PREPARATION OF MONO-SIZED EPOXY/MF MICROCAPSULES IN THE APPEARANCE OF POLYVINYL ALCOHOL AS CO-EMULSIFIER

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ABSTRACT

For epoxy microcapsules embedded in concrete as mechanic-triggered self-healing adhesive, globular shape with uniform size is the basic requirement to ensure the solid shell broken and the liquid core released at a designed stress. In this paper, monodispersed melamine–formaldehyde (MF) resin-walled epoxy E-51 microcapsules were successfully fabricated in an in situ polycondensation process, in which a certain amount of polyvinyl alcohol (PVA) solution was added as co-emulsifier to control the microcapsules' shape and size. Detail investigation shows, with the cooperation of PVA, the microcapsule morphologies and size distribution were ease to be adjusted by the parameters such as emulsifying agents, agitation rate, pH value and acidification time.

1. INTRODUCTION

MF is one of cross-linked polyamino resin synthesized from tripolycyanamide by condensation with methanal. As shell material of microcapsule, MF resin is waterproof and thermal tolerant. It is strong enough to remain intact during manufacture and concrete mixing, but also crisp enough to cause leakage of core materials easily when required. It's ideal for the application of self-healing concrete, in which the microcapsules are expected to have optimum mechanical strength and can rupture under a given mechanical load. Theoretically, the mechanical strength of microcapsules is determined by shell's chemical composition, structure, size and thickness. So it is advantageous to prepare MF microcapsules with a narrow size distribution, which may lead to a narrow strength distribution. Moreover, microcapsules with a narrow size distribution can offer many other benefits, including tight control of the release rate of the core material.

2. MATERIALS AND METHODS

2.1 Materials

Bisphenol A type epoxy resin E-51(industrial reagents) was used as core material. Tripolycyanamide (Melamine, AR) and formaldehyde (37wt% aqueous solution, AR) were purchased from Aladdin-reagent, Shanghai, China. Sodium hydroxide (AR) and citric acid (AR) were received from Tianjin Chemical Plant, China, and used as pH

value regulating agents. All of the emulsifiers used, such as polyvinyl alcohol (PVA, MW=1800), sodium dodecyl benzene sulfonate (SDBS), sodium lauryl sulfate (SLS) are analytical pure agents and purchased from Tianjin Chemical Plant, China, but sulfonated copolymer of styrene and maleic anhydride(SMA, Scripset® 520, AR) are from Ashlande Inc., USA.

2.2 Preparation of microcapsules

Melamine, equimolar formaldehyde and 100ml water were mixed in a 250ml three-neck flask and agitated at 350rpm till melamine was dissolved, then 10 wt% NaOH solution was added slowly to adjust pH value to 8.5, succeeded by elevation of temperature at 2℃/min to 70℃ and keep for 10mins. After cooling, performed MF polymer was obtained.
0.4g emulsifier and 100ml distilled water were poured into an 500ml beaker and mixed, adding 10g epoxy E-51 resin, homogenized at 1000rpm for 30mins, add 2-3 drops of defoamer, latex emulsion of epoxy/water was formed.
Add performed MF polymer into the emulsion, stirred at 350rpm for 10mins. Add 10wt% citric acid solution dropwise to decrease the pH value to 3.5, then drop 0.4wt% PVA solution, meanwhile raise the temperature at 2℃/min to 70℃ again and keep for 1hr. The performed MF polymer will cross-linked with each other at the w/o interface. After cooling, vacuum filtration, water rinse and vacuum drying, the products, epoxy/MF Microcapsules, were acquired.

2.3 Characterization of the microcapsules

The morphology of microcapsules was observed under Hitachi SU-20 SEM, by which the particle diameters and shell thickness were also 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 400 to 4000cm^{-1} wave number region.

3. RESULTS AND DISCUSSION

3.1 Effect of emulsifiers

SMA is an emulsifying agent widely used in the preparation of polyamino resin walled microcapsules. However, in our experiment, it's found the generation of MF prepolymer on SMA-emulsified o/w interface arouses emulsion breaking, leading to a very low encapsulation ratio of epoxy core. SDBS and SLS are unimolecule anionic surfactants. Their stab molecules tend to absorbed on the o/w interface with intensive and highly oriented arrangement, impeding the emergence of demulsification and increasing the efficiency of encapsulation, but the microcapsules have a wide size distribution. PVA can react with formaldehyde to form polyvinyl formal (PVF) in acidic condition. PVF coves on the surface of oil drops and changes the HLB value, making the oil drop size small and uniform. Experimental results shows, SDBS coperated with PVA has very good effects on shape and size controlling of microcapsule, as showing in Fig. 1.

