Thermal conductivity of an organic phase change material/expanded graphite composite across the phase change temperature range and a novel thermal conductivity model

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Abstract

This work studies factors that affect the thermal conductivity of an organic phase change material (PCM), RT44HC/expanded graphite (EG) composite, which include: EG mass fraction, composite PCM density and temperature. The increase of EG mass fraction and bulk density will both enhance thermal conductivity of composite PCMs, by up to 60 times. Thermal conductivity of RT44HC/EG composites remains independent on temperature outside the phase change range (40~45 °C), but nearly doubles during the phase change. The narrow temperature change during the phase change allows the maximum heat flux or minimum temperature for heat source if attaching PCMs to a first (constant temperature) or second (constant heat flux) thermal boundary. At last, a simple thermal conductivity model for EG-based composites is put forward, based on only two parameters: mass fraction of EG and bulk density of the composite. This model is validated with experiment data presented in this paper and in literature, showing this model has general applicability to any composite of EG and poor thermal conductive materials.

Keywords: phase change material; temperature-dependent; thermal conductivity model; expanded graphite; thermal management
1. **Introduction**

Phase change materials (PCMs) – that can store massive amounts of energy during phase changing – have a role in thermal energy storage [1, 2] or passive thermal management systems [3-5]. But the low thermal conductivity of PCMs, typically in the range of 0.15~1 Wm\(^{-1}\)K\(^{-1}\), prevents rapid heat transfer and limits power capacity of those systems. Efforts to improve PCM thermal conductivity have been made through: 1) dispersing thermal-conductive nanoparticles within PCM [6, 7]; 2) inserting a metallic matrix [8, 9]; 3) compositing PCMs with expanded graphite (EG) [10, 11]. Compared with the first two methods, compositing PCMs with EG significantly enhances the PCM thermal conductivity with a small change in phase change enthalpy. Moreover, PCMs/EG composites are form-stable – the capillary and surface tension force of porous EG holds PCMs even they are melted – which reduces requirements for sealing.

Several factors influence thermal conductivity of PCMs/EG composites, but only the mass fraction of EG has been discussed [12-15]. The increase of EG mass fraction increase thermal conductivity, but at a cost of lowering phase change enthalpy.

Recent studies on carbon mixtures [16, 17] have noticed thermal conductivity of EG-based composites increased with packing density. Thermal energy storage capacity per unit volume also increased with packing density, which boosted thermal management performance of a paraffin/EG composite [18].

Changes in physical structure caused by phase change also have a potential
impact on thermal conductivity of PCMs. Lyeo et al. [19] studied the thermal conductivity of Ge$_2$Sb$_2$Te$_5$ from 25 °C to 400 °C, and found an increase with temperature after a solid-solid phase change at 130 °C. Couto et al. [20] observed the effective thermal conductivity of the eutectic alkali nitrate salts/EG composites dropped by 11%-30% after melting. Thermal conductivity of mixtures of organic PCMs and thermal conductive nano-particles, were nearly temperature-independent out of the phase change temperature range; but slightly increased near the phase change temperature [21-23]. However, relationship between thermal conductivity of organic PCMs/EG composites and temperature has never been reported.

In this paper, we measure the thermal conductivity of an organic PCM/EG composite from 30 °C to 60 °C, and systematically discuss effects of mass fraction of EG, packing density and temperature on enhancing thermal conductivity for organic PCMs. A mathematical model is presented to predict thermal conductivity of EG-based composite PCMs— which is based on two input parameters: mass fraction of EG and the bulk density of composites. This model is expected to be universally suitable for thermal conductivity prediction of all organic PCMs/EG composites.

2. Experiment

2.1 Preparation of RT44HC/EG composites

RT44HC (purchased from Ruhr Energy Technology Co., Ltd, Hangzhou, China.) shows great promise for thermal management of power batteries thanks to its high latent heat (over 200 kJ kg$^{-1}$) and proper phase change temperature (44°C), and was
chosen as the basic organic PCM. RT44HC/EG composites with loadings of EG (mass fraction) of 25% and 35% were prepared by submerging EG into liquid RT44HC bath at 60 °C. Then cooled down the composite PCMs, and compressed them into cylinders with size of Φ 40×10 mm and densities from 300 to 900 kg m⁻³. Pictures of the samples are shown in Fig. 1.

