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Design, preparation and properties of microcapsules containing rejuvenator for asphalt

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HIGHLIGHTS

- Microcapsules of asphalt regenerator with urea resin wall were successfully prepared.
- A crack would lead to release the healing agent so that the damaged portions can be coalesced.
- The core/shell ratio, pH and temperature have significant influence on microcapsule preparation.
- Microcapsules can improve the performance of asphalt pavement.

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ABSTRACT

In order to repair the cracks that were caused by the vehicle load and natural environment in the asphalt pavement, a microcapsule containing urea–formaldehyde resin as a core material based on an in situ polymerization method was proposed and prepared for use in self-healing materials. When a crack ruptured the microcapsules, it would lead to a release of the healing agent so that the damaged portions can be coalesced. The shell thickness and shell density increased by adding more prepolymer in the fabrication process. The optimum synthetic conditions were carefully explored to study the microcapsule properties. The thermal stability results indicated that the decomposition temperatures of the microcapsule samples were higher than the melting temperature of asphalt. The healing efficiency was improved by the optimal dosage of microcapsule 38.67%. We conclude that the microcapsules affected the cracks in the asphalt pavement, which would save on maintenance costs and improve the performance of asphalt pavement.

1. Introduction

Asphalt concrete is a composite material that is widely used in civil engineering. Asphalt acts as a binder mixing together with aggregates. Under the effect of vehicle load and natural environment, asphalt would become brittle and crack because the material performance declines. Therefore, continuous efforts are being made to prevent the occurrence of cracks. One of the most effective ways to produce an autonomous self-healing material is to store a rejuvenator inside microcapsules that can partially restore the material properties upon the formation of cracks [1].

The microcapsule method is inspired by biological materials with self-healing capacity [2]. White reported that an autonomous self-healing microcapsule was ruptured by cracks, releasing the healing agent to the crack surface by capillary action [3]. The microcapsule should possess the following properties [4]: First, the microcapsule shells must have a higher thermal stability to resist the melting temperature and a higher mechanical strength to resist the mixing pressure of asphalt in practical application. Second, the shells should break when a microcrack appears or else a macro-crack may be triggered, and shells cannot be ruptured without releasing the rejuvenator.

The microcapsules must meet some specific requirements, such as size distribution, encapsulation ratios and core/shell ratios because these factors would directly influence the performance of the microcapsules [5]. A previous study indicated that the mechanical strength of microcapsules depends on their size [6]. In addition, the shell structure of microcapsules, including thickness, density and molecule structure, can influence the mechanical strength and thermal stability of microcapsules [7,8]. Therefore, we should optimize the parameters for good microcapsule performance. Microcapsulations of an asphalt regenerator with a urea–formaldehyde resin wall were successfully prepared by an in situ

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method in this work. We researched the influence of reaction conditions, such as the emulsifier type, stirring speed, and core/shell ratio, on the microcapsule morphology and performance. A self-healing ductility test was carried out to verify the repairing ability of the prepared microcapsules.

2. Experimental

2.1. Materials

Sodium dodecyl benzene sulfonate (SDBS). Formaldehyde, resorcin, ammonium chloride, hydrochloric acid, sodium hydroxide and octane. The composite rejuvenator, denoted as REA, was prepared in the laboratory by blending lightweight oil containing a high content of aromatics with a chemical compound containing polar epoxy group (see Table 1).

2.2. Fabrication of microcapsule-containing rejuvenator

Urea (1 mol) and formaldehyde (1.5 mol) were placed in a three-necked round-bottom flask containing a certain amount of deionized water. Then, sodium hydroxide aqueous solution was added to adjust the pH value to 8–9. The mixture was stirred in a water bath at 70 °C. After 70 min, urea–formaldehyde prepolymers were obtained. A certain amount of regenerator, deionized water and surfactant were mixed, adjusting the pH to neutral. Then, a high-speed shear apparatus was used to stir the mixture for approximately 15 min in a 50 °C water bath. Finally, an oil-in-water emulsion system was obtained. The regenerator emulsion was placed in another three-necked round-bottom flask. The mixture was continuously stirred to stabilize the emulsion. Then, urea–formaldehyde prepolymers were prepared, and 2 drops of octane-defoaming agent were slowly added to the mixture.

A peristaltic pump was used to control the dilute hydrochloric acid flow to tune the pH value to near 4. At the same time, the reaction temperature was raised to 70 °C and maintained for 3 h under continuous agitation. Then, the system was cooled to room temperature and was filtered and washed several times. Having been dried at room temperature in a dry cupboard, the ultimate microcapsules were produced.

2.3. Optical morphology (OM)

An optical microscope was used to check the fabrication process of microcapsules in emulsion. Approximately 1 ml of the colloidal solution was extracted and spread onto a clean glass slide (3 × 3 cm).Various images were taken at different stages of the microcapsule-forming process.

