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Molecular Self-Assembled Microcapsules Prepared by In Situ Polymerization Technology for Self-Healing Cement Materials

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Abstract Monodisperse core–shell microcapsules have been widely used as self-healing cement materials and paid more attentions. A new series of self-assembled microcapsules containing poly(styrene-divinylbenzene) as shell material were prepared by in situ polymerization technology. The microencapsulating process of core material using mixture of epoxy resins and benzyl alcohol was monitored using optical microscopy (OM). Morphology and shell wall thickness of microcapsule were observed using scanning electron microscopy and OM, respectively. The effects of different weight ratios of core–shell and the agitation rates on the physical properties of microcapsules were investigated. The size and surface morphology of microcapsule can be controlled by selecting different processing parameters.

Keywords Molecular self-assembly · Microcapsule · In situ polymerization · Epoxy resins

1 Introduction

Self-healing cement materials as the promising engineering concrete materials [1–5] have attached great importance to the construction and development of the society. The smart concrete, an intelligent material, is a composite of building materials and intelligent science [6–8]. The appearance of self-repairing concrete indicates that the smart concrete has developed to a higher stage. Moreover, the influence of application environment and cyclic loading which concrete suffering from, results in the appearance of micro-cracks and other damage and reduction of the service life of concrete. The research of making damaged concrete adapt for the environment and performing the self-healing is becoming more and more popular, accordingly to enhance the durability of concrete. When cracks appeared in concrete due to force or other factors, the useful life of concrete will decrease. When cracks appear, the self-repairing concrete will excrete phlegm. The phlegm flows into the cracks and makes them heal and restore, and it can even enhance the performance of concrete.

The existing microcapsules have been applied to many fields such as in pharmaceuticals [9–13], catalysts [14–16], dyes [17, 18], etc. because the core materials such as drugs, water, dyes or oils can be protected by the shell of microcapsules from the damages of environment or can be released under a controlled condition. In order to develop new, versatile applications of microcapsules, the microcapsules filled with healing agents offer tremendous potential for providing long-lived structural materials and saving time and manpower used in repairing concrete. Therefore, microencapsulated liquid healing agents, which can be used to fabricate self-healing concrete, have been paid more attentions. Epoxy resins [19–21] are reactive monomers and can be reacted with wide variety of curing agents or hardeners such as amines of differential functionalities and anhydrides at different temperatures. They are extensively used in many applications such as surface coating, adhesive, and laminates for composite materials

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due to excellent mechanical resistance of the cured products and good adhesion to many substrates [22]. So, they may be used as healing agents for the fabrication of self-healing concrete. Moreover, high thermal decomposition temperature of epoxy resins may endow microcapsules with higher thermal stability. In this study, we adopted in situ polymerization technology in an oil-in-water emulsion to prepare microcapsules.

2 Experimental

2.1 Materials

Epoxy resin used as core material was purchased from Wuxi Resin Plant, China. Sodium dodecylbenzene sulfonate (SDBS) (99% purity) and Arabic gum, used as emulsifier, were purchased from Tianjin Damao Chemical Regents Factory, China. Styrene (St) and divinylbenzene (DVB) used as shell materials were purchased from Tianjin Guangcheng Chemical Plant, China. Potassium peroxydisulfate used initiator was purchased from Tianjin Guangcheng Chemical Plant, China. Benzoyl peroxide (BPO) was purchased from Tianjin Damao Chemical Plant, China.

2.2 Experimental

At room temperature (20 °C), 20 mL epoxy resin, 28 mL benzyl alcohol, 1.51 g SDBS, 0.55 g Arabic gum and 80 mL deionized water were mixed in a 250 mL three-neck round-bottomed flask and equipped with a mechanical stirrer. After stirred 0.5 h, 31 mL styrene, 4.3 mL divinylbenzene and 0.5 g benzoyl peroxide were added to the above solution, keeping the N_2 surrounding, while the solution was slowly heated to the target temperature of 60–65 °C. After 5 h, 2 mL 1% potassium peroxydisulfate was added, after 3 h, the reaction was ended. The obtained suspension of microcapsules were cooled down to ambient temperature, rinsed with deionized water and acetone, filtered and air-dried for 24 h.

