THE EFFECT OF PROCESSING PARAMETERS ON THE FORMATION OF EPOXY/UF RESIN MICROCAPSULES

G. Zhu[1], Z. Wu[1], Y. Zhou[1], J. Tang[1], B. Dong[2], N. Han[2], F. 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; tjn@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

Epoxy E-51/UF resin microcapsules were prepared by traditional two-stepped *in situ* polymerization method and processing parameters affecting the final microcapsules' shape and size were carefully studied in the aim to obtain microcapsule with ideally spherical shape and uniform size. It's found the polycarboxylate surfactant of SMA (styrene-maleic anhydride) is better than the monomolecule sulfate surfactant of SDBS (dodecylbenzenesulphonate) in the emulsification of Epoxy E-51, because the microcapsules from epoxy E-51/SMA emulsion possess good sphericity and clear surface. On the second step of reaction, U/F mole ratio should be controlled in 1.5~2:1 region, and ammonium chloride (NH_4Cl) or m-dihydroxybenzene are strongly recommended to be added to strengthen the shell. For a higher encapsulation ratio, acidification time should be controlled in 2~3h and the end-point pH value of the curing reaction should be controlled at 2~2.5, respectively. The core/shell ratio (weight) is optimal at 2:1 and reaction temperature at 60-65°C.

1. INTRODUCTION

Epoxy encapsulated by urea formaldehyde (UF) resin is a typical repairing agent applied in self-healing concrete. The preparation usually is a traditional *in situ* polymerization process with two steps: first, soluble UF prepolymer forms in an alkaline condition; second, the molecules of UF prepolymer cross-links with each other in an acidic condition to form a hard shell on the emulsified epoxy/water interface. As the polycondensation between urea and formaldehyde is a very complex reaction, so far there are many details on reaction mechanism are still unknown. So it's not surprised that attempts made by many researchers to synthesize epoxy/UF microcapsules with desired shape and size are fail. In order to well understand the formation process and reveal which factor governs microcapsule morphology, the controllable parameters in preparation, such as U/F mole ratio, emulsifying agent, pH value, acidification time, *etc*, were systematically investigated in this paper.

2. MATERIALS AND METHODS

2.1 Materials

Bisphenol A type epoxy resin E-51 was obtained commercially and used without further treatment. Analytically pure urea and 37wt% formaldehyde solution were purchased from Aladdin-reagent, Shanghai, China. Surfactant of SDBS, curing catalyst of ammonium chloride (NH_4Cl), m-dihydroxybenzene (used as chain-extender), triethanolamine and citric acid (both used as pH value regulating agent) were analytical reagents received from Tianjin Chemical Plant, China. SMA (Scripset® 520, AR) were imported from Ashlande Inc., USA.

2.2 Preparation of microcapsules

Urea and formaldehyde solution were mixed in a three-neck flask with U/F mole ratio at 1.5~2:1, adjusting the pH value to 8~9 by triethanolamine. The solution was then heated to 70°C and kept at the temperature for 1h to form UF prepolymer.
Add epoxy E-51, 0.4wt% SMA aqueous solution and 10wt% (of urea) NH_4Cl into a beaker. The mixture was stirred at 800rpm for 20min for emulsification. After cooled to 5°C, the resulting latex was mixed with the UF prepolymer, stirred at 300rpm for 2~3h while regulating pH value at 2.5 by citric acid for acidification. Then elevating the temperature at a very low rate of 1°C/3min to 60°C, commence the curing reaction of UF polymer. After another 2~3h, followed by some post-treatments, such as neutralizing with NaOH, filting and drying, the final products of E-51/UF microcapsules were obtained.

2.3 Characterization of the microcapsules

The morphology of microcapsules was observed under Keyence VHX-600K stereo optical microscope and Hitachi SU-20 SEM. The thermal stability and thermolysis temperature were determined by TA DSC Q200/TGA Q50 thermal analyser. FTIR analysis was conducted on Nicolet 6700 FTIR Spectrometer.

3. RESULTS AND DISCUSSION

3.1 Effect of surfactants

SMA and SDBS are the two emulsifying agents widely used in the preparation of UF resin walled epoxy microcapsules, but there is an altercation over which one is better. Fig. 1(a) and 1(b) shows the effects on emulsification of epoxy E-51 are almost same. However, the microcapsules obtained from the emulsion emulsified by SMA are more regular in spherical shape and narrower in size distribution. The shells are more compact and smoother, as Fig. 1(c) , Fig.1(d) and Fig. 5 shown.

