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# Full Length Article

# Microstructure of neat and SBS modified asphalt binder by small-angle neutron scattering

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#### ABSTRACT

The microstructure of asphalt binders is believed to have a significant impact on the performance of binders used in roadway constructions. However, there are only limited studies of their nanoscale to microscale structures. Here, small angle neutron scattering (SANS) is used to study the nanoscale structure of neat asphalt binder, styrene-butadienestyrene (SBS) block copolymers and SBS modified asphalt binder. The SANS pattern for asphalt binder demonstrates that it exhibits a colloidal structure comprised of asphaltenes surrounded by resins dispersed in saturates and aromatics. Fractal-core-shell model fits to these patterns indicate that the asphaltene core size decreases with increasing temperature. Both SANS and rheology confirm that SBS modified asphalt has a thermo-reversible phase transition around 110 °C, where the SBS micelles swell and lose scattering contrast above this temperature. The thermo-reversibility of this phenomenon indicates that the mechanism of SBS modification is mostly a physical modification of the nanoscale structure as proposed in the colloidal model of asphalt. Modeling of the SANS patterns shows that neat SBS and SBS dispersed in asphalt binder have a lamellar structure surrounded by a shell. These results are useful for understanding the relationship between the nanoscale structure of asphalt binder and pavement performance, as well as potentially developing new types of modified asphalt binders.

# 1. Introduction

Asphalt binder is a major road construction material and has received much attention in the past few decades due to its significance in enhancing the whole in-service performance of the road. As a residual product from crude oil refining, asphalt binder has very complex components and compositions, consisting of thousands of chemical structures. Therefore, it is challenging to establish the relationship directly between the chemical composition and macroscopic asphalt binder properties. To address this challenge and further study of asphalt binder, the complex compositions in asphalt binder were grouped into different fractions based on their chemical similarity [1,2]. One of the commonly used fractionation methods is to separate asphalt binder into four general fractions based on their polarity: saturates, aromatics, resins, and asphaltenes (SARA) [2].

The microstructure of asphalt binder is closely linked to its composition, and has a significant effect on the properties of asphalt binder and the development of modified binder [3]. Asphalt binders are widely considered to have a colloidal structure [1,2,4,5]. Asphaltenes surrounded by resins are generally considered to be the dispersed phase, with the mixture of saturates plus aromatics acting as the dispersing medium or the continuous phase [5]. A variety of techniques have been applied to characterize asphalt microstructure, including parameters such as size and shape of the dispersed phase [6–15].

Theoretical calculations suggest the colloidal features are the result of spinodal decomposition [16]. Although, alternatives to this interpretation are based on limited solubility [17]. A recent review of molecular simulations of asphalt binder highlights the complexity of the molecular interactions present in bituminous materials that lead to molecular associations and segregation [18]. Lesueur's review supports the colloidal model and provides linkage between this microstructure and the binder rheology [19].

The most commonly used techniques to characterize the microstructure of asphalt binders are microscopies, such as optical microscopes (OM, including fluorescence), scanning electron (SEM), transmission electron (TEM), as well as atomic force (AFM). Due to the refractive index contrast between neat asphalt binder and modifier, OM is perhaps the most widely used and most efficient method to analyze the effect of

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modifier on the microstructure of asphalt binders on length scales greater than a micron. Factors such as temperature, concentration, and composition that govern the shape, dimension, size distribution and morphology of the modifier particles have been well studied using OM [6-9]. Based on these prior studies, it can be concluded that size of the modifier phase (SBS, pitch-polymer, polyethylene, etc.) in asphalt is normally micrometer in size. The sub-micron colloid structure is considered to be asphaltene micelles dispersed within the saturates and aromatics continuous phase, which can be observed with SEM or TEM [10-13]. The reported size of asphaltene micelles is in the range of several nanometers to hundreds of nanometers [10,13]. Wang et al. showed that the form of the micelles in non-aged neat asphalt is plate-shaped [13]. Electron microscopes have also been used to measure the SBS polymer modifiers in asphalt. The studies suggested that after blending asphalt with SBS polymer, SBS particles would absorb some components in asphalt and swell, and result in a swollen network [14,15]. One critical disadvantage of SEM and TEM is that the method requires dissolution in a solvent before imaging, which may affect the micelle microstructure.

