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The effect of varying volume fraction of microcapsules on fresh, mechanical and self-healing properties of mortars

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HIGHLIGHTS

- Polymeric microcapsules with sodium silicate used for self-healing in mortars.
- Inclusion of microcapsules does not affect hydration and setting time.
- Increasing dosage of microcapsules slightly increases dramatically the viscosity.
- Increasing dosage of microcapsules slightly reduces the mechanical properties.
- Microcapsules showed good adhesion to the cement matrix.

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ABSTRACT

Spherical polymeric microcapsules, carrying liquid sodium silicate, were used for autonomic self-healing of mortars. Microcapsules were added at varying volume fractions (V_f), with respect to the cement volume, from as low as 4% up to 32% and their effect on fresh, mechanical and self-healing properties was investigated. For this purpose a series of techniques were used ranging from static mechanical testing, ultrasonic measurements, capillary sorption tests and optical microscopy. A detailed investigation was also carried out at the microstructural level utilising scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Results showed that although increasing V_f resulted in a ~27% reduction in the mechanical properties, the corresponding improvement in the self-healing potential was significantly higher. Areal crack mouth healing reached almost 100%. Also, the measured crack depth and sorptivity coefficient reduced to a maximum of 70% and 54% respectively in microcapsule-containing specimens. SEM/EDX observations showed that the regions in the periphery of fractured microcapsules are very dense. In this region, high healing product formation is also observed. Elemental analysis revealed that these products are mainly ettringite and calcium-silicate-hydrate (C-S-H).

1. Introduction

Amongst the self-healing techniques developed in the last twenty years the microencapsulation approach is by far the most studied. Microencapsulation was initially developed for self-healing applications in polymers and composites [1] and developed from the previous systems based on hollow capillary tubes [2]. The two techniques have many similarities, but the use of microcapsules alleviates the manufacturing related issues associated with the incorporation of hollow tubes in matrices. Typically microcapsules have sizes ranging from few microns up to 1 mm, whereas hollow tubes have diameters and lengths ranging from 1 to 5 mm and 10–80 mm respectively. In principle, microcapsules are containers that envelope a healing compound keeping it protected from the manufacturing processes as well as from the surrounding host matrix. The most fundamental principle of self-healing via microencapsulation is that the microcapsules are homogeneously dispersed in the bulk volume of the host material and the release of their healing compound is triggered by the formation of cracks that rupture their shell. Consequent chemical interactions between the encapsulated material(s) and the host matrix heal the crack. In this way, bulk material properties can be partially, or fully, restored.

There is a large number of different techniques and processes that produce an impressive spectrum of different types of microcapsules [3–5]. A wide variety of materials have been investigated as shell and core constituents in the microencapsulate systems. Polymeric shells and epoxy-based cargos are the most broadly used and investigated. The main focus of research over the last

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fifteen years was on the actual development of these systems as well as the optimisation of the production techniques. This involved systematic investigation of the influence of the process parameters such as the agitation speed, the pH, the temperature and the concentration of raw materials on the size, stability, morphology, content loading and mechanical properties of the produced microcapsules [6–9]. In the last few years the concept of using microcapsules has extended to construction materials. While the microcapsules' production techniques do not differ significantly for such applications, the survivability, stability and functionality of microcapsules have been investigated for these non-polymeric host matrices [10–13].

Since the microcapsules are additions within the bulk volume of the host matrix it is expected they will alter its mechanical properties. The degree of this change depends on a large number of parameters: the size and the volume fraction of microcapsules, the mechanical properties of the shell materials and the mechanical interlock between the microcapsules and the surrounding matrix. The extent of self-healing itself depends on four major factors: the type of the healing compound used, the size of the crack, the size of the microcapsules and their volume fraction with respect to the bulk material. In cases where an activator is needed to promote healing, the quality, the particle size and the concentration of the activator also play an important role. It is therefore apparent that the ideal self-healing material should have an optimised balance between an alteration in its original properties due to the inclusion of microcapsules, and the potential self-healing efficiency.

