Interfacial interaction mechanism of graphene/phenolic resin composites: A molecular dynamics study

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Abstract. The outstanding thermal and mechanical properties of graphene/phenolic resin (G/PR) composites are largely related with the interfacial interactions. The interfacial properties of the G/PR composites were studied with molecular dynamics method, based on dozens of G/PR and graphene oxide/PR (GO/PR) interface models. The results showed that, $p$-$\pi/\pi$-$\pi$ and hydrogen bond interactions are the main interactions between the G/PR and GO/PR interfaces, respectively. Strong interfacial interactions were formed between the crosslinked PRs and GO layer grafted with oxygen-containing groups. The obtained results will be beneficial to guide the design and preparation of G/PR composites with special performances.

1. Introduction
Phenolic resins (PRs), which are one of the typical thermosetting resins in the world, are widely used in the fields of electronics, aerospace, transportation and other industries, owing to the good mechanical, thermal resistance performance of PRs.[1] The excellent comprehensive properties of PRs largely depend on the crosslinked structure, which consist of a network of tri-branched phenols that are linked by methylene bridges. However, owing to the inherent defects of the weakness of the C-O and C-C bonds, both the thermal and mechanical properties can hardly be further enhanced with simply optimization of the raw materials or the preparation procedure.

During the past decades, many modification approaches for PR are reported, such as etherification, esterification, chelation and blending, etc. Recently, it is reported that a low loading of nanocarbon materials (such as carbon nanotube (CNT) and graphene) in PR, can significantly enhance the thermal and mechanical properties[2]. Especially, the graphene/PR (G/PR) or graphene oxide/PR (GO/PR) exhibits better thermal property than that of both PR and CNT/PR. Si et al.[3] found that the blending of GO into PR can significantly improve the thermal decomposition temperature ($T_d, 5\%$, 15 °C) and the char yield (800°C, 8%). Yuan et al.[4] prepared GO/PR composites by added 1.7 vol% GO into resole solution, the elasticity modulus of the dried product was 316.8% higher than the unmodified PR. They explained that the phenolic rings near the graphene layer tend to form $p$-$\pi/\pi$-$\pi$ interactions, which lead to catalytic graphitization effect. These studies showed clearly that the apparent properties of G/PR are highly related with the interfacial interactions between the two components.

Molecular dynamics (MD) simulation method has been proved is a powerful tool to reveal the interfacial non-bond interactions. Skoutzos et al.[5] investigated the relationship between the interfacial interactions and mechanical properties of poly(methyl methacrylate)/graphene
nanocomposites, with MD simulation. Desai et al.[6] found that the introduction of CNT and graphene in PR can improve the degree of graphitization, with the aid of MD.

The novelty of this work is that, since it is still a challenge to detaily characterize the interfacial interactions of G/PR composites with experimental approaches, MD simulation method was applied in this work to reveal the physical nature of the interfacial interactions in G/PR and GO/PR. Based on several different interfacial models, the effect of degree of polymerization, the crosslink structure of PR, and the types of the oxygen-containing functional groups on the GO surfaces, on the interfacial interactions were studied.

2. Simulation details

2.1. Model construction
Models with different PR and graphene (or GO) combinations were constructed.

2.1.1. G/PRs with different degree of polymerization. These models are named as G/Boo-2, G/Boo-8, G/Boo-16, G/Bop-2, G/Bop-8, G/Bop-16, in which Boo and Bop stand for the two typical bulk novolac models (Figure 1). The degree of polymerization (DP) of these novolac chains are 2, 8 and 16, respectively.

![Figure 1: Phenolic resin models with different degree of polymerization. The DP is equal to 2, 8 and 16, which is typical DP in the real novolac resins.](image)

2.1.2. GO/PRs with different oxygen-containing groups. These models are named as GO_OH/Boo-8, GO_EP/Boo-8, GO_COOH/Boo-8, GO_OH/Bop-8, GO_EP/Bop-8, GO_COOH/Bop-8, in which GO_OH, GO_EP and GO_COOH stand for GO models that are grafted with hydroxyl (-OH), epoxy (-CH(O)CH-) and carboxyl (-COOH) groups, respectively.

2.1.3. G/PRs and GO/PRs with crosslinked PR. These models are named as G/Boo95, GO/Boo95, G/Bop95 and GO/Bop95. Boo95 and Bop95 stand for crosslinked PR models with 95% o and p sites of the phenolic rings were linked by methylene bridges, which means they are highly crosslinked PR models. The C/O ratio of the GO model is equal to 5:1. The crosslinked PR models were built according to Izumi et al.[7] and Monk et al.’s[8] methodology, which can be briefly described as: i) The o and p active sites in the novolac chains with proper distance were randomly linked by methylene bridges; ii) Geometry optimization or MD relaxation; iii) Link the potential un-linked o and p sites with larger searching radius; iv) End the loop if the searching radius is higher than a specific value (10 Å in this study). All the models above were constructed with the Packmol[9] and LAMMPS[10] software. There are about 6000 atoms for each model.

