Journal of International Scientific Publications:
Materials, Methods & Technologies, Volume 5, Part 1
ISSN 1313-2539, Published at: http://www.science-journals.eu

THE INFLUENCE OF TAILORED NANO/MICRO POLYMERIC AGGREGATES ON MATERIAL PROPERTIES OF CEMENT-BASED SYSTEMS

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Abstract

Durability and service life in civil engineering are largely related to the corrosion-related phenomena affecting the steel reinforcement. Damage initiation and/or the development of structural properties start on nano/micro level. Therefore, modification of the material structure on these levels is more likely to effectively deal with the aforementioned durability issues. This work is part of a comprehensive study on novel approaches for corrosion control in reinforced concrete and includes investigation on the influence of tailored nano/micro range polymeric aggregates on material properties of both steel and concrete. The mechanisms related to corrosion and corrosion control are hereby discussed in terms of the possibility for establishing a durable and sustainable solution i.e. self-healing mechanisms in reinforced concrete by using polymeric micelles, vesicles or hybrid aggregates. The feasibility of self-healing is briefly presented via preliminary tests in model liquid environment. Additionally, the significant impact of minimal concentrations of nano-aggregates on global properties of the cementitious bulk matrix is also discussed.

Key words: *corrosion; micelles; hybrid aggregates; mortar; EIS; PDP; SEM*

1. INTRODUCTION

The corrosion resistance of reinforced cement-based materials is one of the most important factors and concerns in structures durability and safe service life. The increasing focus on durability aspects requires developing of high knowledge-based materials, systems and technologies, which will yield improved or new functionalities and superior performance. 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 involvement of nano particles (e.g. polymeric nano-aggregates, inorganic nano-particles, etc.) in cement-based materials results in modified properties and characteristics [1, 2]. Their influence on the material bulk properties, e.g. mechanical performance, permeability and microstructure were widely investigated [3-8], results indicating increased compressive strength, matrix densification, resistance to penetration of aggressive substances, etc. The majority of literature reports, however, deal separately with either the cement-based bulk matrix only or the steel surface only (as within testing inhibitors for example). Further, and to our best knowledge, there is no investigation considering simultaneously both the steel reinforcement and the cement matrix in the presence of tailored polymeric nano-aggregates. The former, in terms of integration of electrochemistry and concrete material science is essential for a thorough understanding of corrosion phenomena; the latter – employment of tailored

polymeric formations, will result in desired properties and the hereby aimed self-healing mechanisms in the event of detrimental influence.

This work summarizes main results from several series of experiments, so far performed with regard to the above mentioned aims. The hereby presented cases refer to the following research streams:

1. Illustration of the feasibility for self-healing: tests in model solutions, representing the pore water in cementitious materials, where a "self-healing" agent is released from the so called hybrid particles as a result of external trigger (pH change in this case);

2. Assessment of the electrochemical behavior of steel in model solutions, the electrochemical behavior of reinforcing steel and the steel/cement paste interface in reinforced mortar specimens in conditions of chloride induced corrosion, compared to control, non-corroding cases with and without the involvement of polymeric nano-aggregates.

3. Investigation of bulk matrix properties and global parameters (as mechanical strength, water permeability, porosity) of cement-based materials (mortar) in the presence of tailored nano-aggregates (micelles and vesicles).

The outcome from each sub-stream of research is a substantial amount of results so far, revealing the feasibility of the suggested novel approach of using tailored nano/micro-aggregates for corrosion control in reinforced concrete. Moreover, global material properties were found to be positively altered. For more information on different aspects of the work, including elaborated and detailed reports on each research stream, please see [9-18].

