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Low-temperature rheological and morphological characterization of SBS modified bitumen

Olli-Ville Laukkanen^{1,2}, Hilde Soenen³, H. Henning Winter¹, and Jukka Seppälä²

¹ Department of Polymer Science and Engineering and Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts 01003, United States

² Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, P.O. Box 16100, 00076 Aalto, Finland

³ Nynas NV, 2000 Antwerp, Belgium

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.

Keywords: Polymer modified bitumen; Rheology; 4-mm DSR; Bending beam rheometry; Fluorescence microscopy; Temperature-modulated differential scanning calorimetry; Glass transition; Thermorheological complexity; Phase separation

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 ($T_{g,PS} \approx 90\text{ }^{\circ}\text{C}$) and contribute to the strength of SBS, while PB blocks are rubbery ($T_{g,PB} \approx -90\text{ }^{\circ}\text{C}$) and offer the elasticity [10]. Consequently, SBS forms a three-dimensional network structure where rigid PS blocks 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

1 charged groups in bitumen through their π -electrons [17]. As a result, SBS modified bitumen
2 microphase separates into a swollen SBS-rich phase and an asphaltene-rich bitumen phase [18].
3 Moreover, due to the increased asymmetry caused by the absorption of the maltenes, the
4 morphology of PS domains changes from cylindrical to spherical within the SBS-rich phase
5 [16]. When added at low concentrations, SBS is dispersed as a discrete phase in bitumen [15].
6 However, phase inversion occurs when the SBS content is increased (typically around 5 wt%)
7 and the SBS-rich phase becomes the continuous phase [15,19].

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

23 In order to overcome measurement errors associated with the instrument compliance, a
24 group of researchers from the Western Research Institute (WRI) recently developed a
25 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 (sub-zero) 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.

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 12591 (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

SBS modified bitumen samples were prepared by melt blending SBS block copolymers and bitumen at 160-185 °C for 3 hours 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.

Table 3 Composition and basic physical properties of the SBS modified bitumen samples

Sample code	Base bitumen	SBS modification			Penetration [1/10 mm]	Ring-and-Ball softening point [°C]	Penetration index [-]
		Type of SBS	SBS content [wt%]	Chemically crosslinked			
BitA+3%SBS-S	Bitumen A	star	3	No	107	59.0	3.13
BitA+5%SBS-S	Bitumen A	star	5	No	79	98.5	7.82
BitA+7%SBS-S	Bitumen A	star	7	No	64	103.5	7.67
BitA+10%SBS-S	Bitumen A	star	10	No	50	112.5	7.78
BitA+5%SBS-L	Bitumen A	linear	5	No	91	82.5	6.48
BitB+5%SBS-L	Bitumen B	linear	5	No	84	78.0	5.60
BitB+5%SBS-L*	Bitumen B	linear	5	Yes	86	79.5	5.89

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 50x, 100x and 200x. 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 sinusoidal modulation on a linear heating or cooling ramp. In this study, TMDSC experiments were performed on a TA Instruments Q2000 differential scanning calorimeter equipped with a Refrigerated Cooling System (RCS90). The DSC instrument was calibrated with high-purity sapphire and indium standards. Approximately 7-10 mg of the investigated material was weighed into an aluminum pan that was hermetically sealed and transferred to the DSC instrument. Prior to the actual measurement, the samples were annealed inside the DSC at 140 °C for 5 min to remove any effects of thermal history. After the annealing treatment, modulated cooling and heating scans were carried out in the temperature range between -90 and 140 °C. The following modulation parameters were used in the TMDSC experiments: underlying cooling/heating rate = 3 K/min, modulation amplitude = 0.5 K, and modulation period = 60 s. The DSC cell was purged with dry nitrogen gas at a flow rate of 50 ml/min. The data from the TMDSC experiments was analyzed with TA Instruments Universal Analysis 2000 software, version 4.5A.

2.4. Rheological characterization

2.4.1. Bending beam rheometry (BBR) of SBS modified bitumen

Bending beam rheometry (BBR) was used to evaluate the low-temperature rheological properties of the SBS modified bitumen samples in bending. A BBR device from Cannon Instrument Company was used to perform creep experiments in three-point bending according to EN 14771. A constant load of 980 mN is applied at the midspan of a bitumen beam ($127 \times 12.7 \times 6.35 \text{ mm}^3$) at various temperatures ranging from -18 to -36 °C. The deflection at the midspan of the beam specimen is measured as a function of loading time, and the flexural creep

stiffness (S) and creep rate (m) are calculated at $t = 8, 15, 30, 60, 120$ and 240 s. Two replicate beams of each SBS modified bitumen sample were tested and average values are reported.