2.2 Characterization of thermo-physical properties of RT44HC/EG composites

Phase change temperature, specific phase change enthalpy and effective specific heat of the RT44HC/EG composite PCMs were measured with a differential scanning calorimeter (DSC, Q20, TA Instruments Inc), with an average error less than 1.0%. The data were collected with a scan rate of 1 °C min⁻¹ over a temperature range of 30–60 °C.

Thermal conductivity of samples were measured by TPS 2500, a thermal constant analyzer manufactured by HOTDISK, based on transient plane source method. Experiment set-up is shown in Fig. 2. The Sensor 5501 with a radius of 6.403 mm was sandwiched between two samples prepared in Section 2.1. A special container was designed to hold the sample and prevent thermal expansions. To monitor the temperature of PCMs, three K-type thermocouples with errors less than 1 °C were attached to samples from top to bottom as positions shown at left in Fig. 2. Temperature was recorded by an Agilent 34970A data acquisition linked to a laptop. The samples and sensor were put into an oven, where temperature was regulated from 30 °C to 60 °C. Testing temperature included 30 °C, 35 °C, 40 °C, 41 °C, 42 °C, 43 °C,
44°C, 45°C, 50°C and 60°C – smaller temperature interval was set within the phase
change temperature range. At each temperature, it took at least 1 hour for the system
to stabilize. Once the temperature difference among three thermocouples dropped to 0,
measurements were performed by three times and took the average.

3. Mathemetic model

A quick and precise model to predict thermal conductivity of PCMs/EG
composites helps reduce costs of experiment. EG has a pore structure, as shown in Fig. 3. However, models based on porosity ε fail to work, as two types of pores in
composite PCMs — the inherent pores in EG and external pores produced by the
interlocking of particles — raised confusions about how to determine the porosity of
the porous mixture [24].

Numerical methods based on finite element analysis can also calculate thermal
conductivities of pore-structure materials [25-27], assuming that basic cell geometry
was idealized three-dimensional. But numerical models suffer from high
computational cost, and in most cases, irregular shape or size of pores are hard to be
described with regular model.

Models based on mixing law provides another solution. Maxwell-Eucken
model is an exact model that is often used to describe the thermal conductivity of
composites based on dispersed particles into a homogeneous matrix [28].

\[ k_{\text{eff}} = k_m \frac{2k_m + k_f + 2\beta (k_f - k_m)}{2k_m + k_f - \beta (k_f - k_m)} \]  

Where, \( k_{\text{eff}} \), \( k_m \), \( k_f \), and \( \beta \) are effective thermal conductivity of composite, thermal
conductivity of matrix, thermal conductivity of fluids saturated in and volume fraction of fillers. Concerning permeability and field strength, Bruggeman derived a model for dilute suspensions of spheres in a homogeneous medium[29, 30]. Other models have been developed for fillers with special shapes or distribution function [31-34]. All these models treated the matrix as a poor thermal conductive material, fillers are added to improve the thermal conductivity. In EG-based composites, EG is the matrix to hold PCMs, meanwhile it is also the filler to improve the thermal conductivity of PCM, which deviates from original assumptions and caused prediction errors.

Here a simple equation based on the bulk density and EG mass fraction is derived as follows. This model is supposed to predict the effective thermal conductivity of EG-based composite at room temperature.

First, the smallest heat transfer unit is defined as a bulk with the smallest volume that can conduct heat in the macroscopic view.

Then the following assumptions are made:

1) Thermal conductivity of compressed PCM/EG composites is isotropic, as indicated in [35].

2) Thermal network in graphite remains the same even after expanding or compressing. Microscopic structures of RT44HC/EG composites with different bulk densities have small difference, as shown in Fig. 4, which supports this assumption.
3) Contribution of PCMs to thermal conductivity of composites is neglected, due to the much smaller thermal conductivity of organic PCMs than graphite (0.22 W m\(^{-1}\) K\(^{-1}\) vs 129 W m\(^{-1}\) K\(^{-1}\)).

