



A review on encapsulation techniques for inorganic phase change materials and the influence on their thermophysical properties



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ABSTRACT

Phase change materials (PCM) are characterized for storing a large amount of thermal energy while changing from one phase to another (generally solid-liquid states) at a specific temperature and presenting a high specific heat of phase change process. PCMs can be classified as organic, inorganic and eutectic. Such materials present some limitations, including subcooling, phase segregation, flammability, low thermal conductivity and thermal instability, among others. In order to overcome these problems, encapsulation of PCMs is being successfully developed, providing decreased subcooling, large heat transfer area, and controlling the volume change of the storage materials when the phase transition occurs. A considerable amount of studies has been published in the field of encapsulation methods for organic PCMs. Nevertheless, the information available on inorganic PCMs is scattered. Furthermore, the influence of the encapsulation techniques on thermophysical properties of PCMs is not reported in these reviews most of the time. Hence, the aim of this review is to summarize the encapsulation and characterization techniques for inorganic PCMs and to provide the analysis about the influence of synthesis parameters on thermophysical properties of encapsulated PCMs. Two principal types of encapsulated inorganic PCMs were found: core-shell PCMs (core-shell EPCMs) and shape stabilized PCMs (SS-PCMs). Classification of encapsulation methods of core-shell EPCMs and SS-PCMs are reported in this work. Among all the microencapsulation methods, inverse Pickering emulsion, electroplating, solvent evaporation–precipitation method and mechanical packaging are the most common methods described in the literature for the production of core-shell EPCM. On the other hand, for SS-PCMs, mainly sol-gel process, infiltration and impregnation encapsulation methods were found. Scientific works report a reduction in the heat of phase change for core-shell EPCMs. This is mostly because of the low content of salt in the final material. Moreover, an improvement of thermal conductivity was procured for SS-PCMs. Finally, PCM percentage, particle size, stirring rate, type of crosslinking agent and solvent properties were established as principal factors influencing the final properties of the encapsulated materials. For the best of our knowledge, this is the first profound review of encapsulation techniques for inorganic PCM.

1. Introduction

In recent years the increase in energy demand due the growth experienced by the global economy stimulates the search for more

energy efficient technologies to mitigate the negative effects on the environment caused by this growth. Renewable energy sources (RES) such as solar radiation, biomass, geothermal heat and wind, are becoming more and more attractive, clean and sustainable alternative

Abbreviation: CAB, Cellulose acetate butyrate; CS – PCM, Core Shell – Phase Change Material; CSP, Concentrated Solar Plants; DSC, Differential Scanning Calorimetry; DSG, Direct Steam Generation; EA, Ethyl acrylate; EG, Expanded Graphite; ENG, Expanded Natural Graphite; EPCM, Encapsulated PCM. Includes both CS-PCMs and SS-PCM; esd, energy storage density; FA, Formaldehyde; FEP, fluorinated ethylene propylene; HDPE, High Density Polyethylene; HT – TES, High Temperature Thermal Energy Storage; K, Thermal conductivity; K %, Increment on thermal conductivity; LHS, Latent Heat Storage; MDI, Diphenyl methylene diisocyanate; MdiMS, (3 – Mercaptopropyl)-methyldimethoxysiloxane; MMA, Methyl methacrylate; MODS, Trimethoxy(octadecyl) silane; MS, (3 – Mercaptopropyl)-methylsiloxane; ODTMS, Octadecyl trimethoxysilane; PAOS, Poly(ethoxysiloxane); PCM, Phase Change Material; PEG, Poly (ethylene glycol); PIME, Pickering Inverse Mini-Emulsion; PTFE, Polytetrafluoroethylene; PTMS, Propyl trimethoxysilane; PVP, Polyvinyl; RES, Renewable Energy Sources; SDBS, Sodium dodecyl benzene sulfonate; SDS, Sodium dodecyl sulfate; SS – PCM, Shape Stabilized – Phase Change Material; TEOS, Tetraethylorthosilicate; TES, Thermal Energy Storage; Tm/c, melting/crystallization temperature; TMPTA, Trimethylolpropane triacrylate; ΔHm, melting latent heat enthalpy; ΔHm %, Reduction on latent heat

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to conventional energy sources, like nuclear and fossil fuels [1–3]. Solar energy is one of the most promising RES that “persists” and “repeats” day after day, however it is variable and not constant (available only during the day) [1,2]. Although electricity produced from solar radiation in the world power supply system has increased significantly over the past years, the electricity produced from these sources is fluctuating strongly during day over the different seasons of the year [4,5]. This is the reason why thermal energy storage (TES) has been succeeding across the last decades, transferring heat to storage media during the charging period, and releasing it during the discharging step [6]. Sensible heat or latent heat are used in this method, but sensible heat storage materials have the lower storage capacity compared to the latent heat storage materials, which is the reason why sensible heat storage systems are huge and thus space demanders [6]. Therefore, latent heat storage (LHS) is one of the most competent ways of TES, providing high storage density with a small temperature difference between storing and releasing heat. The materials used for LHS are called phase change materials (PCMs) and are characterized by storing a large amount of thermal energy while changing from one phase to other (usually solid-liquid states), at a specific and almost constant temperature, and presenting high heat of phase change (latent heat) [7]. This allows PCMs to change their phase, once the required amount of heat has been received and to release the energy when it is needed. For this reason, their applications such as construction, refrigeration, air conditioning, textiles, food, astronautics and waste heat recovery, among others [8–10], are determined based on their phase change temperature [11].

