

# Surfactant modification of expanded graphite to fabricate composite glycine water-based phase change material for cold energy storage

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## ABSTRACT

To improve the compatibility between expanded graphite (EG) and glycine water-based phase change material (GWPCM), different concentrations of modified expanded graphite (MEG) were prepared by using surfactant of triton x-100 (TX-100) as a modifier. The adsorption capacity of EG and MEG was implemented in detail. Composite GWPCM by using MEG as a porous material was prepared. The thermophysical properties of the prepared MEG/GWPCM were evaluated. The results showed that MEG-0.15 exhibited the best compatibility with GWPCM, and the adsorption capacity increased to 82.87 %. When the addition amount of MEG was 16 wt%, the MEG/GWPCM possessed a suitable melting temperature (-5.75 °C) and a high latent heat (250.77 J/g). Notably, the thermal conductivity was 2.4523 W/(m·K), which was 4.08 folds of GWPCM. The prepared composite materials showed great potential in the low-temperature cold energy storage of photovoltaic refrigeration systems.

**Keywords:** modified expanded graphite, phase change material, cold energy storage, thermal properties

## NONMENCLATURE

### Abbreviations

GWPCM	Glycine water - based phase change material
EG	Expanded graphite
MEG	Modified expanded graphite
PCM	Phase change material

CNTs	Carbon nanotubes
<i>Symbols</i>	
$m_0$	Weights of EG or MEG block before adsorption for GWPCM (g)
$m_1$	Weights of EG or MEG block after adsorption for GWPCM (g)

## 1. INTRODUCTION

It is an effective way to reduce the loss rate of fruit, vegetable circulation and energy consumption by using solar energy as driving energy for cold storage in the field to achieve the first-kilometer refrigeration. However, the fluctuation and intermittency of solar energy will lead to the instability of the off-grid photovoltaic refrigeration system. It is necessary to set up an energy storage device in the system to suppress the impact of photovoltaic fluctuations [1]. Currently, the research of off-grid photovoltaic refrigeration systems at home and abroad mainly focuses on using battery or phase change material (PCM) for energy storage. The investment and maintenance costs of batteries are high, and lifespan is limited. Therefore, the development of off-grid photovoltaic refrigeration system with battery is still restricted [2]. PCM absorbs or releases latent heat through solid-liquid phase change to achieve thermal energy storage.

Water-based PCM, which has the advantages of low cost and high latent heat and shows great potential in cold energy storage applications below 0 °C. Xu et al. [3] prepared a water-based PCM (potassium sorbate aqueous solution) with phase change temperature of -2.5 °C and latent heat of 256.2 J/g. The prepared low-temperature PCM kept the temperature in the cold box range of -2 ~ 0 °C for 14 h. Ma et al. [4] prepared a low

temperature PCM with phase change temperature between -1.7 and -2.3 °C, and the latent heat of the PCM was maintained above 280 J/g. The development of a water-based PCM system with an organic aqueous solution is expected to achieve higher energy storage density. However, the water-based PCM system has the disadvantages of large undercooling and low thermal conductivity [5], which will decrease the rate of cold storage/release [6]. Therefore, solving the problems of large supercooling and low thermal conductivity of water-based PCM has become the key to achieve efficient, stable, and long-term energy storage or release of photovoltaic refrigeration system.

Carbon-based materials, such as carbon nanotubes (CNTs) [7], graphene [8], and expanded graphite (EG) [9] are favored in improving the thermal conductivity of PCM due to their large specific surface area and excellent thermal properties [10]. CNTs are typical one-dimensional cylindrical structures with a high aspect ratio [11], which have the advantages of high thermal conductivity, low density, and large specific surface area. As a two-dimensional carbon material, graphene has a single-layer structure and good thermal conductivity, high specific surface area, and strong mechanical stability [12]. However, due to the high cost of CNTs and graphene, their applications in cold energy storage are limited. EG is often used as a support material for organic PCMs for its large specific surface area, strong adsorption capacity [13], high thermal conductivity, and special worm-like structure [14]. However, due to the hydrophobicity of EG [15], its compatibility with water-based PCMs is poor.