AFM provides structural information concerning the surface of the sample using an atomic-scale mechanical probe. The application of AFM on asphalt microstructure can be traced back to the work of Loeber et al. [10]. Various microstructures were observed on the surfaces of thin-film asphalt binders, such as fine structure, flake-like structure, or bee-structure micelles [20-28]. Among the different kinds of micelles shapes, a "bee-structure" has received significant attention from researchers. However, there is not a uniform explanation on the formation of such bee-structures. Some researchers believe it is caused by asphaltenes fraction [10,21,22]. while others attribute it to wax content [23-25]. The bee-structure is a few micrometers wide and long [26,27]. The dimension of fine or flake-like structure is around or less than 1 µm [28]. Loeber et al. measured the size of asphaltene particles to be in the range of 100-200 nm using AFM and SEM. Further, they observed that of order 100 particles aggregate into a larger mesostructure with a characteristic size of about  $6 \mu m$  [10]. A key limitation of AFM is that it only probes the surface microstructure. Hence, questions arise as to how representative the 2D surface microstructure is for the bulk material microstructure.

Scattering methods, such as X-ray and small-angle neutron scattering (SANS) can complement and overcome many limitations of the aforementioned direct imaging techniques. X-ray scattering reveals polydisperse asphaltene particles of 3–6 nm in asphalt binder, but low contrast limits the measurements [29]. In SANS, elastic neutron scattering is used at small scattering angles to investigate the structure over length scales from about 1 nm to nearly one micron. Since SANS has the advantages of penetrating sufficiently through opaque materials by interacting neutron with nuclei of measured atoms to quantitatively determine the internal structure [30], it is suitable for analyzing materials' spatial microstructure. Even though SANS is a common characterization tool for colloidal materials, biomaterials, and polymers [31,32], it has been rarely used to study asphalt binders.

The early applications of SANS in asphalt materials can be dated back to the microstructure study of asphaltene from crude oil [33–35], followed by some more recent reports [36–38]. Based on this body of research, the size of asphaltene aggregates in oil is found to be in the range of 2–10 nm [34–36,38]. Some measurements show evidence of aggregation into larger fractal structures [35,37,38]. Although these results are important background references for SANS studies of asphalt binders, asphaltenes were dissolved in solvents throughout these measurements. Therefore, it is very difficult to determine how the physical properties of neat asphalt binders related to these asphalt solutions.

There are only a few literatures of SANS patterns for asphalt binders. Schmets et al. used SANS to show that the structural feature observed at the bitumen's surface by AFM were also present in the bulk of the materials [39,40]. Huang et al. used SANS to detect the effect of moisture on the microstructure of foamed asphalt, and the results showed that the foaming process did not alter the nanostructure of the

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Components of the	neat as	phalt l	oinders.

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Asphalt type	Component (%)	Component (%)		
	Asphaltene	Resin	Saturate	Aromatics
Asphalt A Asphalt B	16.63 13.93	14.15 27.24	33.68 28.31	35.54 30.52

asphalt, but did alter the mesoscale structure (> 100 nm) of the asphalt [41]. It can be concluded from these studies that SANS is a viable method to study the microstructure of asphalt binders.

SBS copolymers are added to asphalt binder to improve the pavement performance [42]. The SBS forms micron or larger sized polymerrich inclusions swollen with the aromatic fraction of the maltene phase [19]. This segregation is implicated in the rheological modification both through the concentration of the asphaltene colloidal material in the remaining maltene phase as well as the introduction of additional viscoelasticity through these swollen polymer inclusions [43]. However, questions remain about the nanoscale structure of the SBS within these swollen polymer domains.

