SCIENTIFIC CULTURE
www.sci-cult.com

SCIENTIFIC CULTURE, Vol. 9, No. 2, (2023), pp. 109-116
Open Access. Online & Print

DOI: 10.5281/zenodo.7918407

SYNTHESIS OF ENCAPSULATED HEALING AGENTS AND INTEGRATION IN CULTURAL HERITAGE REPAIR MORTARS FOR ENHANCING THEIR HEALING CAPACITY

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Received: 10/04/2023
Accepted: 07/03/2023
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ABSTRACT

The present work focuses on the synthesis and integration of encapsulated healing agents in ternary mixtures of repair mortars for cultural heritage applications. The research is categorized in three sections: a) the development and characterization of spherical encapsulated healing agents according to optical and scanning electron microscopy, b) the incorporation of different concentrations of capsules in ternary repair mortar mixtures (consisting of white cement, lime and pozzolan) and the study of their survivability during mixing process, their distribution in the matrix and effect on the mechanical properties of the matrix, and c) the identification of the healing products created inside the cracks by scanning electron microscopy. The results revealed that the methodology followed can be efficiently used to prepare encapsulated healing agents with good chemical compatibility with the repair mortars. Capsules presented uniform distribution in the mortar mixtures without significant effect on their mechanical performance. Finally, healing assessment revealed the efficient activation of capsules during damage of the specimens, as well as the contribution of capsules on the healing mechanism.

KEYWORDS: Self-healing, Repair mortars, Encapsulated agents, Healing products

1. INTRODUCTION

The protection and structural safety of architectural monuments over time are the two main axes that determine the type of interventions and the selection of the repair materials. To this direction, the autogenous self-healing ability of mortars has attracted the interest of the research community, as an alternative solution for improving the durability of repair mortars and the structural integrity of the monuments. Several studies have shown the autogenous self-healing ability of mortars to heal the micro-cracks created in their structure, extending their service life, without requiring external intervention (Amenta et al., 2016, De Francesco et al., 2021). However, due to the limited efficiency of this mechanism, new technologies have been proposed to enhance the self-healing performance of mortars (De Belie et al., 2018, Michalopoulou et al., 2020, Mohamed El-Sayed et al., 2022).

A promising approach towards self-healing repair mortars is the development of encapsulated healing agents incorporated into the mortar mixtures during the mixing process (Van Tittelboom and De Belie, 2013; Huang et al., 2016). The healing agent is stored in the core of the capsules, protected by a durable shell. During crack propagation, the shell breaks and the healing agent is released, forming secondary hydration products that heal the crack. The effectiveness of these capsules depends on several parameters (Papaioannou et al., 2021), such as: (i) the reactivity of the healing agent and its compatibility with the matrix, (ii) the ability of the shell to protect the healing agent from the moisture, (iii) the efficient incorporation of capsules into the mortar mixtures, as well as (iv) their successful activation during crack propagation. In addition, the size and concentration of the capsules are significant parameters that affect the self-healing performance and mechanical strength of mortars and should be taken into consideration.

The present work focuses on the synthesis and integration of encapsulated healing agents in ternary mixtures of repair mortars for cultural heritage applications. More specifically, this research is divided in three sections: a) the development of spherical encapsulated healing agents in the macro-scale based on a physical encapsulation methodology, the pan coating, b) the incorporation of different concentrations of capsules in ternary repair mortar mixtures (consisting of white cement, lime and pozzolan), and c) the evaluation of their self-healing capacity, through SEM analysis of the fractured surfaces, after 28 d of healing.