To improve the compatibility of EG with water-based PCM, researchers tried to improve the compatibility of EG with inorganic PCM by coating metal oxides on the surface of EG. Al<sub>2</sub>O<sub>3</sub>-coated EG was used to modify its surface [16], and the compatibility between EG and water was improved after Al<sub>2</sub>O<sub>3</sub> coating. 3D flower-like NiCo<sub>2</sub>O<sub>4</sub> was used to modify the surface of EG [17]. The modified EG showed excellent chemical compatibility with Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O-Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O inorganic phase change materials. Zou et al. [18] improved the compatibility between MEG and CaCl<sub>2</sub>·6H<sub>2</sub>O by coating TiO<sub>2</sub> on the surface of EG. The adsorption capacity of MEG to CaCl<sub>2</sub>·6H<sub>2</sub>O reached 82.6 %. Existing studies have shown that coating metal oxides on the surface of EG can effectively improve the compatibility between EG and inorganic PCM. However, the process of preparing MEG by coating metal oxides is complicated and time-consuming. Therefore, exploring a simple preparation method of cheap and suitable

modifiers for large-scale promotion is an urgent task in the field of cold energy storage.

In this study, to improve the compatibility of EG and GWPCM, the surface modification of EG with different concentrations of surfactant TX-100 was investigated. The adsorption capacity of MEG on GWPCM was effectively improved. Subsequently, the thermal physical parameters of MEG/GWPCM were characterized by DSC. The prepared high-performance MEG/GWPCM material at low temperature showed great potential for cold energy storage applications.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Glycine (ACS, ≥ 98.5%) was purchased from Shanghai Macklin Biochemical Co., Ltd., China. Mannitol (AR, 98.0%), Potassium sorbate (AR), TX-100 and expandable graphite (particle size: 75 μm) were purchased from Aladdin Reagent Co., Ltd. The thermal properties of raw materials listed in table 1.

Table 1 Thermal properties of raw materials

Material	Molecular formula	Melting point /°C	Molecular weight
Glycine	C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	182	75.07
Mannitol	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	166-168	182.172
Potassium sorbate	C <sub>6</sub> H <sub>7</sub> KO <sub>2</sub>	270	150.217
TX-100	C <sub>34</sub> H <sub>62</sub> O <sub>11</sub>	44-46	646.86

### 2.2 Preparation of MEG

Preparation of EG. Firstly, expandable graphite was put in a drying oven at 80 °C for 12 h to remove water. Next, the expandable graphite was put in a microwave oven and heated for 30 s with a power of 700W. Then, EG was prepared.

Preparation of MEG. The surfactant of TX-100 with different concentrations was dissolved in 50 mL ethanol and sonicated for 10 minutes. Then, EG with mass of 0.5g was immersed in TX-100 ethanol solution and sonicated for 40 minutes. Then EG dispersion was dried in a vacuum drying oven at 80 °C for 18 h until the ethanol was completely volatilized.

Table 2 The composites of MEG

Name	TX-100: EG	TX-100/g	EG/g
MEG-0.01	0.01	0.005	0.5
MEG-0.05	0.05	0.025	0.5
MEG-0.1	0.1	0.05	0.5
MEG-0.15	0.15	0.075	0.5
MEG-0.2	0.2	0.1	0.5

