Available online at www.sciencedirect.com

ScienceDirect

Solar Energy 112 (2015) 300–309

SOLAR ENERGY

www.elsevier.com/locate/solener

Preparation and exhaustive characterization of paraffin or palmitic acid microcapsules as novel phase change material

J. Giro-Paloma [a,1], Y. Konuklu [b,c,2], A.I. Fernández [a,*]

[a] Departament de Ciència dels Materials i Enginyeria Metal·lúrgica, Universitat de Barcelona, Martí i Franqués 1-11, 08028 Barcelona, Spain
[b] Nigde University, Nanotechnology Application and Research Center, 51240 Nigde, Turkey
[c] Nigde University, Mechanical Engineering Department, 51240 Nigde, Turkey

Received 29 September 2014; received in revised form 16 November 2014; accepted 3 December 2014
Available online 30 December 2014

Communicated by: Associate Editor Halime Paksoy

Abstract

In this study, two different types of Phase Change Materials (PCM) suitable for Thermal Energy Storage (TES) applications were used as a core material in a microencapsulation process. The wall material for these microencapsulated PCM (MPCM) was Poly(styrene-co-ethylacrylate) (PScEA). Microcapsules were prepared using an emulsion co-polymerization technique. The prepared MPCM were characterized as follows: morphology, shape and size were analyzed by Scanning Electron Microscopy (SEM) and Particle Size Distribution (PSD). Besides, Fourier Transformed Infrared spectroscopy (FT-IR) was used to perform the chemical characterization of the shell microcapsules. Moreover, thermophysical properties were analyzed by Differential Scanning Calorimetry (DSC) for the two PCM in usage (paraffin 42–44 and palmitic acid) meanwhile the thermal stability was evaluated by Thermogravimetrical Analysis (TGA). Mechanical characterization of the prepared microcapsules was performed by using the Atomic Force Microscopy (AFM) as indentor. Experiments were performed at two different temperatures 25 °C and 70 °C, and two parameters were evaluated: the Young's modulus on a punctual area and the vertical force required to plastically deform the MPCM. At the light of the results, it can be considered that these synthesized MPCM were successfully prepared being able to be used in a TES system.

Keywords: Phase Change Material; Microencapsulated phase change material; Atomic Force Microscopy; Differential Scanning Calorimetry; Thermogravimetrical Analysis; Fourier Transformed Infrared spectroscopy

1. Introduction

Phase Change Materials (PCM) are well known for Thermal Energy Storage (TES) applications and are reported as a promising energy technology for improving the energy efficiency (Gil et al., 2010), hence different kind of PCM have been studied for different applications. To avoid the leakage of the PCM and control the variation in the storage material volume as the phase change takes place, the development of microencapsulated phase change materials (MPCM) has become an area of interest (Tyagi et al., 2011; Konuklu et al., 2014; Jamekhorshid et al., 2014; Zhang et al., 2004; Zhao and Zhang, 2011). MPCM are little containers made of polymeric shell and contain PCM inside (Alkan et al., 2009). There are three prerequisites for the microencapsulation process: the construction of the shell involving the PCM, ensuring that no leakage and no impurities are incorporated in the core/shell MPCM

* Corresponding author. Tel.: +34 934021298; fax: +34 934035438.
E-mail addresses: jessicagiro@ub.edu (J. Giro-Paloma), ykonuklu@nigde.edu.tr (Y. Konuklu), ana_inesfernandez@ub.edu (A.I. Fernández).
[1] Tel.: +34 934021298; fax: +34 934035438.
[2] Tel.: +90 3882254492; fax: +90 3882250112.

http://dx.doi.org/10.1016/j.solener.2014.12.008
0038-092X/

system. The second requirement is that the coating material thickness has to achieve the efficiency of the MPCM. By this way, MPCM third specification is being resistant to thermal and mechanical stresses. Besides, there are different methodologies to microencapsulate PCM (Boh and Šumiga, 2008; Jyothi et al., 2010; Sánchez et al., 2008). Based on the mechanisms of microcapsules formation, methodologies are classified in chemical methods, physico-chemical methods, and physical and mechanical methods.

