

PREPARATION AND CHARACTERIZATION OF POLY (UREA-FORMALDEHYDE) WALLED DICYCLOPENTADIENE MICROCAPSULES

W. Xiong¹, G. Zhu¹, J. Tang¹, B. Dong², N. Han², F. Xing², E. Schlangen³

¹Shenzhen 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;

²Department of Civil Engineering, Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, Shenzhen University, Shenzhen 518060, PR China

³Delft University of Technology, Faculty of Civil Engineering and Geosciences, Micromechanics Laboratory (MICROLAB), Stevinweg 1, 2628 CN Delft, Netherlands

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ABSTRACT

Poly (urea-formaldehyde) (PUF) shelled dicyclopentadiene (DCPD) microcapsules were prepared by *in-situ* polymerization technology for self-healing concrete applications. It's found, during the process, sodium dodecyl benzene sulfonate (SDBS) behaves better in emulsification of DCPD than other surfactant of sodium lauryl sulfate (SLS) and styrene maleic anhydride copolymer (SMA), and the addition of ammonia chloride (NH₄Cl) as PUF curing catalyst accidentally leads to a smooth surface of the microcapsule.

1. INTRODUCTION

Dicyclopentadiene (DCPD) is a monomer would conduct ring-opening-metathesis polymerization (RPMP) on Grubbs' catalyst, and the resulting poly-DCPD was regarded as a good healing agent. In recent years, there are many researchers are interested in preparation of encapsulated PCPD for self-healing propose^[1-3]. The most PCPD microcapsules are poly (urea-formaldehyde) walled, which is formed by an *in situ* condensation polymerization process. It's well known that, for the microcapsule applied in self-healing concrete, epoxy was commonly used as the core materials. However, because of its glutinous attribute, epoxy is difficult to be uniformly emulsified and effectively encapsulated in the *in situ* polymerization of urea formaldehyde. DCPD is a white crystalline solid with a very low melting point at 32.5°C. DCPD at slightly-elevated temperature is oily liquid with low viscosity, so ease to be emulsified in water, accordingly the shape and size of microcapsule were apt to be controlled. In this paper, DCPD was attempted dispersed in water by different surfactants, and the PUF-walled microcapsules were synthesized to reveal the simplicity or easiness of DCPD encapsulation.

2. MATERIALS AND METHODS

2.1 Materials

DCPD and resorcinol were received from Aladdin-reagent, Shanghai, China, and were used as core materials and PUF curing agent respectively. Urea, 37wt%

formaldehyde solution, triethanolamine (TEA), citric acid, ammonium chloride (NH_4Cl) and all of emulsifiers, including SDBS, SLS, SMA, PVA, are purchased from Tianjin Chemical Plant, China, in which triethanolamine and citric acid were employed to adjust pH value, and NH_4Cl was used as PUF curing catalyst. All the chemicals are analytical pure.

2.2 Preparation of microcapsules

5g urea and 10.1g formaldehyde are mixed in 250ml three-neck flask, TEA was added to adjust the pH value to 8-9, then the solution was heated to 70°C and persisted for 1h, PUF prepolymer solution was obtained.

0.1g SDBS, 0.5g PVA (used as emulsion stabilizer^[4]), 17.4g DCPD are added in 100ml deionized water, stirred at rate of 600rpm for emulsification for 30min. PUF prepolymer solution, 0.5g resorcinol and 0.5g ammonium chloride are then added into the emulsion. The pH value of the solution is adjusted to 3-4 by 5% citric acid and the temperature was raised slowly to 60°C and kept for 2h for *in situ* polymerization. After cooling, the solution was filtered, and the residue was rinsed by warm deionized water, dried in succession at 50°C for 12h. The whole process is schematically shown in Fig.1.