2. EXPERIMENTAL

2.1 Materials

2.1.1. Polymeric nano- and hybrid aggregates: Three types of polymeric aggregates were investigated: nano-formations – micelles and vesicles and micro formations (hybrid aggregates). The nano aggregates employed in this study were prepared from PEO_{113}-b-$PS_{70/218}$) di-block copolymer. The copolymer was synthesized by atom transfer radical polymerization (ATRP), employing the macroinitiator technique. PEO_{113}-b-$PS_{70/218}$ micelles and vesicles in aqueous media were obtained via dialysis [18]. The micelles (Fig. 1a) were used as a reference case for the influence of polymer formations on microstructural properties of the bulk matrix or on the electrochemical behavior of steel. The vesicles (Fig.1b) served already as "carriers" of active (healing) substance, to be released in the bulk matrix or at the steel/cement paste interface as a result of external trigger (i.e. corrosion initiation, pH drop, carbonation). Both micelles and vesicles were employed in very low concentrations: 0.0024 wt. % of nano-aggregates were present in chloride-free and chloride-containing model solutions; 0.006 wt.% per mortar weight were present in reinforced mortar specimens.

The hybrid aggregates (Fig.1c) are slightly different formation, which at this stage is both micro and nano-sized. The composite particles were synthesized through a layer-by-layer adsorption of oppositely charged ploy-electrolytes on CaO crystals (PDADMAC/PAA/ PDADMAC over CaO). Polyelectrolytes: poly(diallyldimethyl-ammonium chloride) PDADM AC, 4.10^{-2} g/l; Poly(acrylic acid), sodium salt, PAA, 4.10^{-2} g/l. The particles concentration was 3.10^{-2} g/l (in demi-water). In the hereby tested model solutions, particle concentration was $4.9.10^{-4}$ g/l. For more details on investigations with all three formations, please see [9-18].

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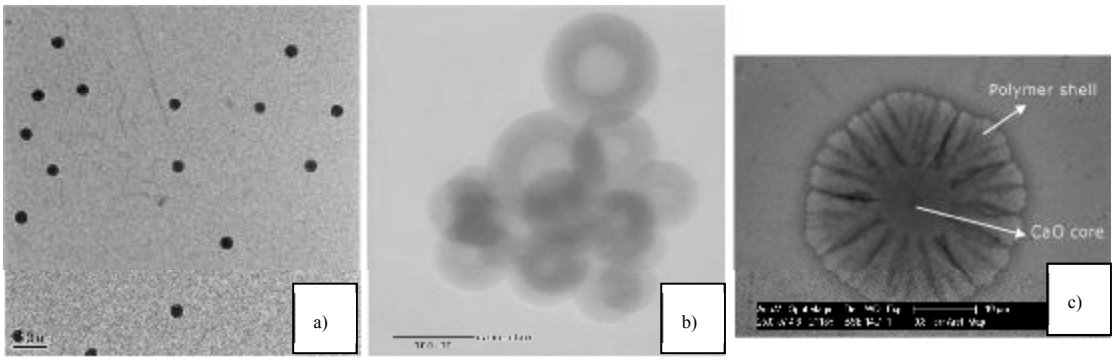

Fig.1 (a) micelles (TEM); vesicles (TEM); hybrid aggregates (ESEM)

2.1.2. Model liquid environment: The model solution (simulating concrete pore water) 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 obtained CE was used as received (as a control case) at pH of 12.6 or modified in two ways: 1st – by adding 5% NaCl (for investigating corrosion behavior of steel electrodes, treated at different time intervals), pH of 12.6 remains; 2nd – by correcting the pH to pH 9 and pH 3 in order to investigate "self-healing" agent release within pH drop.

2.1.3. Steel electrodes in model solutions: Preliminary tests in the above specified solutions were conducted, using steel electrodes (low-carbon steel St37) with service area of 0.7 cm^2 to 4cm^2 i.e. this investigation was related to corrosion behavior of steel in model CE solutions containing nano/micro aggregates (micelles, vesicles and hybrid aggregates). There was no special pretreatment for the steel electrodes, only grinding, polishing, acetone cleaning and water rinsing before testing. The control cases are those, where only nano/micro aggregates are involved and these cases are compared to aggregates-free solutions. The "corroding" cases are those, where 5%NaCl was added to all solution types as corrosion initiator.

