Smart Self-Healing Asphalt Composite Materials Using Microcapsules Containing Rejuvenator

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ABSTRACT

Microcapsules containing rejuvenator are particles, which can be used to enhance the self-healing capability of asphalt. The aim of this work was to directly observe the distribution and stability states of self-healing microcapsules in asphalt binders. Asphalt samples were prepared by mixing bitumen and various weight contents of microcapsules. Experimental tests were carried out to investigate the morphology, integrity, distribution, thermal stability and interface bonding of microcapsules in asphalt binders. Fluorescence microscope morphologies and X-ray computed tomography images showed that microcapsules were homogenously dispersed in asphalt binders without particles aggregation and adhesion. Moreover, microcapsules survived in asphalt resisting high temperature and strong agitation without premature damage. A circular heating-cooling process tests showed that microcapsules still kept a stable state after an extreme temperature change simulating temperature changes in the natural environment. In addition, interface deboning phenomenon did not appear. These results indicate that microcapsules containing rejuvenator can satisfy the requirements of using in asphalt binders.

1. INTRODUCTION

Asphalt is widely used pavement material. Because of the effect of natural environment, loading and other factors, asphalt becomes brittle and microcracks will generate in the asphalt pavement [1]. It is well known that bitumen has a self-healing naturality. Its capability of self-healing is associated with temperature, healing time and aging degree of itself. The aging problem of bitumen will damage the asphalt original properties. Comparing with the deterioration process, this healing capacity of bitumen is not enough to repair the damage like surface raveling and reflective cracking which are caused by aging. Therefore, several methods have been used to improve the self-healing capability of bituminous materials, including rejuvenation, polymer blend, heating induction, and nanoparticles [2]. It has been found that microcapsules containing rejuvenator is one of the most effective methods [3]. In previous researches, it was found that oily rejuvenators nearly could not penetrate into the asphalt pavement more than 2 cm [4]. Encapsulation rejuvenator mixed in bitumen may be an alternative method not only to promote repair capacity but also overcome the disadvantages of oily rejuvenator. When micro-cracks encounter capsules in the propagation and open them, the rejuvenating agents fill the cracks with the help of capillarity; at the same time the released rejuvenator reconstitutes the asphalt binder's chemical composition caused by aging [5].

Several approaches have been reported on exploring novel microcapsules by chemical method. García et al. [6, 7] reported a work to fabricate capsules containing oily rejuvenator using epoxy resin as a coating material and porous sand as a skeleton material. However, the rejuvenator could not be easily released from the porous sands while the capsules were broken owing to extreme viscidity of healing agents. Sun et al. [8] reported a method to fabricate microcapsules using melamine-formaldehyde (MF) resin as shell material. It was also reported by Pei et al. [9] that the core/shell structure of microcapsules could be fabricated by healing agents and melamine-formaldehyde resin. In the previous researches, MF resin is adhered on the surface of liquid core droplets through an in-situ polymerization [10-12]. The mechanism of fabrication of capsules is named as a one-step polymerization (OSP) [13]. However, this structure of microcapsules cannot satisfy with non-penetration in the asphalt pavement. In order to obtain higher compact shells, Su [14] fabricated self-healing microcapsules with a methanol modified melamine-formaldehyde (MMF) resin as shell material which was synthesized through a two-step polymerization (TSP). The formation of shells would be a two-step coacervation due to the interfacial equilibrium. The rigidity and toughness of shells was promoted by using MMF resin.

Bitumen is an asphalt binder, which has a melting point of 180°C. It can be illustrated that self-healing microcapsules need excellent thermal stability and mechanical properties to keep their integrity in asphalt when melt blending with bitumen. It was showed that the size of microcapsules, the shell thickness and the core/shell ratio are the main factors for the stability of microcapsules [15]. In the previous researches, the inorganic/organic composite structure was found to be an efficient shell structure to improve the thermal and mechanical properties of microcapsules [16]. For example, microcapsules had been fabricated with a nano-CaCO3/polymer shell structure [17]. The size of microcapsules did not greatly effect by the structure of microcapsules with nano-inorganic/organic shells. Comparing with that, it was varied that the shell thickness increased owing to the addition of nano-$CaCO_3$. Moreover, microcapsule shells could resist a higher temperature and protect microencapsulated rejuvenator. It was noted that the addition of inorganic enhanced interaction resulting in promoting adhesion between the asphalt and the microcapsules [18]. The self-healing mechanism of asphalt using microcapsules was investigated by mechanical tests; self-healing process contained four steps: the crack generation, microcapsules broken, rejuvenator release and rejuvenator capillarity-diffusion [19]. Oily rejuvenator flowed along cracks with the help of capillarity and diffused into the aging bitumen [5].

