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Low-temperature rheological and morphological characterization of SBS modified bitumen

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HIGHLIGHTS

- Dynamic viscoelastic properties at low temperatures are measured by the recently developed 4-mm DSR technique.
- The formation of continuous SBS-rich network within bitumen results in thermorheological complexity at low temperatures.
- The macro-phase separation of SBS and bitumen leads to deviations in 4-mm DSR and BBR test results.

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ABSTRACT

Polymer modification is widely used to improve the engineering properties of bitumen, the most commonly used polymer modifier being styrene-butadiene-styrene (SBS) block copolymer. Although extensive studies have been performed on polymer modified bitumen (PMB), no reliable data is currently available on the effect of polymer modification on the dynamic rheological properties at low temperatures. In this study, we focus on the rheology of SBS modified bitumen near and below the glass transition temperature (T_g) using the 4-mm DSR technique. In addition, fluorescence microscopy and temperature-modulated differential scanning calorimetry are used to study the phase behavior and interactions in the SBS-bitumen blends. At high SBS concentrations, thermorheological complexity is observed in the investigated temperature range, attributable to the formation of a continuous SBS-rich network structure. In the case of compatible SBS-bitumen blends, a linear correlation is established between the flexural creep stiffness measured by bending beam rheometry (BBR) and the complex shear modulus measured by 4-mm DSR. Deviations from this linear trend are shown to result from the macro-phase separation induced by the poor compatibility of SBS and bitumen.

1. Introduction

Polymers are frequently used as modifiers to improve the engineering properties of bitumen in various industrial applications such as asphalt paving and roofing [1–4]. The most commonly used polymers include plastomers (e.g. polyethylene (PE), polypropylene (PP), ethylene–vinyl acetate (EVA), and ethylene-butyl acrylate (EBA)) and thermoplastic elastomers (e.g. styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), and styrene-ethylene/butylene-styrene (SEBS)) [4]. Most notably, the effect of polymer modification is commonly and distinctively manifested in the rheological behavior. Many studies have shown that viscoelastic properties of polymer modified bitumen (PMB) exhibit reduced temperature dependence as compared to unmodified bitumen, as well as improved elasticity, leading to improved performance both at high and low service temperatures [5–9].

According to Zhu et al. [4], SBS triblock copolymer is the most widely used polymer for bitumen modification. Due to the asymmetric composition of SBS (the styrene content is typically well below 50 wt%), this polymer has a biphasic morphology of cylindrical polystyrene (PS) domains dispersed in a continuous polybutadiene (PB) matrix. Under the usual service temperatures of paving bitumen, PS blocks are glassy ($T_{g,PS} \approx 90\,^{\circ}C$) and contribute to the strength of SBS, while PB blocks are rubbery ($T_{g,PB} \approx -90\,^{\circ}C$) and offer the elasticity [10]. Consequently, SBS forms a three-dimensional network structure where rigid PS blocks

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act as physical crosslinks. When mixed with bitumen, some interactions take place between bitumen and SBS. In particular, it has been frequently reported that PB midblock absorbs the maltenes (oil fractions) from the bitumen and swells up to nine times its initial volume [11–16]. Fourier transform infrared spectroscopy (FTIR) analysis of SBS modified bitumen indicates that this absorption is caused by the interaction of PB blocks with positively charged groups in bitumen through their π-electrons [17]. As a result, SBS modified bitumen microphase separates into a swollen SBS-rich phase and an asphaltene-rich bitumen phase [18]. Moreover, due to the increased asymmetry caused by the absorption of the maltenes, the morphology of PS domains changes from cylindrical to spherical within the SBS-rich phase [16]. When added at low concentrations, SBS is dispersed as a discrete phase in bitumen [15]. However, phase inversion occurs when the SBS content is increased (typically around 5 wt%) and the SBS-rich phase becomes the continuous phase [15,19].

The formation of the continuous SBS-rich phase has been shown to induce large changes in the rheological properties of SBS modified bitumen [15,20]. A dramatic increase in viscosity and elasticity at high service temperatures is well documented [8,9,21–23]. Meanwhile, somewhat less information is available on the effect of SBS polymer modification on the low-temperature rheological properties of bitumen [24]. This is somewhat surprising as it has been reported that binder properties account for 90% of the low-temperature cracking distresses of asphalt pavements [25]. Most of the existing low-temperature studies have focused on the creep properties measured by a bending beam rheometer (BBR), several of them concluding that SBS modification decreases the creep stiffness and creep rate (m-value) of bitumen [20,26,27]. On the other hand, only Lu and coworkers have performed extensive low-temperature investigations on the dynamic viscoelastic properties of bitumens modified with SBS and other polymers [7,26,28–30]. It should be noted, however, that these studies focused mainly on the qualitative comparison between different polymer modifiers and bitumens by temperature sweep experiments, and therefore they did not provide a complete understanding of the complex viscoelastic behavior of these materials at low temperatures.

