Review paper

Critical Aspects in the Development and Integration of Encapsulated Healing Agents in Cement and Concrete

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Abstract

Self-healing cement composites are considered to be an effective solution towards the enhancement of sustainability and service-life of cement and concrete structures, as well as the reduction of repair and maintenance cost. Among the several self-healing technologies, encapsulated healing agents present benefits that include healing of larger cracks and timeless healing potential upon damage. This paper presents a critical overview of the progress made in the development of encapsulated healing agents, along with the main achievements related to their integration in the cement mixtures. Encapsulated healing agents were classified according to their size in two main categories: (i) spherical microcapsules up to 1 mm, and (ii) macrocapsules that include larger spherical capsules (>1 mm) and/or tubular capsules up to 100 millimeters long. The review emphasizes on the performance characteristics of the shell material and the capsule system that are necessary in order to protect the different types of healing agents in the long-term, to provide even distribution and survivability and finally, to ensure efficient triggering and release of the healing agent during crack propagation. The relevant literature is analyzed and discussed according to the above thematic priorities, aiming to locate research gaps and best practices and thus, to enable and facilitate the development of effective encapsulated healing agents that could be scaled-up. To this end, particular emphasis is given on the effect of capsules integration on the properties of both fresh mixtures and hardened cement specimens.

1. Introduction

The development of self-healing cements has been proposed as an innovative approach for enhancing the durability of conventional cement and prolonging the service life of critical concrete structures (Van Tittelboom and De Belie 2013; Huang *et al.* 2016; De Belie *et al.* 2018; Danish *et al.* 2020; Zhang *et al.* 2020). To this direction, encapsulated healing agents have attracted the interest of research community and industry, due to the long-term protection of the healing agent, until crack formation. During crack propagation, the shell is triggered, and the healing agent is released, activating the

healing process.

The long-term protection of the healing agent, the timeless healing ability of capsule-based cement composites and their ability for healing cracks larger than those addressed by the autogenous mechanism (Amenta *et al.* 2016) have led to several different approaches on the topic (Mihashi and Nishiwaki 2012; De Belie *et al.* 2018; Ferrara *et al.* 2018; Paine *et al.* 2019). This work is focused on the capsule-based self-healing additives for cement, the evolution and the achievements in this topic. The increasing interest of the research community in capsule-based self-healing additives is reflected on the number of experimental papers reported in **Fig. 1**. The autogenous self-healing (Amenta *et al.* 2020a) and all other approaches of autonomic self-healing, such as the use of mineral and expansive admixtures (Ahn and Kishi 2010; Roig-flores *et al.* 2015), superabsorbent polymers (Mignon *et al.* 2017; Mechtcherine *et al.* 2021), vascular systems (Li *et al.* 2020b; De Nardi *et al.* 2020) and bacteria (Tziviloglou *et al.* 2016; Chen *et al.* 2019) were excluded from this review, as well as from the papers used in **Fig. 1**. Therefore, the first paper considered in **Fig. 1** is dated in 1994 while the number of papers until 2010 is limited. However, during that period, the research in self-healing materials in general was vivid, resulting much more research papers in the field, as can be seen in the graph presented by Van Tittelboom and De Belie (2013).

Although several different capsules have been proposed for enhancing the autogenous healing capacity, there is no clear-cut answer for the efficiency of each

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type. There are several methodological and technical aspects that need to be further examined, in order to facilitate the establishment of the most suitable technologies and their scale-up for testing in large-scale applications.

The main factors that affect the performance and healing efficiency of encapsulated healing agents and cement composites include:

- The type and reaction mechanism of the healing agent
- The survivability of capsules during the mixing process
- The protection of healing agent in the long-term (watertight and chemically durable shell)
- The triggering efficiency of capsules during crack propagation
- The size, shape and concentration of capsules

This paper aims to present the progress made, as well as the research gaps in the different design and development aspects of capsule-based self-healing cement composites, along with the challenges that need further examination in order to move from the laboratory scale to the market. Particular emphasis is given on the properties of the shell, as well as on issues related to the integration of different capsules in the cement matrix and their effect on the initial performance of cement specimens.

2. Performance of capsules

In order to promote the healing capacity and maintain the original performance characteristics of cementitious material, there are several parameters that need to be considered during the design process of the self-healing system. Besides the physical and chemical properties of the healing agent, emphasis should be given on the stability of the system over time, and thus on the watertightness and durability of the shell that will ensure the long-term reactivity of the healing agent and allow activation of the healing mechanism upon damage. Moreover, the efficient integration of capsules in the cement matrix is a critical subject for research. Due to the vari-

ety of the encapsulation methods, further research is required, concerning the effect of capsules' size distribution, their adhesion strength to the matrix, as well as their concentration on the fresh properties of the mixtures and the mechanical performance of the hardened specimens. Simulation can be a useful tool in this stage for studying the multivariate effect of size, geometry and concentration. In the following sections, the main characteristics of the capsules' shell used so far in self-healing studies are described, along with the scientific progress and the main findings in this field.

2.1 Protective shell

The development of the shell is a crucial stage of capsules' preparation, as it has a dual role: to protect the healing agent from early reaction in the long-term, and ensure the efficient release during damage and crack propagation. To meet these requirements, a set of properties should be optimized, including: (i) size, (ii) water tightness (microstructure), (iii) morphology, (iv) mechanical strength and (v) chemical affinity with the matrix. The potential to control and adjust the surface properties and morphological characteristics of capsules has been proved to be significant for enhancing crucial performance characteristics, such as the adhesion of the shell with the matrix, survivability of capsules during mixing and efficiency of the triggering mechanism. So far, several types of capsules with different shell compositions, healing agents, sizes and other properties have been prepared using traditional and innovative encapsulation techniques. In **Table 1**, the main encapsulation techniques, the corresponding shell materials, as well as the resulted geometry and size of the capsules are categorized according to the type of encapsulation method.

Capsule-based healing agents are classified according to their size in two main categories: (i) microcapsules that concern spherical capsules with diameters up to 1 mm, and (ii) macrocapsules that include larger spherical capsules (>1 mm) and/or tubular capsules up to 100 millimeters long (De Belie *et al.* 2018).

Spherical microcapsules have been extensively studied for self-healing cement applications and have been produced both by chemical and physicochemical techniques. Polymerization techniques, such as interfacial and in situ polymerization and sol-gel reaction are some of the main chemical techniques that have been studied so far. Typical shell materials of this type of capsules include urea formaldehyde, polyurethane, polyurea and silica. Among various physicochemical techniques, complex coacervation and microfluidic encapsulation have been used in order to produce spherical microcapsules. Using complex coacervation, spherical polymeric microcapsules in the range of 300-700 μm , with switchable mechanical properties have been developed, while the use of microfluidic devices allowed the development of acrylic microcapsules with adjustable shell properties.

