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Scientific paper

Early Age Hydration, Microstructure and Micromechanical Properties of Cement Paste Modified with Polymeric Vesicles

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Abstract

The influence of limited concentration, of 0.025 wt.% per cement weight, poly (ethylene oxide) -block -polystyrene vesicles on the hydration process, microstructure and micromechanical properties of cement paste at early hydration age of maximum 7 days are discussed. Isothermal calorimetry and non-evaporable water content tests indicate that the admixed vesicles have no apparent influence on the process of cement hydration, but affect microstructural properties. Whereas nitrogen adsorption tests reveal that the gel pore structure of the vesicles-modified matrix is almost identical to the vesicles-free one, mercury intrusion porosimetry proves refined capillary porosity and reduced total porosity in the presence of admixed vesicles. Nano-indentation supports the above observations and indicates that the admixed vesicles act as nucleation sites, leading to a more uniform distribution of low density hydration products.

1. Introduction

Polymers are widely applied in petroleum engineering, civil engineering and construction applications (Merlin *et al.* 2005). With regard to cement based materials, polymers are applied as superplasticizers, air-entraining admixtures, shrinkage-reducing admixtures, etc. (Folliard and Berke 1997; Zhang *et al.* 2001). The general aim of these applications is improving material properties, e.g. workability, setting time, water requirement and mechanical strength (Aitcin and Neville 2003; Jansen *et al.* 2012; Young 1972), consequently producing high-strength and high-performance concretes (Jansen *et al.* 2012; Li *et al.* 2005; Neville and Aitcin 1998). The influence of admixed polymers on the properties of cement-based materials is reported to be mainly related to their dispersion ability via increasing repulsive forces and hindering the coagulation and sedimentation of the cement particles by introducing electrostatic and/or steric repulsion (Jansen *et al.* 2012; Mollah *et al.* 2000). The reported mechanisms are generally commented with regard to the molecular structure and adsorption characteristics of the investigated polymeric additions

(Uchikawa *et al.* 1997). It is also known that admixed polymers generally influence cement hydration to a significant extent, consequently affect the morphology and microstructure of cement-based materials (Chandra and Flodin 1987; Mollah *et al.* 2000; Young 1972).

More recently, block copolymers have been widely investigated (Park *et al.* 2003) because of the specifics of their highly ordered structures (Hadjichristidis *et al.* 2002; Hamley 1998) and the possibility to develop and design nano-particles with desired size, morphology and composition (Krishnamoorti *et al.* 1998). Unique properties in selective solvents can be obtained with amphiphilic copolymers, consisting of both hydrophilic and hydrophobic blocks (Girod *et al.* 2008). When the environmental conditions (temperature, pH, ionic strength) change, the copolymers self-assemble into micelles, vesicles and/or other supramolecular structures (Gil and Hudson 2004). Therefore, amphiphilic copolymers are widely used in many industrial applications, e.g. templates for the preparation of inorganic nano-particles (Gorna *et al.* 2007; Sun and Gutmann 2004), crystal growth modifiers (Rudloff *et al.* 2002), electrolyte components for rechargeable batteries (Singh *et al.* 2007), “vehicles” of active substances release (Khanal and Nakashima 2005; Kojima *et al.* 2008), etc.

The application of amphiphilic copolymers in the form of nano-architectures for cement-based materials is to our best knowledge not reported. In our previous research, the influence of polymeric micelles and vesicles (with a hydrodynamic radius of 50 nm and 220 nm) respectively on the corrosion performance of reinforced concrete was investigated (Hu *et al.* 2012b, 2011, 2012c). Micelles are polymeric, self-assembled nano-architectures with amphiphilic properties in our case, whereas vesicles are nano-sacs, that enclose a volume, containing water or chosen substances. Both micelles and vesicles were prepared from polyethylene oxide-b-polystyrene (PEO-b-PS) diblock copolymer.

