Chloridion-triggered microcapsule for self-healing concrete application

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ABSTRACT

Sodium monofluorophosphate (Na_2PO_3F) microcapsule shelled with sodium polyacrylate (PAS)'s double-coordination with Ag^+ or/and double-chelate with Cu^{2+} was prepared by spray-drying process, and the microcapsule's respondent behavior to chloride ion in 3.5wt% NaCl artificial sea water was examined subsequently with stereomicroscope. It's found microcapsule shelled with PAS-Ag is very susceptible to hydrosoluble chloride ion, however microcapsule shelled with PAS-Cu has no response, but it possesses hard and brittle shell. The shell consist of the mixture of PAS coordination with Ag^+ or or chelate with Cu^{2+} is compromised in the performance of Cl^- response and mechanics. The shell strength increases with the incremental Cu^{2+}/Ag^+ ratio in central ions, while the sensitivity to chloride ion on the contrary. When Cu^{2+}/Ag^+ is over 1/2, the microcapsule has no answer to chloride ion. It's firmly believed that microcapsule shelled with PAS- ($Ag^+ + Cu^{2+}$) complex could be used in self-healing concrete to spontaneously protect rebar aganst chloride attack.

1. INTRODUCTION

Concrete is the construction material most widely used with the largest amount in the word. About this material, the most concerned problem is deterioration, which is important because of involveing buildings' durability and lifetime. Deterioration is mainly caused by the corrosion of rebar embedded in concrete, and the corrosion are aroused by the permeation of chloridions and carbonate ions. So chloride damage and carbonation are the major problem for a civil engineering. To solve this issue, Cl^--sensitive microcapsules containing corrosion inhibitor was designed and prepared in this article as a demonstration. It's believed, embedment with these microcapsules will endue concrete with anti-corrosion ability, hence improve the construction's service life and reliability.

2. MATERIALS AND METHODS

2.1 Materials

Sodium polyacrylate (PAS) and microcrystalline cellulose (MCC) are tachnical pure materials provided by xumei chemical Co. Ltd., Hnagzhou, Zhejiang, China, and Heshan medicinal materials Limited by Share Ltd, Anhui, China, respectively. $AgNO_3$, NaCl and $Cu(NO_3)_2$ are analytical reagents purchased from Damao Chemical Plant, Tianjin, China. Sodium monofluorophosphate(Na_2PO_3F, AR) is a product of Fenghua Chemical Materials Development Co.,Ltd., Hunan, China.

2.2 Granulation of core materials

Microcrystalline cellulose (MCC) and sodium monofluorophosphate(Na_2PO_3F) mixed in mass ratio of 2:3, then add 3wt% ethanol and 1wt% tween-80 of total mass, remixed, add some water to adjust the dough's viscosity, pelletized into microballoon sphere with diameter of 600~700μm as core.

2.3 Cl^--trigger test of the shell materials

Drop 2% PAS solution into a salt bath by a 1ml syringe, stirred at 200rpm for 10mins. The result microcballoons were washed by deionized water, then filtered, dried under 40°C for 30min. In bath, the salt's concentration was set at 0.5mol/L, but the salt's component was $AgNO_3$, $Cu(NO_3)_2$, or the mixture of them with $Cu(NO_3)_2$/ $AgNO_3$ mass ratio (denoted by Cu/Ag) of 1/4,1/2,3/4 or1/1.