Although many efforts have been carried out to investigate microcapsules containing rejuvenator in bitumen, the states of microcapsules in asphalt mixture have not been studied. Asphalt mixture is a composed of asphalt binder, aggregate particles and air voids. Self-healing process in asphalt mixture normally occurs in the binders. After several years of use, bituminous material loses part of visco-elastic capability. At the same time, microcracks occur and develop at the interface between binder and aggregates. Therefore, microcapsule states in asphalt concrete play an important role in the healing process. In view of the above, the purpose of this work was to analyze the morphology, distribution, thermal stability of microcapsules in asphalt binders. In addition, microcracks were generated to examine the state of microcapsules in binders. Based on the above observation, it conclusion can be deduced about the application possibility of the self-healing microcapsules in asphalt.

2. EXPERIMENTAL METHOD

2.1 Materials

Bitumen was supplied by Qilu Petrochemical of China. The aged bitumen sample (40/50 penetration grade) was artificially produced with 80/100 penetration grade bitumen using a thin film oven method [5]. Rejuvenator (0.905 g/cm^3, 4.24 Pa·s) was obtained from Shanghai Chem. Co., Ltd. of China. Methanol melamine-formaldehyde (MMF) was supplied by Aonisite Chemical Trade Co., Ltd. (Tianjin, China). Styrene maleic anhydride (SMA) was applied as dispersant copolymer (Scripset® 520, Hercules, USA) [14]. Nano-$CaCO_3$ powder (mean size 20 nm) was purchased from Tianjin Sinago Technology Co., Ltd. of China.

2.2 Microcapsules fabrication process

The method of fabrication microcapsules containing rejuvenator was divided into three steps [20]: (1) SMA powder was added into 50 °C water mixing for 2 h, and then the solution was adjusted pH value to 10 by NaOH. Oily rejuvenator was added with a stirring rate stirring speed of 500 r·min^{-1} for 10 min. (2) The above emulsion was transferred into a three-neck bottomed flask. MMF resin was added with a stirring speed of 300 r·min^{-1}. At the same time, temperature was elevated to 80 °C with a speed of 2 °C·min^{-1}. (3) The polymerization was kept for 2 h, and then the temperature was decreased to room temperature. At last, microcapsules were filtered and dried in a vacuum oven.

2.3 Preparation of asphalt samples mixing with microcapsules

Bitumen (40/50) was blended with microcapsules and aggregate particles using a propeller mixer at 165 °C. The mixtures were put into a mold which has lubricants in its inner wall. The mold was installed at the gyratory compactor (AFGC125X, PINE, U.S.) for 100 gyrations under the pressure of 600 kPa. Asphalt samples had a diameter of 100 mm and a height of 67 mm.

2.4 Morphologies observation

The surface morphologies of microcapsules were observed using an Environmental Scan Electron Microscopy at an accelerated voltage of 20 kV (ESEM, XL30, Philips). Self-healing process was analyzed by using a fluorescence microscope (CKX41-F32FL, OLYMPUS). As bituminous material was temperature sensitive, the observation was controlled in an environment under 0 ^{o}C.

2.5 X-ray computed tomography (XCT)

XCT is a microscope that the internal structure of materials can be obtained by X-ray scanning [21]. It can be found the distributed state of self-healing microcapsules in asphalt by XCT. XCT is mainly composed of three parts, including scanning part (X-ray tube, detector and gantry), computer system and image display and storage system. X-rays is generated by the X-ray tube from different directions through the specimen and detected by the detector. Scanning information is stored in the computer. Image is displayed on the screen, which is processed and reconstructed by computer. By comparing X-ray attenuation intensity before and after scanning, the contour information can be obtained, and the contour information is processed to obtain scanning images of the specimen. CT images reflect the extent of absorption of X-rays to the sample with different gray level. Shadow indicates low absorption region, namely low-density areas; the white represents high absorbency zone, that is, high-density areas.