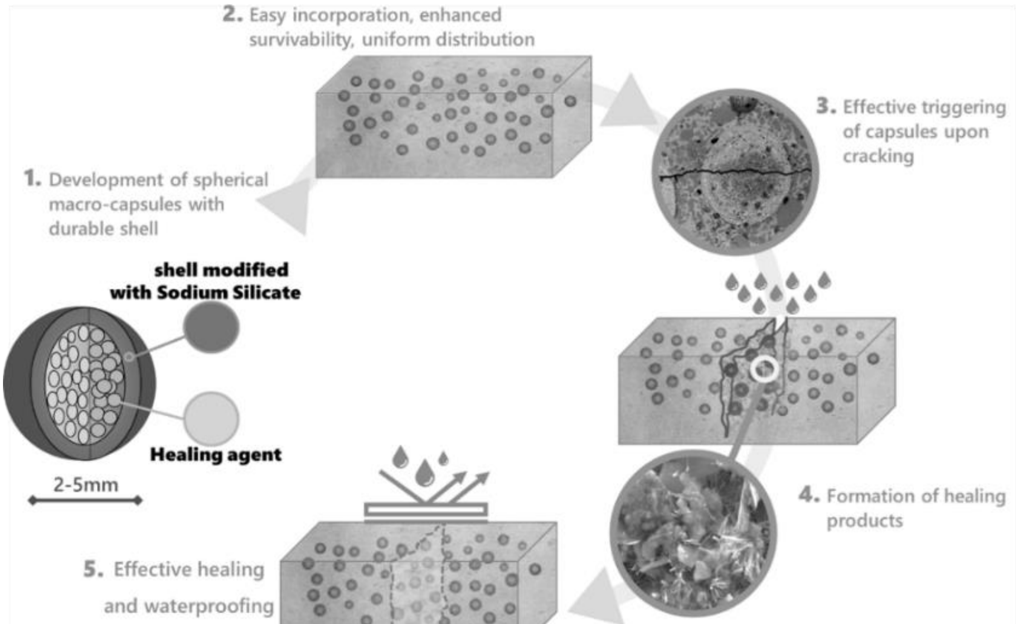

Figure 1. Graphical representation of the design, incorporation and activation of the encapsulated healing agents, inside the matrix of laboratory prepared repair mixtures (Papaioannou et al., 2022).

2. METHODOLOGY

2.1. Materials and methods

Spherical cement-based capsules with a solid healing agent were produced by pan coating, according to the methodology proposed in a previous work (Papaioannou et al., 2022). The healing agent was composed of a mixture of ordinary Portland cement (CEM I 42.5) supplied by TITAN S.A. with 15 wt. % CSA-based (calcium sulfoaluminate) expansive admixture (Denka Company Limited) in order to enhance the reactivity and expansion after activation.

The shell of the capsules was synthesized by applying OPC powder, sprayed by a water solution of alkaline accelerator (DOMOGUNIT L, DOMYLCO Ltd.) to provide early strength development and dense microstructure. The total alkaline accelerator/cement ratio of the shell was 3/10 w/w. The morphology of the capsules was examined using a Leica S6D stereo-microscope, while the shell formation was studied in cross sections of the capsules by scanning electron microscopy (SEM). SEM examination was conducted in a FEI, Quanta Inspect at 25 kV.

Figure 2 shows a representative sample of cement-based capsules produced in the lab. Using core particles between 2 to 4 mm, capsules up to 5 mm of good circularity (circularity index: φ=0.87±0.02) were formed. Macroscopical observation of capsules showed that pan coating can be efficiently used for encapsulating powder healing agents, resulting in the formation of an external protective shell in the range of 100 to 600 μm.

The use of the alkaline accelerator enabled the early strength development of the shell, resulting in a high crushing load under compression equal to 25.5±4 N. The alkaline accelerator is composed mainly of sodium aluminate, providing Na^+ and $[Al(OH)_4]^-$ ions in the cement particles of the shell. During shell formation, $[Al(OH)_4]^-$ ions react with Ca^{2+} and SO_4^{2-} ions present in the liquid phase of the cement, forming AFt (ettringite – $C_6A\hat{S}_3H_{32}$) and AFm (calcium monosulfoaluminate – $C_4A\hat{S}H_{12}$) phases, which reduce the setting time of the cement and increase the density of the hydrated products (Salvador et al., 2016).

