

Molecular Dynamics Simulation of Glass Transition Behavior of Polymer based Nanocomposites

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Molecular Dynamics (MD) simulations were carried out to explore the effect of functionalization of graphene on the visco-elastic properties of epoxy based nanocomposites. Pristine graphene, graphene functionalized with amine ($-NH_2$) group and carboxyl ($-COOH$) group respectively involved in this research. The simulation result shows that glass transition temperature (T_g) of the graphene epoxy based nanocomposites are higher than that of pure epoxy. The computational findings of T_g agrees well with the experimental results. Thus, the present MD simulation study can serve as good computational evidence for the existing experimental results on the T_g of graphene epoxy composites.

Keywords: Glass Transition Temperature, Functionalized Graphene, Epoxy Resin, Molecular Dynamics Simulation

Introduction

Graphene, is a two dimensional (2D) exciting material, composed of by rolling a single layer six member rings nanosheet of sp^2 -hybridized carbon atoms¹. It has excellent thermo-mechanical properties of graphene/epoxy nanocomposites²⁻⁵. Graphene-enhanced composite materials can find uses in aerospace, structural applications, sensing devices and many more⁶. Glass transition temperature (T_g) is one of the remarkable prospect to investigate visco-elastic properties of epoxy and their composites. Xue *et al.*⁷ predicted that the addition of graphene inside a polymer matrix can increase the T_g of the graphene-polymer composites. Jeyranpour *et al.*⁸ investigated T_g of cross-linked epoxy polymer with different curing agents and conclude that T_g of DGEBA/DETDA in all cross linking densities has a higher value than that of DGEBA/TETA epoxy system. Choi *et al.*⁹ predicted coefficient of thermal expansion (CTE) and the elastic stiffness of cross-linked epoxy based nanocomposites using MD simulation. Thus, MD simulations may be a viable solution for prediction the mechanical properties of nanocomposites. In this work, MD simulation using Materials Studio software were carried out to find out the effects of functionalized graphene on T_g of graphene epoxy nanocomposites. T_g of pristine graphene, functionalized graphene with $-NH_2$ and $-$

$COOH$ functional groups respectively, reinforced with cross-linked LY556 epoxy nanocomposites are compared with the neat LY556 epoxy resin samples.

Experimental section

Modeling of cross-linked LY556 epoxy resin

LY556 epoxy resins used as a matrix are thermosetting polymers with more than one epoxide group per molecule having excellent adhesion properties, good thermal stability, high elastic modulus and corrosion resistance was chosen with 10 repeating units in each chain for the molecular model. Due to these remarkable properties, epoxy resins are widely used in variety of engineering areas as polymer matrix to fabricate polymer nanocomposites. The hydrogen atom in the amine ($-NH_2$) groups of the curing agent (di-ethylene toluene di-amine – DETDA) molecule reacts with the epoxide groups of epoxy resin. The resulting cured resin molecule further reacts with epoxy molecules at the site of HN and NH_2 and one curing agent molecule reacts at the site of another epoxide group. Finally, a crosslink between the epoxy resin and the curing agent is formed. As the reaction continues, the epoxy resin and curing agent molecules generate more crosslinks. These crosslinks motion in all directions and generate a mesh of macromolecules^{10,11}.

Simulation models

In this study, LY556 epoxy resin (DGEBA) cross-linked with HY951 curing agent (DETDA) is used as a

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polymer matrix. Single layer graphene sheet, which has 162 carbon atoms in total, was chosen as the nanofiller in the composites as shown in Figure 1. Chemical functionalization may be a viable solution to achieve a good dispersion as well as a strong adhesive interface between the surrounding polymer chains and graphene.

Chemical functionalization is based on the covalent linkage of functional groups onto carbon arena of graphene. There are numerous difficulties that need to be focused upon in order to use graphene as effective reinforcing nanofiller in polymer composites. The dispersion of graphene is one of the most widely considered difficulties. Some of the organic molecules, such as $-NH_2$, $-CH_3$, $-OH$, and $-COOH$ can be formed by chemical covalent bonds between the polymer chains and the functionalized graphene in the composites¹¹. This may overcome the problem of dispersion and agglomeration of graphene in the epoxy matrix. Thus the chemical covalent bond mechanism of functional groups to the surface of the graphene is very useful in maintaining the stable bonds between functionalized graphene and the epoxy.