2.6 Microcapsules stability in asphalt

Various microcapsule/asphalt samples were made to test their thermal stability. A thermal absorbing-releasing method was carried out to analyze the thermal stability using a temperature controlled chest [15, 19]. This method also was successfully applied to test the thermal stability of microcapsules in epoxy [22]. The asphalt samples were heated to 50 ^{o}C and kept for 10 min, and then decreased temperature to -10 °C. The increasing and decreasing temperature speed both was 2 $^{o}C\cdot min^{-1}$. The above increasing-decreasing treatment was repeated 60 times for each sample. After the absorbing-releasing process, a piece of asphalt peeled off and heated to 150 ^{o}C. The melting bitumen was spread on a glass sheet. A fluorescence microscope was used to analyze the morphologies of microcapsules in melting bitumen.

3. RESULTS

3.1 Morphologies of microcapsules containing rejuvenator

In this study, self-healing microcapsules were prepared by in-situ polymerization method using MMF shell. Hydrolyzed SMA was used as an amphiphilic polymeric surfactant. SMA was hydrolyzed by NaOH and absorbed at the oily droplets interface. Rejuvenator droplets owned strong electron negative, which reduced the oil/water interfacial tension. Rejuvenator droplets were formed by high-speed stirring. The oil droplets absorbed MMF prepolymer in order to balance the charge. The coacervation polymers were cross-linked and then formed shells under the effects of acid and heat.

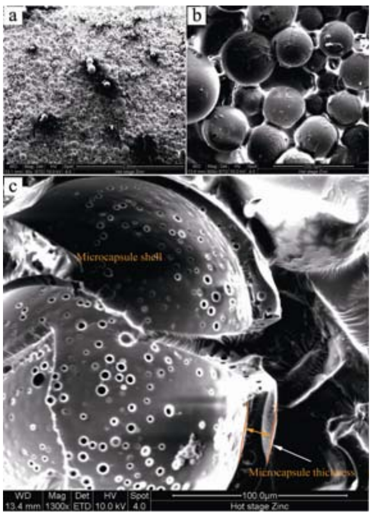

Fig.1 ESEM morphologies of microcapsules containing rejuvenator, (a, b) microcapsules containing rejuvenator with mean size of 50 μm, (c) shell structure of a break microcapsule.

Fig.1(a,b) show ESEM surface morphologies of microcapsules. They keep a regular global shape with a mean size of 100 μm. Shell surfaces were compact and smooth with little adherend. Core-shell structure can be recognized form a break microcapsule in Fig.1(c). It means that the oily rejuvenator has been microencapsulated by polymeric shell material. Usually, larger microcapsules may be more likely to break or crack. Polymer shells can not maintain integrity under an ultimate mechanical strength or thermal stimulation. Therefore, it is important that the microcapsules keep regularity and have the appropriate mean size and shell thickness. For example, the mean size of self-healing microcapsules in asphalt needs to be less than 100 μm avoiding squeeze rapture [5]. It has found that the shell thickness could be controlled by the amount of shell materials [14]. Therefore, all microcapsules in this study had the same core/shell ratio of 2:1 to simplify the complexity.

3.2 Morphologies and integrality states of microcapsules in asphalt binder

Fig.2 shows microcapsule sample (Fig.2a) and asphalt samples (Fig.2b) mixing with various contents of microcapsules. The diameter of samples is 100 mm and the height is 67 mm. The addition ratios of microcapsules are calculated by the contents of microcapsules accounting for bitumen. The practicality of microcapsule self-healing technology could be detected by preparing asphalt concrete samples. By the way, the extent of repairing asphalt concrete would be influenced by the content of microcapsules.

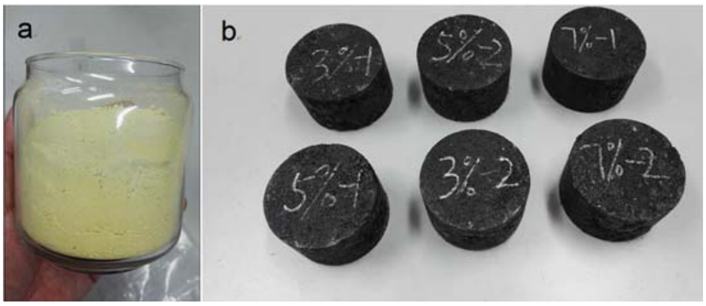

Fig.2 Asphalt samples mixing with microcapsules, (a) A photography of microcapsules containing rejuvenator, and (b) A photography of asphalt samples (MB-3, MB-5 and MB-7) mixing with various contents of microcapsules.