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Initial tests in simulated pore solution (Hu *et al.* 2011) and reinforced mortar in the presence of micelles (Hu *et al.* 2012b) proved that corrosion initiation was delayed on one hand and chloride binding capacity of the mortar was increased on the other. Further investigations on admixed vesicles, and especially Ca-containing ones, where saturated $\text{Ca}(\text{OH})_2$ solution was pre-reserved in their core, (Hu *et al.* 2012c) indicated “self-healing” effect of the corrosion damage in the reinforcement: after corrosion initiation, the steel corrosion resistance was significantly increased and corrosion propagation on the steel reinforcement was halted. The most plausible mechanism is initially related to increased chloride binding capacity of the bulk matrix and further calcium release from the vesicles on anodic locations (active spots) i.e. formation of Ca-substituted iron oxides/hydroxides layers with increased corrosion resistance was observed. The trigger of altered vesicles morphology and core release is modified pore solution chemistry in the presence of chlorides and altered ions/water/oxygen balance on the steel surface within and after corrosion initiation. All together, these processes lead to repair or “self-healing” of the steel surface layer.

Considering the complicated nature of both micelles and vesicles and their effect on permeability, Cl-binding capacity, etc. of a cement system, their influence on bulk matrix properties only, when no steel reinforcement or corrosion phenomena are involved, is logically of interest and deserves investigation for substantiated reasoning behind the postulated “repair” or “self-healing” effects. The effect of micelles, i.e. reduced porosity and water permeability, has been previously reported (Hu *et al.* 2012a). These results were a positive outcome if steel corrosion in reinforced cement-based systems is considered. Corrosion initiation and corrosion propagation depend on the material properties of a reinforced cement-based system, e.g. if the rate of chlorides or CO_2 penetration is limited or none, steel is (generally) in a passive state. Since corrosion initiation depends on the cement matrix permeability and diffusivity, which in turn determine the rate of penetration of aggressive substances, the early age hydration mechanisms are of great importance. To this end, the objective of this study is to clarify the influence of vesicles (empty i.e. not Ca-bearing ones) on material properties: hydration rate and microstructure of cement-based materials at early hydration age. The hydration process was evaluated both by isothermal calorimetry and non-evaporable water content tests; the pore structure of the cement matrix was studied by nitrogen adsorption (for the gel pore structure) and mercury intrusion porosimetry (for the capillary pore structure). Further, nano indentation was conducted to

investigate the influence of admixed vesicles on the formation and distribution of hydration products.

2. Materials and methods

2.1 Materials

2.1.1 Vesicles

The vesicles used in this study were prepared from $\text{PEO}_{113}\text{-b-PS}_{780}$ di-block copolymer (the molecule structure of the copolymer is presented in **Fig. 1**). The copolymer was synthesized by atom transfer radical polymerization (ATRP), employing the macroinitiator technique (Hu *et al.* 2012b; Matyjaszewski and Xia 2001). The vesicles solution was prepared by dialysis: 0.5 g $\text{PEO}_{113}\text{-PS}_{780}$ diblock copolymer was dissolved in 800 ml 1,4-dioxane and 200 ml deionized water were added drop-wise. The vesicles gradually formed at the interface between dioxane and deionized water. The solution was then transferred to regenerated cellulose tubular membrane (MWCO 12,000 g/mol) and dialyzed against deionized water to remove dioxane. The vesicles concentration in solution was 0.5 g/l. The morphology of $\text{PEO}_{113}\text{-b-PS}_{780}$ vesicles is spherical, presenting a membrane of an outer hydrophilic - PEO and an inner, hydrophobic - PS part. The hydrodynamic radius, determined by dynamic light scattering (DLS) measurement, is about 220 nm (Hu *et al.* 2012d) (details about the vesicles preparation can be found in (Hu *et al.* 2012c)).

2.1.2 Cement paste specimens

In this study, Ordinary Portland Cement OPC CEM I 42.5 N (ENCI, **Table 1**) was used to prepare the cement paste specimens; the water-to-cement (w/c) ratio was 0.5.

