Fuel 387 (2025) 134361

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Physicochemical compatibility assessment of bio-additives and bitumen using solubility science-based approaches

Yongping Hu [a], Anand Sreeram [a,b,*], Abir Al-Tabbaa [b], Gordon D. Airey [a]

[a] Nottingham Transportation Engineering Centre (NTEC), Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, UK
[b] Department of Engineering, University of Cambridge, Cambridge CB2 1PZ, UK

ARTICLE INFO

Keywords:
Asphalt
Bio-bitumen
Bio-binder
Hansen Solubility Parameter (HSP)
Compatibility

ABSTRACT

Increasing environmental concerns necessitate the urgent investigation of alternative, sustainable resources as replacement for fossil fuel-derived bitumen; the primary material used for road construction. One of the promising approaches is the use of bio-based alternatives as partial or full bitumen substitutes in asphalt mixtures. Currently, the selection of bio-additives is subjective, resulting in significant variations in the quality of bio-based bitumen produced and its resulting utility as an engineering material. This study utilised solubility-based measurements using the Hansen solubility parameters (HSP) to assess the fundamental physicochemical compatibility between bitumen and two bio-based additives. Firstly, tall oil (bio-additive-1) and waste cooking oil (bio-additive-2) were employed as bio-sourced additives and bitumen was separated into its basic polarity-based building blocks i.e. maltenes and asphaltenes. Afterwards, the HSPs of bitumen, its subfractions and bio-additives were measured. Frequency sweep tests, linear amplitude sweep (LAS) tests and bending beam rheometer (BBR) tests were carried out to assess the rheological properties of blended bio-bitumen and its relation to solubility-based indices. Bio-additive-1 showed better performance and efficiency compared to bio-additive-2 in improving the low-temperature performance, fatigue life and durability of bio-bitumen. The HSP of bio-additive-1 was closer to those of bitumen and its subfractions compared to bio-additive-2, which likely contributes to increased compatibility. The overlapping ratios of Hansen spheres and bitumen subfractions were positively correlated with the rheological properties of the bio-bitumen. Overall, the findings represent a first step towards development of a robust framework for the scientific design of bio-bitumen in future paving applications.

1. Introduction

The volatility of the global oil market has caused oil prices to rise significantly, leading to a corresponding increase in bitumen cost. According to statistical data, the average price of bitumen was approximately $170 per ton in 2000. By 2010, this price nearly tripled, reaching around $480 per ton. In 2022, the price rose to $680 per ton, marking a historic high [1]. This, coupled with rising diesel fuel prices, has remarkably increased the cost of asphalt pavement construction [2]. Bitumen is derived from non-renewable fossil fuel-based resources (crude oil). It has been forecasted that the continuous increase in fossil fuel consumption will ultimately lead to energy shortages [3,4]. Additionally, modern refining processes, including hydrocracking and catalytic cracking are more efficient in extracting high-value products such as gasoline and diesel from crude oil. These processes could leave less high-quality residue for bitumen production [5]. Moreover, the production of bitumen results in excessive CO_2 emissions and energy consumption, which induces increasing environmental concerns [6]. Overall, the rising demand and escalating prices, the alteration of the quality as well as sustainability related concerns necessitate the exigent exploration of alternative, eco-friendly resources for bitumen [7,8].

In this regard, one of the ways to make the paving industry more sustainable is using bio-based alternatives to modify or partially replace bitumen. For example, residues derived through the chemical processing of waste cooking oils, waste woods, animal manures, municipal solid wastes and other industrial bio-based by-products [9–11]. Nowadays, there has been increased interest in the practical application of bio-based construction materials for improving sustainability of road infrastructure [12]. Studies have shown that the use of bitumen derived from biomaterials i.e. bio-bitumen, can provide significant

* Corresponding author at: Nottingham Transportation Engineering Centre (NTEC), Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, UK.
E-mail address: anand.sreeram@nottingham.ac.uk (A. Sreeram).

https://doi.org/10.1016/j.fuel.2025.134361
Received 17 November 2024; Received in revised form 25 December 2024; Accepted 7 January 2025
Available online 11 January 2025

environmental benefits, such as reducing the demand for the unrenewable fossil fuels, reducing the emissions of CO_2 and reducing the demand for landfill by improving circularity of asphalt materials and waste bio resources. [13]. Besides this, the specific application of certain bio-bitumen has also shown benefits in terms of rheological performance, such as improved thermal and fatigue cracking resistance, improved moisture damage resistance, reduced ageing susceptibility and enhanced adhesion between bitumen and aggregates [14,15]. Therefore, the utilisation of bio-bitumen is a promising approach for addressing the future requirements regarding the sustainable development of pavement infrastructure.

Although the use of bitumen modified with bio-additives i.e. bio-bitumen offers a sustainable option, certain drawbacks limit their widespread adoption. For example, due to the large variety of suitable bioresources that can be processed to paving grade additives, the selection of bio-additives is currently arbitrary, resulting in significant variations in the quality of bio-bitumen and its utility as a paving material [16]. Mixing bitumen with less suitable bio-additives may also lead to incompatibility issues and thereby adversely affecting the performance of bio-bitumens [17].

Compatibility refers to the ability of two or more entities to exist, work, or function together without conflict or difficulty, which is one of the most critical factors affecting the quality of bio-bitumen [18]. Poor compatibility can result in issues such as phase separation, leading to performance deterioration of [19]. However, the compatibility-related research of bio-bitumen is limited and there is no established methods to scientifically characterise the compatibility between bio-additives and bitumen [20]. One promising approach to evaluate compatibility is using solubility science. Firstly proposed in 1950, the concept of solubility addresses the compatibility between two materials on the basis of "like dissolves like" [21]. Solubility science could be used to predict chemical reactions, material compatibility and permeation rate. Hansen solubility parameter (HSP) is one of the most commonly used solubility-based models [22]. As per theory, the HSP consists of three parts which reflects the intermolecular forces influencing a given materials solubility, namely dispersion forces (δ_D, in $MPa^{1/2}$), polar interactions (δ_P, in $MPa^{1/2}$), and hydrogen bonding (δ_H, in $MPa^{1/2}$), respectively [22]. Materials which have similar values of HSPs are believed to be soluble and compatible with each other [23].

The HSP approach has been proven to be a useful tool for characterising the solubility of bituminous materials, crude oils, and residues [24]. Moreover, this approach has also been employed to characterise the physicochemical compatibility between bitumen and additives, or different types of bitumen [24]. Previous studies have shown that HSP approach could effectively evaluate the compatibility between styrene–butadiene–styrene (SBS), polyethylene (PE) and polyurethanes (TPU) modifiers and bitumen [17,25,26]. HSP has also been used to address the compatibility between aged/oxidated bitumen and fresh bitumen, providing a fundamental understanding in terms of the interaction mechanism between fresh and aged bitumen when blended [27,28]. Apart from this, HSP based investigations on the interactions between asphaltenes and maltenes speculated that asphaltenes could be possibly dissolved in maltenes [29]. Overall, the HSP approach can effectively provide insights regarding the solubility based physicochemical nature of bitumen, compatibility between bitumen and additives and extenders, and consequentially predict the performance of modified bitumen.

As per the solubility in n-heptane, bitumen can be separated into asphaltenes and maltenes [30]. It has been reported that interactions between the molecules within bitumen, e.g. asphaltenes and maltenes, are the main determinants for its physical properties [31]. The incorporation of bio-additives or extenders will also contribute to the internal interactions within bitumen, thereby determining its overall chemo-rheological properties [26]. In that aspect, there is currently no research investigating the interactions between bitumen fractions and bio-additives. Overall, there is no established framework for the effective selection of bio-additives for bitumen modification and replacement. Current approaches are primarily based on trial and error, lacking scientific basis and fundamental understanding of physicochemical interactions in these complex colloidal mixes. This could result in unsatisfactory performance and lacks quality control for producing adequately performing bio-bitumens. In this regard, this study will evaluate the physicochemical compatibility of bio-additives and bitumen using a solubility science-based approach. This approach is envisaged to lead to a necessary understanding in terms of the influence of compatibility on the physical performance of bio-bitumens.