The main goal of this work is to measure the microstructure of neat asphalt binder and SBS modified asphalt binder and analyze the effect of compositions and temperature on the microstructure of asphalt binder at nanoscale. For this purpose, we studied two different neat asphalt binders and with one type of SBS modifier at two loadings using SANS over the temperature range of 0-130 °C. The results reveal the microstructure of neat asphalt binders, SBS polymer and SBS modified asphalt binder, and how the microstructure of SBS particle in asphalt binder changing with temperatures. It also provides further evidence for the colloid structure of asphalt binder and mechanism of SBS modification. Complementary rheological measurements aid in understanding the connection between this microstructure and binder performance.

#### 2. Materials and methods

# 2.1. Materials

The materials tested were SBS copolymer, two neat asphalt binders and one of these binders modified at two SBS loadings. Two neat asphalt binders from Western Canadian Select (WCS) crude, A and B, were selected to compare the microstructure difference between different asphalt binders. The PG grade of asphalt A is PG58-28 and the PG grade of asphalt B is PG64-22. The SARA fractional percentages of asphalt A and B are tabulated in Table 1. The SBS co-polymer is Kraton D1192 and linear. The modified asphalt binder was made with asphalt A and different percentage of SBS polymer. Asphalt A modified with 1 wt% SBS is named as asphalt  $A_{1sbs}$  and that modified with 4 wt% SBS is named as asphalt  $A_{4sbs}$ . All the sample information is tabulated in Table 2.

#### 2.2. Rheological tests

Rheological measurements were conducted in stress-controlled mode using TA AR-G2 rheometer with 25 mm parallel-plate geometry equipped with an oven for temperature control. The tests followed the

Table 2Tested material sample information.

Number	Materials	Composition/Description
1	Asphalt A	PG58-28 neat asphalt binder
2	Asphalt B	PG64-22 neat asphalt binder
3	SBS	styrene–butadiene–styrene
4	Modified asphalt A <sub>1sbs</sub>	99 wt% asphalt A + 1% wt% SBS
5	Modified asphalt A <sub>4sbs</sub>	96 wt% asphalt A + 4% wt% SBS

protocols developed in the previous study [44]. The gap was set to 1 mm for all the measurements. Temperature ramp tests were conducted on asphalt A, B,  $A_{1sbs}$ , and  $A_{4sbs}$  to identify any changes in rheological behavior beyond simple softening. The samples were heated from 30 °C to 100 °C with 10 °C increment, and equilibrated for 25 min at each measurement temperature. After 25 min equilibration, the samples were immediately sheared for 1 min in the linear viscoelastic regime. The stress sweep test was used to choose the control stress levels at each temperature to make sure the binder was tested in the linear viscoelastic regime. The storage modulus (*G'*), loss modulus (*G''*), and phase angle ( $\delta$ ) were recorded. The temperature sweeps were conducted at a constant shear angular frequency of 10 rad/s.

#### 2.3. SANS sample preparation

The asphalt binder was heated to flow, and then poured into a silica mold. After the asphalt binder cooled to room temperature, it was sand-wiched between two quartz window cells. These were placed between the parallel plates of the rheometer and pressed to a uniform, parallel thickness 1 mm asphalt sample. To avoid the leakage of the asphalt binder during the test at high temperature, Dow Corning<sup>@</sup> 736 heat resistant sealant was used to seal the sample holder. This sample was mounted into standard demountable titanium SANS sample cell holder. The SBS polymer is provided as a powder and was directly loaded into the demountable titanium SANS sample cell holder for SANS measurement.