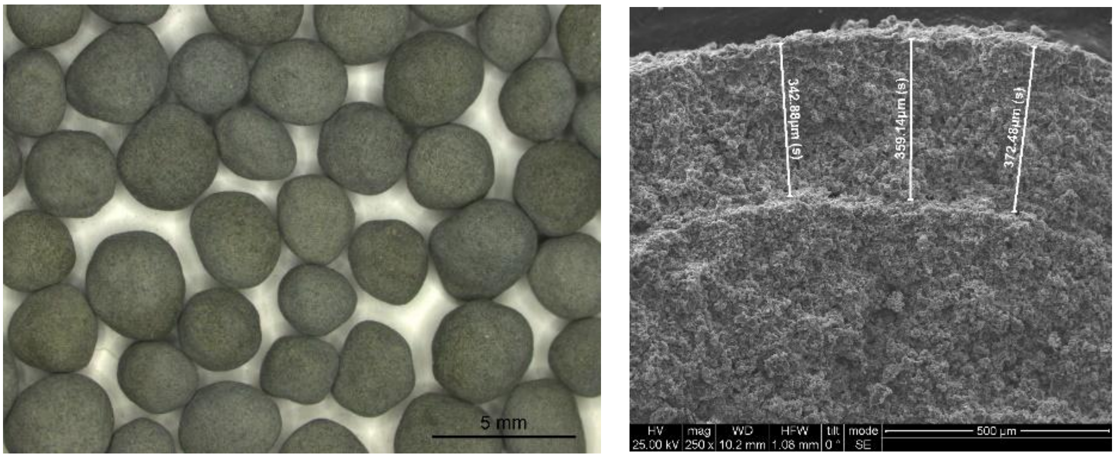

Figure 2. Representative sample of capsules observed in stereomicroscope (left) and cross section of a capsule examined in SEM (secondary e- mode), indicating their shell thickness.

Mortar mixtures of OPC (CEM I 42.5), standard sand (CEN standard siliceous sand by AFNOR) and different concentrations of capsules (10% and 20% as sand replacement by volume) were prepared in order to evaluate the survivability of capsules during mixing process, their distribution in the matrix, as well as their effect on the mechanical performance of the hardened mixtures. Moreover, a healing efficiency assessment was conducted in order to evaluate the contribution of capsules in the healing mechanism. More specifically, the damaged specimens were split after healing under water following their initial crack so that the crack faces would be exposed. Samples of the fractured surfaces were extracted and carbon coated in order to examine the healing products in SEM. The methodology followed for the examination of the above parameters is described in a previous work (Papaioannou et al., 2022).

3. RESULTS AND DISCUSSION

3.1. *Integration in ternary mixtures*

To achieve efficient integration of capsules in a mortar mixture, critical parameters that ensure the maintenance of its original performance and enhancement of its healing efficiency should be fulfilled. Thus, the ability of capsules to survive the mixing process, their effect on the mechanical properties of the matrix, as well as their distribution inside the mortar specimens were studied. The results are presented in the following subsections.

3.1.1. Survivability during mixing process

Survivability ratio of capsules was evaluated by conducting a washing test after the mixing process, in order to collect the intact capsules that survived during mixing and calculate the survivability ratio. The high crushing load of capsules allowed the survivability of the majority of the capsules during the mixing process, which was calculated equal to 77%. It has to be noted that this value could be even higher, since a quantity of capsules is inevitably crushed between the mixer blade and the walls of the bowl, as the gap between the blade and the bowl of the specific mixer is 3±1 mm, while capsules up to 5 mm were used.

3.1.2. Mechanical performance of mortar mixtures

The addition of capsules is expected to modify the properties and mechanical performance of the repair mortars. For that reason, the mechanical properties of specimens with different concentrations of capsules after 28 days of curing under water were studied. The flexural and compressive strength of the mixtures can be seen in Fig. 3. Regarding the flexural strength of the specimens, similar performance is observed when 10% of capsules is added in the mixtures compared to the reference mixtures, while a small decrease of 5.4% is calculated when 20% of capsules is integrated in the mixtures. However, the standard deviation range of the specimens containing 20% of capsules is included in the corresponded range of the reference specimens, indicating the negligible effect of capsules addition. Accordingly, the addition of 10% of capsules improved the behavior of the specimens under uniaxial compression, resulting in an increase of 8.6% after 28 days of curing compared to the reference specimens. Further increase of capsules concentration, at 20%, led in a small decrease of the compressive strength by 7.6%.

