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Technical Note

Thermal oxidative aging mechanism of crumb rubber/SBS composite modified asphalt

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HIGHLIGHTS

- The thermal oxygen aging mechanism of CR/SBSCMA has been discussed.
- IR and group components test have been used for the investigation of aging mechanism.
- The aging process of CR/SBSCMA was different from CRMA and SBSMA.
- The reaction process of group components of CR/SBSCMA was presented.

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ABSTRACT

Crumb rubber/SBS composite modified asphalt (CR/SBSCMA) technology is proposed to combine the advantages of crumb rubber (CR) and SBS. Then, the production cost of the modified asphalt could be reduced, the waste rubber resources could be made full utilization, and the performance of asphalt could be improved. Rotate thin film oven test was used for stimulating the thermal oxidative aging of matrix asphalt, crumb rubber modified asphalt (CRMA), SBS modified asphalt (SBSMA) and CR/SBSCMA. The influences of matrix asphalt, CR and SBS on the aging properties have been investigated based on the composition and structure analysis of asphalt and modified asphalt pre and post aging process. Then, the thermal oxidative aging mechanism of CR/SBSCMA has been discussed. The test results demonstrated that the carbonyl index and sulfoxide index could reflect the aging degree of asphalt well. Moreover, due to the presence of CR and SBS at the same time, the aging process of CR/SBSCMA was different from CRMA and SBSMA. In the aging process of CR/SBSCMA, the modifiers degradation products and asphalt secondary components reacted severely, which resulted in the decrease of aromatics and resin and the increase of asphaltenes and toluene insoluble. Meanwhile, the distribution and colloid structure of composite modified asphalt were changed by the modifiers degradation products, the asphalt secondary components and their reaction products, so were the macroscopic properties of CR/SBSCMA.

1. Introduction

Crumb rubber/SBS composite modified asphalt (CR/SBSCMA) technology is proposed to combine the advantages of crumb rubber (CR) and SBS. Then, the production cost of the modified asphalt could be reduced, the waste rubber resources could be made full utilization, and the performance of asphalt could be improved [1–3]. The current studies about CR/SBSCMA are mainly focus in the asphalt mixture preparation, road construction and performance evaluation and so on. However, the stable ability of the composite modified asphalt is the first problem in order to promote a large-scale application of composite modified asphalt, which requires the study of the modification mechanism directly of composite modified asphalt. At present, the related studies are not well documented, which restricts the application and popularization of CR/SBSCMA technology.

CR/SBSCMA has a good performance at high and low temperature. However, the aging of asphalt in construction and service will make the performance recession greatly of asphalt [4]. Asphalt aging resistance is very important to the use, maintenance and regeneration of paving asphalt. Paving asphalt would experience a series of physical and chemistry changes (such as evaporation,

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condensation, dehydrogenation, oxidation and decomposition) due to exposing to heat, oxygen, and ultraviolet light during storage, mixing, transport and laying down, as well as in service life. Then the asphalt pavement is prone to generate rut and crack, and could not perform its original bonding and sealing effect in the mixture. Aging is this kind of irreversible changes of the asphalt performance, physicochemical properties, colloidal structure and mechanical properties in this process. The asphalt aging is the main factor affecting its performance, and the asphalt aging resistance performance directly affects the service life of the paving asphalt [5,6].

In the aging process of CR/SBSCMA, besides the aging of matrix asphalt, the aging of the modifiers CR and SBS were also influence on the aging properties of composite modified asphalt. Rotate thin film oven test (RTFOT) was used for stimulating the thermal oxidative aging of matrix asphalt, crumb rubber modified asphalt (CRMA), SBS modified asphalt (SBSMA) and CR/SBSCMA. The influences of matrix asphalt, CR and SBS on the aging properties have been investigated based on the composition and structure analysis of asphalt and modified asphalt pre and post aging process. Then, the thermal oxygen aging mechanism of CR/SBSCMA has been discussed.

2. Materials and experimental

2.1. Materials

The selected matrix asphalt was SK-70, whose 25 °C penetration was 7.43 mm, softening point was 48.0 °C, and 15 °C ductility was more than 150 cm. The Furfural extract oil (FEO) which is high in saturates and aromatics is an ideal compatibilizer for the production of modified asphalt. The group components of the FEO were as follows: the content of saturates was 38.54%; the content of aromatics and resins were 57.04% and 4.42%, respectively. Both the SK-70 and FEO were provided by Hubei Guochuang Advanced Material Co. Ltd. The general CR was tyre crumb rubber from Huangshi Second Rubber Factory. The size of CR was 40–60 mesh. YH-791 SBS was supplied by the Hunan Yueyang Changling Petrifaction Co. Ltd. And several kinds of modifying agents included stabilizer and activator.

2.2. Preparation of modified asphalt

The preparation of modified asphalt was consisted of swelling, shearing and breeding. Firstly, mixture of modifier (CR, SBS or CR/SBS) and matrix asphalt with different proportions swelled at 163 °C for 1 h. After swelling, a given amount of fresh matrix asphalt was added to the mixture. The new mixture was high-speed shearing and stirring with 3000 r/min for 1 h at 180 °C. Then, adding 1‰ stabilizer by the total content of the mixture, the modified asphalt was made by breeding the mixture with 1000 r/min for 1 h at 170 °C.