2.4.2. 4-mm DSR of neat and SBS modified bitumen

Shear rheological experiments were performed using a stress-controlled Malvern Kinexus Pro rheometer. The temperature was controlled within ± 0.1 K using a Peltier plate and active hood that were connected to a Julabo CF41 refrigerated circulator. The sample environment was flushed with dry nitrogen gas to avoid moisture uptake and ice formation. Frequency sweeps were conducted from 10 to 0.01 Hz in the temperature range of 10 to -40 °C at 10 K intervals. In order to avoid instrument compliance effects caused by the high stiffness of bitumen in this temperature range [36], 4-mm diameter parallel plate geometry at a gap of 1.75 mm was used to carry out these experiments. The accuracy and reliability of this 4-mm DSR technique, also known as small-diameter parallel plate (SDPP) rheometry, have been established by Laukkanen [31]. The rheometer was operated in a strain-controlled mode, and the strain amplitude was varied in the range of 0.075 to 0.01 % to remain in the linear viscoelastic regime (the strain amplitude was reduced with decreasing temperature as detailed in the Supplementary Material). When the temperature was below 0 °C, the normal force control of the rheometer was utilized to automatically adjust the measurement gap in order to avoid the build-up of negative normal forces in the test specimen while maintaining good adhesion between the plates and the specimen. Further details of the specimen preparation and measurement protocol can be found elsewhere [47].

Although instrument compliance effects can be reduced by the use of a small-diameter parallel plate geometry, it is often necessary to perform instrument compliance corrections on the measured rheological data. This is especially true when measuring rheological properties

near or in the glassy state. Hence, all the rheological data measured in this study were corrected for the torsional instrument compliance, J_i , according to Eqs. (1)-(3) [31,48]:

$$G'_s = \frac{G'_m \left(1 - \frac{J_i}{k_g} G'_m\right) - \frac{J_i}{k_g} G''_m{}^2}{\left(1 - \frac{J_i}{k_g} G'_m\right)^2 + \left(\frac{J_i}{k_g} G''_m\right)^2} \quad (1)$$

$$G''_s = \frac{G''_m}{\left(1 - \frac{J_i}{k_g} G'_m\right)^2 + \left(\frac{J_i}{k_g} G''_m\right)^2} \quad (2)$$

$$\tan \delta_s = \frac{G''_s}{G'_s} = \frac{G''_m}{G'_m \left(1 - \frac{J_i}{k_g} G'_m\right) - \frac{J_i}{k_g} G''_m{}^2} \quad (3)$$

where G'_s , G''_s , and $\tan \delta_s$ denote the true (compliance corrected) values of the storage modulus, loss modulus and loss tangent of the sample, respectively, G'_m and G''_m are the measured values, and k_g is the geometry conversion factor (for the parallel plate geometry, $k_g = 2h / \pi R^4$, where h is the gap between the plates of radius R). The torsional instrument compliance $J_i = 0.00964$ rad/Nm was determined experimentally as outlined in the Supplementary Material. Interactive Rheology Information Systems (IRIS) software was used to analyze and plot the compliance-corrected rheological data [49].

2.4.3. Shear and torsional rheometry of neat SBS

Two rotational rheometers were used to characterize the linear viscoelastic properties of the neat star-branched SBS block copolymer as described in the following.

High-temperature experiments were performed on a stress-controlled Malvern Kinexus rheometer equipped with 8-mm diameter parallel plate geometry. Test specimens were prepared by melt-pressing SBS pellets in a washer at 170 °C for 10 min. During the rheological

experiments, the temperature of the specimen was controlled within ± 0.1 K using a Peltier plate and active hood, and the specimen environment was flushed with nitrogen gas to avoid polymer degradation. Frequency sweeps were conducted from 10 to 0.01 Hz in the temperature range of 180 to 90 °C. Strain amplitudes of 1 % and 0.1 % were employed in the temperature ranges of 180-120 °C and 110-90 °C, respectively, in order to remain in the linear viscoelastic regime.