2.1.4. Mortar and reinforced mortar specimens: Mortar specimens (cubes of 40x40x40 mm) and reinforced mortar (cylinders of h=150 mm, d= 40 mm, embedded "as received steel FeB500 HWL of d=8mm) were cast from OPC CEM I 42.5 (the same cement as used for the model CE solutions). The cement-to-sand ratio was 1:3 and water-to-cement ratio was 0.5. All specimens were cured in fog room (20ºC, 98%RH) before testing (7 days curing). The ordinary mortar mixtures are as above specified; the modified mixtures contained admixed polymeric nano-aggregates (core-shell micelles/vesicles: PEO_{113}-b-PS_{218} for the cylinders and PEO_{113}-b-PS_{70} for the cubes). The micelles (or vesicles) were added to the mortar mixture during casting as a solution (i.e. the mixing water for the modified specimens was a solution of aggregates in concentration of 0.5 g/l; concentration per mortar weight was 0.006 wt.%).

2.2. Methods

With regard to the experimental results and discussion, which this paper briefly summarizes, the following methods and techniques are relevant.

2.2.1. Tests in model solutions and electrochemical behavior of steel:

- Scanning electron microscopy, coupled with EDX analysis (using ESEM Philips XL30);

- Open circuit potential mapping (OCP), Electrochemical Impedance Spectroscopy (EIS) and Potentio-dynamic polarization (PDP), using EcoChemie Autolab.

2.2.2. Mortar and reinforced mortar:

- Standard compressive strength tests, conducted on 40 × 40 × 40 mm^3 mortar cubes, 3 replicates per certain curing age;

- Microstructure and image analysis (for porosity and pore size distribution) ESEM for imaging and visualization of morphological and microstructure investigation; OPTIMAS software was used for image analysis (for image analysis, a set of ESEM images of the cement matrix was obtained in backscattered electron (BSE) mode with the magnification of 500x. The results are an average of 35 locations per sample (details about the sample preparation and procedures as reported in [19-21]).

- Water permeability measurements: the specimens were cured for 7 days in sealed conditions; water saturated before the test and placed in the permeability cells, subject to a constant hydrostatic pressure of about 7 bars. The coefficient of permeability K [m/s] was calculated using Darcy's Law [19].

3. RESULTS AND DISCUSSION

3.1. Hybrid aggregates in model solutions

Identifying micelles and/or vesicles contribution to corrosion control via self-healing agent release is complicated for visualisation, considering the dimension of these particles (50 – 250 nm) and the high level heterogeneity of the concerned systems (cement-based reinforced materials). Further, the intended for use tailored polymeric aggregates (nano or micro) are formations, serving far different purposes, as drug delivery for example, rather then the hereby studied phenomena in alkaline medium (liquid or solid). Consequently, some of the research aspects concern: proper choice of the polymeric formations, proper choice of the substance that they carry, size, behaviour in alkaline medium etc. Additionally, their addition to concrete as a 'solid" electrolyte and the complexity of the involved hydration mechanisms, thus also particles/cement interactions, need to be well clarified in advance. Therefore, the aimed improvement of material properties was initially studied by investigating the performance of the previously introduced hybrid aggregates in model solutions of different pH values.

This preliminary research tries to answer two questions: - first - to determine if and how the morphology of the aggregates (Fig.1c) is altered within pH change, Fig.2 (which would be normally the case within corrosion initiation at the steel surface) and to observe if there will be changes in the CaO concentration within the "core" of the particle, the "shell" and the surrounding bulk; - second – to determine if the hereby used hybrid formations (Fig.1c) have any impact on corrosion behaviour of steel in alkaline medium, with and without chlorides, and thus to make the path for further investigation in a real cement-based system.

