Enhanced Thermal Conductivity in a Nanostructured Phase Change Composite due to Low Concentration Graphene Additives

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ABSTRACT: The liquid-solid phase change enthalpy, crystallization, and thermal conductivity of graphene/1-octadecanol (stearyl alcohol) composite, a nanostructured phase change material, was investigated as a function of graphene content. The thermal conductivity ($\kappa$) of the nanocomposite increased by nearly 2.5-fold ($\sim$140% increase) upon $\sim$4% (by weight) graphene addition while the drop in the heat of fusion (i.e., storage capacity) was only $\sim$15.4%. The enhancement in thermal properties of 1-octadecanol obtained with the addition of graphene is markedly superior to the effect of other nanofillers such as silver nanowires and carbon nanotubes reported previously in the literature. Boosting the thermal conductivity of organic phase change materials without incurring a significant loss in the heat of fusion is one of the key issues in enabling their practical application as latent heat storage/release units for thermal management and thermal protection.

INTRODUCTION

One of the main sources of energy in nature is thermal energy, which could be obtained from sources such as the sun, geothermal fields, and oceans. This type of energy is also released as waste heat from many man-made devices such as power plants, reactors, and engines. There is a large interest to develop efficient systems or materials to scavenge thermal energy and reuse it either directly or convert it to another type of useful energy such as electricity.$^{1–3}$ Solid–liquid organic phase change materials (PCMs) have drawn a lot of attention$^{4,5}$ because they possess a considerable heat of fusion of the order of 100s J/g. PCMs can be used as latent heat storage and release units for thermal management of computers, electrical engines, solar power plants, and for thermal protection of electronic devices.$^4$ However, a major drawback of organic PCMs is their low thermal conductivity ($\kappa$) which leads to large temperature gradients during heat transfer in or out of the material, reduced heat transfer rates, and large time constants. Therefore, increasing the thermal conductivity of the solidified material is one of the main issues in the application of organic PCMs.$^5$ However, although the conductivity needs to be improved, it has to be achieved while maintaining the phase change enthalpy. To achieve this goal, several methods have been developed including improving encapsulation techniques,$^6$ mixing the PCMs with high conductive fillers such as carbon nanotubes$^7$ and silver nanowires,$^8$ and dispersing PCMs in highly conductive cellular structures.$^9,10$

Graphene, a recently discovered form of carbon that consists of a sheet of carbon atoms arranged in a honeycomb lattice,$^{11}$ exhibits a number of fascinating properties including very high thermal conductivity. The value of thermal conductivity ($\kappa$) for single layer graphene is reported to be in the range of 4840–5300 W/mK,$^{12}$ which is more than an order of magnitude higher than that of copper. Graphene is a promising thermally conductive filler because of its ultrahigh thermal conductivity and low density. Nanosheets of graphene have previously been used to improve thermal conductivity of different organic materials$^{13}$ such as epoxy,$^{14–16}$ polypropylene,$^{17}$ polystyrene,$^{20}$ polyethylene, and polyamide.$^{21}$
In the current work, we are proposing to use nanosheets of graphene to improve the thermal conductivity of PCMs. Although the conductivity of the PCM/graphene nanocomposite would be higher than that of the PCM alone, which will help the heat transfer rate, it is expected that the phase change enthalpy would be lower than that of PCM because some of the PCM volume would be replaced by the graphene sheets that do not undergo phase change in the operating temperature range. Therefore, it is important that the enhancement in the thermal conductivity of the PCM should be done with as small as possible a sacrifice in the phase change enthalpy of the PCM. We show in this work that the large increase in thermal conductivity coupled with a small reduction in the heat of fusion for graphene nanocomposites is far superior when compared with the published literature for other nanofillers such as carbon nanotubes and silver nanowires.

**MATERIALS AND EXPERIMENTAL SECTION**

The graphene fillers used in this work were obtained from graphite using the method developed in ref 11. In this method, graphite oxide is prepared by oxidizing graphite in a solution of sulfuric acid, nitric acid, and potassium chlorate for 96 h. Partially oxidized graphene sheets are then generated by the rapid thermal expansion (>2000 °C/min) of the graphite oxide. A transmission electron microscope (TEM) image of a graphene platelet produced by this method is shown in Figure 1a. The graphene flakes have relatively wrinkled surface texture, which could play a beneficial role in enhancing the interlocking of the flakes with each other and enable strong interaction with the matrix.22 Figure 1b is a high-resolution transmission electron microscopy (HRTEM) image of the graphene platelet demonstrating the layered structure of the platelet (inset shows the electron diffraction image).

