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Dissertation

Elucidation of Chemical Ageing Processes in Bituminous Construction Materials

A thesis submitted for the degree of
Doctor of Natural Science under the supervision of

Univ. Prof. Dr.rer.nat. Hinrich Grothe

E165 - Institute of Materials Chemistry
Research Unit Physical Chemistry

submitted at the Technical University Vienna

Faculty of Technical Chemistry

by

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Dissertation

Aufklärung der chemischen Alterungsprozesse in Bituminösen Baumaterialien

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines Doktors der Naturwissenschaften unter der Leitung von

Univ. Prof. Dr.rer.nat. Hinrich Grothe

E165-01 Institut für Materialchemie,
Forschungsbereich Physikalische Chemie

eingereicht an der Technischen Universität Wien

Fakultät für Technische Chemie

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Abstract

Bitumen is an essential component of modern infrastructure, where it is predominantly used as a binder in road engineering and as a sealing material in roofing applications. The unique combination of viscoelastic, waterproofing, and adhesive behaviour has made it a versatile and reliable product. The main problem, however, is that bituminous materials have an expiry date. During use, rheological and mechanical properties deteriorate, which can ultimately lead to material failure. In such cases, repairs or new constructions are unavoidable, which requires resources (raw materials, energy and money) and contributes to increased emissions of carbon dioxide, volatile organic compounds and aerosols. Extensive research has shown that the decline in performance is related to chemical changes in bitumen, but the contributions of individual molecular processes are not fully understood. Furthermore, an effective assessment of the initial quality and chemical degradation of the materials needs to be developed. Therefore, this work evaluated spectroscopic methods that could fill this scientific gap. Based on these studies, an analytical framework was established to investigate field ageing processes in unmodified and styrene-butadiene-styrene (SBS) modified bitumen (PMB) and to determine the strengths and weaknesses of standardised and novel laboratory ageing devices.

Nuclear magnetic resonance (NMR), electron paramagnetic resonance, infrared and fluorescence spectroscopy were used for analysis. The information obtained using these methods and their sensitivity to ageing-induced changes was investigated in preliminary studies with seven samples. These experiments have shown that various parameters, such as carbonyl-, sulfoxide-, organic radical-, vanadyl content, aromaticity, and aromatic system size, are reproducibly obtainable. Vanadyl content, fluorescence properties, and sulfoxide content strongly depended on the crude oil source and manufacturing process, which is potentially valuable for origin determination. Standardised thermal ageing, using the rolling thin-film oven (RTFO, thermal ageing) and the pressurised ageing vessel (PAV, thermal ageing), showed that the amount of carbonyls, sulfoxides, and organic radicals and the amount and size of aromatic systems changed significantly in all samples.

In the field, oxygen was continuously incorporated into the material, producing carbonyls and sulfoxides as main products and aliphatic alcohols and carboxylic acids as by-products. At the same time, molecular groups already present in the starting material (amides/quinolones and porphyrins) were degraded or linked intermolecularly with larger molecular structures during ageing. Analysis of the aromatic systems showed that the content of aromatic molecules decreased due to evaporation and structural rearrangements and that the size of the aromatic systems increased due to polycondensation and dehydrogenative coupling reactions. In a study that compared the ageing in unmodified and polymer-modified bitumen samples, the oxidation rates were shown to be very similar. However, additional reactions at the polymer skeleton (at olefinic and allylic positions) and degradation processes originating from the polybutadiene phase were observed. In PMBs, these processes must be considered as additional influencing factors for rheological and mechanical property deterioration. Interestingly, the aromaticity in the bitumen phase of the field-aged PMB samples did not decrease. This was attributed to direct and indirect protective mechanisms, such as intermolecular bonding (reduction of vapour pressure) and preferential reactions at the polymer backbone (polymer as a sacrificial lamb).

The assessment of laboratory ageing was carried out with the RTFO (thermal ageing), the PAV (thermal ageing), the Viennese binder ageing reactor (VBA, thermochemical ageing) and a photoreactor (light ageing). Studies on thermal ageing (RTFOT, PAV, VBA) have shown that sulfoxide formation is lower compared to field ageing due to competing decomposition reactions. The effects on the aromatic groups were different for all ageing procedures. VBA induced a similar growth of aromatic systems (sizes) as field ageing but, at the same time, led to a higher loss of aromatic structures. On the contrary, PAV ageing simulated the loss of aromatic structures better than VBA but did not lead to the same growth as in the field. The flawed ageing simulation becomes apparent in both cases, probably due to a delicate balance of competing reactions (evaporation vs. degradation vs. oxidation vs. aromatisation).

The light ageing experiments helped to clarify the initial molecular processes on the surface of bituminous materials. Light induced a different range of oxidation products (alcohols, carboxylic acid esters and acids) and impacted aromatic structures more than thermal ageing procedures. The rapid effects of solar radiation (UV and visible light) and the potential influences of sample heterogeneity were investigated by monitoring the oxygen uptake and fluorescence properties of bitumen and its polarity-based fractions. The results indicate oxidation and molecular rearrangement reactions occurring mainly in the oily components, the aromatics and the resins, while the saturates are hardly altered, and the asphaltenes are not altered at all by light ageing.

In this work, a robust and unique analytical framework was created, with the help of which new details on molecular processes in the field could be found. The new findings helped elucidate the differences between field ageing and standardised and novel laboratory ageing methods in detail. Based on the developed/adapted analytics, ageing procedures can be optimised, which can be used to determine the quality of raw materials/industrial products and the influence of additives and recycled materials on the expected service life. The improved quality control and the controllable optimisation of bituminous products thus pave the way for a more sustainable industry.

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Kurzfassung

Bitumen ist ein wesentlicher Bestandteil der modernen Infrastruktur, wo es vor allem als Bindemittel im Straßenbau und als Abdichtungsmaterial im Dachbereich eingesetzt wird. Die einzigartige Kombination aus viskoelastischem, abdichtendem und adhäsivem Verhalten hat es zu einem vielseitigen und zuverlässigen Produkt gemacht. Das Hauptproblem ist jedoch, dass bituminöse Materialien ein Verfallsdatum haben. Im Laufe der Nutzung verschlechtern sich die rheologischen und mechanischen Eigenschaften, was schließlich zum Versagen des Materials führen kann. In solchen Fällen sind Reparaturen oder Neubauten unvermeidlich, was Ressourcen (Rohstoffe, Energie und Geld) erfordert und zu erhöhten Emissionen von Kohlendioxid, flüchtigen organischen Verbindungen und Aerosolen beiträgt. Umfangreiche Forschungsarbeiten haben gezeigt, dass die Verringerung der Performance mit chemischen Veränderungen im Bitumen zusammenhängt, aber die Beiträge der einzelnen molekularen Prozesse sind noch nicht vollständig bekannt. Außerdem müssen wirksame Techniken zur Bewertung der Qualität und des chemischen Abbaus der Materialien entwickelt werden. In dieser Arbeit wurden daher spektroskopische Methoden bewertet, die diese wissenschaftliche Lücke schließen könnten. Auf der Grundlage dieser Studien wurde ein analytischer Rahmen entwickelt, um Alterungsprozesse in unmodifiziertem und Styrol-Butadien-Styrol (SBS) modifiziertem Bitumen (PMB) im Feld zu untersuchen und die Stärken und Schwächen standardisierter und neuartiger Laboralterungsreaktoren zu ermitteln.

Zur Analyse wurden Kernspinresonanz (NMR)-, Elektronenspinresonanz-, Infrarot- und Fluoreszenzspektroskopie eingesetzt. Die mit diesen Methoden gewonnenen Informationen und ihre Empfindlichkeit gegenüber alterungsbedingten Veränderungen wurden in Vorstudien mit sieben Proben untersucht. Diese Versuche haben gezeigt, dass verschiedene Parameter wie der Gehalt an Carbonylen, Sulfoxiden, organische Radikalen, Vanadylen, und die Aromatizität und Größe des aromatischen Systems reproduzierbar ermittelt werden können. Der Vanadylgehalt, die Fluoreszenzeigenschaften und der Sulfoxidgehalt hingen dabei stark von der Rohölquelle und dem Herstellungsprozess ab, was für die Herkunftsbestimmung genutzt werden könnte. Die standardisierte thermische Alterung mit dem rollierenden Dünnschichtofen (RTFO, thermische Alterung) und dem Druckalterungsgefäß (PAV, thermische Alterung) zeigte, dass sich die Menge an Carbonylen, Sulfoxiden und organischen Radikalen sowie die Menge und Größe der aromatischen Systeme in allen Proben deutlich veränderten.

Im Feld wurde kontinuierlich Sauerstoff in das Material eingebaut, wobei Carbonylgruppen und Sulfoxide als Hauptprodukte und aliphatische Alkohole und Carbonsäuren als Nebenprodukte entstanden. Gleichzeitig wurden bereits im Ausgangsmaterial vorhandene Molekülgruppen (Amide/Chinolone und Porphyrine) abgebaut oder während der Alterung intermolekular mit größeren Molekülstrukturen verknüpft. Die Analyse der aromatischen Systeme ergab, dass der Gehalt an aromatischen Molekülen aufgrund von Verdampfung und strukturellen Umlagerungen abnahm und dass die Größe der aromatischen Systeme aufgrund von Polykondensation und dehydrierenden Kopplungsreaktionen zunahm. In einer Studie, in der die Alterung von unmodifizierten und polymermodifizierten Bitumenproben verglichen wurde, erwiesen sich die Oxidationsraten als sehr ähnlich. Es wurden jedoch zusätzliche Reaktionen am Polymerskelett (an olefinischen und allylischen Positionen) und von der Polybutadienphase ausgehende Abbauprozesse beobachtet. Bei PMBs müssen diese Prozesse als zusätzliche Einflussfaktoren für die Verschlechterung der rheologischen und mechanischen Eigenschaften betrachtet werden. Interessanterweise nahm die Aromatizität in der Bitumenphase der feldgealterten PMB-Proben nicht ab. Dies wurde auf direkte und indirekte Schutzmechanismen wie intermolekulare Bindungen (Verringerung des Dampfdrucks) und Vorzugsreaktionen am Polymergerüst zurückgeführt.

Die Bewertung der Laboralterung wurde mit dem RTFO (thermische Alterung), dem PAV (thermische Alterung), dem Wiener Bindemittelalterungsreaktor (VBA, thermochemische Alterung) und mit einem Photoreaktor (Lichtalterung) durchgeführt. Untersuchungen zur thermischen Alterung (RTFOT, PAV, VBA) haben gezeigt, dass die Sulfoxidbildung aufgrund konkurrierender Zersetzungsreaktionen geringer ist als bei der Feldalterung. Die Auswirkungen auf die aromatischen Gruppen waren bei allen Alterungsverfahren unterschiedlich. VBA induzierte ein ähnliches Wachstum der aromatischen Systeme wie die Feldalterung, führte aber gleichzeitig zu einem höheren Verlust an aromatischen Strukturen. Im Gegensatz dazu simulierte die PAV-Alterung den Verlust aromatischer Strukturen besser als die VBA, führte aber nicht zu demselben Wachstum wie im Feld. Die fehlerhafte Alterungssimulation wird in beiden Fällen deutlich, was wahrscheinlich auf ein empfindliches Gleichgewicht konkurrierender Reaktionen (Verdampfung vs. Abbau vs. Oxidation vs. Aromatisierung) zurückzuführen ist.

