Preparation of Cu^{2+}-P(VIm-MMA) complex shelled microcapsule and its respondent behavior to carbonate ion in water

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ABSTRACT
In this paper, a microcapsule sensitive to carbonate ion was prepared and researched. This microcapsule is shelled with a complex made up of copper ion and a copolymer with dangling imidazolyl ligands. When the microcapsule encounters carbonate ion in water, the copper ion is carried off to form copper carbonate precipitate, meanwhile the complex is decomposed to release the contents. The copolymer was synthesized by a simple radical polymerization of 1- vinyl imidazole and methyl methacrylate. The microcapsule was prepared by piercing-bath methode. It's believed the result microcapsule could be applied in concrete to protect the cement matrix against carbonization.

1. INTRODUCTION
Most of the microcapsules used in self-healing materials are stress-triggered, but in many instances, the response of microcapsule to ionic concentration is expected. There are a lot of industrial applications banking on the corresponding microcapsules. For example, pH-sensitive microcapsules could be used as drug carriers with controlled release in medical treatment; chloridion-triggered microcapsules in concrete enable the marine construction from chloride attack. The ion trigger mechanism of these microcapsules usually is based on the disintegration of shell caused by dissolution, decomposion or depolymerization when they react with some ions or molecules, or based on permeability change of shell aroused by swelling. In this paper, microcapsules shelled by polymer ligand-metal ion's complex were prepared for self-healing concrete application. It's designed to uniquely respond the existence of CO_3^{2-} ion, which lowers the pH value in cement, further causes breakdown of the passive layer on rebar. It's believed embedment CO_3^{2-} sensitive microcapsules in concrete will increase the resistance of concrete works to pernicious chemical surroundings, and then heighten the building's durability.

2. MATERIALS AND METHODS
2.1 Materials
1-vinylimidazole(VIm), methylmethacrylate (MMA), azobisisobutyronitrile(AIBN) and all solvents were analytical grade reagents from Alfa Aesar, with purity over 99%. All salts, such as $CuCl_2$, $NaNO_3$, Na_2SO_4 and Na_2CO_3 were analytical pure reagents purchased from Aladdin-reagent, Shanghai, China.

2.2 Preparation of p(Vim-MMA)

VIm and MMA were added into a three-necked flask with mass ratio of 3 :7, then add 50ml tetrahydrofuran (THF) solution containing 0.25g AIBN, heated up to 60°C, tirred at 500rpm and keep at this temperature for 24h. The product was precipitated in diethylether, filtered, and vacuum dried overnight.

2.3 Preparation of Cu^{2+}-p(Vim-MMA) complex microcapsule
Dissolve p(Vim-MMA) in THF, drop into 4% $CuCl_2$ solution by a syringe, then agitate at 200rpm for 12h. The result hollow microcapsule was washed by deionized water, then filtered, dried under 50°C for 5h.

2.4 CO_3^{2-} trigger test
The microcapsule soaked in 5% $NaNO_3$, Na_2SO_4 and Na_2CO_3 aqueous solution respectively, recording the crack time.

2.5 Characterization of p(Vim-MMA) copolymer and Cu^{2+}-p(Vim-MMA) microcapsule
The structure of p(Vim-MMA) was analysed by ^{1}H-NMR. The morphology of microcapsules was observed under Keyence VHX-600K stereo optical microscope and Hitachi SU-20 SEM. FTIR analysis was conducted on Nicolet 6700 FTIR Spectrometer.