The PCM used in the current work is 1-octadecanol (stearyl alcohol), with a melting temperature of ~66 °C which is close to room temperature and has an outstanding solid–liquid phase change enthalpy (~250 J/g). 1-octadecanol is nontoxic, has a relatively low density (0.812 g/cm³), and boils at ~210 °C. To fabricate 1-octadecanol/graphene composites, as seen in Figure 1c, graphene sheets were first dispersed in a 25 mL/mg acetone solution and were ultrasonicated for 15 min (10 s on, 5 s off, 50% power). Then the mixture was heated on a hot plate to 120 °C while being sonicated for another 5 min. The 1-octadecanol was then mixed with the graphene dispersion and was sonicated for another ~15 min on a hot plate at ~120 °C. The mixture of acetone, graphene, and PCM were stirred and heated to ~150 °C to evaporate the remaining acetone. The nanocomposite in liquid phase was then poured into preheated Si rubber molds of cylindrical shape, ~6.35 mm thick and ~12.70 mm in diameter, and was left at room temperature to solidify for ~20 min. The resulting composite was affixed to a sample holder, cut to different thicknesses using a hot blade, and polished on a sand paper pad.

**RESULTS AND DISCUSSION**

The SEM images of the freeze-fractured surfaces of pristine 1-octadecanol and 4% (by weight) graphene/1-octadecanol nanocomposites are shown in Figure 2a,b, respectively. High magnification images of 4% nanocomposite are also shown in Figure 2c,d. As seen in these figures, graphene flakes were dispersed uniformly throughout the matrix providing a three-dimensional network of high thermal conductivity graphene films. Good dispersion and network formation facilitates heat transfer and allows phonons to travel efficiently through the graphene fillers and between the flakes. It is well-known that the type of the polymer matrix, degree of exfoliation of the graphene flakes, orientation of the fillers, and interfacial interaction influences the thermal transport in graphene nanocomposites.23 The SEM image of the fracture surface of an epoxy/graphene composite, fabricated using the same graphene flakes, is shown in Figure 2e, which is comparable to Figure 2d in terms of magnification. However, there is a drastic difference in terms of the interaction of graphene with the surrounding polymer. In the case of graphene/1-octadecanol, the graphene sheets are still covered with a thick layer of polymer, whereas in the case of...
graphene/epoxy, the graphene sheets seem to be completely separated from the epoxy matrix. This suggests that there is a strong interface between graphene and 1-octadecanol molecules.

To measure the heat conductivity of the composites, a steady-state one-dimensional heat conduction method was used. The experimental setup consists of an electrical heater, a heat sink and two thermocouples to measure the temperature gradient (Figure 3a). To minimize the interface thermal resistance, fine-diameter electrically insulated thermocouples were embedded into two soft indium layers to measure the temperature at both sides of a thin cylindrical sample. Pressure is applied using a screw mechanism that is thermally insulated from the sample by a thick Teflon block. The heat losses in the experimental setup were calibrated using glass samples of known conductivity. The thermal conductivity of the pure 1-octadecanol measured with this setup (~0.38 W/mK) matches the value reported in the literature. To measure $\kappa$, the experimental thermal resistance is first obtained from the slope of the temperature difference across the sample as a function of heater power (Figure 3b). Next, the calibrated heat loss ($R_{hl}$) contribution is accounted for by using a parallel thermal resistance network model. To find the intrinsic thermal conductivity ($\kappa$), the interface thermal resistance ($R_{int}$) between the composite sample and the indium layer must be subtracted from the overall conduction resistance ($R_s$). This interface thermal resistance was determined by testing samples with different thicknesses, then extrapolating the plot of $R_s + R_{int}$ vs thickness to zero thickness using linear regression (Figure 3c). The thermal resistance and conductivity of the sample are calculated using the following equations:

$$R_s = -R_{int} + \frac{R_t R_{hl}}{R_{hl} - R_t}$$  \hspace{2cm} (1)

$$\kappa = \left( \frac{1}{R_s A} \right) \times t$$  \hspace{2cm} (2)

Figure 2. Scanning electron microscopy (SEM) image of (a) fracture surface of pristine 1-octadecanol, (b–d) fracture surface of ~4% by weight graphene/1-octadecanol composite with different magnifications, and (e) fracture surface of ~4% by weight graphene/epoxy nanocomposite.
where t and A are the thickness and cross sectional area of the sample, respectively. The value of κ was obtained using the aforementioned method for the samples with different graphene contents. The results are shown in Figure 3d. As expected, thermal conductivity is considerably enhanced by the presence of graphene and reaches ~0.91 W/mK at ~4% graphene content. This value of κ is about 2.5-times higher than the measured κ value (~0.38 W/mK) for pure 1-octadecanol. This increase can be attributed to the high thermal conductivity of the network of graphene fillers that provide a path of lower resistance for phonons to travel. Also, the high aspect ratio and large interfacial contact area of graphene as well as strong interface between graphene and the polymer may help to increase the thermal transport capacity of graphene/PCM nanocomposites.