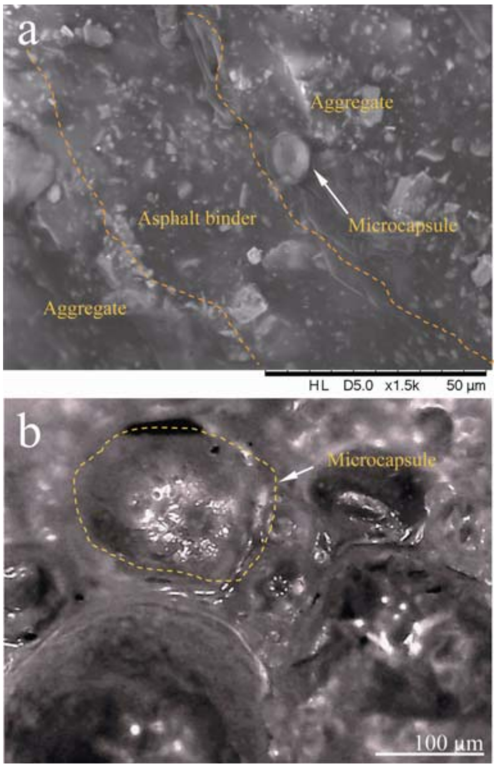

Fig.3 Microstructure morphologies of microcapsules in asphalt sample (MB-7) at room temperature state, (a) ESEM morphology of asphalt with aggregate and bitumen binder, and (b) a fluorescence microscope morphology of microcapsules in bitumen binders.

In previous work, it had been reported that microcapsules could survive and in melting pure bitumen under 180-200 °C [20]. The results confirmed that the miccapsules had satisfactory properties of interface stability, thermal stability, and mechanical stability, which meet the needs of application in bitumen. However, no references can be used to image states of self-healing microcapsules in the asphalt binder. In Fig.3(a), fine aggregates and bitumen are mixed together. Asphalt binder was pointed by an arrow. Comparing with the total mass of asphalt concrete, it can be concluded that the bitumen was used rarely and it was only in the aggregates gap. The amount of microcapsules healing aging bitumen and the increasing of road cost is in an acceptable range, compared to traditional repairing methods. From the point of view of the morphologies of asphalt binder, adding microcapsules did not affect the performance of asphalt. In other words, compatibility of microcapsules with bitumen performed well so that microcracks were not generated by microcapsules departing from the asphalt mixtures. Fig.3(b) shows a fluorescence microscope morphology of microcapsules in asphalt binder. The surface of microcapsules was completely adhered by bitumen binder. It can be obviously seen a fusion of microcapsules and bitumen. Stability of microcapsules performed very well and rupture was not produced at the shell materials. The microcapsules were not damaged by agitation in the molten asphalt.

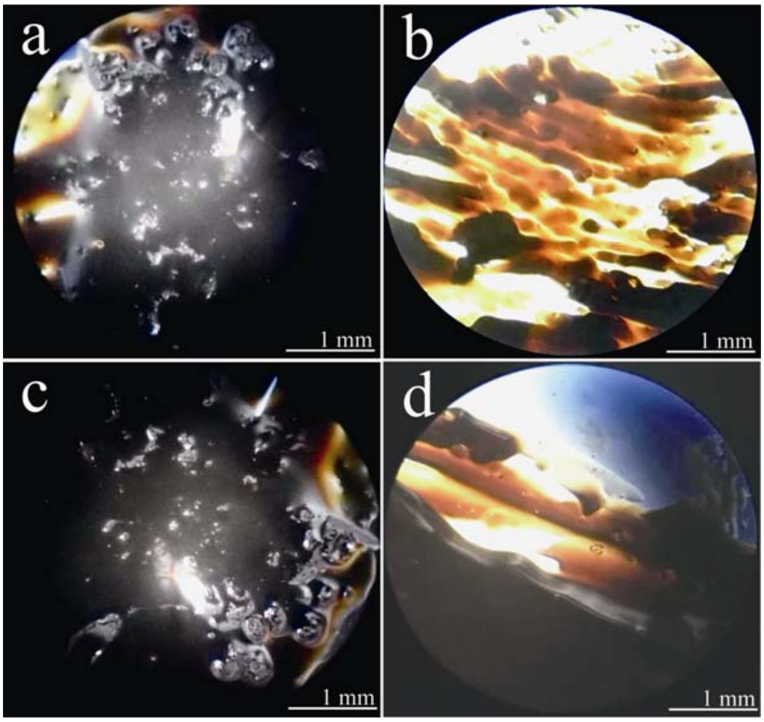

Fig.4 Optical morphologies of microcapsules in melting bitumen peeled from asphalt samples (MB-3) under high temperature, (a,b) 180 °C and (c,d) 200 °C.

