

Tailor-made Nano Materials for Corrosion Control and Improved Matrix Characteristics in Cement-based Systems

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ABSTRACT

Polymeric nano-aggregates (PEO₁₁₃-b-PS₂₁₈ micelles) in a very low concentration (0.025 wt. % per dry cement weight) were investigated for their ability to exert superior corrosion performance of carbon steel in simulated pore solution. The presence of these tailored made polymeric aggregates was found to exert morphological changes and altered composition of the passive layer on the steel surface, resulting in improved electrochemical behavior. Further, these nano-aggregates when admixed in cement paste appeared to alter microstructural characteristics and global parameters as porosity and permeability. Whereas bulk matrix characteristics were largely affected in a positive direction, alterations in hydration rate and modified cement hydration mechanisms were not recorded for the micelle-containing mixtures compared to the non-modified such. The paper discusses main aspects of this investigation, emphasizing on the mechanisms, related to the influence of micelles on the microstructural characteristics of the cement-based bulk matrix. Mainly considered is the “nucleation sites” effect, as actually supported by the results from nano-indentation investigation, isothermal calorimetry and pore structure analysis.

Keywords: Corrosion; Polymeric nano-aggregates; Microstructure; Mortar; MIP; Nano-indentation.

1. Introduction

Next to water, concrete is the most used material on earth. Reinforced concrete has the potential to be durable and capable of withstanding a variety of adverse environmental conditions. One of the major difficulties in the engineering practice, however, is the multi-dimensional nature of reinforcement corrosion. Corrosion-related durability issues are constantly increasing especially for older structures. Therefore, the major challenge, and thus the primary goal of a comprehensive investigation, this work being part of it, is to significantly improve the civil structures performance by incorporating entirely innovative for these applications materials i.e. tailored nano-polymers.

The main hydration product in cement paste, calcium silicate hydrate (CSH) gel, is a natural nano-structured material [1-3]. The incorporation of nano materials into a cement matrix is a challenging way to control corrosion of embedded reinforcement and/or modify the material properties of the bulk matrix and the steel/cement paste interface. Thus the aim is to achieve superior material performance, starting at the nano-scale level. A comprehensive review on nanotechnology in concrete material science [4] gives a detailed overview of recent advancements in the application of nano-materials for altered properties of cement-based systems. Nano-TiO₂ particles [5], nano-Fe₂O₃, nano-SiO₂ particles [6] etc., were investigated for their effect on cement hydration, mechanical properties, microstructure alterations, resistance to water penetration, etc., showing promising results. Polymeric micro-particles (e.g. admixed

poly (ethylene-co-vinyl acetate) copolymer), [7] or polycarboxylic acid-based copolymers [8, 9] were reported to result in altered morphology and composition of hydration products and to behave as nucleation sites for the formation of new ones. In other words, when a cement-based system is modified with inorganic nano-particles or organic micro-particles, superior material properties are achieved. The influence of organic nano-particles is rarely reported. This work presents the investigation on the effect of polymeric nano-particles on both corrosion performance of embedded steel and microstructural properties of the cementitious bulk matrix.

2. Experimental materials and methods

2.1. Polymeric nano-aggregates: The polymeric micelles employed in this study were prepared from PEO₁₁₃-b-PS₂₁₈ di-block copolymer [10]. The micelles (Fig.1) were used as additions to model liquid environment (solutions simulating concrete pore water, [10]), or admixed in plain mortar [11,12] reinforced mortar [13] and the hereby discussed cement paste. The micelles were employed in very low concentrations: 0.0024 wt. % in chloride-free and chloride-containing model solutions; 0.025 wt. % per cement weight were admixed in cement-based materials.

