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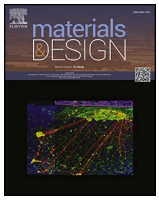

Engineering bitumen for future asphalt pavements: A review of chemistry, structure and rheology

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ABSTRACT

Bitumen, a product mostly used as a binder in road construction, has been subject of numerous scientific investigations with the goal to optimise its function as an engineering material. Although a lot of research has been devoted to the three main pillars of bitumen characterisation, chemistry, structure and rheology, less attention has been paid to addressing their respective interrelationship. This critical review revisits modern theories, research advancements and methods, with a primary focus on how techniques like spectroscopy, chemical separation, rheology and microscopy can help to identify issues related to processes like modification and ageing of bitumen. Finally, an overview of current advancements of trying to correlate and interrelate these different schools is given. These individual studies highlight that a considerable amount of research is still required to understand the link between chemistry, mechanical behavior and structure of bitumen which can be related to its complex nature that depends on factors like crude oil origin and refinement process. In addition to that, more advanced characterisation tools and statistical methods, via the developing field of bitumen chemomechanics, can also help to solve modern issues related to future questions. Obtaining the required knowledge will ultimately help design and engineer future paving materials.

List of Abbreviations

UV	Ultraviolet
ROS	Reactive Oxygen Species
SBS	Styrene Butadiene Styrene
SARA	Saturates Aromatic Resins Asphaltenes
MD	Molecular Dynamics
GPC	Gel Permeation Chromatography
HPLC	High-Pressure Liquid Chromatography
ATR-FTIR	Attenuated Total Reflectance - Fourier Transform Infrared
SNV	Standard Normal Variant
PCA	Principal Component Analysis
LDA	Linear Discriminant Analysis
THF	Tetrahydrofuran
SEE	Synchronous Excitation Emission
FEEM	Fluorescence Excitation-Emission Mapping
NMR	Nuclear Magnetic Resonance
EPR	Electron Paramagnetic Resonance
TOF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometry
SANS	Small-Angle Neutron Scattering
SAXS	Small-Angle X-Ray Scattering
WAXD	Wide-Angle X-Ray Diffraction
AFM	Atomic Force Microscopy
CLSM	Confocal Laser Scanning Microscopy
ESEM	Environmental Scanning Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
DSR	Dynamic Shear Rheometer
TTSP	Time-Temperature Superposition Principle
LAS	Linear Amplitude Sweep
MSCR	Multiple Stress Creep Recovery
VBA	Viennese Binder Ageing
PAV	Pressure Ageing Vessel
PTR	Proton Transfer Reaction
2D-FFT	Two-dimensional Fast-Fourier Transformation

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1. Introduction

Bitumen, at ambient temperature, is a sticky, highly viscous, black or dark-coloured material, also commonly known as asphalt (Southeast Asia) or asphalt binder (North America). Chemically, bitumen is a complex blend of hydrocarbons and other heteroatoms such as oxygen, sulfur and nitrogen that are acquired through the distillation process of crude oil [1]. It is most used in road construction as a binder or adhesive for asphalt concrete, but it is also used to a limited extent for the production of roofing membranes, waterproofing materials, and some types of sealants. During the process of refining crude oil through distillation, a range of hydrocarbon products such as gasoline, kerosene, diesel, and lubricating oil are generated. These are typically recognised as high-value refined products. The remaining material, often referred to as short residue, is commonly identified as straight-run bitumen. Here, it is crucial to highlight that the characteristics of high-value distillation products, such as gasoline, undergo stringent control measures. As a result, the variations in chemical composition among sources of crude oil are significantly accentuated in the resultant short residue or straight-run distilled bitumen. To this end, the original property of each bitumen is greatly influenced by the methods used to produce and process it as well as the properties of the crude oil from which it is derived [2]. Generally, heavier crude oil tends to yield higher quantities of bitumen and hence, selecting the right crude oil and refining it using appropriate techniques is an important consideration for bitumen producers [3]. Nevertheless, it should be noted that bitumen is often not the main product of the refining operation.

Currently, the majority of the bitumen produced worldwide is used predominantly as a binder in the asphalt paving industry [4]. This involves mixing bitumen with aggregates to create asphalt concrete mixes, typically through a hot mixing process at temperatures over 150 °C. Although other techniques exist, such as using foamed bitumen, warm mix and cold mix technology, they are not commonly used, accounting for a small percentage of the total asphalt mix production [5–7]. In situations where straight-run bitumen does not meet the specifications for pavement applications, producers resort to additional processing methods. This involves the manipulation of key variables, including the proportional blending of various binders, the selection of specific techniques and chemical catalysts (such as air blowing or half air blowing), and the incorporation of additives to modify properties [1]. Refineries employ optimisation strategies for these variables to engineer a bitumen that adheres to consumer requirements while minimising overall production costs.

One of the most important characteristics of bitumen is that it exhibits a temperature-dependent viscoelastic behaviour, indicating its physical response as an engineering material falls within the continuum between a viscous fluid and an elastic solid. This distinctive property highlights their inherent time-dependent nature, wherein their mechanical response evolves over time. More specifically, bitumen as an organic material is prone to oxidise or "age" during its service life. During this ageing process, the material is exposed to environmental factors such as elevated temperatures, UV and visible sunlight, moisture or water as well as reactive oxygen species (ROS) present in the atmosphere [8–12]. Moreover, as a road paving material, it shows different behaviour depending on the service temperature and loading time. At high temperatures and under slow-moving loads, it behaves as a purely viscous material and is prone to plastic deformations and rutting. At low temperatures and high rates of loading, it behaves as an elastic and eventually brittle material, leading to low-temperature cracking [13]. Hence, depending on the climatic region, bitumen with different properties is used in paving applications to meet performance requirements. It is also common nowadays to modify bitumen with modifiers such as polymers at various percentages to improve its service properties [14–17]. The incorporation of modifiers in bitumen is undertaken to enhance its rheological and functional characteristics and widen the temperature window of application in asphalt pavements. The selection of an appropriate modifier is pivotal from both engineering and economic perspectives to achieve desired properties for paving applications. Extensive research has explored materials such as polyolefins, natural rubber, thermoplastic elastomers, and crumb rubber as potential modifiers [18,19]. However, only a limited number of these have proven to be satisfactory in terms of both performance and cost-effectiveness. Out of these, styrene butadiene styrene (SBS) is a commonly used modifier, well recognised for improving the overall rheological properties of bitumen [20]. Such modification primarily targets the enhancement of fundamental properties, including rigidity, elasticity, brittleness, storage stability, durability, and resistance to accumulated damage. Other types of modification reported include recycled polymers, thiourea, isocyanate-functionalised prepolymers and phosphogypsum waste [21–24].

Lastly, another important class of additives are rejuvenators, which are used commonly to regenerate the rheological properties of bitumen after extended ageing in-situ. The main purpose of rejuvenation is to increase the recycling rate of the aged asphalt materials by recovering their properties [25–27]. However, issues such as phase discontinuity, poor dispersion, and instability with the use of such additives can complicate the production and application of modified materials in practice [28–31]. Overall, the engineering of bituminous materials to meet design requirements, especially in the face of increased traffic loads and the onset of climate change is an ongoing challenge for practitioners and engineers [32].

1.1. Importance of bitumen in pavement engineering

Globally, asphalt pavement is predominantly favored for its exceptional performance on roads, its straightforward rehabilitative processes, and the comfort it provides for driving conditions. As mentioned, the mechanical properties of asphalt mixtures are inherited from the bitumen and dependent on time, temperature, and age [33]. Bitumen generally constitutes a mere 4–8 % of the asphalt mixture by weight, whereas from a volumetric perspective, typical compositions feature 9–18 % bitumen, 78–85 % mineral aggregates, and 3–6 % air voids. Despite its modest mass or volume fraction, bitumen commands a substantial portion of the material costs in asphalt mixture production [34]. This emphasises the considerable influence of bitumen prices, often linked to crude oil costs, on the overall economic dynamics of asphalt mixtures.

In essence, understanding the behaviour and performance of asphalt mixtures requires comprehension of the characteristics and performance of bitumen. Specifically in terms of rheological properties, the resistance to plastic deformation and rutting in asphalt mixtures is provided by both the aggregate structure as well as the bitumen, with the contribution of the bitumen being significant and crucial for predicting and understanding rutting [35]. Similarly, the failure of asphalt mixtures is also often caused by the displacement of bitumen from the aggregate particle surface, known as stripping, due to moisture. The ability of the interface between bitumen and aggregate to withstand such damage is determined by the physical and chemical surface characteristics of the bitumen as well as the aggregate [36]. Lastly, an essential characteristic of asphalt pavements is their resistance to cracking induced by thermal shrinkage during temperature reductions or by repeated action of traffic loads, typically exacerbated by ageing. Decreasing air and pavement temperatures lead to the development of tensile stresses within the asphalt mixture. Owing to bitumen's intrinsic viscoelastic properties, it possesses the ability to relax and thereby reduce these tensile stresses over time. This phenomenon ensures that the cumulative tensile stresses remain within the bitumen's strength threshold, highlighting the material's ability to mitigate thermal-induced cracking [13].

1.2. Need for this review

There is wide consensus in the pavement engineering community

that the behaviour and performance of bitumen are fundamental in predicting the performance of asphalt mixtures and pavements. However, it can be also contended that in mixtures, bitumen is used exclusively with aggregates and the behaviour of asphalt mixtures as a whole is naturally consequential when considering it as a structural entity. Although such statements hold partial merit, it is crucial to emphasise that the durability of the asphalt mixtures heavily depends on the quality of the bitumen, and it is essential to choose one that is well-suited for the prevailing climatic and traffic conditions. This ensures adequate performance as a first step towards designing a well-performing asphalt mix. Developing and manufacturing bitumen with enhanced qualities can lead to significant enhancements in the longevity and lifecycle expenses of asphalt mixtures and pavements [37,38]. This is still a challenging prospect as the chemistry of the bitumen is complicated and many of its chemical characteristics that eventually dictate rheological performance are topics of ongoing research. In that regard, the comprehension of bitumen chemistry is critical to appreciate and engineer its properties during all its life stages i.e., the production stage, service life and end of life. Such knowledge is important to appreciate several critical characteristics of bitumen such as modifications, extensions, bitumen ageing and eventual recycling with possible utilisation of rejuvenation.

