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## Effect of structural characteristics and surface functional groups of biochar on thermal properties of different organic phase change materials: Dominant encapsulation mechanisms



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Laiquan Lv , Jiankang Wang , Mengting Ji , Yize Zhang , Shengyao Huang, Kefa Cen , Hao Zhou $^{\ast}$ 

State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou, 310027, PR China

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## ABSTRACT

In this article, waste phoenix leaf biochar was introduced into three most used organic phase change materials (PCMs) to prepare shape-stable composite PCMs by the vacuum impregnation method. The encapsulation capacity and encapsulation efficiency of steam activated biochar for paraffin, stearic acid, and polyethylene glycol were 59.28% and 49.14%, 63.03% and 57.62%, 71.38% and 46.84%, respectively, which was related to the mechanisms of biochar encapsulated organic PCMs. The dominant mechanisms of biochar encapsulated organic PCMs are summarized as pore-filling, hydrogen-bonding, hydrophobic interaction between biochar and PCMs, and other potential mechanisms. Influence degree  $\eta$  was introduced to illustrate the effect of biochar on organic PCMs, 16.56%, 8.72%, and 35.75% for steam activated biochar on paraffin, stearic acid, and polyethylene glycol. In addition, compared with original PCMs, the thermal conductivity of biochar-based composite PCMs first decreased and then increased with the increase of biochar pyrolysis temperature. Moreover, biochar encapsulated organic PCMs and organic PCMs in thermal energy storage, building energy conservation, solar energy utilization, and battery thermal management system.

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## 1. Introduction

In recent decades, people have noticed the severe detriment of fossil fuel combustion on the environment, such as air pollution, acid rain, greenhouse effect, etc. Renewable energy has the ability of natural supplement and can effectively reduce the impact of energy consumption on the environment and society, which has attracted extensive attention [1,2]. However, unlike fossil fuel, renewable energy needs to be harvested when available and stored until required [3], which means reliable energy storage systems are requisite for the utilization of renewable energy.

Latent heat storage (LHS) system employs PCM for thermal energy storage, which can realize heat storage and release almost without temperature variation [4]. Moreover, LHS system has more excellent energy storage density than sensible heat storage system

\* Corresponding author. E-mail address: zhouhao@zju.edu.cn (H. Zhou). [5]. PCMs are categorized based on the type of materials as organic and inorganic PCMs, and the former is widely used in solar energy storage systems [6,7], building applications [8,9], and textile [10,11] due to non-toxic, non-corrosive and low supercooling. However, the easy leakage and poor thermal conductivity of organic PCMs will result in energy loss and poor heat transfer performance.

In view of the poor thermal conductivity of PCMs, scholars put forward numerous ways to overwhelm the problem, such as adding high thermal conductivity nanoparticles, porous support, and other materials into PCMs. Porous support encapsulated organic PCMs can not only solve the problem of leakage but improve the thermal conductivity [12], mechanical [13] and chemical stability [14]. At present, the shape-stable composite PCMs based on expanded graphite (EG) [15,16], carbon nanotubes (CNTs) [17,18], porous minerals [19,20], graphene [21,22], mesoporous silica [23,24] and metal foam [25,26] were investigated extensively. For example, Zhou et al. [16] used the "impregnation and compression" method to prepare xylitol/EG shape-stable composite PCM. The SEM, DSC,



Nomenclature			thermogravimetry X-ray powder diffractometer
Abbreviat BET BJH CNT CPL DSC DTG EG FT-IR LHS PA PEG PCM PL SA SEM SEI	tion Brunauer-Emmett-Teller Barrett-Joyner-Halenda carbon nanotube CO <sub>2</sub> activated phoenix leaf biochar differential scanning calorimeter derivative thermogravimetry expanded graphite Fourier transform infrared latent heat storage paraffin polyethylene glycol phase change material phoenix leaf biochar stearic acid scanning electron microscope staam activated phoenix leaf biochar	symbols C $D_{average}$ E m R $S_{BET}$ $T_m$ $T_s$ $V_{total}$ $W_i$ $W_t$ Y $\eta$ $\Delta H_m$ $\Delta H$	encapsulation capacity [%] average pore diameter [nm] encapsulation efficiency [%] mass [g] empirical parameter BET specific surface area [m <sup>2</sup> /g] melting temperature [°C] solidification temperature [°C] total pore volume [cm <sup>3</sup> /g] initial mass of biomass sample [g] mass of biochar sample after pyrolysis or activation [g] yield of biochar [%] influence degree [%] melting enthalpy [kJ/kg] solidification enthalpy [kJ/kg]
	r r r r r r r r r r r r r r r r r r r		FJ [-5/*8]

and thermal conductivity results indicated that the composite PCM with 10% EG had little leakage of xylitol and the thermal conductivity improved to 3.91 W/(m·K), 9.54 times of pure xylitol. Wu et al. synthesized a melamine foam/graphene oxide/paraffin wax form-stable PCM with solar-to-thermal energy ability. The composite PCM possessed great encapsulation capacity and excellent energy storage ability. Nonetheless, the porous materials mentioned above still have several fatal problems, such as the hazardous media being applied during the preparation process, complex synthesis operation, and high cost, which are contrary to environmental sustainability [27].

