



# Effect of microencapsulated phase change materials on the flow behavior of cement composites

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## HIGHLIGHTS

- Minislump tests were performed on cement pastes prepared at different water-to-cement ratios.
- The effect of addition of three different types of MPCM (hydrophilic, amphiphilic and hydrophobic) was investigated.
- Rheological behavior of cement pastes with hydrophilic MPCM and different amounts of superplasticizer was studied.
- The paste with the hydrophilic MPCM went from shear thinning to shear thickening when more superplasticizer was added.

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## ABSTRACT

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

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## 1. Introduction

Several studies are focused on the incorporation of microencapsulated phase change materials (MPCMs) in a cementitious matrix [1–6]. The interest in MPCMs has increased in the last years, with the aim to decrease the energy consumption of buildings while maintaining thermal comfort [7–9]. In addition, the incorporation of MPCMs in cementitious materials can potentially prevent

thermal cracking caused by early age temperature rise due to cement hydration and freeze-thaw damage [10–13]. MPCMs are able to store energy above their phase change temperature and dissipate energy below that temperature. They are usually composed of an organic core (usually paraffin) and a polymeric shell to prevent leaching when the core is in its liquid state [14,15].

The rheological behavior of cement pastes and mortars can be influenced by a number of factors [16], such as type and amount of additives [17–19], sulfate source [20–22], fillers and supplementary cementitious materials [23–27], as well as the mixing procedure [28,29]. Accordingly, the optimization of the parameters

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involved in the processing of cement pastes is key to control the setting time and the hardened state properties, such as porosity, bulk density, mechanical strength and durability. Several models have been reported [30] to describe the rheological behavior of cement pastes with different compounds, such as silica fume, limestone [31] as well as high range water reducer additives (HRWRA), also known as a superplasticizers (SP) [32].

While previous studies are focused on the durability of such composites, the literature concerning the rheological behavior of cement pastes containing MPCMs is less abundant. However, the addition of a MPCM is expected to have a considerable influence on the flow properties of the pastes. For instance, Cao et al. [33] studied the evolution with time of a geopolymer paste with low amounts of different MPCMs, and found that the early stage viscosities were much more affected by particles with a hydrophilic surface than particles with a hydrophobic surface. A fresh state characterization based on flow tables and rheology in aerial lime mortar has also been reported [34], and it was found that the addition of 10 and 20 wt% of MPCM added to the total solid content, does not compromise the hardened state properties. In addition, Luigi et al. [35] described the increased water demand of a cement mortar with addition of MPCM.

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

## 2. Material and methods

### 2.1. Materials

Three types of MPCM with different shells (hydrophilic, hydrophobic and amphiphilic) were used: a) the hydrophilic MPCM (denoted MF-PCM) was purchased from Microtek Laboratories Inc., and contains a core of paraffin (*n*-octadecane) encapsulated in a melamine formaldehyde (MF) polymer shell [36]. It has been reported that the encapsulating polymer shell of these microcapsules is strong enough to survive the mixing process during the preparation of mortars [37]; b) the amphiphilic MPCM (denoted PE-PCM) was synthesized by spray drying. It is composed of a paraffin Rubitherm®RT27 core which is coated by a low density polyethylene (LDPE) and ethylvinylacetate (EVA) copolymer shell (LDPE-EVA). LDPE is hydrophobic, while EVA is amphiphilic [38,39]; c) the hydrophobic MPCM (denoted St-PCM) was prepared through a suspension-like polymerization technique with a Rubitherm®RT27 core encapsulated in a poly(styrene-divinylbenzene) shell [40]. Both non-commercial MPCMs (PE-PCM and St-PCM) contain the same core.

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

### 2.2. Material characterization

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

The particle size distribution of the powders was measured by laser diffraction with a Malvern Mastersizer 2000, using a dry chamber. Both morphology and size of the different MPCMs were studied through Scanning Electron Microscopy (SEM) (model Quanta 250, FEI Company) with a tungsten filament operating at a working potential of 15 kV. Density measurements of the MPCMs were carried out with a Helium pycnometer (Accupyc II 1340). Melting point and latent heat storage capacity of the MPCMs were measured in a differential scanning calorimeter (DSC)

(model Q100 from TA Instruments) equipped with a refrigerated cooling system and nitrogen as the purge gas. Measurements were carried out in the temperature range from –40 to 80 °C with heating and cooling rates of 3 °C/min [41]. The microstructure of the fracture surface of the optimized paste, at 28 days of hydration, was observed by SEM. Zeta potentials and hydrodynamic radii of suspensions were measured by a Möbiuξ from Wyatt Technology at 20 °C.

### 2.3. Paste preparation

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

Pastes for rheological measurements were prepared at w/c of 0.5, with different contents of SP, and 45 wt% MPCM (or 70 wt% Poraver®) with respect to the cement content. The water that forms part of the SP was taken into account in the preparation of the pastes (added water). For a better comparison, Table 1 also shows the equivalence between weight percentages and volume percentages of the MPCM and Poraver® in these pastes. The measured density values of MF-PCM, PE-PCM and St-PCM are 0.85, 0.86, 0.90 g·cm<sup>-3</sup>, respectively. The density of Poraver® was provided by the supplier as 1.40 g·cm<sup>-3</sup>, and the theoretical density of PC is 3.15 g·cm<sup>-3</sup>. Since the density values of the three MPCMs are not very different, the volume percentages of these materials are similar. In the case of the paste with 70 wt% of Poraver® (with respect to cement), the vol% data is similar to the pastes with 45 wt% MPCM (61.2 and about 62 vol% for Por and MPCM pastes, respectively), see Table 1.