2.3 Characterization

The microcapsules size distribution and shell thickness were investigated using OM technology, and size analysis was performed using OM on data sets of at least 250 measurements. Morphology of the microcapsules was observed by an XL30 FEG scanning electron microscope (SEM), while their sizes were measured with a MasterSizer 2000 size analyzer.

2.4 Determination of the Microcapsules Core Content

The core content of the resultant microcapsules was determined by extraction with acetone. Firstly, the microcapsule samples were ground with a mortar and pestle at room temperature. A certain amount of the dried and ground microcapsules (W_0) was sealed in a filter paper bag. Then, the bag with the ground microcapsules was dried for 5 h in a vacuum oven at 55 °C, cooled in a vacuum desiccator and precisely weighed (W_1). Afterwards, the sample bag was placed in a Soxhlet apparatus, extracted with acetone for 24 h, and dried in a vacuum oven at 55 °C. After cooling in a vacuum desiccator, the sample bag was weighed again (W_2). Eventually, the core content of the microcapsules, α, was calculated by:

$$\alpha = \frac{W_1 - W_2}{W_0} \times 100\%.$$

3 Results and Discussion

3.1 Size Distribution

Figure 1 shows the size distribution of microcapsule samples. The microcapsule size is in a wide range of 50–360 μm. The reason is that the fluid flow around the propeller is turbulent, in the region of flow away from the propeller, many larger micro eddies exist, and in the vicinity of the propeller blades, many smaller micro eddies exist, which result in a wider length scale. The microcapsules size can be controlled by the adjusting agitation rate. In this study, the mean diameter of the prepared microcapsules is 143 μm.

3.2 Microcapsule Shell Thickness

Wall shell thickness of microcapsule, which determines the mechanical properties of microcapsule and the release

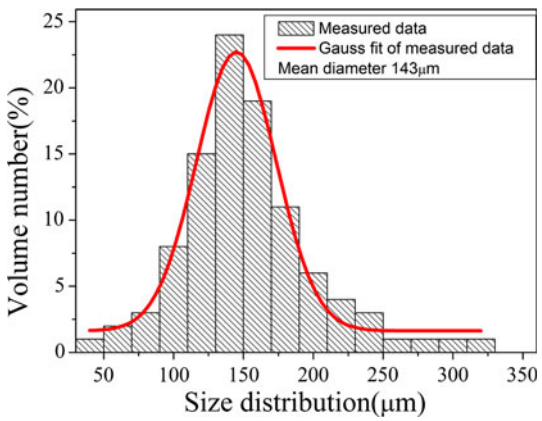

Fig. 1 Size distribution of microcapsule samples

model of core material, largely depends on the manufacturing parameters such as the ratio of core–shell material, agitation rate and so on. Figure 2 shows the OM micrographs of microcapsule samples embedded in epoxy matrix. The black ring area represents the wall shell material. In this study, the wall thickness of microcapsule sample falls consistently between 15 and 40 μm.

3.3 Effects of Initial Ratio of Core–Shell Material

The effect of different initial weight ratios of core–shell material on the size and morphology of microcapsules were investigated. The initial weight ratio of core–shell material is varied from 2.0 to 5.0.

Figure 3a, b shows the SEM micrograph of microcapsule sample. The surface of microcapsule is rough and scraggly, and it is composed of styrene nanoparticles protruding from the surface. The protuberant nanoparticles can increase the surface areas of microcapsules and enhance surface adhesion.

Figure 3 shows the SEM micrographs of microcapsules, indicating that the surface of microcapsule becomes smooth with the increase of core material. Figure 3 shows the relationship of initial weight ratios of core–shell material to microcapsule size. The diameters of microcapsules increase with the enhancement of weight ratio of core–shell material. The main reason is that the size of core droplet in emulsion is larger when the weight ratio of core–shell is higher and the other processing parameters are kept constant. Although the wall shell thickness may decrease owing to the increase of core material, it slightly affects the diameter of microcapsule when the core material obviously changes. But excess core materials cause poor dispersion, promoting aggregation of core droplets, resulting in lower yield of microcapsule sample. Moreover, the microcapsules prepared by selecting higher weight ratio of core–shell material are easily fractured due to the thinner wall shell.