Generally, the good mechanical performance of the specimens with embedded capsules is attributed both to the good adhesion of the capsules' shell with the matrix, as well as to the fact that the capsules were added as replacement of sand, keeping the total volume of sand/capsules stable. Small deviations compared to the reference mixtures are due to the slight modification of the packing density of the aggregates (sand/capsules system), as well as to the different chemical and physical characteristics of the capsules compared to the sand particles.

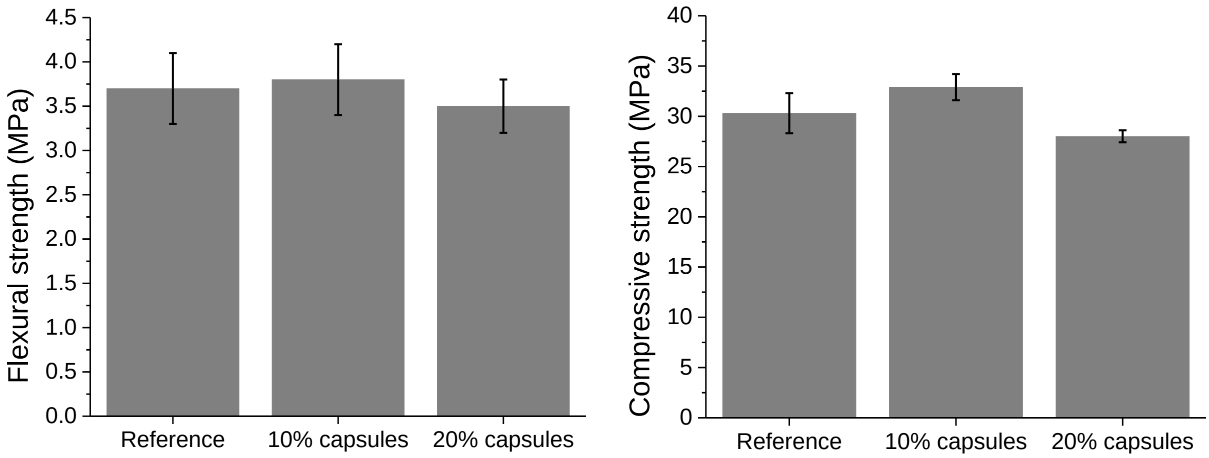

Figure 3. Effect of capsules concentration on the flexural (left) and compressive strength (right) of ternary mortar mixtures, after 28 days of curing under water.

3.1.3. Distribution of capsules in mortar mixtures

Capsules distribution is another parameter that affects the original performance of mortars, as well as the efficiency of the healing mechanism. The distribution coefficient of capsules inside the mortar specimens was calculated for the different concentrations of capsules, as shown in Fig. 4. In both cases the distribution coefficient is above 0.5, indicating the satisfactory distribution of the capsules in the mortar mixture thanks to their hydrophilicity that enabled their homogenization with the rest ingredients of the mixture. As the concentration of capsules increases from 10% to 20%, a more homogenous distribution is achieved. The good distribution revealed by the examination of the cross sections of the specimens is a good indicator that phenomena like wasting of reactive components due to agglomerates of capsules and inappropriate homogenization are not presented using this type of capsules.

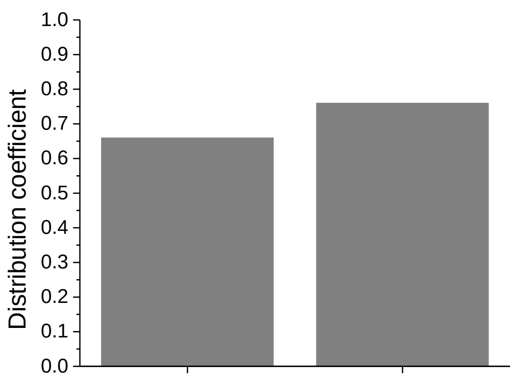

Figure 4. Effect of capsules concentration on their distribution coefficient, after their integration in the mortar specimens.

