Microstructure and Mechanical Properties of Polyphosphoric Acid Modified Asphalt

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Abstract. Based on atomic force microscopy (AFM), PPA modified asphalt, SBS modified asphalt and PPA composite modified asphalt were tested. The microstructure and Micro-Mechanical Properties of the three modified asphalts before and after aging were analyzed with different evaluation indexes. The results show that PPA modified asphalt has good adhesion and deformation resistance, and the anti-deformation ability is more remarkable after aging, which is obviously superior to the other two kinds of modified asphalt in anti-aging performance; PPA modified asphalt and PPA modified asphalt have higher peak density, larger surface free energy and better adhesion performance, which is conducive to improving the interface adhesion between asphalt and mineral. For PPA composite modified asphalt, the addition of PPA improves the storage stability and aging resistance of SBS modified asphalt, which is superior to SBS modified asphalt in deformation resistance and cracking resistance, and has the effect of taking into account both high and low temperature performance. The micro-performance of asphalt based on AFM provides a basis for macro-performance analysis.

1. Introduction
Polyphosphoric acid (PPA), as a chemical modifier of asphalt, has been used in asphalt modification in the United States for a long time[1]. PPA can improve the performance of asphalt obviously, and can improve the high-temperature PG classification of asphalt, but has no effect on the low-temperature PG classification[2]. Liang, P. also proved that PPA can significantly improve the stability and rutting resistance of asphalt at high temperature without affecting the low temperature stiffness[3]. However, there is no consensus on the low temperature performance at home and abroad. Some researchers believe that PPA modifier can significantly improve the low temperature performance of asphalt, while others have verified that PPA has a negative effect on low temperature performance [4-6]. In order to improve the low-temperature performance of asphalt, SBS or SBR are usually used as modifiers. The high-temperature and low-temperature properties of the modified asphalt are improved after compounding[7]. At present, the research on PPA modified asphalt is mostly focused on macro-characteristics analysis, while the research on micro-structure and properties is relatively small. With the development of engineering material testing technology, micro-
instruments such as SEM, AFM, TEM and so on have been applied. Among them, atomic force microscopy (AFM) can measure the three-dimensional morphology of materials at micro-scale, and has been widely used in the micro-structure of asphalt materials in recent years. Visual structure test [8]. Researchers at home and abroad generally scan and analyze the micro-morphology of asphalt material by AFM, and study the adhesion characteristics of asphalt material under Peak-force mode [9]. In addition, the physical bonding characteristics of asphalt material can also be analyzed by testing the physical interaction between probe and asphalt surface [10]. Other studies have shown that different kinds of asphalt surface may have different roughness. Based on AFM, the roughness of asphalt surface can be measured accurately, which provides a basis for the study of the interface adhesion between asphalt and aggregate [11]. Atomic force microscopy (AFM) can simultaneously detect the micro-morphology and mechanical properties of asphalt, thus providing insights into how micro-morphology affects the micro-rheological properties of samples [12]. In this paper, based on AFM technology, PPA modified asphalt, SBS modified asphalt and PPA composite modified asphalt were tested. The microstructure and Micro-Mechanical Properties of three modified asphalts before and after aging were analyzed with different evaluation indexes.

2. Experimental materials
The base asphalt is Panjin No. 90 asphalt, the content of PPA (PPA concentration is 116%) in modified asphalt is 2.0% (mass fraction), the content of SBS in SBS (4303 star type) modified asphalt is 4.0% (mass fraction), the content of SBS in PPA composite modified asphalt is 3% (mass fraction), and the content of PPA is 1.0% (mass fraction).

Short-term aging: Rotating film oven aging test (RTFO [R]: 163℃/85 min), long-term aging: pressure aging test (PAV [P]: 90℃/2.1 MPa/20 h).

Table 1. Matrix asphalt and modified asphalt technology index.

| index                  | 90 # asphalt | PPA | SBS | PPA &SBS |
|------------------------|--------------|-----|-----|----------|
| Penetration (/25℃/0.1mm) | 85           | 44.3| 62.0| 51.0     |
| softening point /℃     | 51.5         | 66.0| 61.5| 65.6     |
| Ductility (/5℃/mm)     | 94           | 56  | 202 | 130      |

3. Testing equipment and methods

3.1. Test method
The modified asphalt was tested by CSPM4000 atomic force microscope. The imaging mode was tapping mode, the test temperature was room temperature, the maximum resonance amplitude was set to 1.4V, the resonance frequency was set to 260kHz, the reference point was set to 0.8V, the scanning area was 15μm×15μm, and the image clarity was 512×512. The probe used in the test is SNL-10 silicon nitride probe with a frequency of 65 kHz and an elastic constant of 0.35N/m.