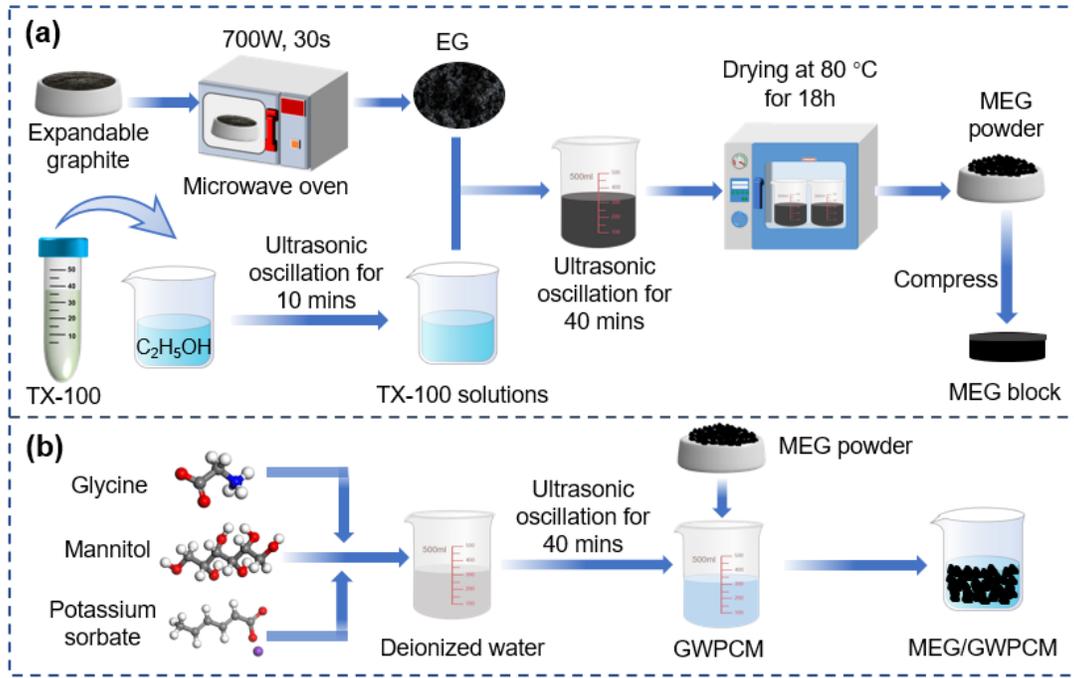


Fig. 1 Preparation process of MEG and MEG/GWPCM

Thus, MEG with different concentrations of TX-100 was obtained, which named MEG-0.01, MEG-0.05, MEG-0.1, MEG-0.15, MEG-0.2, as shown in Table 2. The preparation process of MEG is shown in Fig.1(a).

### 2.3 Preparation of composite MEG/GWPCM

Preparation of GWPCM. Firstly, mass fractions of 6% glycine, 1.5% mannitol, 0.1% potassium sorbate and 92.4% deionized water were put into the beaker, and the beaker was put into the ultrasonic cleaning instrument. Then the solution evenly mixed by ultrasonic oscillation for 40 mins, and the glycine water-based phase change material (GWPCM) was prepared.

Preparation of MEG/GWPCM. MEG/GWPCM was prepared by natural adsorption method. Firstly, MEG-0.15 powders with mass fractions of 10 %, 12 %, 14 %, 16 %, and 18 % were placed in a beaker, and then GWPCM with mass fractions of 90 %, 88 %, 86 %, 84 %, and 82 % were added, respectively. The GWPCM was repeatedly adsorbed by MEG by stirring the glass plate for 5 min. The preparation process of MEG/GWPCM composite is shown in Fig.1(b).

## 2.4 Section of results Characterization

### 2.4.1. Characterization of thermal physical properties

The thermal properties of GWPCM and MEG/GWPCM composites were characterized via differential scanning calorimeter (DSC, METTLER DSC3+, Switzerland). The thermal conductivity of GWPCM and

MEG/GWPCM composites was at 25 °C by thermal conductivity meter (DRE-III, Xiangtan City Instrument & Metre Co., Ltd., China).

### 2.4.2. Adsorption capacity and leakage test

To analyze the adsorption capacity of EG and MEG on liquid GWPCM, an adsorption experiment was carried out. The MEG powders were compressed to blocks, the adsorption capacity of EG and MEG blocks on liquid GWPCM was calculated by Eq. (1):

$$y = \frac{m_1 - m_0}{m_1} \times 100\% \quad (1)$$

where  $m_0$  and  $m_1$  represented the weights of EG or MEG block before and after adsorption for GWPCM, respectively.

To determine the optimal adsorption capacity of MEG, leakage experiments of MEG/GWPCM samples with mass fractions of 10%, 12 %, 14 %, 16 %, and 18 % of MEG were conducted at 25 °C. MEG/GWPCM samples were placed on filter paper until there was no liquid leakage in MEG/GWPCM.

## 3. RESULTS AND DISCUSSION

### 3.1 Adsorption performance of EG on GWPCM

In order to investigate the effect of particle size of EG on the adsorption capacity of GWPCM, the adsorption experiments of EG with particle size of 20 mesh (EG-20), 40 mesh (EG-40), 60 mesh (EG-60), 80

mesh (EG-80) and 100 mesh (EG-100) were carried out, and the results are shown in Fig.2.