# 2.4. Small-angle neutron scattering

The experiments were carried out on the 30 m NGB30SANS instrument at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) in Gaithersburg MD [45]. The measurements were conducted at three detector distances: high Qrange: 1.33 m sample-to-detector distance (SDD) with 6 Å neutrons for 100 s counting time for each sample, intermediate Q: 4 m SDD with 6 Å neutrons for 300 s counting time, and low Q: 13 m SDD with 6 Å neutrons for at least 1500 s counting time. The range of the scattering wave vector covers from about  $0.004 \text{ Å}^{-1} < Q < 0.4 \text{ Å}^{-1}$ . The wavelength spread  $\Delta\lambda/\lambda$  was 0.15. Demountable titanium cells with quartz windows and a path length (thickness) of 1 mm were used for all samples. For asphalt binder A,  $A_{1sbs}$ ,  $A_{4sbs}$  and SBS, the measurements were performed in ascending temperature order from10 °C, 30 °C, 60 °C, to 110 °C. Samples  $A_{1sbs}$  and  $A_{4sbs}$  were also measured at 0 °C after 110 °C testing. For asphalt binder B, the test temperatures were 30 °C, 60 °C, and 130 °C. The sample was held for at least 25 min at each temperature to reach the thermal equilibrium. Standard NIST SANS data reduction protocol was performed by the IGOR Pro program to obtain the corrected and radially averaged SANS scattering spectra [46].

As shown in Fig. 1, the scattered intensity of a SANS measurement is collected as a function of scattering angle,  $\theta$ , which is typically reported as the magnitude of the momentum transfer vector or scattering vector Q with the amplitude given by [47]

$$Q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \tag{1}$$

in which  $\lambda$  is the wavelength of the incident neutrons beam. The scattering wave vector Q has dimensions of inverse length, e.g.,  $Å^{-1}$ . The experimental data are typically reported as a function of Q. Bragg's law relates the length scale in reciprocal space Q to the characteristic length scale in real space, d via the following relationship [30], i.e.,

$$d = \frac{2\pi}{Q} \tag{2}$$

Hence, structures observed in SANS pattern are inversely related to the real-space features in the sample.



Fig. 1. Schematic of SANS measurement. A monochromatic incident neutron beam was chosen by the neutron velocity selector. Neutrons were guided to illuminate the asphalt binder sample. Scattered neutrons were detected by the 2D position sensitive detector installed in a vacuum chamber. And the scatter angle,  $\theta$ , was calculated based on the position of probed neutrons on the 2D detector.

# 3. Results and discussions

#### 3.1. Temperature dependence of the rheological behavior

To develop the relationship between macroscopic rheological behavior and the microstructure of asphalt binder, the rheological behavior as a function of temperature is reported in this section, and will be compared with SANS measurements in the following section. Fig. 2 plots the storage moduli, loss moduli and phase angles dependence on the temperature. As shown in Fig. 2(a), both storage modulus and loss modulus decrease with increasing temperature, confirming the asphalt binder softens with increasing temperature. The measured moduli decrease slower at large temperatures as shown in Fig. 2(a). Furthermore, the loss modulus values are larger than the storage modulus over the measured temperature range, indicating the viscous nature of the



**Fig. 2.** Temperature dependence of (a) modulus and (b) Tan (phase angle) for the studied binders. G' and G'' are indicated in open and closed symbols, respectively, and tan (delta) with symbols line.

binder at these conditions. This is confirmed in Fig. 2(b) showing tan  $(\delta) > 1$  for all samples in this temperature range.

The curves of tan ( $\delta$ ) versus temperature for different binders are shown in Fig. 2(b). Importantly, the binder behavior switches from viscoelastic flow to Newtonian flow at high temperature. When this occurs, the phase angle approaches 90°, and tan ( $\delta$ ) is infinite for purely viscous materials. Thus, the data collected at and above this transition temperature are not shown in the curve. This transition temperature is termed the  $\alpha$ -relaxation temperature and is associated with the temperature dependence on the asphaltene phase. As shown in Fig. 2(b),  $\alpha$ relaxation temperature for neat asphalt binders is around 80 °C and is above 100 °C for SBS modified asphalt binders. Our results show that the phase transition temperature of asphalt binders increases with adding SBS polymer, confirming that SBS copolymer can make the asphalt binder more stable at higher temperature [19].