Besides the morphologies of microcapsules embedded in asphalt, it is an essential issue to verify the integrity of microcapsules in binder. In order to directly observe microcapsules, a piece of asphalt was peeled from an asphalt sample and heated to melt state under temperature of 180 °C and 200 °C. Then melting bitumen without aggregates was spread on a microscope slide. Fig.4(a,b) show the optical morphologies of microcapsules in melting bitumen from asphalt samples (MB-3) under a high temperature of 180 °C. As the arrows pointing, the microcapsules are keeping an intact globe shape without rapture. Even under temperature of 200 °C, as Fig.4(c,d) shows, the microcapsules still keep their integrity without premature rapture. It indicates that the microcapsules resisted high temperature and strong squeeze during the asphalt samples formation process. It is in agreement with the previous conclusions based on microcapsules in pure bitumen [20].

3.3 Distribution of microcapsules in asphalt binder

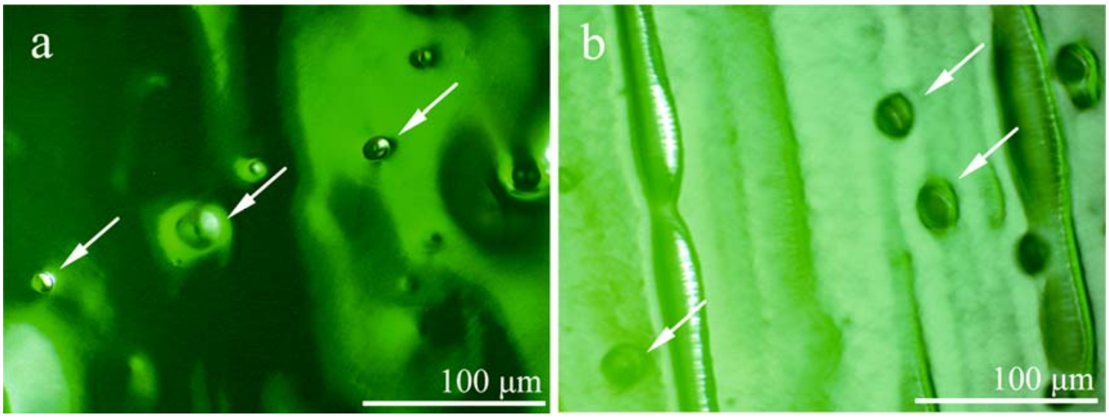

Fig.5 In-situ observation of microcapsules dispersing in asphalt binder by a fluorescence microscope: morphologies of (a) MB-3 and (b) MB-7.

Agglomeration of microcapsule particles in asphalt should be avoided because it may greatly influence the self-healing effective [23]. Fig.5 shows the in-situ fluorescence microscope morphologies of microcapsules dispersing in asphalt samples of MB-3 and MB-7. As the arrow pointed, the microcapsules disperse in asphalt binders homogenously without adhesion. In this study, shells have an inorganic/organic composite structure, the electrostatic interaction between particles does not increase the appearance of the phenomenon of agglomeration. Comparing Fig.5(a) and Fig.5(b), the weight ratio increasing of microcapsules in binder also do not affect the dispersion of microcapsules. It can be imaged that the uniform dispersion of microcapsules in binders will enhance the uniformity of the material structure. Self-healing occurs in binders. With the aging of bitumen, the generated microcracks will break microcapsules and release the oily rejuvenator. If the microcapsules did not disperse well, microcrack might pierce fewer microcapsules. In other words, the self-healing process will be affected by an inhomogeneity of the structure of the binders.

