# Thermal enhancement of graphene/ polyethylene glycol (PEG) by interfacial crosslinking modification: molecular dynamics simulation

Xuehong Wu<sup>a,b\*,</sup> Mengyao Liu<sup>a</sup>, and Yanping Du<sup>c,\*</sup>

a School of Energy and Power Engineering, Zhengzhou University of Light Industry, Zhengzhou, Henan 450000, China;

*b* International Joint Laboratory for Efficient Energy Conversion and Utilization of Henan Province, Zhengzhou, Henan 450000, China;

c School of Engineering, Lancaster University, Lancaster LA14YW, UK \* Corresponding author: wuxh1212@163.com, y.du17@lancaster.ac.uk

Abstract: Polyethylene glycol (PEG) phase change materials (PCMs) are widely used in energy storage applications due to their excellent thermal properties. This study investigates, at the molecular level, the effects of graphene (GN) functionalization and the number of graphene layers on the interfacial thermal conductivity of composite phase change materials (CPCM) using the velocity rescaling method. By calculating the phonon density of states (PDOS), the study elucidates the mechanism through which functional groups enhance the interfacial thermal conductivity of GN/PEG composites. Additionally, the radial distribution function of carbon atoms in graphene with varying numbers of layers and PEG is analyzed. Finally, the thermal conductivity of the composite material is predicted using the effective medium theory. The results show that crosslinking modification significantly improves the thermal conductivity of the composite material, with -C7H15GN demonstrating the most notable enhancement in the GN/PEG interfacial thermal conductivity. When the filler volume fraction is 15%, the thermal conductivities of the graphene based CPCM achieves  $6.17 \text{ W/(m \cdot K)}$  or more, which is 643% higher than the corresponding values of composite phase change materials with 1% volume fraction of graphene.

**Keywords:** Composite phase change materials (CPCM); Covalent modification; Interfacial thermal conductivity; Molecular Dynamics Simulation; Effective Medium Theory

#### 1. Introduction

Due to the energy crisis and environmental issues caused by the overuse of fossil fuels, effects have been made on sustainable energy technologies[1, 2]. Phase change materials address energy concerns by reversibly storing large amounts of thermal energy, helping to alleviate energy scarcity to some extent[3, 4]. Latent heat storage utilizes phase change materials that store thermal energy through the solid-liquid phase transition[5, 6], Its energy density is much higher than that of conventional sensible heat storage systems, which is beneficial to save materials and space[7]. Polyethylene glycol has garnered significant attention as a primary medium for latent heat storage due to its high latent heat, excellent cyclic stability, and non-toxicity[8]. However, the low thermal conductivity of these phase change materials limits their practical applications[9, 10]. To address this issue, researchers have proposed various methods, primarily by incorporating high thermal conductivity fillers to form functional composite phase change materials (CPCM), thereby enhancing thermal conductivity[11, 12]. For example, high thermal conductivity fillers such as graphene and carbon nanotubes are widely used to enhance the thermal conductivity of phase change materials[13]. As a novel carbon-based material, graphene has been extensively applied in CPCM due to its exceptional thermal conductivity. However, when graphene is incorporated into a polymer matrix, challenges arise due to weak interfacial bonding and lattice mismatch, which result in significant interfacial thermal resistance. This presents a challenge in understanding the key factors that govern interfacial heat transfer performance[14]. Previous studies have mostly focused on experimental methods at the macroscopic level to determine the effect of graphene on the thermal conductivity of composite phase change materials. To the knowledge of authors, there are few experimental research examining the promotional effect of graphene from a microscopic perspective.