Intermediate- and low-temperature experiments were carried out on a stress-controlled Anton Paar Physica MCR 301 rheometer equipped with a SRF 12 torsion bar fixture. Rectangular test specimens were prepared by melt-pressing at 170 °C for 10 min and cut into dimensions of $32 \times 10 \times 0.65$ mm³. During the rheological experiments, the specimen temperature was controlled to an accuracy of better than ± 0.5 K using a CTD 450 convection oven. Below room temperature, the oven was connected to an EVU 10 evaporation unit and cooled with liquid nitrogen. Frequency sweeps were performed from 1 to 0.01 Hz in the temperature range of 90 to -120 °C. The strain amplitude was varied between 0.05 and 0.01 % to remain in the linear viscoelastic regime over the whole temperature range. A constant tensile force of 0.2 N (equal to a tensile stress of approximately 0.03 N/mm²) was applied to the test specimen during these experiments to keep the sample slightly stretched. Due to the small free length of the clamped test specimen ($l_{act} = 18$ mm), corrected values for the specimen length were calculated according to Eq. (4) [50,51]. The rheological data measured using the torsion bar geometry were consequently corrected for this “effective” specimen length l_{corr} , resulting in 35-39 % decrease in the measured G' and G'' moduli values.

$$l_{corr} = l_{act} \left[1 - K(u, v) \frac{w}{l_{act}} + 0.12886 \left(\frac{w}{l_{act}} \right)^2 \right] \text{ for } 10 < l_{act} < 30 \text{ mm} \quad (4)$$

where w and l_{act} are the width and free length of the rectangular test specimen, and

$$K(u, v) = \frac{(1 + \nu)(1 + z^2)}{250} \left[25 \left(4 \frac{1 - z^2}{1 + z^2} - 1 \right) k - 5(1 - \nu) \times (1 + z^6)k^3 - 2(1 + \nu)z^2k^5 \right] \quad (5)$$

with

$$k^2 = -(3/2)(1 + u^2) + \sqrt{[(3/4)(1 + u^2)]^2 + \left(\frac{5}{2(1 + \nu)}\right)\left(4\frac{u^2 - 1}{1 + z^2}\right) - u^2} \quad (6)$$

and $z = 1/u$ and ν is the Poisson's ratio.

3. Results and discussion

3.1. Fluorescence microscopy (FM)

Figs. 1(a)-(d) show the evolution of the SBS modified bitumen morphology with increasing SBS content. In these FM micrographs, the SBS-rich phase appears light yellow, whereas the bitumen-rich phase appears dark. SBS is observed to be finely dispersed in bitumen at all concentrations studied, and it appears that the SBS-rich phase forms a continuous network already at relatively low concentrations. The phase inversion between 3 and 5 wt% SBS content is more clearly depicted in Figs. 1(e) and 1(f) that provide magnifications of Figs. 1(a) and 1(b), respectively. The formation of continuous network is also reflected in the physical/mechanical properties. For example, an abrupt jump in the Ring-and-Ball softening point is observed when the SBS content is increased from 3 to 5 wt% (Table 3).

Fig. 1 The effect of SBS content on the morphology of SBS modified bitumen: (a) BitA+3%SBS-S, (b) BitA+5%SBS-S, (c) BitA+7%SBS-S, (d) BitA+10%SBS-S. Parts (e) and (f) are magnifications of parts (a) and (b), respectively, highlighting the formation of a continuous SBS-rich network structure between 3 and 5 wt% SBS content.

As noted in Table 2, bitumen B was expected to have poor compatibility with SBS. This is confirmed in Figs. 2(a) and 2(b) that show the FM micrographs of BitB+5%SBS-L before and after annealing the specimen at 140 °C for 1 h, respectively. Pronounced macro-phase

separation occurs especially during the high-temperature annealing, resulting in the formation of discrete SBS-rich particles within continuous bitumen-rich matrix. The macro-phase separation can be largely mitigated by chemical crosslinking as shown in Figs. 2(c) and 2(d). It is notable that the good dispersion of the chemically crosslinked BitB+5%SBS-L* sample is preserved even after the high-temperature annealing (Fig. 2(d)).

Fig. 2 The effect of chemical crosslinking on the morphology of SBS modified bitumen. Parts (a) and (b) show the FM micrographs of the poorly compatible BitB+5%SBS-L blend before and after annealing at 140 °C for 1 h, respectively. Parts (c) and (d) show the FM micrographs of the chemically crosslinked BitB+5%SBS-L* blend before and after annealing at 140 °C for 1 h, respectively.

