Observation and characterization of asphalt microstructure by atomic force microscopy

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Abstract: The microstructure of asphalt is investigated by atomic force microscopy (AFM). In order to analyze the impacts of asphalt types on microstructures, two neat asphalts with different penetration grades (50# and 70#) and one styrene-butadiene-styrene (SBS) modified asphalt are chosen. The influence of short-term aging is also studied. Based on the knowledge of asphalt's microproperties, the relationship between microstructures and healing property is analyzed. The results indicate that the microstructures of three asphalts are quite different and the effects of aging on the surface characteristics for different asphalts are also different. It is proposed that the bee structure is a type of wax crystal and it has a close relationship with the "bridge-healing" mechanism. The findings may reveal the formation mechanism of microstructure and the healing property for asphalts.

Key words: asphalt; atomic force microscopy (AFM); microstructure; self-healing property

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Researchers have conducted many extensive and in-depth studies on the macro properties of asphalt material for decades. However, due to the limitations of research scale and techniques, the achieved results were phenomenological. Only with a full understanding of micro characteristics of asphalt, can researchers modify asphalt with the proper addictives to produce high-performance asphalt. To achieve this goal, asphalt should be studied at micro level and a relationship between micro and macro properties should be established. With the progress of science and technology, obstacles of lacking advanced instruments can be overcome. Atomic force microscopy (AFM) is one of the most advanced tools in nanotechnology, which has gained prominence during the last decade in asphalt research. With the aid of AFM, researchers can extend the all-round understanding of the structure-function relationship by observing and analyzing the microstructure of asphalt. It is worthwhile noting that the AFM can provide unique information.

AFM was first applied in the research of asphalt by Loeber et al[1]. In the AFM image of gel asphalt, a number of microstructures with the diameter up to several microns and the height of only tens of nanometers were observed. Because the stripes look like bees, Loeber et al. named this structure as "bumble bees". Bees were found to exist in the gel asphalt which contained much asphaltene, so they thought that this structure was formed by the aggregation of asphaltene. At present, researchers generally agree that the colloid model, with the aggregation of asphaltene being the core, can explain the micro properties of asphalt. However, the size of the core in the colloid model (several nanometers) is quite different from that of the bee structures (several micrometers). Researchers remain puzzled by this contradiction.

Since the 21st century, an increasing number of experts in Western countries have begun to use AFM to investigate the micro property of asphalt. Some researchers found that there is a close relationship between the number of bee structures and the proportion of asphaltene, which supports Loeber et al.'s opinion. However, Masson et al. [2] argued that the bees were connected to the content of vanadium and nickel. By comparing AFM images of asphalt before and after aging, Wu et al. [3] concluded that the bee structure was associated with agglomerates of asphaltene. In recent years, more and more researchers have attributed the bee to the wax crystal[4-6].

It is believed that asphalt is a sophisticated system. The bee structures should not be simply attributed to the asphaltene or wax. Multiple factors contribute to the formation of this structure. Furthermore, microstructures have profound influences on macroproperties of asphalt and researchers are making great effort to build a relationship between them. One of the most miraculous properties of asphalt is its self-healing property and it has roused public interest. However, knowledge of self-healing at micro scale is limited and this study aims to narrow this gap. Based on the observed phenomenon, the crystal healing mechanism is proposed as a supplement for the traditional interdiffusion healing theory.

The objectives of this study are as follows: 1) Selecting an effective method for sample preparation; 2) Com-

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paring microstructures from different asphalts before and after aging; 3) Interpreting bee structure; 4) Establishing the relationship between the bee structure and the bridge-healing mechanism of asphalt. All the achievements in this study aim to provide a basic understanding of microstructure and self-healing property of asphalt at micro scale.

1 Equipment and Materials

AFM (Dimension ICON) is used in this study. All the samples are imaged in ScanAsyst mode. The scanning parameters are listed in Tab. 1.

