

# SELF-ENCAPSULATION OF EPOXY RESIN BY A CONTROLLED INTERFACE CURING PROCESS IN EPOXY/WATER EMULSION

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## ABSTRACT

The microcapsules of epoxy E-51 resin encapsulated by cured itself were prepared by interfacial curing reaction, in which ethylenediamine (EDA) was employed as curing agent and sulfonated copolymer of styrene and maleic anhydride (SMA) as emulsifying agent. It's found the morphology of microcapsules strongly depend on reaction time and EDA dosage. Usually, the microcapsules were formed in 20mins, Extension of the time doesn't change the morphology but thicken the shell and strengthen the microcapsules. Large dose of EDA bring about smooth surface of microcapsules. It's believed that this simple process to fabricate epoxy microcapsules is more suitable for the application of self healing concrete, because it is ease to be industrialized and can be produced in large scale.

## 1. INTRODUCTION

Epoxy resin is widely used in concrete as the crack repairing agent, but so far, there are no epoxy microcapsules are commercially available to be embedded in concrete for self healing propose. The reason may be traced to the glutinous attribute of epoxy, as adhesive materials is difficult to be uniformly emulsified and effectively encapsulated, especially in the *in situ* polymerization of urea formaldehyde as wall materials. In this paper, a novel and simple method is developed to prepare epoxy/epoxy microcapsule based on the idea of core materials partially hardened at the o/w emulsion interface by the diffusion of curing agent from aqueous phase to oil phase.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Epoxy resin E-51 was industrial reagent and used without further purification. Ethanediamine and acetone were analytical pure reagents purchased from Aladdin-reagent, Shanghai, China. Sulfonated copolymer of styrene and maleic anhydride (SMA, Scripset® 520, AR ) was received from Ashlande Inc., USA.

## 2.2 Preparation of microcapsules

Add 20g epoxy E-51 and 100ml 3wt% SMA solution into a 250-ml three-necked round-bottomed flask with thermometer and mechanical stirred equipment at room temperature. The mixture was then heated to 50°C, and agitated for at least 30mins at 750rpm for emulsification. After that, elevating temperature to 60°C and increasing agitation rate to 300-400rpm, commence the controlled curing reaction by adding EDA dropwise and slowly. After finished, keep stirring at that temperature for 2hr, then cooling and rest for 24hr, skimming off the solution, rinsing the white powder with acetone, then filtered and air-dried for 24 hr.

## 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 the wave number range from 400 to 4000 $\text{cm}^{-1}$ .

## 3. RESULTS AND DISCUSSION

### 3.1 The effect of EDA dosage

EDA is a commonly-used hydrosoluble curing agent for epoxy. However, unlike normal curing process, EDA molecules can't contact with epoxy directly in epoxy/water emulsion. They are supposed to diffuse through the o/w interface comprised of SMA. So it's deduced the concentration gradient of EDA plays an important role in the progress.

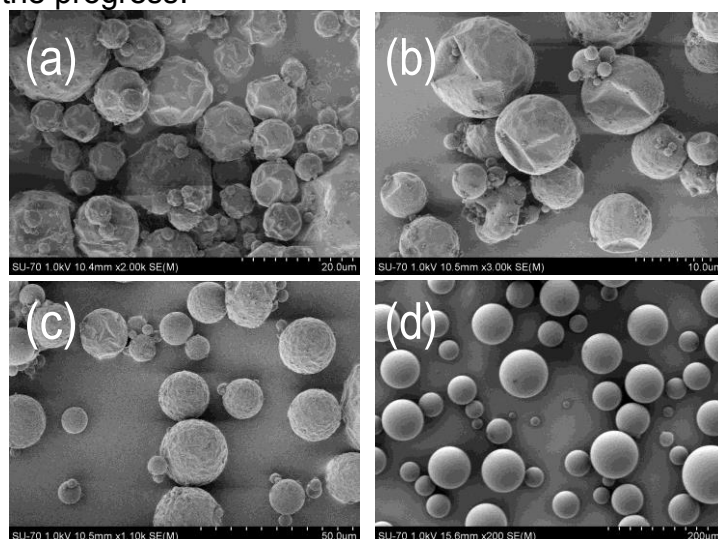


Figure 1: SEM images of the microcapsules synthesized by epoxy reacted for 1hr with different weight ratio of EDA (E-51:EDA): (a) 10:1, (b) 5:1, (c) 4:1, (d) 2:1

Fig.1 clearly shows, with increasing EDA concentration, the microcapsules obtained have better sphericity and more smooth surface. It reveals that small dose of EDA results thin and weak shell, causing the microcapsules were prone to collapse or

crumple in the stirred emulsion. Large dose of EDA not only causes the microcapsules' shell thickened quickly, but also raised the shell's density.

### 3.2 The effect of reaction time

The shell strength of microcapsules enhanced with curing time. At the beginning, the shell is so thin and soft that was ease to be broken or welded with each other because of collision and convection current, as fig. 1 (a)-(c) shown, but after 20mins, the shell is strong enough to keep its shape.

