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DOI
10.1617/s11527-022-02068-7

Publication date
2022

Document Version
Final published version

Published in
Materials and Structures

Materials and Structures (2022)55:239
https://doi.org/10.1617/s11527-022-02068-7

RILEM TC REPORT

RILEM TC272 PIM: phase morphology of bituminous binders with liquid additives

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Received: 22 November 2021 / Accepted: 19 October 2022

Abstract In the past years, the use of liquid additives as bitumen modifiers has increased to tailor the rheology of bitumen for a wide range of applications. Their chemical composition and mutual interaction result in specific phase morphologies in the binders. Hence, there is a need to evaluate the phase morphology of complex binders and the impact of additives on their physical properties. The RILEM Technical Committee 272-PIM 'Phase and Interphase behaviour of innovative bituminous Materials', Task Group TG1 assessed the phase and interphase properties of bituminous binders. Some preliminary results are presented on blends using three liquid additives and a neat 35/50 bitumen. The goal of formulating the blends was to achieve similar consistency of a pen grade 70/100 bitumen at the original state and to evaluate the binders at both original and after aging. Physical properties were evaluated through rheological characterisation using a dynamic shear rheometer (DSR) in a wide range of conditions. The phase

Published online: 16 November 2022

morphology was assessed using atomic force microscopy (AFM). Differential scanning calorimetry (DSC) was also used for the characterisation of the thermal behaviour of the binders. While conventional properties, as obtained from the routine binder testing methods, hardly distinguish between blends, the crossover temperature, derived from DSR measurements, enabled to dictate the impact of liquid additives on the physical properties of bituminous binders at intermediate temperature. AFM confirmed a difference in phase morphology between the blends, whereas some binders displayed new phases at original and aged conditions. Glass transition, as determined by DSC, also showed a difference in the low-temperature domain that may be explained with the difference in phase morphology. Overall, an in-depth understanding of microstructure morphology and glass transition behaviour of complex binders can assist in designing future specifications to distinguish durable bituminous materials better.

Keywords Bitumen · Crossover temperature · Glass transition · Phase morphology · Atomic force microscopy · Differential scanning calorimetry

1 Introduction

Over the past two decades, the oil industry has evolved greatly with more variability in crude oil sources and complexity in petroleum refineries. Changes were observed in the refining of crude oil processes with an emphasis on upgrading the 'upstream' products of the refineries. It has introduced changes in the bitumen production processes in the past years and, as a result, the chemical composition and rheological properties have also varied, while a limited selection of crude oil feedstocks can result in quality bituminous products [1]. At the same time, the demand for quality pavement has also evolved, with more focus on durability, warranty on performance, and sustainability. In this context, alternative materials to bitumen have entered the bitumen supply chain to adjust properties and end-performances [2]. As a result, the use of liquid additives for bitumen modification has become common for the purpose of corrective measures and to obtain desirable binder properties in relation to specific applications. These additives may have different chemical origins and physical properties. For example, with increasing demand for recycling applications, additives for asphalt recycling markets, historically known as 'rejuvenators', have expanded to restore the lost properties of aged bitumen [3]. The use of such additives has resulted in new classes of bituminous binders, where the molecular composition is more complex than neat bitumen. To assess these new classes of binders, a novel approach, where analytical tools can reliably evaluate the phase and interphase morphology of binders, will bring more understanding and robustness in addressing binder behaviour.

In the RILEM TC231 NBM, 'Nanotechnology-based bituminous materials' (2008–2013), an extensive effort was made to assess the bitumen morphology through differential scanning calorimetry (DSC) and atomic force microscopy (AFM). The experimental plan included four different binders with varying wax contents, one expected to be wax-free, two with natural wax, and one containing added-wax. A total of seven labs participated with DSC and AFM measurements with detailed test procedures [4]. The motivation was to determine repeatability and reproducibility of the tests, identifying any specific correlation between the morphology as observed through AFM and thermal behaviour with DSC, and finally, propose some recommendations. The outcomes on DSC were that temperature scan between −80 °C and 140 °C should cover thermal transition phenomena in bitumen and provided reasonably good reproducibility. With AFM, three labs performed temperature-related AFM and showed that three phases in the materials with wax could be distinguished by the different responses in phase-contrast imaging mode [5].

While this RILEM TC was considering wax, in continuation of these works, the RILEM TC 272-PIM 'Phase and Interphase behaviour of innovative bituminous Materials' in its Task Group-TG1 aims at combining advanced characterisation methods to

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evaluate the complex bituminous binders with various modifiers [6] on physical properties and morphology structure. This work involved 17 different labs around the world combining their capabilities, not only by addressing the conventional binder properties, but also with an in-depth insight into the fundamental assessment of binders. While the current specifications, either in pen grading or Superpave PG grading, were developed for petroleum-based bituminous binders, the question should be raised on their suitability to assess complex binders that include various modifiers and additives. The objective of these inter-laboratory activities was not performing a round-robin test on conventional binder properties and testing, but rather having different labs using various methods to go beyond the routine level of specifications, and finally answer the question of whether the current specifications are suitable for characterising the complex binders and its durability aspects. The results presented here emphasise more on the evaluation of two paving grade bitumen, commonly used in Europe, and the effect of three liquid additives on the rheological properties of the base binders at different temperature regimes using a dynamic shear rheometer (DSR) and phase morphology and thermal properties by AFM and DSC, respectively.

