Design and preparation of chloridion- triggered microcapsule for chemical self-healing application

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ABSTRACT

Ion- sensitive microcapsule has attracted much attention of the researchers in biologic and medicinal fields, but most of them are triggered by pH value. In this paper, a chloridion-responsive microcapsule was designed and synthesized for the application of chemical self-healing materials, such as the seawater-corrosion resistant concrete.

The microcapsule is shelled by polymethylmethacrylate (PMMA), in which small particles of lead sulfate ($PbSO_4$) are embedded as chloridion switches. It is stable in freshwater but not in seawater. When chloridion appears in water, the $PbSO_4$ precipitant will dissolve because of the following complexing reaction:

$$PbSO_4\downarrow + 4Cl^- \rightarrow PbCl_4^{2-}(s) + SO_4^{2-}(s)$$

Distinctly, the response time rests with Cl^- concentration. In 3.5% NaCl artificial sea water, it's about 5 hours.

1. INTRODUCTION

In concrete, chloridion is the main factor causing the corrosion of rebar. It's expected there is a chloridion-sensltive microcapsule containing chloridion absorbent, corrosion inhibitor, or repairing additives embeded beforehand in concrete. If so, the microcapsule will release its contents spontaneously to retard the permeation or to block the diffusion path of chloridions once they make an incursion. Hence, durability of the concrete works built in high salinity area will be improved greatly.

To prepare a chloridion-triggered microcapsule used in concrete, the microcapsule's shell should be waterproof as it must withstand a long cement hydration period, so it's better to be made up of hydrophobic polymer and indissoluble veneers of inorganic salt. If the metallic cation of the salt is able to coordinate with chloridion to form a soluble complex ion, the inorganic salt veneers will be vanished. After water penetrates from the left hole, collapse of microcapsule will be aroused by swelling of core materials. Lead sulfate is one of the few inorganic salts.

2. MATERIALS AND METHODS

2.1 Materials

$Pb(NO_3)_2$, Na_2SO_4, NaCl, dichloromethane(DCM), cetane are analytical reagents from Tianjin chemical reagent factory, Tianjin, P.R. China. Polymethyl methacrylate (PMMA) (MW≈100,000g/mol) is tachnical pure polymer received from Aladdin reagent Co., Shanghai, P.R. China.

2.2 Preparation of microcapsules

$PbSO_4$ embeded PMMA walled microcapsule with hexadecane core was prepared by solvent evaporation approache: mixed hexadecane, PMMA, fine $PbSO_4$ powders in DCM to obtained a suspensoid, then add PVA aqueous solution as surfactant, stirred for emulsification, heating-up to 40°C, removing DCM from the emulsion by evaporation. The optimal condition is: core/shell ratio (mass): 1.5:1; stirring rate: 400rpm; PVA concentration: 5wt%; evaporation temperature: 40°C; evaporation time: 2.0~3.0h.

2.3 Characterization of the microcapsules

The morphology of microcapsules was observed under Hitachi SU-20 SEM, by which the particle diameters and shell thickness were also measured. The thermal stability and thermolysis temperature were determined by TA DSC Q200/TGA Q50 thermal analyser. The chemical composition of microcapsules was confirmed by Nicolet 6700 FTIR Spectrometer in the wave number range from 400 to 4000cm^{-1}.

3. RESULTS AND DISCUSSION

3.1 The effect of Emulsifier concentration

Concentration of PVA plays an important role in the formation of microcapsule. Low-concentration results in nonuniform dispersion of $PbSO_4$ powders, in other hand, high-concentration leads to conglomeration of microcapsule. When the concentration is moderate, as 5% in Fig. 1, the result microcapsules present very good sphere shape, narrow particle size distribution and uniform $PbSO_4$ embedment.

Fig.1 SEM images of as-prepared microcapsules with different concentration of PVA

3.2 The effect of temperature

The boiling point of DCM is 39.8°C. If the evaporation temperature was set at a little bit above this point, the viscosity of suspension increased gradually, resulting good shape and dispersal of microcapsules. Evaporated at higher themperature, like 50°C, 60°C in Fig. 2, the rapid change of viscosity brought out agglomeration of microcapsules or gathered $PbSO_4$ powders on the shell. Obviously, the appropriate temperature is 40 °C.

