Incorporation of Hybrid Biopolymer/Silicate-Based Microcapsules in Cementitious Mixtures for Potential Uses in Self-healing Technology with Renewable Materials

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Abstract. The high demand for cement for repairing concrete structures leads to adverse environmental impacts, reducing the cement industry's sustainability. For that reason, using renewable materials to develop self-healing cement-based materials is desirable to diminish cement consumption for rehabilitation and increase the durability and reliability of concrete structures. Evaluation of hybrid organic/inorganic microcapsules for autonomous self-healing of cementitious materials offers a solution for microcracking, meanwhile conferring better characteristics to construction materials. Microcapsules evaluated in this study with a core of Silicate-based (MC-SS) and Biopolymer/Silicate-based (MC-SS-St) resins covered by a Silica shell were synthesized and added in replacement of microsilica in cement pastes at a dosage of 2.5, 5.0 and 7.5% by weight of cement. The microcapsules and microsilica were characterized by XRD, SEM, and FTIR. Performance of cement pastes with microcapsules addition was followed by flexural and compressive strength of prismatic specimens of $1 \times 1 \times 6$ cm^3 at 7 and 28 days of curing immersed in water at room temperature. Total porosity was followed by MIP at 28 days of curing. Also, the workability of samples with 2.5% microcapsules was compared with a cement reference mixture (CEM I) and cement with microsilica (MS) as the blank sample. Obtained results show differences in the morphology of microcapsules compared with microsilica. Moreover, as was expected, the water/binder ratio (w/b) increases with microcapsules addition, which reduces mechanical resistance. However, with the higher substitution of microcapsules, the obtained values accomplish the current regulations. Therefore, the proposed microcapsule-based system under evaluation is a promising product designed for self-healing cementitious mixtures.

Keywords: Self-Healing concrete · silica · biopolymer · silicate · microcapsules

A. Jędrzejewska et al. (Eds.): SynerCrete 2023, RILEM Bookseries 44, pp. 853–864, 2023.
https://doi.org/10.1007/978-3-031-33187-9_78

1 Introduction

Durability in concrete is a parameter that stands for the efficiency of civil engineering constructions in terms of cost and safety. Concrete structures are affected by different loads and environmental conditions that affect their stability, causing microcracking and permitting the entrance of harmful substances that can deteriorate the characteristic strength of that construction material. In addition, using cement to repair or rehabilitate structures leads to expensive and negative environmental impacts since the cement industry is one of the most contaminants worldwide because of its production capacity, energy consumption, and CO_2 emissions. Thus, using self-healing materials to overcome microcracking in concrete is a good alternative to producing sustainable, durable, and low-cost construction materials [1, 2]. Moreover, replacing cement with these smart materials in concrete formulations improves that industry's environmental and social performance [3]. Additionally, adding renewable or waste materials to the mixture increases profits without negatively affecting concrete properties [4].

The influence of admixtures on cementitious formulations has been widely studied [5, 6]. Inorganic, organic, and biological admixtures have been assessed [7, 8]. Nonetheless, when a new substance or mixtures of substances are designed to be added to a concrete formulation, their effect on the performance of concrete needs to be evaluated, including their physicochemical properties and their impact on the fresh and hardened concrete properties. Effects of nanosilica and silica fume have been the most studied due to their application in Ultra-High Performance Concrete (UHPC) mixtures determining the relationship between the physicochemical characteristics, i.e., morphology, size, type of crystallinity, the fresh properties of cementitious mixtures, i.e., consistency and setting time, and the hardened properties, i.e., mechanical strength and durability. Significant effects are related to an increasing compressive strength because of the improvement of the paste-aggregate interface [9].

In terms of competitiveness in the market, microsilica has advantages compared to nanosilica in terms of price and availability. The former amorphous silica is cheaper and more available because it comes from the dust collected as a by-product of the silicon and ferrosilicon production in the baghouse filters, and the applications are extensive, so its consumption is approximately 500.000 metric tons per year [10]. Despite the advantages of microsilica, its use in long-term durability composites does not include microcracking control, where the objective separates into autogenous healing of the cracks at early ages and autonomous healing at longer ages. For that reason, new materials from renewable and inorganic sources need to be developed to overcome microcracking with a desirable improvement of the concrete properties or, if it is not possible, without impact negatively these.