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

### 2.4. Minislump test

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

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

where (w/c)<sub>MPCM</sub> corresponds to the water-to-cement (w/c) value of the pastes prepared with MPCM which resulted in a minislump diameter of 75 mm; and (w/c)<sub>control</sub> is the w/c, for the paste without MPCM which resulted in the same minislump diameter of 75 mm.

### 2.5. Rheological measurements

Rheological measurements of cement pastes were carried out in a Thermo HAAKE Viscometer VT550 with a serrated coaxial cylinder sensor to reduce slippage (SV2P), provided with a lid to minimize evaporation. Flow curves (controlled rate measurements) were measured with sweeps of 6 s in the shear rate range between 0 and 100 s<sup>-1</sup>, for a total of 12 sweeps. A further decrease from 100 to 0 s<sup>-1</sup> shear rate was performed by following the same sweeps. Prior to the measurements, all pastes were pre-sheared for 30 s at 100 s<sup>-1</sup>. All measurements were carried out at 20 °C.

## 3. Results and discussion

### 3.1. Characterization of the raw materials

Table 3 shows the elemental composition of both the PC and Poraver®, and Table 4 shows selected physical properties of the three MPCMs. The three materials exhibit similar melting points, which are close to the human comfort temperature (22–25 °C). However, the latent heat of the hydrophilic MPCM (MF-PCM) is about 55% higher than the other two MPCMs due to the higher paraffin content. The particle size distribution of the three MPCMs and Poraver® are displayed in Fig. 1.

**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 (C-paste)	0 (C-paste)	0 (C-paste)	0.6	0.6	60	0	36.0	–
0 (C-paste)	0 (C-paste)	0 (C-paste)	0.7	0.7	60	0	42.0	–
0 (C-paste)	0 (C-paste)	0 (C-paste)	0.8	0.8	60	0	48.0	–
0 (C-paste)	0 (C-paste)	0 (C-paste)	0.9	0.9	60	0	54.0	–
0 (C-paste)	0 (C-paste)	0 (C-paste)	1	1.0	60	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	–
15	13	MF-PCM: 35.6; PE-PCM: 35.4; St-PCM: 34.3	0.6	0.5	52.2	7.8	31.3	–
15	13	MF-PCM: 35.6; PE-PCM: 35.4; St-PCM: 34.3	0.7	0.6	52.2	7.8	36.5	–
15	13	MF-PCM: 35.6; PE-PCM: 35.4; St-PCM: 34.3	0.8	0.7	52.2	7.8	41.8	–
15	13	MF-PCM: 35.6; PE-PCM: 35.4; St-PCM: 34.3	0.9	0.8	52.2	7.8	47.0	–
15	13	MF-PCM: 35.6; PE-PCM: 35.4; St-PCM: 34.3	1	0.9	52.2	7.8	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	–
30	23	MF-PCM: 52.5; PE-PCM: 52.2; St-PCM: 52.1	0.6	0.5	46.2	13.8	27.7	–
30	23	MF-PCM: 52.5; PE-PCM: 52.2; St-PCM: 52.1	0.7	0.5	46.2	13.8	32.3	–
30	23	MF-PCM: 52.5; PE-PCM: 52.2; St-PCM: 52.1	0.8	0.6	46.2	13.8	37.0	–
30	23	MF-PCM: 52.5; PE-PCM: 52.2; St-PCM: 52.1	0.9	0.7	46.2	13.8	41.6	–
30	23	MF-PCM: 52.5; PE-PCM: 52.2; St-PCM: 52.1	1	0.8	46.2	13.8	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
45	31	MF-PCM: 62.5; PE-PCM: 62.2; St-PCM: 61.1	0.5	0.3	41.4	18.6	20.7	0.4
45	31	MF-PCM: 62.5; PE-PCM: 62.2; St-PCM: 61.1	0.5	0.3	41.4	18.6	20.7	0.8
45	31	MF-PCM: 62.5; PE-PCM: 62.2; St-PCM: 61.1	0.5	0.3	41.4	18.6	20.7	1.2
45	31	MF-PCM: 62.5; PE-PCM: 62.2; St-PCM: 61.1	0.5	0.3	41.4	18.6	20.7	1.6
45	31	MF-PCM: 62.5; PE-PCM: 62.2; St-PCM: 61.1	0.5	0.3	41.4	18.6	20.7	2.0
45	31	MF-PCM: 62.5; PE-PCM: 62.2; St-PCM: 61.1	0.5	0.3	41.4	18.6	20.7	2.4
45	31	MF-PCM: 62.5; PE-PCM: 62.2; St-PCM: 61.1	0.6	0.4	41.4	18.6	24.8	–
45	31	MF-PCM: 62.5; PE-PCM: 62.2; St-PCM: 61.1	0.7	0.5	41.4	18.6	29.0	–
45	31	MF-PCM: 62.5; PE-PCM: 62.2; St-PCM: 61.1	0.8	0.6	41.4	18.6	33.1	–
45	31	MF-PCM: 62.5; PE-PCM: 62.2; St-PCM: 61.1	0.9	0.6	41.4	18.6	37.3	–
45	31	MF-PCM: 62.5; PE-PCM: 62.2; St-PCM: 61.1	1	0.7	41.4	18.6	41.4	–
70 (Poraver®)	41.2	61.2	0.5	0.3	41.4	29.0	20.7	–
70 (Poraver®)	41.2	61.2	0.6	0.4	41.4	29.0	24.8	–
70 (Poraver®)	41.2	61.2	0.7	0.5	41.4	29.0	29.0	–
70 (Poraver®)	41.2	61.2	0.8	0.6	41.4	29.0	33.1	–
70 (Poraver®)	41.2	61.2	0.9	0.6	41.4	29.0	37.3	–
70 (Poraver®)	41.2	61.2	1	0.7	41.4	29.0	41.4	–