Biochar, a by-product of the pyrolysis from carbon-rich biomass under oxygen-limited conditions, has high micropore volume, high aromaticity, and attractive specific surface area. Due to the above properties, biochar has been widely used to solve the environmental issues, including adsorbing contaminants [28], reducing greenhouse gas emissions [29], composting [30], wastewater treatment [31], soil remediation [32], energy production [33], and catalyst [34] et al. In addition, biochar can be extracted from waste biomass, with simple preparation process, no harmful substances, and sound economy, which makes biochar an ideal PCM support material [35]. Many scholars investigated the performance of PCM encapsulated by biochar. Hekimoğlu et al. [36] developed two kinds of biochar carbonized and chemically activated from walnut shells. The encapsulation capacity of biochar and activated biochar for methyl palmitate were 43% and 45%, respectively, and the thermal conductivity of the composites increased to 1.9 and 1.58 times that of the original PCM after adding biochar. Zhang et al. [37] prepared a carbonization corn cob/lauric-steric form-stable composite PCM with a high encapsulation capacity of 77.9% for PCM, and the thermal conductivity of the composite PCM was 1.93 times of the original PCM. There are many other biochars derived from different biomass precursors to encapsulate PCM, such as potato [38], abandoned rice [39], white radishes [40], cotton [41], pinecone [42], towel gourd [43], weed plants [44], wheat bran [45] and so on. Further, biochar-based composite PCMs whose support was pyrolyzed from miscanthus straw, oilseed rape, and sewage sludge feedstock under 700 °C were prepared by Atinafu et al. [27]. The biochar-based PCMs represented appropriate heat transfer performance, amplified thermal stability, and chemical compatibility. More importantly, it also was found that biochar-based composite

PCMs' thermal properties were affected by the type of biomass, pyrolysis temperature, structural characteristics, surface functionality, and intermolecular interaction between biochar and PCM [46].

Admittedly, there are plenty of studies about biochar encapsulated PCM, but the investigations mainly focus on the thermal properties changes of PCM after adding biochar pyrolyzed from different biomass precursors [38–41]. Besides, some scholars have studied the internal mechanism of biochar encapsulated PCM, such as structural characteristics, surface functionality, and intermolecular interaction. However, the effects of biochar and physically activated biochar (richer structural characteristics and surface functional groups) on the thermal properties of different types of organic PCMs and the dominant mechanisms of biochar encapsulated organic PCMs have not been systematically investigated.

Consequently, this article investigated the effect of biochar with and without physically activated on the thermal properties of different kinds of organic PCMs, and the dominant mechanisms of biochar encapsulated organic PCMs were summarized. The waste phoenix leaf was applied to produce biochar pyrolyzed under 450 °C, 500 °C, 550 °C, and 600 °C. The structural characteristics of biochar pyrolyzed under different temperatures were evaluated, and the biochar with better structural characteristics was activated by carbon dioxide and steam. Three most used organic PCMs, including paraffin (PA), stearic acid (SA), and polyethylene glycol (PEG) were applied as PCMs to obtain the effect of structural characteristics and surface functional groups of biochar on thermal properties of different organic PCMs. In addition, the impact of biochar on the thermal conductivity of PCMs was studied. This article aimed to provide valuable information for the mechanisms and applications of biochar encapsulated organic PCMs, which positively impacted the reuse of waste biomass.

#### 2. Material and experimental

#### 2.1. Materials

Three organic PCMs: paraffin, stearic acid (purity: 98%), and polyethylene glycol (average Mn: 6000) were purchased from Aladdin Chemistry Co. Ltd., Shanghai Macklin Biochemical Technology Co. Ltd., and Sinopharm Chemical Reagent Co. Ltd., respectively. The three PCMs used were analytical-grade reagents and needed no further purification.

## 2.2. Pyrolysis and activation of biochar from phoenix leaf

Waste phoenix leaf composed of cellulose, hemicellulose, and lignin (Fig. 1) and used for biomass pyrolysis were collected at the campus of Zhejiang University. Firstly, to remove the impurities from the collected leaves, the phoenix leaf was cleaned with water carefully and dried in a 105 °C oven (GZX-9030, MBE) for 24 h. Then it was subsequently crushed to pass through a 0.5 mm sieve. Next, the prepared crushed leaf (200 g) was pyrolyzed in a self-made muffle furnace (ZK-12-300, diameter: 300 mm, length: 600 mm) under a nitrogen atmosphere (5 L/min) with a heat rate of 10 °C/min [31,47]. The leaf powder was pyrolyzed at a fixed temperature (450 °C, 500 °C, 550 °C, and 600 °C) for 120 min. Finally, the biochar was taken out and calculated the yield until the temperature in the muffle furnace dropped to room temperature. The biochar obtained at different pyrolyzed temperatures is PL-450, PL-500, PL-550, and PL-600, respectively.

In this article, the activation of biochar was realized by the physical method using CO<sub>2</sub> or superheated steam under high temperature. More specifically, 60 g PL-500 biochar was heated from room temperature to 800 °C in the muffle furnace under a nitrogen atmosphere (5 L/min) with a heat rate of 10 °C/min. Then the nitrogen was quickly switched to CO<sub>2</sub> (5 L/min [48])/steam and treated for 60 min. Superheated steam was produced by heating deionized water (1.5 mL/min [32]) in a preheating furnace at 250 °C. The activated biochar treated by CO<sub>2</sub> and steam were called CPL and SPL, respectively.