Force field and simulation procedure

We used COMPASS force field, which is implanted in Material studio 6.0. The valence parameters were derived using COMPASS force field, ab-initio parameterization techniques and validated using condensed phase properties in addition to empirical data for molecules in isolation. The

COMPASS force field consists of three categories of energy terms: the bonded energy terms, the cross-terms, the non-bonded energy terms, a Coulombic function for electrostatic interactions and a 6-9 Lennard-Jones potential for vander Walls interactions and are follows in Equation 1.

$$E_{total} = E_b + E_\theta + E_\phi + E_\chi + E_{b,b'} + E_{b,\theta} + E_{b,\phi} + E_{\theta,\phi} + E_{\theta,\theta'} + E_{\theta,\theta',\phi} + E_q + E_{vdw} \quad \dots (1)$$

Where,

E_b = covalent bond-stretching energy,

E_θ = bond-angle bending energy,

E_ϕ = torsion-angle rotation energy,

E_χ = out-of-plane energy,

E_q = electrostatic energy,

E_{vdw} = van derWalls energy and,

$E_{b,b'}$, $E_{b,\theta}$, $E_{b,\phi}$, $E_{\theta,\theta'}$, $E_{\theta,\theta',\phi}$ = cross terms representing the energy due to the interaction between bond stretch-bond stretch, bond stretch-bond bend, bond stretch-bond torsion, bond bend-bond torsion, bond bend-bond bend and bond bend-bond bend-torsion, respectively. The size of the simulation cell is adjusted to set the density of LY556 epoxy resin as 1.20 g/cc. In order to obtain a well relaxed start structure with the correct density, firstly, the lowest energy configuration was chosen from the minimized boxes in discover tool in Material Studio, was further relaxed by performing an 'anneal cycle' from 300 to 650 K at intervals of 50 K to remove unfavorable interaction in the initial configuration. To bring the

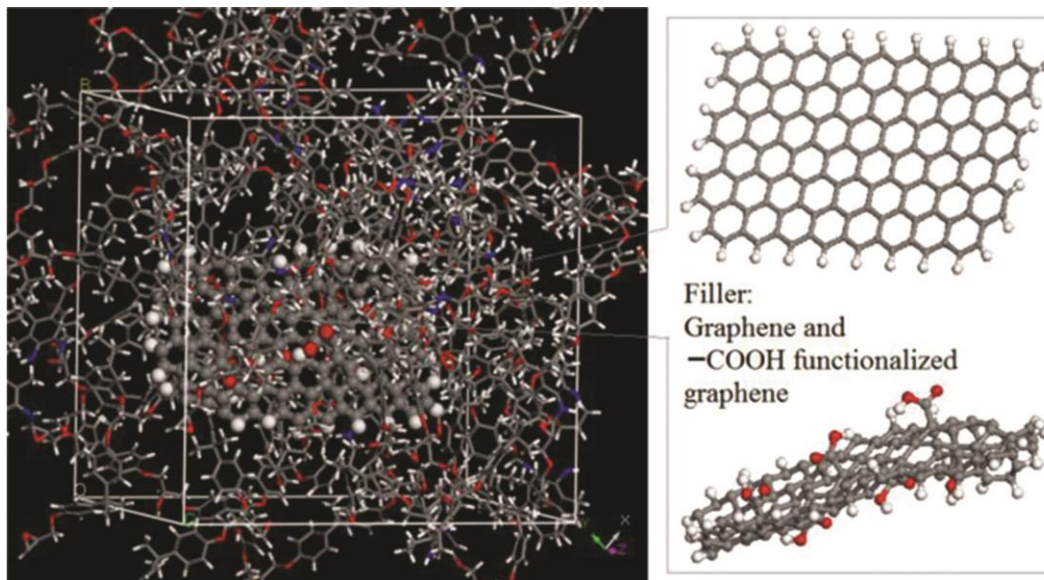


Fig. 1 — Nanocomposite unit cell consists of cross-linked LY556 epoxy resin as matrix and graphene or modified graphene as filler.