Smart materials have been developed with properties of healing themselves. Microcapsules containing an adhesive or reactive core are candidates with good performance for healing microcracks in concrete since no polymeric shell covers the healing agent. Innovative microcapsule-based systems have been developed, and their comparison with nanosilica and microsilica performance and influence on concrete characteristics or its improvement have also been studied [11, 12]. However, when the core-shell configuration changes in its components, studies need to be developed from time to time to assess the proposed design.

In that sense, this study evaluates a microcapsule-based system as hybrid organic/inorganic microcapsules for autonomous self-healing of cementitious materials, with a core of Silicate-based (MC-SS) and Biopolymer/Silicate-based (MC-SS-St) resins, covered by a Silica shell, previously synthesized in the laboratory. The evaluation of the influence in cementitious formulations and its comparison with silica fume replacements of cement were studied in pastes at a dosage of 2.5, 5.0, and 7.5% by weight of cement. Characterization of the microcapsules and the microsilica (used as reference) in terms of morphological and compositional characteristics was done, and its performance was followed by workability and mechanical strength properties.

2 Materials and Methods

2.1 Materials

Microsilica® 940 (MS) was purchased from Elkem (Kristiansand, Norway). Microcapsules (MC) with a Silica shell and a core of Silicate-based resin (MC-SS) and Biopolymer/Silicate-based resin (MC-SS-St) were synthesized at laboratory scale by sol-gel method and interfacial polymerization using tetraethoxysilane, ethanol, and ammonium hydroxide purchased from Merck (Darmstadt, Germany), polycarboxylic acid from Loba Chemie (Mumbai, India), and biopolymer from Sigma-Aldrich (Saint Louis, USA), all these reagents were of analytical grade. Sodium silicate and surfactants were provided by Sika Colombia S.A.S. (Tocancipá, Colombia), and mineral oil was purchased from Lega Químicos (Bogotá, Colombia). The latter three reagents were commercial grade. Cement Portland Type I 42.5 R (CEM I 42.5 R) and deionized water were used for the cement paste formulation, provided by the Instituto de Ciencias de la Construcción “Eduardo Torroja” – IETcc (Madrid, España).

2.2 Synthesis of Microcapsules

Microcapsules MC-SS and MC-SS-St were synthesized using a modified methodology based on previous procedures reported in the literature [11, 13, 14]. The primary synthesis method was sol-gel using TEOS as a silica precursor, and it was hydrolyzed for 5 h using polycarboxylic acid (1,03M COOH) and ethanol as the reaction medium. Then encapsulation of each microcapsule type was carried out employing a W1/O/W2 emulsion using a Silicate-based resin for MC-SS and a Biopolymer/Silicate-based resin for MC-SS-St as core solutions. Through interfacial polymerization, the hydrolyzed silica solution was condensed, using an aqueous and basic medium with NH4OH (1M), over the resin drops of the W1/O solution, which was previously stabilized using an adequate surfactant. Purification of the obtained material was done by centrifugation, and finally, it was dried at 40 °C for 12 h.

2.3 Characterization of Microcapsules and Microsilica

Morphology was determined by Scanning Electron Microscopy (SEM) using a HITACHI S-4800 (Japan) Scanning Electron Microscope with a tungsten lamp filament operated

at 20.0 kV. Samples were previously sputter-coated with carbon. The amorphous silica phase of microcapsules and microsilica was determined by X-Ray Diffraction (XRD) using a Diffractometer Bruker AXS D8 ADVANCE (USA) with a Copper X-ray tube Anode producing Kα1.2 radiation and tungsten Cathode; data were taken at angle 2θ in a range of 5° to 60°. Infrared absorption spectra data of the microsilica samples were recorded by FTIR spectrophotometer Bruker VERTEX 70V in the wavenumber range from 4000 to 400 cm^{-1} using the KBr pellet method for sample preparation. For the microcapsules, the measurement range was from 4000 to 550 cm^{-1} using a FTIR Spectrophotometer Shimadzu (Japan).

