Designed-in Molecular Interactions Lead to Superior Thermo-mechanical Properties in Nanocomposites

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ABSTRACT

The effect of the nanofiller chemistry on the mechanical behaviour of thermoset polymer matrix nanocomposites is investigated. The interaction between a crosslinked polymer resin and the reinforcing nanofibers driven by their chemistry is revealed by molecular dynamics simulations. Specifically, crosslinked network systems of neat epoxy and epoxy-P(St-*co*-GMA) are modeled to discuss the effect of various molecular interactions as a function of temperature on a molecular basis. At 433K˚, incorporation of single molecule of bonded P(St-*co*-GMA) and nonbonded P(St-*co*-GMA) lead to increase in Young's modulus by 10% and 6%, respectively, compared to neat epoxy system.

INTRODUCTION

Crosslinked epoxy resins are often preferred in variety of applications such as polymeric coatings, adhesives and composites. Consequently, they are subject of numerous research works which include molecular dynamics (MD) simulations to improve the understanding of epoxy crosslinked networks [1-8]. This study also presents an investigation by MD simulations, specifically towards the epoxy matrix nanocomposite mechanical behavior. The reinforcing materials of interest are surface reactive P(St-*co*-GMA) nanofibers. They contain epoxide ring and are promising compatible materials in reinforcing and toughening of the epoxy resin [10-11] and epoxy based carbon fiber prepregs [12,13]. Dynamic thermo-mechanical tests under flexural loads revealed significant increase in the mechanical response. This increase was attributed to the combined effect of the two factors: the inherent cross-linked fiber structure and the surface chemistry of the electrospun fibers leading to cross-linked polymer matrix−nanofiber interfacial bonding. In this study, correlation of the MD simulations and experimentally observed effect of the nanofiller chemistry on the mechanical properties of thermoset polymer matrix-based nanocomposites is sought. This article is organized as follows: First, MD simulation methodologies are described. The design of cross-linked epoxy structure is presented in detail. Next, the mechanical properties of neat and reinforced epoxy systems are obtained and discussed. In reference to earlier studies in this field [5-7] diglycidyl ether of bisphenol F (EPON862®) and triethylenetetramine (TETA ®) were chosen as epoxy unit monomer and the curing agent, correspondingly.

THEORY

Molecular dynamics methodology

In order to construct the initial molecular structures and implement all ensemble simulations and post-processes, the molecular simulation program Material Studio ® 4.4 [9] has been used, and ab initio Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) forcefield is applied to describe inter- and intra-atomic interactions. In COMPASS forcefield, intra-molecular interactions are quite complex compared to other force fields in polymers. Particularly, bond stretching is represented by a polynomial with terms of order two, three, and four. Nonbonded terms due to interactions between pairs of atoms that are separated by two or more atoms or for different molecules, utilizes Coulombic and Lennard-Jones functions for electrostatic and van der Waals interactions. The van der Waals interactions use the Lennard-Jones 9-6 function. In calculating the non-bonded potentials, the atom-based summation with a cutoff radius of 8.5 Å is used. Electrostatic interaction by Coulomb potential can be calculated using the Ewald summation method. In terms of force-field based simulation, Dreiding2.21 and COMPASS have been employed to study thermoset materials [5-7,8]. Xu et al concluded that the COMPASS is more favorable than the Dreiding2.21 for crosslinked epoxy systems and demonstrated the importance of a well-tuned forcefield for an accurate prediction of structure and properties [8].

Material constants for mechanical behavior

In the MD simulations, the mechanical properties of all atomistic unit cells are calculated using the Parrinello–Rahman fluctuation method [14, 15] where uniform external stress is applied to the unit cell. Stiffness matrix was calculated from the second derivative of potential energy (U) with respect to strain (ε):

$$C_{ij} = \frac{1}{v}\frac{\partial^2 U}{\partial \varepsilon i \partial \varepsilon j} = \frac{\partial \sigma i}{\partial \varepsilon} = \frac{\sigma_+ - \sigma_-}{2\varepsilon j} \qquad (1)$$

$$\lambda = \frac{1}{3}(C_{11} + C_{22} + C_{33}) - \frac{2}{3}(C_{44} + C_{55} + C_{66}) \qquad (2)$$

$$\mu = \frac{1}{3}(C_{44} + C_{55} + C_{66}) \qquad (3)$$

Two Lame constants are obtained from equation (2) and (3). Mechanical properties such as Young's modulus (E), shear modulus (G), bulk modulus (B) and Poisson's ratio (*v)* can then be computed.