system in equilibrium, the conjugate gradient minimization method with high convergence root mean square force (1×10^{-3} Kcal/mol Å). Afterwards, a “cooling process” was initiated by lowering the temperature stepwise by 25 K starting at 550K (the modified graphene–polymer module starting at 550 K which was under the thermal degradation temperature of the composite) by using the forcite quench dynamics run. Further simulated annealing dynamics tool is used in a mid-circle temperature of 2075 K. The thermal annealing procedure involves heating the system from 300 to 2075 K in 25 K increments followed by cooling to 300 K using the Forcite tool of Material Studio. The time interval and the simulation run were set at 1.0 ps and 17.9 ps, respectively. All the MD simulations were performed using NVT ensemble and a pressure of 0.1 MPa.

Results and Discussions

T_g of functionalized graphene epoxy composites

The glass transition is mainly caused by the freezing of the motion of chain segments i.e. local chain movement²². Therefore there are two factors to be considered, (a) free volume and (b) themobility of chain segments, which will directly affect a polymer when it is cooled down and turned to its glassy state. Our simulated result shows that the epoxy matrix with functionalized graphene can enhance T_g . As shown in Figure 2, the COOH-graphene and NH_2 -graphene epoxy composite has a higher T_g of 456.8 K and 461.4 K, which was 40 K and 45 K higher than T_g of neat bulk epoxy resin respectively. The simulation results show that the epoxy matrix reinforced with functionalized graphene can increase T_g . The main reason for the large enhancement of T_g is the modified groups which provided a stronger interlocking between the graphene and epoxy molecules. Jayranpour *et al.*¹² performed a comparative study concerning the effect of nanofillers including expanded graphite (EG), single walled nanotubes (SWNTs) and, functionalized graphene sheet (FGS) on the T_g of the epoxy nanocomposites. In case of FGS epoxy nanocomposites the great shift of T_g nearly 30 K. Whereas, in SWNT epoxy nanocomposites no significant shift of T_g was observed. As seen from above computational results of T_g were in good agreement with the experimental data¹² indicating that the simulation method can be effective way to predict T_g of graphene based epoxy nanocomposites.

Radial distribution function/Pair correlation function

The radial distribution function (RDF) or pair correlation function (PCF), $g_{a-b}(r)$ which is obtained directly from the MD simulations using forcite analysis in MS software. It is an important parameter which gives a measure of probability and used to study the influence of several factors, such as filler, cross-linking density, and additives, on the local structure (both solid and liquid packing) of the constructed epoxy nanocomposites system¹³. $g(r)$ is also defined as the probability of findings an atom in a spherical shell at a distance r from an arbitrary atom¹⁴. The RDF is calculated by given Equation 2

$$g_{a-b}(r) = \frac{V (\sum_{i \neq j} \delta(r - |r_{Ai} - r_{Bj}|)) 4\pi r^2 dr}{N_A N_B - N_{AB}} \quad \dots (2)$$

Where, i and j are the i th and j th atom of the group A of N_A atoms and B of N_B atoms respectively; N_{AB} is

