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Characterisation of cement pastes with innovative self-healing system based in epoxy-amine adhesive

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ABSTRACT

Two innovative additions are considered for the development of self-healing concrete: epoxy-containing silica microcapsules and amine-functionalized nanosilica. The effect of two concentrations of the additions on the microstructure of a cement paste with silica fume is studied. The results indicate a proper dispersion of the additions within the matrix, a pozzolanic reaction induced by nanosilica and the stability of the microcapsules that reliably isolate the epoxy from the paste. As the concentration of additions increases, a preferential orientation of the portlandite phase is observed, together with a decrease of the compressive strength due to the presence of a minor content of macropores and to the low strength of the capsules. The self-healing efficiency is confirmed in concrete specimens for 150 μm wide cracks and a particular concentration of the additions. These results will be essential for the subsequent development of a reliable self-healing concrete based in the epoxy-amine adhesive.

1. Introduction

The revolutionary paper by White and co-workers published in 2001 [1], presented the development of a structural polymeric material with the ability to autonomously heal cracks in its structure. Since that time, a wide variety of self-healing materials and mechanisms have been studied. In the field of construction materials, self-healing may be accomplished by components already present in the cementitious matrices (autogenous approach) or caused by engineered additions specific for this action (autonomous approach) [2]. The final objective in both cases is to prevent the development of cracks at the macroscopic scale, thus improving the long-term durability and mitigating the ageing effects on the materials. This translates into an increase of their service-life and a reduction of the costs associated to maintenance and repair [3–6].

Within this context, our group is developing an innovative cementitious material in which the self-healing mechanism is based in the combined action of two additions. On the one hand, silica microcapsules containing an epoxy compound are added to the paste and get bound to the matrix as it hardens. On the other hand, amine functionalised silica nanoparticles are added in order to react with the clinker during the hydration process to give rise to an amine functionalised cementitious matrix. Upon breakage of the capsules' shell due to the appearance of damage in the material at the micro-scale, the epoxy would spread and come into contact with the amine groups that act as the curing agent to seal the micro-cracks. The healing mechanism, based in the chemical reaction between the epoxy and the amine groups bonded to the silicate chains of the matrix, is depicted in Fig. 1.

The development of such a smart material has to be addressed stepwise, considering the following main issues:

i. The proper dispersion of the additions within the cementitious material and their chemical compatibility with the matrix.
ii. The stability of the microcapsules upon mixing and hydration processes that is important to assure the stability of the polymer and its availability when crack appears.
iii. The influence of the healing system on the microstructure developed upon the hydration of the concrete.
iv. The definition of a proper proportion of each addition with respect to the rest of concrete components and also the relative proportion between the two addition.
v. The assessment of the self-healing capacity of the concrete.
vi. Finally, the effect of the additions on the mechanical performance and durability of the final self-healing concrete.

In order to analyse the three first questions, it is more adequate to consider cement paste specimens instead of concrete ones, as

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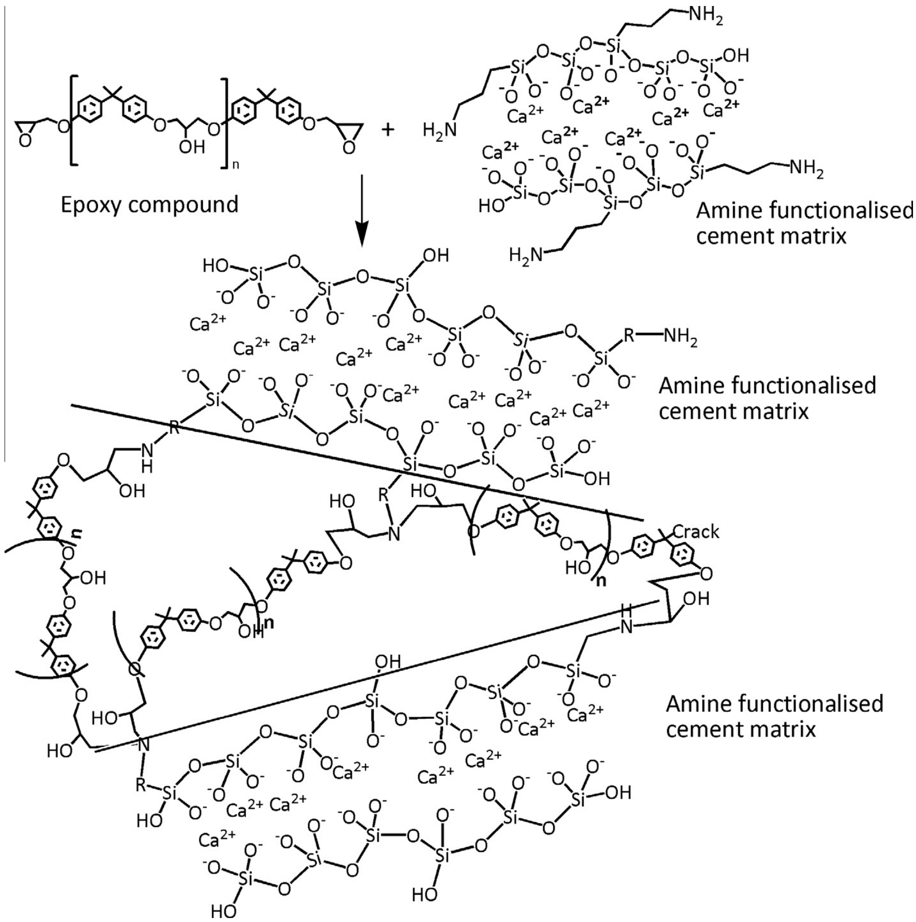