Die Experimente zur Lichtalterung trugen zur Klärung der anfänglichen molekularen Prozesse an der Oberfläche von bituminösen Materialien bei. Licht induzierte ein anderes Spektrum von Oxidationsprodukten (Alkohole, Carbonsäureester und Säuren) und beeinflusste die aromatischen Strukturen stärker als thermische Alterungsverfahren. Die raschen Auswirkungen der Sonnenstrahlung (UV- und sichtbares Licht) und die potenziellen Einflüsse der Probenheterogenität wurden durch die zeitaufgelöste Bestimmung von Sauerstoffaufnahme und der Veränderungen der Fluoreszenzeigenschaften von Bitumen und seinen Polaritätsfraktionen untersucht. Die Ergebnisse deuten auf Oxidations- und molekulare Umlagerungsreaktionen hin, die hauptsächlich in den öligen Komponenten, den Aromaten und den Resinen stattfinden, während die Saturates kaum und die Asphaltene überhaupt nicht durch Lichtalterung verändert werden.

In dieser Arbeit wurde ein robuster und einzigartiger analytischer Rahmen geschaffen, mit dessen Hilfe neue Details über molekulare Prozesse im Feld gefunden werden konnten. Die neuen Erkenntnisse trugen dazu bei, die Unterschiede zwischen der Alterung im Feld und den standardisierten und neuartigen Alterungsmethoden im Labor im Detail aufzuklären. Auf der Basis der entwickelten/adaptierten Analytik können so Alterungsverfahren optimiert werden, die zur Qualitätsbestimmung von Rohstoffen/Industrieprodukten und zur Ermittlung des Einflusses von Additiven und Rezyklaten auf die zu erwartende Lebensdauer eingesetzt werden können. Die damit ermöglichte Qualitätskontrolle und kontrollierbare Optimierung von bituminösen Produkten ebnet den Weg für eine nachhaltigere Industrie.

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List of Abbreviations

AI	Ageing index based on FTIR
ASTM	American Society for Testing and Materials
ATR	Attenuated total reflection
CEN	European Committee for Standardization
DOSY	Diffusion-ordered spectroscopy
EN	European Norm (European Standards)
EPR	Electron paramagnetic resonance
FEEM	Fluorescence excitation-emission map
FTIR	Fourier transformation infrared spectroscopy
FS	Fluorescence spectroscopy
HMA	Hot-mix asphalt
HMBC	Heteronuclear multiple bond correlation
HSQC	Heteronuclear single-quantum coherence
LTA	Long-term ageing
NMR	Nuclear magnetic resonance
OR	Organic radical
PAV	Pressure ageing vessel
PB	Polybutadiene blocks of SBS
PEN grade	Penetration grade of bitumen
PMB	Polymer-modified bitumen
PPM	Parts per million
PS	Polystyrene blocks of SBS
RAP	Reclaimed asphalt pavement
ROS	Reactive oxygen species
RTFOT	Rolling thin-film oven test
SARA	Saturates, aromatics, resins, and asphaltenes
SBS	Styrene-butadiene-styrene
STA	Short-term ageing
TFOT	Thin-film oven test
UV/VIS	Ultraviolet/Visible
VBA	Viennese binder ageing
VO^{2+}	Vanadyl ion
VOC	Volatile organic compound
WMA	Warm-mix asphalt

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1. Introduction

1.1. Bituminous construction materials

Bitumen has a long and fascinating history as a construction material, spanning thousands of years and evolving from simple waterproofing and adhesive uses in prehistoric and ancient times to sophisticated road construction and industrial applications today. Its natural occurrence in seeps made it readily available to prehistoric civilizations, where the roots of the use of bitumen can be traced back to hunter-gatherers in the Palaeolithic period, who recognised the adhesive properties of bitumen and used it to make hunting tools from wooden handles and stones[1, 2]. The Mesopotamians incorporated bitumen extensively in their architectural endeavours, employing it for waterproofing baths, boats, and as mortar in the construction of iconic structures like ziggurats and city walls[1-3]. The Egyptians imported bitumen for embalming and mummification[1, 2], while the Greeks and Romans recognized its valuable waterproofing and adhesive properties[2, 4]. Throughout medieval times, bitumen continued to be used[5], although greater interest did not revive until the Renaissance[6, 7].

The turning point for bitumen came in the 18th century with the development of modern road construction techniques in Europe, particularly in England and France[8-10]. Bitumen emerged as a binding agent with mineral aggregates, leading to the paving of roads. Paris took a pioneering role in constructing the first modern bituminous roads, laying the foundation for today’s asphalt pavement[8, 9]. Another critical step was the development of the modern oil refining industry, which started in the 19th century with the discovery of abundant oil reserves and the development of refining techniques[11, 12]. The rise of automobile usage in the 20th century prompted the global expansion of bitumen road construction to facilitate better road networks[13]. Technological advancements followed, including the development of hot-mix asphalt and new forms of road surface treatments[14]. Beyond roads, bitumen became a staple in waterproofing, roofing materials, and insulating products[15]. In many application areas, adding modifiers became necessary to meet the required specifications[16]. Particularly, the advent of synthetic polymers, such as thermoplastic elastomers (e.g. polyethylene (PE), polypropylene (PP) and ethylene-vinyl acetate (EVA)) and plastomers (e.g. styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIB)), has contributed to the worldwide use and commercialisation of modified bituminous products[16-18]. Polymer modification has proven itself over many years and has significantly expanded the application possibilities of bitumen[16-18].

However, bituminous materials have finite lifespans[15, 19]. Molecular processes alter the interactions in the material, which impacts the rheological and mechanical properties and can lead to material failure[15, 19]. The shorter the average service life of the products, the more repairs or reconstructions are necessary, which increases the consumption of raw materials and the generation of CO_2, volatile organic compounds (VOCs) and aerosols[20-23]. Therefore, research into the degradation of asphalt and a correlation between degradation and starting materials (which binders are ‘good’?), process parameters (how to improve it?), and additives (performance improvements?) is essential to extend the use-life of bituminous products and lay the foundations for a sustainable industry. Other innovations like warm-mix asphalt[1] (WMA)

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[1] WMA: Production, placement and compaction of asphalt pavement at lower temperatures than hot-mix asphalt

technologies and reclaimed asphalt pavement (RAP)[2] are heading in the same direction, as they aim to reduce emissions (gaseous species and aerosol particles), minimise short-term ageing contributions[24, 25], and optimise the use of material resources[26-28]. Ultimately, all these approaches are intended to reduce the consumption of bituminous raw materials, energy, costs, and environmental impact.

This thesis focused on the investigation of chemical ageing processes and the evaluation and adaptation of suitable analysis methods. Therefore, a detailed introduction to bitumen's elemental, molecular and structural composition and the known aspects of ageing is given first. This is followed by a summary of the open questions, the aim of this work and the methodology. Finally, the scientific publications that form the basis of this work are presented and discussed in detail.

1.2. Bitumen chemistry

Bitumen is a complex mixture of organic molecules[15, 19, 29]. However, it has no strictly definable molecular composition. The reasons for the structural variety are differences in the natural formation processes and the manufacturing processes in the refinery[30]. Petroleum formation is a geological process that takes place over millions of years, involving the transformation of organic matter into hydrocarbons. It begins with the accumulation of organic debris, such as microscopic algae and marine plankton, in sedimentary basins. As layers of sediment bury these organic materials, the combination of heat, pressure, and time leads to the decomposition of the organic matter into a waxy substance called kerogen. Further geological processes, including thermal maturation and migration, cause the kerogen to undergo additional transformations, yielding liquid hydrocarbon mixtures. These hydrocarbons migrate through porous rock formations until they are trapped in reservoirs, forming petroleum deposits. The composition of crude oil varies widely, reflecting the types of organic matter present and the geological conditions of the source rock[31, 32].

Detectable bioorganic structures, such as porphyrins, isoprenoids, and steranes, strongly indicate the biological origin of crude oil[29, 33]. Those are the primary sources of hydrogen and carbon. Abundant heteroatoms (nitrogen, oxygen, and sulfur) and metals can be traced back to biological structures and (thermo-bio)chemically reduced minerals from the oil source rock. The high content and variability of sulfur are especially interesting. The incorporation of sulfur happens mainly in the kerogen state. Anaerobic bacteria reduce sulfate to hydrogen sulfide (H_2S). If metal ions (e.g., Fe^{2+} or Cu^{2+}) are absent in the surrounding minerals, H_2S is (bio)chemically oxidized to elemental sulfur, which reacts with kerogen to form organic sulfides. The amount of organic sulfides present in crude oil depends on the minerals surrounding the crude oil deposits (trap sulfur in metal sulfides, which do not react with kerogen) and the thermal history (high temperatures lead to loss of sulfur)[33].

The next step towards bituminous products is the crude oil refining process. The crude oil is heated in a furnace and fed into a distillation tower. Inside the tower, the crude oil is heated at the bottom, causing it to vaporize. As the vapours rise through the rectification column, they gradually cool and condense at different heights based on their boiling points. During distillation, bitumen and other heavy components, such as fuel and lubricating oil, remain at the

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[2] RAP: Asphalt pavements that are removed for reconstructions, resurfacing, or other construction activities

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bottom of the distillation tower, known as the residue. While crude oil distillation separates bitumen from lighter fractions such as gasoline, diesel, and kerosene, it does not produce bitumen as a distinct product. Once separated, the atmospheric residue may undergo further processing, such as vacuum distillation or bitumen blowing, to enhance its properties for specific applications like road construction or waterproofing[11, 15, 34].

In order to understand the impact of distillation and to elucidate the differences between bitumen and coal tar (frequently used in road construction in the past[15]), the elemental compositions of these three organic mixtures were compared in Table 1 and Table 2. The H/C ratio[3] is lower in bitumen than in crude oil due to the loss of small and medium-sized aliphatic hydrocarbons (with a high H/C ratio) during distillation. The comparison with coal tar shows that the latter contains more (poly-)aromatic functionalities and fewer aliphatic side chains, indicated by a low H/C ratio and an extraordinarily high carbon content. Besides the hydrocarbon basic building blocks, heteroatoms such as sulfur, oxygen, and nitrogen are present. Their abundance varies based on the crude oil source and the manufacturing process in the refinery[15]. Depending on the direct geological environment of the crude oil source, traces of metals are also regularly detected in bitumen[15]. The most frequently occurring are vanadium (avg. 254 ppm, 7-1590 ppm), nickel (avg. 83 ppm, 10-139 ppm), iron (avg. 67 ppm, 5-147 ppm), calcium (avg. 118 ppm, 1-335 ppm), and sodium (avg. 63 ppm, 6-159 ppm) [35, 36].

Table 1. Elemental composition of crude oil, bitumen, coal and coal tar.

Element	**Crude oil** [11, 33, 34, 37, 38]	**Bitumen**[15, 29, 35, 36]	**Coal tar**[39, 40]
Hydrogen (%)	10.00-15.00	9.80-11.70	4.32-4.79
Carbon (%)	82.00-87.00	80.20-87.10	91.85-92.90
Sulfur (%)	0.05-6.10	0.50-6.90	0.43-0.79
Oxygen (%)	0.05-1.62	0.20-2.25	0.97-1.16
Nitrogen (%)	0.10-2.00	0.20-1.20	1.47-1.58

Table 2. H/C ratio of crude oil, bitumen, and coal tar.

Parameter	**Crude oil**[38]	**Bitumen**[15, 29, 35, 36]	**Coal tar** [39, 40]
H/C ratio (-)	1.72-2.27	1.42-1.59	0.56-0.62

Those elements form a wide range of molecules in the material. Many structural motifs and functional groups have been found and described based on structure identification with spectroscopic and mass spectrometric techniques[15, 19, 29]. Table 3 summarises those functionalities and groups them in aliphatic, aromatic, (multiple) heteroatom-containing, and metastable compounds.

---

[3] H/C ratio: The average ratio of the number of hydrogen atoms to the number of carbon atoms. Indicates the degree of saturation in organic mixtures. Saturated molecules (H/C~2) increase the ratio, while (poly)aromatic molecules (≤1) decrease the ratio in typical hydrocarbon mixtures.

