Study on Microcosmic Characteristics of Gussasphalt after Superheat Aging based on FTIR Technology

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Abstract. Gussasphalt concrete has many excellent characteristics, such as good impermeability, strength, elasticity and so on. In recent years, it has been widely used in large and medium bridges, especially in steel deck pavement. But different from ordinary mixture, gussasphalt needs to undergo long period of high temperature aging during mixing and transportation. In order to reveal the microscopic mechanism of superheat aging of gussasphalt, fourier transform infra-red spectroscopy (FTIR) is mainly used in this paper. The changes of functional groups of gussasphalt before and after aging were analyzed from the microscopic point of view. The results show that there is no new absorption peak of lake asphalt when it is added to the matrix asphalt, the asphalt is mainly physically modified by lake asphalt, and the aging degree of gussasphalt can be quantitatively characterized by carbonyl coefficient.

1. Introduction
In order to make steel bridge deck pavement have excellent performance and long-lasting service life, besides reasonable bridge structure, pavement structure, mixture composition design and construction technology, the technical performance of asphalt mixture is also required, especially, whether asphalt and its mixture can withstand the aging at 240°C is particularly important. In the life cycle of steel bridge deck pavement, the most severe aging stage of gussasphalt is the short-term aging stage in the process of secondary mixing, transportation and paving. The excessive heat aging will not only cause the viscosity of the gussasphalt mixture to increase rapidly, but also become difficult to be constructed. Even if the pavement is completed, it is easy to produce temperature shrinkage crack and fatigue crack under the comprehensive action of environment temperature and the traffic loading, which will affect the service life and service performance of the pavement[1].

Therefore, fourier transform infrared spectroscopy (FTIR) is mainly used to analyze the changes of functional groups before and after aging of gussasphalt on a microscopic scale in this paper. The superheat aging mechanism of gussasphalt is revealed from the microscopic level. The research results can provide theoretical basis for the design of gussasphalt aging resistance and the formulation of maintenance strategy.

2. Principle and test design
Fourier transform infra-red spectrometer is one of the most commonly used method in the qualitative and quantitative analysis of the chemical structure on organic polymers. Compared with other structural analysis instruments, the FTIR method is convenient to use and maintain, which can quickly provide abundant information of structural components. The principle is: when the infrared light is irradiated, the substance absorbs the infrared light of a certain wavelength, which causes the transition of vibration-rotational energy level of the molecule, and records the changing curve of the transmittance (or
absorbance) of different wavelengths by means of the instrument. That is, the infrared spectrum of the substance [2]. FTIR is an effective method in analyzing the changes of functional groups in asphalt aging process. It can be used to study the molecular structure of substances, determine the functional group composition of organic compounds and speculate the process of chemical reaction [3]. The principle of infrared spectrum quantitative analysis of asphalt aging is based on Lambert-Beer's law. At present, quantitative analysis is mostly carried out by measuring the absorbance at the absorption peak of infrared spectrum. The absorbance of carbonyl group reflects the concentration of carbonyl group in the sample. Because a large amount of carbonyl group is produced during asphalt aging, the higher the degree of aging is, the higher the carbonyl concentration is. The carbonyl concentration of asphalt before and after aging can truly reflect the aging degree of asphalt [4].

In order to reveal the mechanism of superheat aging of gussasphalt, in this study, the Bruker Alpha infrared spectrometer is used for test. The resolution is $4\text{cm}^{-1}$, the number of scanning is 32 times, and the range of wave number is $4000\sim400\text{cm}^{-1}$. Firstly, the functional groups of 70# matrix asphalt, TLA lake asphalt and the gussasphalt by mixing matrix and lake asphalt were tested and analyzed separately. Then 70# matrix asphalt and TLA lake asphalt were heated with the temperature of 163 ℃ about 6h, and the changes of functional groups of gussasphalt was analyzed before and after aging. On this basis, the aging law of gussasphalt was discussed for five kinds of superheat temperature.

3. Results and discussion

3.1 Analysis of functional groups for 70# asphalt and lake asphalt

During the test, the mixed asphalt of TLA:70#asphalt=60:40 was prepared as the gussasphalt sample. The infrared spectra of 70# matrix asphalt, lake asphalt and gussasphalt are shown in Figure 1.

![Figure 1](image)

Figure 1. Comparison of infrared spectra for the three kinds of samples

It can be seen from figure 1 that there are several distinct characteristic absorption peaks of the three kinds of asphalt. Among them, peak at 2924 cm$^{-1}$ and 2854 cm$^{-1}$ is stretch vibration absorption peak of CH$_2$. Peak at 1603 cm$^{-1}$ is benzene ring vibration absorption peak. Peak at 1455 cm$^{-1}$ is bending vibration absorption peak of CH$_3$. According to spectral analysis, asphalt is mainly composed of saturated hydrocarbons, aromatic compounds and hetero-atomic derivatives.

The characteristic peaks of the three kinds of asphalt are: both TLA Lake Asphalt and gussasphalt have stretching vibration absorption peaks of carboxylic acids in 1702 cm$^{-1}$. This is due to the fact that the lake asphalt and the gussasphalt mixed with the lake asphalt contain natural and long-lasting oxidized substances, which is related to the formation mechanism of the lake asphalt.

While there is no absorption peak in 70# matrix asphalt, which indicates that it has not been oxidized or aged. The obvious strong absorption peak of TLA lake asphalt and gussasphalt is vibration absorption peak of cyclopropane at 1033 cm$^{-1}$. This is mainly due to the presence of some minerals, such as quartz and clay in the asphalt contain a lot of silicon-oxygen bond.