3.1.4. Triggering mechanism of capsules

Fig. 5 shows representative images of fractured surfaces of the specimens with embedded capsules obtained in stereomicroscope. The images show some capsules that have been mechanically activated during crack propagation, releasing the active components from the core particles. At the same time, other capsules that have not been activated were found in the fractured surfaces, since the crack passed between the shell and the matrix, without damaging the shell. This is attributed to the high mechanical properties of the capsules' shell compared to the strength of the ternary matrix at 28 d, combined with the existence of weak areas between the shell and the matrix which attracted the cracks, leading in debonding of the capsules from the matrix. Moreover, as shown in the images, in some cases the binder from the matrix has stuck in the surface of the capsules that have not been ruptured during crack propagation. This is attributed to the good adhesion of the shell with the matrix and the strong interfacial transition zone created, combined with the high strength of capsules compared to the matrix that did not allow their activation. The graphical representation of these two triggering mechanisms can be seen in Fig. 6.

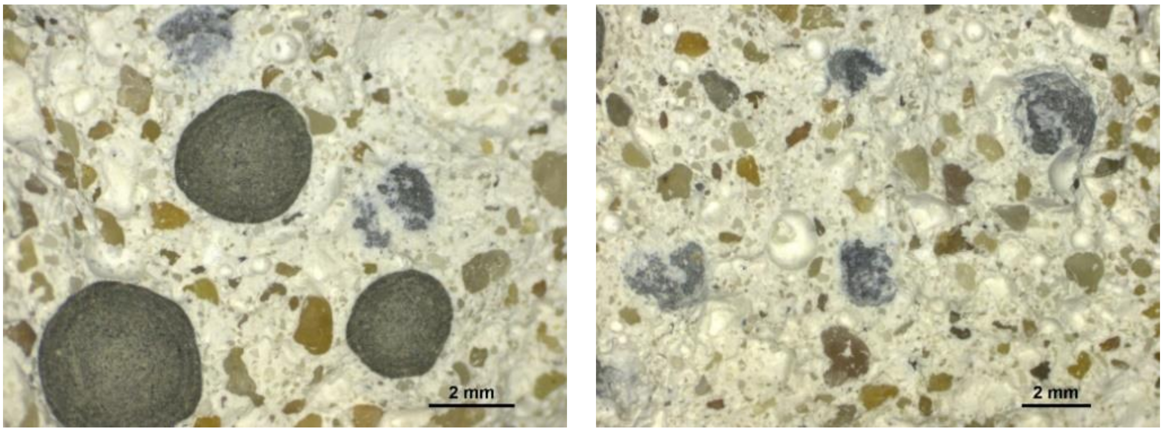

Figure 5. Examination of the triggering mechanism of capsules integrated in mortar specimens under stereomicroscope.

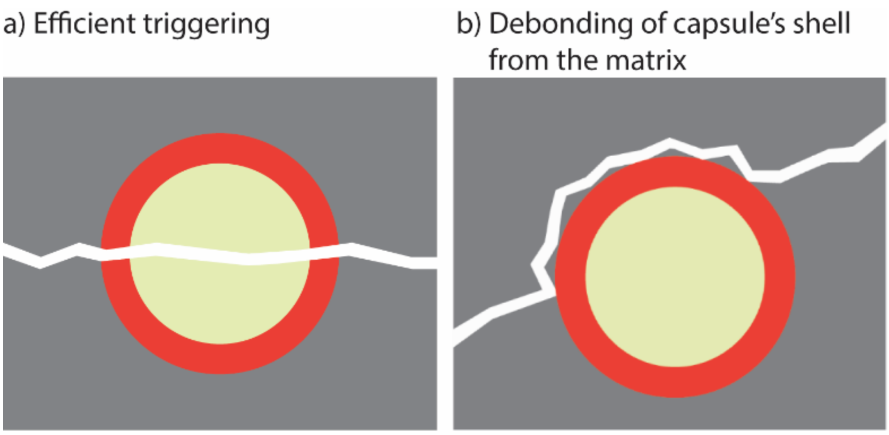

Figure 6. Possible scenarios during crack propagation: a) efficient triggering of capsule, and b) debonding of the shell from the matrix.