Then take a smallest heat transfer unit of natural graphite with a cross section area of 1 m\(^2\) and normalize its layer height \(h_G\) to 1 for benchmark. According to Fourier’s law, with the same area \(S\) and temperature gradient \(dT\), the power \(Q\) is dominated by thermal conductivity \(k\) and thickness \(h\), which corresponds to the layer height shown in Fig. 5.

\[
\frac{Q}{S} = -k \frac{dT}{h} = -k_G \frac{dT}{h_G} = -k_{EG} \frac{dT}{h_{EG}}
\]

(2)

Where \(k_G\) is the thermal conductivity of graphite, which equals to 129 W m\(^{-2}\) K\(^{-1}\), \(k_{EG}\) and \(h_{EG}\) is the thermal conductivity and layer height of EG.

Assumption 2 indicates that expanding or compressing natural graphite only does not change the bulk thermal conductivity of graphite remains constant— which means \(k_G = k_{EG}\). But thickness of the smallest heat transfer unit is changed, and the increase in thickness will reduce thermal conductivity of EG. The effective thermal conductivity \(k_{eff}\) is a combination of \(k\) and \(h\):

\[
k_{eff} = \frac{k_G}{h_{EG}}
\]

(3)

\(h_{EG}\) must be calculated before we can solve \(k_{eff}\). There is m mass conservation for graphite and EG:

\[
m = \rho_G V_G = \rho_{EG} V_{EG}
\]

(4)

\[
V_{EG} = \frac{\rho_G V_G}{\rho_{EG}}
\]

(5)
Where \( m \) is the mass of graphite, \( \rho_G, V_G, \rho_{EG} \) and \( V_{EG} \) are the density and volume of graphite and compressed EG. \( \rho_G = 2333 \text{ kg m}^{-3} \) and \( V_G = 1 \text{ m}^3 \).

\[
h_{EG} = \frac{V_{EG}}{S} = \frac{\rho_G \times 1 \text{ m}^3}{\rho_{EG} \times 1 \text{ m}^2} \quad (6)
\]

\( S \) is the cross section area of this unit, \( 1 \text{ m}^2 \).

\[
\rho_{EG} = \rho_c \phi \quad (7)
\]

\( \rho_c \) is the bulk density of the composite and \( \phi \) is the mass fraction of EG in the composite.

Finally,

\[
k_{\text{eff}} = \frac{k_G \rho_c \phi}{\rho_G} \quad (8)
\]

4. Results and discussions

4.1 Phase change characteristics of RT44HC

Fig. 6 shows the heating curves by DSC of paraffin/EG composite PCMs. RT44HC/EG composites have two phase change peaks near 40.5 °C and 43.0 °C. The first weak peak represents a solid-solid phase change and the second strong peak represents a solid-liquid phase change. These two peaks match the data of pure RT44HC, which is shown in the same figure. The phase change enthalpy of composites with EG mass fraction of 35% and 25% are 152.5 kJ kg\(^{-1}\) and 168.1 kJ kg\(^{-1}\), just as the product of the mass fraction and phase change enthalpy of pure RT44HC (226.1 kJ kg\(^{-1}\)).

Fig. 7 shows the curve of the specific heat versus temperature. The average specific heat of the composite with 25% EG is 2.1 kJ kg\(^{-1}\) °C\(^{-1}\) at the temperature
below 40 °C and above 45 °C. For the composite with 35% EG, the average specific heat is 1.3 kJ kg\(^{-1}\) °C\(^{-1}\). As the effective heat capacity includes both the sensible and latent heat, the effective specific heat rises sharply to 60~90 kJ kg\(^{-1}\) °C\(^{-1}\) within the phase change temperature range.

### 4.2 Temperature-dependent thermal conductivity

The temperature dependent thermal conductivity of RT44HC/EG composites (EG fraction: 25%wt) is shown in Fig. 8. Compared with pure RT44HC, effective thermal conductivity of RT44HC/EG composites at room temperature is increased by 20~60 times, which depends on its packing density.

