

Excellent heat transfer and thermal energy storage performance of erythritol/graphene composite phase change materials

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ABSTRACT

Erythritol as a phase change material has a main disadvantage: low thermal conductivity. In this paper, we proposed a novel erythritol/graphene composite phase change material and its thermal properties were predicted by molecular dynamics method. The effects of graphene mass fraction, size and number of layers on thermal conductivity were analyzed. The mechanism of graphene on thermal conductivity was revealed from the microscopic point of view. The results show that graphene can efficiently improve the thermal conductivity of the composites, thus improving the thermal properties of erythritol. The thermal conductivity of the composites increases with the increase of graphene amount, size and number of layers. When the mass fraction of graphene increased to 8 wt%, the thermal conductivity is doubled. This study can provide guidance for the design and application of erythritol-based composite phase change materials.

Keywords: Erythritol, Composite phase change material, Thermal conductivity, Microscopic mechanism, Molecular dynamics simulation.

NONMENCLATURE

Abbreviations

PCMs	Phase change materials
C ₄ H ₁₀ O ₄	Erythritol
CFs	Carbon fibers
MD	Molecular dynamics simulation
PPPM	Particle–particle particle-mesh
NEMD	Non equilibrium molecular dynamics
MFP	Mean free path
vdW	van der Waals
VDOS	Vibration density of states

1. INTRODUCTION

During the development process of human society, the exploitation and utilization of energy are intimately integrated with us. For a long time, the energy structure has been dominated by fossil fuels, but it is a non-renewable energy. With the consumption of fossil fuels, the energy tension situation are further worsening, and the environment has been seriously polluted. Therefore, the development and utilization of clean energy is of great significance. How to improve the energy utilization rate and realize the efficient utilization of energy has become a hotspot. Phase change energy storage technology uses phase change materials (PCMs) to store energy artificially for use when needed, which reduces the waste of energy to a certain extent. In recent years, phase change energy storage technology has been widely used in the fields of electric peak load shifting [1], solar energy utilization [2], energy saving of building [3] and so on.

Because PCMs are used as the medium in phase change energy storage technology, the performance of PCMs plays a decisive role. Erythritol (C₄H₁₀O₄) is a kind of sugar alcohol organic PCM, which has the advantages of non-toxic, non-corrosive, high stability and easy to obtain. The phase transition temperature of erythritol is about 120 °C. Compared with other PCMs in low-to-medium temperature region (320-540 K), erythritol has a high phase transition enthalpy (340 kJ/kg), which makes it have greater application potential. However, erythritol still has the common disadvantage of organic PCMs---low thermal conductivity, which affects the heat storage/release rate and degrades the energy utilization efficiency.

In order to solve the above issue, researchers have made a lot of attempts. The results show that the thermal conductivity of erythritol can be improved by adding nanomaterials such as carbon nanotubes [4],

carbon fibers (CFs) [5], graphene oxide nanosheets [6], graphene nanoparticles [7]. Generally, these nanomaterials have excellent thermal performance, which can improve the thermal conductivity of PCMs to different degrees. For example, with 10 wt% long CFs, the thermal conductivity increased nearly 4-fold [5]. When 1.0 wt% graphene oxide nanosheets were added, the thermal conductivity can be enhanced by 200% compared to pure erythritol [6]. Graphene with 1 wt% addition increased thermal conductivity of erythritol by 53.1% [7]. Among them, graphene is often added to various PCMs, such as paraffin [8], palmitic acid [9], 1-octadecanol [10], due to its excellent two-dimensional thermal transport properties.

In this paper, the thermal conductivity and phase change properties of erythritol/graphene composite PCM were calculated by molecular dynamics (MD) simulation. The effects of the temperature, mass fraction, layers and the size of graphene on the thermal conductivity were analyzed, and the effects of graphene on the melting point and supercooling degree of composite were also obtained. The influence mechanism of graphene nanoparticles on thermal conductivity and phase transition properties was analyzed from the micro-scale view of point. This provides clear guidance for the design of composite PCMs with nanoparticles in the future.

