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

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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 ºC and 70 ºC, 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.

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 contains 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 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 may be 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; Giro-Paloma, *et al.*, 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

MCPMs 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 ($FeSO_4·7H_2O$) (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 MPCMs 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 minutes at 40 ℃. 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 ℃. The solution was stirred for 5 hours and then 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 hours at room conditions.

2.3 Characterization of microcapsules

2.3.1 Scanning Electron Microscopy (SEM)

The morphology of the samples was characterized using an environmental Scanning Electron Microscopy (Zeiss Evo 50, Zeiss, UK). The samples were fixed on the sample holder using a double-sided tape and then the particle size and the morphology of the samples were observed. The conditions were low vacuum and high voltage (15 kV), obtaining the image by secondary electrons.

2.3.2 Particle Size Distribution

The average particle size and size distribution of the micro-nanoPCMs were determined using a Nano Zetasizer (Malvern Instruments Ltd., UK). Measurements were carried out at 25 ℃. To avoid multiple scattering effects, firstly, MPCM was mixed with water (1:100) and stirred 30 minutes in ultrasonic bath. The mean particles diameters were calculated from the average of three measurements.

2.3.3 Fourier-Transformed Infrared Spectroscopy (FT-IR)

FT-IR spectroscopy is a potent technique to identify functional groups in organic polymers or compounds. The chemical characterization of the MPCM shells was performed by a Fourier

Transformed Infrared (FT-IR) spectroscopy. It was used through FT-IR Spectrum Two™ from Perkin Elmer using a working range from 400 to 4000 cm^{-1}.

2.3.4 Differential Scanning Calorimeter (DSC)

The thermal properties melting and solidification temperature and the melting/solidification enthalpy of the two types of microcapsules containing PCM were evaluated with a DSC (Perkin Elmer Diamond) with a heating-cooling rate of 5 ºC·min^{-1} in the range of 10 - 80 ºC. During DSC analysis, about 5 mg of sample was used. This technique shows the melting temperature (T_m) and solidification temperature (T_s) of the sample and the enthalpy value for each process (melting and solidification, H_m and H_s respectively) which is equivalent to the area under the curve. The determination of the phase change material content in the MPCMs followed from the formula:

$$PCM\ (\%) = {^{\Delta H_{microPCM}}}/_{\Delta H_{corePCM}} \cdot 100 \qquad\qquad \text{Equation 1}$$

2.3.5 Thermogravimetrical Analysis (TGA)

The thermal stability of the microcapsules was evaluated with a Simultaneous SDTQ600 TA Instruments under N_2 and air atmosphere. The scanning rate was 10 ºC·min^{-1} in the temperature range between 25 and 600 ºC for 5.4420 mg of sample for both samples.

2.3.6 Atomic Force Microscopy (AFM)

Samples were suspended in ethanol, and 50 μl of suspension was poured on freshly cleaved mica and gently dried with a nitrogen stream. Then, sample was imaged in air. The experiments were performed in air using a Peak Force Quantitative NanoMechanics mode (QNM) with a system Multimode 8, Nanoscope V electronics. The AFM probe was a diamond MDNISP one, with a nominal spring constant: 388 nN·nm^{-1}. The sensitivity was 68.2 nm·V^{-1} with a set point between 400 and 550 nN. Moreover, the working conditions for the peak force amplitude were 150 nm, and the DMT Modulus limit 1 TPa. Both samples A and B were more soluble in ethanol than water. In order to break the aggregates, the samples were sonicated until the solution was homogeneous. Capsules A was tested at 25 ºC and 50 ºC, and Capsules B at 25 ºC and 70 ºC to evaluate the different behavior of the MPCM when the PCM is solid (around 25 ºC) and liquid (up to 43 ºC for A and up to 63 ºC for B). It was measured the maximum force that is needed to apply at the top of a capsule to break it, as well as a Young's modulus map and Young's modulus histogram for some capsules at different temperatures.

161   Individual indentation tests were made in diverse particles of the upper flat-top part of the
162   capsules in order to avoid tip slippage due to sample curvature. For all the force *vs.* Z graph
163   representations, the blue line corresponds to tip sample approach process and the red one corresponds
164   to the tip retraction from the sample. The first region corresponds to the no contact between the tip
165   and the sample. Then, when the tip touches the surface of the sample, the cantilever applies an
166   increasing force on the sample, deforming it elastically. Finally, the retraction of the AFM probe is
167   represented by the red line. It is essential to notice that a three-sided dent in the upper site of the
168   particle can be observed when it is plastically deformed by the AFM probe. Also, it has to be
169   remarkable that usually the general profile of the particles seem to be triangular due to the pyramidal
170   form of the AFM tip, and not due to the real profile of the particle. To calculate the force F, the
171   following equation is used:

172
$$F = k \cdot \Delta_z \hspace{4cm} \text{Equation 2}$$

173   where *k* is the AFM probe, and Δ_z is cantilever deflection in the z axis. Besides, the cantilever
174   deflection is expressed in Equation 3 as:

