# Rheological characterization of styrene-butadiene-styrene block copolymer modified bitumens

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## ABSTRACT

This study investigates rheological characteristics of various styrene-butadiene-styrene (SBS) triblock copolymer modified bitumens, with emphasis on the low-temperature behavior. Fluorescence microscopy is employed as a supplementary characterization technique to study the morphological properties of the SBS modified bitumens and their correlations with the observed rheological behavior.

## INTRODUCTION

During the last few decades, dramatically increased traffic volumes and loads have forced asphalt engineers to find ways to improve the engineering properties of road bitumens. In this context, one of the most popular approaches is the polymer modification of bitumen[1,2]. Currently, the most commonly used polymer for bitumen modification is styrene-butadiene-styrene (SBS) triblock copolymer that can be classified as a thermoplastic elastomer. The widespread use of SBS is due to its relatively good dispersibility in bitumen as well as the superior engineering performance (i.e. improved high-temperature rutting and low-temperature cracking resistance) and acceptable cost of SBS modified bitumen[1].

SBS copolymers have a biphasic morphology where glassy polystyrene (PS) domains ($T_g \approx 90$ °C) are dispersed in the rubbery polybutadiene (PB) matrix ($T_g \approx -90$ °C). At the usual service temperatures of paving bitumen, SBS forms a three-dimensional network structure where rigid PS blocks act as reversible physical crosslinks between soft PB blocks that provide elasticity[3]. When SBS is mixed with bitumen, some specific interactions occur. Most notably, PB midblocks are believed to interact with positively charged atoms or functions in bitumen through their $\pi$-electrons[4], and are known to absorb the maltenes (oil fractions) from the bitumen and swell up to nine times their initial volume[5].

In the present study, rheological properties of SBS modified bitumens are studied over a wide temperature range. In particular, small-amplitude oscillatory shear (SAOS) testing is extended to sub-zero temperatures, which is a temperature range at which the dynamic oscillatory properties of SBS modified bitumens have not been studied extensively in the past. The effects of SBS concentration and architecture, base bitumen type, and sulfur vulcanization are investigated. Furthermore, fluorescence microscopy is used to investigate the morphology of the SBS modified bitumens and to further elucidate the origins of the observed rheological behavior. Finally, correlations between the low-temperature rheological properties measured in shear and in bending are briefly analyzed.

## EXPERIMENTAL

### Materials

Two commercial SBS triblock copolymers with different architectures were blended with two base bitumen in various proportions to produce seven SBS modified bitumen samples for analysis. The properties of the SBS copolymers and base bitumens are summarized in Tables 1 and 2, respectively.

A summary of the prepared SBS modified bitumen samples and their basic properties is given in Table 3. These samples were prepared by mixing bitumen and SBS powder in a propeller mixer (160-185 °C, 3 h). Based on preliminary observations, it was expected that Bitumen B is poorly compatible with SBS. Therefore, in one of the samples a minor amount of sulfur was added to the blend of Bitumen B and linear SBS to enhance the compatibility of the blend components.

### Methods

Optical microscopy was performed with a Carl Zeiss Axioskop 40F1 equipped with a digital camera DP200a. Samples were prepared using the freeze fracture method[6] and fluorescence microscopy in reflection mode was performed. A magnification of 200x was used.

Frequency sweep measurements ($f$ = 10 … 0.01 Hz) were performed with two stress-controlled rheometers: an Anton Paar MCR 301 rheometer equipped with 25-mm parallel plate geometry at a gap of 1 mm was used at high temperatures ($T$ = 20 … 120 °C), while a Malvern Kinexus Pro rheometer equipped with 4-mm parallel plate geometry at a gap of 1.75 mm was employed at low temperatures

Table 1. Molecular and thermal properties of the SBS triblock copolymers.

| | Radial SBS | Linear SBS |
|---|---|---|
| Commercial name | Calprene 411 | Kraton D1101 |
| Architecture | 3-arm star | linear chain |
| Styrene content [wt%] | 30 | 31 |
| SB diblock content [wt%] | 8 | 16 |
| $M_n$ [kg/mol] | 311 | 193 |
| $M_w$ [kg/mol] | 343 | 219 |
| $M_w/M_n$ [-] | 1.11 | 1.13 |
| $T_g$ (PB/PS) [°C] [a] | -90/89 | -91/89 |

[a] measured by DSC at a heating rate of 10 K/min

Table 2. Conventional properties of the base bitumens.

| | Bitumen A | Bitumen B |
|---|---|---|
| Pen [1/10mm] [a] | 177 | 145 |
| $T_{R\&B}$ [°C] [b] | 38.4 | 39.8 |
| $T_g$ [°C] [c] | -18.7 | -19.5 |

