



# Coarse-grained molecular dynamics simulations of epoxy resin during the curing process



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## ABSTRACT

Motivated by the need to establish a multiscale understanding of the mechanical and thermal properties of polymers used for nano-, meso- and macro-composites, we are presenting an investigation of the cross-linking process (associated with curing) of an epoxy phenol novolac and bisphenol-A melt system via coarse-grained molecular dynamics simulations. In particular, we are focusing on the associated structural and physical behaviors of the melts of different cross-linking degree under Couette and Poiseuille flow conditions. At the nanoscale, we also investigated the stress, heat flux and temperature fields that are computable from the quantities of the coarse-grained model of the epoxy resin melt with the extended Hardy's theory to multibody potentials. We have established that the epoxy resin chains tend to reorient along the direction of the imposed Couette flow, and the degree of alignment increases with the cross-linking degree and shear rate. The pronounced reorientation of cross-linked epoxy resin melts can be ascribed to the inter-bonded chains. This conformational change explains the shear thinning behaviors of cross-linked melts that initiate at low shear rates. The cross-linked melts under Poiseuille flow possess less pronounced velocity profiles, accompanied with the smaller temperature rise from the applied gravity force. Due to the size of the nanoscale channel height, the epoxy resin melts under Poiseuille flow can only be approximately predicted via the continuum theory. We have shown that the discrepancies between atomistic simulations and continuum predictions increase as the wall/epoxy interaction strength reduces. This study reveals the variations of important rheological properties during the cross-linking process and elucidates the roles played by the topological changes in the shear flow, thus can contribute to the design and manufacturing of the epoxy-resin based nanocomposites.

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## 1. Introduction

Nanocomposites made out of polymers populated by micro/nano-particles and fibers have drawn a lot attention from scientists and manufacturers for the past few decades, due to their enhanced mechanical and thermal properties [1]. In the macro scale, thermoset polymers, such as certain epoxy resins, are widely used as matrix polymers especially for carbon-fiber-reinforced composites. The epoxy resins are formed by the cross-linking of the epoxy monomers bearing multiple epoxy groups and the curing agents with active hydrogens such as hydroxyls and amines. The cross-linking reaction is commonly referred to as curing. Due to the strong covalent bonding between individual chains, thermoset epoxy resins often exhibit excellent mechanical properties

and have found increasing usage for applications that benefit from weight reduction such as their employment in the manufacturing of structural macrocomposites.

With the aim to design and manufacture high performance epoxy resins, a fundamental understanding of the changing behaviors from the monomer state, i.e. from the uncured to the cured state, is vital. A first-principles-based computational approach, as a powerful supplement to experimental and analytical approaches, has been utilized to characterize the curing process especially at the atomistic length scale [2–9]. Xu et al. conducted full atomistic molecular dynamics (MD) simulations of the curing process of the epoxy resin based on diglycidyl ether bisphenol-A (DGEBA) and isophorone diamine (IPD); this study employed the COMPASS force field – and achieved a cross-linking ratio up to 93.7% [3]. In their study, the degree of cross-linking has been shown to have an important effect on the glass transition temperature ( $T_g$ ) [5]. Using the representative cross-linked unit and sequential scale bridging methods, Cho et al. constructed Al<sub>2</sub>O<sub>3</sub>/epoxy

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nanocomposites and investigated the size effect of  $\text{Al}_2\text{O}_3$  particles on their mechanical properties [8]. Among the limited coarse-grained molecular dynamics (CGMD) simulations of cross-linked epoxy resins [6,10–13], Komarov et al. adopted a mapping/reverse mapping approach to bridge the full atomistic and CGMD models, and cross-linked the epoxy monomers through Monte Carlo (MC) simulations [10]. The degree of cross-linking has been found to increase the glass transition temperature ( $T_g$ ). Recently, Qu et al. has demonstrated a CGMD model for the epoxy phenol novolac (EPN) – bisphenol-A (BPA) epoxy system composed of EPN as the epoxy monomer and BPA as the curing agent [6]. They parameterized the inter-bead potentials of the CGMD model by fitting to certain key thermomechanical properties from experiments and full atomistic simulations. Thus the developed CGMD model is capable of predicting a number of thermomechanical properties of epoxy resin systems. In these studies, chemical reactions are considered possible between the epoxy monomer and curing agent when the reactive sites approach a fixed distance.

The rheological behavior of epoxy resin is another important aspect to investigate in order to optimize the material design in the curing process. Shear thinning is a commonly observed behavior for polymer melts under shear flow; i.e. the viscosity decreases with increasing shear rates [14–16]. This behavioral deviation from Newtonian fluids of the polymer melts is believed to be related with the topological constraints such as entanglements in the polymer matrix, which prevents the flow-induced conformational changes of polymer chains [17,18]. Chen et al. investigated the nature of shear thinning of both untangled and entangled linear polymer melts using nonequilibrium molecular dynamics (NEMD) simulations [14]. Three distinct regimes characterized by the different dependence of shear viscosity  $\eta$  on the shear rate  $\dot{\gamma}$  have been found. In the study of polymer nanocomposites (PNCs), a network formed between the filler and polymers has been revealed to have a significant influence on the dynamics of the PNCs under shear [16]. Adding nano-fillers may enhance the shear thinning effects by inducing high degrees of orientation of polymer chains. The reports on the shear properties of epoxy resins are relatively limited. In an experimental study on the rheology of double-walled carbon nanotubes (CNTs)/RTM6-Epoxy suspension using differential scanning calorimeter (DSC), the effect of shear thinning has been found more pronounced at high temperatures [19]. These shear flow experiments, however, were carried out at low temperatures to avoid the curing reaction. The effects of the strain rate and temperature on the shear yield strength and shear strength are studied for epoxy resins with various molecular weights between cross-linkings. Both the shear yield strength and shear strength have been found to increase exponentially with the strain rate [19].