2. MODEL AND METHODOLOGY

2.1 Physical model

The structure of erythritol and graphene in the system is shown in Fig.1, and the graphene size in Fig.1 (b) is 5.11 nm × 2.95 nm, containing 576 C atoms. The erythritol molecule in Fig.1 (a) is filled into the box containing graphene nanosheets. The composite structure is optimized by energy minimization to obtain

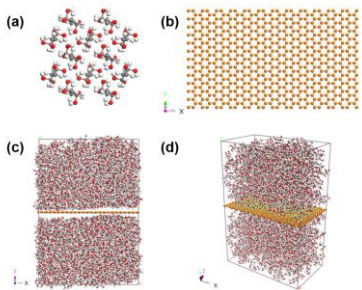


Fig 1 (a) 12 erythritol molecules; (b) Monolayer graphene nanosheets; (c) Erythritol/graphene composite structure (front view); (d) Erythritol/graphene monolayer composite structure (perspective view).

a stable state. In order to explore the influence of the mass fraction of graphene nanosheets, the mass fraction of graphene was changed by changing the size of the box in z direction, that is, changing the number of erythritol molecules. By keeping the mass fraction constant (10 wt%), the effects of graphene size was obtained. The sizes of the graphene are 2 nm × 3 nm (240 C atoms), 3 nm × 3 nm (336 C atoms), 4 nm × 3 nm (480 C atoms), 5 nm × 3 nm (576 C atoms), 6 nm × 3 nm (672 C atoms). Because the number of graphene layers has a significant impact on the heat transfer characteristics, we constructed 1-4 layers of graphene under the condition of the same mass fraction and the same size of graphene.

2.2 Simulation method

In MD simulation, the selection of force field plays a decisive role in the accuracy of calculation results. We choose the GROMOS 54A7 force field [11] to describe erythritol. The force field is optimized on the basis of GROMOS 53A6 force field [12], which improves the stability of protein, alcohol and lipid simulation. This force field has been used to simulate erythritol [13,14]. Tersoff potential [15] was selected to describe the C atoms within each layer graphene, and the interaction between the layers of graphene and graphene-erythritol is described by Lennard-Jones (L-J) potential. $\epsilon=2.39$ meV and $\sigma=3.412$ Å are used for the interaction between the layers of graphene. The L-J parameters of graphene-erythritol are all from Ref. [17] and the L-J potential is given by:

$$E(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (1)$$

According to Lorentz-Berthelot mixing rules, $\epsilon_{ij} = \sqrt{(\epsilon_i \cdot \epsilon_j)}$, $\sigma_{ij} = \frac{(\sigma_i + \sigma_j)}{2}$, where ϵ and σ are the potential well constant (eV) and equilibrium constant (Å) respectively, and subscripts i, j refer to different atom species. A cutoff distance of 14 Å was used for the L-J potential interaction. All MD simulations in this paper were carried out in LAMMPS (Large Scale Atomic Molecular Massively Parallel Simulator) software [18], while the OVITO (open visualization tool) package was used for visualization [19].

In the MD simulation process, periodic boundary conditions were used in all three directions, and the time step was 0.5 fs. The initial velocity of atoms in the simulation system was randomly distributed at the specified temperature and obeyed Gaussian distribution. The Velocity Verlet [20] algorithm was applied to solve the Newton's equations of motion. The long-distance

electrostatic interaction was solved by PPPM (particle–particle particle-mesh) method with an accuracy of 10^{-4} . At the beginning of the simulation, the standard conjugate gradient algorithm was used to minimize the energy, so that the system can obtain stable structure. The system first relaxed 250 ps under the NPT (constant temperature and constant pressure) ensemble at the target temperature and 1 atm. The Nosé–Hoover [21] thermostat and barostat were used to adjust the temperature and pressure of the system, respectively. Remove the NPT ensemble, and then relaxed 250 ps under the NVE ensemble to ensure the full stability of the system. Finally, the relevant parameters were calculated by running 2 ns under the NVE ensemble, and the data of the last 1 ns was chosen as the calculation results.

