

HIGHLIGHTS

- Minislump tests of cement pastes prepared at different water-to-cement ratios and at different amounts of three different types of MPCM (hydrophilic, amphiphilic and hydrophobic) have been measured.
- The rheological behavior of cement pastes containing the hydrophilic MPCM and different amounts of superplasticizer has been studied ($w/c=0.5$). The paste with the hydrophilic MPCM exhibited a shear thinning behavior when small amounts of superplasticizer were added (<1.2 wt%); however, when higher amounts were added, the paste was shear thickening.

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24 paste was shear thickening.

25

26 ABSTRACT

27 Microencapsulated phase change materials (MPCMs) were incorporated into cement pastes of
28 Portland cement (PC). Minislump tests and rheological properties of cement pastes containing
29 three MPCMs with different surfaces (hydrophilic, amphiphilic and hydrophobic) were
30 measured, and the water demand of MPCM in the cement matrix was evaluated. The hydrophilic
31 MPCM was chosen for a more thorough rheological study, since it was found to be more
32 compatible with the cement matrix. The dispersion of a high amounts (45 wt% with respect to
33 the cement content, which corresponds to about 62 vol% of the total solids) of the hydrophilic
34 MPCM in the cement pastes was achieved by optimization of the amount of superplasticizer
35 through rheological measurements. For the viscometer tests, a Power Law model was found to
36 give the best fit to the experimental data. While pastes (with 45 wt% of hydrophilic MPCM)
37 prepared with low superplasticizer contents (<1.2 wt%) were found to be shear thinning, the
38 paste exhibited a shear thickening behavior in the presence of higher amounts of superplasticizer.
39 The shear thickening is probably caused by high water adsorption onto the microcapsules
40 combined with deflocculation of the cement particles at high concentrations of superplasticizer.
41 After the optimization of the superplasticizer content, homogeneous pastes were obtained, where
42 the particles of the hydrophilic MPCM were well dispersed and unaltered after 28 days of
43 hydration.

44

45 1. INTRODUCTION

46 Several studies are focused on the incorporation of microencapsulated phase change
47 materials (MPCMs) in a cementitious matrix [1-6]. The interest in MPCMs has increased in the
48 last years, with the aim to decrease the energy consumption of buildings while maintaining

49 thermal comfort [7-9]. In addition, the incorporation of MPCMs in cementitious materials can
50 potentially prevent thermal cracking caused by early age temperature rise due to cement
51 hydration and freeze-thaw damage [10-13]. MPCMs are able to store energy above their phase
52 change temperature and dissipate energy below that temperature. They are usually composed of
53 an organic core (usually paraffin) and a polymeric shell to prevent leaching when the core is in
54 its liquid state [14, 15].

55 The rheological behavior of cement pastes and mortars can be influenced by a number of
56 factors [16], such as type and amount of additives [17-19], sulfate source [20-22], fillers and
57 supplementary cementitious materials [23-27], as well as the mixing procedure [28, 29].
58 Accordingly, the optimization of the parameters involved in the processing of cement pastes is
59 key to control the setting time and the hardened state properties, such as porosity, bulk density,
60 mechanical strength and durability. Several models have been reported [30] to describe the
61 rheological behavior of cement pastes with different compounds, such as silica fume, limestone
62 [31] as well as high range water reducer additives (HRWRA), also known as a superplasticizers
63 (SP) [32].

64 While previous studies are focused on the durability of such composites, the literature
65 concerning the rheological behavior of cement pastes containing MPCMs is less abundant.
66 However, the addition of a MPCM is expected to have a considerable influence on the flow
67 properties of the pastes. For instance, Cao et al. [33] studied the evolution with time of a
68 geopolymer paste with low amounts of different MPCMs, and found that the early stage
69 viscosities were much more affected by particles with a hydrophilic surface than particles with a
70 hydrophobic surface. A fresh state characterization based on flow tables and rheology in aerial
71 lime mortar has also been reported [34], and it was found that the addition of 10 and 20 wt% of

72 MPCM added to the total solid content, does not compromise the hardened state properties. In
73 addition, Luigi et al. [35] described the increased water demand of a cement mortar with addition
74 of MPCM.

75 In the present study, the effect of different types of MPCM in a fresh state cement matrix is
76 investigated using three types of MPCM, with hydrophilic, hydrophobic and amphiphilic shells,
77 and the behavior is compared to an inorganic material (expanded glass). The water demand of the
78 different types of MPCM in the cement matrix was evaluated through minislump tests, and the
79 effect of the superplasticizer content in pastes with the hydrophilic MPCM was examined. The
80 percentage of superplasticizer was optimized to prepare homogeneous pastes (with low water
81 content and a high content of hydrophilic MPCM) and mortars.

82 **2. MATERIAL AND METHODS**

83 *2.1 Materials*

84 Three types of MPCM with different shells (hydrophilic, hydrophobic and amphiphilic) were
85 used: a) the hydrophilic MPCM (denoted MF-PCM) was purchased from Microtek Laboratories
86 Inc., and contains a core of paraffin (*n*-octadecane) encapsulated in a melamine formaldehyde
87 (MF) polymer shell [36]. It has been reported that the encapsulating polymer shell of these
88 microcapsules is strong enough to survive the mixing process during the preparation of mortars
89 [37]; b) the amphiphilic MPCM (denoted PE-PCM) was synthesized by spray drying. It is
90 composed of a paraffin Rubitherm[®]RT27 core which is coated by a low density polyethylene
91 (LDPE) and ethylvinylacetate (EVA) copolymer shell (LDPE-EVA). LDPE is hydrophobic,
92 while EVA is amphiphilic [38] [39]; c) the hydrophobic MPCM (denoted St-PCM) was prepared
93 through a suspension-like polymerization technique with a Rubitherm[®]RT27 core encapsulated

94 in a poly(styrene-divinylbenzene) shell [40]. Both non-commercial MPCMs (PE-PCM and St-
95 PCM) contain the same core.

96 Portland cement (PC) Type I 52.5 R from FyM Heidelberg Cement Group (Málaga, Spain)
97 was used. A high range water reducer agent (HRWRA), which is a polycarboxylate-based
98 superplasticizer (SP), KHEMEFLOW 1030®, with a 35 wt% of solid residue was provided by
99 Kheme Chemical S.L (Valencia, Spain). The added amounts of SP (0.4-2.4 wt%) are with
100 respect to the total solid content, and calculated from the commercial additive (from the bottle).
101 Poraver® (0.04-0.125 mm size) expanded glass spheres, from Dennert GmbH (Germany), were
102 used in specific studies for the sake of comparison.

103 *2.2 Material characterization*

104 The oxide composition of the cement and the silica addition was obtained through X-Ray
105 fluorescence (XRF) in a ARL ADVANT'XP+ from Thermo with a Rhodium X ray tube and a
106 goniometer with three collimators, 4 crystals and 2 detectors.

