Analysis of Asphalt Aging Behavior Evaluation Method Based on Infrared Spectrum

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Abstract: In order to analysis under microscopic scale fast evaluating asphalt asphalt aging mechanism and aging degree, Fourier transform infrared spectroscopy were used respectively to solvent method and ATR method to transmission spectra analysis of matrix asphalt, secondly by ATR method of matrix asphalt tested functional characteristics before and after the RTFOT aging, qualitative and quantitative analysis of the functional groups. The results show that there is no difference between the infrared spectra of the solvent method and the ATR method. Some carbon and sulfur elements in asphalt are oxidized to form carbonyl C=O and sulfoxide S=O functional groups during the aging process, and the oxidation of sulfur element is the main one. The sulfoxide index (SI) and carbonyl index (CI) are well correlated with the penetration degree of asphalt, the correlation coefficient reaches 0.83 and 0.84, respectively. The aging of asphalt increases the sulfoxide index (SI) and carbonyl index (CI), and the asphalt becomes hard and the penetration degree decreases. Infrared spectroscopy can effectively evaluate the aging behavior and degree of asphalt, which provides a new method for rapid detection of aging asphalt.

1. Introduction

By the end of 2020, some expressways in Jiangsu Province have been in operation for more than 15 years. For example, the length of expressways that have been in operation for more than 10 years has also reached 77%. By the end of the 13th Five-Year Plan, this proportion will further increase, and the operation time of the overall road network is generally longer. With the deepening of the aging of the provincial expressway, the evaluation of the asphalt aging condition of the pavement surface will gradually become the focus of the pavement evaluation. The asphalt aging has a significant impact on the attenuation of the pavement performance. Therefore, a fast and simple evaluation method of asphalt aging is urgently needed in the face of the huge pavement aging detection demand. The traditional asphalt aging evaluation uses the extraction and recovery method. Due to the many interfering factors of the original pavement asphalt, the long time and the need for a large amount of asphalt mixture, the detection results are difficult to characterize the performance of the aging asphalt, and it is difficult to meet the urgent needs of the current pavement asphalt aging evaluation.

Fourier Transform Infrared Spectroscopy (FT-IR) is an important method to analyze the structure of chemical compounds. In recent years, with the development of computer technology, FT-IR has been widely used in petrochemical industry, material science and other fields. The research shows that the changes of characteristic functional groups during asphalt aging can be measured by FT-IR. However,
there are still three problems in using FT-IR to study the aging mechanism of asphalt. First, due to the insufficient research on the aging mechanism of asphalt from the microscopic perspective at home and abroad, there is still a big gap between the practical application. 2 it is lack in the asphalt ir test analysis with asphalt road macroscopic quantitative indicators to evaluate asphalt aging, is three commonly used methods for ir test with solvent method and attenuated total reflection (ATR) method, The lack of a variety of methods of test results contrast, causing the difference between evaluation results appear.

In view of this, this paper first adopted Fourier Transform Inf rared Spectrometry (FT-IR) solvent method and ATR method to carry out transmission spectrum contrast test on the selected five kinds of matrix asphalt, and compared and analyzed the differences of different test methods, so as to determine the appropriate test and evaluation method. Secondly, ATR method is used to carry out transmission spectrum test on aging asphalt, and qualitative analysis of aging characteristics of asphalt from the microscopic point of view, and establish the relationship between Sulfoxide index (SI) and Carbonyl index (CI) and asphalt macroscopic road performance. In order to provide technical support for the evaluation of the aging condition of asphalt surface of Jiangsu expressway and national expressway, The micro-composition variation characteristics of asphalt were studied quantitatively by combining the macroscopic road performance and infrared spectrum.

2. Test

2.1. Test Materials
Five kinds of asphalt samples were selected, including 200# asphalt produced by Jiangsu Xinhai Stone Chemical Co., Ltd. (JXSC), 70# asphalt produced by Jiangsu Baoli Asphalt Co., Ltd. (JB), Korea Shuanglong Asphalt (KS), 70# asphalt produced by China Petroleum and Chemical Corporation (CPCC), and 70# asphalt produced by China National Petroleum Corporation (CNPC).

