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Research Paper

Thermogravimetric study of a Phase Change Slurry: Effect of variable conditions

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HIGHLIGHTS

- Dry or wet PCS present differences in their thermal behavior.
- The optimum conditions of dry PCS were determined by TGA.
- Type of atmosphere and heating rate were the variables under consideration.
- T_{peak} can be accurately determined at 1 °C·min^{-1} in N_2.
- Fusion/latent heat can be best determined at 10 °C·min^{-1}.

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ABSTRACT

Microcapsules containing Phase Change Materials (MPCM) are widely used for passive systems in energy storage. When MPCM are mixed with a carrier fluid, Phase Change Slurries (PCS) are used for heat transfer fluids in active systems or heat transport systems. The thermal behavior of PCS can be measured as dry or wet basis, resulting in important differences in weight losses. This study explores the optimum conditions for analyzing the thermal behavior of dried PCS by thermogravimetric analysis (TGA) varying the parameter conditions for obtaining peak temperature and heat flow (latent heat). The factors that were taken into account were the atmosphere of study (air and nitrogen) and the heating rate (0.5, 1, 5, and 10 °C·min^{-1}). The best conditions to determine peak temperature are at 1 °C·min^{-1} and in N_2 atmosphere, whereas the decomposition fusion/latent heat of the sample is improved at higher heating velocities towards 10 °C·min^{-1}.

1. Introduction

Energy efficiency in buildings is nowadays an important objective to take into account for energy policy at an international level [1]. Thermal Energy Storage (TES) in buildings includes both the storage as sensible heat and latent heat. The former is performed by changing the temperature of the storage material (when it is heated or when the heat is removed from it) and is directly related with its specific heat capacity. The latter involves the heat release during the phase change of a material and it requires smaller volumes for storing the same amount of energy than the first case [2]. In this sense, Phase Change Materials (PCM) have attracted increasing attention because of their potential use in heat transfer and TES applications due to their high energy storage density over a small temperature range [3–5]. PCM are substances with a high heat of fusion that melt and solidify at a certain temperature and are capable of storing and releasing large amounts of energy by absorbing or releasing heat when the material changes from solid to liquid or liquid to solid, respectively [6,7]. These materials are well known in many fields, such as textiles [8], packaging, food [9,10], and buildings [11,12].

The major concern in PCM applications is the fixation of the liquid phase when the PCM is melted for avoiding its leakage and migration. In order to overcome this problem, PCM can be microencapsulated in a polymeric shell of micron sized particles to form Microencapsulated Phase Change Material (MPCM). There are other reasons for encapsulating PCM; in some cases it allows minimizing leaching or volatilization risks [13–15] while preventing agglomeration of the melted paraffin wax when PCM is used for heat storage. Hence, it is important to develop a MPCM shell that is stable enough to support rough conditions [16–19]. For instance, MPCM are used in piping systems when they are mixed with a

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carrier fluid, commonly water [20] or other organic compounds such as glycerol [21]. These mixtures are called Phase Change Slurries (PCS) and are used for heat transfer fluids in active systems or heat transport systems [22,23]. They allow enhancing the energy efficiency while also reducing the amount of thermal fluids [24]. The most employed shell material in a MPCM or PCS is methacrylate [25,26] while *n*-octadecane is widely used as PCM [27,28]. In order to evaluate the capacity of a PCS to withstand hard environments (e.g. pumping conditions), a test rig can be performed in which the sample is subjected to different thermal cycling as described by Gschwander et al. [29].

Thermal properties of PCS can be determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The former measures the stored heat while the latter consists of the measurement of the amount and rate of mass loss of a material when it is heated at a given rate under a controlled atmosphere. By this manner, a TGA curve of mass loss vs. heating temperature can be obtained. Thus, a material that exhibits loss or gain of mass due to thermal decomposition, oxidation or dehydration, can be analyzed by this technique [30].

Different TGA curves recorded at different heating rates can provide accurate information regarding the mechanism and the kinetics of a polymeric degradation process [31]. Thermal stability has been used in MPCM characterization, such as in Tyagi et al. [32], Ma et al. [33], Qiu et al. [34] studies. Su et al. [35], Zhang et al. [16], and Li et al. [36] evaluated MPCM degradation by using TGA curves. However, in the case of PCS, TGA has been scarcely employed [37]. Taking into account the importance of thermal analysis in characterizing the PCS for properly describing a sample [38], the main goal of this study is to define and explore the best parameters and optimum conditions for analyzing the decomposition of PCS using TGA and DSC. The factors that were taken into account were the state of the sample (liquid and air-dried), the atmosphere, and several heating rates. By this manner, a comprehensive characterization and evaluation of the thermal properties may facilitate the understanding of PCS performance.