107 The particle size distribution of the powders was measured by laser diffraction with a Malvern
108 Mastersizer 2000, using a dry chamber. Both morphology and size of the different MPCMs were
109 studied through Scanning Electron Microscopy (SEM) (model Quanta 250, FEI Company) with
110 a tungsten filament operating at a working potential of 15 kV. Density measurements of the
111 MPCMs were carried out with a Helium pycnometer (Accupyc II 1340). Melting point and latent
112 heat storage capacity of the MPCMs were measured in a differential scanning calorimeter (DSC)
113 (model Q100 from TA Instruments) equipped with a refrigerated cooling system and nitrogen as
114 the purge gas. Measurements were carried out in the temperature range from -40 to 80°C with
115 heating and cooling rates of 3°C/min [41]. The microstructure of the fracture surface of the
116 optimized paste, at 28 days of hydration, was observed by SEM. Zeta potentials and

117 hydrodynamic radii of suspensions were measured by a Möbiuξ from Wyatt Technology at 20
118 °C.

119 *2.3. Paste preparation*

120 Pastes were prepared by mechanical stirring according to a modified standard procedure (EN
121 196-3:2005) using a mechanical stirrer at higher speed (800 rpm for 90 seconds, 30 seconds
122 without stirring, and mixing at 800 rpm for 90 seconds) to improve the homogeneity of the
123 pastes. Pastes for the minislump tests were prepared at different water-to-cement ratios (w/c),
124 from 0.5 to 1.0, as described in Table 1. They were prepared with different MPCM types (MF-
125 PCM, St-PCM, PE-PCM), and contents (0, 15, 30, 45 wt% with respect to cement, which
126 corresponds to 0, 13, 23 and 31 wt% with respect to the total solids, and about 0, 35, 52 and 62
127 vol% with respect to total solids, respectively). They were also prepared without or with different
128 contents of superplasticizer (SP). The water-to-solid (w/s) ratio is also included in Table 1, where
129 pastes with values as low as 0.35 were prepared. In general, samples are labeled in Table 1
130 according to the MPCM type (MF-PCM, St-PCM, PE-PCM) or Poraver (Por) and wt% with
131 respect to the cement content (0, 15, 30, 45 or 70 wt%).

132

133 *Table 1. Cement paste dosage for the minislump tests*

MPCM content with respect to cement (wt%)	MPCM content with respect to total solids (wt%)	MPCM content with respect to total solids (vol%)	w/c	w/s	Cement (g)	MPCM (g)	Water (g)	SP (wt%)
0 (C-paste)	0 (C-paste)	0 (C-paste)	0.5	0.5	60	0	30.0	-
			0.6	0.6			36.0	
			0.7	0.7			42.0	
			0.8	0.8			48.0	
			0.9	0.9			54.0	
			1	1.0			60.0	
15	13	MF-PCM: 35.6 PE-PCM: 35.4 St-PCM: 34.3	0.5	0.4	52.2	7.8	26.1	-
			0.6	0.5			31.3	
			0.7	0.6			36.5	
			0.8	0.7			41.8	
			0.9	0.8			47.0	
			1	0.9			52.2	
30	23	MF-PCM: 52.5 PE-PCM: 52.2 St-PCM: 52.1	0.5	0.4	46.2	13.8	23.1	-
			0.6	0.5			27.7	
			0.7	0.5			32.3	
			0.8	0.6			37.0	
			0.9	0.7			41.6	
			1	0.8			46.2	
45	31	MF-PCM: 62.5 PE-PCM: 62.2 St-PCM: 61.1	0.5	0.3	41.4	18.6	20.7	0
							0.4	0.4
							0.8	0.8
							1.2	1.2
							1.6	1.6
							2.0	2.0
			2.4	2.4				
			0.6	0.4			24.8	-
			0.7	0.5			29.0	
			0.8	0.6			33.1	
0.9	0.6	37.3						
1	0.7	41.4						
70 (Poraver®)	41.2	61.2	0.5	0.3	41.4	29.0	20.7	-
			0.6	0.4			24.8	
			0.7	0.5			29.0	
			0.8	0.6			33.1	
			0.9	0.6			37.3	
			1	0.7			41.4	

134

135 Pastes for rheological measurements were prepared at w/c of 0.5, with different contents of SP,
 136 and 45 wt% MPCM (or 70 wt% Poraver®) with respect to the cement content. The water that
 137 forms part of the SP was taken into account in the preparation of the pastes (added water). For a
 138 better comparison, Table 1 also shows the equivalence between weight percentages and volume

139 percentages of the MPCM and Poraver® in these pastes. The measured density values of MF-
 140 PCM, PE-PCM and St-PCM are 0.85, 0.86, 0.90 g·cm⁻³, respectively. The density of Poraver®
 141 was provided by the supplier as 1.40 g·cm⁻³, and the theoretical density of PC is 3.15 g·cm⁻³.
 142 Since the density values of the three MPCMs are not very different, the volume percentages of
 143 these materials are similar. In the case of the paste with 70 wt% of Poraver® (with respect to
 144 cement), the vol% data is similar to the pastes with 45 wt% MPCM (61.2 and about 62 vol% for
 145 Por and MPCM pastes, respectively), see Table 1.

146 Table 2 shows the amounts of commercial SP, added from the bottle and calculated with respect
 147 to the total solid content (cement and MPCM), and the amounts of MF-PCM and Poraver® used
 148 in the pastes for the rheological study. Different amounts of pastes are used for the rheological
 149 study than for the minislump tests.

150 *Table 2. Mix proportions of cement pastes used in the rheological study (w/c=0.5).*

Sample [#]	Cement(g)	Water(g)	SP (wt%)	MF-PCM(g)	Poraver®(g)
C-Paste			-	-	
45MF-0.6			0.6		
45MF-1.2			1.2	18.6 (62.5	
45MF-1.6			1.6	vol% with	
45MF-2.0	41.4	20.7	2.0	respect to	
45MF-2.4			2.4	solids)	
70Por-1.6			1.6		
70Por-2.0			2.0		29.0 (61.2 vol% with respect to solids)

151 [#]C-Paste is the OPC cement paste control sample (without SP). 45, 70 correspond to the wt. percentage of
 152 microparticle addition (MF-PCM) and Poraver®, respectively, with respect to cement content. The corresponding
 153 vol. percentage of microparticle addition (MF-PCM) and Poraver® is shown in the brackets. The last name
 154 corresponds to the SP percentage (with respect to the total solid weight).

155

156 2.4. Minislump test

157 A minislump test (39 mm cone), adapted to cement pastes, was performed. The water demand of
158 the MPCM in the cement pastes was calculated according to Equation 1:

159
$$\text{Additional water compared to control (\%)} = \left(\frac{\left(\frac{w}{c}\right)_{\text{MPCM}}}{\left(\frac{w}{c}\right)_{\text{control}}} - 1 \right) \cdot 100 \quad \text{Eq. 1}$$

160 where $(w/c)_{\text{MPCM}}$ corresponds to the water-to-cement (w/c) value of the pastes prepared with
161 MPCM which resulted in a minislump diameter of 75 mm; and $(w/c)_{\text{control}}$ is the w/c, for the paste
162 without MPCM which resulted in the same minislump diameter of 75 mm.

163

164 2.5 Rheological measurements

165 Rheological measurements of cement pastes were carried out in a Thermo HAAKE Viscometer
166 VT550 with a serrated coaxial cylinder sensor to reduce slippage (SV2P), provided with a lid to
167 minimize evaporation. Flow curves (controlled rate measurements) were measured with sweeps
168 of 6 s in the shear rate range between 0 and 100 s^{-1} , for a total of 12 sweeps. A further decrease
169 from 100 to 0 s^{-1} shear rate was performed by following the same sweeps. Prior to the
170 measurements, all pastes were pre-sheared for 30 s at 100 s^{-1} . All measurements were carried out
171 at $20 \text{ }^\circ\text{C}$.