2.4 Evaluation of Cement Pastes with Microcapsules and Microsilica

The cement paste preparation and mini-slump test procedure was done as follows. Weighing and mixing mechanically powder mixture with deionized water with a stainless-steel two-blade impeller at 300 rpm for 2 min, with 30 secs of homogenization and finally, the mixture was left to stand for 1 min. The total mass of the cementitious materials was 80 g. The reference mixture (CEM I in Table 1) was prepared only with cement (c) and water (w) at a w/c ratio of 0.27. For the blank sample, 20wt% of microsilica (MS20 in Table 1) was used in replacement of cement at a w/b ratio of 0.455. The samples with microcapsules (MC) were prepared by adding the synthesized materials MC-SS and MC-SS-St in proportions of 2.5, 5.0, and 7.5wt% in replacement of microsilica at a w/b ratio of 0.465. The nomenclature for these materials can be observed in Table 1. These water additions were determined previously employing the Normal Consistency Test according to the Standard UNE-EN-196-3 using the Manual Vicat Apparatus.

Table 1. Cement pastes formulations with microsilica and microcapsules.

Sample	Component of the paste			
	CEM I 42.5 R (g)	MS (g)	MC (g)	H_2O (g)
CEM I	80	0	0	21.6
MS20	64	16	0	36.4
MC-SS2.5	64	14	2	37.2
MC-SS5.0	64	12	4	37.2
MC-SS7.5	64	10	6	37.2
MC-SS-St2.5	64	14	2	37.2
MC-SS-St5.0	64	12	4	37.2
MC-SS-St7.5	64	10	6	37.2

After the water demand required for the reference sample CEM I was determined, mini-slump test was done and the diameter of the spread obtained for CEM I was (52.5 ± 1) mm, this value was chosen as the fixed parameter to determine the w/b ratio for the samples with additions of MS and microcapsules that maintain adequate workability of

these unknown mixtures because until now; it was not clearly established in literature how it can be determined acceptable workability for blends where part of the cement is replaced by synthesized admixtures. Then, through the mini-slump test, the plastic behavior of cement pastes with different additions of microsilica from 12.5% to 20% with increments of 2.5% in replacement of cement was assessed and for the samples CEM I, MS20, MC-SS2.5.

Prismatic specimens of $1 \times 1 \times 6\,cm^3$ were prepared of cement pastes with microsilica and microcapsules addition, according to the formulations seen in Table 1, for hardened properties measurement. The procedure for the mechanical strength evaluation was based on the UNE-EN-196-1 standard at the different curing ages, the methodology for the flexural strength was determined by three-point loading of the prismatic test specimen, and for the compressive strength, the failure and breakage were done on each half of the test probes at a loading rate of 0.07 kN/s. Porosimetry measurements were carried out for pieces of 1 cm^3 using a Mercury Intrusion Porosimeter (MIP) Micromeritics AutoPore IV 9500 (USA).

3 Results and Discussion

3.1 Morphology and Composition of Microcapsules and Microsilica

Images of Scanning Electron Microscopy (SEM) in Fig. 1 show a regular spherical form of synthesized materials. In Fig. 1a microcapsules with silicate-based resin (MC-SS) with smooth surfaces and narrower particle size distribution with values under 200 μm can be observed, as well as pore-like morphologies. Similar results were found for microcapsules containing hybrid biopolymer/silicate-based resin (MC-SS-St) with more pore-like surfaces, as seen in Fig. 1b. In general, no signal of core solutions outer microcapsules shell was exhibited, and a free-flowing powder was obtained. In the microsilica micrograph, Fig. 1c, broader particle size distribution was found with smaller particle sizes of less than 0.5 μm. Moreover, the spherical shape was evidenced as well as the presence of agglomerates.

The composition of microcapsules and microsilica was analyzed through X-Ray Diffraction (XRD). Figure 2 shows the results for amorphous SiO_2 in all cases with a wide peak at 23° at an angle 2θ [9]. For microcapsules, that peak is broader and more intense than for microsilica, which means a size effect confirmed by SEM with higher-sized diameters for microcapsules [11]. Furthermore, the composition of microcapsules is confirmed as pure SiO_2 due to no presence of sharp peaks; it indicates the absence of impurities [15]. An opposite view is seen for microsilica, where the main content is amorphous silicon dioxide [16] but with the presence of typical impurities [10]. It was confirmed by the sharp peaks at 28° and 35° (Angle 2θ) corresponding to crystalline MgO [17] and SiC [18], respectively.