Fig. 1 Evolution of the number of papers referred to the use of encapsulated healing agents in self-healing cementitious materials.

Table 1 Reported encapsulation techniques for self-healing concrete applications.

	Preparation method			
	Chemical	Physical	Physicochemical	Commercial
Publications merit (%) per category	41.7	22.0	7.1	29.1
Technique	Polymerization, sol-gel reaction	Extrusion, 3D printing, pan coating, spray drying	Complex coacervation, microfluidic fabrication	Injection
Geometry	Spherical	Spherical or tubular	Spherical	Tubular
Size range	5-600 μm	Spherical: 0.6-4 mm diameter, Tubular: up to 100 mm long, 10 mm diameter	70-700 μm	Up to 100 mm long
Shell materials	UF, PU, PUrea, poly(phenol-formaldehyde), silica	Polymer modified cement, PMMA, PS, PLA, PVA, SS-PS-LS, cement	Gelatin, acacia gum, polyacrylate	Glass, ceramic
References	(Yang <i>et al.</i> 2009, 2011; Ge <i>et al.</i> 2011; Dong <i>et al.</i> 2012, 2016, 2017; Li <i>et al.</i> 2013, 2016a, 2016b, 2017, 2020a; Wang <i>et al.</i> 2013, 2015, 2017b, 2018, 2019a, 2020; Song <i>et al.</i> 2013; Gilford <i>et al.</i> 2014; Litina <i>et al.</i> 2014; Perez <i>et al.</i> 2015a, 2015b; Mostavi <i>et al.</i> 2015; Zhou <i>et al.</i> 2015; Giannaros <i>et al.</i> 2016; Tan <i>et al.</i> 2016; Lv <i>et al.</i> 2016a, 2016b, 2020b; Van Stappen <i>et al.</i> 2016; Arce <i>et al.</i> 2017; Al-Ansari <i>et al.</i> 2017, 2019; Kim <i>et al.</i> 2017; Milla <i>et al.</i> 2017; De Nardi <i>et al.</i> 2017; García Calvo <i>et al.</i> 2017; Souza and Al-Tabbaa 2018; Kim <i>et al.</i> 2018; Liu <i>et al.</i> 2018; Mao <i>et al.</i> 2018; Beglarigale <i>et al.</i> 2018; Milla <i>et al.</i> 2019; Sun <i>et al.</i> 2019; Han <i>et al.</i> 2020; Ren <i>et al.</i> 2020, 2020; Sidiq <i>et al.</i> 2020; Xu <i>et al.</i> 2020; Du <i>et al.</i> 2020a)	(Formia <i>et al.</i> 2015b, 2016; Sisomphon <i>et al.</i> 2011; Van Tittelboom <i>et al.</i> 2012; Dong <i>et al.</i> 2018a, 2018b, 2014, 2015; Formia and Irico 2015; Hilloulin <i>et al.</i> 2015; Gruyaert <i>et al.</i> 2016; De Nardi <i>et al.</i> 2017; Araújo <i>et al.</i> 2017, 2018; Choi <i>et al.</i> 2017a, 2017b; Alghamri <i>et al.</i> 2018; Fang <i>et al.</i> 2018; Anglani <i>et al.</i> 2019, 2020a, 2020b; Du <i>et al.</i> 2019, 2020b; Oh <i>et al.</i> 2019; Rodríguez <i>et al.</i> 2020; Wu <i>et al.</i> 2020)	(Souza <i>et al.</i> 2015; Giannaros <i>et al.</i> 2016a, 2016b; Kanellopoulos <i>et al.</i> 2016, 2017; Souza and Al-Tabbaa 2018; Al-Tabbaa <i>et al.</i> 2019; Litina and Al-Tabbaa 2019, 2020)	(Li <i>et al.</i> 1998; Van Tittelboom <i>et al.</i> 2011a, 2011b, 2013, 2014, 2015, 2016, 2018; Escobar <i>et al.</i> 2013; Tsangouri <i>et al.</i> 2013a, 2013b, 2013c, 2014, 2015, 2019; Maes <i>et al.</i> 2014; Feiteira <i>et al.</i> 2014, 2016a, 2016b; Van Belleghem <i>et al.</i> 2015, 2016a, 2016b, 2018a, 2018b, 2018c, 2019; Kanellopoulos <i>et al.</i> 2015; Qureshi <i>et al.</i> 2016; Heede <i>et al.</i> 2016; Karaikos <i>et al.</i> 2016; Anbarlouie <i>et al.</i> 2018; Van Mullem <i>et al.</i> 2018; Hu <i>et al.</i> 2018; Wu <i>et al.</i> 2019; Lv <i>et al.</i> 2020a; Mao <i>et al.</i> 2020)

Table 2 Classification of the shell materials tested in self-healing cement applications.

