

TRACING THE SUPERIOR THERMO-MECHANICAL PROPERTIES IN NANOCOMPOSITES OF CROSSLINKED FILLERS AND INTERFACES: MOLECULAR POINT OF VIEW

E. Özden-Yenigün^{1*}, C. Atılğan¹, Y. Z. Menceloğlu¹, M. Papila¹⁻²

¹ Faculty of Engineering and Natural Sciences, Material Science and Engineering, Sabanci University, Tuzla-İstanbul 34956

² currently in Department of Aeronautics&Astronautics, Stanford University, Stanford CA, USA

*elifozden@sabanciuniv.edu

Keywords: nanocomposites, molecular dynamics, crosslinked interface, surface modification

Abstract

This study presents an investigation by molecular dynamics (MD) simulations, specifically focus on epoxy matrix nanocomposite mechanical behavior. Reinforcing materials of interest are surface reactive P(St-co-GMA) nanofibers. Effect of the nanofiller chemistry on mechanical behavior of thermoset polymer matrix nanocomposites is explored. Molecular dynamics simulations are employed to address the differences in the temperature dependence of the bulk, shear and Young's modulus when the characteristics of fiber-epoxy interface in the nanocomposites are modified. The results indicated that at 493K°, incorporation of single molecule of bonded P(St-co-GMA) and nonbonded P(St-co-GMA) lead to increase in Young's modulus by 9% and 6%, respectively, compared to neat epoxy system. Glass transition temperatures of composite systems are also studied. Results corroborating the experiments suggest that the manipulation in glass transition temperature at the interface may be designed by modifying the chemistry of the constituents.

1 Introduction

Nanofiber reinforced polymer composites have attracted an increasing amount of interest. They are commonly designed with the primary aim of obtaining superior mechanical properties in advanced structural applications but they are also promising candidates as functional materials [1]. It has been widely demonstrated that nanofibers can carry out the reinforcing function, particularly when they have good fiber-matrix adhesion [2-4]. Crosslinked epoxy resins are often preferred as matrix in nanofiber reinforced composites [1]. Thus, they are subject of numerous research works which include molecular dynamics (MD) simulations to improve the understanding of epoxy crosslinked networks [5-11]. This study also presents an investigation by MD simulations, specifically towards the epoxy matrix nanocomposite mechanical behavior and the chemical interactions between matrix and filler. The reinforcing materials of interest are surface reactive P(St-co-GMA) nanofibers, as it was discussed in our earlier experimental studies [2-4]. They contain epoxide ring and are promising compatible materials in reinforcing and toughening of the epoxy resin [2-4] and epoxy based carbon fiber prepregs [12]. 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. Next, the mechanical properties of neat and reinforced epoxy systems are obtained and discussed. Glass transition temperature of crosslinked neat epoxy and reinforced epoxy systems are presented in detail. In reference to earlier studies in this field [9-10] diglycidyl ether of bisphenol F (EPON862®) and triethylenetetramine (TETA ®) were chosen as epoxy unit monomer and the curing agent, correspondingly.

1 Theory

1.1 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 ® 6.0 [13] 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 [9-11]. 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 [11].

1.2 Material constants for mechanical behavior

If the body is in equilibrium, the external stress must be exactly balanced by internal forces. Therefore, in the MD simulations the *shear moduli* (G) of all atomistic unit cells are calculated using Material Studio ® 6.0 [13] where uniform external stress is applied to the unit cell. Stiffness matrix (C) calculated from the second derivative of potential energy (U) with respect to strain (ε):

$$C_{ij} = \frac{1}{v} \frac{\partial^2 U}{\partial \epsilon_i \partial \epsilon_j} = \frac{\partial \sigma_i}{\partial \epsilon} = \frac{\sigma_+ - \sigma_-}{2\epsilon_j} \quad (1)$$

For small deformations, compliance matrix (S) could be expressed by generalized Hook's law and is defined by Eq. 2.

$$\epsilon_{lm} = S_{lmnk} \sigma_{nk} \quad (2)$$

where σ is the stress and S_{lmnk} denotes the compliance components.