FTIR spectra of synthesized materials are shown in Fig. 3a, and there were observed the main peaks, also confirmed for microsilica in Fig. 3b, where the presence of Si-O bond vibrations corresponding to the amorphous silica bond interactions is evident. A first IR band characteristic of O-Si-O bending vibrations is located at 481 cm^{-1}, and symmetric stretching vibrations of Si-O-Si present the IR band at 810 cm^{-1} for MS, and 790 cm^{-1} for microcapsules. Also, a strong and sharp IR band at 1119 cm^{-1} for MS, and

1070 cm^{-1} for microcapsules, correspond to Si-O-Si asymmetric stretching vibration. Other less intense IR bands at 1632 cm^{-1} and 3450 cm^{-1} for MS, and 1640 cm^{-1} and 3410 cm^{-1} for microcapsules, referred to bending and stretching vibrations of OH- from water molecules absorption [19].

In the case of MC, the described peaks corresponding to the amorphous silica are more intense than for microsilica. Also, wider peaks for the absorbed water molecules are notorious, and it was also observed the presence of CO_2 gas at 2348 cm^{-1}. Likewise, additional peaks were found for microcapsules at 580 cm^{-1} and 960 cm^{-1}, related to vibrations of the Si-O bond, where a silicon tetrahedron could be disconnected to one or more neighbor oxygen atoms and possibly bound to OH- groups [11]. It has sense considering the peak at 580 cm^{-1} is more pronounced for MC-SS-St than for MC-SS, and it is not present in the MS sample, maybe due to the bonds of Si-OH, where hydroxyl groups are from the carbohydrate structure. Peaks at 1450 and 1550 correspond to -CH_2- and N-H bending vibrations, respectively [20]; also, another slight peak appears at 2920 cm^{-1}, referred to as C-H vibrations [11], these organic compounds vibrations are in accordance with the remanent organic fractions involved in the synthesis process of the microcapsules.

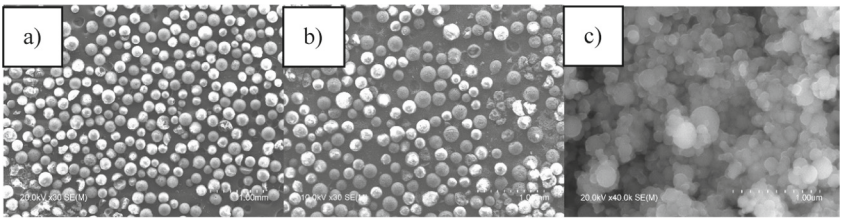

Fig. 1. SEM micrographs of microcapsules a) MC-SS and b) MC-SS-St at a magnification of 30X and c) microsilica with a different magnification of 40 kX.

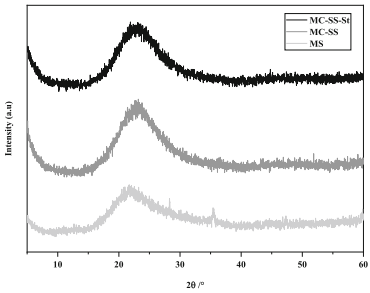

Fig. 2. XRD Pattern of microcapsules and microsilica.

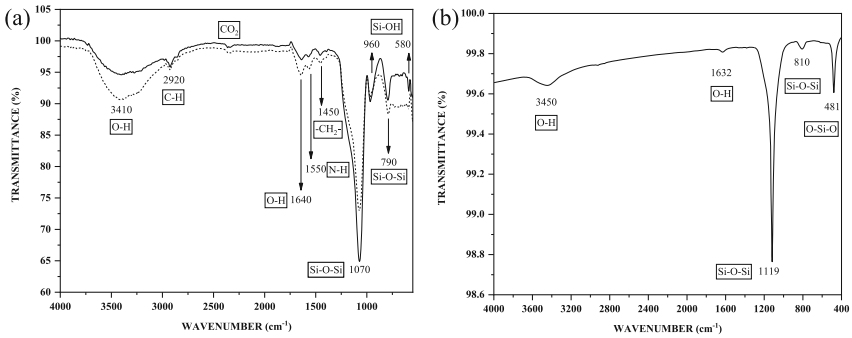

Fig. 3. FTIR Spectra of (a) microcapsules MC-SS (straight line) and MC-SS-St (dash line), and (b) microsilica (MS).