Shell material	Number of papers	Geometry	References
Glass	35	Tubular	(Van Tittelboom <i>et al.</i> 2011a, 2011b, 2013, 2015, 2016, 2018; Escobar <i>et al.</i> 2013; Tsangouri <i>et al.</i> 2013a, 2013b, 2013c, 2014, 2015, 2019; Maes <i>et al.</i> 2014; Van Tittelboom <i>et al.</i> 2014; Feiteira <i>et al.</i> 2014, 2016a, 2016b; Van Bellegem <i>et al.</i> 2015, 2016a, 2016b, 2018a, 2018b, 2018c, 2019; Kanellopoulos <i>et al.</i> 2015; Qureshi <i>et al.</i> 2016; Heede <i>et al.</i> 2016; Karaikos <i>et al.</i> 2016; Restuccia <i>et al.</i> 2017; Anbarlouie <i>et al.</i> 2018; Van Mullem <i>et al.</i> 2018; Hu <i>et al.</i> 2018; Wu <i>et al.</i> 2019; Mao <i>et al.</i> 2020)
UF-PU-PUrea	29	Spherical	(Dong <i>et al.</i> 2012, 2016, 2017; Wang <i>et al.</i> 2013, 2017, 2018, 2019, 2020; Song <i>et al.</i> 2013; Litina <i>et al.</i> 2014; Gilford <i>et al.</i> 2014; Mostavi <i>et al.</i> 2015; Zhou <i>et al.</i> 2015; Li <i>et al.</i> 2016b, 2017, 2020a; Tan <i>et al.</i> 2016; Al-Ansari <i>et al.</i> 2017; Arce <i>et al.</i> 2017; Kim <i>et al.</i> 2018, 2017; Liu <i>et al.</i> 2018; Mao <i>et al.</i> 2018; Beglarigale <i>et al.</i> 2018; Bonilla <i>et al.</i> 2018; Milla <i>et al.</i> 2019; Sidiq <i>et al.</i> 2020; Xu <i>et al.</i> 2020; Han <i>et al.</i> 2020)
Silica-based	10	Spherical	(Yang <i>et al.</i> 2011; Litina <i>et al.</i> 2014; Perez <i>et al.</i> 2015a, 2015b, 2017; Choi <i>et al.</i> 2017; García Calvo <i>et al.</i> 2017; Wang <i>et al.</i> 2017; Oh <i>et al.</i> 2019; Ren <i>et al.</i> 2020a)
Gelatin-gum Arabic	7	Spherical	(Giannaros <i>et al.</i> 2016a, 2016b; Kanellopoulos <i>et al.</i> 2016, 2017; Al-Tabbaa <i>et al.</i> 2019; Litina and Al-Tabbaa 2019, 2020)
Cementitious	8	Spherical or tubular	(Sisomphon <i>et al.</i> 2011; Formia and Irico 2015; Formia <i>et al.</i> 2015a, 2016; Anglani <i>et al.</i> 2020a, 2020b; Ren <i>et al.</i> 2020b; Lv <i>et al.</i> 2020a)
PMMA, PLA, PS	8	Tubular	(Hilloulin <i>et al.</i> 2015; Araújo <i>et al.</i> 2017, 2018; Choi <i>et al.</i> 2017a, 2017b; Anglani <i>et al.</i> 2019; Rodríguez <i>et al.</i> 2020; Wu <i>et al.</i> 2020)
PVA	2	Spherical	(Alghamri <i>et al.</i> 2018; Kim <i>et al.</i> 2019)
Paraffin	3	Spherical	(Peng <i>et al.</i> 2019; Du <i>et al.</i> 2020a, 2020b)
Ethyl cellulose	4	Spherical or tubular	(Gruyaert <i>et al.</i> 2016; Wang <i>et al.</i> 2016; Dong <i>et al.</i> 2018a, 2018b)
Other	11	Spherical or tubular	(Ge <i>et al.</i> 2011; Van Tittelboom <i>et al.</i> 2012; Li <i>et al.</i> 2013, 2016a; Dong <i>et al.</i> 2015; Xiong <i>et al.</i> 2015; De Nardi <i>et al.</i> 2017; Fang <i>et al.</i> 2018; Souza and Al-Tabbaa 2018; Wang <i>et al.</i> 2019a; Lv <i>et al.</i> 2020b)

Macro-scale capsules include larger capsules that could be either spherical with solid healing agent or tubular, typically used for liquid healing agents. Pan coating is among the most commonly used techniques for spherical macro-capsules. It is the oldest industrial encapsulation process for the production of coated particles, usually larger than 0.5 mm. Polyvinyl alcohol (PVA), polystyrene (PS) and cement (OPC) are some of the materials most commonly used for the formation of spherical macro-capsules' shell. Regarding the tubular

capsules, they are usually made of commercial glass capsules, as well as of polymeric containers produced by 3D printing or extrusion techniques. Except from polymers, polymer modified cement has also been used to produce tubular macrocapsules by extrusion.

In Fig. 2 and Table 2 the occurrence of the different shell materials as well as the relevant literature are summarized, while in the next sections, the performance characteristics of the protective shell are described and discussed according to the published data for both types of capsules (micro- and macro-scale capsules)

Fig. 2 Overview of shell materials tested in self-healing cement applications.

2.1.1 Water-tightness and chemical durability

The primary purpose of encapsulation is to avoid the early-stage consumption of the healing agent and ensure the long-term protection, inside a water impermeable shell with enhanced chemical durability. In case of a water-permeable shell, the healing agent may react with moisture, dissolved CO₂, or with unreacted cement and form secondary healing products, with no healing capacity. Therefore, discontinuities, cracks and defects that allow the penetration of moisture or water solutions inside the capsules, have to be eliminated. In some cases, premature consumption of the healing agents has been reported in the literature. For instance, the examination of fractured specimens with embedded PU microcap-

sules (29 μm average diameter) under SEM (Beglarigale *et al.* 2018), showed that the encapsulated sodium silicate was in the form of spherical solid particles inside the capsules. It was concluded that sodium silicate was consumed due to cracks on the surface of the capsules that allowed an air-drying process to take place. Additionally, tubular macrocapsules prepared by extrusion and 3D-printing usually present issues of waterproofing (Anglani *et al.* 2019, 2020a). According to the procedure followed in these methods, the containers are initially prepared, filled with a liquid healing agent, and subsequently sealed, creating weak points between the interfaces of the containers and the lids. Sand and polymeric coatings are used to overcome issues of watertightness observed in this type of capsules and enhance the bonding with the cement matrix (Anglani *et al.* 2019, 2020b).

Looking at the effect of the shell properties on water permeability of the capsules, for a given shell material, a correlation between water permeability and shell thickness was observed (Souza and Al-Tabbaa 2018). EDS analysis of the core material from ruptured acrylic microcapsules indicated that shells with thickness below 10 μm were water permeable. More specifically, the water used as dispersion medium of the healing agent had been evaporated and only portlandite and PVA were detected in the core of the capsules. As the shell thickness of the capsules was increased, the water permeability of the shell was decreased.

So far, there is no specific methodology developed for the evaluation of the water tightness of the shell. In tubular macrocapsules with liquid healing agents, the water tightness of the shell is usually evaluated by macroscopical observation of the specimens during controlled damage. If during fracture, fresh liquid healing agent is observed, it is assumed that the shell efficiently protected the core material (Van Belleghem *et al.* 2018c). On the contrary, in case of microcapsules, the evaluation of water tightness cannot be directly assessed and the availability of active healing agent in the long-term is unknown. This presents an additional difficulty on the comparison and interpretation of the healing capacity results from different research projects, since the load of active components inside the capsules is not comparable. Consequently, the microstructure of the shell and the ability to isolate the healing agent from the surrounding environment need to be examined. Scanning electron microscopy has been proposed for this purpose, in order to qualitatively characterize the reactivity of a healing agent over time (Souza and Al-Tabbaa 2018).

Another parameter related to the protection of the healing agent is the chemical durability of the protective shell. During early hydration of cement, a highly alkaline solution (pH values between 12.5 and 13.8) is created inside the pores for prolonged time. During this period, where elevated humidity and pH values occur, the integrity of the shell needs to be verified. In most studies, the capsules are integrated in the cement mixtures without prior evaluation of shell's chemical dura-

bility. The integrity of the capsules is studied a posteriori through examination of the shell morphology, in fractured specimens, by scanning electron microscopy. However, a simple test has been proposed for evaluating the chemical durability of PVA used for the encapsulation of mineral pellets in the range of 0.6-4 mm (Alghamri *et al.* 2018). According to this, PVA films are immersed in a high alkaline solution and their mass change is calculated after 24 h. It was observed that the films retained their integrity, while according to the weight measurements they were slightly soluble (4% weight loss) in alkaline environment. Although this is an easy, fast and low-cost procedure, it should be noted that for smaller capsules (≤ 1 mm) the feasibility of the above methodology has to be examined.