172 **3. RESULTS AND DISCUSSION**

173 3.1. Characterization of the raw materials

174 Table 3 shows the elemental composition of both the PC and Poraver®, and Table 4 shows
175 selected physical properties of the three MPCMs. The three materials exhibit similar melting
176 points, which are close to the human comfort temperature ($22\text{-}25^\circ\text{C}$). However, the latent heat of

177 the hydrophilic MPCM (MF-PCM) is about 55% higher than the other two MPCMs due to the
 178 higher paraffin content. The particle size distribution of the three MPCMs and Poraver® are
 179 displayed in Figure 1.

180 *Table 3. XRF data of PC and Poraver® expressed as oxides in weight percentage*

Oxide	PC (wt%)	Poraver® (wt%)
CaO	63.3	9.0
SiO ₂	19.4	71.9
Al ₂ O ₃	4.9	2.5
Fe ₂ O ₃	3.1	0.4
MgO	1.2	2.1
SO ₃	3.3	0.1
K ₂ O	1.0	0.8
Na ₂ O	0.3	13.2
P ₂ O ₅	-	-

181

182 *Table 4. Physical properties of MPCMs.*

MPCM	Melting point (°C)	Latent heat (J/g)	Core/shell wt%/wt%
MF-PCM	21.9*	154	85/15*
PE-PCM	25.8**	98	60/40**
St-PCM	24.9	100	49/51

183 * Data taken from [42]. ** Data taken from [38].

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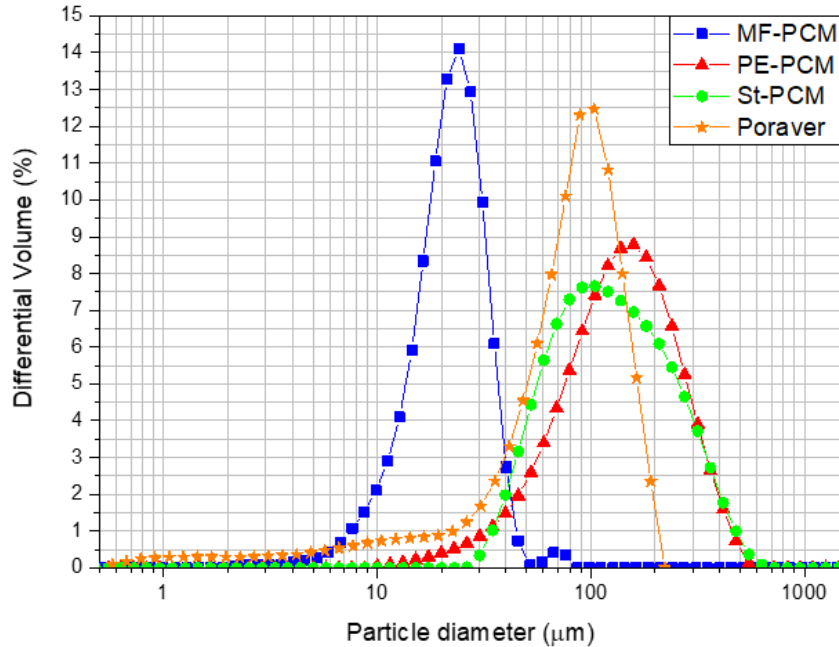


Figure 1. Particle size distribution of the three MPCMs and Poraver®.

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189 Values of D_{v10} , D_{v50} and D_{v90} of the three MPCMs are shown in Table 5. The corresponding
 190 values for Poraver® and PC are also shown for the sake of comparison. The three MPCMs and
 191 Poraver® are polydisperse (Fig. 1), where MF-PCM exhibits the smallest median particle size
 192 (D_{v50}), and PE-PCM the largest one (Table 4). It is known that the particle size of a material
 193 affects the rheological behavior. For less concentrated samples, an increased particle size will
 194 normally result in higher viscosities [43]. However, for samples with high amounts of solids, the
 195 quantity of liquid adsorbed onto the particles becomes an important factor. Since smaller
 196 particles have a larger surface area per volume, they can adsorb more water onto the surface.
 197 Accordingly, the amount of free water is reduced, leading to a higher effective concentration of
 198 solids. This causes the viscosity to increase and induces more intraparticle interactions. The
 199 water affinity of the particles also play an important role, as hydrophilic particles will adsorb
 200 much more water on the surface than hydrophobic particles [44]. In addition, factors such as
 201 particle shape and the addition of superplasticizers will affect the rheology of the samples.

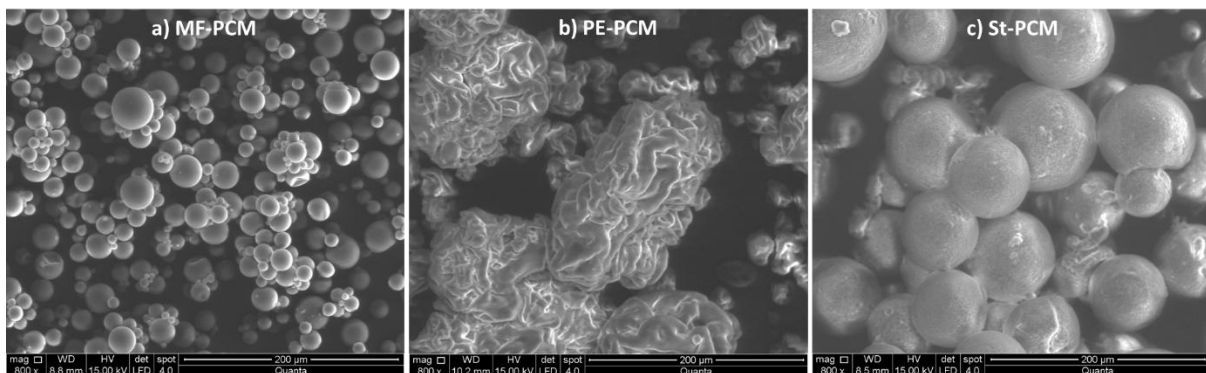
202 *Table 5. Particle size values for all powders studied*

	D_{v10} (μm)	D_{v50} (μm)	D_{v90} (μm)
MF-PCM	12.8	23.5	35.8
PE-PCM	67.7	170.1	352.7
St-PCM	67.3	149.0	359.3
Poraver®	17.4	77.4	133.2
PC	1.7	8.7	27.9

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204 *3.2. MPCM water demand*

