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Proceeding Paper

Rheological and Aging Characteristics of Polymer-Modified Asphalt with Addition of Sulfur †

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Abstract: The polymer modification of asphalt binders was first introduced in Europe in the 1980s and has gained use, as lower-quality asphalt binders did not perform well under increasingly heavier traffic loading on pavements. The influence of chemical cross-linkers such as sulfur on the rheological, morphological, and aging characteristics of the polymer-modified asphalt (PMA) binder has been experimentally examined. The PMAs were prepared, blending different sulfur contents (0.03, 0.1, 0.3, and 0.5% by wt. of binder) with a neat binder. The samples were aged by a rolling thin film oven (RTFO) and a pressure aging vessel (PAV) and examined through rheologic investigations. Using models, including master curves, the Glover–Rowe parameter, and aging indexes, the effect of the aging resistance of the asphalt binder modified with sulfur was analyzed. The results indicate that adding sulfur up to 0.3% improved the performance grade range, elasticity, low-temperature cracking resistance, and rutting resistance of the PMA. Additionally, the introduction of sulfur improved the aging resistance of the PMA.

Keywords: asphalt binder; sulfur; polymer-modified asphalt; rheology; aging; performance

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1. Introduction

The polymer modification of asphalt binders improved their rheological and viscoelastic properties, allowing the pavement to achieve the performance needed for the current traffic demands [1,2]. The copolymer elastomer styrene–butadiene (SB) block is the most common polymer asphalt modifier. The styrene improves the strength of the material, and the butadiene component contributes to the elasticity of the material [3].

To reduce the phase separation between polymer and asphalt binder, crosslinking agents are used to improve their compatibilization [1,3]. Elemental sulfur is the most widely used crosslinking agent, which promotes the vulcanization of SB by chemically crosslinking the elastomer through the unsaturated bond of butadiene and chemically connecting polymer and asphalt molecules via sulfide and/or polysulfide bonds [4]. Most recent studies have placed more attention on the effect of sulfur on PMA's stability, and only a few [5,6] have addressed the improvement in the aging susceptibility and improved rheological properties of the binder.

During the mixing and service life, the binder is subjected to aging. Due to thermo-oxidation, the polymer and polymer network degradation can occur, displaying chain scission, causing the embrittlement of the asphalt [4,7,8]. Cuciniello [9] analyzed the anti-oxidative effect of sulfur in PMA and stated that crosslinked polymer-modified binders had a lower oxidative susceptibility than non-cross-linked binders.

An improvement in the aging resistance of the binder can increase pavement durability and decrease the maintenance cost over its life cycle. Thus, this paper aims to investigate the effects of adding elemental sulfur, an inexpensive, abundant, and available cross-linking agent, to PMA and its concentration on the rheological properties of the asphalt binder that affect pavement performance and durability. Additionally, the use of sulfur as an antioxidant in PMA and its effects on the aging susceptibility were evaluated through the Glover–Rowe parameter and dynamic modulus and phase angle master curves.

2. Materials and Methods

2.1. Materials

The neat asphalt binder used in this study was classified as PG 64-22S, according to Superpave performance grading (PG). For the polymer modification of the asphalt, a thermoplastic elastomer was used: a linear diblock copolymer composed of blocks of styrene and butadiene since it is one of the most effective ways of improving the binder performance [10]. The sulfur used as a crosslinking agent was a 100-mesh powder with 99.5% purity.

For this study, the properties of a control sample, a binder modified with sulfur, and five PMAs with different sulfur contents were compared. The first step consisted of slowly incorporating 3% of SB by weight into the neat, heated asphalt at 180 °C using a high-shear mixer at 4000 rpm and subsequently stirring for 60 min at 1500 rpm. Then, the PMA was mixed with a calculated ratio (0.075, 0.03, 0.1, 0.3, 0.5 wt.%) of sulfur using a mechanical agitator applying lower shear at 160 °C and 800 rpm for 4 h.

2.2. Methods

The asphalt binders were compared by their Superpave performance grades and rheological properties. The binder grading was performed following the AASHTO M 320 specification, which has a set of characterization tests that determines the temperature range in which the binder is suitable to be used in pavement construction. The Multiple Stress Creep Recovery (MSCR) measures the percent recovery and non-recoverable creep compliance of the binder, can be an indicator of rutting sensitivity, and was tested in accordance with AASHTO TP 70. The rheological master curve represents the asphalt binder characteristic in a viscoelastic region. It is a model based on a time–temperature principle that predicts the performance of the material over a range of temperatures and loading times or frequencies. In this work, dynamic shear modulus and phase angle master curves were used to describe the influence of the sulfur on the behavior of the binder.

Using a Dynamic Shear Rheometer (DSR), the magnitude of the dynamic shear modulus $|G^*|$ and the phase angle δ were measured at 60 °C at low strain before and after aging. The aging index was the ratio of both values, and lower values represented lower aging susceptibility. The Glover–Rowe (G–R) parameter evaluated the cracking performance of asphalt binders and could be used as an aging parameter by evaluating the durability of the binder regarding non-load cracking.

3. Results

As given in Table 1, the modification of the neat binder with polymer improved the high-temperature PG.

Table 1. Binder PG and MSCR results.

Sample	PG	Sample	PG
C	64-22	C + SB + 0.075 S	76-22
C + SB	72-22	C + SB + 0.1 S	76-22
C + 0.075 S	68-22	C + SB + 0.3 S	76-22
C + SB + 0.03 S	76-22	C + SB + 0.5 S	76-18

Figure 1 shows that up to 0.3% of sulfur blended increased the elasticity of the binder, improving recovery and decreasing Jnr, a parameter that was related to rutting susceptibility.

