

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 Thermogravimetric Analysis (TGA). Mechanical characterization of the prepared microcapsules was performed by using the Atomic Force Microscopy (AFM) as indenter. Experiments were performed at two different temperatures 25 °C and 70 °C, 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.

31 *Keywords:* Phase Change Material, Microencapsulated Phase Change Material, Atomic Force
32 Microscopy, Differential Scanning Calorimetry, Thermogravimetric analysis, Fourier Transformed
33 Infrared spectroscopy

34 1. Introduction

35 Phase Change Materials (PCM) are well known for Thermal Energy Storage (TES) applications
36 and are reported as a promising energy technology for improving the energy efficiency (Gil, *et al.*,
37 2010), hence different kind of PCM have been studied for different applications. To avoid the leakage
38 of the PCM and control the variation in the storage material volume as the phase change takes place,
39 the development of microencapsulated phase change materials (MPCM) has become an area of
40 interest (Tyagi *et al.*, 2011; Konuklu *et al.*, 2014; Jamekhorshid *et al.*, 2014; Zhang *et al.*, 2004; Zhao
41 and Zhang, 2011). MPCM are little containers made of polymeric shell and contains PCM inside
42 (Alkan *et al.*, 2009). There are three prerequisites for the microencapsulation process: the construction
43 of the shell involving the PCM, ensuring that no leakage and no impurities are incorporated in the
44 core/shell MPCM system. The second requirement is that the coating material thickness has to
45 achieve the efficiency of the MPCM. By this way, MPCM third specification is being resistant to
46 thermal and mechanical stresses. Besides, there are different methodologies to microencapsulate PCM
47 (Boh and Šumiga, 2008; Jyothi *et al.*, 2010; Sánchez *et al.*, 2008). Based on the mechanisms of
48 microcapsules formation, methodologies may be classified in chemical methods, physico-chemical
49 methods, and physical and mechanical methods.

50 There are several possibilities or combinations of shell and core materials as a MPCM. Typical
51 used shells are Poly(methyl methacrylate) (PMMA) (Alkan and Sari, 2008; Wang *et al.*, 2011) and
52 melamine formaldehyde (MF) (Özonur *et al.*, 2006), and the more usual PCM are paraffin (Sánchez-
53 Silva *et al.*, 2010) and particularly *n*-octadecane (Salunkhe and Shembekar, 2012; Zhang *et al.*, 2012).
54 Thus, there are a lot of recent studies with the preparation of MPCM made of PMMA and paraffin
55 wax (Wang *et al.*, 2012; Castellón *et al.*, 2010; Ma *et al.*, 2010), PMMA and *n*-octadecane (Giro-
56 Paloma, *et al.*, 2013; Giro-Paloma, *et al.*, 2014), MF and paraffin wax (Su *et al.*, 2012; Šumiga *et al.*,
57 2011), and finally MF and *n*-octadecane (Zhang and Wang, 2009). Although these two polymers are
58 the most popular ones due their characteristics, polystyrene (PS) is also a popular container used as a
59 shell in MPCM manufacturing. It can be mixed with different type of PCM, depending on the
60 application and in the comfort temperature. Borreguero *et al.* (2011) produced by suspension
61 polymerization technique microcapsules containing RT-27 and PS as a shell material. Although the
62 MPCM was obtained, they concluded that for this kind of PCM is much better a shell of PE-EVA
63 (polyethylene - ethyl vinyl acetate) because its thermal stability is better. Moreover, Sánchez *et al.*
64 (2010) synthesized by suspension like polymerization MPCM for textiles made PS as a shell and
65 paraffin wax as a core. Other authors used the same polymeric shell and changed the PCM obtaining