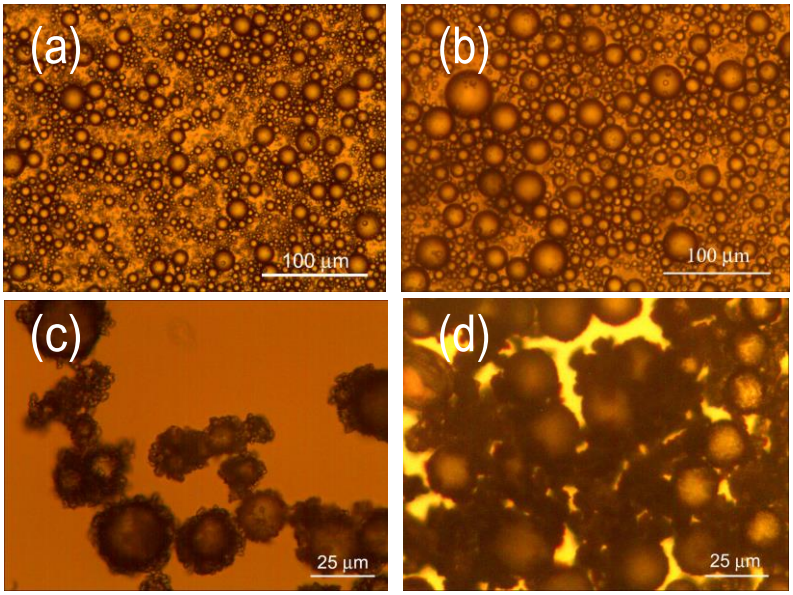

Figure 1: The stereo optical microscope images of epoxy E-51 emulsions [(a) and (b)] and the corresponding microcapsules [(c) and (d)], in which (a) and (c) emulsified by SDBS, (b) and (d) emulsified by SMA.

3.2 Effect of NH_4Cl

Urea reacts with formaldehyde in a complicated way. When the U/F mole ratio locates in 1.5-2:1 region, the UF polymer should be cross-linked, but the degree of crosslinking varies in a large range. In many occasions, the curing process is conducted very slowly, causing the growing microcapsule broken or deformed because the shell is too weak to withstand collision and convection flux. Fig. 2 shows the situation at the very beginning 5mins of the reaction system with U/F mole ratio of 2:1 and pH value of 2.5. It's clear that, the neonatal microcapsule was prone to rupture in flowing solution. It presages the failure of encapsulation or very low encapsulation ratio.

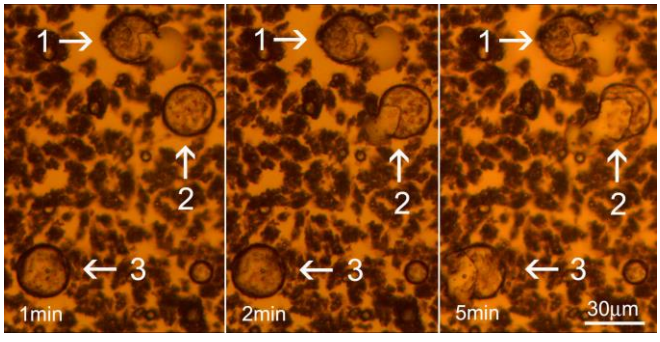

Figure 2: the rupture process of microcapsule shell not strengthened by NH_4Cl

In order to promote the curing reaction, catalyst of NH_4Cl was added. Fig. 3 illustrates the effect. Moreover, the appearance of NH_4Cl changes microcapsule's morphology observably. The microcapsules derived from the reaction with NH_4Cl present a perfect spherical shape and smooth surface (see Fig. 5).

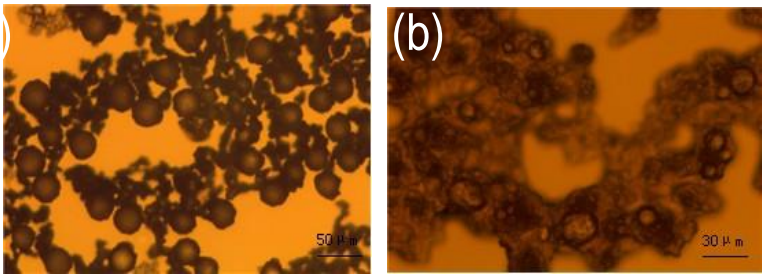

Figure 3: The dried microcapsule powder: (a) with NH_4Cl, (b) without NH_4Cl

3.3 Effect of pH value and acidification time

The formation of epoxy E-51/UF microcapsules is very susceptible to pH value of the reaction end point. At a carefully controlled temperature, a slight fluctuation of pH value will frustrate the encapsulation. In our experiments, the pH value was adjusted or controlled by dilute solution of citric acid added by a precise injection pump.
The acidification time usually should be longer than 1h. Insufficiency in acidification time leads to thin shell of the microcapsules and irregular shape.
As a summary, the optimal processing parameters are as follows:
first step: U/F mole ratio, 1.5-2:1; pH value, 8-9, accurately adjusted by injection of triethanolamine; reaction temperature, 70℃, elevated from room temperature at 1℃ /min; reaction time, 1h; agitation rate, 800rpm. The product (UF prepolymer) is transparent viscous solution.
Second step : (1) emulsification of epoxy E-51. core/shell weight ratio, 2:1; emulsifier, 0.4wt% SMA solution + 10wt% (of urea) NH_4Cl ; agitation rate, 800rpm; emulsifying temperature, 45℃; emulsifying time, 20min; (2) mixture. The emulsion mixed with UF prepolymer solution at 45℃, agitation rate, 300rpm. (3) acidification. pH value, 2.5, accurately adjusted by injection of 0.1M citric acid solution; reaction temperature, 45℃; reaction time, 2-3h. (4) curing reaction. reaction temperature, 60℃, elevated from 45℃ at 1℃/3min, preserved for 2-3h. (5) afterprocessing. neutralized with 0.1M NaOH solution, rinsed with distilled water, filtered, air-dried for 24h.