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

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

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

**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 <sub>2</sub>	19.4	71.9
Al <sub>2</sub> O <sub>3</sub>	4.9	2.5
Fe <sub>2</sub> O <sub>3</sub>	3.1	0.4
MgO	1.2	2.1
SO <sub>3</sub>	3.3	0.1
K <sub>2</sub> O	1.0	0.8
Na <sub>2</sub> O	0.3	13.2
P <sub>2</sub> O <sub>5</sub>	–	–

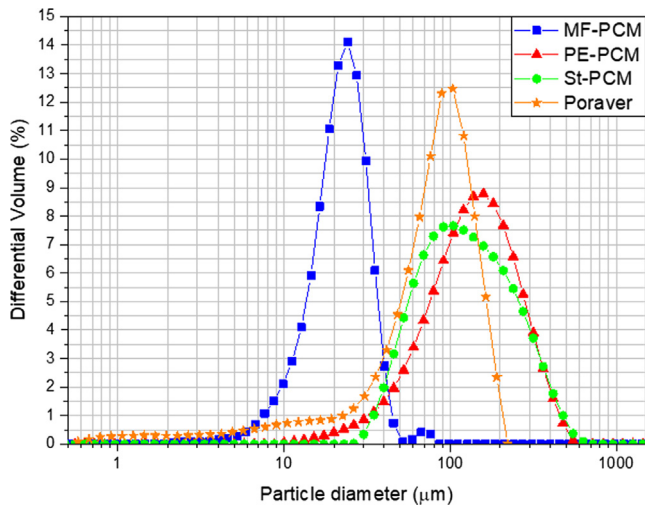
Values of  $D_{v10}$ ,  $D_{v50}$  and  $D_{v90}$  of the three MPCMs are shown in Table 5. The corresponding values for Poraver® and PC are also shown for the sake of comparison. The three MPCMs and Poraver® are polydisperse (Fig. 1), where MF-PCM exhibits the smallest median particle size ( $D_{v50}$ ), and PE-PCM the largest one (Table 4). It is known that the particle size of a material affects the rheological behavior. For less concentrated samples, an increased particle size will normally result in higher viscosities [43]. However, for samples with high amounts of solids, the quantity of liquid adsorbed onto the particles becomes an important factor. Since smaller particles have a larger surface area per volume, they can adsorb more water onto the surface. Accordingly, the amount of free water is reduced, leading to a higher effective concentration

**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

\* Data taken from [42].

\*\* Data taken from [38].



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

**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

of solids. This causes the viscosity to increase and induces more intraparticle interactions. The water affinity of the particles also play an important role, as hydrophilic particles will adsorb much more water on the surface than hydrophobic particles [44]. In addition, factors such as particle shape and the addition of superplasticizers will affect the rheology of the samples.

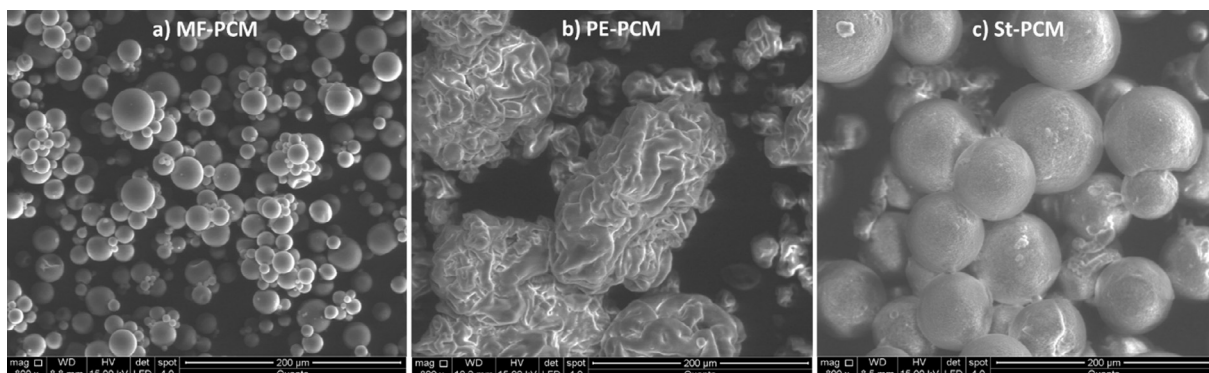
### 3.2. MPCM water demand

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

A minislump test was used to evaluate the water demand of the cement pastes of **Table 1**. First, the effect of the type and amount of MPCM on the pastes prepared at different w/c ratios (0.5–1.0) was studied without additives. **Fig. 3a–c** show the minislump (diameter of spread paste) for pastes with 15, 30 and 45 wt% of MPCM (with respect to cement) prepared without SP. The control paste (C-paste, cement paste without MPCM nor SP) is also shown in the figures for the sake of comparison.