The tests for morphological changes and composition of the hybrid particles include experiments in 12 types of solutions (6 cases are hereby briefly presented, for more information, pls see [13]). The solution, containing hybrid particles in concentration of 3.10^{-2} g/l was as received with a pH of 11.8. This solution was corrected for pH to values of 9 and 3. Similarly, model solutions (cement extract with $4.9.10^{-4}$ g/l hybrid particles) were prepared: CE (as received) at pH 12.6 and CE corrected to pH 9 and 3. A droplet of each solution was vacuum evaporated on a glass holder and observed by ESEM and EDX for morphological changes of the particles and composition of the core/shell at different pH values (semi-quantification is derived by EDX i.e. relative values are hereby discussed, absolute concentrations are not claimed). The results at different pH values "visualise" the mechanisms of particle core "release" due to pH induced changes (i.e. the event of "self-healing" agent release as a result of external trigger).

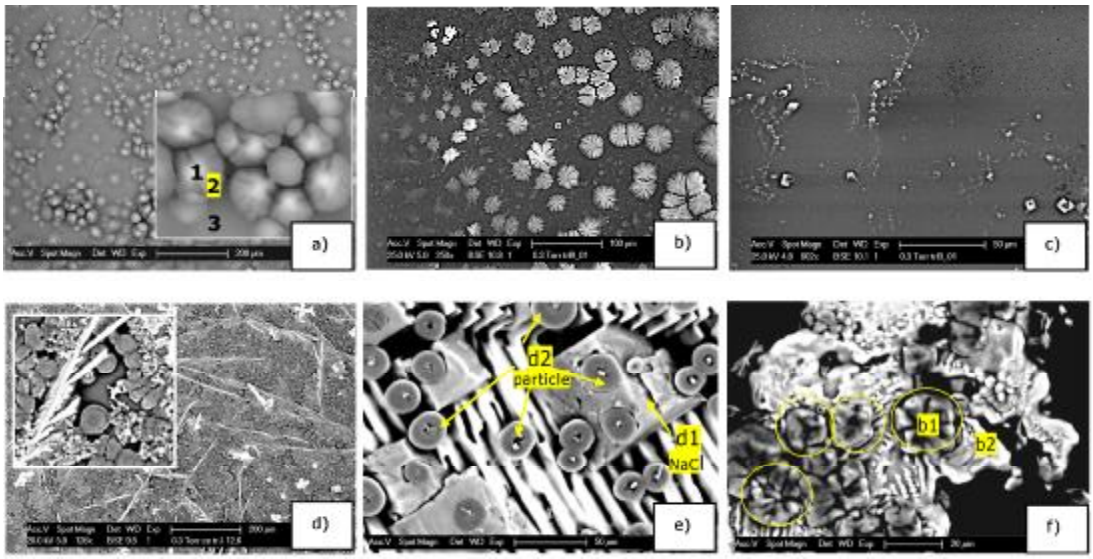

Fig.2 Hybrid particles (from as received solution, demi water) at pH 11.8 (a), pH 9 (b) and pH 3 (c); Hybrid particles from CE solution at pH 12.6 (d), pH 9 (e) and pH 3 (f) [22].

Fig. 2 presents the morphology of the hybrid aggregates at pH 11.8, as received (a), at pH 9 (b) and at pH 3 (c). Similarly Figs. 2 d) to f) present the observation of particle morphology in cement extract at pH levels 12.6, 9 and 3. Table 1 gives the EDX analysis for Ca content in the particles' core and shell for the as received solutions (Fig.2 a-c) and for the CE solutions (Fig.2 e-f).

Table 2 – EDX spot analysis for Ca

as received solution	***pH 11.8***		***pH 9***		***pH 3***	
	core	shell	core	shell	core	shell
	43.2	17.2	14.7	24.6	7.8	8.2
CE + particles	***pH 12.6***		***pH 9***		***pH 3***	
	63.9	7.6	43.1	4.6	12.3	9.6

In both solutions (as received of particles in demi-water and in CE with particles) the changes in amounts of calcium denotes for CaO release (originally in the core) towards the shell and further in the bulk. As can be observed from Fig.2, the morphology of the particles changes within a pH drop from 11.8 to 9, corresponding also to a decrease of the Ca content in the "core" and increase in the "shell". Further, within a pH change from 9 to 3, the polymers vanish (dissolve) and are not detected for the 'as received" solution (Fig.2c), calcium-containing compounds are only detected in the bulk, whereas for CE + particles solution, the hybrid aggregates, although significantly re-structured are still present at pH 3 (Fig.2f).