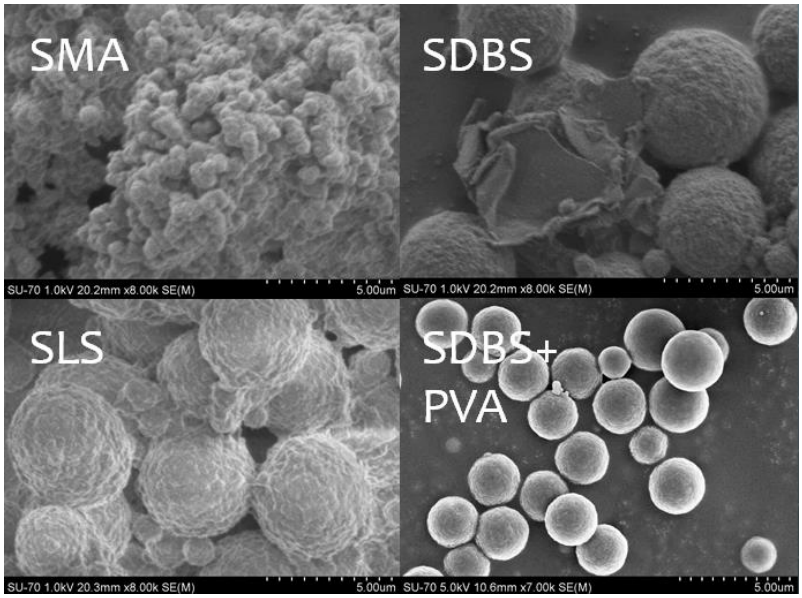


Figure 1: Microcapsules prepared from epoxy/water emulsion with different surfactants

3.2 Effect of pH value and acidification time

During the second period of the *in situ* polymerization of MF, *i.e.*, the cross-linking of performed MF polymer in acid solution, the reaction time and end reaction point (pH value) is very important in microcapsules' morpha controlling. Overlong reaction time will cause partial emulsion drops broken, resulting the microcapsules agglomerate because of the appearance of epoxy resin. Setting end reaction point at higher pH value leading to obtain large-sized microcapsules with rough and loose MF shell, but at lower pH value will arouse wide size distribution. The optimal end reaction point is at 3.5-4 in pH, and the appropriate time is about 1hr. at that condition, the microcapsules received are spheroidal in shape, and with smooth surface and narrow size distribution.

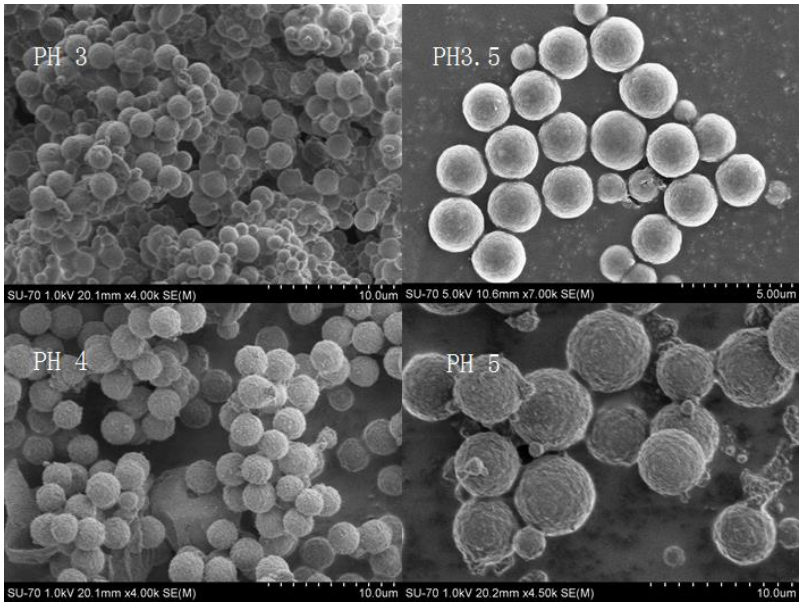


Figure 2: The SEM images of epoxy/MF microcapsules synthesized at different pH values (emulsifier: SDBS+PVA, reaction time: 1hr)