Non equilibrium molecular dynamics simulation (NEMD) was used to calculate the thermal conductivity. The system is divided into 20 layers. The Langevin [22] temperature control method is used to set the hot zone temperature at 310 K and the cold zone temperature at 290 K, respectively, Then the thermal conductivity of the system is obtained by Fourier's law:

$$k = -\frac{J}{A\nabla T} \quad (3)$$

Where k is the thermal conductivity of the system (W/mK), J is the heat flow (W), $J = \frac{dE}{dt}$, A is the cross-sectional area along the heat flow direction (m^2), and ∇T is the temperature gradient between the cold region and the hot region (K/m).

3. RESULTS AND DISCUSSIONS

3.1 Thermal conductivity of erythritol/graphene composites

The thermal conductivity of the composites containing graphene is highly anisotropic, and the heat will be transferred preferentially along the in-plane direction rather than out-of-plane direction, so the in-plane thermal conductivity plays a leading role [23]. Hence, in the following discussion, we will only focus on in-plane thermal conductivity.

3.1.1 Influence of graphene mass fraction

Many experimental results show that the thermal conductivity of the composite is strongly affected by the amount of particles used for thermal enhancement. However, due to many factors in the actual operation, the amount of nanoparticles is controlled to be below a certain value, otherwise serious agglomeration will occur and deteriorate the thermal transport. Here, we calculated the thermal conductivity of

erythritol/graphene (5 nm × 3 nm) composites with different mass ratios (5-10 wt%). As shown in Fig.2 (a), with the increase of the mass ratio of graphene nanosheets, the thermal conductivity of the composite increases, but the growth trend becomes slow and

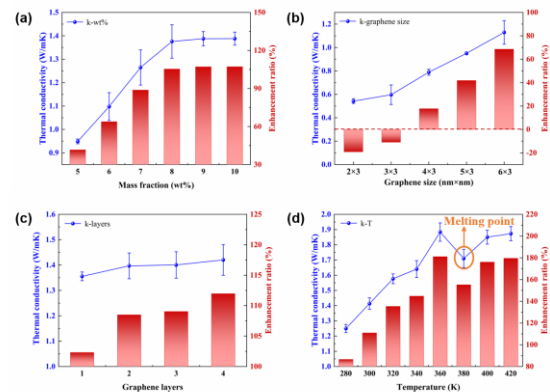


Fig 2 (a) Thermal conductivity of composite with different graphene mass fraction; (b) Thermal conductivity of composite with different graphene sizes; (c) Thermal conductivity of composite with different graphene layers; (d) Thermal conductivity of composite under different temperatures.

gradually tends to a stable value, which indicates that the thermal conductivity enhancement effect is no longer significant when the mass ratio of graphene exceeds a certain amount (8 wt%). At this time, the thermal conductivity was increased by 107% compared with pure erythritol. This can provide clear guidance for the experimental preparation of erythritol-based composites.

3.1.2 Influence of graphene size

In order to explore the influence of graphene size on the thermal conductivity, under the condition of ensuring the mass ratio of 5 wt%, five kinds of graphene models with different sizes were constructed, and the thermal conductivity of the composite was calculated. It can be found that when the size of graphene is very small (2 nm × 3 nm and 3 nm × 3 nm), the thermal conductivity of the composite was lower than that of pure erythritol (Fig.2 (b)). In this case, the phonons in graphene are strongly scattered by the boundary, and the addition of "heat conduction enhancement material" is equivalent to the introduction of impurities. With the increase of graphene size, the thermal conductivity of the composites increases, showing a strong size dependence, which is mainly due to the strong size effect of single-layer graphene. The phonon mean free path (MFP) of graphene is about 700-800 nm [24]. When the geometric size of graphene is smaller than that of MFP,