However, based on molecular dynamics (MD) methods, significant progress has been made in the thermal conductivity improvement of graphene-based CPCM[15]. Yu et al[16] selected PEG as the phase change material and used molecular dynamics simulations to achieve chemical crosslinking between graphene and PEG and analyzed the thermal conductivity and phase transition temperature at different conditions. The results showed that when the surface coverage of graphene reached 12%, the thermal conductivity of the composites increased by 85.8% and 93.3%, respectively, due to the existence of carboxyl and amino modifications. Liu et al[17] demonstrated that non-covalently functionalized graphene enhances composite thermal conductivity by up to 183.66% while reducing interfacial thermal resistance by 21.58%, achieved through optimized phonon coupling and improved nanofiller dispersion. Yang et al[18] revealed that polar functional groups (particularly hydroxyl groups) significantly enhance the interfacial thermal conductivity of grapheme /PVA composites by strengthening interfacial Coulomb interactions and hydrogen bond networks. Yan et al[19] demonstrated that covalent functionalization approaches, particularly carboxylation modification, simultaneously enhanced the composite's thermal conductivity by 156.56% while reducing interfacial thermal resistance by 41.84%. This remarkable performance improvement originates from the synergistic optimization between optimal phonon matching and graphene dispersion achieved at a functionalization degree of 11.96%, providing crucial theoretical guidance for designing high-performance thermally conductive composites. Guo et al[20] conducted molecular dynamics simulations to study the phase transition process and thermal physical properties between functionalized graphene and PEG. It was found that the higher the degree of functionalization on the graphene surface, the lower the interfacial thermal resistance between graphene and PEG. Huang et al[21] established non-equilibrium molecular dynamics (NEMD) models to investigate the thermal conductivity of CPCM incorporated with graphene of different morphologies. The results showed that non-covalent functionalization of the graphene surface contributed significantly to the change of the thermal properties. Compared to single-layer graphene, graphene oxide reduced the mean square displacement (MSD) and lowered the intrinsic mean free path due to the surface groups. This not only makes graphene oxide an excellent thermal conductor but also enhances the interfacial heat transfer between graphene and paraffin. Zabihi et al[22] carried out molecular dynamics simulations to study the thermal conductivity of graphene/paraffin nanocomposites. The results revealed that introducing methyl and phenyl functional groups at the nanocomposite interface significantly enhanced the thermal conductivity of the CPCM. With the increasing of the functional coverage, the thermal conductivity increased significantly. It was reported that the phenyl functional group was the most effective modifier for improving the thermal conductivity of the graphene/nanocomposites, as it helps form a more efficient thermal conduction network within the paraffin. Jamshideasli[23] adopted the NEMD simulation method to examine the interfacial thermal conductivity (ITC) of multilayer graphene with an octadecane ( $C_{18}H_{38}$ ) matrix in both parallel and perpendicular directions to the heat flow. The results showed that systems with thinner graphene layers exhibited higher ITC values. Salehi[24] simulated the effects of monolayer, bilayer, and trilayer graphene or graphene oxide on the thermal performance of the CPCM. The results indicated that more graphene/ graphene oxide layers increased the irregularity of the interface, leading to a 64.4% decrease in thermal conductivity. It was pointed that both the layers number and the arrangement of graphene or graphene oxide contributed substantially to the interfacial thermal resistance.

Although the research on graphene/PEG composites has attracted widespread attention, the microscopic effects of the type of functionalization, coverage, and number/ arrangement of graphene layers of mechanisms on interfacial heat transfer are not fully understood. Therefore, further studies on the enhancement effects of functionalized graphene and multilayer graphene on the thermal performance of graphene/PEG composites is of importance. To address this, our study explores how functionalized and multilayer graphene affects the thermal performance of PEG-based phase-change materials at the molecular level. Using the velocity rescaling method, we quantify interfacial thermal conductivity and systematically evaluate different graphene modifications. Specifically, we examine PEG composites containing graphene (GN), as well as functionalized graphene with hydroxyl (-OHGN), carboxyl (-COOHGN), methyl (-CH<sub>3</sub>GN), butyl (-C<sub>4</sub>H<sub>9</sub>GN), and heptyl (-C<sub>7</sub>H<sub>15</sub>GN) groups, each with varying grafting densities. Additionally, we analyze how the number of graphene layers (ranging from 1 to 9) impacts thermal conductivity. To uncover the microscopic mechanisms behind these effects, we combine phonon density of states calculations and radial distribution function analysis to identify key factors influencing interfacial heat transfer. We also apply effective medium theory to predict the thermal conductivity of composites at different graphene volume fractions. The results show that functionalized graphene significantly enhances the interfacial thermal conductivity of the composites, with -C7H15GN exhibiting the most pronounced enhancement. However, as the number of graphene layers increases, the interfacial thermal conductivity of PEG-GN composites gradually decreases. These insights deepen our understanding of graphene's role in improving thermal transport in PEG and provide valuable guidance for designing highly efficient thermally conductive composites.

