

# A Biomass-derived Carbon Packed Polyethylene Glycol with Enhanced Thermal and Solar Energy Storage Performance

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## ABSTRACT

A biomass-derived hierarchical porous carbon-carbonized rice (CNR) with high porosity (80.9%) and large pore volume (3.45 cm<sup>3</sup>/g) was prepared using natural and accessible biomass rice as template. Then the CNR was applied to pack polyethylene glycol 2000 (PEG2000) phase change material (PCM) via vacuum impregnation method. The phase change property, thermal storage/release and solar photothermal conversion performance of the materials were explored. The results show that the maximum loading of PEG2000 is 75 wt%. Compared with pure PCM, the supercooling degree of PEG2000/CNR composite material is reduced by 57%, that is, CNR promotes the heterogeneous nucleation of PEG2000. The enthalpy value of PEG2000/CNR composite is up to 137.22 J/g with an encapsulation ratio of 81.6%, showing a better thermal performance than commonly used mesoporous silicon-based, carbon-based and metal-organic framework composite PCMs. The biomass-derived CNR can significantly increase the energy storage/release rate and solar photothermal conversion efficiency (54.7%) than that of pure PCM. This work provides a new idea for the design of phase change composite materials with high heat storage density and stability for thermal and solar energy storage.

**Keywords:** biomass-derived, hierarchical porous carbon, polyethylene glycol, composite phase change material, thermal properties, solar photothermal conversion

## NONMENCLATURE

### Abbreviations

CNR	Carbonized rice
PEG	Polyethylene glycol
PCM	Phase change material

SEM	Scanning electron microscopy
XRD	X-ray diffraction
DSC	Differential scanning calorimetry
EDS	Energy dispersive spectrum

### Symbols

wt%	Mass percentage
$m_1, m_2$	Mass
$I_D, I_G$	Intensity
$R$	Encapsulation ratio
$T_m, T_f$	Phase change point
$\Delta H_m, \Delta H_f$	Latent heat enthalpy

## 1. INTRODUCTION

At present, phase change energy storage technology has attracted much attention because of its ability to achieve efficient use of energy [1]. However, the single solid-liquid phase change material (PCM) is easy to leak out and corrode the environment in the utilization process, thus limiting its application. In recent years, porous framework has been proposed to encapsulate PCM and can effectively alleviate the contradiction between thermal storage and heat transfer introduced by the package of single PCM, taking into account the energy storage density and thermal conductivity [2-3]. The porous framework has gradually developed from millimeter-scale macropores to nanometer-scale mesopores or even micropores [4]. However, the loading of PCM cannot exceed 70 wt% due to the limitation of nanopores [5]. And the smaller the pore size, the stronger the capillary force of the framework, which may restrict the movement of the PCM molecules, resulting in a limited crystallization of the PCM [6]. Consequently, it is expected to obtain a multi-stage porous framework to increase the energy storage density as well as ensure the thermal stability of the material.

Inspired by nature, it is not difficult to find that the hierarchical structure of natural organisms has endowed biological organizations with many unexpected functions. The micro-nano structure of papilla enables the lotus leaf to be self-cleaning [7], the micro-nano layer of spider silk makes the specific strength about 5 times that of steel [8], and the overlapping arrangement of micro-nano crystal layer leads to the fracture toughness of shell nacre about 3,000 times that of inorganic aragonite [9]. Studies have shown that hierarchical porous frameworks prepared by using natural biomass materials (wood, straw, eggplant, etc.) as template have the advantages of green, renewable and low cost [10-12].

In this study, a kind of natural biomass rice was selected as a template to synthesize hierarchical carbon-carbonized rice (CNR) through a high-temperature carbonization method. The vacuum impregnation method was used to pack the medium-low temperature PCM polyethylene glycol 2000 (PEG2000). The thermal properties of the composite material were explored, and the results were compared with that of the other common composite PCMs. This study provides some data for the structural-thermal design of such composite PCMs.