2.3. Thermal oxidative aging test of matrix asphalt and modified asphalt

RTFOT was used for stimulating the thermal oxidative aging of matrix asphalt and modified asphalt during storage, mixing, transport and laying down, as well as in service life. RTFOT was conducted according to the standard test method GB/T 0610-2011. RTFOT 75 min (not including the 10 min heating time) and RTFOT 270 min (not including the 10 min heating time) were performed respectively for stimulating the thermal oxidative aging.

2.4. FTIR analysis of matrix asphalt and modified asphalt

The changes of main functional groups of matrix asphalt and modified asphalt pre and post thermal oxidative aging were analyzed by Impact 420 Attenuated total reflectance-Fourier transform infrared spectrophotometer (ATR-FTIR) (Nicolet, USA). The solid asphalt specimen was placed in the optical path to conduct IR analysis, which was convenient and accurate.

2.5. Measurement of group components of matrix asphalt and modified asphalt

Asphalt is usually divided to four groups: saturates, aromatics, resins and asphaltenes. The group components of matrix asphalt and SBSMA pre and post thermal oxidative aging could be measured according to the standard test method GB/T 0618-1993. While CRMA and CR/SBSCMA contained the CR component, and there was only a few fraction of CR which is dissolved in toluene, therefore, CRMA and CR/SBSCMA which should be divided into five groups: toluene insoluble, saturates, aromatics, resins and asphaltenes. At first, the CRMA or CR/SBSCMA was divided into heptane solubles (saturates, aromatics and resins) and heptane insoluble (asphaltenes and toluene insoluble) as the standard test method GB/T 0618-1993. Then the heptane insoluble was heated with toluene to reflux for more than 6 h. Finally, the toluene solubles were just as asphaltenes, and the residue was toluene insoluble.

3. Results and discussion

3.1. IR analysis of asphalt pre and post aging

IR analysis of the matrix asphalt, CRMA, SBSMA and CR/SBSCMA pre and post RTFOT have been conducted to check the changes of the main functional groups absorption peak during the aging process, which was conducive for understanding the aging behavior. The IR spectra of asphalt before and after aging were shown in Figs. 1–4.

As shown in the IR spectra, the characteristic absorption peak position of the matrix asphalt and modified asphalt was basically same pre and post aging. There was only a new absorption peak appearing at 1700 cm^{-1}. The new absorption peak and the absorption peak of 1030 cm^{-1} have been enhanced during aging process. According to the characteristics absorption frequency of organic compound groups, the 1030 cm^{-1} and 1700 cm^{-1} absorption peak were carbonyl peak and sulfoxide peak, respectively. The appearance of carbonyl peak showed that there were a series of oxidation reactions of asphalt in aging process, which generated ester, ketone, aldehyde and carboxylic acids containing carbonyl peak. The enhancement of the sulfoxide peak showed that the sulfur oxidation occurred in the aging process and had an important influence. In addition, the enhancement degree of carbonyl peak and sulfoxide peak were different for the matrix asphalt and three kinds of modified asphalt, which could be calculated quantitatively.

Because the sample thickness was different, the quantitative calculation may affect the absorption peak intensity. Internal standard method has been used to eliminate the effect of specimen thickness on absorbance in this study. The absorption peak area of C—CH_3 asymmetric bending vibration at 1460 cm^{-1} as a benchmark was used to calculate the relative content of carbonyl and sulfoxide [7,8] for each sample. Then, the asphalt aging index has been characterized by the ratio between the carbonyl and sulfoxide absorption peak area and C—CH_3 asymmetric bending vibration absorption peak area. The carbonyl index (CI) and sulfoxide index (SI) could be calculated as following equations:

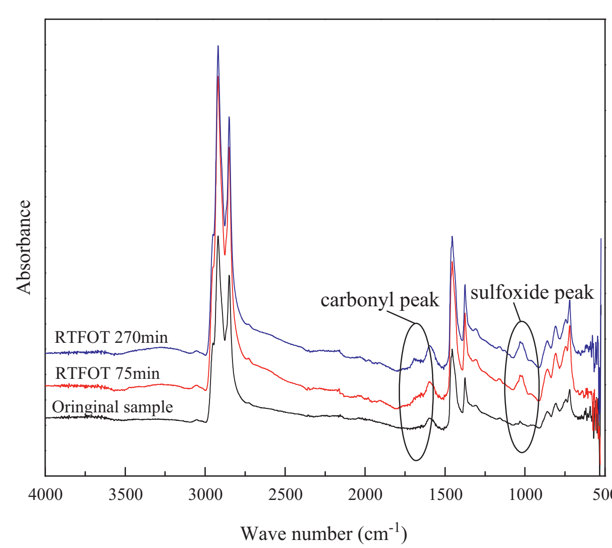

Fig. 1. IR spectra of matrix asphalt pre and post RTFOT.