2. Scope

This study investigates the use of solubility science to evaluate physicochemical interactions and compatibility between bitumen and bio-additives. Bitumen was separated into asphaltenes and maltenes, then the HSP of bitumen, asphaltenes, maltenes, and two bio-additives were measured. The overlapping ratios of the Hansen spheres were calculated to elucidate the compatibility between the bio-additives and bitumen, asphaltenes and maltenes. Frequency sweep tests, linear amplitude sweep (LAS) tests and bending beam rheometer (BBR) tests were also carried out to assess the rheological performance of bio-bitumens. Overall, this work provides significant understanding of the fundamental physicochemical interactions within bio-bitumens and insights towards the future development of a framework for designing future paving materials.

3. Materials and methods

3.1. Materials

A penetration grade 70/100 bitumen and two bio-sourced additives were employed in this study. The fundamental properties of the bitumen and bio-additives are listed in Table 1. SARA represents the contents of saturate, aromatic, resin and asphaltene fractions within bitumen.

The chemical functional groups of bitumen and bio-additives analysed using FTIR are shown in Fig. 1.

Fig. 1 highlights that both bitumen and bio-additives contain a significant amount of alkenes. Bio-additive-1 predominantly includes both alkyls and ketones, along with considerable amounts of alkenes and aromatic esters, and smaller traces of sulfate ester, 2-quinolone, and alkenyls. On the other hand, Bio-additive-2 mainly consists of alkyls, carboxylic acids, sulfate ester, and sulfones, accompanied by minimal amounts of aromatics and alkenes.

The HSPs of bitumen and bio-additives were measured by dissolving the materials into 33 different solvents with a wide range of known Hansen solubility parameters, as listed in Table 2.

Table 1
Technical properties of bitumen and bio-additives.

Key properties of bitumen			
Penetration (0.1 mm)	**Softening point (°C)**	**PG**	**SARA**
81	45.4	PG 64–22	4:59:21:16
Key properties of bio-additives			
Code	Bio-additive 1	Bio-additive 2	
Description	Distilled tall oil	Recycled very viscous cooking oil residue	
Density (kg/l)	0.908	0.878	
Appearance			

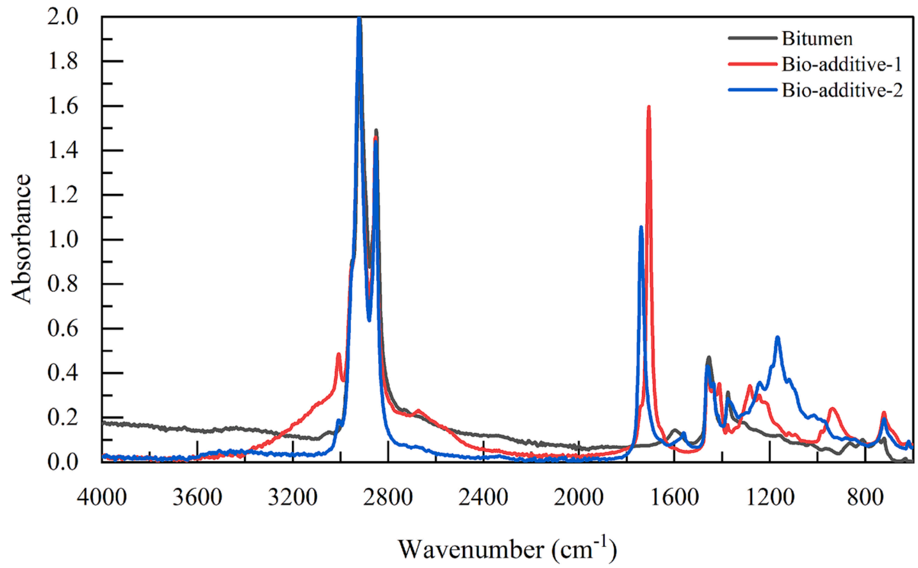


Fig. 1. FTIR spectra of bitumen and bio-additives.

Table 2
Solvents for the measurement of Hansen solubility parameters.

Chemicals	δ_D (MPa$^{1/2}$)	δ_P (MPa$^{1/2}$)	δ_H (MPa$^{1/2}$)	Chemicals	δ_D (MPa$^{1/2}$)	δ_P (MPa$^{1/2}$)	δ_H (MPa$^{1/2}$)
n-Butyl Acetate	15.8	3.7	6.3	Methanol	14.7	12.3	22.3
Acetophenone	18.8	9	4	2-Butanone	16	9	5.1
Cyclohexanone	17.8	8.4	5.1	Methylene Dichloride	17	7.3	7.1
Cyclopentanone	17.9	11.9	5.2	Methylene Diiodide	22	3.9	5.5
Benzyl Amine	19	4.6	9.4	Tetrahydrofuran	16.8	5.7	8
2-Ethyl-1-Hexanol	15.9	3.3	11.8	Toluene	18	1.4	2
Ethylene Glycol	17	11	26	Isooctane	14.1	0	0
n-Heptane	15.3	0	0	Water	15.5	16	42.3
Styrene	18.6	1	4.1	o-Xylene	17.8	1	3.1
Hexyl Acetate	15.8	2.9	5.9	Glycerol	17.4	11.3	27.2
Isopropyl Acetate	14.9	4.5	8.2	3-Methyl-2-Butanol	15.6	5.2	13.4
1-Methyl Naphthalene	19.7	0.8	4.7	4-Methyl-2-Pentanone	15.3	6.1	4.1
1,4-Dioxane	17.5	1.8	9	1,2-Dimethoxybenzene	19.2	4.4	9.4
Acetone	15.5	10.4	7	Diethyl Ether	14.5	2.9	4.6
Dimethyl Formamide	17.4	13.7	11.3	Mesityl Oxide	16.4	7.2	5
Lauryl Methacrylate	14.4	2.2	5.1	Diethylene Glycol Dibutyl Ether	15.8	4.7	4.4
Butyraldehyde	15.6	10.1	6.2				

3.2. Methods

3.2.1. Bitumen separation

Bitumen was dissolved into n-heptane at a concentration of 10 mg/ml in a jar [30]. The solution was then heated to 80 °C using a laboratory hotplate and stirred with a magnetic stirrer for 60 min. Afterwards, it was filtered using filter paper, leaving behind asphaltenes, while the filtered solution containing maltenes was collected in glass bottles. Finally, maltenes were recovered and collected from the filtered solution by heating it to 120 °C for 45 min [32].

3.2.2. Bio-bitumen production

Bitumen was preheated to 160 °C in an oven and then placed on a laboratory hotplate to maintain this temperature throughout the production process. Afterwards, the accurately weighted bio-additives were mixed with bitumen at a percentage of 7 wt% and blended for 10 min using a laboratory mixer. This percentage was determined as per previous studies [10]. This study aims to investigate the correlation between the solubility and effectiveness of the two bio-additives as bitumen modifiers and replacements. Therefore, the same percentage was selected for both additives for comparison purposes. Finally, the obtained blends were labelled as bio-bitumen 1 and bio-bitumen 2 and subjected to rheological tests.

3.2.3. Measurement of HSP

For the measurement of the HSPs of bitumen and its subfractions, 0.5 g of each material were dissolved in 5 ml of each solvent listed in Table 2 in capped glass vials [17]. For the measurement of the HSPs for bio-additives, 5 ml of bio-additives were added to 5 ml of solvents, as illustrated in Fig. 2.

The vials were then shaken at regular intervals and stored in a fume hood for 24 h [33]. For solvents that could dissolve bitumen or its subfractions, homogeneous solutions were observed, and these solvents were scored as 1. For solvents that could not dissolve bitumen or its subfractions, the bitumen or its subfractions precipitated at the bottom of the containers, and these solvents were scored as 0. Regarding the solubilities of bio-additives, if the bio-additives and solvents were mutually soluble, homogeneous blends were observed. If they were insoluble, distinct boundaries between the materials were observed. Scores of 0 and 1 were marked for insoluble and soluble solvents, respectively. Finally, the results of 0 and 1 were input to HSPiP software and the HSPs of each material were calculated. For the HSPiP algorithm, the objective is to minimise the distance between the solubility sphere's surface and the data points representing the solvents. HSPiP uses