## 2. Molecular simulation (MD) model

#### **2.1. Model construction**

In this study, the non-equilibrium molecular dynamics (NEMD) method was used to investigate the thermal transport properties of graphene/PEG composites, with a focus on analyzing the effects of graphene surface functionalization and the number of graphene layers on the interfacial thermal conductivity of the composites. Simulations was done to analyze the thermal transport behavior at the PEG-graphene interface, including interactions between PEG and functionalized graphene and multilayer graphene. The modeling was initially carried out using the Materials Studio software. As shown in Figure 1(a), the PEG model consists of a single-chain structure of  $C_{50}H_{102}O_{26}$ , with each polymer chain containing 25 monomers, serving as the polymer matrix. Figure 1(b) presents the structural model of monolayer graphene. As a thermal conductive filler, graphene was modeled with dimensions of 3.68 nm × 3.41 nm. This is reasonable because the dimensions, were capable of capturing the primary phonon contributions to the interfacial thermal conductivity in terms of results reported by Luo et al[25] On this basis, a simulation model with dimensions of 36.83  $\times$  34.03  $\times$  192.98 Å and a density of 1.18 g/cm<sup>3</sup> was established by embedding monolayer graphene into the PEG phase change material (as shown in Figure 1(c)). The system consists of 100 PEG chains and square graphene fillers. To investigate the effect of surface functionalization on the graphene/PEG interfacial thermal conductivity, five common chemical functional groups were used to modify the surface of graphene. The established models are shown in Figure 1(d-i), representing GN, -OHGN, -COOHGN, -CH<sub>3</sub>GN, -C<sub>4</sub>H<sub>9</sub>GN, and -C<sub>7</sub>H<sub>15</sub>GN, respectively. The functional groups are covalently grafted onto the surface of graphene, with an equal and random distribution of functional groups on both sides. This study simulated the thermal transport behavior across graphene/PEG interfaces with 1-9 layers under perpendicular heat flux. For clarity of presentation, the single-layer graphene system is shown as a representative example (systems with other layer numbers exhibit similar structures to that shown in Figure 1(c)). The regulatory effects of introducing multilayer graphene on interfacial thermal transport characteristics were analyze.



Figure 1. (a) single-stranded structure diagram of peg-C<sub>50</sub>H<sub>102</sub>O<sub>26</sub>; (b) single-layer graphene structure diagram; (c) System structure diagram of single-layer graphene and polyethylene glycol; Structural diagrams of (d-i)GN, -OHGN, -COOHGN,

-CH<sub>3</sub>GN, -C<sub>4</sub>H<sub>9</sub>GN and -C<sub>7</sub>H<sub>15</sub>GN.

#### 2.2. Force field settings

A force field (also known as a potential function) is a mathematical model used to describe both intramolecular and intermolecular interactions, including the force field expressions and parameters. The potential function can be derived through methods such as experimental fitting, semi-empirical approaches, and machine learning. Due to the diversity of research topics and objectives, there is currently no universal force field that applies to all substances. To meet the needs of different systems and application scenarios, scientists have developed various specialized potential functions. The core of molecular dynamics simulation lies in solving Newton's equations of motion. Therefore, the selection of force field is crucial to the accuracy and reliability of the simulation results. In this study, the PCFF[26] force field was adopted to describe polyethylene glycol and the functional groups. This force field has been widely applied in simulating the thermal transport properties of polymer

molecules and has yielded favorable results. The interactions between carbon atoms within graphene were described using the modified Tersoff potential by Lindsay and Broido[27], which effectively modeled the properties of graphene[28] The van der Waals interactions between polyethylene glycol, functionalized graphene, and graphene of different layers were described using the Lennard-Jones (LJ) 12-6 potential[23] The LJ parameters for graphene were  $\sigma = 3.412$  Å and  $\varepsilon = 0.055091$  kcal/mol, with the cross parameters calculated using the Lorentz–Berthelot mixing rule[29] Additionally, in the functionalized system, the non-bonded interactions of the PCFF force field and the cutoff radius of the Lennard-Jones potential were both set to 14.0 Å. In the multilayer graphene system, these cutoff radii were set to 10.0 Å and 12.0 Å, respectively, to accommodate their unique thermal transport properties. This parameter configuration provides strong support for the accuracy and reliability of the simulated system.

#### 2.3. Computational methods

In this study, the heat transfer process was simulated using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) code. The entire simulation process was carried out using the LAMMPS software[30]. Due to the high-frequency vibrations of hydrogen atoms, a smaller time step of 0.25 fs was used in this study, with periodic boundary conditions applied in all three directions. After constructing the initial model of functionalized graphene/PEG, energy minimization was firstly performed using the conjugate gradient method. The model was then equilibrated at a high temperature of 400 K for 2 ns, followed by rapid cooling to 300 K at a rate of 0.4 K/ps, resulting in an amorphous model. For the initial models of graphene/PEG with different numbers of layers, the models were fully equilibrated at 300 K for 2 ns. The temperature and pressure were controlled using the Nose-Hoover thermostat and barostat. The model was equilibrated for 0.5 ns under both NPT and NVT ensembles to obtain a stable amorphous model at 300 K. During the NPT ensemble equilibration process, the pressure in the XYZ directions was independently controlled and maintained at 1.01325 bar. Subsequently, nonequilibrium molecular

