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Mechanical response evaluation of microcapsules from different slurries

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ABSTRACT

Thermal energy storage (TES) is one method to accumulate thermal energy. In TES, latent heat storage using phase change materials (PCM) has attracted a lot of interest, recently. Phase change slurries (PCS) consist on a carrier fluid binary system composed of water as the continuous phase and micro-encapsulated PCM as the dispersed phase. In this paper, two PCS to be used for TES in buildings were studied: Micronal® DS 5007 X, from BASF company, and PCS28, a laboratory made sample. Both samples were characterized using particle size distribution and scanning electron microscopy, to observe the regular spherical microcapsules, the surface morphology, and the wall shell thickness of the microcapsules. Atomic force microscopy was used to analyze the force needed to break the PCS microcapsules, a critical parameter when the PCS are to be used in active pumpable systems, and also to evaluate the effective Young's modulus. Both samples were studied with the microcapsules broken and unbroken. The physicochemical and thermal properties were reported in a previous paper, and it can be concluded that both are proper candidates to be used in TES building heating and cooling applications, but the acrylic shell microcapsules present better breakage resistance to be used in active systems.

1. Introduction

Phase Change Materials (PCM) are well known in Thermal Energy Storage (TES) because of their capacity to absorb and slowly release the latent heat involved in the phase change process [1], as well as the ability to store a large amount of energy in relatively small volumes. TES with PCM achieves energy conservation in buildings with thermal comfort [2]. Energy storage is very important where the energy source is intermittent, as in solar energy field, and it can decrease the time between energy supply and energy demand. For this reason, energy storage is essential in energy conservation issues. There are some reported methods to include PCM in building walls [3] such as with impregnation. There is also in the literature some studies [4,5] exposing the introduction of PCM in constructive materials [6], such as gypsum [7,8], concrete [9], wood [10], etc. As there is leakage when mixing PCM with building materials, PCM has to be encapsulated for technical use and microcapsules were considered to address this issue [11]. Microencapsulated Phase Change Materials (MPCM) [12–14] are small vessels with a hydrophobic core material and a hard covering that accepts size alterations, maintains its shape and avoids corrosion problems. MPCM temperature remains unchanged during the heat absorption/release process and these can be applied in passive storage systems such as component in buildings envelopes [15], as well as, in sandwich panels [16]. MPCM can also be added to a fluid in order to be transported or pumped in an active storage system. They can be used in active storage systems such as pumping slurries [17–19], which are microcapsules suspensions or emulsions [20–22] using a dispersant agent in order to stabilize the distribution of the microcapsules in order to enhance its thermal behavior. These slurries are known as Phase Change Slurries (PCS).

Different core/shell combinations that have been studied take into account the external polymer and the PCM nature (inorganic or

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organic) [23,24]. In this particular case, the core samples are saturated hydrocarbon paraffin wax as the PCM. In this paper, two samples were characterized: Micronal® DS 5007 X provided by BASF® and a laboratory prepared suspension of microcapsules based on analysis and experimental optimization of in situ polymerisation technology for its preparation from scientific and patent literature [25]. This comparison aspect between both types of MPCM is very important as it is wanted to identify the best MPCM laboratory manufactured, or at least, the most similar commercial MPCM in a laboratory preparation. The two samples have melting temperatures around 24–28 °C that are considered close to the indoor comfort temperature in buildings [26]. The physicochemical and thermal properties were evaluated in a previous paper [27].

The main objective of this study is to compare the physical and mechanical behavior of two PCS samples able to be used in active systems in order to discern the most proper microcapsules for using them in a TES media for heating and cooling applications.

2. Materials and methods

2.1. Materials

Two types of PCS were studied in this paper. Micronal® DS 5007 X which has an acrylate polymer as a shell in a slurry medium, with a proportion of 2:5, (slurry + dispersant):water, and paraffin wax in the core. The other sample is PCS28 which is a laboratory made sample, and the shell was prepared with a melamine-formaldehyde (MF) resin. The paraffin wax inside the microcapsules PCS28 is *n*-octadecane. The phase change temperature of PCS28 is around 28 °C and the proportional relation is 1:2, (slurry + dispersant):water [27]. The main reason for choosing these two types of MPCM was to compare the different mechanical behavior related to the MPCM polymeric shell (acrylic or MF) and to decide which shell is better to microencapsulate the PCM.