2.2. Molecular dynamics simulation

2.2.1. Equilibration. After construction, these models were fully relaxed with several cycles of annealing, until the energy and density reach equilibrium. To achieve the fully equilibrated configurations of these models, three NPT-MD anneal circles (200-800 K) were conducted for all the above models, with a heating rate of 50 K/500 fs. The Berendsen barostat[11] was used for the anneal process. OPLS-AA force field[12] was applied in the MD simulations. The force field parameters C, H
and O elements in PR were referenced from the Izumi and Monk et al.’s work [7, 8]. The time step and vdW interaction cut-off distance was 1 fs and 12.5 Å, respectively.

2.2.2. Interfacial interaction calculation. After the anneal simulation, further 1ns NVT simulation (300 K) were performed to obtain the required trajectories. The trajectories with totally 1000 frames for each model were generated with a frequency of 1 frame/1000fs. The hydrogen bond number, the radial distribution function (RDF) of O-O pairs and phenol-phenol ring pairs between the interface were calculated, based on the latter half of the trajectory for each model. The total van der Waals and electrostatic interaction energies were also calculated. The total interfacial interaction energy (\( <E_{int}> \)) is defined as,

\[
\langle E_{int}\rangle = \frac{E_{A/B} - (E_A + E_B)}{S}
\]

where \( <E_{int}> \) is the total interfacial interaction energy, which is in the unit of kcal·mol\(^{-1}\)·Å\(^{-2}\). The angle brackets refer to that it is an averaged value from 500 frames. \( E_{A/B} \) is the total energy of the composite model of A/B (such as G/PR). \( E_A \) and \( E_B \) are the independent energies of A and B when they were put into the same box size with A/B. S is the cross-sectional area along the interface of the composite model of A/B. \( <E_{vdW}> \) and \( <E_{elec}> \) can be calculated with the similar way.

3. Results and discussion

3.1. The effect of degree of polymerization

It can be speculated that there will be \( p-\pi/\pi-\pi \) interactions between both the G/PR and GO/PR interfaces, and hydrogen bond interactions between GO/PR. Zheng et al. [13] suggested that, the distribution function or density profile of the phenolic rings and hydroxyls along the normal direction of the graphene plane will useful to disclose the interfacial \( p-\pi/\pi-\pi \) and hydrogen bond interactions. The typical distance for \( p-\pi/\pi-\pi \) stack is within the range of 3.5-4.2 Å. These differences can be reflected by the RDF of the oxygen atom pairs and phenolic ring pairs. During the calculation, the oxygen atoms and phenolic rings in the graphene or GO layer were regard as the referential objects, and the distribution functions of the oxygen atoms and phenolic rings in the novolac components along the Z direction were calculated.

The distribution functions of the oxygen atoms or phenolic rings in the novolac along the Z direction (vertical to the graphene or GO layer) will provide the first clues about the nonbond interaction types between the two components in G/novolac composite models. The distribution functions plots (Figure 2) of the oxygen atoms and the phenolic rings show that there exist \( \pi-\pi \) and \( p-\pi \) (CH-\( \pi \), OH-\( \pi \)) interactions between the graphene/novolac interfaces. The left two sub-figures in Figure 2 are the distribution function plots of the oxygen atoms in the novolac systems along the Z direction, in which the carbon atoms in the graphene layers are regarded as reference atoms for RDF calculation. The first peaks of these plots are appeared within the range of 1.2-5.0 Å, these are largely attributed to the OH-\( \pi \) interactions. The right two sub-figures in Figure 2 are the distribution function plots of the centroid of the phenolic rings atoms in the novolac systems along the Z direction. The first peaks of these plots are appeared within the range of 2.0-7.0 Å, these are attributed to both the \( p-\pi \) and \( \pi-\pi \) interactions.

The degree of polymerization of the novolac chain have significantly effects on the peak shape of these plots. Roughly speaking, it can be found that the first peaks of these curves tend to decrease or move to the higher parts, along with the degree of polymerization. The main reason for this phenomenon is the rigidity of the novolac chains. The higher the degree of polymerization, the less possibility they can form nonbond interactions with the graphene layers. But for the composite systems with higher degree of polymerization, the tangled molecular chains mainly played the role of winding the graphene layers together.
The top two are from the graphene/Boo-x systems, while the lower two are from the graphene/Bop-x systems. The number x (2, 8 and 16) refer to the degree of polymerization. The distribution function curves were calculated based on the obtained MD trajectories for each model. The higher the first peaks around 3.5 Å, the more hydrogen bonds formed between the interfaces. The higher the peaks around 4.5 Å, the more p-π and π-π interactions formed between the interfaces.