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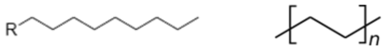
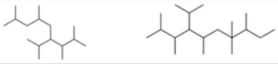
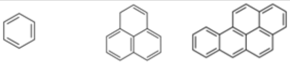
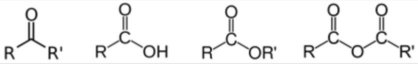
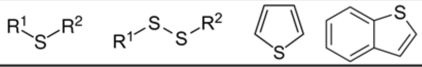
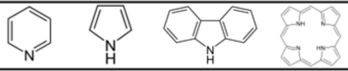
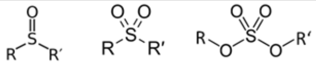
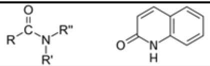
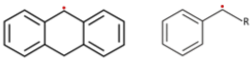
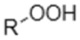
Table 3. Molecular structures in bitumen. General Functionalities, structural motifs, and examples[15, 19, 29, 35].

General functionality	**Structural Motif/Functional group**	**Structural examples**
Aliphatic compound	Linear chains	
	Branched aliphatic structures	
	Cyclic structures (naphthenes)	
Aromatic compound	Aryl compounds	
	Aromatic and polyaromatic compounds	
Heteroatom containing compounds	Ketones, carboxylic acids, esters, anhydrides	
	Aliphatic alcohols, aromatic alcohols (Phenols)	
	Sulfides, Disulfides, (Benzo-)Thiophenes	
	Pyridines, pyrrols, carbazoles, porphyrines	
Compounds with multiple heteroatoms	Sulfoxides, sulfones, sulfates	
	Amides, quinolones	
Metastable compounds	Organic radicals	
	Peroxides	

Aliphatic functionalities are found as singular molecules and attached to aromatic and heteroaromatic compounds. They appear as linear, branched, and cyclic structures. According to Strausz et al., n-alkanes are the dominant species, while isoprenoids and higher-branched alkanes follow in significantly lower concentrations[29]. Aromatic compounds occur from single-ring to polycondensed multi-ring systems and in aryl structures (e.g., biphenyl and triphenyl)[29]. Additional aromatic groups that contain heteroatoms, such as pyrroles, pyridines, carbazoles, quinolines, porphyrins, and (benzo)thiophenes, widen the range even further[19, 29]. Sulfur is mainly present in open-chained and cyclic (thiolanes, thianes) sulfides[29]. Oxygen-containing structures are formed during oxidation, comprising ketones, carboxylic acids, carboxylic anhydrides, and alcohols[19]. Other structures with multiple heteroatoms are quinolones, sulfoxides, sulfones, sulfates, and metal porphyrins[19, 29]. Rarely discussed structural units are organic radicals, whose occurrence and stability have been confirmed in numerous studies [41-44], and peroxides, whose involvement in the ageing process has been described theoretically. [19, 45].

In the characterization of bitumen, separating molecules based on polarity has become an important analytic step to facilitate the detection of the functionalities mentioned above [15]. Bitumen is dissolved in n-alkanes, resulting in a non-dissolvable black residue (asphaltenes) and a brown solution (maltenes). Using chromatographic techniques facilitates the fractionation of maltenes into saturates, aromatics, and resins. The fractions obtained are known under the generic name SARA (saturates, aromatics, resins, asphaltenes)[15]. Average aromaticity, heteroatom content, and molecular size usually increase from low polarity (saturates) to high polarity (asphaltenes)[15]. Based on this categorization, elemental analysis, and structural information from spectroscopy and mass spectrometry, model compounds have been postulated to represent the average SARA molecule (see Figure 1)[46-49]. Those molecular models are used for molecular simulations[46-49], but they also help to understand that most of the appearing molecules are combinations of the structural motifs shown in Table 3.

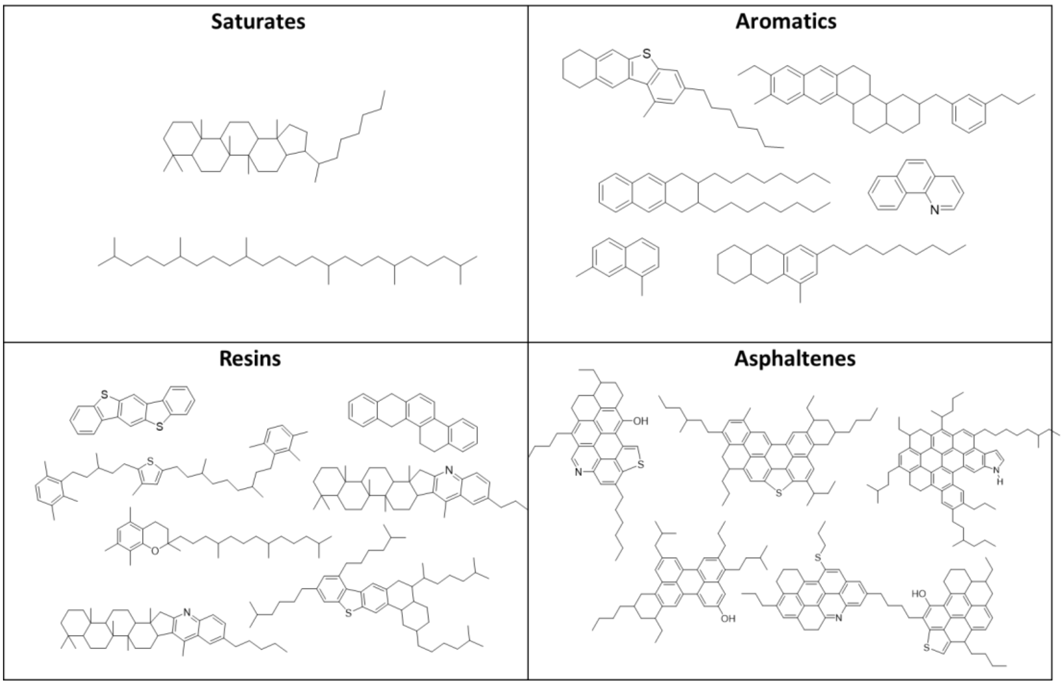


Figure 1. Average molecular structures of the SARA fractions as used in molecular dynamics simulations[46-49].

In particular, asphaltenes play a critical role in intermolecular interactions, aggregation processes, and the formation of nano- and microstructures[50-52]. Gray et al. [50-52] traced island[4] and archipelago[5] structures in the asphaltenes and found source and processing parameter dependencies in their relative distributions. Archipelago architectures mainly contribute to the formation of nano- and microaggregates due to a higher degree of freedom of interactions between multiple groups[50]. The most impactful drivers for aggregation[50] were acid-base, free radical pancake bonding[53], and charge transfer interactions. Medium to weak contributors were determined as van der Waals, polar group dipole-dipole, hydrogen bonding, and π-π interactions[50]. The molecular weights of the nanoaggregates reached up to 40 kDa[50]. A theoretical framework from nanoaggregates to nano- and microstructures was proposed in the 60s and further developed in recent years [54-56]. Based on X-ray and neutron scattering techniques, structures of different size ranges have been observed and thoroughly discussed[57]. Heterogeneity within the bituminous phase has been demonstrated with microscopic studies of the surfaces revealing elongated structures in the µm size range, referred to as 'bee' structures[58, 59].

However, as discussed in Chapter 1.1, neat bitumen binders' mechanical and rheological properties are insufficient for some applications. In such cases, polymers modify the rheological and mechanical properties. But what does this mean regarding bitumen chemistry?

---

[4] Island structures: Compounds with a single aromatic core with (up to) seven fused rings and alkyl side chains

[5] Archipelago structures: Compounds with multiple aromatic cores that are linked by covalent bonds

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This section focuses on the triblock copolymer Styrene-Butadiene-Styrene (SBS), one of the most used polymers in road construction[16]. The molecular structure is represented in Figure 2. The polystyrene (PS) block contains the phenylic ring, a methin group in the α position (benzylic position), and a methylene group in the β position to the aromatic ring. The polybutadiene (PB) groups consist of olefinic units in the polymeric backbone (cis or trans configuration) or in the side chains, referred to as vinyl functionalities. Furthermore, in the regions with the olefinics in the backbone, methylene groups in the α position are present. At the same time, the monomeric units containing vinyls have a methin group in the α position and a methylene group in β position to the vinyl group.

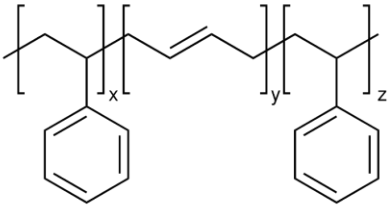

Figure 2. Molecular structure of the linear triblock copolymer styrene-butadiene-styrene (SBS).

The addition of SBS changes the chemistry of polymer-modified binders (PMBs) on multiple levels. Elementally, carbon and hydrogen's relative contents increase while the shares of heteroatoms and transition metals decrease [60]. Molecularly, olefinic, and allylic structural motifs are introduced, which might influence the reactivity and susceptibility of the whole product (detailed discussion in chapter 1.4)[16]. Due to aromatic subunits, those macromolecules also exhibit autofluorescence behaviour[61-64], which has to be considered when analysing the fluorescence properties of the composite. Linear SBS forms physically interlinked networks on a (molecular) structural level[17, 18, 65, 66]. Elasticity is attributed to PB blocks, while PS blocks are the main contributors to the sturdiness[17]. The PMB composite forms a two-phase system consisting of a polymer-rich and a bitumen-rich phase[15, 67, 68]. The continuous phase depends on the SBS content and the miscibility between bitumen and polymer[15]. Phase stability is influenced by physical segregation due to differences in density/weight during storage or transportation and chemical exchange processes between the phases[17, 18, 67, 69-71]. The latter refers to the absorption or intermolecular linkage of low-polar bitumen molecules (e.g., molecules from the saturates and aromatics fraction) to the PS subunits of the polymer (=polymer swelling)[17, 18, 67, 71].

In road engineering, bituminous binder materials are mixed with mineral aggregates to form asphalt mixtures[15]. Exemplary minerals are limestone and basalt, which consist of $CaCO_3$, MgO, Fe_2O_3, SiO_2, and Al_2O_3[72, 73]. Additionally, small inorganic aggregates are added (filler, 2-12 wt.% of the total mineral content, US classification: <75 µm, European classification: <63 µm), which form the so-called mastic phase with bitumen[15]. The interactions between bitumen molecules and aggregates are another critical point influencing the structural stability of bituminous products. In particular, adhesion and absorption tendencies of bitumen molecules towards mineral aggregates strongly depend on the aggregates' geometry (size distribution, shapes, total surface area) and the chemical characteristics of both phases[15, 74-80]. Thus, there is a link between bitumen chemistry and performance related parameters of bituminous construction materials. The variability of bitumen chemistry (based on crude oil source, manufacturing process), and the changes throughout its use-life might impact the interactions between aggregates and bitumen matrix. However, a detailed discussion of this topic was avoided at this point, as the analytical framework did not include any studies on mastics and asphalt mixtures.

1.3. Bitumen analysis

One of the basic techniques for analysing bitumen's composition and structural properties is the polarity-based separation into the SARA fractions: saturates, aromatics, resins, and asphaltenes[15, 81]. The standardized method is ASTM D4124, developed by Corbett[82, 83], but many adaptations of this technique have been reported in the literature[81, 84]. They all share that asphaltenes are separated from maltenes based on their insolubility in n-alkanes (e.g., n-heptane). The maltenes are applied to a chromatographic system (e.g., thin plates[85], packed glass columns[82], solid-phase extraction columns[81]) in which three groups of molecules, saturates, aromatics, and resins are obtained. In bitumen research, SARA fractionation is used to evaluate fractional content and estimate colloidal indices[15, 86]. Besides that, SARA separation reduces the system's complexity, facilitating the detection of additional molecular functionalities[87, 88].