It is clear that there is no specific methodology to directly evaluate the water-tightness of the shell. The shell can be characterized indirectly by SEM as to its thickness, microstructural defects and morphology of the healing agent. Additionally, the chemical durability of the shell for capsules with diameter ≥ 0.5 mm can be evaluated by immersion of capsules in alkaline solution and mass change examination. The feasibility of this methodology should be evaluated for capsules in the micro-scale.

2.1.2 Mechanical durability - Survivability during mixing

For the successful incorporation of capsules in large-scale cement mixtures, that involve the use of aggregates, their survivability during the mixing process should be guaranteed. The shell of the capsules should exhibit sufficient strength in order to withstand the friction and the stress forces applied during the mixing process, but simultaneously, it should be ruptured during crack propagation in order to activate the healing mechanism. Therefore, an optimum balance between survivability and triggering efficiency should be defined, through the control of the mechanical properties of the shell (De Nardi *et al.* 2017). The mechanical properties of the shell depend mainly on: i) the material used for the fabrication of the shell, ii) the size and geometry of the capsules, and iii) the shell thickness.

The shell material is the key parameter that determines the behavior of the capsules during the mixing process. This can be easily understood in the case of tubular glass capsules, that have been widely used as containers for liquid healing agents. The brittleness of the glass ensures the efficient damage of the capsules during crack propagation, however the fragility of glass is considered as a serious weakness in the mixing process. In order to increase the resistance of the glass shell during the mixing process, the application of an external sand coating has been proposed (Restuccia *et al.* 2017). Nevertheless, the effect of this coating on the survivability of the glass capsules has not been evaluated, since the capsules were manually added in the cement mixture at the end of the mixing process.

Tubular polymeric capsules are expected to exhibit better robustness during mixing. PLA, PS, and P(MMA/n-BMA) have been examined as shell materials due to the low glass transition temperature (59, 102, and 59°C respectively) that make them brittle at room temperature and rubbery at elevated temperature (Hilloulin *et al.* 2015). To take advantage of this property, the capsules can be heated before the mixing process to transit to the rubbery state. It has been found that this is beneficial since almost all the preheated capsules survived the mixing procedure, in contrast to the reference capsules, that only a small portion resisted.

Another approach for enhancing the mechanical performance of the shell is the modification of the capsules' size, geometry and shell thickness. The parameters that affect the size and shell thickness of capsules prepared by different encapsulation methods, have been studied in several papers. In physical methods, the adjustment of the size, geometry and shell thickness is possible, by modifying the production procedure. For instance, in capsules produced by extrusion this can be achieved by the modification of the conveyor speed of the extruder, which results in capsules of varying shell thickness (Araújo *et al.* 2017). Similarly, in chemical methods, such as in situ polymerization, the size and shell thickness can be controlled, by modifying the synthetic conditions (agitation rate, reaction temperature, etc.) (Lv *et al.* 2016b).

Generally, when tubular macrocapsules are used, in most cases, the cement paste is prepared according to the standard procedure and the capsules are placed in a specific point of the mould/specimen during casting (Hu *et al.* 2018; Van Belleghem *et al.* 2018a, 2018b; Tsangouri *et al.* 2019; Anglani *et al.* 2020b; Lv *et al.* 2020a). A simple procedure for the calculation of the survivability ratio of macrocapsules has been proposed (Hilloulin *et al.* 2015; Choi *et al.* 2017a). According to this procedure, the capsules are separated from the mixture by performing a washing test, immediately after the mixing process, and the number of intact capsules is related to the original number of capsules added in the mixture. For larger mixtures, containing a high number of capsules, a testing procedure, based on the setting behavior of concrete, has been proposed (Araújo *et al.* 2018).

Concerning the survivability of microcapsules, several mixing procedures have been used for their incor-

poration into a cementitious matrix. The microcapsules can be either added inside the mixer during the mixing process (Du *et al.* 2019; Tsangouri *et al.* 2019), or dispersed in the water, prior to mixing (Kanellopoulos *et al.* 2017). Also, in some cases, the microcapsules are manually added to the mortar mixture, after the mixing process, to avoid their damage. Up to now, the only method to estimate the survivability of microcapsules during the mixing process is the examination of the capsules' condition in fractured sections of the specimens under SEM. If no fragments of the shell are observed, it is assumed that the microcapsules were successfully integrated into the matrix (Kanellopoulos *et al.* 2017).

2.2 Triggering mechanism

To ensure the activation of the autonomous healing process, capsules should be efficiently ruptured during crack propagation in order to release the active compounds. The adhesion of the shell to the cement matrix, as well as its mechanical strength are the major properties that determine the triggering efficiency. As discussed in the previous section, the mechanical properties of the shell depend mainly on: i) the material used for the shell fabrication, ii) the size and geometry of the capsules, and iii) the shell thickness. The adhesion strength between the cement matrix and the shell depends on the surface properties of capsules (e.g. wetting behavior and roughness), the material used for the shell and therefore, the resulted chemical affinity of the cement/shell interface. Lack of chemical affinity and adhesion strength may cause insufficient triggering of the healing process.

Figure 3 summarizes and describes the possible scenarios that may result during crack propagation in a self-healing composite (Kanellopoulos *et al.* 2016; Lv *et al.* 2020a) and highlights the equilibrium that should be achieved between adhesion and strength of the shell for efficient triggering.

In the case of low adhesion between the shell and the cement matrix, the crack goes around the capsule without affecting their integrity (**Fig. 3a**). For instance, the lack of adhesion between cement matrix and poly(phenol-formaldehyde) (PPF) microcapsules revealed that when cracks came across the capsules, only a small portion was damaged. In most microcapsules, the shell was peeled off from the matrix and the crack

Fig. 3 Possible scenarios during crack propagation: a) debonding of shell, b) crack deflection, and c) mechanical triggering of the shell.

passed around the capsules without activating the healing agent (Lv *et al.* 2020b). The examination of the fractured specimens under SEM, revealed the presence of small voids in the shell-matrix interface, which caused debonding of the microcapsules from the matrix. By improving the bond between the shell and the matrix in the above example, the probability of efficient activation of the shell is increased, while almost all the capsules in the fractured surface were found ruptured. The surface modification of the PPF microcapsules with phenolic resin [3-(2-Aminoethylamino) propyl] trimethoxysilane (KH-792), resulted in enhanced interfacial adhesion with the cementitious matrix (Lv *et al.* 2020a) and thus enhancement of the triggering mechanism efficiency.