2 Materials & methods

2.1 Material and preparation

Two bituminous binders were used in this research: a 35/50 pen graded bitumen (Bit1) was used as a control base bitumen, and a 70/100 pen graded bitumen was used as a reference bitumen. Both binders were obtained from the same source and expected to have similar phase morphology. Three different liquid additives were evaluated in blend with Bit1:

- Blend1 used a commercial bio-based asphalt recycling additive (4 wt.% of binder), based on tall oil distillate. The specific aliphatic structure of this additive enables it to interact with the agglomerated asphaltenes as occurring due to aging [7]. This additive is readily miscible in bitumen, it enables to restore the lost properties of the aged binder at intermediate and low temperatures, keeping the advantage of high temperature and with a durable effect over aging.
- Blend2 used a re-refined engine oil bottom; REOB (8 wt.% of binder). It has been used for years as softening agent or even sometimes as a rejuvenator with diverse outcomes. Some limitations were highlighted, causing low-temperature susceptibility cracking depending on the exact process and source of the REOB, especially in the case of excessive dosages.
- Blend3 used a paraffinic oil (4 wt.% of binder), which is commonly not used in the asphalt industry. The paraffinic nature of the additive was presumed to be shown in multiphase morphology, especially at low temperatures.

The basis of the choice of the liquid additives was to have a wide range of different chemistries of the additives. The typical properties of the additives are listed in Table 1.

Table 1 Typical properties of the additives

Additives	Nature	Physical properties	Additional remark
1	Bio-based asphalt recycling agent based on tall oil	Viscosity at 60 °C 22 mm^2/s	Clear liquid at ambient temperature
		Flash point > 280 °C	
		Cloud point < −25 °C	
2	Refined Engine Oil Bottom [8]	Viscosity at 60 °C < 50P *	Brown, viscous liquid at ambient temperature
		Flash point > 232 °C	
		Pour point -28 °C	
3	Paraffinic oil	Viscosity at 40 °C 67–74 mm^2/s	Clear transparent liquid at ambient temperature
		Flash point > 240 °C	
		Pour point < −18 °C	

* as reported from reference [8] in this unit

The dosage of liquid additives in Bit1, the 35/50 pen grade, has been determined to target paving grade binders with similar range of intermediate temperature consistency, as based on penetration value at 25 °C, of Bit2, a 70/100 pen grade. The control bitumen, Bit1, was first heated to 160 °C, and then the additives were added. The blends were prepared by hand-stirring for about 10 min until they became visually homogeneous, where no high shear or maturation time was required. A single lab performed the blending and then was dispatched to each participant. Later, all samples were aged by each lab, first using the Rolling Thin Film Oven Test (RTFOT), where 35 g binder per bottle was kept in a pre-heated oven for 75 min after stabilisation at 163 °C. Afterward, the samples were long-term aged in a Pressure Aging Vessel (PAV) unit for 20 h at 100 °C and 2.1 MPa. All binders were characterised by conventional tests. Between three and seven labs performed the full pen grading characterisation of the binders; and between three and four performed the full PG grading. Table 2 provides the basic properties of the five binders (before and after aging) and PG grading, resulting in average of all measurements.

2.2 Dynamic shear rheometer (DSR)

Rheological tests were conducted by dynamic shear rheometer (DSR) on all samples at the different aging states to reveal their high and intermediate temperature response. While the analysis and comparison between laboratories has been already reported [9] the analysis here was made on measurements from one laboratory in temperature ramping from low to high temperature at fixed frequency of 1.59 Hz (10 rad/s). This choice was dictated to keep focus on comparison between different testing approach with DSC and AFM.

2.3 Atomic force microscope (AFM)

2.3.1 Sample preparation

All samples were prepared by applying approximately 15 mg of sample on the 8 mm AFM sample substrate (i.e., steel disks of 0.5 mm thickness). The samples were then heated for 30 s at 100 °C on a heating plate to obtain a smooth bitumen film. Later, to have the same thermal history for all samples, they were conditioned in an oven at 100 °C for 15 min. Prior to AFM imaging, the samples were stored in closed petri dishes at the imaging temperature of 21 °C for 24 h. This method has been used successfully to characterise the surface morphology and phase-interphase properties of bitumen [10–12]. In this context, the results of the RILEM TC PIM aims at extending the findings to more complex bituminous binders.