Other approaches involve the use of spectroscopic and scattering methods. These techniques rely on the interaction of electromagnetic radiation with matter, leading to the absorption, emission, or scattering of light at different wavelengths. The whole spectral range, the electromagnetic spectrum, the different subsections, exemplary spectroscopic techniques, and the ongoing processes in molecules, atoms, and nuclei are shown in Figure 3.

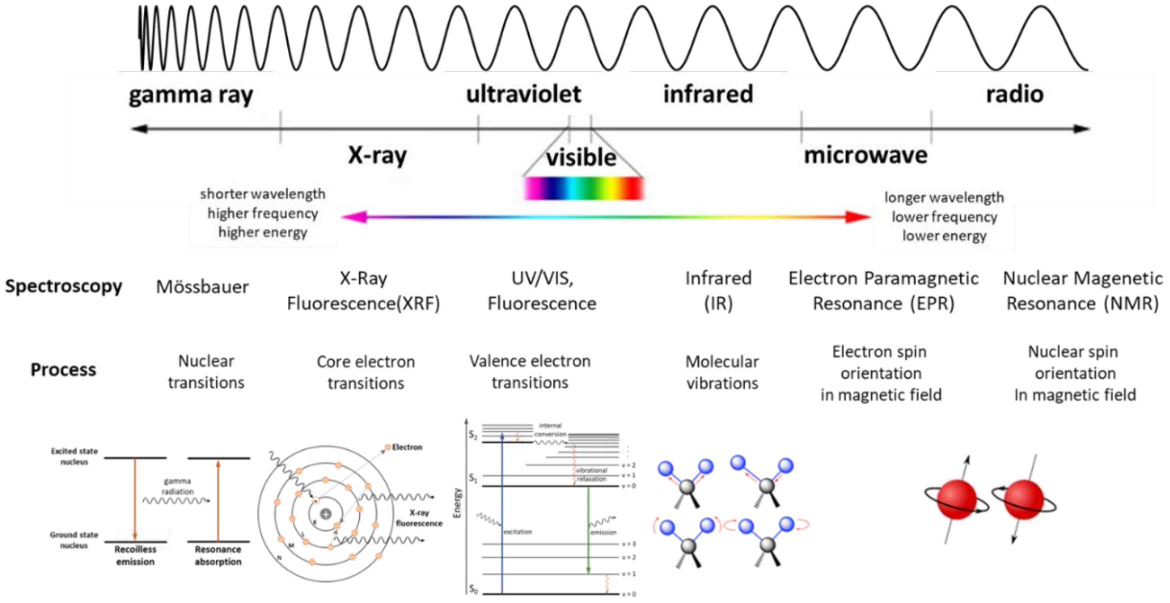

Figure 3. Electromagnetic spectrum, spectral ranges, exemplary spectroscopic techniques, fundamental processes.

All these methodologies can be used to obtain specific information about materials. Figure 4 gives an overview of typically applied techniques and their value in the analysis of bituminous products.

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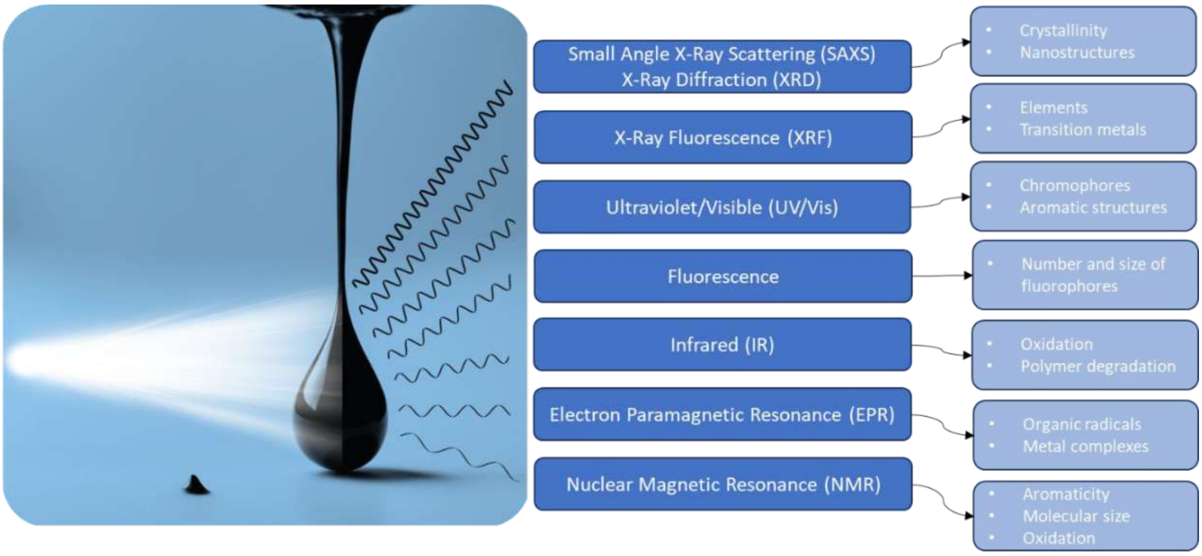

Figure 4. Physico-chemical techniques and available information in bitumen analysis. This image was created with the assistance of DALL·E 2.

Of the techniques mentioned, nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), infrared (IR) and fluorescence spectroscopy were used extensively in the studies of this thesis. Their theoretical background is therefore presented in the upcoming paragraphs.

NMR spectroscopy examines the magnetic properties of atomic nuclei. When subjected to a strong magnetic field and radiofrequency radiation, specific nuclei (e.g., ^{1}H, ^{13}C, ^{14}N, ^{31}P) absorb and emit energy at characteristic frequencies, offering detailed insights into their chemical environments. Key information extracted from these techniques includes[89]:

- Chemical shifts: Resonant frequency of atomic nuclei relative to a standard in a magnetic field. These shifts, influenced by the electronic environment, enable the identification of functional groups within a compound.
- Integration: The area under a peak in the spectrum correlates with the number of nuclei contributing to that peak, offering quantitative insights into the relative abundance of different functionalities.
- Spin-spin coupling: Interactions of different spin states (of NMR active nuclei) through chemical bonds (scalar coupling, J coupling) or through space, resulting in the splitting of NMR signals.

Researchers have demonstrated that NMR spectroscopy can yield molecular parameters (e.g., aromaticity, aliphatic side chain length, number of alkyl substituents) of bitumen, which are used to gain unique insights into ageing processes[43, 44, 90-95].

EPR spectroscopy investigates materials with unpaired electrons, like free radicals and transition metal ions. It relies on the absorption of microwaves by these unpaired electrons in a magnetic field, yielding information on electronic structure, spin dynamics, and chemical environment[96]. Only organic radicals and vanadyl (VO^{2+}) ions are detectable in bitumen[43, 44]. The usually very reactive carbon-centred organic radicals are metastable in bitumen, proven by their presence and persistence in samples from ancient Egyptian mummies[41]. Vanadyl ions appear as central ions of organic complexes, such as porphyrins. Vanadyl content is stable during ageing and can aid in geographic origin evaluation (content is source-dependent)[43]. The content of organic radicals, on the other hand, increases with ageing, and thorough studies have shown the kinetics of this increase[43].

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Molecules exhibit vibrational motion when exposed to infrared light. This process is the basis of IR spectroscopy, which has become one of the cornerstones for the routine analysis of organic compounds. IR techniques can quickly and easily provide information about structural units and their changes in molecules and complex mixtures[97]. The main usage of IR in bitumen research is in ageing studies, where the oxidation processes are monitored by quantifying spectral bands that can be linked to carbonyls and sulfoxides[19, 87, 88, 92, 98-100]. Further studies expand the evaluation to aromatic, aliphatic, and polymeric groups or even employ multivariate data analysis for improved assessment of the ageing state[43, 44, 101-104].

Fluorescence spectroscopy is based on the absorption of electromagnetic radiation in the visible and ultraviolet range. This excitation step is followed by various processes such as vibrational relaxation, internal conversion, intersystem crossing, and emission of light at longer wavelengths (compared to excitation, Stokes shift)[105]. The occurrence of fluorescence is strongly dependent on the molecular structure, functional units and measurement conditions (temperature, concentration, solvent)[105]. In organic mixtures, mainly molecules with conjugated double bonds, such as (poly)aromatic, heteroaromatic (porphyrins, flavins), and polyenic structures, exhibit fluorescence[105]. The higher the degree of conjugation (more conjugated double bonds), the higher the Stokes shift (red shift)[105, 106]. Fluorescence is also observed in bitumen and is mainly linked to the abundance of aromatic structures within the material[107]. Ageing studies have shown that the overall intensity goes down and that the position of the maximum signal shifts to longer wavelengths[108, 109].

With the help of all these techniques, it was possible to describe the chemical system of bitumen very precisely and thus create a basis for chemical ageing tests. The most groundbreaking findings from these investigations are summarised and discussed in the next chapter.

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1.4. Bitumen ageing

Ageing in bituminous construction materials refers to molecular, structural, and mechanical alterations during production, construction, and application. These changes happen permanently and influence each other, as illustrated in Figure 5. Generally, bitumen ageing can be separated into two distinguishable phases. The first phase, short-term ageing (STA), refers to the processes happening at elevated temperatures (>150°C) during production, transport, mixing, and paving for short periods at the beginning of the use-life. The second phase, long-term ageing (LTA), describes all processes at moderate temperatures (max 60-80°C) between STA and the end-of-life of bituminous products[19].

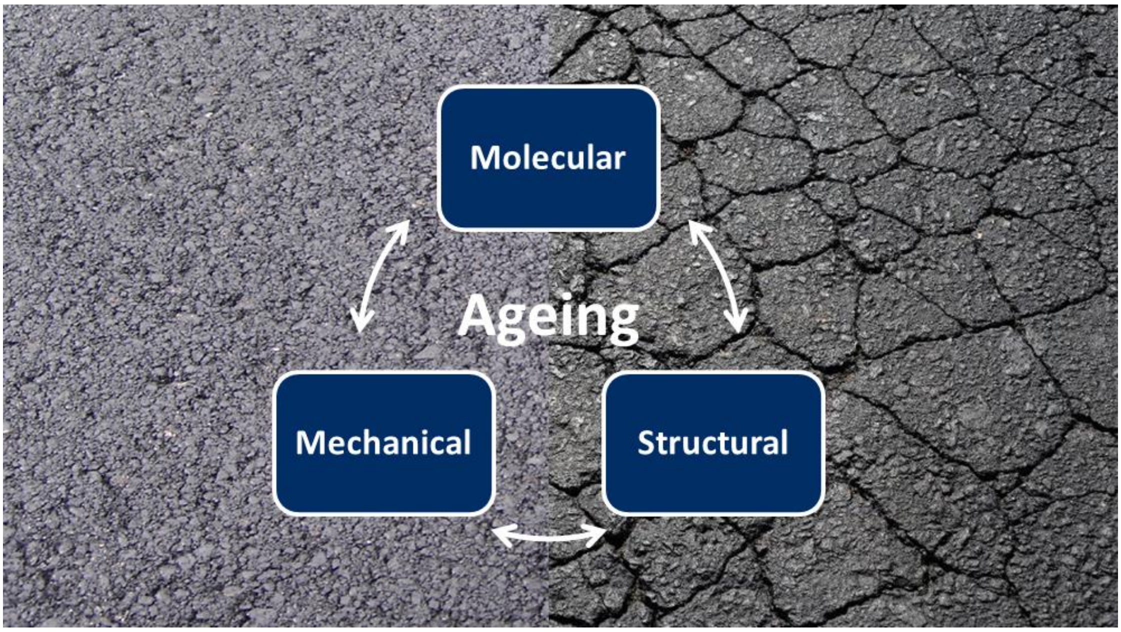

Figure 5. Illustration of the three levels of ageing in bituminous construction materials.

