Optical characterization of temperature- and composition-dependent microstructure in asphalt binders

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Summary
We introduce noncontact optical microscopy and optical scattering to characterize asphalt binder microstructure at temperatures ranging from 15°C to 85°C for two compositionally different asphalt binders. We benchmark optical measurements against rheometric measurements of the magnitude of the temperature-dependent bulk complex shear modulus $|G'(T)|$. The main findings are: (1) Elongated (~5 × 1 μm), striped microstructures (known from AFM studies as ‘bees’ because they resemble bumble-bees) are resolved optically, found to reside primarily at the surface and do not reappear immediately after a single heating–cooling cycle. (2) Smaller (~1 μm²) microstructures with no observable internal structure (hereafter dubbed ‘ants’), are found to reside primarily in the bulk, to persist after multiple thermal cycles and to scatter light strongly. Optical scattering from ‘ants’ decreases to zero with heating from 15°C to 65°C, but recovers completely upon cooling back to 15°C, albeit with distinct hysteresis. (3) Rheometric measurements of $|G'(T)|$ reveal hysteresis that closely resembles that observed by optical scatter, suggesting that thermally driven changes in microstructure volume fraction cause corresponding changes in $|G'(T)|$.

Introduction
An asphalt mixture is a composite composed of approximately 5% asphalt binder or bitumen and 95% mineral aggregates. Though only a small weight fraction, the bitumen is primarily responsible for a road’s mechanical properties, and must be engineered to withstand wide climatic variations. Ideal binders possess high stiffness at high temperatures, low stiffness with high relaxation rates at low temperatures and high resistance to fatigue cracking at intermediate temperatures. To choose or engineer a binder suited to a given climate, its temperature-dependent macroscopic properties must be well known. Such bulk properties are conventionally measured with rheometers, but the chemical composition of binders can vary unpredictably among nominally identical binders. The resulting uncertainty can lead to multimillion-dollar errors in materials designed for highway construction. A better understanding of the interrelationship between the chemical composition, internal microstructure and mechanical properties of a bitumen is critical to design and build durable and long-lasting pavements. The study of this interrelationship has been a subject of several research studies in the past few decades (Robertson, 2000; Lesueur, 2009). More recently, researchers have reported on the microstructure of bitumen using Atomic Force Microscopy (AFM; Loeb et al., 1996; Jäger et al., 2004; Schmets et al., 2009; DeMoraes et al., 2010; Pauli et al., 2011; Allen et al., 2012; Das et al., 2013; Hofko et al., 2015; Jahangir et al., 2015).

In this work, we explore the connection between variations in bulk properties of bitumen and corresponding changes in its internal microstructure. The presence of temperature- and composition-dependent micrometer-sized structures in bitumen is known almost exclusively from AFM (DeMoraes et al., 2010; Pauli et al., 2011), which images their distinctive shapes with high resolution. As examples, the AFM images in Figures 1(A) and (B) show elongated, rippled microstructures that are widely observed on the surfaces of binders at room temperature (RT), and have been dubbed ‘bees’ because their shape resembles that of bumble-bees. Most AFM research, however, has focused on understanding the relationship between observed microstructures and a binder’s chemistry and various external factors. Very little work has investigated the relationship between observed microstructures and bulk engineering properties of the bitumen. Moreover, AFM suffers from three shortcomings if it were to be developed as a microstructure diagnostic tool. First, it can only image surface structures. Thus, it is not well-suited for exploring connections between subsurface structures and bulk rheology. Secondly, because scanning is required, it is slow and limited to micrometer-sized...
areas. Thus, it is not well-suited for rapid, high-volume sample screening, which is particularly important if such a tool is to be used for bitumen research, design and production on a routine basis. Thirdly, because it requires contact with a sample, it has great difficulty imaging structures at elevated temperatures at which bitumen becomes a sticky liquid. Thus, it is not well-suited for probing variations in binder properties at high temperatures that are critical to the durability of pavements in hot climates.