The Eq.3 and Eq.4 are for the Reuss and Voight definitions, while the Hill values are defined as the average of the other two:

$$G_{VOIGHT} = \frac{1}{15} (C_{11} + C_{22} + C_{33} + 2(C_{44} + C_{55} + C_{66}) - C_{12} - C_{13} - C_{23}) \quad (3)$$

$$G_{REUSS} = \frac{15}{4(S_{11}+S_{22}+S_{33}-S_{12}-S_{13}-S_{23})+3(S_{44}+S_{55}+S_{66})} \quad (4)$$

Bulk modulus (K) in Eq. 5 is computed by the reverse of isothermal compressibility using the equation below;

$$K = \frac{k_B T \langle V \rangle}{\langle V^2 \rangle - \langle V \rangle^2} \quad (5)$$

where V is the volume of the unit box, T is the temperature in °K units and k_B is Boltzmann constant.

Young's Modulus (E) is calculated by combining bulk modulus (K) data from trajectory and shear modulus (G) data from dynamic method as in Eq. 6:

$$E = \frac{9KG}{G+3K} \quad (6)$$

Glass transition temperatures (T_g) of these systems were determined by two different methods. In the first method, shear and Young's modulus data points are fitted to Boltzmann sigmoidal function to detect transition temperatures. Secondly, T_g is estimated from the relation of mean density of the system- temperature.

2.3 Designing representative neat and reinforced 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 [9,11], we investigated the properties of five epoxy unit designs as representative molecules, described as in reference [14]. Since there is no tractable difference between the five designs, and 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 which is indicated as *neat epoxy case* in this study. After the cell construction containing five different crosslinked units, all the unit cells were simulated at fifteen different temperatures (283,303,323,343,353,363,373,388,403,418,433,453,463, 473 and 493°K) using 5 ns of NVT and 3 ns of NPT 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 at least 10 different simulations in each case are averaged for computational accuracy. Two models, *noncrosslinked reinforced system model* - the Epon 862® matrix reinforced with nonbonded P(St-co-GMA) and *crosslinked reinforced system model* Epon 862 matrix reinforced with bonded P(St-co-GMA) are studied. In the crosslinked case, the P(St-co-GMA) is bonded directly to a molecule of epoxy. The detailed temperature sweep is also performed on these reinforced models structure.

3. Discussion

3.1 Temperature effect on neat and reinforced crosslinked epoxy

First bulk modulus was computed by the reverse of isothermal compressibility using the trajectory from the last 2 ns at each temperature which was divided into 5 chunks of 400-ps length, each with 400 data points. The results emphasize that bulk modulus (K) decreases as the temperature increases, and all three system converges to a plateau, as in Fig. 1 (a). Hill shear moduli of three systems follow the same trend with bulk moduli. However, the transition temperatures between the high modulus and low modulus zone were more distinctive in Fig. 1 (b). In Fig. 1 (c) the calculated values of the Young's modulus for the systems of neat epoxy versus those containing reinforcing agents were presented. Comparison of the MD based Young's moduli predictions for P(St-co-GMA) nonbonded and bonded to epoxy molecules correlates with the macro-scale experimental finding [2-4]. 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 experiment are represented in our MD simulations. Therefore, the order of magnitude of the reinforcing effect is significantly different compared to experimental results. 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% and 6% at 493 K, respectively.