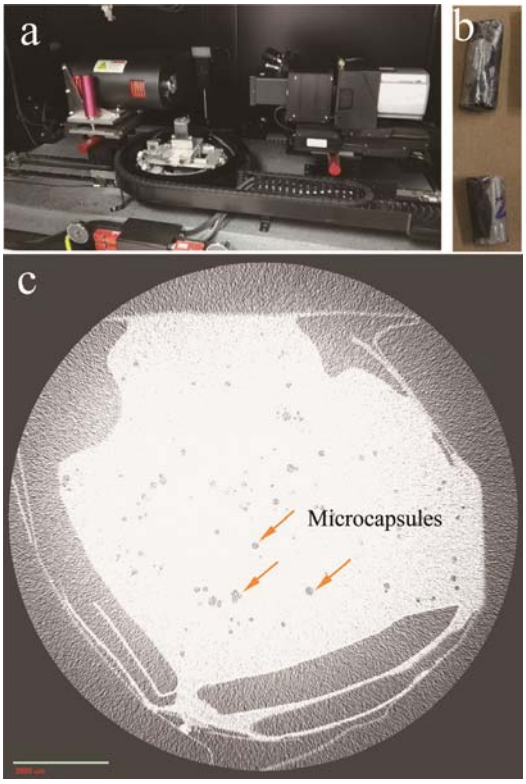

Fig. 6 XCT investigation of microcapsules in pure bitumen, (a) a photography of X-ray scanning part of XCT instrument, (b) a photograph of testing microcapsules/bitumen samples with cylindrical shape (3.0 wt.%, microcapsules), and (c) XCT image of microcapsules dispersing in pure bitumen.

In order to investigate the state of microcapsules in asphalt, XCT was used to observe their dispersion. As the shell has inorganic nano-$CaCO_3$, the shape of microcapsules can be identified due to the density difference between bitumen and inorganic material. Fig.6(a) shows a photography of X-ray scanning part of XCT instrument. Fig.6(b) shows a picture of the bitumen/microcapsules samples with cylindrical shape (3.0 wt.%, microcapsules). A CT scan makes the user to observe the inside of an object without rapture using computer-processed combinations of many X-ray image slices. These slices can be taken from different angles of specific areas of a scanned object. Fig.6(c) is a typical tomographic slice of bitumen/microcapsules sample. The global shape of microcapsules can be clearly identified as the arrows pointed. Microcapsules disperse in bitumen homogenously without the phenomenon of particle agglomeration. It can be seen that the microcapsules were covered with inorganically particles due to the density difference. The darker part size is about of 30 μm, which is equal to the mean size of microcapsules. This is proved from the other side that the darker parts are well dispersing microcapsules. Otherwise the darker parts can not have a global shape and the same size of microcapsule's diameter. A CT slice corresponds to a certain thickness of asphalt. Therefore, voxels can compose to a CT slice image; pixels compose to a typical digital image.

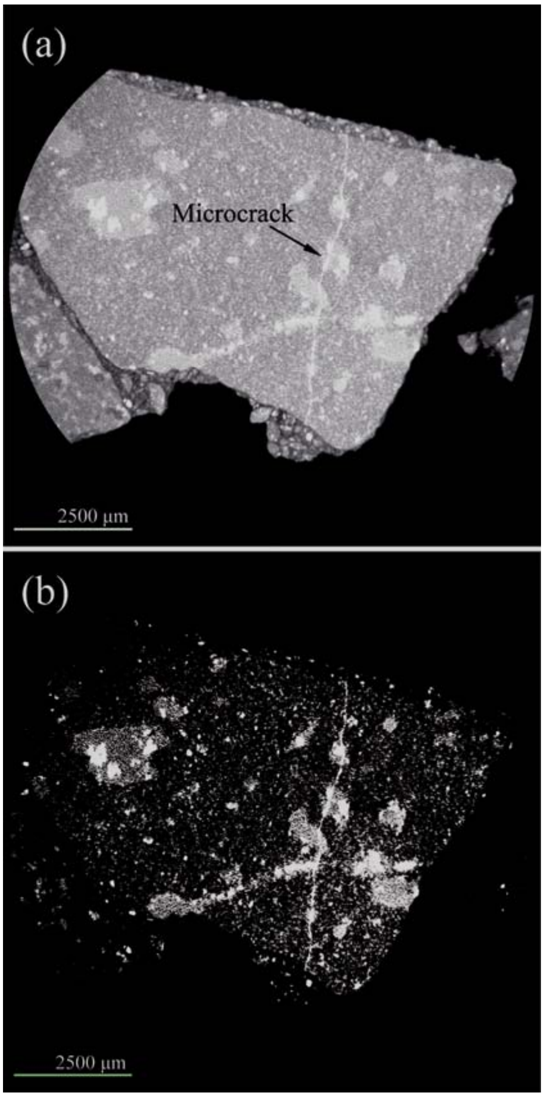

Fig.7 XCT images of microcapsules in asphalt binder (BM-7), (a) a XCT slice of microcapsules dispersing in asphalt sample, (b) a 3D-image of microcapsules dispersing in asphalt sample.