2.2. Methodology

The size of the microcapsules was studied analyzing the Particle Size Distribution (PSD). Also, by using Scanning Electron Microscopy (SEM) the dimensions of the microcapsules can be measured. Finally, they were analyzed by Atomic Force Microscopy (AFM) [12,28,29], which is commonly used to examine the nano- or microscale properties of the surface and in close proximity surface regions. AFM is a powerful tool for evaluating polymeric materials on a sub-micrometer scale because it admits lesser forces and higher upper resolutions than nanoindenters [30]. In this study, it was identified the maximum force that can be applied on the top of microcapsules (dried PCS) to break them, analyzing the typical deflection-indentation curves. Besides, it was calculated the Effective Young's modulus (E) distribution in a specific region of each microsphere for the two studied samples. The tests were done at 23 °C and 45 °C for both samples, which is with the core material in solid and liquid phase.

2.2.1. Particle size measurements and scanning electron microscopy

The Particle Size Distribution (PSD) was analyzed using a Beckman Coulter® LSTM 13 320 with Universal Liquid Module. The results were analyzed applying the Mie mathematical model, because it fits well for homogenous, spherical, and transparent or opaque particles with diameter below 50 μm. Afterwards, each sample was circulated separately a total of 10 min in order to estimate sample volume changes, to evaluate possible MPCM degradation or MPCM accumulation.

Samples morphologies were observed by Scanning Electron Microscopy (SEM) using a Jeol JSM-6510 instrument under vacuum atmosphere, high voltage (15 kV), and images obtained by secondary electrons. Furthermore, the microcapsules were broken in purpose applying a compressive strength to study the wall shell thickness, which is directly related with the mechanical properties of the microcapsules.

2.2.2. Atomic force microscopy (AFM)

The AFM equipment used to evaluate the mechanical properties of microcapsules (two dried PCS samples) was Multimode 8 and Nanoscope V electronics from Bruker with a Peak Force Quantitative Nanomechanics mode (QNM). The diamond probe used was from Bruker, with a 388 nN nm^{-1} spring constant. Therefore, the peak force amplitude was 300 nm, the peak force frequency was 0.5 kHz, and finally, the maximum vertical force was 500 nN. One aliquot of each PCS was diluted in water in a small beaker. Then, 50 μl of this solution were poured on a freshly cleaved mica surface under a N_2 stream until complete dryness. The samples were observed and mechanically tested without further treatment.

The goal of the first assay is to quantify the highest vertical force that the samples were able to resist after creating a permanent elastic deformation executing a force. It was obtained microcapsules images at 23 °C, and after that, it was applied a force on the top of the microcapsule until breaking the shell to perform a force curve. Subsequently, the particle was imaged again. This process was repeated three times at 23 °C for each microcapsule (PCM in solid state); following that, PCS microcapsules temperature was raised to 45 °C (PCM in liquid state), and the whole process was repeated again three times for each sample. A total of 18 tests were performed. The second set of experiments consists on testing the stiffness and calculate the Effective Young's modulus (E) of the dried PCS microcapsules at the two different temperatures performing two repetitions at 23 °C and 45 °C (PCM in solid and liquid state, respectively). In all the cases, the temperature was measured with a micro-thermocouple type-K in contact with the sample holder.

3. Results and discussion

3.1. Particle size measurements

3.1.1. Particle size distribution (PSD)

PSD was evaluated following the Mie mathematic model, and Table 1 lists the main results obtained. The parameter d_{10} means that 10% of the volume of the particles had a diameter below the given value; for d_{50}, 50% of the particles had a diameter below the given value, and finally, 90% of particles had a size volume below d_{90}.

At the light of the results, PCS28 presents lower values than Micronal® DS 5007X. Thereby, the repeatability over the measurements is shown in Fig. 1 for Micronal® DS 5007 X. The profile curves obtained are almost identical, showing a quite narrow distribution, being assured the repeatability between the different experiments.

The evolution over time for PCS28 results is plotted in Fig. 2. This graph illustrates that at the beginning of the experiment there was

Table 1
Particle Size Distribution results from microcapsules under study.

	Micronal® DS 5007 X	PCS28
PSD d_{10} (μm)	2.79	0.14
PSD d_{50} (μm)	4.88	3.46
PSD d_{90} (μm)	7.48	6.62
PSD mean (μm)	4.88	3.14
Standard deviation (μm)	2.09	2.62