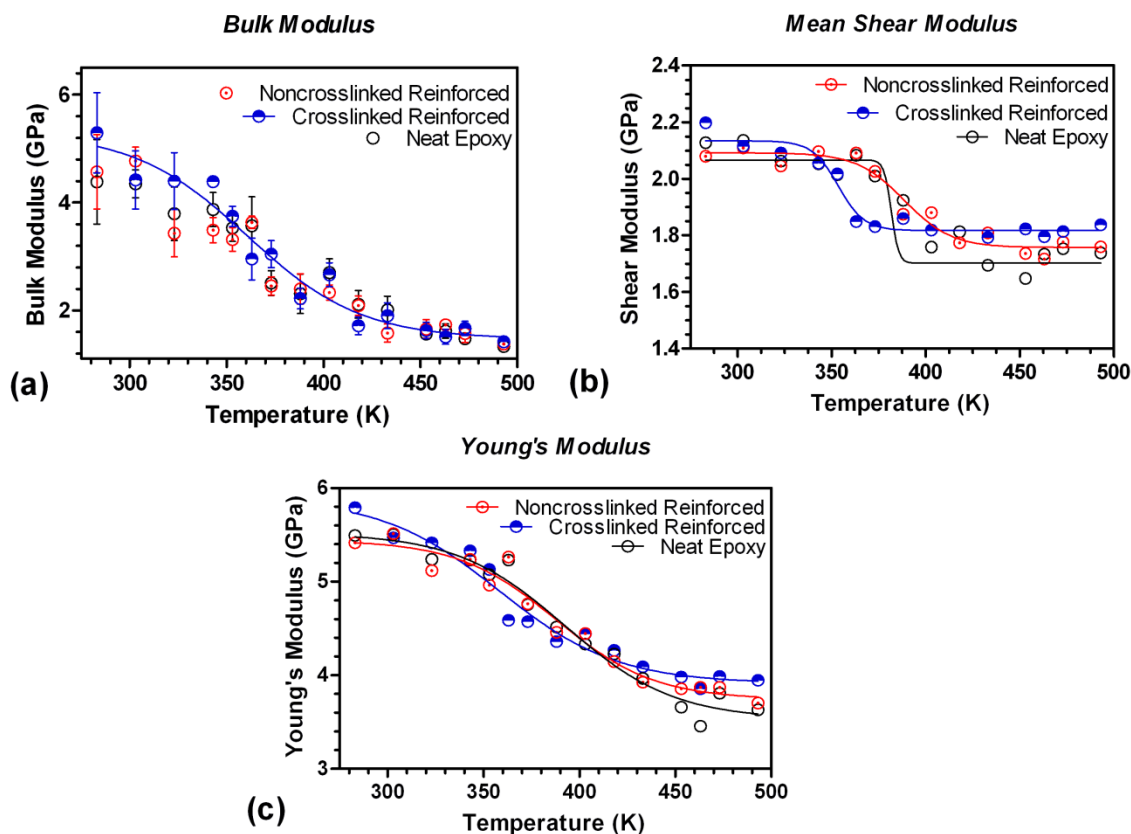


Figure 1. (a) Bulk modulus (b) shear modulus (c) Young's modulus vs temperature results of neat (black dotted), noncrosslinked (red dotted) and crosslinked (blue dotted) reinforced epoxy system.

3.2 Glass Transition Temperature Determination

Bulk, shear and Young's modulus versus temperature results demonstrated that the mechanical response of these three systems exhibit two plateau and a transition region. Determination of T_g would be interpreted from this transition region. Shear and Young's modulus data points were fitted to boltzmann sigmoidal function, best fit-V50 values indicated T_g of different systems, as presented in Table 1.