3.2. Temperature-modulated differential scanning calorimetry (TMDSC)

Table 4 summarizes results from TMDSC heating scans. Of particular interest here are the glass transition properties that can be determined from reversing heat flow curves. It should be noted that only the glass transition of the bitumen-rich phase can be detected in SBS modified bitumen, while the glass transitions of the SBS-rich phase are too weak to be observed or outside the investigated temperature range. Fig. 3(a) illustrates the effect of SBS content on the glass transition in the compatible blends of bitumen A and star-branched SBS. The glass transition is observed to shift to slightly lower temperatures with increasing SBS content. This trend is particularly notable in $T_{g,end}$ values, while $T_{g,onset}$ is practically unaffected by the addition of SBS. In addition, ΔC_p at T_g is observed to drastically decrease with increasing SBS content in these blends. These observations indicate that the interaction of SBS and bitumen leads to a decrease in the amount of the material phase that is responsible for the high-temperature end of the glass transition. According to Masson et al. [53], the maltene-asphaltene interphase has a T_g of approximately -5 °C, and therefore it seems likely that SBS hinders interactions between maltenes and asphaltenes and to some extent prevents the formation of the maltene-asphaltene interface. This, in turn, is presumably caused by the steric exclusion of asphaltenes from the interphase [53]. Furthermore, as reported earlier by Collins et al. [54], a decrease in the cold crystallization enthalpy (ΔH_{cc}) and melting enthalpy (ΔH_m) with increasing SBS content is observed; see Figs. 3(b) and 3(c) for the determination of ΔH_{cc} and ΔH_m from the non-reversing and total heat flow curves, respectively). This indicates that a significant portion of the crystalline fractions present in bitumen A are absorbed by SBS, and these absorbed fractions do not melt or crystallize in the investigated temperature range.

Table 4 Summary of the parameters determined from the TMDSC heating scans. $T_{g,onset}$, $T_{g,midpoint}$ and $T_{g,end}$ are the onset, midpoint and end temperatures of the glass transition region,

respectively, $\Delta T_g = |T_{g,onset} - T_{g,end}|$ is the width of the glass transition region, ΔC_p at T_g is the heat capacity change at the glass transition, ΔH_{cc} is the cold crystallization enthalpy, and ΔH_m is the melting enthalpy. The standard errors are estimated from four replicate measurements.

	$T_{g,onset}$ [°C]	$T_{g,midpoint}$ [°C]	$T_{g,end}$ [°C]	ΔT_g [K]	ΔC_p at T_g [J/(g K)]	ΔH_{cc} [J/g]	ΔH_m [J/g]
<i>Standard error</i>	± 0.3	± 0.3	± 0.5	± 0.6	± 0.020	± 0.2	± 0.4
Bitumen A	-35.6	-18.7	-1.8	33.8	0.470	1.7	3.5
BitA+3%SBS-S	-35.4	-19.4	-3.6	31.8	0.433	1.2	3.4
BitA+5%SBS-S	-35.4	-19.8	-4.3	31.1	0.353	0.6	3.1
BitA+7%SBS-S	-36.2	-20.7	-5.3	30.9	0.346	0.7	2.4
BitA+10%SBS-S	-35.7	-21.1	-6.7	28.9	0.299	0.4	1.3
BitA+5%SBS-L	-35.7	-19.4	-3.1	32.6	0.401	1.1	2.1
Bitumen B	-29.3	-19.5	-9.8	19.6	0.347	0.0	0.0
BitB+5%SBS-L	-29.5	-18.5	-7.4	22.0	0.301	0.0	0.0
BitB+5%SBS-L*	-34.7	-21.5	-8.3	26.4	0.380	0.0	0.0

Fig. 3 The effect of SBS modification on the (a) reversing, (b) non-reversing and (c) total heat flow curves of bitumen. The curves are shifted vertically for clarity. The numbers indicate the SBS content in wt%. The dashed and solid lines in part (a) show the evolution in the onset, midpoint and end temperatures of the glass transition region with increasing SBS content. The exotherms corresponding to the cold crystallization and endotherms corresponding to wax melting are shown in parts (b) and (c), respectively.

The composition dependence of T_g in miscible polymer blends and random copolymers can be predicted by the Fox equation [55]. For binary blends:

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{1 - w_1}{T_{g,2}} \quad (7)$$

where T_g is the glass transition temperature of the blend, $T_{g,1}$ and $T_{g,2}$ are the glass transition temperatures of the pure components, and w_1 and $1 - w_1$ are the weight fractions of the components. As evidenced by Adedeji et al. [16] and Masson et al. [17], only the PB midblock of SBS interacts with bitumen and is thus able to change its T_g , while the PS endblocks of SBS have negligible interaction with bitumen and its T_g . Therefore, the T_g values and weight fractions of PB and bitumen were used in the Fox equation to predict the T_g of the bitumen-rich phase of SBS modified bitumen. $T_{g,PB} = -90$ °C was measured by conventional DSC at a heating rate of 10 K/min. However, as shown in Fig. 4 and reported earlier by Adedeji et al. [16], the Fox equation significantly overpredicts the shift in T_g when SBS is added to bitumen. The measured shift is only about one-third of the predicted one. Adedeji et al. attributed this discrepancy to the incomplete mixing of bitumen with the PB midblock of SBS, as also supported by microscopic evidence.