#### 2.3. Synthesis of biochar/activated biochar-based composite PCMs

The vacuum impregnation method was applied to synthesize biochar-based composite PCMs, while the fabrication procedure is displayed in Fig. 1. Firstly, approximately 30 g PCM was melted in a 90 °C water bath (HH-51BS/300 °C/ $\pm$ 0.5 °C) until it was transparent. Then, the biochar prepared under different conditions (10 g) was added to liquid PCM and stirred for 10 min to get an evenly

distributed mixture. Secondly, the mixture was placed in a 90 °C vacuum oven (DZF-6020) for 24 h to impregnate PCM into the mesoporous of biochar completely. Finally, the black mixture was poured onto the filter paper and put into an oven at 90 °C, then changed the filter paper regularly to filter out the excess liquid PCM. It was considered that shape-stable composite PCM was obtained until no liquid PCM remained on the filter paper after the mixture was dried for 30 min under 90 °C. The composite obtained by impregnating biochar pyrolyzed at 500 °C with PA, SA, and PEG are PA/PL, SA/PL, and PEG/PL, respectively. The composite encapsulated PA into biochar activated with CO<sub>2</sub> and steam is PA/CPL and PA/SPL.

### 2.4. Characterization methods

The microstructure of biochar, activated biochar, and biocharbased composite PCMs was observed by field emission electron microscopy (FESEM, SU8010, HITACHI, Japan). The Brunauer-Emmett-Teller (BET) specific surface area, pore volume, and average pore diameter of the biochar samples were investigated by a nitrogen (N<sub>2</sub>) sorption isotherm analyzer (ASAP 2460, micromeritics, USA). The textural properties were evaluated under 77 K over the relative pressure range (P/P<sub>0</sub>) of 0.05–0.15. An X-ray diffractometer (X'pert Powder, PANalytical B.V., Netherland) with Cu K-alpha radiation (k = 1.540598 Å) from 10° to 90° was employed to characterize the crystal size of biochar/activated biochar. The scanning rate and step size were 0.1°/min and 0.02°. Fourier transform infrared (Vertex 70, Bruker, Germany) was applied to evaluate the chemical compatibility between PCMs and biochar support with the wavenumber range 500–4000 cm<sup>-1</sup>.

The melting temperature, solidification temperature, heat enthalpies of original PCMs and composite PCMs were measured by the DSC (DSC 25, TA, USA, accuracy:  $\pm 0.01$  °C,  $\pm 0.1\%$ ) with a 50 mL/ min constant stream of nitrogen. All the samples were heated from 25 °C to 120 °C to eliminate the thermal history with a heating rate of 20 °C/min, then cooled from 120 °C to 0 °C and heated from 0 °C to 120 °C at 5 °C/min to get endothermic and exothermic peak. A thermogravimetric analyzer (TGA 5500, TA, USA, accuracy:  $\pm 0.1$  °C,  $\pm 0.01\%$ ) was employed to test the thermal stability of original PCMs



Fig. 1. Fabrication procedure of biochar/activated biochar-based composite PCMs.

and biochar-based composite PCMs samples under a nitrogen atmosphere of 60 mL/min by for the size of samples 6–7 mg with the temperature range and heating rate of 25–600 °C and 10 °C/min.

The samples' thermal conductivity was characterized by a thermal constant analyzer (TCi, C-Therm, Canada, accuracy:  $\pm 1\%$ ) at room temperature of  $18\pm0.5$  °C. Considering the morphological differences between original PCM samples and biochar-based PCMs, the PCM samples were melted at 90 °C and poured into a 50 mm mold for cooling to obtain PCM blocks with a diameter of 50 mm. For biochar-based composite PCM samples, we ground them into powder, then poured into a 50 mm mold and pressed them in 10 MPa tablet press for 1 min. Both surfaces of all blocks were then carefully polished for thermal conductivity test to avoid the experimental error caused by the samples as much as possible. The result that was significantly different from the average value obtained by the test without abnormal results was applied as the thermal conductivity result.

#### 3. Result and discussion

#### 3.1. Structural characteristics of biochar and activated biochar

The specific surface area and pore volume of biochar and activated biochar were evaluated based on BET specific surface area and BJH absorption pore distribution. The specific surface area ( $S_{\text{BET}}$ ), total pore volume ( $V_{\text{total}}$ ), average pore diameter ( $D_{\text{average}}$ ), and yield of biochar pyrolyzed under different temperatures and after physical activation are listed in Table 1 and plotted in Fig. 2. The yield of biochar Y is calculated as follows:

$$Y = \frac{W_t}{W_i} \tag{1}$$

Where  $W_i$  is the initial mass of biomass sample, and  $W_t$  is the mass of biochar sample after pyrolysis or activation.

As we know from Table 1, the  $S_{BET}$ ,  $V_{total}$ , and  $D_{average}$  of biochar samples first increased and then decreased with the rise of pyrolysis temperature, while the yield decreased with the increase of temperature. This may be attributed to the fusion of mesopores [49,50], which was consistent with the results of average pore diameter. Notably, the BET specific surface area of PL-500 biochar increased sharply after physical activation, from 14.182 m<sup>2</sup>/g of PL-500 to 139.40 m<sup>2</sup>/g of CPL-500 and 421.993 m<sup>2</sup>/g of SPL-500, increased by 9.83 and 29.756 times, respectively. Concurrently, the average pore diameter of biochar reduced from 8.707 nm of PL-500 to 6.249 nm of CPL-500 and 4.465 nm of SPL-500, respectively, as shown in Fig. 2 (b, d). The possible reason was that  $CO_2$  or steam reacted with the retained products that were not completely pyrolyzed during the pyrolysis process, which enriched the structural characteristics by opening, expanding, or creating new pores [29]. In addition, the pore diameter of biochar without physical activation was mainly distributed between 1.8 and 4.8 nm, but larger

 Table 1

 BET specific surface area, pore volume, and yield of different biochar samples.