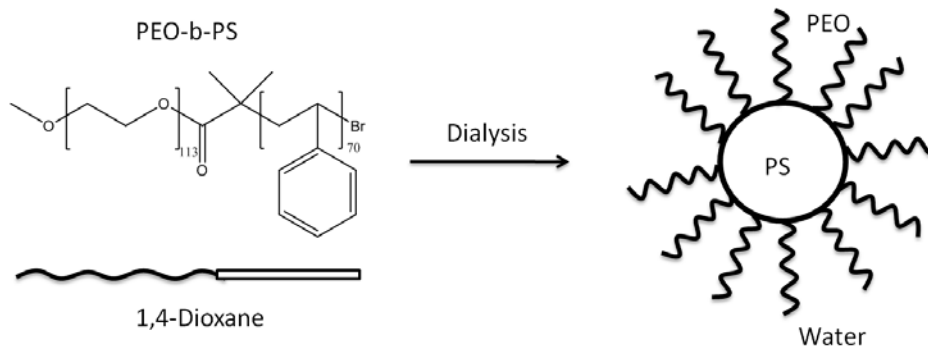


Fig. 1 Formation of frozen core-shell micelles from PEO₁₁₃-b-PS₇₀ di-block copolymer (with the size of 50 nm) in aqueous media

2.2. Tests in model solutions:

- *Model liquid environment*: The model solution was cement extract (CE), prepared by mixing Portland cement CEM I 42.5 and water in a ratio of 1:1 and filtrating the suspension after 24h. The so prepared CE (pH of 12.6) was used as received (as a control case) or modified by adding 10% NaCl (for investigating corrosion behavior of steel electrodes, treated at different time intervals).

- *Steel electrodes in model solutions*: The tests in the above specified solutions were conducted, using steel electrodes (low-carbon steel St37) with service area of 4cm² i.e. this investigation was related to corrosion behavior of steel in model CE solutions containing nano-aggregates (micelles). Before testing, grinding, polishing, acetone cleaning and water rinsing were performed for the steel electrodes.

- *Electrochemical behavior and surface analysis*: Open circuit potential (OCP), Electrochemical Impedance Spectroscopy (EIS) and Potentio-dynamic polarization (PDP), using Eco-Chemie Autolab were performed for evaluating corrosion performance of the steel electrodes; Scanning electron microscopy, coupled with EDX analysis (using ESEM Philips XL30) and X-ray photoelectron spectroscopy (XPS) were employed for surface analysis of the product layers on the steel surface.

2.3. Tests in mortar:

- *Isothermal calorimetry* was performed on 3 replicate specimens of cement paste using an eight channel micro-calorimeter (TEM Air 314) at 20 °C. The mixing tools and materials were stored at a constant temperature of 20 °C for 24 hours before mixing. The entire mixing period was maintained within 60±5 seconds. The rate of hydration was measured as power (mW) and was normalized per gram of cement. The standard deviation for the accumulative heat release at 7 days hydration age was 4.02 J/g (1.24%) for micelle-free specimens (OPC) and 4.37 J/g (1.36%) for micelle-containing specimens (OPCm)

- *Nano indentation* tests were conducted using U9820A Agilent Nano Indenter G200 (MTS systems corporation) to determine the elastic modulus E of different phases (e.g un-hydrated cement particles and CSH). The mechanical properties at the nano-scale can be determined from the indentation load and displacement measurement. The investigation was performed on the top trowel surface of equally prepared and handled specimens. Information on the mechanical properties was obtained from a matrix of a minimum of 120 indents covering a representative area of at least 40×230µm² on the surface. The selected indent spacing was 10 µm.

- *Mercury intrusion porosimetry (MIP)* was conducted by using Micromeritics Poresizer 9320 (with a maximum pressure of 207 MPa) to determine the porosity and the pore size distribution of the specimens. The Washburn equation [14] was used to calculate the diameter of pores intruded at each pressure step. The surface tension of mercury was 484 ×10⁻³ N/m and the contact angle was 130°. 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. According to Washburn equation [14], the pore size range detected is from 350 µm to 0.007 µm.