[a] Needle penetration at 25 °C (EN 1426)
[b] Ring-and-Ball softening point (EN 1427)
[c] measured by temperature-modulated DSC (linear heating rate = 3 K/min, modulation amplitude = 0.5 K, modulation period = 60 s)

Table 3. Summary of the prepared SBS modified bitumen samples and their basic properties.

| Sample code | Base bitumen | SBS modification | | Pen [1/10mm] | $T_{R\&B}$ [°C] | $T_g$ [°C] [a] |
|---|---|---|---|---|---|---|
| | | Type | Amount [wt%] | | | |
| BitA+3%SBS-R | Bitumen A | Radial SBS | 3 | 107 | 59.0 | -19.4 |
| BitA+5%SBS-R | Bitumen A | Radial SBS | 5 | 79 | 98.5 | -19.8 |
| BitA+7%SBS-R | Bitumen A | Radial SBS | 7 | 64 | 103.5 | -20.7 |
| BitA+10%SBS-R | Bitumen A | Radial SBS | 10 | 50 | 112.5 | -21.1 |
| BitA+5%SBS-L | Bitumen A | Linear SBS | 5 | 91 | 82.5 | -19.4 |
| BitB+5%SBS-L | Bitumen B | Linear SBS | 5 | 84 | 78.0 | -18.5 |
| BitB+5%SBS-L +sulfur | Bitumen B | Linear SBS | 5 | 86 | 79.5 | -21.5 |

[a] measured by temperature-modulated DSC (linear heating rate = 3 K/min, modulation amplitude = 0.5 K, modulation period = 60 s)

($T$ = 10 … -40 °C). Both of the rheometers were equipped with a Peltier plate and hood, connected to a refrigerated circulator, to provide an accurate temperature control of the test specimen. All frequency sweep measurements were performed in the linear viscoelastic regime. The low-temperature frequency sweep data were corrected for torsional instrument compliance as described elsewhere[7].

Repeated creep-recovery experiments were performed with the Anton Paar MCR 301 rheometer equipped with 25-mm parallel plate geometry at a gap of 1 mm. In these repeated creep-recovery experiments, ten successive creep-recovery tests (1-s creep / 9-s recovery) were carried out at multiple creep stress levels ranging from 25 to 25,600 Pa at a constant temperature of 50 °C.

Bending beam rheometer (BBR) is used routinely in the asphalt industry to evaluate low-temperature creep properties of asphalt binders. In this study, BBR tests were conducted according to EN 14771 standard at temperatures ranging from -18 to -36 °C.

## RESULTS AND DISCUSSION

Fluorescence micrographs clearly demonstrate the ability of SBS polymer (or its PB midblock, to be more exact) to absorb light fractions of the bitumen and swell considerably. At low concentrations, SBS is estimated to swell approximately nine times its initial volume, conforming to the findings of other researchers[5]. Furthermore, as a result of the swelling, phase inversion occurs already at a relatively low SBS content and the polymer-rich phase becomes the continuous phase in the SBS-bitumen blend. For example, a continuous network of SBS-rich phase is detected in sample BitA+5%SBS-R that contains only 5 wt% of SBS. However, at the highest SBS concentrations investigated the swelling is significantly reduced.

Frequency sweep measurements reveal that SBS modification results in a remarkable increase in stiffness and elasticity at temperatures above 10 °C. One of the most convenient ways to visualize the enhancement in the elastic properties is by means of the Booij-Palmen plot $\delta(\log|G^*|)$ (also known as the van Gurp-Palmen plot). In this plot, SBS modified bitumens show a sharp minimum peak, signifying the existence of highly elastic, rubbery behavior. Furthermore, a systematic increase in the complex modulus value corresponding to the minimum phase angle $G^*(\delta_{min})$ is observed with increasing SBS content; this trend will be analyzed in more detail in a future publication.

The effect of SBS modification on the high-temperature rheological properties can also be quantified using the Winter plot $\eta^*(G^*)$[8]. This plot clearly reveals a transition from Newtonian to highly non-Newtonian flow behavior at 60 °C with increasing SBS content. Furthermore, this data is indicative of the semi-solid like characteristics of SBS modified bitumens at this temperature (cf. the analysis of wax modified bitumens in Laukkanen and Soenen[9]).

As opposed to high temperatures, SBS modification is observed to remarkably decrease the stiffness of bitumen at low temperatures ($T$ < 10 °C). Consequently, the temperature dependence of viscoelastic properties is significantly reduced in SBS modified bitumens. In addition, SBS modification results in the reduction of bitumen elasticity (increase in phase angle values) at the lowest measurement temperatures.