In the present study, we perform NEMD simulations to investigate the rheological behaviors of the EPN–BPA epoxy resins under Couette flow and Poiseuille flow [20,21], with different cross-linking degrees during the curing process. A CGMD model of the epoxy resin is employed. We also adopt an atomistic–continuum bridging method, which has been applied to polyethylene polymers in our previous work [22,23], to compute stress and heat flux of the non-cross-linked and cross-linked epoxy resin melts. Through this method, a comprehensive approach for understanding the manufacturing process of epoxy resin-based composites is provided.

## 2. Numerical modeling and setup

### 2.1. Coarse grained molecular model of the epoxy resin

The epoxy system investigated in our study is composed of EPN as the epoxy monomer and BPA as the cross-linking agent, i.e.

hardener. The CGMD model (Fig. 1) and parameters for the EPN–BPA epoxy system is modified from that initially developed by Qu et al. [6]. This set of parameters enables the prediction of the density, the glass transition temperature ( $T_g$ ), and Young's modulus ( $E$ ) in good agreement with the reference [6], as observed from our simulations. The epoxy chains are composed of 3 backbone beads (yellow), each linked to a reactive branching bead (purple) (Fig. 1a). The hardeners are represented by two reactive beads (blue) attached to one center bead (white) (Fig. 1b). All the beads are identical, having the mass of 1  $m$ , and assumed to interact through Lennard–Jones (LJ) potentials. The system consists of 2000 EPN chains and 3000 BPA chains, totally 21,000 beads. The curing process of the epoxy system includes three major steps: (i) the epoxy ring on an EPN monomer opens, (ii) the hydrogen atom transfers from the BPAs' hydroxyl groups to the oxygen atom on the broken ring of the EPN, and then (iii) the free carbon atom on the broken ring of the EPN is bonded with an oxygen atom in the BPA, thus linking the EPN and BPA. In this NEMD simulation, the cross-linking process is considered by a bond creation procedure between the reactive beads of EPNs and BPAs (Fig. 1c). If the distance between the EPN reactive bead and the BPA reactive bead is within  $1.3\sigma$ , the chance that a bond formed between the two beads is set to be 1%. The curing (cross-linking) degree is thus defined by the ratio of number of formed bonds to the maximum number of bonds that can be created in the system. In our study, the curing degree of 20%, 40%, and 60% are considered for subsequent rheological tests, and the bond creation is deactivated after the respective curing degree is reached. The epoxy systems with representative curing degree (0%, 20%, 40%, and 60%) are chosen in order to investigate the variation of rheological behaviors during the curing process. The nonbonded beads separated by at least three bonds interact through the LJ potential,

$$U_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (2.1)$$

where  $r$  is the interbead distance. The interaction is truncated at  $r = r_c^{LJ} = 2.5\sigma$ .  $\sigma$  and  $\epsilon$  are calibrated to be  $1.519 \text{ kcal mol}^{-1}$  and  $4.383 \text{ \AA}$  [6]. The bond stretching between adjacent beads are described by the potential function (Eq. (2.2)),

$$U_{stretch}(r) = U_0 + k_4(r - r_c)^2(r - b_1 - r_c)(r - b_2 - r_c)H(r_c - r) + 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 + \frac{1}{4} \right] \quad (2.2)$$

where  $H(x)$  is the Heaviside step function,  $k_4 = 1434.3 \text{ } \epsilon/\sigma^4$ ,  $b_1 = -0.7598 \sigma$ ,  $b_2 = 0$ , and  $U_0 = 67.2234 \text{ } \epsilon$ , and  $r_c = 1.343 \sigma$ . The bending deformation is described by the harmonic function:

$$U_{bend}(\theta) = k_\theta^{(i)} \left( \theta - \theta_0^{(i)} \right)^2 \quad (2.3)$$

All the bending angles formed by beads within each EPN is of type 1, for which  $\theta_0^{(1)} = 180^\circ$  and  $k_\theta^{(1)} = 1.612 \text{ } \epsilon/\text{rad}^2$ . The angle formed by the three beads in a BPA monomer is of type 2, for which  $\theta_0^{(2)} = 100^\circ$  and  $k_\theta^{(2)} = 6.308 \text{ } \epsilon/\text{rad}^2$ . The bending angle involving both the EPN bead and BPA bead is of type 3, with  $\theta_0^{(3)} = 180^\circ$  and  $k_\theta^{(3)} = 1.908 \text{ } \epsilon/\text{rad}^2$ . The epoxy liquid mixture, with the ratio between epoxy and curing agent chains 2:3, is at first equilibrated at  $0.8 \text{ } \epsilon/k_B$  under NPT ensemble for 2E5 steps at zero pressure with a time step size of  $0.005 \tau$  ( $=\epsilon/m\sigma^2$ ) $^{-1/2}$  (6.48 fs) first before the curing process is launched, where  $k_B$  is the Boltzmann constant. Note that standard reduced LJ unit is adopted throughout the paper unless otherwise stated, which means all physical quantities are expressed in terms of  $m$ ,  $\sigma$ ,  $\epsilon$ , and  $k_B$ . The LAMMPS Molecular Dynamics Simulator developed by Sandia National Lab was used for all the MD simulations.

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