3. RESULTS AND DISCUSSION

3.1 Structure of copolymer

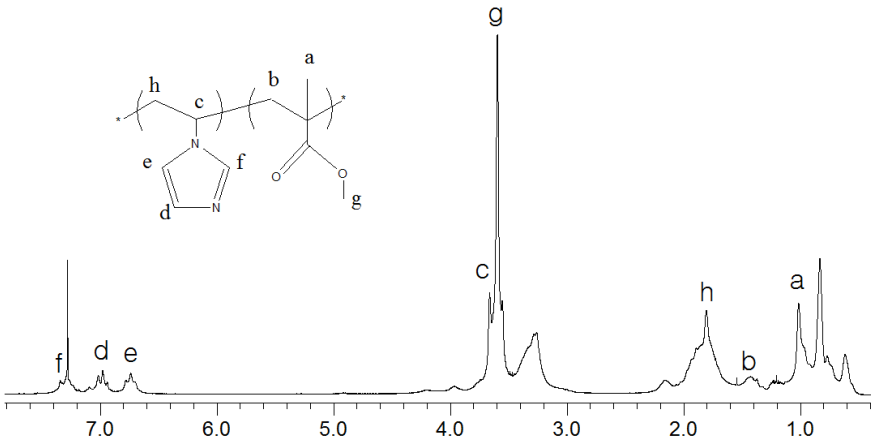
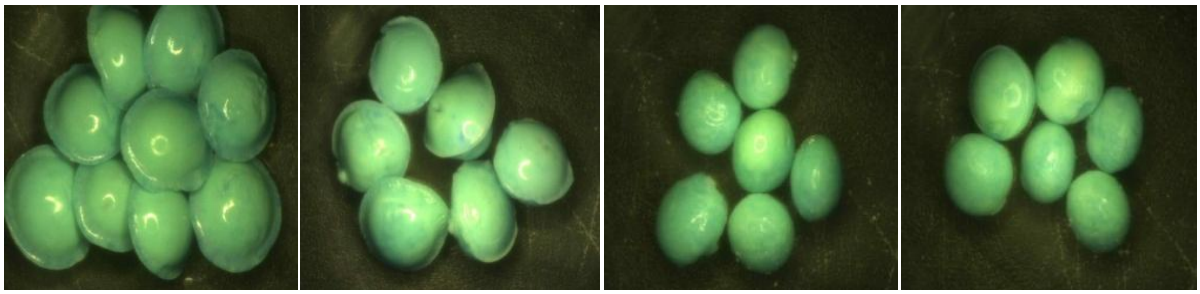


Fig.1 ^{1}H-NMR spectrum of p(Vim-MMA) copolymer

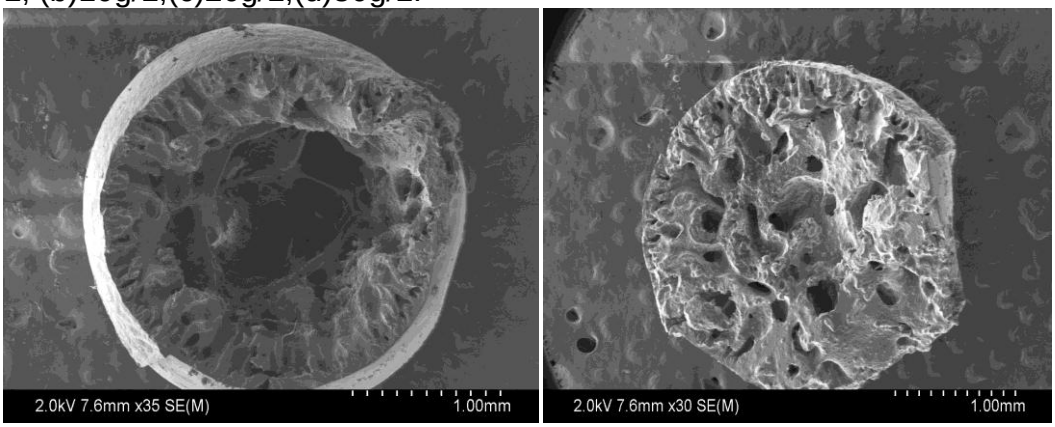
The assignments of the peaks in Fig.1 are as follows:
^{1}H-NMR（400MHz,$CDCl_3$）δ(ppm)：1.18-1.19(s, 3H)，1.59-1.62(s, 2H), 3.84-3.85(s, 1H), 7.14-7.16(m, 1H), 6.91-6.92(m, 1H), 7.52-7.53(s, 1H), 3.76-3.77(dd, 1H), 1.97-1.98(d, 2H). All the chemical shiff values are consistent with the theoretical, indicating the target product was synthesized successfully.
GPC shows the average molecular weight of p(Vim-MMA) is 16112.