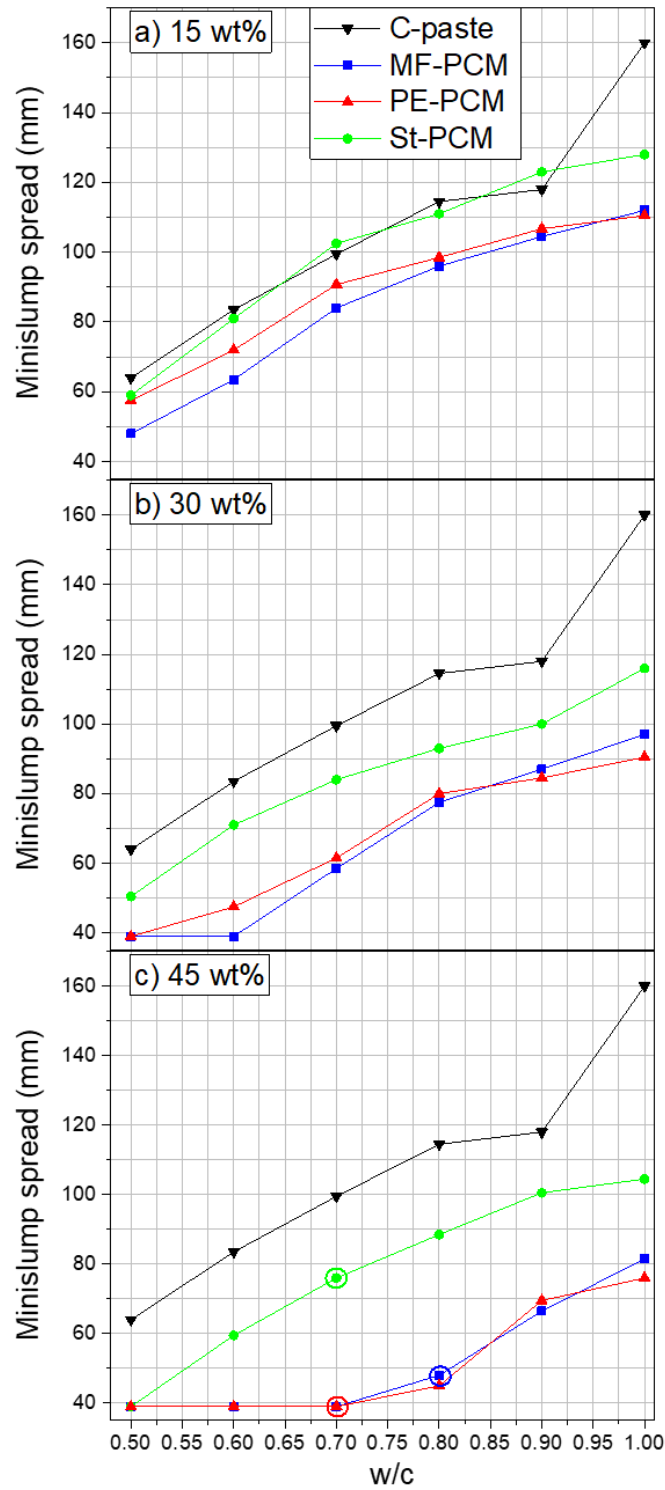
205 Figure 2 shows SEM micrographs of the three types of MPCM. MF-PCM and St-PCM are
 206 spherical with smooth surfaces while PE-PCM has an irregular shape and a rough surface. The
 207 micrographs confirm the average particle size shown in Table 5; MF-PCM exhibits the smallest
 208 particle size, and St-PCM the largest one. The surface area (BET) values of the three MPCMs
 209 were measured, but they were too small to provide trustable values. However, it is expected that
 210 MF-PCM has the highest surface area due to the lowest particle size, and St-PCM probably has
 211 the smallest surface area due to its large particle size combined with a smooth surface.



212 *Figure 2. SEM micrographs of MF-PCM (a), PE-PCM (b) and St-PCM (c) particles*
 213
 214

215 A minislump test was used to evaluate the water demand of the cement pastes of Table 1. First,
 216 the effect of the type and amount of MPCM on the pastes prepared at different w/c ratios (0.5-
 217 1.0) was studied without additives. Figures 3a, 3b, and 3c show the minislump (diameter of

218 spread paste) for pastes with 15, 30 and 45 wt % of MPCM (with respect to cement) prepared
219 without SP. The control paste (C-paste, cement paste without MPCM nor SP) is also shown in
220 the figures for the sake of comparison.



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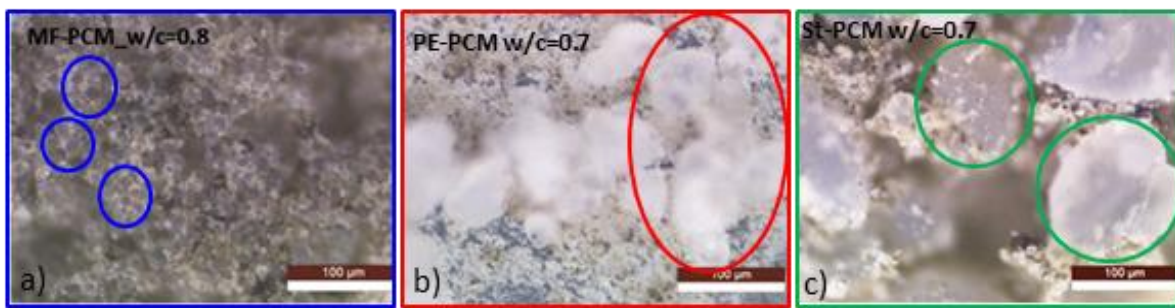
Figure 3. Minislump (diameter of spread paste) of pastes prepared with a) 15 wt%, b) 30 wt% and c) 45 wt% of different MPCMs (with respect to cement) with different w/c ratios (without superplasticizer). The Control-paste is shown for the sake of comparison.

227 As expected, the minislump increases when the w/c ratio is raised. The addition of MPCM
228 reduces the minislump. This illustrates that MPCM induces poorer workability to the paste. This
229 is due to an increased solid content, and adsorption of water on the surface of the MPCM
230 particles. Due to the hydrophobic character of St-PCM, it adsorbs very little water [42, 44]. In
231 addition, the large particle size (and smooth surface) are indications of a low surface area onto
232 which water might be adsorbed. Accordingly, the minislump of St-PCM is close to the reference
233 without MPCM at the lowest MPCM concentration (15 wt%), and higher than MF-PCM and PE-
234 PCM at all conditions.

235 At the lower studied w/c ratios (0.5-0.7) for the two lowest MPCM concentrations, pastes
236 containing MF-PCM have a lower minislump than PE-PCM. This is related to the hydrophilic
237 polymer shell but also to the much lower particle size of MF-PCM (Figure 1). As mentioned
238 previously, the small particles (with a corresponding large surface area), and a hydrophilic
239 surface promotes adsorption of water onto the particles. Accordingly, the amount of free water is
240 reduced, which increases the effective concentration of solids in the sample. This results in a
241 higher viscosity, which gives a lower slump. The effect of adsorbed water is more pronounced at
242 the lower studied w/c ratios, since less water is available in the pastes. For 30 and 45 wt%
243 MPCM (with respect to cement), the difference between the pastes with MPCM and the C-paste
244 increases when the MPCM content is raised. This is mainly related to the higher solid content,
245 since the w/c ratio is fixed. In general, the minislump of the PE-pastes is slightly higher than for
246 MF-pastes. The superplasticizer was not utilized to disperse these samples. Accordingly, the
247 small difference between the PE-PCM and MF-PCM pastes may be caused by agglomeration
248 and water trapped inside the PE-PCM agglomerates [42]. The minislump of St-pastes is located
249 between the C-paste and the other pastes with MPCM. The minislump of St-pastes also decrease

250 by increasing the MPCM content, but less than for MF-PCM and PE-PCM pastes. The high St-
251 PCM content will make it more difficult to disperse the particles in the cement matrix. The St-
252 PCM will therefore form agglomerates (see Figure 4) that will trap water inside. This decreases
253 the minislump and raises the viscosity, which prevents segregation.