Fig. 4 Measured and predicted T_g s in SBS modified bitumen, plotted as a function of PB midblock content. See text for the explanations of the different curves.

We point out that another possible explanation for this discrepancy is the so-called self-concentration effect. According to the model proposed by Lodge and McLeish [56], the average composition of the local environment around any chosen segment is enriched by the same

species because of chain connectivity effects. Consequently, this segment experiences, on average, an effective local concentration ϕ_{eff} given by:

$$\phi_{eff} = \phi_s + (1 - \phi_s)\phi \quad (8)$$

where ϕ is the bulk concentration and ϕ_s is the self-concentration defined as

$$\phi_s = \frac{C_\infty M_0}{k\rho N_A V} \quad (9)$$

where C_∞ is the characteristic ratio, M_0 is the repeat unit molar mass, k is the number of backbone bonds per repeat unit, ρ is the density, N_A is the Avogadro constant, and V is a volume defined by the Kuhn length l_k as follows: $V = l_k^3$. Using the parameter values found in the literature [57], the self-concentration of PB is calculated to be $\phi_{s,PB} = 0.33$. Consequently, effective PB concentrations $\phi_{eff,PB}$ are calculated according to Eq. (8) and a prediction of the modified Fox equation for effective T_g , $T_g^{eff}(\phi) = T_g(\phi)|_{\phi=\phi_{eff}}$ is plotted in Fig. 4:

$$\frac{1}{T_g^{eff}} = \frac{\phi_{eff,PB}}{T_{g,PB}} + \frac{1 - \phi_{eff,PB}}{T_{g,bitumen}} \quad (10)$$

Although the predictions for the T_g of SBS modified bitumen become better when self-concentration effects are taken into account, they still overestimate the shift in T_g by a factor of two. It is therefore clear that the self-concentration model cannot completely explain the smallness of the T_g shift upon the addition of SBS in bitumen. It is also notable that similar observations have been made by Savin et al. [58] who concluded that in polymer-solvent mixtures the T_g of the diluent is nearly unaffected by the presence of the polymeric component. They attributed this finding to the small persistence length of the solvent, leading to a large self-concentration ($\phi_s \sim 1$). In practical terms, this means that the solvent senses only a very local environment in the mixture and retains its own T_g until most of its nearest neighbors are polymer segments. However, as mentioned above, it is also probable that the partial

immiscibility (i.e. incomplete mixing) of SBS and bitumen affects the concentration dependence of T_g in this case.

Fig. 4 also shows a prediction for the concentration dependence of T_g when ϕ_s is used as a fitting parameter. In this case, the self-concentration model is observed to provide a good fit to the experimental T_g data when $\phi_s = 0.67$. However, this parameter value cannot be considered realistic or physically meaningful as it deviates strongly from the theoretically calculated value of $\phi_s = 0.33$.

3.3. Low-temperature rheological properties in bending (BBR)

Low-temperature creep properties measured by BBR are summarized in Table 5. Following the standard procedure, the flexural creep stiffness and creep rate (m -value) are evaluated at a loading time of 60 s. Furthermore, critical low temperatures $T_{c,S}$ and $T_{c,m}$ are determined as temperatures at which the criteria $S(60 \text{ s}) = 300 \text{ MPa}$ and $m(60 \text{ s}) = 0.30$, respectively, are met. The BBR data was further analyzed by calculating the ratio of the flexural creep stiffness to the creep rate, S/m , and the temperature difference $\Delta T_c = T_{c,S} - T_{c,m}$. The S/m value is directly related to the rate of creep compliance $J'(t)$ and to the amount of dissipated energy [59], and it has been proposed as a physically meaningful indicator of the low-temperature anti-cracking performance of asphalt binders [60]. Correspondingly, ΔT_c can be used to describe the non-load related cracking potential of asphalt binders [61].