2.3.2 AFM operating mode and parameters

The phase and interphase properties at the surface of the original bitumen and the binders were characterised by AFM. The AFM measurements were performed by one laboratory only. Dimension Icon AFM set-up from Bruker was used for this study where 'Tapping mode' AFM was used to characterise the binders. RTESPA silicon AFM probes from Bruker were used for the measurement. An AFM probe is a sharp tip attached to the end of a micro-cantilever. The nominal end radius of the tip of each RTESPA probe was 8 nm and the cantilever had a nominal resonance frequency of 300 kHz and spring constant of 40 N/m.

Table 2 Properties of the binders

Sample	Penetration value at 25 °C, 0.1-mm		Softening point temperature, °C		PG	
	Original	After RTFOT + PAV	Original	After RTFOT + PAV	Exact	Grade
Bit1	39	18	54.0	66.6	74–23	70–22
Bit2	79	29	46.2	60.0	65–27	64–22
Blend1	89	32	45.6	59.8	67–29	64–28
Blend2	76	29	47.8	63.4	69–29	64–28
Blend3	69	30	48.0	63.0	68–29	64–28

The probe was scanned at 1 Hz (1 line/s) over the sample surface by a piezoelectric scanner at ambient temperature condition (21 °C) during the AFM measurement in tapping mode. The topography and phase images were collected simultaneously in a $10 \times 10\ \mu m^2$ scan size with a pixel resolution of 512×512. In Tapping mode AFM, the probe is driven near its first resonant frequency. While the probe is scanned across the sample, the amplitude is kept constant. In this way, the tip maintains an intermittent contact over the sample surface by exerting a moderate force, which is suitable for the characterisation of the bituminous binders. The oscillating cantilever dissipates different amounts of energy as it meets different local mechanical properties on the sample surface. As a result, topography and phase-contrast data are generated simultaneously. Topography images provide information of the relative height of the surface features of the material and phase-contrast images present relative damping of an oscillating cantilever, which can be related to the cumulative measure of modulus and adhesion force of the individual phase [13–16].

Phase images obtained using tapping mode AFM provide only qualitative evidence of the differences of mechanical properties between the bituminous phases. The mechanical property contrast observed in a phase image is the cumulative contribution of all different mechanical responses, such as modulus, adhesion, deformation at the applied force and energy dissipation between the loading and unloading tapping cycles [16]. It is difficult to decouple the individual mechanical response properties from the AFM phase images alone. Different phases in bitumen can be quantitatively distinguished using another AFM mode 'Peak Force Quantitative Nanomechanical Mapping' (QNM). Peak Force QNM provides the mechanical property maps, such as modulus, probe-sample adhesion force, deformation, and dissipated energy of bitumen phases at the microstructural level [12, 16].

In this research, as a first step towards characterising bituminous binders with liquid additives, a semi-quantitative approach was explored using Tapping mode AFM. Gwyddion's software package was used to extract some quantitative features of the microstructures, such as the quantity, size, and phase fraction of the dispersed phase (i.e., inclusions) [16]. Statistical quantities such as the mean length along the long axis were calculated from the total dispersed phase in the scanned area. To distinguish the inclusions from the continuous matrix phase, the images were first converted to binary images, and from that phase fractions were calculated using 'ImageJ' open source software. This approach helped to determine the potential of such a technique in complex binder characterisation.

2.3.3 *Differential scanning calorimetry (DSC)*

At low temperature regime, the aged binders become brittle at a relatively higher temperature, reflecting the adverse impact of aging on material embrittlement, and ultimately showing susceptibility to thermal cracking [17, 18]. Mitigation of aging-induced embrittlement can be achieved by shifting the *glass transition temperature* (T_g) values toward lower temperatures by incorporating various agents, such as liquid additives. The liquid modified binders can have lower T_g values, mainly because the liquid additives turn out to be in the glassy state at much lower temperatures than of neat bituminous binders.

In the present DSC experimental program, the heat flow curves of studied materials have been obtained by conducting temperature modulation DSC (TM-DSC) and temperature linear DSC (TL-DSC) measurements. The measured heat flow is a function of the heating or cooling rates, sample heat capacity, and endothermic or exothermic events occurring in the sample. The weight of samples ranged from 10 to 15 mg to minimise the thermal lag, and annealing was conducted before any measurement to remove any polar association existed in binders due to their thermal history.

A schematic representation of heat capacity (C_p), which was calculated from the heat flow signal wherein the inflection point that corresponds to the glass transition of the sample is shown as well. In fact, the increase of C_p takes place during the transition from that of glass to an amorphous state. Further details about the calibration of measurements and the protocols employed to evaluate the glass transition changes in bituminous binders are discussed extensively in RILEM TC 272-PIM [19].

3 Results and discussion

3.1 Rheological behaviour

One laboratory was able to run the different samples in temperature ramping range between -20 °C and 80 °C at a fixed frequency of 1.59 Hz (10 rad/s), thus providing the full range of rheological behaviour. Figure 1 shows the shear modulus of all binders on original and after long-term aging, RTFOT + PAV. Bit1 can distinguish from the other ones with higher shear modulus, while the different blends overlapped the Bit2 profile. With aging, the same trend was observed. On physical properties, all blends regardless of the liquid additives showed a limited difference.