the heat transfer mode is mainly quasi-ballistic transport [25]. The size has a great influence on this mode, which directly leads to the size effect of thermal conductivity. At the same time, because graphene usually has low intrinsic phonon scattering, its thermal conductivity generally increases with the increase of sample size, which is also confirmed by NEMD simulation of Huang *et al.* [26]. When the size of graphene nanosheets is less than 10 μm , the thermal conductivity will increase with the increase of the size [27]. Therefore, the thermal conductivity of the composite PCMs increased in the range of our simulation.

3.1.3 Influence of graphene layers

In practice, there are not only monolayer graphene, but also multilayer graphene. Under the conditions of 5 nm \times 3 nm size and 10 wt% graphene mass ratio, we constructed 1-4 layers graphene composite models (Fig.3 (a)-(d)), and the thermal conductivity results are shown in Fig.2 (c). Theoretically, at the same temperature, the thermal conductivity of graphene decreases with the increase of the number of layers, which are stacked

together by van der Waals force. Compared with the free vibration of carbon atoms in single-layer graphene, the vibration of carbon atoms in multi-layer graphene is suppressed by its adjacent layers, which increases the resistance to phonon transport in the in-plane direction [28]. Interestingly, however, the thermal conductivity of the composites increases with the increase of the number of layers, which is opposite to that of pure graphene, and this trend is consistent with the results of [29]. With the increase of the number of graphene layers, the number of graphene atoms per unit area increases when the heat flow passes through. More graphene in the inner layer can interact with erythritol molecules, resulting in higher interface adhesion energy (E_I). The interface adhesion energy is given as follows [29]:

$$E_I = |E_T - (E_{ery} + E_g)|$$

where E_T is the total energy of the system, E_g is the energy of graphene without interaction with erythritol, and E_{ery} is the energy of erythritol without interaction with graphene. The interface adhesion energy increases with the increase of graphene layers, as shown in Fig.3 (g). The non-contact layer in the middle of graphene sheet can exert attraction on erythritol molecules through van der Waals (vdW) interaction. High interfacial adhesion energy usually leads to small interfacial thermal resistance [29], and the energy loss at the

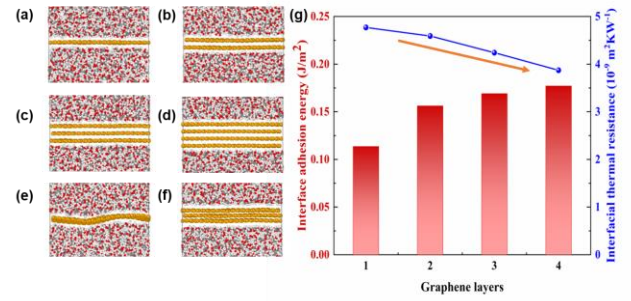


Fig 3 (a)-(d) Models of erythritol/graphene (1-4 layers) composites; (e) Final state of erythritol/graphene (monolayer) composite; (f) Final state of erythritol/graphene (three layers) composite. (g) Interface adhesion energy and interfacial thermal resistance between erythritol and graphene in the composites with various graphene layers. interface decreases, so the thermal conductivity of erythritol/graphene composite increases.

In addition, by observing the trajectory file, we found that monolayer graphene nanosheets formed obvious folds, as shown in Fig.3 (e), while multilayer graphene (such as three layers) did not exhibit obvious folds (Fig.3 (f)). The folding of graphene nanosheets is due to the effect of intermolecular shear force. Thin graphene sheets may be more elastic than thick multilayer graphene sheets, so it is easy to form folds in the matrix [30]. The more the folds, the lower the thermal conductivity of graphene. With the increase of graphene layers, the shear force and van der Waals force counteract each other, which reduces the number of folds and improves the thermal conductivity of the composites.

