and strength, good thermal stability, high water resistance, low cure shrinkage and ease of processing. However, their application is restricted by their very low fracture toughness, typically below $1 \text{ MPa m}^{1/2}$ [1]. High crosslinking density increases stiffness in most epoxy resins but tends to decrease the fracture toughness [2]. As a result, numerous efforts have focused on engineering toughening mechanisms on these materials [3–5]. An effective approach is inducing a second phase that helps hinder crack propagation by adding thermoplastic polymers into the epoxy resin [6]. The mixture is usually in a homogeneous, single-phase state before curing of the thermoset. During the crosslinking process, the molecular weight of the epoxy gradually increases leading to an increase of the free energy of the mixture relative to that of the two-phase system. This can eventually lead to phase separation. Depending on the composition of the blend and curing conditions, the final morphology of a phase separated polymer mixture is a result of two competing processes:

the chemical crosslinking reaction and the phase separation during curing. The phase separation in such a system is termed as reaction-induced phase separation (RIPS). The increase in toughness over the pure epoxy resins depends on the phase morphology: volume fraction, domain size and phase structure [7,8]. A fundamental understanding of RIPS is, thus, of great interest from an applied science point of view to design optimal processing conditions to achieve desired morphologies and properties. As we will describe next, open basic science questions also remain regarding RIPS.

While the fact that fracture toughness can be significantly improved with bicontinuous or phase-inverted morphologies is well established [9] and that characteristic size of the toughening phase in the order of micrometers is desirable [10], the optimal microstructure is not known. Furthermore, given a desired morphology, the processing route to achieve it can only be determined today by experimental trial and error and expert opinions based on similar systems. Thus, optimizing toughness of epoxy/thermoplastic mixture requires lengthy experimental effort which could be reduced via predictive simulation tools and a fundamental understanding. Our work aims at contributing towards this goal by establishing general relationships between processing and microstructure development during RIPS.

Computer simulations using both continuum and particle-based approaches have been used to study RIPS since the 1990s. For example, Ohnaga et al. [11] used the nonlinear Cahn-Hilliard

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equation and Flory-Huggins free energy equation to describe phase separation phenomena in thermoset/thermoplastic mixtures. Tanaka et al. [12] proposed a modified version of the linear Cahn-Hilliard equation in the form of a reaction-diffusion equation. Chan and Rey [13,14] also modeled RIPS with the nonlinear Cahn-Hilliard and Flory-Huggins equations but with a second order of rate equation to describe the process of curing. Liu et al. [15] studied RIPS of ternary mixtures based on a modified time-dependent Ginzburg-Landau equation. Based on a similar time-dependent Ginzburg-Landau equation, Zhang et al. [16] studied the spinodal decomposition by the coupling of polymerization and crosslinking reactions. Herderson and Clarke [17] studied pseudo-interpenetrating polymer networks in polydisperse polymer blends using a modified version of Cahn-Hilliard equation combined with the Flory-Huggins theory. While these numerical simulations brought some insights into the interaction between chemical reaction and phase separation as well as the formation of morphology, the results are mostly limited to two dimensions and based on approximate expressions for the free energy of each phase and their kinetics. On the other hand, researchers have made some efforts using molecular simulations for the RIPS studying. Jo et al. [18] considered the effect of crosslinker reactivity on the phase structure of sequential interpenetrating polymer networks using Monte Carlo simulations. Dumont et al. [19] used molecular dynamics (MD) to calculate the diffusion coefficients of thermoplastics and epoxy precursors to understand the molecule mobility but did not consider resin crosslinking in their model. Lee [20,21] studied the kinetics of microphase separation in the forming process of a polymer dispersed liquid crystal by MD simulations using Lennard-Jones particles. The results of the time-evolution of the structure factor indicated the growth of liquid crystal droplets follows a power law scaling. Toxvaerd [22,23] performed MD simulations on two-dimensional binary mixtures with simple chemical reactions that change a particle from one specie to another or merge two particles of different species into a particle of third specie and showed a larger reaction rate results in a smaller domain size. Krishnan and Puri [24] also performed MD simulations on binary mixture with simple chemical reaction that change one specie into another randomly, but in three dimensions. They found that not only the average domain size shows a power-law dependence on reaction time but also the equilibrium length in steady state follows a power-law scaling with the reaction rate.