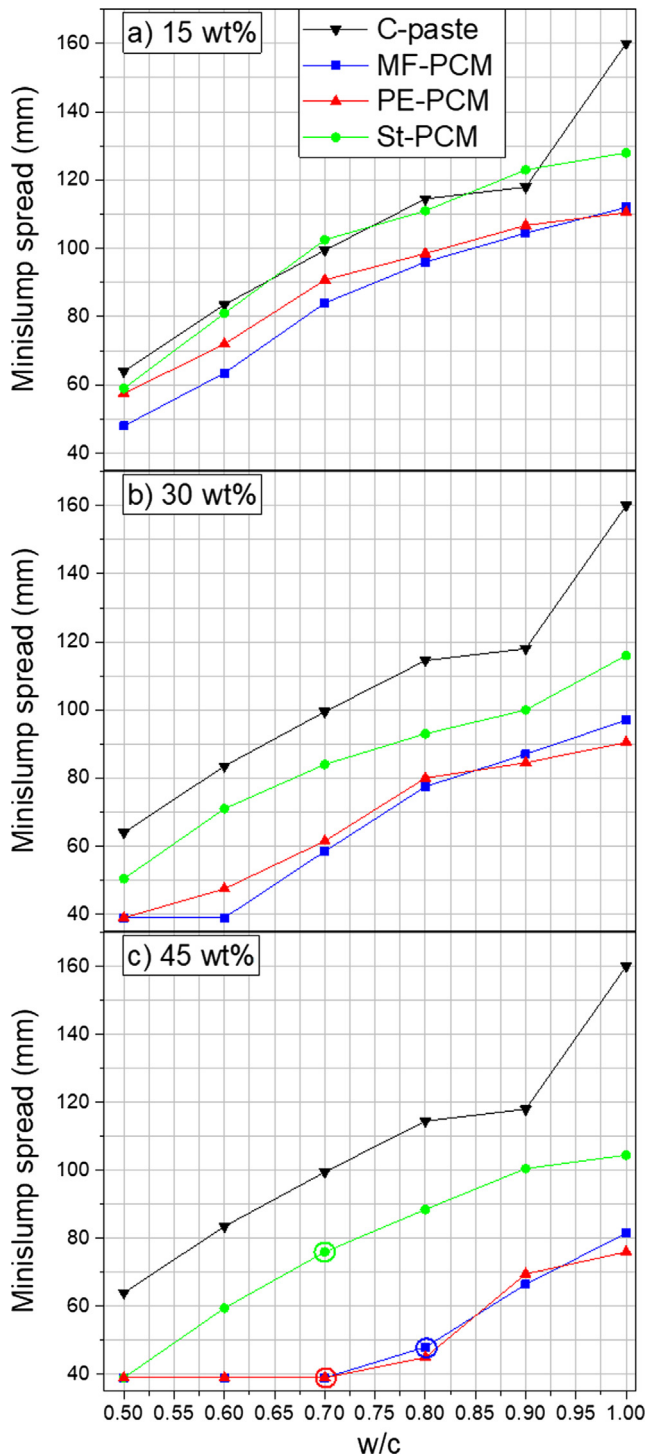
As expected, the minislump increases when the w/c ratio is raised. The addition of MPCM reduces the minislump. This illustrates that MPCM induces poorer workability to the paste. This is due to an increased solid content, and adsorption of water on the surface of the MPCM particles. Due to the hydrophobic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

At the lower studied w/c ratios (0.5–0.7) for the two lowest MPCM concentrations, pastes containing MF-PCM have a lower minislump than PE-PCM. This is related to the hydrophilic polymer shell but also to the much lower particle size of MF-PCM (**Fig. 1**). As mentioned previously, the small particles (with a corresponding large surface area), and a hydrophilic surface promotes adsorption of water onto the particles. Accordingly, the amount of free water is reduced, which increases the effective concentration of solids in the sample. This results in a higher viscosity, which gives a lower slump. The effect of adsorbed water is more pronounced at the lower studied w/c ratios, since less water is available in the pastes. For 30 and 45 wt% MPCM (with respect to cement), the difference between the pastes with MPCM and the C-paste increases when the MPCM content is raised. This is mainly related to the higher solid content, since the w/c ratio is fixed. In general, the minislump of the PE-pastes is slightly higher than for MF-pastes. The superplasticizer was not utilized to disperse these samples. Accordingly, the small difference between the PE-PCM and MF-PCM pastes may



**Fig. 2.** SEM micrographs of MF-PCM (a), PE-PCM (b) and St-PCM (c) particles.





**Fig. 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.

be caused by agglomeration and water trapped inside the PE-PCM agglomerates [42]. The minislump of St-pastes is located between the C-paste and the other pastes with MPCM. The minislump of St-pastes also decrease by increasing the MPCM content, but less than for MF-PCM and PE-PCM pastes. The high St-PCM content will make it more difficult to disperse the particles in the cement matrix. The St-PCM will therefore form agglomerates (see Fig. 4)

that will trap water inside. This decreases the minislump and raises the viscosity, which prevents segregation.