The samples for mercury intrusion porosimetry (MIP), N_2 adsorption and nano indentation tests were prepared in plastic bottles. After casting, the samples were rotated for 24 hours to avoid sedimentation and then cured in sealed conditions at room temperature. After curing for 1, 3 and 7 days, standard sample preparation for ceasing cement hydration was employed: the samples were submerged in liquid nitrogen and further placed in a vacuum freeze-dryer at -28°C (water sublimation) until achieving a constant weight. For isothermal calorimetry

Fig.1 Molecule structure of $\text{PEO}_{113}\text{-PS}_{780}$ diblock copolymer used in this study.

Table 1 Chemical compositions of OPC CEM I 42.5 N (ENCI, NL).

Chemical compositions of OPC CEM I 42.5 N											
Oxide	CaO	SiO ₂	Al ₂ O ₃	SO ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	Mn ₂ O ₄
Weight (%)	64.4	20.36	4.96	2.57	3.17	2.09	0.14	0.64	0.35	0.18	0.14

and non-evaporable water content tests, parallel groups of cement paste (same mixtures) were prepared (procedures' details are described further below). Two main groups were investigated in this study: group "OPC" as control, vesicles-free specimens cast with tap water and group "OPCv" as vesicles-containing specimens cast with the as produced vesicles' solution instead of tap water. The vesicles concentration was thus 0.025 wt. % (by weight of dry cement) in cement paste for specimen OPCv.

2.2 Methods

2.2.1 Hydration rate and hydration degree

Isothermal calorimetry was performed on 3 replicates for each specimen using a micro-calorimeter (TEM Air 314) at 20 °C. Before the tests, the mixing tools and materials were stored at 20 °C in the same room for 24 hours. Cement was mixed with tap water (for specimen OPC) or vesicles' solution (for specimen OPCv) within 60±5 seconds; then about 10 g cement paste was carefully poured into glass calorimeter ampoules (the rest of the cement paste was tightly sealed in plastic bottles for the measurement of non-evaporable water content). The whole procedure was completed within 3 min. The heat flow and the cumulative heat release were recorded until 168 h (7 days). The rate of hydration was measured as power (mW) and was normalized per gram of cement.

Non-evaporable water content ($W_{n/c}$): The hydration degree of the cement paste was obtained by determining the non-evaporable water content ($W_{n/c}$). $W_{n/c}$ is defined as the weight loss per gram of original cement paste, measured between the temperatures of 105 °C and 1000 °C (Copeland and Hayes 1953). At each hydration age (1 day, 3 days and 7 days), the samples were ground to powders and then 3 replicates were dried in an oven at 105 °C for at least 12 hours; the samples were then ignited at 1000 °C in a furnace for 3 hours (details about the procedure and calculation are as described in Copeland and Hayes (1953) and Molina (1992).

2.2.2 Microstructure evaluation

Nitrogen adsorption: For nitrogen adsorption tests, the samples were first crushed into small pieces (with a weight of less than 0.05 g). The crushed samples were weighted and placed in a glass tube, the latter positioned in the chamber of Germini VII 2390 Surface Area Analyzer. The glass tube was evacuated first, and then filled with pure nitrogen. p and p_0 were defined as the nitrogen pressure in the tube and the saturated pressure respectively. During the measurement, the adsorption amounts of nitrogen at different relative pressures (p/p_0) from 0.05 to 0.95 were recorded. The pore size distribution was determined by Barrett-Joyner-Halenda (BJH) method (Barrett *et al.* 1951).

Mercury intrusion porosimetry (MIP), using Micro-metric Poresizer 9320 (with pressure limits from 0.0036 to 210 MPa) was performed. The measurement was conducted in two stages: the first stage was at low

pressure, from 0 to 0.0036 MPa and the second stage was at high pressure running from 0.0036 to 210 MPa, followed by an extrusion running from 210 to 0.14 MPa. The surface tension of mercury was 484×10^{-3} N/m and the contact angle was 130°. According to Washburn equation (Washburn 1921), the pore size range detected in this study is from 350 µm to 0.007 µm. There were 2 replicates for both nitrogen adsorption and MIP tests.