254 To evaluate whether the MPCMs were destroyed during the paste preparation, selected pastes
255 prepared with 45 wt% MPCM (with respect to cement) were examined by an optical microscope.
256 The agglomerates of the three MPCMs in the cement matrix can be seen in Figure 4, where the
257 circles of Fig. 3c correspond to the selected pastes of the images. The microscope images
258 confirmed that the microcapsules were not visibly damaged during the preparation of the pastes.

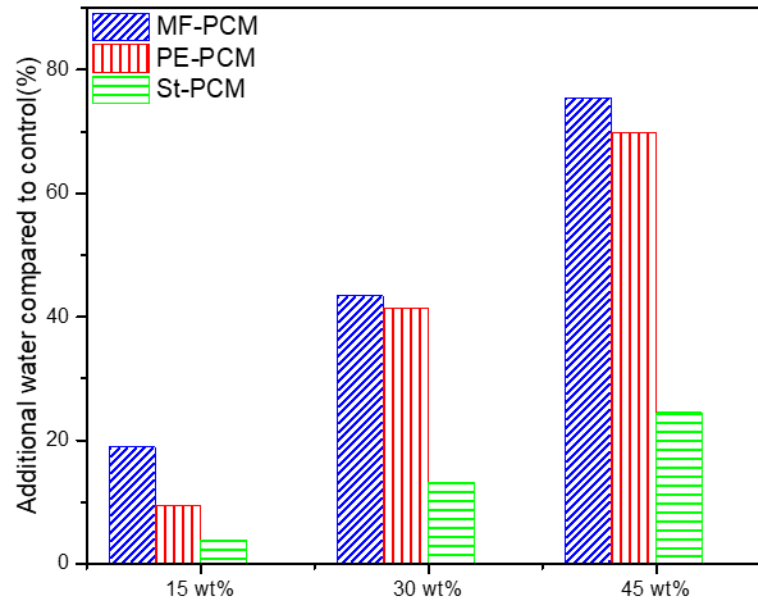


259
260 *Figure 4. Optical microscope photographs of selected pastes prepared with 45 wt% MPCM (with respect to*
261 *cement): a) MF-PCM-paste at $w/c=0.8$, b) PE-PCM-paste at $w/c=0.7$, and c) St-PCM-paste at $w/c=0.7$.*
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263 In order to quantify the water demand of the MPCMs, Figure 5 shows the additional water
264 needed to achieve a minislump diameter of 75 mm (Eq. 1). The water demand is a consequence
265 of the water adsorbed onto the surface of the particles, and the water trapped between particles;
266 the latter will depend on particle size, morphology and nature of the MPCM and agglomeration
267 of the particles. The additional water needed by the pastes increases when more MPCM is added.
268 At a low MPCM content, MF-PCM needs more additional water (almost double) than the PE-
269 PCM paste to achieve the same minislump diameter. However, when the MPCM concentration is
270 raised, the differences between MF-PCM and PE-PCM pastes are lower.

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Figure 5. Additional water needed by pastes with 15, 30 and 45 wt% MPCMs (with respect to cement) prepared without superplasticizer, compared to the control-paste, to achieve a minislump of 75 mm ($w/c=0.5$).

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Concentrated (low w/c) and homogeneous pastes and mortars are required to prepare dense and flawless materials. This can provide mortars with high mechanical strengths, low permeability, increased resistance to weathering, improved bonds between concrete and reinforcements, reduced volume change from drying and wetting, and reduced shrinkage cracking [45]. This is favored by the addition of an optimized amount of SP, which will increase the homogeneity of the pastes and decrease the water demand. Figure 6 shows the effect of SP concentration on the minislump diameter of pastes with the lowest studied w/c ratio (0.5) and the highest content of MPCM (45 wt% with respect to cement). The pastes were characterized at the highest MPCM concentration, since these samples will exhibit the best thermal properties for future applications. The MF-PCM paste needs a relatively high amount of SP to become flowable under these conditions. The spread increases when the SP content is sufficiently raised. Homogeneous pastes with MF-PCM were prepared without any segregation, with 2.0 wt% SP

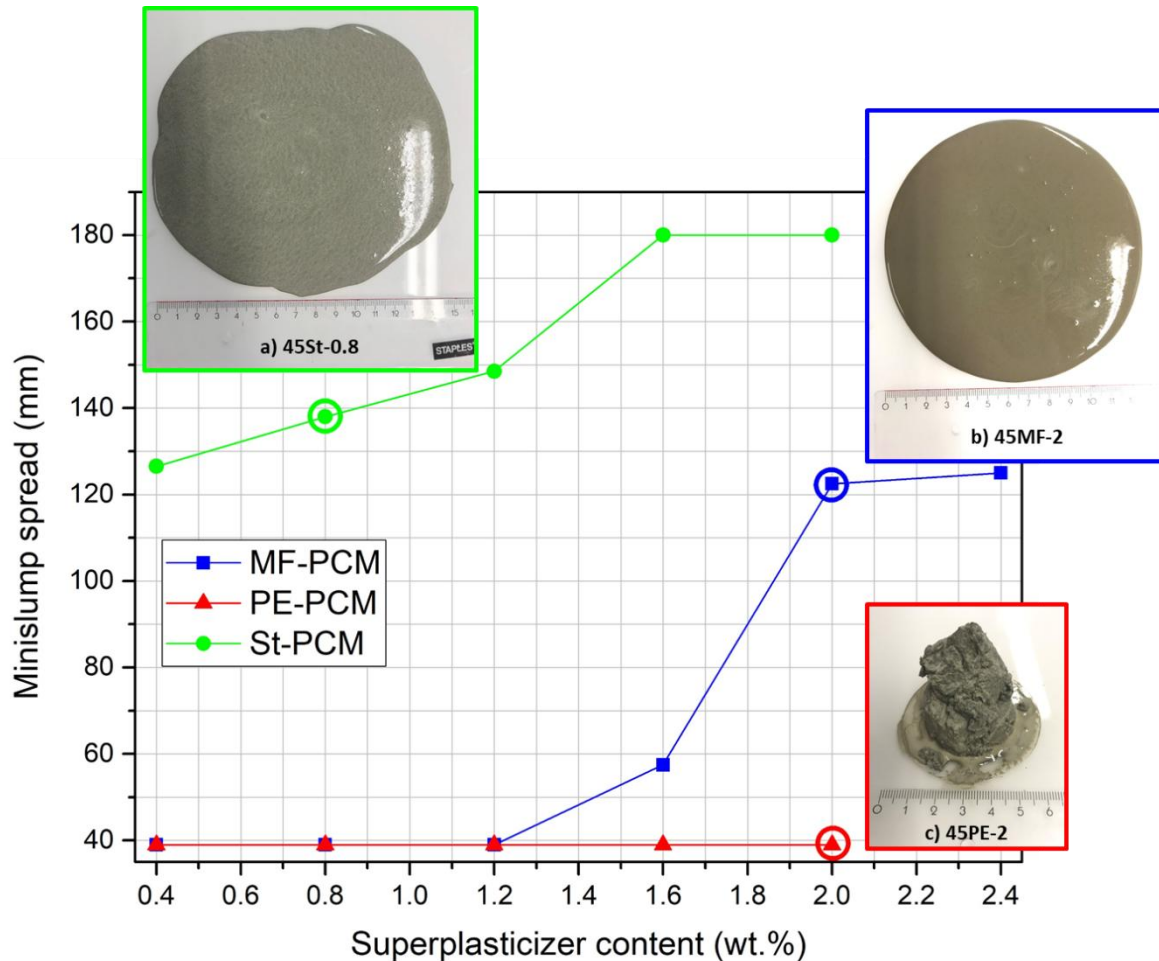
289 (Figure 6). The spread of the PE-PCM paste does not improve with the addition of the SP, and
290 strong segregation was observed for all samples (Figure 6). Even with the highest SP
291 concentration no significant effect was observed for the PE-PCM paste. This suggests that the SP
292 might be adsorbed onto the PE-PCM particles, thereby preventing the SP from interacting with
293 the cement matrix.