Tab. 1 Parameters of AFM

Spring constant/ ($N \cdot m^{-1}$)	Cantilever length/μm	Resonance frequency/kHz	Scanningrange/ (μm × μm)	Image pixel
0.4	125	70	40 × 40	512 × 512

Two neat asphalts, named 50# and 70#, and one SBS modified asphalt are selected for this study. The basic properties are given in Tab. 2.

Tab. 2 Properties of asphalt

Asphalt	Penetration (25 ℃)/0.1 mm	Ductility (10 ℃)/cm	Softening point/℃
50# asphalt	52	30.5	56
70# asphalt	71	62.0	50
SBS modified asphalt	53	68.2	77

The casting method and the solution method are used to prepare samples for AFM observation, respectively.

Samples are prepared by the casting method according to the following steps: 1) Asphalt is heated to liquid; 2) About 0.5 g asphalt is poured onto the slide (40 mm × 15 mm × 1 mm); 3) The samples are put inside the oven at 150℃ for 10 min to make the asphalt spread with a diameter of about 1 cm; 4) The samples are removed from the oven and cooled in two ways. One is cooled in the air to the room temperature for 1 h, the other is cooled in the refrigerator for 1 h and then cured at room temperature.

According to the solvent method, samples are prepared in the following steps: 1) Asphalt is dissolved with trichloroethylene; 2) Drops of solvent are dripped on the central of the slides placed in the centrifuge (333 r/min); 3) After 10 min, the samples are put in a sealed container to become volatile in a refrigerator.

Samples for 70# asphalt are prepared using two methods. The more convenient and effective method to prepare AFM samples is determined by the comparison between AFM images. The aged asphalt is performed using the thin film oven test (TFOT, 163 ℃, 5 h).

All the samples were scanned at (20 ± 3) ℃.

2 Results and Analysis

2.1 Determination of sample preparation method

It has been proved in other studies that both methods can be applied to the sample preparation. But for the same asphalt, quite different phenomena were observed in this study.

For the samples using the casting method (see Figs. 1 (a) and (b)), the bee structures can be observed. However, they differ remarkably in distribution, size and shape. It is known that the asphalt is a mixture which can be divided into asphaltene, resin, aromatics and saturates. The coordination of these four fractions controls the stability of the internal state. It has been accepted widely that bee structures are wax crystal. Here, the state of bees under different cooling rates is in favor of this viewpoint since crystal morphology is affected by the cooling rate. According to the growth rule of wax crystal, when wax molecular begins to crystallize, polar molecules are taken as the crystal nucleus. If the temperature falls sharply, due to the slow diffusion of the molecules, they cannot relax back to their normal distribution where the energy is minimum. In this way, the crystal will be extremely small and the number of crystals will increase significantly. It is known that asphaltene has the highest polarity and molecular weight. It contains many hetero-atoms. At the same time, metallic elements (vanadium, nickel and other metals) which have high polarity are known to exist in asphaltene. Based on these properties, asphaltene is often regarded as the major source of nucleus of wax crystallization. Due to the gradient of polarity, resins wrap the asphaltene before the wax and oil molecules with long chains can wrap the asphaltene. Therefore, from the view of composition, asphaltene/metal, resin, wax and other components all contribute to the formation and state of the bee structure.

However, bee structures cannot be observed from samples prepared using the solvent method (see Fig. 1(c)). The possible reasons are listed as follows:

1) The solvent is not appropriate so that the chemical bonds within the binder may be affected;

2) The sample is not annealed;

3) The curing temperature is too low and the film is too thin.

Because samples prepared with the casting method have the phenomenon coming from "bees", the casting method is selected to prepare AFM samples of asphalts.

2.2 Observation of microstructures from different asphalts before and after aging

Bee structures in AFM images mainly consist of microcrystal wax. However, this kind of wax, with a carbon number of over 40, is different from paraffin in morphology. By comparing images of three different asphalts (see Figs. 2(a), (c) and (e)), it is found that bees are vastly different, particularly for those of 50# asphalt. This indicates that the properties of bees are dependent on the crude source of asphalt.