3.2 Workability of Cement Pastes with Microsilica and Microcapsules Addition

Figure 4a shows a clear linear trend between increases in the dosage of MS and the w/b ratio keeping the diameter of spread in the fixed range of (52.5 ± 1) mm. That was an expected result, considering MS has a low particle size distribution leading to higher interparticle and intermolecular interaction and more attraction for water molecules as its amount increases. Similar results were obtained in comparison with the reference mixture (CEM I) and the cement pastes with the addition of microcapsules in replacement of MS. Figure 4b reveals the mixing water required was higher for the samples with 2.5% by cement weight of microcapsules in replacement of MS (MC-SS2.5 and MC-SS-St2.5) with a notorious difference to the reference sample CEM I but only one point above the w/b of the blank sample (MS20).

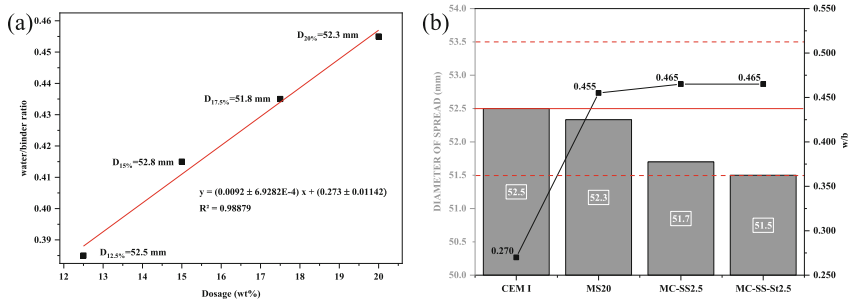

Fig. 4. (a) Water demand for cement mixtures with different additions of MS. (b) Mini-slump of cement paste mixtures: Reference sample (CEM I), blank sample with 20wt% MS addition (MS20), and with 2.5wt% MC additions (MC-SS2.5 and MC-SS-St2.5).

This behavior means the replacement of cement by MS increases by 68.5% the mixing water required for the paste preparation to guarantee acceptable workability, and the water demand when part of this MS is replaced by microcapsules is a little bit more. Although the spread diameter of the samples is set between the range (52.5 ±

1) mm, the workability decreases when the replacement of MS by the microcapsules is carried out due to the higher hydrophilicity of the microcapsules because no size effect is considered as the particle size of microcapsules is 400 times bigger than the microsilica. Even more interesting is the fact that the competition for water molecules between the two types of microcapsules suggests more interaction for the samples with the hybrid biopolymer/silicate-based resin MC-SS-St, determining a more hydrophilic character of this material compared with the microsilica and the microcapsules with solely silicate-based resin MC-SS. This result is fully validated by the FTIR spectra of these materials analyzed above, where MC-SS-St presented more hydroxyl groups from water adsorbed, which is also coherent with the lower workability with the same amount of mixing water compared with MC-SS.

3.3 Mechanical Resistance Evolution and Microstructure of Cement Pastes with Microsilica and Microcapsules Addition

The results of the workability of the evaluated samples are clearly related to the mechanical strength evolution of the mixtures because higher w/b ratios led to lower mechanical resistances, as was expected for the analyzed samples. The water demand for this unknown cement pastes with synthesized microcapsules was higher than the required to guarantee adequate workability, instead of setting the correct proportion of w/b required to achieve proper strength evolution. In that manner, this methodology allowed us to understand the synthesized admixtures' behavior in the cementitious matrix.