Nano indentation: Before nano indentation tests (performed for samples at hydration age of 7 days only), the samples were ground with silicon carbide papers (fineness in the range from 320 to 4000) and then polished with diamond pastes of sizes 6, 3, 1 and 0.25 µm to obtain a very flat and smooth surface. After polishing, the specimens were cleaned in an ultrasonic bath. Nano indentation is a method providing information on micromechanical properties via indentation load and displacement measurements, including distribution of un-hydrated particles, calcium silicate hydrate (CSH) and calcium hydroxide (CH) at micro and sub-micro scale. **Fig. 2** presents a typical data curve of indentation load-displacement as recorded in this study. The Continuous Stiffness Method (CSM Method) developed by Oliver & Pharr (Oliver and Pharr 2004) was used for the analyses of the results and the average E-modulus was determined in the loading range between 200 and 800 nm depths.

Agilent Nano Indenter G200 equipped with a pyramid-shaped Berkovich diamond indenter probe was applied to determine the micromechanical properties of cement paste. Nano indentation mapping was used to investigate the local elastic modulus properties between two adjacent un-hydrated particles. Before the indentation, two adjacent cement grains were located and marked via ESEM. The investigated matrix covered an area of at least $40 \times 340 \mu\text{m}^2$ with a minimum of 175 indents. The selected indent spacing was 10 µm. At least 6 locations were measured for each specimen.

ESEM and EDX analysis: An environmental SEM (ESEM Philips XL30), in backscattered electrons (BSE) mode (working distance of 10 mm, accelerating voltage at 20 keV), combined with energy dispersive X-ray analysis (EDX) was employed for morphology observa-

Fig.2 Typical data curve of indentation load-displacement.

tion and qualitative and semi-quantitative analysis of the cement matrix. These enable an assessment and correlation of the nano indentation results, the morphology of the corresponding surface and the composition of relevant (indented) phases.

3. Results and discussions

3.1 Hydration process of cement paste in the presence of admixed vesicles

The rate of heat release and the cumulative heat for both specimens during the first 168 h are presented in **Fig. 3**. It can be observed that the admixed vesicles slightly decelerated the hydration rate of tri-calcium silicate (C_3S , corresponding to the main peak in **Fig. 3(a)**) by about 36 minutes. Similarly, the total heat release for the modified cement paste was also slightly reduced by the admixed vesicles: at 7 days (168 h) hydration age, the cumulative heat release was 315.69 J/g for specimen OPC and 306.35 J/g for specimen OPCv respectively. The isothermal calorimetry results are in line with those for degree of hydration, determined by the non-evaporable water content ($W_{n/c}$), shown in **Fig. 4**.

The degree of hydration for both vesicles-free (OPC) and vesicles containing (OPCv) cement pastes is very similar at each hydration age, **Fig. 4**: e.g. at 7 days, for specimen OPC - 49.53 %, for specimen OPCv - 49.43 % are relevant. These results are in contrast to the previously recorded ones for micelles-modified cement paste (Hu *et al.* 2012a). For completeness, a comparison of the influence of admixed micelles and vesicles on the hydration process of cement paste at 7 days hydration age is presented in **Table 2**. Compared to vesicles, although again minimal difference, but yet opposite trends of slightly increased degree of hydration for the micelles-modified matrix was observed i.e. at the age of 7 days, the cumulative heat release and hydration degree of micelles-modified specimens was 314.92 J/g and 50.80 ± 0.55 %, compared to 315.69 and 49.27 ± 0.98 % for the non-modified matrix. These results are as expected to a certain extent, considering the larger surface area of micelles (50 nm), compared to the hereby investigated vesicles (220 nm) and therefore the possibility of more pronounced “nucleation sites effect” in the former, rather than in the latter case. Additionally, some reports on retardation of early hydration of cement paste due to admixed PEO-containing polymers (normally used as superplasticizers for cement-based materials) need to be also considered (Sakai *et al.* 2006; Winnefeld *et al.* 2007) as contributing factors. The retardation effects are reported to be mainly relevant to the hydration of C_3S

Fig.3 (a) Hydration rate and (b) Cumulative heat evolution of the cement paste in the absence (specimen OPC) and presence (specimen OPCv) of admixed vesicles respectively

Fig.4 Hydration degree of the cement paste determined by non-evaporable water content.