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

In order to quantify the water demand of the MPCMs, Fig. 5 shows the additional water needed to achieve a minislump diameter of 75 mm (Eq. (1)). The water demand is a consequence of the water adsorbed onto the surface of the particles, and the water trapped between particles; the latter will depend on particle size, morphology and nature of the MPCM and agglomeration of the particles. The additional water needed by the pastes increases when more MPCM is added. At a low MPCM content, MF-PCM needs more additional water (almost double) than the PE-PCM paste to achieve the same minislump diameter. However, when the MPCM concentration is raised, the differences between MF-PCM and PE-PCM pastes are lower.

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

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

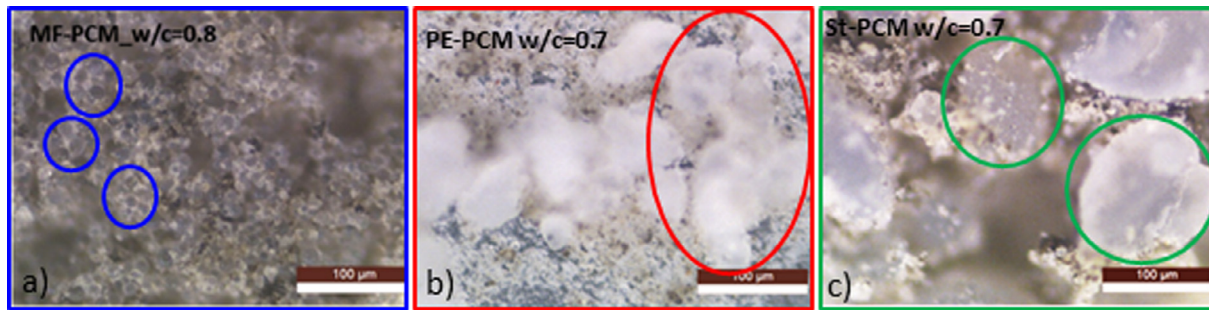


Fig. 4. Optical microscope photographs of selected pastes prepared with 45 wt% MPCM (with respect to cement): a) MF-PCM-paste at  $w/c = 0.8$ , b) PE-PCM-paste at  $w/c = 0.7$ , and c) St-PCM-paste at  $w/c = 0.7$ .

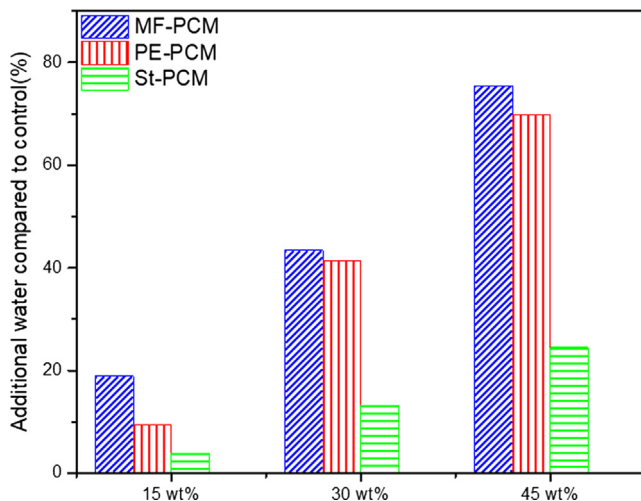


Fig. 5. Additional water needed by pastes with 15, 30 and 45 wt% MPCMs (with respect to cement) prepared without superplasticizer, compared to the control-paste, to achieve a minislump of 75 mm ( $w/c = 0.5$ ).

potential of the microcapsules to values close to that of the SP is therefore a good indication of adsorption of SP onto the surface of the microcapsules [46].

To further explore the preference of the SP to adsorb onto the PE-PCM, an alternative cement paste with 45 wt% PE-PCM (with respect to cement) was prepared in a different way. The cement was added to water containing SP, thereby allowing it to be adsorbed onto the cement particles. The PE-PCM was added afterwards. This paste exhibited the same behavior as for the previous mixing procedure. This indicates that in the competitive adsorption of SP on cement and PE-PCM [47], the SP preferably adsorbs onto PE-PCM (resulting in a desorption from the cement particles).

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

### 3.3. Rheological behaviour

The addition of MF-PCM into the PC paste causes an increase of the viscosity. The SP is adsorbed by both the hydrophilic MPCM and the cement particles [48–50]. This is analogous to the adsorption of admixtures on the laminar structures of  $C_3A$  hydration products, which decrease the admixture content available for the silicate phases [51]. Fig. 7a shows the viscosity curves of the selected cement pastes (with 45 wt% MF-PCM with respect to cement,  $w/c = 0.5$ , and different amounts of SP). For the sake of comparison, the PC paste without MPCM or SP (C-paste) is also shown ( $w/c = 0.5$ ).

