Phase-Change Materials and Biochar: Some New Composite Materials in Recent Literature

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Abstract

A phase change material (PCM) is a substance absorbing and releasing energy at phase transition. The substance is therefore useful for heating and cooling applications. Here we review the recent literature about the use of biochar and PCMs for composite materials, to obtain phase change composites (PCCs).

Keywords: PCM, PCC, Biochar, Composite Materials, Biomass-Based Porous Carbon, Phase Change Composites, Thermal Management, Latent Heat Storage Biocomposite, LHSBC.

Subject Areas: Materials Science.

1. Introduction

A phase change material, PCM, is a substance absorbing and releasing energy at phase transition. The substance is therefore useful for heating and cooling applications. Generally the transition is between solid and liquid phases. However, phase transition may also be considered between crystalline phase structures, which have different energy states. An example of PCM based on fusion is the ice (heat of fusion, 333.55 J/g). Water/ice is therefore a well-known phase change material, which can be used to store winter cold to cool buildings in summer [1].

By melting and solidifying at the given phase change temperature, a phase change material is able to store or release energy. In the case of water, heat is absorbed or released when the material changes from solid to liquid and vice versa. Therefore, PCM are latent heat storage (LHS) materials.

In the past, water was considered the main, or let us tell, the only available PCM. In the last few decades, several substances, such as hydrocarbons and paraffin, have been adapted to have further applications to a wide temperature range. For instance, PCMs are used for Ultra Low Tem-
perature (ULT) freezers, so that the World Health Organization, WHO, is mentioning them in its logistic guidance for vaccination [2]. In fact, PCMs are mainly used in ULT logistics, where thermal energy storage is fundamental. This logistics takes advantage of the fast progress in materials science, which is providing new substances for PCMs, and also of the technologies which are receiving support from these materials.

Actually, several researched are aimed at enhancing PCM's performance. The main drive of these researches is mainly the huge potential market for building heating and cooling [3]. For buildings, other materials are under investigation, such as biochar, for CO$_2$ absorption [4]. Here, let us consider literature about the use of biochar in PCMs. Let us remember that biochar is charcoal produced by pyrolysis of biomass in the absence of oxygen, which has its main application in soil management [5].

To see the microscopic structure of biochar, see please [6] (an example in given in the Figure 1). It is the biochar structure which is interesting for the encapsulation of phase-change substances.

![FESEM Image 3D Mesh](image)

**Figure 1.** From a FESEM image of a biochar sample, a 3D mesh can be obtained [6].

### 2. Literature

Objective of the research proposed in [7] was the characterization of a latent heat storage bio-composite (LHSBC), based on biochar, which can be used as a novel material useful for latent heat storage insulation. "In particular, this paper [7] analyzed the chemical stability, latent heat storage performance, thermal conductivity, and thermal stability of LHSBCs". "As a result, the LHSBCs showed a maximum latent heat storage capacity of 74.6 J/g and a low thermal conductivity of 0.030 W/mK at the maximum, confirming that LHSBCs have a high latent heat storage..."
As observed in [8], PCMs are a promising solution in the field of thermal energy storage. "However, the low thermal conductivity and form stability over cycles of charging and discharging of PCM are challenges to address". In [8], the authors are proposing a study concerning a novel and low cost biochar-PCM hybrid latent heat energy storage material. According to [8], the new composite material possesses superior thermal conductivity over pure PCM, "as well as better stability due to the high carbon content and porosity of the developed biochar". "The heat of fusion is calculated to be 179.4 J/g. The thermal conductivity of the PCM is enhanced up to 13.82 times with the addition of water hyacinth biochar as a supporting matrix. The addition of aluminum metal powder further increases the thermal conductivity by 17.27 times higher than that of PCM alone" [8]. PCM is based on paraffin wax.

"To obtain high thermal performance composite phase change materials (PCMs), various other supporting materials have been utilized to encapsulate organic PCMs" [9]. In the study proposed in Ref. [9], four carbon materials (biochar, activated carbon, carbon nanotubes, and expanded graphite) were introduced to support heptadecane. "The latent heat storage capacity ranged from 53.3 J/g to 195.9 J/g. It was observed that the intermolecular interactions between the PCM and supporting materials and the surface functionality of the encapsulating agents play a leading role in the thermal performance of the composite PCMs. Furthermore, pore structures such as specific surface area, total pore volume, and pore size distribution have a combined effect on the crystallinity of heptadecane in the composite PCMs" [9].

Data about four composite PCMs (carbon nanotube, CNT; expanded graphite, EG; biochar, BC; activated carbon, AC; heptadecane, HD) are the following: HD/BC, HD/AC, HD/CNTs, and HD/EG exhibited latent heat capacities of 53.3 J/g, 85.4 J/g, 163.3 J/g, and 195.9 J/g, respectively [9]. All the composite PCMs exhibited a decrease in heat enthalpy when compared with the pure PCM. "This is due to the pore structure of the supporting materials that restrict the normal movement of the HD chain" [9].

However, biochar is an environmentally friendly material. In [10], a composite material is studied, obtained by means of biochar derived from bamboo, multiwalled carbon nanotubes and liquid n-dodecane for a new energy storage material. "The hybrid material provides favorable morphological and interconnected framework structures for PCM encapsulation and energy storage capacity in the composite PCMs. The PCM loading capacity of biochar, biochar-CNT, and CNTs reached 51.3%, 70.6%, and 83.2% with latent heat of 93.4 ± 1.1, 127.3 ± 1.1, and 152.3 ± 1.3 J/g, respectively". "The obtained composite PCMs exhibited outstanding shape and thermal stabilities and chemical compatibilities". The synthesis strategy proposed in [10] "is expected to create a platform for fabricating biochar-based multifunctional PCMs for desired applications".

Biochar, in general recognized as an environmentally friendly product, is consider for being used in buildings too. "The spread of low-energy buildings increases the impact of embodied energy in the life cycle of buildings. Moreover, environmental concerns push for the use of biobased materials". Ref. [11] summarizes the literature on biobased phase change materials (PCMs). "When implemented in testing huts, these biobased PCMs are able to perform as expected, decreasing the energy needed for cooling buildings" [11].

Ref. [12] tells that "Biochars have been suggested as cheap, eco-friendly, and commercially available media for adsorbing various organic and inorganic target compounds". Further inves-
tigations are necessary for the "design of shape and thermally stable organic phase-change materials (PCMs)". In [12], composite PCMs based on standard biochars and organic PCMs (1-dodecanol and n-dodecane) have been developed. "Among these biochar-derived composites, one from oilseed rape exhibited high heating enthalpy of 73.7 and 90.5 kJ/kg for 1-dodecanol and n-dodecane, respectively". "The synthesis of 1-dodecanol-based composite appeared to be influenced by specific surface areas of the biochars and intermolecular interactions owing to the highly sensitive hydroxyl group of the organic PCM".

Biochar belongs to the family of the bio-carbons. Some of them, obtained from walnut shell (WS) as "lightweight, porous, low-cost and environmentally friendly supporting matrix", have been studied too [13]. "The produced walnut shell carbon (WSC) and activated WSC (AWSC) were evaluated as novel shape stabilizer and thermal conductivity enhancer for methyl palmitate (MP) preferred as phase change materials (PCM) for thermal controlling applications in buildings". "The DSC measurements indicated that the melting temperatures of WSC/MP and AWSC/MP were 26.27 and 26.65°C, and corresponding fusion enthalpies were 108.3 and 138.1 J/g, respectively". "All findings revealed that the leak-free composite PCMs can be used as admixture in the manufacture of lightweight, cost-effective, eco-friendly and energy-saving construction elements utilized for solar thermal controlling of buildings" [13].

In [14], we find stressed that the practical application requires a shape-stable phase change composite (PCC). "A shape-stable PCC was fabricated by incorporating poly(ethylene glycol) (PEG) with biomass-based porous carbon that was produced via freeze-drying and carbonization using a low-cost and environmentally friendly fresh towel gourd. ... The shape-stable PCC demonstrated excellent thermal reliability and a high melting latent heat of ~164.3 J/g". The study in [14], as told by the authors, "provided an innovative strategy for the design and development of shape-stable PCCs for great potential in heat-insulating protective textiles, solar thermal energy storage, energy-saving buildings, and infrared stealth of military targets".

Also in [15], we can find a new form-stable composite phase change material (PEG/ASB) composed of almond shell biochar (ASB) and polyethylene glycol (PEG). "The supporting material ASB, which was cost effective, environmentally friendly, renewable and rich in appropriate pore structures, was produced from agricultural residues of almond shells by a simple pyrolysis method, and it was firstly used as the matrix of PEG". "The thermogravimetric analysis (TGA) and thermal cycle tests demonstrated that PEG/ASB possessed favorable thermal stability. The differential scanning calorimetry (DSC) curves demonstrated that the capacities for latent heat storage of PEG/ASB were enhanced with increasing PEG weight percentage. ... All the study results indicated that PEG/ASB had favorable phase change properties, which could be used for thermal energy storage" [15].

Pinecone biochar is used in [16]. A "form-stable phase change material (PA/PB) was fabricated using pinecone biochar (PB) as the supporting material of palmitic acid (PA)". Analyses demonstrated "that the PA was physically absorbed by the PB and the crystal structure of the PA was not destroyed. The results of DSC showed that the fusing and crystallization points of the form-stable phase change material with the maximum content of PA (PA/PB-4) were 59.25 °C and 59.13 °C, and its fusing and freezing latent heat were 84.74 kJ/kg and 83.81 kJ/kg, respectively. ... Thus, the study results indicated that the PA/PB-4 had great potential for thermal energy storage applications" [16].
Ref. [17] is studying infiltration properties of PCMs in biochar. "Three different n-alkanes (such as dodecane, tetradecane, and octadecane) are used as PCMs. The PCMs were infiltrated in the biochar network via the vacuum impregnation method. Among the biochar/n-alkane composites, one from octadecane exhibited a high latent heat storage capacity of 91.5 kJ/kg, 15.7 % and 25.9 % higher than that of dodecane and tetradecane-based composites, respectively. The molecular length of the PCMs and intermolecular interaction between the functional groups play an imperative role. The infiltration ratio of PCM in the biochar reached 50.1 % with improved thermal stability and chemical compatibility".

As previously told, a very important application of PCMs is in the enhancement of the energy efficiency of buildings. The base is in the integration of common construction materials with latent heat storage biocomposites [18]. These composites are prepared "by vacuum impregnating the phase change material into biochar. Biochar is used because it is highly utilized and environmentally-friendly, and the selected phase change materials are fatty acid type which are bio-based material and have a low risk of depletion". In [18], authors tells that "results of the numerical analysis showed further that latent heat storage biocomposite efficiently reduced the maximum energy consumption of reference building models by 531.31 kWh per year. Thus, both results validate the claim that latent heat storage biocomposite is a promising building material".

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