294 To check whether the SP adsorb onto the PE-PCM, zeta potentials of aqueous suspensions of
295 the components were determined. The SP has a zeta potential of -24 ± 5 mV, and a
296 hydrodynamic radius (R_h) of 4.6 ± 0.7 nm. The PE-PCM is too large to make stable suspensions,
297 as it floats to the surface. Suspensions were therefore made by mixing PE-PCM with the aqueous
298 solvent, and sonicating the sample for 10 s. This resulted in a diluted suspension of the smallest
299 PE-PCM particles. The resulting suspension was separated from the unsuspended larger particles
300 (still floating on top of the sample) and measured with and without the addition of SP. PE-PCM
301 was found to have a zeta potential of -98 ± 4 mV, and a R_h of 141 ± 6 nm (confirming that only
302 the smallest particles were present in the suspension). When SP was added to the suspension, the
303 sizes were the same within the experimental error (134 ± 6 nm). However, the zeta potentials
304 were shifted to -34 ± 1 mV, which is close to that of the SP (-24 ± 5 mV). Since PE-PCM is
305 much larger than the SP, the scattering from the microcapsules will dominate the results, and the
306 measured zeta potentials are that of the microcapsules [46]. The zeta potential probes the charge
307 on the surface of the particles. The shift of the zeta potential of the microcapsules to values close
308 to that of the SP is therefore a good indication of adsorption of SP onto the surface of the
309 microcapsules [46].

310 To further explore the preference of the SP to adsorb onto the PE-PCM, an alternative cement
311 paste with 45 wt% PE-PCM (with respect to cement) was prepared in a different way. The

312 cement was added to water containing SP, thereby allowing it to be adsorbed onto the cement
313 particles. The PE-PCM was added afterwards. This paste exhibited the same behavior as for the
314 previous mixing procedure. This indicates that in the competitive adsorption of SP on cement
315 and PE-PCM [47], the SP preferably adsorbs onto PE-PCM (resulting in a desorption from the
316 cement particles).

317 For St-PCM pastes, a large minislump diameter was measured, which increased with the SP
318 content up to 1.6 wt%, after which the minislump diameter was constant. However, all the St-
319 PCM pastes segregated (Figure 6a). This segregation is related to the hydrophobic nature of the
320 MPCM combined with the low viscosity of the cement pastes in the presence of the SP.
321 Consequently, the St-PCM particles were not trapped in the cement matrix as they were in the
322 paste without SP (Fig.4). The increasing flowability of the paste with the addition of SP is related
323 to the better dispersion of the cement particles. A higher SP content is needed to improve the
324 flowability of the MF-PCM paste compared to the St-PCM paste, since the hydrophilic MF-PCM
325 particles are also adsorbing the SP additive. A percentage of 2.0 wt% of SP was found to be
326 appropriate for preparing homogeneous pastes without segregation. A higher percentage of SP
327 did not increase the minislump spread significantly. The MF-PCM pastes were selected for
328 further studies, since these are the only samples that did not segregate.

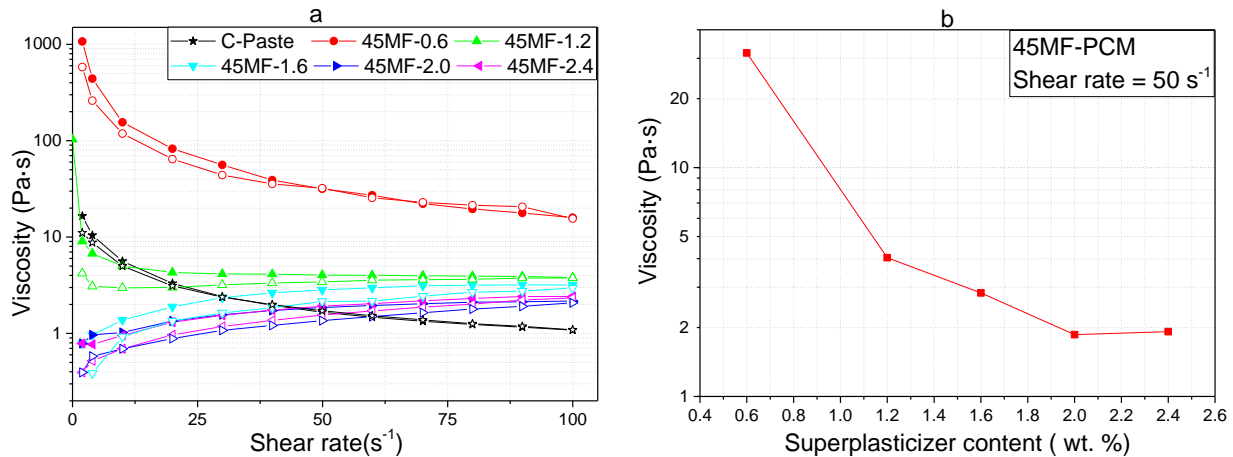


330
 331 *Figure 6. Minislump of pastes prepared with 45 wt% (with respect to cement) of the indicated MPCMs ($w/c=0.5$) as*
 332 *a function of the superplasticizer concentration. Inset: photographs of the minislump cake for a) St-PCM with 0.8%*
 333 *SP (some segregation observed), b) MF-PCM with 2.0% SP and c) PE-PCM with 2.0% SP (strong segregation).*
 334

335 3.3. Rheological behaviour

336 The addition of MF-PCM into the PC paste causes an increase of the viscosity. The SP is
 337 adsorbed by both the hydrophilic MPCM and the cement particles [48-50]. This is analogous to
 338 the adsorption of admixtures on the laminar structures of C_3A hydration products, which
 339 decrease the admixture content available for the silicate phases [51]. Figure 7a shows the
 340 viscosity curves of the selected cement pastes (with 45 wt% MF-PCM with respect to cement,

341 w/c=0.5, and different amounts of SP). For the sake of comparison, the PC paste without MPCM
 342 or SP (C-paste) is also shown (w/c=0.5).



