Solar Energy Materials and Solar Cells 174 (2018) 380–387

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Novel shapeable phase change material (PCM) composites for thermal energy storage (TES) applications

Nurten Şahan*, Halime Paksoy

Çukurova University, Chemistry Department, Adana 01330, Turkey

ARTICLE INFO

Keywords:
Shapeable PCM composite
TES
Microcapsules
Engineering applications of TES

ABSTRACT

Phase change materials (PCMs) have recently found a wide range of new application opportunities. One of their main constraints is their integration in complex geometries. Present work has prepared shapeable polymer composites with PCM capsules for thermal energy storage (TES) systems – ones that especially need specific integration requirements. Different preparation methods of PCMs are necessary to meet the integration obstacles. With the goal of filling the R & D gap, stearic acid was encapsulated in two different kinds of shells of SiO_2 and PMMA and then incorporated into the PMMA matrix to form shapeable composites. Thermal, chemical, and physical properties of composites and their components were studied in comparison to the matrix material. This initial study showed that our novel shapeable PCM composites come with many advantages: less volume, no leakage, suitable storage capacities, as well as flexible shapes that can be easily engineered in various TES systems.

1. Introduction

Thermal energy storage (TES) – by forming a bridge between renewables and end-users – plays an important role in meeting increasing energy demand of the world in a sustainable way. The three main techniques used in TES are thermochemical, sensible, and latent heat.

Phase change materials (PCMs) are the energy storing materials in latent heat storage systems. Storage performance of a PCM plays a vital role in efficient latent heat storage applications. Many applications can benefit from storing latent heat.

Mismatch between supply and demand of renewables or waste heat can be narrowed with latent heat storage. Using PCMs also regulate or maintain optimum temperatures in electronic devices [1], buildings [2], food and medical material [3,4], greenhouses [5] and vehicles [6].

PCMs may exhibit advantages and disadvantages depending on their chemical classification and application types. Leakage is a common problem in all types of PCMs, which makes them difficult to integrate into melting/freezing cycles. Several techniques have been developed to address this problem being: using special packages or containers [7], embedding into supporting materials [8,9], and encapsulation [10,11]. In recent years, solid-solid PCMs are suggested as alternative storage materials that do not leak. However, these materials are not preferred widely as heat storage candidates, because they have high transition temperatures, lower storage capacities, and instability in comparison to solid-liquid PCMs.

Recovering surplus heat – even in small amounts – as well as providing the optimum operating temperature of devices or systems with PCMs is an important research subject. The containers for PCMs should meet the engineering requirements for compatible design as well as possess suitable volumes and geometries.

The objective of our study is to develop PCM composites that can be used with coating at specific thicknesses and shapes, thus enable easy integration for various TES applications avoiding any leakage or interactions of PCM with surroundings. There are limited previous studies directly associated with this study. The encapsulated PCMs were tested in composites for specific applications in several studies. For example, capsules have been placed into concrete for building applications [12] and tested in cotton fabrics for providing thermal buffering of clothes [13]. Sarı et al. mixed microcapsules of PCMs with polycaprolactone powder by blending method to investigate their thermophysical properties. The resulting composite was not shapeable and form stable [14]. One of the closest studies done is by Jamekhorshid et al., who prepared composite of wood-plastic encapsulated PCMs by using compression molding method for thermal management of buildings. They found that thermal properties of composite remained reasonable; however, mechanical strength was reduced [15]. As the reason for the low mechanical strength mixing these components at high temperatures was given. Furthermore, they saw that microcapsules were more favorable additives with regard to the leakage problem in comparison to non-encapsulated PCMs in their composite samples [15]. In addition to

* Corresponding author.
E-mail address: nurtenshn@gmail.com (N. Şahan).

http://dx.doi.org/10.1016/j.solmat.2017.09.022
Received 5 June 2017; Received in revised form 25 August 2017; Accepted 12 September 2017
Available online 25 September 2017
0927-0248/

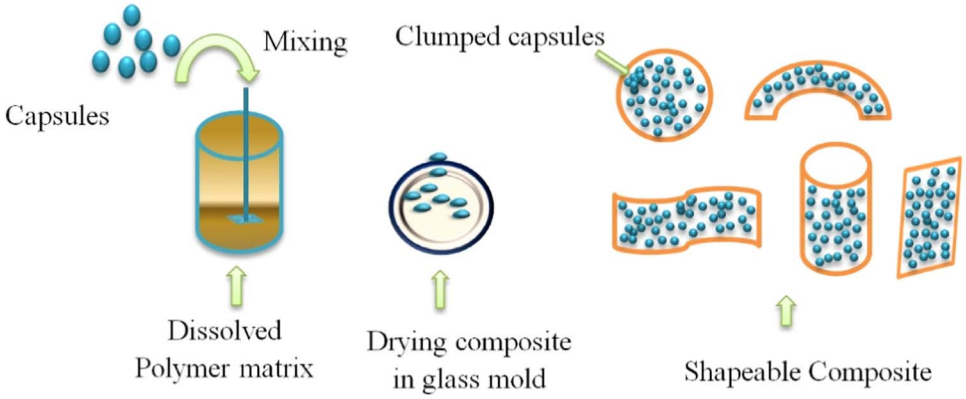

Fig. 1. Schematic illustration of solution casting method for preparation of shapeable PCM composite.