The extensive knowledge on in situ polymerization facilitated the study of several organic compounds for the development of a protective shell. Polyurea, urea-formaldehyde, and polyurethane is a group of polymers that have been studied as shell materials, providing an extensive feedback on the triggering mechanism and the adhesion strength with cement matrix. Due to the high thermal stability, polyurea was used for the preparation of microcapsules for oil well cement (Mao *et al.* 2020). The examination of specimens with embedded microcapsules in SEM indicated that the microcapsules were broken, and the shells were not detached from the matrix, suggesting good bonding. Urea-formaldehyde microcapsules exhibited similar fracture behavior. During crack propagation, they were mechanically damaged, releasing effectively the epoxy resin-based agent (Wang *et al.* 2019). A modification of the above process, using sulfonic acid as polymerization catalyst (Al-Ansari *et al.* 2017) reduced the adhesion strength at the shell interface, due to the non-hydrated cement particles that agglomerated on the shell surface. Finally, the use of polyurethane capsules embedded in cement substrate (Yang *et al.* 2009; Beglarigale *et al.* 2018; Sidiq *et al.* 2020) demonstrated sufficient interfacial bonding with the matrix, while the majority of capsules were damaged during crack propagation. However, small areas of the shell debonded from the matrix were detected.

Inorganic silica-based shells have been proposed for encapsulating a healing agent, as a more compatible option that could support elevated adhesion strength. Indeed, the examination of silica capsules embedded in cement paste under electron microscope, in conjunction with elemental analysis (EDS), demonstrated a reaction zone confirming the pozzolanic reaction of the silica microcapsules and the cement matrix (García Calvo *et al.* 2017).

The performance of commercial tubular glass capsules used for liquid healing agents introduces another parameter that controls the triggering mechanism, that of brittleness or brittle behavior. For commercial glass capsules, even if the adhesion of the capsules' surface to the cement matrix is reduced, the mechanical triggering is achieved due to the brittleness of the glass. As an al-

ternative option for tubular capsules, polymeric (PMMA, PLA, PS) tubes have been proposed and evaluated as containers for liquid healing agents (Hilloulin *et al.* 2015; Araújo *et al.* 2017, 2018; Anglani *et al.* 2019). For enhancing their adhesion to the cement matrix and avoid slipping during crack propagation, an external sand layer is usually added (Araújo *et al.* 2018; Anglani *et al.* 2019).

Along with the adhesion strength of the shell, its mechanical performance is an important factor that influences the triggering mechanism. It has been noticed that when a strong shell is formed around the healing agents and high adhesion strength is appeared as well, the elevated toughness of the composite may result in deflection of the crack path and formation of secondary cracks in the opposite side of the crack front (**Fig. 3b**) (Kanellopoulos *et al.* 2016). Consequently, to ensure the successful activation of the healing agents, the mechanical performance of the shell, in conjunction with the adhesion strength, have to be optimized and adjusted according to the expected level of damage.

As already mentioned in the previous section, the mechanical performance of the capsules can be controlled by modifying the shell material, size of the capsules and shell thickness. Based on this approach, Lv *et al.* (2016a) suggested the development of capsules with different levels of load sensitivity, that will be activated depending on the level of damage and the crack width (Lv *et al.* 2016a). Thus, by producing a batch of capsules of varying size and shell thickness, it is possible to develop a self-healing composite of multi-scale triggering mechanism.

An alternative mechanism to the mechanical triggering is the development of capsules with pH sensitive shell, which is activated by the reduction of the pH inside the cement matrix (Wang *et al.* 2015, 2016). Compared to the traditional mechanical triggering, this approach lies on the activation by the weathering solutions, assuming that even when nano-cracks are created, the pH of the solution that penetrates will break all the capsules. However, a significant restriction of this approach is the assumption that the weathering solution will have lower pH values of the cement and that this pH will not alter during penetration and diffusion within the cement matrix. Another alternative suggests the use of chloride ions responsive capsules (Xiong *et al.* 2015), especially for applications in marine environments. The triggering efficiency of Ag-alginate capsules has been studied and the results indicated total disintegration of the shell and release of the healing agent, in the presence of chloride ions (Xiong *et al.* 2015).

Therefore, for efficient mechanical triggering of capsules during crack propagation, balanced adhesion and mechanical strength of the shell is needed. Adhesion strength of the surface of capsules to the cement matrix is the major factor that determines the triggering mechanism. In cases of chemical bonding of the shell with the cement matrix, elevated adhesion is created,

resulting in efficient triggering. Simultaneously, the mechanical properties of the shell should enable their survivability during mixing and fracture during crack propagation. Finally, chemical triggering has been proposed as an alternative mechanism for the release of the healing agent in cement mixtures made for specific applications, such as marine environment.

2.3 Integration of capsules in the cement matrix

The addition and integration of capsules in a cementitious mixture is expected to modify the initial performance of the matrix in terms of rheological properties of the mixture and mechanical properties of the hardened specimens. The effect of capsules addition on the initial properties of the cement mixture depends mainly on: i) the loading of capsules, ii) the size and distribution of capsules, iii) the interfacial bonding between the capsules and the cement matrix, and iv) the mechanical properties of capsules. Therefore, during the development of a self-healing cement composite the enhancement of the healing potential is studied, aiming to the minimum alteration of the initial performance characteristics of the cement.

The papers published so far that discuss the effect of capsules addition on the rheology and mechanical properties of cement mixtures, concern mainly spherical microcapsules, since this is the only type of capsules that is mixed together with the cement mixture. In contrast, when tubular macrocapsules are used, they are manually integrated in the casted cement mixtures and placed in specific positions, in the middle of the specimens, in order to ensure their integrity and activation during controlled damage. Usually, one or two tubular macrocapsules are placed in each specimen, since they are able to provide large volume of healing agent. So far, the studies related to tubular macrocapsules are mainly focused on the development and optimization of capsules properties and the assessment of their healing efficiency, while the effect of their integration on the cement properties has not been investigated.

2.3.1 Rheology of wet-cement mixtures

The incorporation of microcapsules into a cement mix-

ture is expected to modify the rheological properties of the mixture, since it affects the grain size distribution and the packing density of the mixture. Rheological properties can be monitored either by viscosity measurements (Kanellopoulos *et al.* 2016) or by the flow table test (Alghamri *et al.* 2018).

The viscosity of a suspension depends not only on the volume fraction of the added particles, but also on the particle size distribution. According to the Einstein's viscosity theory, for dilute dispersions of small spherical particles, the viscosity of the suspension is linearly correlated with the volume fraction of the added particles (Equation 1).

$$\eta = \eta_{\text{medium}} \cdot (1 + 2.5\varphi) \quad (1)$$

where η is the viscosity of the suspension, η_{medium} is the viscosity of the medium and φ is the volume fraction of the spherical particles in the suspension.