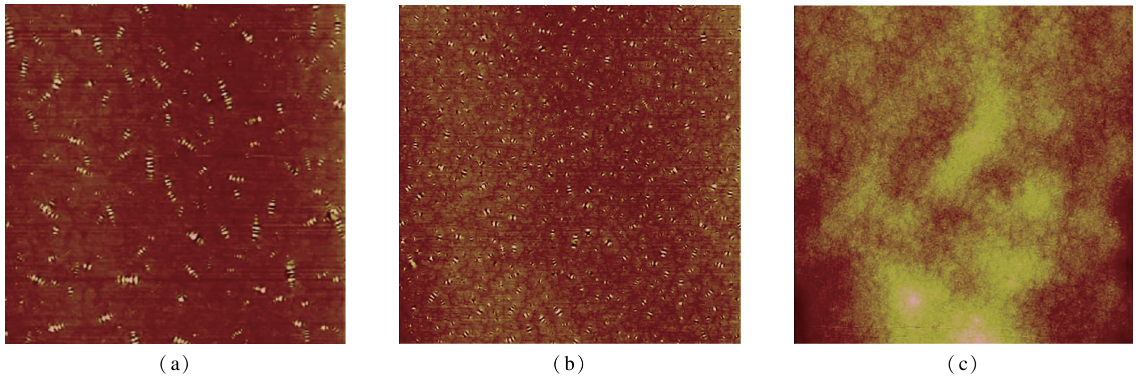

Fig. 1 Images of 70# asphalt with different preparation conditions (40 μm × 40 μm). (a) Casting method, air cooled; (b) Casting method, cooled in the refrigerator; (c) Solvent method, cooled in the refrigerator

Based on the observation of asphalt morphology before and after aging (see Figs. 2(b), (d) and (f)), changes of microstructures from each asphalt can be found. For 50# asphalt, bees become thinner and smaller; for 70# asphalt, bees become bigger and longer while the number of bees decreases; for the SBS modified asphalt, more bees appear but their size becomes smaller.