dynamics simulations were performed to investigate the thermal transport properties of polyethylene glycol and graphene/PEG composite materials. The heat source and heat sink were set as shown in Figure 2. 10 Å at both ends of the model were fixed, with 15 Å on either side of the fixed regions designated as the heat source and heat sink. The velocity rescaling method was applied to increase the particle velocities in the heat source region and decrease the particle velocities in the heat sink region, thereby establishing a stable heat flux between the heat source and heat sink. The heat flux was set to 4 kcal/(mol·ps). After 4 ns of stable simulation in the NVE ensemble, a steady temperature gradient was formed. Subsequently, the block averaging method was used to statistically average the temperature data over the following 2 ns, yielding the temperature distribution curve along the heat flux direction. Due to the presence of the graphene interface, a noticeable temperature jump ( $\Delta$ T) appeared on both sides of the interface. Based on this, the interfacial thermal conductivity of the graphene/PEG composite material was calculated.

$$R_0 = \frac{q}{\Delta T} \tag{1}$$

Here,  $\Delta T$  represents the temperature jump at the graphene interface, and q is the heat flux.



Figure 2. Schematic diagram of heat transfer of simulation system.

#### 3. Model and force field validation

To validate the effectiveness of the chosen force field, simulation methods, and model, the phase transition temperature, thermal conductivity of polyethylene glycol, and interfacial thermal conductivity between polyethylene glycol and graphene were calculated. As the temperature increases, the polyethylene glycol system gradually transites from a solid to a liquid state. The thermal motion of the molecules significantly intensifies, leading to noticeable changes in diffusion behavior. The self-diffusion coefficient increases dramatically, indicating a phase transition in the system. By calculating the mean square displacement and self-diffusion coefficient of the polyethylene glycol system within the temperature range of 280–340 K, the phase transition temperature was investigated. The results are shown in Figure 3(a-b), where the phase transition temperature of polyethylene glycol was found to be 316.37 K. The temperature distribution of the polyethylene glycol system along the heat flux direction (Z-axis) is shown in Figure 3(c). The thermal conductivity of polyethylene glycol at 300 K and atmospheric pressure was measured to be  $0.15 \pm 0.001$  W/(m·K), which is in good agreement with both the simulated value[16] and the experimental results[31]. The temperature drop in the PEG-GN system arises due to interfacial thermal resistance, whereas pure PEG lacks such an interface, resulting in a smooth temperature gradient. The temperature distribution of the graphene/PEG system along the Z-direction is presented in Figure 3(d). As can be seen from the figure, the temperature exhibits a linear distribution along the heat flux direction, with a significant temperature jump on both sides of the graphene interface. Based on the above, the interfacial thermal conductivity between polyethylene glycol and graphene was calculated as 33.23 mW/m<sup>2</sup>·K. This value (33.23 mW/m<sup>2</sup>·K) serves as a reference for studying the effects of functional group types and grafting density on the enhancement of interfacial thermal transport in the polyethylene glycol/graphene composite system.





Figure 3. (a) MSD curves of PEG at different temperatures; (b) self-diffusion coefficient of PEG at different temperatures; (c) the steady-state temperature distribution of PEG along the z direction; (d) The steady temperature distribution of PEG-GN system along the Z direction.

#### 4. Effects of graphene (GN) functionalization on the heat transport of CPCMs

## 4.1. Improvement of interfacial thermal conductivity

The variation of interfacial temperature difference and thermal conductivity between polyethylene glycol and graphene covalently modified with five functional groups (-OH, -COOH, -CH<sub>3</sub>, -C<sub>4</sub>H<sub>9</sub>, and -C<sub>7</sub>H<sub>15</sub>) with respect to grafting density is shown in Figure 4. It is seen that with the increase of the grafting density, the interfacial temperature difference between graphene and polyethylene glycol decreases, leading to an increasing interfacial thermal conductivity. The large initial temperature jump is attributed to poor phonon coupling at low grafting density. As grafting density increases, improved interfacial bonding enhances phonon transmission, reducing the temperature difference. With different functional groups, the enhancement of interfacial thermal conductivity varies significantly. Compared to -OH and -COOH, alkyl chain-modified graphene exhibits a more pronounced enhancement in the interfacial thermal conductivity with polyethylene glycol. Among the alkyl chains, the -C7H15 functional group shows the most significant improvement in interfacial thermal conductivity, followed by -C<sub>4</sub>H<sub>9</sub>, and CH<sub>3</sub>, respectively. When the grafting density is lower than 6, the interfacial thermal conductivity of graphene functionalized with different functional groups is approximate. However, as the