3.1.4 Influence of temperature

In the case that the size of graphene nanosheets is 5 nm \times 3 nm and the mass ratio is 10 wt%, the temperature gradient is set to 20 K to study the variation rule of thermal conductivity within the temperature range of 280 K-420 K (Fig.2 (d)). With the increase of the temperature, the thermal conductivity of the composite material firstly increases gradually. However, at 380 K, the thermal conductivity suddenly decreases, and the thermal conductivity of the composite material continues to increase as the temperature continues to rise. Through the calculation of melting point in section 3.3.2, it is found that the melting point of this case is around 380 K. Under that temperature, the erythritol changes from solid state to liquid state, and the whole system changes from ordered to disordered state. The heat conduction in the phase transition region is hindered, and thus the thermal conductivity decreases

greatly. However, the thermal conductivity is still 5 times higher than that of the pure erythritol liquid (0.3 W/mK), indicating that the addition of graphene is conducive to heat conduction in both solid and liquid state.

3.2 VDOS and overlap energy

Figure 4 (a) shows the Vibration density of states (VDOS) of erythritol and graphene with different layers. It is clearly seen that the vibration of graphene and erythritol do not match each other. However, the overlap energy results (Fig.4 (b)) show that with the increase of layers, the matching degree between

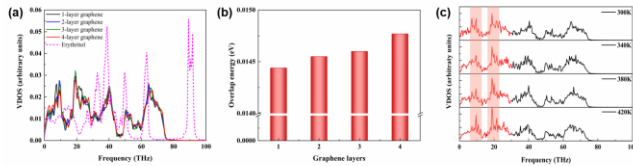


Fig 4 (a) VDOS of erythritol and graphene with different layers; (b) Overlap energy between erythritol and graphene with different layers; (c) VDOS of graphene under different temperature..

graphene and erythritol is improved, which boosts the efficiency of interfacial thermal transport. This is also an internal reason for the increase of thermal conductivity with the increase of layers.

The VDOS of graphene at different temperatures is shown in Fig.4 (c). With the increase of temperature, the vibration peak of graphene at low frequency increases significantly. The 0-30 THz phonon dominates the thermal transport in graphene, and the strong transport ability of phonon is excited, thus increasing the heating conductivity (a positive effect). At the same time, by increasing the temperature, the phonon-phonon interaction will increase, resulting in an increase in the phonon scattering and hence a decrease in the thermal conductivity (a negative effect). These two effects jointly determine the change trend of thermal conductivity. It can be seen from Fig.4 (c) that the low-frequency peak increases slightly with the increase of temperature, so the overall thermal conductivity still increases, which is consistent with Fig.2 (d).

4. CONCLUSIONS

In order to solve the problems of low thermal conductivity of erythritol as phase change material, we calculated the thermal characteristics of erythritol/graphene by molecular dynamics simulation, and analyzed the effects of graphene mass fraction, size and number of layers on the thermal conductivity The

results show that graphene can effectively improve the thermal conductivity of the composites. When the mass fraction of graphene reaches 8 wt%, the thermal conductivity is almost no longer improved, and the thermal conductivity is increased by 107%. Due to the ballistic transport, the increase of graphene size is beneficial to improve the overall thermal conductivity. Increasing the number of graphene layers can reduce the number of folds, improve the interface adhesion energy, and reduce the loss of interface energy. At the same time, the vibrational coordination between erythritol and graphene is improved with the increase of graphene layers, which is beneficial to phonon thermal transport. The increase of temperature stimulates the low frequency phonon vibration of graphene and enhances the phonon phonon scattering. The change of thermal conductivity is the result of competition between the two. It is of great significance for the application of erythritol in the field of phase change energy storage, and provide a theoretical guidance for the design of erythritol composite phase change materials.

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