Effect of different curing agents on the fracture behavior of epoxy-shelled bio-microcapsule under stress

Guangming Zhu[1], Yuanchun Luo[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*

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ABSTRACT

Besides natural biopolymers, such as alginate, chitin, cellulose, gelatin, etc, epoxy also is a candidate of shell-materials in microencapsulation of bacteria, because epoxy and its amine curing agents, such as N-(amino-ethyl)-amino-propyl trimethoxy silane (silane coupling agent KH-792), M-Xylene Diamine(MXDA), 2,4,6-Tris (dimethylaminomethyl) phenol (DMP-30), are proved harmfulless to the spores. Epoxy shell is admittedly superior in waterproofing quality, which is very important to the dormancy of spores, but sometimes epoxy shell is too strong to be broken. In this work, epoxy E-51-shelled microcapsules cured with KH-792, MXDA, DMP-30 were prepared respectively, and their fracture behavior was examined and compared. It's found microcapsule with E-51/KH-792 shell is hard to break up, however, that with E-51/MXDA and E-51/DMP-30 shell are more easy. Bending best shows, E-51/KH-792 shell is very tenacious, while E-51/DMP-30 shell is brittle. It can be concluded that fracture behavior of microcapsules depends on the molecular chain flexibility of curing agents and the degree of crosslinking of cured epoxy. The molecular of amine curing agent with a long flexile chain or less reactive group will lead to an elastic shell, otherwise, to a fragile shell.

1. INTRODUCTION

Microbe is a good repairing agent for concrete cracks, as some bacteria are able to metabolize calcium ion and excrete lime carbonate to fill the crevices. So self-healing concrete could be actualized by embedding mcroencapsulated these bacteria inside. In consideration of biocompatibility, the shell materials of bio-microcapsule are normally selected from natural polymers, such as algin, chitin, glutin, etc. Unfortunately, all the polymers are hydrophilic, can be dissolved or swellen in water, hence not suitable for self-healing concrete application. In this article, epoxy E-51 was empolyed as shell material in the formation of water-proof bio-mcroencapsules. To ensure the shell be able to break in concrete, the shell's mechanical performance was studied in comparison of epoxy E-51 resin cured with different agents.

2. MATERIALS AND METHODS

2.1 Materials

Koch's bacilli DSM6307 were supplied by school of life science, Shenzhen university, Shenzhen, Guangdong, China, with microcrystalline cellulose(MCC) carrier. Polydimethylsiloxane(PDMS) were purchased from Aladdin Reagent Co., Shanghai, China. Epoxy resin of E-51 and its' curing agents, KH-792, MXDA and DMP-30 were products of Tianjin Chemical Plant, Tianjin, China. All the chemicals used are analytical pure.

2.2 Biocompatibility test

Take some amount of spores mixed with epoxy E-51, KH-792, MXDA, DMP-30 and water respectively, rest for 160mins, isolate and collect the spores, cultured for 24hrs, then extract the culture medium solution to determine the optical density by 490nm-ultraviolet absorption value (denoted by OD_{490}). That value was used to represent the bacterial concentration because they are positively correlated.

2.3 Preparation of microcapsules

3g Koch's bacillus DSM6307 spores, 250g culture medium (yeast powder: inosine: Na_2NO_3 = 25:5:150) and 150g MCC were mixed with 150ml water, the dough obtained was delivered into a twin-screw granulator (mini250, Xinyite Sci. and Tech. Co., Ltd, Shenzhen, China) for granulation, then cryodesiccated, the core particles were obtained.

Weighing 10g core powders, 10g epoxy E-51, curing agent, mixed in a flask at 50°C for 40mins. Add 200ml PDMS, agitated at 300rpm for 60mins, the microcapsule was formed.

The dosage of curing agent was determined by the reactive hydrogen atom (H*) number in their molecules. The principle is H* in equimolar amount of epoxy group. It's known all of KH-792, MXDA and DMP-30 are amine compounds, the reactive hydrogen atoms are from amidos, but they are different from each other. MXDA has two primary amine groups, there are 4 H*s per molecule, so the molar ratio of E-51/MXDA is 4:2, i.e. the dosage of MXDA is 15.5wt% of E-51. KH-792 has one secondary amine group and one primary amine group, there are 3 H*s per molecule, so the molar ratio of E-51/ KH-792 is 3:2, i.e. the dosage of KH-792 is 28.5wt% of E-51. DMP-30 has three tertiary amine groups, which without H*, but it's an efficient curing catalyst. The dosage of DMP-30 was determined by experience, usually 10wt% of E-51.

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.

2.5 Determination of viability

Weighing 1g core particles as a blank copy, ground into fine powders, then added into liquid nutrient medium, diluted 10^8 times with deionized water, extract 100μL solution into ϕ90 petri dish, cultured for 24hrs, counting the number of colonies and calculating the amount of spores.