However, as the volume fraction of the capsules increases, a more inhibited flow field is created, resulting in higher values of viscosity and greater sensitivity to changes in particles' loading (Faroughi and Hube 2014). A representative study of how the amount of capsules (average diameter of 300 μm) affects the viscosity of the cement mixture is provided in the work of Kanellopoulos *et al.* (2016). It was found that for loadings up to 12%, there was a slight increase of the viscosity up to 36%. For higher loadings (up to 32%), the viscosity increased more than 200% in comparison to the reference mixture.

Moreover, depending on the size distribution of the added particles, an amount of the matrix, called dead fluid, is trapped between them. As the dead fluid increases, the flowability of the suspension significantly decreases (Fig. 4).

An alternative approach, in order to minimize the effect of the capsules on the rheology of the mixture, is to add the capsules as partial replacement of sand. According to this approach, different amounts of polymeric capsules in the range of 0.6-4 mm diameter were added in cement mixtures, by replacing equal mass of the aggregates (Alghamri *et al.* 2018). The flow table test was used for studying the workability and consistency of the

Fig. 4 Schematic representation of the dead fluid volume in binary systems with different size ratios and the same volume fraction of particles.

Table 3 An overview of the effect of microcapsules on the compressive strength of the cement matrix.

Shell material	Microcapsule size (μm)	Loading of microcapsules	Effect on compressive strength	Reference
Gelatin/gum Arabic	~ 300	1, 2, 3, 4, 8, 16 and 32 % by volume of cement	Negligible effect for 4 and 8% of microcapsules. Up to 24% reduction of compressive strength for higher microcapsules loadings.	(Giannaros <i>et al.</i> 2016a; Kanellopoulos <i>et al.</i> 2016; Litina and Al-Tabbaa 2019)
	500	1, 2, 3 and 4 % by volume of cement	~ 11 % decrease for 1% of microcapsules. Up to 16% decrease for higher microcapsules loadings.	(Giannaros <i>et al.</i> 2016b)
Urea/ formaldehyde	70	0.5, 0.75, 1.0 and 1.25 % by weight of cement	Less than 10% decrease.	(Al-Ansari <i>et al.</i> 2017)
	166	3, 6 and 9 % by weight of cement	Increase of 9% with 3% of microcapsules. Decrease of 35% with 9% of microcapsules.	(Wang <i>et al.</i> 2013)
	132, 180 and 230	2, 4, 6 and 8 % by weight of binder	Decrease of 3.7, 5.6 and 5.9% for 2% of microcapsules and 23.0, 24.9 and 27.6% for 8% of microcapsules.	(Dong <i>et al.</i> 2017)
Polyurea	~ 120	1, 2, 3, 4, 5 and 7.5 % by weight of cement	Up to 12% decrease for 1% microcapsules and 26 and 40% decrease for 7.5% microcapsules, depending on the shell properties (rigid or rubbery).	(Giannaros <i>et al.</i> 2016b; Mao <i>et al.</i> 2020)
Silica	~ 4	1.5 % by weight of cement	Increase of compressive strength	(Yang <i>et al.</i> 2009)
	5-180	5 and 10 % by weight	Decrease of 15% and 30% for 5 and 10% of microcapsules respectively.	(García Calvo <i>et al.</i> 2017)
Polyphenol formaldehyde	250-500	3 % by weight of cement	82.5% of the reference samples. For capsules with surface modification the compressive strength is decreased up to 60.7% of the reference.	(Lv <i>et al.</i> 2020b)
Cement	150	2, 4, 8, 16, 32 % of the total volume	75% of the reference samples for 32% capsules.	(Ren <i>et al.</i> 2020b)
Paraffin	20-700	1.5, 3, 4.5, 6 % by mass ratio	By 1.5 and 3% of microcapsules, the compressive strength is increased.	(Du <i>et al.</i> 2019)

mixtures. By increasing the loading of the capsules, the flow values decreased, since due to the lower density of the capsules in comparison to the sand, the same weight percentage corresponded to higher volume. Subsequently, the increased volume fraction of capsules has inhibited the flowability of the mixture, resulting in lower flow values.

Depending on the type of the shell, the ability of some capsules to absorb water during the mixing process may result in elevated viscosity values. For instance, the use of water permeable shells, such as gelatin/gum Arabic and polyurea may increase the viscosity of the mixture up to 50%, (Giannaros *et al.* 2016), even for very small amounts of microcapsules (4%). Simultaneously, the rheology of the mixtures may be affected by the damage of the capsules and the uncontrolled release of the healing agent during the mixing process

(Alghamri *et al.* 2018). In this case, part of the initial mixing water is consumed due to reaction with the healing agent and therefore, additional water is required for achieving the same consistency.

Generally, the packing density of the cement mixture, and therefore its rheological properties, are modified by the addition of capsules. The effect of capsules addition on the rheology of the cement mainly depends on the size distribution and concentration of capsules. Moreover, the consumption of part of setting water from the healing agent of the capsules should be considered, as the shell of the capsules usually presents issues of water tightness and low survivability. Therefore, an effective approach in order to avoid the modification of the packing density is to replace part of the sand volume by equal volume of encapsulated healing agents.

2.3.2 Mechanical properties of cement mixtures

Table 3 summarizes the effect of various types of microcapsules on the compressive strength of the cementitious matrix. So far, the effect of microcapsules in the range of 4-700 μm has been examined. The relevant papers are focused either on the preparation procedure of the macro-scale capsules, or on the assessment of the self-healing efficiency.

In most cases, the addition of microcapsules results in the decrease of compressive strength, except some cases where a slight increase is observed. The alteration of the mechanical properties is attributed to the modification of the packing density of the mixture and the (micro-) filler effect of the capsules. Depending on the size of microcapsules and the grain size distribution of the solid particles in different cement mixtures, there is an optimum amount - at low concentrations - where microcapsules act as filler and fill the empty space within the solids. Thus, the packing density of the matrix is enhanced and the compressive strength of the hardened specimens is increased (Wang *et al.* 2013; Du *et al.* 2019). Above that optimum amount, the packing density decreases again, and the matrix of the mixture becomes looser (Giannaros *et al.* 2016a, 2016b; Dong *et al.* 2017). The loose microstructure results in the formation of larger pores (Dong *et al.* 2017) and thus, the compressive strength of the matrix is decreased.

Another parameter that affects the compressive strength of the cement matrix is the mixtures' viscosity. As the content of microcapsules increases, the mixture's viscosity is also increased and this may result in the decrease of compressive strength, since higher w/c ratio is required for the same rheology (Giannaros *et al.* 2016a; Amenta *et al.* 2017).