3. Results and Discussion

3.1. Model solutions: electrochemical behavior of carbon steel.

The influence of polymer nano-aggregates on the corrosion performance of carbon steel and morphology and composition of the product layers on the steel surface were investigated in model solutions (cement extract, simulating concrete pore water). The variables within this investigation were: solutions without (control cases) or with (corroding cases) admixed chlorides.

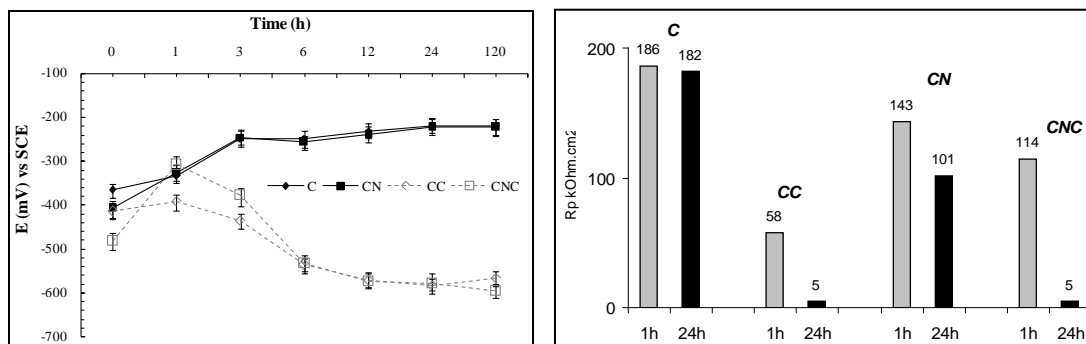


Fig.2 OCP readings for all studied cases (left) and Rp values (right)

Further, with respect to the influence of nano-aggregates, both control and corroding cases consisted of micelle-free and micelle-containing solutions. The control cases are designated C (micelle-free) and CN (micelle-containing) cases; the corroding ones are designated CC (mi-

celle-free) and CNC (micelle containing) cases. The steel electrodes, treated in these solutions and discussed hereby maintain identical sample designation. Figure 2 (left) depicts the OCP readings for all specimens within treatment; the summarized polarization resistance (R_p) values for 1h and 24h conditioning are given in Fig.2 (right). Figure 3 presents the behavior of the steel electrodes with external polarization after 24h treatment (Fig.3(left), overlay of PD curves) and the EIS response (Fig.3(right)) from 1h and until 24h for the corroding cases (for the complete and comprehensive investigation of these experimental series, pls see [10]).

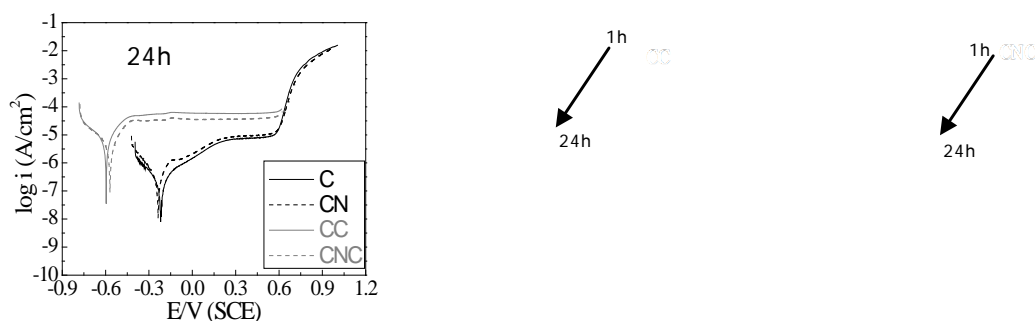


Fig.3 Potentio-dynamic curves for all cases after 24h treatment (left) and EIS response for CC and CNC (corroding) cells within treatment of 1h – 24h (right)

As seen from the plots (Figs.2, 3), electrochemical measurements present similar behavior of the steel electrodes in both micelle free (C and CC) and micelle-containing (CN and CNC) solutions. Both control cases C and CN present (as expected) high corrosion resistance (Fig.2). For the corroding cases, except at earlier time intervals (Fig.2, right) the corrosion resistance of the steel electrodes was not affected by the presence of micelles to a significant extent. However, capacitance values for the oxi/redox process in the product layers (C_{red}) as well as double layer capacitance (C_{ct}) (derived via EIS, Fig.3, left) show lower values for the steel treated in micelle-containing solutions i.e. superior properties of the otherwise electrochemically behaving as „corroding“ cells CNC.

