Study on poly (urea-formaldehyde) microcapsules embedded self-healing composite

Haiyan Li, Rongguo Wang, Xiaodong He, Wenbo Liu
Center for composite materials, Harbin institute of technology, Harbin, P.R. China 150001

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Abstract

The aim of this study was to develop a novel microcapsules applied to self-healing composites. The microcapsules were synthesized by In-situ polymerization technology with poly(urea-formaldehyde) (PUF) as a shell material and dicyclopentadiene (DCPD) as core materials. The effect of processing parameters on the microcapsule's performance was analyzed. The chemical structure of microcapsule was characterized using fourie-transform infrared spectroscopy (FTIR), Morphlogy and shell wall thickness of microcapsule were observed using scanning electron microscopy (SEM). The thermal properties and the stability were analysis using thermal gravity analysis (TGA). The results indicate that PUF microcapsules containing DCPD can be synthesized successfully.

1 Introduction

Polymer composites pressure vessel are susceptible to microcracking in the process of repeating use. Microcracks often lead to some damage including fiber/matrix debonding and ply delamination [1] which will result in the life-span decreased. The microcracks are deep into within the structure where detections and repair are very difficult. Self-healing polymers and composites with microencapsulated healing agents offer tremendous potential for providing long-lived structural materials [2]. Microcapsules have been applied to many fields such as electronic inks, dyes, food additives, pharmaceuticals etc.[3] 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. There are many methods to autonomic repair the microcrack such as employing a solid-sate repair system for a thermosetting resin, embedding hollow fibers filled with healing agent, embedding microcapsules in composite matrix [4, 5]. In this study, we adopted in-situ polymerization technology in an oil-in water emulsion to prepare PUF microcapsules filled with DCPD.

2 Experimental

2.1 Materials

DCPD used as core material was purchased from Hangzhou Yangli chemical company, China. Urea (U) and 37wt% formaldehyde (F) used as shell materials were purchased from Tianjin Chemical Plant, China. Ammonium chloride, used to control the pH of solution, was purchased from Harbin Chemical Plant. Styrene/maleic anhydride copolymer (SMA) used as dispersant was prepared in our laboratory. Triethanotamine(TEA), used to control the pH of solution, and sodium dodecylbenzene sulfonate (SDBS) (99% purity), used as emulsifier, were purchased from Tianjin Chemical Regents Factory, China. All the materials are commercial products and were used without further purification.

2.2 Preparation of Microcapsules

PUF microcapsules were prepared by In-situ polymerization technique.

- At room temperature, Urea (U) and 37wt% formaldehyde (F) were mixed in a 250 ml there-neck round-bottomed flask with the reflux condenser and mechanical stirred equipment. The weight ratio is U: F=1:2. The pH of mixed solution was adjusted to 8-9 with TEA. The temperature of system was raised to 70℃, and kept for 1 h, and then the U-F pre-polymer solution was obtained.

- PUF microcapsules were prepared in the acidic condition. The process of preparation was list in figure 1.