Table 5 Summary of the BBR test results

Parameter	$S(60 \text{ s})$ [MPa]				$m(60 \text{ s})$ [-]				$S(60 \text{ s})/m(60 \text{ s})$ [MPa]				$T_{c,S}$	$T_{c,m}$	ΔT_c
Temperature [°C]	-18	-24	-30	-36	-18	-24	-30	-36	-18	-24	-30	-36	[°C]	[°C]	[°C]
BitA+3%SBS-S	151	351	-	-	0.389	0.297	-	-	388	1182	-	-	-22.9	-23.8	0.9
BitA+5%SBS-S	119	242	522	-	0.375	0.300	0.226	-	316	808	2315	-	-25.7	-24.0	-1.7
BitA+7%SBS-S	49.4	129	176	-	0.369	0.328	0.360	-	134	394	488	-	-34.0	N/A ^a	N/A ^a
BitA+10%SBS-S	-	35.6	96.8	246	-	0.470	0.428	0.345	-	75.6	226	712	-37.3	-39.3	2.0

BitA+5%SBS-L	144	318	-	-	0.378	0.300	-	-	381	1060	-	-	-23.6	-24.0	0.4
BitB+5%SBS-L	145	395	-	-	0.431	0.302	-	-	336	1308	-	-	-22.4	-24.1	1.7
BitB+5%SBS-L*	101	301	-	-	0.471	0.343	-	-	215	876	-	-	-24.0	-26.0	2.0

^a $T_{c,m}$ could not be reliably determined due to the inconsistent temperature dependence of the m -value, and thus also the temperature difference ΔT_c could not be calculated

The effect of SBS content on the flexural creep stiffness is highlighted in Fig. 5. A systematic and significant stiffness decrease is observed with increasing SBS content, as also reflected by the decrease in the corresponding $T_{c,s}$ temperatures (Table 5). Moreover, SBS modification appears to increase the slope of the creep stiffness curve, i.e. the m -value, although the trend is not as systematic as in the case of the creep stiffness values. This, in turn, results in decreasing $T_{c,m}$ temperatures as can be seen from Table 5. The S/m value is observed to decrease with increasing SBS content (corresponding to decreasing creep stiffness and/or increasing m -value), which indicates improved resistance against low-temperature cracking. No clear trends can be discerned in the ΔT_c values. Generally speaking, the reported BBR results are in good agreement with the findings of Lin et al. [24]. Some authors, however, have argued that the BBR test often underestimates the low-temperature performance of SBS modified bitumen [30,62,63]. Section 3.5. provides further discussion on the BBR test results in relation to 4-mm DSR test results.

Fig. 5 The effect of SBS content on the flexural creep stiffness master curves.

3.4. *Low-temperature rheological properties in shear (4-mm DSR)*

In order to gain more comprehensive understanding of the linear viscoelastic properties of SBS modified bitumen at low temperatures, rheological characterization was performed using the 4-mm DSR technique. It can be demonstrated that dynamic oscillatory experiments, such as frequency sweep tests, provide more comprehensive description of viscoelastic materials than simple creep tests. For example, the elastic and viscous components of the material response are more readily separated in frequency sweep data than in creep data.

The effect of SBS content on the dynamic rheological properties of compatible SBS/bitumen blends is demonstrated in Fig. 6. Both the frequency-dependent complex modulus and phase angle values are plotted to properly analyze the viscoelastic characteristics of the investigated materials. Furthermore, frequency sweep data for the neat star-branched SBS block copolymer is shown for comparison purposes. The effect of SBS modification is found to be highly temperature- and frequency-dependent. The addition of SBS to bitumen is observed to increase the stiffness of the resulting blend at 10 °C (Fig. 6(a)), whereas the trend is reversed at sub-zero temperatures (Figs. 6(b) and 6(c)). The observed decrease in the low-temperature stiffness with increasing SBS content is consistent with the results from the BBR experiments (Fig. 5). The aforementioned observations highlight the reduced temperature dependence of SBS modified bitumen, resulting from the very weak temperature dependence of the neat SBS block copolymer (cf. the curves for neat SBS in Figs. 6(a)-(c)).

Fig. 6 The effect of SBS modification on the complex modulus and phase angle values at (a) 10°C , (b) -10°C and (c) -40°C . The data for the neat SBS sample is shown for comparison purposes.

Correspondingly, the SBS modification is found to increase bitumen elasticity at temperatures close to 0°C (Figs. 6(a) and 6(b)), but a reverse trend is observed at the lowest measurement temperatures (Fig. 6(c)). These findings, once again, demonstrate the reduced temperature dependence of the viscoelastic properties of SBS modified bitumen. The observed decrease in elasticity (increasing phase angle) at low temperatures is somewhat counterintuitive considering the almost purely elastic behavior of the neat SBS block copolymer in this temperature range. The reduced low-temperature elasticity of the SBS/bitumen blends (as compared to the pure blend components) may be attributed to the decreased elasticity of the

SBS-rich phase plasticized by the light oils absorbed from the bitumen. Indeed, this explanation is consistent with the experimental results of Lu et al. [18] who reported an increase in the phase angle of the separated SBS-rich phase in the low-temperature regime.