To overcome these limits, we adopt optical microscopy and optical scattering as primary diagnostic tools of bitumen microstructure. As shown by the 100× optical micrographs of RT ‘bee’ structures in Figures 1(C) and (D), optical microscopy rivals AFM in its ability to resolve microstructures of interest. Such optical images require no scanning, and thus can be acquired rapidly, even in real time, limited only by the camera frame rate. At low magnification, even though internal structure is no longer resolved, such microstructures appear as near-point-like optical scattering centres, whose areal density can be monitored in real-time over mm² to cm² areas (see Figs 1E and F). All microstructures within the optical absorption depth contribute to the observed optical scattering. Thus, optical probes provide access to subsurface structures. Finally, optical diagnostics require no mechanical contact with the sample surface. Thus, they can characterize bitumen microstructures equally well at any temperature, whether the sample is frozen or heated beyond its melting point. A previous example of optical characterization of internal microstructure of bitumen was confocal microscopy of laser-induced fluorescence from asphaltene aggregates in a continuous maltene matrix (Bearsley et al., 2004).

We acquire optical data from samples of bitumen with two variations in chemical composition for temperatures $T$ in the range $15 \leq T \leq 65°C$. We then explore the relationship between temperature-dependent optical data and the temperature-dependent complex shear modulus $G^*(T) = |G^*(T)| \exp i\delta(T)$ of identical bitumen samples measured by a dynamic shear rheometer (DSR). Here, $|G^*(T)|$ is the magnitude of the complex shear modulus, defined as the ratio of shear stress to shear strain amplitudes in steady state when a sample is subjected to oscillating shear stress at a specific frequency. The higher $|G^*(T)|$, the stiffer the binder. The phase angle $\delta(T)$ measures delay between a periodic shear force and appearance of deformation at a given $T$. A lower value of $\delta(T)$ indicates a relatively more elastic than viscous response of the material: for example, $\delta = 0$ indicates an elastic material that is time-independent. $|G^*(T)|$ is a critical property of the binder that dictates its performance in an asphalt mixture. For example, $|G^*(T)|/\sin(\delta(T))$ at a frequency of 10 rad s⁻¹ at high temperature is used as a measure of the susceptibility of the binder to permanent deformation or rutting. It is also well established that the complex shear modulus of an asphalt binder is a time- (or rate-) , temperature- and age-dependent property (McGennis et al., 1994). Precise knowledge of $|G^*(T)|$ is therefore an important property that ultimately dictates the performance of the asphalt mixture used in roadway construction.

An important finding of DSR measurements presented here is that $|G^*(T)|$ exhibits significant hysteresis – i.e. $|G^*(T)|$ at any given temperature differs by as much as 22% between the heating and cooling portions of a thermal cycle. Ambiguities in $|G^*(T)|$ of this magnitude can critically influence judgment of the suitability of a binder for a given climate. A major finding of optical measurements presented here is that temperature-dependent optical scattering from the same binders exhibits a similar hysteresis, suggesting a possible connection between hysteretic variations in $|G^*(T)|$ and the density and size of microstructural inclusions in the binder. This information is potentially one of the most important and first steps in
establishing the relationship between bitumen microstructure and its mechanical properties.

**Experimental procedure**

**Materials and specimen preparation**

Two variations of a single bitumen were used in this study. The parent binder had a performance grade (PG) of PG 64-22 – i.e. the binder is appropriate for a maximum (minimum) pavement design temperature of 64°C (−22°C) – based on the Superpave PG specification (Pavement Interactive, 2008). PG 64-22 binder is commonly used in the paving industry, particularly in warm climates. The second binder was composed of the original PG 64-22 and a wax additive, commercially known as Sasobit, which accounted for approximately 1% of the new binder’s weight. Hereafter the original PG 64-22 binder is termed ‘unmodified’ whereas the PG 64-22+Sasobit binder is termed ‘high wax’. The choice of Sasobit as a modifier was based on the findings from previous studies that indicated a significant change in the microstructure of the binder observed using an AFM due to the addition of waxes (Schmets et al., 2009; Menapace et al., 2015).

To prepare samples for optical studies, a small solid bead of bitumen was placed onto a glass microscope slide mounted on an aluminium frame. Mount, slide and sample were then heated with a flexible silicone rubber heater (Omega Engineering, Inc.) and held at 120°C for approximately 1–2 min until the bitumen flowed freely. The binder was then either left exposed to air, or covered with a glass cover slip to suppress topological features from forming on its surface during cooling. The sample was then allowed to cool to RT over 10 min. Optical studies were carried out in reflection from the flat free or glass-covered surface of the RT sample, and during subsequent heating and cooling cycles up to 65°C.