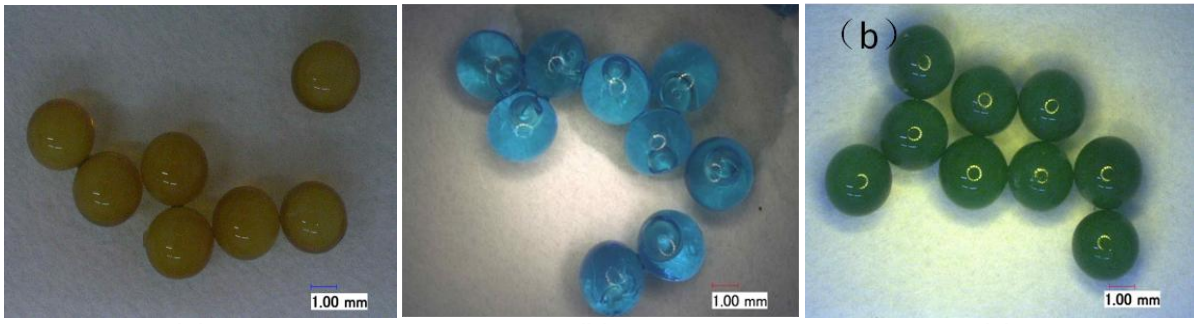
2.4 Preparationof microcapsules

Weighing 15g sodium polyacrylate (PAS) per 100g core powders, dissolved into water to become 3wt% solution, mixed with core powders for suspension, then sprayed drying. The PAS-shelled powders were soaked in the salt bath for 10mins, a PAS-(Ag or/and Cu) shelled Na_2PO_3F microcapsule was obtained.

3. RESULTS AND DISCUSSION

3.1 Cl^--response of PAS complex shelles

Fig.1 shows the solid microballoon of the shell materials. It's clear that, PAS-Ag is soft yellow ball, PAS-Cu is a very hard blue ball, and the mixed complex PAS-Cu/Ag balls are in betweenness, colored secondary green, varying from light to dark with increased Cu/Ag ratio from 1/4 to 1/1.



(a) (b) (c)

Fig.1 stereomicroscope images of microballoon: (a) PAS-Ag, (b) PAS-Cu, (c)PAS-Cu/Ag(1/2)

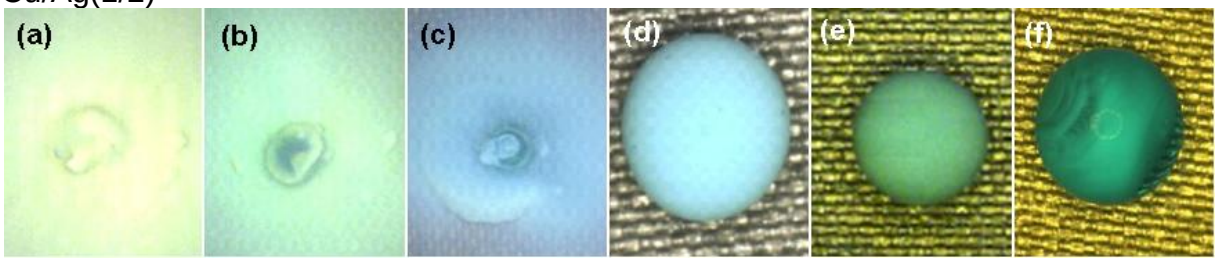


Fig.2 morphologies of PAS-Cu/Ag microballoons in 3.5wt% NaCl solution at different time. Cu/Ag: (a) 0/1, 3mins;(b) 1/4, 4mins, (c) 1/2, 5mins, (d) 3/4, 24hrs, (e) 1/1, 24hrs, (f) 1/0, 48hrs.

When PAS complex microballoons were soaked in NaCl solution, PAS-Cu/Ag balls of which Cu/Ag ratio is less than 1/2 responded to Cl^- very quickly, ba able to scatter in 5mins. However, that balls Cu/Ag ratio greater than 1/2 didn't disperse, even soaked for a longer time.