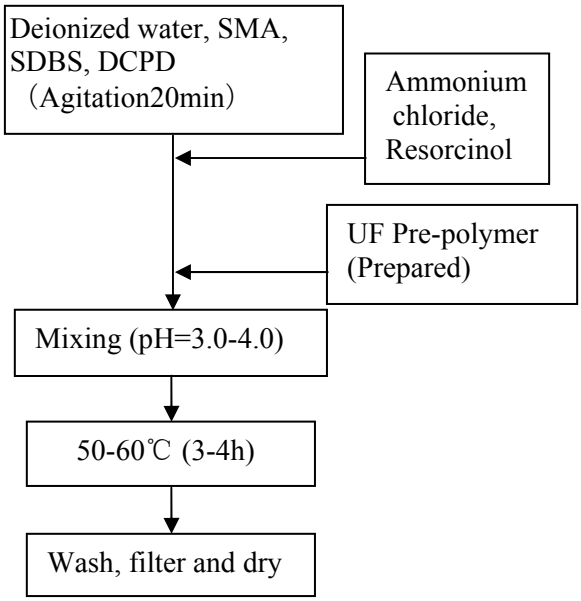

Fig.1. Polymerization process of UF microcapsules

2.3 Characterization

Microcapsule size analysis was performed with optical microscope. The size distribution and average size of microcapsules were measured. Surface morphology and capsule shell thickness were examined by scanning electron microscopy (XL 30 ESEM-FEG, PHILIPS). The infrared spectrometric analyzer (EQUINOX-55) was used to identify the chemical structure of DCPD and UF microcapsules. The thermal properties and the stability were analysis using thermal gravity analysis (ZRY-2P), microcapsules samples were combusted at a heating rate of 10℃/min from 20-600℃.

3 Results and Discussion

3.1 Microcapsules Diameter

The diameters of microcapsules and the size distribution were infected by many factors, such as temperature of reaction, ratio of heated, ratio of agitation. Among these factors, the ratio of agitation was the most important. The relationship between diameter and agitation rate was obtained. The average microcapsule diameter was controlled by agitation rate between 200-1000 rpm as shown in figure 2. A linear relation exists between log (mean diameter) and log (agitation rate).

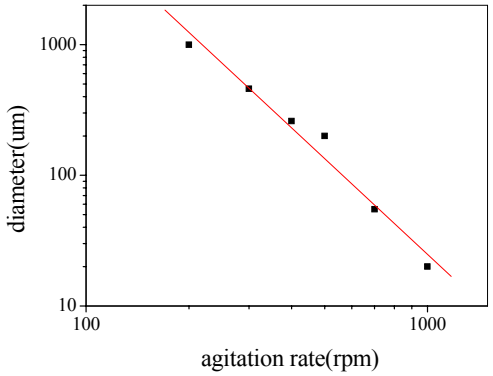

Fig.2.Mean microcapsule log(diameter) vs. log(agitation rate).

3.2 Surface Morphology and Thickness

Figure3 and figure 4 were the surface morphology of microcapsule observed by OM and SEM. At the same time the thickness can be measured by SEM.

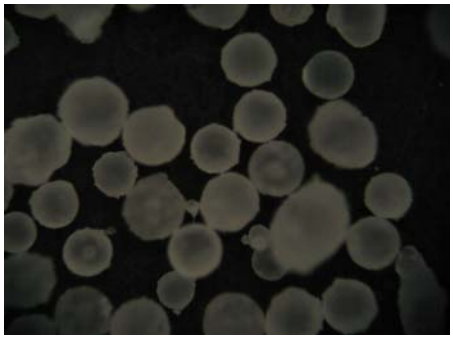

Fig.3.OM image of microcapsule

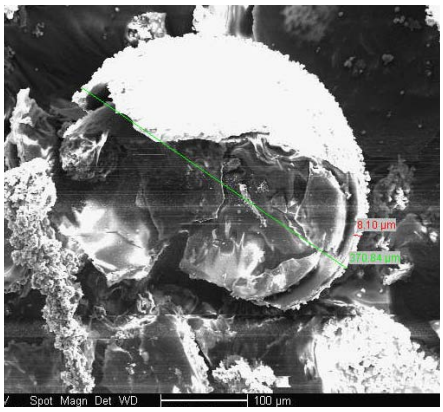

Fig.4.SEM image of rupture microcapsule

The shell wall thickness was in the range of 5-10 µm by measuring many ruptured microcapsules, which is larger than the report by White [1].

3.3 Chemical Structure of Microcapsule

The chemical structure of DCPD and microcapsules were studied by using a FTIR spectrometer as showed in figure 5. The sample was prepared by grinding with a potassium bromide (KBr) or by attaching sample to a KBr disc.