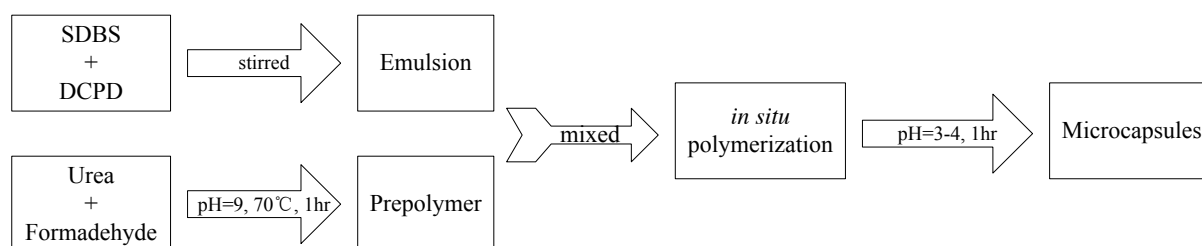


Figure 1: The schematic of preparation of microcapsules

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 Effects of different emulsifiers

Fig. 2 (a)-(c) show the OM images of DCPD oil droplet in water emulsified by SDBS, SLS and SMA respectively, and Fig. 2 (d)-(f) show the OM images of corresponding microcapsules. It is clear that the emulsifying effect of monomolecule sulfate surfactants, such as SDBS and SLS, is much better than the polycarboxylate surfactant, SMA.

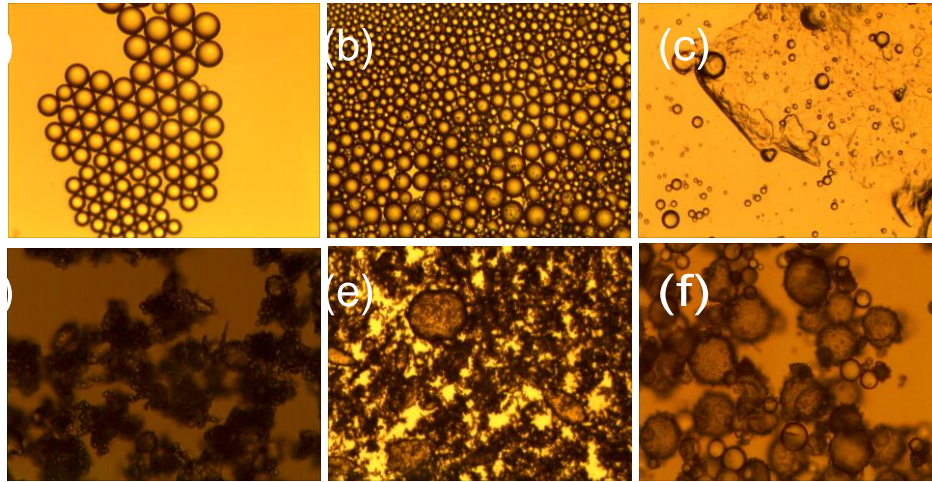


Figure 2: OM images of DCPD oil droplet (200×) emulsified by (a) SDBS, (b) SLS, (c) SMA, and the corresponding PUF/DCPD microcapsules (400×): (d) SDBS, (e) SLS, (f) SMA.

3.2 The influence of NH_4Cl on microencapsulation process

It is well known that NH_4Cl is a curing catalyst commonly used in the cross-linking reaction of PUF resin, but the mechanism is still unknown. Zhou et al regards NH_4Cl promotes the micro-encapsulation reaction comes of the fact it debases pH value^[5]. As there are so much many chemicals can lower pH value, so NH_4Cl is dispensable in the preparation of PUF microcapsules^[6,7]. It's only a curing accelerant. However, in our experiments, it's found NH_4Cl plays an important role in morphology controlling. As shown in Fig. 3 and Fig. 4, the PUF microcapsules synthesized with NH_4Cl presents very smooth surface, meanwhile the microcapsules derived from reaction without NH_4Cl exhibits tough appearance, just like most of PUF microcapsule does. This phenomenon should be brought to the forefront because microcapsule with smooth surface is not appropriate for the application in self-healing concrete.

