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Optimization of synthesis technology to improve the design of asphalt self-healing microcapsules

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HIGHLIGHTS

- A synthesis technology for preparing asphalt self-healing microcapsule was put forward.
- The microcapsules prepared by optimal synthesis technology do enhance the self-healing capability of the asphalt.
- The microcapsules prepared by optimal synthesis technology have high thermal stability and storage stability.

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ABSTRACT

Microcapsules are considered as a potential method to enhance self-healing capability in asphalt materials. This study aims to investigate the optimization of self-healing microcapsule synthesis technology. According to prepolymer synthesis test results, the melamine-urea-formaldehyde (MUF) terpolymer, which contains 20 wt% urea, is selected as shell material. Fluorescence Microscope (FM) is employed to observe the rejuvenator emulsion and prepared microcapsules. The result reveals that Sodium Dodecyl Sulfate (SDS) has the best emulsion performance and can be determined as emulsifier of core material. By means of FM and microcapsule size calculation, sixteen sets of microcapsules prepared under different conditions are investigated to determine the optimization of reaction condition. The optimal MUF microcapsule is synthesized under core/shell ratio as 2:1, end point reaction temperature as 65 °C, emulsifying speed as 1500 r/min, emulsifier content as 0.7% and end point pH as 3. Scanning Electronic Microscope (SEM) result shows that the microcapsules are spherical and intact without damage. Fourier Transform Infrared Spectroscopy (FTIR) result indicates that with the increase of core/shell ratio, shell material in microcapsules becomes less. Thermo-gravimetric analysis (TGA) result shows that the mass loss of microcapsules is not distinct after maintained at 180 °C for 1 h, indicating that the optimal microcapsules can meet the temperature requirement of asphalt mixing and compaction. Finally, the self-healing process of microcapsules in asphalt binder is observed to prove the healing efficiency.

1. Introduction

Microencapsulation technology is one of the most widely studied self-healing techniques developed in the past twenty years [1]. Generally, microcapsules have diameters ranging from 3 to 800 μm and composed of 10 to 90 wt% core materials [2].

So far, a wide variety of microcapsules containing different shell and core materials have been developed, among which polymeric shells and epoxy cores are the most widely investigated. Microcapsules were initially invented to enhance self-healing capability in polymers and composites [3]. White et al. [3] prepared dicyclopentadiene-filled microcapsules with urea-formaldehyde (UF) shell to incorporate into cracked epoxy matrix. The fracture experiments yield as much as 75% recovery in toughness using these microcapsules and Grubbs' Ru catalyst. Based on this previous study, it was found that the size and concentration of microcapsules strongly affect fracture toughness [4]. One year later, those microcapsules were proved to prolong fatigue life of self-healing epoxy matrix with a carefully timed rest [5]. Urea-formaldehyde walled microcapsules have limited heat resistance and complicated preparation process. Therefore, melamine-formaldehyde (MF) resin and melamine-urea-formaldehyde

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(MUF) polymer were developed to be shell constituents of microcapsules [6,7].

There are various microcapsules synthesis methods such as in-situ polymerization [3,8–13], complex coacervation [14–16], interfacial polymerization [17,18], adsorption [19–21] and emulsion/solvent evaporation method [22]. Among these numerous methods, in-situ polymerization is considered to be the easiest, lowest-cost and the most effective method. Thus, in-situ polymerization is the most broadly used and investigated to synthesize self-healing microcapsules. According to previous studies, the average diameters of microcapsules are typically less than 500 μm. Core constituents are typically rejuvenators and shell constituents are polymers such as UF, MF or MUF mentioned above. The in-situ polymerization process of microcapsules can be divided into two steps: (i) dissolving applicable emulsifier into water and adding rejuvenator to the emulsion. Then stirring at required speed for a definite time to obtain a uniform and stable core emulsion. (ii) adding the prepolymer (shell material) to the emulsion, then stirring under the condition of changed temperature and pH, causing polycondensation reaction on the surface of the core materials. The prepolymer shapes cross-linked structure to form microcapsule shell with enough thickness and strength. White et al. [3] synthesized UF microcapsules by in-situ polymerization. They adjusted pH of the emulsion to 3.5 by means of NaOH solution. The reaction mixture was stirred at 454 rpm and the temperature after adding formaldehyde was raised from room temperature to 50 °C. These microcapsules had average diameter as 220 μm with 80% yield. On this basis, the method was improved by Brown et al. [4,23]. The temperature was changed to 55 °C and pH of the reaction mixture was 2.6–3.5. It was found that average sizes of microcapsules ranged from 10 to 1000 μm as adjusting agitation rate from 200 to 2000 rpm, which was also proved to affect the yield. Liu et al. [7] introduced synthesis of MUF microcapsules containing 5-ethylidene-2-norbornene (ENB)-based core healing agents. The agitation rate was set to 500 rpm and reaction temperature was set to 86 °C. These MUF microcapsules had diameters in the range of 113–122 μm. In addition, MUF microcapsules were proved to exhibit superior thermal stability and mechanical properties compared to UF microcapsules.