The electrochemical behaviour of steel electrodes in these model solutions (with and without particles and with and without NaCl) was investigated. The measurements were performed at certain time intervals (from 1h to 7 days), during which the electrodes were immersed (at OCP) in the relevant solutions.

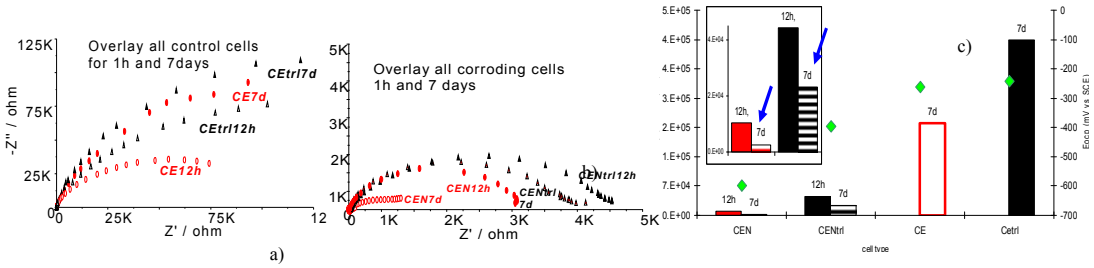

Fig.3 EIS response for control cells (a)[13], corroding cells (b)[13] and Rp values for all cases (c)

Figure 3 presents the EIS response of the control (non-corroding) groups of steel electrodes, in particles-free cement extract and in particle-containing cement extract (Fig.3a), the relevant corroding cases i.e. particles-free and particles-containing 5%NaCl solution of CE (Fig.3b) and the calculated from PDP tests polarization resistance values (Fig.3c). As evidenced by the results from electrochemical measurements, a concentration of $4.9.10^{-4}$ g/l leads to increased corrosion resistance of steel, especially in NaCl containing solutions. The observed behaviour is in first approximation denoted to increased barrier properties of the layers, when particles are present. Additionally, the particles probably act as nucleation sites and therefore a more uniform and compact layer is formed on the steel surface (for more details on the electrochemical study of steel in hybrid-aggregates containing solutions, pls see [13]).

The preliminary study on the performance of the hereby investigated hybrid aggregates, containing a CaO core and a polymer shell, in model solutions as well as the electrochemical behaviour of steel in such solutions resulted in very promising results. The outcomes clearly show the possibility for CaO release within pH changes in the environment, which will in turn positively influence the electrochemical behaviour of steel. Research on admixing these type of aggregates in cement-based materials is on-going.

3.2. Reinforced mortar, containing PEO_{113}-b-PS_{218} micelles.

Considering the above preliminary studies, subject to this part of the work is microstructural investigation of the steel/cement paste interface and the bulk matrix in reinforced mortar specimens, with and without polymer nano-aggregates. Two main groups were investigated: group “Or” were specimens without admixed nano-aggregates, group “Pr” were specimens cast with polymeric nano-aggregates. The specimens, immersed in water, denoted as “Or” and “Pr” served as “reference” specimens for a comparison of microstructural and electrochemical parameters with the “corroding” specimens (treated in 10%NaCl), denoted “Oc” and “Pc”. Figure 4 presents the steel/cement paste interface in the “control” groups Or(a) and Pr(b) and the “corroding” groups Oc(c) and Pc(d). Similar morphology was observed for both Or and Pr, except that for the micelles-containing specimens Pr, a more uniform and visually higher percentage of calcium-containing (CaO, $Ca(OH)_2$) compounds are predominantly deposited in the vicinity of the steel surface (Fig.4b) as well as the interfacial transition zones (ITZs) of aggregate and cement paste. For the “corroding” specimens, with and without micelles, corrosion products were observed at the steel/cement paste interface. For the specimens without micelles (Oc, Fig.4c), a significant accumulation and further propagation (more than 400 μm away from the steel surface) of corrosion products into the bulk matrix was observed, whereas only a few isolated locations of accumulated corrosion products, propagating approximately 20 μm only into the bulk matrix, was recorded for the micelles-containing specimens Pc (Fig.4d).