2.2. Test equipment
Tensor27 research grade Fourier transform infrared spectrometer, product of Bruker (Broker), Germany, has a signal-to-noise ratio of 5000:1, resolution of 1-0.4cm⁻¹, scanning speed of 3 images /s, and spectral testing range of 4000-400cm⁻¹. SYD-3061 (85) type asphalt film rotary oven is a product of Changzhou DeDu Precision Instrument Co., Ltd. The studio temperature is 163℃, The temperature control accuracy is ±0.5℃, The rotary speed is 15±0.2r/min, and the air flow rate is 4000±200ml/min.

2.3. Test methods
(1) Infrared spectroscopy solvent test, The asphalt was dissolved in carbon tetrachloride (CCl4) solution, and then injected into the liquid pool for testing.
(2) In the Attenuated Total Refraction (ATR) test, The ATR attachment was first placed in the optical path of the infrared spectrometer, and the air background was scanned. Then the asphalt was smeared on the infrared translucent crystal surface of the ATR attachment, and then the scanning test was performed [1][2].
(3) Rolling Thin Film Oven Test (RTFOT) was conducted in accordance with JTG E20-2011 Test Rules for Asphalt and Asphalt Mixtures in Highway Engineering. The test temperature was 163℃±0.5℃. Heating time is 0, 45, 85, 180, 240, 300min.
(4) The asphalt injection degree test was carried out in accordance with JTG E20-2011 Test Rules for Asphalt and Asphalt Mixtures in Highway Engineering. The test temperature was 25℃, The load was 100g, and the penetration time was 5s.

3. Test results and analysis

3.1. Comparison between solvent method and ATR method
Using solvent method and ATR method of five kinds of asphalt samples infrared spectrum experiment, quantitative comparison, using similarity of each sample solvent method is used to test the first parallel
reference spectrum, and the rest of the solvent method to test the spectra of the sample spectra and test by ATR method compared with the reference spectra analysis. The spectrogram is shown in Figure 1~ Figure 5. The statistical results of infrared spectrum similarity between the solvent methods and ATR methods are shown in Table 1.

**Table 1 Similarity statistics of infrared spectra of five bitumen solvents and ATR methods**

| Serial number | The test method | 200# asphalt produced by JXSC | 70# asphalt produced by JB | asphalt produced by KS | 70# asphalt produced by CPCC | 70# asphalt produced by CNPC |
|---------------|----------------|-------------------------------|---------------------------|-----------------------|-------------------------------|-------------------------------|
| 1             | Solvent method | 100%                          | 100%                      | 100%                  | 100%                          | 100%                          |
| 2             | ATR method     | 99.86%                        | 99.77%                    | 99.83%                | 99.71%                        | 99.80%                        |
| 3             | Solvent method | 99.96%                        | 99.69%                    | 99.83%                | 99.71%                        | 99.80%                        |
| 4             | ATR method     | 99.68%                        | 99.77%                    | 99.83%                | 99.71%                        | 99.80%                        |
| 5             | Solvent method | 99.41%                        | 99.77%                    | 99.83%                | 99.71%                        | 99.80%                        |
| 6             | ATR method     | 91.18%                        | 89.33%                    | 94.16%                | 89.56%                        | 89.23%                       |
| 7             | ATR method     | 85.45%                        | 89.25%                    | 93.75%                | 89.23%                        | 89.23%                        |
According to the results in Table 1, the similarity of the ATR spectrogram tested by the solvent method was all below 95%, which was somewhat different from the infrared spectrogram tested by the solvent method, mainly manifested in the position and intensity of the absorption peaks of 2729 cm$^{-1}$ and 1200-1000 cm$^{-1}$, as shown in Figure 1 to 5. It can be seen from a small part of the spectra tested by solvent method that there are weak absorption peaks at 2729 cm$^{-1}$, 1196 cm$^{-1}$, 1179 cm$^{-1}$, 1132 cm$^{-1}$ and 1076 cm$^{-1}$. However, in the infrared spectra tested by ATR method, there is basically no absorption peak at 2729 cm$^{-1}$, 1196 cm$^{-1}$, 1179 cm$^{-1}$, 1132 cm$^{-1}$ and 1076 cm$^{-1}$.