Considering the very high theoretical conductivity of graphene (4840–5300 W/mK), one might expect a more dramatic improvement in thermal conductivity of the composite with the addition of graphene fillers. However, it has been reported that since the dominant heat transfer mechanism is due to the lattice vibrations or phonons; poor phonon coupling in the vibrational modes at the polymer—filler and filler—filler interfaces cause thermal resistance, also called the Kapitza resistance, which decreases the overall thermal conductivity of the material.24–27 Introduction of defects associated with the oxidation and thermal exfoliation of graphite can also reduce the thermal conductivity below the ideal value for defect-free graphene. Previous studies have also shown that the thermal conductivity enhancement due to the addition of conductive nanofillers differs depending on the type of nanofiller and the polymer matrix. For example, an up to 4-fold increase in thermal conductivity can be attained by adding 5% graphene platelets (by weight) into epoxy while only ~20%6 and ~26%7 increase in thermal conductivity were observed by adding the same amount of silver nanowires and multi wall carbon nanotubes into PCMs, respectively. Besides these factors, a minor mechanism affecting the heat transfer could be related to the change in the volume fraction of the crystalline phase of the polymer. The crystallinity of the organic PCM could be lowered by the addition of graphene fillers.29 In the current work, the changes in crystallinity and crystallization mechanism were observed via differential scanning calorimetry (Figure 4). The crystallization and melting of 1-octadecanol has been well studied.30 It was shown that 1-octadecanol has a stable γ phase (monoclinic) crystal structure at room temperature, however melting transition does not proceed directly from the γ phase to liquid but an intermediate rotator phase exists. Therefore, during melting the γ phase transforms to the rotator phase and upon further heating, the rotator phase melts into the liquid state. During melting the solid—solid (γ-rotator) and solid—liquid (rotator-liquid) phase transitions occur very close to each other (within 1–2°C), therefore, show up as a single melting peak. However, during crystallization, the two phase transitions appear as distinct peaks (8–10°C apart from each other). In our results, these characteristics are clearly seen in Figure 4a,b; the nanocomposite shows two crystallization temperatures, both of these temperatures decrease with increasing filler content suggesting that crystallization became more difficult in the presence of graphene. These results were highly reproducible and the data from the first heating cycle were identical to the subsequent ones.

The phase change enthalpy is a critical factor in PCMs. The phase change enthalpy could be used as a measure to evaluate the thermal energy storage capacity of the PCM. Figure 4c shows that with the addition of graphene platelets, the melting enthalpy of 1-octadecanol decreases. The decrease is ~15% in the case of ~4% graphene filler content. This is expected given that some of the PCM volume is now replaced by the graphene sheets that do not undergo phase change. We did not increase the graphene weight fraction beyond 4% to avoid further reduction in the melting enthalpy. In the case of silver nanowire/PCM nanocomposites,4 in order to achieve the same (~2–3-fold) increase in the thermal conductivity of graphene/PCM, about ~45% silver nanowires (by weight) needs to be used, which also leads to ~50% decrease in phase change enthalpy, and hence, the heat storage capacity. Therefore, compared to silver nanowires, the graphene loading is an order of magnitude lower and the reduction in phase change enthalpy is also ~3 times lower than silver nanowires. Similarly, adding ~2% by weight of multiwalled carbon nanotubes leads to ~9% increase in thermal conductivity and ~9% decrease in the phase change enthalpy of the PCM,6 whereas adding ~2% by weight of graphene platelets leads to ~63% increase in the thermal conductivity and only ~8.7% decrease in the phase change enthalpy of the PCM used in the current work (Figure 3d and 4c). These comparisons with silver nanowires and multiwalled carbon nanotubes indicate the superiority of graphene as a conductive nanofiller for organic phase change materials. We also measured the melting temperature of 1-octadecanol as a function of graphene loading (Figure 4d); no significant change in the melting temperatures was observed.
CONCLUSIONS

It is shown that adding graphene platelets to organic phase change materials significantly boosts their thermal conductivity without incurring a large reduction in their liquid—solid phase change enthalpy. Addition of ~4% graphene (by weight) to 1-octadecanol led to a ~140% increase in thermal conductivity with only ~15% decrease in the phase change enthalpy. These improvements were markedly superior to other nanofillers such as multiwalled carbon nanotubes and silver nanowires. These results indicate that graphene is a promising candidate for the enhancement of thermal conductivity of organic phase change materials.

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Figure 4. (a) Differential scanning calorimetry (DSC) plots of graphene/1-octadecanol composites for various graphene concentrations showing the melting and crystallization events. (b) The change in the first and second crystallization temperature for graphene/1-octadecanol composites for various graphene concentrations. (c) The change in heat of fusion for graphene/1-octadecanol composites for various graphene concentrations. (d) Melting temperature of 1-octadecanol shown as a function of the graphene weight fraction in the composite.