3.2. Sample preparation
The asphalt samples were prepared by thermoforming method. First, the asphalt samples were heated in the oven at 160℃, then the glass slides were preheated on the heating plate at 140℃. Then the glass slides were dipped in the asphalt and dripped on the glass slides, which were flattened in a circular film shape. Then the glass slides were heated on the heating plate for about 10 minutes to make the asphalt show smoothness and uniformity. Finally, it is cooled to room temperature for test.

4. Analysis of Microstructure Characteristics

4.1. Topographic analysis
Fig. 1-6 is the surface micro-morphology and three-dimensional diagram of modified asphalt. It can be seen that the surface of asphalt has obvious interlaced structure of light and dark stripes. Because of its shape like bees, it is called "bee-shaped structure", which is a unique structure in asphalt. It can also be
seen that there are two distinct phases in asphalt, namely, dispersed phase with "bee-shaped structure" (asphaltene) as the core and dispersed phase surrounded by "bee". Continuous phase dominated by light components around the "shape structure".

![Figure 1. Topographic image of PPA modified asphalt](image1)

(a) Original; (b) RTFOT; (c) PAV

![Figure 2. 3D image of PPA modified asphalt](image2)

(a) Original; (b) RTFOT; (c) PAV

![Figure 3. Topographic image of SBS modified asphalt](image3)

(a) Original; (b) RTFOT; (c) PAV

![Figure 4. 3D image of SBS modified asphalt](image4)

(a) Original; (b) RTFOT; (c) PAV

Fig. 1 is the morphology of PPA modified asphalt. It can be seen that the bee-shaped structure in PPA modified asphalt before aging is clearly visible and uniformly dispersed, forming a stable network structure in asphalt, which improves the stability of asphalt. With the deepening of aging
degree, the bee-shaped structure in PPA modified asphalt has changed significantly, and the size of bee-shaped structure has become smaller. But not after long-term aging, the bee-like structure appeared obviously.

From the figure 2, it can be seen that the surface of PPA modified asphalt before aging is uneven, showing obvious peak shape. With the deepening of aging, the surface becomes rough, and the peak shape is not obvious.

Figure 3 shows the morphology of SBS modified asphalt. Compared with the other two kinds of modified asphalt, the "bee-shaped structure" is different in size and concentrated in distribution. With the deepening of aging, the "bee-shaped structure" changes greatly, and the bright part of the "bee-shaped structure" becomes larger and longer, showing strip shape. From the three-dimensional graph of Figure 4, it can also be seen that the bright part of the aging is continuous. The brightness of the image is enhanced by aggregation, and the bright part has no peaks. This is because SBS modifier is a block copolymer of styrene(S)-butadiene(B)-styrene(S), which crosslinks with each other. Asphaltenene has strong polarity and is adsorbed by SBS and distributes more centrally.

4.2. Peak density analysis
Based on the roughness theory, peak density (S_\text{ds}) is selected as the main index to evaluate the surface roughness of asphalt. Peak density divides the image into M×N rectangular areas, and calculates the number of maximum elevation in the unit area. Formula (1), in which M and N are small rectangular, is used to analyze and calculate the peak density of asphalt using NanoScope Analysis software.
According to the roughness theory, the higher the peak density is, the rougher the surface is. When the asphalt contacts with the surface texture of the aggregate, the adhesion between the asphalt and the aggregate will be improved. Before and after aging, the peak density of modified asphalt: PPA&SBS > PPA > SBS. The combination of PPA and SBS can obviously improve the peak density of asphalt, showing better adhesion characteristics, followed by PPA modified asphalt. With the deepening of aging degree, the peak density of modified asphalt decreases, which is due to the decrease of light components, the increase of heavy components and the aggregation of asphaltene molecules. Compared with pre-aging, the decreasing range of peak density after aging is SBS > PPA > PPA&SBS, which indicates that PPA and PPA composite modified asphalt are less affected by aging, while in the process of short-term aging to long-term aging, the decreasing range of peak density is SBS > PPA&SBS > PPA, which indicates the aging resistance of PPA modified asphalt. Compared with SBS modified asphalt, PPA&SBS has better aging resistance.