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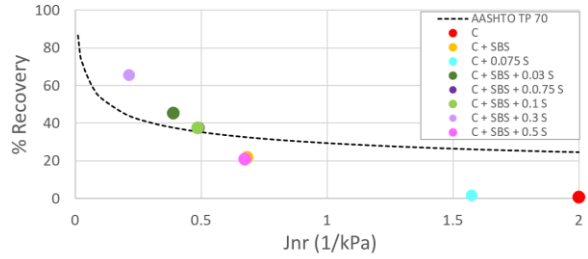
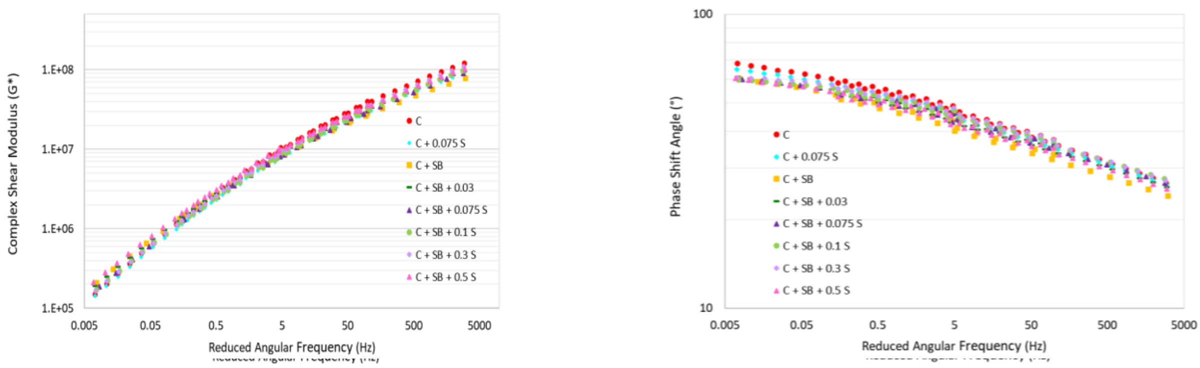


Figure 1. Elastomeric behavior of PMA.

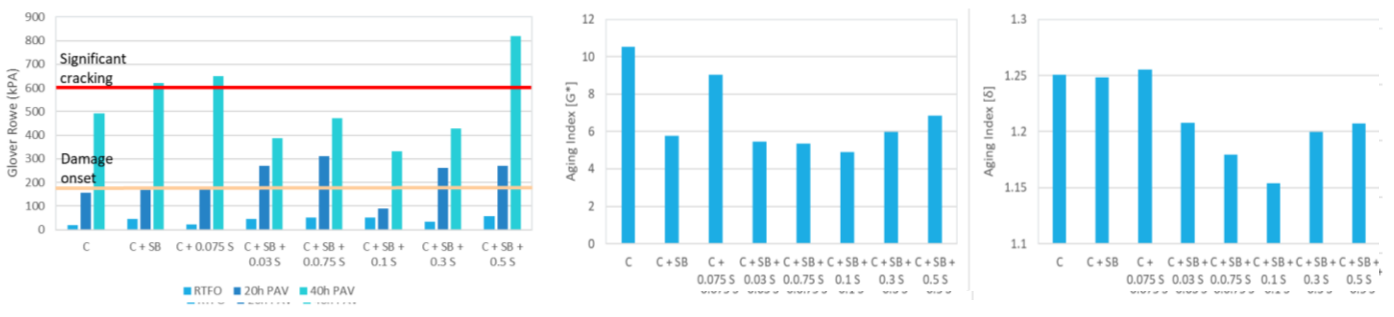
Based on the Williams-Landel-Ferry (WLF) model and using 15°C as a reference temperature, the master curves for complex shear modulus (G*) and phase angle (δ) were constructed and are shown in Figure 2. Lower frequencies represent slow traffic speeds, a condition that the binder is more prone to rutting, and higher frequencies correspond to shorter loading times. The addition of sulfur to PMA slightly decreased G* at lower frequencies, G* increased at higher frequencies, and the binder became marginally more viscous. Despite the outcome, the PMA with sulfur performed better than the neat binder.



(a) (b)

Figure 2. Master curves (a) Complex Shear Modulus; (b) Phase Shift Angle.

The effect of sulfur as an antioxidant is suggested through the Glover-Rowe parameter and aging indexes, shown in Figure 3.



(a) (b)

Figure 3. Aging of PMA (a) Glover-Rowe parameter; (b) Aging Indexes (G* and δ).

Figure 3a shows that PMA increased susceptibility to cracking after long-term aging compared to the neat binder, and the addition of sulfur up to 0.3% could attenuate those effects. Figure 3b evaluates aging through the changes in G* and δ and shows that the aging

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effects. Figure 3b evaluates aging through the changes in G* and δ and shows that the aging susceptibility decreases when sulfur is added to the PMA blend, with the best formulation being with 0.1% of sulfur, complying with the Glover–Rowe parameter analyses.

4. Conclusions

This research investigated the effect of the addition of sulfur on PMA's rheological properties and aging mechanism. The following conclusions can be drawn.

- The content of sulfur has a significant impact on the extent of the changes in PMA, in which it has a positive effect of up to 0.3% by the total weight of the binder.
- Up to 0.3% sulfur improved the performance grade, elastomeric behavior, and low-temperature cracking resistance of PMA.
- The addition of sulfur decreased the aging susceptibility of PMA.

Therefore, the decrease in cracking and aging susceptibility can potentially increase the serviceability of the pavement, improve the ride quality, and require less maintenance over the pavement's life cycle.

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