(Lothenbach *et al.* 2007; Pourchet *et al.* ; Winnefeld *et al.* 2007) and the proposed mechanisms (Gu *et al.* 1994; Jansen *et al.* 2012; Mollah *et al.* 2000) can be summarized as: (1) polymers adsorption on the surface of cement grains, hindering the diffusion of water and Ca^{2+} ions at the cement grain/solution interface; (2) impeded growth of hydrate phases due to the presence of polymers; (3) dispersive ability and effect of the polymers which alter the growth kinetics and morphology of the hydration products. These effects are not necessarily

Table 2 Comparison of the influence of micelles and vesicle on the hydration process of cement paste at the hydration age of 7 days.

Mixing water	Accumulative heat release (J/g)	Hydration degree (%)
Tap water	315.69	49.53
Micelles solution	314.92	50.80
Vesicles solution	306.35	49.43

Note: the parameters for cement paste casting with micelles solution was previously reported in [Hu *et al.* 2012a]

relevant for the present investigation, mainly because of: 1) the type and size of the hereby PEO-b-PS - based vesicles, being in the nano-range; 2) these self-assembled architectures are in a minimal concentration of 0.025 wt.% per cement weight. Moreover, the hydration of C_3S in specimens OPCv was only delayed for 36 minutes (**Fig. 2(a)**), whereas the reported retardation in C_3S hydration is in the range of 3-17 h (Sakai *et al.* 2006; Winnefeld *et al.* 2007), relevant to concentration of 0.1-0.5 wt. % by cement weight (Sakai *et al.* 2006; Winnefeld *et al.* 2007; Yamada *et al.* 2000). However, dispersive effects can't be excluded and need further investigation, which is beyond the scope of this study and will be further reported.

3.2 Microstructural alterations of cement paste in the presence of the admixed vesicles

3.2.1 Gel pore structure

Nitrogen adsorption test, which is widely used for the investigation of the microstructure of cement-based materials (the pore size determined by nitrogen adsorption test is normally in the range from 1 nm to 300 nm) (Aligizaki 2006; De Belie *et al.* 2010; Garci Juenger and Jennings 2001), was applied in this study to evaluate the influence of the admixed vesicles on the gel pores structure of cement paste (normally ranging from 0.5 nm to 0.01 μm (Mindess and Young 1981). **Figure 5** presents the total porosity and pore size distribution of both

Fig.5 Porosity and pore size distribution of the specimens at 7 day hydration age, derived from N_2 adsorption test.

specimens at 7 day hydration age, derived from N_2 adsorption tests (due to the limitation of the nitrogen adsorption tests, the determined pore size range was only from 3 nm to 80 nm in this study).

As seen from the plots, the total gel porosity was similar for both specimens OPC (0.855 ml/g) and OPCv (0.856 ml/g). The gel pores with large size (pore size range from 40-80 nm) for specimen OPCv were slightly more pronounced than for specimen OPC (**Fig. 5(a)**). The critical pore size of the gel pores was also identical for both specimens OPC and OPCv, as shown in **Fig. 5(b)**. From these results it is obvious that the gel pore structure of cement paste was not significantly influenced by the admixed vesicles.

3.2.2 Capillary pore structure

MIP, which can evaluate a much wider pore size range than N_2 adsorption test (the pore size range determined by MIP was between 0.007 μm and 350 μm in the present study), was employed to investigate the microstructural alterations of cement paste in the presence of admixed vesicles.

The cumulative intruded volume curves (**Fig. 6(a)**) and differential distribution curves (**Fig. 6(b)**) derived from MIP at 7 days hydration age are shown in **Fig. 6**. At

Fig.6 Porosity and pore size distribution of the specimens at 7 day hydration age, derived from MIP test: (a) Cumulative intruded volume curves; (b) Differential distribution curves.