The narrow difference between the effective thermal conductivity of composite PCMs below 35 °C and above 45 °C negligible. But it is noticeable that thermal conductivity nearly doubles within the phase change temperature range. For example, the composite PCM thermal conductivity (density: 700 kg m\(^{-3}\)) rises up to 14.7 W m\(^{-1}\) K\(^{-1}\) at 42 °C from 8.8 W m\(^{-1}\) K\(^{-1}\) at 30 °C and 8.4 W m\(^{-1}\) K\(^{-1}\) at 60 °C.

This steep increase in thermal conductivity may attribute to PCM’s superior capability in keeping temperature constant during phase changing. Figure 9 shows the thermal diffusion coefficient of PCM during phase changing is an order of magnitude lower, which imposes a great difficulty in changing the temperature inside PCM.

Whether attached to a boundary with a constant heat flux or constant temperature, the PCM whose temperature stops increasing throughout the phase change range enables a more efficient heat transfer by:
1) Minimizing the heat source temperature while keeping the temperature difference between heat source and PCMs constant, for the first-kind thermal boundary with a constant heat flux.

2) Maximizing the temperature difference between heat source and PCMs for the second-kind thermal boundary with constant temperature.

This finding is interesting and deserves further studies on enhancing heat transfer during the phase change.

As the difference between thermal conductivity of RT44HC/EG composites at 60 °C and 30 °C is within 10 %, effective thermal conductivity of RT44HC/EG composites out of melting range is considered as temperature-independent, which may be explained with the weakly temperature-dependent thermal conductivity of EG—that interlocks to form a network to hold PCMs and conduct heat.

However, as indicated by Couto [20], thermal conductivity of inorganic salts/EG composites dropped nearly 50% after melting, which might show it is inappropriate to neglect the contribution of inorganic salts to thermal conductivity of composites, as salts have higher thermal conductivity and more sensitive to changes in physical structure.

4.3 Effects of density and mass fraction of EG

The increase in mass fraction of EG reduces heat capacity and latent heat of the composite PCMs, but increases their thermal conductivity. Fig. 10 compares thermal conductivity of composites with different percentage of EG and densities. At the same
density, the thermal conductivity of composites with 35% EG is 30% higher than 25% EG.

But packing density of composites has a stronger impact on thermal conductivity of EG-based composites. Fig. 10 shows the effective thermal conductivity increases linearly with packing density. Thermal conductivity of the composite with 25 wt% EG at the density of 300 kg m$^{-3}$ is only 4.3 W m$^{-1}$ K$^{-1}$, but rises up to 10.7 W m$^{-1}$ K$^{-1}$ at the density of 900 kg m$^{-3}$, almost an increase by 150%. Increasing density compacts the thermal network and shortens the heat conduction pathway. Moreover, the volumetric heat capacity (both the sensible and latent capacity) increases with density, which can provide expanded thermal storage capacity in a fixed volume. Therefore, the increase of density is always desirable.

4.4 Validation of the thermal conductivity model

Theoretical predictions is compared with experiment data and Maxwell-Eucken model, results are shown in Fig. 11. The average relative deviation from experiment data of our model is less than 10%, smaller than 24% by Maxwell-Eucken model. Our model neglects the contribution of materials with low thermal conductivity and has the potential to predict thermal conductivity of any organic PCMs/EG composite.

We also compare predicting results with data presented in [35] and [27], which studied the thermal conductivity of sebacic acid (melting point: 135 °C, thermal conductivity: 0.372 W m$^{-1}$ K$^{-1}$)/EG (mass fraction: 15%) composites, and paraffin (melting point: 58–60 °C, thermal conductivity: not mentioned)/EG composite with a
constant density of 1061 kg m$^{-3}$. Fig. 12(a–b) shows the maximum deviation of our model from data in literature is less than 1.4 W m$^{-1}$ K$^{-1}$, which further proves the wide applicability of this model.

