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Synthesis and characterization of epoxy encapsulating silica microcapsules and amine functionalized silica nanoparticles for development of an innovative self-healing concrete

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ABSTRACT

Silica microcapsules encapsulating an epoxy compound (CAP) and silica nanoparticles functionalized by an amine group (NS) are synthesized to be used as self-healing system for smart cementitious composites. The innovative character of this system comes from the use of silica shell microcapsules to improve the durability and compatibility with the cement and from the use of functionalized nanosilica to obtain an amine functionalized cementitious matrix. Characterization of the particles indicates that they are amorphous and possess a proper morphology and size to be considered as additions to cement. The stability of the epoxy compound inside the microcapsules and the presence of amine groups bonded to silica nanoparticles are also confirmed. Moreover, NS shows a pozzolanic activity superior to that of the silica fume used as reference, while CAP is to a high degree stable upon reaction with lime. The results confirm that the synthesized particles are a suitable starting point to address the development of a smart self-healing concrete.

1. Introduction

Cement composites are one of the most important materials in the modern world. These materials show good mechanical properties and they are relatively inexpensive, both of which make them ideal for use in large quantities. However, during the lifetime of structures, they are subjected to several actions that invariably form cracks. These cracks often lead to durability problems that undermine structural integrity, reduce their performance and result in the need of costly repair works. In order to improve the long-term durability of cement composites, material scientists have recently challenged the traditional way of designing structures —which aims to prevent damage— by developing smart materials that mimic natural living materials and their ability to adapt and respond to their environment by self-repairing. Even though a number of approaches to self-healing materials had been explored before, it was really White et al. who revolutionized this field with their 2001 Nature article *"Autonomous Healing of Polymer Composites"* [1], by using polymeric microcapsules encapsulating a curing compound as a self-healing system for an epoxy resin matrix. After publication of this article, research into self-healing spread to different materials, including cement composites [2–8]. In general three different approaches have been explored [9]: the introduction of vascular systems with curing agents mimicking human veins, the maximization of the intrinsic healing capacity of the matrix mainly by the activation of unreacted material within the matrix, and the addition of repairing component sequestered into capsules. Although some researchers are working on the use of bacteria as healing agents, polymers are still the most widely studied healing compounds for cementitious materials [4]. Polymeric systems consist almost invariably of two components and reaction only takes place when they meet. In some cases, one of the components is just water or air and the main difficulty relies on keeping them away from the polymer to prevent premature reaction. Also, and because of their reactivity with water and air, these type of polymers are more complex to encapsulate (in dry and inert environment). On the contrary, when the second

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component is another chemical compound except water or air, it must also be introduced into the matrix. Of the whole range of polymers available, epoxy resin is one of the adhesive compounds studied for self healing applications [10]. Several epoxy monomers have already been successfully encapsulated due to their good emulsivity in aqueous environments [11,12]. However, the incorporation of suitable hardeners is rather challenging [10] and for the self-healing system to work it requires that both materials (epoxy and hardener compounds) should be available nearby to meet and react when and where the microcrack occurs. In addition to the chemical compatibility with the epoxy resin, the long term and thermal stability of the shell of the microcapsules, generally made of organic compounds, are strongly influenced by the corrosive hardener [13].

Taking the above into account we are developing an innovative self-healing system for cement-based materials based on a two-component epoxy-amine curing agent but with several different characteristics from other epoxy-amine healing systems found in the literature [7,13]. On one hand, and to overcome the possible shell degradation in the long run, the epoxy compound in our system is encapsulated in silica shell microcapsules unlike in some other studies where the epoxy was encapsulated in organic microcapsules [7]. Silica is known to have high chemical resistance and good mechanical strength [14] which is also an important characteristic in order to withstand the mixing process for the preparation of cementitious materials. Furthermore, since the shell is made of silica we expect it will have good interaction with the cementitious matrix, whose major component is the calcium silicate hydrate (C–S–H gel). This is an important feature because we want the microcracks, when they form, to also break the microcapsules instead of going around them. Yang et al. [5] have also used silica shell to encapsulate both parts of the curing system, which in their case was the monomer methylmethacrylate with triethylborane as a catalyst. They indicated that a strong bonding was expected between the silica microcapsules and the cement matrix because the silica of the shell could participate in pozzolanic reactions with the portlandite of the cement matrix.