343 *Figure 7. (a) Viscosity curves of cement pastes with 45 wt% MF-PCM (with respect to cement) and different*
 344 *contents of SP (w/c=0.5). Filled symbols correspond to the up-curve and empty symbols to the down-curve. The C-*
 345 *paste is included for comparison (PC paste without MF-PCM or SP, w/c=0.5). (b) The deflocculation curve of the*
 346 *same pastes prepared with 45 wt% MF-PCM and SP (shear rate of 50 s⁻¹).*

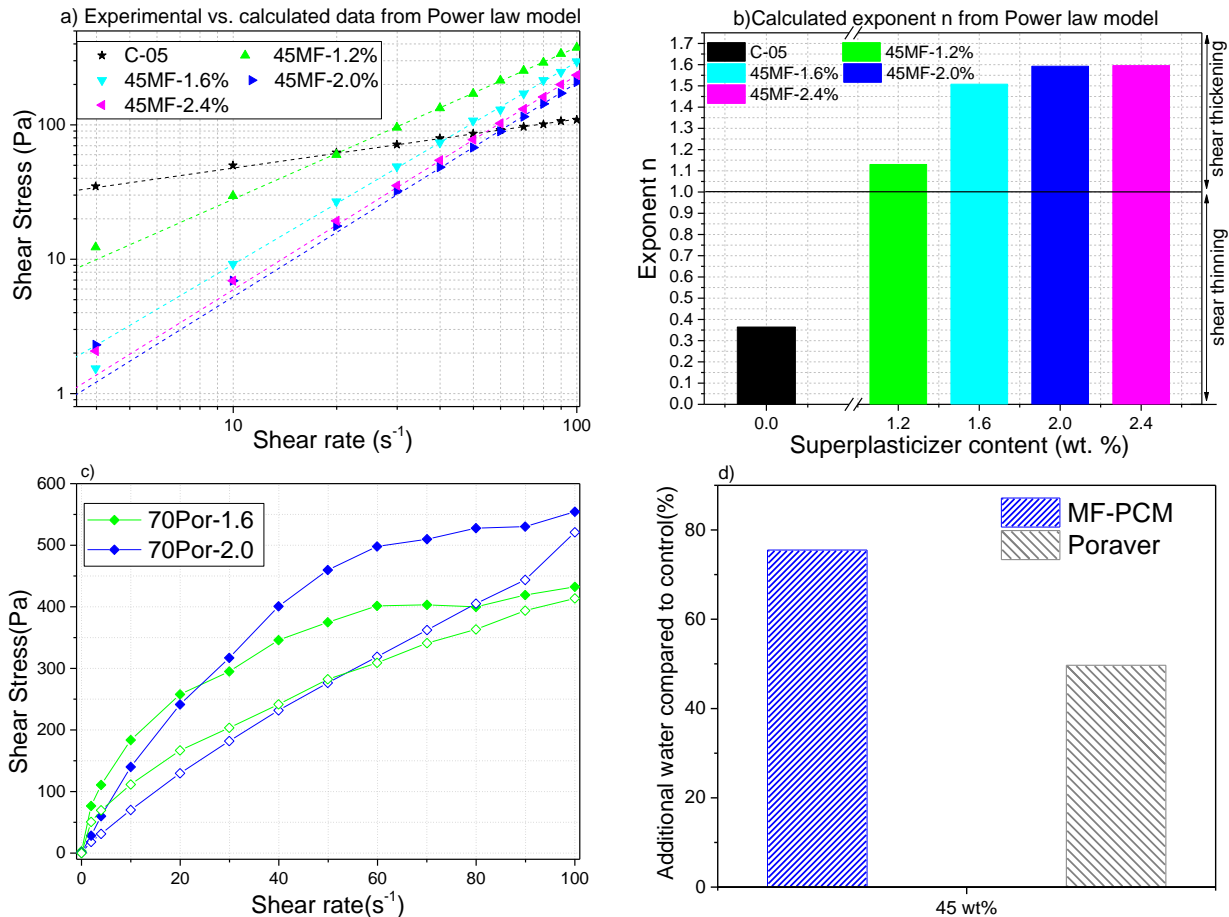
347
 348 Figure 7b shows the deflocculation curve of the pastes at a shear rate of 50 s⁻¹ (values taken
 349 from the up-curve). The viscosity decreases when the SP content is raised up to 2.0 wt%, after
 350 which it remained almost constant. The point where the viscosity is no longer decreasing is
 351 called “the saturation point” by Aitcin et al. [52]. At this point, the sample is fully coated with
 352 admixture. 2.0 wt% SP is therefore selected as the optimal quantity, and this concentration will
 353 be for further experiments. These results are in agreement with the minislump data (Figure 6b),
 354 where the flowability increased (higher minislump spread) by adding up to 2.0 wt% SP. At
 355 higher SP contents no significant improvement was found by further increasing the SP
 356 concentration (there is a plateau from 2.0 to 2.4 wt% SP). Interestingly, while pastes show a
 357 shear thinning behavior at low SP concentrations (Figure 7a), a shear thickening behavior is
 358 observed for samples containing more than 1.2 wt% SP. The combination of MF-PCM addition
 359 and a sufficiently high concentration of SP was found to be needed for the shear thickening
 360 behavior to occur. In order to quantify this effect, different rheological models (Power Law,

361 Bingham, Herschel-Bulkley and Modified Bingham) were evaluated [53-59] and compared with
 362 the experimental data (Figure 8a). The Power Law model was found to be best suited to describe
 363 the experimental data, and was therefore selected for further data analyses. The Power Law
 364 model (Eq. 2), also known as Ostwald-de-Waele model, describes the shear stress (τ) as a
 365 function of the consistency index (K) and the flow behavior index (n):

366
$$\tau = K\dot{\gamma}^n$$
 Eq. 2

367 where $n=1$ for Newtonian fluids, $n<1$ for shear-thinning fluids and $n>1$ for shear-thickening
 368 fluids.
 369

370



371 *Figure 8. a) Flow curves (from the up-curve) of the same cement pastes shown in Figure 7 (symbols), and curves*
 372 *fitted with Eq. 2 (stippled lines). b) The flow behavior index (n). c) Shear stress (up-filled, down-empty) of Poraver®*
 373 *samples. d) Water demand of Poraver® and MF-PCM pastes prepared with similar volume content of admixtures.*
 374 *Refer to Table 2 for sample notation.*
 375

376 Figure 8a illustrates that the Power Law model fits well to the experimental data. The paste
377 prepared with 0.6 wt% SP is very viscous and heterogeneous due to the low content of
378 superplasticizer (Figure 7a) and was therefore not included in the analysis.

379 The flow behavior index (n) increases when the SP concentration is raised (Figure 8b). The
380 shift from $n < 1$ to $n > 1$ illustrates that the shear thinning behavior at low SP concentrations are
381 gradually shifted to shear thickening when high admixture concentrations are added. Similar
382 behavior has been observed previously [60-63]. There are several theories regarding the origin of
383 shear thickening of concentrated colloidal suspensions (such as cement pastes). It has been
384 suggested that the shear thickening is due to an order-disorder transition [64]. It has also been
385 argued that the shear thickening is caused by a mechanism where high shear forces induce
386 hydro-clusters [65-67] due to strong hydrodynamic coupling between particles. Newer studies
387 claim that shear thickening is due to frictional forces, which becomes stronger as the shear rate
388 increases [68-70]. As can be seen from Figure 8a, the shear stress becomes lower throughout the
389 whole shear rate region when the concentration of SP is increased. Based on this observation,
390 Kwan et al. [63] suggested that SP causes a higher reduction of shear stress at low shear rates
391 than at high shear rates, resulting in an apparent shear thickening behavior. However, Brown et
392 al. [71] demonstrated that shear thinning of flocculated samples can mask the shear thickening
393 behavior. This is in good agreement with the current observations. When more SP is added to the
394 samples the cement particles becomes better dispersed, as illustrated by the reduced viscosities
395 (Figure 7a) and lower shear stress (Figure 8a). Accordingly, they become less shear thinning
396 (reduced amount of agglomerates that can be broken apart), and the shear thickening becomes
397 the dominant effect.