When designing asphalt mixtures for high-end pavement applications, it would be practical to screen and engineer bitumen with superior mechanical properties. Additionally, the rise in traffic speed and load and unpredicted climatic events have resulted in decreasing the life of asphalt pavements [39,40]. This leads to higher maintenance costs and an increased risk to users. One of the ways that practitioners are looking to address this issue is through bitumen enhancement and the incorporation of various additives to improve its performance properties. However, the eclectic nature of bitumen and complicated chemistry makes it a difficult material to comprehend and engineer for pavement practitioners. One of the main knowledge gaps that exists as of this review's writing is understanding the relationship between the chemistry, rheology and morphological structure or microstructure of bitumen. It has long been speculated that the links between these three pillars may be the key to fully understanding the material and engineering its performance to the best possible extent. Moreover, current studies and research efforts do not employ the full potential of existing experimental tools for bitumen research, while the sample preparation and standardisation of these techniques need to be also carefully considered. Thus, the purpose of this review article is to disseminate the current state of the art in bitumen with an emphasis on the latest developments and comprehension in chemistry, rheology, and microstructure. Based on this, the future direction and required research to achieve superior levels of understanding and engineering performance of the material is deliberated. The three pillars of relevance in this review are depicted schematically in Fig. 1 together with the direct relationships represented by the given arrows.

1.3. Scope and outline of this review

This review article presents the current state of the art in relation to bitumen as a binder material for asphalt pavements. It is important to note that this critical review is aimed at providing a succinct overview of the subject matter and is not an exhaustive review of all available literature, for which the reader is referred elsewhere [12,41]. In view of that, the article is mainly divided into five distinct sections. In the first three sections, the chemistry, structure and rheology of bitumen are deliberated. Each section provides a synopsis of the current state of knowledge in these areas including the latest research advancements over the past years. Next, the interrelationship between the properties is contemplated with an emphasis on bitumen characterisation, ageing and modifications. Lastly, based on the critical evaluation of existing literature, the future directions of research including vital knowledge gaps that need to be addressed are discussed. Overall, this critical review article is expected to be helpful for researchers, engineers, and policy-makers as a reference guide to understand the current information on this topic and identify key areas for impactful future research.

2. The chemistry

This section focuses on the chemistry of bitumen and illustrates various analytical methods that can be used for its characterisation. These techniques include separation techniques as well as a broad variety of spectroscopic analysis tools that can give valuable insight into the chemical nature of the material.

2.1. Identification and simplification of bitumen chemistry by separation techniques

2.1.1. SARA fractionation

Bitumen is a complex engineering material consisting of a multitude of different molecules. To simplify its study, the characterisation and identification of bitumen including its chemical composition has been a topic of interest for more than 50 years [42–46]. In 1957 Stewart used chromatographic separation techniques and infrared spectroscopy to identify the chemical composition of unaged and field-aged fractions of

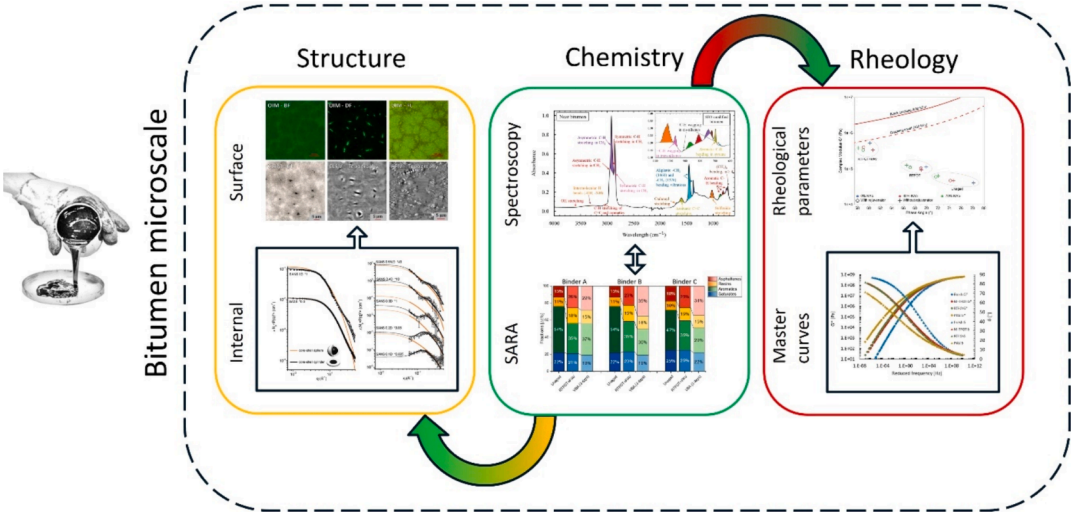

Fig. 1. The three pillars of bitumen focus of this review article.

roofing bitumen. A separation of asphaltenes and maltenes was achieved by using n-pentane as a solvent [42]. Roughly 10 years later, Corbett proposed elution-adsorption chromatography to separate bitumen into four fractions the saturates, naphthene aromatics, polar aromatics and asphaltenes [44]. This separation has since been further developed with slight adaptations to the solvents or different names of the fractions. For example, the proprietary method of SARA-AD of the Western Research Institute (WRI) provides even further subfractions of the four main SARA fractions [47]. However, the overall concept of separating the material into polarity-based fractions, the SARA (Saturates, Aromatics, Resins and Asphaltenes) has remained the same. This led to the standardisation in the ASTM D41 24–01 [48], where the binders get separated into saturates, naphthenic aromatics (renamed aromatics), polar aromatics (renamed resins) and asphaltenes. It is worth noting that this separation is not a strict separation into a precise set of molecules but rather a separation along a polarity gradient. This indicates that saturates, resins or asphaltenes can also contain small or large aromatic structures. Typically, such a polarity-based separation is a tedious and time-consuming procedure. Thus, modern adaptations have led to new methods that utilise automatised separation or fast, small-scale approaches. One example is the approach developed by Sakib et al. [49], where solid phase extraction was used to separate 400 mg of binder, yielding the four desired SARA fractions with quick execution and excellent repeatability. This method has already been implemented in other international research groups [50–53] and the miniature apparatus can be seen in Fig. 2. Mirwald et al [50,51] looked at the spectroscopic information of these SARA fractions and their respective changes during ageing. Guo et al. characterised the effect of rejuvenators on the SARA fractions [53] and attempted to link the SARA fractions to molecular dynamic (MD) simulations [52]. Work by Schettmann et al. [54] used a similar solid phase extraction and compared it to column chromatography. Their work investigated virgin and aged bitumen via gravimetric determination and also analysed the fractions chemically. Thus, all these separation methods mostly served the same purpose i.e. to evaluate the polarity distribution of these fractions and determine their composition. It should be noted that the exact chemical constituents of the SARA fractions such as carbon, oxygen, sulfur and nitrogen can only be revealed via elemental analysis [55]. However, this method only provides an elemental overview of the material and does not provide any insight to how these elements are linked to each other. Thus, their insight needs to correlated to a specific chemical question.

2.1.2. Gel permeation chromatography (GPC)

Another important chromatographic technique used to characterise bitumen is gel permeation chromatography (GPC), which provides information on the molecular weight distribution of bitumen [56–58]. Larger molecules require less time to travel through the column compared to smaller ones. Thus, the resulting chromatogram shows the molecular weight distribution in correlation to elution time. In 1979, Such et al [45] used GPC and high-pressure liquid chromatography (HPLC) to characterise bitumen. The SHRP report from 1993 also reports results from GPC of the SHRP binders AAA-AAG [59] indicating that the method can account also for the interaction between their molecules. Thus, GPC is used to address differences in bitumen ageing [60–63], impact of additives such as polymers like SBS [64–66], crumb rubber [67,68], alternative materials such as bio-based binders [69], the effect of recycling and rejuvenation agents [63] or the usage of antioxidants [70]. A drawback of the method is that it requires specific equipment

Fig. 2. The small-scale apparatus developed for SARA fractionation (reprinted from [49].

and dissolved samples, which leads to a more complicated sample preparation procedure. The obtained results also are slightly dependent on other characteristics of the test setup. Therefore, it is not a commonly used chemical characterisation technique in bitumen and asphalt research.

2.2. Spectroscopic techniques

2.2.1. Fourier Transform infrared (FTIR) spectroscopy

The most common analytical technique used in the field of bitumen research is Fourier Transform Infrared (FTIR) spectroscopy [71]. A material can be characterized by FTIR if it contains IR active functional groups that absorb infrared light. IR light absorption leads to a change in dipole momentum and the molecules start to rotate or vibrate, which creates a characteristic band for a specific functional group. Fig. 3 summarises most of the functional groups found in bitumen documented by Petersen et al. [72]. The ketones and sulphoxides are particularly relevant in bitumen analysis as they are formed during the ageing process and can thus be traced with FTIR spectroscopy in a semi-quantitative way.

A typical FTIR spectrum of an unmodified (blue) and a polymer-modified bitumen (green) is shown in Fig. 4. The respective functional group and assigned vibration of the bands shown in Fig. 3 are listed in Table 1 (hydrocarbons), Table 2 (oxygen-containing functional groups) and Table 3 (sulphur-containing functional groups).

In order to determine the significance of these functional groups, the changes of their respective intensities upon chemical processes such as ageing need to be considered. Starting with the hydrocarbon-containing functional groups, it can be said that the alkyl bands listed in Table 1 remain mostly unaffected by ageing. Thus, these functional groups often act as a reference band. The aromatic bands at 1600, 850, 810 and 750 cm^{-1} increase slightly, which can be attributed to the dehydrogenation of perhydro-aromatics such as 9.10-dihydroantracenes, which are assumed to be the initial molecules reacting with oxygen, starting a chain oxidation mechanism [9]. For bitumen ageing quantification, the ketone and sulphoxide functional groups at 1700 and 1030 cm^{-1} are mainly of interest, as they change significantly with ageing. Other groups such as 2-quinolones, carboxylic acids [9,50] or esters are mostly found in the resins fraction or are formed during ageing [46,73,74].

Looking back at the early stages of bitumen characterisation, Stewart was one of the first to report the infrared spectra of roofing binders [42]. During the first FTIR trials with bitumen, the binders had to be prepared and measured in transmission mode [46,75,76]. Since bitumen in its solid-state lack's transparency, and it needs to be dissolved and applied onto a compatible substrate, such as a KBr, CsI, or NaCl crystal window [77]. This was a tedious process and consumed a lot of time, which diminished the methods practicality. After the implementation of the attenuated total reflection (ATR) geometry, where the solid bitumen sample can be placed directly onto the ATR crystal, the method's usability increased significantly. Most ATR crystals are made of diamond, germanium, or zinc selenide.

