



Form stable composite phase change materials from palmitic-lauric acid eutectic mixture and carbonized abandoned rice: Preparation, characterization, and thermal conductivity enhancement



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ABSTRACT

In this study, novel form stable composite phase change materials (FS-CPCMs) from palmitic-lauric acid (PA-LA) eutectic mixture and carbonized abandoned rice (CAR) were prepared via vacuum impregnation. The CAR served as a good supporting material to prevent PA-LA from leaking and enhanced the thermal conductivity of PA-LA. SEM results showed that the CAR has a highly porous structure consisting of rough micro-pores and PA-LA did not leak from the CAR during the solid-liquid phase transition. DSC indicated that the latent heat and temperature of PA-LA/CAR FS-CPCMs during melt were 135.4 J/g and 34.3 °C, respectively, whereas, these values were 124.8 J/g and 28.6 °C during freezing, respectively. The thermal conductivity of PA-LA/CAR FS-CPCMs was 1.83 times that of PA-LA. The heat storage/release rate of the PA-LA/CAR FS-CPCMs is significantly more than that of PA-LA for practical applications. The results obtained from FTIR demonstrated that no new chemical bonds were formed between PA-LA and CAR. TGA and 200-cycle experiments showed that the PA-LA/CAR FS-CPCMs exhibit excellent thermal stability and form-stable performance. The PA-LA/CAR FS-CPCMs thus prepared were safe, environmentally friendly, and cost-effective; hence, they can be used as potential building materials for the applications of thermal energy storage.

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1. Introduction

Solar energy can cope with the energy crisis because it is environment friendly, cost-free, abundant, sustainable, and renewable [1–4]. The solar energy concept has been applied to solar heating/cooling systems [5], solar chimney [6], and solar cooking settings [7]. Thermal energy storage (TES) is a promising method for energy savings and energy conservation enhancement, including heat storage, latent heat storage, and reversible chemical reaction heat storage [1,8]. Latent heat storage using phase change materials (PCMs) is the most efficient way of utilizing TES, because PCMs have extensively advantages such as high energy storage density, isothermal behavior, excellent time and space constraints, and

small temperature differences between heat and release storage [8–11].

In the past few years, PCMs have gained research attention and have been used in the fields of smart textiles, building energy conservation, air-conditioning systems, heat pumps, waste heat recovery, and thermal insulation [12–15]. According to composition, PCMs are usually categorized into organic and inorganic PCMs. Organic PCMs have been widely used owing to competitive pricing, high latent heat density, wide melting temperatures for suitable phase transition temperatures, and stable physical and chemical properties for long-term usage [1,10,11]. Fatty acids obtained from common vegetables oils are a kind of typical organic PCMs, which have excellent performance such as high latent heat capacity, non-toxic, non-corrosive, good chemical and thermal stability, little or no supercooling during phase transitions [16–19]. Although fatty acids exhibit a host of superior properties, fatty acids with high melting points cannot be directly used in buildings in some cases [19]. According to the ideal solution model, the phase change temperatures of fatty acids are regulated by adjusting the composition

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and mass ratio of fatty acid in their eutectic mixture [18–21]. Wei et al. [18] studied the heat transfer characteristics of capric-myristic-stearic acid eutectic mixture. Li et al. [20] prepared binary fatty acid and the binary fatty acids/diatomite composite phase change materials. Wang et al. [22] did experimental studies on the fatty acid eutectic/polymethyl methacrylate composite PCMs for thermal energy storage. Although some studies on the preparation and the properties of fatty acid eutectic mixture have been carried out, the study on the fatty acid eutectic is not systematic or even complete. There are still several challenges for the applications of fatty acid PCMs. For example, it is difficult to handle the materials during the phase change from solid to liquid. Moreover, low thermal conductivity leads to hysteresis of thermal responses. Such drawbacks may degrade the performance for energy storage and thermal regulation during the melting and freezing cycles and restrict their final applications.

In recent years, form stabilization, has been used as a new packaging technology and developed to overcome the above problems [10,23,24]. FS-CPCMs have been prepared by using expanded vermiculite [25,26], expanded perlite [11,27,28], diatomite [23,29], halloysite nanotube [30,31], and kaolin [32], which can maintain a solid shape even when the temperature is above the melting point of the PCMs [11,23]. It has been proven that this method is the most effective approach to resolve leaking. However, the low thermal conductivities of expanded vermiculite, expanded perlite, diatomite, halloysite nanotube, and kaolin decrease the thermal exchange rates during the melting and freezing cycles. To overcome the low thermal conductivities, carbon-based nanostructures (nano-fibers, nano platelets, and graphene flakes), metals (Ag, Fe, Au, and Cu), metal oxides (Al_2O_3 , CuO, MgO, and TiO_2), and metallic nanowires (Ag, Au, and Cu) have been investigated as the filler to enhance the thermal conductivity [4,33–38]. Moreover, many studies on the preparation and characterization of the FS-CPCMs have used porous carbon materials [39], such as porous carbon [40], graphite [41], expanded graphite [42–44], carbon nanospheres [45], and carbon nanotubes [46,47]. The porous carbonaceous materials possess some attractive features, such as chemical and thermal stability, high surface areas, porous structures, and excellent thermal conductivities.