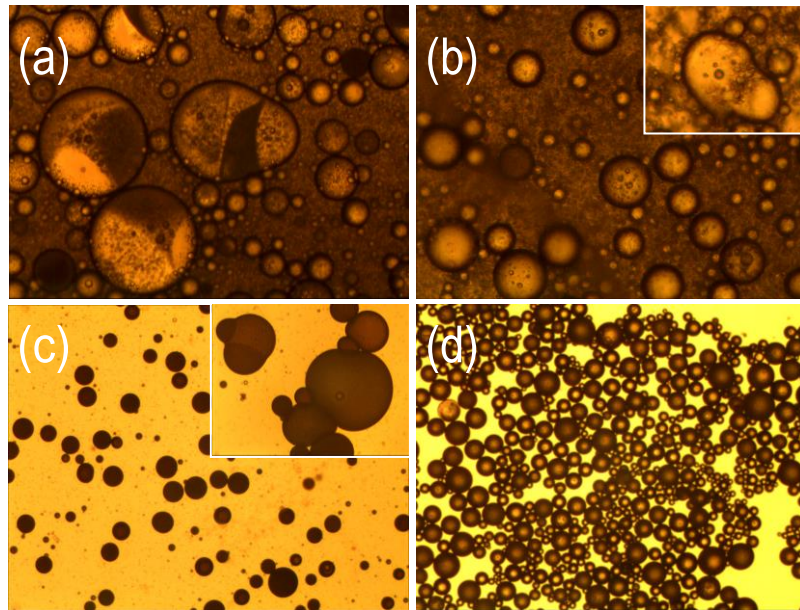


Figure 2: Optical microscope images (100x) of the microcapsules formed at different reaction time (weight ratio of E-51:EDA): (a) 10mins, (b) 15mins, (c) 19mins, (d) 20mins

### 3.3 Analysis of the microcapsules

Fig.3 shows clearly the shell/core structure of the microcapsule. It has a smooth inner surface, and the shell thickness is  $7.78\mu\text{m}$ .



Figure 3: SEM images of a broken microcapsule showing its inner structure.

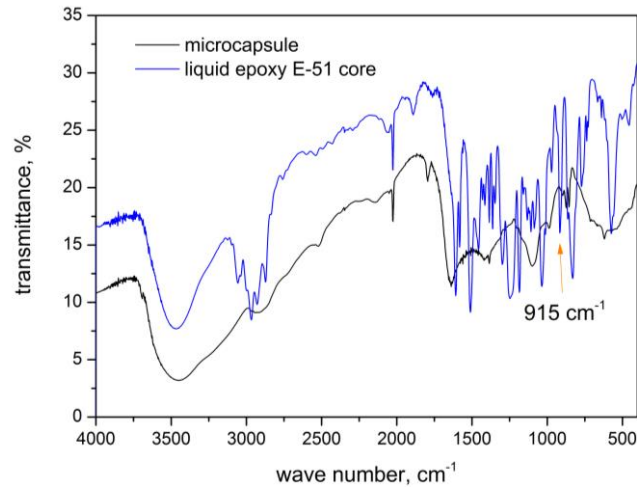


Figure 4: FTIR spectra of epoxy/epoxy microcapsule and the liquid epoxy core.

In FTIR spectrum of microcapsule, the stretching vibration band of epoxy group located at  $915\text{cm}^{-1}$  was disappeared, confirmed the shell was composed of completely-cured epoxy E-51 resin.

Thermal analysis indicates the epoxy/epoxy microcapsule is heat-resistant. The pyrolysis temperature is up to  $343.44^\circ\text{C}$ .

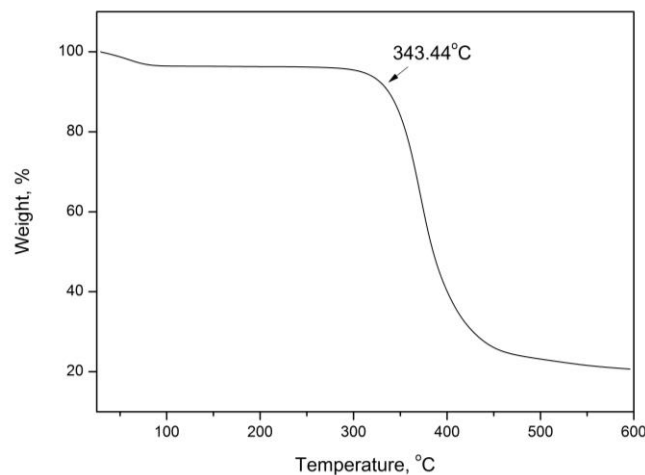


Figure 5: TG curve of epoxy/epoxy microcapsules

#### 4. CONCLUSION

A novel and simple method is developed to prepare epoxy/epoxy microcapsule based on the idea of core materials partially hardened at the o/w emulsion interface by the diffusion of curing agent from aqueous phase to oil phase. The resulting microcapsules are almost consubstantial in shell (solidified epoxy) and core (liquid epoxy), and the size and wall thickness can be adjusted by stirring rate and curing temperature. When weight ratio of EDA to epoxy E-51 is greater than 1:2 and reaction at  $60^\circ\text{C}$  lasts over 20mins, the microcapsules obtained will possess perfect spherical shape and smooth surface. We consider this process is easy to be industrialized it's simpler than the traditional *in situ* polymerization methods in which the shell material is different from the epoxy core.

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