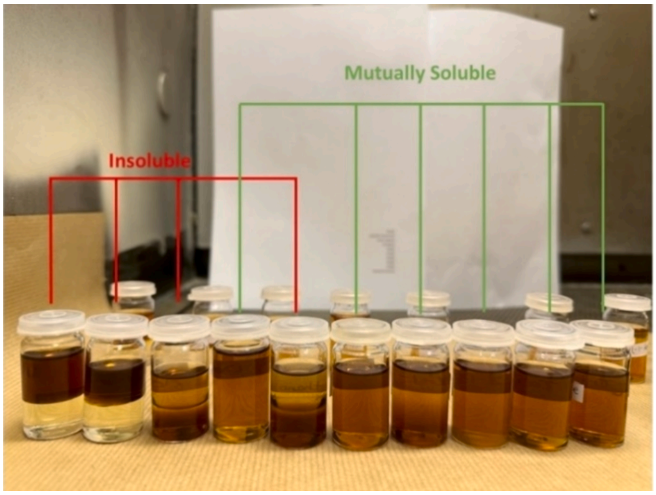


Fig. 2. Solubility measurements of bio-additives.

iterative algorithms to adjust the sphere's parameters until the best fit is achieved. This involves calculating the total interaction energy for each solvent and comparing it with the experimental solubility results. Once the best fit is found, the software provides the HSP values (δ_D, δ_P, δ_H) for the material, indicating the centre of the solubility sphere, and the radius of the Hansen sphere. Based on the HSP values and their radii, three-dimension Hansen spheres could be constructed to illustrate the compatibility between different materials. The Hansen sphere encompasses its entire solubility of a material in Hansen space. Fig. 3 shows the schematic of HSP for bitumen and some representative solvents based on a prior work conducted by the authors [27].

Based on the HSP, the solubility distance (R_a) between two materials can be computed as per Equation (1) and the relative energy difference (RED) could be computed as per Equation (2).

$$R_a^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 \quad (1)$$

$$RED = \frac{R_a}{R_0} \quad (2)$$

Where, R_0 is the radius of Hansen sphere of bio-additives.

3.2.4. Rheological properties tests

Frequency sweep tests, as per ASTM D7175 [34], and linear amplitude sweep (LAS) tests, as per AASHTO T391 [35] were caried out using a dynamic shear rheometer (DSR). Bending beam rheometer (BBR) tests, as per ASTM D6648 [36] were also carried out for examining the rheological performance of bitumen. In the frequency sweep tests, the bitumen samples were heated in a glass vial for 10 min then poured into a silicone mould with a diameter of 25 mm and thickness of 1 mm. Then the samples were cooled down at room temperature before testing. The frequencies ranged from 0.1 rad/s to 100 rad/s, and the temperatures ranged from 10 °C to 70 °C in 10 °C intervals, with a strain level of 0.2 %, and two replicates were tested. For the LAS tests, the bitumen samples were heated in the same situation then poured into a silicone mould with a diameter of 8 mm and thickness of 2 mm. Three replicates were tested at 25 °C. For the BBR tests, the bitumen samples were heated in a metal can and poured into the metal mould with a length of 127 mm, width of 12.7 mm and thickness of 6.4 mm. Before testing, the sample beams were conditioned at testing temperature for 45 min. There were two replicates being tested at −12 °C, −18 °C, and −24 °C, respectively.

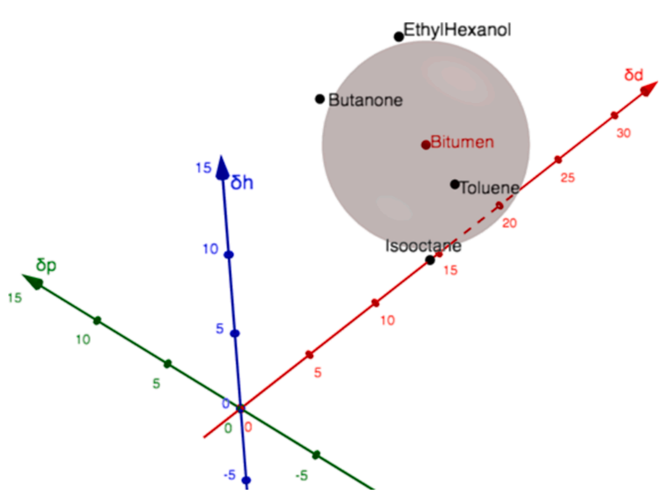


Fig. 3. Schematic of HSP for bitumen and solvents.

3.3. Data processing methods

3.3.1. Frequency sweep

The Christensen–Anderson–Marasteanu (CAM) model [37] was selected to construct master curves of bitumen based on the results of frequency sweep tests [38].

The master curves of complex modulus ($|G^*|$) and phase angle (δ) of bitumen were built at the reference temperature of 25 ℃, as per Equation (3) and (4).

$$G^* = \frac{G_g^*}{\left[1 + (f_c/f_r)^k\right]^{m/k}} \quad (3)$$

$$\delta = 90I - (90I - \delta_m)\left\{1 + \left[\frac{\log(f_d/f_r)}{R_d}\right]^2\right\}^{-m_d/2} \quad (4)$$

Where, G^*_g is glass complex modulus, f_c is crossover frequency, f_r is reduced frequency, and m and k are fitting parameters. δ_m is the phase angle constant at f_d, which is the value at the inflexion, f_d is location parameter with dimensions of frequency, at which δ_m occurs, R_d, m_d are shape parameters, and $I = 0$ if $f > f_d$, and $I = 1$ if $f \le f_d$.

3.3.2. Linear amplitude sweep tests

In the T391-20 standard, the damage failure of bitumen corresponds to the 35 % reduction in undamaged $|G^*|sin\ \delta$. The damage accumulation at failure (D_f) is defined as per Equation (5).

$$D_f = (0.35\frac{C_0}{C_1})^{\frac{1}{C_2}} \quad (5)$$

Where, C_0 is the average value of $|G^*|sin\ \delta$ from the 0.1 % strain interval, in MPa, C_1 and C_2 are the fitting coefficients derived from Equation (6) [39].

$$\log(C_0 - |G^*|\sin\delta) = \log(C_1) + C_2\log(D) \quad (6)$$

The fatigue life can be calculated as per Equation (7) with the interest strain γ.

$$N_f = A_{35}(\gamma)^B \quad (7)$$

Where, the parameters A_{35} and B are material-specific parameters for calculating the fatigue life of bitumen, as shown in Equations (8) and (9).

$$A_{35} = \frac{f(D_f)^k}{k(\pi I_D C_1 C_2)^\alpha} \quad (8)$$

$$B = -2\alpha \quad (9)$$

Where, f is the testing frequency, I_D is the initial value of $|G^*|$ from the 1 % applied strain intervals, in MPa, and k can be calculated using Equation (10).

$$k = 1 + (1 - C_2)\alpha \quad (10)$$

3.3.3. Bending beam rheometer (BBR) tests

The stiffness (S) and creep rate (*m-value*) were measured to characterise the low-temperature performance of bitumen. Two critical temperatures, controlled by S ($T_{C,S}$) and *m-value* ($T_{C,m}$), respectively, were calculated. The difference between $T_{C,S}$ and $T_{C,S}$ is defined as ΔT_C, as per ASTM D7643 [40].

4. Results and discussion

4.1. Solubility based interactions

The HSPs of the materials employed in this study were calculated using the HSPiP software, as shown in Fig. 4. It was seen that the interactions between the bituminous and biomaterials with solvents varied, as a consequence of their varying solubilities. Based on the Hansen solubility parameter of each material, a 3D sphere could be plotted. The green dots within the centres of Hansen spheres represent the Hansen solubility parameters of each material. The blue dots within the spheres are solvents which can dissolve the materials, indicating these chemicals were soluble with the tested materials. The red squares apart from the spheres are solvents which cannot dissolve the materials, indicating these chemicals were insoluble with the materials. It was seen from Fig. 4 that the Hansen sphere of the bio-additive-1 was the biggest, indicating that it is highly compatible with other types of materials/solvents while it was opposite for the sphere of asphaltenes, as it was the smallest, which suggested its limited compatibility.

To quantitively assess the Hansen solubility parameters and their correlations with compatibility, the HSPs of the materials tested in this study are listed in Table 3. All the three dimensions of Hansen solubility parameters of asphaltenes were greater than those of maltenes, while the values of HSP of bitumen were greater than those of asphaltenes and smaller than those of maltenes. This observation and values obtained were comparable with previous studies [24,29]. The radius of Hansen sphere of maltenes was 9.0, around 1.4 times of that for asphaltenes, suggesting that maltenes were of a more soluble composition than asphaltenes.