## 2. EXPERIMENTAL PREPARATION

The natural material rice was obtained from the restaurant. PEG2000 was purchased from 3A-Chemicals. Hierarchical porous carbon framework CNR was prepared by carbonizing the rice at 600°C [13]. Then put the CNR buck and excess PEG2000 in a 50 mL beaker, which was subsequently kept in a vacuum drying oven at 80°C for 3 h. Finally, the sample was placed on the filter paper and put in a drying oven at 80°C to remove the excess PEG2000. The PEG2000/CNR composite material was obtained until there was no oil appeared on the filter paper.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of carbon framework

Fig. 1a and Fig. 1b represents the actual and scanning electron microscope (SEM) image of CNR, respectively. It can be seen that the framework is disordered and highly porous. X-ray diffraction (XRD) (Fig. 1c) shows that CNR has weak and broad characteristic peaks at 22.5° and 44.6° (2θ), corresponding to the (002) and (101) diffraction of carbon materials [14]. The Raman characterization result (Fig. 1d) exhibits that CNR has D peak and G peak at 1350 cm<sup>-1</sup> and 1591 cm<sup>-1</sup>,

respectively, indicating that CNR contains sp<sup>3</sup> and sp<sup>2</sup> hybrid carbon atoms, that is, the sample contains both amorphous and graphite structures.

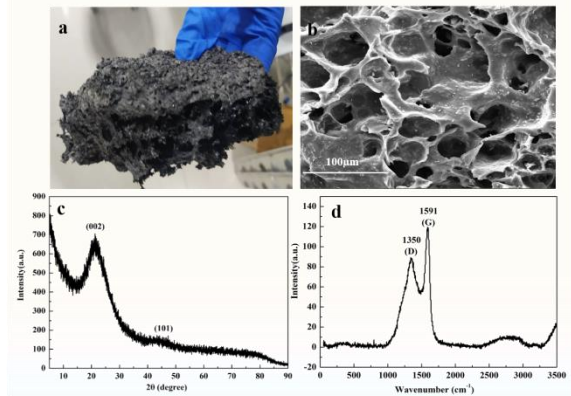


Fig. 1. (a) Biomass-derived carbon framework and its (b) SEM (c) XRD and (d) Raman spectra

The structural parameters of the material were obtained by mercury intrusion test, and the pore size distribution is shown in Fig. 2. The average pore diameter of CNR is 3.64 μm with a high porosity of 80.9% and a large pore volume of 3.45 cm<sup>3</sup>/g. The CNR pore size distribution percentage was further explored. The pore diameter of CNR framework is mainly distributed in the range of 1-50 μm, accounting for 48% of the total pores. The proportion of nanopores (pore diameter < 1 μm) is 6%, proving that CNR has a hierarchical porous structure.

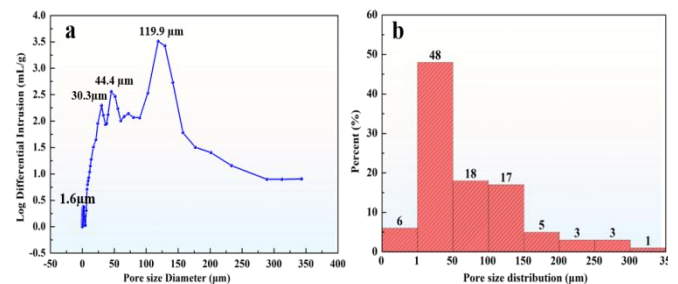


Fig. 2. (a) Pore size distribution and (b) pore size distribution percentage of carbon framework

### 3.2 Characterization and thermal storage property of composite material

Fig. 3A shows the leakage test of the PEG2000/CNR composite material. There is no PEG impregnation on the filter paper after 4 h, indicating that the excess PCM has been completely removed. The maximum loading of PEG2000 in the composite material is:

$$wt\% = \frac{m_2 - m_1}{m_2} \times 100\% \quad (1)$$

Where wt% is the mass percentage of PCM,  $m_1$  and  $m_2$  stands for the mass of CNR framework and