175
$$\Delta_z = \frac{\Delta V}{S} \hspace{4cm} \text{Equation 3}$$

176   where ΔV is the increment in photodetector vertical signal as the tip contacts the sample. The S value
177   is the sensitivity, which is the slope of the contact region of a force curve performed on a rigid
178   sample. It is also needed to take into account the sample penetration (δ) because of the applied force
179   value:

180
$$\delta = z - \Delta_z \hspace{4cm} \text{Equation 4}$$

181   where *z* represents the piezo-scanner displacement in the axis perpendicular to the sample plane. The
182   F vs. z graphs achieved at a certain force value, and it was evaluated by the Hertz model in the elastic
183   region with Equation 5:

184
$$F = \left(\frac{3}{4} \cdot E_{eff} \cdot R^{1/2} \right) \cdot \delta^{3/2} \hspace{3cm} \text{Equation 5}$$

185   Besides, the Young Modulus is considered following Equation 6:

186
$$\frac{1}{E_{eff}} = \left[\frac{(1 - v^2)}{E} \right] + \left[\frac{(1 - v_i^2)}{E_i} \right] \hspace{2cm} \text{Equation 6}$$

187   and Young Modulus (E_{eff}) value can be obtained using Equation 6, taking into consideration that v is
188   the Poisson ratio with 0.33 as a value. Furthermore, the subindex *i* corresponds to the mechanical
189   properties of the AFM probe, SiO_2. The values for the E_i and v_i are 76 GPa (Namazu and Isono, 2003)
190   and 0.17 respectively (Oliver and Pharr, 1992).

191

3. Results and discussion

3.1 Scanning Electron Microscopy (SEM)

Figure 1 shows SEM micrographs of the PScEA shell microcapsules obtained using emulsion co-polymerization technique. As it can be seen, microparticles almost have a spherical structure and the microcapsule stability after the coating process was confirmed.

Figure 1.

3.2 Particle Size and Distribution Analysis (PSD)

Particle sizes distributions of sample A and sample B are shown in Figure 2. Mean particle diameters for sample A and sample B were 165 and 265 nm, respectively. Smaller and uniform microcapsules were obtained with PScEA + paraffin.

Figure 2.

3.3 Fourier-Transformed Infrared Spectroscopy

The FTIR spectra of core material, shell material and MPCM are shown in Figure 3 and Figure 4. Each of the characteristic peaks belonging to the core material preserves itself after microencapsulation. These results in Transmittance (%) vs. Wavenumber (cm^{-1}) confirm that the encapsulation of paraffin and palmitic acid could be prepared within PScEA.

Figure 3.

Figure 4.

In general, FT-IR spectroscopy is used to describe the microcapsules shell structure. In this work, FT-IR shell spectra of the two samples under study were given in Figure 5 to verify the presence of PScEA in both MPCM.

220

221   Figure 5.

222

223   **3.4 Differential Scanning Calorimeter (DSC)**

224   Figure 6 provides the curves of the DSC samples containing 32.1 wt.% paraffin and 47.8 wt.%

225   palmitic acid at 5 ℃·min^{-1} scanning rate. Moreover, in Table 1 is shown the DSC numerical results for

226   capsule A PScEA with Paraffin 42 - 44 in the core, and capsule B PScEA with palmitic acid as the

227   PCM. It is indicated the onset melting temperature (T_{om}) of the DSC curve, the melting peak

228   temperature (T_{pm}), the endset melting tempertaure (T_{em}), the melting enthalpy (H_m), onset the

229   crystallazing temperature (T_{oc}), the cristallazing peak temperature (T_{pc}), the endset cristallizing

230   temperature (T_{ec}), and finally the cristallization enthaply (H_c). Figure 6a and Table **1** indicate that the

231   peak temperatures of melting and freezing were determined to be 44.23 ℃ and 36.84 ℃ for non-

232   encapsulated A and 42.39 ℃ and 37.41 ℃ for capsule A. Furthermore, Figure 6b and Table 1 indicate

233   that the peak temperatures of melting and freezing were determined to be 64.57 ℃ and 57.00 ℃ for

234   non-encapsulated B and 62.66 ℃ and 56.22 ℃ for capsule B. It is clear that, there is no significant

235   temperature change observed after microencapsulation process. It was determined that, the

236   microcapsules obtained in this study, capsule A and capsule B, are very suitable for thermal energy

237   storage applications. Moreover, the enthalpy values are 49 J·g^{-1} for capsule A and 97 J·g^{-1} for capsule

238   B, which are very good values according to the reported data for the studied temperature ranges, thus

239   being a good alternative for solar thermal applications.