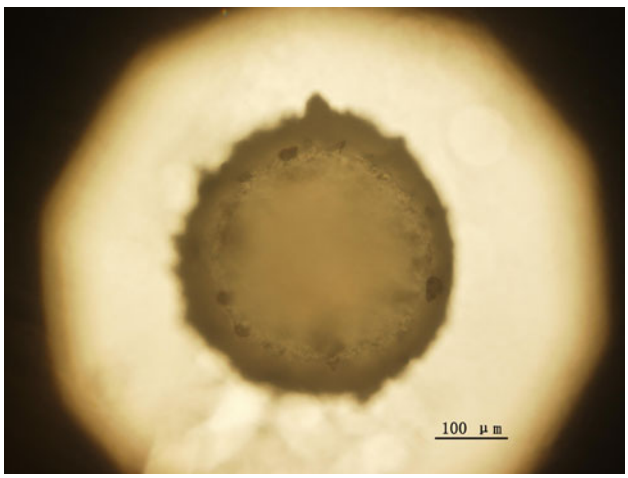

Fig. 2 OM micrographs of microcapsule embed in epoxy matrix

3.4 Agitation Rate

Adjusting agitation rates between 200 and 500 rpm can produce microcapsules with mean diameter in the range of 85–261 μm. Figure 4 shows the size distributions of microcapsules prepared by selecting different agitation rate from 200 to 500 rpm. As the agitation rate increases, the microcapsule size distribution becomes narrow, the microcapsule size decreases and the smaller microcapsules become dominant. The reason is that the epoxy resins come under larger shear stress and their sizes are smaller when the agitation rate is higher, and accordingly, the prepared microcapsule diameters become smaller.

3.5 Stability

The weight loss of microcapsules is about 1.03 wt% at room temperature for 80 days, and the longer of exposed time, the larger of weight loss of microcapsules, indicating that the microcapsules exposed to room temperature can maintain well in 80 days. The weight loss of microcapsules heat-treated increases with the enhancement of heating temperature and time, indicating that the microcapsules cannot be exposed to heat surrounding timelessly, which cause the larger weight loss of microcapsules. The main reason of weight loss of microcapsules at different temperatures is the diffusion of core material throughout the wall shell.

4 Conclusions

Microcapsules filled with epoxy resin by in situ polymerization of styrene and divinylbenzene in an oil-in-water emulsion were prepared to develop the self-healing concrete composites. During the microencapsulation process, the epoxy resins are hardly affected by the surrounding media and the use of microcapsules is potential. The rough outer surface of microcapsule is composed of styrene nanoparticles. The size and the surface morphology of microcapsule can be adjusted by weight ratio of core–shell and agitation rate. In general, this research provides novel microcapsules for the self-healing composites and the effects of the microcapsules on the polymeric composites will be further examined in our future study.