While the applicability of ATR-FTIR increased the method's popularity significantly, it led to questions regarding routine measurement and universal applicability. Since there is currently no standard for measuring bitumen with FTIR spectroscopy, various measurement routines and approaches for spectral evaluation have been developed. Typical spectral evaluation involves normalisation and integration of regions of interest, such as the region of carbonyl around 1700 cm^{-1} or sulphoxides at 1030 cm^{-1}. Lamontagne et al., the Belgian Road Research Centre (BRRC), Laboratoire central des ponts et chaussées (LCPC) and participants from the MURE evaluated FTIR spectra using the valley-to-valley or tangential integration method [75,78–81]. Work by Hofko et al. [82] tackled the topic of repeatability and sensitivity regarding the effects on oxidation comparing raw data and normalised spectra as well as full-baseline and tangential (valley-to-valley) integration methods. Follow-up work by Mirwald et al. investigated the impact of sample preparation and the impact of thermal history (heating time and temperature). They furthermore reported the influence of storage time and storage conditioning of different unmodified and modified bitumen with ATR-FTIR spectroscopy [73,83]. A more sophisticated spectral data evaluation approach was investigated by Weigel et al. [77,84] who applied standard normal variant (SNV) transformation and coupled it with multivariance analysis to detect differences in binder origins to predict its properties. Ma et al. [85] also utilised principal component analysis (PCA) and linear discriminant analysis (LDA) models to investigate the effects of ageing via FTIR spectroscopy and correlated specific bands or wavenumber regions to bitumen source, type, and ageing state. Primerano et al. [86] also utilised multivariance analysis to find

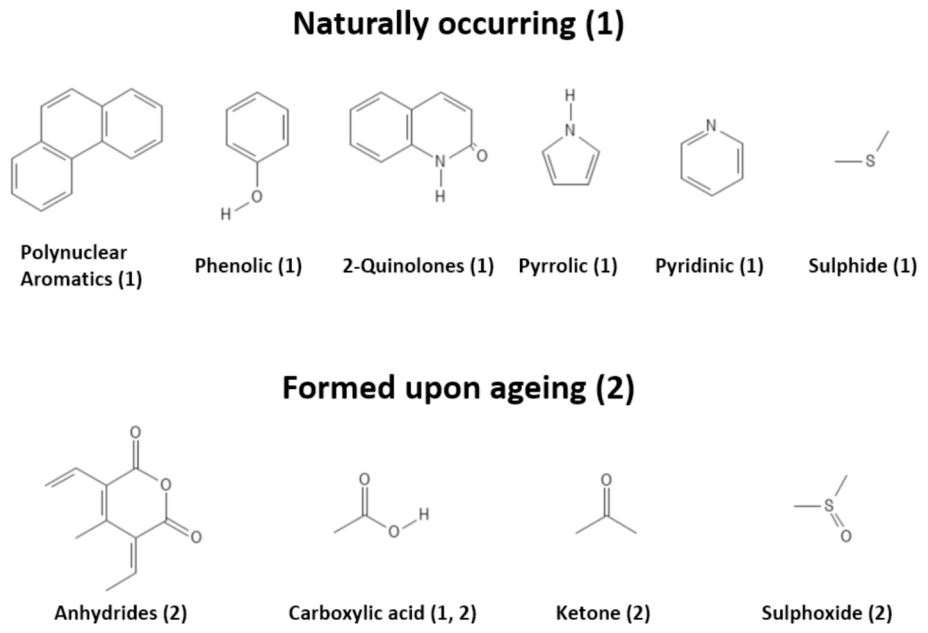

Fig. 3. Functional groups found in bitumen reported in literature (. adapted from [72])

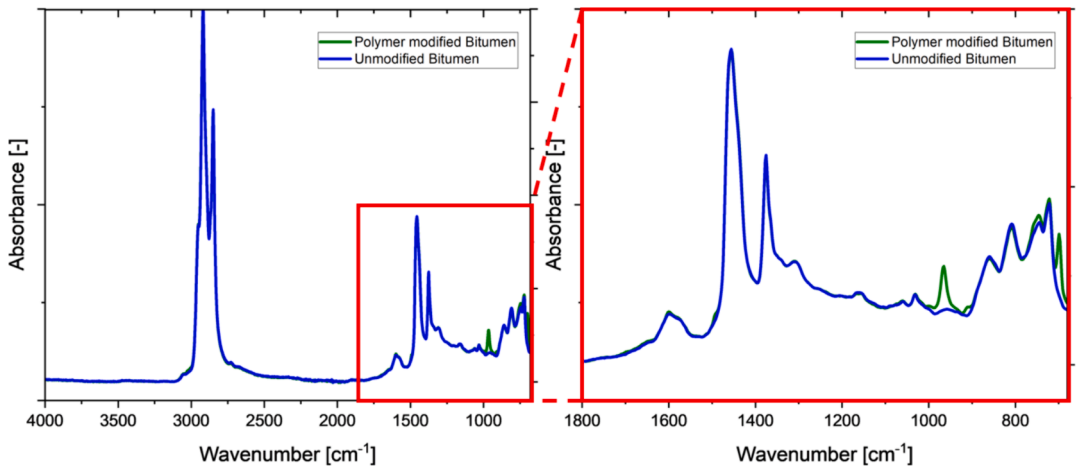

Fig. 4. Exemplary FTIR spectra of an unmodified (blue) and polymer-modified bitumen (green) shown at full spectral range (left) and in the fingerprint region (right). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Hydrocarbon functional groups found in bitumen (taken from [50]).

Functional Group	Assigned Vibration	Appearing Band [cm^{-1}]
Alkyls	ν_{as} CH_2/CH_3	2920
Alkyls	ν_s CH_2/CH_3	2850
Alkyls	δ_{as} CH_2/CH_3	1455
Alkyls	δ_s CH_2/CH_3	1380
Alkyls	ρ (CH_{2n})	720
Aromatic	ν C=C	1600
Aromatic	γ CH_{aro}	860
Aromatic	γ CH_{aro}	810
Aromatic	γ CH_{aro}	750
Alkene	δ (CH)	960

Table 2
Possible oxygen-containing functional groups found in bitumen (taken from [50]).

Functional Group	Assigned Vibration	Appearing Band [cm^{-1}]
Ketone	ν C=O	1700
2-Quinolone	ν C=O	1655
Carboxylic Acids	ν C=O	1730

Table 3
Possible Sulphur-containing functional groups found in bitumen (taken from [50]).

Functional Group	Assigned Vibration	Appearing Band [cm^{-1}]
Sulphoxides	ν S=O	1030
Sulphones	ν SO_2 (out-of-phase)	1310
Sulphones	ν SO_2 (in-phase)	1160
Sulphate Ester	ν_{as} SO_3	1260
Sulphate Ester	ν_s SO_3	1080
Sulphate Ester	ν S-O-C	810

differences in FTIR spectra of various laboratory and field long-term aged bitumen and highlighted the influence of different ageing-inducing factors.

FTIR spectroscopy can also be used to characterise prominent bitumen modifiers such as SBS. Since both styrene and butadiene are IR-active functional groups, they can be tracked with infrared spectroscopy [87–89]. In the FTIR spectra, the band assigned to the polybutadiene can be seen at 966 cm^{-1} and the polystyrene at 699 cm^{-1}. These bands can either be used to identify whether bitumen contains SBS or if the polymer is changing upon phenomena like ageing. As an example, Sun et al. used FTIR spectroscopy to quantify the amount of SBS polymer contained in different bitumen, ranging from 2 to 6 % [88]. On the other hand, Mouillet et al. used FTIR spectroscopy to quantify the degradation of SBS polymer upon UV ageing via the evolution of the butadiene double bond band at 966 cm^{-1} [90]. The same principle applies to other additives such as rejuvenators or other extenders, where FTIR can be used as a characterisation tool if the materials contain IR active functional groups. A representative FTIR spectrum, including information about all possible functional groups in conventional and polymer-modified bitumen, is shown in Fig. 5.

2.2.2. UV Vis and fluorescence spectroscopy

Light in the visible and ultraviolet domain can also be used to obtain characteristic information of the chemical composition of bitumen. Soenen et al. [91] studied laboratory aged bitumen dissolved in tetrahydrofuran (THF) with UV–vis absorption spectrophotometry and showed changes in absorption at longer wavelengths around 600 nm which increased upon ageing. Hou et al. [92] and Hung et al. [93] have also obtained similar results, where ageing causes an increase in the wavelength domain of 700 – 900 nm, which was linked to the increase in asphaltene content.

Buisine et al. [59] studied different bitumen samples using synchronous excitation emission (SEE) fluorescence spectroscopy, revealing a strong fluorescence signal in the range between 250 – 600 nm. These can be assigned to aromatic rings of different sizes, where an increase in wavelength corresponds to an increased aromatic ring size. Handle et al. [94] and Grossegger et al. [95] conducted similar fluorescence spectroscopic measurements on unmodified, solid bitumen and its SARA fractions. Excitation scans, emission scans and fluorescence excitation-emission mapping (FEEM) revealed an overall strong loss in fluorescence intensity, that can be linked to the decrease in aromatic content during ageing. The analysis of the SARA fractions revealed that most of the intensity comes from the aromatic fraction as its fluorescence intensity is two orders of magnitude higher compared to the rest of the fractions. The overall intensity loss upon ageing can be explained by the fact that the aromatic fraction decays the most.

Mirwald et al. [96] coupled fluorescence spectroscopy with optical fluorescence and darkfield microscopy to investigate the differences between various long-term ageing procedures. FEEM results showed that besides the overall decrease in the fluorescence intensity, a shift towards a higher emission wavelength and possible quenching effects were observed.