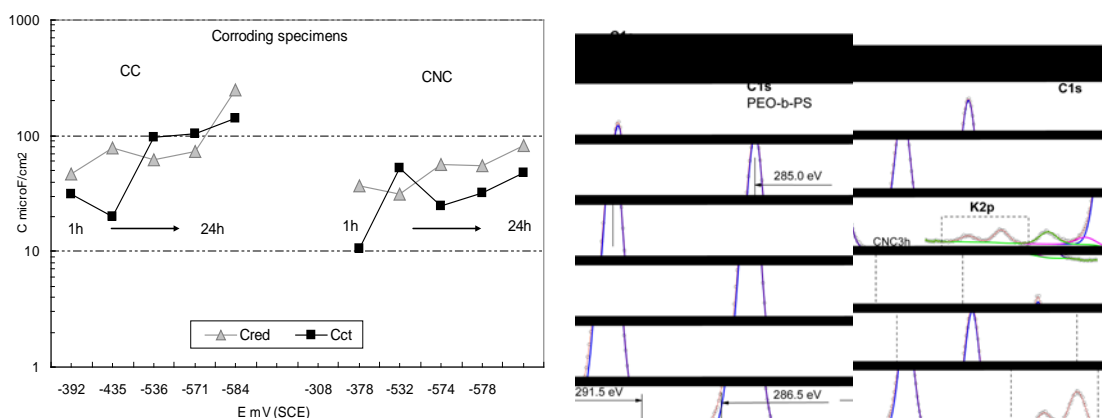


Fig.4 (left) C_{red} and C_{ct} capacitance values (from EIS measurements [10]); (right) Detailed C1s spectra for micelles only and for corroding cells CN and CNC [10].

This observation was supported by X-ray analysis of the steel surface, showing indeed the presence of micelles on the steel surface (Fig. 4, right). and consequently increased barrier effects of the formed layer, compared to CC specimens The XPS analysis thus revealed that the presence of only 0.0024 wt. % micelles in the initial testing solutions leads to increased barrier effects (at least on earlier stages) but also results in “blocking” the steel surface and

less oxygen content. Therefore, an initially more hydrated film (as in CC), along with an easier chloride penetration, result in faster corrosion initiation and propagation. In contrast, a more dehydrated film, as would be initially in specimens CNC (micelle containing) would be less prone to chloride attack, which in addition to the partially “blocked” by micelles steel surface will result in an impeded Cl⁻ penetration and consequently corrosion delay. These latter mechanisms are actually evidenced by the lower chloride content in the surface layer of corroding specimens CNC [10], compared to corroding specimens CC, which in turn means better properties for CNC from a corrosion view point.

3.2. The influence of admixed micelles on hydration and microstructure of cement paste [15].

3.2.1 Hydration rate in the presence of micelles: Isothermal calorimetry was performed for both the control specimen and the micelles-containing specimen to study the effect of admixed micelles on the hydration rate of the cement paste. The data collected up to 7 days, starting from the time of mixing cement with water, were analyzed, which is shown in Fig.5. The main peak of the heat release is related to the reaction of C₃S. It can be observed that the admixed micelles did not significantly accelerate the hydration rate of C₃S (only about 6 minutes time difference between the two specimens (the cumulative heat release was also similar for both specimens at 7 days hydration age: specimen OPC 315.69 J/g; specimen OPCm 314.92 J/g). The results indicate that the cement hydration rate is practically not influenced by the admixed micelles.