66 MCPMs to be used for Phase Change Slurries (PCS) and phase change emulsions, as Yang *et al.*
67 (2003), where they prepared and characterized microcapsules containing *n*-tetradecane for improving
68 the heat transfer ability and energy transport ability. Besides, Fang *et al.* (2008) studied
69 nanoencapsulated PCM with PS *n*-octadecane, as a shell and as PCM, respectively. Their conclusion
70 was that these capsules were successfully prepared by the ultrasonic assistant miniemulsion in-situ
71 polymerization. Also, Sánchez-Silva *et al.* (2010) studied the MPCM of styrene mixed with another
72 polymer in paraffin. The preparation of the microcapsules was done by suspension - like
73 polymerization, and the main conclusion for the styrene-methyl methacrylate with paraffin was that it
74 is impossible to microencapsulate the paraffin wax when the MMA/St is equal to 2.0. Also, styrene
75 can be copolymerized with other substances creating the ABS (Acrylonitrile-Styrene-Butadiene), AB
76 (Acrylonitrile-styrene copolymer), and the SBS (Styrene-butadiene-styrene). Examples of these are
77 the ones of Yang *et al.* (2009) and Kenisarin and Kenisarina (2012), respectively. The first one
78 prepared MPCM of ABS and AS with *n*-tetradecane in the core, remarking that their potential and
79 flexibility as a shell material. The SBS MPCM study includes microparticles with paraffin wax as a
80 core material and others with lauric acid.

81 In our literature survey, none reported preparation of paraffin and palmitic acid microcapsules
82 with Poly(styrene-co-ethylacrylate) (PScEA) shells. In this paper is reported the microencapsulation
83 and full characterization of paraffin and palmitic acid in PScEA shells by the emulsion co-
84 polymerization method to obtain micro-nanocapsules for low temperatures solar thermal applications
85 by Scanning Electron Microscopy (SEM), Particle Size Distribution (PSD), Fourier Transformed
86 Infrared Spectroscopy (FT-IR), Differential Scanning Calorimeter (DSC), Thermogravimetical
87 Analysis (TGA), Atomic Force Microscopy (AFM).

88

89 **2. Materials and methods**

90 **2.1 Materials**

91 Paraffin 42 - 44 and palmitic acid were used as core PCM. Styrene (> 99 %; Sigma Aldrich
92 Company, USA) and ethyl acrylate, C₅H₈O₂ (> 99 %; Merck, Germany) were used as a shell material;
93 ethylene glycol dimethacrylate (EGDMA), C₁₀H₁₄O₄ (Merck, Germany) was used as a crosslinking
94 agent and it was distilled before use. The initiator of ammonium peroxodisulfate (Merck, Germany)
95 and other analytical reagents tert-butylhydroperoxide (70 %; Merck, Germany), Triton X-100 (Merck,
96 Germany), iron (II) sulfate 7-hydrate (FeSO₄·7H₂O) (Panreac, Spain), and sodium thiosulfate
97 (Na₂S₂O₃) (Merck, Germany) were used without further purification.

98

99 **2.2 Preparation of microcapsules**

100 A typical emulsion polymerization process technique was used in the preparation of MPCMs with
101 PScEA shell. The emulsion co-polymerization method consists on mixing the polymer in an oiled
102 system, adding an emulsifier. An emulsification is needed to create a water/oil emulsion and to
103 generate a crosslinked system. Then, it will be needed the wash of the emulsion, to eliminate the oil,
104 creating isolated microcapsules. Firstly, 120 ml of deionized water, 1.60 g of Triton X100, 28 g of
105 core material were stirred for 30 minutes at 40 °C. Then 14 g of styrene, 14 g of ethyl acrylate, 8 g of
106 EGDMA, 1 ml of FeSO₄·7H₂O solution and 0.25 g of ammonium peroxodisulfate was stirred in a
107 beaker, then added to emulsion and stirring was continued at 1000 rpm. Then 0.25 g of Na₂O₃S₂, 1 ml
108 of tert-butylhydroperoxide was added to the emulsion and heated to 95 °C. The solution was stirred
109 for 5 hours and then it was cooled down to room temperature and washed with water five times.
110 Finally, the microcapsules were rinsed with deionized water, filtered and dried approximately 72
111 hours at room conditions.

112

113 **2.3 Characterization of microcapsules**

114 **2.3.1 Scanning Electron Microscopy (SEM)**

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

119

120 **2.3.2 Particle Size Distribution**

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

126

127 **2.3.3 Fourier-Transformed Infrared Spectroscopy (FT-IR)**

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

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

132

133 **2.3.4 Differential Scanning Calorimeter (DSC)**

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

$$141 \quad PCM (\%) = \frac{\Delta H_{microPCM}}{\Delta H_{corePCM}} \cdot 100 \quad \text{Equation 1}$$

142

143 **2.3.5 Thermogravimetric Analysis (TGA)**

144 The thermal stability of the microcapsules was evaluated with a Simultaneous SDTQ600 TA
145 Instruments under N₂ and air atmosphere. The scanning rate was 10 °C·min⁻¹ in the temperature range
146 between 25 and 600 °C for 5.4420 mg of sample for both samples.