Recent work by Werkovits et al. [97,98] combined fluorescence spectroscopy with FTIR spectroscopy and Nuclear Magnetic Resonance (NMR) spectroscopy to investigate the ageing effects on bitumen and its

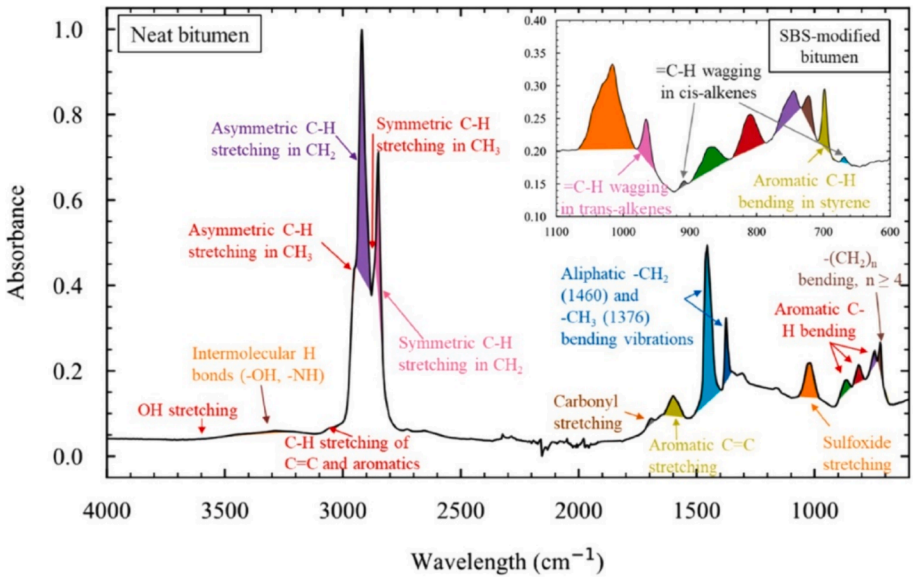

Fig. 5. Possible functional groups in FTIR spectra of conventional and polymer-modified bitumen (reprinted from [85]).

SARA fractions (Fig. 6). Emission scans and FEEM maps confirmed a shift towards higher wavelengths upon long-term ageing. These trends were also highlighted in differential FEEMs, where the loss of small aromatics was observed in the saturates and aromatics, which reappeared in the fractions with higher polarity.

Similar to FTIR spectroscopy, fluorescence spectroscopy can also be used to identify SBS polymers within polymer-modified bitumen. This can be explained by the fact that SBS exhibits autofluorescence on a significantly higher level than the bitumen itself. A study by Mirwald et al. was able to identify the contribution of SBS in fluorescence spectroscopy, revealing a strong signal around 350 nm when measured in excitation mode. Surfaces containing different amounts of SBS show different intensities of the respective signal around 350 nm [99,100].

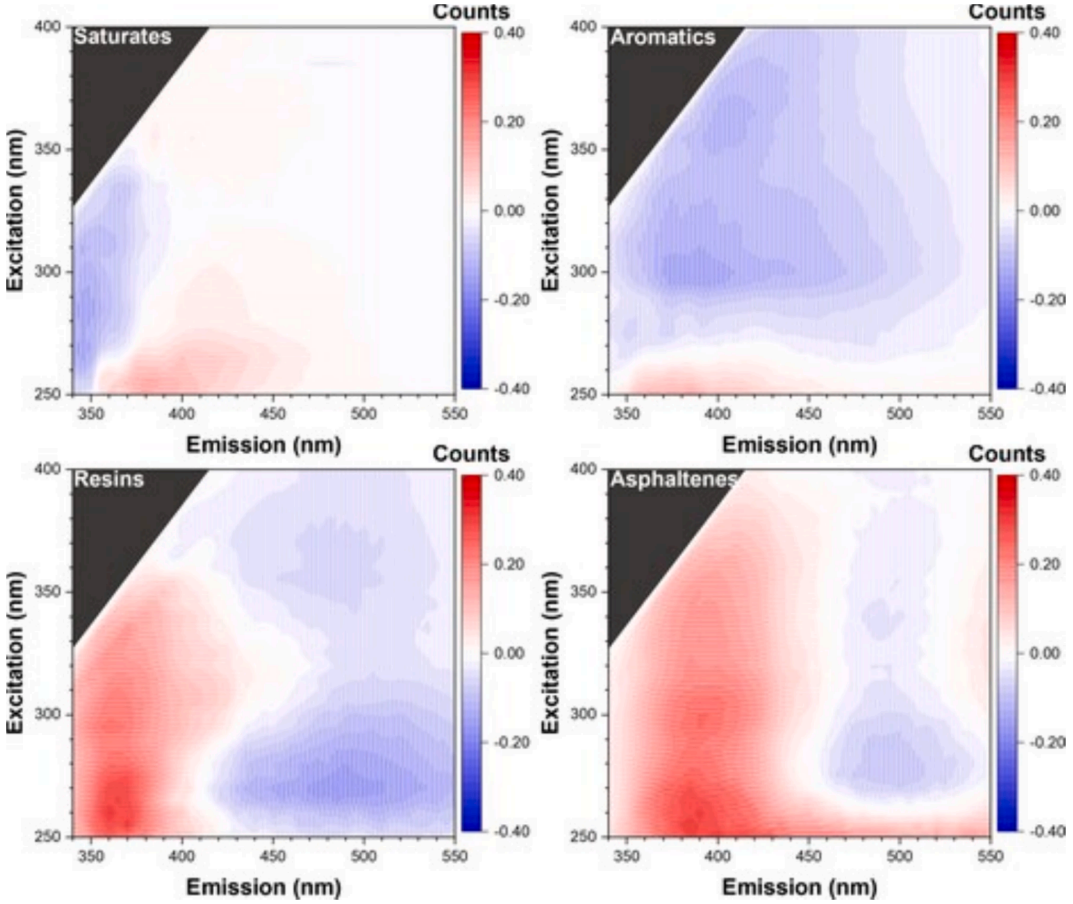

Fig. 6. Typical FEEM of the SARA fractions (reprinted from [98]).

2.2.3. Nuclear Magnetic Resonance (NMR) spectroscopy

NMR is a spectroscopic technique which is used for materials that contain elements with an odd number of protons, such as hydrogen, carbon or phosphorous. Since organic materials like bitumen mostly consist of these elements, it would be an ideal candidate for NMR spectroscopy. However, since bitumen contains millions of different molecules [37], the resulting outcome can show overlapping signals and lead to unclear results. Nonetheless, researchers have investigated binders with ^{1}H and ^{13}C NMR spectroscopy, typically regarding changes induced by laboratory ageing [101–107]. Most of these studies showed many overlapping bands, making it difficult to come to a precise answer. Thus, the post-separation spectral analysis becomes a necessary step. On the bitumen level, Woods et al. [108], Guo et al. [52] and Huang [109] investigated the SARA fractions with ^{1}H and ^{13}C NMR spectroscopy. Results showed an increase in aromatic carbon ratio as well as a cycloalkane carbon decrease with rising polarity (Saturates < Aromatics < Resins < Asphaltenes). Furthermore, poly-condensed aromatic rings were found in the aromatics, resins and asphaltenes. However, the necessity for separation also makes this method quite inconvenient and unpractical. Thus, another possible approach to tackle the issue of overlapping signals was addressed by the combination of different NMR techniques. Such a combination was mostly conducted on crude oil fractions [110], from feeds in the refinery process [111] or on heavy fuel oils [112]. However, recently Werkovits et al. [97] applied different NMR techniques, such as HSQC and ^{31}P NMR, on various bitumen and its SARA fractions, which provided insight into the H/C ratio, aromatic systems and average molecular size of binder and fractions. A typical HSQC NMR spectrum of bitumen can be found in Fig. 7. Notable conclusions were that the fractions contain varying chain lengths of aliphatic substituents. Functional groups such as esters or amides are found in the resins, which was indicated by a characteristic shift. ^{31}P NMR revealed the presence of minor amounts of alcohols and carboxylic acids.

Overall, it can be inferred that the utilisation of NMR spectroscopy has risen in recent times, but fundamental knowledge at the chemical fractions level as well as a its use as a combination with other techniques is required to come to meaningful conclusions.

2.2.4. Electron paramagnetic resonance (EPR) spectroscopy

Analogous to the principle of NMR spectroscopy, where the electromagnetic field is used to analyse nuclei of the molecules, electron paramagnetic resonance (EPR) spectroscopy makes use of the electromagnetic field but investigates the unpaired electrons or their spins. Pipintakos et al. [102,113] investigated the oxidation mechanism of bitumen using EPR spectroscopy and combined it with FTIR spectroscopy, ^{1}H NMR and Time-of-flight secondary ion mass spectrometry (TOF-SIMS). The EPR analysis revealed that carbon-centred radicals form upon oxidation, while vanadyl-porphyrins remain mostly unchanged. Rossi et al. [114] also analysed the effect of antioxidants on the ageing process by investigating asphaltenes and maltenes via EPR and combined it with rheological investigations. EPR results showed the effectiveness of the antioxidants, as a lower content of radicals was determined for the fractions containing the antioxidants.

2.2.5. Time-of-Flight secondary ion mass spectrometry (ToF-SIMS)

Mass spectrometry can also be used to determine the chemical composition of the surface of the material. An ion beam (primary ions) bombards the surface of the material, emitting secondary ions. These ions are then separated according to their different masses using a time-of-flight analyser. Not a lot of literature and research has been conducted using this method, which can mainly be attributed to the fact that it is an expensive device and that the information gained from a complex material like bitumen is limited. On top of that, most mass spectrometers work under vacuum, which requires special attention during preparation and measurement. Nonetheless, various researchers have studied different binders using ToF-SIMS [101,115–118]. Results mainly indicate that hydrocarbon ions $C_xH_y^+$ dominate the positive ion spectra, while the negative ion spectra show peaks from heteroatom-containing ions.

3. The structure

The previous section on chemistry reviewed the use of techniques, such as chromatography and spectroscopy, to examine the variety of molecular species in bitumen based on polarity, molecular size and functional groups. However, most of these spectroscopic techniques fail to realise the structure of the material i.e. the spatial distribution of the different molecular species. Thus, microscopic and other characterisation techniques are required to resolve the morphology and structure of the material.