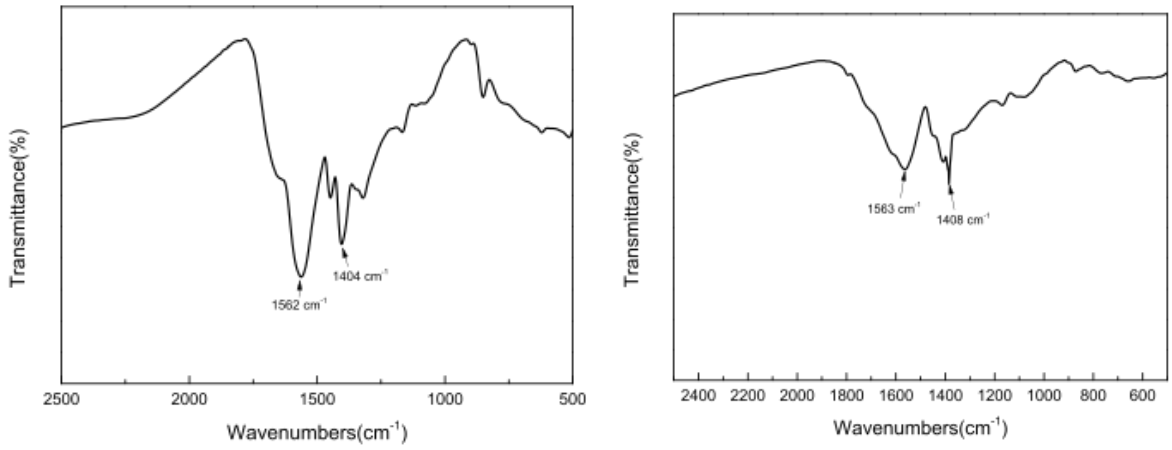


Fig.3 FTIR spectra of (a) PAS-Ag and (b) PAS-Cu

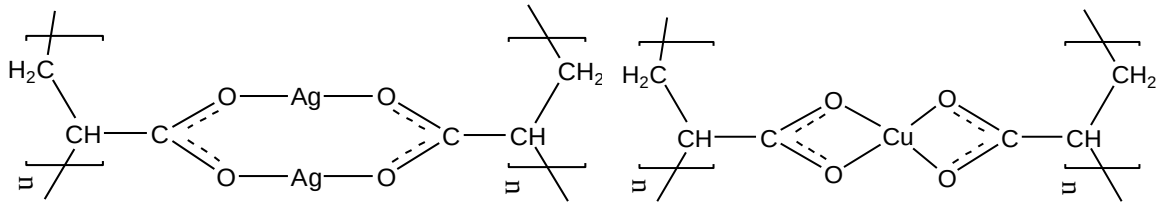


Fig.4 molecular structure of PAS-Ag and PAS-Cu

FTIR spectra reveals that COO^- group in PAS-Cu and PAS-Ag is a bidentate ligand. As shown in Fig. 3(a), the antisymmetric stretching vibration absorption peak (V_{as}) and symmetric stretching vibration peak (V_s) of COO^- are located at 1562cm^{-1} and 1404cm^{-1} respectively. Their difference ($\Delta V=V_{as}-V_s$) equals to 158cm^{-1}. In Fig. 3(b), $\Delta V=V_{as}-\Delta V_s$=1563$cm^{-1}$ –1408cm^{-1} = 155cm^{-1}. Both are less than 166 cm^{-1}, ΔV value of COO^- in sodium carboxylate, indicating COO^- is bidentate[1],. As the coordination number of Ag^+ is 2, while of Cu^{2+} is 4, the coordination mode in PAS-Ag is bidentate-bridge type, in PAS-Cu is bidentate-chelate type[1], as Fig. 4 shows. Bidentate-chelate type coordinate bond is more strong than bidentate-bridge type, so PAS-Cu ball is harder and more stable in NaCl solution than PAS-Ag.

3.2 Cl^--response of microcapsule

The microcapsules has a very uniform size narrowed in 600~700μm. After soaked in NaCl solution, the microcapsules shelled by PAS-Ag and PAS-Cu/Ag(1/2) can release contents very quickly. The reponse time is 3mins and 5mins respectively.

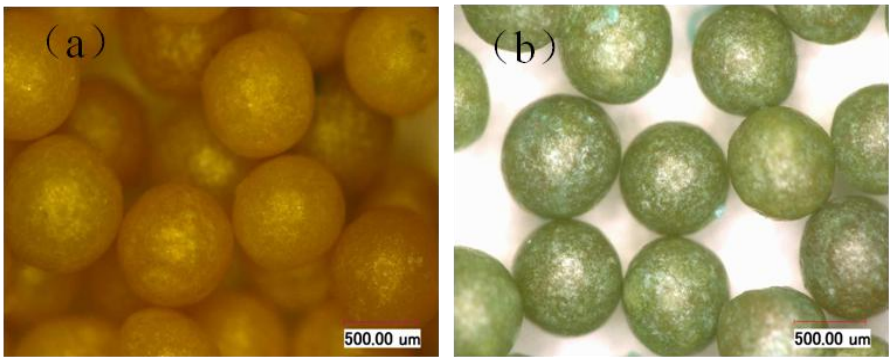


Fig.5 stereomicroscope images of microcapsules shelled with: (a)PAS-Ag，(b) PAS-Cu/Ag(1/2).