Unlike unmodified bitumens[10], highly SBS modified bitumens are observed to exhibit thermorheologically complex behavior at low temperatures as illustrated by the Booij-Palmen plot. In this case, the thermorheological complexity is believed to result from the distinctly different temperature dependences of the relaxation times of SBS- and bitumen-rich phases. This conclusion is supported by the microscopic observation of a continuous SBS-rich phase in highly modified bitumens.

Despite this thermorheological complexity, qualitatively satisfactory master curves could be constructed for the investigated materials over a wide range of frequencies by combining the frequency sweep data measured at high and low temperatures. The effect of SBS modification is particularly visible in the storage modulus master curves that display a plateau region at intermediate frequencies (corresponding to the minimum peak in the Booij-Palmen plot). This suggests that SBS is able to form entanglements even when it is blended at relatively low concentrations with bitumen. Therefore, in principle, SBS modified bitumens can be considered as semidilute entangled polymer solutions, a concept that will be discussed in more detail in a later publication. Interestingly, the master curves of highly SBS modified bitumens also exhibit critical gel-like behavior ($G' \approx G'' \sim \omega^{1/2}$)[11] over approximately three decades of frequency above the plateau region. Additionally, the analysis of the master curves reveals that the crossover frequency (the frequency at which $G'(\omega) = G''(\omega)$ above the plateau region) decreases with increasing SBS content.

The temperature dependence of the investigated materials can be further investigated by analyzing the horizontal shift factors $a_T$ obtained from the master curve construction. The temperature dependence of the shift factors of both unmodified and SBS modified bitumens is found to follow the modified Kaelble equation[12] over the entire experimental temperature range, that is both below and above $T_g$.

Relaxation time spectra were calculated from the experimental dynamic data using the method of Baumgaertel and Winter[13]. It is observed that with increasing SBS content, a distinct peak at long relaxation times develops. This peak can be attributed to the entanglement behavior of SBS.

Repeated creep-recovery experiments at 50 °C reveal a drastic decrease in non-recoverable (permanent) creep deformation and increase in elastic recovery with increasing SBS content. These measurements also indicate that the network structure formed by swollen SBS is relatively strong as only moderate nonlinearity is observed in the shear creep properties of the SBS modified bitumens when the creep stress is increased up to 25,600 Pa. It is also observed that significant normal stresses develop in SBS modified bitumens when sheared at high creep stresses, a phenomenon that is caused by the enhanced elastic properties of these materials. Furthermore, the zero-shear first normal stress coefficient, defined as $\Psi_{1,0} = N_1/\dot{\gamma}^2$ when $\dot{\gamma} \rightarrow 0$, is found to increase dramatically with increasing SBS content.

The effect of SBS architecture on the rheological properties of SBS modified bitumen was investigated by means of samples BitA+5%SBS-R and BitA+5%SBS-L. It is found that radial SBS has a more pronounced impact on the rheological properties of Bitumen A than linear SBS, indicating that star-shaped polymer architecture is more suitable for bitumen modification than linear one. This finding can be at least partly explained by morphological differences, as fluorescence microscopy reveals a continuous SBS-rich phase only in BitA+5%SBS-R and not in BitA+5%SBS-L. However, it should be also noted that the different molecular weights of the SBS polymers may also influence this result.

The poor compatibility of SBS and Bitumen B was confirmed by fluorescence microscopy that revealed the coalescence of SBS particles in sample BitB+5%SBS-L. Rheologically, this incompatibility appears to manifest itself as reduced elasticity and thermorheological complexity at high temperatures. The addition of a minor amount of sulfur to this SBS-bitumen blend is observed to significantly improve the dispersibility of SBS in bitumen and to increase the temperature dependence of viscoelastic properties at low temperatures.

Finally, the low-temperature rheological properties of all investigated SBS modified bitumens were analyzed and a comparison was made between the properties measured in shear and in bending. A very good correlation ($R^2 = 0.981$) is found between the complex modulus measured with 4-mm parallel plate geometry in a rotational rheometer and the creep stiffness measured by BBR if sample BitB+5%SBS-L is excluded from the analysis. The reason why this sample does not follow the correlation as observed for the other samples is speculated to be the poor compatibility of BitB+5%SBS-L blend, a characteristic that presumably leads to macro-phase separation or to other morphological differences between the 4-mm parallel plate and BBR test specimens.

## CONCLUSIONS

SBS block copolymers are observed to greatly affect the rheological properties of bitumen, especially its elasticity. This is mainly due to SBS polymers' ability to swell and form a continuous network structure in bitumen already at relatively low concentrations. At low temperatures, SBS modification is found to reduce the stiffness of bitumen and to cause thermorheological complexity.

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