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Fabrication and characterization of self-healing microcapsules containing bituminous rejuvenator by a nano-inorganic/organic hybrid method

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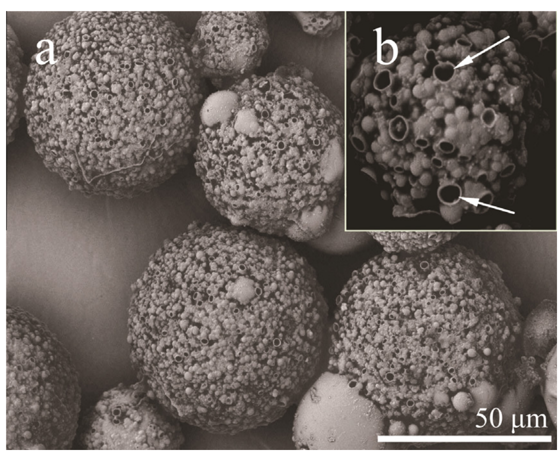
HIGHLIGHTS

- Self-healing microcapsules containing rejuvenator were fabricated with nano-inorganic/organic hybrid shells.
- The mechanical and thermal properties of these microcapsules had been improved.
- The nano-particles on microcapsules decreased the deformation possibility of shells.

GRAPHICAL ABSTRACT

ESEM morphologies of microcapsules with 10% nano-$CaCO_3$ composite shells.



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ABSTRACT

The aging problem of bitumen leads to pavement failure after years of usage. Microcapsules containing rejuvenator is a promising chemical product applied to improve the self-healing ability of bitumen. The aim of this work was to fabricate and characterize the self-healing microcapsules containing bituminous rejuvenator with nano-inorganic/organic hybrid shells. The shell had a two-layer structure: the inside layer material was the cross-linked methanol modified melamine-formaldehyde (MMF) resin and the outside materials was composed of methanol modified MMF resin and nano-particles of calcium carbonate (nano-$CaCO_3$). The forming mechanism of the two-layer structure was described based on a twice-condensation process. Fourier transform infrared spectroscopy (FT-IR) and Energy Dispersive Spectroscopy (EDS) results confirmed the nano-inorganic/organic hybrid structure of shells. The ideal content of nano-$CaCO_3$ particles was optimized through the morphologies observation. The addition of nano-$CaCO_3$ particles did not greatly influence the mean size of microcapsules. On the contrary, the nano-$CaCO_3$ particles increased the shell thickness of microcapsules owing to the loosely composite structure of shells. Thermal stability tests showed that the microcapsules could survive in the bitumen

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with a temperature of 200 °C. Moreover, the microcapsules could resist a violent temperature change process without destruction attributing to the protection of nano-$CaCO_3$ particles. The nano-particles on microcapsules decreased the deformation possibility of shells tested by nanoindentation.

1. Introduction

Bitumen is the most common surface material of the pavement. After some years of use, the bitumen becomes brittle and cracks occur owing to a result of oxidation of the binder and the mechanical failure of the load repetition [1]. It will lose service-life without timely reparation or cracks elimination. Bitumen itself owns an inherent self-healing ability, which depends on its physiochemical properties. However, the self-healing ability is rather complex influencing by environmental temperature, loading and aging [2]. Hereinto, the aging problem of bitumen leads to pavement failure, including surface raveling and reflective cracking. It therefore increases the cost of renovating and preserving bituminous pavements [3]. In recent years, several physical and chemical attempts have been carried out to improve the self-healing ability of bituminous materials [4]. One of the most effective methods arouses researches interest: mixing powder microcapsules containing rejuvenator in asphalt [5]. The self-healing mechanism was the microcapsules broke by microcracks and leaked the oily-liquid rejuvenator into microcracks [6,7]. With the help of capillarity, the rejuvenator filled the cracks with a movement speed mainly determined by the volume of microcapsules in bitumen. A diffusion phenomenon was also observed by using a fluorescence microscope. Rejuvenating agents have the ability to reconstitute the binder's chemical composition and they consist of lubricating and extender oils that contain a high proportion of maltene constituents [8]. In other words, rejuvenator can soften the aged binder and provide comprehensive rejuvenation that replenishes the volatile and dispersing oils while simultaneously promoting adhesion [9].