Fig. 7b shows the deflocculation curve of the pastes at a shear rate of  $50 \text{ s}^{-1}$  (values taken from the up-curve). The viscosity decreases when the SP content is raised up to 2.0 wt%, after which it remained almost constant. The point where the viscosity is no longer decreasing is called “the saturation point” by Aitcin et al. [52]. At this point, the sample is fully coated with admixture. 2.0 wt% SP is therefore selected as the optimal quantity, and this concentration will be for further experiments. These results are in agreement with the minislump data (Fig. 6b), where the flowability increased (higher minislump spread) by adding up to 2.0 wt% SP. At higher SP contents no significant improvement was found by further increasing the SP concentration (there is a plateau from 2.0 to 2.4 wt% SP). Interestingly, while pastes show a shear thinning behavior at low SP concentrations (Fig. 7a), a shear thickening behavior is observed for samples containing  $>1.2$  wt% SP. The combination of MF-PCM addition and a sufficiently high concentration of SP was found to be needed for the shear thickening behavior to occur. In order to quantify this effect, different rheological models (Power Law, Bingham, Herschel-Bulkley and Modified Bingham) were evaluated [53–59] and compared with the experimental data (Fig. 8a). The Power Law model was found to be best suited to describe the experimental data, and was therefore selected for further data analyses. The Power Law model (Eq. (2)), also known as Ostwald-de-Waele model, describes the shear stress ( $\tau$ ) as a function of the consistency index ( $K$ ) and the flow behavior index ( $n$ ):

$$\tau = K\dot{\gamma}^n \quad (2)$$

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

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

The flow behavior index ( $n$ ) increases when the SP concentration is raised (Fig. 8b). The shift from  $n < 1$  to  $n > 1$  illustrates that the shear thinning behavior at low SP concentrations are gradually shifted to shear thickening when high admixture concentrations are added. Similar behavior has been observed previously [60–

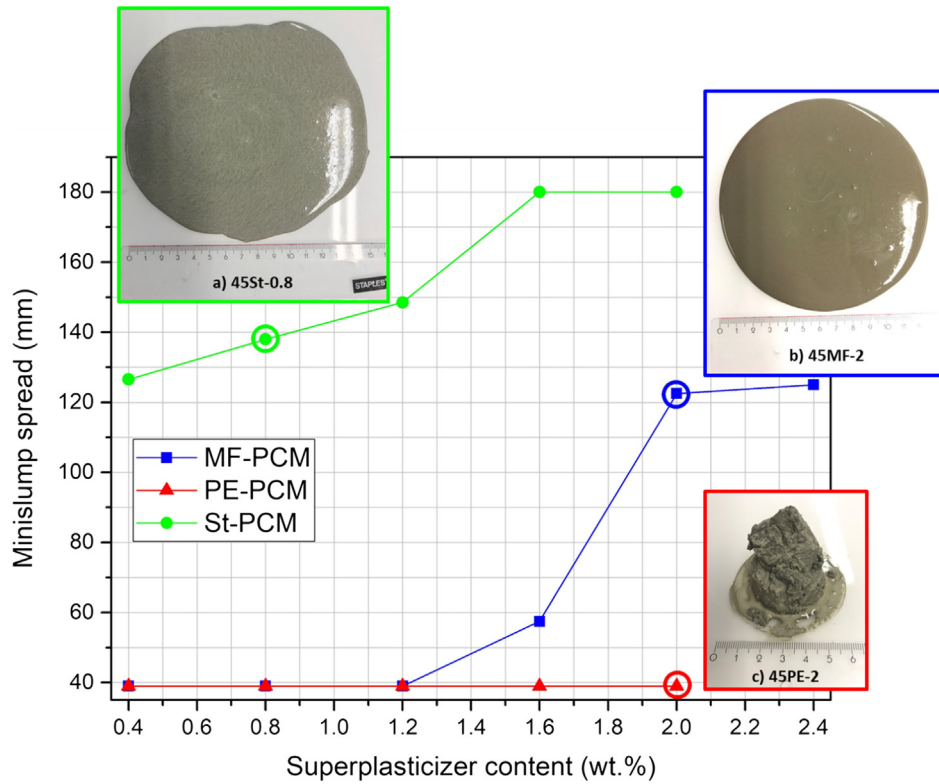


Fig. 6. Minislump of pastes prepared with 45 wt% (with respect to cement) of the indicated MPCMs (w/c = 0.5) as a function of the superplasticizer concentration. Inset: photographs of the minislump cake for a) St-PCM with 0.8% SP (some segregation observed), b) MF-PCM with 2.0% SP and c) PE-PCM with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

