Effect of rubber powder modification on the aging resistance of asphalt binder

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Abstract. The rubber powder produced by waste rubber was used to modify asphalt, which was conducted in aging test. The effect of rubber powder modification on the aging resistance of asphalt binder was studied by the means of basic physical properties test, dynamic shear rheological test and infrared spectrum analysis. Results indicate that the addition of rubber powder can reduce the degradation of aromatic, which makes the rubber powder modified asphalt shows better aging resistance and lower temperature sensitivity. After aging, the change of rheological properties of rubber modified asphalt is relatively small, and it also shows a stable high temperature performance.

1. Introduction

Asphalt is the binding material of mixture which plays a very important role in the application of road engineering. With the continuous growth of traffic volume and the heavy traffic in China, and the improvement of road service life requirements, ordinary asphalt has been unable to meet the needs of road construction and service [1]. Asphalt is prone to dehydrogenation, condensation and oxidation under the environment, which lead to aging of asphalt, resulting in hardening and embrittlement of asphalt cement, and seriously reducing the service performance of asphalt mixture [2, 3]. The high-strength and wear-resistant characteristics of waste rubber make it difficult to degrade in nature. The rubber powder milled by waste rubber can not only solve the problem of environmental pollution and transform waste materials into resources, but also effectively improve the performance of asphalt pavement [4-6]. Rubber powder modified asphalt has been paid more and more attention and applied because of its good performance, environmental benefits and economic benefits [7-9].

In order to study the influence of the rubber powder modification on the aging resistance of the base asphalt, this research is based on the preparation of the rubber powder modified asphalt from SK70# asphalt, and the rotary film oven test was used to aging the SK70# asphalt and the modified asphalt, and the change of its basic physical properties were tested, as well as the difference of its rheological energy was analyzed. Combined with the infrared spectrum, the improvement effects of the rubber powder modification on the aging resistance of the asphalt and modification mechanism were discussed.
2. Raw Materials And Experimental Methods

2.1 Raw Materials
The technical indexes of SK70# asphalt used in this study are listed in Table 1. The size of rubber powder is 250, of which the technical indexes are listed in Table 2. The laboratory prepare process for the rubber powder modified asphalt was as follow: The SK70 # asphalt is heated to 180 oC and adds the rubber powder (20 percent of the mass of asphalt), which shearing for 90 min at the stirring rate of 5000 r/min, then the rubber powder modified asphalt will be obtain after swelling for 15 min.

| Test indexes               | Results |
|---------------------------|---------|
| Penetration (25°C,0.1mm)  | 67      |
| Ductility (15°C,50mm/min) | > 100   |
| Softening point (℃)       | 50.2    |
| Viscosity (135℃,Paꞏs)    | 0.46    |

Table 2. General technical properties of the rubber powder

| Test indexes                       | Results |
|------------------------------------|---------|
| Natural rubber content(%)          | 44      |
| Rubber hydrocarbon content(%)      | 46.5    |
| Acetone extract content(%)         | 12      |
| Ash content(%)                     | 5       |
| Carbon black content(%)            | 35      |
| Metal content(%)                   | 0.009   |
| Fiber content(%)                   | 0.03    |
| Water content(%)                   | 0.5     |

2.2 Experimental methods
The Rolling Thin Film Oven Test (RTFOT) simulated the short-term aging of asphalt binders, and the main parameters in the tests are 4000ml/min air flow rate, 163 ℃ aged temperature and aging time 5 h.

The penetration, ductility and softening point of two kinds of asphalt before and after aging were tested, and the aging degree was analyzed by the change of basic performance indexes before and after aging. The Dynamic Shear Rheological Test (DSR) was used to analyze the high temperature performance of the asphalt binder. The temperature scanning was carried out under the mode of controlling strain, and the scanning range was 30 ℃ - 70 ℃, and the heating rate was 1 ℃/ min.

The change of molecular structure caused by asphalt aging was analyzed by infrared spectrum. The asphalt was dissolved in CS2 solvent to obtain asphalt carbon disulfide solution (5% mass concentration). A drop of asphalt carbon disulfide solution was titrated on the blank potassium bromide film after scanning. After the evaporation of CS2, the sample was scanned by infrared spectrum, and the wave number scanning range is 4000-1 - 500cm-1.

3. Results And Discussion

3.1 Aging performance analysis
In this study, residual penetration ratio (penetration ratio before and after aging, PRR), residual ductility ratio (ductility ratio before and after aging, DRR), softening point change (softening point difference value before and after aging, SPI), viscosity aging index (viscosity ratio before and after aging, VAI) were used to evaluate the aging performance of asphalt [6]. The larger the value of PRR and DRR, the smaller the change of penetration and ductility before and after asphalt aging, and the smaller the degree of asphalt aging. The smaller the value of SPI and VAI, the smaller the change of softening point and viscosity, which mean that the Asphalt has a low degree of aging.