Biochar	$S_{\text{BET}} (m^2/g)$	V <sub>total</sub> (cm <sup>3</sup> /g)	D <sub>average</sub> (nm)	Yield (%) <sup>a</sup>
PL-450	7.427	0.015	10.882	40.10
PL-500	14.182	0.024	8.707	39.45
PL-550	8.608	0.017	14.540	37.85
PL-600	6.285	0.015	18.277	36.80
CPL	139.400	0.189	6.249	27.39
SPL	421.993	0.253	4.465	28.01

<sup>a</sup> Uncertainty: ±0.006%.

mesoporous increased significantly after physical activation, which was also caused by the expanding of CO<sub>2</sub> or steam.

The representative morphologies of the biochar with and without physical activation are revealed in Fig. 3. Ambiguous pore structure with disorderly distribution, different sizes, and irregular shape for biochar without physical activation could be observed, as displayed in Fig. 3 (a–d). After physical activation, a clear and orderly pore structure could be followed, and the porosity increased significantly, as shown in Fig. 3 (e, f). Moreover, the pore wall of biochar activated with steam was thinner and smaller than that of biochar activated with  $CO_2$ , which further increased the BET specific surface area, which was consistent with the results from Table 1. As described, physically activated biochar had higher specific surface area and richer structural characteristics than biochar, whose encapsulation capacity for PCM would be enhanced effectually.

## 3.2. Surface microstructure and chemical compatibility of biocharbased composite PCMs

The surface microstructure of biochar-based shape-stable composite PCMs could reflect the encapsulation of PCM into support biochar. The SEM morphologies of the composite PCMs with three kinds of PCMs encapsulated in different biochar are shown in Fig. 4. Due to the impregnation of PCM, the mesopores of biochar were almost filled, and only a small amount of mesopores could be observed, which indicated that the structure and surface characteristics of biochar could effectively encapsulate the three kinds of PCMs. Therefore, it could be concluded that biochar-based shape-stable composite PCMs have been successfully synthesized.

The FT-IR spectra of biochar samples, original PCMs, and PA, SA, PEG/PL, CPL, SPL biochar-based composite PCMs are shown in Fig. 5. As can be seen from Fig. 5 (a), biochar had a broad and intense absorption peak with wave number of 3427-3435 cm<sup>-1</sup>, corresponding to the stretching vibration of -OH, which was mainly caused by the stretching vibration of -OH associated with hydrogen bonds [51]. The strong absorption peak centered at 2917-2919  $\text{cm}^{-1}$  was due to the asymmetry of fatty  $-\text{CH}_2$  and the stretching vibration of symmetrical C-H, which mainly came from carbon hydrates, aliphatic compounds, and alicyclic compounds in organic compounds [52]. A moderate intensity absorption peak appeared at 1562-1633 cm<sup>-1</sup>, indicating a particular form of shear vibration in the aromatic ring skeleton or C=0 bending vibration, concerned with the complete vibration formed by the material adsorbing water [53]. The absorption peaks located at 868- $870 \text{ cm}^{-1}$  and  $1401-1408 \text{ cm}^{-1}$  were attributed to the C-H out of plane bending vibration and C-H in-plane bending vibration of olefins, respectively [51]. Although the pyrolyzed biochar under different temperatures and activated biochar had the above functional groups vibration, the vibration intensity of different samples was quite different. For instance, the vibration intensity of biochar before and after activation was very different at 1562-1633 cm<sup>-1</sup> and 1401-1408 cm<sup>-1</sup>, which may affect the thermal properties of biochar-based composite after PCM encapsulation.

As displayed in Fig. 5 (b–d), the absorption peaks between 2750 and 3000 cm<sup>-1</sup> were due to the symmetrical stretching vibration of  $-CH_3$  and  $-CH_2$  groups from PCMs [54]. In the spectrum of PA, the peaks centered at 1468 cm<sup>-1</sup> and 725 cm<sup>-1</sup> were due to the rocking vibration of  $-CH_2$  and the deformation vibration of  $-CH_2$  and  $-CH_3$  groups, respectively [55,56]. Concerning SA, the absorption peaks located at 1462 cm<sup>-1</sup> and 1298 cm<sup>-1</sup> corresponded to the in-plane bending vibration of -OH [57], and the absorption peaks centered at 1701 cm<sup>-1</sup>, 943 cm<sup>-1</sup>, and 721 cm<sup>-1</sup> were caused by the stretching vibration of  $-CH_2$  and the bending and swinging vibration of -OH, respectively [58,59]. In the



Fig. 2. Structural characteristics of biochar samples: (a) N<sub>2</sub> sorption-desorption isotherms, (b) BJH pore distribution of biochar treated with different temperatures, (c) N<sub>2</sub> sorption-desorption isotherms, (d) BJH pore distribution of biochar treated with and without physical activation.



Fig. 3. SEM morphologies of (a) PL-450, (b) PL-500, (c) PL-550, (d) PL-600, (e) CPL and (f) SPL.

spectrum of PEG, the characteristic absorption peaks located at  $3429 \text{ cm}^{-1}$  and  $1466 \text{ cm}^{-1}$  were due to the tensile vibration of O-H, and the absorption peaks at  $2883 \text{ cm}^{-1}$  and  $1466 \text{ cm}^{-1}$  corresponded to the tensile vibration and bending vibration of C-H

groups [60]. As described, compared with the original FT-IR spectra of PCMs, there were no occurrences of additional characteristic peaks in biochar-based PCMs' spectra, indicating excellent chemical compatibility.



