

# Synthesis and characterization of novel mechanical triggered phenol-formaldehyde microcapsules containing a rejuvenator for self-healing cement-based materials

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## ABSTRACT

In this paper, a novel type of microcapsules was synthesized by in situ polymerization with phenol-formaldehyde (PF) as a shell and dicyclopentadiene (DCPD) as a healing agent. The microencapsulating process of the microcapsules was examined using optical microscopy (OM). The morphology were investigated using scanning electron microscopy (SEM). The breakage test demonstrates that the microcapsules containing the rejuvenator can be triggered when a crack passes through the capsules.

## 1. INTRODUCTION

Cement-based materials is one of the most commonly used materials in the area of civil engineering. During the process of cement hydration, setting and solidification, some micro-cracks emerged. These micro-cracks will further develop into macro-cracks because of the stress overload, fatigue, and freeze-thaw and dry-wet cycles[1], which can pose a potential safety hazard for the performance and service life of cement-based material [2]. To compensate for the decrease in mechanical properties and increased permeability, the concept of self-healing technology has been proposed for cement-based materials by incorporating healing agents according to the concept of bio-mimetic theory.

Dry [3-6] was the first group using glass tube containing healing agent to repair cement cracks. After that, many new healing agents have been inspired and demonstrated over the past ten years [7-10]; while microcapsules, serving as the most promising healing agent, have some intrinsic advantages compared with other repair mechanisms. In this study, we present a new type of microcapsule using PF resin as the wall material. The formation process and morphologies were observed by optical microscopy (OM) and scanning electronic microscopy (SEM). The simulation of microcapsules breaking processes were operated under glass plate and cement matrix were monitored.

## 2. MATERIALS AND METHODS

Dicyclopentadiene (DCPD) was purchased from Shanghai Aladdin Co. (China). Phenol, formaldehyde (37%) and the emulsifier, sodium polyacrylate (PAA-Na), were obtained from Tianjin Damao Co. (China). The pH regulators, sodium hydroxide and citric acid, were provided by Tianjin Forever Chemical Reagent Co. (China). Portland cement was a commercial product supplied by Anhui Conch Cement Co. (China).

The DCPD/PF microcapsules were prepared using the following three steps: (1) Phenol, formaldehyde and deionized water were mixed in a three-necked flask, a solution of NaOH was added to adjust the pH value to 9 at 90°C for 90min (2) 10 g DCPD was added to 100 g surfactant aqueous solution containing PAA-Na at 65°C and stirred at 1,000 rpm for 20 min to separate the DCPD from the water. (3) Sodium hydrate solution was added to the flask to adjust the pH value to approximately 1. The system temperature was then increased to 80°C and maintained for 200 min. Once the reaction was completed, the products were filtered using a sieve and washed with deionized water. Then, the fully covered MF microcapsules were obtained.

After that, 8 wt.% of DCPD/PF microcapsules was added to a cement paste (water/cement ratio = 0.4) and poured into a  $\phi 10$  mm $\times$ H30 mm cylindrical mould. After being cured for 28 days, the mortar specimens were obtained.

## 3. RESULTS AND DISCUSSION

The formation process of the microcapsule was examined by optical microscopy. Fig. 1 shows the optical morphologies of the formation process of microcapsules after 1.5, 2, 3 and 4 h. The core material was already been enwrapped at 1.5 h, whereas the shell was still soft and the microcapsules were stuck together at that time (Fig. 1a). With increasing reaction time, at 2 h, the thickness of the shell increases continuously, and the dispersion of microcapsules is increased (Fig. 1b). When the reaction progressed for 3 h, a separated micro-ball was completely formed with a compact wall and global shape. As the condensation continued to progress, the thickness and strength of the shell of microcapsules increased further (Fig 1d)

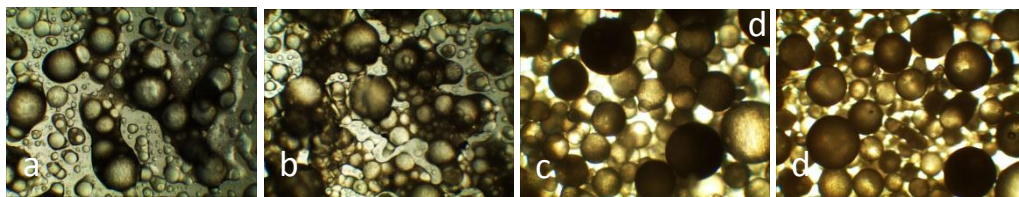


Fig. 1 Morphologies of microcapsules prepared after different reaction times: (a) 1.5 h, (b) 2 h, (c) 3 h, and (d) 4 h

