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Self-healing features in cementitious material with urea–formaldehyde/epoxy microcapsules

Biqin Dong, Guohao Fang, Weijian Ding, Yuqing Liu, Jianchao Zhang, Ningxu Han, Feng Xing *

School of Civil Engineering, Guangdong Province Key Laboratory of Durability for Marine Civil Engineering, The Key Laboratory on Durability of Civil Engineering in Shenzhen, Shenzhen University, Shenzhen 518060, PR China

HIGHLIGHTS

- A microcapsule designed for mechanics/permeability self-healing in concrete.
- Crack in concrete is filled by healing agent releasing from the microcapsules.
- Influence on the healing effect of mechanical properties/permeability is analyzed.

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ABSTRACT

Urea–formaldehyde/Epoxy microcapsule is designed and prepared for the crack recovery of cementitious materials, using epoxy resin E-51 as a healing agent. The obtained microcapsules have an excellent surface texture (such as the roughness), suitable size and remarkable thermal stability. The viability of microcapsule during mixing process is investigated first. The breakage of microcapsules upon cracking and the crack-healing results are verified by SEM/EDS. Self-healing capacity is evaluated by crack-healing effect and mechanical property as well as chloride permeability. The experimental results reveal that the crack-healing ratios are in the range of 20.71–45.59%, indicating that the system actually work on the crack-healing. In addition, the healing ratio of compressive strength and impermeability is about 13% and 19.8%, respectively.

1. Introduction

Cementitious materials are the mostly used construction material world-widely in civil engineering [1]. However, micro-cracks can be initiated in this type of brittle material due to inappropriate curing, freeze–thawing, temperature gradients, mechanical loading and so on. This will negatively impact the durability of the structures [2–4]. Thus, controlling and healing cracks are important issues as far as the application of cementitious materials is concerned. Up to now, several methods are developed for crack controlling and healing [5–7]. Incorporating Alkali resistant (AR)-glass fibers into cementitious materials can control the early-age emerged cracks due to shrinkage [8]. On the other hand, some new binder materials are applied to reduce the initial cracks and to form a very dense, low-porosity microstructure [9–11]. This sort of performance enhancement has a positive effect on the initial crack-restraining, but do not prevent the lately emerged cracks caused by freeze–thawing, temperature gradients and mechanical loading, etc.

A new repair system called self-healing cementitious material has been proposed for solving of the long-term cracking problem [12–16]. However, for practical application, the self-healing cementitious material needs to be less costly, passively smart and easily to be distributed uniformly. The development of a smart concrete is then governed by engineering feasibility, performance level and economical usage of material from the application point of view. Therefore, one of the important efforts is to fabricate self-healing cementitious material by adding microcapsules. Firstly, the healing agent is sealed by microcapsules. Researches related to the microcapsule synthesis technologies have been carried out and some results have been already obtained [17,18]. To obtain better healing results, the mix proportion of microcapsules and concrete matrix is very important. In addition, the geometry and texture of microcapsules are also critical towards healing efficiency and it is found that spherical microcapsules can reasonably fulfill this in cement-based material [13,15]. As a crack initiates and propagates, the embedded microcapsule at the crack tip will be broken.

* Corresponding author.
E-mail address: xingf@szu.edu.cn (F. Xing).

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The healing agent inside the microcapsule is then released by capillary action to achieve the healing effect. The above described concept of self-healing cementitious material has been proved to be feasible by several researchers. A successful novel attempt has been made by the authors [19–21], with promising results using organic microcapsules in cementitious material. The preliminary study suggested that the encapsulation is a promising approach for self-healing. However, there still two main problems in microcapsules based self-healing system needed to be conquer. The problems are: (1) the quality of healing agent filled in the microcapsules is limited to a very small amount; (2) the bond strength between the microcapsules and the cementitious matrix needed to be stronger than the strength of the microcapsules [22]. As for employing of urea formaldehyde or epoxy composite as healing agent, enough though several researches have been carried on this attempt the comprehensive investigation of its healing feature in cementitious materials has not achieved yet [23,24].

In order to study self-healing cementitious materials with urea–formaldehyde/epoxy microcapsule, the curing mechanism based this healing agent is investigated first [25]. As shown in Fig. 1, the theoretical background of curing reaction mechanism is clearly identified. The chemical reaction mechanism of healing system consisting of epoxy resin E-51, BGE(butyl glycidyl ether) and harden agent (MC 120D) is occurs by a step-growth process. In the first step, tertiary amines attacks the epoxy functional group to generate the adduct. In the second step, the newly generated adduct attacks another epoxy group to produce the clathrate consisting of positive and negative ions. In the last step, the anion in clathrate is used as active center to catalyze the copolycondensation of epoxy group in order to create terpolymer. This terpolymer made up of epoxy resin, thinner and imidazole has strong connective property. Based on this mechanism, therefore, epoxy resin E-51 is chose as core materials of microcapsules (healing agent) , BGE as thinner agent and MC120D as harden agent which are premixed in cement pastes. Theoretically, once the microcapsules are triggered upon cracking, the healing agent (epoxy resin E-51) inside the microcapsule is released and reacts with the curing agent (BGE and MC120D) to form healing products and fill the cracks. In addition, in order to conquer the key problems in microcapsules based system (small size of microcapsule and the weak bond strength between microcapsule and cementitious material), the synthetic technique is improved to design suitable microcapsule for this system. What more, the self-healing feature of urea–formaldehyde/epoxy microcapsules based cementitious materials are comprehensively studied in the research.