1.4.1. Thermal ageing during production, transportation, mixing, and paving

Bitumen is heated to roughly 160°C (in HMA, up to 185°C for PMBs) to lower the viscosity, improve workability, and guarantee complete coverage of the mineral aggregates in asphalt mixtures. The high temperatures induce the evaporation of volatile organic compounds (VOCs)[21, 110, 111] and the incorporation of oxygen[19, 44, 112]. The loss of volatiles leads to a change in the remaining bitumen matrix and the formation of secondary organic aerosols, which impact air quality, health and the climate[22]. Several studies examined the chemical changes during STA, focusing on oxidation kinetics[19, 43-45, 90, 113]. The extensive studies by Petersen et al. showed that sulfoxides (dominantly) and ketones are formed in the initial phase[19]. Sulfoxide formation during this phase is reportedly temperature-dependent as sulfoxide decomposition (at elevated temperatures) becomes a limiting factor[19, 114]. Further results show slight changes in aromatic systems, aliphatic structures, and the formation of organic radicals, while vanadyl content remains constant[43, 44]. The impact of the formation and the extension of aromatic systems was (theoretically) linked to enhanced interactions between the emerging molecules[19]. Those interactions (e.g., π bonding) lead to agglomeration processes, which increase the average size of the structures in the system[42, 50-52, 115, 116].

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1.4.2. Field ageing process

Understanding the processes that take place during short-term ageing is well-advanced. This is reflected in the reproducible simulation methods that have been developed over the years. However, when looking at long-term ageing in the field, the complexity of the process increases, making accurate simulations a difficult task. The main reason for this limitation is that standardised ageing methodologies (e.g., pressure ageing vessel (PAV)) only consider thermal ageing. In field ageing processes, however, many other factors can play a role[19, 117]. They are, therefore, summarised and described in detail in Figure 6.

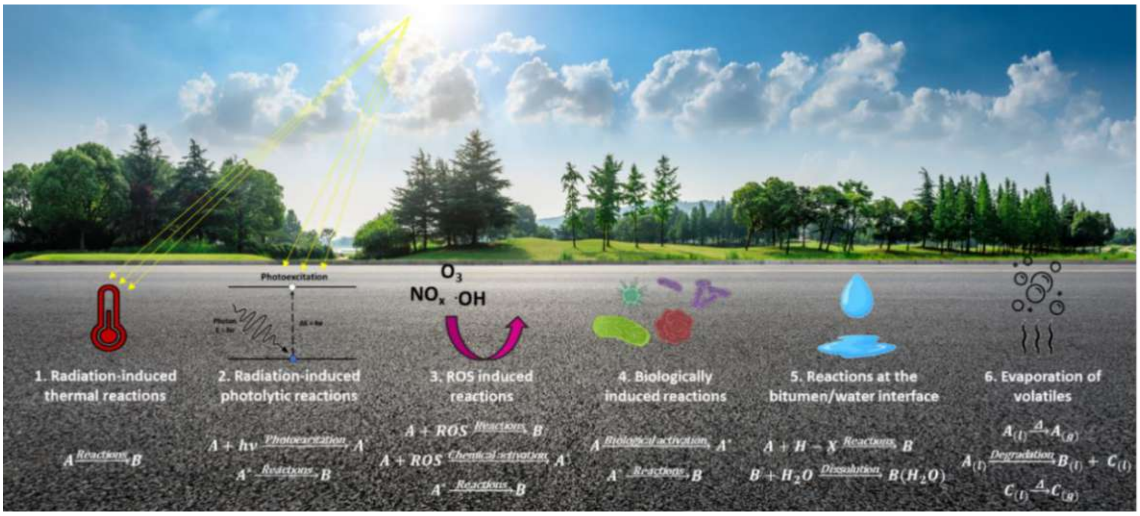

Figure 6. Illustration of possible mechanisms that lead to permanent changes in bitumen chemistry. This image was used under license from ABCDstock - stock.adobe.com.

Ageing during the service life of bituminous materials takes place at much lower temperatures than during production and varies greatly depending on climate, region (rural or urban) and layer depth[19, 118]. Petersen et al. determined carbonyls and sulfoxides as the main oxidation products and anhydrides and carboxylic acids as the minor oxidation products[19, 113]. Two oxidative periods were differentiated based on viscosity increase and oxygen uptake: a spurt reaction and the long-term oxidation period[19, 45, 113]. Experiments at 40 °C showed that the spurt induction period lasted roughly 20 h and that sulfoxide formation was dominant (less thermal decomposition reactions) [19, 114]. The ketone formation rate was almost linear and very small. Based on these results, an increase in viscosity was linked to sulfoxide formation and an increase in aromaticity in the initial phase[19]. The second phase was linearly correlated with the ketone formation. This behaviour was observed for multiple binders; however, the sensitivities/slopes were sample-dependent, which indicates the differences in ageing susceptibility based on the properties of the binder[19].

Based on extensive studies, reaction mechanisms for both oxidative phases have been proposed[19]. Initial reactions are triggered by the reaction of oxygen with highly reactive hydrocarbons (e.g., 9,10 dihydroanthracene). Therein, aromatic structures and reactive (hydro)peroxide intermediates are formed. Those react at low temperatures mainly with sulfides to form sulfoxides or decompose to reactive radicals. Additionally, reactive benzylic carbon precursors form low initial amounts of ketones. Consumable perhydroaromatics limit this spurt reaction. After that, carbonyl and sulfoxide formation rates are reduced. H-abstraction facilitates ketone formation on benzyl carbons at the α position (benzylic position) of the aromatic rings. The radical (after H-abstraction) reacts with oxygen to form peroxides. Follow-up reactions lead to the formation of carbonyls, sulfoxides, and aliphatic and aromatic alcohols.

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Thus, the expected main oxidation products are ketones and sulfoxides, while minor products comprise alcohols[19, 45, 113].

All oxidation products contribute to the polarity of the system. Davis and Petersen highlighted the importance of polarity and related performance parameters such as weathering durability and cracking resistance to the binder's susceptibility to polarity increase[19, 119]. The binders with higher polarity after specific laboratory ageing procedures were less durable. The cause of this was investigated using SARA analysis, among other methods. During LTA, asphaltene content rises, which is linked to the increase in viscosity[19, 119]. Asphaltenes grow in size and number as maltene molecules intermolecularly bond or transform during ageing[91]. One suggestion was that the ketones formed in oxidation induce agglomeration, which initiates asphaltene formation and growth. The characterization of asphaltenes produced in ageing processes confirmed that they have the same impact on viscosity as native asphaltenes[19]. Combining all of this, a correlation between ketone formation and viscosity increase was proposed[19]. Besides autoxidation, the potential catalytic properties of transition metals (e.g., vanadyl complexes) in bitumen have also been discussed[120]. The ageing extent depended on the organic ligands (in metal complexes, e.g., porphyrins) and the central ion (Ni^{2+} vs. VO^{2+}). Non-porphyrin vanadium complexes and nickel porphyrins were inactive in promoting oxidation reactions[19]. Notably, Gooswilligen et al. found that known oxidation catalyst poisons, such as potassium cyanide (KCN) and sodium nitride (NaN_3), reduced the oxidation rate in bitumen, which is an indication that metal catalysts play a role in oxidative ageing[19, 121].

Besides reactions and interactions in the bituminous phase, the impact of mineral aggregates must be considered in asphalt mixtures. Oxidation studies have shown that mineral aggregates can catalyse reactions in saturates and aromatics but have little to no effect on resins and asphaltenes (considering the ageing of the isolated systems). However, no effects were observed when the entire asphalt was aged[19]. This was explained by the fact that the polar fractions (resins and asphaltenes) preferentially adsorb on the minerals and thus passivate the active catalytic sites[19]. Studies on the impact of mineral aggregate fillers (e.g., limestones) have shown that they can interact with asphaltenes[15, 76] (adsorption of asphaltenes) and reduce the formation rate of oxidation products and the hardening rate[19, 76].

Another critical parameter is air void content. It was shown that air void content impacts ageing degree and ageing depth. However, pavement permeability and accessible voids (surface voids) also need to be considered. In studies on the depth profile of bitumen ageing, time proved to be a crucial factor. Only the uppermost surface (~1.5 cm) was impacted during the first months. Measurable impact after 47 months reached 4 cm into the material, while 109 months of field ageing was enough to exceed the limit of the study, which was roughly 5 cm[19, 122].

As emphasised in Figure 6, ageing in the field depends on many factors. In order to better understand the overall influence, the contributions of the individual parameters must be investigated in detail. Studies on the effects of solar radiation, in particular, have attracted much attention in recent years. The initial excitation of molecules by photons initiates various reactions, such as photodissociation, hydrogen abstraction, cycloaddition, photosubstitution, and photooxidation, which differ from thermal reactions[123-125]. In bitumen, light induces oxidation processes and molecular rearrangements and generates organic radicals, which may additionally catalyse radical chain reactions, thereby gradually compromising its structural integrity over time[126-128]. However, the penetration depth of light is limited[129, 130]. Zeng et al.[130] evaluated the maximum penetration depth of UV light and light at 500 nm as 4.5 µm and roughly 15 µm, respectively. These values resemble the direct radiational impact on the material. Ageing

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beyond these thresholds (~2200 µm) was reported and attributed to diffusion processes from oxidized surface molecules into the bulk[130]. Li et al.[129] analysed the impact of irradiance and monitored oxidation and changes in the complex modulus and the phase angle during light ageing. They found that ageing depth depended on time, wavelength, and irradiance[129].

Further ageing factors omnipresent in tropospheric gas composition are reactive oxygen species (ROS)[131]. The collective term ROS includes gaseous oxidants such as tropospheric ozone (O_3), nitrogen oxides (NO_X) and the hydroxyl radical ($OH\cdot$)[131]. These structures are highly reactive and can initiate reactions in several materials. Accelerating ageing with ROS in the laboratory was introduced recently [132-135]. The impact of O_3 and NO_X was looked upon, and it was shown that NO_2 is the most effective oxidant, especially when another oxygen source (e.g., O_2) is present[133]. Compared to that, the reactivity of O_3 was rather low and binder-dependent [133].

The permanent oxygen uptake during ageing also changes the solubility of the materials. Glattke et al. studied photo-induced ageing processes in bitumen, maltenes and asphaltenes[126, 136, 137]. They found that photo-ageing can induce the formation of water-soluble compounds [136, 137]. The dissolution of organic compounds impacts the bituminous matrix (loss of molecules). Other leaching studies of asphalt pavements measured trace amounts of heavy metals[138, 139], potentially impacting the surrounding vegetation[138, 139].

Bituminous construction materials also contain volatile organic compounds that can be emitted at elevated temperatures (e.g., on hot summer days). The emission of molecules and organic aerosols has been intensively studied with regard to the assessment of health risks[21, 22, 111, 140]. Besides health, the potential impact of aerosols on the climate is analysed and evaluated in recent publications[22]. Additionally, the loss of organic compounds also means that the molecular composition of bitumen changes, potentially affecting the (micro)structure- and phase stability. Further studies looked at microbial/bacterial abundance in crude oil/bitumen and their potential influence on ageing [141, 142]. The presence of bacterial communities in crude oil contaminated soils was demonstrated[142]. In an investigation on the potential impact of different microorganisms in laboratory-based ageing tests, it was found that certain microbes can degrade light bituminous compounds, while the larger, more polar structures (e.g., asphaltenes) were more resistible[141].