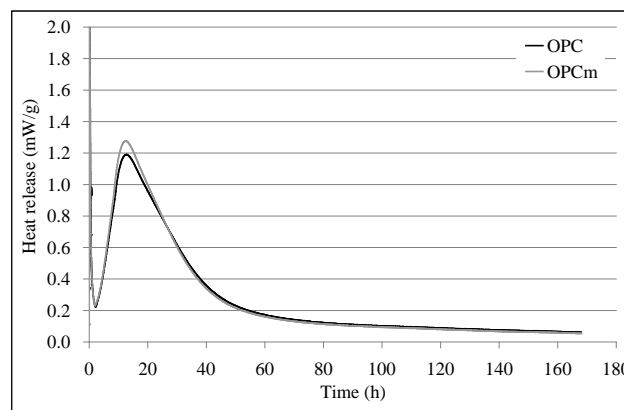


Fig.5 Hydration rate (heat release evolution) for both non-modified, OPC and micelles-modified, OPCm specimens within 7 days of hydration [15]

3.2.2 Nano indentation: Fig.6 presents the maps of elastic modulus E of the tested area in the cement paste, together with the corresponding ESEM images (within the rectangular area in the ESEM images). The highest value of the modulus was detected in the core of the un-hydrated cement particles (this is corresponding to the un-hydrated cement particles shown in the ESEM images); the modulus gradually decreased from the un-hydrated particles into the matrix of cement hydration products with the modulus value between 20-40 GPa [16, 17]; The lowest modulus values (0-15 GPa) are related to the pores in the matrix. Well known is that two types of calcium-silicate-hydrates (CSH) exist in cement paste: high-density (HD) CSH (formed around the un-hydrated cement particles) and low-density (LD) CSH (formed in the matrix) [18]. The reported elastic modulus values are generally in the range of 29.1-31.4 GPa for HD CSH and 18.2-23.4 for LD CSH [16]. According to the modulus maps (Fig. 6), there is no significant difference in the formation of HD CSH for the two specimens (the amount of HD CSH formed around the un-hydrated cement particles was similar for both

specimens). However, a more uniform distribution of LD CSH was observed for the micelles-containing specimen OPCm, compared to micelles-free specimen OPC, evidenced by much larger area corresponding to the modulus value between 15-30 GPa in the modulus map for specimen OPCm.

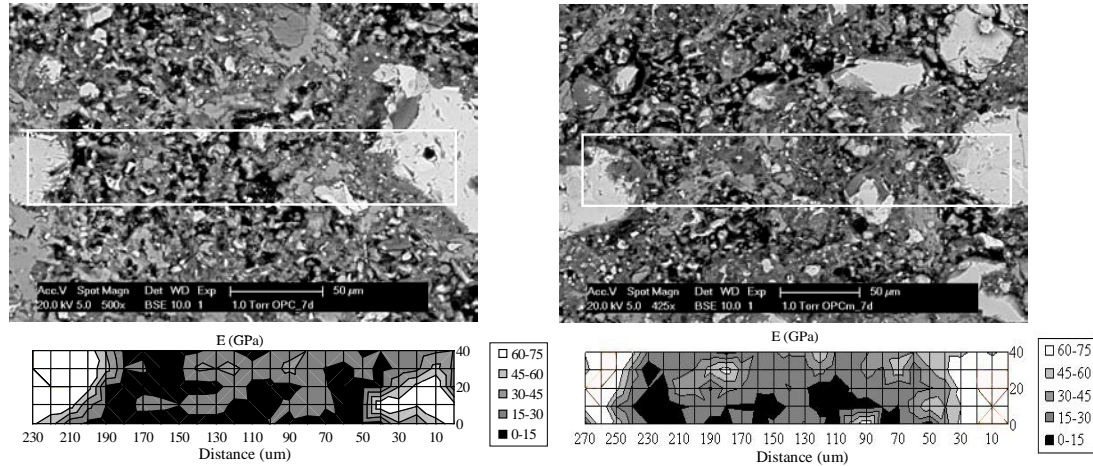


Fig.6 Maps of elastic modulus E of the test area in cement paste, together with the corresponding ESEM images for OPC_7d (left) and OPCm_7d (right) [15]

On the other hand, the area corresponding to the pores in the matrix (i.e. area with modulus value between 0-15 GPa) was significantly larger for specimen OPC. The results indicate that the admixed micelles lead to a more homogeneous and denser matrix of the cement paste.