PEG2000/CNR, respectively. Hence, the maximum loading of PEG2000 is determined to be 75 wt%. Fig. 3B (a) and (b) represents the SEM and energy dispersive spectrum (EDS) image of the composite with 75 wt% loading, respectively. It can be seen that the PEG2000 has occupied the pores of CNR and is evenly distributed in the pores. The nano-pores of the porous framework can provide strong capillary force to prevent the PCM from leaking out during the phase change process, and the larger pore volume and porosity greatly increase the loading capacity to the PCM.

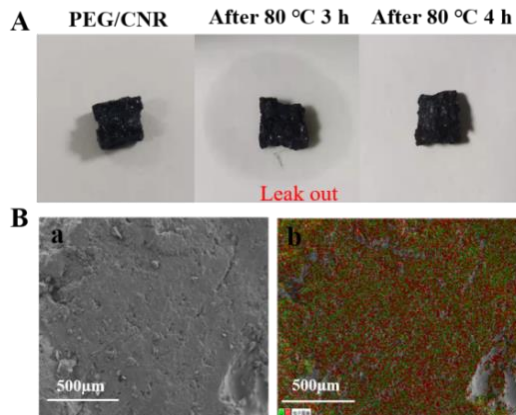


Fig. 3. (a) Leakage test of PEG2000/CNR, (b) SEM and (c) EDS element mapping images of the composite

The phase change point and latent heat enthalpy of PEG2000 and composite material were measured by differential scanning calorimetry (DSC). The melting and freezing point of pure PEG2000 is 55.14 °C and 19.18 °C, respectively. The corresponding latent heat enthalpy is 168.09 J/g and 155.46 J/g, respectively. For the PEG2000/CNR bulk material, the phase change point and latent heat are the average test values at multiple points. The heat flow curves versus temperature of PEG and composite material are shown in Fig. 4, and the results are summarized in Table 1. We used the encapsulation ratio  $R$  to reflect the influence of the framework on the phase change enthalpy:

$$R = \frac{\Delta H_{m,comp}}{\Delta H_{m,PEG}} \times 100\% \quad (2)$$

Where  $R$  is the encapsulation ratio,  $\Delta H_{m,comp}$  and  $\Delta H_{m,PEG}$  is regard as the melting enthalpy of the composite and PEG2000, respectively. The average melting and cooling point of the PEG2000/CNR is 50.61 °C and 35.17 °C respectively. The corresponding latent heat is 137.22 J/g and 132.57 J/g, respectively, and the encapsulation ratio of the composite can reach up to 81.6%.

The phase change characteristics of composite materials were compared with that of the popular silicon-based, carbon-based and metal-organic

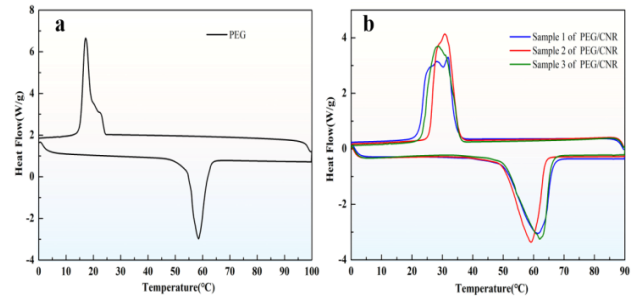


Fig. 4. Heat flow curves versus temperature of PEG and PEG2000/CNR composites

Table 1. Phase change point and latent heat text results of PEG and composites

Samples	$T_m/T_f$ (J/g)	$\Delta H_m/\Delta H_f$ (J/g)	$R$ (%)
PEG	55.14/19.18	168.09/155.46	-
PEG2000/CNR-1	50.15/34.40	133.05/129.56	79.2
PEG2000/CNR-2	50.10/35.51	137.41/133.12	81.7
PEG2000/CNR-3	51.59/35.61	141.12/135.02	84.0