PCMs can be classified as organic, inorganic and eutectic. Organic PCMs can be divided into two types, paraffin and non-paraffin. Organic PCMs have been widely employed for TES, due to their non-corrosiveness behaviour and for having congruent melting and self-nucleation capacity. Inorganic PCMs include salt hydrates, metals and alloys. Additionally, the main advantages of inorganic PCMs are high latent heat, relatively high thermal conductivity, non-toxicity, non-flammability and low cost, compared to organic PCMs [8]. In consequence, inorganic PCMs offer a high potential for building [12–14], concentrated solar plants (CSP) [15–17] and thermal management of Li-ion batteries [18–20], among other applications. However, LHS presents some limitations to be overcome depending on the nature of the material employed, including subcooling, leakage, phase segregation, flammability, low thermal conductivity and thermal instability, among others. The subcooling and phase segregation problem can be solved by the addition of some nucleating [7,21,22] or thickening agents [7,22,23]. Lately, the encapsulation of PCM has been successfully developed, providing a large heat transfer area and reducing the reactivity of the materials with the outside environment. Also, this technique ensures the decreasing of subcooling and controlling the volume change of the storage materials during the phase transition. The encapsulation methods can be classified based on the shape of the material, as core-shell and shape-stabilized PCMs (CS-PCMs and SS-PCMs, respectively). Different materials are employed to encapsulate PCMs, i.e.: acrylics, urea, formaldehyde and silica based polymers, metals and carbon based composites as graphene and graphite, among others. The application of these encapsulating methods allows improving the thermophysical performance of PCM. This has been already demonstrated for organic PCMs [7,22,24,25]. Nevertheless, the information available on encapsulation of inorganic PCMs is scattered, is limited and not integrated in a single source. Also, only two publications (in 1988) regarding the encapsulation inorganic PCMs before 2002 were found. Half of papers belong to the last 3 years (Fig. 1).

Hence, the aim of this review is to summarize the encapsulation techniques for inorganic PCMs, as well as to provide an analysis about the influence of synthesis parameters on the thermophysical properties of encapsulated PCM.

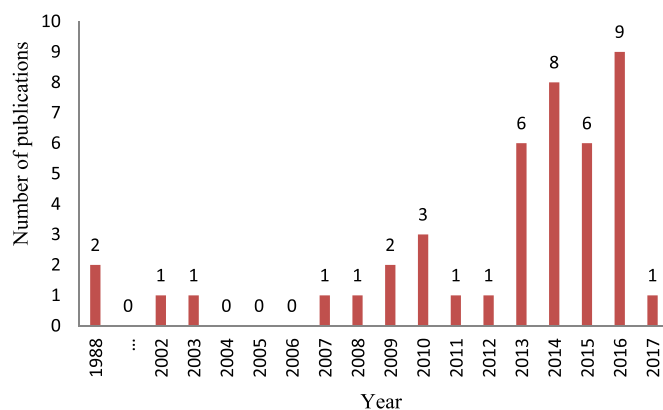


Fig. 1. Publications per year on encapsulation of inorganic PCMs.

2. Encapsulation methods for inorganic PCMs

The encapsulated PCMs can be classified as core-shell materials (CS-PCMs) and shape-stabilized PCMs (SS-PCMs), depending on the design of the material. Core-shell materials are composed of particles of PCMs (core) covered by another material (shell) (Fig. 2), which encapsulates the PCMs, while SS-PCMs are composites of PCMs with other materials that retain molten PCMs by capillarity [16] (Fig. 3).

In general, the encapsulation methods can be classified as in-situ polymerization, complex coacervation, sol-gel and solvent extraction/evaporation [22,24,26]. In-situ polymerization is divided into three more categories: interfacial polycondensation, suspension polymerization and emulsion/mini-emulsion polymerization. Organic PCMs present a large variety of encapsulation techniques, and a great number of review papers can be found for this type of materials [7,22,24,25,27–29]. On the other hand, Su et al. claim that solvent extraction/evaporation was the only method that could be found for inorganic PCMs [22].

Nevertheless, the present review establishes that some methods can be applied not only for organic PCMs but also for inorganic PCMs. The comparison of methods available for organic and inorganic PCMs is summarized in Table 1.

Suspension polymerization, dispersion, coacervation, electrostatic encapsulation, spray-drying and supercritical CO₂-assisted methods have not been employed for inorganic PCMs, mainly because of solubility and system stability concerns.

The currently available encapsulation techniques for inorganic CS-PCMs and SS-PCMs as well as the changes of thermophysical properties due to the encapsulation are described below.

2.1. Core-shell encapsulation methods

Table 2 summarizes the core-shell encapsulation methodology revealed for inorganic PCMs. In this work, it is classified as chemical, physicochemical and mechanical packaging. Chemical methods include in situ polymerization, emulsion (direct emulsion, inverse emulsion and Pickering inverse emulsion (PIE)), electroplating and interfacial

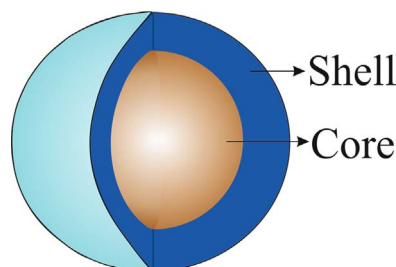


Fig. 2. Representation of a capsule of core-shell encapsulated PCM.

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