Molecular Dynamics Simulation on Dielectric Constant and Thermal Conductivity of Crosslink Epoxy/functionalized graphene Nano-composites

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Abstract. Nanoscale graphene fillers are expected to enhance electronic and thermal properties of polymers owing to the superior performances of graphene. In this paper, dielectric constant and thermal conductivity of crosslink epoxy/functionalized graphene nano-composites were investigated using molecular dynamics simulations. The results show that graphene nanoplatelets (GN) can improve performances of polymer matrix, covalent functional groups can further enhance this improvement. Among different functional groups, hydroxyl is more effective than carboxyl and amino in reducing dielectric constant. Correspondingly, the introduction of graphene fillers also leads to an increase in thermal conductivity. GN and amino functionalized GN raise thermal conductivity of crosslink epoxy by 30.69% and 44.86% respectively. All the results demonstrate that functionalization of GN can suppress polarization and enhance thermal transportation.

1. Introduction

Owing to the remarkable electronic, mechanical and thermal properties of graphene, polymer based nano-composites with graphene fillers have attracted significant attention in the past few years [1-4]. A large amount of research has indicated that electronic and thermal properties of such nano-composites could be enhanced, thus they hold great potential in a wide range of practical application [5-7]. One of the most promising applications is in insulation material. Insulation material demand for low dielectric constant and high thermal conductivity. In sharp contrast to the low thermal conductivity of common insulation material such as crosslink epoxy (EP), graphene has extremely high thermal conductivity in the range of 2000-5300 Wm⁻¹K⁻¹ [4,8]. Dispersing graphene fillers into polymer is a promising approach to improve performances of insulation material. When graphene is dispersed into polymer, the resultant composite performances are influenced by interfacial interaction between graphene and polymer [7]. Previous research found that covalent functional groups can enhance interaction between molecules and improve performances of nano-composites. Jen-Yu Wang et al. performed experiments and discovered that graphene oxide can not only enhance mechanical properties of polyimide but also reduce dielectric constant of polyimide by 39.4% [9]. Using Molecular Dynamics (MD), Yu Wang et al. discovered that the thermal resistance...
between epoxy and graphene functionalized by carboxyl and hydroxyl has decreased by 54.8% and 31.2% respectively compared to pristine graphene [10].

Using experiments to evaluate the relationship between structure and properties of nano-composites is challenging because of the associated variables such as the extent of conversion, extent of dispersion, and experimental temperature etc. An alternative method: MD simulation was applied throughout this study. MD simulation allows for an atomic-scale description of the interactions between graphene and polymer matrix. Thereby, it has been widely used in research on nano-composites. Upon analyzing the results from simulation system, an evaluation upon nano-composites’ performances can be given.

The purpose to the present article is to explore dielectric constant and thermal conductivity of EP doped with graphene nanoplatelets (GN). Models of unmodified epoxy (EP) and epoxy doped with GN (EP-GN) were firstly established. Then GN fillers functionalized by hydroxyl (-OH), carboxyl (-COOH) and amino (-NH₂) functional groups was established and dispersed into EP. This is followed by the calculation of dielectric constant and thermal conductivity of the five models respectively. Performances of nano-composites were compared to the performances of EP and amongst themselves to study the influence of different fillers to the polymer matrix. We close the paper by summarizing the results in the conclusion part.

2. Preparation of model structures

Establish model of Biphenyl A epoxy resin. The monomer and curing agent of biphenyl A epoxy resin are diglycidyl ether of bis phenol A (DGEBA) and 3,3’-diaminodiphenyl sulfone (33DDS). Molecular structures of DGEBA and 33DDS are shown in Figure 1. The model was built and structurally optimized using Material Studio software. The intra- and intermolecular forces that governed the behavior of the molecular models were described by CAMPASSII [11] force field.