Fig. 4. SEM morphologies of (a) PA/PL, (b) PA/CPL, (c) PA/SPL; (d) SA/PL, (e) SA/CPL, (f) SA/SPL; (g) PEG/PL, (h) PEG/CPL and (i) PEG/SPL biochar-based composite PCMs.

# 3.3. Thermal properties of biochar-based composite PCMs and dominant mechanisms of biochar encapsulated organic PCMs

The thermal properties such as melting temperature  $(T_m)$ , solidification temperature ( $T_s$ ), melting enthalpies ( $\Delta H_m$ ), and solidification enthalpies  $(\Delta H_s)$  of original PCMs and shape-stable composite PCMs were evaluated by DSC analyses. Fig. 6 reveals the DSC curves of PA, SA, PEG, and biochar-based composite PCMs, and the corresponding data are summed up in Table 2. There was no appreciable change in the DSC peaks of the three organic PCMs after adding different kinds of biochar, as shown in Fig. 6 (a-c), further indicating that no chemical reaction between biochar and PCM. Among them, the DSC curves of PA composite PCMs demonstrated two phase transition peaks during endothermic and exothermic processes. It was reported that N-alkane showed a rotator phase during the phase transition process, which led to the homogeneously nucleated liquid to the rotator phase for the first peak and the heterogeneously nucleated rotator phase to the crystalline phase for the second one [61,62].

Fig. 6 (d) plots the melting and solidification enthalpies of original PCMs and biochar-based composite PCMs. The melting and solidification enthalpies of pure PA, SA, and PEG were 225.24 kJ/kg and 227.13 kJ/kg, 231.87 kJ/kg and 231.98 kJ/kg, 188.79 kJ/kg and 182.85 kJ/kg, respectively. The heat enthalpies of PCMs decreased significantly after adding biochar, but the difference between melting and solidification enthalpies remained consistent, such as the melting and solidification enthalpies of PA/PL, PA/CPL, and PA/

SPL was 111.02 kJ/kg and 114.06 kJ/kg, 111.16 kJ/kg and 113.88 kJ/kg 110.69 kJ/kg and 113.08 kJ/kg, respectively.

To illustrate the effect of structural characteristics and surface functional groups of biochar on the thermal properties of three kinds of PCMs, the melting temperature, solidification temperature, melting enthalpies, and solidification enthalpies were investigated in detail. Fig. 7 (a) displays the melting temperature and solidification temperature of original PCMs and corresponding shapestable composite PCMs. In the case of PA, the addition of biochar hardly affected its phase transition temperature. From the perspective of SA, whose melting and solidification temperature decreased slightly after adding biochar, the sample with biochar activated by steam was more prominent. For PEG, the addition of biochar without activation increased the melting and solidification temperature, while the activated biochar decreased the melting temperature but increased the solidification temperature, indicating the abatement of supercooling.

Given the above, biochar had different effects on the phase transition temperature of three PCMs, which may be related to the various interaction between biochar surface functional groups and different PCM molecules [27]. However, it should be noted that, unlike other carbon support materials, biochar had an inconspicuous effect on the phase transition temperature of various PCM, which was attributed to the fact that biochar did not promote heterogeneous nucleation of PCM [63].

To clarify the effect of structural characteristics and surface functional groups of biochar on the melting and solidification



Fig. 5. FT-IR spectra of (a) biochar prepared under different conditions, (b) PA and PA/PL, CPL, SPL, (c) SA and SA/PL, CPL, SPL, (d) PEG, PEG/PL, CPL, SPL shape-stable composite PCMs.

enthalpies of different PCMs, we introduced encapsulation capacity C [43] and encapsulation efficiency E [64], which could be calculated by the following equations:

$$C = \frac{m_{composite} - m_{biochar}}{m_{composite}}$$
(2)

$$E = \frac{\Delta H_{m,composite} + \Delta H_{s,composite}}{\Delta H_{m,PCM} + \Delta H_{s,PCM}}$$
(3)

Where  $m_{\text{composite}}$  was the mass of shape-stable composite,  $m_{\text{biochar}}$  was the mass of biochar in the shape-stable composite.  $\Delta H_{\text{m,composite}}$ ,  $\Delta H_{\text{s,composite}}$ ,  $\Delta H_{\text{m,PCM}}$  and  $\Delta H_{\text{s,PCM}}$  were the melting and solidification enthalpies of shape-stable composite and original PCM, respectively.

Fig. 7 (b) shows the encapsulation capacity and encapsulation efficiency for PA, SA, and PEG of biochar with and without activation. The encapsulation capacity of activated biochar (especially activated by steam) was greater than that of biochar for three kinds of PCMs (Table 2), which may result from the large specific surface area and rich structural characteristics of activated biochar (Section 3.1). However, PEG represented worse encapsulation capacity in biochar activated by steam than biochar activated by CO<sub>2</sub>, which may be related to the larger molecular weight of PEG and the narrower pore of biochar activated by steam. It was reported that molecular weight could affect the adsorption mechanism [65] and the steric hindrance occurred when the pores were too narrow [66]. More interestingly, the encapsulation capacity of biochar for PEG was the largest, followed by SA and PA, which may be caused by the structural characteristics of biochar, hydrogen bond, surface

functional groups interaction, or hydrophobic interaction between biochar and PCMs [46,67].

Table 3 summarizes the thermal properties of reported biocharbased composite PCMs. Waste phoenix leaf biochar-based composite had high encapsulation capacity and attractive heat enthalpies for three kinds of PCMs than other biochar-based composites PCMs, making waste phoenix leaf biochar-based composite PCMs have broad application prospects.