Studies have shown that molecular structure and external environmental factors, such as material state, sample preparation method and solvent effect, have certain influence on group frequency. In the solvent test, the bitumen samples were pretreated by dissolving the bitumen in a solution of carbon tetrachloride and drying it for 10-15 minutes under a high temperature drying lamp (temperature 80-90 °C). Some infrared spectra tested by solvent method are different from those tested by ATR method, possibly due to the pretreatment of the sample. Therefore, the infrared spectra tested by different test methods basically have no influence on the results.

3.2. Qualitative analysis of ATR method

The rotating film short-term aging test was carried out on 70# matrix asphalt produced by Jiangsu Baoli Asphalt Co., Ltd. The heating time was 0, 45, 85, 180, 240 and 300 min. The aging asphalt was subjected to infrared spectrum test using ATR method. The test results are shown in Figure 6 and Figure 7 below.

The results in Figure 6 and Figure 7 show:(1) Compared with the graph of the original matrix asphalt after aging, the position of the entire absorption peak in the graph does not change. There are obvious absorption peaks in the maps of both the original matrix asphalt and the aging asphalt, including 6 absorption peaks near 3441, 2921, 2853, 1617, 1457, and 1375 cm$^{-1}$, among which 2921 cm$^{-1}$ and 2853 cm$^{-1}$ are the symmetric stretching absorption peaks of C-H and -CH$_2$- groups, respectively. And these two peaks have the highest absorption. The absorption peak at 1617 cm$^{-1}$ was caused by the C=C skeleton vibration and C=O absorption of the benzene ring, and the absorption peak at 1457 cm$^{-1}$ was formed by the superposition of the -CH$_2$- bending vibration and the C-CH$_3$ asymmetric bending vibration close to it. The absorption peak at 1375 cm$^{-1}$ is formed by the symmetric bending vibration of -CH$_3$ [3][4][5].

(2) By comparing the atlases of the original matrix asphalt and the aging asphalt, it is found that the absorption peak transmittance of the aging asphalt after RTFOT has a significant change. In the functional group region, 3441 cm$^{-1}$ is the absorption peak of -NH- group. With the increase of aging time, the transmittance of the absorption peak at this place is significantly enhanced, indicating that -NH- absorption is enhanced and some -NH- reacts with hydroxy-OH to form hydrogen bonding.
compounds, indicating that asphalt aging occurs. The absorption peak transmittance of carbonyl C=O functional group near 1700cm⁻¹ also increases with aging time, indicating that part of carbon elements are oxidized into -C=O- group and C=O carbonyl tube energy group is formed during asphalt aging process. In addition, the absorption enhancement phenomenon also exists in the absorption peaks of -CH₂- and -CH₃, indicating that the number of -CH₂- and -CH₃ groups increases to varying degrees during asphalt aging [6][7][8][9]. In the fingerprint region, with the increase of aging time, the sulfoxide absorption peak near 1030cm⁻¹ also gradually increased, indicating that sulfur elements in asphalt generated S=O sulfoxide functional group.

3.3. Quantitative analysis of ATR method

In order to quantitatively analyze the aging degree of asphalt, the sulfoxide index (SI) and carbonyl index (CI) were proposed to characterize the content of sulfoxide and carbonyl. SI = sulfoxide S=O absorption peak area/reference absorption peak area and CI = carbonyl C=O absorption peak area/reference absorption peak area[10]. The sulfoxide index (SI) and carbonyl index (CI) were calculated by obtaining the area of characteristic absorption peaks of carbonyl and sulfoxide in the infrared spectra before and after aging of 70# asphalt produced by Jiangsu Baoli Bituminous Co., Ltd., as shown in Fig. 8 below.

