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Effects of polymerized sulfur on rheological properties, morphology and stability of SBS modified asphalt

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HIGHLIGHTS

- This work revealed polymerized sulfur had delayed vulcanization effect on SBS modified asphalt.
- The morphology indicated polymer domains tend to be smaller as the elongation of mixing time.
- Viscosity of SBS modified asphalt decreases as polymerized sulfur content increases.
- SBS modified asphalt with high level of polymerized sulfur shows the improved storage stability.

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ABSTRACT

The objective of this study was to investigate effects of polymerized sulfur on viscosity functions, morphology and storage stability of SBS modified asphalt, as compared to elemental sulfur. Viscosity functions including complex viscosity, steady flow viscosity and dynamic viscosity were measured by dynamic shear rheometer (DSR) and Brookfield viscosity rheometer. The morphology and microstructure of modified asphalt were observed using fluorescence microscopy and Fourier Transform Infrared spectroscopy (FTIR). The results revealed that the increment in viscosity of modified asphalt containing polymerized sulfur was slower than that of elemental sulfur. Vulcanization rate decreases with the increase of polymerized sulfur, i.e. delayed vulcanization effect. In morphology, large polymer domains progressively transform to the fine dispersed SBS phase with smaller dimensions as the elongation of mixing time; whereas a fine polymer phase was found for elemental sulfur at the initial stage of mixing, which is significant evidence of delayed vulcanization. Moreover, the FTIR results verify the decrease of unsaturation of poly-butadiene block and the formation of C—S bond. Viscosities of asphalt with polymerized sulfur were always lower than those of elemental sulfur and decreased with the increase of polymerized sulfur content. SBS phase domain vulcanized by polymerized sulfur is larger than that of elemental sulfur and tends to become larger with the increase of polymerized sulfur content. Lastly, SBS modified asphalt with higher level of polymerized sulfur shows the improved storage stability.

1. Introduction

The vast majority of road pavements in the world are made of asphalt binders due to its adhesive, impermeable, and viscoelastic properties [1]. However, increased traffic factors (e.g. heavier loads, higher traffic volume, and higher tire pressure) as well as extreme weather events are the great threats to pavement performance, causing pavement distress such as permanent deformation, fatigue cracking, and thermal cracking [2,3]. These undesirable distresses shorten pavement service life and increase maintenance cost of pavement. In order to increase longevity of pavement, high-performance asphalt that has the stronger resistance to high-temperature rutting and low-temperature cracking is desired in paving construction. Polymer modification for asphalt has been an effective method to achieve this goal. To date, the most popular polymer for asphalt modification is styrene-butadiene styrene (SBS) tri-block copolymers, which provides asphalt better mechanical behavior at high temperatures and elastic properties at low temperatures [4,5]. The SBS triblock chains involve a starting

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polystyrene block, followed by an intermediate polybutadiene block, ending with another polystyrene block, which presents a two-phase morphology of glassy polystyrene domain dispersed in the flexible polybutadiene matrix. Within the service temperature range of pavement, the glassy polystyrene domains contribute to the stiffness of SBS while the polybutadiene blocks offer the elasticity [6,7]. This special behavior of physically crosslinking elastic network makes SBS to be a popular polymer modifier for asphalt.

However, SBS in asphalt matrix is prone to separate out from bulk phase at high temperatures because of their thermodynamic instability [8,9]. It is common and inevitable for SBS modified asphalt to be stored at high temperatures without stirring in paving field for several days or even more than weeks at a time [10]. The storage instability of SBS modified asphalt is regarded as one of the most critical issues that significantly impairs the thermo-mechanical properties and rheological properties of modified asphalt. Thus, many efforts have been done to prevent the occurrence of phase separation [11–15]. It is commonly believed that the most effective and practical approach is to use sulfur, usually elemental sulfur, to improve the stability of SBS modified asphalt through sulfur vulcanization.

As early as 1958, Welborn and Babashak [16] reported that the addition of sulfur to the blends of rubber or latex and asphalt can greatly improve their storage stability. Maldonado et al. [17] developed a method for preparation of the storage-stable SBS modified asphalt by adding sulfur. Unfortunately, these attempts are not put into field practice owing to the excessive viscosity of modified asphalt. Until 1990, the storage-stable polymer modified asphalt mixed with sulfur was prepared and applied in the real paving project [18]. After that, a number of studies have focused on optimizing the preparation process, improving the performance, understanding the reaction mechanism, and reducing the cost for SBS modified asphalt with sulfur [19–22].