Weighing another copy of 1g core particles, microencapsulated, whereafter crushed, then treated as the blank copy.

$$\text{fraction surviving} = \frac{\text{the amount of spores in blank copy}}{\text{the amount of spores in microencapsulated copy}}$$

2.6 Waterproofing test

Soak the microcapsules in fresh water at room temperature, observe the shape change under JPL1350 optical microscope.

2.7 Preparation of concrete specimen

Microcapsule, water, Portland cement were mixed with mass ratio of 1:10:20, poured into a steel mold, demolding after 24hr hydration, then curing for 7days in a room at 20±2°C and 95%RH.

2.8 Stress-trigger test and crack-healing test

The concrete specimen was compressed on a mechanical tester to make a crack, examining the fracture surface, or soaked in nutrient solution, cultured in an incubator for 30days.

3. RESULTS AND DISCUSSION

3.1 Biocompatibility of raw materials

As shown in Fig.1, the OD_{490} values of E-51, DMP-30, MXDA and KH-792 are only slightly less than 57.2%,that of sterile water. It means these raw materials are micro - poisonous to the spores.

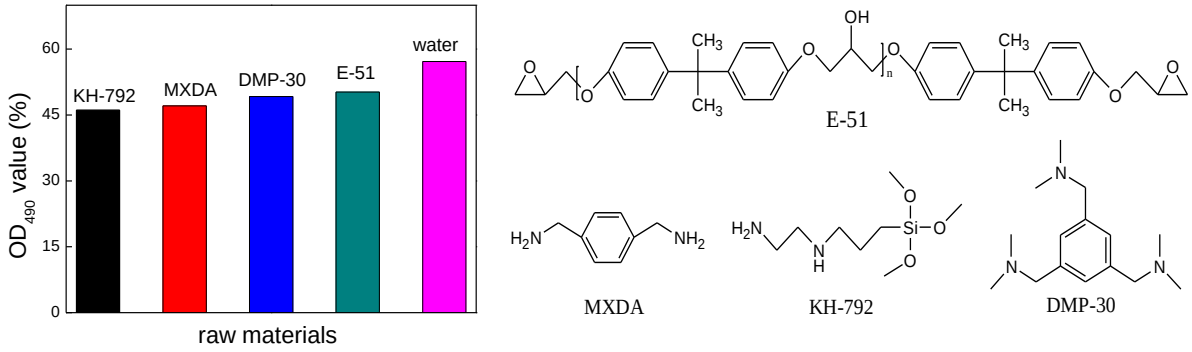


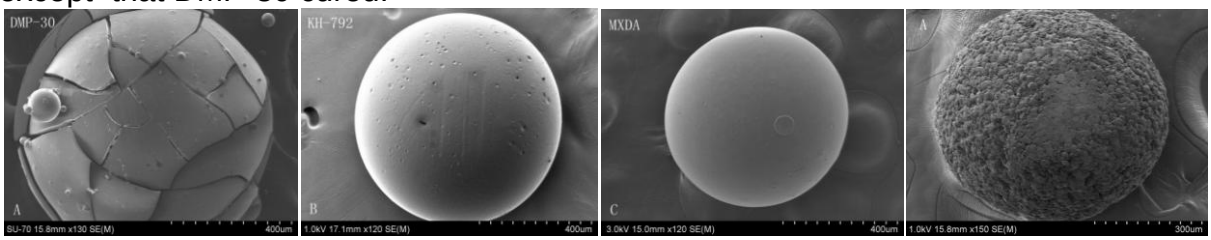
Fig.1 The molecular structures and OD_{490} values of raw materials

3.2 Viability of the microencapsulated spores

The fractions of surviving spore in all the microcapsules are over 90%.

3.3 Morphologis of microcapsules

All the microcapsules prepared are perfect sphere ball with a hard and smooth shell. The shell thickness is 30-75μm. The microcapsules are not easy to be brocken except that DMP-30 cured.



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

Fig.2 The SEM images of microcapsules microcapsules prepared by different curing agents : (a) DMP-30, (b)KH-792, (c) MXDA, (d)bare core.

3.4 Watertightness

Saoked all the microcapsules in water for 1 month, there were no any change in shape, size and color observed. So it can be concluded the microcapsules have excellent waterproof performance.