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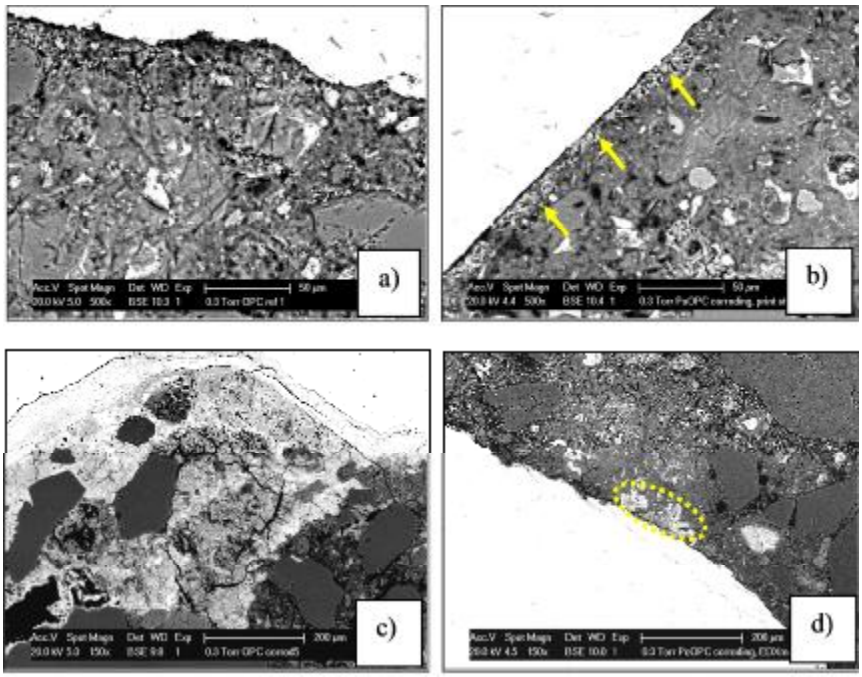

Fig.4 Micrographs of the steel/cement paste interface: reference (control) specimens Or(a) and Pr(b); corroding specimens Oc(c) and Pc(d)

Figure 5 presents a comparison of porosity values for the bulk matrix (more than 600 μm away from the steel surface) and porosity of the steel/cement interface (up to 50 μm from the steel surface into the bulk) for all investigated conditions. As seen form the plot, the most homogeneous structure was found to be in the control, micelles-free specimen Or and the corroding, micelles-containing specimen Pc, since their bulk and interfacial porosity are almost equal. The slight differences in porosity between corroding specimens Oc and Pc (micelle-free and micelle-containing specimens, Fig.5) can not explain the corrosion delay observed in specimens Pc i.e. the positive effect of micelles on electrochemical behaviour is not only related to decreased porosity in chloride containing environment. The most plausible mechanism is increased chloride threshold and thus corrosion delay (for more details on these mechanisms please see [16]).