To prepare samples for rheometric studies, 25 mm diameter circular cylindrical bitumen ‘tablets’ were prepared by heating bitumen to 120°C and pouring it into silicone moulds, then cooling to RT, as specified by ASTM standard D7175-08 (ASTM, 2015). These tablets thus had the same thermal history as samples used for optical studies. A tablet was placed between the 25-mm diameter parallel plates of the DSR (described in ‘Rheometric measurements’). The plates were heated to 50°C to ensure proper adhesion of binder tablet to plates. The top plate then squeezed the tablet to a thickness of 1050 μm. The tablet was then trimmed and further squeezed to a thickness of 1000 μm.

Some samples were thermally cycled to 120°C and back to RT multiple times using the format described above. Optical and rheological properties of these samples were indistinguishable from those that had been cycled to 120°C and back to RT only once. Evidently, internal shear resistance and microstructure re-form completely and reproducibly upon cooling for ~10 min from a 120°C melt.

**Optical measurements**

To resolve the internal structure of individual microstructures, slide and heater were mounted on the stage of a compound optical microscope (Leitz Ergolux) equipped with a 100× objective (Olympus LMPFLN, numerical aperture 0.80, working distance 3.4 mm). A 20W halogen lamp emitting a spectrum peaked at 630 nm with FWHM (full width at half maximum) 150 nm illuminated the samples from above. A 14 megapixel CMOS digital camera (AmScope MU1403) recorded images in reflection. Typical high-resolution images, shown in Figures 1(C) and (D), resolve internal stripes of individual ‘bees’, which correspond to height variations of only a few hundred nanometers (Pauli et al., 2011), along with a featureless background of specularly reflected light from the uniform matrix.

To characterize the statistical properties of many microstructures over a large volume, we used 40× dark field microscopy. The sample, mounted on a thermoelectric stage (TS-4-MP, Physitemp Instruments) with a temperature range of 0°C–125°C and subdegree temperature resolution, was illuminated at a 45° angle from the surface normal with white light from a halogen lamp (Vicon 191 Illuminator, Chapman-Huffman), with a spectrum similar to that of the microscope lamp, collimated via a fibre optic cable. Most of this radiation reflected specularly from the smooth surface of the matrix and was not detected, but a small portion of it scattered from microstructures over a wide angular range. A Nikon 40× long working distance objective collected light scattered into a narrow cone centred on the surface normal. A 14MP CMOS digital microscope camera (AmScope) recorded an image of the scattered light. With dark field microscopy, detected light originated solely from the microstructures, enabling rapid estimates of their areal density and average size. Figures 1(E) and (F) show typical dark field micrographs of freshly prepared unmodified and high wax bitumen samples, respectively. Analysis of such micrographs using the public-domain image processing software ImageJ (Rasband, 2015) yielded a fractional areal density of scattering centres within the field of view. For uniformly distributed bulk microstructures, area density yielded volume fraction of material occupied by microstructures when combined with knowledge of the light penetration depth.

The relative contributions of surface and bulk microstructures to dark field images such as these is determined in part by the depth distribution of the microstructures themselves, and in part by the penetration depth $\alpha^{-1}(\lambda)$ of the incident light, which in general depends on wavelength $\lambda$. Here, $\alpha(\lambda)$ is an absorption coefficient that relates intensity $I(\lambda, z)$ transmitted through a film of thickness $z$ to the incident intensity $I_0(\lambda)$ via Beer’s Law: $I(\lambda, z) = (1 - R) I_0(\lambda) \exp[-\alpha(\lambda)z]$, where $R$ is the reflectivity of the front surface. Multiple internal reflections are negligible for $\alpha z > 1$. Necessary conditions for bulk microstructures to dominate optical scattering are that $\alpha^{-1}(\lambda)$
significantly exceed the dimensions of the microstructures, and that $\alpha z > 1$. We measured $I(\lambda, z)$ over the wavelength range $350 < \lambda < 1500$ nm using a Cary 5000 UV-Vis-NIR spectrophotometer (Agilent) for bitumen films of four different thicknesses deposited on flat glass slides. The film thickness was measured using a Dektak 6M Stylus Profilometer (Brucker). The black curve in Figure 2 shows the penetration depth determined from these measurements. Nearly identical curves were obtained for unmodified and high wax samples.