On the other hand, in our self-healing system, we have also brought in another innovative and, to the best of our knowledge, unique approach, which is the way the second component is introduced into the matrix. The amine group, which is necessary to harden the epoxy resin, is not introduced encapsulated to maintain it isolated from the matrix [7] but is intended to become part of it. To do so, we have developed amine functionalized silica nanoparticles that are added to the cementitious material during the mixing process. Thanks to the expected large reactivity of the nanoparticles, they would induce a pozzolanic reaction that would result in the production of an amine functionalized cementitious matrix. Once a propagating crack breaks the microcapsules, the epoxy compound would be liberated and meet the amine functional groups that are tethered in the silicate chains of the matrix. The two components of the adhesive would then react and the hardened epoxy would end up permanently attached to the matrix, thus sealing the crack.

In this article the synthesis process of both types of particles, together with their characterization, will be described. Furthermore, and as a first step toward developing a self-healing smart concrete, their pozzolanic activity will be assessed. As aforementioned, this property is critical because the whole self-healing system relies on the reaction of the additions with the matrix. The results for silica fume (SF) will also be presented for comparative reasons, as this is a pozzolanic addition commonly used by the cement industry [15].

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS, 98% (GC)), 3-aminopropyltriethoxysilane and ammonium hydroxide (ACT Reagent, 28–30%) were purchased from Sigma–Aldrich. Ethanol (EtOH, 96% v/v PA) and hydrochloric acid (37% chemically pure) were from Panreac and EPOTHIN® was bought from Buehler. Solutions of ammonium hydroxide 0.1 M and hydrochloric acid 1 M were prepared for the reaction from the concentrated solutions. Distilled water was used in all cases. Silica fume used as reference material was ELKEM 940U.

2.2. Synthesis of silica microcapsules encapsulating Epothin®

The microencapsulation of the material Epothin® has been based on the procedure used by Ahn et al. [16]. A sol–gel reaction followed by an oil-in-water emulsion has been used for the synthesis. In a first step a precursor is obtained by hydrolysing 11.2 mL (0.05 mol) of TEOS with water in acidic conditions (pH~2) during 5 h in a reflux at 40 °C. The molar ratio of the reactants used in this first step is 1:4:1:3 × 10^{-3} of TEOS:EtOH:H_2O:HCl. In the next step, 3 mL of Epothin® is added to the precursor, followed by 25 mL of water and a mechanical stirrer is used at 600 rpm to form an emulsion. Ammonium hydroxide solution 0.1 M is added to the emulsion drop wise until the pH is around 10. After the addition of NH_4OH a white solid can be seen in the reaction mixture. The suspension of microcapsules is left aging for an hour and the solid is collected by centrifuge. This solid is washed 3 times with water and collected every time by centrifuge and finally dried at room temperature. The yield of microcapsules with Epothin® is around 2 g (1.90 g–2.30 g).

2.3. Synthesis of propylamine functionalized silica nanoparticles

The route of synthesis is based on the Stöber method [17] and in this case the tetraethoxysilane is reacted with 3-aminopropyltriethoxysilane in a one pot reaction to obtain the amine functionalization [18]. Ethanol (4 L), water (83.3 mL), tetraethoxysilane (121 mL, 0.542 mol) and 3-aminopropyltriethoxysilane (13.2 mL, 0.0566 mol) are added to a round bottom flask. To this, concentrated ammonium hydroxide (39 mL) is added and the reaction is left stirring for three days. After these three days, a white colloidal dispersion is obtained. The solid is separated from the solvent by centrifuge and decanting. The solid is washed three times with ethanol to remove any reactants and centrifuged and decanted to collect it. The white solid obtained is air dried. The yield of the nanoparticles is around 40 g (35 g-41 g).

2.4. Characterization of synthesized materials

Morphology and elemental composition were studied with a Hitachi S-4800 scanning electron microscope (SEM-EDX) and a FEI Quanta 200 environmental scanning electron microscope that has an energy dispersive X-ray microanalysis (EDX). In the first case, samples were previously coated with a carbon layer to avoid surface charging. In some cases, the results were complemented with dynamic light scattering measurements carried out in a Malvern Zetasizer in order to quantify particle size distribution.

Solid-state ^{29}Si and ^{13}C NMR experiments for the aminopropyl silica nanoparticles were performed on a 400 MHz Bruker Advance III, while the solid-state ^{29}Si NMR characterization of the silica microcapsules was carried out on a 300 MHz Bruker Advance DSX300 NMR spectrometer. Infrared transmission spectra (FTIR) of the samples under study were measured in a Nicolet 6700