To further study the temperature sensitivity, the curves of complex viscosity versus 1/T for the studied binders are drawn to compare the flow activation energy of different binders, as shown in Fig. 3. The solid line is the fit to an Arrhenius expression (shown in Eq. (3)), which represents the data well at low to moderate temperatures, and the dotted line is the extrapolation to higher temperatures for reference. The fitting results are tabulated in Table 3. The obtained activation energy ( $E_a$ ) is approximate to the values in the literature [48]. The activation energy for binder A decreases upon addition of SBS, which helps explain the thermal stability imparted by SBS. The deviation from this behavior for these modified binders at higher temperatures may reflect changes in the microstructure, which will be discussed next.

$$\eta^* = A e^{\frac{-u}{RT}} \tag{3}$$

where  $\eta^*$  is the complex viscosity (Pa.s), *T* is the absolute temperature (K), A is the pre-exponential factor (Pa.s),  $E_a$  is the activation energy (kJ/mol) and *R* is the universal gas constant (J/(mol.K)).

#### 3.2. Microstructure of neat asphalt binder

The SANS patterns of asphalt binder A and asphalt binder B after subtracting the background are shown in Fig. 4. To guide the eye, the intensity curves were vertically shifted relative to that for the lowest temperature. It can be seen that the intensity decreases monotonically with increasing scattering vector Q, as has been reported previously [19]. As the intensity continues to rise with decreasing Q, the scattering contrast in these samples arises from objects larger than ~180 nm. These objects are believed to be the asphaltene phase cluster, and their extent could be probed in the future by methods such as USANS.

The shape of the SANS patterns are qualitatively similar to each other at all measured temperatures, suggesting that the microstructures are similar at these length scales for the studied temperature range. The







**Fig. 4.** SANS patterns of (a) binder A and (b) binder B. The temperature was varied in ascending order at 10 °C, 30 °C, 60 °C, and 110 °C for binder A and 30 °C, 60 °C, and 130 °C for binder B. The solid lines are the fitting curves using the fractal-core-shell model. For clarity, the curves were vertically shifted relative to that at the lowest temperature. The shifting magnitudes were indicated in each figure.

SANS patterns obtained in this study are similar to that reported by Huang et al.'s for foamed asphalt [41], suggesting that the microstructures of asphalt binder and foamed asphalt are similar. Quantitative differences between experiments are evident, however, and so a quantitative analysis proceeds by modeling these patterns as follows.

Based on the pattern shape and the colloidal structure theory of asphalt binders [1,11], the patterns were fitted using the fractal-core-shell model shown in Eq. (4). SLD are calculated to be  $1.30 \times 10^{-6} \text{\AA}^{-2}$  for asphaltene core, and  $0.8 \times 10^{-6} \text{\AA}^{-2}$  for resin shell.

$$I(Q) = P(Q)S(Q) + \text{background}$$
(4)

where P(Q) is the core-shell form factor [46] and S(Q) is the Teixeira [49] fractal structure factor both of which are given below:

#### Table 4

The fitting parameters of the binders at different temperature.

Binder Type	Temperature (°C)	Parameters		
		Core Radius (Å)	Shell Thickness (Å)	Fractal Dimension
Asphalt A	10	$24.5 \pm 0.1$	$21.1~\pm~0.3$	~3
	30	$23.7 \pm 0.1$	$21.4 \pm 0.3$	
	60	$22.8 \pm 0.1$	$11.9 \pm 0.3$	
	110	$18.4 \pm 0.1$	$20.7~\pm~0.3$	
Asphalt B	30	$18.8 \pm 0.0$	$18.7 \pm 0.1$	
	60	$16.1 \pm 0.1$	$19.5~\pm~0.1$	
	130	$8.2~\pm~0.2$	$24.5~\pm~0.4$	

$$P(Q) = \frac{\varphi}{V_s} \left[ 3V_c(\rho_c - \rho_s) \frac{\sin(qr_c) - qr_c\cos(qr_c)}{(qr_c)^3} + 3V_s(\rho_s - \rho_{solv}) \frac{\sin(qr_s) - qr_s\cos(qr_s)}{(qr_s)^3} \right]^2$$
(5)

