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Solar Energy Materials & Solar Cells
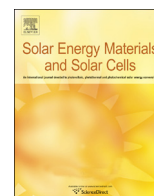
Development of content-stable phase change composites by infiltration into inorganic porous supports

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ARTICLE INFO

ABSTRACT

The performance of the vacuum infiltration technique to develop content-stable phase change composites is thoroughly analyzed for a representative spectrum of solid supports that cover a wide range of pore sizes, from micropores (> 0.6 nm) to macropores (< 200 μm). Particularly, the discussion of the results addresses how the porous features affect the amount of embeddable PCM, the phase change properties and the cycling stability of the composites. In terms of latent heat and cycling stability, conventionally used solid supports, such as bentonite, zeolites, diatomaceous earth and expanded graphite, appear to be less advantageous than mesoporous silica. The content stability provided by the nanosized pores of the composite developed with mesoporous silica reduces the risk of PCM leakage and makes this composite suitable for use in building materials without requiring a protective coating. The characterization of the phase change features is also accomplished by thermodiffractometric measurements on composite samples to analyze their main crystallographic properties. Finally, the effect of nano-confinement within the porous matrix on the phase change properties is discussed by focusing on the shifts observed for supercooling and melting point depression.

1. Introduction

Thermal energy storage based on the latent heat of phase change material (PCM) has attracted the attention of researchers and engineers in different fields due to its high energy storage density and nearly invariable operating temperature [1–4]. One of the most important applications of PCMs is building energy conservation, where the PCM is used for two purposes. The first is to store solar energy that does not necessarily match the energy needed for building heating at all times and the second is to shift the building heating or cooling load from peak to off peak electricity periods. With regard to the latter, absorbing solar energy during periods of solar isolation peak and releasing it gradually during off-peak periods or during night times into the conditioned space involves peak shaving of electric load of buildings, improves the efficiency of electricity systems and achieves significant economic savings.

Several techniques have been used to incorporate PCMs inside building components. Although some initial studies accounted for the direct incorporation of the unmodified PCM into plasterboard [5], the exudation problems of in-use conditions led to the search for new solutions. The most usual one is based on the use of PCMs contained within tight capsules fabricated on metallic or polymeric materials [6,7]. These capsules can be easily placed in room walls and ceilings, but have some disadvantages such as high cost, incompatibility with some inorganic building materials, or in some cases, the need for additional supporting structures [8]. Another alternative to incorporate PCMs into building components is based on the infiltration into porous supports [9,10]. There are two types of infiltration methods. The first, called natural infiltration, is carried out under atmospheric pressure, while the second is assisted by vacuum and have proved to be more efficient [11,12]. The benefit of infiltrating PCMs into porous materials lies in the low cost, ease of fabrication and widespread application of the porous supports in building industries. Despite there are plenty of commercially accessible porous materials, they can easily be designed to fit the required porosity features using the sol–gel process [13–15].

Previous studies have shown how phase change composites can be prepared by infiltration of a PCM into common macroporous materials such as expanded graphite and perlite [9,11,16,17]. Other authors have also developed this kind of composites by using macroporous metal foams as supports [18,19]. More recently, some researchers have prepared composites based on mesoporous supports [20–23]. However, to the best of our knowledge, none of them

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have considered the stability to thermal cycles that resemble in-use conditions in the absence of a container or a coating that prevents PCM leakage. This aspect proves to be crucial if the developed material is to be incorporated in a building component, such as plasterboard. In fact, as mentioned above, pioneer studies described undesirable PCM exudation during in-use conditions. Although the confinement of PCM into metallic or polymeric macrocapsules can overcome this problem [12,20,24], it increases the cost of production and thus, it is worth investigating if PCMs infiltrated in porous supports can avoid PCM leakage as well.

To this end, this current study has selected a representative spectrum of solid supports that cover a wide range of pore sizes, from micropores (>0.6 nm) to macropores (<200 μm). The research begins by evaluating the most fundamental operational parameters in order to optimize the preparation process of phase change composites by vacuum infiltration using hexadecane as reference PCM. The thermal cycling behaviour of all developed composites is then analyzed under parameters that resemble in-use conditions. According to the results herein described, although composites prepared from conventional porous materials such as bentonite, zeolites, diatomaceous earth and expanded graphite, might present an initially appealing latent heat, they suffer a considerable amount of PCM leakage caused by exudation from the macropores and the inter-granular space during thermal cycling. On the other hand, the stability towards the exudation provided by the mesoporous silica reduces leakage, thus making this material the most appropriate support to prepare content-stable phase change composites by means of vacuum infiltration. The effect of nano-confinement within the porous matrix on a range of PCMs (hexadecane, octadecane, an eutectic mixture of fatty acids, and butyl stearate) is also analyzed in terms of thermodiffractometric measurements and of the shifts observed for supercooling and melting point depression.