Fig.2 shows the morphology of the DCPD/PF microcapsules prepared under an optimized reaction condition. As shown in Fig. 2a, the microcapsule has a regular globe shape with smooth and flawless surfaces; these properties are beneficial for the microcapsules to sense the isotropic mechanical trigger in concrete from all directions. Fig. 2b shows that the microcapsule has a typical egg-like structure, the shell of the microcapsules is homogeneous and brittle. In Fig. 2c, the microcapsules are fully covered by PF resin without agglomeration. The diameter is approximately 300 $\mu$ m. Once the microcapsules are pressed to rupture by compressive force, the

microcapsules will crack, and healing agent will flow out immediately. The thickness of the shell is approximately 25  $\mu\text{m}$  (Fig. 2d).

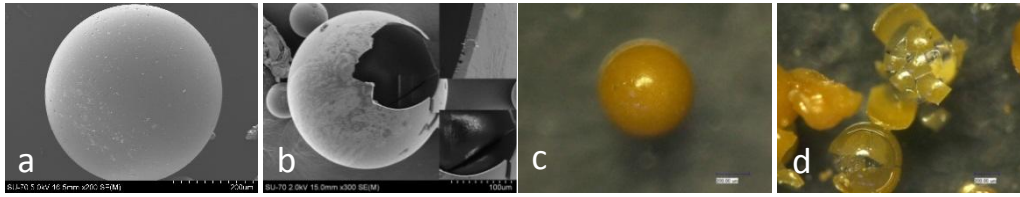


Fig.2 SEM and optical microscopic images of (a) the typical surface morphology of the microcapsule, (b) the ruptured microcapsule with its wall thickness, (c) a single microcapsule, and (d) microcapsules compressed between glass sheets.

Fig. 3(a) shows microcapsules containing the healing agent which was crushed by two parallel glass sheets. It can be seen that the shell of the microcapsule is uniform and brittle with a thickness of approximately 34.65 $\mu\text{m}$ , and the healing agent (DCPD) was completely stored in the wall materials. Fig. 3(b) shows the optical morphologies of the microcapsule triggered by a crack crossing the section in the cement matrix. The microcapsule was ruptured when the crack passed through the matrix, which indicates that PF microcapsules are sensitive to the mechanical trigger produced by the crack. The binding strength between the PF shell and cement matrix is sufficiently strong to ensure that the crack will not pass around the capsule.

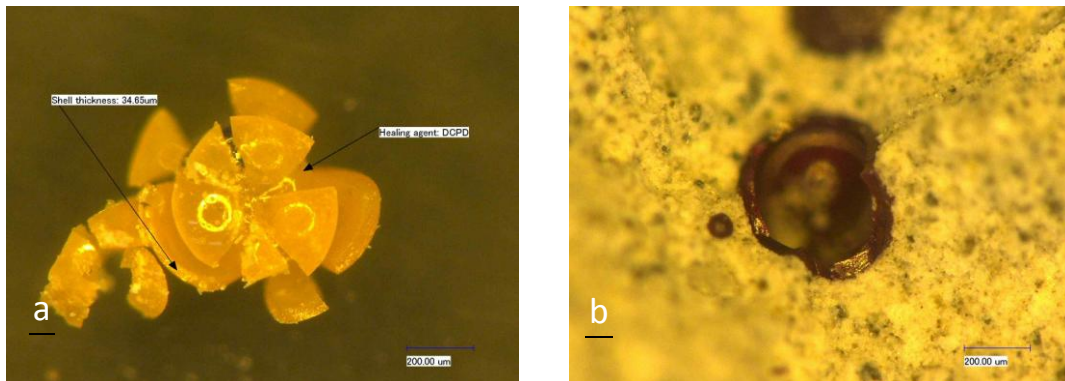


Fig. 3 OM photographs of the microcapsules triggered by mechanical force: (a) microcapsules crushed by compressive stress and (b) microcapsules in cement triggered by the crack

#### 4.CONCLUSION

A novel type of microcapsule containing a healing agent for self-healing cement-based materials was successfully synthesized using in situ polymerization. Phenol-formaldehyde resin was applied as a shell to protect the microcapsules from being affected by the process of hydration and poor conditions upon further application. Further testing demonstrated that the microcapsules we synthesised can survive in the extreme condition of cement hydration and when a crack passes through the capsules, the capsules are sensitive to the mechanical trigger and could be ruptured by the tensile force generated by the crack.

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