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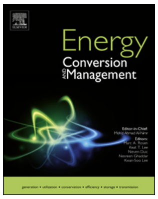

Preparation and investigation of distinct and shape stable paraffin/SiO_2 composite PCM nanospheres

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ABSTRACT

The synthesis of a shape stable paraffin/SiO_2 composite PCM, for use in latent heat storage, comprised of distinct nanospheres, using a novel and simple chemically aided infiltration method was investigated and the produced samples were characterized. SiO_2 spheres were synthesized, with the sol-gel method, and then used to encapsulate paraffin wax using several different preparation ratios of paraffin to SiO_2. The samples' constitution and morphology were characterized by FT-IR spectroscopy and scanning electron microscopy (SEM) respectively. Thermogravimetric analysis (TGA) was used for the paraffin mass percentage determination. The results were indicative of paraffin encapsulation inside the porous network of the SiO_2 spheres. DSC was used to investigate the thermophysical properties of the composite samples and for their evaluation as PCMs. The sample with the highest encapsulation ratio (B4 at 78.15%) had a paraffin mass percentage of 80% and a latent heat of ~ 156 J/g. The encapsulation's influence on paraffin's thermal properties was investigated and an optimum preparation ratio was determined. The composite nanoparticles retained a large amount of the paraffin's latent heat while showing no signs of aggregation -a novelty for paraffin/SiO_2 nanoPCM- and presenting enhancements that make them promising materials for heat storage applications (LHTES).

1. Introduction

As the limited supply of non-renewable energy sources, such as fossil fuels, continues to deplete, more attention is given to renewable energy. The efficiency and quality of service of fluctuant renewable energy systems can be increased with the use of thermal energy storage. In has been estimated that the global thermal energy storage market for 2015–2019 will cross US$1300 million in revenue, with the highest growth expected to be in Europe, Middle East, and Africa followed by the Asia-Pacific region [1]. Latent heat storage systems offer higher energy storage density than sensible storage systems and have less cost than techno-chemical based systems [1]. Latent Heat Thermal Energy Storage (LHTES) systems use the latent heat absorbed and expelled during phase transitions of materials, called Phase Change Materials (PCM).

PCM can be utilized for heating, cooling, temperature regulation and insulation [2] applications in buildings [3–6], solar systems [3,5,7], off-peak electricity utilization [3,8–10], electronics, space crafts, biomedical applications [11] and the automotive industry [5,11]. For a PCM material to be considered for use in thermal energy storage applications, several thermal, physical, kinetic, chemical and economical properties must be considered [3,4]. Among them, high latent heat and thermal conductivity, suitable phase transition temperature, small volume change during transition, good chemical compatibility and stability are desired properties in a PCM for use in LHTES applications. Conversely, inadequate long term stability may be caused by poor material stability and/or by corrosion between the PCM and its container [11]. Also, a large temperature difference between charging and discharging is undesirable for efficient energy storage applications [1].

So far, we have been unable to identify a pure material that presents ideal quality for all of its properties as PCM leading to a necessary compromise [12]. A way to improve on the properties of PCM materials is by creating composite materials by combining two or more pure materials in different configurations, thus modifying and enhancing desirable properties. One such method is PCM encapsulation, the placement of the main PCM material inside another support material. With encapsulation we can achieve form stability and by encapsulating PCM

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Nomenclature

T_m	melting onset point, °C
T_s	freezing/solidification onset point, °C
ΔT	difference between melting and solidification onset points
T_{mp}	melting curve peak (DSC graphs), °C
ΔH_m/LHF	latent heat of fusion (melting), J/g
ΔH_s	latent heat of solidification (freezing), J/g

Subscripts

m	melting
s	solidification
PCM	corresponding to the pure PCM (paraffin)
encapPCM	corresponding to the composite PCM (paraffin/SiO_2)

Abbreviations

PCM	phase change material
LHTES	latent heat thermal energy storage
SEM	scanning electron microscopy
FT-IR	fourier transform infrared spectroscopy
TGA	thermogravimetric analysis
DSC	differential scanning calorimetry

Chemical compounds

TEOS	tetraethoxy silane
EtOH	ethanol
NH_3	ammonia
CH_2Cl_2	dichloromethane
PVP	polyvinylpyrrolidone

in a large number of distinct capsules of a specific shape, the area for heat transfer can dramatically increase [7]. With a proper encapsulant, non-compatibility of a PCM with its surroundings (such as containers and heat transfer fluids) and characteristics such as toxicity, corrosiveness and inflammability can be circumvented because in that case, it is the encapsulant material, and not the PCM, that would be interacting directly with the environment. In order for a material to contain a PCM, certain requirements have been proposed [7,13,14] and among the chief concerns for encapsulation [15] is the reactivity between materials and the accommodation of the PCM's volumetric expansion, during melting, by the encapsulant.