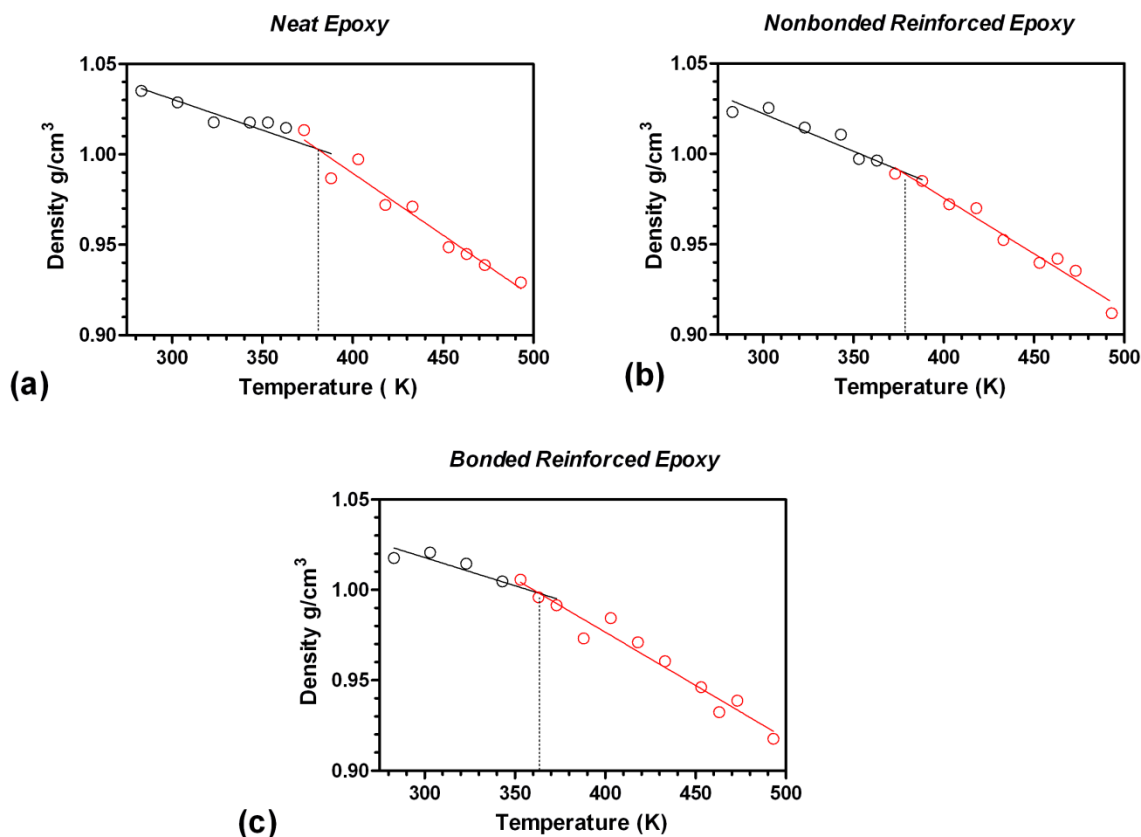
System	T_g		T_g		T_g
	from Young's Modulus	R^2	from Shear Modulus	R^2	
Neat Epoxy	$392.7 \pm 6.443^\circ\text{K}$	0.9729	$381.8 \pm 21.35^\circ\text{K}$	0.8091	$381.26 \pm 10.089^\circ\text{K}$
Noncrosslinked	$388.05 \pm 6.562^\circ\text{K}$	0.9651	$388.6 \pm 4.563^\circ\text{K}$	0.9562	$377.28 \pm 4.453^\circ\text{K}$
Crosslinked	$358.2 \pm 9.078^\circ\text{K}$	0.9648	$353.5 \pm 2.671^\circ\text{K}$	0.9536	$366.16 \pm 3.823^\circ\text{K}$

Table 1. T_g determination of neat, noncrosslinked and crosslinked epoxy systems using the methods of the mechanical response and density average.

The second method was to estimate T_g from the relation of average density- temperature (See Fig. 2). The density of the cell at each temperature from 493 °K to 283 °K was obtained in each equilibrium state of the last 2 ns NPT runs for all three cases. The results demonstrated that T_g was depressed within the addition of P(St-co-GMA) which has lower T_g than EPON862 epoxy matrix. Our experimental results showed that T_g of Poly(St-co-GMA) was around 95° C (368K°) [2]. On the other hand, experimentally reported T_g values of EPON862-TETA hardener matrix was around 140° C (413 ° K) [15]. Thus, depletion in T_g could be understood in terms of observed kinetics of reinforcing agent and polymer matrices.