In this paper, the further development of urea–formaldehyde/epoxy microcapsule based self-healing cementitious material is presented. Microcapsules made of an epoxy resin E-51/urea–formaldehyde resin are in-situ polymerized and characterized. The viability of microcapsule during mixing process is investigated. The breakage of microcapsules upon cracking and the crack-healing results are verified by SEM/EDS. The crack-healing process is monitored by means of Mercury Intrusion Porosimetry (MIP) test. The crack-healing effect against chloride penetration is measured with different crack width. Compressive strength test is applied to investigate the healing effect of mechanical property. Permeability is evaluated with the help of Rapid Chloride Migration (RCM) test.

2. Experiments

2.1. Microcapsule fabrication

Microcapsules are produced using UF (urea–formaldehyde)/ep oxy resin at a urea/formaldehyde molar ratio of 1:1.5 by means of in-situ polymerization procedure. Briefly, a mixture of urea and 37% formaldehyde is adjusted to pH 8.0–9.0 with 78% triethanolamine aqueous solution. The UF prepolymer is prepared by stirring at 70 °C until the mixture became transparent. The temperature is then reduced to 40 °C. Simultaneously, the oil/water emulsion is prepared by adding a mixture of 0.5% SDBS (sodium dodecyl benzene sulfonate) aqueous solution and epoxy resin – BGE mixture (epoxy resin/BGE = 100/17.5). This oil/water emulsion is added to the UF prepolymer. The reaction liquid is adjusted to pH 2.0–3.0 with 2% sulfuric acid solution. The resulting mixture is stirred at 60 °C for two hours, then cooled to room temperature. After filter and air-dry for 24 h, the resultant microcapsules are washed with pure water and dried in a vacuum oven. In order to study microcapsules with different sizes four types of griddles (sieve diameter = 100 μm; 150 μm; 200 μm and 250 μm.) are applied to sieve microcapsules with three interval (Group A: 100–150 μm; Group B: 150–200 μm; Group C: 200–250 μm). The particle size distribution is shown in Fig. 2. The mean diameter of three type microcapsules are 132, 180 and 230 μm, respectively.

2.2. Specimens preparation and pre-processing

The chemical composition of the cement is given in Table 1. The physical and mechanical properties of cement specimens are listed in Table 2. Three different groups of mortar matrix are made and

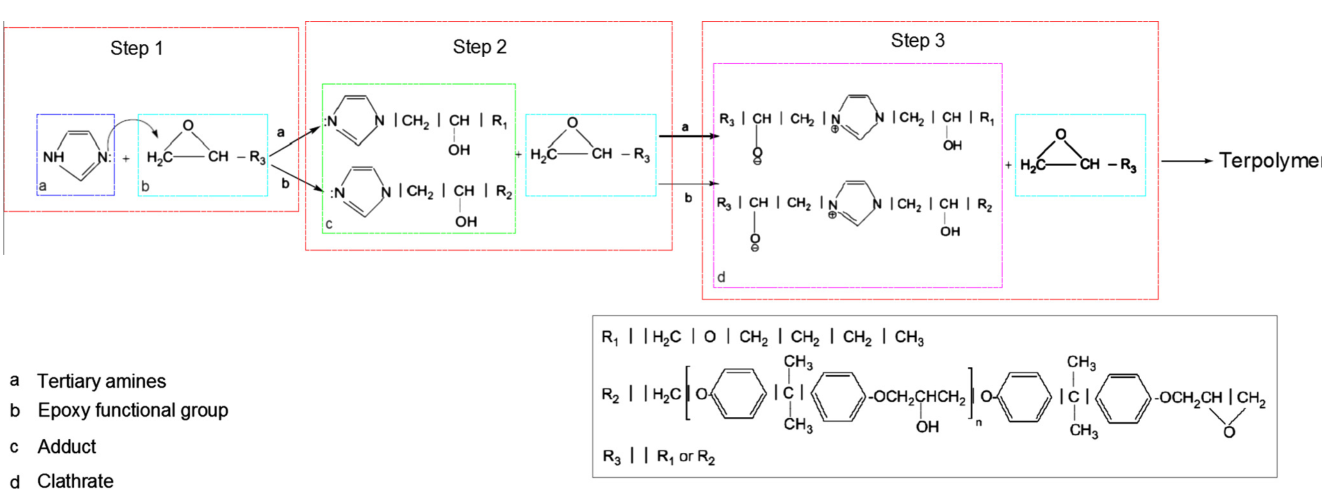

Fig. 1. Chemical reaction mechanism of self-healing system.