Regarding encapsulation size scales, the surface area to volume ratio increases as the capsule size decreases which leads to higher heat transfer rates [16]. Furthermore, microencapsulation offers faster charging and discharging rates due to the smaller distance for heat transfer [15], better adaptation to the thermal expansion/contraction during the phase change processes [7] and, when comparing with macroencapsulated PCM, better thermal reliability and chemical stability [16]. Phase change slurries, systems of microscopic-sized PCM particles with a protective coating suspended in a continuous phase (e.g. water), have a wide array of applications [6]. With encapsulation in general, however, it is necessary to sacrifice energy storage media mass for encapsulant material mass in order to achieve proper encapsulation. Encapsulation in the nanoscale seems even more promising. The enhancement of the heat transfer speed due to the ratio of surface area to volume of nanoencapsulated PCM has been considered as an effective counterbalance to the low thermal conductivity problem that organic PCM face [17]. Furthermore, nanocapsules have been considered more structurally stable compared to micro- and macrocapsules [16].

Paraffin presents large amounts of latent heat [3,18], is safe, noncorrosive, chemically inert and stable bellow 500 °C while having small volume change during its phase change and small vapor pressure [3]. It has a very small (to non-existent) degree of supercooling [3,6] due to good nucleation properties. Paraffins have been considered to be among the more promising PCM for thermal storage applications for the temperature area of -10 °C to 100 °C, in related studies [12]. Though the quality of paraffin wax varies a lot in the commercial market [19,20] due to its wide use in different products, it has been found to have reasonably good thermal stability regarding melting temperature and variations in latent heat of fusion during the thermal cycling process [21]. Furthermore, due to it being an organic compound, the cost of paraffin is relatively low and its availability high [6]. Finally, its undesirable characteristics of low thermal conductivity, moderate flammability, non-compatibility with plastic containers [3] along with the oxidation of organic compounds [22] and production of toxic compounds [6] due to paraffin wax's exposure to the environment, can be sufficiently rectified by proper nano-encapsulation with a suitable encapsulant material. The problem of low thermal conductivity can be counterbalanced by the high heat transfer speeds resulting from the high surface area to volume ratio of nanoencapsulation [17] and the issues of flammability and compatibility are suppressed since the encapsulant material will be the one to interact with the PCM's environment.

Several materials have been investigated as potential micro-PCM encapsulants such as Polystyrene [23], polymethylmethacrylate (PMMA) [24] and urea-formaldehyde polymer [25]. However the inflammability, toxic gas release possibility and other concerning factors regarding most of the proposed materials, limit their applicability. A promising material for that purpose is inorganic SiO_2. Silica is characterized by its non-toxicity, excellent thermal stability and good mechanical properties [26]. SiO_2 is a fire resistant [26] material with a high melting point that presents ease of synthesis and cost effectiveness when used as the encapsulant material for a PCM [27]. Additionally, it is a generally chemically inert biocompatible material with a degree of elasticity and good compatibility with many other materials. An organic PCM with an inorganic coating can be considered as a preferred encapsulation choice [28] and SiO_2 shells have been considered as a good encapsulant material for paraffin that can improve the thermal stability in the microcapsules [29,30].

Polymers, along with paraffin and other PCM, are often used in order to prepare composites in various works [17,31–34]. A common method for the preparation of composites using paraffin, is by impregnating it in support materials such as expanded graphite [35], expanded perlite [36] and diatomite [37–39]. However, diatomite and expanded perlite, as supporting materials for PCMs, have been thought to have clear drawbacks due to their large pore size and the lower latent heat of their fabricated composites (often requiring the complex vacuum impregnation method in order to increase the energy storage capacity) [2]. SiO_2 has also been used as the supporting material for the preparation of paraffin/SiO_2 composites with several different methods such as sol-gel [29,40–42], in situ emulsion interfacial hydrolysis and polycondensation [30,43] and chemical precipitation [26]. A known method for the preparation of paraffin/silica composites is natural infiltration, the mixing of melted paraffin with silica, where paraffin infiltration can be aided by the good wetting ability of porous silica [18]. Li et al. produced a form stable material with the absorption of paraffin in different types of hydrophilic and hydrophobic nanosilica, namely fumed silica, precipitated silica and silica aerogel. The direct impregnation method was used without vacuum treatment by gradually adding nanosilica in melted PCM [44]. In their work Zhou et al. studied the encapsulation, by natural infiltration, of paraffin in porous silica prepared with the sol gel method. The infiltration was performed by submerging the silica in melted paraffin [18]. Hydrophobic nano-SiO_2