Models of dopants were established afterwards, including graphene nanoplatelets (GN), carboxyl functionalized graphene nanoplatelets (GNCOOH), hydroxyl functionalized graphene nanoplatelets (GNOH), and amino functionalized graphene nanoplatelets (GNNH₂). Generally, hydroxyl groups are attached to the basal plane of graphene nanoplatelets whereas carboxyl and amino groups are decorated at the edge sites [12]. The models of GN, GNCOOH, GNOH, and GNNH₂ are displayed by Figure 2.
In this simulation, 50 DGEBA and 25 33DDS were placed into a simulation box. In the cross-linking process, the scattered epoxy monomer and curing agents formed chemical bonds with each other. Next, the four kinds of dopants were placed respectively into the simulation box with the uncrosslink epoxy monomer and curing agents. Models of the four nano-composites were established repeating the cross-linking process. The following abbreviations were used to represent the nano-composite models in the paper: EP-GN, EP-GNCOOH, EP-GNOH, and EP-GNNH$_2$. Parameters of the nano-composites are given in Table 1 and the models are displayed by Figure 3.

The established models of EP and nano-composites were relaxed in an NPT ensemble. The temperature, pressure, and time settings of the relaxation process were 298K, 1 atm, and 100ps respectively. Structures of the crosslink models were closer to the actual situation after relaxation. The resultant models were adopted as test objects in subsequent simulation. The simulation was performed in the open-source large-scale atomic-molecular massively parallel simulator (LAMMPS) [13].
Figure 3. Model of Nano-composites.

Table 1. Parameters of Models.

| Model       | Number of Atoms in models | Molecular Weight | Mass Fraction of Dopants in Nano-composites |
|-------------|---------------------------|------------------|---------------------------------------------|
|             | C  | H  | N  | O  | S  |                                 |
| EP          | 1350 | 1500 | 50  | 250 | 25 | 23228.4                          |
| EP/GN       | 1548 | 1538 | 50  | 250 | 25 | 25644.9  9%                      |
| EP/GNCOOH   | 1558 | 1539 | 50  | 270 | 25 | 26086  11%                      |
| EP/GNOH     | 1548 | 1548 | 50  | 260 | 25 | 25815  10%                      |
| EP/GNNH₂    | 1548 | 1549 | 60  | 250 | 25 | 25796.1  10%                    |

3. Calculation of dielectric constant

In principle, dielectric constant can be calculated by measuring total dipole moment \( M \) of the model. During the simulation process, the five models were firstly relaxed in an NVT ensemble at 300K for 50ps. Then the relaxed models ran MD simulation in an NVT ensemble at 300K for 50ps. The simulation was performed for 10 times repeatedly. For each simulation, total dipole moment of model was obtained, dielectric constant \( \varepsilon \) can be described by [14]

\[
\varepsilon = 1 + \frac{1}{3Vk_B T \varepsilon_0} \left( \langle \vec{M}^2 \rangle - \langle \vec{M} \rangle^2 \right)
\]

(1)

\( V \) and \( T \) are volume and temperature of the models, \( k_B \) is the Boltzmann’s constant. \( \varepsilon_0 \) is the dielectric constant of vacuum. \( \langle \vec{M}^2 \rangle \) is the average value of the dipole moment squared, \( \langle \vec{M} \rangle^2 \) is the square of the mean dipole moment values. The dielectric constants obtained by repeating the calculation of each model were averaged, the resultant dielectric constants of the five models are shown in Figure 4.
The dielectric constant of EP was calculated as 2.909. This value is in good agreement with 2.5-6.0 as observed by other researchers. Dielectric constants of nano-composites generally have lower dielectric constant than EP. EP-GNOH has the lowest dielectric constant of 2.156, which is 25.9% lower than dielectric constant of EP and 9.4% lower than dielectric constant of EP-GN. This phenomenon can be explained by the polarization mechanism of epoxy. The polarization mechanism of epoxy is dipole polarization, which depends on the mobility of chain segments. The sp²-carbons in GN can form strong π–π stacking interactions with aromatic rings in EP. The interactions intensified the constraints on chain segments in EP-GN and reduced its dielectric constant. Molecular structure of hydroxyl can introduce strong hydrogen bonds. The bonds enhanced the constrains on chain segments and further reduced dielectric constant of EP-GNOH.

4. Calculation of thermal conductivity

A common method to calculate thermal conductivity in MD simulation is nonequilibrium molecular dynamics (NEMD) [15]. In NEMD, a heat flux is imposed on the simulation system and the thermal conductivity is related to the resultant temperature gradient by:

$$\kappa = -\frac{J_x}{\partial T/\partial x}$$

(2)

$J_x$ is the heat flux which is defined as the amount of energy transferred in a given time through a surface of given area perpendicular to the flux direction (x direction in this case). $\partial T/\partial x$ is the temperature gradient along x direction.