Although a very large number of scientific articles discuss all the above mentioned parameters, the studies focusing on the effect of microcapsule addition on the mechanical properties of hardened cementitious matrices under static and dynamic load conditions are limited. Similarly, studies reporting on the effect of microencapsulate additions on the fresh properties, such as viscosity and curing time, are even scarcer. Brown et al. [14], in one of the most comprehensive studies on the effect of microcapsule addition on epoxy matrices-reporting that both the elastic modulus and ultimate stress decreased when increasing the percentage of microcapsules. More specifically they investigated microcapsule additions from as low as 6%, by volume of host matrix, up to 33%. The maximum reduction in elastic modulus and ultimate stress was reported as 30% and 64% respectively, for 33% of microcapsules, when compared to a matrix without additions. These findings verified similar trends reported earlier in the literature for epoxy composites containing polymeric microcapsules or microspheres [15–17]. Although mechanical properties are affected negatively by the addition of microcapsules, the composite matrices were found to have increased stiffness. This is evident from fracture toughness values increasing with increasing percentage of microencapsulate additions [14,18,19]. This increase of stiffness was observed regardless of the size of the microcapsules used. Smaller microcapsules exhibited higher stiffness at lower volume fractions (up to 10%). At higher volume fractions (>20%), regardless of the size of the microcapsules, the measured fracture toughness peaks reach an equivalent plateau [14]. In another study [20], it was reported that a high concentration of microcapsules increased the viscosity of the epoxy composite substantially during manufacture; however no specific data was provided. Similarly, Koh et al. [21] showed that incorporation of large volume fractions of microcapsules (>25%) in paint coatings affect significantly their hardening time- extending it by almost 70%.

In terms of healing, the majority of published data report that larger volume fractions of small sized microcapsules are required for the same size of cracks to achieve same level of healing. Brown et al. [14] reported maximum healing efficiency using 180 μm microcapsules at 5% volume fraction, whereas for 50 μm microcapsules the maximum healing was reached at a concentration of 20%. Similar observations were made by other researchers [18,22–24]. However, the percentage and type of catalysts used as well as the mechanical properties of the host matrix play an important role in the observed healing efficiency [25–27].

In the field of construction materials, the concept of introducing microcapsules for self-healing is relatively new. The earliest reported studies were conducted by Pelletier and Bose [28] and Yang et al. [29] for the production of self-healing concrete, while more recently the development of microcapsules for use in bituminous materials was also reported [30]. Following from the scarcity of data in the field of polymers on the effect of microcapsules addition, one can understand that the lack of such data in the field of construction materials is more pronounced. The vast majority of articles in the field mainly deal with production methods, characterisation and survivability issues and in the best case report some preliminary healing results. Pelletier et al. [31] in their proposed system of polyurethane microcapsules, ranging from 40 μm to 800 μm, reported a reduction of 12% in compressive strength of mortars containing 2% of microcapsules. In terms of toughness, they report negligible change while the observed healing, by means of load recovery, reached 24% compared to 12% of the control samples. Gilford et al. [32] reported that urea-formaldehyde microcapsules, with diameters in the range of 400 μm, at a volume fraction of 5% do not alter the modulus of elasticity. However, when the microcapsule concentration reduced to 2.5% and 1% inexplicably the modulus of elasticity dropped by 21% and 27% respectively. On another study using double-walled polyurethane/urea-formaldehyde (PU/UF) microcapsules, encapsulating sodium silicate, it was found that 2.5% addition of microcapsules increased the modulus of elasticity by ~14% [33]. In the same study when microcapsule concentration was doubled the modulus of elasticity dropped by ~5%, compared to the control samples. The modulus in this instance was measured using ultrasonic p-wave velocity. Mostavi et al. [33] also reported maximum healing efficiency, by means of crack depth measurements, 24% and 35% for microcapsules concentration of 2.5% and 5% respectively. The original crack depths in this study varied from ~78 mm for specimens with 2.5% microcapsules to ~88 mm and ~90 mm for samples with no microcapsules and 5% microcapsules respectively.

Wang et al. [34] examined the effect of UF microcapsules, added up to 9% by cement weight, on the mechanical properties of mortars. Their findings suggest that there was no significant change in compressive and flexural strength up to 6% addition of microcapsules. However, at 9%, a reduction of 35% and 25% was observed for compressive and flexural strength respectively. In terms of healing efficiency, the epoxy-carrying microcapsules exhibit their best performance at 9% reaching almost 100%. Healing efficiency in this case was measured in terms of load recovery as well as reduction in chloride permeability. J.Y. Wang et al. [35] embedded in mortar different percentages, up to 5%, of melamine formaldehyde microcapsules containing bacteria. The reported results show a significant reduction on both tensile and compressive strengths for the first 28 days. The reduction for both properties was gradual with increasing percentage of microcapsules and reached 25% and 34% for tensile and compressive strength respectively. J.Y. Wang et al. [35] also reported that after three months of curing the observed difference on the tensile strength was not statistically significant, whereas the difference on the compressive strength was increased further to 47%. In this work, the effect of the addition of microcapsules on the produced heat of hydration was also investigated. The results showed that the cumulative heat production was very similar when comparing the control mix with mixes containing 3% and 5% of microcapsules.

From the above discussion it is obvious that only a very limited number of studies have dealt with the effect of different