$$E = \mu\frac{3\lambda+2\mu}{\lambda+\mu} \qquad (4)$$

$$G = \mu \qquad (5)$$

$$B = \lambda + \frac{2}{3}\mu \qquad (6)$$

$$v = \frac{\lambda}{2(\lambda+\mu)} \qquad (7)$$

Designing representative crosslinked systems using MD simulations

It is not possible to exactly reproduce atomic models of the epoxy-based polymers that are used in the experiments. Following earlier studies [5,8], we investigate the properties of five epoxy unit designs as representative molecules, exhibited in Fig. 1. In the MD simulations, the NVT (constant number of molecules or atoms, volume and temperature) ensemble is used. 1 fs

time step is employed. Temperature is set at 373° K. Temperature is controlled by the Andersen–Berendsen method [9]. The target density of all unit cells is 1.23 g/cm^3[5] in conformity with the measured density value. To validate the resulting polymer network model, 5,000 steps of energy minimization is performed on the initially generated model, followed by 1 ns of MD simulation. Elastic constants are calculated using the Parrinello–Rahman method [9,14-15]. This method is applied on five representative equilibrated configurations obtained at 100 ps intervals from the MD simulations for each of the five crosslinked system.

The results are evaluated so as to design a final representative structure. Each system yields a Poisson's ratio of 0.35 and they exhibit similar mechanical performance. Since there is no tractable difference between the five designs, and since the degree of crosslinking is not totally controllable in the experiments, we use a final network structure containing all five of the different types of crosslinked units The detailed temperature sweep is performed on this mixture structure, and all the following results are reported from these simulations which we describe next.
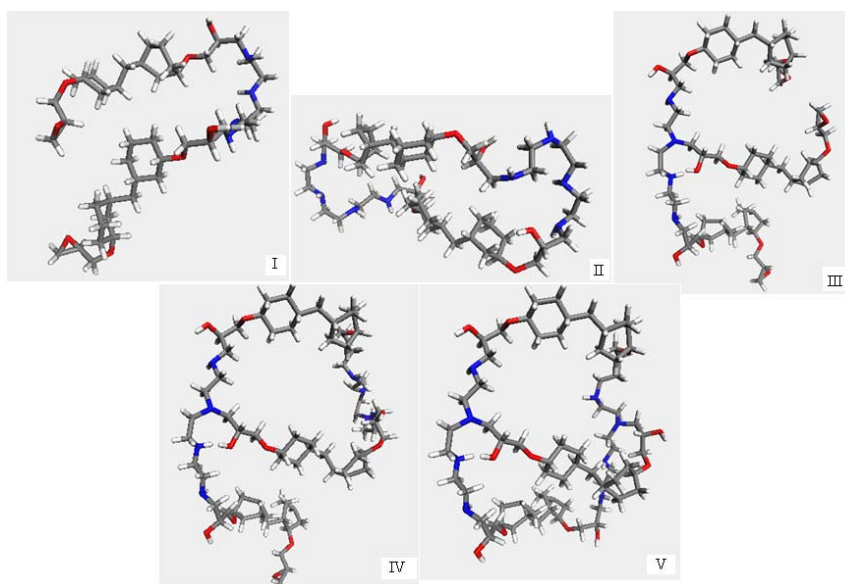

Figure 1 Five different representative cross linked units containing EPON 862 and TETA hardener.

Molecular dynamics simulation of final crosslinked representative unit and reinforced epoxy network

After the cell construction containing 1 molecule of I and 2 molecules each of II, III, IV, V crosslinked units, (See Fig. 2 a) all the unit cells were simulated at 303, 323, 343, 373, 403 and 433 °K using 1 ns of NVT simulation. At each temperature, the elastic modulus of the mixture unit cell structure is obtained using the same method as described in the previous subsection, and the results of five different simulations in each case are averaged for computational accuracy. Two models, the Epon 862® matrix reinforced with nonbonded P(St-*co*-GMA) (Fig. 2b), and Epon 862 matrix reinforced with bonded P(St-*co*-GMA) are studied (Fig. 2c). In the latter case,