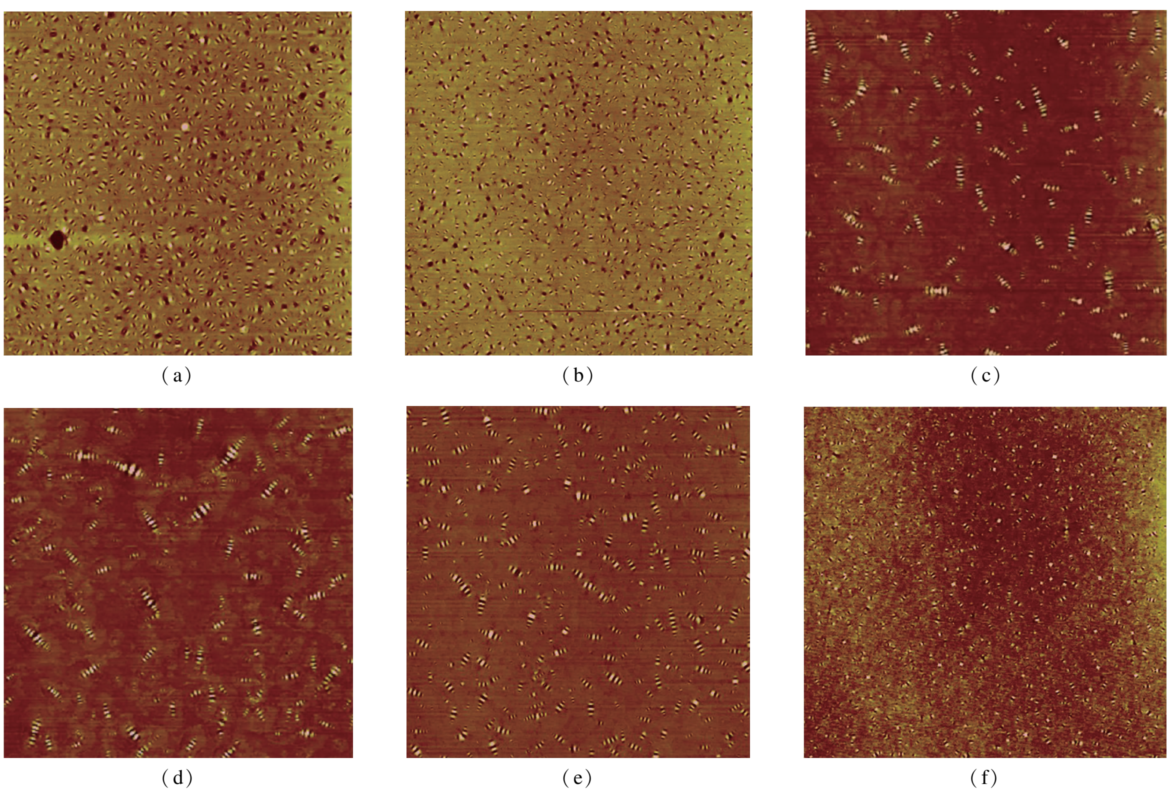

Fig. 2 Images of different asphalt before and after aging (40 μm × 40 μm). (a) 50# asphalt, virgin; (b) 50# asphalt, aged; (c) 70# asphalt, virgin; (d) 70# asphalt, aged; (e) SBS modified asphalt, virgin; (f) SBS modified asphalt, aged

2.3 Interpretation of bee structure

During the process of aging, properties and contents of four fractions change. When the contents of asphaltene and resin increase, there is much more nucleus for the wax to crystallize with, and asphaltene and resin aggregate on the surface of wax crystal, working as a natural depressant to reduce the surface free energy and strength of the wax. This effect impedes wax from co-crystallizing. From the perspective of crystallography, asphaltene with long chains will precipitate, working as the nucleus. Then the resin with strong polarity will wrap the asphaltene rapidly, hindering the aggregation of asphaltene. After this, the wax begins to crystallize around the resin. When the crystal grows to a certain size, the asphaltene and resin will attach to the surface of the crystal. Simultaneously, the asphaltene and resin in the oil phase form an electric double layer. The layer of directional dipolar molecules formed in the surface of wax crystal may not outwardly diffuse, but it can induce the secondary molecular layer to go into adjacent liquid phase. Therefore, a coating forms outside the wax crystal and prevents the wax from connecting. However, when the asphaltene increases to a certain content, the resin is not able to wrap the asphaltene fully so asphaltene aggregation occurs. Then the asphaltene for the nucleus becomes less and the effect of the depression decreases. Finally, crystals merge together and become larger[8-9].

This interpretation can be verified by the following experimental phenomenon observed by Masson et al[7]. When the morphological changes were correlated to endothermic and exothermic phase transitions, the domains around the rippled dispersions (bees) were found to be rich in naphthene and polar aromatics.

At the same time, for the puzzling and unexplained terracing structure in Schmets' study (see Fig. 3), it can also be interpreted thus. When the crystal nucleus is deposited on the wax crystal, the second layer grows and expands on the first layer. A new edge forms because there are defects in the growing process of the layer. Other wax molecules will connect at this place and grow in a spiral way, forming a screw dislocation[8-9].

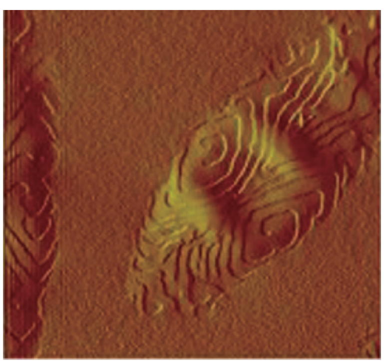

Fig. 3 Terracing structure (4 μm × 4 μm)[5]