In order to overcome measurement errors associated with the instrument compliance [31–33], a group of researchers from the Western Research Institute (WRI) recently developed a rheological characterization method that uses 4-mm diameter parallel plate geometry on a standard rotational rheometer [34,35]. This technique, commonly known as "4-mm DSR", allows an accurate determination of the rheological properties of bituminous binders near and within the glassy state where the shear modulus approaches a limiting value of $G_g \approx 1$ GPa. As described in a technical report by the WRI researchers [36], the 4-mm DSR technique has been successfully employed in the low-temperature rheological characterization of a wide variety of bituminous materials, such as asphalt emulsion residues [37], field-aged asphalt binders [38,39] and wax modified bitumen [40]. However, at the time of writing, no research has been published that systematically examines the low-temperature rheological properties of PMBs by 4-mm DSR.

In this study, we focus on the low-temperature rheological characterization of SBS modified bitumen by 4-mm DSR. We note that this is, to our knowledge, the first systematic study of the dynamic viscoelastic properties of PMBs at low (subzero) temperatures using this technique. In addition, complementary calorimetric and microscopic studies are performed to better understand and explain the rheological observations. High-temperature rheological properties of the SBS modified bitumen are outside the scope of this paper and are discussed elsewhere [5,41].

2. Experimental

2.1. Materials

Two base bitumens and two commercial SBS triblock copolymers (one with linear and one with star-branched structure) were used to produce SBS modified bitumen samples investigated in this study. Some basic properties of the base bitumens are listed in Table 1. Correspondingly, information about the SBS block copolymers is provided in Table 2.

SBS modified bitumen samples were prepared by melt blending SBS block copolymers and bitumen at 160–185 °C for 3 h using a Silverson high shear mixer. The SBS concentration was varied in the range of 3–10 wt% as detailed in Table 3. Moreover, the blend of bitumen B and linear SBS was chemically crosslinked to enhance the compatibility between the blend components; this sample is labelled BitB + 5%SBS-L*. For the sake of brevity, the analysis presented in this paper focuses mainly on the effect of SBS content on the investigated material properties (i.e. samples Bitumen A, BitA + 3%SBS-S, BitA + 5%SBS-S, BitA + 7%SBS-S and BitA + 10%SBS-S are compared). However, for completeness, information about the effect of SBS structure (BitA + 5%SBS-S vs. BitA + 5%SBS-L), base bitumen type (BitA + 5%SBS-L vs. BitB + 5%SBS-L) and chemical crosslinking (BitB + 5%SBS-L vs. BitB + 5%SBS-L*) is also provided.

2.2. Fluorescence microscopy (FM)

The morphology of the SBS modified bitumen samples was studied using a Carl Zeiss Axioskop 40 FL epifluorescence microscope, equipped with a DeltaPix DP200 digital camera. A set of three filters was used in the fluorescence imaging: a BP 450–490 nm excitation filter, a FT 510 nm beam splitter, and a LP 515 nm emission filter. FM micrographs were taken at original magnifications of 50×, 100× and 200×. FM specimens were prepared by the freeze fracture method as described by Soenen et al. [42] and the micrographs were taken at room temperature. In addition, selected specimens were imaged after high-temperature annealing (140 °C for 1 h) as discussed in Section 3.1. The FM micrographs were analyzed using an ImageJ image processing and analysis software, version 1.50i (National Institutes of Health, Bethesda, MD, USA; https://imagej.nih.gov/ij/) [43]. The uneven illumination of the field of view was corrected using a posteriori shading correction plugin developed by Bonnet and coworkers [44].

2.3. Temperature-modulated differential scanning calorimetry (TMDSC)

Developed by Reading and coworkers [45,46], temperature-modulated differential scanning calorimetry (TMDSC) is an extension of the conventional DSC technique. TMDSC allows a separation of the total heat flow into its heat capacity-related (reversing) and kinetic (non-reversing) components by superimposing a

Table 1
Basic properties of the base bitumens.

	Test method	Bitumen A	Bitumen B
Penetration [1/10 mm]	EN 1426	177	145
Ring-and-Ball softening point [°C]	EN 1427	38.4	39.8
Penetration index [-]	EN 12,591 (Annex A)	−1.30	−1.46
SARA fractions	IP-469		
Saturates [wt%]		4.7	6.6
Aromatics [wt%]		54.3	50.0
Resins [wt%]		22.9	21.8
Asphaltenes [wt%]		18.2	21.6
Colloidal index [−]	$(w_{aromatics} + w_{resins})/(w_{saturates} + w_{asphaltenes})$	3.4	2.5

Table 2
Chemical properties of the SBS block copolymers.

	Test method	Star SBS	Linear SBS
Polymer architecture		3-arm star	linear
Styrene content [wt%]	information provided by the material supplier	30	31
SB diblock content [wt%]	gel permeation chromatography (GPC)	8	16
M_n [kg/mol]		311	193
M_w [kg/mol]		343	219
M_w/M_n [−]		1.11	1.13