398 Shear thickening seems to be a general trend of hard-particle suspensions at high
399 concentrations [71], it becomes stronger at higher volume fractions of solids [65, 72, 73], and
400 can be reduced or completely masked by shear thinning of flocculated samples [71]. This seems
401 to be in good agreement with the recent theory of frictional forces as the cause of the shear
402 thickening effect [68-70].

403 Interestingly, cement pastes without microcapsules did not become shear thickening when SP
404 was added to the samples (data not shown). In order to investigate the dominating factors that
405 causes the shear thickening in the cement pastes containing both MF-MCM and high amounts of
406 SP, inert expanded glass spheres (Poraver®) was used as an addition. It should be noted that MF-
407 PCM and Poraver® have different densities (0.85 and 1.40 g/cm³, respectively). To take this into
408 account, pastes with different amounts of both powders were added (Table 1).

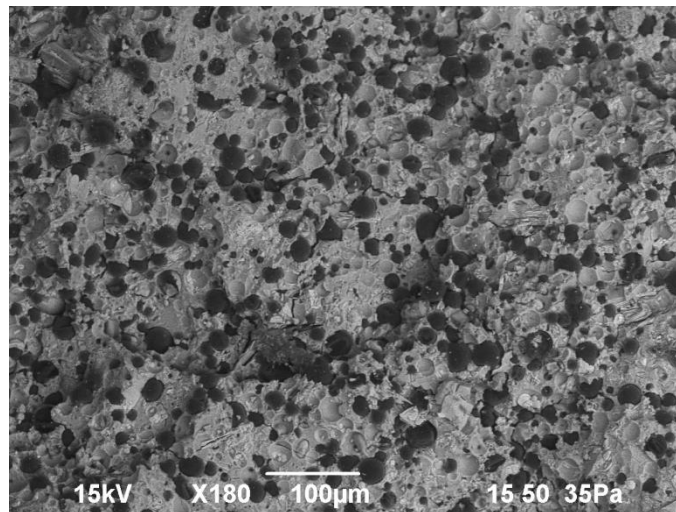
409 Figure 8c shows the flow and viscosity curves of the paste with 70 wt% Poraver® (with respect
410 to cement) with different SP contents (1.6 and 2.0 wt%) prepared at the same w/c ratio (0.5).
411 Both flow curves show a shear thinning behavior with a wide thixotropic cycle, where the up-
412 curves follow the Power Law model, but the down-curves exhibit a Bingham behavior. Pastes
413 with 1.6 wt% SP (70-Por-1.6) have the smallest thixotropic cycle, indicating that the Poraver®
414 paste with 2.0 wt% SP (70-Por-2.0) contains an excess of SP. The shear thinning behavior of the
415 samples are illustrated by the flow behavior index, where $n = 0.57$ and 0.86 for 1.6 % and 2.0 %
416 Poraver®, respectively.

417 The different particle size (Figure 1), particle packing, and lower water adsorption of Poraver®
418 compared to MF-PCM (Figure 8d) contributes to the differences in rheological behavior between
419 the pastes containing Poraver® (shear thinning) and MF-PCM (shear thickening). A larger
420 amount of SP is expected to be free in the aqueous medium in the Poraver®-paste, which should

421 result in less shear thinning and therefore stronger shear thickening (see discussion above).
422 However, since much more water adsorbs onto the MF-PCM (Figure 8d), the effective
423 concentration of solids becomes higher. A larger volume fraction of solids enhances the shear
424 thickening behavior [65, 72, 73], and the high water adsorption of MF-PCM is therefore
425 probably one of the causes for the observed shear thickening effect. Combined with the SP-
426 induced deflocculation of the cement particles (which reduces the shear thinning), this causes the
427 observed shear thickening in the presence of MF-PCM and high amounts of SP.

428 3.3. Microstructure of MF-PCM pastes

429 Figure 9 shows a SEM micrograph of a fresh fracture section of the cement optimized paste (45-
430 MF-2.0) ($w/c=0.5$) at 28 days of hydration (see Table 2). The paste shows a homogeneous
431 microstructure, where the MF-PCM particles are properly dispersed (and unaltered) in the
432 cement matrix. This illustrates that the MF-PCM particles are strong enough to withstand the
433 mixing process without breaking.



434
435 *Figure 9. SEM micrograph of the fracture section of the paste with 45% of MF-PCM (with respect to cement)*
436 *prepared with 2.0 wt% SP ($w/c=0.5$) at 28 d of hydration (45-MF-2.0).*
437

438 **4. CONCLUSIONS**

439 The effect of three different microencapsulated phase change materials (MPCM): hydrophilic
440 (MF-PCM), amphiphilic (PE-PCM) and hydrophobic (St-PCM) on the flowability of cement
441 pastes prepared with different water-to-cement (w/c) ratios has been examined. The effect of
442 different amounts of MPCM (15, 30 and 45 wt% with respect to cement, corresponding to
443 respectively 0, 13, 23 and 31 wt% with respect to total solids, or 0, 35, 52 and 62 vol%) was
444 investigated.

445 Pastes with 15 wt% of MF-PCM and PE-PCM (without superplasticizer, SP) exhibited similar
446 (but not identical) minislump-behavior. The St-PCM paste has a similar spread diameter as the
447 C-paste (control-paste without MPCM), due to its hydrophobic nature. However, when more
448 MPCM were added, the difference between the pastes with MPCM and the C-paste increases. At
449 these concentrations, St-PCM pastes exhibit an intermediate behavior between the C-paste and
450 the other pastes. When SP (a polycarboxylate-based superplasticizer) was added to the cement
451 pastes with 45 wt% MPCM (with respect to cement), only the paste with the hydrophilic MPCM
452 (MF-PCM) did not segregate. This sample was therefore selected for further studies. The
453 optimum amount of SP was found to be 2.0 wt% with respect to the total solid content (minimum
454 viscosity values) for the MF-PCM paste. MF-pastes with low amounts of SP (<1.2 wt%)
455 exhibited a shear thinning behavior, while MF-pastes with SP contents higher than 1.2 wt% was
456 shear thickening. This is probably caused by the combination of two effects. The high water
457 adsorption onto the MF-PCM particles causes the sample to behave as if the concentration of
458 solids were higher. In addition, SP-induced deflocculation of the cement particles reduces the
459 shear thinning of the samples, thereby causing the shear thickening to become more dominant
460 [71]. Pastes with 45 wt% MF-PCM (with respect to cement) exhibit a homogeneous

461 microstructure, where the MF-PCM particles are well dispersed and unaltered at 28 days of
462 hydration.

463

464 **Acknowledgement**

465 This work was supported by The Research Council of Norway, grant number 238198, and by
466 Spanish MINECO and FEDER (BIA2017-82391-R) and I3 (IEDI-2016-0079).

467

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