framework composite PCMs [5,6,14-19]. As shown in Fig. 5, the biomass-derived PEG2000/CNR composite material possess a better thermal performance, and the latent heat enthalpy is higher than that of the MOFs-derived hierarchical porous composite material [5]. Furthermore, the supercooling degree ( $T_m-T_f$ ) of the composite (15.44 °C) is 57% lower than that of pure PEG2000 (35.96 °C), that is, the CNR framework promotes the crystallization of PEG2000, which can improve the phenomenon that the latent heat cannot be released in time during the energy utilization process [20].

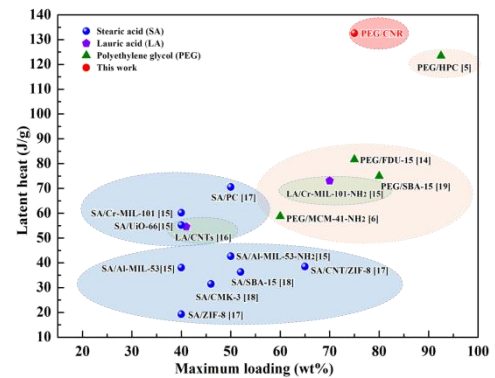


Fig. 5. Comparison of latent heat of different mesoporous/nanoporous composite materials<sup>[5,6,14-19]</sup>

Furthermore, an infrared thermal imager was used to record the surface temperature changes of pure PEG2000 and PEG2000/CNR composites during heating and cooling process to compare their thermal storage/release performance. During the heating process, the samples was placed on a ceramic heating

plate and the temperature was gradually raised to about 48 °C , then followed by a cooling process. The representative infrared thermographic images of two samples were shown in Fig. 6a. The temperature of PEG2000/CNR material rises faster than that of pure PEG, and similar phenomena can be also observed during the cooling process. Fig. 6b shows the temperature distribution of two samples at the center of the surfaces. It can be seen that the heating and cooling rate of the composite material is higher than that of pure PCM, indicating that the rice-derived hierarchical porous carbon can significantly increase the thermal conductivity of the material, thereby increasing the energy storage/release rate, thus would realize rapid charging and discharging in the practical thermal energy storage system.

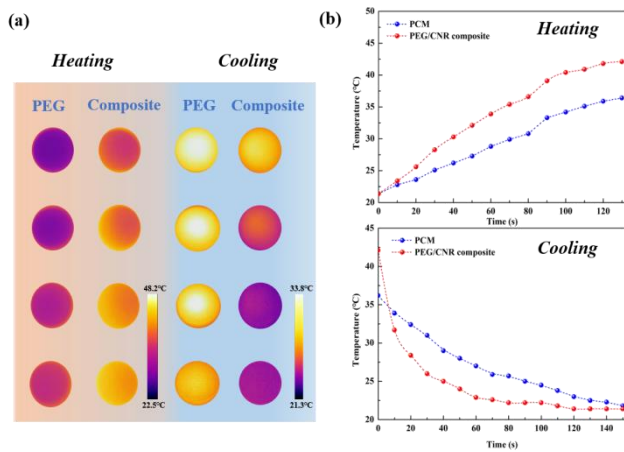


Fig. 6. (a) Representative infrared thermography of PEG2000 and composite materials and (b) Temperature curves with time in the heating and cooling process