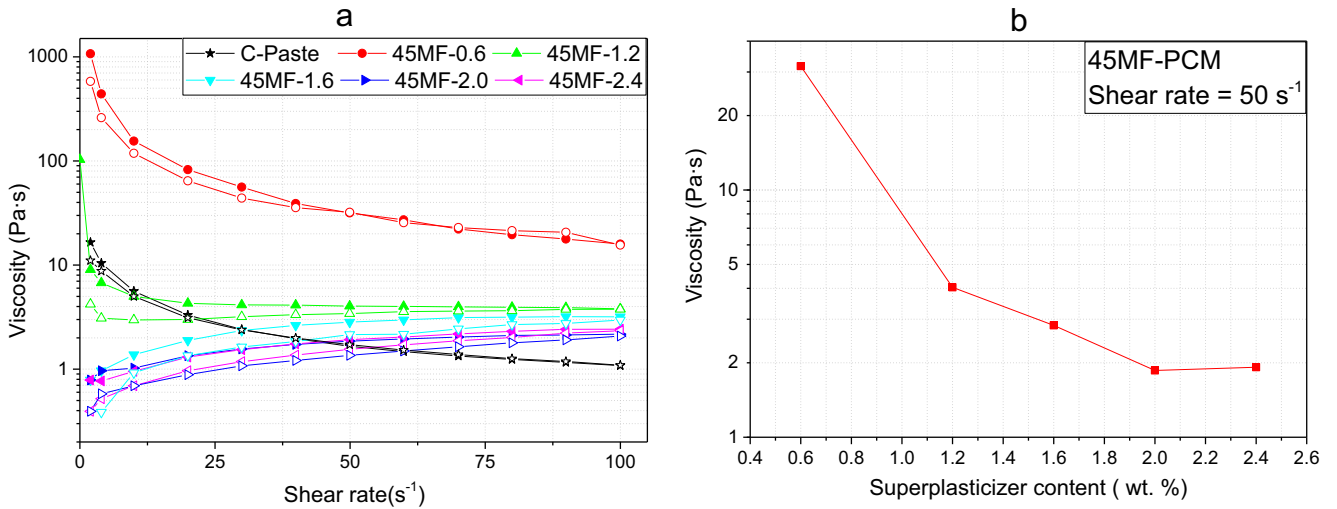
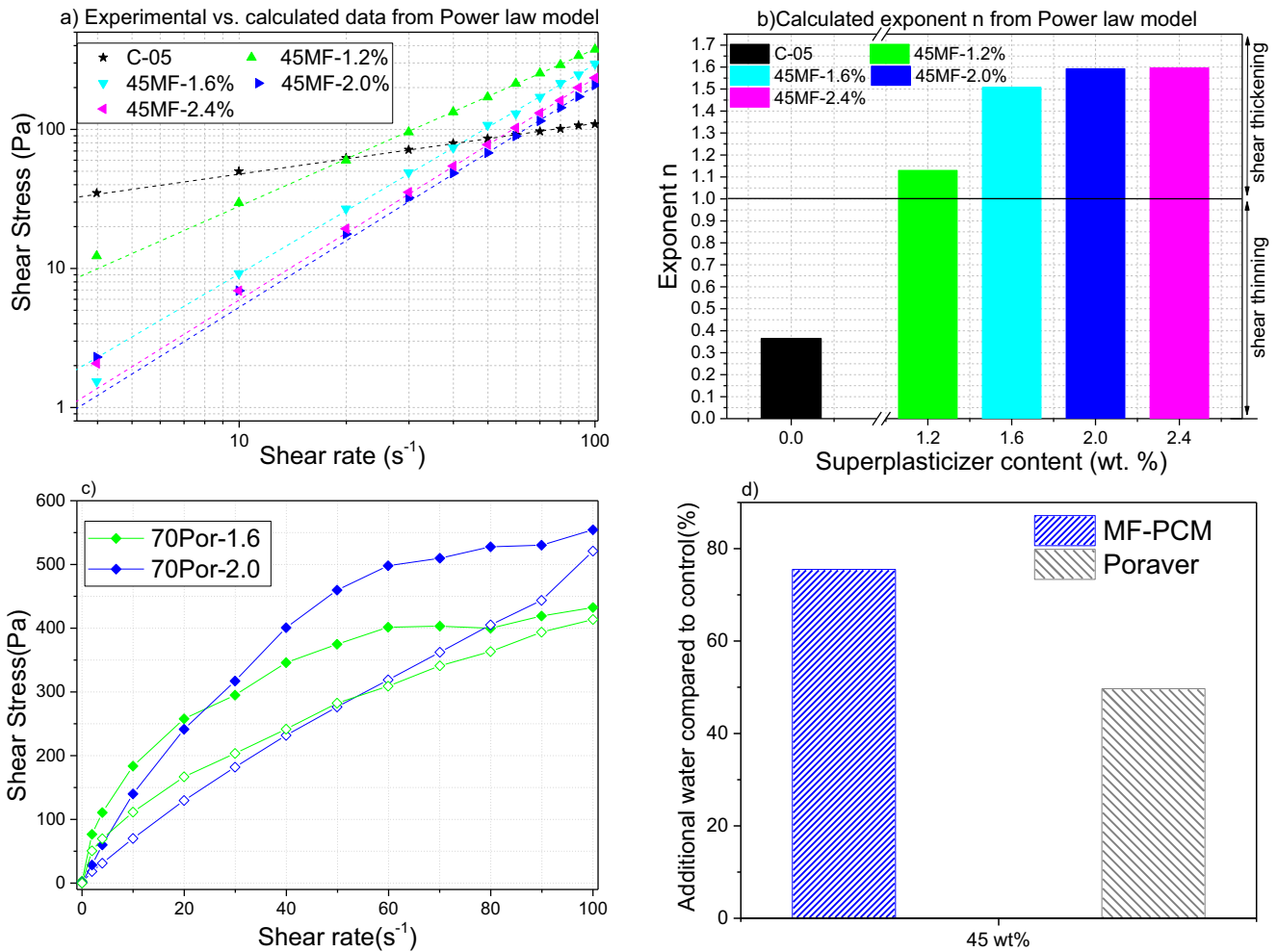