The good chemical bonding between the shell and the cement matrix is a parameter that can reduce the negative effect of elevated capsule loading and benefit the overall performance of the composite mixture. For instance, the addition of both types of cement and urea/formaldehyde microcapsules, decreased the compressive strength of the mortar. However, this negative effect was more intense when only urea/formaldehyde microcapsules have been used (Ren *et al.* 2020b).

During the evaluation of such experimental results, it should be taken into consideration that any compounds released from the capsules which are damaged during the mixing process may modify the hydration process of the composite material, and therefore affect the development of the mechanical strength. For instance, the release of sodium silicate from broken microcapsules resulted in the formation of C-S-H that enhanced the compressive strength of the mixture (Sidiq *et al.* 2020). Therefore, during the evaluation of the mechanical properties of self-healing cements the contribution of accidentally released healing agent has to be considered.

Therefore, the mechanical properties of the composite self-healing cement depend on: i) the packing density of the mixture, ii) the viscosity of the fresh mixture, iii) the

chemical bonding between the shell of the capsules and the matrix, and iv) the accidental release of healing agent due to fracture of capsules during mixing. The effect of different types of microcapsules in the range of 4-700 μm has been examined, while the effect of macro-scale capsules has not been investigated so far.

2.3.3 Distribution of capsules in the cement matrix

The possibility of a crack to hit a capsule is maximized when a uniform distribution of capsules in the cement matrix is achieved. Although this is a critical parameter for self-healing, there are limited papers dealing with this subject.

Modeling of the distribution, size and amount of capsules could constitute one of the most important tools for designing mixtures with optimum healing capacity. Computational studies have been used in order to investigate the optimum size and percentage of capsules added to cement. Two analytical models have been developed to calculate the probability of a crack to cross a capsule during crack propagation (Zemskov *et al.* 2011). Depending on the distribution of capsules into the matrix, the optimum loading and size of capsules can be calculated and used as a reference value for further experimental investigation. Moreover, the geometry of capsules is an important parameter that affects the healing efficiency. In a recent study (Fang *et al.* 2021), the effect of capsules' size and shell thickness on the healing efficiency has been studied through analytical models developed for this purpose, concerning three common capsule shapes: spherical, tubular, and tubular with spherical tips. The results showed that the self-healing efficiency is proportional to the diameter of the capsules and increases approximately linearly by increasing the aspect ratio of the tubular capsules.

So far, limited experimental results are available about the distribution of capsules in the matrix. X-ray micro-tomography has been used to estimate the distribution of tubular PMMA and glass capsules into concrete specimens (Araújo *et al.* 2018). According to the 3D rendering of the specimens, the PMMA capsules were not homogeneously dispersed inside the matrix and it was found that due to their floating behavior, they accumulated in the top surface of the specimens. This observation highlights the critical role of surface wetting properties and density on the dispersion of self-healing capsules inside the cement matrix.

Alghamri *et al.* (2018) followed another methodology to evaluate the distribution of spherical capsules with diameter of 1.2 mm inside the hardened concrete specimens. Cylindrical specimens with embedded capsules were prepared and sawn into equal discs, and the distribution of the capsules was determined and quantified. The dispersion coefficient α was calculated as an exponent of $-\phi(x)$ according to the following equation (Torigoe *et al.* 2003; Oh *et al.* 2019):

$$\phi(x) = \sqrt{\frac{\sum_i^n (x_i - \bar{x})^2}{n}} / \bar{x} \quad (2)$$

$$a = \exp[-\phi(x)] \quad (3)$$

where a is the dispersion coefficient, n is the number of examined regions, x_i the amount of capsules in the arbitrary region and $\bar{x}$ the average amount of capsules in each region.

The dispersibility of the capsules is considered satisfactory when the coefficient value is above 0.5. In the specific research, when 10% of capsules was incorporated in a standard cement mixture, the distribution coefficient was 0.27, while when a high fluidity mixture was used, the value of the coefficient was above the target (> 0.5). This method can be facilitated by image analysis software, especially when a high number of capsules is used.

3. Large-scale tests

The existing large-scale tests on self-healing cement composites concern field application of technologies that are close to the market exit, such as microencapsulation of bacterial-based healing systems (i.e., Basilisk) or feasibility studies, such as performance evaluation of vascular systems, which are ideal for tests in large-scale. Evaluation of capsule-based self-healing cement composites in the field is limited, since they are still at laboratory stage.

In the context of M4L research project (2013-2016), a 1.8 m high panel with gelatin-acacia gum capsules (diameters of 300-700 μm) was cast in the UK, aiming to replicate a conventional field application (Davies *et al.* 2018; Al-Tabbaa *et al.* 2019). The microcapsules had switchable mechanical properties, and more specifically 'rubbery' behaviour when hydrated and brittle when dried, in order to survive during concrete mixing and then get fractured during crack propagation in hardened concrete. Although the development of microcapsules had been investigated by the University of Cambridge, their large-scale production required the collaboration with Lambson chemical manufacturer company, indicating the necessity of up-scaling the capsules production before moving into large-scale trials. According to laboratory experiments, the content of microcapsules was set to 8% of cement volume. Besides the improved healing potential that was reported in terms of crack depth closing, water permeability and strength recovery, the authors have also commented on the condition of the healing agent, in the time of investigation. Microstructural analysis showed that liquid sodium silicate, used as healing agent, may had partially solidified, since the core material was in a solid/crystalline form (Al-Tabbaa *et al.* 2019). This indicates the importance of controlling the water tightness of the shell in order to maintain the original state and properties of the healing agent and avoid reduced efficiency. Moreover, analytical data on

the condition of the healing agent will allow better discrimination between autogenous and autonomic mechanisms, which in many cases act simultaneously.

Furthermore, the large-scale application of encapsulated polyurethane was evaluated by Magnel Laboratory (Belgium), through the construction of reference and self-healing concrete beams (150 mm x 250 mm x 3000 mm), which were controlled damaged under four-point bending test (Van Tittelboom *et al.* 2016). In this case, 350 glass tubular capsules (50 mm long) were manually filled with polyurethane and positioned with a network of wires in specific points of the mould. In this field trial it became evident that the use of glass capsules has a demanding and time-consuming preparation process, which is not possible to be applied yet in real scale constructions. The main reason is the brittleness of glass that does not allow mixing of capsules with cement, water and aggregates without them been damaged. Further research is conducted in this area, in order to improve the mixing behavior of glass capsules and consequently decrease the preparation time.

The limited number of field applications and large-scale trials indicates the difficulties of scaling-up the different technologies studied at laboratory scale. Among other challenges that are faced in large-scale trials, is the survivability of capsules during the mixing process with gravel for concrete production. The development of capsules with shell properties that withstand the mechanical stresses applied during mixing, is a critical step necessary to avoid crushing of the capsules' shell and uncontrolled release of the healing agent. The damage of capsules should be eliminated, since apart from useless consumption of the active components, it causes modification of mortar's composition and properties (Sidiq *et al.* 2020).