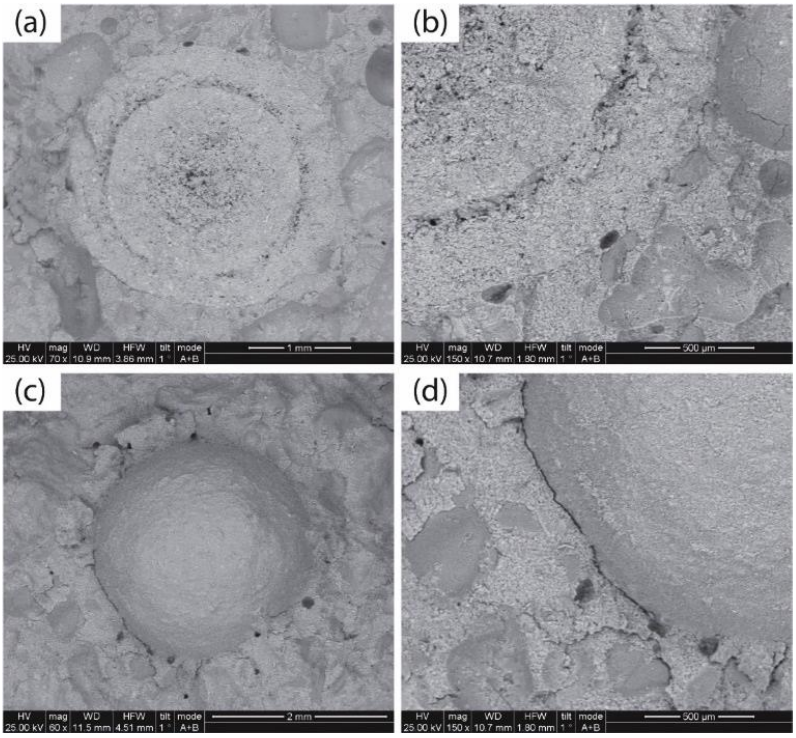

Figure 7. Examination of the fractured surfaces of the specimens containing capsules in SEM (BS mode), showing both mechanically triggered capsules (a, b), and capsules that have not been activated during crack propagation (c, d).

The fractured surfaces of the specimens were also examined in SEM, in order to evaluate the triggering mechanism of capsules and the adhesion between the shell and the binder. The zone between the shell of the capsules and the binder is called Interfacial Transition Zone (ITZ) and is differentiated by the microstructure of the bulk binder as seen in Fig. 7. An efficiently activated capsule and a capsule that has not been triggered, are presented in Fig. 7a and Fig. 7c respectively. Images of higher magnification (x150) focusing on the ITZ are also presented in Fig. 7b and 7d. As seen in Fig. 7b, good adhesion between the shell and the matrix has been created, due to the good chemical compatibility of the shell materials with the matrix, that allowed the efficient rupturing of the shell during crack propagation. In the second case (Fig. 7d), delamination of the capsule from the binder and crack deflection was observed, due to the gap presented in the interface of the binder and the capsule, that led the crack to this direction.

3.2. Examination of the healing products

Fractured surfaces of the specimens were examined in SEM after 28 days of healing in order to characterize the healing products formed inside the cracks. Representative images of the healing products formed inside the cracks of the reference specimens and the specimens containing capsules are presented in Fig. 8 and 9. In both cases healing products were rich in calcite and portlandite due to the autogenous healing mechanism of the binder, attributed to on-going hydration. Moreover, due to the pozzolanic reaction (Cai et al., 2018) between metakaolin and calcium hydroxide in the presence of water, secondary calcium-silicate-hydrate (C-S-H) was formed inside the cracks. In specimens containing capsules, additional C-S-H and ettringite were produced due to the hydration of the healing agent.