Figure 5 show the mechanical strength evolution, flexural and compressive strength, of the evaluated mixtures CEM I, MS20, and MC-SS and MC-SS-St, at the three different additions. It established an increase of the mechanical strength from 7 to 28 days of curing for all the samples, which agrees with the normal evolution of cement paste hydration. That outcome means that the microcapsules do not interfere with the hydration reactions in the cementitious matrix. The blank sample MS20 presented a flexural and compressive strength lower than reference sample CEM I due to the higher w/b ratio. In other studies, additions of microsilica lead to stronger mechanical strength in different formulations but keeping the same w/b and w/c ratios than the samples without MS additions [3, 9, 16, 18]. In case of part of the MS were replaced by microcapsules, a decrease in the flexural and compressive strength at 7 and 28 days of curing would be evident when the dosage of microcapsules increases, which confirms that a lower interfacial interaction between microcapsules and the cementitious matrix is taking place. However, at 7 days of curing, for the sample MC-SS-St at 2.5%, the flexural strength value was 9.5% higher than for MS20. At 28 days of curing, the highest value was obtained for the MC-SS at 2.5% with an increment of 11.4%, followed by MC-SS-St2.5 with an increment of 1.9% compared with MS20. That result means that the chemical compatibility of the microcapsules with the cementitious matrix is satisfactory and competitive with the microsilica material, despite organic groups on the surface of the microcapsule, which can diminish the interfacial interactions presented in the mixture. Regarding the compressive strength, the highest at 7 days of curing value was obtained for MC-SS-St2.5 with an increment of 5.7% with respect to MS20. However, after 28 days of curing, the value for MS20 was the highest, with 57.93 MPa above the value of 51.95 MPa obtained for MC-SS2.5

and 57.30 MPa for MC-SS-St2.5. Despite these differences, all the obtained values are in accordance with regulations.

A comparison of the two systems of microcapsules shows values for flexural and compressive strength higher for the three additions of the MC-SS-St than for the system MC-SS at the two ages, except for the sample MC-SS at a dosage of 2.5% at 28 days of curing, which was 8.6% higher than MC-SS-St in flexural strength. It could be explained by the biopolymer content of the MC-SS-St in replacement of silicate resin. The biopolymer could inhibit the reactivity of the healing resin at longer ages. Nevertheless, this is not a probed reason to consider in the mechanism of hydration and healing because MC-SS-St presented better behavior at higher dosages. Additionally, in the case of compressive strength (Fig. 5b), the higher values were obtained for the system MC-SS-St at 28 days of curing for all three dosages, except for MC-SS5.0 at 7 days of curing with an increment of 2.3% above MC-SS-St5.0. Then, the primary trend between these two materials is clear, as the better performance was achieved by the system MC-SS-St. Though, more studies are required to determine the influence of the biopolymer contained in the microcapsule-based system on the properties of the cementitious mixtures. Those synthesized microcapsule-based systems have shown the potential to be promising materials with greater particle size but almost the same performance as microsilica. Meanwhile, the expected result was that the rate of reaction decreases as silica particle size increases as the comparison between nanosilica and microsilica performance was analyzed in other works [21].

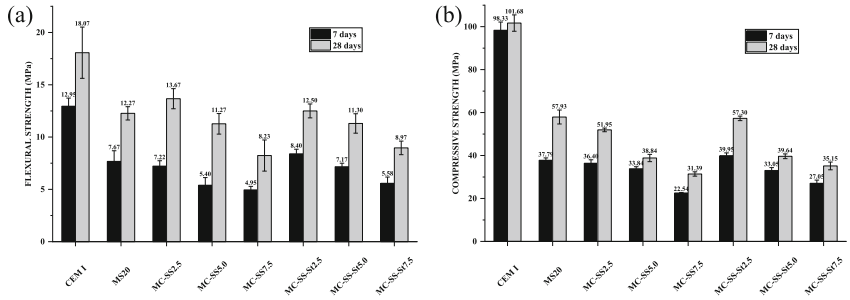

Fig. 5. (a) Flexural strength and (b) compressive strength evolution of cement paste mixtures: Reference sample (CEM I), blank sample with 20wt% MS addition (MS20), and samples with 2.5, 5.0 and 7.5wt% MC additions.

Related to the microstructure of the cementitious matrix with microcapsules, an augmentation in the porosity with the increments of dosage for both systems MC-SS and MC-SS-St was found, as can be observed in Fig. 6a. However, a slight refinement of microporosity was presented in the samples at 2.5wt%, showing a total porosity not so far from the reference CEM I (6.07%). This result is coherent with the decreased slump value for these samples compared to the reference one, where the workability was slightly diminished, leading to poor compaction and higher porosity [22]. Despite in previous works [23] the microcapsules could act as weak points within the cementitious matrix with no high values of total porosity. Opposite to the presented work, higher values of