3.2.3 MIP tests: Porosity and pore size distribution of the cement paste derived from MIP test at 7 days hydration ages are shown in Fig. 7: Fig.7 (left) shows the cumulative intruded volume curves and Fig.7 (right) shows the differential distribution curves.

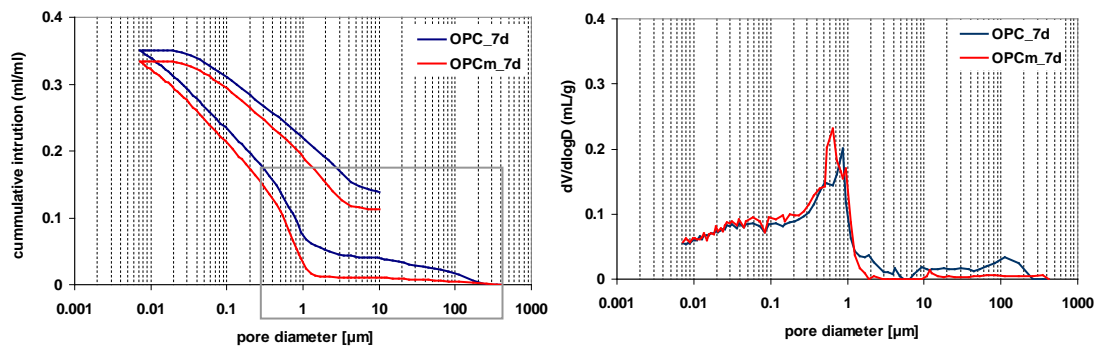


Fig.7 Porosity and pore size distribution at 7 days hydration age.

Obviously, the total porosity of the cement paste decreased when the micelles were incorporated in the matrix: the total porosity for specimens OPCm was 33.35%, compared to 35.02% for specimens OPC. Moreover, the pores with larger size in the matrix (pore size larger than 1 μm) for specimens OPCm were significantly less than specimens OPC, meaning that the admixed micelles lead to a more uniform distribution of the hydration products.

The critical pore size was determined from the differential distribution curve; the critical pore size is closely related to the transmissivity of the cement-based materials and normally the larger critical pore size corresponds to the higher connectivity of the pores. At 7 days curing age, the critical pore size for specimen OPCm was slightly lower, compared to specimen

OPC (Fig.7 (right), 0.66 μm for specimen OPCm and 0.89 μm for specimen OPC). The lower critical pore size for specimen OPCm denote for a lower pore connectivity of the cement matrix.

4. Conclusions

In conclusion, this paper briefly summarized main outcomes from an on-going investigation on a novel approach to corrosion control in reinforced cement-based systems. The approach contains two main aspects: implementation of tailored nano aggregates for improved steel corrosion resistance on one hand and improved bulk matrix characteristics on the other.

Preliminary tests in model solutions with regard to the former aspect so far prove to be a feasible approach for corrosion control, evidenced by the significant influence of minimal concentration of nano aggregates on material properties: achieved corrosion delay, altered product layer composition and contribution to increased passivity, rather than enhanced barrier effects only.

The latter aspect (improved bulk matrix characteristics) is still under investigation. Preliminary results, however, show the feasibility of the concept itself. In cement paste, the hydration rate was not significantly influenced by the admixed micelles, evidenced by the isothermal calorimetry measurements. The nano indentation results reveal that the admixed micelles lead to a more uniform distribution of hydration products and a denser matrix. The MIP analysis confirms the microstructure alterations in the presence of admixed micelles: the total porosity and critical pore size were lower for the micelle-modified specimens OPCm, compared to the micelle-free specimens OPC. At this stage of the investigation, it is suggested that the responsible mechanism for the observed behavior is mainly related to the “nucleation sites” effect of the micelles, leading to a reduced porosity and a more homogeneous cement matrix.