grafting density increases further, the enhancement effect of  $-C_7H_{15}$  on interfacial thermal conductivity increases more rapidly. In the condition that the grafting density reaches 18, the interfacial thermal conductivity of  $-C_7H_{15}GN/PEG$  and  $-C_4H_9GN/PEG$ can reach 1.29 times (43.11 mW/m<sup>2</sup>·K) and 1.24 times (41.33 mW/m<sup>2</sup>·K) of the GN/PEG interface, respectively. With a grafting density of  $-CH_3$  in the range of 6-18, the interfacial thermal conductivity of  $-CH_3GN/PEG$  rises from 34.59 mW/m<sup>2</sup>·K to 40.82 mW/m<sup>2</sup>·K. The MD results show that both -OH and -COOH are beneficial to enhance the interfacial thermal conductivity between graphene and polyethylene glycol. As the grafting density increases, the enhancement effect of -OH and -COOH on the GN/PEG interfacial thermal conductivity increases at a relatively slower rate.



Figure 4. Interface temperature difference and thermal conductivity of graphene. and polyethylene glycol with five functional groups under different grafting numbers.

#### 4.2. Phonon density of states analysis

In solid-state physics, phonons are quasiparticles used to describe the quantized energy of lattice vibrations. This concept is also applicable to amorphous materials. Despite of the random distribution of atoms and the lack of a lattice structure in amorphous solids, phonons can still be used to characterize the atomic vibrational behavior. In solid materials, the main carriers of heat conduction typically include electrons and phonons. For polymer nanocomposites, where free electrons are usually absent, heat transfer primarily relies on phonons. Based on the acoustic and diffusion mismatch models, the overlap of the vibrational density of states between graphene fillers and polyethylene glycol is considered as a crucial factor determining the interface thermal conductivity. The phonon density of states can be calculated through the Fourier transform of the velocity autocorrelation function (VACF). Specifically, by performing a Fourier transform on the normalized atomic velocity autocorrelation function, the phonon density of states distribution in the frequency domain can be obtained:

$$D(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} \frac{\langle \sum_{n=1}^{N} v_n(0) \cdot v_n(t) \rangle}{\langle \sum_{n=1}^{N} v_n(0) \cdot v_n(t) \rangle} dt$$
(2)

Alternatively, the discrete cosine transform can be used instead.

$$D(\omega) = \int_{-\infty}^{\infty} \frac{\langle \sum_{n=1}^{N} v_n(0) \cdot v_n(t) \rangle}{\langle \sum_{n=1}^{N} v_n(0) \cdot v_n(t) \rangle} \cos(\omega t) dt$$
(3)

Here, N is the total number of atoms,  $v_n(0)$  and  $v_n(t)$  are the velocities of atom n at the initial and t -th time steps, respectively, and  $\langle \rangle$  denotes the ensemble average.

This study calculated the PDOS of graphene fillers, functionalized graphene, and PEG. As shown in Figure 5, the characteristic peaks of the PDOS of graphene are primarily located around 5–40 THz and 51 THz, while the characteristic peaks of the PDOS of PEG appear around 0–10 THz, 30–45 THz, and 88 THz. This indicates a significant mismatch in the vibration modes between graphene and PEG, which limits the interface thermal conductivity. By covalent modification of graphene with different functional groups, the poor PDOS coupling was improved to varying degrees. Specifically, -OH modification enhanced the PDOS of graphene in the frequency ranges of 3–13 THz and 25–29 THz, and introduced a new characteristic peak at 56.77 THz. Both functional groups improved the low-frequency PDOS coupling between graphene and PEG to some extent. It is evident that the introduction of alkyl functional groups significantly improved the overlap of the PDOS between graphene at 43.64

THz and introduced new characteristic peaks at 86.34 THz and 89.9 THz. However, only partial overlap was achieved at 86.34 THz and 89.9 THz. In contrast,  $-C_4H_9$  and  $-C_7H_{15}$  modifications introduced stronger new characteristic peaks in the high-frequency region (88 THz) except for the peak at 43 THz. This significantly improved the PDOS coupling between graphene and PEG, thereby significantly enhancing the interfacial thermal conductivity. In other frequency regions, compared to other types of graphene, the PDOS peak shapes of  $-C_7H_{15}$ -modified graphene and PEG were more similar, showing a more predominant overlap. This suggests that functionalized graphene can act as a "thermal bridge," effectively coupling the vibrational modes of graphene with those of the PEG chains, thereby reducing phonon scattering and enhancing the interfacial thermal conductivity. To more accurately describe the linear correlation between the PDOS of different functionalized graphene and PEG in the 0–100 THz frequency range, the Pearson correlation coefficient (R) is calculated using the following equation:

$$R = \frac{n(\sum^{V} PDOS_{1}PDOS_{2}) - (\sum^{V} PDOS_{1})(\sum^{V} PDOS_{2})}{\sqrt{[n(\sum^{V} PDOS_{1}^{2}) - (\sum^{V} PDOS_{1})^{2}][n(\sum^{V} PDOS_{2}^{2}) - (\sum^{V} PDOS_{2})^{2}]}}$$
(4)