Fig. 2. Penetration depth versus wavelength for bitumen films (black curve, left vertical axis), with overlay of spectral bands created by passing white light through BG39 (blue) and RG850 (red) coloured glass filters (right vertical axis).

The blue and red curves in Figure 2 show the spectral intensity of two nonoverlapping bands centred at 550 and 870 nm that we created by passing halogen lamp light incident on the sample through Corning coloured glass filters BG39 and RG850, respectively. For the 550 nm band $\alpha^{-1}(550\text{nm}) \approx 3 \mu m$, comparable to or smaller than the dimensions of the ‘bee’ structures in Figures 1(A)–(D). It was therefore predominantly a probe of surface microstructures. The 870 nm band, on the other hand, yielded $\alpha^{-1}(870\text{nm}) \approx 25 \mu m$, thus the subsurface and surface microstructures could be probed.

To test for the presence of subsurface scattering centres, we compared dark field images of optical scattering from 2 and 100 $\mu m$ thick bitumen films using the 550 and 870 nm frequency bands. The thicknesses of these films were determined, and verified to be uniform, by measuring their absorption spectra with the spectrophotometer and comparing it to the calibrated absorption depth curve in Figure 2. Figures 3(A) and (B) show scattered light from the 2 $\mu m$ film for 550 and 870 bands, respectively. Figures 3(C) and (D) show corresponding scattering from the 100 $\mu m$ film. For 550 nm light, the areal density of scattering centres was only 50% greater for the 100 $\mu m$ film (C) than for the 2 $\mu m$ film (A), consistent with scattering primarily from surface microstructures within the ~3 $\mu m$ penetration depth. For 870 nm light, on the other hand, the areal density of optical scattering centres was 870% greater for the 100 $\mu m$ film (D) than for the 2 $\mu m$ film (B). This increase must be attributed to additional optical scattering centres present between 2 $\mu m$ and the 25 $\mu m$ penetration depth of 870 nm light in the thicker film. We conclude that most of the 870 nm light’s optical scattering originates from bulk microstructures. As discussed below, placing a cover slip over, or thermally cycling, the sample selectively suppresses surface optical scattering centres. Note that 870 nm light then scatters almost entirely from bulk microstructures. Optical scattering data reported below is taken with 870 nm light, except where surface structures are the main interest.

For temperature-dependent optical studies, sample temperature was varied between a low (typically 15°C) and high (65°C–85°C) value in 5 degree increments, using both heating and cooling sequences. Each temperature increment was held for 5 min to ensure the binder had equilibrated at the set point temperature, after which dark field images were captured. The ‘high’ temperature in these studies was significantly lower than the 120°C used in preparing the samples initially, and did not cause the sample to flow freely. Each thermal cycle was repeated multiple times to check reproducibility of results.

Rheometric measurements

Rheometric measurements were obtained with an AR-2000X DSR (TA Instruments) with parallel plate setup enclosed in an environmental chamber. The bottom circular plate was fixed; the top parallel plate could move vertically or oscillate azimuthally. We performed a temperature ramp
oscillatory shear test. For one complete cycle, the binder started at its low temperature (typically 10°C or 15°C), was heated in 5 degree increments to its high temperature (typically 50°C, but varied from 45°C to 65°C), and was then cooled in 5 degree increments to its starting temperature. As in the optical measurements, each temperature increment was held for 5 min to ensure equilibration of the binder. A dummy sample with an embedded thermocouple was used to ensure that thermal equilibrium was achieved in this duration of time. Oscillatory shear stress sufficient to cause 0.1% strain amplitude was then applied at frequency 10 rad s$^{-1}$ to the binder tablet. Each measurement consisted of 10 preparatory oscillation cycles to stabilize the waveform to a steady state (constant stress-strain phase difference), followed by 10 data collection cycles. All binder specimens underwent several such thermal cycles. To ensure repeatability, at least two consecutive thermal cycles were repeated with identical temperature ranges. However, a full test included cycles of different temperature ranges in order to observe the effect of variable high and low temperatures.