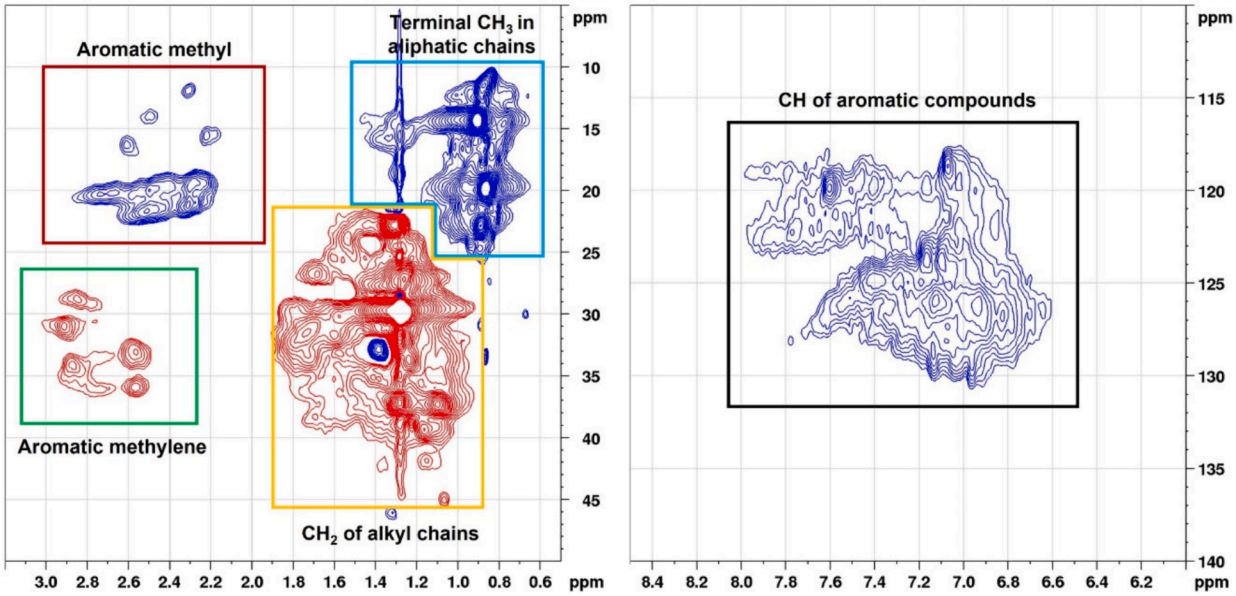

Fig. 7. HSQC NMR spectrum of bitumen depicting the aliphatic and aromatic regions (reprinted from [97]).

3.1. Modern theories of bitumen's structure

The internal structure of bitumen has long been of interest to researchers, in part because of the possible connection to its viscoelastic performance. Theories about the structure of bitumen are rooted back to 1914 when Rosinger shaped the idea of the colloidal structure [119]. This model was adopted and further discussed by Nellensteyn, describing bitumen as a colloidal suspension of asphaltenes and maltenes, in which resins surround the asphaltenes contributing to a stabilising effect in this suspension [120]. This idea was widely accepted by the scientific community for many years as it found basis as an explanation of the sol–gel behaviour of bitumen [121,122]. More specifically, bitumen can behave as a Newtonian or non-Newtonian fluid-like material, depending on the aggregation and interaction potential of the asphaltenes inside the oily maltene medium [123].

Another theory put forward for the structure of bitumen is widely known as dispersed polar fluid [124–126]. It was speculated that since an elastic plateau cannot exist for a gel bitumen [127], then it should be a purely homogeneous fluid of all the SARA fractions in a mutual solution. The SARA fractions do have different solubilities in this solution, while a phase separation could be explained by a reduction in the system's entropy and by successive enthalpy compensation.

Based on contemporaneous theories from colloids science, Yen initially hypothesised bitumen structure in a hierarchical way forming cores, micelles and aggregates consisting of asphaltenes [128]. Mullins further developed this idea by classifying the structure of bitumen based on the propensity of asphaltenes to form nanoaggregates and clusters [129,130]. This theory is known as the Yen-Mullins model (Fig. 8) and various sophisticated spectroscopic and scattering techniques have partially validated its rationale [131,132].

3.2. Modern theories of bitumen's surface microstructure

It appears that bitumen has a strong tendency to form peculiar surface microstructural patterns, as observed by different modes of microscopy. To explain these surface features, theories have been developed over the years in the scientific community. It has long been a matter of debate which one could explain their formation supporting also a reasonable thermodynamical balance. As expected, each school of thought has its merits and deficiencies.

On the one hand, the 'wax theory' has its basis on the paraffinic wax that can exist in bitumen's composition [133–135] whereas the 'asphaltene theory' attributes these microstructures to the most polar of the SARA fractions [136]. The former supports that the crystallisable components that exist by means of paraffinic or microcrystalline waxes can crystallise in large, thin flat plates or small crystals of a few micrometres respectively [137–139]. When crystallised the waxes are considered responsible for the formation of the surface microstructures in bitumen [140].

The 'asphaltene theory' is built around the premise that the polar asphaltene micelles can be stabilised in the maltene matrix. The association of the hierarchically structured agglomerations of asphaltenes and the various sizes of the surface microstructures is considered the most sound argument of this theory [141–143]. It is worth mentioning that the asphaltene theory put forward attempts to bridge the gap between bulk and surface microstructure as well as its chemical composition.

3.3. Internal and surface structure

3.3.1. Small-Angle Neutron (SANS), x-ray scattering (SAXS) and Wide-Angle X-ray Diffraction (WAXD)

To elucidate the internal structure of bitumen in the scale of nano-observations, scholars have utilised scattering techniques such as SANS, SAXS and WAXD. The advantage of these techniques is the investigation of the bulk of bitumen. It additionally provides information regarding the orientation and composition of the captured units, assumed to be asphaltene nanoaggregation, as shown in Fig. 9 [144,145]. The basic working principle of these techniques is based on the different reflections at varying scattering angles that the various bitumen molecules experience. It can provide an estimation for the type and organisation of these agglomerations when compared with standard probe materials [134,146].

SANS is particularly used to study isolated asphaltenes nanoaggregation in dissolutions whereas SAXS and WAXD are more applicable to study the parent bitumen. The morphology and size of aggregation are made possible via these techniques. Moreover, paraffins, when present in bitumen, are found to be typically organised in orthorhombic unit cells [131,147]. Several studies report that the asphaltene nanoaggregation ranges between 60 and 300 \AA whereas their shape varies somewhere between disk and spherical [148–150]. Asphaltenes aggregate in 'islands' in low concentrations while in higher concentrations they form 'clusters'.

3.3.2. Atomic Force Microscopy (AFM)

Several microscopic techniques have been applied to study the surface microstructure of bitumen. To name some of them, Environmental Scanning Electron Microscopy (ESEM) [151], Scanning Transmission Electron Microscopy (STEM) [139], Confocal Laser Scanning Microscopy (CLSM) [152], Brightfield and Darkfield Microscopy [153,154] have been successfully applied to bitumen applications. Out of these, the technique that has been used largely is Atomic Force Microscopy (AFM). An example of microscopic images of the same bitumen in different modes is shown in Fig. 10.

AFM has been used to study the topography, adhesion, stiffness and phase contrast at the microscale level [155,156]. Sample preparation for AFM plays a crucial role in the surface-driven patterns that can be captured and is conducted either via spin or heat casting [157,158]. Operation of a typical AFM can be performed in near-contact, tapping and non-contact mode, while recent developments provide also a coupling with peak force and nanomechanical or chemical mapping [159]. It should be noted that bitumen modification, like SBS, cannot be

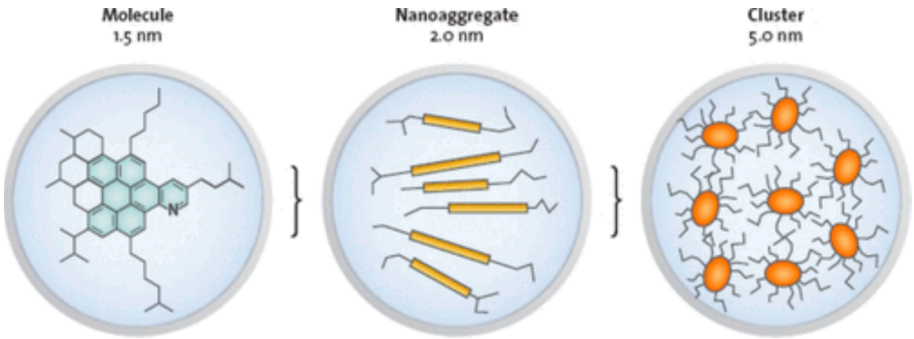

Fig. 8. Simplified representation of the Yen-Mullins model (reprinted from [129]).

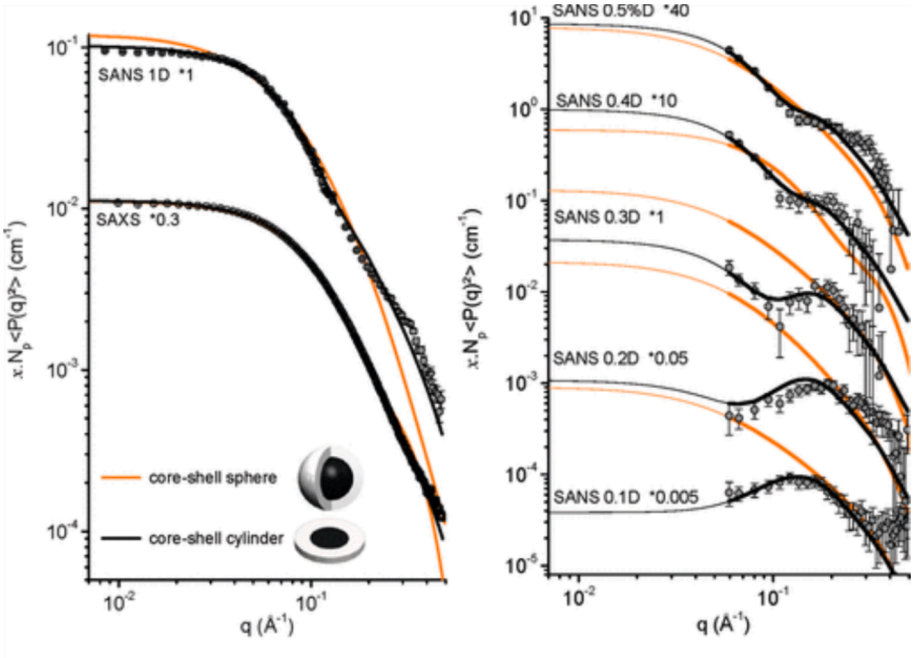

Fig. 9. Experimental support for the composition of nanoaggregation via SANS and SAXS (reprinted from [131]).