Compared with existing models, our thermal conductivity model is simple, reliable, and has a wide applicability. Besides predicting thermal conductivity based on EG mass fraction and bulk density, in turn, this model can be also used to calculate EG mass fraction or density if given a desirable thermal conductivity, which guides researchers to prepare PCM/EG composites based upon needs.

5. Conclusions

In this paper, we investigate factors that affect the thermal conductivity of RT44HC/EG composites with experiments. The following conclusions could be made:

1) Thermal conductivity of RT44HC/EG composites is temperature-independent outside the melting range, but increases sharply during the phase change – which is a consequence of superb capability of PCMs in keeping temperature constant;

2) The increase of EG mass fraction will increase thermal conductivity of RT44HC/EG composites, but decrease their specific heat and specific latent heat;

3) Thermal conductivity of EG-based composites increases with packing density, and is more sensitive to packing density than EG mass fraction.

4) A mathematic model based on inputs of bulk density and mass fraction of EG, is presented to predict the thermal conductivity of EG-based composites. This
model is validated with experiment data in this paper and in literature. This model is applicable to any kind of PCM/EG composites, only if the thermal conductivity of the pure PCM is low.

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Reference


Figures and Captions

Fig. 1  Pictures of samples that have been compacted.

Fig. 2  Experiment set-up to measure the thermal conductivity across the phase change temperature
Fig. 3  Scanning electron microscope (SEM) photo of EG

Fig. 4  SEM photos of RT44HC/EG composites with different densities: a) 300kg m$^{-3}$, b) 500kg m$^{-3}$, c) 700kg m$^{-3}$, d) 900kg m$^{-3}$,
Fig. 5  The illustration of the smallest heat transfer unit

![Diagram showing the smallest heat transfer unit with labeled dimensions and effective thermal conductivity.]

Fig. 6  DSC curves of RT44HC and its composites with EG.

![DSC curve graph with temperature on the x-axis and heat flow on the y-axis. The graph shows three curves for pure RT44HC, 25% EG, and 35% EG, with peak enthalpies of phase change: 35%: 152.5 J/g, 25%: 168.1 J/g, pure: 226.1 J/g.]

Fig. 7  Heat capacity of RT44HC/EG composites

![Heat capacity graph with temperature on the x-axis and heat capacity on the y-axis. The graph compares the heat capacity of 35% EG and 25% EG.]

The temperature dependent thermal conductivities of RT44HC/EG composites (EG: 25%wt)

![Graph showing thermal conductivity vs temperature for different packing densities.]

The temperature dependent thermal diffusivities of RT44HC/EG composites (EG: 25%wt)

![Graph showing thermal diffusivity vs temperature for different packing densities.]

Thermal conductivity of composites with different packing density

![Graph showing thermal conductivity vs temperature for different packing densities.]

Fig. 11  The comparison of the predicted results with experiment data and Maxwell-Eucken Model

Fig. 12  The comparison of the predicted results with experiment data: (a) sebacic acid/EG composites[35] and (b) paraffin/EG composites[27].
(a) Graph showing the relationship between density (kg m$^{-3}$) and thermal conductivity ($k$ (W m$^{-1}$ K$^{-1}$)) for experimental and predicted data.

(b) Graph showing the relationship between EG mass fraction (%) and thermal conductivity ($k$ (W m$^{-1}$ K$^{-1}$)) for experimental and predicted data.
### Nomenclature

- **k**: thermal conductivity (W m\(^{-1}\) K\(^{-1}\))
- **Q**: heat power (W)
- **T**: temperature (K)
- **h**: layer height of a smallest heat transfer unit (m)
- **m**: mass of graphite (kg)
- **V**: volume of a smallest heat transfer unit (m\(^3\))

**Subscripts**
- **S**: cross section area of a smallest heat transfer unit (m\(^2\))
- **eff**: effective

**Greek letters**
- **ε**: porosity
- **β**: volume fraction of fillers
- **φ**: mass fraction of EG
- **ρ**: density (kg m\(^{-3}\))

**Subscripts**
- **f**: fluid
- **m**: matrix
- **c**: composite PCMs
- **G**: natural graphite
- **EG**: compressed EG