The microcapsule responsive to chloride ion

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ABSTRACT

Several kinds of microcapsules with a shell responsive to free chloride ion were designed according to the reaction of: (1) precipitation, (2) complexation, (3) corrosion, or based on (4) swelling effect. These microcapsules could be prepared with spray drying, solvent evaporation or phase separation method for self-healing concrete usage. If these microcapsules carries chloridion absorbents, corrosion inhibitors, or repairing additives insight, they can release contents to prevent chloride-attack spontaneously. In this article, the chloridion-responsive microcapsules presented is only for the illustration of the distrinct chloridion trigger principles. They are not described in details.

1. INTRODUCTION

Concrete is a very durable construction material widely used in the world, but in some extreme conditions, for example, a chloride environment, premature deterioration often occurs. For reinforced cement concrete (RCC), deterioration is mainly due to the corrosion of steel used in concrete, and the rebar corrosion is mainly caused by ingress of chloride ions and diffusion of CO_2. In the past several decades, concrete structures bulted in littorals had suffered from safety and serviceability problems because of chloride damage and carbonation.

Chloride ion is an accelerant of the corrosion reaction of rebar. The best way to prevent penetration of chloridions is embedding beforehand a chloridion-sensltive microcapsule containing chloridion absorbent, corrosion inhibitor, or repairing additives in concrete. Once there is an incursion of chloridion, the microcapsule will release its contents spontaneously to retard the permeation or to block the diffusion path of chloridions. It's believed, embedment with these microcapsules will endue concrete with anti-corrosion ability, hence improve the construction's service life and reliability.

2. DESIGN OF THE MICROCAPSULE

Chloridion is so stable in aqueous solution that there is few substance can react with. However there are still two way to combine with free chloridions : (1) precipitation, (2) complexation. Ag^+ and Pb^{2+} are the two of few cations able to form chloride deposits. The K_{sp} values of $AgCl$ and $PbCl_2$ at 25°C are 1.8×10^{-10} and 1.7×10^{-5} respectively, very lower than other deposits of Ag^+ and Pb^{2+}. Theoretically, all the indissoluble compounds of Ag^+ or Pb^{2+} of which K_{sp} value or reciprocal of complexing constant is greater than K_{sp} values of $AgCl$ or $PbCl_2$ can make up of the shell. These compounds could be carboxylates (e.g. stearate, laurate, oleate, etc.), polycarboxylates (e.g PAS, alginate etc.), coordination or chelates compounds (i.e organic metal complex, such as MOFs) of Ag^+ or Pb^{2+}. The trigger process is disappearance of these compounds accompanied by the formation of AgCl or $PbCl_2$.

Chloridion is also an active ligand to many metal ions. Some indissoluble salts, such as $PbSO_4$, CuCl, etc can combine with Cl^- to form a soluble complex anions. Embedding the powder of these salts on a ploymer shell could make the microcapsules respond to chloridions. The trigger reaction should be :

(1) For $PbSO_4$ $PbSO_4 + 4Cl^- \rightarrow (PbCl_4)^{2-}, + SO_4^{2-}$

(2) For CuCl $CuCl + Cl^- \rightarrow (CuCl_2)^-$ and $(CuCl_2)^- + Cl^- \rightarrow (CuCl_3)^{2-}$

As chloridion causes the corrosion of many metals, the microcapsules shelled with these metals, such as Al, Cu, Fe, etc, could be responsive to chloridion. The trigger mechanism is pitting of these metal shelles aroused by chloridion.

Polymer are offen used as the shell materials of microcapsule. Their permeabilities are strongly affected by ionic strength, solvent, or concentration of certain anions. If the shell is formed by a complexation reaction of a polymer ligand with a metal cation, the penetrability of water can be controlled by the concentration of given ion. As an instance, Ag^+-polycarboxylate shelled microcapsule could respond to concentration of Cl^- because of permeability change.

3. PREPARATION OF MICROCAPSULE

3.1 Pb-stearate shelled microcapsule

Microcrystalline cellulose (MCC), sodium monofluorophosphate(Na_2PO_3F, core material) and lead stearate (shell material) mixed in mass ratio of 4:5:1, 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, heated at 120°C for 3mins, a lead stearate shelled Na_2PO_3F microcapsule obtained.

3.2 PAS-Ag shelled microcapsule

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.

Weighing 15g sodium polyacrylate (PAS) per 100g core powders, dissolved into water to become a 3wt% solution, mixed with core powders for suspension, then sprayed drying, soak the powders in 0.5mol/L $AgNO_3$ solution for 10mins, a PAS-Ag shelled Na_2PO_3F microcapsule obtained.

3.3 $PbSO_4$-PMMA shelled microcapsule

PMMA and liquid core materials dissolved into dichloromethane (DCM), add $PbSO_4$ powders, stirred for suspension, then poured into 5wt% PVA aqueous solution, stirred at 400rpm, evaporating DCM at 50°C for 2~3hrs.