Furthermore, the data set can be analysed using a Black space plot and displayed in Fig. 2. Such plots are independent of temperature or frequency and provide the correlation between phase angle and shear modulus. With a high shear value, in the low-temperature domain, the material is stiff and predominantly elastic with low phase angle. For low shear modulus values, in the high-temperature domain, the material is softer and predominantly viscous with a phase angle close to 90°. All original binders almost overlapped with limited rheological differences. After long-term aging, some slight differences may be observed in the curvature. Usually, with aging, the curves tend to become flattened, less temperature susceptible. Blend1 tends to keep its initial curvature as compared to Blend2 and Blend3.

Rheological datasets were analysed to determine different rheological parameters commonly used as specification performance indicators for bituminous binders. First, high temperatures parameters of the binders were compared at different aging conditions. These DSR parameters were initially included in the Performance Grading (PG) system [20], even though multiple stress creep recovery tests have been introduced for high temperatures.

In this work, the temperature at which $|G^*|/\sin\delta$ is equal to 1 kPa for the original and 2.2 kPa after RTFOT were determined, respectively. The specific PG high temperature was the minimum of both values. Performance at intermediate temperature was addressed by the PG criteria after RTFOT + PAV, where loss modulus equals 5000 kPa. In addition to these basic properties as per the routine level of

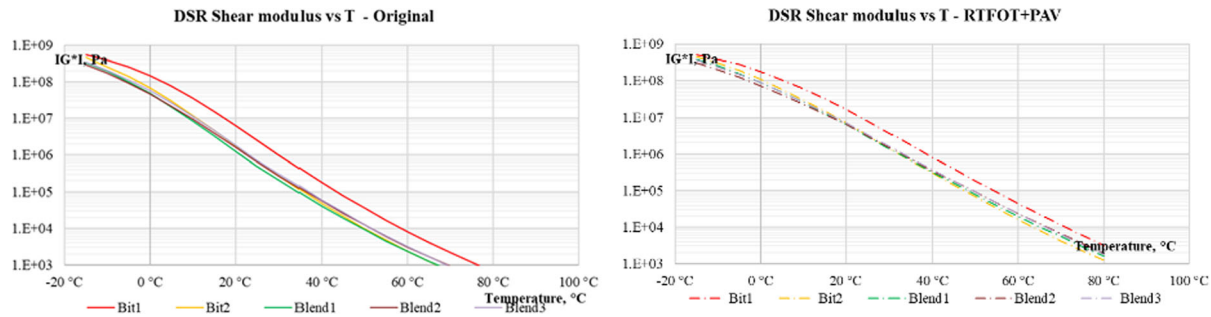

Fig. 1 Shear complex modulus against temperature for all binders, original and after RTFOT + PAV

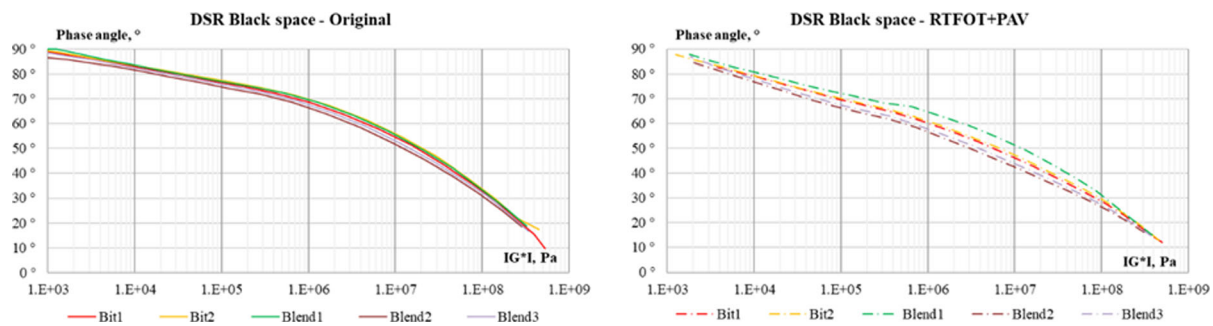

Fig. 2 Black space for all binders, original and after RTFOT + PAV

specifications, the cross-over temperature at different aging states was determined.

Figure 3 shows the PG parameters for high temperature on the original binders after RTFOT and the intermediate temperature after RTFOT and PAV. The error bars are for the lowest and highest values as recorded within all laboratories. As expected, Bit1 showed the highest values, close to PG76. While the temperature for Bit2 and the three blends were in the same range within PG64. After aging, a similar trend and ranking are observed in all the binders. Hence, from the high-temperature criteria, different blends could not be distinguished easily. Furthermore, the intermediate temperature was evaluated by the loss modulus $|G^*|\sin\delta$ after long-term aging at the value of 5000 kPa. Similar to the high-temperature domain, Bit1 had a higher value than Bit2, and all the three blends showed a similar response in the intermediate temperature domain. From this parameter, the different blends could not be distinguished either.