2.4. Scan electron microscopy (SEM)

The dried microcapsules were adhered onto double-sided conductive adhesive tape without cracking the shells. The surface morphologies were observed using a JSM-5610LV at an accelerated voltage of 20 kV.

2.5. Average size of microcapsules

For each microcapsule sample, the average diameter is the mean value of the valid microcapsules that were measured from the SEM morphology image.

2.6. Shell thickness and density of microcapsules

The thickness and density of shells are also critical properties for the thermal stability and compactness of microcapsules. It is unacceptable for the rejuvenator to leak or penetrate outside, losing shell protection. The shell thickness of the microcapsule was determined by numerical calculations according to the Madan theoretical formula [9].

$$h = \frac{m_w}{m - m_w} \times \frac{\rho_c}{\rho_w} \times \frac{\bar{d}}{6} \quad (1)$$

where h is the shell thickness of the microcapsules, m is the weight of the microcapsules, m_w is the weight of the shell, ρ_w is the density of the shell, ρ_c is the density of the rejuvenator, and $\bar{d}$ is the average size of the microcapsules. The dispersion degree of microcapsules is also a repair effect factor that could influence the uniform distribution in the repair matrix, and good dispersion can evenly distribute the microcapsule throughout the matrix. At a microcapsule fracture stimulated by rupture, the regenerator can outflow from the shell and spread evenly around the cracks of asphalt softening, so as to achieve repair. In contrast, microcapsule dispersion was poor in the matrix, with cracks having little or no microcapsules, and even if there were many fractures due to cracks, the regenerator could not completely improve the properties and repair effect of asphalt. Therefore, it is necessary to verify the dispersion of microcapsules, and the number of microcapsules per unit area is used to characterize the dispersion density of the microcapsules in the paper.

2.7. Thermogravimetric analysis (TG)

Thermal stability characterization of microcapsules was performed on a NETZSCH STA 449C at a scanning rate of 10 °C min^{-1} with an N_2 flow of 20 ml min^{-1}.

2.8. Mechanical properties test

The nanoindenter (Multifunctional Nanomaterials Test 600, Micro Materials Ltd, UK) was used to form curves and extract the mechanical properties of the microcapsule and its shell. The core of the nanoindenter is a nanometer probe that is designed for data collection. The microcapsules were fixed with epoxy resin, and the surface was kept clean and smooth at 25 °C for 24 h carefully separated on a smooth glass slide. Another glass slide with a thin layer of strong glue was used to conglutinate the separated microcapsules. A Berkovich tip was used to process the indentation testing. At the beginning of the tests, the microscope was turned on to find a single microcapsule. Then, the tip slowly shifted to the surface of the single microcapsules. The load that was placed on the indenter tip increased as the tip penetrated further into the specimen and soon reached a user-defined value. The indentation depth was 1500 nm, the largest load rate was 0.2 m s^{-1}, the time for the load was 5 s, and the experimental conditions are presented in Table 2.

3. Results and discussion

3.1. The effect of the core material emulsion stirring speed on the average size of the microcapsules

Compared to the aqueous solution, the regenerator viscosity was too great for the mechanical mixing regenerator to fully emulsify the aqueous solution; thus, the regenerator emulsification in aqueous solution was completed by a high-speed shear emulsifying machine. The emulsion stirring rate in the emulsion state directly affects the droplet size in the emulsion solution and determines the particle size of the microcapsule product. In order to explore the effect of the stirring rate on the droplet size, Figs. 1–3 shows the average diameters of the microcapsule (core/shell ratio of 1.5/1) under various emulsion stirring rates of 200 r/min, 500 r/min and 800 r/min.

When the stirring speed was 200 r/min, the droplet size increased slightly, and the droplet number decreased; thus, the droplet distribution could not be reflected. Therefore, 325 valid data points were collected as shown in Fig. 1(a). According to the data analysis, it is concluded that the droplet size distribution histogram and the fitting curve were calculate with $\sigma_{200} = 19.105$ as shown in Fig. 1(b). The size distribution of the droplet is very extensive and mainly ranges from 5 μm to 35 μm. In addition, there are also many droplet diameters greater than 35 μm, and a

Table 1
The physical properties and chemical components of the rejuvenators.

	Index	REA
Physical properties	Flash point (°C)	>220
	Viscosity changing ratio after TFOT aging	1.6
	Weight loss after TFOT aging (%)	1.7
Chemical components	Saturates content (%)	14.3
	Aromatics content (%)	61.1
	Resins content (%)	15.8
	Asphaltenes content (%)	8.7

Table 2
Condition and number of nanoindentation tests.

Sample	Depth of impression (nm)	Load speed (0.2 mN s^{-1})	Load time (s)
Microcapsules	1500	0.2	5
Epoxy resin	1200	0.1	5