3.4 Analysis of the microcapsules

On the FTIR spectrum of microcapsule, characteristic peaks of epoxy E-51 in 3000-3100 $cm^{-1}$and 1600-1450cm^{-1} become vestigial while peak at 1643cm^{-1} (allophanyl group) and peak at 3440cm^{-1}(-NH) are clear indicates epoxy E-51 is enwrapped by UF. The powder has a core/shell structure.

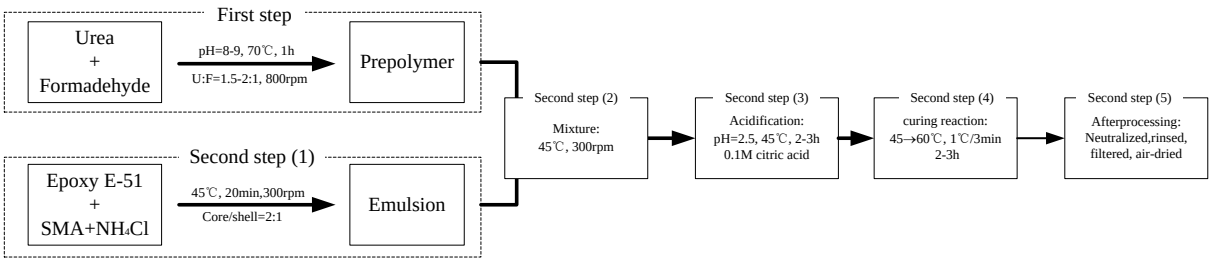

Figure 4: The schematic of the optimal process

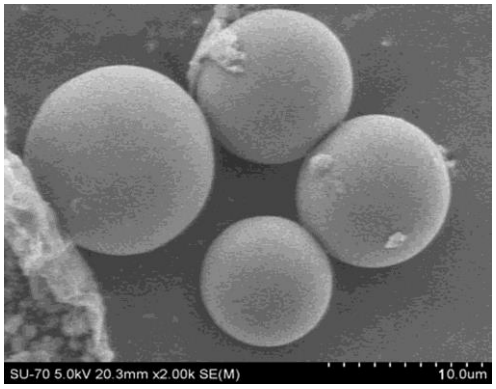

Figure 5: the SEM picture of E-51/UF microcapsules synthesized in optimal process

The TG curve shows, when the microcapsule is heated, epoxy core decomposed at 254.30℃ first, then UF shell pyrolyzed at 356.67℃.

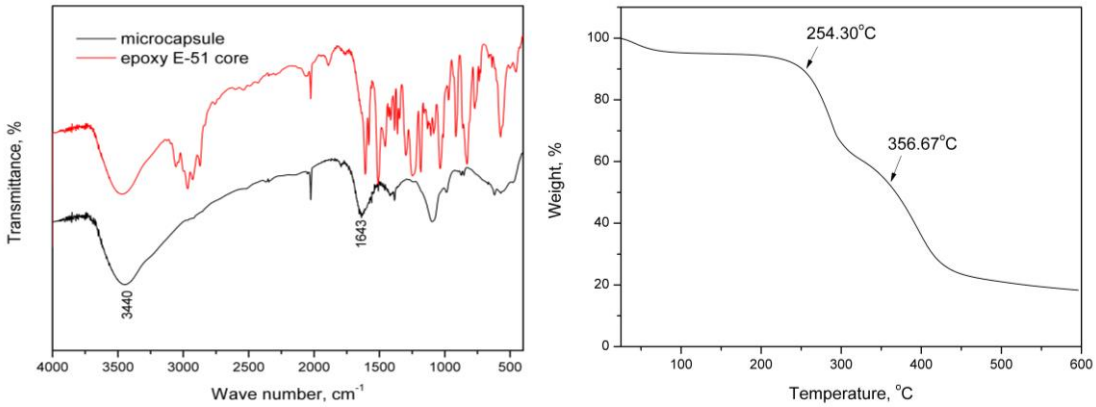

Figure 6: FTIR spectra (left) and TG curve (right) of E-51/UF microcapsules synthesized in optimal process

4. CONCLUSION

Epoxy E-51/UF resin microcapsules were successfully prepared by traditional two-stepped *in situ* polymerization method, and the processing parameters were systematically examined. It's found addition of NH_4Cl promotes the curing reaction greatly and the formation of microcapsule is susceptible to the pH value of the reaction end point. Based on all the experiments, the main processing parameters could be summarized as: pH value at end point controlled at 2.5, acidification time 2-3h, reaction temperature 60℃, agitation rate 300rpm, U/F mole ratio 1.5-2:1, core/shell weight ratio 2:1.

ACKNOWLEGDEMENTS

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