3.4 CuCl-PS shelled microcapsule

Add cuprous chloride powders into 0.8wt% ethanol solution of citric acid, stirred at room temperature for 4hrs for modification, then filter to obtain oxidation-resisting CuCl.

Weighing PS and epoxy E-51(as core materials) in mass ratio of 1 :1.5, dissolved into dichloromethane (DCM), add some modified CuCl powders, stirred for suspension, then poured into 5wt% PVA aqueous solution, stirred at 400rpm, evaporating DCM at 50°C for 2~3hrs.

3.5 Al shelled microcapsule

Put Na_2PO_3F+MCC core powders into a vacuum evaporation device, vapor depositing Al on the powders for 3-5 mins while keep vibration. Conditions:

vacuum: 10^{-4}mbar, temperature: 1300~1400°C, Al wire purity: 99.99%. the thickness of Al shell is about 2μm.

3.6 Ag^+-p(VIm/AA) embedded PMMA shelled microcapsule

Add 2.7mL(0.03mol) 1- vinyl imidazole (VIm) and 2.5mL(0.03mol) acrylic acid (AA) into a flask, then add 2.0wt% (of total mass of Vim + AA) N,N'-methylene bis acrylamide (MBA) as crosslinking agent and 1.0wt% (of total mass of Vim + AA) ammonium peroxydisulfate as polymerization initiator p(VIm/AA), heating-up to 70°C, stirred at 200rpm, react with reflux condensation for 24h. The products were washed with deionized water, filtrated, vacuum dried at 50°C, a yellowish p(VIm/AA) copolymer powder was obtained. Soaking p(VIm/AA) in $AgNO_3$ solution for 12h, white Ag^+-p(VIm/AA) is formed.

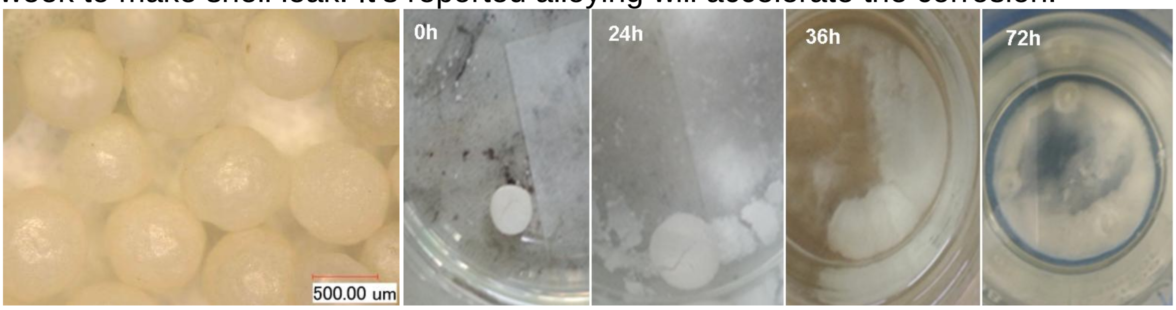
Add 1g polymethylmethacrylate (PMMA) into 30ml dichloromethane, after dissolved, mixed with insoluble core powders and 1wt% PVA solution to obtain a O/W emulsion, then remove dichloromethane by evaporation at 45°C for 4h, white microcapsule is formed.

4. RESULTS AND DISCUSSION

All the microcapsules prepared above are able to respond to chloridion, but response time is quite different, from several mins to several days, as shown in Fig1~5.

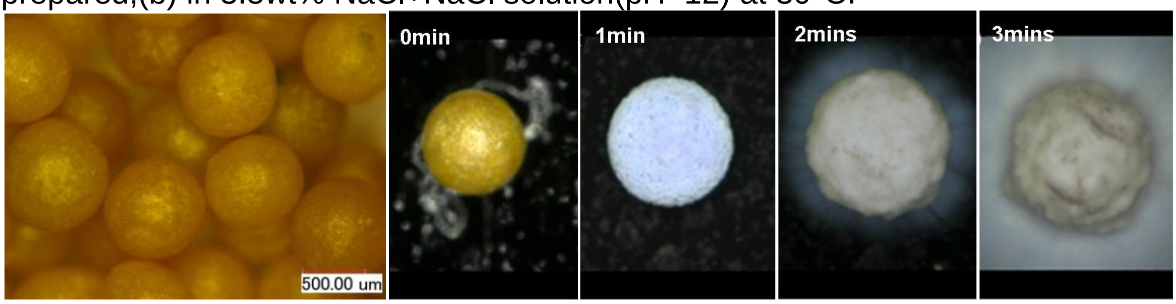
There was no response when Pb-stearate was immersed in 3.5wt% NaCl solution, because the resultant of reaction, Na-stearate, is only slightly soluble in water. So it's estimated Pb-lauricide can respond to chloridion in 3.5wt% NaCl solution. However, it's not intelligible that Pb-stearate shelled microcapsule could be triggered by chloridion in alkaline solution. More experiments should be done to figuer it out, we think.