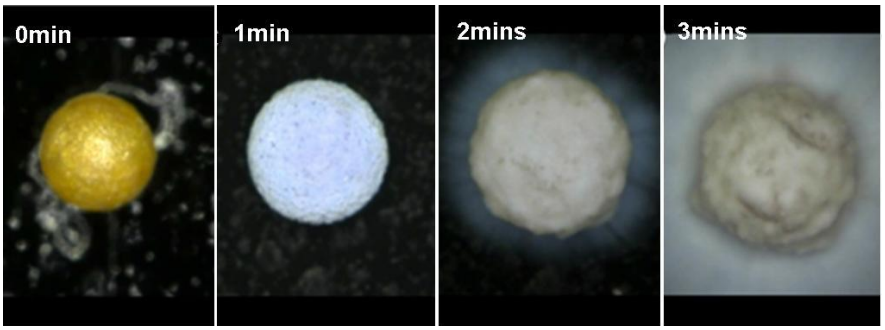


Fig.6 Trigger procedure of PAS-Ag microcapsule in 3.5% NaCl solution at 25°C.

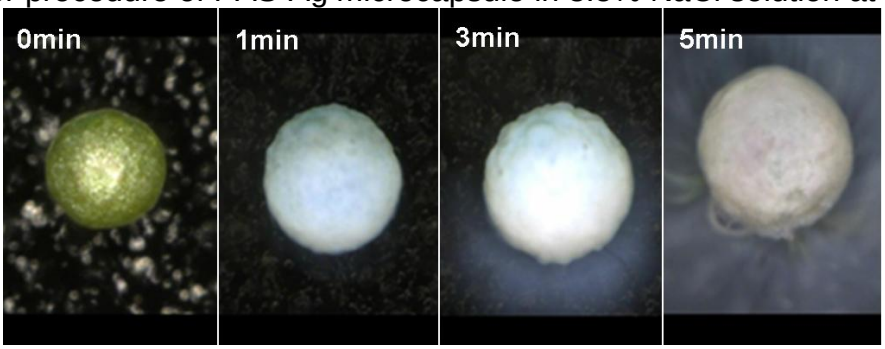


Fig.7 Trigger procedure of PAS-Cu/Ag(1/2) microcapsule in 3.5% NaCl solution at 25°C.

After triggered, the precipitant formed during the process was collected and analysized by XRD. As shown in Fig. 8, it's comprised with AgCl only, indicating the trigger reaction is as follows : $[CH_2CHCOOAg]_n+nNaCl \rightarrow [CH_2CHCOONa]_n+nAgCl\downarrow$.

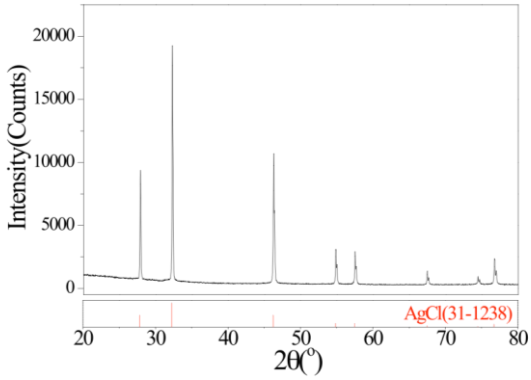


Fig.8 XRD of the precipitant formed in Cl^--trigger procedure.

4. CONCLUSION

PAS-Ag shelled microcapsule containing Na_2PO_3F as the rusty retardant of rebar can be triggered by chloridion in artificial seawater (3.5wt% NaCl). Partial substitution of Ag^+ by Cu^{2+} in the PAS complex will harden the shell.

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