Based on the successful applications of microencapsulation techniques in polymers and composites, some researchers have considered microcapsules as a potential method to enhance self-healing capability in asphalt materials [9,10,24–29]. The microcapsules used in the asphalt mixture have special requirements on the structure and properties. Shell thickness, size and surface morphology of microcapsules have effect on their fracture behavior as well as release efficiency of rejuvenators. Su et al. [10] considered that the diameter of microcapsules should be controlled within 50 μm because thickness of asphalt membrane between aggregates in asphalt mixture is about 50 μm. Hence, they controlled diameter of microcapsules ranging from 5 to 23.5 μm. While, Chuang et al. [9] and Shirzad et al. [27] produced microcapsules, whose diameters were greater than 100 μm. Besides, Al-Mansoori et al. [28,29] prepared calcium-alginate microcapsules containing sunflower oil with the diameter of 2.9 mm. Their microcapsules were both proved successfully enhancing asphalt concrete self-healing capability. It has been found that agitation rate is the main influencing factor of microcapsule sizes. Precisely, higher agitation rate produces smaller microcapsule size. The pH of emulsion is regarded as one of the main factors for the microcapsule surface morphology. Su et al. [25] found that lower core/shell ratio and slower prepolymer dropping speed contributed to better thermal stability of microcapsules based on TGA (thermogravimetric analysis) investigation. Appropriate strength of microcapsules is the key to their application in asphalt mixture. Su et al. [10] investigated the strength of microcapsules by nanoindenter, and found that microcapsules with larger sizes and thicker shells had higher Young's modulus.

In this paper, we focused on the optimization of melamine-urea-formaldehyde (MUF) microcapsules synthesis technology via an in-situ polymerization method. The optimal mass ratios of core materials and shell materials were discussed. The properties

Table 1
Properties of rejuvenator used in this study.

Binder	135 °C Viscosity/Pa·s
Neat asphalt	0.549
5 h TFOT-aged asphalt + 3 wt% rejuvenator	0.492
24 h TFOT-aged asphalt + 3 wt% rejuvenator	1.095

Table 2
Prepolymer synthesis test.

Code	Mass ratio of urea /%	Mole ratio F: (M + U)	The time it takes for generating massive polymer/min
Sample 1	0	3.0	20
Sample 2	10	2.7	38
Sample 3	20	2.5	80
Sample 4	30	2.3	95
Sample 5	80	1.6	120
Sample 6	100	1.4	145

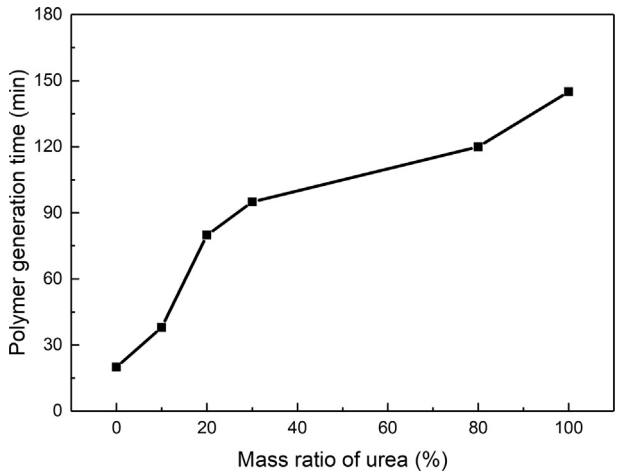

Fig. 1. Effect of urea content on polymer generation time.

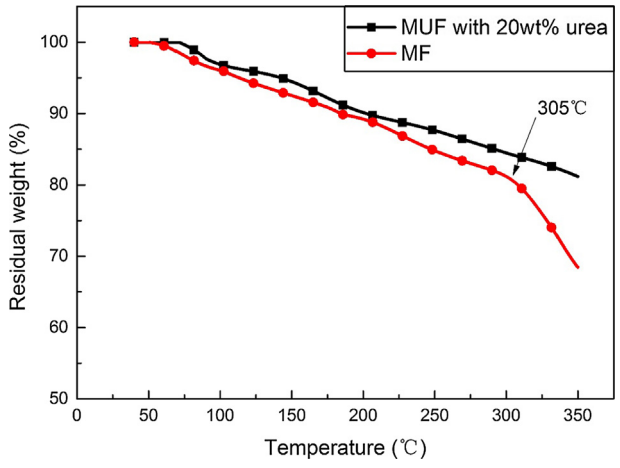

Fig. 2. TGA results of MUF and MF.