The trigger process of Al shelled microcapsule is a very slow motion. It need one week to make shell leak. It's reported alloying will accelerate the corrosion.



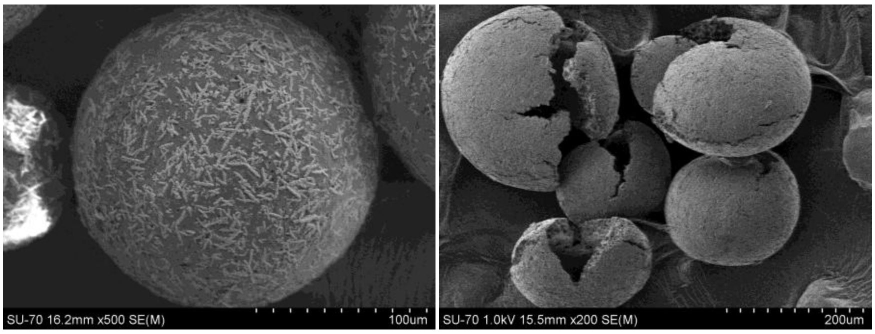
(a) (b)

Fig. 1 Pb-stearate shelled microcapsule containing CMC+Na_2PO_3F: (a) as-prepared,(b) in 3.5wt% NaCl+NaCl solution(pH=12) at 30°C.



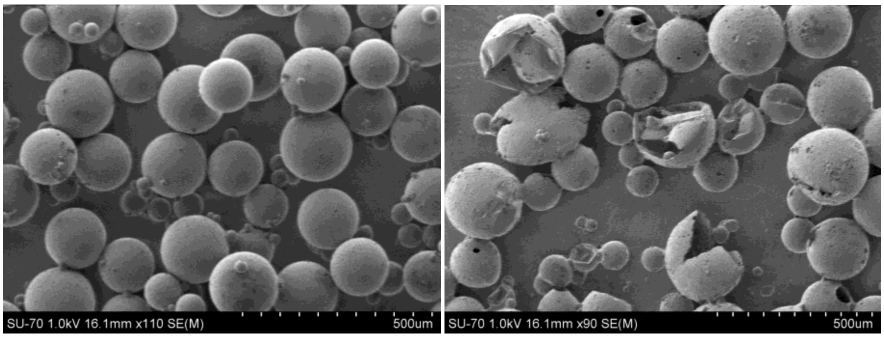
(a) (b)

Fig. 2 PAS-Ag shelled microcapsule containing CMC+Na_2PO_3F: (a) as-prepared,(b) in 3.5wt% NaCl solution at 25°C.



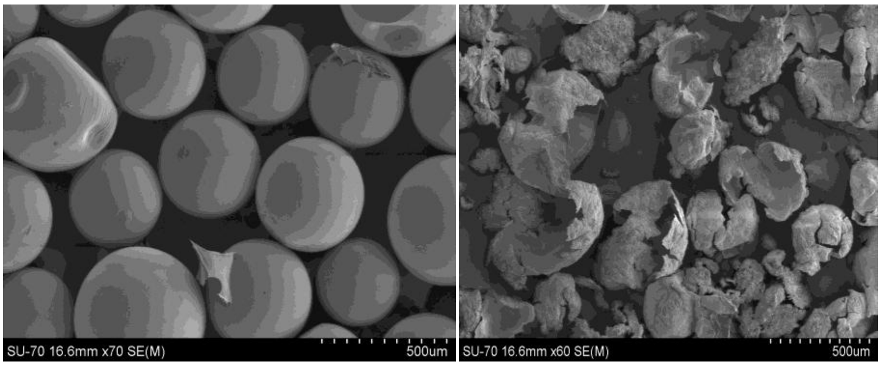
(a) (b)

Fig. 3 $PbSO_4$-PMMA shelled microcapsule :(a) as-prepared, (b) soaked in 3.5wt% NaCl solution for 20hrs.



(a) (b)

Fig. 4 CuCl-PS shelled microcapsule:(a) as-prepared, (b) soaked in 3.5wt% NaCl solution for 1hr.



(a) (b)

Fig. 5 [Ag^+-p(VIm/AA)]-PMMA shelled microcapsule:(a) as-prepared, (b) soaked in 3.5wt% NaCl solution for 48hrs.

5. CONCLUSION

Several chloridion-triggered microcapsules were designed and prepared to illustrate the trigger principles. All the microcapsules works well in 3.5wt% NaCl solution except Pb-stearate shelled microcapsule.

Based on the mechanism, all the microcapsules also can be triggered by OH^- as the K_{sp} value of $Pb(OH)_2$ (1.43×10^{-20}) and AgOH (2.0×10^{-8}) are very low, too. Concrete is a alkaline matrix, so microcapsules embedded in concrete maybe is not stable.

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