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The research for structural characteristics and modification mechanism of crumb rubber compound modified asphalts

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HIGHLIGHTS

- The lack of physical properties of CRM asphalt was pointed out.
- The way for improving the physical properties of CRM by using SBS or sulfur was provided.
- The effect of SBS and sulfur on the structural characteristics of CRM asphalt before and after ageing was studied carefully.
- The major ways for studying the structural characteristics of CR compound asphalt were displayed fully.

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ABSTRACT

The crumb rubber (CR) compound modified asphalt with improved tenacity and high- or low-temperature properties was prepared by the addition of styrene–butadiene–styrene (SBS) and the stability of CR/SBS-modified (CRSM) asphalt was improved by the addition of sulfur. Rheological testing demonstrated the improved high-temperature performance of modified binders and indicated the susceptibility of vulcanizated binder to dynamic shear. Morphology observation showed the compatibility between CR and asphalt was improved greatly by vulcanization or ageing. Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) analysis showed the characteristics and distribution of the major functional groups of modified asphalt before and after ageing. In thermal analysis, DSC curve showed the effect of ageing and modifier on the molecule weight distribution and constituents of asphalt. The thermal stability and susceptibility of each binder to thermal decomposition were evaluated by using TG and DTG curves, which indicated the structural characteristics of binder and demonstrated the conclusion drawn by DSC analysis further.

1. Introduction

Asphalt as the binder of aggregate has been widely used in road pavement. Unfortunately high-temperature rutting and low-temperature cracking of asphalt cement or coating layer due to the severe temperature susceptibility limit its further application. Therefore it is necessary to modify asphalt. Among the modifiers of asphalt, crumb rubber (CR) is most widely used in road pavement. The research and application of CRM asphalt can date back to several decades ago in the United States, Canada and other countries [1,2]. The past research and application showed that CRM asphalt had many good characteristics such as improved resistance to rutting due to higher viscosity, higher softening point and better resilience, improved resistance to surface initiated, reduced fatigue/reflection cracking, reduced temperature susceptibility, improved durability and lower pavement maintenance costs, and saving in energy and natural resource by using waste products etc [1]. CR is the second used polymer to modify asphalt, following SBS [3]. In China, the research and application of CRM asphalt began in the 1980s. In recent years, with the rapid development of automobile industry, the volume of scrap tires has followed the rapid increasing. According to statistics, in 2004, the new tire production was 239 million tons and scrap tire amount was over 112 million tons [2]. In 2006, the tire production of China was as high as 280 million tons, ranking first in the world. At the same year, the scarp tire also was up to 140 million tons. It is estimated that, by 2010, China's auto volume kept 70 million tons, and scrap tire output kept 200 million tons [4]. In this background, the research and application of CRM asphalt in road engineering in China has been gained more attention. The use of CRM asphalt is environmentally correct solution, since the use of this material

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partially reduces the need for new raw materials, and improves the performances and life cycle of asphalt pavements [5,6].

A great deal of researchers have made a lot of study on the CRM asphalt. It is found that the improvement of CRM asphalt depended on many factors such as the particle size, the surface characteristics of CR, blending conditions, the manner in which CR devulcanizes, the chemical/physical properties of base asphalt, as well as its source and microstructure [3,7–13]. Thodesena et.al developed an empirical model depicting the changes in values of $G^*/\sin \delta$ and failure temperatures [14]. Liu et al. evaluated the performance of different modified binders with different CR contents, the particle size or type by using the analysis of variance method [15].

Although lots of study has been done on the properties of CRM asphalt, the study for the compound modification of CRM asphalt is still very scarce in many publications. Actually the major physical properties of CRM asphalt are still poor and cannot compete with those of SBS-modified asphalt, due to the low activation and quality of CR, which restricted the application of CRM asphalt in different climates or traffic conditions to great extent. Therefore it is necessary to modify CRM asphalt further by the addition of other modifiers, however the corresponding research is still scarce yet, especially for the detailed research for the structural characteristics and modification mechanism of CR compound asphalt.

In this study, CRM asphalt, crumb rubber/SBS modified (CRSM) asphalt and crumb rubber/SBS/sulfur modified (CRSSM) asphalt were prepared by the addition of CR, SBS and sulfur respectively in order to improve the lack of the tenacity and storage stability of CRM asphalt. We studied the physical properties of base asphalt, CRM, CRSM, CRSSM asphalts before and after ageing carefully. To investigate the structural characteristics and modification mechanism of each binder further before and after ageing, we used various research methods including rheological testing, morphology observation, FTIR, ^{1}H NMR and thermal analysis.