References:

1. Taylor H.F.W., Nanostructure of CSH: current status, *Adv Cem Bas Mater.* 1 (1993) 38–46.
2. Richardson I.G., The nature of the hydration products in hardened cement paste, *Cem Concr Compos.* 22 (2000) 97–113.
3. Zhang X.Z., Nanostructure of calcium silicate hydrate gels in cement paste, *J Am Ceram Soc.* 83(10) (2000) 2600–2604.
4. Sanchez F., Sobolev K., Nanotechnology in concrete – A review, *Constr.Build.Mater.* 24 (2010) 2060-2071.
5. Jayapalan A.R., Lee B.Y., Fredrich S.M., Kurtis K.E., Influence of additions of anatase TiO_2 nanoparticles on early-age properties of cement-based materials, *Transportation Research Record* 2141 (2010) 41-46.
6. Li H., Xiao H., Yuan J., Ou J., Microstructure of cement mortar with nano-particles, *Composites B.* 35 (2003) 185–189.
7. Silva D.A., Monteiro P.J.M., Hydration evolution of C_3S –EVA composites analyzed by soft X-ray microscopy, *Cem. Concr. Res.* 35 (2005) 351–357.
8. Uchikawa H., Hanehara S., Sawaki D., The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixture, *Cem. Concr. Res.* 27 (1) (1997) 37-50.
9. Uchikawa H., Hydration of cement and structure formation and properties of cement paste in the presence of organic Admixture, Conference in Tribute to Micheline Moranville Regourd ‘Importance of Recent Microstructural Developments in Cement and Concrete’ (Sherbrooke, Canada), p.63, Concrete Canada, 1994.
10. Hu J., Koleva D.A., de Wit J.H.W., Kolev H., van Breugel K., Corrosion Performance of Carbon Steel in Simulated Pore Solution in the Presence of Micelles, *Journal of the Electrochemical Society.* 158 (3) C76-C87, (2011)
11. Koleva D.A., Ye G., Zhou J., Petrov P., van Breugel K., Material properties of mortar specimens at early stage of hydration in the presence of polymeric nano-aggregates, Intern.Conference on "Microstructure related

Durability of Cementitious Composites, Nanjing, China, 13th-15th October, RILEM Publications SARL 2008, pp 161-168.

12. Hu J., Koleva D.A., van Breugel K., Microstructure analysis and global performance of mortar with tailored nano aggregates. 2nd International Symposium on Service Life Design for Infrastructure (SLD2010), 4-6, October, Delft, The Netherlands. RILEM Publications SARL 2010, PRO 70 (2) 791-797.
13. Koleva D.A., van Breugel K., Boshkov N., Mol J.M.C., de Wit J.H.W., Electrochemical and microstructural studies in reinforced mortar, modified with core-shell micelles, ECS Transactions 25 (24), 79-85 (2010)
14. Washburn E.W., The dynamics of capillary flow, Physical Review. 17(3) (1921) 273-283.
15. Hu J., Koleva D.A., Ma Y., Schlangen E., van Breugel K., Petrov P., The influence of Admixed polymeric micelles on the microstructural properties and global performance of cement-based materials, Submitted to Cem. Concr. Res. 2011.
16. Constantinides G., Ulm F.J., Vliet K. van, On the use of nanoindentation for cementitious materials, Mat Struct. 36 (2003) 191-196.
17. Hughes J.J., Trtik P., Micro-mechanical properties of cement paste measured by depth-sensing nanoindentation: a preliminary correlation of physical properties with phase type, Mater Charact. 53 (2004) 223-231.
18. Jennings H.M., A model for the microstructure of calcium silicate hydrate in cement paste, Cem. Concr. Res. 30 (1) (2000) 101-116.