3.2 Formation of Cu^{2+}-p(Vim-MMA) microcapsule
Concentration of p(Vim-MMA) in THF solution affects the formation of microcapsule strongly. Low-concentration means low viscosity. When the solution drops into $CuCl_2$ bath, the driplet was shaped by the surface tension of $CuCl_2$ solution into a discoid ball. However, High-concentration led to a solid ball, no hollow microcapsule was formed, as Fig.3 shown.



(a) (b) (c) (d)

Fig.2 Influence of p(Vim-MMA) concentration on the formation of microcapsules: (a)5g/L, (b)10g/L,(c)20g/L,(d)30g/L.



(a) (b)

Fig.3 SEM images of the microcapsules prepared with (a)20g/L, (b)30g/L p(Vim-MMA) solution.

3.3 Analysis of Cu^{2+}-p(Vim-MMA) microcapsule

The microcapsule formation process is a coordination reaction of p(Vim-MMA) with Cu^{2+}. Fig.4 confirms the occurrence of that reaction. Comparing FTIR spectra of the p(Vim-MMA) and Cu^{2+}-p(Vim-MMA), the stretching vibration peak of C=CH bond in imidazole ring at 3116cm^{-1} and N=CH bond of imidazole ring at 1484 cm^{-1} on p(Vim-MMA) FTIR spectrum are shifted to 3133cm^{-1} and 1498 cm^{-1} on Cu^{2+}-p(Vim-MMA) FTIR spectrum respectively, but the absorption peak of other groups remains the same. It means the imidazole coordinates with Cu^{2+} in Cu^{2+}-p(Vim-MMA).

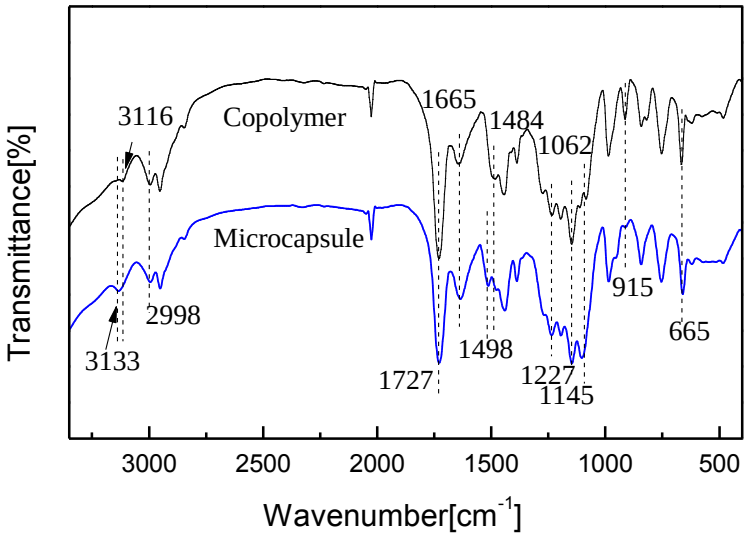
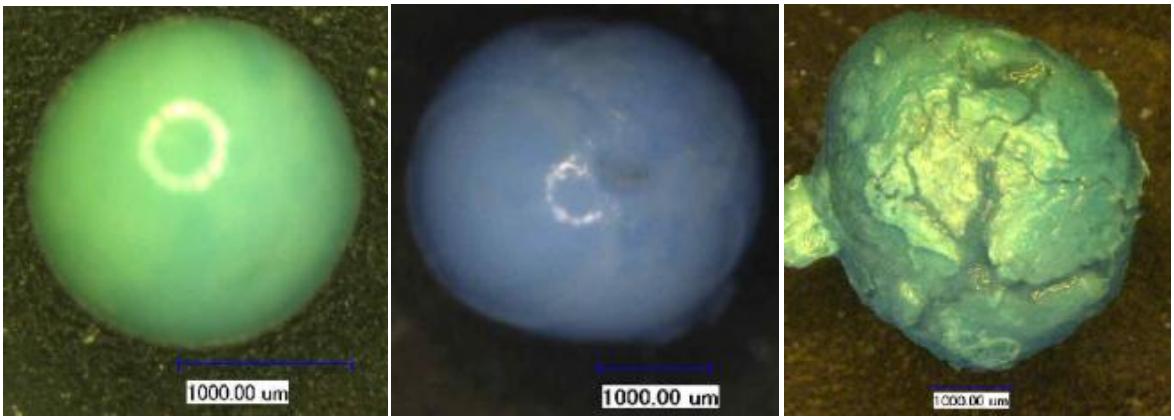