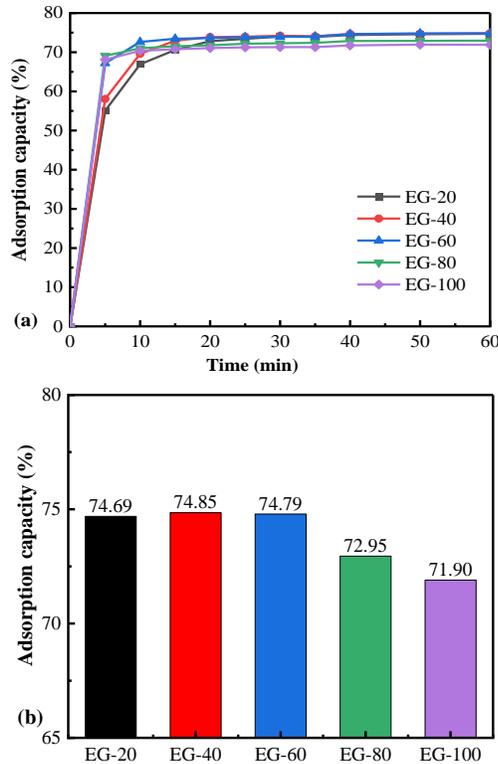


Fig. 2 Adsorption capacity of EG with different mesh

The results showed that when the mesh of EG was between 20 and 100, the adsorption capacity of GWPCM range from 71.90 % to 74.85 %. EG with particle size of 40 mesh possessed the maximum adsorption capacity of 74.85 %. When the mesh of EG was larger than 60 mesh, the adsorption capacity of GWPCM decreased slightly. EG with 40 mesh was selected as the supporting material in this study.

### 3.2 Adsorption performance of MEG on GWPCM

To verify the compatibility of EG and MEG with GWPCM, the adsorption experiment of GWPCM was carried out, and the results are shown in Fig.3. After TX-100 modification, the adsorption capacity of MEG-0.01, MEG-0.05, MEG-0.1, MEG-0.15 and MEG-0.2 on GWPCM was effectively improved, which was 75.54%, 78.71 %, 82.55 %, 82.87 % and 82.69%, respectively. The results showed that the compatibility of MEG and GWPCM was better than that of EG. TX-100 is a non-ionic surfactant with a long molecular chain, which will occupy the layers of EG, and introduce hydrophilic functional groups -OH and ether bonds composed of oxygen-containing groups, thereby improving compatibility with GWPCM.

In addition, with the increase of TX-100 concentration, the adsorption capacity of MEG to

GWPCM slightly decreased. The main reason is that the high concentration of TX-100 attached to the layer of EG, thus leads to the decrease of EG lamellar space, which reduces the adsorption capacity. MEG-0.15 showed the best compatibility with GWPCM, and the adsorption capacity increased from 74.85% to 82.87% compared with EG. Therefore, MEG-0.15 was selected as the porous carrier of GWPCM in this study.

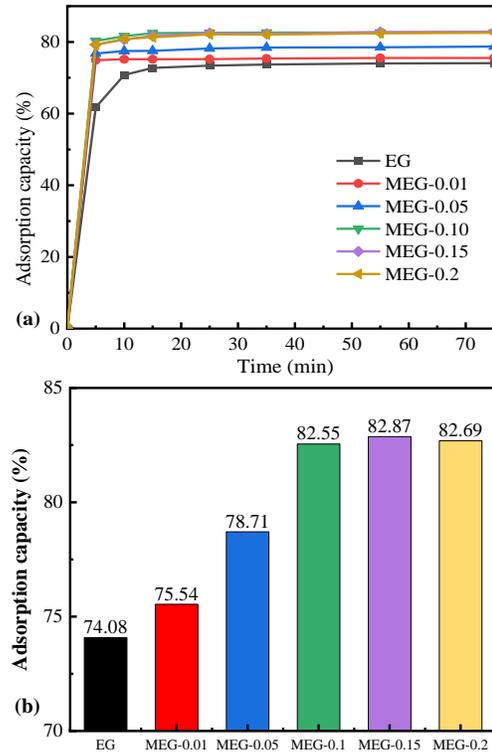


Fig. 3 Adsorption capacity of MEG

### 3.3 Leakage test of MEG/GWPCM

The leakage test of MEG/GWPCM with 10wt %, 12 wt%, 14 wt%, 16 wt% and 18 wt% MEG-0.15 was carried out, and the results are shown in Fig.4. When the mass fraction of MEG-0.15 was 16 % and 18 %, there was no obvious leakage trace on the filter paper. When the mass fraction of MEG-0.15 was less than 16%, obvious leakage marks on the filter paper could be observed. Thus, the MEG/GWPCM composites were prepared by selecting MEG-0.15 with a content of 16%, and the thermophysical properties of GWPCM by adding MEG was further analyzed.