$$S(Q) = 1 + \frac{D_f \Gamma(D_f - 1)}{[1 + 1/(q\xi)^2]^{(D_f - 1)/2}} \frac{\sin[(D_f - 1)\tan^{-1}(q\xi)]}{(qr_s)^{D_f}}$$
(6)

where  $\varphi$  is the volume fraction of particles,  $V_s$  is the volume of the whole particle,  $V_c$  is the volume of the core,  $\rho_c$ ,  $\rho_s$  and  $\rho_{solv}$  are the scattering length densities of the core, shell, and the solvent respectively,  $r_c$  and  $r_s$  are the radius of the core and the radius of the core plus shell respectively,  $D_f$  is the fractal dimension, and  $\xi$  is the correlation length.

The fitting results are also shown in Fig. 4 as black, solid lines. It can be seen that the fractal-core-shell model can accurately fit the intensity patterns of the asphalt binders. The radius and thickness parameters are reported in Table 4. As seen in Table 4, the core radius is around 20 Å, which is similar to the results obtained by Eyssautier and co-workers. [38] This confirms that the asphaltene size in asphalt binder is similar to the asphaltene size previously measured in solvents. The core radius decreases slightly when increasing temperature. This result is consistent with those shown for asphaltene aggregates in crude oil and precipitated asphaltenes redispersed in deuterated solvents [37,50]. The asphaltene phase may dissolve into the maltene phase with an increase of temperature. The shell thickness does not show significant temperature dependence.

The structure factor yields fractal dimensions for both asphalt binders under different temperatures that are very close to  $d_f \sim 3$ , which would imply that the aggregates are very dense. However, given the limited range of the data available and that the pattern clearly extends to much high intensity reflecting larger sizes, an alternative interpretation for this power law behavior at low Q may be the surface fractal of the asphaltene aggregate. Note that values of  $d_s \sim 2.5$  were observed for a related material, coal [51], and this interpretation of a rough interface may be more representative of the asphaltene aggregates. Further investigations at lower Q using USANS may help resolve this.

#### 3.3. Microstructure of SBS polymer

The SANS patterns for the neat SBS copolymer with temperature are shown in Fig. 5(a). A strong scattering peak is evident in the intensity pattern, which is indicative of a characteristic repeat distance in the sample associated with the microstructure of the SBS copolymer. The intensity curves are identical at 10 °C, 30 °C, and 60 °C. However, increasing the temperature to 110 °C, the peak increases in amplitude and sharpens, without substantially changing position.

To provide a more quantitative analysis of the microstructure in the SBS polymer, the Teubner-Strey (TS) model [52] was used to fit the SANS patterns of the SBS polymer. The TS model has the following functional form:





**Fig. 5.** SANS patterns of the SBS polymers before (a) and after (b) vertically shift. The temperature was changed in ascending order at 10 °C, 30 °C, 60 °C, and 110 °C. The solid lines are the fitting curves using the Teubner-Strey model.

$$I(Q) = \frac{1}{a_2 + c_1 Q^2 + c_2 Q^4} + \text{background}$$
(7)

where I(Q) is the scattering intensity, and  $a_2$ ,  $c_1$ , and  $c_2$  are composition-dependent coefficients. The correlation length,  $\xi$ , and the *d*-spacing (characteristic of a domain size or periodicity) are:

$$\xi = \left[\frac{1}{2} \left(\frac{a_2}{c_2}\right)^{1/2} + \frac{1}{4} \frac{c_1}{c_2}\right]^{-1/2}$$
(8)

$$d = 2\pi \left[ \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{1/2} - \frac{1}{4} \frac{c_1}{c_2} \right]$$
(9)

The solid lines in Fig. 5(b) are the model fits. The curves for T > 10 °C were vertically shifted for better viewing. It can be seen that the model fits the peak very well. The correlation length  $\xi$  and the quasi-periodic *d*-spacing characterizing the lamellar phases are summarized in Table 5. These are almost constant over the temperature

Table 5							
The correlation	length	and	the	d-spacing	for	the	SBS.