This study has considered the crossover temperature to assess binder at the intermediate temperature range. This is the temperature at which the phase angle equals 45°, where the storage and loss modulus are equal. This parameter provides insights on the transition between a predominant elastic behaviour, where $\delta < 45°$ to a predominant viscous behaviour, where $\delta > 45°$ [21]. The lower the crossover temperature, the longer the binder can dissipate energy [17, 22]. Figure 4 displays the cross-over temperature after different aging conditions. The original binder, Bit1 had a crossover temperature of 11 °C, and Bit2 had a lower value, 4 °C, which is consistent from the "hardness" point of view. Whereas, Blend1 shows a lower crossover temperature of 2 °C, as compared to the other blends, including Bit2. After aging, a clear trend of increasing crossover temperature was observed for Blend2 and Blend3 compared to Bit2 and Blend1. The increase between original and RTFOT + PAV states was almost 15 °C for Blend2 and Blend3 compared to Bit2 and Blend2, which were limited to 10 °C. Thus, the crossover temperature has shown the potential to be an indicator to distinguish complex binders. This may designate some difference in mobility of the structure and resulting properties between the blends at the intermediate temperature range.

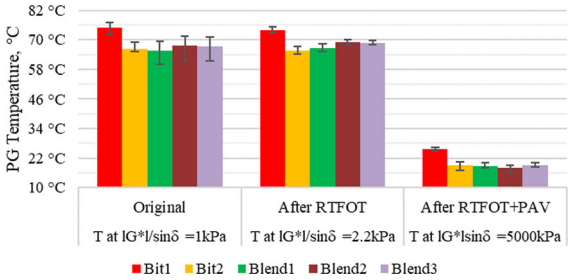

Fig. 3 DSR, high and intermediate temperature continuous grades

3.2 Phase morphology

The phase and interphase surface properties of the bitumen and the blends are obtained as AFM micrographs. The binders display distinct phase-separation characteristics at original and aged conditions. Mutual compatibility of liquid additives and the base bitumen can be revealed by the phase morphology of the blends [13–16]. The study of phase images reveals any possible incompatibility caused by a discontinuity in the molecular weight distribution in the binders [13]. This phenomenon may occur in aged bitumen and the presence of a liquid additive, which is not fully compatible with the base bitumen, showing distinct phase morphology.

Figure 5a and b present 10 × 10 μm^2 AFM topography and phase images of Bit1 and Bit2, respectively. Additionally, AFM micrographs of Blend1, Blend2 and Blend3 are presented in Fig. 5c, d and e, respectively. Topography images of Bit1 and Bit2 confirmed a flat morphology without any significant structuring, wherein the characteristic "bee-structures" were absent. This morphology is commonly seen in the bitumen of non-waxy and naphthenic origin [15, 16, 23]. Additionally, phase images confirmed that the bitumen showed mostly continuous phase with fine (i.e., submicron) dispersed phase of size.