7 days hydration age, the total porosity of cement paste was slightly reduced by the admixed vesicles: the total porosity was 36.78 % for specimen OPCv and 37.81 % for specimen OPC, **Fig. 6(a)**. Further, it is observed in **Fig. 6(b)** that the critical pore size was similar for both specimens, which is as derived by N_2 adsorption tests; however, the critical pore size for the capillary pores (normally ranging from 0.01 μm to 10 μm (Mindess and Young 1981)) decreased in the presence of the admixed vesicles (0.44 μm for specimen OPCv and 0.51 μm for specimen OPC). Therefore, it can be stated that in the presence of admixed vesicles, the slightly denser pore structure and reduced critical pore size (which is the smallest pore size of a connected pore network) would result in reduced pore network connectivity (a similar effect was also observed in the presence of micelles, (Hu *et al.* 2012a)). Therefore, if the vesicles are admixed in reinforced concrete, chloride penetration is expected to be halted, leading to a delay of corrosion initiation and further propagation on the steel reinforcement. Since on the other hand hydration rate and hydration degree were not affected or showing a slightly reversed trend (**Figs. 3, 4**), the observed microstructural alterations in the presence of admixed vesicles can only be related to their influence on the formation and distribution of hydration products, which will be discussed in what follows.

3.3 Distribution of hydration products in the presence of vesicles

Figure 7 presents the morphology of the cement matrix for both specimens OPC and OPCv at the hydration age of 7 days (ESEM observation). Distinguishing the admixed vesicles in the cement matrix is impossible due to their nano-size, however, their influence on the development of the bulk microstructure is obvious: the cement matrix was denser for specimen OPCv (**Fig. 7(b)**), compared to specimen OPC (**Fig. 7(a)**), presenting significantly lower amount of pores in the former and higher amount in the latter case (pore space indicated as circled areas in **Fig. 7**). Further, the distribution of hydration products was also altered in the presence of vesicles: for specimen OPC, the hydration products were predominantly formed around the un-hydrated cement particles (high density CSH (Jennings 2000; Richardson 1999)), whereas for specimen OPCv visually higher amount of hydration products were observed in the bulk matrix (low density CSH (Jennings 2000; Richardson 1999)).

Nano indentation tests confirmed these observations. **Figure 8** presents the ESEM images (magnification of 500 $\times$) and maps of elastic modulus E of the test area in cement paste for both specimens. The nano indentation test was conducted in the area between two adjacent un-hydrated cement particles, which is marked as the

Fig.7 ESEM images (a) OPC; (b) OPCv both at 500 $\times$ magnification at 7 days hydration age.

Fig.8 Maps of elastic modulus E of the test area in cement paste, together with the corresponding ESEM images (marked rectangular areas corresponds to the modulus maps).

rectangular area in the corresponding ESEM images. As well known, the CSH gel in cement paste can be classified into two different morphological forms (Jennings 2000; Richardson 1999): high density (HD) CSH with an elastic modulus values in the range of 29.1-31.4 GPa and low density (LD) CSH with an elastic modulus values in

the range of 18.2-23.4 GPa (Constantinides and Ulm 2004; Constantinides *et al.* 2003; Zhu *et al.* 2007).

These two distinct phases are also characteristic in this study. The influence of admixed vesicles on the formation of HD CSH was not obvious, confirmed by the similar distribution of modulus value between 30 and 45

Fig.9 ESEM images and the corresponding EDX pattern for: (a) un-hydrated cement grains, (b) HD CSH, (c) LD CSH and (d) CH) in OPC (left column) and OPCv (right column) (the test points – nano-indents - are well visible in the images of un-hydrated grains)

GPa for both specimens (the percentage of nano indents with a modulus value between 30 and 45 GPa was 9.71 % for specimen OPC and 10.86 % for specimen OPCv respectively in Fig. 8). However, the distribution of LD CSH was significantly altered in the presence of vesicles: for specimen OPCv, a larger area corresponding to LD CSH (the percentage of nano indents with a modulus value between 15 and 30 GPa was 25.14 % for specimen OPCv, compared to 21.14 % for specimen OPC) was observed; the area corresponding to the pores in the cement matrix was also larger for specimen OPC (the percentage of nano indents with a modulus value between 0 and 15 GPa was 41.71 % for specimen OPC, compared to 34.29 % for specimen OPCv). The results indicate that the admixed vesicles lead to a more uniform distribution of low density hydration products and a more homogeneous and denser cement matrix (a result, which was also observed previously in the presence of micelles, (Hu *et al.* 2012a)).