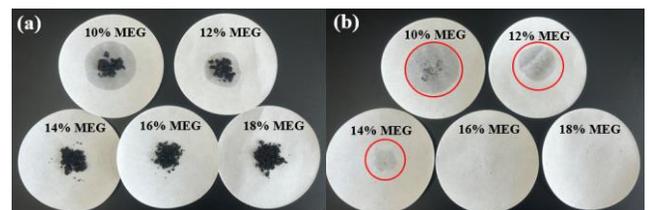


Fig.4 The prepared EG and MEG block

### 3.4 Thermal properties of MEG/GWPCM

The phase change temperature and latent heat are two important factors in cold energy storage applications of photovoltaic refrigeration system. The latent heat and phase change temperature of GWPCM and MEG/GWPCM were characterized via DSC, as shown in Fig.5. The prepared liquid GWPCM had a large latent heat (292.21 J/g) and a suitable melting temperature (-5.53 °C). The thermal conductivity was 0.6017 W/(m·K). When the additional amount of MEG powder was 16 wt%, the melting temperature and latent heat of MEG/GWPCM were -5.75 °C and 250.77 J/g, respectively. Notably, the thermal conductivity was reached to 2.4523 W/(m·K), which was 4.08 folds of GWPCM, as shown in Fig.6.

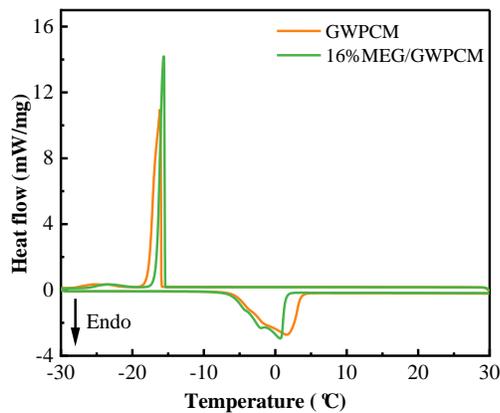


Fig. 5 DSC results of GWPCM and MEG/GWPCM

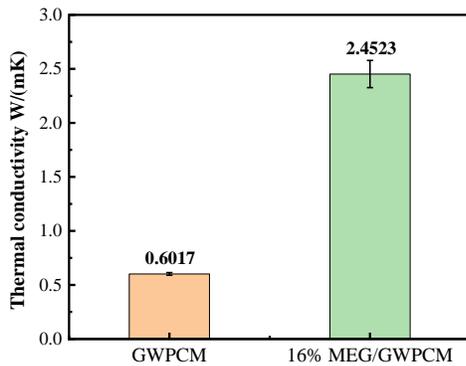


Fig. 6 Thermal conductivity of GWPCM and 16% MEG/GWPCM

## 4. CONCLUSIONS

In this paper, low-temperature composite materials of MEG/GPCM with different concentrations of MEG were prepared by the natural adsorption method. The adsorption capacity of GWPCM was effectively improved after the modification of EG by surfactant TX-100. The thermal properties of MEG/GWPCM were analyzed. The prepared composite PCMs of MEG/GWPCM showed great potential in cold energy

storage. The main conclusions of this study can be drawn:

(1) The effect of the particle size of EG on the adsorption capacity of GWPCM was investigated, and the results showed that the adsorption capacity of GWPCM ranged from 71.90 % to 74.85 % with the particle size of EG between 20 and 100 mesh. EG with a particle size of 40 mesh possessed the maximum adsorption capacity of 74.85 %.

(2) Surfactant of TX-100 effectively improved the compatibility of GWPCM and EG. The results showed that MEG-0.15 exhibited the best compatibility with GWPCM, and the adsorption capacity increased from 74.85 % to 82.87% compared with EG.

(3) The leakage test results showed that the liquid GWPCM can be effectively encapsulated by MEG when the additional amount of MEG was 16 wt%. The composite material of MEG/GWPCM with 16% MEG possessed a suitable melting temperature (-5.75 °C) and higher latent heat (250.77 J/g). Notably, the thermal conductivity was 2.4523 W/(m·K), which was 4.08 folds of GWPCM.

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## DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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