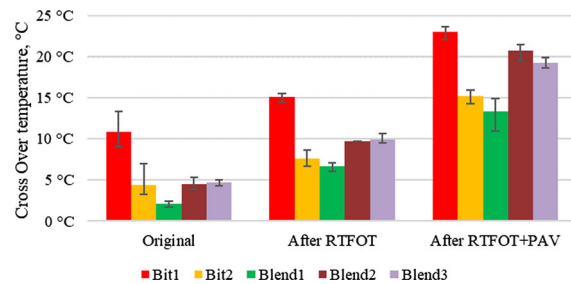

Fig. 4 DSR cross-over temperatures

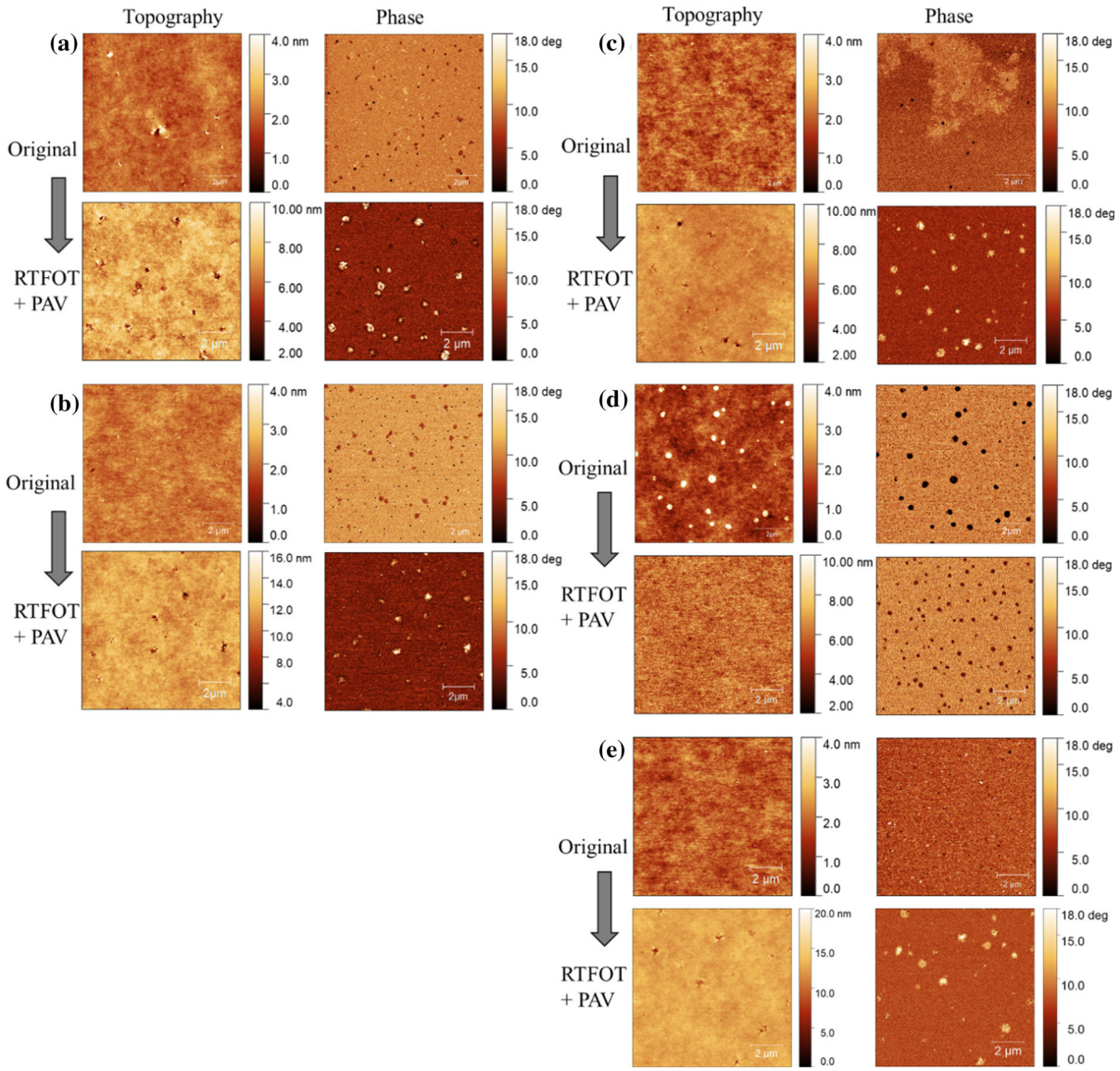

Fig. 5 Phase behaviour of **a** Bit1 and (**b**) Bit2 (**c**) Blend1, **d** Blend2 and **e** Blend3 at fresh and aged conditions (AFM 10 × 10 μm^2 topography and phase images)

Phase images resulted from the cumulative local mechanical properties of the scanned surface, such as stiffness modulus [13, 24]. From the earlier published work of controlled nano-mechanical measurement by AFM, it is known that the phase showing higher phase shift corresponds to a stiffer and less adhesive phase and vice-versa [14]. The difference in phase shift is perceived from the colour bars of the AFM micrographs presented in Fig. 5, where the brighter colour corresponds to the higher value and the darker, the lower. In Fig. 5a and b, the dispersed submicron phases of Bit1 and Bit2 displayed a lower phase shift, hence are softer than the matrix phase. Phase images of these bitumen after aging revealed an emergence of a new spherical phase with higher stiffness peaks, which suggests that this phase is higher in modulus than the matrix phase. This new phase may have resulted due to an increased agglomeration of molecules in oxidised bitumen after the RTFOT and PAV aging conditions.

The topography of the original Blend1 showed similar properties as the original Bit1, as seen in Fig. 3c. At some locations in the phase image of the original Blend1, an incompatibility was observed. Whereas the incompatibility is no longer apparent after aging, and the phase images displayed similar structures as Bit2: stiffer inclusions in the matrix. In Fig. 5d, the original Blend2 displayed a spherical phase of submicron size in the topography image protruding from the surface. Phase images depicting a lower phase angle than the matrix phase confirmed that this phase was softer than the matrix phase. After aging, the topography showed that the earlier observed phase had been embedded into the matrix phase. Moreover, the phase image after aging confirmed that the spherical phase was still apparent as softer inclusions. Topography and phase images of the original Blend3 revealed a homogeneous morphology in Fig. 5e. Phase image of original Blend3 demonstrated fine nano-domains, which could be a result of precipitated wax from the additive. The aged Blend3 showed similar properties as the aged Bit2. These observations corroborate the differences seen with the crossover temperature, were Blend2 and Blend3 displayed stiffer phase morphology.