240

241   Figure 6.

242

243   Table 1.

244

245   **3.5 Thermogravimetrical Analysis (TGA)**

246   Thermal stabilities of the MPCM samples were evaluated by the TGA analysis. The two type of

247   capsules showed two-step decomposition profiles (Figure 7). The first-step weight loss of the

248   microcapsules is due to the degradation of the core materials (paraffin wax and palmitic acid) and the

249   second-step decomposition results from the degradation of the PScEA copolymer shell. Over 470 °C

250   the microcapsules decomposed completely. For capsule A the first weight loss corresponds to the

decomposition of the PCM paraffin wax around 200 ºC and the associated loss is around a 40 % of the sample. The second mass loss involves approximatelly the 60 % of the sample mass with an onset temperature around 275 ºC, being completely decomposed at 430 ºC. Moreover, it can be observed the thermal degradation for the capsule B, where the first weight loss is due to the palmitic acid decomposition, representing almost the 50 % by weight, and the second one fits with the shell, being completeley decomposed at 450 ºC. From these results, capsule B with higher melting point is more stable than capsule A.

Figure 7.

3.6 Atomic Force Microscopy (AFM)

Considering one isolated capsule, and selecting a specific delimited area, it can be studied a Young´s modulus map and the histogram of the sample A at 25 ºC, as Figure 8 shows. The mean Young's modulus value for this specific region is 106 MPa.

Figure 8.

In Figure 9 is shown the vertical force (µN) *vs*. sample penetration (nm) curve obtained by processing the measurement of the cantilever deflection at 25 ºC. In view of all the equations and considerations explained previously, the average breakthrough force after three repetitions for sample A at 25 ºC is 3.9 µN. It can be noticed in b) point that there is a slight change in the slope curve, due to the breakage of the microcapsule shell.

Figure 9.

It is needed to increase the temperature up to 50 ºC to observe the mechanical differences. Around this value is reached the phase change temperature, so the PCM will be in liquid state.

It is seen in Figure 10 that the average Young's modulus histogram for the specific area delimited in the left image is 160 MPa. For this reason, it can be concluded that for sample A the Young´s

9

280 modulus value looks independent from temperature, because the values obtained at room temperature
281 and at 50 ºC are extremely small.

282

283 Figure 10.

284

285 Besides, in Figure 11 is shown that the sample A at 50 ºC has a maximum force before breaking
286 at 5.4 μN, which is almost the same than at room temperature.

287

288 Figure 11.

289

290 For sample A it can be concluded that the differences in temperature are not very significant,
291 because the results at both temperatures (25 ºC and 50 ºC) are quite similar for the Young's modulus
292 value and also for the maximum force that can be applied on the top of the microcapsules before
293 breaking them. For this reason, it can be concluded that this sample A is suitable for using it at both
294 temperatures without suffering any mechanical deformation. Otherwise, when sample B is studied, we
295 can observe some more evidence differences.

296 Then, in Figure 12 is evaluated the Young's modulus in the specific area delimited with the black
297 frame at 25 ºC for sample B. The result gives a mean value of 422 MPa.

298

299 Figure 12.

300

301 The typical graph of loading-unloading is shown in Figure 13 and denotes that for capsule B at
302 room temperature there is a breakthrough force of 17.3 μN.

303

304 Figure 13.

305

306 For capsule B case, it was decided to increase the temperature until 70 ºC due to the phase change
307 temperature of the PCM.

308   These microcapsules gives a result of 517 MPa at 70 ºC when it is evaluated its Young´s modulus,

309   as Figure 14 shows. Young´s modulus values for room temperature and 70 ºC are low, for this reason,

310   the difference between them is not representative; hence, it can be assumed that E values do not

311   change in front of the temperature.

312

313   Figure 14.

314

315   Besides, in Figure 15 it is shown the result for the maximum allowed force on the top of the

316   capsule B at 70 ºC. This value is around the 1.8 µN, ten times lower compared with 25 ºC due to the

317   experimental temperature. This result is really important because this sample can be damaged in an

318   easiest way than the capsule A at higher temperatures.

319

320   Figure 15.

321

322   **4. Conclusions**

323   In this research, paraffin and palmitic acid were microencapsulated with a Poly(stirene-co-

324   ethylacrylate) PScEA shell via an emulsion co-polymerization technique. SEM results confirm that

325   paraffin (capsule A) and palmitic acid (capsule B) encapsulated successfully in this study, and the

326   diameters for capsule A and capsule B were analyzed by PSD being 166 nm and 265 nm, respectively.

327   Besides, the encapsulated paraffin and palmitic acid can be considered to have good potential for

328   energy storage. Also, TGA results denoted a slightly higher thermal stability for sample B in the same

329   working conditions. The FTIR results proved that paraffin and palmitic acid encapsulated successfully

330   with a PScEA shell in this study. AFM results confirm that there are no differences in capsule A for

331   Young's modulus and force applied to break the microcapsule at different temperatures (25 ºC and 50

332   ºC) because the results are similar. Capsule B does not have the same mechanical behavior at 25 ºC

333   and 70 ºC, the force is ten times lower at 70 ºC comparing the results with those at 25 ºC although the

334   Young's modulus has a similar value.

335

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