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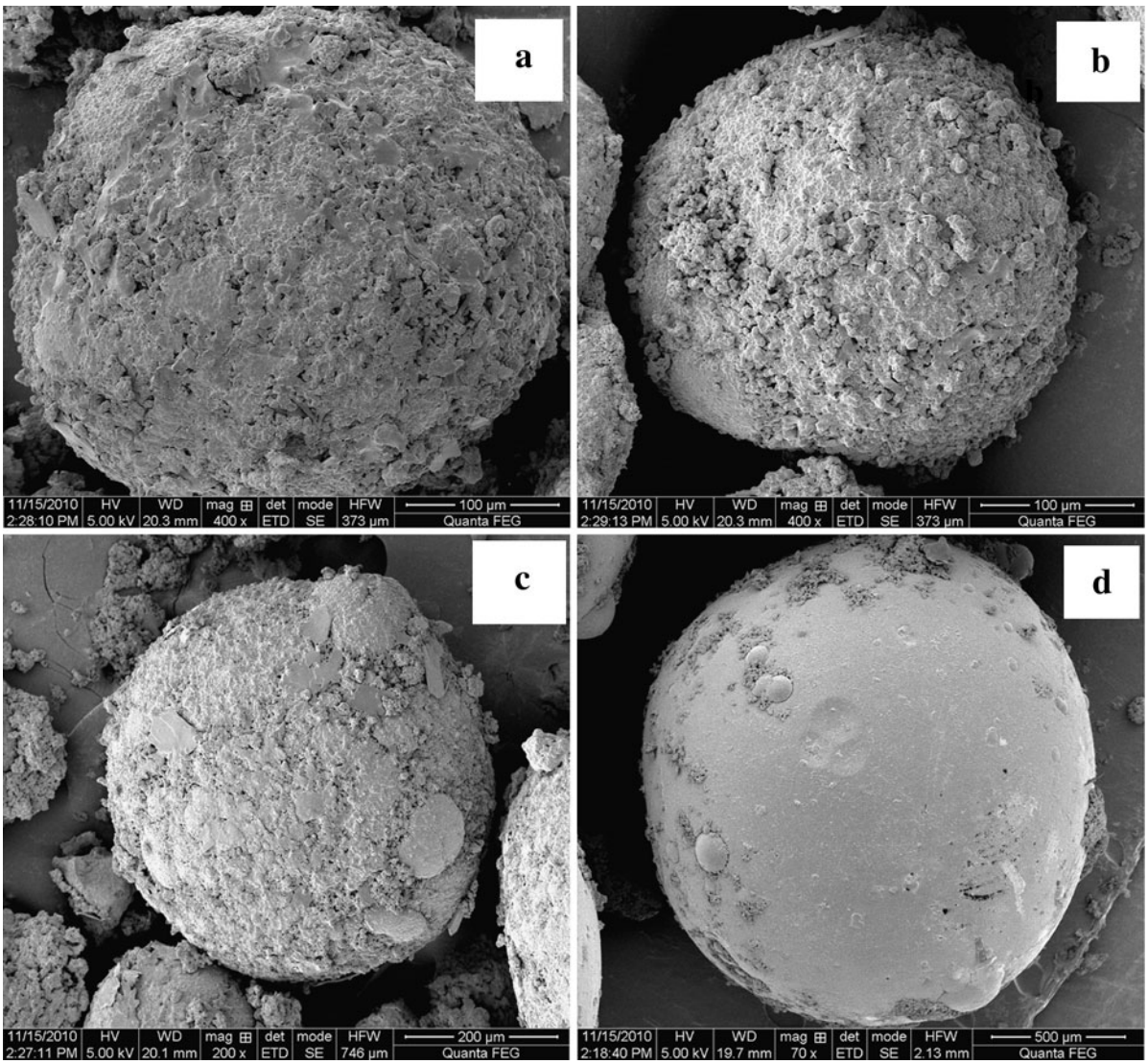

Fig. 3 SEM micrographs of microcapsules with different ratios of core–shell materials (**a** 2, **b** 3, **c** 4, **d** 5)

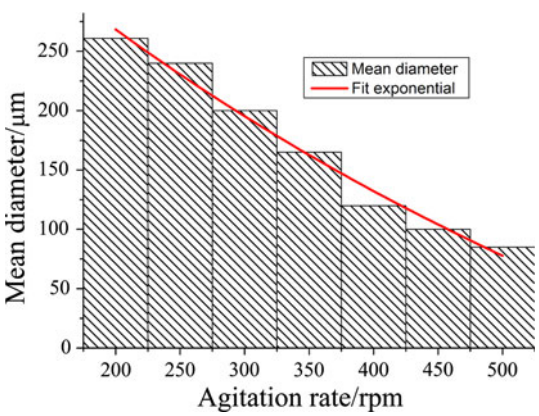

Fig. 4 Mean diameter of different agitation rate

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