In this study, the bitumen was pre-mixed with microcapsules. It might be imaged that the microcapsules were dispersed homogenously in asphalt binders. However, it is not clear about the influence of aggregate on the distribution of microcapsules. XCT still offers a good solution to solve this problem. Fig.7(a) shows a XCT slice of microcapsules dispersing in asphalt sample (BM-7) with a microcrack. XCT data generally take from a sequence of image files, which can be visualized through a 3D-based image tool. Fig.7(b) illustrates the 3D-XCT image of asphalt sample (BM-7). Based on the same observation angle, the microcrack still can be found along the same direction. As listed in Table 1, the aggregates size is in a range of 0.075 to 13.2 mm. Particles with the size less than 0.075 mm can be identified in this image. It can be ascribed to the presence of microcapsules. Moreover, the microcapsules have a full range distribution in asphalt. This result is very important for self-healing asphalt using microcapsules containing rejuvenator because a randomly generated microcrack in asphalt has the same probability to meet microcapsules. The mechanism of self-healing of asphalt using microcapsules is clear that oily rejuvenator flow out from microcapsules and fill the whole microcrack through capillarity [5, 23]. As microcapsules are homogeneously distributed, rejuvenator quickly penetrates and diffuses through both sides of a microcrack. The homogeneous dispersion of microcapsules also will help to accelerated diffusion speed under given conditions [23].

3.4 Thermal stability of microcapsules in asphalt

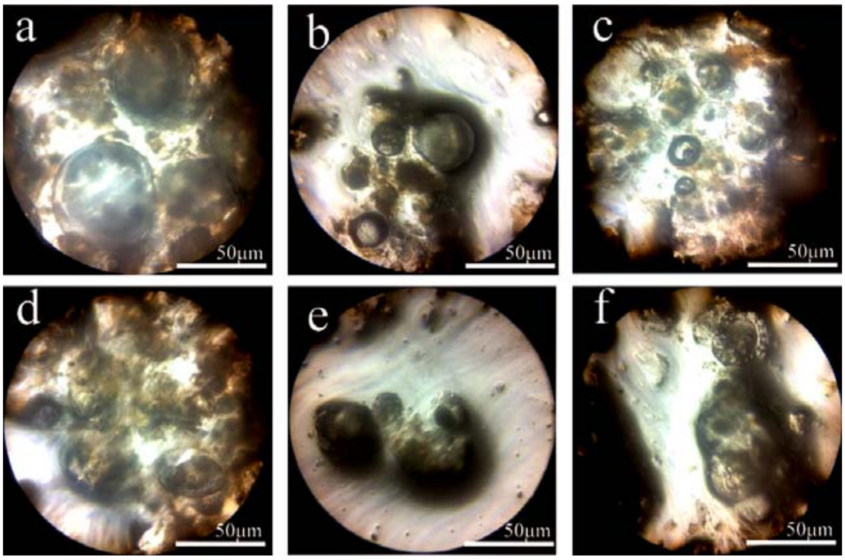

Fig.8 Morphologies of microcapsules in asphalt sample (MB-7) under various temperatures, (a) 100 ^{o}C, (b) 140 ^{o}C, (c) 180 ^{o}C, (d) 220 ^{o}C, and (e,f) 260 ^{o}C.

The initial decomposition temperature of microcapsules was affected by the factors including core/shell ratio, morphology and shell material dropping speed [15]. In this study, the same microcapsules were used to reduce the complexity of the differences in microstructure. Thermal tests also showed that the microcapsules with nano-$CaCO_3$/polymer shells survived in 180-200 ^{o}C bitumen [20]. Although microcapsules can safely survive in asphalt, it is still required to prove that microcapsules can resist some under extreme heat conditions. It is a well-known and accepted fact about overheating when asphalt operates under extreme heat conditions, which in turn results on stable state of microcapsules. On another hand, asphalt in real application of environmental conditions withstands the external temperature changes. The temperature change cycles may cause to the breakdown of microcapsules. This will significantly reduce the possibility of microcapsule rupture only when the microcracks appear.