The efficient protection of the healing agent is the primary purpose of capsule-based healing agents and therefore it is considered an essential feature of the capsules. However, so far only a limited number of papers deal with this issue. This raises doubts about the long-term reactivity and efficiency of encapsulated healing agents and also creates an additional difficulty in the comparison of the various capsule-based systems, since the actual content of the active healing agent inside the capsules remains unknown, due to water penetration through the shell and early consumption of the healing agent. As a consequence, before moving to large scale applications, the validation of the efficient protection of the healing agent would be useful and could contribute to the production of more valuable and accurate results.

The number of large-scale self-healing projects is also limited by the lack of standard methodologies for evaluating the healing efficiency of the composite material. Flourishing research in the last decade has led to the development of numerous healing technologies and methodologies for assessing the healing efficiency. However, the large variety of methodologies proposed to assess the efficiency of the various self-healing tech-

nologies makes it necessary to provide a unified framework for the validation and comparative evaluation of the several self-healing technologies. To this direction the members of the RILEM Technical Committee TC 221-SHC has undertaken the initiative in order to summarize the knowledge generated by the international research community, define a common terminology and provide information on the different experimental techniques that have been used to evaluate the healing efficiency (De Rooij *et al.* 2013).

Among the several techniques used to characterize the healing efficiency of a cementitious material, the recovery of the compressive strength, recovery of stiffness and the characterization of water absorption, water permeability and resistance to chloride penetration are the most widely studied (Huang *et al.* 2016; Ferrara *et al.* 2018; Xue *et al.* 2019; Amenta *et al.* 2020b, 2021; Van Mullem *et al.* 2020). For maximizing the reliability of the results, microstructural analysis of the healing products formed inside the crack is considered useful. Regardless of the examined property for evaluating the healing efficiency, a preliminary stage of controlled damage of the specimen is required. The level and type of damage, the age of cracking, the healing duration and the curing conditions are the main variables that affect the healing efficiency. Therefore, for accurate, representative and comparable results, all these parameters should be taken into account. In this context, six inter-laboratory tests have been conducted under the framework of the EU COST Action 15202 SARCOS focused on different self-healing technologies: (i) concrete with mineral additions, (ii) concrete with the addition of magnesium oxide (Amenta *et al.* 2021), (iii) concrete with crystalline admixtures, (iv) high performance fibre reinforced concrete with crystalline admixtures, (v) concrete with macrocapsules containing a polymeric healing agent (Van Mullem *et al.* 2020), and (vi) concrete with encapsulated bacteria. The scope of this program was to evaluate the feasibility and repeatability of several healing assessment methodologies, as well as to identify the main challenges for quantifying the healing efficiency in concrete specimens, instead of cement paste or mortar, typically used in laboratory experiments.

4. Concluding remarks

The development of capsule-based self-healing cement composites is a complex and multiparametric research topic that requires comprehensive research in several stages of capsules' design and development, in order to ensure reproducible performance at different application scales. This has resulted in examination of many different encapsulation approaches.

According to the literature reviewed, capsule-based healing agents can be classified in spherical microcapsules (<1 mm) and macrocapsules.

Microcapsules are produced by chemical (polymerization, sol-gel reaction) and physicochemical techniques,

such as complex coacervation and microfluidic encapsulation. Typical shell materials of this type of capsules include urea formaldehyde, polyurethane, polyurea and silica.

Macro-scale capsules are either spherical (>1 mm) or tubular of several millimeters. Pan coating is among the most commonly used techniques for spherical macrocapsules, while tubular capsules are usually made of commercial glass and polymeric containers, produced by 3D printing or extrusion techniques. Polyvinyl alcohol (PVA), polystyrene (PS), cement (OPC) and polymer modified cement (PMC) are some of the materials most commonly used for macro-capsules' shell.

Although there are both theoretical and experimental data for the different proposed encapsulated healing agents, further research is required before transitioning from laboratory experiments to the market.

The limited field applications conducted so far, confirmed the premature stage of this technology and revealed the main challenges that need to be addressed, regarding both the performance characteristics of the capsules, and the up-scaling of the encapsulation methodology. Simultaneously, the lack of standard methodologies for evaluating the healing efficiency creates an additional difficulty on the exploitation of this technology as the comparison of the several self-healing approaches remains unclear.

The main areas that require further research before moving to large-scale applications can be summarized below as follows:

- (1) Water tightness of individual capsules is the main parameter that affects the long-term reactivity of the healing agent. In the majority of the papers cited in this work, the evaluation of water tightness is not directly assessed, while the reactivity, availability and amount of the healing agent in the long-term are unknown. This presents an additional difficulty on the comparison and interpretation of the healing capacity results from different research projects, since the load of active components inside the capsules is not comparable. The development of appropriate characterization techniques for the evaluation of the capsules' performance is hereby of utmost importance.
- (2) For efficient mechanical triggering of capsules during crack propagation, balanced mechanical strength of the shell and adhesion with the cement matrix is needed. Adhesion strength of the surface of the capsules to the cement matrix is the major factor that determines the triggering mechanism. In cases of chemical bonding of the shell with the cement matrix, elevated adhesion is created, resulting in efficient triggering of capsules. Simultaneously, the mechanical properties of the shell should enable their survivability during mixing and fracture during crack propagation.
- (3) Survivability of capsules during mixing is of critical importance for the effective use of capsules in large-scale applications. Strength properties of the shell af-

fect the survivability of capsules during mixing and effective triggering mechanism of the healing agent upon damage. However, relevant studies that investigate the behavior of capsules in this stage are limited. Especially for microcapsules, there is no reported methodology for the quantification of the survivability ratio, while the only reported way to estimate their survivability is to examine fractured areas of specimens under SEM.

- (4) The incorporation of capsules into the cement matrix affects the rheological properties of the fresh cement and mechanical strength of the hardened mixture. Thus, an optimum combination of capsules' properties and concentration should be found. Computational studies would be useful in this stage to study the effect of size, geometry, surface properties and percentage of capsules on both healing efficiency and final performance characteristics of the composite material.

It should be noted that besides chemical, mineralogical and mechanical properties, the development of encapsulated healing agents should include further issues, such as complexity of the production process, production cost, environmental impact, as well as health and safety aspects. The above issues have not been addressed in any paper, indicating the premature stage of the capsule-based systems.

Overall, capsule-based self-healing additives offer an easy and reliable solution with several modification alternatives, for the development of self-healing cement and concrete composites. In contrast to other self-healing approaches, such as the vascular system, capsule-based additives do not require any alteration of the traditional building or casting process, and offer a great potential for fast technological growth and exit to large-scale projects in the near future.

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