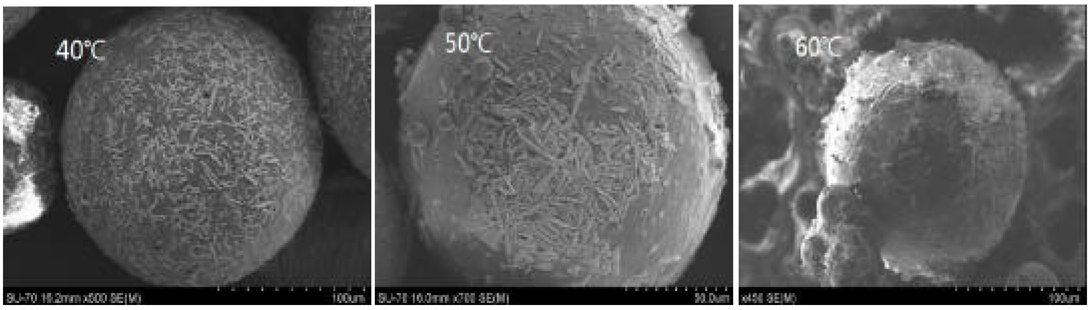

Fig.2 SEM images of microcapsules formed at different temperatures

3.3 Analysis of the microcapsules

Fig. 3 shows morphology and structure of microcapsule. It's clear, the microcapsule was provided with standard core/shell structure, and the $PbSO_4$ powders was infixed in the cross section of shell. During preparation, $PbSO_4$ powders does not change.

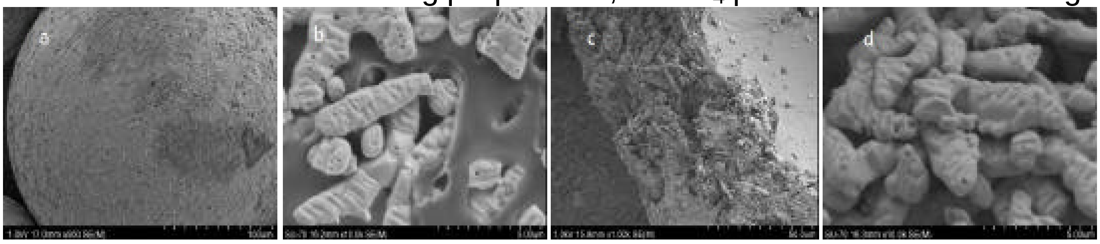

Fig. 3 SEM images of : (a)microcapsule, (b) impaction of $PbSO_4$, (c) cross-section of shell, (d) $PbSO_4$ powders.

3.4 Cl^--trigger test

Soaked in 3.5wt% NaCl solution, the shell of microcapsules start dehiscing after 5hrs. At 30th hour, all the microcapsules are cracked. XRD shows, after Cl^--trigger test, all the peaks indicating $PbSO_4$ are disappeared, only amorphous peak of PMMA is left, illustrating all the $PbSO_4$ salts are dissolved.

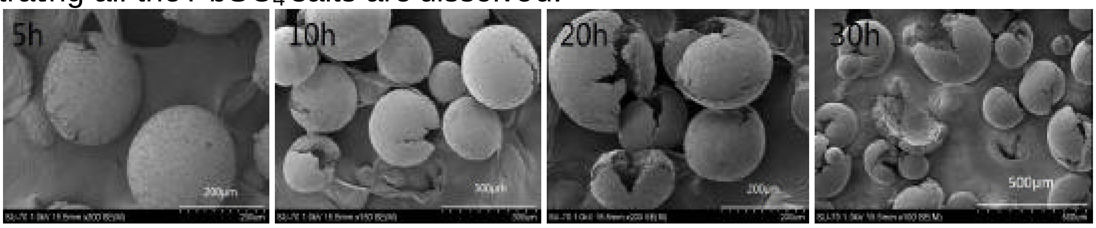

Fig.4 SEM images of microcapsules soaked in 3.5wt% NaCl solution at different time.

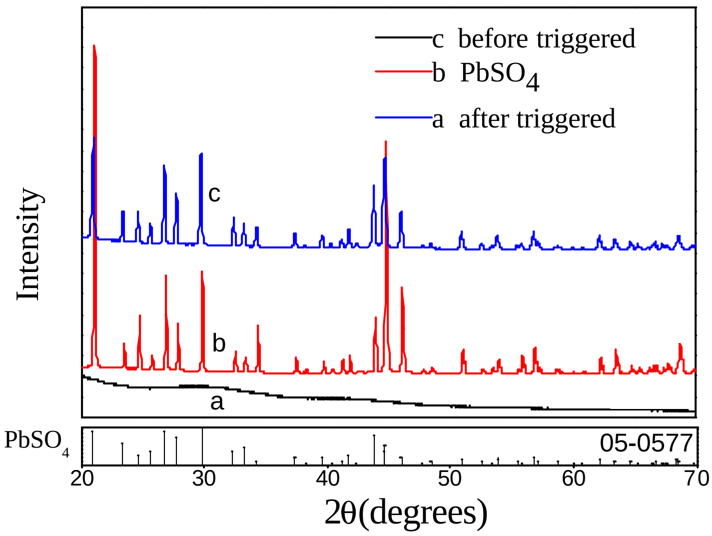

Fig.5 XRD of $PbSO_4$ powders and the shell $PbSO_4$ embedded in before and after Cl^--triggered

4. CONCLUSION

$PbSO_4$ shows good response to chloridion. $PbSO_4$-embedded PMMA shell is able to dehisce spontaneously in 3.5wt% NaCl solution after 5hours, indicating the microcapsule could be used in self-healing concrete against chloride damage. Of course, further research is needed.

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