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Comparison of phase change slurries: Physicochemical and thermal properties

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ABSTRACT

Phase change slurries (PCS) consist on a carrier fluid binary system, where water is mostly used as continuous phase and micro-encapsulated phase change materials (MPCM) are used as dispersed phase. PCS are used in Thermal Energy Storage (TES) for building applications, combining the latent heat capacity of the MPCM with the sensible heat capacity of the carrier fluid, and at the same time giving the PCM pumpable properties. In this study, two PCS samples are compared and characterized, the commercial Micronal® DS 5007 X from BASF and a laboratory made PCS28. Thereby, in this paper thermal stability is studied by using thermogravimetrical analysis (TGA) and the main components of the MPCM have been studied using Fourier transformed infrared spectroscopy (FT-IR). Moreover, TGA coupled with FT-IR is used to study deeply the thermal decompositions of the PCS microcapsules and products derived thereof. Finally, differential scanning calorimetry (DSC) is performed to study the melting enthalpy and the melting temperature range of the phase change material (PCM). This paper concludes that both types of PCS have good potential from thermal energy storage purposes such as solar space heating applications.

1. Introduction

Phase Change Materials (PCM) absorb energy during the heating process and release the energy to the environment during the cooling process. One of the biggest drawbacks of the PCM incorporation for technical used is due to the liquid migration (leakage). Accordingly, microcapsules were thought to solve this problem. Microencapsulated Phase Change Materials (MPCM) are composed by a PCM as a core [1] and a polymer or an inorganic wall used as shell [2]. They are micro-containers with a hydrophobic core material and a hard shell which accept volume changes, maintaining the shape to conserve the form and avoid the PCM leakage when the phase change occurs. MPCM attribute thermoregulatory properties to materials [3] and they must be enclosed in thin and resistant polymer shells for changing solid to liquid phase change and back again within the shells.

Organic PCM have been proposed as one of the most significant thermal energy storage materials [4–6] because of their advantageous thermal and heat transfer characteristics [7]. Moreover, PMMA is also a widely used polymer as a shell [8–12]. Nevertheless, the PCM which is mainly used and studied is *n*-octadecane [13–16]. This PCM is commonly encapsulated with melamine-formaldehyde shell [7,17–19], although there are a lot of PCM possibilities as a core, and materials as a shell [20,21]. It is known that the physicochemical properties of all type of microcapsules after several thermal cycles change [22], and these changes are attributed to a partial degradation of the microcapsules by breakage [23].

Encapsulating PCM in a firm substance with small enough diameter to be suspended in a liquid (partially melting and

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solidifying slurries) can be done with high energy densities and heat transfer rates [24]. Phase change slurries (PCS) consist on a carried fluid binary system (water is mostly used as a continuous phase) and MPCM (as a dispersed phase) [25], and may be used in active or passive systems [26–28], having several applications in different fields [29] such as heating [30], air-conditioning [31] and ventilation [32], refrigeration [33] and heat exchangers, most of them in buildings [34–38].

In this study, an evaluation between two PCS able to be used for thermal energy storage (TES) in buildings was performed. The main objective is the characterization and the comparison of two different PCS, a commercial one and a laboratory made one. The most important reason to compare two PCS samples with different types of microcapsules is based on deciding the best candidate to be used in a TES field for active systems in building applications. Besides, as novelty, two different PCS sources (commercial and laboratory made) were compared to ensure that the obtained thermal properties for both samples are similar and good enough to choose both as possible samples to apply in an active system. This paper includes thermophysical and chemical properties of the two studied slurries, while other properties will be covered in a second paper [39]. It was evaluated different techniques to compare them physicochemically and thermally. Thermogravimetrical analysis (TGA) and differential scanning calorimetry (DSC) were used to measure the thermophysical properties and the thermal stability of the PCS under study. Furthermore, to study the composition of the polymer used as the shell of the microcapsules it was performed a Fourier transform infrared (FT-IR). Besides, the characterization of the chemical functionality for the volatile emissions during the decomposition of the PCS microcapsules was studied with TGA coupled with FT-IR.

2. Materials and methods

2.1. Materials

Micronal® DS 5007 X from BASF company is a microencapsulated slurry sample which is used in active systems and composed of an acrylic shell and *n*-octadecane as PCM with an average size of the microcapsules is around 7.5 μm. The other sample is a laboratory suspension of microcapsules prepared at the University of Ljubljana (Slovenia) named PCS28 based on analysis and experimental optimization of in situ polymerisation technology composed of melamine-formaldehyde (MF) as a shell and *n*-octadecane as PCM, and with an average size of 6.6 μm. Working temperatures for both samples are around 24–28 °C, considered close to the indoor comfort temperature in buildings.