In order to examine the influence of the SBS modification more quantitatively, relative changes in the complex modulus and phase angle values with respect to the unmodified bitumen were calculated at different temperatures and frequencies. As an example, Figs. 7(a) and 7(b) show the effect of 5 wt% SBS addition on these rheological properties (similar plots for the other SBS modified bitumen samples are provided in the Supplementary Material). Most notably, these figures are intended to illustrate the remarkable softening (up to ~35 % decrease in the complex modulus) and elasticity reduction (up to ~50 % increase in the phase angle) at low temperatures and/or high frequencies. These changes are even more pronounced at higher SBS concentrations as shown in the Supplementary Material.

Fig. 7 The effect of 5 wt% SBS modification on the (a) complex modulus and (b) phase angle values of Bitumen A at various temperatures and frequencies. Only selected measurement frequencies are shown for clarity.

Fig. 8(a) shows the effect of SBS content on the shape of the curves in the Booij-Palmen plot $\delta(G^*)$, also known as the van Gorp-Palmen plot [64,65]. Most notably, the curves corresponding to the bitumen samples modified with 7 and 10 wt% of SBS show discontinuities in this plot, resulting from the poor overlap of the frequency sweep data measured at different temperatures. This observation is further illustrated in Figs. 8(b) and 8(c), clearly revealing the thermorheological complexity of these samples. In this case, the thermorheologically complex behavior is believed to originate from the continuous SBS-rich network structure detected by fluorescence microscopy (Section 3.1.). More specifically, it is expected that the relaxation mechanisms of the elastic network formed by the swollen SBS have different temperature dependence than those of the bitumen-rich phase. Indeed, this type of discrepancy in the temperature dependence of different material components (and their viscoelastic properties) is well known to lead to thermorheological complexity [66]. As a consequence of the thermorheological complexity, it is not possible to construct master curves of rheological material functions in the case of highly polymer modified bitumens. It should also be noted that thermorheological complexity appears to be exclusive for polymer modified bitumens as unmodified bitumens from various different crude oil sources and refining processes are reported to show invariably thermorheologically simple behavior [47,67].

Fig. 8 (a) The effect of SBS content illustrated in the Booij-Palmen plot. Note that the neat SBS data was collected over a wide temperature range of 180 to -120 °C, while the data for the other samples was measured in the range of 10 to -40 °C. The thermorheological complexity of the highly-modified samples BitA+7%SBS-S and BitA+10%SBS-S is highlighted in parts (b) and (c), respectively.

Another interesting observation from Fig. 8(a) is the change in the overall shape of the curves with increasing SBS content. All the curves appear to converge in the glassy state (the bottom right corner of this plot), but deviate when moving towards the liquid state (the top left corner of this plot). Following the interpretation introduced in our previous publications [68,69], increasing SBS content appears to broaden the viscoelastic transition from the glassy to the liquid state. However, the TMDSC results presented in Section 3.2. indicate that the width of the calorimetric glass transition, ΔT_g , decreases with increasing SBS content. It is indeed surprising and counterintuitive to observe such opposing trends, in contrast with our earlier findings on different types of petroleum fluids [69]. This non-trivial result cannot be fully explained with the present results, but it can be speculated that the multiphase morphology and/or strong dynamic asymmetry of the blend components may play a role here. As an additional note, the broadening of the viscoelastic glass transition is also reflected in the broadening shapes of the dynamic moduli master curves (Fig. 9(a) and 9(b)) and of the relaxation time spectrum (Fig. 9(c)).

Fig. 9 The effect of SBS content on the (a) storage modulus and (b) loss modulus master curves, as well as on the (c) relaxation time spectrum. The reference temperature is -40 °C. Note that the highly-modified samples BitA+7%SBS-S and BitA+10%SBS-S are not included in these plots due to their thermorheological complexity (see Figs. 8(a) and 8(b)). The relaxation time spectra were calculated using the method of Baumgärtel and Winter [70,71].

3.5. Correlation between the low-temperature rheological properties in bending and shear

In previous studies by Farrar and coworkers [35,36] and Riccardi and coworkers [72], linear correlations have been established between the stiffness and m -values determined by BBR and 4-mm DSR. These studies, however, included almost exclusively unmodified bitumen samples; only one PMB was investigated in both studies. Consequently, no one has yet systematically studied the correlations between the BBR and 4-mm DSR data of PMBs. To bridge this knowledge gap, Fig. 10 provides such a comparison for the SBS modified bitumen samples investigated in this study. The measurement conditions at which the BBR and 4-mm DSR data were compared were selected to be as similar as possible considering the time-temperature equivalence (a longer loading time or a lower frequency corresponds to a higher temperature, and vice versa).