The models were firstly heated integrally in NVT ensemble at 300K for 50ps. Then the models were heated partially in NVE ensemble for 100ps. In the partial heating process, the simulation box was divided into 20 “slices” along x direction. The slices at the two end of the box were set as fixed layer displayed by Figure 5. A “hot” plate and a “cold” plate were artificially placed next to the two fixed layer. The hot plate and cold plate were also known as heat source and heat sink. In each time step, kinetic energy of the hottest atom in the heat sink exchange with kinetic energy of the coldest atom in the heat source. The exchanging process produced a heat flux from the heat source to the heat sink, which led to a temperature gradient in the intervening region. Temperature of the slices were calculated at each iteration. Once the model reached a steady state, thermal conductivity of the material can be calculated.
Take x direction of EP model as an example, heat flow with the change of simulation time is displayed by Figure 6. When a stable, linear temperature profile is reached, temperature gradient of the model is displayed by Figure 7. Repeat the above-mentioned process on the five models, for each model the simulation was performed in x, y, and z direction. Each calculation was performed for five times with a spontaneous initial energy of the molecule. Take the average of five calculation results as the thermal conductivity. The integral thermal conductivity of the model was represented by the arithmetic mean of the thermal conductivity in three directions. The results are shown in Table 2.

Table 2. The thermal conductivity of five epoxy models.

| thermal conductivity \( \kappa/Wm^{-1}K^{-1} \) | x direction | y direction | z direction | integral |
|-----------------------------------------------|-------------|-------------|-------------|----------|
| EP                                            | 0.1484      | 0.1551      | 0.1285      | 0.1440   |
| EP-GN                                         | 0.1988      | 0.2647      | 0.1009      | 0.1882   |
| EP-GNCOOH                                      | 0.2060      | 0.2744      | 0.1207      | 0.2004   |
| EP-GNOH                                       | 0.2619      | 0.1537      | 0.1661      | 0.1939   |
| EP-GNNH\(_2\)                                 | 0.2601      | 0.2585      | 0.1073      | 0.2086   |

The thermal conductivity of EP was calculated as 0.1440 Wm\(^{-1}\)K\(^{-1}\). This is in reasonable disparity with the value of 0.19 Wm\(^{-1}\)K\(^{-1}\) given by experiments [16]. Nano-composites with dopants have larger thermal conductivity compared to EP. GN, GNCOOH, GNOH, and GNNH\(_2\) enhanced thermal conductivity of EP by 30.69%, 39.17%, 34.65% and 44.86% respectively.

It can be concluded from the results that thermal conductivity of z direction in nano-composites is smaller than thermal conductivity of x and y direction. This can be attributed to interfacial thermal resistance (also known as Kapitza resistance) cause by the large distinction of thermal properties between graphene and EP [17]. Covalent functional groups in nano-composites can enhance
interaction between dopants and polymer matrix as well as diminish interfacial thermal resistance. Hence, thermal conductivity of nano-composites with functional groups was increased.

5. Conclusion
In this study, MD simulation was performed to investigate the dielectric constant and thermal conductivity of five crosslink models. The five models include crosslink epoxy and four epoxy based nano-composites. The model of crosslink epoxy was built as comparison to the nano-composites. The fillers of nano-composites were graphene nanoplatelets, carboxyl functionalized graphene nanoplatelets, hydroxyl functionalized graphene nanoplatelets, and amino functionalized graphene nanoplatelets. The influence of different dopants to the performances of nano-composites were examined.

- Calculate the dielectric constant by counting dipole moment of the simulation system. Among the different covalent groups, hydroxyl is the most effective one in reducing dielectric constant, lowering dielectric constant by 25.9% compared to EP.
- Calculate the thermal conductivity applying NEMD method. All nano-composites had different degree of enhancement in thermal conductivity. EP-GNNH₂ had the largest thermal conductivity which is 44.86% larger compared to thermal conductivity of EP.

The present findings provide a review on dielectric constant and thermal conductivity of epoxy doped with functionalized graphene nanoplatelets. The results can offer a useful guidance for the future development of graphene-epoxy nano-composites in insulation material.

6. References
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Acknowledgments
This study is supported by the State Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources(Grant No.LAPS19006).