Here, subscripts 1 and 2 represent graphene and polyethylene glycol, respectively. The value ranges from -1 to +1. In the condition that the absolute value of R is approximate to 1, the PDOS shower relatively higher similarity. R characterizes the degree of overlap in the vibrational density of states between different materials, which in turn reflects the interfacial thermal conductivity performance. As shown in Figure 5, the R values for graphene functionalized with -COOH, -OH, -CH<sub>3</sub>, -C<sub>4</sub>H<sub>9</sub>, and -C<sub>7</sub>H<sub>15</sub> groups exhibit a gradual increase, while the R value for unmodified graphene with PEG is the lowest. This indicates that functional group modification effectively enhances the coupling between graphene and PEG, thereby improving the interfacial thermal conductivity between graphene fillers and PEG.



Figure 5. Comparison and correlation coefficient analysis of phonon state density between unmodified graphene and polyethylene glycol modified with five functional groups.

## 4.3 Evaluation of the overall thermal performance by effective medium theory

After calculating the interfacial thermal conductivity, it is crucial to relate it to the overall thermal conductivity of the graphene/PEG composite material. This can be achieved using the effective medium theory[32]. The overall thermal conductivity of the composite phase-change material can be predicted using the interfacial thermal

conductivity of graphene when randomly dispersed. It has been found that the predicted results are in good agreement with the experimental data. When graphene sheets are randomly dispersed in the phase-change material matrix, the thermal conductivity of the composite material can be expressed as:

$$K^{*} = k_{m} \frac{3 + f \left[ 2\beta_{11}(1 - L_{11}) + \beta_{33}(1 - L_{33}) \right]}{3 - f \left[ 2\beta_{11}L_{11} + \beta_{33}L_{33} \right]}$$
(5)

In the equation:

$$\beta_{11} = \frac{k_{11}^c - k_m}{k_m + L_{11}(k_{11}^c - k_m)}, \quad \beta_{33} = \frac{k_{33}^c - k_m}{k_m + L_{33}(k_{33}^c - k_m)}$$
(6)

$$k_{11}^{c} = \frac{k_{f}}{1 + \gamma L_{11} k_{f} / k_{m}}, \quad k_{33}^{c} = \frac{k_{f}}{1 + \gamma L_{33} k_{f} / k_{m}}$$
(7)

$$L_{11} = \frac{p^2}{2(p^2 - 1)} + \frac{p}{2(1 - p^2)^{3/2}} \cos^{-1} p$$
(8)

$$L_{33} = 1 - 2L_{11} \tag{9}$$

$$\gamma = (1+2p)a_k / a_3 \tag{10}$$

$$p = a_3 / a_1 \tag{11}$$

$$a_k = k_m / G_k \tag{12}$$

In this equation,  $K^*$ ,  $k_f$  and  $k_m$  represent the thermal conductivities of the composite material, graphene filler, and PEG matrix, respectively. f is the volume fraction of the filler.  $a_1$  and  $a_3$  represents the thickness and length of the graphene sheets.  $a_k$  denotes the thermal resistance radius.  $G_k$  is the interfacial thermal conductivity. p represents the ratio of the length to the thickness of graphene. The value of p is less than 1; Both  $L_{11}$  and  $L_{33}$  are geometric factors dependent on the shape of the graphene. Based on the above simulation results, the parameters required in the effective medium theory can be assigned. Among them, the value of  $k_m$  is assumed as 0.15 W/(m·K). The length of graphene  $a_3$  is 5 µm, and the

thickness  $a_1$  is taken as 0.335 nm. Although the thermal conductivity of graphene can reach as high as 5000 W/(m·K) or even higher[33] its interaction with the surrounding polymer significantly suppresses phonon transport within the graphene. Studies have shown that at room temperatures, the thermal conductivity of graphene is approximately 600 W/(m·K), primarily due to the reduction in its mean free path[34, 35]. Therefore, in the case where the effects of functional groups on the thermal conductivity and volume of graphene fillers are neglected, the thermal conductivity of graphene is typically assumed as 600 W/(m·K)[36].