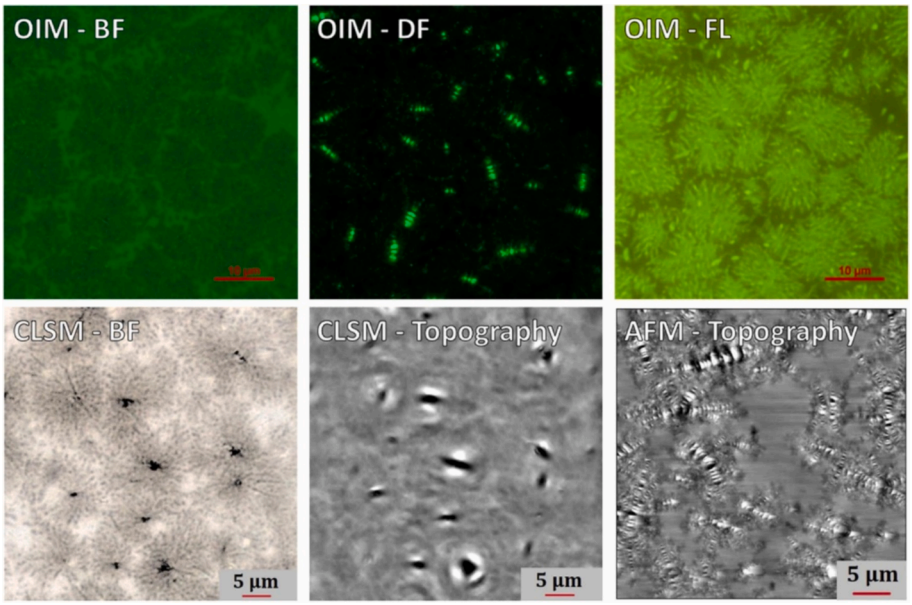

Fig. 10. Typical microscopic images of bitumen with different microscopes (reprinted from [153]).

easily distinguished with the use of AFM or similar microscopes.

Except for the fibril structure of bitumen that can be mainly revealed by ESEM, AFM and all the other microscopes have demonstrated that rippled-like patterns can be found on the surface of bitumen. In a cross-section, these patterns look like wavy wrinkles realised by a sequence of valleys and depths. They are widely known in literature as 'bee structures' of bitumen [135,140,160]. Scholars showed that by simply changing surface from air to a different interface or the thermal history of the specimen, the 'bee structures' can change [140,161,162].

3.3.3. *Fluorescent Microscopy*

Fluorescent microscopy is also used for the identification of surface microstructure for both conventional and modified bitumen. However, its main application remains for use in characterising polymer-modified bitumen. It has been used extensively as a rapid check of the phase morphology of the modified bitumen, the homogeneity as well as blending efficiency of the polymer, i.e. SBS, within the bitumen matrix [163]. The dispersion of the polymer is a key aspect for such types of binders in relation to potential phase separation, storage stability issues and the compatibility of the type and content of polymer with them. It also explains to a certain degree, via the visual information that is captured the chemical composition of modified bitumen.

In terms of the working mechanism, the ability of the polymer to swell while it absorbs part of the bitumen composition, namely the aromatic compounds, and its fluorescence allows the identification of the polymer-rich phase under UV light. The principle is in fact based on the different UV excitation responses of the polymer and bitumen, with the polymer exhibiting a higher fluorescence [158]. Typically, the

wavelength of the light source ranges between 450 to 510 nm depending on the filter and splitter that is utilised.

It has been reported that the sample preparation of the bitumen drop under investigation plays a crucial role in the observed morphology. In particular, at a specific temperature, based on the bituminous blend, there is a critical liquid–liquid demixing behaviour, which if exceeded results in phase separation, whereas in lower temperatures keeps them miscible [164]. It becomes apparent that the sample preparation conditions are crucial for the depicted morphology [154]. This was confirmed in recent studies coupling fluorescent microscopic information with the excitation spectra via fluorescent spectroscopy to investigate the degree of ageing severity [96].

A few studies have utilised image processing approaches to quantify the polymer dispersion and degree of compatibility with the bitumen matrix [163]. It should be noted that the borders between the different morphology phases are not always clear and are rather prone to software package errors. Instead, 2D-FFT has been successfully applied to study morphological parameters with greater accuracy [165].

3.3.4. Link between the bulk and surface

Microscopy has been utilised to study the effect of the near-surface characteristics of bitumen. However, there are only a few studies that have attempted to establish the links between the bulk information and the surface observations. To tackle this, scholars have employed fractured surfaces of frozen samples to explore these links [166,167]. Interestingly, literature supports that different morphology or microstructure can be found in the absence of air i.e., in the bulk of the bitumen compared to the surface. More specifically, it has been shown that the bee structures are most likely a surface phenomenon that can be only restored in fractured surfaces upon reheating [167]. Studies support that at the bulk of bitumen 'ant structures' appear which are considerably different than the bee structures [162].

A step further, the link between the internal, compositional structure and the bulk microstructure is even more challenging, considering the limitations and the effects of the sample analysis. Due to this, the correlation between thermoanalytical techniques and microscopic investigations becomes challenging. As an example, the prior thermal contact treatment that WAXD requires before analysis compared to the freezing, and subsequent heating till the ambient temperature for the AFM fractured specimens illustrates the existing experimental challenges. Nevertheless, few researchers have examined the influence of bulk microstructure on the rheology of bitumen [168,169].

4. The rheology

In the two previous sections, the underlying chemistry and (micro) structure of bitumen were reviewed. Undoubtedly, understanding the fundamental mechanisms that govern the chemistry and structure of bitumen is critical in modifying its composition. From an engineering perspective, the performance of bitumen is assessed based on its rheological and physical properties. To obtain a complete overview of the material, this section reviews the latest advancements in bitumen rheology.

4.1. Bitumen classification

As mentioned earlier, one of the main advantages of bitumen for road-related applications lies in its viscoelastic and waterproofing properties [170]. Typically, bitumen is classified in Europe based on certain physical properties such as the penetration depth and softening point. However, these properties together with bitumen viscosity remain somewhat limited in differentiating clearly between newly-introduced complex binders. As such, modern efforts in the United States are shifting towards an overall classification of the product based on a more meaningful mechanical and physical characterisation as well as the incorporation of CAS numbers to maintain the quality of bitumen. It becomes apparent that recent crude oil sanctions affect the quality of bitumen, especially in Europe since bitumen producers need to find alternative crude oil sources [171,172]. This implies an even more complicated assurance of bitumen quality while at the same time, contractors are relying only on a rather semi-empirical classification. Following such categorisation not only makes the use of blending charts for asphalt mixture composition problematic but may also provide a false view of the long-term performance of the bitumen and the asphalt pavement.

4.2. Advanced mechanical characterisation

It has long been speculated that the physical properties of bitumen may not be sufficient enough to fully comprehend its material behaviour. The Strategic Highways Research Programme (SHRP) adopted in its categorisation the time and age-dependent mechanical properties of bitumen, widely known as rheology [173]. More specifically, bitumen, and successively asphalt pavements, may appear to crack excessively in low temperatures when they are too stiff and at high temperatures they become softer and are prone to rutting. Two metrics that were utilised to roughly evaluate the ability of bitumen to overcome such distresses are the fatigue and the rutting factor. Both parameters are derived from the norm of the complex shear modulus and phase angle.

All these parameters can be extracted by a Dynamic Shear Rheometer (DSR) under a strain or stress-controlled test. The basic principle of this device is rather simple. A rotation/oscillation of constant strain of an upper plate is applied on a sandwiched bituminous sample between two plates, from which the bottom remains clamped, and the measured stress can finally provide the norm of the complex shear modulus (G*) and the phase angle of the material. The former represents the stiffness of bitumen whereas the latter is the phase lag between the stress and strain. Besides the magnitude of the complex modulus, other fundamental parameters of critical significance include the storage or elastic modulus G' (the in-phase part of G*) and the loss modulus G'' (the out-of-phase part of G*). Practically, choosing the right controlled stress or strain is vital to meet the linearity conditions of the viscoelastic domain where most rheological evaluations are conducted.

Different tests have been developed with the DSR for the rheological evaluation of bitumen. A common test to fingerprint the rheological properties of a material is the frequency-temperature sweep, which comprises a testing programme with different temperatures at a range of frequencies. The phase angle and complex modulus vary depending on the frequency and temperature. For instance, when the phase angle values are low, the material acts more like an elastic solid, while high phase angle values suggest a viscous fluid-like behavior. The information obtained from isothermal charts can be adjusted in accordance with the time–temperature superposition principle (TTSP). This information can then be applied to construct models of the complex modulus and phase angle across an expanded spectrum of frequencies and temperatures, ultimately forming a continuous representation referred to as a master curve.

The master curves have been used effectively to study the ageing degree of bitumen, its modification and the potential susceptibility to certain types of distress when used in a specific climatic region. Typical master curves of a conventional bituminous binder and the effect of ageing on it are depicted in Fig. 11.

Moreover, the phase angle versus the complex modulus (black space diagram) can depict how rheologically complex the studied bitumen is. These types of graphs as shown in Fig. 12, can also show the polymer activity, by means of 'curling' in this diagram and the existence of any other additive in its composition [89,175]. Moreover, for polymer-modified bitumen, a characteristic 'feathering' effect is seen in its master curve especially when the polymer is active. In parallel, in search of imposing certain limits above which bitumen may be unable to perform as intended, a number of meaningful parameters related to the different distresses have been introduced during the last decade. Table 4

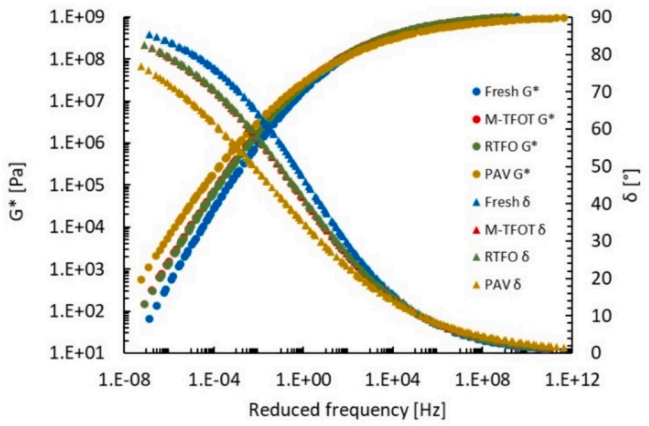

Fig. 11. Master curves of complex modulus and phase angle and the evolution of them with ageing (reprinted from [174]).

summarises the current state of knowledge related to these parameters, its potential use, and its relationship with ageing.