Table 2 Adhesion of modified asphalt before and after aging (nN)

| Asphalt type | Origin | RTFOT | PAV |
|--------------|--------|-------|-----|
| SBS          | 21.3   | 16.8  | 12.4|
| PPA          | 23.8   | 20.7  | 15.9|
From Table 2, it can be seen that the adhesion force of PPA modified asphalt before and after aging is greater than that of SBS modified asphalt, and PPA composite modified asphalt has the best adhesion force, showing better adhesion characteristics. With the deepening of aging degree, the adhesion force of modified asphalt decreases gradually, which is due to the increase of hardness of asphalt after aging and the change of interaction force between probe and asphalt. It can also be seen from Figure 8 that, compared with Figure 8 before aging, the viscous zones of three modified asphalts in Figure 9 (a), (b), (c), after aging are obviously narrowed and the cohesion of asphalt is weakened. Among them, the viscous zones of SBS modified asphalt shrink most obviously after TFOT to PAV, which shows that the adhesion properties of SBS modified asphalt are relatively affected by aging, while PPA and PPA composite modified asphalt. Asphalt exhibits good aging resistance.

5.2. Young modulus
Young's modulus is a physical quantity describing material's resistance to deformation. The larger the value, the less likely it is to be deformed. In this study, Hertz model is used to fit the Young's modulus. Formula (2) shows that \( F \) is the adhesion force. From the above force-curve, \( E \) is the Young's modulus, \( \nu \) is the Poisson's ratio of the sample (This study takes 3.0), \( R \) is the radius of the probe indenter, and \( \delta \) is the indenter parameter. Young's modulus of modified asphalt before and after chemical modification is shown in Figure 10.

\[
F = \frac{4}{3} \frac{E}{(1-\nu^2)} \sqrt{R} \delta^3
\]  

(2)

From Figure 10, we can see that the Young's modulus of modified asphalt before and after aging is PPA > PPA&SBS > SBS, which shows that PPA modified asphalt has better deformation resistance and more significant deformation resistance after aging, while the Young's modulus of SBS modified asphalt is the smallest, showing weaker deformation resistance. With the deepening of aging degree, Young's modulus of modified asphalt increases obviously. This is due to the decrease of light components and the increase of heavy components in asphalt after aging, which makes asphalt harden and has certain stiffness, and Young's modulus increases accordingly. The increase of Young's modulus can improve the rutting resistance of asphalt at high temperature, but has a negative impact on the cracking resistance of asphalt at low temperature. PPA modified asphalt not only improves the high temperature performance, but also has a negative impact on the low temperature performance. PPA modified asphalt is better than SBS modified asphalt in deformation resistance and cracking resistance, and has both high and low temperature performance.

5.3. Surface free energy
The surface free energy of asphalt is measured by atomic force microscopy, which reflects the adhesion between asphalt and aggregate at micro-level. In this study, the surface free energy of asphalt is calculated by using JKR and Fowken models in contact mechanics. As shown in equation \( F_{ad} = 1.5\piRW \), \( F_{ad} \) is the adhesion force, \( R \) is the radius of curvature of probe tip and \( W \) is the adhesion work. The obtained adhesion work is transformed into surface free energy by Fowken model. As
shown in equation $W = 2\sqrt{\gamma_a \gamma_b}$, $\gamma_a$ is the surface free energy of asphalt, and $\gamma_b$ is the probe. In this study, SNL-10 silicon nitride probe with $\gamma_b$ of 1352.67 mJ/m$^2$ was used. The surface free energy of modified asphalt before and after aging was shown in Figure 11.

From Figure 11, it can be seen that the surface free energy of PPA composite modified asphalt before and after aging is the largest, followed by PPA modified asphalt and SBS modified asphalt. This shows that PPA and PPA composite modified asphalt have strong adhesion performance, while SBS modified asphalt has relatively weak adhesion performance, which is consistent with the analysis results of asphalt roughness in 4.2. It shows that asphalt surface roughness is related to asphalt surface. Freedom energy has an important impact. With the deepening of aging degree, the surface free energy of modified asphalt decreases obviously, which indicates that the adhesion property of modified asphalt decreases after aging. When aging degree increases, the increase of heavy components will reduce the adhesion strength between asphalt and aggregate. However, the adhesion between asphalt and aggregate is also related to the effect of embedding and friction. Therefore, the aging effect on the adhesion property is related to the effect of embedding and friction. It also needs to be verified by asphalt mixture test.

6. Conclusion

(1) PPA modified asphalt has good adhesion and deformation resistance, and the anti-deformation ability is more remarkable after aging, which is better than SBS modified asphalt and PPA composite modified asphalt in aging resistance.

(2) PPA modified asphalt and PPA composite modified asphalt have higher peak density, larger surface free energy and better adhesion performance, which is conducive to improving the interface adhesion between asphalt and aggregate.

(3) For PPA composite modified asphalt, the addition of PPA plays a similar role as stabilizer for SBS modified asphalt, promotes the dispersion of polymer molecules, improves the storage stability of asphalt, and enhances the aging resistance and deformation resistance.

(4) PPA composite modified asphalt is superior to SBS modified asphalt in deformation resistance and cracking resistance. It has both high and low temperature properties.

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