Fig.4 FTIR spectra of microcapsules and copolymer

3.4 Anion-response of Cu^{2+}-p(Vim-MMA) microcapsule

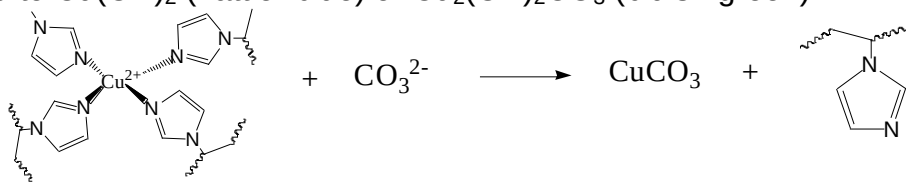
Cu^{2+}-p(Vim-MMA) microcapsule saoked in water only responds to carbonate ions. As shown in Fig.5, Cu^{2+}-p(Vim-MMA) microcapsule in NO_3^- or SO_4^{2-} solution does not crack. Even if soak time was prolonged to 1month, they were still the same, but that in CO_3^{2-} solution was broken in 48hrs.



(a) (b) (c)

Fig.5 Cu^{2+}-p(Vim-MMA) microcapsule saoked in 5% solution of (a) $NaNO_3$, (b) Na_2SO_4, (c)Na_2CO_3 for 48hrs.

The trigger principle is illustrated in Fig. 6. In water, $CuCO_3$ is more stable than Cu^{2+}-p(Vim-MMA) complex, so carbonate ion capturing Cu^{2+} from Cu^{2+}-p(Vim-MMA) complex will lower the shell's strength. However, compared with $Cu(OH)_2$ (K_{sp} at 25°C= 2.2×10^{-20}), $CuCO_3$(K_{sp} at 25°C= 1.4×10^{-10}) is unstable relatively, will be transmuted to $Cu(OH)_2$ (nattier blue) or $Cu_2(OH)_2CO_3$ (bluish green).



$$CuCO_3 + H_2O \longrightarrow Cu(OH)_2 + CO_2$$

$$Cu(OH)_2 + Na_2CO_3 \longrightarrow Cu_2(OH)_2CO_3$$

Fig.6 CO_3^{2-} response mechanism of Cu^{2+}-p(Vim-MMA) microcapsule in water

4. CONCLUSION

P(Vim-MMA) copolymer was synthesized, and it's Cu^{2+} coordination microcapsule was prepared successfully. When the concentration of p(Vim-MMA) copolymer is 20g/L, the formed microcapsule is a hollow ball with best sphericity. Not only that, this microcapsule is able to crack when soaked in CO_3^{2-} solution, generating a more stable sediment.

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