147 **2.3.6 Atomic Force Microscopy (AFM)**

148 Samples were suspended in ethanol, and 50 µl of suspension was poured on freshly cleaved mica
149 and gently dried with a nitrogen stream. Then, sample was imaged in air. The experiments were
150 performed in air using a Peak Force Quantitative NanoMechanics mode (QNM) with a system
151 Multimode 8, Nanoscope V electronics. The AFM probe was a diamond MDNISP one, with a
152 nominal spring constant: 388 nN·nm⁻¹. The sensitivity was 68.2 nm·V⁻¹ with a set point between 400
153 and 550 nN. Moreover, the working conditions for the peak force amplitude were 150 nm, and the
154 DMT Modulus limit 1 TPa. Both samples A and B were more soluble in ethanol than water. In order
155 to break the aggregates, the samples were sonicated until the solution was homogeneous. Capsules A
156 was tested at 25 °C and 50 °C, and Capsules B at 25 °C and 70 °C to evaluate the different behavior of
157 the MPCM when the PCM is solid (around 25 °C) and liquid (up to 43 °C for A and up to 63 °C for
158 B). It was measured the maximum force that is needed to apply at the top of a capsule to break it, as
159 well as a Young's modulus map and Young's modulus histogram for some capsules at different
160 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:

$$172 \quad F = k \cdot \Delta_z \quad \text{Equation 2}$$

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:

$$175 \quad \Delta_z = \Delta V / S \quad \text{Equation 3}$$

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:

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

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:

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

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

$$186 \quad \frac{1}{E_{eff}} = \left[\frac{(1 - \nu^2)}{E} \right] + \left[\frac{(1 - \nu_i^2)}{E_i} \right] \quad \text{Equation 6}$$

187 and Young Modulus (E_{eff}) value can be obtained using Equation 6, taking into consideration that ν 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, SiO₂. The values for the E_i and ν_i are 76 GPa (Namazu and Isono, 2003)
 190 and 0.17 respectively (Oliver and Pharr, 1992).

191

192 **3. Results and discussion**

193 **3.1 Scanning Electron Microscopy (SEM)**

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

197

198 Figure 1.

199

200 **3.2 Particle Size and Distribution Analysis (PSD)**

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

204

205 Figure 2.

206

207 **3.3 Fourier-Transformed Infrared Spectroscopy**

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

212

213 Figure 3.

214

215 Figure 4.

216

217 In general, FT-IR spectroscopy is used to describe the microcapsules shell structure. In this work,
218 FT-IR shell spectra of the two samples under study were given in Figure 5 to verify the presence of
219 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 °C·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 °C and 36.84 °C for non-
232 encapsulated A and 42.39 °C and 37.41 °C 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 °C and 57.00 °C for
234 non-encapsulated B and 62.66 °C and 56.22 °C 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 Thermogravimetical 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

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

258

259 Figure 7.

260

261 3.6 Atomic Force Microscopy (AFM)

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

265

266 Figure 8.

267

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

273

274 Figure 9.

275

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

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

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

282

283 Figure 10.

284

285 Besides, in Figure 11 is shown that the sample A at 50 °C 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 °C and 50 °C) 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 °C 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 °C due to the phase change
307 temperature of the PCM.

308 These microcapsules gives a result of 517 MPa at 70 °C when it is evaluated its Young's modulus,
309 as Figure 14 shows. Young's modulus values for room temperature and 70 °C 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 °C. This value is around the 1.8 μN, ten times lower compared with 25 °C 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 °C and 50
332 °C) because the results are similar. Capsule B does not have the same mechanical behavior at 25 °C
333 and 70 °C, the force is ten times lower at 70 °C comparing the results with those at 25 °C although the
334 Young's modulus has a similar value.

335

336 Acknowledgment

337 The work is partially funded by the Spanish government (ENE2011-28269-C03-02). The authors
338 would like to thank the Catalan Government for the quality accreditation given to their research group
339 DIOPMA (2014 SGR 1543). The research leading to these results has received funding from the
340 European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n°
341 PIRSES-GA-2013-610692 (INNOSTORAGE). Also, preparation of microcapsules funded by The
342 Scientific & Technical Research Council of Turkey (TUBITAK) (The Project Code: TUBITAK
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344

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