Chloridion response of the microcapsule shelled with polystyrene-cuprous chloride composite

Guangming Zhu[1], Yongxing He[1], Jiaoning Tang[1], Ningxu Han[2], Feng Xing[2]

[1]*Shenzhen Key Laboratory of Special Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, PR China,E-mail: gzhu@szu.edu.cn;*
[2]*Department of Civil Engineering, Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, Shenzhen University, Shenzhen 518060, PR China*

Keywords: microcapsule, chlorid attack, cuprous chloride, concrete

Abstract ID No : 97

ABSTRACT

Microcapsules with response to chemicals have a variety of potential applications, for example, embedding chloridion- triggered microcapsule containing repairing agent or corrosion inhibitor in steel reinforced concrete is considered to be an effective measures to protect marine construction against chloride attack. In this paper, a chloridion- sensitive microcapsule was designed and synthesized based on the following reaction :

$$CuCl\downarrow + Cl^- \rightarrow [CuCl_2]^-(s)$$

This microcapsule was consists of polystyrene-cuprous chloride (PS-CuCl) composite shell and epoxy resin core. It forms in a solvent-evaporation process at 40°C. Soaked the result microcapsule in 3.5% NaCl artificial sea water, cuprous chloride was dissolved in a short time. SEM observation shows the shell was hiascent in one houre, and collapsed after 5 hours.

1. INTRODUCTION

Cuprous chloride (CuCl) is a catalyst widely used in chemical industy for synthesys of acrylonitrile, vinyl acetylene, etc.Iit's also extensively used as desulfurizer, decolorant and releaseagent in petrochemicals. As CuCl is inclined to CO sequestration,it's well-known as a gas absorbent.

It's noticed, besides coordinating with carbon monoxide, CuCl could have a further complexation with chloridion for form a soluble complex-ion. Besed on this reaction, a Cl^--response microcapsule can be designed. However, CuCl is prone to being oxidized, so antioxidation treatment is required.

In this article CuCl was embedded in polystyrene (PS) shell. The corresponding composite-shelled microcapsule was prepared by solvent evaporation approach specially for the application of self-healing concrete with immunity against chloride damage.

2. MATERIALS AND METHODS

2.1 Materials

CuCl,NaCl, dichloromethane(DCM) are analytical reagents from Tianjin chemical reagent factory, Tianjin, P.R. China. Polystyrene (PS) (MW≈100,000g/mol) is tachnical pure polymer received from Aladdin reagent Co., Shanghai, P.R. China. Epoxy E-51 is also tachnical pure polymer provided by Dongfeng chemical plant, Guangzhou, guangdong, China.

2.2 Antioxidation treatment of CuCl

Add cuprous chloride powders into 0.8wt% ethanol solution of citric acid, stirred at room temperature for 4hrs for modification, then filtered out.

2.3 CuCl-PS shelled microcapsule

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.

2.4 Characterization of the microcapsules

The morphology of microcapsules was observed under Hitachi SU-20 SEM, by which the particle diameters and shell thickness were 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 Characterization of microcapsule

SEM observation shows the E-51/PS-CuCl microcapsule has a standard core/shell structure. The particle size is about 150μm. The shell thickness is around 20 microns. Fig. 1 shows morphology and structure of microcapsule. EDS elemental analysis tell us the atomic ratio of Cu :Cl is about 1 :0.7, generally demonstrating most of CuCl was kept in existence during the microencapsulation.

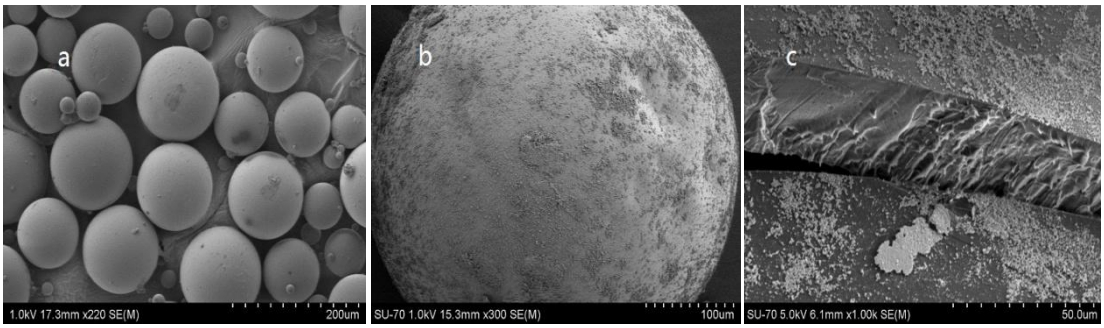

Fig.1 The surface morphology of composite microcapsules

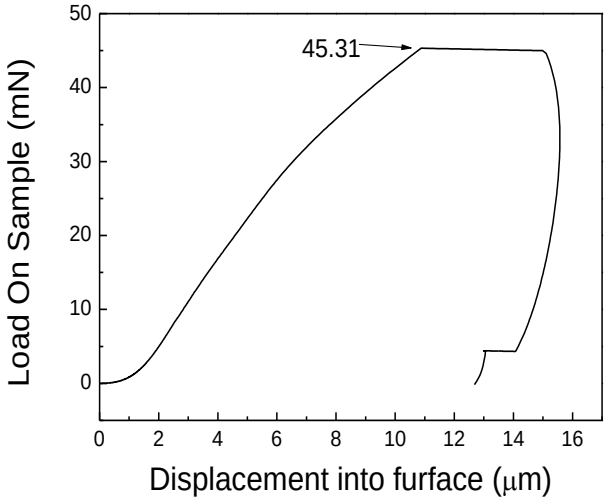

Fig.2 Load-displacement curve of E-51/PS-CuCl microcapsule

From the load-displacement curve acquired from nanoindentation measurement on G200 nanoindenter, the hardness and Yang's modulus of CuCl-PS composite shell were calculated. the results are 0.029 GPa and 2.01GPa respectively. It means the composite shell is hard enough but can be broken in adequate stress. So it's suitable for self-healing concrete application.