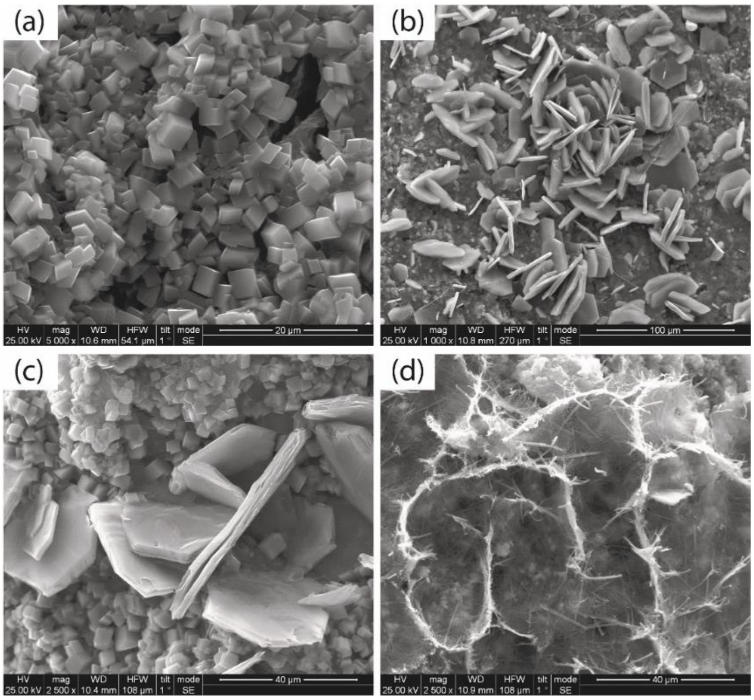

Figure 8. Morphology of autogenous healing products observed in fractured surfaces of reference specimens in SEM (SE mode), indicating the formation of calcite crystals (a), portlandite (b, c) and calcium silicate hydrates (d) during healing period.

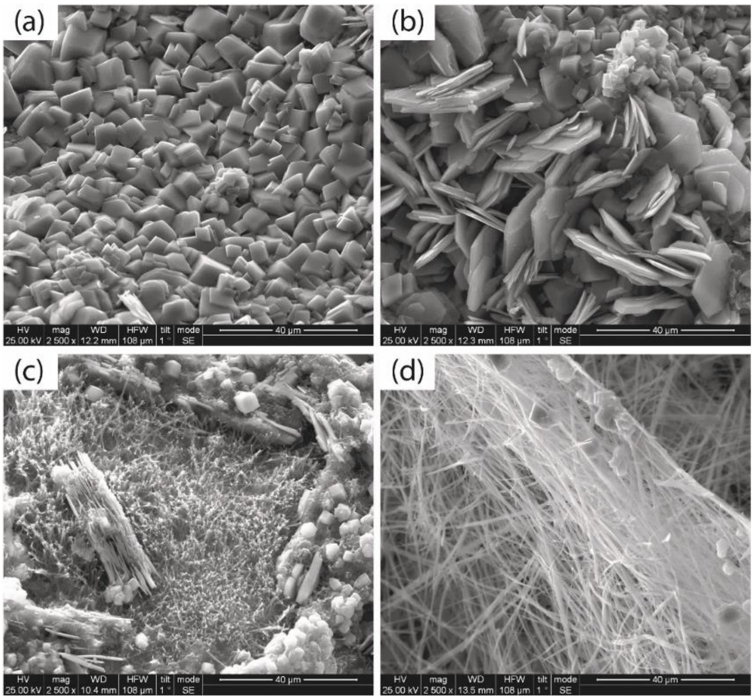

Figure 9. Morphology of autogenous and autonomous healing products observed in fractured surfaces of specimens containing capsules in SEM (SE mode), indicating the formation of calcite crystals (a), portlandite (b) and ettringite (c, d) during healing period.

4. CONCLUSIONS

The results revealed that the pan coating technique can be efficiently used to prepare encapsulated healing agents for improving the autogenous self-healing of repair mortars. The produced capsules exhibited high survivability ratio during the mixing process, indicating their feasible use in large scale applications. In addition, the hydrophilicity and compatibility of the capsules enabled their uniform distribution in the matrix without significant effect on the mechanical performance of the matrix. The examination of the triggering mechanism revealed that some capsules were not efficiently activated during crack propagation due to their increased strength compared to the matrix, highlighting the need for optimization of the shell properties. Finally, the examination of the healing products in SEM showed the beneficial contribution of capsules on the healing mechanism, indicating the potential use of the self-healing capsules, especially after the initial setting period, when the autogenous mechanism will have been diminished.

Author Contributions: Conceptualization: S.P and I.K; Methodology: S.P, M.A, I.K; Investigation, S.P; Resources, V.K; Writing—original draft preparation: S.P; Writing—review and editing: S.P, V.K, D.G, I.K; Supervision: I.K; funding acquisition: I.K. All authors have read and agreed to the published version of the manuscript.

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