![Figure 8 Calculation results of sulfoxide index (SI) and carbonyl index (CI)](image)

As shown in Fig. 8, with the aging time, The carboxyl index Ci has a gentle growth trend, while the sulfoxide index Si has a slow growth trend in the early stage and a rapid growth trend in the later stage, indicating that the contents of carbonyl and sulfoxide are increasing after asphalt aging, and the oxidation of sulfur element is a major part of asphalt aging [11].

Furthermore, penetration tests were carried out on the 70# asphalt produced by Jiangsu Baoli Bitumen Co., Ltd. with different aging times. Based on the penetration test results, The correlation between carbonyl index Ci and sulfoxide index Si and penetration was established. The results are shown in Figure 9, Figure 10, and Figure 11.

![FIG. 9 Variation diagram of needle penetration of asphalt at different thermal aging times](image)

![FIG. 10 Correlation between CI of carbonyl index and insertion degree](image)
FIG. 11 Correlation between sulfoxide index SI and insertion degree

As shown in Fig. 9, with the increase of thermal aging time, penetration degree showed a trend of gradual decrease, which was contrary to the change trend of sulfoxide index (SI) and carbonyl index (CI) with the increase of thermal aging time. According to Fig. 10 and Fig. 11, sulfoxide index (SI) and carbonyl index (CI) have a good correlation with the penetration degree of asphalt. With the increase of sulfoxide index (SI) and carbonyl index (CI), the penetration degree of asphalt has a trend of gradual decrease, indicating that the content of carbonyl and sulfoxide is increasing after asphalt aging. The functional group combines with oxygen to form polar or amphoteric groups such as carbonyl group and sulfoxide, which enhances the interaction between asphalt molecules, thus hardening asphalt and increasing its stiffness.

In summary, the relative content of functional groups of carbonyl and sulfoxide can represent the aging degree of asphalt. Both carbonyl and sulfoxide are chemical products of oxygen reaction of the constituent molecules of asphalt. The greater the increase of carbonyl index and sulfoxide index, the more serious the aging of asphalt will be. Therefore, carbonyl index Ci and sulfoxide index Si can characterize the aging degree of asphalt to a certain extent, which indicates that it is feasible to determine the aging degree of asphalt by using infrared spectrum test technology combined with modern analysis method, which provides a new method for rapid detection of aging asphalt.

4. conclusion
In this paper, comparison and analysis of infrared spectra of solvent method and ATR method of test results, and then using ATR method of aging asphalt transmission spectra experiment was carried out, from the microcosmic point of view, The qualitative and quantitative analysis of asphalt aging characteristics and establish sulfoxide index (SI) and carbonyl index (CI) and the macro road asphalt performance, The relationship between the following main conclusions:

(1) The similarity of asphalt samples tested by ATR method is all below 95%, which is somewhat different from the infrared results of solvent method, mainly manifested in the position and strength of 2729cm⁻¹ and 1200-1000cm⁻¹ absorption peaks. It is due to the sample pretreatment before the test that the results of solvent method and ATR method are different. Therefore, Solvent method and ATR method have little effect on the test results.

(2) Compared with the graph of the original matrix bitumen, the position of the whole absorption peak in the graph of the aged bitumen does not change, but the transmittance of the absorption peak in the graph of the aged bitumen with RTFOT significantly changes. In the tube energy group region, the absorption peak transmittance of C=O carbonyl functional group increases with aging time, indicating that part of carbon atoms are oxidized to form -C=O- group during asphalt aging process. In the fingerprint region, as the aging time increases, the sulfoxide absorption peak transmittance also gradually increases, indicating that sulfur elements form S=O sulfoxide functional groups with the aging of asphalt.

(3) Sulfoxide index (SI) and carbonyl index (CI) have a good correlation with asphalt penetration. After asphalt aging, The content of carbonyl and sulfoxide is increasing, and functional groups combine
with oxygen to form polar or amphoteric groups such as carbonyl and sulfoxide, so that the interaction between asphalt molecules is enhanced, which makes asphalt hardener and stiffer. The results show that infrared spectroscopy can effectively evaluate the aging behavior and degree of asphalt.

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