2. Experimental procedure

2.1. Materials

The sample under study was Micronal® DS 5045 X from BASF (M). It consists of a suspension made of a highly cross linked methyl methacrylate (MMA) shell and *n*-octadecane as core PCM, with a phase change between 24 and 28 °C. The original sample was tested in liquid state and after being air-dried, MD. Drying took place for 24 h at room temperature to avoid any thermal degradation. These drying conditions were chosen as reported by Giro-Paloma et al. [39].

2.2. Methods

2.2.1. Physico-chemical characterization

In order to characterize the shape and size after the thermal reliability process of M sample, Scanning Electron Microscopy (SEM) JEOL JSM-6510 was used. Unlike conventional methods, the preparation of the sample required using N_2 as freezing system to solidify the PCS. Hence, a Cryo Unit GATAN accessory (Alto 1000 model) for observing the size and shape of the sample was used. Due to the nature of the sample a conductive carbon coating was also required. The images were obtained by secondary electrons (SE) at 10 kV. Moreover, Fourier-Transformed Infrared spectroscopy (FT-IR) using a FT-IR Spectrum Two™ from Perkin Elmer (400–4000 cm^{-1} working range) with Attenuated Total Reflectance (ATR) was used to chemically characterized the microcapsules shell.

2.2.2. Thermal analysis

Thermogravimetrical analysis (TGA) was performed by means of a SDT Q600 from TA Instruments under N_2 and air atmosphere. The scanning rates were 0.5, 1, 5 and 10 $°C·min^{-1}$ for both atmospheres (50 $mL·min^{-1}$) in a temperature range between 20 °C (T_0) and 600 °C (T_f). The preparation of the solid sample prior TGA was always performed in the same manner and the amount was kept in a mass range of 10.0 ± 0.5 mg using alumina 90 μL crucibles. The differences observed in the TGA studies were evaluated by assessing the weight loss (%), the Derivative Thermogravimetry (DTG), and the simultaneous Differential Scanning Calorimetry (s-DSC) signal obtained from the Differential Temperature Analysis (DTA).

Close to melting interval temperatures of PCM (*n*-octadecane), a DSC analysis was performed to obtain complementary and more accurate information using a Mettler-Toledo DSC-30 calorimeter. The experimental conditions consisted of using aluminum crucibles of 40 μL in volume in a dry N_2 atmosphere with a 50 $mL·min^{-1}$ flow rate at 0.5, 1, 5, and 10 $°C·min^{-1}$.

3. Results and discussion

3.1. Physico-chemical characterization

Fig. 1 shows the size and shape of M sample after freezing with a cryogenic N_2 system. As it shows, microcapsules are uniformly distributed and embedded in the water matrix. The size of the

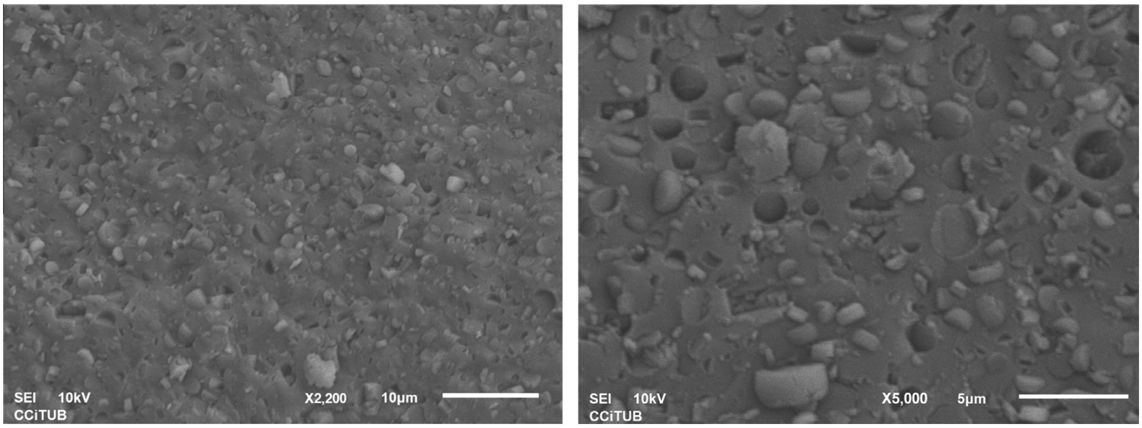

Fig. 1. SEM micrographies for M sample, Micronal® DS 5045 X (magnification: 2200× left and 5500× right).