As a matter of fact, it is not an easy task to produce the storage-stable SBS modified asphalt because the complexity and variation of asphalt compositions and the poor compatibility among polymer and asphalt. However, the exact mechanism of sulfur reacting with SBS and asphalt is still unclear. It is commonly agreed that sulfur chemically bond the polymer chains and couple polymer and asphalt by means of sulfides and/or polysulfide bonds. In terms of reaction mechanism, researchers [23–25] argued that the additional reaction of double bond and substitution of allylic hydrogen atoms mainly account for the linking between sulfur and SBS chains, giving rise to the decrease of unsaturation, the shifting of the double bonds, and the molecular isomerization. While the dehydrogenation of asphalt components and sulfur radicals may occur in the linking reaction of sulfur and asphalt [2,26–28]. On the other hand, sulfur vulcanization for SBS is an anti-plasticization process and leads to the formation of more complex higher-molecular weight networks, which easily results in gel formation. SBS is susceptible to vulcanization and the dosage of sulfur should be precisely tuned to prevent gelation. However, the properties of SBS modified asphalt varies greatly even using the same dosage of sulfur because the vulcanization reaction process as well as the degree of vulcanization is not easily controllable and tunable. Wen et al. [29,30] considered sulfur vulcanization as a process of dynamic vulcanization and this dynamic process will sustain until cooling down.

Based on above considerations, technical methods should be developed to slow down and finely control sulfur vulcanization process and thus the degree of sulfur vulcanization, thus reducing the susceptibility of SBS to vulcanization and preventing the gel formation. Although previous researches have studied optimizing mixing conditions and sulfur content, little work has considered the vulcanization process. Besides, vulcanization of SBS in asphalt by polymerized sulfur is not available from the literature. Polymerized sulfur, an amorphous allotrope of sulfur, is a metastable linear polymer of sulfur, which has an average molecular weight from 100,000 to 300,000 [31,32].

The objective of the present study is to investigate the effect of polymerized sulfur on the viscoelastic properties and storage stability of SBS modified asphalt. This will achieve the goal of controlling vulcanization process and reaction degree, thus decreasing susceptibility of SBS to vulcanization, reducing potential gelation, and improving storage stability. Therefore, elemental sulfur, various polymerized sulfur, SBS, and asphalts were used to prepare SBS modified asphalt containing different polymerized sulfur contents. The effect of polymerized sulfur content on the performance of SBS modified asphalt was evaluated by viscosity functions measured from dynamic oscillation shear, steady state shear, and rotating shear modes. The variations of viscosity functions with time were also investigated. Stabilities of SBS modified asphalt mixed with different level of polymerized sulfur were monitored by viscoelastic function variations.

2. Experimental testing

2.1. Materials

Two types of paving asphalt with 80/100 penetration grade were used as base asphalts, which are abbreviated as ZH and K in this study. Conventional properties such as penetration [33], softening point [34], and viscosity [35] are presented in Table 1. The SBS is a linear polymer with 30 wt% styrene and its weight-average molecular weight is around 110,000. The elemental sulfur and polymerized sulfur are commercial products. The elemental sulfur was noted as S_0. Three types of polymerized sulfur used in this study are noted as S_{40}, S_{60} and S_{90}, respectively. The S_{40} contains 40% weight of polymerized sulfur and the remaining 60% is elemental sulfur. The contents of polymerized sulfur in S_{60} and S_{90} are 60% and 90% accordingly.

2.2. Preparation of SBS modified asphalt with polymerized sulfur

SBS modified asphalt was prepared by melt blending method [37,38] using a high speed disintegrating mixer at 4000 rpm and 170 °C for one hour. The operating conditions such as temperature control, rotating speed, shearing rate, as well as stirring period were optimized in order to maximize the rheological performance and to minimize degradation of asphalt and polymer [39]. The content of SBS was 3% by weight of the blend for all samples. After shear blending process, a propeller with clovers was applied to stir the blends. At the meantime, sulfur was added by weight of 0.2% of blends. Lastly, the blends were divided into small samples into containers, cooled down to room temperature, and sealed by aluminum foil for further characterization. For the sake of brevity, the SBS modified asphalt (ZH, K) mixed with elemental sulfur,

Table 1
Physical properties and chemical composition of the base asphalts.

	Test specifications	Results	
		Asphalt ZH	Asphalt K
Physical properties			
Penetration (25 °C, dmm)	ASTM D 5 [33]	89	90
Softening point (R&B, °C)	ASTM D 36 [34]	42.2	41.6
Viscosity (135 °C, Pa·s)	ASTM D 4402 [35]	0.36	0.38
Chemical composition (wt%)			
Saturates	ASTM D4124 [36]	22.8	30.9
Aromatics		32.1	27.5
Resins		39.1	41
Asphaltene		6	0.6