Fig. 1. Depiction of the curing reaction between the epoxy compound and the amine functionalized cement matrix.

some aspects are more easily evaluated in this simpler material. Taking this into account, this work is devoted mainly to study the effect of the additions on cement pastes and vice versa. In particular, the compatibility of the two additions previously described with an ordinary Portland cement paste and their stability during mixing and curing processes will be assessed. Furthermore, an in-depth study of the effect of two different amounts of the healing additions on the microstructural properties and on the mechanical strength development of the pastes upon hydration will be assessed. Characterisation techniques such as X-ray diffraction, thermal analysis, mercury intrusion porosimetry and scanning electron microscopy with energy dispersive X-ray microanalysis are considered for the study, as well as compressive strength tests.

Although such a previous analysis is of great interest in order to understand the subsequent behaviour of the additions in the more complex concrete matrix, this type of studies is scarcely found in the literature [7]. In fact, many works on self-healing cementitious materials have been published, as collected in several recent reviews [3–6]. However, they are mainly devoted to the description of a particular self-healing system and of its effectiveness for repairing damage in concrete.

Finally, the assessment of the self-healing capacity of the system formed by the epoxy-containing microcapsules and the amine functionalized nanosilica is essential to assure that the previous study on cement pastes will be useful for the development of an innovative self-healing concrete. Taking this into account, a preliminary test on the sealing capacity of the proposed system is performed in cracked concrete specimens through capillary absorption testing.

2. Materials and methods

Silica microcapsules containing the epoxy sealing compound (CAP) and amine-functionalised nanosilica particles (NS) were synthesized in our laboratory by a sol–gel method described elsewhere [8,9]. The microcapsules had diameters in the range 5–180 μm [8] and BET specific surface area of 343.6 m^2/g [10]. The particle size of NS is about 150 nm with a specific surface area of 36.7 m^2/g [9,10]. Silica fume (SF) is commercially available under the name of Elkem Grade 940-U undensified. Particle size is smaller than 1 μm although they are partially agglomerated into elongated particles generally smaller than 45 μm.

Cement paste prismatic specimens of $1 \times 1 \times 6\ cm^3$ were prepared. The blends considered include 24 g of distilled water, 3.2 g of superplastizicer (Structuro 351 from Fosroc) and 20 g of additions (CAP, NS and silica) per 80 g of ordinary Portland cement type CEM I 52.5 N. The exception is sample CEM constituted by 100 g of cement per 24 g of water and 3.2 g of superplastizicer. Table 1 collects the composition of the different cement pastes studied. Substitution quantities of 5% and 10% by weight of cement for the microcapsules were considered for samples CAP 5/MIX 5 and CAP 10/MIX 10, respectively. The amount of NS was calculated to keep a value of 0.75 for the CAP:NS ratio. Both CAP and NS were added in substitution to silica fume.

In the case of NS, the addition was added to the water with the superplastizicer and ultrasonicated for 5 min using an ultrasonic probe (a Bandelin Sonopuls Ultrasonic homogenizer, 20 kHz). On the contrary, SF and CAP were mixed with the cement powder and stirred for 1 min at 300 rpm before pouring on them the water