Fig. 10 The relationships between the low-temperature rheological parameters measured in bending (BBR) and shear (4-mm DSR). Part (a) shows the linear correlation between the flexural creep stiffness and complex shear modulus. Sample BitB+5%SBS-L deviates from this linear trend due to macro-phase separation and is thus not included in the linear fit shown as a solid line. Part (b) shows the relationship between the m -value and phase angle.

The relationship between the flexural creep stiffness and complex shear modulus – measured by BBR and 4-mm DSR, respectively – is depicted in Fig. 10(a). Except for sample BitB+5%SBS-L, a strong linear correlation can be observed between these two parameters. The deviation of BitB+5%SBS-L from the linear trend can be attributed to the macro-phase separation occurring in this blend. More specifically, elevated temperatures employed during BBR specimen preparation (typically 160-185 °C) severely promote phase separation in the test specimens, leading to a morphology similar to that of the annealed FM specimen in Fig. 2(b). On the contrary, macro-phase separation can be largely avoided in 4-mm DSR testing owing to much lower specimen preparation temperatures (typically 60-80 °C). As a further proof of this, the discrepancy between the stiffness values measured by BBR and 4-mm DSR is shown to disappear upon chemical crosslinking, i.e. in the case of sample BitB+5%SBS-L*. As shown in Fig. 2(d), the improved compatibility of this blend helps to avoid macro-phase

separation even after prolonged high-temperature annealing. Furthermore, FM confirmed that no severe macro-phase separation occurs during the annealing of the compatible blends of Bitumen A and SBS (the micrographs are not shown in this paper for brevity).

Figure 10(b) provides further comparison of the BBR and 4-mm DSR results by illustrating the relationship between the m -value and phase angle. It is obvious from this figure that there is no simple correlation between these two parameters. This observation is in contrast with the findings of Rowe [73] who reported a linear correlation between the m -value and phase angle in unmodified bitumen samples. In the case of bitumen samples modified with large amounts (7-10 wt%) of SBS, the m -value appears to increase dramatically with increasing SBS content, whereas the phase angle value is not very sensitive to this quantity. We presume that this deviation between the two trends is partly due to the thermorheological complexity of these blends (see Section 3.4.). However, further studies on different types of PMBs need to be conducted in order to fully understand these interrelationships.

4. Conclusions

This paper focused on the rheological characterization of SBS block copolymer modified bitumen at low temperatures. In particular, the 4-mm DSR technique was employed for the first time to systematically study the dynamic rheological properties of PMBs near and below T_g . Fluorescence microscopy (FM) and temperature-modulated differential scanning calorimetry (TMDSC) were used to examine the phase morphology and interactions in SBS-bitumen blends. FM demonstrated a dramatic swelling of SBS by the light oily components of bitumen, as well as the formation of a continuous SBS-rich network structure at relatively low SBS concentrations (~ 5 wt%). TMDSC revealed only a minor shift in T_g with the addition of SBS to bitumen. This shift is considerably smaller than what is predicted by the Fox equation

1 for miscible blends, even when the self-concentration effects are taken into account. This
2 discrepancy between the theoretical and experimental values is attributed to the partial
3 immiscibility of the blend components.

4 In contrast to thermal properties, rheological properties in the vicinity of the glass transition
5 are significantly affected by the SBS polymer modification. The low-temperature stiffness is
6 significantly reduced by the addition of SBS as evidenced both by BBR and 4-mm DSR results.
7 Furthermore, the 4-mm DSR technique was shown to provide new insights into the viscoelastic
8 behavior of SBS modified bitumen at low temperatures. Highly SBS modified bitumens are
9 observed to be thermorheologically complex in the investigated temperature range, presumably
10 due to the formation of a continuous SBS-rich network in bitumen. Moreover, in compatible
11 SBS-bitumen blends, a linear correlation is established between the flexural creep stiffness and
12 complex shear modulus measured by BBR and 4-mm DSR, respectively. As evidenced by FM
13 micrographs, deviations from this linear trend result from the occurrence of macro-phase
14 separation induced by the poor compatibility of SBS and bitumen. Further studies are
15 recommended to evaluate the low-temperature rheological properties of a wider variety of
16 PMBs using the 4-mm DSR technique, and to relate these properties with the field performance
17 of corresponding asphalt mixtures.

19 **Conflicts of Interest**

20 The authors declare no conflict of interest.

23 **Acknowledgments**

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