Comparation of FTIR spectra of core and microcapsule can reveal the microcausules' tructure. In Fig. 3, the absorption at 2920cm-1 corresponds to stretching vibration (V_S) of $–CH_2$- group, both that at 1609cm^{-1} and 1507cm^{-1} represent the vibration of C=C in benzene ring. The peaks at 913cm^{-1}and 831cm^{-1} are the characteristics of epoxide group. It makes known the epoxy E-51 was encapsulated by PS.

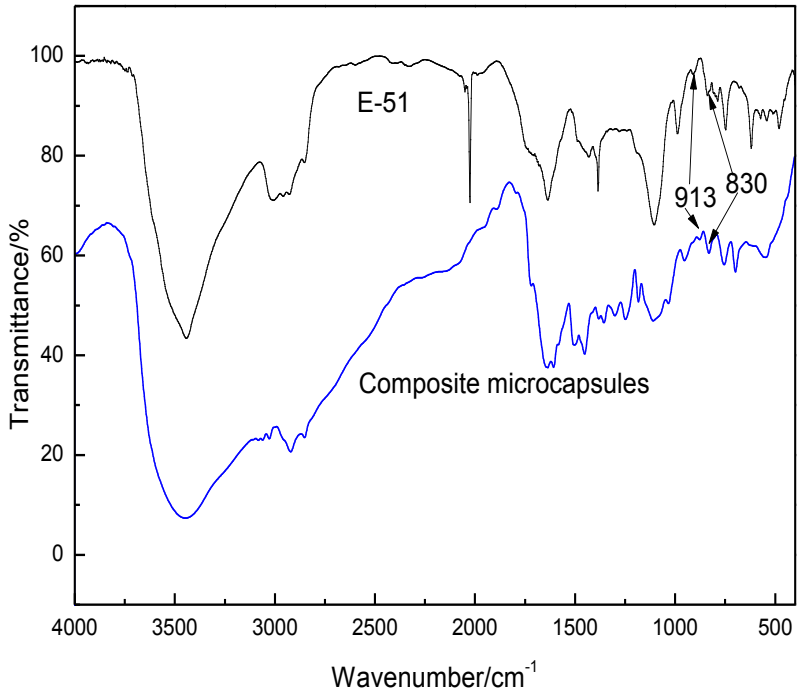

Fig.3 FTIR spectrograms of epoxy E-51 core and PS-CuCl shelled microcapsule

3.2 Cl^--trigger test

As shown in Fig. 4, after soaked in 3.5wt% NaCl solution, the microcapsules were cracked in 1h. If the soaking time is rolonged to 5hrs, the shell will be widely opened.

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

After triggered in NaCl solution, the shell fragments was collected and washed by acetone to remove the epoxy E-51 core. XRD shows, the peaks indicating CuCl on

the X-diffractogram of the Cl^--triggered shell are disappeared, illustrating all the CuCl salts are dissolved and translated to other salt of copper.

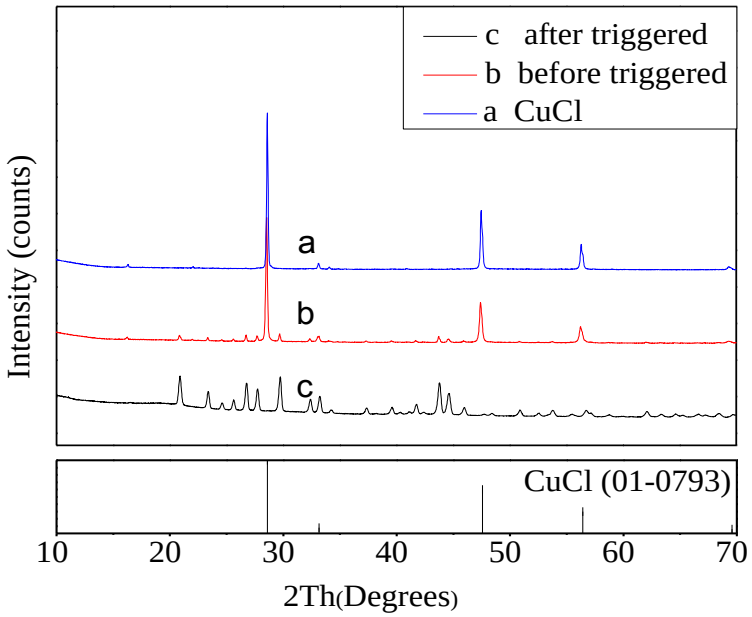

Fig.5 XRD of PS-CuCl composite microcapsules before and after triggered in 3.5wt%NaCl solution, in comparison with that of CuCl.

4. CONCLUSION

CuCl shows good response to chloridion. CuCl-embedded PS shell is able to dehisce spontaneously in 3.5wt% NaCl solution in 1hours, indicating the microcapsule could be used in self-healing concrete against chloride damage.

ACKNOWLEGDEMENTS

The authors would like to acknowledge financial support provided by National Natural Science Foundation of China (No.51120185002/U1301241), Science and Technology Project of Shenzhen City (JCYJ20140418091413518), and Collaborative Innovation Center for Advanced Civil Engineering Materials, Nanjing, P. R. China.