The connection patterns of the novolac chain also influence the peak shape of these plots. For the RDF plots of oxygen atoms (Figure 2a and 2b), only the plot of G/Boo-2 has a sharp peak around 3.5 Å, while both the plots of G/Bop-2 and G/Bop-8 have apparent peaks within the range of 1.2-4.5 Å. For the RDF of the phenolic rings (Figure 2c and 2d), the areas under the first peak of the RDF curves of G/Bop-2, G/Bop-8 and G/Bop-16 are higher than that of G/Boo-2, G/Boo-8 and G/Boo-16, respectively. These phenomena are derived from the different nonbond interaction mechanism in the Boo-x/Bop-x models. Since the hydroxy groups in the Boo-x models can form more intra hydrogen bonds than that in the Bop-x models, this led to more curled novolac chains in Boo-x and less possibility to form interfacial non-bond interactions with the graphene layer. However, there are many hydroxyl and benzene groups available near the interface to form OH-π and π-π interactions with the graphene layer.

3.2. The effect of oxygen containing groups

The distinctive feature of graphene oxide is the various kinds of oxygen-containing groups (such as hydroxyl, epoxy and carboxyl groups) distributed on the GO surface. The constitution, number and distribution of these groups have decisive effects on the interfacial interactions, as well as the relative thermal and mechanical properties of the GO/polymer composites. In the below section, single layer GO models with different degree of oxidation and grafted with different oxygen-containing groups were built, their interfacial interactions with Boo-8 and Bop-8 were also studied. For GO_OH, GO_EP (grafted with epoxy group) and GO_COOH, the oxygen-containing groups were randomly distributed on the both sides of the GO surfaces.

The distribution function curves of these GO/novolac models show different trends, owing to the different nonbond interaction formation mechanism between GO and the three kind of oxygen-containing groups with the novolac systems. It can be seen that the areas of the first peaks for both the O atoms and the phenolic rings for the GO_COOH/Boo-8 and GO_COOH/Bop-8 are significantly larger than that of the other curves. Since both the two oxygen atoms in the carboxylic group can form hydrogen bonds with the hydroxyl groups in the novolac systems, especially with that in Bop-8, the strongest nonbond interactions can be formed in GO_COOH/Bop-8 (Figure 3c and 3d). Meanwhile, as the carboxylic groups are “longer” than hydroxyl and epoxy groups, they can embed within the
novolac systems and form more hydrogen bonds or OH-π interactions. It can also be found that because of the intra hydrogen bonds in Boo-8, small amount of hydrogen bonds were found in the GO/Boo-8 (Figure 3a), but many π-π interactions can still be found in GO/Boo-8 (Figure 3c).

**Figure 3.** Distribution functions of oxygen atoms (a and b) and phenolic rings (c and d) along the Z direction in GO/novolac composite models. The top two are from the GO/Boo-8 systems, while the lower two are from the GO/Bop-8 systems. GO_OH, GO_EP and GO_COOH refer to the GO models with hydroxyl, epoxy and carboxyl groups grafted on the GO layers, respectively. There are strong RDF peaks can be found between the GO/Bop-8 interfaces, which means that many interfacial hydrogen bonds were formed, compared with the GO/Boo-8.

### 3.3. The effect of crosslink

In most application fields, PR can only be used after cured. Thus, the interfacial interactions of crosslinked G/PR and GO/PR should be studied. Four typical composite models were constructed, based on almost fully crosslinked PR models of Boo95 and Bop95, in which “95” represents for 95% of o- and p- sites of phenolic rings in the PR models (originated from Boo-8 and Bop-8) were crosslinked together. The three type of oxygen-containing groups were randomly on the both sides of the GO layer.

According to the distribution function curves of oxygen atoms (Figure 4a) and phenolic rings (Figure 4b) along the Z direction in the G/PR and GO/PR composite models, hydrogen bonds and p-π/π-π interactions can be verified. As the crosslinked models of Boo95 and Bop95 were constructed based on novolac models of Boo-8 and Bop-8, respectively, a comparison between G/Boo95 and G/Bop95, G/Boo95 and G/Bop95 and G/Boo95 and G/Bop95, G/Bop-8 and G/Bop95 will offer further clues about the effect of crosslink. The first peak of the distribution curve of oxygen atoms (Figure 4a) of G/Boo95 is higher than that of G/Bop95, which is similar to that of G/Boo-8 versus G/Bop-8. This means that crosslink have little effect on the interfacial OH-π interactions of G/PR, this is in accord with the distribution curves of the phenolic rings (Figure 4b).