1. Rheological testing was used to investigate the effect of modifier and ageing on the rheological behaviour and structural characteristics of asphalt by comparing master curves.
2. Morphology observation was used to study the morphological characteristics of binder and the compatibility between polymer and asphalt under different ageing or modification conditions.
3. FTIR and ^{1}H NMR tests were used to investigate the effect of modifier and ageing on the distribution of the major functional groups of modified asphalt.
4. Thermal analysis was used to evaluate the thermal stability of each binder. The effect of modifier and ageing on the structural characteristics of binder was studied further by comparing thermodynamic parameters and enthalpy curves.

2. Materials and measurements

2.1. Materials

Hulian-70 paving asphalt, was obtained from the Fuzhou Petroleum Asphalt Factory, China. The physical properties were as follows: penetration, 61 dmm (0.1 mm, 25 °C, ASTM D 5); softening point, 49.1 °C (ASTM D 36); viscosity, 0.35 Pa.s (135 °C, ASTM D 4402). SBS1301 is linear polymer, containing 30 wt% styrene, the average molecule weight is 110,000 g/mol. Superfine sulfur powder (500 mesh number) is a commercial product (industrial grade) of Wenhe Chemical Co., Ltd., China. The general crumb rubber (60 mesh) was tyre crumb rubber from Haihong Rubber Factory, China, and the physical properties and chemical compositions is listed in Table 1.

2.2. Preparation of samples

The modified asphalts were prepared using a high shear mixer (made by Qishuang Machine Co., Ltd., China). Firstly, asphalt (300 g) was heated until it became fluid in an iron container, then upon reaching about 180 °C, the SBS and crumb rubber powder (based on 100 parts asphalt) were added. The shearing time was 1 h and then the modifiers (based on 100 parts asphalt) were added, heated until reaching about 180 °C and sheared 1 h at the shearing speed of 4500 r/min, subsequently the blend was stirred by a mechanical stirrer at 180 °C for 2 h to make sure the fully swelling of the modifiers in the asphalt. After that, the preparation has been finished. The proportion for CRM, CRSM, CRSSM asphalts is listed in the following:

CRM asphalt: CR modified asphalt (15 wt% 60 mesh CR).
CRSM asphalt: CR/SBS1301-modified asphalt (15 wt% 60 mesh CR; 3 wt% SBS1301).
CRSSM asphalt: CR/SBS1301/sulfur-modified asphalt (15 wt% 60 mesh CR; 3 wt% SBS1301; 0.2 wt% sulfur).

2.3. The ageing of modified asphalt

The ageing of modified polymer asphalt was performed using the thin film oven test (TFOT, ASTM D 2872) simulates the changes in the properties of asphalt during the hot mixing and the lay down process.

2.4. Physical properties test

The physical properties of asphalts, including softening point, penetration, toughness and tenacity, ductility, elastic recovery were tested in accordance with ASTM D 36, D 5, D 5801-95, D113, D 6084-97 respectively.

2.5. Storage stability test

The storage stability of modified asphalts was measured as follows. The sample was poured into an aluminum toothpaste tube (32 mm in diameter and 160 mm in height). The tube was sealed and stored vertically in an oven at 163 °C for 48 h, then taken out, cooled to room temperature and cut horizontally into three equal sections. The samples taken from the top and bottom sections were used to evaluate the storage stability of a polymer modified asphalt (PMA) by measuring their softening points. If the difference of the softening points between the top and the bottom sections was less than 2.5 °C, the sample was considered to have good high-temperature storage stability. If the softening points differed by more than 2.5 °C, the PMA was considered unstable.

2.6. Rheological characterization

A strain-controlled dynamic shear rheometer (DSR, Annton Paar, MCR 102, Germany) with parallel plate geometry (25 mm or 8 mm in diameter), was used to determine the rheological behaviour of asphalts.

High temperature sweeps (from 30 to 120 °C, 25 mm parallel plate, 1 mm gap) with 2 °C increments were applied at a fixed frequency of 10 rad/s and variable strain. Frequency sweeps were applied over the range of 0.1–100 rad/s at a fixed strain amplitude at 60 °C.

In each test, about 1.0 g of sample was applied to the bottom plate, covering the entire surface, and the plate was then mounted in the rheometer. After heating to the softening point of the binder, the top plate was brought into contact with the sample, and the sample was trimmed. The actual strain was measured to calculate various viscoelastic parameters such as complex viscosity (η^*) and phase angle (δ). All tests were performed within the linear viscoelastic range of the sample.

2.7. Morphology observation

The sample morphology was observed using an optical microscope made by Nikon Co., Japan. Squashed slides of modified binders were prepared using very small amounts of the heated sample and viewed under the microscope at a magnification of 400.

Table 1
Physical properties and chemical compositions of crumb rubber (60 mesh).

Physical properties	Density ratio (g/cm^3)	1.15
	Moisture content (%)	0.45
	Break strength (MPa)	10.0
	Elongation at break (%)	400.0
Chemical compositions	Ash content (%)	3.6
	Acetone extract (%)	11.5
	Carbon black content (%)	28.4
	Rubber hydrocarbon content (%)	56.6