Dispersion interactions play a crucial role in relatively non-polar hydrocarbons and represent the dominant molecular interactions in bitumen, asphaltenes, maltenes, and bio-additives. These interactions significantly influence cohesive strength and stability. Materials with lower dispersion forces tend to exhibit reduced colloidal and thermodynamic stability, making them more prone to aggregation after

Table 3
Hansen solubility parameters of materials used in this study.

Material	δ_D (MPa$^{1/2}$)	δ_P (MPa$^{1/2}$)	δ_H (MPa$^{1/2}$)	R
Bitumen	17.3	4.6	2.4	8.0
Asphaltenes	18.9	6.2	3	6.6
Maltenes	17.2	4.5	0.9	9.0
Bio-additive 1	15.9	7.6	10.2	13.5
Bio-additive 2	15.5	2.6	6.3	7.8

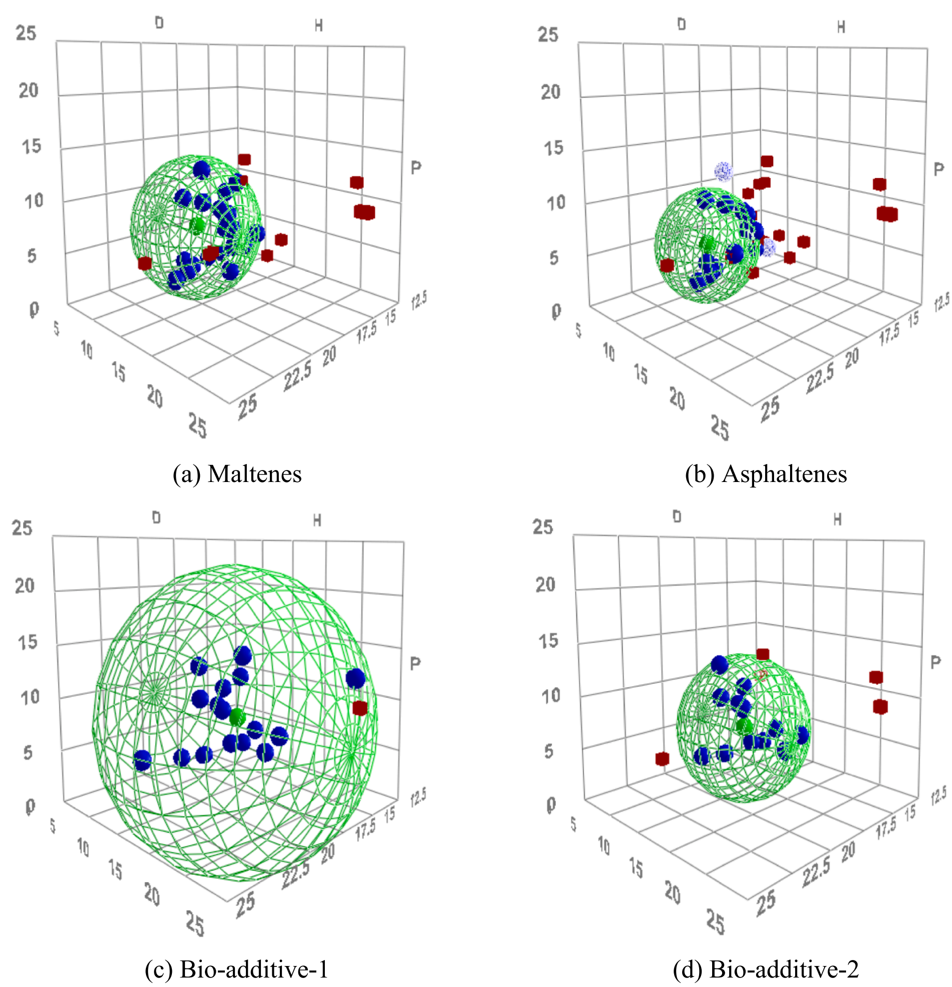


Fig. 4. Measurements of Hansen solubility parameters using HSPiP software.

exposure to thermal cycles [41]. The polar interactions indicates material polarity. Since asphaltenes are more polar than maltenes, they are expected to dissolve readily in highly polar solvents. Although asphaltenes in bitumen do not precipitate under normal conditions, bitumen aggregation can still disrupt phase balance, thereby impacting its macroscopic properties [41]. Hydrogen bonding strength is primarily influenced by the content of heteroatoms such as oxygen and nitrogen within bitumen and its subfractions. A higher heteroatom content corresponds to stronger hydrogen bond interactions. Structurally, asphaltene molecules are characterised by pericondensed ring systems enriched with nitrogen or sulphur functional groups [42].

To understand the differences and interactions between the HSPs of asphaltenes and maltenes, their Hansen spheres were plotted together, as shown in Fig. 5. It was seen that the Hansen sphere of asphaltenes was almost entirely covered by that of maltenes. This indicated that different solubility properties of asphaltenes and maltenes is insufficient to result in insolubility between them and thus the asphaltenes could be dissolved to some extent in the maltenes, instead of simply being dispersed [24]. Therefore, bitumen is considered structurally stable as its subfractions are compatible with each other in terms of solubility related chemistry. Fig. 5 also showed that n-heptane was inside the HSP sphere of maltenes but outside that of asphaltenes. In contrast, toluene was inside the HSP spheres of both asphaltenes and maltenes. This explained why both maltenes and asphaltenes are dissolvable in toluene, while only maltenes are dissolvable in n-heptane. Based on Equations (1) and (2), the RED for asphaltenes and n-heptane was 1.604, while for asphaltenes and toluene, it was 0.688. In contrast, the REDs for maltenes with these two chemicals were 0.558 and 0.406, respectively. The value of RED greater than 1.0 indicates that the chemical is a nonsolvent for the tested materials [43].

When investigating the internal molecular level interactions within bitumen, it can be seen from Table 3 that the polar interaction and hydrogen bonding interactions of asphaltenes were higher than those of maltenes. Previous studies have suggested that polar interactions and hydrogen bonding interactions are critical when considering the elasticity related properties of bitumen [44]. This finding illustrates that after ageing, bitumen gets more elastic in terms of phase angle response, as ageing produces more asphaltenes [45,46]. The values of dispersive interactions for bitumen were almost identical with that for maltenes, while only slightly different from that of asphaltenes. Therefore, it is assumed that the dispersive interactions have limited impact on the physical and rheological properties of bitumen [44].

4.2. Hansen solubility parameters of bio-additives

To visualise the solubility parameters of bio-additives and subfractions of bitumen, the Hansen spheres of two bio-additives and maltenes as well as asphaltenes are shown in Fig. 6.

The visualised HSPs of two bio-additives were significantly different.

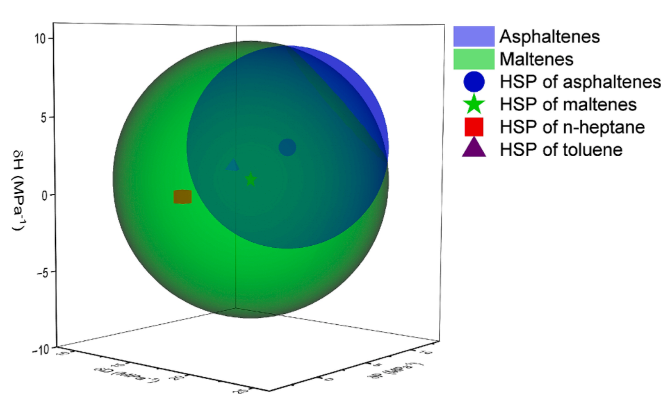


Fig. 5. HSP spheres of asphaltenes and maltenes.

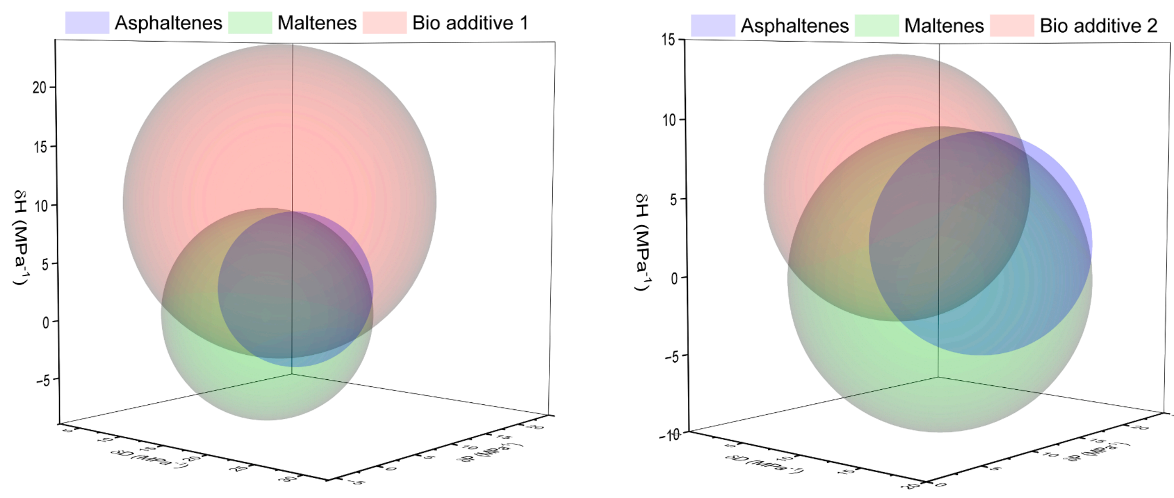
The Hansen sphere of asphaltenes was almost entirely covered by that of bio-additive 1 while partially covered by that of bio-additive 2. In terms of the Hansen sphere of maltenes, it overlapped partially with both bio-additive 1 and bio-additive 2. The overlapping ratios of each pair of spheres were calculated, as shown in Fig. 7. The overlapping ratio of the Hansen spheres of asphaltenes and maltenes was 96.99 %. Moreover, it was observed that asphaltenes were more soluble in bio-additives compared to maltenes. The overlapping ratios of Hansen sphere of asphaltenes with bio-additive 1 and bio-additive 2 were 97 % and 52.81 %, respectively, which were 45.9 % and 35.2 % higher than the overlapping ratios of maltenes and bio-additives. It should be noted that the Hansen radius of maltenes was greater than that of asphaltenes, indicating that maltenes were more soluble than asphaltenes, which explained why the overlapping ratios between maltenes, and bio-additives were relatively smaller. However, the overlapping ratios between maltenes and bio-additives were still reasonably high, indicating that the affinity and compatibility between maltenes and bio-additives to be adequate.

Previous studies have postulated that bitumen is considered compatible with modifiers and additives when their Hansen spheres partially overlap [17,33]. Therefore, given that the Hansen spheres of both maltenes and asphaltenes were significantly overlapped with those of bio-additives, it can be assumed that the bio-additives employed in this study were theoretically compatible with bitumen to a large extent. However, it is noteworthy that bio-additives employed in this study had different compatibilities with bitumen fractions. This is expected to be reflected in their rheological performance and will be verified in the following subsections.

4.3. Master curves and black space diagrams

The master curves and black space diagrams were plotted based on the frequency sweep tests. As shown in Fig. 8(a), the incorporation of bio-additives significantly softened bitumen as the master curves for complex modulus moved downwards after the addition of the bio-additives. It was also noted that the addition of bio-additives had more pronounced impact on the complex modulus at low-frequency (high-temperature) range. Two bio-additives showed similar effect on the complex modulus of bio-bitumen as the master curves of the two bio-bitumen were almost parallel, though bio-additive 1 showed higher efficiency compared to bio-additive 2 as bio-bitumen 1 was softer than bio-bitumen 2. When it comes to the master curves for phase angle, it was observed that the bio-bitumen was more viscous than the control bitumen as the master curves for phase angle moved upwards. It was noteworthy that bio-additives had more significant impact on the phase angle at high-frequency (low-temperature) range, which was opposite to the impact on complex modulus. It has been reported that higher phase angle at low-temperature is beneficial for the relaxation properties of bitumen [47], therefore, the incorporation of bio-additives could significantly improve the thermal cracking resistance of bio-bitumen. The impact of bio-additive 1 was more pronounced than bio-additive 2 in terms of increasing the phase angle of bio-bitumen, which was consistent with that for complex modulus. As the bio-bitumen was softer and more viscous than control bitumen, its high-temperature performance might be compromised. Therefore, these bio-additives were more suitable to be used as softeners or rejuvenators for softening the aged bitumen to recover its performance.

G-R parameter is proven to be highly correlated with the durability of asphalt pavements [48]. A lower value of G-R parameter suggests that the bitumen is more durable and less susceptible to fatigue cracking. The observation from Fig. 8(b) indicated that both control bitumen and bio-bitumen fell within the "safe zone", suggesting that these materials were less likely to encounter durability issues. Being in the "safe zone" implied that the properties and performance characteristics are within acceptable limits. Notably, the addition of bio-additives lowered the G-R parameters of the bio-bitumen, indicating better durability.



(a) Hansen spheres of bio-additive-1 and bitumen subfractions

(b) Hansen spheres of bio-additive-2 and bitumen subfractions

Fig. 6. Hansen spheres of bio-additives and bitumen subfractions.

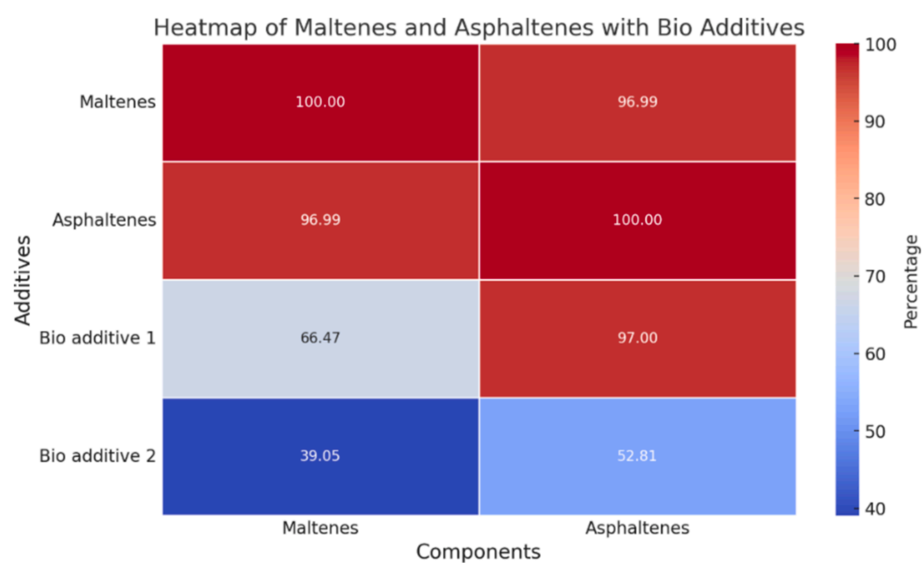


Fig. 7. Overlapping ratios of Hansen spheres between bitumen subfractions and bio-additives.

Furthermore, bio-additive 1 showed more pronounced effectiveness. The observations from Fig. 8 aligned with the HSP results. The improvement or lack of detrimental effect in term of rheological properties could be reflected by the high compatibility between bio-additives and bitumen subfractions. Moreover, bio-additive 1 was more compatible with bitumen subfractions compared to bio-additive 2, therefore, the rheological properties of bio-bitumen 1 were seemingly superior to those of bio-bitumen 2.

4.4. Fatigue performance of bitumen with bio-additives

The most used data analysis techniques for linear amplitude sweep (LAS) tests include stress–strain curves, fatigue life and strain dependence. Stress–strain curves illustrate the stress response against strain, which could be used to identify the linear viscoelastic properties of bitumen. Previous studies have reported that the fatigue life of bitumen is highly strain-dependent [49,50]. Therefore, in this study, the fatigue life was calculated at strain levels of 2.5 %, 5 %, 7.5 %, 10 %, 12.5 % and 15 % to comprehensively characterise the impact of bio-additives on the fatigue performance of bio-bitumens. The strain dependency could be illustrated by the slope of fatigue life versus strain curves, which is related to the *Parameter B* as defined by Equation (10). The fatigue properties of bio-bitumen and control sample are shown in Fig. 9.

Fig. 9 indicated that the bio-additives had significant influence on fatigue properties of bitumen. As observed in Fig. 9(a), the addition of bio-additives reduced stress of bitumen significantly when bitumen was subjected to identical strains. It has been reported that higher stress levels could result in more serious cracking related damage of bitumen [51]. Therefore, the incorporation of bio-additives could significantly mitigate the risk of damage for bio-bitumen when subjected to accelerated fatigue testing, thereby prolonging the durability of asphalt pavements.