Among these parameters, the Glover-Rowe parameter is typically used as a surrogate for ductility measurement and propensity to crack with threshold limits of crack onset (180 KPa) and severe, critical cracking (600 KPa) for unmodified bitumen [176,177]. Similar thresholds have been suggested for example for the ΔT_c parameter, with values of −2,5 and −5 °C for the cracking onset and severe cracking respectively [178]. It should be noted that ΔTc was originally developed to detect the presence of re-refined engine oil REOB in bitumen and later was used to evaluate low-temperature performance using a Bending Beam Rheometer (BBR). However, recent developments allow for its calculation using a 4 mm DSR plate for the same values at the same temperature domain with a satisfying conversion and with the advantage of using less material [152]. Obviously, the advantages of DSR are incomparable especially when the material cannot be obtained in large quantities which is the case with aged binders extracted and recovered from the pavement.

Two other useful rheological testing programmes in DSR are the Linear Amplitude Sweep (LAS) test based on the American standard AASHTO TP101-14 and the Multiple Stress Creep Recovery (MSCR) test based on both American and European specifications, i.e. the EN 16659:205. LAS is useful to evaluate the damage susceptibility of bitumen utilising viscoelastic continuum damage theory and investigate its cracking resistance [185]. It can even adopt different strain levels to simulate a weak or strong pavement structure [186]. While LAS makes use of 8 mm DSR geometry, MSCR uses a 25 mm plate geometry at different stress levels over ten cycles including a loading and a recovery period. The latter can extract parameters, such as the non-recoverable

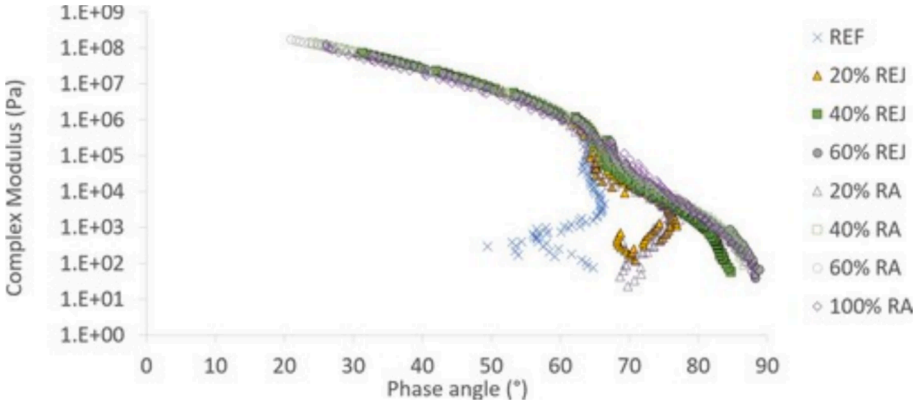

Fig. 12. Black space diagram of polymer-modified binder including rejuvenator and reclaimed polymer-modified binder showing its characteristic curling effect (reprinted from [89]).

Table 4
Recently introduced rheological parameters [56].

Rheological value	Formula	Definition	Plate geometry	Evolution with ageing	Indication
Crossover modulus (G_c)	Respective values derived by a master curve where a phase angle is $\delta = 45^{\circ}$	The modulus, frequency and temperature at the point where the loss modulus G´´ coincides with the storage modulus G´	8 and 25 mm	↓	Elastic/viscous transition, brittleness, hardness [180,181]
Crossover frequency (ω_c)					
Crossover temperature (T_c)				↑	Rutting and cracking [182]
Shape parameter (R)	$R = \log G_g - \log G_c$ where G_g is the glassy modulus and G_c is the crossover modulus	Difference between the moduli of glassy behaviour and crossover point	4, 8 and 25 mm	↑	Width of relaxation spectrum, fatigue cracking [180,183]
Glover-Rowe (G-R)	$G-R = \frac{G^* \bullet (\cos\delta)^2}{\sin\delta}$ where G^* and δ the complex shear modulus and phase angle at 15 °C, 0.005 rad/s	A parameter based on the complex modulus and phase angle under a specific frequency in correspondence with ductility at the same temperature and specific elongation rate	8 mm	↑	Durability, non-load related cracking [178,184]
ΔT_c	$\Delta T_c = T_{c,G} - T_{c,m}$ where $T_{c,G}$ and $T_{c,m}$ the temperatures where the DSR values of G (60) = 143 MPa andm (60) = 0.275 respectively [179]	Difference of two lower continuous grading temperatures related to creep stiffness and relaxation	BBR or 4 mm DSR	↓	Ageing-induced cracking [178]

creep compliance Jnr and the recovery percentage R% at the end of each cycle. These are related to the relaxation of the bitumen and its resistance to permanent deformation.

4.3. Ageing, modification and rejuvenation in rheology

Ageing, modification and rejuvenation of bitumen can often be seen via changes in its rheological properties. Firstly, an apparent increase in the complex shear modulus is observable accompanied by a decrease in phase angle with ageing, whereas the opposite effect is seen with the incorporation of rejuvenators. Moreover, a decrease of the ΔTc and the crossover modulus and an increase of the crossover temperature, frequency, R-value and G-R have been reported with ageing [187]. Fatigue life as predicted via LAS is in general seen to increase with ageing for strong pavement structures while the ability to relax as evaluated by MSCR is seen to decrease [188]. An example of the effect of ageing and rejuvenation for the G-R parameter is shown in Fig. 13 together with its corresponding cracking limits.

While similar effects can be found for polymer-modified bitumen, it should be noted that the majority of the newly introduced rheological parameters from frequency sweeps were developed for rheologically simple, i.e. conventional bituminous binders. Thus, the use i.e. of the G-R parameter should be undertaken with caution. MSCR is considered the most appropriate test for elastomeric polymer-modified bitumen which exhibits enhanced J_{nr} and R%. Other rheologically complex bituminous binders such as waxy, REOB, bio-derived or nanomaterial-induced binders should be always evaluated for the applicability of the TTSP and the effect i.e. of internal phenomena in the bulk. For example, it has been shown that the crystallisation of certain paraffinic components in waxy bitumen has a significant effect on the selected DSR testing programne and the obtained results, i.e. the discontinuity in the black space diagram [189].

5. The interrelationship between chemistry, structure and rheology

Understanding the links between chemical compositions, microstructure and rheology of bitumen is crucial to fully comprehend its characteristics. The authors of this work are of the view that care should be exercised in order to conclude meaningful relationships between the chemistry, structure, and rheology of binders. When considering the ageing-related hardening of binders, the oxidative processes fundamentally modify the chemical composition, particularly affecting the asphaltene fractions [13]. To this end, the structural rearrangement within the fractions contributes to the changes in rheological behaviour. Similarly, the viscoelastic properties of bitumen exhibit pronounced changes with temperature which can be traced to the delicate equilibrium between asphaltene and maltene fractions. Polymer and extender modification introduces an additional layer of complexity to these interrelationships imparting unique structural characteristics to the binder and enhancing its chemical composition with the introduction of different molecules [16]. Several laboratory investigations have been conducted to develop links between the rheological properties and the chemical composition of bitumen. Initial studies primarily qualitatively explored the impact of individual asphalt components on performance, while subsequent research has concentrated on quantitatively establishing correlations. These correlations naturally involve performance parameters and physicochemical attributes of individual components, encompassing viscosity, complex modulus, phase angle, molecular weight, polarity, content of oxidised functional groups or a combination of these factors.

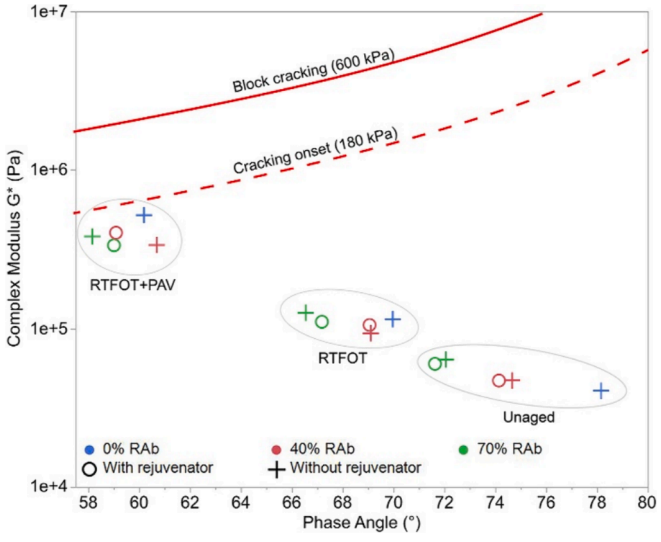

Fig. 13. Evolution of Glover-Rowe parameter with lab ageing and the effect of rejuvenation (reprinted from [187]).

In terms of qualitative analysis, the Strategic Highway Research Programme (SHRP) undertook extensive studies to investigate the links between the chemical composition and rheological characteristics of bitumen [3,190]. These studies aimed to gauge the strength of molecular interactions within bitumen, specifically focusing on their polarity, which were quantified through the dielectric constant. Moreover, the reports from these studies employed regression analysis to establish mathematical relationships between various chemical parameters and their corresponding rheological properties. Apart from this, Simpson et al. separated asphaltene precipitate residues into resins, aromatics, and saturates using fractionation procedures and their findings indicated that resins positively affected viscosity, saturates had a negative impact, and aromatics marginally heightened the shear sensitivity [191]. Corbett further elucidated the contributions of these fractions to the bitumen properties. The study highlighted the roles of saturates and naphthalene aromatics in providing fluidity, asphaltenes as thickeners, and polar aromatics influencing ductility, collectively controlled by their mixing ratios [192]. Bukka et al. observed that despite containing more than twice the amount of asphaltenes, Athabasca bitumen possesses a lower viscosity than that of Asphalt Ridge bitumen [193]. This indicates that the viscosity of bitumen is affected not solely by the asphaltene content but also by the polar constituents present in resins and aromatics. The observation that carboxylic acids within resins increase viscosity via hydrogen bonding with asphaltenes highlights their role as a significant contributing factor. Additionally, higher resin content was experimentally verified to improve bitumen ductility. Elseifi et al. used high-performance gel permeation chromatography to characterise molecular fractions in bitumen, highlighting the role of paraffinic maltenes in ductility and rutting resistance [194]. Sultana showed that mixing the polar fraction in proportionate amounts with the original bitumen samples led to an increase in hardness and tensile strength [195].

Efforts to create quantitative links between the physicochemical attributes and chemical parameters of bitumen have been ongoing. The reports from SHRP revealed significant correlations between fraction chemistry parameters and the rheological index, employing regression analysis on collected experimental data. [3]. Neural networks were used to determine the relationships between the chemical composition of bitumen (indicated by average molecular parameters) and rheological characteristics such as the creep slope at low temperatures and high temperature stiffness. [196].