The encapsulation efficiency of different biochar was all lower than the encapsulation capacity (Fig. 7 (b) and Table 2), indicating that biochar evidently affected the heat enthalpies of original PCMs. The behaviors of PA and SA were similar, but the encapsulation efficiency of PEG encapsulated in biochar activated by CO<sub>2</sub> and steam decreased seriously. Similar phenomena had also been reported in Refs. [72,73]. Several reasons may account for the phenomenon: (1) The intense hydrogen bond interaction between the surface of biochar and PCMs restricted the freedom of motion required for phase change [24,74]. (2) The hydrophilic interaction between biochar and PCMs may restrain the crystallinity of PCMs [72,73]. (3) Other potential mechanisms, such as the interaction of other functional groups,  $\pi$ - $\pi$  EDA interaction, electrostatic attraction, and so on [67].

The influence degree  $\eta$  was introduced to illustrate the effect of structural characteristics and surface functional groups of biochar on heat enthalpies of PCMs. The influence degree  $\eta$  could be calculated as follow:

$$\eta = \left(1 - \frac{E}{C}\right) \times 100\% \tag{4}$$

As we can see from Fig. 7 (c), the influence degree of physically



Fig. 6. DSC curves ((a) PA, (b) SA, and (c) PEG) and (d) melting enthalpies and solidification enthalpies of original PCMs and biochar-based composite PCMs.

Table 2

Thermal properties of original PCMs and biochar-based composite PCMs, and encapsulation capacity (C), encapsulation efficiency (E), and influence degree ( $\eta$ ) of biochar on PCMs.

Sample	$T_{\rm m}$ (°C)	$\Delta H_{\rm m}  (\rm kJ/kg)$	$T_{s}$ (°C)	$\Delta H_{\rm s}  ({\rm kJ/kg})$	C (%)	E (%)	η (%)
РА	57.73	225.24	55.19	227.13	-	-	-
PA/PL	58.24	111.02	55.28	114.06	$54.11 \pm 0.06$	$49.76 \pm 0.08$	$8.04 \pm 0.17$
PA/CPL	58.01	111.16	55.28	113.88	$57.93 \pm 0.06$	$49.75 \pm 0.08$	$14.13 \pm 0.15$
PA/SPL	58.31	110.69	54.96	113.08	$59.28 \pm 0.05$	$49.47 \pm 0.07$	$16.56 \pm 0.14$
SA	70.87	231.87	67.17	231.98	-	-	-
SA/PL	70.60	129.06	68.64	129.19	$60.25 \pm 0.05$	$55.68 \pm 0.08$	$7.60 \pm 0.16$
SA/CPL	70.39	126.15	65.89	125.88	$61.99 \pm 0.05$	$54.33 \pm 0.08$	$12.35 \pm 0.15$
SA/SPL	70.16	133.61	65.40	133.28	$63.03 \pm 0.05$	$57.54 \pm 0.08$	8.72 ± 0.16
PEG	61.67	188.79	41.36	182.85	-	-	-
PEG/PL	62.04	122.06	42.24	120.25	$69.41 \pm 0.04$	$65.20 \pm 0.10$	$6.06 \pm 0.16$
PEG/CPL	59.68	109.26	42.02	104.62	$73.38 \pm 0.04$	57.55 ± 0.09	$21.58 \pm 0.13$
PEG/SPL	60.03	88.43	43.67	82.01	$71.38 \pm 0.04$	$45.86 \pm 0.07$	$35.75\pm0.10$

activated biochar on PCMs was more notable than that of biochar, which was attributed to the more functional groups on high specific surface area and increase of oxygen-containing functional groups after activation [31,75]. Among the three PCMs, activated biochar had the most significant effect on the enthalpy of PEG, increasing from 6.06% of PL to 35.75% of SPL, followed by PA and SA. Significantly, the biochar activated by steam had the highest specific surface area (Table 1), but the impact on SA is lower than that of biochar activated by CO<sub>2</sub>, which may be attributed to the change of surface functional groups (Fig. 5 (a)) and intermolecular interaction between biochar and SA. Fig. 7 (d) gives the influent degree of reported other carbon support materials (EG, CNT and graphene) and biochar on PCMs. Compared with other carbon support materials,

biochar had relatively poor encapsulation capacity and a higher influence degree on the encapsulated organic PCMs.

To summarize, the structural characteristics, surface functional groups interaction (mainly hydrogen-bonding and hydrophobic interaction), and other potential mechanisms significantly impacted the encapsulation capacity and encapsulation efficiency of biochar encapsulated PCMs, as depicted in Fig. 8. As described, the larger specific surface area and rich structural characteristics would increase the encapsulation capacity of organic PCMs. Simultaneously, the turn of structural characteristics and the increase of surface functional groups may reduce the encapsulation efficiency of PCMs (especially for polymer polar substances, such as PEG), which requires a trade-off in practical applications.



Fig. 7. (a) phase transition temperature of original PCMs and biochar-based composite, (b) encapsulation capacity and encapsulation efficiency of different biochar for PCMs, (c) influence degree of different biochar on PCMs, and (d) influence degree of biochar that in other reported work and this work on different PCMs.

Table 3
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Thermal properties of reported biochar-based composite PCMs.