Consequently, the concentration of 0.006 wt.% admixed micelles was able to influence the process of corrosion initiation in terms of a significant corrosion delay as well as structural alterations (reduced bulk matrix porosity). The influence of the micelles on corrosion behavior of the steel reinforcement, as well as on bulk matrix properties and steel/cement paste interface, originates from the presence of the micelles themselves and their influence on structural and material properties and is essentially denoted to enhanced nucleation effect, resulting in re-distribution of hydration products (for a more detailed information on the influence of PEO_{113}-b-PS_{218} micelles on microstructure and corrosion behavior, please see [10-13, 16,17])

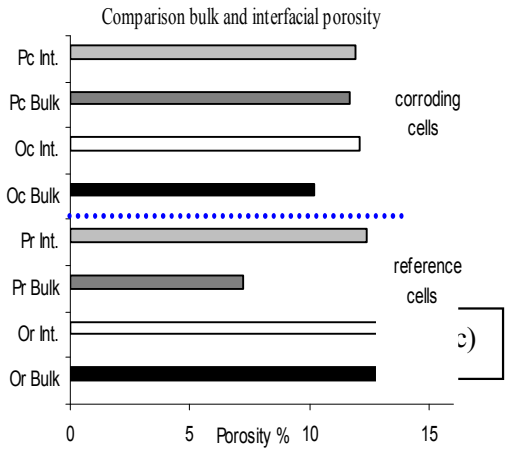

Fig.5 Bulk matrix and steel/cement paste interface porosity for control specimens Or and Pr and corroding specimens Oc and Pc

3.3. Plain mortar, containing PEO_{113}-b-PS_{70} micelles and vesicles.

The investigations with hybrid aggregates and micelles in model solutions, plain and reinforced mortar (as partly presented above) have shown very promising results [10, 11, 17, 18, 22, 23] in terms of increased corrosion resistance, reduced porosity, slightly increased compressive strength etc. The presently on-going investigation on corrosion control in reinforced concrete concerns micelles and vesicles comprising shorter hydrophobic blocks (PS_{70}). These were admixed in mortar, using the same as previously employed concentration of 0.006 wt.% per mortar weight. A brief introduction to part of the results so far is presented in this section (for more details on reported results from these still on-going investigations, please see [9-18]).

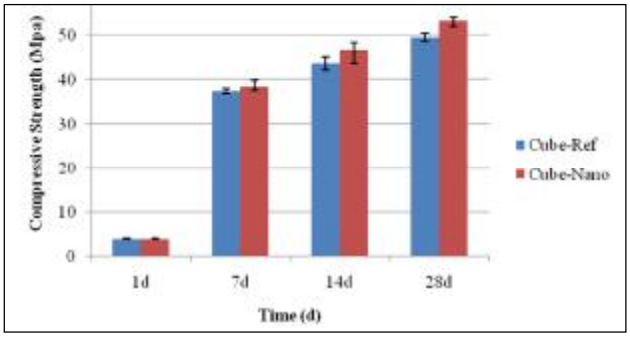

Fig.6 Compressive strength for micelle-free (ref) and micelle-containing (nano) mortar at hydration ages of 1day, 7 days, 14days and 28 days [15].

Compressive strength was recorded for micelle-containing mortar cubes at different hydration ages. The results for both control (micelle-free) and “nano” (micelle-containing) mortar cubes are shown in Fig. 6. Except for the 1d stage, the compressive strength of the “nano” sample was slightly higher than that of the control sample. The results indicate that the compressive strength of mortar is slightly improved when micelles are present in the matrix.