The change of basic performance indexes of sk70# asphalt and its rubber powder modified asphalt
after aging is shown in Table 3. It can be seen from the table that the residual penetration ratio of crumb modified asphalt is higher than the sk70# asphalt after aging, indicating that the short-term thermal oxygen aging degree of crumb modified asphalt is smaller than that of sk70# asphalt. And the residual ductility ratio of crumb rubber modified asphalt is much higher than that of matrix asphalt, which indicates that the aging degree of crumb rubber modified asphalt is relatively small after aging. The softening point of the sample increases after aging, and that shows more evidence of SK70# asphalt, while the aging degree of rubber powder modified asphalt is relatively small, and the increment of softening point is relatively small. The viscosity of sk70 asphalt and its modified asphalt with rubber powder increases after aging. And it can be obtained that the viscosity change amplitude of the modified asphalt with rubber powder is smaller than that of SK70# asphalt after aging. It is not difficult to find that the basic performance index of aged rubber powder modified asphalt shows certain advantages.

Table 3. Physical property change index of asphalt after aging

| Asphalt type               | Residual penetration ratio /% | Residual ductility ratio /% | Softening point increment /°C | Viscosity aging index |
|----------------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------|
| SK 70# asphalt             | 70%                           | 25%                         | 6.2                           | 1.6                   |
| rubber powder modified asphalt | 81%                           | 67%                         | 1.7                           | 1.35                  |

3.2 Rheological properties analysis

Figure 1 and Figure 2 show the rheological properties of the two asphalts before and after aging. It can be observed from Figure 1 that the complex modulus of asphalt material decreases with the increase of temperature. For SK70# asphalt, the complex modulus of SK70# asphalt significant increases, which is due to the evaporation or oxidation of light components of asphalt after aging, and then the increase of heavy components in the asphalt composition. The proportion of asphalt composition changes greatly, which is reflected in the increase of elastic response of asphalt. The addition of rubber powder makes the composition of asphalt system very complex, but through the comparison of macro rheological properties, it can be seen that the aging resistance of rubber powder modified asphalt is significantly better than that of matrix asphalt, and the complex modulus changes little before and after aging.

Figure 2 shows that the phase angle of SK70# asphalt increases with the increase of temperature, and it still has this change trend after aging, while the phase angle of SK70# asphalt decreases after aging at the same temperature, indicating that the viscosity response of asphalt decreases due to aging.

The change of phase angle of crumb rubber modified asphalt is different from that of matrix asphalt. With the increase of temperature, the phase angle of crumb rubber modified asphalt first increases and then decreases, but the change amplitude of crumb rubber modified asphalt is smaller than that of matrix asphalt, which shows that the addition of rubber powder makes the viscosity response of asphalt change little, and the thermal sensitivity is reduced.
3.3 Structural change analysis

The macro performance of asphalt is molecular structure determined. So the change of performance can be understood essentially by studying the change of molecular structure before and after aging of asphalt. The structure type and content of the characteristic functional group can be inferred from the absorption frequency position and the corresponding absorption peak area shown in the infrared spectrogram [10, 11]. Fig. 3 and Fig. 4 show the infrared spectrum of the base asphalt and its rubber powder modified asphalt before and after aging.

It can be found that the absorption peaks of 2924 cm\(^{-1}\), 2852 cm\(^{-1}\), 1601 cm\(^{-1}\), 1462 cm\(^{-1}\), 1377 cm\(^{-1}\), 1032 cm\(^{-1}\), 866 cm\(^{-1}\), 812 cm\(^{-1}\) and 723 cm\(^{-1}\) can be found in the infrared spectrum of the base asphalt and the rubber powder modified asphalt before and after aging.

The rubber powder modified asphalt has one more absorption peaks of wave number 996 cm\(^{-1}\) than the base asphalt. According to previous studies, the absorption peak can reflect the stretching vibration of C = C bond, which is the characteristic functional group of rubber powder. The characteristics of functional groups represented by other wave numbers are shown in Table 4.
Figure 3. Infrared spectra of base asphalt before and after aging

Figure 4. Infrared spectra of crumb rubber modified asphalt before and after aging

Table 4. Characteristics of functional groups characterized by different wave numbers

| Wave numbers (cm$^{-1}$) | Characteristics of functional groups                      | Wave numbers (cm$^{-1}$) | Characteristics of functional groups                      |
|-------------------------|-----------------------------------------------------------|-------------------------|-----------------------------------------------------------|
| 2924                    | Asymmetric stretching vibration of C-H                    | 1601                    | Skeleton vibration of benzene ring                         |
| 1462                    | In plane bending vibration of -CH2-                      | 1377                    | Out of plane bending vibration of -CH3-                   |
| 1032                    | Stretching vibration of S=O                               | 866                     | Stretching vibration of benzene ring                       |
| 812                     | Stretching vibration of benzene ring                      | 723                     | Synergistic vibration of methylene segments               |
| 2852                    | Symmetric stretching vibration of C-H                    |                          |                                                           |