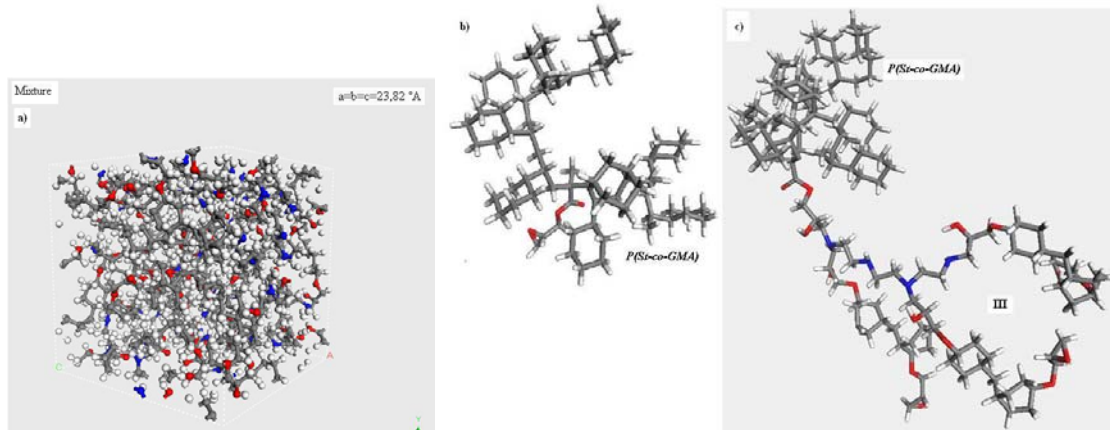the P(St-*co*-GMA) is bonded directly to a molecule of III. These reinforced cases are simulated at 303, 373 and 433 ˚K.

Figure 2 a) Molecular model systems generated: ball-stick model (red for oxygen, gray for carbon, white for hydrogen, blue for nitrogen) **b)** P(St-*co*-GMA) **c)** Representative crosslinked unit bonded to P(St-*co*-GMA).

DISCUSSION

Temperature Effect on neat crosslinked epoxy

We find that the Poisson's ratio is within the range of general polymer materials 0.33-0.38 (Fig. 3). The COMPASS forcefield reproduced experimental measurements of *v* and we consider the designed systems to be well-equilibrated. The results emphasize that the Young's modulus (E) decreases as the temperature increases, and converges to a plateau beyond the T_g of epoxy which is 350 ˚K [7]. MD results reveal that the shear modulus (G) follow the same trend as the Young's modulus.
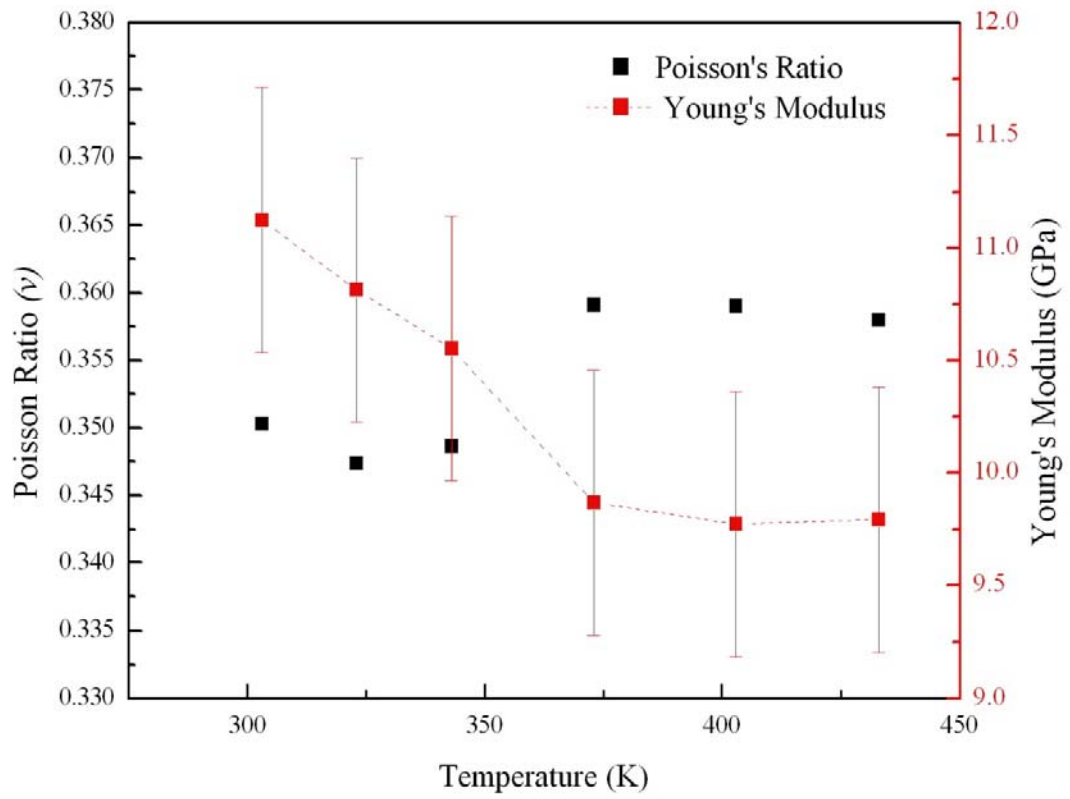
Figure 3 Poisson's Ratio and Young's Modulus obtained from temperature scan for equilibrated neat epoxy system.
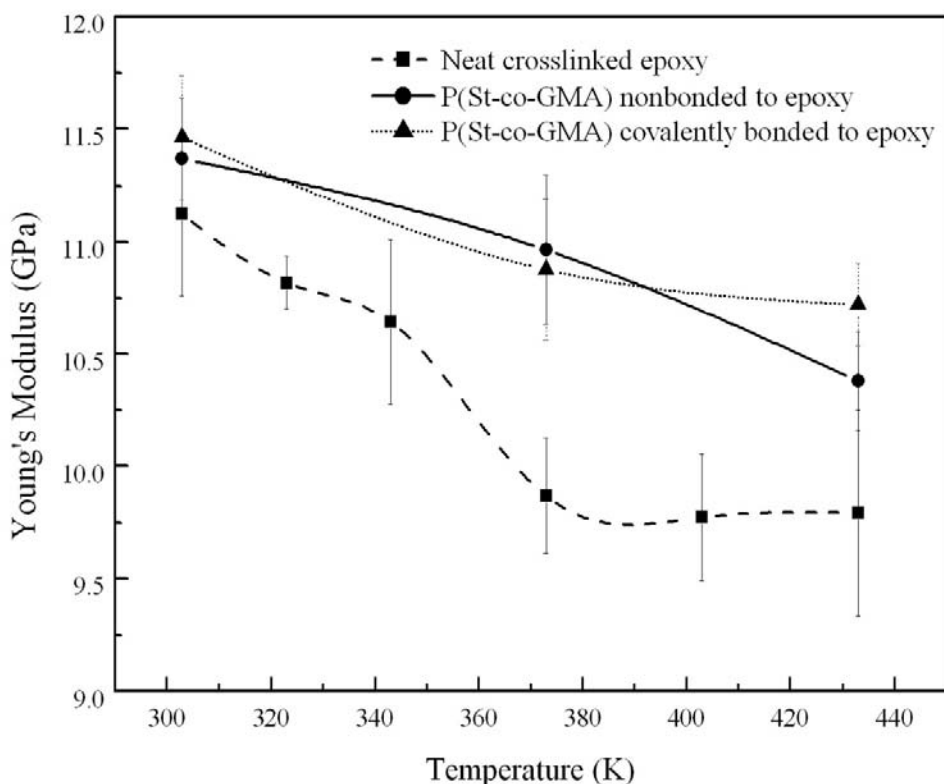
Figure 4 Young's Modulus for equilibrated reinforced epoxy systems.