2. Experimental

2.1. Characterization methods

The porosity of macroporous supports was assessed by mercury intrusion porosimetry using a PoreMaster 60 from Quantachrome Instruments. Surface area and pore size distribution of micro- and mesoporous solid supports were estimated by the measurement of N_2 adsorption isotherms at 77 K in a NOVA 1200e Surface Analyzer from Quantachrome Instruments. The pore size distribution was modeled by density functional theory (DFT) as implemented in ASiQwin program of Quantachrome (ASiQwin V1.11, October 2010). All the samples were dried under vacuum at 250 °C for 8 h to eliminate solvent guest molecules prior to measurement. The microstructures of the porous supports and of the PCM composites were studied by means of a scanning electron microscope (SEM) ULTRAplus from Zeiss Company equipped with a Gemini column and an energy-dispersive X-ray spectrometer (EDS; OXFORD INCA Synergy microanalysis system). Physicochemical features of the samples were further studied by measuring FTIR spectra in a Perkin-Elmer Spectrum ONE, from 450 to 4000 cm^{-1} with a resolution of 2 cm^{-1} using KBr discs. X-ray diffraction (XRD) experiments on polycrystalline samples were carried out using a Bruker D8 Advance Vantec diffractometer equipped with Cu-$K\alpha$ ($\lambda=1.5418$ Å) and low temperature chamber. XRD patterns were recorded from 8 to 35 °C, over the range $5 < 2\theta < 38°$ using a step size of 0.033° and an acquisition time of 0.8 s per step. The indexation of the profiles (pattern-matching analysis) was made by means of FULLPROF program [25] on the basis of the space group and the cell parameters found for

isostructural compounds in the Cambridge Structural Database (CSD; v5.35 November 2013) [26].

To study the thermal stability of developed composite materials and to estimate the amount of embedded PCM, thermal gravimetric analysis (TGA) were performed in a *Q series Q600-0802-SDT* from TA Instruments. Thermograms were acquired in air atmosphere from 25 °C to 300 °C using a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) was used to evaluate the thermal properties (freezing–melting temperatures and enthalpies) of the prepared *PCM-porous support* composites. The DSC measurements were carried out from -10 to $+50$ °C under nitrogen atmosphere in a HP DSC827 calorimeter of Mettler Toledo, using around 5–10 mg as sample weight. Prior to measuring the samples, the calorimeter was calibrated with indium and zinc as standard reference materials. The phase change temperature corresponds to the onset temperature (T_s) obtained by drawing a line at the point of maximum slope of the leading edge of the DSC peak and extrapolating the baseline on the same side as the leading edge of the peak [27]. The latent heat of phase change was calculated by numerical integration of the area under the peaks.

2.2. Phase change materials and solid supports

Hexadecane (HE) and octadecane (OC) were selected as representative paraffinic PCMs. With a purity of 98% and 99%, respectively, both were purchased from Across Organics Company. Concerning the fatty acid type PCMs, an eutectic mixture (FA) of capric acid and lauric acid was prepared. Each component, with a purity of 99%, was acquired from Across Organics Company. Finally, an ester was selected, butyl stearate (BE) to be precise, with a purity of 99% and provided by Sigma-Aldrich. Table 1 shows their main phase change properties, which were determined by differential scanning calorimetry (see details in Section 2.1). These values provide a reference point for the assessment of the results obtained for the phase change composites.

Regarding the solid supports, four of them, expanded graphite (EG), bentonite (BT), diatomaceous earth (DE), and zeolite Y (ZY) were acquired from different suppliers, while the fifth one (mesoporous siliceous material: MS) was prepared following the procedure described below (Section 2.3). Expandable graphite was supplied by Technografit GmbH Company. Expanded graphite was obtained by rapid expansion in a furnace at 900 °C for 30 s. Bentonite and diatomaceous earth were acquired from Sigma-Aldrich, and they were used as commercially obtained without further chemical treatment. H form Zeolite Y was sourced from Zeolyst Company. The obtained material was washed thoroughly with distilled water and then dried in a furnace at 100 °C for 24 h. For the synthesis of the mesoporous silica the following reagents were acquired from Sigma-Aldrich and used without further purification: tetraethylortosilicate (TEOS, 98%), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, $\geq97.0\%$), and sodium dodecyl sulfate (SDS, 99%).

Table 1

Main phase change properties of selected phase change materials[a].

PCM	T_F (°C)	T_C (°C)	ΔH_F (J g^{-1})	ΔH_C (J g^{-1})
Hexadecane (HE)	17.66	16.15	220	224
Octadecane (OC)	27.77	26.75	195	19
Eutectic mixture of fatty acids (FA)	19.15	18.68	14	14
Butyl stearate (BE)	17.58	20.49	10	10

[a] All data were determined by differential scanning calorimetry (see details in Section 2.1). T_F: melting point. T_C: crystallization temperature. ΔH_F: melting enthalpy. ΔH_C: crystallization enthalpy.