A quantitative analysis was also performed on the AFM images using 'Gwyddion' and 'ImageJ' software packages, and the results are shown in Table 3. It presents properties of dispersed spherical phase, such as comparative stiffness difference, phase shift, number of spheres, average size, area fraction. After aging, Bit1 showed more agglomerates molecules and appeared as a more spherical dispersed phase as compared to Bit2. Where the agglomerates in Bit1 are larger compared to Bit2. The base bitumen used to prepare all the blends was Bit1. Blend1 showed a higher number of dispersed spheres as compared to Bit1 after aging. Whereas the mean sphere size was lower than the base Bit1. This suggests that after oxidation, Blend1 was less susceptible to agglomeration. Blend2 showed softer particles at the original state. The particles remained softer after aging but became smaller and more dispersed. Blend3 showed again stiffer particles with an average size comparable to Bit1 after aging.

3.3 Glass transition behaviour

The T_g values of all binders and blends are reported in Table 4, whereas no significant systematic difference between the participating labs was observed. Four laboratories conducted DSC. Nevertheless, there was an apparent difference in glass transition with the aging and the incorporation of liquid additives in Bit1.

All binders exhibited a single and distinct T_g, as illustrated in Fig. 6 with the results from one lab, indicating that they behaved as homogeneous systems. When blended, the single T_g could also be attributed to the compatibility of additives with Bit1. The molecules of liquid additives were flexible enough, and the intermolecular forces between the molecules of additives and Bit1 were relatively weak to shift the T_g of

Table 3 Quantitative analysis of the AFM images

Binders	Condition	Dispersed spherical phase				
		Relative stiffness to the matrix phase	Phase shift $\Delta\phi$ ($\phi_{spheres}$-ϕ_{matrix})	No. of spheres	Average size (μm)	Phase area fraction (%)
Bit1	Original	–	–	–	–	–
	RTFOT + PAV	Stiffer	12	20	0.46 ± 0.09	3.28
Bit2	Original	–	–	–	–	–
	RTFOT + PAV	Stiffer	10	19	0.30 ± 0.11	1.47
Blend1	Original	–	–	–	–	–
	RTFOT + PAV	Stiffer	11	27	0.26 ± 0.12	3.09
Blend2	Original	Softer	− 8	31	0.28 ± 0.08	4.93
	RTFOT + PAV	Softer	− 7	88	0.18 ± 0.06	6.48
Blend3	Original	–	–	–	–	–
	RTFOT + PAV	Stiffer	8	26	0.37 ± 0.16	2.46