In view of the above facts, several approaches have been reported to fabricate capsules containing rejuvenator for bitumen. García et al. [10,11] found a method to prepare rejuvenator capsules by using an epoxy resin as a coating and porous sand as a skeleton. Pei et al. [12] fabricated microcapsules containing rejuvenator using urea-formaldehyde resin as a shell material based on an in-situ polymerization. To produce microcapsules containing rejuvenator by chemical means, the cost, complexity, and capacity must be considered for the construction industry. This core-shell structure powder needs to meet specific requirements in terms of size distribution, encapsulation ratio, and non-biodegradability because the factors influence their service performance [13]. Based on these considerations, Su [14] reported a method of fabrication microcapsules using a modified melamine-formaldehyde (MMF) resin as microcapsule shell material. The shell was synthesized through a twice polymerization method, which was named as a two-step coacervation (TSC) [14]. The design and construction of microcapsules containing rejuvenator were systematically described [6]. For example, it was found that a lower MMF-prepolymer dropping rate made a better homogeneity of the microcapsules. The hardness and Young's modulus results of single microcapsule indicated that the MMF shell had an elastic-plastic deformation character. The size and shell thickness were two main factors influencing the micro-mechanical properties of the microcapsules. Interestingly, a novel multi-self-healing behavior was found in bitumen/microcapsules composites because the microcapsules could break at different time [15].

Bitumen is a binder between mineral aggregates, which usual has a temperature of 180 °C in a melting state. On the other hand, the microcapsules need an ability to resist an external force keeping their integrity in asphalt [6]. Therefore, excellent thermal stability and mechanical properties are necessary demands for the microcapsules. It has been proved in previous report [9] that MMF-microcapsules own an appropriate thermal stability with a decomposition temperature beyond the melting temperature of asphalt (180 °C). Excess demands still motivate researcher to fabricate microcapsules surviving in bitumen with complex and rigidity conditions.

A literature review shows that the inorganic/organic composite may be an efficient structure for microcapsules with improved thermal and mechanical properties [16]. Relative researches indicated that the thermal stability, mechanical property and chemical resistance of microcapsules could be regulated by the addition of inorganic particles such as nano-clays, nano-SiO_2, nano-$CaCO_3$, carbon nano-tubes, nano-Al_2O_3 [17–20]. All these microcapsules had a nano-composite shell structure. Considering the operational practicality and economic applicability of the particles, the nano-$CaCO_3$ powder was usually selected as the addition. Yu et al. [21] had synthesized microcapsules with the nano-$CaCO_3$ in shells, which had good performances of anti-osmosis and service durability. However, the pure inorganic microcapsules with calcium carbonate shell cannot be satisfied with non-permeable need owing to its porous structure [22]. Long et al. [23] synthesized microcapsules with the nano-$CaCO_3$/polymer shells. It was found that the nano-$CaCO_3$ made the shell with lower permeability and higher mechanical strength. Moreover, the low cost and easy availability are also advantages of nano-$CaCO_3$ particles besides its high performance [24]. All these results indicate that nano-$CaCO_3$/polymer composite shell may be a feasible way to form microcapsules with satisfying properties.

Herein, an approach was reported to explore simple, cheap, robust and environmental-friendly microcapsules containing rejuvenator with the enhanced thermal stability and mechanical properties applied in asphalt. The main aim of this work was to design the reliable microcapsules using a nano-inorganic/organic hybrid method. The shell structure was composed of methanol modified melamine-formaldehyde (MMF) resin and nano-$CaCO_3$ particles, which was adjusted by polymerization process and nano-$CaCO_3$ content [23]. The relationship between shell structure (morphology, thickness and diameter) and shell properties (thermal stability and mechanical property) was investigated systematically.

2. Experimental

2.1. Materials

The core material used as rejuvenator is dense, aromatic oil (density is 0.905 g/cm^3, viscosity is 4.25 Pa s) obtained from Shanghai Zili Chem Co., Ltd. (ERA-C, Shanghai, China). The core material was emulsified by styrene maleic anhydride (SMA) co-polymer (Scripset® 520, Hercules, USA) [3]. The shell material of microcapsules was commercial prepolymer of methanol modified melamine-formaldehyde (MMF, solid content was 78.0%) purchased from Aonisite Chemical Trade Co., Ltd. (Tianjin, China). The nano-$CaCO_3$ powder was supplied by Tianjin Yuoer Technology Co., Ltd. (20 nm, Tianjin, China). The bitumen used in this study was 80/100 penetration grade obtained from SINOPEC QILU Co., Ltd. The aged bitumen 40/50 penetration grade was artificially produced by thin film oven test [3,15].

2.2. Microcapsules fabrication process

The method of fabrication microcapsules containing rejuvenator was conducted by a coacervation precede, which could be divided into three steps [6]: