



Phase change materials and carbon nanostructures for thermal energy storage: A literature review

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ABSTRACT

The high thermal conductivity of carbon based nanostructures (CNs) has been recognized appropriate to be integrated into phase change materials (PCMs) to enhance the overall thermal properties of the obtained nanocomposites. The equilibrium of the possibility to enhance the thermal conductivity of the PCMs and the latent heat capacity are the key for their ability to store or dissipate a large amount of energy in a short period of time. This paper gives an update overview summarizing the state-of-the-art concerning nanocomposites prepared using PCMs and CNs with emphasis on the improvement of the latent heat capacity and of the thermal conductivity. Focus is directed towards experimental research studies regarding the enhancement of the thermal properties (thermal conductivity and the latent heat capacity) of PCMs obtained by the addition of the CNs by means of the encapsulation method.

The majority of the reported research studies focus mainly on the thermal characterization of PCMs nanocomposites, however there is scarce information about the mechanisms explaining why/how the thermal properties are enhanced. This review outlines the results of the thermal conductivity and the latent heat capacity of PCMs/CNs nanocomposites, trying to identify the features that lead to the improvement of their thermal properties.

1. Introduction

For the two last decades, the European Union (EU) has been working on new and stricter legislation to reduce energy consumption in all sectors and promote the use of renewable energy sources. In particular, the building sector is responsible for consuming around 40% of the total final energy and producing nearly 40% of the total CO₂ emissions [1,2]. Indeed, this sector is one of the major energy consumers [3,4].

In what regards the building sector, the basic premise of energy efficiency is to decrease energy consumptions, without compromising thermal comfort and indoor air quality in buildings [5]. Considering that buildings active systems for cooling and heating consume a large amount of energy to keep the indoor temperature within the comfort

range, many new and optimized solutions based on passive cooling and heating strategies have been developed in order to minimize the energy consumption. In fact, some have been passed onto commercial solutions are presently available on the market.

Amongst the strategies mentioned above, Thermal Energy Storage (TES) systems have gained much attention in the last decade, particularly as a potential approach to improve the energy efficiency in buildings. In this context, PCMs appear as a potential solution to increase the energy efficiency in new and refurbished constructions, since they can store more energy, in the latent form, than the typical sensible energy stored by common materials, as for example: clay, brick, wood, concrete and others [6,7]. The integration of latent heat thermal energy storage systems (LHTES) using PCMs increases the thermal inertia, and when coupled with other active systems can

Abbreviations: AC, acetamide; CA, capric acid; CNFs, carbon nanofibers; CNs, carbon nanostructures; CNTs, carbon nanotubes; MWCNTs, multi-wall carbon nanotubes; EG, expanded graphite; EU, European Union; GNPs, graphene nanoplatelets; GNs, graphite nanosheets; GO, graphene oxide; HD, hexadecane; HP, heptadecane; HVAC, heating, ventilation and air conditioning; LA, lauric acid; LHTES, latent heat thermal energy storage; L-MWCNTs, long multi-wall carbon nanotubes; MF, melamine- formaldehyde; MWCNTs, multi-wall carbon nanotubes; NDG, nitrogen doped graphene; NG, nano graphite; O-GNs, oriented graphite nanosheets; PA, palmitic acid; PA6, polyamide 6; PCMs, phase change materials; PD, pentadecane; PEG, polyethylene glycol; PMMA, poly(methyl methacrylate); PU, polyurethane; PVP, dispersing agent; R-GNs, randomly distributed graphite nanosheets; SA, stearic acid; S-MWCNTs, short multi-wall carbon nanotubes; SSPCMs, shape-stabilized phase change materials; SWCNTs, single-wall carbon nanotubes; TD, tetradecane; TES, thermal energy storage; UF, urea-formaldehyde; UMF, urea-melamine- formaldehyde; xGNPs, exfoliated graphite nanoplatelets

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increase the energy efficiency in new and refurbished buildings. The main advantage of LHTES is the high storage density for small temperature intervals. In consequence, it is demanding to contribute to solve the time mismatch between the energy supply and demand of these systems [7–10].

A simple way to increase the energy efficiency of new and existing buildings is to incorporate PCMs in the building external envelope wall solutions, as well as in other components such as glazing, enclosure facade and partitions walls, ceiling, and active HVAC (heating, ventilation and air conditioning) systems. In addition to the increase of energy storage, PCMs help to reduce the temperature peaks and attenuate the comfort asymmetry and temperature swing in building spaces through storing and releasing energy, functioning as a thermal regulator. Additionally, for hot climates, PCMs potentially reduce the overheating during the summer period [9,11].

However, the low thermal conductivity of PCMs limits the use of the full potential of these materials since it slows down the heat transfer process associated with the charging and discharging processes. The solution to this problem may be tackled by the incorporation of high thermal conductivity nanofillers such as CNs or other additives that can increase the thermal conductivity of the final composites [12,13]. Other strategies have been studied, in order to improve the thermal properties of PCMs, for example, shape stabilization of the PCMs [14–16] and the PCMs microencapsulation [17,18]. Among the various nanofillers reported in literature (inorganic and organic fillers), CNs have been preferred due their extremely high thermal conductivity and relatively low density [12,13,19]. Improvement of energy storage capacity of PCMs/CNs nanocomposites inevitably requires the increase of the thermal conductivity whilst minimizing the variation of the latent heat capacity of the nanocomposite and ideally increases it. In other words, materials should be able to store or dissipate a large amount of energy in a short period of time. The equilibrium between these parameters (thermal conductivity and latent heat capacity) in PCMs/CNs nanocomposites is the key factor for the development of many TES applications such as energy storage and thermal protection systems as well as in active and passive cooling of electronic devices, for thermal management of computers clusters, solar energy storage use, energy saving constructions, electrical engines, recovery of waste heat, smart textiles and heat transfer media.

Several reviews have been published regarding the characterization and applications of PCMs composites for thermal energy storage. However, there are just a few recent reviews focusing on methods developed to enhance the thermal properties of the PCMs composites by the addition of nanoparticles using encapsulation methods. Liu et al. [20] summarized and listed experimental and theoretical methods to enhance the thermal conductivity of the PCMs by the incorporation of additives such as CNs and metals or their oxides. These authors discussed and compared several methods to enhance the thermal conductivity of PCMs. Ibrahim et al. [21] reviewed separately the thermal conductivity enhancement strategies of the PCMs using porous materials, nanoparticles and low density materials, and the heat transfer enhancement of the PCMs with fins, heat pipes and using multiple PCMs. Huang et al. [22] focused their review on ways to improve the thermal conductivity and heat transfer of the PCMs using the incorporation of nanomaterials and porous materials, as well as encapsulation methods. Qiu et al. [23] presented an extensive review about the characterization of the microencapsulated PCMs slurries with the identification of the increase/decrease of thermal conductivity and latent heat capacity enhancement of microencapsulated PCMs slurries under the laminar and turbulent flow conditions. Milián et al. [24] summarized the encapsulation and characterization techniques for two types of encapsulated inorganic PCMs: core-shell PCMs and shape-stabilized PCMs. In addition, this review presents the effects of materials used for encapsulation and the parameters of encapsulation methods on PCMs thermal conductivity and on PCM latent heat capacity.

Despite of the contributions referred above, a comprehensive review focusing on the enhancement of the thermal properties (thermal conductivity and the latent heat capacity) of PCMs as a result of the addition of the CNs using the encapsulation method has not yet been carried out. This review gives an overview of the experimental research that has been reported concerning the improvement of the energy storage capacity and thermal conductivity of PCMs/CNs nanocomposites and the factors that determine the thermal performance of these nanocomposites. Therefore, and for a better understanding of this issue, this review focuses primarily on the fundamental properties of the individual PCMs and CNs and after on the PCMs/CNs nanocomposites. Next, the enhancement of the thermal properties (thermal conductivity and the latent heat capacity) of PCMs/CNs obtained from macro, micro and nanoencapsulation methods, including shape stabilized methodologies are discussed.

This review is organized as follows:

- 1) Discussion and identification of the most relevant parameters that can influence the enhancement of the thermal properties of PCMs/CNs composites using the referred methods.
- 2) Organization of the relevant information in tables: for the enhancement of the thermal properties of PCMs/CNs, the tables contain the variance of the latent heat capacity and the thermal conductivity increase for different types of PCMs and CNs (with different loading content); for the enhancement of the thermal properties of PCMs by the encapsulation method, the tables contain the latent heat capacity and the thermal conductivity values for different shell materials.
- 3) Detailed description of the most relevant experimental studies regarding innovative results, and identification of the critical reason(s) for the observed increase of the thermal conductivity and of the latent heat capacity, are separately presented.

Therefore, the present work gives an overview of different ways to improve the thermal properties of the PCMs, by enumerating in detail the most relevant experimental research studies to enhance the thermal conductivity and the latent heat capacity of the PCMs. Thus this work helps identifying the current status, potential existing problems and future directions in relation to research.

2. Phase change materials (PCMs)

2.1. Definition and operation principles

Materials with solid-liquid phase change, which are suitable for heat or cold storage applications, are commonly referred to as phase change materials (PCMs). In this context, PCMs appear as a potential solution to increase the thermal regulation in buildings since they can store more energy, in the latent form, than typical sensible energy stored by common building materials [25–27].

The sensible heat storage is the most common method for heat storage (ΔQ) [28], and this process can be expressed by Eq. (1):

$$\Delta Q = C \cdot \Delta T = m \cdot c \cdot \Delta T \quad (1)$$

where, the heat capacity, C , is given by the amount of material, m , and by the specific heat of the material, c , and ΔT represents the thermal amplitude between the final and initial temperature. Each material has a different heat capacity, C , so the sensible heat is influenced by the materials properties and by the imposed temperature [28].

Another method for thermal energy storage determination is the latent heat physical process. This method uses the phase change process of the material to store energy, in the latent form. Usually this type of materials suffers a small volume change, less than 10%, when the phase change process occurs. As Fig. 1 shows, for a solid-liquid phase change, when the melting temperature of the phase change is reached, the temperature of the PCM is constant and the stored heat

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