4. Conclusion

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. 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 . In atomistic-scale a kinetic parameter T_g can be detected and manipulated in composite polymeric systems. 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 .

**Figure 2.** The mean density values versus temperature (a) neat epoxy (b) noncrosslinked reinforced epoxy and (c) crosslinked reinforced epoxy

References

- [1] Zucchelli, A., Focarete, M. L., Gualandi, C. and Ramakrishna, S., Electrospun nanofibers for enhancing structural performance of composite materials. *Polym. Adv. Technol.*, **22**, 339–349 (2011).
- [2] Özden E., Menceloğlu Y.Z., Papila M., Engineering Chemistry of Electrospun Nanofibers and Interfaces in Nanocomposites for Superior Mechanical Properties. *ACS Appl. Mater. Interfaces* **2** (7), 1788–1793 (2010).
- [3] Özden E., Menceloğlu Y.Z., Papila M., Proceeding in *Mechanical Behavior at Small Scales — Experiments and Modeling*, edited by Lou J.; Lilleodden E.; Boyce B.; Lu L.; Derlet P.M.; Weygand D.; Li J.; Uchic M.D.; Le Bourhis E.; (Mater. Res. Soc. Symp. Proc. 1224, Warrendale, PA.), 1224-FF10-23 (2010).
- [4] Özden-Yenigün E., Menceloğlu Y.Z., Papila M., Papila MWCNTs/P(St-co-GMA) Composite Nanofibers of Engineered Interface Chemistry for Epoxy Matrix Nanocomposites. *ACS Applied Materials & Interfaces* **4** (2), 777-784 (2012).
- [5] Stevens MJ., Manipulating connectivity to control fracture in network polymer adhesives. *Macromolecules* **34**, 1411-5, (2001).
- [6] Stevens MJ., Interfacial fracture between highly cross-linked polymer networks and a solid surface: Effect of interfacial bond density. *Macromolecules* **34**, 2710-8, (2001).
- [7] Tsige M, Stevens MJ., Effect of cross-linker functionality on the adhesion of highly cross-linked polymer networks: A molecular dynamics study of epoxies. *Macromolecules* **37**, 630-7, (2004).
- [8] Tsige M, Lorenz CD., Stevens MJ., Role of network connectivity on the mechanical properties of highly cross-linked polymers. *Macromolecules* **37**, 8466-72 (2004).
- [9] S.Yu, S., Yang, M.Cho Multi-scale modeling of cross-linked epoxy nanocomposites. *Polymer* **50**, 945–95 (2009).
- [10] Zhua R., Pana E., Roy A.K., Molecular dynamics study of the stress–strain behavior of carbon-nanotube reinforced Epon 862 composites. *Materials Science and Engineering A* **447**, 51–57 (2007).
- [11] Wu C., Xu W., Atomistic molecular modelling of crosslinked epoxy resin. *Polymer* **47** 6004-6009 (2006).
- [12] Bilge K.; Özden-Yenigün E.; Şimşek E.; Menceloğlu Y.Z.; Papila M. Structural Composites Hybridized with Epoxy Compatible Polymer/MWCNT Nanofibrous Interlayers. *Compos. Sci. Eng.*, (2011), submitted.
- [13] Accelrys Inc., San Diego, www.Accelrys.com
- [14] Ozden E., Atilgan A.R., Bilge K., Menceloglu Y.Z., Atilgan C. and Papila M., Designed-in Molecular Interactions Lead to Superior Thermo-mechanical Properties in Nanocomposites in *Mater. Res. Soc. Symp. Proc. Vol. 1304*, Boston, USA (2011).
- [15] Sun L., Warren G.L., O'Reilly J.Y., Everett W.N., Lee S.M.D., Lagoudas D. Mechanical properties of surface-functionalized SWCNT/epoxy composites *Carbon*, **46**, 320–328,(2008).