For the microcapsules product, the peak at 3386 cm^{-1} is characteristic of –NH , The highlighted peak at 2962 cm^{-1} is characteristic of –CH. There existed the peak of -CH from DCPD, which is weak, indicating the formation of new –CH. The highlighted peak at 1645 cm^{-1} and 1550 cm^{-1} are characteristics of –C=O and –CN- functional group respectively. The four primary peaks at 3386 cm^{-1}, 2962 cm^{-1}, 1645cm^{-1} and 1550 cm^{-1} indicated the formation of UF. Comparing the DCPD Infrared spectrum with microcapsules products, the cycloolefin characteristic peak of H-C= at 3050 cm^{-1} and the peak of double bong of dicycolpentadiene at 1620 cm^{-1} were found. The peaks at the 2930 cm^{-1} and 1050 cm^{-1} were the characteristic of fatty saturated hydrocarbon C-H and the C-H. These characteristic peaks indicated that the core of DCPD has been packed.

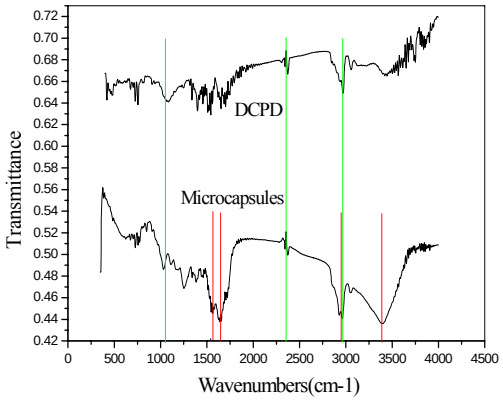

Fig.5.IR spectra of DCPD and urea- formaldehyde microcapsules.

3.4Thermal Behavior Analyses

Thermal stability of DCPD, UF and microcapsules were examined by TGA. The TG curves of three materials were showed in figure 6.The loss in weight of DCPD occurred at temperature of 55℃-200℃. The rate of loss in weight was quick. The decomposed of UF wall occurred from 60℃ and it didn't conclude until 600℃. For microcapsules, the first lose in weight occurred at temperature of 64℃-132℃. The reason was there existed unpacked DCPD, absorbable water outer microcapsules surface and partial wall material. The curve decrease slowly at temperature of 132℃-215℃, indicating there are a little lose in weight of UF wall and no lose in weight of DCPD. So the core of DCPD was packed well. The rate of loss in the weight was quick at 215℃-260℃ because the wall was cracked and the core of DCPD was decomposed. The rate of loss in weight was slower than the single DCPD because of the enveloped effect of wall. The wall material was decomposed again after 260℃and it didn't conclude until 600℃.

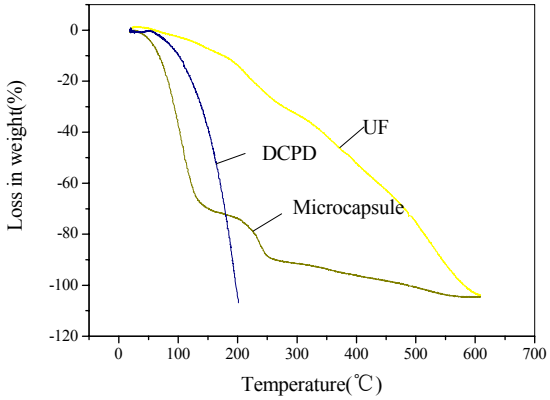

Fig.6. TAG of DCPD, microcapsules and UF

4 Conclusions

1. Urea-formaldehyde resin encapsulated DCPD healing agent (210μm in diameter) can be successfully prepared by pre-polymerizing urea and formaldehyde.
2. A linear relation exists between log(mean diameter) and log(agitation rate). The means size is about 210 μm at agitation rate of 500rpm.
3. The surface of microcapsules was smooth and compact as the diameter was small; the wall thickness was measured as 5-10 μm by SEM. Infrared spectrum and thermal behavior analyses of DCPD and microcapsules verified the formation of wall and the partial healing agent had been packed.

References

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