The infrared spectrum of gussasphalt contains same vibration absorption peak in 70# matrix asphalt and TLA lake asphalt, and almost in the same place. Although the area of some absorption peaks has changed after the addition of lake asphalt, there is no new absorption peak appear, which indicates that there is no chemical reaction in the mixing process of TLA lake asphalt and 70# matrix asphalt.
3.2 The functional groups analysis of 70# matrix asphalt and TLA lake asphalt before and after aging

70# matrix asphalt and TLA lake asphalt were aged at 163℃ for 6h respectively. The changes of functional groups before and after aging were observed. The original absorption peaks of 70# matrix asphalt and TLA lake asphalt are basically the same before and after aging, but the absorbance intensity is different. A new characteristic absorption peak, carbonyl functional group, was produced in the vicinity of 1702 cm⁻¹ after aging of 70# matrix asphalt, and the area of absorption peak of TLA lake asphalt at this location was enhanced. The results show that both 70# matrix asphalt and TLA lake asphalt produce oxide during aging. The absorption peak of 70# matrix asphalt near 1030 cm⁻¹ corresponds to the sulfoxide functional group produced by oxidation. The absorption peak of TLA lake asphalt is stronger than that of the matrix asphalt. It is mainly caused by the original clay and quartz composition in lake asphalt and the superposition effect of sulfoxide functional groups produced by aging. So it is not advisable to use sulfoxide functional groups to evaluate the aging of lake asphalt.

3.3 The functional groups analysis of gussasphalt before and after aging

In this paper, the improved rolling thin film oven is used to aging the gussasphalt samples, and the aging time is 6h. The aging temperature of the gussasphalt samples respectively is 163℃, 180℃, 200℃, 220℃, 240℃. Infrared scanning test of five groups aged gussasphalt was carried out by infrared spectrometer. The test results are shown in figure 2.

![Figure 2. Comparison of infrared spectra under different superheat aging](image)

The carbonyl of gussasphalt at different aging temperatures at 1702 cm⁻¹ was quantitatively analyzed by baseline method. The aging degree of gussasphalt samples at different temperatures was analyzed by measuring the variation of carbonyl absorbance. According to the principle of infrared spectrum measurement, the intensity of absorption peak at different characteristic peak can be affected by quantitative calculation due to the different thickness of coating film. Therefore, the aging degree can't be evaluated directly by the absolute value of absorption peak area of carbonyl characteristic absorption peak. Because the saturated C-H flexural vibration bond is stable, the effect of coating thickness on absorbance can be removed by internal standard method. The relative content of carbonyl group is calculated by the absorbance (area of absorption peak) of saturated C-H bond (1455 cm⁻¹) and the carbonyl coefficient CI, as shown in Formula 1.

\[
CI = \frac{S_{C=O}}{S_{C-H}}
\]

In the formula, CI is the carbonyl coefficient, \( S_{C=O} \) is the integral area of the carbonyl absorption peak, and \( S_{C-H} \) is the saturated C-H integral area. The characteristic absorption peaks of carbonyl group and saturated C-H bond under different aging conditions were integrated by opus infrared spectrum processing software, and the respective absorption peak areas were obtained. The carbonyl coefficient CI was calculated according to the above Eq.1 as shown in Table 1. It is observed that there is no obvious relationship between the peak area of carbonyl group and saturated C-H bond with aging temperature. But the carbonyl coefficient increases with the increase of aging temperature. As shown in Fig. 3, the increase of carbonyl coefficient is...
relatively small under 220 °C, which indicates that the aging degree of gussasphalt is lower. While, the carbonyl coefficient increases rapidly when the temperature exceeds 220 °C, which indicates that the aging degree of gussasphalt is deepening. The association of macromolecules or polar functional groups has a great influence on asphalt properties, which increases the viscosity of asphalt. Therefore, the mixing temperature should be kept within 220 °C as far as possible.

Table 1. CI of gussasphalt at different aging temperatures

| Aging temperature | SC=O (1702cm⁻¹) | SC-H (1455cm⁻¹) | carbonyl coefficient CI |
|-------------------|-----------------|-----------------|------------------------|
| 163°C             | 1.14            | 6.52            | 0.175                  |
| 180°C             | 1.38            | 7.31            | 0.189                  |
| 200°C             | 2.65            | 12.57           | 0.211                  |
| 220°C             | 0.91            | 4.12            | 0.221                  |
| 240°C             | 2.11            | 7.93            | 0.266                  |

Figure 3. Changing curve of CI with aging temperature

4. Conclusions
In this paper, the microscopic properties of 70# matrix asphalt, TLA lake asphalt and the gussasphalt under different aging conditions were studied by Fourier transform infrared spectroscopy. The main conclusions are as follows:

1. The vibrational absorption peaks of gussasphalt are similar to those of lake asphalt and matrix asphalt, which almost appear in the same position. Although the area of some absorption peaks changed with the addition of lake asphalt, there was no new absorption peak appear when the lake asphalt was added to the matrix asphalt. Therefore, the lake asphalt was mainly physical modified to the matrix asphalt.

2. A new absorption peak carbonyl functional group was produced near 1702cm⁻¹ after aging, and the area of absorption peak of lake asphalt at this wave number was enhanced. The characteristic absorption peak of lake asphalt near 1030cm⁻¹ is mainly caused by the aging of the original clay and quartz components in lake asphalt. It is not advisable to use sulfoxide functional groups to evaluate the aging degree of lake asphalt and mixed asphalt.

3. The aging degree of gussasphalt can be quantitatively characterized by carbonyl coefficient, and the carbonyl coefficient increases with aging temperature. Especially the increasing trend is fastest between 220 °C and 240 °C.

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