There are several possibilities or combinations of shell and core materials as a MPCM. Typical used shells are Poly(methyl methacrylate) (PMMA) (Alkan and Sarı, 2008; Wang et al., 2011) and melamine formaldehyde (MF) (Özonur et al., 2006), and the more usual PCM are paraffin (Sánchez-Silva et al., 2010) and particularly *n*-octadecane (Salunkhe and Shembekar, 2012; Zhang et al., 2012). Thus, there are a lot of recent studies with the preparation of MPCM made of PMMA and paraffin wax (Wang et al., 2012; Castellón et al., 2010; Ma et al., 2010), PMMA and *n*-octadecane (Giro-Paloma et al., 2013, 2014), MF and paraffin wax (Su et al., 2012; Šumiga et al., 2011), and finally MF and *n*-octadecane (Zhang and Wang, 2009). Although these two polymers are the most popular ones due their characteristics, polystyrene (PS) is also a popular container used as a shell in MPCM manufacturing. It can be mixed with different type of PCM, depending on the application and in the comfort temperature. Borreguero et al. (2011) produced by suspension polymerization technique microcapsules containing RT-27 and PS as a shell material. Although the MPCM was obtained, they concluded that for this kind of PCM is much better a shell of PE–EVA (polyethylene–ethyl vinyl acetate) because its thermal stability is better. Moreover, Sánchez et al. (2010) synthesized by suspension like polymerization MPCM for textiles made PS as a shell and paraffin wax as a core. Other authors used the same polymeric shell and changed the PCM obtaining MCPM to be used for Phase Change Slurries (PCS) and phase change emulsions, as Yang et al. (2003), where they prepared and characterized microcapsules containing *n*-tetradecane for improving the heat transfer ability and energy transport ability. Besides, Fang et al. (2008) studied nanoencapsulated PCM with PS *n*-octadecane, as a shell and as PCM, respectively. Their conclusion was that these capsules were successfully prepared by the ultrasonic assistant miniemulsion in-situ polymerization. Also, Sánchez-Silva et al. (2010) studied the MPCM of styrene mixed with another polymer in paraffin. The preparation of the microcapsules was done by suspension – like polymerization, and the main conclusion for the styrene–methyl methacrylate with paraffin was that it is impossible to microencapsulate the paraffin wax when the MMA/St is equal to 2.0. Also, styrene can be copolymerized with other substances creating the ABS (Acrylonitrile–Styrene–Butadiene), AB (Acrylonitrile–styrene copolymer), and the SBS (Styrene–butadiene–styrene). Examples of these are the ones of Yang et al. (2009) and Kenisarin and Kenisarina (2012), respectively. The first one prepared MPCM of ABS and AS with *n*-tetradecane in the core, remarking that their potential and flexibility as a shell material. The SBS MPCM study includes microparticles with paraffin wax as a core material and others with lauric acid.

In our literature survey, none reported preparation of paraffin and palmitic acid microcapsules with Poly(styrene-co-ethylacrylate) (PScEA) shells. In this paper is reported the microencapsulation and full characterization of paraffin and palmitic acid in PScEA shells by the emulsion co-polymerization method to obtain micro-nanocapsules for low temperatures solar thermal applications by Scanning Electron Microscopy (SEM), Particle Size Distribution (PSD), Fourier Transformed Infrared spectroscopy (FT-IR), Differential Scanning Calorimeter (DSC), Thermogravimetrical Analysis (TGA), Atomic Force Microscopy (AFM).

2. Materials and methods

2.1. Materials

Paraffin 42–44 and palmitic acid were used as core PCM. Styrene (>99%; Sigma Aldrich Company, USA) and ethyl acrylate, $C_5H_8O_2$ (>99%; Merck, Germany) were used as a shell material; ethylene glycol dimethacrylate (EGDMA), $C_{10}H_{14}O_4$ (Merck, Germany) was used as a crosslinking agent and it was distilled before use. The initiator of ammonium peroxodisulfate (Merck, Germany) and other analytical reagents tert-butylhydroperoxide (70%; Merck, Germany), Triton X-100 (Merck, Germany), iron (II) sulfate 7-hydrate ($FeSO_4{\cdot}7H_2O$) (Panreac, Spain), and sodium thiosulfate ($Na_2S_2O_3$) (Merck, Germany) were used without further purification.

2.2. Preparation of microcapsules

A typical emulsion polymerization process technique was used in the preparation of MPCM with PScEA shell. The emulsion co-polymerization method consists on mixing the polymer in an oiled system, adding an emulsifier. An emulsification is needed to create a water/oil emulsion and to generate a crosslinked system. Then, it will be needed the wash of the emulsion, to eliminate the oil, creating isolated microcapsules. Firstly, 120 ml of deionized water, 1.60 g of Triton X100, 28 g of core material were stirred for 30 min at 40 °C. Then, 14 g of styrene, 14 g of ethyl acrylate, 8 g of EGDMA, 1 ml of $FeSO_4{\cdot}7H_2O$ solution and 0.25 g of ammonium peroxodisulfate was stirred in a beaker, then added to emulsion, and stirring was continued at 1000 rpm. Then, 0.25 g of $Na_2O_3S_2$, 1 ml of tert-butylhydroperoxide was added to the emulsion and heated to 95 °C. The solution was stirred for 5 h and after this it was cooled down to room temperature and washed with water five times. Finally, the microcapsules were rinsed with deionized water, filtered and dried approximately 72 h at room conditions.