Temperature (°C)	Correlation length $\xi(\text{\AA})$	d-spacing (Å)
10 30 60 110	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$



**Fig. 6.** SANS spectra of the SBS polymer modified asphalt binders for (a) binder  $A_{1sbs}$  (1 wt%SBS) and (b) binder  $A_{4sbs}$  (4 wt%SBS). The temperature changes from 10 °C to 110 °C and then decreases to 0 °C. The curves were vertically shifted by the corresponding factor for clarity.

range from 10 °C to 60 °C. However, heating to 110 °C leads to a significant increase in the correlation length, which is consistent with the formation of well-defined lamellae. The *d*-spacing also increases, again consistent with a transition to a more ordered microstructure. The repeat distance in SBS (*d*-spacing) is comparable to that observed by Hashimoto et al. [53]. Fitting a power-law, slope to the low *Q* range yields a value around 4, which suggests sharp interfaces in the SBS sample on a much larger length scale.

# 3.4. Effect of SBS on asphalt binder microstructure

The SANS patterns of the SBS modified asphalt binders with different SBS weight percentages over a range of temperatures are shown in Fig. 6. In this experiment, the temperature was increased from 10 °C to 110 °C and then was decreased to 0 °C to determine if any thermal transitions in the microstructure were thermo-reversible. At each temperature, the samples were maintained at least 25 min for equilibration before any measurement. As shown in Fig. 6(a), the peak intensity arising from SBS is evident in the overall scattering intensity at the same location as for the neat SBS, as well as a strong upturn at low-Q, indicative of a phase-separated sample. Essentially, the SBS phase dominates the scattering intensity even though its concentration is low. Upon heating, there is a negligible change in this feature, but at 60 °C there is a marked decrease in the low-Q scattering. Further heating to 110 °C eliminates the correlation peak, suggesting the SBS dissolves in the asphalt. Importantly, cooling to 0°C restores the original microstructure. This trend is observed for both 1 and 4 wt% SBS addition. Thus combing the rheological measurement results, our SANS results indicate that the SBS phase acts to increase the softening temperature of



(b) Binder A4sbs(4wt%SBS)

Fig. 7. SANS patterns of the SBS polymer in the asphalt binders for (a) binder  $A_{1sbs}$  (1 wt%SBS) and (b) binder  $A_{4sbs}$  (4 wt%SBS).

the asphalt binder by swelling with the light components of the maltene phase [14]. Our measurements show a reversible dissolution of the SBS into the asphalt binder at about 110 °C. Note that the  $\alpha$ -transition temperature from rheology (Fig. 2) is above 100 °C for the SBS modified samples.

Adedeji et al. [14] studied a similar system by TEM and showed that at these low SBS loadings, the microstructure consists of SBS 'microgel' domains dispersed in the asphalt. At 4 wt% SBS, they report SBS microdomains of ~200 nm size dispersed in the asphalt. Although a lamellar structure was observed for SBS at moderate to high asphalt loadings, for a sample at 6 wt% SBS, they reported a transition to PS core micelles with swollen PB domains as a corona. Our results show that the SBS remains as a dispersed phase in the asphalt binder with similar structure as in the neat copolymer over the conditions measured, but that it dissolves into the binder at 110 °C.

To fully analyze the microstructure of SBS copolymer dispersed in our asphalt binder, the weighted intensity of asphalt binder was subtracted from the intensity of the SBS modified asphalt binder to better reveal the contribution to the overall intensity of the dispersed SBS copolymer, as shown in Fig. 7. The TS model was also used to fit the scattering peak, and the fitted correlation length and d-spacing values in Table 5 were used for the fitting. The fitted scale value for binder  $A_{1sbs}$  is around 1% and for binder  $A_{4sbs}$  is around 4%, which confirms the SBS percentage in the samples. The fitting results are shown in the solid line in Fig. 7. The data in the low *Q* region was fitted with powerlaw function with a slope of -4, and the fitting lines are also shown in Fig. 7. This power-law behavior suggests the presence of domains of SBS that are greater than a micron in scale. USANS or other methods will be required to resolve the extent of these domains.