A small number of tests were carried out using 1% strain amplitude at 10 rad s$^{-1}$ and 0.1% at 1 rad s$^{-1}$ frequency. Results were independent of strain amplitude (0.1% and 1%), indicating that the tablet was responding linearly within this range of strains. The shear modulus exhibited qualitatively similar temperature-dependence at 1 and 10 rad s$^{-1}$, but its quantitative value differed. For brevity, the results discussed in the subsequent section are based on 0.1% strain amplitude at 10 rad s$^{-1}$.

Results

Free surface ‘bee’ microstructures

Figure 4 plots the areal density of microstructures observed from the free surfaces of unmodified (black squares) and high wax (red circles) bitumen, as derived from dark field micrographs at 550 nm wavelength during the first thermal cycle after sample preparation. During heating from RT (filled data symbols), optical scattering first intensified, reaching a peak at 35°C (45°C) for unmodified (high wax) samples (see points (a) and (b) in Fig. 4). At this point, rippled ‘bee’ structures, like those observed on the surfaces of the freshly prepared samples at RT (see Figs 1C and D), were observed prominently in high-resolution micrographs of the heated sample (see Figs 5A and B). Upon further heating, scattered intensity from both samples decreased sharply (see points (c) and (d) in Fig. 4). Corresponding high-resolution micrographs of the same area of each surface showed that the ‘bees’, though still discernible, had faded considerably (Figs 5C and D). Upon heating to 55°C (85°C), ‘bee’ microstructures disappeared completely (not shown). Upon heating to 60°C (unmodified, see point (e) in Fig. 4) or 90°C (high wax, see point (f) in Fig. 4), no optical scattering could be detected in dark field micrographs, nor were any microstructures at all discernible in high-resolution micrographs (Figs 5E and F). The point at which all evidence of microstructure disappeared served to define the maximum temperature for thermal cycles.

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Apart from absence of ‘bees’ during the first thermal cycle, the size, shape and density of ‘ant’ structures remaining in the cover slip samples after the first cycle were indistinguishable from those shown in Figures 5(G) and (H), suggesting that they reside in the underlying bulk. These results show that the optical scattering during the first thermal cycle is dominated by the changing structure of surface microstructures, which are responsible for the contrasting behavior of unmodified and high wax samples shown in Figures 4 and 5. They further suggest that the first thermal cycle removes strongly scattering surface microstructures, so that the temperature-dependent behavior of smaller bulk microstructures, which are more likely to be connected to bulk rheology, can be studied unobstructed on subsequent thermal cycles.

**Bulk microstructure hysteresis**

Figure 7(A) shows a sequence of dark field micrographs acquired during a thermal cycle of unmodified bitumen with cover slip using 870 nm light. Very similar images were acquired from the free surface of an uncovered sample during the second (and subsequent) thermal cycles. For these data, we were able to brighten the 870 nm light several times above the level used to study the first cycle of the uncovered sample, in order to maximize visibility of bulk ‘ant’ structures. This was not possible for the first cycle of the uncovered sample because intense optical scattering from the larger surface ‘bee’ structures caused the detector to saturate. During heating from 15°C to 65°C, scattered intensity dropped to zero (top five frames). Upon cooling, scattered intensity recovered, although it remained weaker than during heating at intermediate temperatures. In contrast to the first thermal cycle of the uncovered sample (see Fig. 4), however, scattered intensity recovered completely to its starting level upon cooling back to 15°C (bottom five frames).

Figure 7(B) and (D) shows quantitative plots of the areal density of microstructures versus temperature for unmodified and high wax binders, respectively, obtained from dark field images such as those in Figure 7(A) using ImageJ. In both samples, optical scattering from microstructures was significantly stronger for a given temperature during the heating leg of the cycle than during cooling, but returned to its starting value upon cooling to 15°C. To highlight this hysteresis, Figures 7(C) and (E) show plots of the difference $\Delta I = I_{heat} - I_{cool}$ in areal density of microstructures versus temperature for unmodified and high wax samples, respectively. $I$ and $\Delta I$ were both about 50% stronger for the high wax sample in the temperature range $15 < T < 65$°C. However, $\Delta I$ peaked near 25°C and trended towards zero at temperature above 40°C and at 15°C for both samples.