Redelius employed linear fitting methods to examine the association between the rheological properties of bitumen and parameters of solubility models, utilising penetration, softening point, viscosity, and solubility parameters to predict the complex modulus and phase angle. [197]. Pipintakos et al. employed spectroscopic methods and rheological assessments to extract chemical and rheological parameters, demonstrating that both chemical composition and rheological

properties undergo similar alterations. This observation was derived in the context of laboratory aging, particularly following the rapid-rate phase of a dual oxidation scheme and short-term laboratory aging. [174]. Oyekunle investigated the relationship between SARA fraction parameters and bitumen properties and reported a non-linear relationship between ductility and the percentage of resins. Additionally, robust correlations of all SARA fraction parameters with the softening point were also reported [198]. Weigel et al. analysed the content and average molecular weight of SARA fractions, exploring the relationships between linear combination parameters and various characteristics including physical, rheological, aging, and adhesion parameters [16]. Wang et al. employed a linear combination approach to examine the links between chemical parameters, including SARA contents and indices of FTIR functional groups, and rheological characteristics [199]. Primerano et al. conducted chemo-mechanical correlations to identify ageing methods that are realistic to field ageing employing various techniques in their analysis. It was reported that the field ageing level could not be reached either with Viennese Binder Ageing (VBA) or with multiple PAV cycles. However, VBA could be a better approximation compared to the standard ageing procedures in lab [200]. Lastly, scholars have also investigated certain relationships that may exist with the surface microstructural patterns and the chemistry of bitumen, reporting trends between its compositional information (paraffinic waxes or asphaltenes) and various characteristics of the bee structures [140,162,201]. It has been speculated that the links between them could characterise the compositional nature of different bitumen.

6. Lessons learned and future directions

6.1. Use of appropriate evaluation techniques

The information provided in this review underscores the role of comprehending the complex nature of bitumen for practitioners to effectively use the tools described to address future engineering challenges. One of the main considerations in that aspect lies in evaluating the efficacy of commonly employed techniques in acquiring an understanding of the complex nature of bitumen. For example, a significant hurdle in the study of bitumen arises from its inherent variability. This variability poses a substantial challenge in interpreting results in a meaningful and applicable manner. While bitumen rheology and related indices prove advantageous in offering general applicability, the same cannot be readily said for the study of bitumen chemistry and microstructure. The diverse outcomes and testing methods available in literature further complicate the comprehension of different results in this domain, making it a formidable task to navigate for researchers. When considering the different tests utilised to evaluate the effectiveness of bitumen, empirical-based research in this field has consistently highlighted distinct differences in the meaningfulness of various testing methodologies. This prompts a fundamental question concerning the purpose and justification for conducting less impactful tests for the assessment of bitumen.

Take, for instance, the microstructure assessment of bitumen utilising AFM and other microscopy-based methods. Despite the considerable investment of several decades in research endeavours, the outcomes have yet to yield universally applicable insights beyond the mapping of microstructure and possibly some micromechanical-related properties [159]. The connection between these microstructural details and macroscopic properties remains largely speculative, posing a significant challenge and risk in establishing a cohesive and conclusive understanding. This raises a poignant question regarding the fundamental utility of these tests. Considering the limited progress in bridging the gap between micro- and macrolevel observations thus far, it becomes even more imperative to assess the value proposition of these methods in contributing substantively to the broader field of bitumen analysis and engineering applications. Various analytical techniques, including FTIR and GPC, have exhibited promise in extracting valuable insights concerning different facets of bitumen chemistry. Despite their potential utility, the persistent issue of result variability still raises significant concerns.

Addressing this challenge calls for a concerted effort to standardise both experimental procedures and analytical methodologies. Variable parameters such as material handling can become a concerning issue, depending on the level of observation from the respective analysis technique. This highlights the importance of temperature as well as loading both on rheologically complex binders and also on the obtained microscopic images. By establishing standardised protocols and norms for both experimentation and analysis, the research community can adopt a more cohesive foundation for interpreting results and drawing meaningful conclusions from these techniques. Related to this, the use of chemometrics to account for the role of temperature and loading could be a useful tool to unravel their influence on rheology and microstructure.

Nevertheless, it is also crucial to underscore the limitations of these methods. While FTIR, GPC, and similar approaches contribute valuable information, they inherently represent supplementary tools within the domain of bitumen analysis. More simply, these methods offer useful insights, yet they fall short of capturing the full complexity inherent in binders as they merely provide qualitative information related to the chemistry of the material. No absolute values are generated, making it difficult to interpret the obtained output compared to the results from mechanical testing, in which respective values like stiffness can directly be compared among a group of materials. Therefore, it is essential to acknowledge the inherent limitations and delineate these techniques as adjunctive rather than exhaustive. This also prompts a holistic consideration of the various analytical tools to navigate the intricacies of bitumen characterisation effectively. In this regard, directing the focus of future studies towards tests that elucidate the complex chemical processes within bitumen, notably utilising advanced techniques such as NMR, Proton Transfer Reaction (PTR) Mass Spectrometry and EPR, becomes paramount. Despite the inherent challenges in analysing and interpreting results from these methods, the potential dividends are considerable. These techniques hold the promise of unravelling key aspects of bitumen behaviour, thereby offering valuable insights for engineering superior materials to meet future challenges.

Previous research has emphasised the need to establish material level connections across diverse length scales, spanning from molecular and nanolevel to micro-, meso-, and macroscales, to comprehensively understand the performance of bitumen. Nevertheless, numerous unresolved questions persist, including whether fundamental changes occur at a comparable level in the chemistry and rheology of bitumen during various physicochemical processes. A substantial gap remains in the understanding of the evolving trends of specific chemical products concerning performance-related parameters. For example, the role of thermodynamic relaxation on the effectiveness of recycling agents on properties of aged bitumen can be better understood via the developing area of MD simulations. As mentioned, several studies have dedicated efforts to establishing correlations between ageing indices derived from FTIR spectroscopy and similar methods, representing oxygenated functional groups, and rheological indices. Despite these efforts, the universal applicability of results is hindered by the inherent variability in outcomes reported in literature. A key contributing factor is the infrequent use of statistical tools in bitumen analysis, often constrained by small datasets. To address this limitation effectively, there is a pressing need to extend datasets, either through experimental means or by leveraging information available in existing literature. Adopting more robust statistical analysis approaches, such as multivariate methods or non-parametric analyses is essential to further understanding the applicability of results. This aspect is notably absent in current bitumen research and represents a critical missing link that warrants the attention of the community. Nevertheless, it is emphasised that the physical significance underlying the observed results must be explored to ensure that they represent more than simply statistical correlations.

6.2. Extending pavement life and future paving materials

As we enter the next phase of circular economy in road construction, the adoption of higher levels of recycling is becoming imperative within the pavement industry. A key strategy for reducing material usage involves extending the lifespan of existing pavements. It is believed that a durable and sustainable material usage can only be achieved by a comprehensive understanding of the bitumen's nature via the interrelationships mentioned in the previous sections. Central to this objective is the careful consideration of ageing, a factor in relation to bitumen which influences pavement longevity and its recyclability. In-depth comprehension of the various facets of ageing, coupled with the development of engineering methods to mitigate its effects will continue to be an ongoing area of essential research for the community. Primarily, a sustained focus on understanding the ageing and oxidation phenomenon is paramount. Methods such as the FTIR, GPC, SARA analysis and others have emerged as reliable tools, demonstrating its effectiveness in tracking fundamental oxidation-related products such as carbonyls and discretisation of molecular groups. While analysis and results within the realm of individual studies may offer comparative results, the challenge again lies in the limited possibility of comparing outcomes across different research endeavours. Furthermore, the often-overlooked issues of repeatability and reproducibility also warrant careful consideration.

Most importantly, many commonly employed methods only provide superficial results when addressing the fundamental chemistry related to ageing. To gain a more profound understanding at molecular, nano-, and microscales, the use of more advanced instrumentation becomes imperative. Overcoming uncertainties and risks associated with underutilised spectroscopic, microscopic, and thermoanalytical tools necessitates a strategic approach as mentioned previously. By employing more advanced methods, it is possible to acquire a more profound understanding and fingerprint the ageing mechanisms and specific bitumen characteristics at higher chemical resolutions. This will empower practitioners to make informed design decisions and utilise specific additives such as antioxidants effectively to mitigate or reduce the extent of ageing. For example, when considering the use of antioxidants, there is a growing expectation that the use of such additives will become more prevalent as it can help significantly increase the longevity of pavements [202–204]. However, to optimise their application, it is essential to obtain fundamental information related to bitumen/antioxidant pairs that are tailored to specific use cases and utilities. Specifically, there is a need to further explore the interaction mechanisms between antioxidants and understand specific bitumen chemistry changes with the addition of such modifiers. This is essential in expediting the widespread adoption of this technology, providing a robust foundation for making well-informed decisions. In its absence, it merely ends up as a trial-and-error approach which is not conducive to large-scale viability. Similar can be said about any other type of less understood bitumen modifications such as the extended use of polymers, plastics or biomaterials.

6.3. Crucial aspects for future research

It is apparent from the information presented in this review that bitumen research has developed rapidly over the last few years, offering a multitude of data and scientific perspectives. There are several crucial aspects identified for further research.

First, the true impact of the scientific capabilities of underutilised techniques for bitumen can only be grasped when a multidisciplinary approach is adopted. This is of paramount importance to be realised by scholars worldwide in order to unravel the complex nature of bitumen. Only through such an interdisciplinary approach and collaboration among engineers, chemists, and physicists such techniques can be used to their maximum potential. Moreover, the data post-processing could be enhanced to capture hidden patterns that routine processing may not be capable of identifying.

The second point of future attention lies in the lack of standardised protocols for sample preparation, data analysis and processing. Often the existing illustrations of bitumen data at chemical, structural or rheological level are rather individual efforts, often missing the raw data or repeatability. Future research works are encouraged to provide and publish the datasets, analysis settings as well as detailed sample preparation steps. In that way, the reproducibility of the experimental works can be significantly enhanced. Finally, given that a sufficient number of datasets become available for researchers in a digital format, efforts can be directed to more sophisticated, machine-learning approaches.

CRediT authorship contribution statement

Georgios Pipintakos: Writing – review & editing, Writing – original draft. **Anand Sreeram:** Writing – review & editing, Writing – original draft, Conceptualization. **Johannes Mirwald:** Writing – review & editing, Writing – original draft. **Amit Bhasin:** Writing – review & editing, Writing – original draft.

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.

Data availability

No data was used for the research described in the article.

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