Other processes can also take place in polymer-modified bitumen, but these depend heavily on the chemistry of the polymer. The natural ageing processes in SBS-modified bitumen have been extensively analysed[143]. The main processes are oxidation reactions, which produce ketones, carboxylic acids, sulfoxides, sulfones and their corresponding sulfinic and sulfonic acids. Additionally, loss of aromatic groups and evaporation were observed. Regarding the polymers, scission/degradation of the block copolymers into PS and PB fragments and oxidative crosslinking of PB fragments were measured[143]. A decrease in the molecular size of the polymers was also reported in laboratory-aged PMB samples[144]. The degradation processes of SBS molecules increased the chemical similarity of polymer fragments and bituminous molecules, which, according to Mouillet[145], resulted in a more homogeneous PMB matrix. Further studies also analysed the evolution of olefinic groups with ageing and found significant decreases in those structures[145-147].

This literature review shows that the chemistry of bitumen and the induced ageing processes are highly complex. A robust analytical framework is needed to analyse and understand them in detail. The structure of such an analytic system, the methods used, their characteristics and their significance are described in the following chapters.

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2. Statement of the problem

Atmospheric contributors and solar radiation induce changes in the mechanical and rheological properties of bituminous construction materials. These modifications accelerate material deterioration and, in the worst case, cause material failure (e.g., fatigue cracking). Thus, critical infrastructure, such as asphalt roads, roofing membranes, and products for water insulation applications, has an expiry date and must be regularly maintained or completely replaced, which costs money, time, and resources. One approach to solving this problem is to find the fundamental causes. To achieve this goal, it is necessary to go down to the molecular level, where oxidative and structural modifications are the foundation for macroscopic change. Exploration and determination of molecular parameters are accomplished with a wide range of spectroscopic and mass spectrometric techniques. However, due to the complexity of the molecular system of bitumen, the characterisation of reaction products and quantification of chemical changes is challenging and produces ambiguous results. It is unclear which methods to use to assess the material's chemistry best, whether they are sensitive enough, and whether they are representative to evaluate ageing.

Another critical topic is the quality assessment of bituminous products through their response to accelerated ageing methodologies. Here, the main problems of standardised ageing procedures are the high temperatures and pressures that induce completely different molecular processes. Open questions are if they are sufficient to mimic the ageing in the field and if improvements can be made by reducing the temperature and adding atmospheric contributors such as reactive oxygen species and solar radiation. Lastly, many bituminous products incorporate polymers to enhance and modify material properties. One extensively utilised polymer is the copolymer styrene-butadiene-styrene (SBS). Despite its prevalent use, the polymer's influence on the composite's ageing processes remains unknown. The changes occurring in the SBS phase during ageing, alongside those in the bitumen phase, and the impact of ageing on overall ageing processes in PMB require further research.

3. The aim of this work

This thesis focuses on utilising spectroscopic methods to characterise bituminous products. The first goal is to adapt and develop efficient methodologies to assess the ageing state. With that premise, oxidation products and structural changes typical in field ageing can be examined. The next goal is to evaluate the conventional and novel laboratory ageing methods and analyse similarities and differences to field ageing. Finally, the impact of polymers on the ageing mechanisms should be tackled within this work. By improving the understanding of the ongoing processes and introducing ways to characterise the material of interest qualitatively and quantitatively, we aim to provide a physicochemical toolbox for refineries, road construction, and roofing companies to assess the quality of their products/raw materials. Furthermore, the findings should address researchers/research facilities that implement novel modifiers or use recycled materials. The implementation of the characterisation methods facilitates the correct assessment/evaluation of the impact of novel additives, waste materials from other industries, and recycled bitumen on the performance and longevity of the composites. The overall aim of these investigations is, therefore, to contribute to extending the durability of bituminous products. The more efficient use of resources such as energy and raw materials should thus help to ensure a more sustainable bitumen industry. This leaves three research questions that build the foundation of this thesis.

1. Which methods can improve the characterisation of bitumen and its ageing states?
2. How does field ageing compare to conventional and novel laboratory ageing procedures?
3. What impact do polymers have on the ageing processes of bituminous products?

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4. Methodology

The scientific approach chosen to tackle the stated research questions is discussed in this chapter. It contains a critical perspective on the choice of materials and ageing methods, the screening and evaluation of analytical techniques, and the adaptation of spectroscopic methods for ageing investigations.

4.1. Choice of materials

As highlighted in Chapter 1.2, bitumen is a very complex material. The elemental and molecular composition depends on the origin of crude oil, refinery processes, and production standards, which means there are many different types of bitumen with a wide range of properties on the market[15, 30]. However, not only the initial state of the material is highly variable, but also its susceptibility to external influences. Therefore, any analytical investigation of this material should include a broad spectrum of different types of bitumen to be able to make scientifically sound, generally valid statements. This was only possible to a limited extent in the scientific publications of this thesis due to the high costs of the individual measurements and the overriding goal of correlating new methods while maintaining the readability/comprehensibility of the articles. Nevertheless, the work is based on extensive investigations on larger sample sets, where rheological parameters, crude oil sources, refineries, and presence/absence of polymers were varied. The sample set chosen for these preliminary studies is shown in Table 5.

Table 4. Sample set for the preliminary studies with needle penetration, softening point, performance grade (PG), and information on polymer modification.

Binder	Penetration at 25°C (*0.1 mm)	Softening point (°C)	Performance grade (-)	Polymer modification
A	62	49.6	64-28	-
B	84	45.8	58-28	-
C	91	46.8	58-22	-
D	73	46.6	64-28	-
E	168	38.4	46-34	-
F	48	83.5	82-28	SBS
G	79	68.4	76-28	SBS

4.2. Choice of ageing setups

In the laboratory setting, we used the standardised methods for short-term ageing (rolling thin-film oven test (RTFOT)[148] and thin-film oven test (TFOT)[149]) and long-term ageing (pressure ageing vessel (PAV)[150]) to simulate thermal ageing processes. These methods were also used as reference techniques for comparative studies and method development. Furthermore, using the Viennese binder ageing (VBA) cell[132], we were able to carry out fundamental investigations on the influences of the ageing atmosphere (different ROS species, ROS concentration, synergies between oxygen and ROS), humidity, temperature, and duration. The surface-relevant light ageing processes were simulated with a photo reactor. This device facilitated the control of the surface temperature, the ageing atmosphere, and the lamps' irradiance. The field ageing studies contained samples from a test field of asphalt slabs (2012-2017) and an Austrian road (2005-2022) (for detailed information, see Chapter 9.1.2).

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4.3. Screening and evaluation of spectroscopic methods

This chapter describes the adaptation of spectroscopic methods for analysing bituminous materials. Each technique's information content, repeatability and uniqueness were determined using seven different samples. The focus was on NMR, EPR, infrared, and fluorescence spectroscopy.

4.3.1. Nuclear magnetic resonance (NMR) spectroscopy

The ^{1}H NMR spectra of unmodified and polymer-modified bitumen are shown in Figure 7. The abscissa represents the chemical shift of the hydrogen nuclei in the sample (relative to a standard compound (e.g., tetramethylsilane)) and the ordinate, the intensity. The experiments were conducted in solution using deuterated chloroform ($CDCl_3$) as a solvent. The solubility of bitumen and PMBs was sufficient in this solvent; however, when analysing highly oxidised samples (e.g., from roofing membranes) or highly modified PMBs, an evaluation of the solubility before the NMR experiment (for highly oxidised samples, e.g. deuterated methanol or DMSO) is recommended. The obtained spectra reveal the challenges inherent in analysing mixtures. Instead of sharp signals, broad bands with low intensities are measured, owing to the thousands of different contributing molecules. Another drawback in the semi-quantitative evaluation of bitumen is that the solvent peak of $CDCl_3$ interferes with the aromatic signals of bitumen. Eliminating this peak by data processing tools or changing the solvent (e.g., deuterated tetrachloroethane[44]) are ways to cope with this problem.

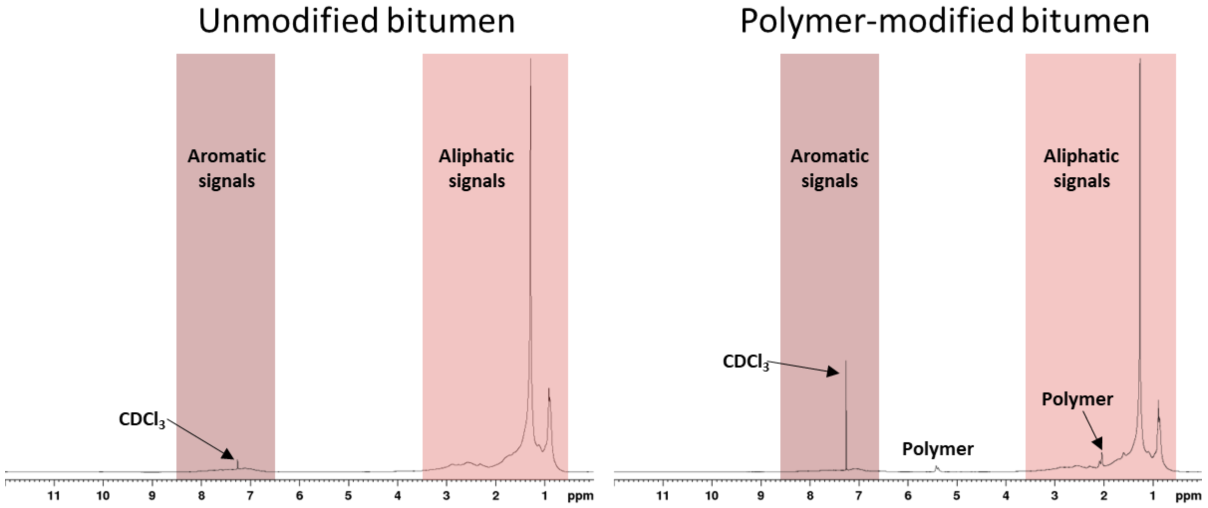

Figure 7. ^{1}H NMR spectra of unmodified (left) and polymer-modified (right) bitumen dissolved in $CDCl_3$. Aromatic and aliphatic regions, polymer signals, and solvent signals are labelled.

The chosen approach to enhance spectral resolution and analytical depth was heteronuclear single-quantum coherence (HSQC) spectroscopy, a 2-dimensional NMR technique. This method correlates nuclei (e.g., carbon and hydrogen) that are covalently bonded and provides multiplicity information (CH vs CH_2 vs CH_3) in the phase-sensitive mode[151]. Hence, further differentiation of methyl/methine and methylene groups and the characterization of alkyl groups attached to aromatic rings, olefinic structures, or heteroatoms is possible. An exemplary spectrum is shown in Figure 8, where characteristic bitumen, polymer, and solvent signals are labelled. The abscissa represents the chemical shifts of the hydrogen nuclei, and the ordinate represents the chemical shifts of the carbon-13 isotopes (^{13}C).

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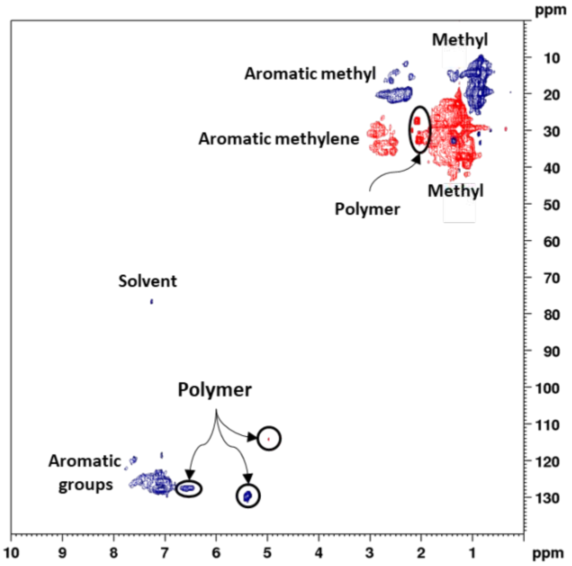

Figure 8. ^{1}H-^{13}C HSQC NMR spectrum of polymer-modified bitumen (modified with SBS). Characteristic bitumen, polymer, and solvent signals are labelled.