We found that the hysteresis curves shown in Figures 7(B)–(E) reproduced indefinitely without perceptible change, and without reappearance of surface ‘bee’ microstructures, on subsequent thermal cycles. The temperature range $15 < T < 2015 The Authors. Journal of Microscopy published by John Wiley & Sons Ltd on behalf of Royal Microscopical Society. 262, 216–225
Fig. 7. (A) Dark field images of unmodified bitumen with cover slip during heating (top row) and cooling (bottom row) cycle. Temperatures (left to right) were 15°C, 25°C, 35°C, 45°C and 55°C. (B) Areal density of microstructures and (C) hysteresis $\Delta I = I_{\text{heat}} - I_{\text{cool}}$ versus temperature for unmodified bitumen. (D and E) same as (B and C), but for high wax binder.

65°C thus appears to represent a chemically stable regime in which the bulk 'ant' microstructures can disappear completely upon heating, although retaining the ability to re-form completely upon cooling.

Shear modulus hysteresis

Figure 8(A) presents results from the measurements of the complex shear modulus ($|G^*(T)|$) of unmodified (black squares) and high wax (red circles) bitumen at 10 rad s$^{-1}$. Upon heating from 15°C to 50°C (see solid data symbols), $|G^*_\text{heat}(T)|$ dropped by a factor of ~200 for both samples. This is consistent with the generally observed linear behavior between $\log |G^*_\text{heat}(T)|$ versus temperature (McGennis, 1994). Upon cooling back to 15°C (see open data symbols), $|G^*_\text{cool}(T)|$ increased, returning very nearly to its initial value at 15°C. However, during the cooling leg of the cycle, $|G^*_\text{cool}(T)|$ was lower than $|G^*_\text{heat}(T)|$, by as much as 13% (22%) for unmodified (high wax) samples. Note that Figure 8(A) is in log scale, which makes the discrepancy appear small even though it
significant difference in the spatial structure of the domains in the bulk, referred to as ‘ants’ in this study, was consistently observed even after several thermal cycles. However, the ‘bee’ structures observed on the bitumen surface did not reappear immediately after the first heating cycle.

The strikingly similar hysteresis observed in areal density of microstructures by dark field microscopy (see Figs 7C and E) and in the dynamic shear modulus $|G^*(T)|$ by DSR (see Fig. 8B) during thermal cycling of chemically identical bitumen samples constitutes one of the main results of this study. Both hysteresis phenomena peak at 25°C, are of the same sign (microstructure areal density and $|G^*(T)|$ larger during heating than during cooling), and are prominent over identical temperature ranges (approximately 20°C < T < 40°C), exhibit the same 2-fold stronger magnitude for high wax compared to unmodified bitumen, and repeat similarly over multiple temperature cycles. These similarities suggest that thermally driven modulation of microstructure size and/or density is the cause of the corresponding 10–20% modulation in $|G^*(T)|$.

Although a quantitative model of this causal relation is beyond the scope of this paper, the general connection between the size, density, viscoelasticity and interfacial properties of microstructural inclusions, on the one hand, and bulk mechanical properties of composite materials, on the other, has been well established in colloidal science for over a century. For example, Einstein calculated the viscosity of a suspension of rigid spheres in a Newtonian liquid as early as 1906 (Einstein, 1906). Later work extended Einstein’s treatment to elastic spheres (Fröhlich & Sack, 1946), dilute emulsions of spherical drops of one Newtonian liquid dispersed in another (Taylor, 1932), flowing liquid emulsions (Oldroyd, 1955), highly concentrated composites (Kerner, 1956), nonlinear effects (Showalter et al., 1968) and polydisperse emulsions with interface surfactants (Palierne, 1990). For the present samples, the volume fraction occupied by ‘ant’ inclusions is less than 1% (see Fig. 7, right-hand vertical scale), and they appear to be of only a single material species and of similar size. Thus, for a qualitative discussion, we can treat the samples as a dilute emulsion of spherical droplets of common radius $R_i$ of one incompressible viscoelastic fluid (the ‘ant’ microstructures) dispersed in another (the bitumen matrix). Moreover, the independence of $|G^*|$ from strain amplitude indicates that $|G^*|$ is linear. For this case, the average linear complex shear modulus $|G^*|$ of the composite medium has the general form (Palierne, 1990)