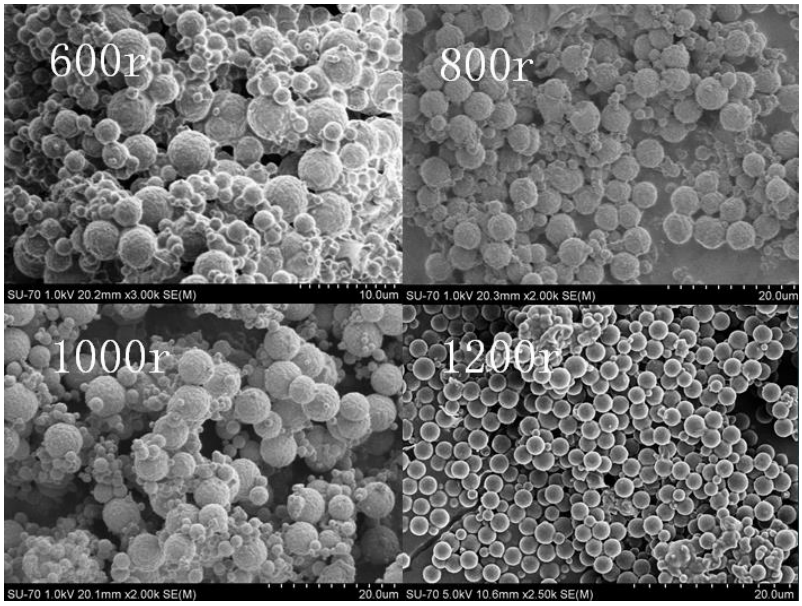
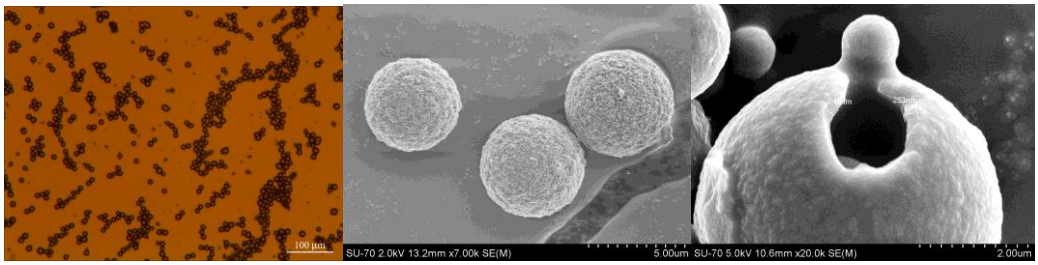


Figure 3: the SEM images of epoxy/MF microcapsules synthesized at different revolution
number of agitator per min (emulsifier: SDBS+PVA, reaction time: 1hr, pH value: 3.5)

3.4 Morphological analysis of epoxy/MF microcapsules

Based on the experiments described above, one of the optimal process to obtain mono-sized epoxy/MF microcapsules can be summarized as follows: adding melamine, formaldehyde and water (molar ratio 1:6.3:105) to a three neck flask equipped with stirrer, thermometer and acidimeter, adjusting pH to 9 by 0.1M NaOH solution, heating to 70℃ at 2℃/min and keep at that temperature for 10min to obtain MF prepolymer, then dissolving 4g SDBS into 100ml water in a beaker, adding 10g epoxy E-51 as core materials, stirred for 10min to emulsify, then mixed with the MF prepolymer, decreasing pH value to 3.5 by 4wt% citric acid dropwise, pump-injected 100ml 4wt% PVA solution at rate of 3.3ml/min while raising the temperature again to 70℃ and keep for 1hr. After standing for 24h, white epoxy/MF microcapsule powders were obtained.



(a) (b) (c)

Figure 4: the image of epoxy E-51/MF microcapsules under (a) optical microscopy, (b) and (c) SEM.

Fig. 4 shows the image of the products. It's clear that the shape of microcapsule is perfect sphere. The particle diameters are narrowly centered on 5μm and the shell is

smooth with thickness about 0.2μm. Calculation tells us the efficiency of core encapsulation is about 92% and epoxy core content of a microcapsule is about 64%.

3.5 characterization of the epoxy/MF microcapsule

FTIR analysis shows, the spectrum of microcapsules is same with that of pure MF resin, no epoxy absorption peak found, indicating all of the epoxy core materials was successfully encapsulated. TG analysis tells us, the microcapsule pyrolysis goes through 4 stages in turn: (1) lost 2wt% adsorbed water under 100℃, (2) Removal of formaldehyde from MF shell at 173.28℃, (3) epoxy E-51 decomposed at 245.98℃, (4) MF shell decomposed at 370.87℃.

4. CONCLUSION

Monosized epoxy E-51/MF microcapsules can be prepared in the emulsion employing right amount of PVA as co-emulsifier. With cooperation of PVA, the shape, size and surface roughness of microcapsules can be easily controlled by changing emulsifying agents or adjusting agitation rate, pH value and reaction time. In an optimal condition, the microcapsules obtained are dispersed and almost monosized. The shape is perfect sphere. However, it should be noted that the particle size is usually less than 10μm. That's too small for application in self-healing concrete. So further work is needed.

ACKNOWLEGDEMENTS

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