Fig. 8. Schematics of the SBS structure in different length scales and at different temperatures.

To compare the microstructure of SBS and SBS in asphalt binders, the intensity pattern of SBS at 10 °C is also shown in Fig. 7(a) for reference. The curve shape and peak position for SBS and SBS in asphalt binders are similar. This confirms that the nanostructure of SBS copolymer is similar in asphalt binder as in the neat copolymer. It can be seen from Fig. 7 that for both binder A<sub>1sbs</sub> and binder A<sub>4sbs</sub>, the powerlaw function together with the TS model can fit the curve well. This means that the SBS micelles in asphalt binder can still be considered as domains containing the lamellar structure; the schematic of the SBS structure is shown in Fig. 8. The SBS micelle is a sphere containing a lamellar structure in nano length scale. The d-spacing in the lamellar structure keeps almost the same when the temperature is lower than 60 °C, and increases when the temperature increases to 110 °C. Furthermore, the sphere size and the distance between the spherical micelles increase with the increase of temperature to 110 °C. However, all the structure parameters can be reversible when cooling back to 0 °C, as shown in Fig. 8.

This microstructural analysis is significant as swelling of the copolymer was thought to cause the increase in modulus shown in Fig. 2. As summarized by Lesueur et al., one reason for the improvement in mechanical properties of SBS modified asphalt binder is that swelling of the copolymer causes a decrease in the maltene content, leading to an increase in its asphaltene content when compared to the initial material composition [43]. Alternatively swelling of the copolymer by the liquid phase is thought to yield a viscoelastic polymer network [54], although it was not clear if the polymer actually dissolves or just disperses. Our measurements resolve this question - namely that the SBS co-polymer disperses into the maltene phase without significant swelling of the copolymer core below 110 °C. Aggregation of these nanoparticles of copolymer into fractal-like aggregates in the liquid component of the asphalt binder may be sufficient to impart viscoelasticity and stabilize the binder at higher temperatures. Swelling into the liquid phase above 110 °C is evident, which could then lead to a viscoelastic polymer interpenetrating network. Either way, the high loading of the asphaltene colloids must impart significant mechanical properties as compared to the SBS modified liquid phase. Our observations are consistent with the prior rheological observations of the improvement in high temperature viscosity, elasticity of SBS modified asphalt binders which identified the formation of "a rubber-elastic network within the modified binder". [54] This motivates the need for future studies of SBS in the maltene rich phase of the binder to ascertain its specific contribution to the overall thermal rheology.

#### 4. Summaries and conclusions

SANS & rheology studies of the microstructure of neat asphalt binders, SBS polymers and modified asphalt binder are performed as a function of temperature, binder type, and SBS modifier content. SANS of the neat asphalt binder shows scattering from the asphaltene phase dispersed in the maltene. The intensity curve can be well described by the fractal-core-shell model which proves that asphalt binders have colloidal structure, that is asphaltenes surrounded by resins are dispersed in the mixture of saturates plus aromatics. The asphaltene core size decreases with an increase of temperature. There is a strong scattering peak in the SANS intensity for the neat SBS polymer and a TS model fit suggests that the SBS polymer may have lamellar structure. The microstructure of SBS polymer was also observed in the SBS modified asphalt binder, showing that the SBS disperses in the binder while maintaining its nanoscale structure. Thermal cycling above 110 °C, where this characteristic peak disappears, is reversible suggesting that the SBS phase maintains its integrity even after melting. This phenomenon means that the SBS modified mechanism is a physical modified process. When the temperature is higher than 110 °C, the SBS micelle swells and possibly dissolves. When compared to the rheological measurements and literature results, our SANS measurements confirm that the SBS copolymer disperses into the maltene phase and swells significantly at high temperature to impart viscoelasticity at high temperatures.

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