Biochar	PCM	Melting temperature (°C)	Encapsulation capacity (%)	Fusion enthalpy (kJ/ kg)	Enhancement of thermal conductivity	References
Softwood	n-eicosane	37.0	26.4	52	-	[46]
Oil palm kernel shell	Paraffin	29.2	31.04	57.3	-	[68]
Wheat straw	n-eicosane	37.0	37.1	75	-	[46]
Oilseed rape	1-dodecanol	21.9	38.4	73.7	-	[27]
	n-dodecane	-4.1	60.2	90.5	-	[27]
Wheat bran	Stearic acid	68.2	40	84.91	1.87	[45]
Cabbage mustard	Tetra decanoic acid	50.6	57.07	103.55	2.18	[69]
Pinecone	Palmitic acid	59.25	60	84.74	1.44	[42]
Corn cob	Lauric-stearic acid	35.1	77.9	148.3	1.88	[37]
Abandoned rice	Palmitic-lauric acid	34.3	78.8	135.4	1.83	[39]
Towel gourd	PEG 2000	59.6	94.5	164.3	-	[43]
Potatoes	PEG 4000	56.67	50	91.80	-	[38]
Almond shell	PEG 4000	62.76	60	82.73	1.60	[70]
Potatoes	PEG 4000	56.5	85.36	158.8	10.51	[40]
White radishes	PEG 4000	56.5	89.77	159.7	4.09	[40]
Wood	1-tetradecanol	36.92	73.4	165.8	2.14	[71]
Walnut shell	Methyl palmitate	26.27	43	108.32	1.89	[36]
Activated walnut shell	Methyl palmitate	26.65	55	138.32	1.58	[36]

3.4. Thermal conductivity of biochar and biochar-based composite PCMs

The transient plane heat source method was employed to survey the thermal conductivity of original PCMs and shape-stable composite PCMs. The thermal conductivity of PA/PL, SA/PL and PEG/PL decreased from 0.302 W/(m·K), 0.385 W/(m·K), and 0.406 W/ (m·K) for original PA, SA and PEG to 0.3 W/(m·K), 0.331 W/(m·K), and 0.333 W/(m·K), respectively, as revealed in Fig. 9 (a). However, the thermal conductivity of PA/CPL, SA/CPL, and PEG/CPL increased to 0.456 W/(m·K), 0.405 W/(m·K), and 0.507 W/(m·K), respectively. It was attributed that the thermal conductivity of biochar



Fig. 8. Summary of dominant mechanisms of biochar encapsulation organic PCMs.



Fig. 9. Thermal conductivity of (a) Original PCMs and biochar-based composite PCMs and (b) biochar powder and PA biochar-based composite PCMs, and (c) XRD patterns of biochar samples and (d) schematic diagram of thermal conductivity test.

was inseparable from the types of biochar precursors and pyrolysis conditions [8,76]. The effect of biochar addition on the thermal

conductivity of PCMs reported in the published literature can be found in Table 3.



Fig. 10. TG ((a) PA, (c) SA and (e) PEG) and DTG ((b) PA, (d) SA and (f) PEG) curves of pure PCMs and shape-stable composite PCMs.

Therefore, the thermal conductivity of biochar powder prepared under different conditions and PA biochar-based composite PCMs was measured (Fig. 9 (d)), and the results are shown in Fig. 9 (b). The thermal conductivity of biochar would improve with the rise of pyrolysis temperature, increasing from 0.056 W/(m·K) for PL-450 to 0.06 W/(m·K) for PL-600. The phenomenon could be explained by the XRD patterns of biochar, as displayed in Fig. 9 (c). Dahn et al. [77] employed an empirical parameter R (ratio of the height of Bragg peak to the background) to get the number of carbon sheets arranged as single layers. The greater the R value, the higher degree of the graphitization, which suggested a larger concentration of the parallel single [78]. The R value of biochar increased with the increase of pyrolysis temperature, which accounted for the positive proportional relationship between pyrolysis temperature and the thermal conductivity of biochar. Moreover, the graphitization degree of biochar should increase with the rise of pyrolysis temperature [78], but the activated carbon obtained at higher activation temperature had lower graphitization degree and higher thermal conductivity, which may be due to the edge effect caused by the chemical reaction between activated gas and biochar, resulting in the decrease of the graphitization degree of edge. It was worth noting that the thermal conductivity of biochar was obtained from biochar powder, so it was different from the composite PCM measured in bulk.

Adding biochar with different pyrolysis temperatures to PCM could obtain shape-stable composite PCM with adjustable thermal conductivity, which would have a broader range of practical applications of PCM, for example, building thermal insulation materials [8] or thermal energy storage materials [79].

## 3.5. Thermal stability performance of biochar-based composite PCMs

The TG and DTG curves of original PCMs and shape-stable composite PCMs are shown in Fig. 10. It could be observed that original PA. SA. and PEG decomposed from approximately 178 °C. 176 °C, and 194 °C, and the maximum degradation temperature of that was 265 °C, 255 °C, and 370 °C, respectively. After adding biochar, the TG curves of PA and PEG composite PCMs shifted backward evidently, and the maximum degradation temperature of PA/SPL and PEG/SPL increased to 282 °C and 375 °C, respectively. This phenomenon was consistent with the influence degree of biochar on PCMs mentioned in Section 3.3. The higher the influence degree, the stronger the hydrogen-bonding, hydrophilic, or other intermolecular interaction between PCM and biochar, which would increase the stability of composite PCM. The thermal stability of SA/ PL, SA/CPL, and SA/SPL was similar to original SA, which may be caused by the weak molecular interaction between SA and biochar. In a word, the addition of biochar could improve the stability of organic PCMs, which was conducive to the practical application of organic PCMs.