$$|G^*| = |G_M^*| (1 + F_i \Phi_I) ,$$

where $|G_M^*|$ is the complex shear modulus of the matrix without inclusions, $\Phi_I$ is the volume fraction occupied by the inclusions and $F_i$ is a dimensionless coefficient that depends on $R_i$, the difference $|G'| - |G_M^*|$ in shear moduli of the materials of the inclusions (I) and matrix (M), and interfacial tension coefficients. The linear relation between $\Phi_I$ and $|G^*|$ in Eq. (2) provides a simple framework for understanding the observed
hysteresis correlation: \( \Phi_I \) is directly proportional to the areal density of microstructures, the quantity measured by dark field microscopy. Thus, hysteresis in \( \Phi_I \) naturally leads to corresponding 10–20% modulation of [\( G''(T) \)] over the background value \( [G''_m(T)] \) of the pure matrix. The material-dependent coefficient \( F_I \) governs the magnitude of the latter, and should be amenable to microscopic modelling and fitting of data such as that presented here.

The authors would also like to point out that the ‘ant’ inclusions suspended in a matrix as observed in this study are similar to the hypothesized colloidal structure of the bitumen that has been extensively discussed in the literature (Lesueur, 2009) and has also been used to computationally model the bitumen as a composite (Eberhardsteiner et al., 2015). However, additional work is needed to establish the chemical makeup of the microstructures observed in this study.

Conclusion

We applied optical microscopy and optical scattering to track variations in the size, shape and density of microstructural inclusions in PG 64–22 bitumen and a high wax variant as temperature varied over the approximate range 15 < \( T \) < 65°C. Choosing a wavelength band centred in either the visible (550 ± 50 nm) or near infrared (870 ± 50 nm) spectral region enabled selective probing of surface or bulk microstructures, respectively. Rippled ‘bee’ microstructures of \( 5 \text{ (} 20) \mu \text{m length in unmodified (high wax) bitumen, although they dominated optical scattering during the first heating ramp after sample preparation from melts, were found to be concentrated at the surface, and to be annealed away by this initial heating. Smaller quasi-spherical ‘ant’ microstructures of \( \leq 1 \mu \text{m radius then became clearly visible upon first cooling back to 15°C, and dominated 870 nm optical scattering on subsequent thermal cycles.}

‘Ant’ microstructures were found to reside primarily in the bulk, to disappear each time samples were heated to ~65°C, then to reappear reproducibly without diminution in size or density upon cooling for an indefinite number of cycles. At intermediate temperatures in each cycle, the size and density of bulk microstructures was higher during heating than during cooling, resulting in distinct hysteresis in optical scattering intensity. Hysteresis peaked at 25°C, was most pronounced in the range 20 < \( T \) < 40°C, and was \( \approx 2 \times \) stronger in high wax than in unmodified bitumen.

Parallel mechanical measurements of the magnitude of the complex shear modulus \( [G''(T)] \) of identical samples during identical thermal cycles revealed hysteresis of the same sign, same peak temperature, same temperature range and same contrasting magnitude between unmodified and high wax samples as observed by optical scattering. \( [G''(T = 25°C)] \) was 13% (22%) higher during heating than during cooling for unmodified (high wax) bitumen, differences large enough to significantly impact the expected performance of the material. This strikingly similar hysteretic behavior between the microstructure’s optical scattering and \( [G''(T)] \) suggests that internal microstructures contribute significantly to the shear stiffness of bitumen, and that thermal modulation of microstructure size and/or density similarly modulates the mechanical strength of a binder. Our results should stimulate quantitative theoretical modelling of the relationship between microstructure and shear modulus, which is well established from a century of colloidal material science. Finally, our results demonstrate that optical microscopy and optical scattering provide fast, noncontact probes of internal bulk microstructure of asphalt binders that are suitable for high-volume screening and testing.

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