The phase separation of liquid mixtures is often characterized by three different growth regimes: diffusive regime, viscous regime and hydrodynamic regime [25,26]. The growth rates in these regimes are very different but all show power-law scaling between domain size and time. Some molecular simulations have observed similar scaling phenomenon for binary or ternary mixtures [27,28], but the existence of power law scaling during RIPS or for branched polymers has not been established. Additional questions remain to be answered. For example: At what crosslinking degree does phase separation begin? How does composition affect the onset of RIPS process? What is the role of the curing temperature and reaction rate in RIPS? How does the domain size or phase structure depend on crosslinking degree? Any scaling phenomena related to the crosslinking degree? Our objective is to provide answers to some of these open questions. We simulate the RIPS by a coarse-grained MD model designed to mimic an epoxy resin and thermoplastic mixtures. Various processing conditions in the practical curing for epoxy resins will be examined.

2. Coarse-grained model for a RIPS system

We start the simulations with a mixture of the uncured epoxy resin and a linear thermoplastic, all described via coarse-grained

particles and we model the process of crosslinking. The model is composed of three types of molecules: particles **E**, representing the bifunctional epoxy, particles **X** representing a tetrafunctional crosslinker such as a diamine, and particles **TP** representing monomers in linear thermoplastic chains. Epoxy and crosslinker molecules are considered as the first phase and they react with each other to form a thermoset polymer network. The linear thermoplastic chains are nonreactive and considered as the second phase. Our purpose is to understand the fundamental mechanisms of phase separation during cure of a network forming epoxy mixed with a linear polymer and opposed to the details of specific systems. Thus, non-bond interactions are described with the Lennard-Jones potential with the identical parameters (energy and distance) for all interactions, including like and unlike particles. All coarse-grained particles have equal masses. Epoxy particles **E** can form up to two bonds with crosslinker particles. Particles **X** can form up to four bonds with other epoxy particles. The molecular weight of the thermosetting phase increases during cure but the thermoplastic phase remains composed of particles. This mixture represents an epoxy resin mixed with low molecular weight thermoplastics as toughening phase. Molecular simulations of systems with longer thermoplastic chains would be valuable and deserve study.

We will use Lennard-Jones dimensionless units throughout the paper, i.e., distance is measured in units of $x^* = x/\sigma$, density in $\rho^* = \rho\sigma^3$, energy and temperature in $U^* = U/\epsilon$, $T^* = Tk_B/\epsilon$ and time in $t^* = t(\sqrt{\epsilon/m}/\sigma)$. The bond interaction between **E** and **X** beads in the thermoset and thermoplastic are described by a simple harmonic form $U_b = k_b(r - r_0)^2$ with bond parameters obtained by matching the LJ potential equilibrium distance and curvature at the minimum, resulting in $k_b = 40$, $r_0 = 1.12$. Harmonic angle terms $U_a = k_a(\theta - \theta_0)^2$ are used to control the shape of the liner thermoset ($\theta_0 = 180^\circ$) and network ($\theta_0 = 109^\circ$), with a very small stiffness ($k_a = 0.001$). No four-body terms are included. We use a time step of $0.0005 t^*$ to integrate the equations of motion. All simulations are performed in parallel using the open-source software package LAMMPS [29] on computing facilities at Purdue University.

Three different compositions with the number ratio: **E:X:TP** = 16:8:2, 14:7:5, 8:4:14 are simulated. The purpose of this number ratio choice is to keep the epoxy and crosslinker particle in 2:1 ratio for perfect stoichiometry to potentially reach 100% crosslinking. Each thermoplastic chain contains one TP particle. The total number of particles in these systems are 208,000. The volume fraction of thermoplastics in the three systems studied are approximately 8%,19% and 54%.

3. Simulation on chemical reactions

We start by building a small system with desired ratio of particles with a mass density set to 1.0. The simulation systems (208,000 particles) are then generated by replicating unit cells multiple times in three directions. The initial packed systems are relaxed for 10^6 timesteps under NVT condition at temperature $T = 5$. This temperature can be compared with the critical phase separation temperature $T_c \approx 1.4$ for binary LJ liquids in three dimensions driven by molecular interactions $\epsilon_{AA} = \epsilon_{BB} = \frac{1}{2}\epsilon_{AB}$ [30].

The crosslinking process is adapted from MDPOs, a crosslinking method for all-atom simulations [31]. We periodically perform chemical reactions between reactive particles (**E** and **X**). New bonds are formed based on a distance criterion compared with a pre-defined cutoff. New bonds are created periodically between pairs of **E** and **X** particles within the cutoff if they are not fully reacted. Each cycle of bond creation is followed by 5×10^5 steps of relaxation using energy minimization and 10^6 MD steps to thermalize the

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