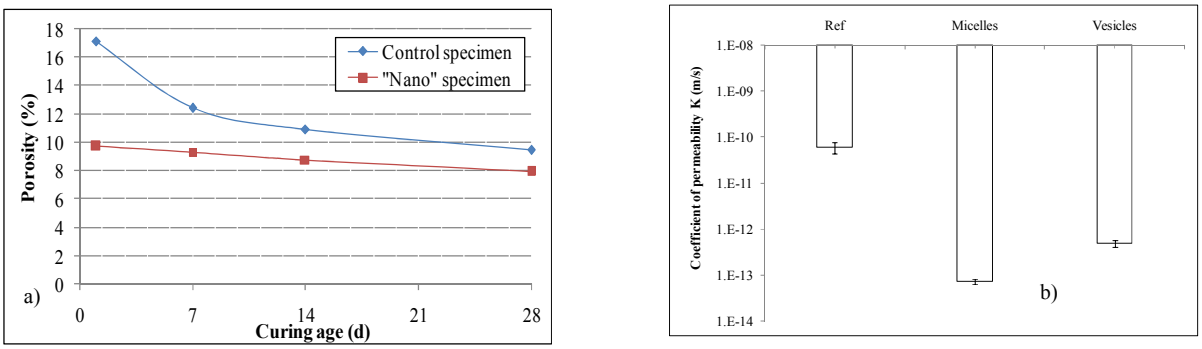

Fig.7 Porosity values at different hydration ages for micelle-free (control) and micelle-containing (nano) specimens (a); water permeability for control, micelle-containing and vesicle-containing specimens (b)

Porosity and permeability of the bulk cementitious matrix are considered to be one of the most important parameters, affecting concrete durability. Concrete with higher permeability allows faster penetration of gases, liquids and other aggressive aggregates such as chlorides, resulting in rapid corrosion of the reinforcing steel. The permeability of concrete is related to its microstructure, especially the volume, size distribution, connectivity and shape of the pores [24].

The porosity of both the control and nano specimens is shown in Fig.7a). The results were calculated from the image analysis of 35 locations per sample. As seen from the plot, the incorporated micelles have a significant influence on the microstructure of the cement matrix, especially at early stages: at 1day of cement hydration approx. 15% porosity is relevant for the control specimen, whereas approx. 9% porosity is recorded for the "nano" specimen. Apparently, the micelles (even in the very low concentration of 0.006 wt%) resulted in a significant densification of the bulk matrix which is well in line with the lower water permeability results for the "nano specimen" – Fig.7b).

Fig.7b) depicts the recorded water permeability for a control (aggregates-free) matrix, compared to micelle- and vesicle containing mortar matrix (permeability was recorded after 7 days curing). As seen from the plot, the coefficient of water permeability K for the "Nano samples" is about 3 orders of magnitude lower than the control (Ref) ones ($7.32*e^{-14}$ m/s for nano sample, compared to $6.09*e^{-11}$ m/s for control sample). Obviously, a very low concentration of PEO_{113}-b-PS_{70} micelles is able to significantly reduce the water permeability of the mortar matrix. Similarly, the permeability is reduced in the presence of vesicles, resulting, however, in slightly higher permeability values, compared to the micelle-modified matrix.

The effect of PEO_{113}-b-PS_{70} micelles on the global bulk matrix properties (including microstructural properties) is due to the "role" of the micelles, acting as nucleation sites for the formation of new hydration products, thus resulting in a more uniform matrix, The investigations are in line with the previously reported results on the effect of PEO_{113}-b-$_{PS}PS_{218}$ micelles [10-13, 16, 17] part of which were previously presented and discussed hereby. The investigation on vesicles ("empty" such and already including a "self-healing" agent) is on-going.

4. CONCLUSIONS

In conclusion, this paper briefly summarized main outcomes from on-going investigation on a novel approach to corrosion control in reinforced cement-based systems. The approach contains two main

aspects: innovative for the field of civil engineering implementation of tailored nano/micro aggregates and autonomous self-healing.

The former (tailored aggregates) so far proves 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, substantial reduction of water permeability and reduced porosity.

The latter (self-healing aspects) is still under investigation. Preliminary results in model solutions show promising results, "visualizing" the feasibility of the concept itself: the investigated hybrid aggregates, containing a Ca-rich core and a polymer shell appear to be affected by pH change in the environment, exhibiting altered morphology and re-structuring, which in turn leads to the release of the Ca-rich substance. Further, steel electrodes, treated in solutions in the presence of hybrid aggregates, exhibits increased corrosion resistance.

On-going is the investigation on corrosion control via self-healing mechanisms in the presence of nano-aggregates (vesicles) and hybrid aggregates in reinforced mortar specimens.

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