Figure 6 shows the calculated thermal conductivity of the composite material when graphene sheets covalently modified with different functional groups are randomly dispersed in the polyethylene glycol matrix. It can be observed that the thermal conductivity of the composite material increases linearly with the volume fraction of graphene. When the graphene volume fraction increases from 2% to 20%, the thermal conductivity of GN/PEG rises from 3.99 W/ (m·K) to 28.97 W/ (m·K). For the same volume fraction of filler, the thermal conductivity of the composite material decreases in the following order:  $-C_7H_{15}GN/PEG$ ,  $-C_4H_9GN/PEG$ ,  $-CH_3GN/PEG$ , -OHGN/PEG, and -COOHGN/PEG. When the filler volume fraction is 20%, the thermal conductivities of  $-C_7H_{15}GN/PEG$  and  $-C_4H_9GN/PEG$  reach 34.54 W/ (m·K) and 33.57 W/ (m·K), respectively, which are 1.19 times and 1.16 times higher than that of GN/PEG.





Figure 6. curves of thermal conductivity of graphene-polyethylene glycol and graphene-polyethylene glycol composite systems with different functional groups and grafting numbers with graphene volume fraction.

#### 5. Effect of graphene layers on the thermal performance of CPCMs

## 5.1 Reduction in thermal conductivity



Figure 7. shows the interfacial temperature difference and interfacial thermal conductivity between 1-9 layers of graphene and polyethylene glycol.

Figure 7 illustrates the variation of the interfacial thermal conductivity with the change of number of graphene layers in the polyethylene glycol/graphene composite system, where the heat flux is applied perpendicular to the graphene plane, as obtained through NEMD simulations. As seen in the figure, when graphene is monolayer, the interfacial thermal conductivity of the system is 21.09 mW/m<sup>2</sup>·K. When the number of graphene layers is less than 5, the interfacial thermal conductivity decreases significantly with the increase of the layer number. After the layer number exceeds 5, the interfacial thermal conductivity stabilizes as 18.3 mW/m<sup>2</sup>·K, which is consistent with the results reported in literature. This trend is primarily due to the dominant ballistic phonon transport mode in monolayer graphene, where phonon collisions are the minimal and scattering is reduced. With multilayers of graphene, however, phonons interact and scatter with interlayer particles, and there is also an occurrence of phonon backscattering. The enhanced scattering effect reduces the heat transfer capability of graphene, leading to a decrease in its thermal conductivity. With a further increase of the number of graphene layers, phonon scattering becomes more pronounced, resulting in a more significant reduction in thermal conductivity.

#### 5.2 Radial Distribution Function Analysis

The Radial Distribution Function (RDF) is a characteristic physical quantity that reflects the microscopic structure of a material. It represents the probability of finding another atom at a distance r from a reference atom, and is defined as:

$$g_{AB}(r) = \frac{1}{\rho_{AB} 4\pi r^2 \delta r} \frac{\sum_{t=1}^{k} \sum_{j=1}^{N_{AB}} \Delta N_{AB}(r \to r + \delta r)}{N_{AB} \times k}$$
(13)

Where:  $N_{AB}$  are the numbers of atoms A and B in the system, k is the time step,  $\delta r$  is the distance interval width,  $\Delta N_{AB}$  represents the number of B (or A) atoms found within the range from atom A (or B) at position r to position  $r+\delta r$ , and  $\rho_{AB}$  is the density of the system.



Figure 8. The radial distribution function between PEG-C and Graphene-C when the heat flux is applied perpendicular to the graphene plane.

RDF can reveal the interaction modes and nature between non-bonded atoms in the system. The range of hydrogen bonding is 2.6-3.1 Å, while the range of van der Waals interactions is 3.1–5 Å. Figure 8 shows the RDF between polyethylene glycol carbon atoms and graphene carbon atoms when the heat flux is applied perpendicular to the graphene plane. As shown in the figure, the primary interaction between the polymer carbon atoms and the graphene carbon atoms is van der Waals (vdW) interaction. As the number of graphene layers increases, there is no significant change in the shape of the RDF, indicating that the interaction mode between the two remains unchanged with the variation in graphene layers. However, the peak value of the RDF gradually decreases with the increase in the number of graphene layers, and this decline slows down over time. This is due to the increase in the total number of graphene carbon atoms as the number of layers increases, which enlarges the denominator in the RDF calculation formula, resulting in a gradual reduction in the RDF peak. However,  $\Delta N_{AB}$  remains unchanged. This suggests that, with the increase in graphene layers, the atomic interactions at the interface do not undergo fundamental changes.