Wave number/cm$^{-1}$
The functional groups reflected by each absorption peak represent different components in the modified asphalt, 1377 cm\(^{-1}\), 1601 cm\(^{-1}\), 1700 cm\(^{-1}\), and 1032 cm\(^{-1}\) can be used to analyze branched aliphatic functional groups, aromatic components, C=O and S=O, which can be used to reflect the aging of asphalt. In this paper, the change of the content of functional groups in the molecular structure is characterized by the area ratio of each absorption peak, which reflected the aging degree difference of asphalt. Specifically, IB, and IAr represent the change of aliphatic compound structure in asphalt and aromatic ring structure, respectively. IC=0 and IS=0 represent oxygen functional group index in asphalt. IG=G represents the change of functional group in rubber powder, and the corresponding area ratio calculation can be obtained by the following formula.

\[
I_B = \frac{A_{1377}}{A_{1462} + A_{1377} + A_{723}} \quad (1)
\]

\[
I_{Ar} = \frac{A_{1601}}{\sum A} \quad (2)
\]

\[
I_{C=O} = \frac{A_{1700}}{\sum A} \quad (3)
\]

\[
I_{S=O} = \frac{A_{1032}}{\sum A} \quad (4)
\]

\[
I_{C=C} = \frac{A_{996}}{\sum A} \quad (5)
\]

In the formula, \(\sum A = A_{2924} + A_{2852} + A_{1700} + A_{1601} + A_{1462} + A_{1377} + A_{1032} + A_{996} + A_{866} + A_{812} + A_{723}\). According to the experimental results in Fig. 3, Fig.4 and formula (1) - (5), the molecular structure changes are shown in Fig. 5.

| Asphalt types                  | IB    | IAr   | IC=O | IS=O | IC=C |
|--------------------------------|-------|-------|------|------|------|
| SK70# asphalt                  | 0.272 | 0.070 | 0    | 0.017| 0    |
| SK70# asphalt after aging      | 0.321 | 0.046 | 0.012| 0.032| 0    |
| Rubber powder modified asphalt | 0.291 | 0.069 | 0.015| 0.015|      |
| Rubber powder modified asphalt after aging | 0.310 | 0.055 | 0.061| 0.026| 0.013|

It can be seen from Fig. 5 that the value of IB for the SK70# asphalt increases by 18% after aging, while the value of IAr increases by 33% after aging. And the phenomenon shows that the aromatic components of asphalt are transformed into other components in the aging process, which leads to the asphalt harden. The chain reaction, chain condensation and oxidation reaction of asphalt gel system after aging lead to the increase of oxygen-containing functional groups, then the carbonyl group was found in the infrared spectrum scanning of aging samples. In addition, the content of sulfoxide group increased significantly after aging, 46% higher than that of sulfoxide group.

Compare with SK70# asphalt, the value of IB for the modified asphalt increases by 7% after aging, while the value of IAr increases by 20% after aging, which indicating that the change range of the molecular structure of the modified asphalt is slightly smaller, and the increase range of the absorption peak area ratio of carbonyl is also smaller, showing slightly stronger stability than SK70# asphalt. The sulfoxide group of rubber powder modified asphalt increased by 73% after RTFOT aging. In addition, due to the existence of rubber powder, the IC=C of rubber powder modified asphalt is significantly larger after long-term thermal oxygen aging. At the same time, the existence of rubber powder intensifies the decomposition of C=O functional groups, promotes the formation of S=O and C=C, and thus leads to the increase of both functional groups. Through the above analysis, it can be found that the aromatic compounds of rubber powder modified asphalt decrease after aging while the analytical structure of oxygen functional group increases. For the rubber powder modified asphalt, the aromatic compounds decrease relatively small, but the IC=O and IS=O are significantly larger.
4. Conclusions
(1) The aging performance of asphalt can be studied by analyzing the index of PRR, DRR, SPI or VAI. It is found that the aging degree of rubber powder modified asphalt is less than that of SK70# asphalt under the same aging environment.

(2) The complex modulus of SK70# asphalt after aging is significantly increased, while the change range of complex modulus of rubber powder modified asphalt after aging is relatively small; the addition of rubber powder has prompted the temperature sensitivity of rubber powder modified asphalt lower.

(3) The addition of rubber powder can reduce the reduction of aromatic compounds in asphalt, so as to ensure its good aging resistance.

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