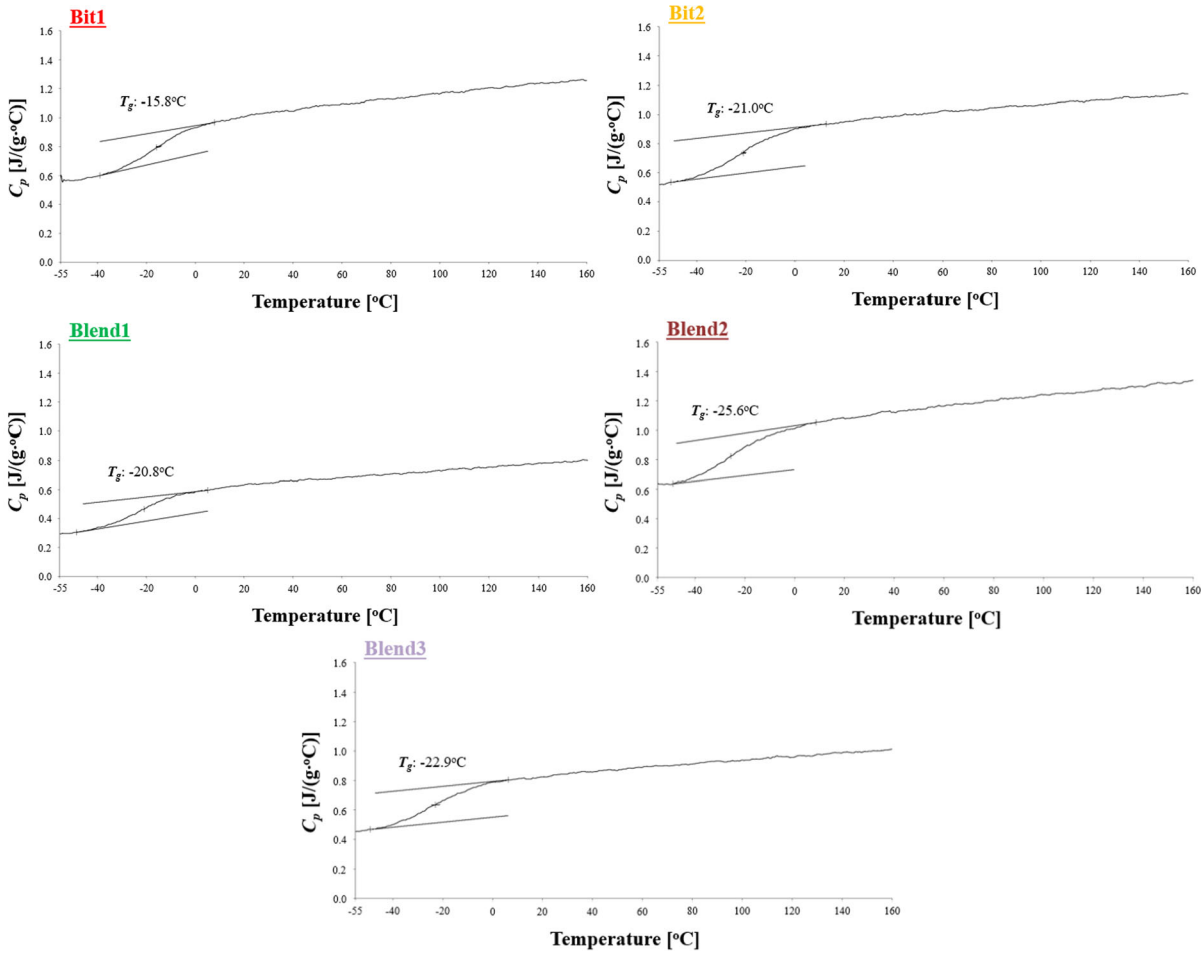

Fig. 6 Glass transition behaviour of studied binders after RTFOT + PAV

Table 4 Glass transition temperature values of binders

Binders	Glass transition temperature [°C]			
	Original		After RTFOT + PAV	
	Average	St dev	Average	St dev
Bit1	− 17.26	0.94	− 15.97	0.23
Bit2	− 22.02	0.93	− 20.17	1.17
Blend1	− 23.79	2.17	− 21.07	0.37
Blend2	− 25.91	3.49	− 25.69	0.12
Blend3	− 23.86	0.12	− 22.84	0.08

Bit1 to lower values. A high T_g also manifests a rigid molecular network in a binder. In Bit1, the REOB had a slightly higher effect on reducing the glass transition of binder compared to the bio-based additive in Blend1. The change of T_g values of blends with aging has been studied, showing that their glass transition was increased after aging. The increase of stiffness modulus of the homogeneous microstructures of aged blends was noticed in Fig. 5, together with the appearance of some bright (or high phase angle) spots. The T_g values were also increased after aging, dictating the possible increase of the number of strong intermolecular forces and thus the transition to more brittle blends.

4 Conclusions

The RILEM TC 272-PIM TG1 have conducted fundamental studies to assess binder properties at different temperature regimes reliably. Within the scope of

this study, bitumen of different penetration grades and blended with liquid additives were characterised by using state-of-the-art assessment techniques for rheology, phase, interphase morphology, and thermal properties of materials.

Conventional DSR high-temperature criteria hardly distinguish between the different blends with liquid additives. However, the crossover temperature can distinguish the physical viscoelastic properties of complex binders at intermediate temperature regime and can be considered as a promising parameter.

AFM confirmed to be a promising tool for distinguishing morphology properties of both neat and aged bitumen and the complex binders at the nano to micrometer length scales. From AFM micrographs, it is revealed that all liquid additives show relatively good compatibility with the base binder except Blend2, containing REOB, which shows a distinct morphology with the presence of a new phase. This suggests a possible incompatibility arising from the additive REOB. Furthermore, AFM has the potential to assess any possible agglomeration of molecules due to aging, which results in different phases which are apparent in the microstructure of the aged binder.

Next to the phase-interphase properties assessed by AFM, the glass transition behaviour of the binders can be interpreted by conducting TM-DSC analyses. The bio-based additive in Blend1 showed a slightly lower effect on lowering the T_g values of Bit1 compared to the REOB in Blend2. The T_g values were generally decreased by incorporating the liquid additives in Bit1, and the opposite attribute was observed after aging. Thermal events like enthalpy related to association-dissociation of molecular classes from low to high temperature range might provide information on the hierarchy of structures within the bulk of bitumen, which could be the topic of a future study.

Combining the assessment tools for rheology, phase-interphase characteristics to thermal properties of the binders have demonstrated a promising approach to evaluate more complex binders and eventually establish a structure–property relationship. Furthermore, the results obtained from these binder characterisation methods can support the selection of binders with desired performance properties for a specific application. The knowledge developed further following this approach can provide valuable insights for updating current binder specifications.

Acknowledgements The authors acknowledge RILEM TC 272 PIM – TG1 'Phase and interphase behaviour of innovative bituminous materials' for providing the materials and valuable discussions. This article was prepared by a task group within RILEM TC 272-PIM: Phase and Interphase behaviour of bituminous Materials. The article has been reviewed and approved by all members of the TG and the TC.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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