Compared with G/crosslinked PR (G/Boo95 and G/Bop95), there are little difference between the distribution curves of oxygen atoms of GO/crosslinked PR (GO/Boo95 and GO/Bop95). Meanwhile, the distribution curves of oxygen atoms of GO/un-crosslinked PR (GO_OH/Boo-8 and GO_OH/Bop-8, etc.) shown different peak distribution characteristics. This could largely be owing to the strong hydrogen bond formed between the oxygen containing groups and phenolic hydroxyl groups in GO/un-crosslinked PR systems. After crosslinked, the potential groups (phenolic hydroxyl and phenyl group) that can form interfacial interactions were “frozen” in the crosslinked network. The oxygen containing groups on the GO layer can hardly stretch into the crosslinked PR network, and consequently, the possibility of hydron bonds and p-π/π-π formation in the deep area of PR network reduced. On the other hand, the oxygen containing groups on the GO layer with various lengths have
more chance to form hydrogen bonds or $p$-$\pi$ interactions. A competition result of these phenomena is that, very strong interfacial interaction was formed between the GO/crosslinked PR interfaces, compared with the other G/PR or GO/PR models (Table 1).

![Figure 4. Distribution functions of oxygen atoms (a) and phenolic rings (b) along the Z direction in G/PR and GO/PR composite models. The black-dashed, black-solid, red-dashed, red-solid lines represent for G/Boo95, GO/Boo95, G/Bop95 and GO/Bop95, respectively. Strong peaks can be found between the G/Boo95 and G/Bop95 interfaces within the range of -5 to 5 Å, which means that many interfacial $p$-$\pi$-$\pi$ interactions were formed, compared with the GO/Boo95 and GO/Bop95.](image)

3.4. Interface interaction energy

The interfacial interaction energies, including total ($<E_{\text{Int}}>\), van der waals ($<E_{\text{vdW}}>\) and electrostatic ($<E_{\text{Coulomb}}>\) interaction energies, of the above G/PR or GO/PR composite models were quantitative calculated (Table 1).

| Models    | $<E_{\text{Int}}>$ | $<E_{\text{vdW}}>$ | $<E_{\text{Coulomb}}>$ | Models    | $<E_{\text{Int}}>$ | $<E_{\text{vdW}}>$ | $<E_{\text{Coulomb}}>$ |
|-----------|------------------|------------------|------------------|-----------|------------------|------------------|------------------|
| G/Boo-2   | -0.594           | -0.562           | 0                | G/Bop95   | -0.595           | -0.563           | 0                |
| G/Boo-8   | -0.547           | -0.515           | 0                | G/Boo-16  | -0.547           | -0.515           | 0                |
| GO_OH/Boo-8| -0.580         | -0.464           | -0.082         | GO_OH/Bop-8| -0.684           | -0.460           | -0.191         |
| GO_COOH/Boo-8| -0.655       | -0.451           | -0.166         | GO_COOH/Bop-8| -0.714           | -0.455           | -0.220         |
| G/Boo95   | -0.464           | -0.289           | -0.149         | G/Boo95   | -0.915           | -0.575           | -0.363         |
| G/Bop95   | -0.684           | -0.413           | -0.238         | G/Bop95   | -0.959           | -0.578           | -0.316         |

Note: $<E_{\text{Int}}>$, $<E_{\text{vdW}}>$ and $<E_{\text{Coulomb}}>$ represent the total, van der waals and electrostatic interaction energies per unit area, the unit area is the section plane perpendicular to $Z$ direction of the box (approximately parallel to G or GO layer).

It can be found that, for both the G/PR and GO/PR systems, the interaction energy is mainly contributed from van der waals ($p$-$\pi$-$\pi$, hydrogen bond) interactions, which is in accordance with the above RDF analysis results. There is no electrostatic interaction between the G/PR interfaces. While for GO/PR systems, electrostatic interactions contribute about 10–40% in the total interaction energies. As the degree of polymerization increases, the interaction energy decreases. For most G/PR or GO/PR systems, the interfacial interaction energies of $o$-$p$ type are stronger than that of $o$-$o$ type PR. Carboxyl groups on the GO layer contribute more electrostatic interactions than that of hydroxyl and
epoxy groups. The oxygen containing groups with various lengths distributed on the GO layer lead to strong interfacial interaction between the GO/PR interfaces.

4. Conclusion
In this study, the interfacial interaction mechanism between the G/PR and GO/PR composites was investigated by molecular dynamics simulation, based on different composite models. The p-π/π and hydrogen bond interactions are the main interactions between the G/PR and GO/PR interfaces, respectively. For G/PR systems, the higher the degree of polymerization, the less possibility the novolac chains can form non-bond interactions with the graphene layers. For both the G/PR and GO/PR systems, the o-p type novolac systems have more possibility to form interfacial hydrogen bonds and p-π interactions with the GO layer, compared with o-o type systems. Strong interfacial interaction can be formed between crosslinked PR and GO with proper ratio of grafted oxygen-containing groups.

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