Fig. 7. (a) Viscosity curves of cement pastes with 45 wt% MF-PCM (with respect to cement) and different contents of SP (w/c = 0.5). Filled symbols correspond to the up-curve and empty symbols to the down-curve. The C-paste is included for comparison (PC paste without MF-PCM or SP, w/c = 0.5). (b) The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

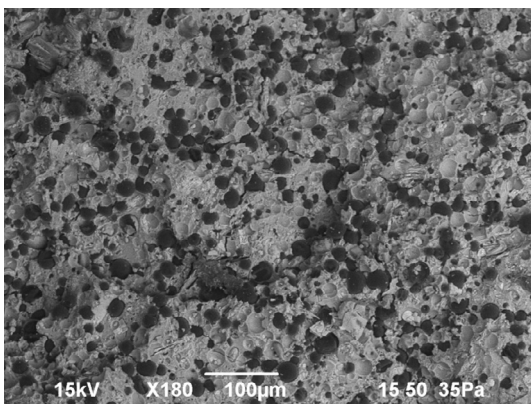
[63]. There are several theories regarding the origin of shear thickening of concentrated colloidal suspensions (such as cement pastes). It has been suggested that the shear thickening is due to an order-disorder transition [64]. It has also been argued that the shear thickening is caused by a mechanism where high shear forces induce hydro-clusters [65–67] due to strong hydrodynamic coupling between particles. Newer studies claim that shear thickening is due to frictional forces, which becomes stronger as the shear rate increases [68–70]. As can be seen from Fig. 8a, the shear stress becomes lower throughout the whole shear rate region

when the concentration of SP is increased. Based on this observation, Kwan et al. [63] suggested that SP causes a higher reduction of shear stress at low shear rates than at high shear rates, resulting in an apparent shear thickening behavior. However, Brown et al. [71] demonstrated that shear thinning of flocculated samples can mask the shear thickening behavior. This is in good agreement with the current observations. When more SP is added to the samples the cement particles becomes better dispersed, as illustrated by the reduced viscosities (Fig. 7a) and lower shear stress (Fig. 8a). Accordingly, they become less shear thinning (reduced





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



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

amount of agglomerates that can be broken apart), and the shear thickening becomes the dominant effect.

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

of frictional forces as the cause of the shear thickening effect [68–70].

Interestingly, cement pastes without microcapsules did not become shear thickening when SP was added to the samples (data not shown). In order to investigate the dominating factors that causes the shear thickening in the cement pastes containing both MF-MCM and high amounts of SP, inert expanded glass spheres (Poraver®) was used as an addition. It should be noted that MF-PCM and Poraver® have different densities (0.85 and 1.40 g/cm<sup>3</sup>, respectively). To take this into account, pastes with different amounts of both powders were added (Table 1).

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

The different particle size (Fig. 1), particle packing, and lower water adsorption of Poraver® compared to MF-PCM (Fig. 8d) contributes to the differences in rheological behavior between the pastes containing Poraver® (shear thinning) and MF-PCM (shear



thickening). A larger amount of SP is expected to be free in the aqueous medium in the Poraver<sup>®</sup>-paste, which should result in less shear thinning and therefore stronger shear thickening (see discussion above). However, since much more water adsorbs onto the MF-PCM (Fig. 8d), the effective concentration of solids becomes higher. A larger volume fraction of solids enhances the shear thickening behavior [65,72,73], and the high water adsorption of MF-PCM is therefore probably one of the causes for the observed shear thickening effect. Combined with the SP-induced deflocculation of the cement particles (which reduces the shear thinning), this causes the observed shear thickening in the presence of MF-PCM and high amounts of SP.

#### 3.4. Microstructure of MF-PCM pastes

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

#### 4. Conclusions

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

Pastes with 15 wt% of MF-PCM and PE-PCM (without superplasticizer, SP) exhibited similar (but not identical) minislump-behavior. The St-PCM paste has a similar spread diameter as the C-paste (control-paste without MPCM), due to its hydrophobic nature. However, when more MPCM were added, the difference between the pastes with MPCM and the C-paste increases. At these concentrations, St-PCM pastes exhibit an intermediate behavior between the C-paste and the other pastes. When SP (a polycarboxylate-based superplasticizer) was added to the cement pastes with 45 wt% MPCM (with respect to cement), only the paste with the hydrophilic MPCM (MF-PCM) did not segregate. This sample was therefore selected for further studies. The optimum amount of SP was found to be 2.0 wt% with respect to the total solid content (minimum viscosity values) for the MF-PCM paste. MF-pastes with low amounts of SP (<1.2 wt%) exhibited a shear thinning behavior, while MF-pastes with SP contents higher than 1.2 wt% was shear thickening. This is probably caused by the combination of two effects. The high water adsorption onto the MF-PCM particles causes the sample to behave as if the concentration of solids were higher. In addition, SP-induced deflocculation of the cement particles reduces the shear thinning of the samples, thereby causing the shear thickening to become more dominant [71]. Pastes with 45 wt% MF-PCM (with respect to cement) exhibit a homogeneous microstructure, where the MF-PCM particles are well dispersed and unaltered at 28 days of hydration.

#### Conflict of interest

The authors declare that we have no conflict of interest with respect to this paper.

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