Figure 9 presents ESEM images (in BSE mode), emphasizing on different phases ((a) un-hydrated cement particle (UH), (b) HD CSH, (c) LD CSH and (d) CH) and the corresponding EDX analysis (the test points are also marked in the images) for specimen OPC after the nano indentation test. Well known is that the different mineral phases in a cement matrix exhibit different grey levels in the BSE images. Skedros *et al.* (1993) and Ye (2003) demonstrated that the grey-scale level in BSE images corresponds to the average atomic number and mineral density of each phase. Based on these well-known dependencies and considering the BSE images obtained in the present study, the main mineral phases in both OPC and OPCv can be distinguished by the order of grey-scale intensity values as follows: UC > CH > HD CSH > LD CSH > pore structures.

EDX analysis indicates the presence of Ca and Si for the different mineral phases (Fig. 9) (EDX analysis was performed as qualification and semi-quantification only; no absolute values are claimed in this study, but rather relevant contents via peaks intensity for equal current/voltage characteristics of the beam and live seconds of investigation). Based on the combination of the nano indentation tests (the nano indents can be easily observed

in the ESEM images after the tests, as shown in Fig. 9, top row), ESEM images and EDX analysis, the phase on which each nano indent contacted the matrix can be easily determined. Therefore, with a large number of indentation data (the number of total nano indents was more than 1000 for both specimens), the average indentation modulus values of HD CSH and LD CSH for both specimens were calculated by statistical analysis, the average values as shown in Fig. 10.

The calculated average modulus of the individual mineral phases further confirms the nano indentation mapping results: the modulus value of HD CSH was not influenced by the admixed vesicles; the modulus value of LD CSH was slightly higher in the presence of vesicles. Because the mechanical properties of the LD CSH and HD CSH are intrinsic to cement paste (Constantinides and Ulm 2004; Constantinides *et al.* 2003; Zhu *et al.* 2007), the most plausible reason for the lower modulus value of LD CSH for specimen OPC is related to a more porous microstructure of the cement matrix. As afore-mentioned in the “Introduction” section, the PEO-containing polymers influence the properties of fresh cement paste: they can hinder the coagulation and sedimentation of un-hydrated cement particles by increasing the electrostatic and/or steric repulsive forces (Jansen *et al.* 2012; Mollah *et al.* 2000). This effect would influence the distribution of hydration products in the hardened cement paste. Further, as reported (Nicoleau 2010), PEO-containing polymers can act as nucleation sites for the formation of new hydration products. In this study, considering that the here investigated vesicles contain -PEO- architectures, similar effects are to be expected: dispersion effects together with “nucleation effects” would contribute to a more uniform distribution of hydration products and a denser pore network in the presence of admixed vesicles.

4. Conclusions

The hydration process and microstructure alterations of cement paste in the presence of admixed poly(ethylene oxide)-block-polystyrene (PEO₁₁₃-b-PS₇₈₀) vesicles at early hydration age were investigated. The results indicate that at early hydration age, the admixed vesicles slightly retard the hydration rate of the cement paste, evidenced by isothermal calorimetry and non-evaporable water content tests. The admixed vesicles did not significantly change the gel pore structure of the cement matrix, which is consistent with the slightly retarded hydration rate. This observation is in contrast to the opposite trend, previously observed and reported for PEO-b-PS micelles and is denoted to the larger surface area of the latter (core-shell structure of 50 nm), compared to the former (nano-sacs of 220 nm). However, at the stage of 7 days, a denser capillary pore structure was observed in the presence of the here investigated vesicles. Nano indentation tests confirmed micro-mechanical alterations and proved that the admixed vesicles act as

Fig.10 Average indentation modulus values of both LD CSH and HD CSH in the cement paste for specimen OPC and OPCv.

nucleation sites, leading to a more uniform distribution of low density hydration products. An additional, plausible mechanism could be related to initial dispersion effects on the un-hydrated cement particles and is subject to on-going research (including zeta-potential alterations) in the presence of vesicles.

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