In terms of the fatigue life of bitumen, it was seen that the fatigue life decreased linearly with strain at a log–log scale. When the strain levels

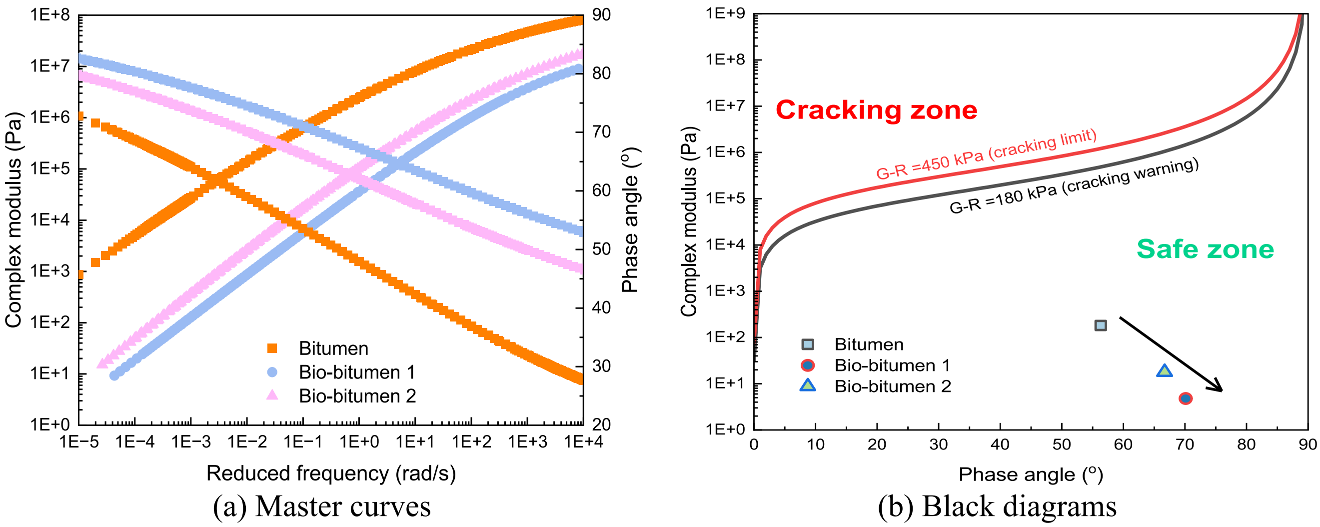


Fig. 8. Rheological properties of bitumen.

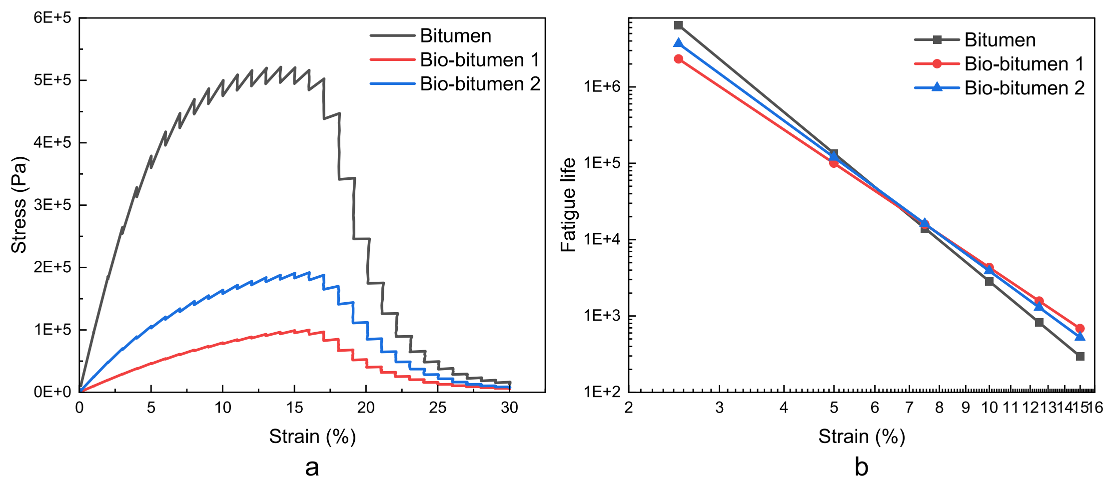


Fig. 9. Fatigue properties of bitumen:(a) Stress–strain curves, and (b) Fatigue life.

were relatively low, e.g. lower than 7.5 %, the fatigue life of control sample was higher than that of the bio-bitumen, while opposite trend was observed when the strain levels were relatively high [52]. The results suggested that the addition of bio-additives could effectively increase the fatigue life of bitumen and asphalt pavements when the traffic load is heavy or when the thickness of pavement layers is small [53]. Moreover, it was also found that the slope of fatigue life versus strain curves of bio-bitumen were smaller, indicating that the bio-bitumen was less susceptible to strain compared to the control one [54]. The results of fatigue properties of bio-bitumen suggested that the two bio-additives employed in this study could effectively improve the durability of bitumen. It is noteworthy that the bio-additive 1 performed better than bio-additive 2, as the fatigue life of bio-bitumen 1 was 30.5 % higher than that of bio-bitumen 2 at the strain level of 15 %.

4.5. *Low-temperature performance of bitumen with bio-additives*

The critical temperatures and the difference between critical temperatures, ΔTc, of bio-bitumen and control sample are shown in Fig. 10. The incorporation of bio-additives significantly improved the low-temperature performance (thermal cracking resistance) of bitumen. For the control sample, its performance grade (PG) was PG 64–22, while for the two types of bio-bitumen, their performance grades were PG 64–40 and PG 64–34, which improved three and two grades,

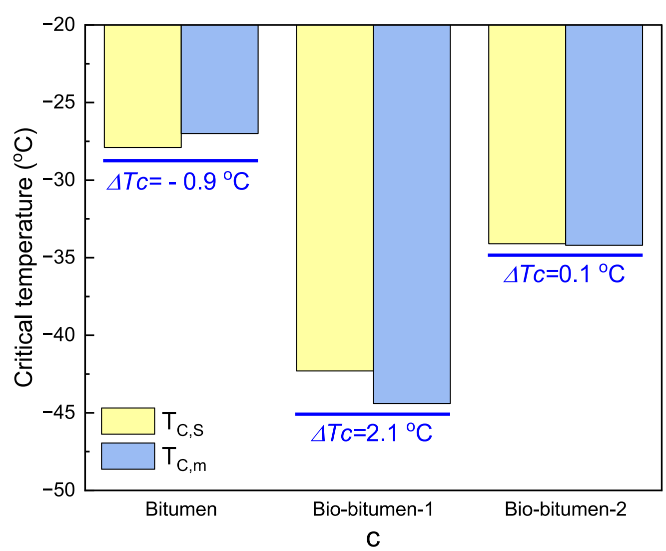


Fig. 10. Low-temperature properties of bitumen.

respectively. The incorporation of bio-additives also improved the relaxation properties of bitumen, denoted by the shifting of lower PG from *m-value* controlled to *stiffness* controlled. More negative values of ΔTc are correlated with higher susceptibility to thermal cracking [55].

It is evident from Fig. 10 that after the modification, the bio-bitumen was less susceptible to thermal cracking. Therefore, the incorporation of bio-additives improves the low-temperature performance of bitumen in two ways: lowering the critical temperature and reducing the cracking susceptibility. Overall, the incorporation of bio-additives effectively improved the thermal cracking resistance of bitumen at low-temperature. This observation was conducted on unaged samples, further testing is required for aged samples. It was also observed that bio-additive 1 was more effective than bio-additive 2 in terms of improving the thermal cracking resistance of bitumen. Combining the low-temperature performance of bio-bitumen and the results of Hansen solubility parameters, it could be assumed that HSP is correlated with low-temperature performance of bio-bitumen, as the overlapping ratios of Hansen spheres were positively correlated with the low-temperature performance. When the same dosage of bio-additives was added to bitumen, the bio-additive with higher Hansen sphere overlapping ratio could improve the thermal cracking resistance of bitumen more significantly. It is likely that although adding higher dosage of bio-additives could improve the low-temperature performance of bitumen due to a softening effect, incompatibility issues might arise. Therefore, it is believed that bio-additives with higher overlapping ratio could be more efficient and compatible in terms of material chemistry. In relation to this, the HSP-based solubility science could potentially be used to select highly effective additives or extenders for bio-based bitumens.