The share of characteristic CH-functionalities (e.g., aromatic, methyl, methylene, SBS) was calculated by comparing the integrals in specific areas to the total integrals of all signals. These characteristic 'normalized areas' are shown for 7 different samples in Figure 9.

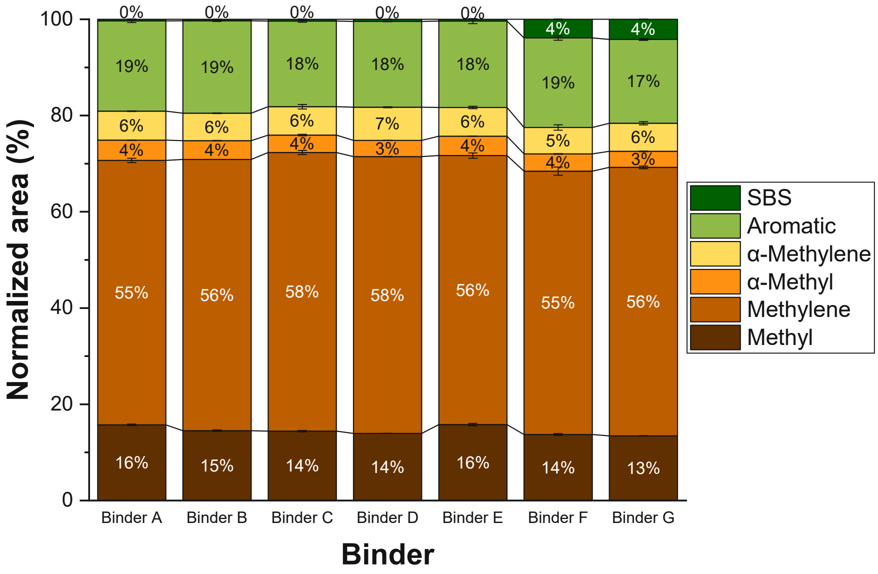

Figure 9. NMR properties of 7 different binders.

The variations of the functionalities are only minor (±3 %) throughout all samples. The comparison of binders from the same refinery but with different PEN grades (Binder A (50/70), B (70/100), and E (160/220)) shows only a slight increase of aliphatic groups from hard to soft binders. The evaluation of the PMB samples proves that SBS is measurable in PMBs. Furthermore, the negligible spectral overlaps between polymer and bitumen signals in HSQC (see Figure 8) facilitate the determination of bitumen functionality distribution, which improves comparability between unmodified and SBS-modified binders. Determining the SBS content is possible by external calibration (SBS in bitumen) and additional evaluation of the background intensity of the bitumen precursor (bitumen specific). The latter factor off-sets the estimated polymer content by about 0.5-1 %.

Despite these capabilities, limitations exist, notably the inability of ^{1}H NMR and HSQC to detect quaternary carbons (in polyaromatic structures and carbonyls), which play crucial roles in the ageing processes[19]. Heteronuclear multiple bond correlation (HMBC) spectroscopy was applied to evaluate these moieties. This technique correlates nuclei (e.g., carbon and hydrogen) that are multiple (2-4) bonds apart, which facilitates the qualitative assessment of quaternary carbons in polyaromatics and carbonyl compounds[151]. We used HMBC to evaluate the distribution of carbonyl groups in the SARA fractions. Another possibility for measuring carbonyls is by selective derivatization of bituminous OH/NH moieties with a phosphorous reactant[152, 153]. Only two functionalities are reactive under the employed conditions in bitumen: alcohols and carboxylic acids. Thus, this technique facilitates the assessment of minor oxidation products (qualitatively and quantitatively). Another NMR technique used was diffusion-ordered NMR spectroscopy (DOSY). This technique exploits differences in diffusive molecular motion based on geometric properties (e.g., size, shape) in a solution[154]. Based on that condition, it is possible to estimate the average hydrodynamic radius and molecular weight of the molecules within a mixture[154]. In our studies, we used this technique to evaluate the size distribution of molecules among the SARA fractions and investigated the size changes of bitumen and SBS structures in various ageing procedures.

4.3.2. Electron paramagnetic resonance (EPR) spectroscopy

The capabilities of EPR spectroscopy have been tested to characterize molecular structures containing unpaired electrons in bituminous materials. Figure 10 depicts the EPR spectrum of bitumen, where the most intense signal in the centre of the analysed range is assigned to carbon-centred organic radicals. The other signals stem from the characteristic splitting pattern of vanadyls (VO^{2+}). A detailed description of sample preparation, data acquisition, and data processing is given in chapter 9.1.1.

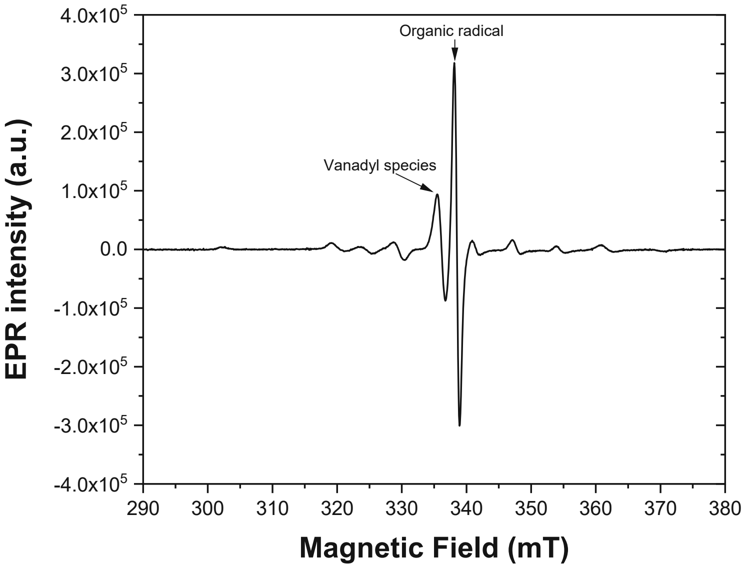

Figure 10. EPR spectrum of bitumen.

Quantitative information is obtained by double integrating the extracted organic radical/vanadyl spectrum (derived via spectral fitting simulations). The content of both molecular groups (number of spins per g) was estimated using regression functions determined by external standards (see details in Chapter 9.1.1.). The results of the quantitative analysis of both molecular groups are given in Figure 11. The vanadyl content depended on the crude oil origin (e.g., compare binder A and binder D) and the manufacturing process (e.g., compare binders A,

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B, and E, increasing PEN grade/same refinery). The content of organic radicals was slightly influenced by the production process (decrease from harder to softer binder; A, B, and E). The dependency of vanadyl and organic radical content on the PEN grade can be linked to the variations in SARA fraction distribution, particularly to the relative share of resins and asphaltenes (containing vanadyl complexes and most organic radicals).

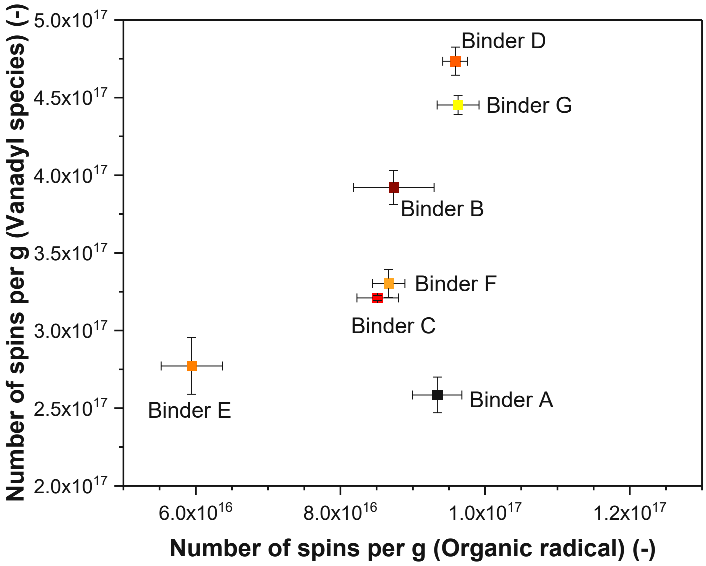

Figure 11. Organic radical and vanadyl content of 7 different binders.

4.3.3. Infrared spectroscopy

The most extensively used spectroscopic technique in bitumen research is attenuated total reflection Fourier transformation infrared spectroscopy (ATR-FTIR). Bitumen is measured in solid state; typically, four samples are prepared for each binder/ageing state[155]. A typical bitumen spectrum with highlighted spectral regions is shown in Figure 12. Based on these spectra, qualitative and quantitative information on oxidation products (carbonyls, sulfoxides, alcohols), aromaticity, aliphatic side chains, polymer content (for PMBs), and contaminants (filler, solvents) is accessible. A detailed assignment of all bands to specific functional groups is given in Chapter 6.5.

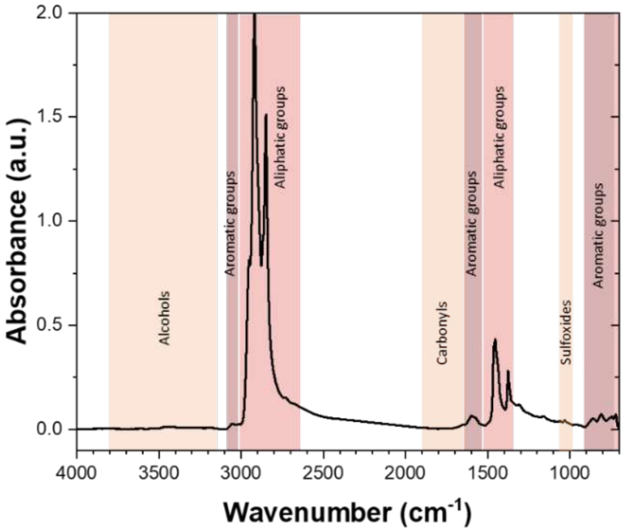

Figure 12. FTIR spectrum of bitumen with highlighted regions of interest.

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Semi-quantitative evaluation of polar groups (CO and SO index), aliphatic groups (branching index), and aromatic groups (aromaticity and aromatic ratio) was employed with the following equations.

$$CO\ index = A_{CO} \tag{1}$$

$$SO\ index = A_{SO} \tag{2}$$

$$Branching\ index = \frac{A_{CH_3}}{A_{CH_2+CH_3}} \tag{3}$$

$$Aromaticity = A_{C=C} \tag{4}$$

$$Aromatic\ ratio = \frac{A_{=C-H_{o.o.p.}}}{A_{C=C}} \tag{5}$$

A_{CO}…	Baseline integrated area between 1800 and 1660 cm^{-1}, C=O stretching vibrations (-)
A_{SO}…	Baseline integrated area between 1079 and 984 cm^{-1}, S=O stretching vibrations (-)
A_{CH_3}…	Baseline integrated area between 1400 and 1350 cm^{-1}, CH_3 bending vibrations (-)
$A_{CH2+CH3}$…	Baseline integrated area between 1525 and 1400 cm^{-1}, overlapping CH_2 and CH_3 bending vibrations (-)
$A_{C=C}$…	Baseline integrated area between 1630 and 1550 cm^{-1}, C=C stretching vibrations (-)
$A_{=CH_{o.o.p.}}$…	Baseline integrated area between 900 and 738 cm^{-1}, =C-H o.o.p. bending vibrations (-)

CO and SO indices are used to evaluate the carbonyl and sulfoxide content in the samples. The branching index compares the amount of methyl groups (CH_3) to the total amount of methyl and methylene functionalities, providing first insights into the molecular architecture of aliphatic groups. Aromaticity gives the share of aromatic groups in the sample, while the aromatic ratio is introduced to analyse the average size of aromatic structures. The evaluation of those parameters for 7 different binders is shown in Figure 13. Differentiation of the samples is possible regarding SO indices and aromaticity, while the CO index, branching index, and aromatic ratio produce overlapping data. Binders from the same source but with different PEN grades (binders A, B and E) show a decrease in polar groups and aromaticity from hard to soft binder.

