Effects of aging methods on properties of rubber powder modified asphalt

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Abstract. Three types of aging methods were conducted on rubber powder modified asphalt, and the basic physical properties test, dynamic shear rheological test and infrared spectrum analysis were adopted to study the effect of aging methods on properties of rubber powder modified asphalt comprehensively. Results show that effects of different aging methods on physical properties of rubber powder modified asphalt are inconsistent. There is a slight influence of aging on its rheological properties, which means a better aging resistance. Through microanalysis, it can be found that there is a significant aging for rubber powder modified asphalt after pressurized aging, followed by the ultraviolet aging. The aging degree of rubber powder modified asphalt is relatively small after short-term thermal-oxidative aging.

1. Introduction
Asphalt pavement is the main form of high-grade highway pavement in China, and the performance of asphalt has always aroused the strong attention of the experts in transportation industry. Research shows that as ordinary asphalt materials struggles to keep up with the improvement of traffic volume and traffic load [1]. And, the use of waste materials for modified asphalt has always been popular among researchers. The cracking of waste rubber to produce rubber powder and applied for modified asphalt can not only solve the problem of environmental pollution and turn waste materials into resources, but also effectively improve the performance of asphalt pavement [2-4]. Rubber powder modified asphalt which has good performance, environmental benefits and economic benefits has attracted a lot of attention and application in road engineering [5-7]. However, its aging behaviors such as dehydrogenation, condensation and oxidation are related with the preparation environmental just like regular asphalt, which could reduce the performance of the modified asphalt [8, 9].

In this study, the rubber powder modified asphalt was prepared based on SK 70# asphalt, and the asphalt was aged by rotary film oven test, pressure aging test and UV aging test. The aging behavior of crumb rubber modified asphalt under different aging modes was analyzed and evaluated by testing the basic properties and rheological properties of aging samples and combining with infrared spectrum. It has a certain theoretical guiding significance for the durability prediction of asphalt pavement, can produce a positive effect on the treatment and utilization of waste rubber, and has certain
environmental and economic benefits.

2. Raw Materials And Experimental Methods

2.1 Raw Materials
The base asphalt used to prepare modified asphalt is SK 70 # asphalt, and its technical properties are shown in Table 1. The particle size of the rubber powder used in this study is 250 μm, and its technical properties are shown in Table 2.

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 500 r/min, then the rubber powder modified asphalt will be obtain after swelling for 15 min.

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

Table 2. General technical properties of the rubber powder

| Test indexes                  | Results |
|-------------------------------|---------|
| Natural rubber content(%)     | 44      |
| Carbon black content(%)       | 35      |
| Rubber hydrocarbon content(%) | 46.5    |
| Metal content(%)              | 0.009   |
| Acetone extract content(%)    | 12      |
| Fiber content(%)              | 0.03    |
| Ash content(%)                | 5       |
| 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 Pressure Aging Test (PAV) simulated the long-term thermal oxygen aging of asphalt binders, and the main parameters in the tests are 2.1 MPa pressure, 100 ℃ test temperature, and 20 h aging time. And the Ultraviolet Aging Test (UV) simulated the long term aging in the condition of open field with light and oxygen of asphalt binders, and the main parameters in the tests are 60 ℃ environment, 800μW/cm2 ultraviolet light and 6 d aging time.

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 Effect of aging mode on general properties
In this study, residual penetration ratio (PRR), residual ductility ratio (DRR), softening point change
(SPI), viscosity aging index (VAI) were used to evaluate the aging performance of asphalt [4], and the definitions of this index are shown in formula (1) - (4):

\[
PRR = \frac{P}{P_0} \times 100\% \\
DRR = \frac{D}{D_0} \times 100\% \\
SPI = \frac{S - S_0}{S_0} \\
VAI = \frac{\eta}{\eta_0}
\]

In the formula, P, D, S and \(\eta\) are the penetration (unit: 0.1mm), ductility (cm), softening point (℃) and viscosity (Pꞏs) of the sample after aging, respectively. And \(P_0\), \(D_0\), \(S_0\) and \(\eta_0\) are the values of the sample before aging. 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 Figure 1. It can be observed from Figure 1 that under the three different aging modes, short-term aging has little effect on penetration and ductility of crumb rubber modified asphalt, UV aging has little effect on softening point of crumb rubber modified asphalt, and the three aging modes have no significant difference on viscosity of crumb rubber modified asphalt.

![Figure 1. Aging performance of SK70# asphalt and rubber powder modified asphalt](image_url)

3.2 Effect of aging mode on rheological properties

Asphalt is a kind of viscoelastic material, which has elastic properties at low temperature and viscous properties at high temperature. Figure 2 and figure 3 show the complex modulus and phase angle of crumb rubber modified asphalt under different aging modes, respectively.