4.6. Correlations between solubility science and rheological properties

The correlations between solubility properties (in term of overlapping ratio) and rheological properties of bitumen are shown in Fig. 11. The overlapping ratios of bio-additive 1 with asphaltenes and maltenes were greater than those of bio-additive 2 with asphaltenes and maltenes. Specifically, the overlapping ratios of bio-additive 1 with maltenes and asphaltenes were 45.9 % and 35.2 % higher than that between bio-additive 2 and maltenes and asphaltenes, respectively. Consequently, the improvement ratios in G-R parameter, fatigue life, and low-temperature performance of bio-bitumen 1 were 438 %, 70 % and 200 % greater than those of bio-bitumen 2, respectively. This indicated that the overlapping ratio is positively correlated with the rheological performance of bio-bitumen when additive content used is the same. Moreover, the higher overlapping ratios of Hansen spheres of asphaltenes and bio-additives may ensure that more polar fractions such as asphaltenes can be dispersed homogeneously in the bio-additives.

These observations clearly indicate that solubility science could be useful to identify the efficiency of bio-additives. Based on the correlations between solubility science and performance of bio-bitumens and other physical properties such as viscosity, a framework of designing the most optimum and closest matching bio-based material to conventional bitumen could be established in the future. Highly efficient bio-additives could have similar HSPs with bitumen and its subfractions to assure the maximum compatibility between them.

5. Key findings and conclusions

This study investigates the use of solubility science to evaluate fundamental physicochemical interactions and compatibility between bitumen and bio-additives. It demonstrates that solubility science can effectively guide the development and selection of bio-additives for modifying bitumen. By establishing a link between solubility parameters and bitumen performance, this research fills a gap in the literature in providing practical insights for designing sustainable and high-performing bio-based bitumen.

The findings indicates that the employed bio-additives enhance low-temperature performance of bitumen by lowering critical temperatures and reducing cracking susceptibility. They also improve fatigue performance by reducing stresses, prolonging fatigue life, and decreasing strain dependency. The addition of bio-additives lowers the complex modulus of bio-bitumen while increasing its phase angle, improving the relaxation properties and durability of bio-bitumen. Bio-additive-1 demonstrated superior performance compared to bio-additive-2 at identical modification levels. For example, bio-bitumen 1 exhibited a 438 % greater G-R parameter, 70 % longer fatigue life, and 200 % higher thermal cracking resistance than bio-bitumen 2. These enhancements were attributed to the higher overlapping ratios of Hansen spheres between bio-additive-1 and the bitumen subfractions maltene and asphaltenes, which were 45.9 % and 35.2 % greater, respectively, than those for bio-additive-2.

Overall, solubility science-based approaches is a promising tool for selecting bio-additives to partially replace conventional bitumen. The

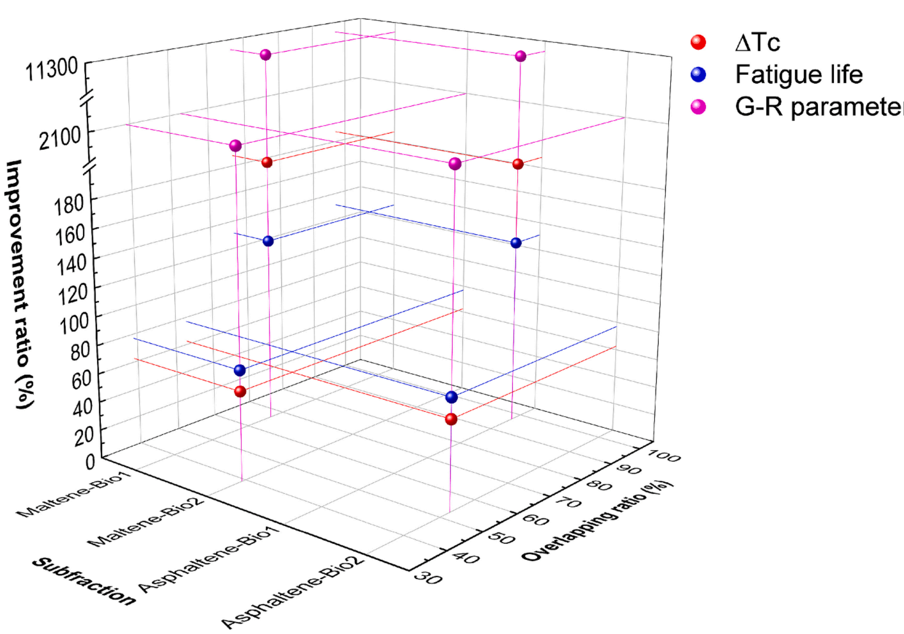


Fig. 11. Correlations between solubility science and rheological properties.

overlapping ratios between bio-additives and bitumen subfractions correlated positively with the rheological properties of bio-bitumen, providing a reliable indicator of compatibility. Highly efficient bio-additives had similar Hansen solubility parameters (HSP) to bitumen and its subfractions, ensuring better interaction and improved material properties.

It should be noted that only two bio-additives and one bitumen were assessed in this study, it is recommended to incorporate more materials in future studies to populate this method. Moreover, this study used overlapping ratio as the method to establish solubility and the direct correlations between dispersive forces, polar interactions, hydrogen bonding interactions and rheological properties has not been established yet. It is recommended to investigate the solubility parameters in further depth to correlate it with the rheological properties more precisely. Lastly, ageing has significant impact on the properties of bitumen, therefore, it is suggested to investigate the compatibility between aged bitumen and bio-additives, as well as bitumen with varying ageing situations using solubility science-based approaches.

CRediT authorship contribution statement

Yongping Hu: Writing – original draft, Software, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation. **Anand Sreeram:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Abir Al-Tabbaa:** Writing – review & editing, Supervision, Resources. **Gordon D. Airey:** Writing – review & editing, Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Yongping Hu would like to acknowledge the financial support from China Scholarship Council (grant number 202106560001). Anand Sreeram would like to acknowledge the funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 101034337.

Data availability

Data will be made available on request.