5.3 Calculated thermal conductivity based on effective medium theory

Figure 9. The variation in thermal conductivity of the graphene-polyethylene glycol composite system with different graphene layer numbers as a function of graphene volume fraction.

Figure 9 shows the calculated thermal conductivity of the composite material with different graphene layer numbers dispersed in the polyethylene glycol matrix. As seen in the figure, the thermal conductivity of the composite material increases with the increase of the graphene volume fraction. For the same filler volume fraction, the thermal conductivity of the composite material decreases in the following order: 1-layer GN/PEG, 3-layer GN/PEG, 5-layer GN/PEG, 7-layer GN/PEG, and 9-layer GN/PEG. When the filler volume fraction is 15%, the thermal conductivities of 1-layer GN/PEG, 3-layer GN/PEG, 5-layer GN/PEG, 7-layer GN/PEG, and 9-layer GN/PEG are 7.58 W/ (m·K), 7.14 W/ (m·K), 6.17 W/ (m·K), 6.35 W/ (m·K), and 6.34 W/ (m·K), respectively. These values are 7.02, 6.87, 6.43, 6.48, and 6.47 times higher than the corresponding values of composite phase change materials with 1% volume fraction of graphene.

## 6. Conclusions

This chapter investigates the effects of graphene functionalization and layer

number on the interface thermal conductivity and heat transfer properties of composite phase-change materials. Using the velocity rescaling method, the interface thermal conductivity of GN/PEG and functionalized graphene with different grafting numbers, including -C<sub>7</sub>H<sub>15</sub>GN/PEG, -C<sub>4</sub>H<sub>9</sub>GN/PEG, -CH<sub>3</sub>GN/PEG, -OHGN/PEG, and -COOHGN/PEG, was calculated. Additionally, the interface thermal conductivity of 1 to 9-layer graphene/polyethylene glycol systems was also computed. The mechanism of interface thermal conductivity enhancement in graphene/polyethylene glycol systems due to different functional groups was explained through PDOS analysis. Additionally, the thermal conductivity of composite systems with varying graphene volume fractions was predicted using effective medium theory. The key findings of the study are as follows:

(1) Different functional groups have distinct effects on enhancing interface thermal conductivity. -COOH and -OH functional groups do not significantly improve the interface thermal conductivity of GN/PEG. In contrast, alkyl functional groups show a moe pronounced enhancement, with interface thermal conductivity increasing as the number of functional groups rises. When the grafting number reaches 18, the interface thermal conductivity of  $-C_7H_{15}GN/PEG$  and  $-C_4H_9GN/PEG$  can reach 1.29 and 1.24 times that of the GN/PEG interface, respectively. When the graphene consists of a single layer, the interface thermal conductivity of the system is 21.09 mW/m<sup>2</sup>·K. As the number of graphene layers increases, the interface thermal conductivity decreases significantly when the number of layers is fewer than five. Once the graphene layers exceed five, the interface thermal conductivity of the system stabilizes.

(2) The nature of the interface thermal resistance can be explained from the perspective of PDOS overlap. The poor PDOS coupling between graphene and polyethylene glycol leads to inefficient interface heat transfer. Introducing covalent functional groups can improve the poor PDOS coupling to varying degrees. Specifically, -OH and -COOH functional groups enhance the low-frequency PDOS coupling between graphene and polyethylene glycol, while alkyl functional groups

significantly strengthen the high-frequency PDOS coupling, thereby effectively improving the thermal conductivity at the interface. Notably, the PDOS peak shape of  $C_7H_{15}GN$  is most similar to that of polyethylene glycol, with the highest overlap, which is the reason for  $C_7H_{15}GN$  showing the most significant enhancement of the interface thermal conductivity in the GN/PEG system.

(3) The thermal conductivity of graphene randomly dispersed in a polyethylene glycol matrix was calculated using the effective medium theory. The results show that, under the same filler volume fraction,  $-C_7H_{15}GN/PEG$  and  $-C_4H_9GN/PEG$  exhibit the highest thermal conductivity. When the filler volume fraction is 20%, the thermal conductivities of  $-C_7H_{15}GN/PEG$  and  $-C_4H_9GN/PEG$  reach 34.54 W/ (m·K) and 33.57 W/ (m·K), respectively, which are 1.19 and 1.16 times that of GN/PEG. In addition, the calculation results also show that the thermal conductivity of composite materials with graphene of different layers dispersed in the PEG matrix increases approximately linearly with the increase of the graphene volume fraction.

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