2.2. Methods

2.2.1. Fourier transform infrared spectroscopy (FT-IR)

Chemical characterization of PCS shell composition was carried out using FT-IR spectroscopy. A Spectrum Two™ from Perkin Elmer supported by Dynascan™ interferometer and OpticsGuard™ technology was used to perform the analyses. This equipment can measure substances at liquid and solid state, and it was optimized by a wavelength range between 4000 cm^{-1} and 350 cm^{-1} and its standard spectral resolution is 0.5 cm^{-1}.

2.2.2. Thermogravimetrical analysis (TGA)

The thermal stability of the samples under study was evaluated with a Simultaneous SDTQ600 from TA Instruments under nitrogen flow. The heating rate applied was 0.5 K min^{-1} between 25 and 30 °C. Then, the temperature was increased applying 1 K min^{-1} heating rate from 30 to 100 °C. The last heating ramp was using 5 K min^{-1} heating rate from 100 to 600 °C. Sample mass used was around 38 mg for both samples.

2.2.3. TGA coupled with FT-IR

The TGA coupled with IR was performed in order to characterize the chemical functionality of volatile emissions during the decomposition of the microcapsules. The temperature range used to perform the evaluation of the microcapsules degradation was between 25 °C and 250 °C applying 10 °C min^{-1} heating rate. All measurements were performed in alumina vessels (90 μL) under 50 mL min^{-1} flow rate of N_2.

2.2.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to assess the melting range, melting enthalpy, as well as thermal stability of compounds [40–42]. The analyses were carried out using a DS 822e by Mettler Toledo at 0.5 K min^{-1} heating/cooling rate between 10 and 45 °C under constant 80 mL min^{-1} flow of N_2. Furthermore, crucibles used were 40 μL closed aluminium.

3. Results and discussion

3.1. Fourier transformed infrared spectroscopy (FTIR)

3.1.1. Micronal® DS 5007 X

The spectrum of Micronal® DS 5007 X is shown in Fig. 1. In this figure, it is shown the spectra of wet and dried sample, just to evaluate the suspension, comparing both spectra. Hence, the sample was dried at 35 °C during 24 h in an oven to obtain the ratio microcapsules: water, being 1:2.4. The broad intense peak in Fig. 1 at 3368.9 cm^{-1} corresponds to the aqueous suspension of the microcapsules. Then, the sharp intense peaks at 2921.0 cm^{-1} and 2852.0 cm^{-1} are due to the presence of the aliphatic C–H stretching vibration. The two peaks related to the presence of ester carbonyl group stretching vibration are in 1729.5 cm^{-1} for the dried sample and 1646.0 cm^{-1} for the slurry one. This wavenumber difference may be attributed to two possible reasons. The first one ascribed to the hydrogen bounding with the presence of the carbonyl group enfeebles the molecule producing a peak at less frequency. The second probable cause of this displacement may be assigned to the presence of monomers in the slurry, and when the air dried process is achieved, these monomers are evaporated causing a displacement of the carbonyl peak at higher frequencies. Besides, the peak at 1466.6 cm^{-1} was associated to the C–H bending vibration. The broad peak ranging at 1123.5 cm^{-1} is explained owing to the C–O

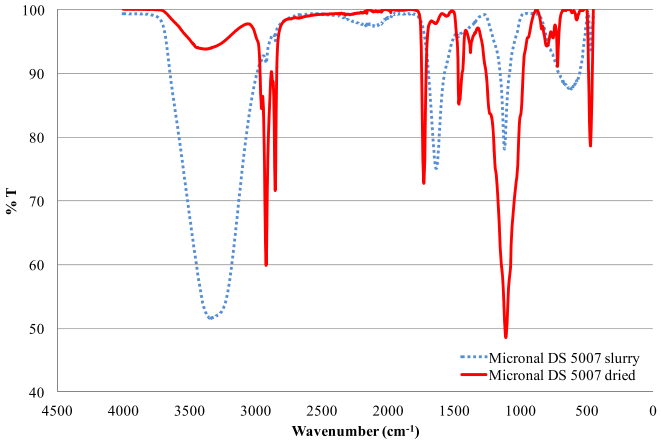

Fig. 1. FT-IR spectrum of Micronal® DS 5007 X in PCS form and dried form.