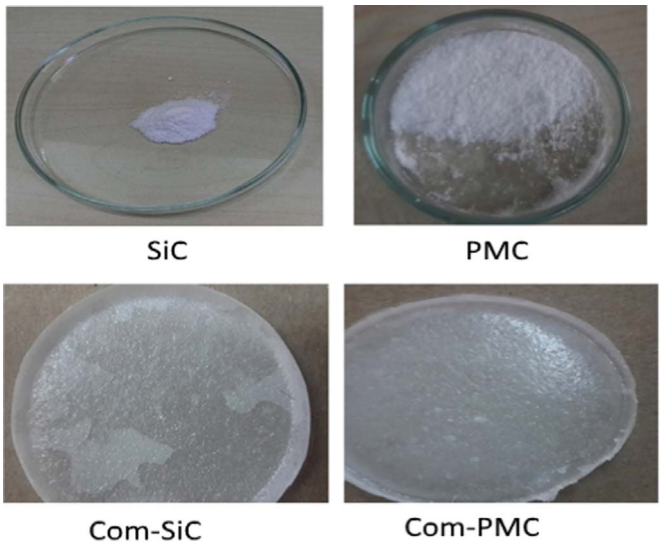

Fig. 2. Photos of microcapsules and composites.

these, there are form-stable composites of PCMs with graphite and polymer matrices. Such composites were suggested as storage materials in a limited number of TES applications [16,17].

This paper attempts to present new and shapeable sheets with PCM, that can be easily integrated and are compatible in small volumes for many TES applications. In this novel study, stearic acid was encapsulated with poly-methyl methacrylate (PMMA) and SiO_2 by emulsion polymerization, in situ emulsion interfacial hydrolysis and polycondensation techniques, respectively. These microcapsules were mixed in polymer matrix (PMMA) by solution casting method to obtain the shapeable composites. PMMA films have wide ranges of applications such as in optoelectronics, advanced electronics, and transistors. It can be used in thin film synthesis with spin coating method [18]. Hence, shapeable polymer-sheets with PCM capsules can be more advantageous than in previous studies –with their controllable thicknesses, shapes, and abilities to be used as coating in different TES applications. Thermal, physical and chemical properties of new shapeable composites were investigated to find out their suitability for TES applications.

2. Experimental

2.1. Materials

Stearic acid (Merck) with melting points of 68–70 °C was used as the core material for two different kinds of capsules. The materials used in the synthesis of SiO_2 shell were tetraethyl orthosilicate ($Si(OC_2H_5)_4$ – TEOS) purchased from Sigma Aldrich and n-amyl alcohol ($C_5H_{11}OH$), cetyltrimethylammonium bromide ($C_{19}H_{42}NBr$ – CTAB), ammonia solution (NH_4OH, 25 wt%), ethanol (CH_3CH_2OH) also purchased from Merck Company. Methyl methacrylate (MMA, Merck) was used as monomer for the synthesis of PMMA shell. Ethylene-glycol dimethacrylate (EGDM, Merck), Triton X-100 (Merck) was used as the cross-linking agent and the surfactant, respectively. Tert-butyl hydroperoxide ($C_4H_{10}O_2$), ferrous sulfate ($FeSO_4{\cdot}7H_2O$), ammonium persulfate ($(NH_4)_2S_2O_8$), and sodium thiosulfate ($Na_2S_2O_7$) were used as the initiators, which were obtained from Merck Company for PMMA capsules. All materials were in analytical grade and were used without any further purification.

2.2. Preparation of PCM composite

Synthesis of composite involves two stages. In the first stage, microencapsulated stearic acid was prepared. In the second stage, prepared microcapsules were mixed into polymer matrix with solution casting method for preparation of composite.

2.2.1. Microencapsulation of stearic acid

Two different microencapsulation methods for stearic acid were used. For capsules with PMMA shell emulsion polymerization and for SiO_2 shell in situ emulsion interfacial hydrolysis and polycondensation were used in the synthesis [10,19]. The steps of the synthesis are given below:

- Emulsion polymerization:
  1. Homogeneous oil-in-water emulsion was prepared for PMMA capsules. Stearic acid, monomer (MMA), EGDM and Triton X-100 were stirred in distilled water at a speed of 3000 rpm and 70 °C for 1 h for obtaining the emulsion phase.
  2. Polymerization reaction started by using initiator agents at 65 °C for 4 h.
  3. Microcapsules with PMMA shells were filtered out and washed with distilled water.
  4. Capsules were dried in a vacuum oven at 40 °C for 1 day.

- In situ emulsion interfacial hydrolysis and polycondensation:
  1. Stearic acid mixture is dissolved in ethanol by using CTAB and n-amyl alcohol to obtain oil /water emulsion.
  2. TEOS was added drop by drop into emulsions and mixture was stirred at a speed of 1000 rpm at 60 °C for 2 h.
  3. The hydrolysis step and polycondensation reactions were initiated by ammonia solution at 60 °C.
  4. Microcapsules with SiO_2 were washed, filtered out and dried in a vacuum oven at 40 °C for 2 days.

2.2.2. Preparation of composite

Solution casting method was used in preparing the composites. First, PMMA sheets were dissolved in ethanol to be used as the matrix