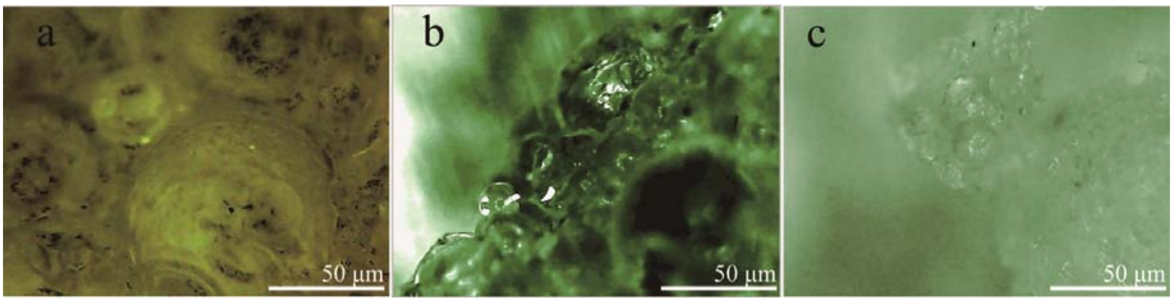

Fig.9 Fluorescence microscope morphologies of microcapsules in asphalt binders (MB-7) with a thermal treatment process repeated for different times: (a) 50, (b) 70 and (c) 100 times. One temperature change cycle: heated to 50 ^{o}C with a rate of 2 °C·min^{-1} and keeping for 10 min, and then decreased the temperature to -10 °C a rate of 2 °C·min^{-1}.

Firstly, a fast heating process was applied to simulate a thermal shock of microcapsules. An asphalt sample was placed in a temperature controlled oven to increase the temperature from room temperature to 200 ^{o}C at a rate of 5 °C·min^{-1}. Then fluorescence microscope was used to observe the states of microcapsules in asphalt binder under various temperatures. In Fig.8, morphologies of microcapsules in asphalt sample (MB-7) were showed under various temperatures of 100, 140, 180, 220, and 260 ^{o}C, respectively. In Fig.8(a-d), it can be seen that the microcapsules keep their original shape without rapture under such a violent thermal shock. The reason may be that the bitumen in asphalt binders does not create enough interior stress to break microcapsules. At the same time, the shells of microcapsules have the capability of resisting to a high temperature (180 ^{o}C). With the increase of temperature to 220 ^{o}C, rejuvenator has been released form the rapture microcapsules as shown in Fig.8(e,f). .Traces of oily rejuvenator can be clearly identified

Secondly, a simulation method was applied to investigate the thermal stability of microcapsules in asphalt binder under an alternating temperature process. Asphalt sample (MB-7) was heated to 50 ^{o}C then decreased the temperature to -10 °C with the rate of 2 °C·min^{-1}. This process was repeated 50-100 times. After the absorbing-releasing process, a piece of sample was peeled off and heated to 150 ^{o}C, then the melting bitumen was evenly coated on glass slides and observed by a fluorescence microscope. In Fig.9(a), microcapsules still compact particles without rapture dispersing in bitumen. It means that they resist the alternating temperature process repeated for 50 times. With an alternating temperature process repeated for 70 times, as shown in Fig.9(b), it can be found that the particles are brighter and their diameter has been enlarged. It is attributed to the rejuvenator of penetrating into bitumen. The shells at this state can not encapsulate the rejuvenator safely. After an alternating temperature process repeated for 100 times, it can be seen the release trace of rejuvenator in Fig.9(c). This phenomenon also has been found in previous work. When the microencapsulated rejuvenator has been released, microcapsules can help rejuvenator to diffusion in a relative accurate location comparing to the normal method of applying rejuvenator on the surface of asphalt [5]. Some microcapsules may have been reputed by the thermal action. It needs to be mentioned that self-healing microcapsules may be broken at different conditions, which will supply a continuous rejuvenator into bitumen during the aging process.

4. CONCLUSIONSC

The states of self-healing microcapsules containing rejuvenator in asphalt binders were investigated. Experimental tests were carried out to observe the morphology, integrity, distribution, thermal stability, interface bonding and triggered rupture of microcapsules in asphalt. The results showed that microcapsules containing rejuvenator were homogenously dispersed in binders avoiding particle aggregation and adhesion. They survived in asphalt resisting high temperature and strong agitation without premature damage. Microcapsules still kept a stable state after a circular heating and cooling process.

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