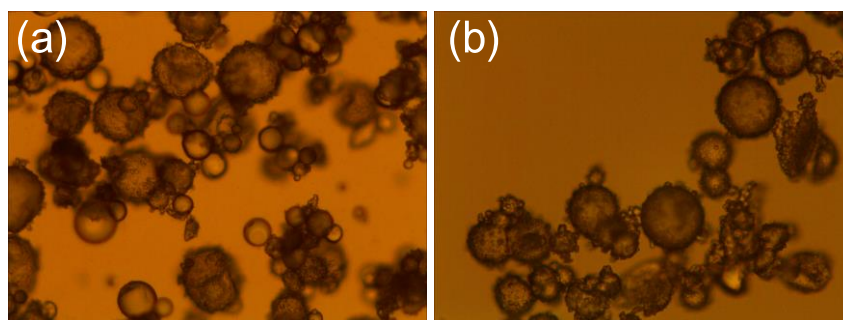


Figure 3: OM images of microcapsules (400×) synthesized (a) with or (b) without NH_4Cl .

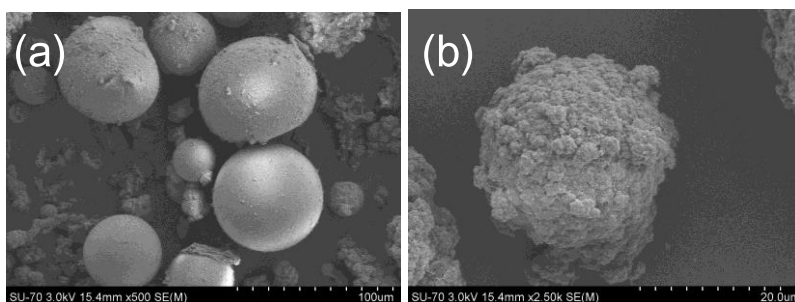


Figure 4: SEM images of microcapsules synthesized (a) with or (b) without NH_4Cl .

3.3 FTIR spectra of microcapsules

On the microcapsule FTIR spectrum, the absorption peaks located at 3060 cm^{-1} and 1630 cm^{-1} belong to of $=\text{CH}$ group, indicating the inner content is DCPD. Existence of the absorption peak of $-\text{NH}$ group at 3240 cm^{-1} and $-\text{OH}$ group at 3500 cm^{-1} affirms the shell of PUF is formed.

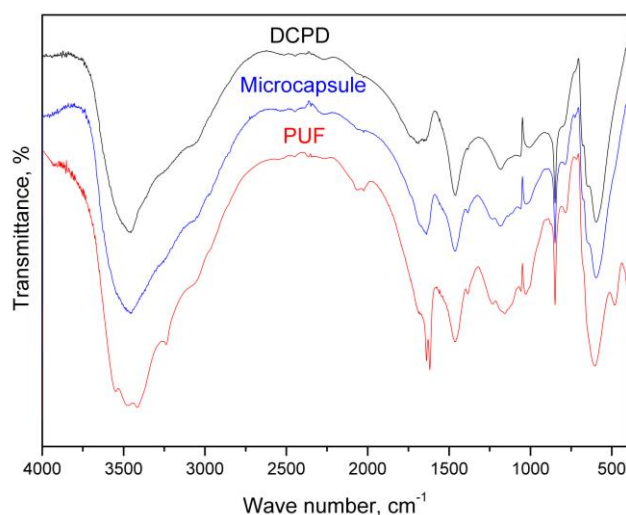


Figure 5: FTIR spectra of the microcapsules and its core and shell materials

4. CONCLUSION

PUF microcapsules filled with DCPD are successfully synthesized. It's found SDBS and SLS are good surfactants for DCPD emulsification in water. Addition of NH_4Cl results smooth surface of microcapsules, brings worry on them to be used in self healing concrete.

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