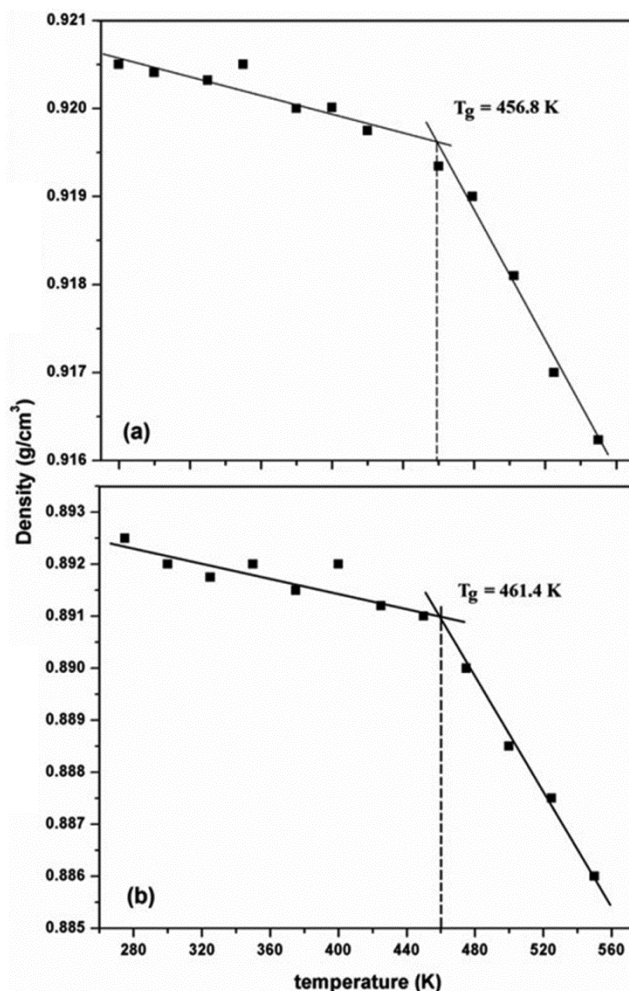


Fig. 2 — Density versus temperature graph for functionalized graphene reinforced epoxy system (a) graphene modified by –COOH (b) graphene modified by –NH₂.

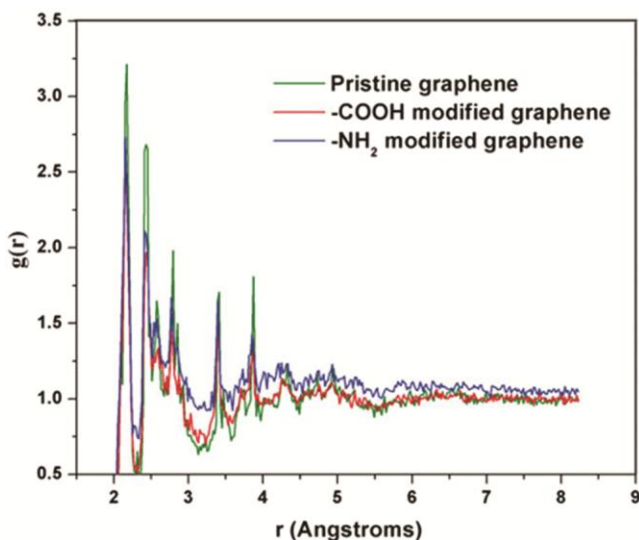


Fig. 3 — Total radial distribution function for three different epoxy composites at room temperature.

the number of atoms common to both groups A and B. Figure 3 shows the RDF curve, which is estimated for all three simulated models. The first peaks around 2.1 Å and 2.32 Å correspond to chemical bond distance between hydrogen and other atoms¹⁶. The second peaks at around 2.4 Å and 2.5 Å corresponds to the distance between bonded and non bonded carbon atoms. The subsequent intra-molecular peaks results from distance between atoms, including hydrogen and carbon atoms in H-C-C sequences ($r = 2.16$ Å) and carbon atoms in C-C-C sequences ($r = 2.44$ Å)¹⁴. As the content of graphene increases, the overall molecular RDFs decrease for the direct chemical bonds between hydrogen and other atoms. However, the RDFs behavior changes for other bonds¹⁵.

Conclusions

In this study, the effects of functionalized graphene as an addition of cross-linked epoxy resin LY 556 were studied using MD simulation. Three different types of cross-linked epoxy systems were used for analysis, of which one has pristine graphene and two have different functional groups (NH₂-graphene and COOH-graphene). The simulation results show that for modified graphene epoxy composites of the estimated T_g are found to be 461.4 K (for NH₂-graphene) and 456.8 K (for COOH-graphene) which are higher than that of neat bulk epoxy resin. Furthermore, the effects of graphene on the growth of the local structures were deliberated by analyzing their RDFs.

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