The leakage of shape-stable PCMs was a crucial parameter affecting its practical application. To assess the leakage performance of biochar-based composite PCMs, we placed them in a 90 °C oven for more than 30 min and then recorded the leakage of shape-stable PCMs. As shown in Fig. 11, PCMs were well encapsulated into biochar and no leakage was observed, which benefited from the structural characteristics of biochar and the strong intermolecular interaction and hydrogen-bonding between biochar and PCMs.

In addition, the 100 thermal cyclic test was implemented to evaluate the thermal stability and reliability of biochar-based composite PCMs. Fig. 12 plots the DSC curves of PA/PL, PA/CPL, and PA/SPL biochar-based composite PCMs before and after the 100 thermal cvclic test. The experimental results showed that the melting/solidification temperature decreased from 58.24/55.28 °C. 58.01/ 55.28 °C, and 58.31/54.96 °C of PA/PL, PA/CPL, and PA/SPL to 57.01/ 53.65 °C. 56.95/53.41 °C. and 56.80/53.71 °C after the thermal cyclic test. On the other hand, the melting/solidification enthalpies of PA/ PL, PA/CPL, and PA/SPL decreased by 4.90%/5.57%, 5.03%/6.13%, and 0.83%/1.12%, respectively. The enthalpies change of PA/PL and PA/CPL before and after the thermal cyclic test were more evident than PA/ SPL, which may be caused by different intermolecular interaction between biochar and PA. All in all, the slight change of phase transition temperature and enthalpies of biochar-based PCMs further indicated the stability of biochar-based PCM in practical application.

## 3.6. Potential applications of biochar-based shape-stable composite PCMs

The waste phoenix leaf biochar-based composite PCMs possessed better thermal stability, variable thermal conductivity, and satisfactory heat enthalpies. PCMs, especially biochar-based shape-stable composite PCMs with high fusion enthalpies and low thermal conductivity, can effectively prevent heat loss and maintain the indoor temperature, to achieve the purpose of building energy conservation [80].

Among the battery thermal management system, the temperature-sensitive Li-ion battery requires a strict thermal



Fig. 11. The leakage performance photos of (a) PA, (b) SA, and (c) PEG biochar-based composite PCMs.



Fig. 12. The DSC curves of (a) PA/PL, (b) PA/CPL, and (c) PA/SPL biochar-based composite PCMs before and after the 100 thermal cyclic test.

environment between 20 and 55 °C, which could be fulfilled with appropriate phase transition temperature, high fusion enthalpies and high thermal conductivity biochar-based composite PCMs [81] to improve the safety and service life of the battery. Besides, biochar-based shape-stable composite PCMs could be applied in solar energy utilization, thermal energy storage and so on [82].

## 4. Conclusion

In summary, the biochar and activated biochar was prepared by the pyrolysis of waste phoenix leaf and physically activation by CO<sub>2</sub> and steam. Biochar-based shape-stable composite PCMs with SA, PA, and PEG were synthesized by the vacuum impregnation method. Based on the physical characterizations, the structural characteristics and surface microstructure of biochar and thermal properties, chemical compatibility, and thermal stability and reliability of biochar-based composite PCMs were investigated. The effect of structural characteristics and surface functional groups of biochar on the thermal properties of different organic PCMs and the dominant mechanisms of biochar encapsulated organic PCMs were summarized. The primary findings of the article are as follows:

- (1) The BET specific surface area, total pore volume, and average pore diameter of waste phoenix biochar first increased and then decreased with the rise of pyrolysis temperature. Physically activated biochar (especially activated by steam) had higher specific surface area and richer structural characteristics than biochar, whose encapsulation capacity for PCM would be enhanced effectually.
- (2) The surface microstructure and Fourier transform infrared spectra of composite PCMs showed that biochar-based shape-stable composite PCMs had been successfully synthesized and represented excellent chemical compatibility.
- (3) Larger specific surface area, richer structural characteristics, and surface functional groups of biochar (such as steam activated biochar) may enhance the intermolecular interaction and hydrogen-bonding between biochar and organic PCMs (high influence degree of biochar on organic PCMs), which would improve the encapsulation capacity of organic PCMs (especially for PEG) effectively but decrease the encapsulation efficiency.
- (4) The biochar pyrolyzed under lower temperature had an adverse effect on the thermal conductivity of PCMs. XRD results revealed that higher pyrolysis temperature led to higher graphitization degree of biochar, which would increase the thermal conductivity of biochar. Hence, the thermal conductivity of shape-stable composite PCMs was positively correlated with the pyrolysis temperature of biochar in a particular range, and the physically activated biochar had positive effect on the thermal conductivity of PCMs as well.
- (5) Biochar-based composite PCM had better thermal stability, concerned with the strength of intermolecular interaction, hydrogen-bonding, and hydrophobic interaction between biochar and organic PCMs. The 100 cyclic thermal test showed that biochar-based composite PCMs had good reliability.

Biochar-based PCMs have incomparable advantages over other porous support materials. The application of biochar-based PCMs in energy storage and management will be explored in our future work.

#### **CRediT authorship contribution statement**

**Laiquan Lv:** Formal analysis, Investigation, Data curation, Writing – original draft, Project administration. **Jiankang Wang:** Data curation, Writing – original draft. **Mengting Ji:** Resources, Data curation. **Yize Zhang:** Visualization, Investigation. **Kefa Cen:** Writing – review & editing. **Hao Zhou:** Conceptualization, Methodology, Validation.

#### **Declaration of competing interest**

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.

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