In this study, abandoned rice (AR) was used to prepare the CAR, and the PA-LA eutectic mixture was prepared through melt-blending followed by ultra-sonication. Finally, the PA-LA/CAR FS-CPCMs was obtained from the pure PA-LA and CAR via a method of vacuum impregnation. The AR is not edible, and the re-use of it is in line with the spirit of economic recycling. The AR with a form shape structure could act as raw materials to prepare the CAR. The CAR with a highly porous structure consisting of rough micro-pores not only can act as a good supporting material to prevent PA-LA from leaking, but also enhance the thermal conductivity of PA-LA. Compared to the expanded vermiculite, expanded perlite, diatomite, halloysite nanotube, and kaolin, the use of CAR to prepare the FS-PCMs with high thermal conductivity is easy. Moreover, CAR is inexpensive than graphite, expanded graphite, carbon nanospheres, and carbon nanotubes. The PA-LA/CAR FS-CPCMs are potential candidates for applications in the fields of energy efficient buildings.

2. Experimental

2.1. Characterization

Scanning electron microscopy (SEM, JSM-5610LV, and JEOL) was utilized to observe the morphology of CR and the PA-LA/CAR FS-CPCMs. X-ray diffraction (XRD, Model XD-3) and a Renishaw in Via Raman microscope equipped with 532 nm laser diode

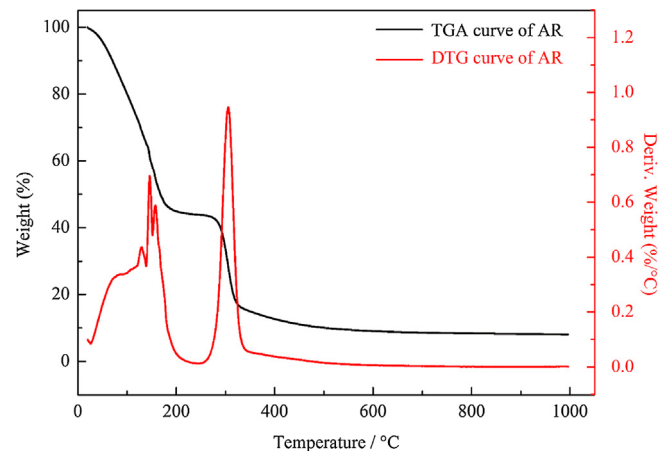


Fig. 1. The TGA and DTG curves of AR.

were employed to analyze the CAR. Fourier transform infrared spectroscopy (FTIR, SHIMADZU FTIR 8400) was conducted in the wavenumber range of $400\text{--}4500\text{ cm}^{-1}$ to investigate the chemical compatibilities in the PA-LA/CAR FS-CPCMs. The thermal properties of the PA-LA and the PA-LA/CAR FS-CPCMs were determined by differential scanning calorimetry (DSC, TA Instruments, Q2000) with an indium standard and using a heat/cool/heat program of $0/100/0^\circ\text{C}$ at $5^\circ\text{C}/\text{min}$ heating/cooling rate. The thermogravimetric analysis (TGA, TA Instruments, Q50) and derivative thermogravimetric (DTG) measurements were conducted to investigate the thermal stability and decomposition properties of the specimens. The nitrogen flow rate was adjusted to $50\text{ mL}/\text{min}$, and TGA data was recorded in the temperature range from room temperature to 600°C at a heating/cooling rate of $10^\circ\text{C}/\text{min}$. The thermal conductivity of sample was measured using a laser flash apparatus (XFA500).

A 200-cycle experiment was carried out to determine the stability of the thermal properties and the stability of the chemical structure of the PA-LA/CAR FS-CPCMs. The PA-LA/CAR FS-CPCMs were placed on a plate and covered with filter paper. They were then placed in a thermostatic chamber equipped with a temperature controller. The PA-LA/CAR FS-CPCMs were first heated to 50°C and then cooled to 20°C and cycled 200 times. The filter paper was substituted every 10 cycles [35].

2.2. Materials

The abandoned rice (denoted as AR) used in the experiment was obtained from leftover rice in the cafeteria. Palmitic acid (denoted as PA, CP) and lauric acid (denoted as LA, CP) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.3. Modification of abandoned rice by carbonizing

Fig. 1 shows the percentage loss in weight as a function of temperature. Three distinct zones are observed. The $20^\circ\text{C}\text{--}200^\circ\text{C}$ zone represents the evaporation of water and other easily volatile materials. The $250\text{--}350^\circ\text{C}$ range represents degradation. The $350\text{--}600^\circ\text{C}$ zone represents the continuous degradation.

The AR was washed with deionized water several times for removing impurities on the surface of leftover rice. The products were then dried in an oven at 100°C for evaporating excess distilled water absorbed on the surface of the AR. The CAR was obtained by carbonizing AR in at high temperatures under nitrogen atmosphere. Fig. 2 shows the schematic preparation of the CAR. According to the TGA and DTG curves of the AR, the prepared system of the CAR was heated in a temperature programmed manner from 20°C to 200°C

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