total porosity for the increasing additions were found, this outcome indicates possibly a lack of compatibility in the interfacial zone with the consequent reduction of mechanical strength for both systems compared with the reference one, as can be seen in Fig. 6b. This situation can be improved with the use of admixtures and a reduction of the w/c and w/b ratios, to enhance mechanical performance and avoid the entrance of harmful substances that could be produced microcracking. Making a comparison within the systems, the MC-SS microcapsules had better linear correlation then the MC-SS-St, which make more predictable the behavior of the cementitious mixture containing this kind of materials at other dosages. Nevertheless, the mixture with MC-SS-St microcapsules presented higher porosity but higher compressive strength, possibly due to the more reactivity of the hybrid biopolymer/silicate-based resin. Then, the less weak and more compact cementitious microstructure was produced using MC-SS-St microcapsules than the mixture with MC-SS containing the solely silicate-based resin.

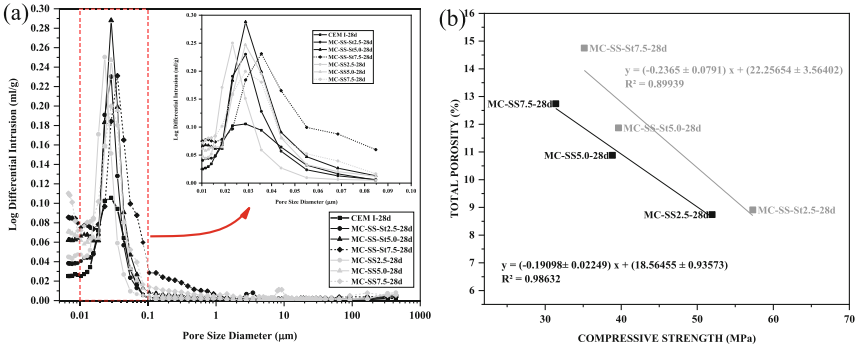

Fig. 6. (a) Pore size distribution and (b) Total porosity and Compressive strength correlation of cement paste mixtures: Reference sample (CEM I), and samples with 2.5, 5.0 and 7.5wt% MC additions.

4 Conclusions

Synthesized microcapsules obtained remarkable physicochemical characteristics and performance in cementitious mixtures compared to microsilica. It gives a light of a possible introduction of smart and environmentally innovative materials for self-healing concrete with competitive features into the construction market. The morphology and compositional properties of the microcapsules are in accordance with a silica material as it is part of the core-shell configuration. The core content based on silicate resins showed to be a good complement for the accomplishment of the proposed system. Even more, the biopolymer content of the core of the second microcapsule-based system presented better capability than the solely inorganic one. As it is known, more mixing water than required for the chemical reaction with the cementitious material reduces strength. That was the reason for reducing the mechanical properties of the evaluated cement paste mixtures. Although, this outcome is interesting as the developed methodology allowed us

to determine the effect of the additions of microsilica and microcapsules, where more than the stoichiometric water is added, resulting in adequate workability of the cement pastes with these admixtures. The optimal dosage of microcapsules was established as 2.5% in replacement of microsilica, although the maximum dosage of 7.5% was also according to regulations for mechanical strength. Further studies need to be developed to determine the self-healing efficiency of repairing microcracking by autonomous mechanism and decide the best formulation of the smart material. Specifically, further improvement of the compatibility on the interfacial zone should be done to ensure the application of the microcapsules in self-healing cementitious materials. Then, this work is a starting point that offer a solution for microcracking by means of microencapsulated systems meanwhile confers better characteristics to construction materials.

Acknowledgments. Authors gratefully acknowledge the financial support of the PID2020-113223RB-I00, funded by the Spanish Government (Ministerio de Ciencia e Innovación), to the Instituto de Ciencias de la Construcción "Eduardo Torroja" of the Spanish Research Council – IETcc CSIC, as well as, the FONDO NACIONAL DE FINANCIAMIENTO PARA LA CIENCIA, LA TECNOLOGÍA Y LA INNOVACIÓN "FRANCISCO JOSÉ DE CALDAS" by means of an interinstitutional contract between the company SIKA Colombia S.A.S., the Universidad Nacional de Colombia – Sede Bogotá, and Minciencias: Contrato de Financiamiento de Reembolso Condicional FP44842-351-2017.

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