### 3.3 Solar photothermal conversion performance of PEG/CNR composite material

Nowadays, solar energy is widely concerned by many researchers as a kind of new energy. To study the solar energy conversion performance of pure PEG2000 and the composite material, the light absorption capacity was first characterized by a UV-vis-NIR spectrophotometer. As shown in Fig. 7a, the PEG2000/CNR composite exhibits a higher solar absorbance in the visible range. The solar radiation with a power density of 100 mW/cm<sup>2</sup> generated by the solar simulator was used to illuminate the samples, as shown in Fig. 7b. The temperature evolution curves were shown in Fig. 7c. Compared with pure PEG2000, the temperature of the composite material rises more rapidly, due to the black surface of the composite material which can effectively capture solar photons and

heat the PEG2000 molecules to a point higher than its phase change temperature. The temperature of the samples drops rapidly after the light source was removed. The freezing platform means the solidification process of PCM in the composite material. The solar photothermal conversion efficiency of the samples can be calculated as :

$$\eta = \frac{m\Delta H}{PS(t_0 - t_e)} \times 100\% \quad (3)$$

Where  $\eta$  is solar photothermal conversion efficiency,  $m$  stands for the mass,  $\Delta H$  represents the melting latent heat,  $P$  is the optical power density,  $S$  is the radiated area, and  $t_0$  and  $t_e$  are light-driven phase change time during the melting process of the sample, respectively. The result was shown in Fig. 7d. It can be seen that the solar photothermal conversion efficiency of PEG2000/CNR composite is 54.7%, which is a significant improvement than that of pure PCM (0). Therefore, the PEG2000/CNR composite can achieve great solar photothermal conversion performance.

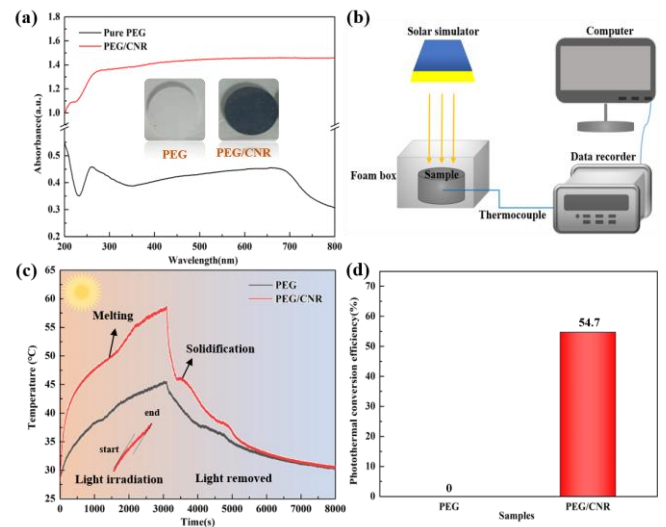


Fig. 7. (a) UV-vis-NIR absorption spectra of PEG2000 and composite materials (b) Schematic experimental setup (c) Temperature distribution at the center of the sample (d) Solar photothermal conversion efficiency of the samples

## 4. CONCLUSIONS

In this paper, the natural biomass rice, which is easily available and environmentally friendly, was used as the template to prepare biomass-derived hierarchical porous carbon by a high-temperature carbonization method, and the organic PCM PEG2000 was further loaded. The phase change property, thermal storage/release and solar photothermal conversion performance were explored. The main conclusions are as follows:

(1) The maximum loading of CNR to PEG2000 is 75 wt%. The nano-pores of framework can provide strong capillary force to prevent the PCM from leaking out, and the larger pore volume and porosity increase the heat storage density of the PCM.

(2) Compared with pure PCM, the supercooling degree of the composite material is reduced by 57%, and the latent heat is as high as 137.22 J/g, which is higher than that of the common mesoporous silicon-based, carbon-based and metal-organic framework composites.

(3) The rice-derived hierarchical porous carbon can significantly increase the energy storage/release rate of PCM, and the PEG2000/CNR composite exhibits great improvement of solar photothermal conversion efficiency (54.7%) than that of pure PEG (0). It is a potential candidate material in the field of thermal energy storage system.

#### ACKNOWLEDGEMENT

This work is financially supported by the National Key R&D Program of China (No.2018YFA0702300), National Natural Science Foundation of China (No.51876007, No.52176054) and Beijing Natural Science Foundation (No.3192022).

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