3.5 Mechanical performance of shell

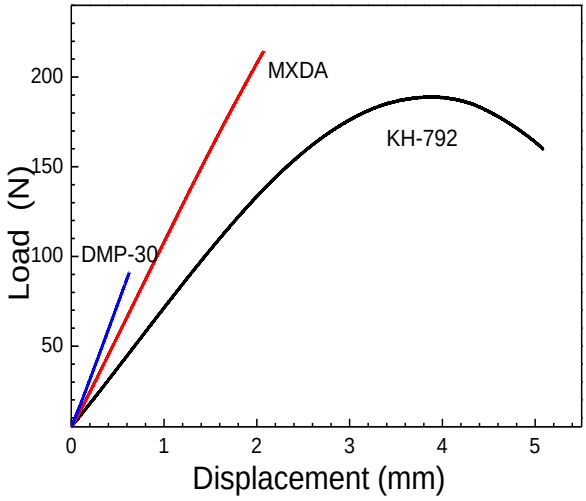
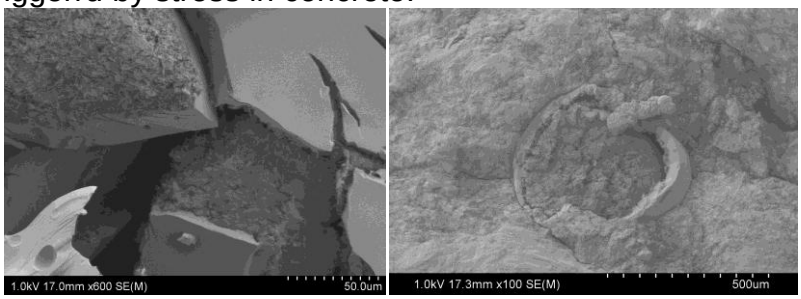


Fig.2 The Load-displacement curve of E-51 specimen in mechanical bend testing

Epoxy resin E-51 mixed with curing agent was cast into a mould to form a rectangle specimen with size of 60mm×10mm×5mm for three point bending test, where the span is 50mm, loading rate is 1mm/min^{-1}. The results are shown in Fig. 2. It's clear that, the specimen of DMP-30 and MXDA are brittle. Of them, flexural strength of DMP-30 is much less than MXDA. So it's believed DMP-30 cured E-51 microcapsule is more easy triggerrd by stress in concrete.



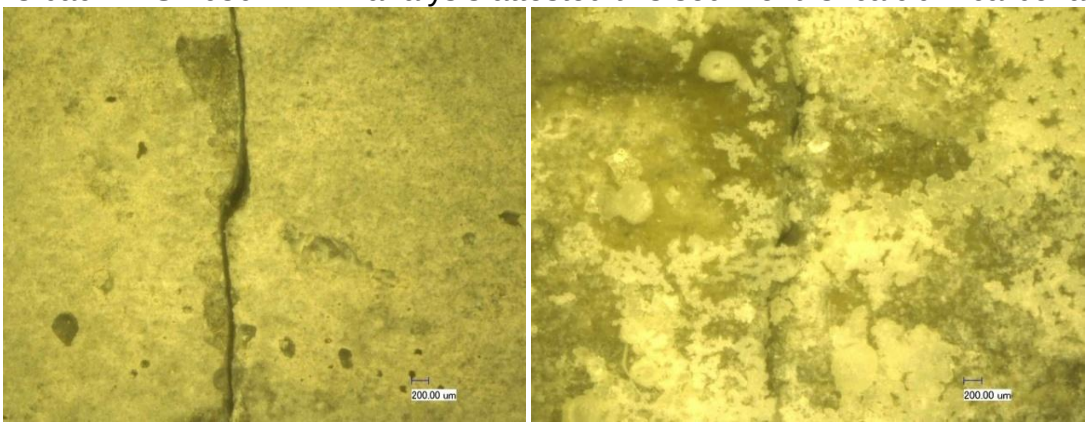
(a) (b)

Fig.3 The SEM images of (a) ground E51/DMP-30 microcapsule, (b)stress-broken E-51/DMP-30 microcapsule in concrete specimen.

Although E-51/DMP-30 microcapsule is hard enough for concrete application, it's easy to be ground into fine powders in mortar. Embedded in 30mm×30mm×30mm sized concrete cube, E-51/DMP-30 microcapsule is able to be mechanical triggered under compressive stress, as Fig. 3(b) shown

2.6 Biological self- repairing effect

After soaked in nutrient solution for 30days, the cracked concrete cube was almost repaired. Fig. 4 shows, a 100μm-width macrocrack was filled in by the metabolite of Koch's bacilli DSM6307. XRD analysis attested this sediment is calcium carbonate.



(a) (b)

Fig.4 OM pictures of macrocrack on concrete cube: (a) before and (b) after bioremediation.

4. CONCLUSION

A tertiary amine like DMP-30 is a better curing agent in microencapsulaion of spores than primary amine and secondary amine like MXDA or KH-792. The E-51/DMP-30 shell is more brittle and biocompatible than others. E-51/DMP-30 microcapsule containing Koch's bacilli DSM6307 spors is able to be brocken in concrete and self-repaire the cracks.

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