It is found that bee structures have peaks and valleys (see Fig. 4). The distance between two adjacent peaks is about 0.5 μm. All the crystals grow in the directions of x axle and y axle. The height in the z axle is only dozens of nanometers. It is proved that wax tends to crystallize at the asphalt/air interface. These bees, like "boats" floating in the asphalt, are more likely to be a surface phenomenon. However, the issue whether the bee structure is a bulk phenomenon or not, which has drawn great attention worldwide, is still unknown unless the fracture surface is analyzed. Yet it is observed that these bee structures disappeared/appeared in the heating/cooling

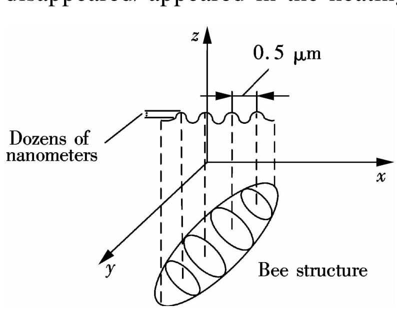

Fig. 4 Diagram of bee structure

cycles, which indicates that bee structures may appear in the fracture asphalt surface because of the environmental temperature cycles.

2.4 Establishment of relationship between bee structure and healing property of asphalt

According to the above analysis, it is reasonable to divide the asphalt surface into amorphous regions and crystalline regions. The crystalline region is thought to be rich in wax molecules with long chains, which have a higher mobility than asphaltene and resin and contribute more to the healing interface than oil in asphalt. It is notable that the phase change of bee structures is related to the healing property in other studies[5].

It is worthwhile noting that there a boundary value problem exists to crack healing, which requires contact between the fractured surfaces at a distance of 10 nm. Nevertheless, from a recently published thesis[10] investigating the bridge-healing mechanism of asphalt, it was found that the healing crack size was several micrometers. The author concluded that the bridge structure developed in two steps: first by the flowing and cooling of crystallisable molecules and aromatic side-chains and secondly by the diffusive build-up of entanglement. Through our research, crystallisable wax molecules forming the bee structures are thought to be responsible for the bridge structure.

In this way, a crystal healing mechanism in asphalt is proposed in this paper. If the crystals are supposed to begin to melt at T (glass transition temperature), the crystal will hinder the inter-diffusion of asphalt molecules because of its low mobility below T. But when the temperature is above T, wax molecules will have enough energy to move across the interface, which is driven by the gradient of density. During cooling, the re-crystallization of bee structures works as the anchor to bridge two surfaces to create strength. It can be found that the crystallization has opposite effects on healing and T may be the optimum healing temperature.

3 Conclusions

1) The casting method is an effective and convenient way to prepare the samples for the observation with AFM.

2) The observed bees are likely to be wax crystals. The properties and distribution of microstructures are quite different for different asphalts before and after aging.

3) The formation of bees can be interpreted with the following mechanism: Asphaltene with high polarity works as the core. Then resin, wax and oil wrap the core layer by layer. When the crystal grows to a certain size, asphaltene and resin outside the crystal will stop the crystal growing and connecting with other crystals. Finally,

numerous bee structures form. These structures tend to gather at the asphalt/air interfaces and float like "boats". But whether bees exist in bulk or not is unknown.

4) The relationship between bees and four fractions of asphalt (saturates, aromatics, resins and asphaltenes) needs to be investigated intensively.

5) Crystal plays a vital role in the process of healing. The crystallization and interdiffusion of molecules simultaneously promote the healing of microcracks.

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基于原子力显微镜的沥青微观结构观察与表征

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摘要: 利用原子力显微镜进行沥青微观结构的观察与表征. 选用针入度分别为50#和70#的2种基质沥青及一种SBS改性沥青,分析沥青种类及短期老化对微观结构的影响. 基于对微观特性的认识,讨论了沥青微观结构与自愈性能之间的联系. 研究表明:对于不同沥青,其微观结构形态相差较大,且结构随老化而变化的规律也各不相同. 初步推断观测到的蜂状结构是一种结晶体,其分子组成与已有研究观测到的"桥接"自愈现象关系密切. 相关结论为沥青微观结构机理和自愈性能研究提供了新的思路.

关键词: 沥青;原子力显微镜;微观结构;自愈性能

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