Reinforcement/filler chemistry effect

We present in Fig. 4 the calculated values of the Young's modulus for the systems of neat epoxy versus those containing reinforcing agents. Comparison of the MD based Young's moduli predictions for P(St-co-GMA) nonbonded and bonded to epoxy molecules correlates with the macroscale experimental finding [10-11]. The experimentally observed benefit in the mechanical response due to the presence of the filler is preserved at elevated temperatures by supplementary GMA−epoxy interactions. However, we should emphasize that neither the high molecular weight polymers nor the incorporation of 2 wt % of nanofibers in the experiments are represented in our MD simulations. Therefore, the order of magnitude of the reinforcing effect is significantly different. Nonetheless, integration of a single molecule of P(St-*co*-GMA) , either bonded or nonbonded increases the Young's modulus compared to the neat epoxy system by 9.7% and 6.2% at 433 K˚, respectively. Preliminary results demonstrate that the observed difference mainly originates from repulsive non-bonded interactions, while electrostatic and dispersive non-bonded interactions do not influence the relative values of the moduli.

CONCLUSIONS

MD simulations are employed to address the differences in the temperature dependence of the Young's modulus when the characteristics of fiber-epoxy interface in the nanocomposites are modified. A representative cross-linked molecular unit method is proposed for an efficient cross-linking simulation. Since the degree of crosslinking in the network is an important design parameter, a mixture containing five different crosslinked representative units at the atomistic scale is utilized. We find that the contribution of both covalently and non-covalently bonded P(St-co-GMA) molecules have the similar influence of retaining a more elevated Young's modulus at temperatures above T_g. Results corroborating the experiments suggest that enhanced adhesion between nanofiber and matrix may be designed by modifying the chemistry of the constituents to retain a high modulus beyond the T_g.

ACKNOWLEDGMENTS

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