It can be observed from Figure 2 that the complex modulus of crumb rubber modified asphalt decreases with the increase of test temperature. The complex modulus of crumb rubber modified asphalt increases under same temperature, because the light component of asphalt changes into the heavy component, which results in the increase of elastic response of modified asphalt system. Specifically, the complex modulus is the largest after PAV aging, and the influence of ultraviolet aging and short-term aging is almost the same. In contrast, the influence of the three aging methods on the complex modulus of crumb rubber modified asphalt is almost negligible at the temperature above 55 ℃, which also reflects the better aging resistance of crumb rubber modified asphalt.

It can be seen from Figure 3 that the phase angle of crumb rubber modified asphalt increases first and then decreases with the increase of temperature, and tends to be gentle at 60 ~ 70 ℃, which shows such complex phase angle change, indicating that the addition of crumb rubber makes the binder
system more complex, and the change rule of viscosity is not single. The angle of crumb rubber modified asphalt decreases after aging, which shows that the viscosity of crumb rubber modified asphalt to decrease after aging. The influence of pressure aging and ultraviolet aging on the phase angle is almost the same, which is stronger than that of short-term aging.

3.3 Effect of aging mode on molecular structure
The physical properties and rheological properties of asphalt binder are closely related to its structural composition. It is a very effective method to analyze its performance differences by studying the differences of chemical molecular structure of asphalt [10, 11]. According to the absorption frequency position shown in the infrared spectrum and the corresponding absorption peak area, the structural type and content of the characteristic functional groups can be inferred [12, 13]. The infrared spectrum of rubber powder modified asphalt after different aging methods are show in the Fig.4. 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. Specifically, the functional group characteristics corresponding to each wave number in the infrared spectrum shown in Fig. 4 are listed in Table 3.
Table 3. 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 | 2852                | Symmetric stretching vibration of C-H |
| 1700                | Stretching vibration of C=O           | 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 |

The change of the content of functional groups in the molecular structure is characterized by the area ratio of each absorption peak, which reflects 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.

\[
I_B = \frac{A_{1377}}{A_{1462} + A_{1377} + A_{\gamma23}} \quad (5)
\]

\[
I_{Ar} = \frac{A_{1601}}{\sum A} \quad (6)
\]

\[
I_{C=O} = \frac{A_{1700}}{\sum A} \quad (7)
\]

\[
I_{S=O} = \frac{A_{1032}}{\sum A} \quad (8)
\]

\[
I_{C=C} = \frac{A_{996}}{\sum A} \quad (9)
\]

In the formula, \( \sum A = A_{2924} + A_{2852} + A_{1700} + A_{1601} + A_{1462} + A_{1377} + A_{1032} + A_{996} + A_{866} + A_{812} + A_{\gamma23} \). According to the experimental results in Fig. 4 and formula (5) - (9), the molecular structure changes are shown in Fig. 5.
Figure 5. Changes of molecular functional groups of two kinds of asphalt binders

It can be seen from Fig. 5 that the value of IB increases by 7% after short-term aging, increases by 21% after UV aging and increases by 14% after pressure aging; the value of IAr decreases by 20% after RTFOT aging, decreases by 26% after UV aging and decreases by 38% after PAV aging. One of the most significant phenomenon is the discovery of C=O structure. Pressure aging results in the most molecular structures containing functional groups, followed by ultraviolet aging, and the short-term aging is relatively small. So the functional group can be used as the evaluation index of aging degree of rubber powder modified asphalt. The sulfoxide group of rubber powder modified asphalt after RTFOT aging, UV and PAV increased by 73%, 203% and 291%, respectively. And the most IG=G was produced by pressure 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. Under the three aging modes, the aging resistance of rubber powder modified asphalt is the largest after pressure aging, followed by that caused by ultraviolet light, and the aging caused by short-term thermal oxygen environment is relatively small.

4. Conclusions

(1) From macro perspective, in addition to almost no difference in viscosity of different aging methods, however it has different effects on other physical properties of crumb rubber modified asphalt.

(2) The influence of three aging methods on the complex modulus of crumb rubber modified asphalt is very little, which reflects the aging resistance of crumb rubber modified asphalt to a certain extent. However, the effects of pressure aging and ultraviolet aging on phase angle are similar.

(3) C=C functional group can be used to characterize the aging of crumb rubber modified asphalt. Through micro analysis, the aging resistance of rubber powder modified asphalt is the largest after pressure aging, followed by that caused by ultraviolet light, and the aging caused by short-term thermal oxygen environment is relatively small.

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