References

[1] MAA, Prevailing Monthly Price for Asphalt, 2024. https://mdasphalt.org/asphalt-index/. (Accessed 14 June 2024).
[2] Fini EH, Al-Qadi IL, You Z, Zada B, Mills-Beale J. Partial replacement of asphalt binder with bio-binder: characterisation and modification. Int J Pavement Eng 2012;13(6):515–22.
[3] He M, Tu C, Cao DW, Chen YJ. Comparative analysis of bio-binder properties derived from different sources. Int J Pavement Eng 2019;20(7):792–800.
[4] Wang X, Ma B, Yu M, Mao W, Si W. Testing and modeling of incomplete phase change heat storage and release of epoxy resin/microcapsule composite phase change materials for asphalt pavement. J Storage Mater 2025;105:114672.
[5] Lapidus AL, Kerimov VY, Mustaev RN, Movsumzade EM, Salikhova IM, Zhagfarov FG. Natural Bitumens: Physicochemical Properties and Production Technologies. Solid Fuel Chem 2018;52(6):344–55.
[6] Thives LP, Ghisi E. Asphalt mixtures emission and energy consumption: A review. Renew Sustain Energy Rev 2017;72:473–84.
[7] Zhou S, Long K, Zhang Z, Li S, Ai C, Yan C. Development of sustainable Lignin-Based coatings for layered double Hydroxides: Enhancing synergistic Anti-Aging properties in bitumen. Fuel 2025;380:133166.
[8] Shi K, Ma F, Falchetto AC, Fu Z, Yuan D, Song R, et al. Comprehensive review on the composition, influence, and inhibition of asphalt fumes. Journal of Traffic and Transportation Engineering(English Edition) 2025.
[9] Ingrassia LP, Lu X, Ferrotti G, Conti C, Canestrari F. Investigating the "circular propensity" of road bio-binders: Effectiveness in hot recycling of reclaimed asphalt and recyclability potential. J Clean Prod 2020;255:120193.
[10] Hu Y, Ryan J, Sreeram A, Allanson M, Pasandín AR, Zhou L, et al. Optimising the dosage of bio-rejuvenators in asphalt recycling: A rejuvenation index based approach. Constr Build Mater 2024;433.
[11] Hu Y, Omairey E, Hughes D, Bailey H, Watkins M, Twitchen J, et al. Recovering the properties of aged bitumen using bio-rejuvenators derived from municipal wastes. Constr Build Mater 2024;438:137268.
[12] Espinosa LV, Vasconcelos K, Alvarez AE, Bhasin A, Bernucci L. Moisture damage susceptibility of a wood-based bio-binder for total replacement of asphalt binders. Road Mater Pavement 2024;25(sup1):45–55.
[13] Samieadel A, Schimmel K, Fini EH. Comparative life cycle assessment (LCA) of bio-modified binder and conventional asphalt binder. Clean Techn Environ Policy 2018;20(1):191–200.
[14] Gaudenzi E, Cardone F, Lu X, Canestrari F. Performance assessment of asphalt mixtures produced with a bio-binder containing 30% of lignin. Mater Struct 2022;55(8):221.
[15] Hu Y, Sreeram A, Airey GD, Li B, Si W, Wang H. Comparative analysis of time sweep testing evaluation methods for the fatigue characterisation of aged bitumen. Constr Build Mater 2024;432:136698.
[16] Musco A, Tarsi G, Tataranni P, Salzano E, Sangiorgi C. Use of bio-based products towards more sustainable road paving binders: A state-of-the-art review. Journal of Road Engineering 2024;4(2):151–62.
[17] A. Sreeram, A. Filonzi, S. Komaragiri, K. Lakshmi Roja, E. Masad, A. Bhasin, Assessing impact of chemical compatibility of additives used in asphalt binders: A case study using plastics, Constr Build Mater 359 (2022).
[18] Lv S, Liu J, Peng X, Jiang M. Laboratory experiments of various bio-asphalt on rheological and microscopic properties. J Clean Prod 2021;320:128770.
[19] Shirzad S, Zouzias H. Enhancing the performance of wood-based bio-asphalt: strategies and innovations. Clean Techn Environ Policy 2024.
[20] Yang X, Mills-Beale J, You Z. Chemical characterization and oxidative aging of bio-asphalt and its compatibility with petroleum asphalt. J Clean Prod 2017;142:1837–47.
[21] Hildebrand J, Scott R. Solutions of nonelectrolytes. Annu Rev Phys Chem 1950;1(1):75–92.
[22] Hansen CM. The Universality of the Solubility Parameter. Ind Eng Chem Prod Res Dev 1969;8:2–11.
[23] Hansen CM. Hansen solubility parameters: a user's handbook, Second. Edition ed. Boca Raton: CRC Press; 2007.
[24] Redelius P. Bitumen Solubility Model Using Hansen Solubility Parameter. Energ Fuel 2004;18(4):1087–92.
[25] Gallu R, Méchin F, Gérard J-F, Dalmas F. Influence of the chain extender of a segmented polyurethane on the properties of polyurethane-modified asphalt blends. Constr Build Mater 2022;328.
[26] Gallu R, Méchin F, Dalmas F, Gérard J-F, Perrin R, Loup F. On the use of solubility parameters to investigate phase separation-morphology-mechanical behavior relationships of TPU. Polymer 2020;207.
[27] Sreeram A, Leng Z, Hajj R, Bhasin A. Characterization of compatibility between aged and unaged binders in bituminous mixtures through an extended HSP model of solubility. Fuel 2019;254:115578.
[28] Sreeram A, Leng Z, Hajj R, Ferreira WLG, Tan Z, Bhasin A. Fundamental investigation of the interaction mechanism between new and aged binders in binder blends. Int J Pavement Eng 2020;23(5):1317–27.
[29] Li M, Ren T, Sun Y, Xiao S, Wang Y, Lu M, et al. New Parameter Derived from the Hansen Solubility Parameter Used to Evaluate the Solubility of Asphaltene in Solvent. ACS Omega 2022;7(16):13801–7.
[30] ASTM, Standard Test Method for Separation of Asphalt into Four Fractions, ASTM International, West Conshohocken, PA, 2018.
[31] Redelius P, Soenen H. Relation between bitumen chemistry and performance. Fuel 2015;140:34–43.
[32] Sakib N, Bhasin A. Measuring polarity-based distributions (SARA) of bitumen using simplified chromatographic techniques. Int J Pavement Eng 2019;20(12):1371–84.
[33] Hu Y, Sreeram A, Xia W, Wang H, Zhou L, Si W, et al. Use of Hansen Solubility Parameters (HSP) in the selection of highly effective rejuvenators for aged bitumen. Road Mater Pavement 2024:1–19.
[34] ASTM, Standard Test Method for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer, ASTM International, Pennsylvania, 2023.
[35] AASHTO, Estimating Fatigue Resistance of Asphalt Binders Using the Linear Amplitude Sweep, American Association of State Highway and Transportation Officials, Washington D.C., 2020.
[36] ASTM, Standard Test Method for Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer (BBR), ASTM International, Pennsylvania, 2016.
[37] Christensen D. Analysis of creep data from indirect tension test on asphalt concrete. J Assoc Asphalt Paving Technol 1998;67:458–92.
[38] Bahia HU, Hanson DI, Zeng M, Zhai H, Khatri MA, Anderson RM. Characterization of Modified Asphalt Binders in Superpave Mix Design. Washington, D.C.: Transportation Research Board; 2001.
[39] Hintz C, Velasquez R, Johnson C, Bahia H. Modification and Validation of Linear Amplitude Sweep Test for Binder Fatigue Specification. Transport Res Rec 2011;2207(1):99–106.
[40] ASTM, Standard Practice for Determining the Continuous Grading Temperatures and Continuous Grades for PG Grades Asphalt Binders, ASTM International, West Conshohocken, PA, 2022.

[41] Yuan H, Nili A, Chen J, Ding H, Liu H, Qiu Y. Solubility and structural parameters of asphaltene subfractions separated from bitumen via an improved method. Fuel 2023;344.
[42] Schabron JF, Rovani Jr JF, Sanderson MM. Asphaltene Determinator Method for Automated On-Column Precipitation and Redissolution of Pericondensed Aromatic Asphaltene Components. Energ Fuel 2010;24(11):5984–96.
[43] Redelius PG. Solubility parameters and bitumen. Fuel 2000;79(1):27–35.
[44] Redelius P, Soenen H. Correlation between Bitumen Polarity and Rheology. Road Mater Pavement 2011;6(3):385–405.
[45] Hu Y, Xia W, Xue Y, Zhao P, Wen X, Si W, et al. Evaluating the Ageing Degrees of Bitumen by Rheological and Chemical Indices. Road Mater Pavement 2023.
[46] Petersen JC, Branthaver JF, Robertson RE, Harnsberger PM, Duvall JJ, Ensley EK. Effects of physicochemical factors on asphalt oxidation kinetics. Transport Res Rec 1993;1391.
[47] Primerano K, Mirwald J, Bhasin A, Hofko B. Low-temperature characterization of bitumen and correlation to chemical properties. Constr Build Mater 2023;366:130202.
[48] Rowe GM, King G, Anderson M. The Influence of Binder Rheology on the Cracking of Asphalt Mixes in Airport and Highway Projects. J Test Eval 2014;42(5):1063–72.
[49] Chen H, Bahia HU. Proposed asphalt binder fatigue criteria for various traffic conditions using the LAS or the G-R parameters. Mater Struct 2022;55(1):24.
[50] Hu Y, Sreeram A, Bahia HU, Airey GD, Si W, Li B, et al. Assessing correlations between two linear amplitude sweep (LAS) standards for evaluating the fatigue properties of aged bitumen. Int J Pavement Eng 2024;25(1):2375419.
[51] Shi C, Cai X, Yi X, Wang T, Yang J. Fatigue crack density of asphalt binders under controlled-stress rotational shear load testing. Constr Build Mater 2021;272:121899.
[52] Wu W, Jiang W, Xiao J, Yuan D, Wang T, Ling X. Investigation of LAS-based fatigue evaluation methods for high-viscosity modified asphalt binders with high-content polymers. Constr Build Mater 2024;422:135810.
[53] Cheng H, Sun L, Yang R, Zhang Y, Liu L. Relating Field Moduli of Asphalt Mixture Layer Under Vehicular Loading and its Dynamic Moduli Under Laboratory Loading. Transport Res Rec 2021;2676(2):567–79.
[54] Shi K, Ma F, Fu Z, Song R, Yuan D, Ogbon AW. Enhancing aged SBS-modified bitumen performance with unaged bitumen additives. Constr Build Mater 2024;412:134768.
[55] T.A.C. Asphalt Institute, State-of-the-Knowledge: Use of the Delta Tc Parameter to Characterize Asphalt Binder Behavior, 2019.