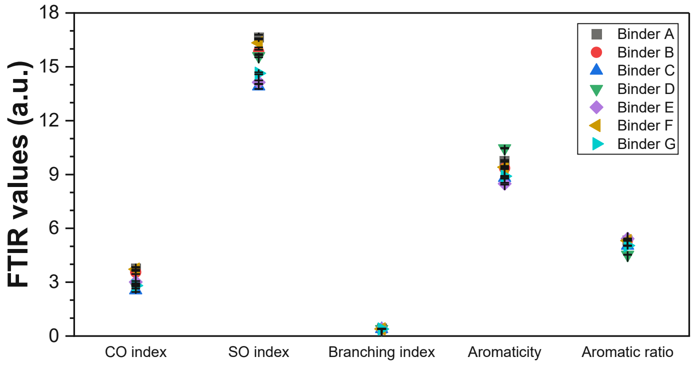

Figure 13. Characteristic FTIR values of 7 different binders.

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4.3.4. Fluorescence spectroscopy

The main fluorescence emitters (fluorophores) in bitumen are polyaromatic and heteroaromatic compounds[107]. Bitumen contains multiple different subclasses of those fluorophores. As a result, the fluorescence signals are usually rather broad. The reabsorption of emitted light and non-radiative energy transfer processes (inner-filter effects) must also be considered in these concentrated fluorophore mixtures[105, 156]. These phenomena can lead to extended emission shifts, attenuation, or complete annihilation of fluorescence[105]. When autofluorescent polymers (e.g., SBS) are added to the mixture (in PMB), further structures (aromatic functionalities) contribute to the fluorescence signals[61-64]. Bitumen mixtures are measured in 'solid state' or dissolved in a suitable solvent (=no interfering autofluorescence, no interactions with bituminous molecules). Data acquisition is based on measuring fluorescence (emission spectra) at fixed excitation wavelengths. By the stepwise increase of the excitation wavelength, 3-dimensional contour plots (fluorescence-excitation-emission maps, FEEMs) can be generated with excitation and emission wavelength on the y- and x-axis and the intensity represented by different colours. A comparison of 'solid' and dissolved bitumen spectra is shown in Figure 14. Dissolving bitumen reduces the wavelength range of the maximum and shifts it towards smaller wavelengths (blue shift).

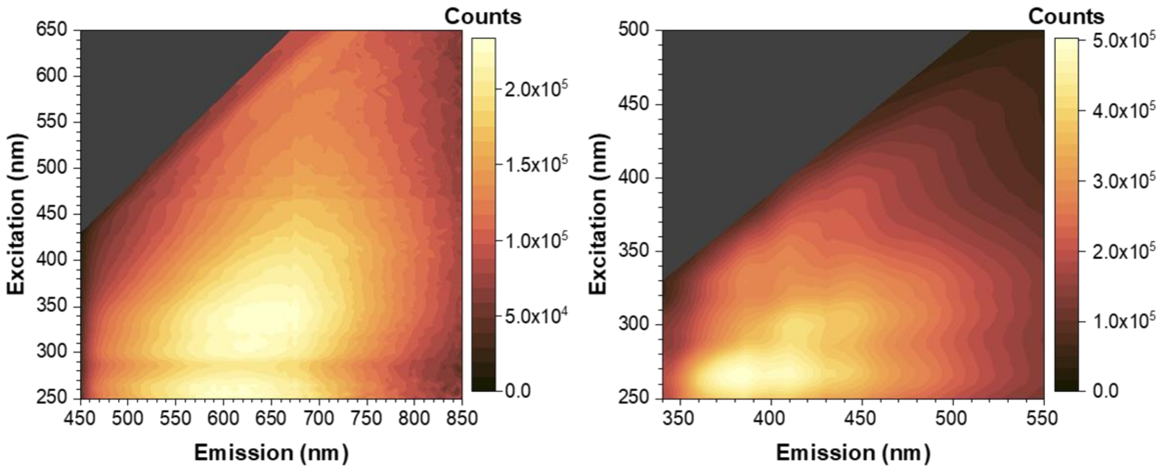

Figure 14. Fluorescence excitation-emission maps of unaged bitumen in solid state (left) and dissolved in dichloromethane (1 mg/l) (right).

Preliminary studies on the fluorescence behaviour of a set of 7 different binders are shown in Figure 15. These measurements show that fluorescence is a property that occurs in all samples. By combining the information from fluorescence intensity and the position of the maximum, all binders (other than B and D) can be distinguished. No significant trends regarding crude oil source, manufacturing procedure, and presence/absence of SBS are observed.

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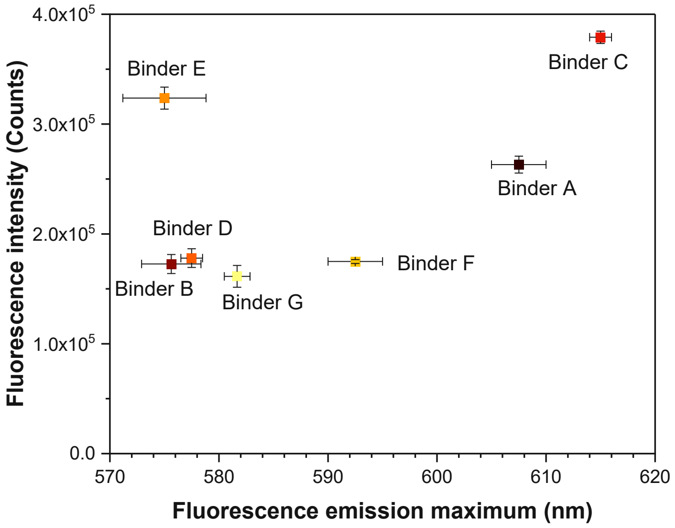

Figure 15. Fluorescence intensity and fluorescence emission maximum of 7 different binders.

4.4. Sensitivity towards ageing-induced changes

In order to explore the applicability of these techniques for ageing experiments, we assessed the sensitivity of the introduced/adapted parameters in standardized ageing procedures. The same sample set was used, and the chosen ageing procedures were RTFOT (short-term ageing (STA) simulation) and RTFOT+PAV (long-term ageing (LTA) simulation). The collected data and a short discussion of the results are provided in the upcoming chapters.

4.4.1. Nuclear magnetic resonance (NMR) spectroscopy

The HSQC NMR analysis of the impact of STA and LTA ageing is represented in Figure 16 for four different binders (B, D, F, and G; see Table 5 for detailed information). The structural properties of bitumen (and the polymer) change slightly (±1 %) during thermal ageing. This indicates that the high temperatures during production, transportation, and paving have a restricted influence on the overall structural parameters. However, ageing factors such as light and ROS might cause or intensify bitumen/polymer structure changes in field applications. Therefore, this technique was also used in the ageing studies in the field (see chapters 6.4 and 6.6) and in the light/ROS ageing studies (in Chapters 6.5 and 6.6).

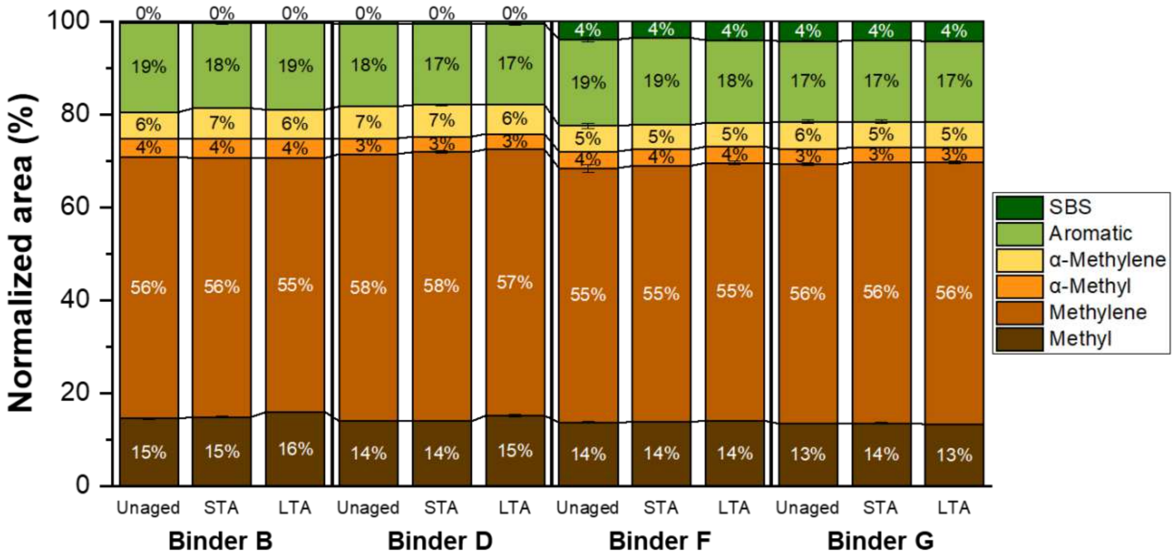

Figure 16. NMR properties of 4 exemplary binders in 3 ageing states. Unaged, STA-, and LTA.

4.4.2. Electron paramagnetic resonance (EPR) spectroscopy

The analysis of ageing-induced changes in the vanadyl and organic radical content is highlighted in Figure 17.

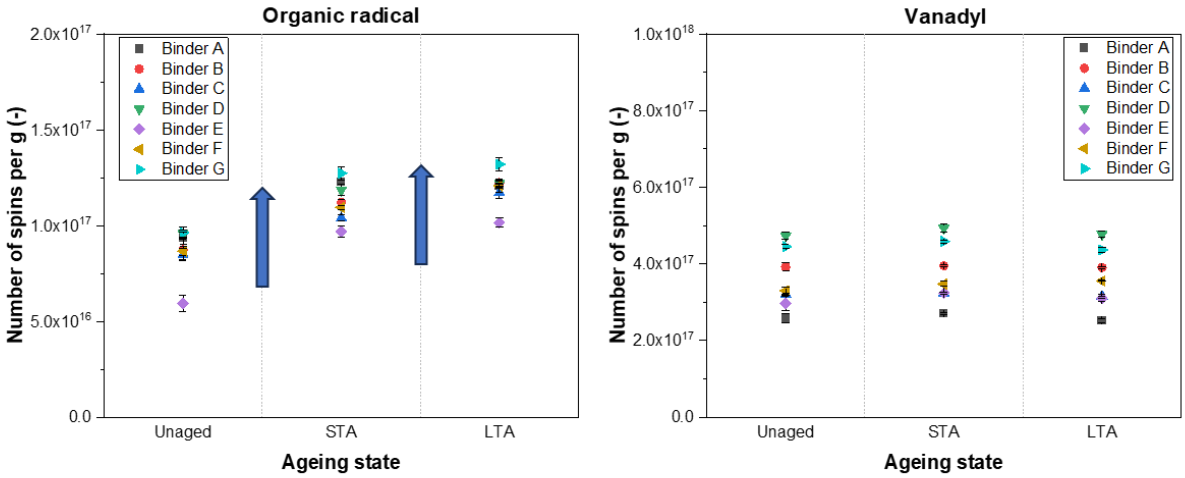

Figure 17. Organic radical (left) and vanadyl (right) content of 7 different binders in 3 ageing states: unaged, STA, and LTA.

As was reported by Pipintakos et al.[43, 44], thermal ageing induces no significant change in vanadyl content in all investigated samples (see Figure 17, right). Thus, no vanadyl-containing molecules are lost in evaporation processes in heated bitumen samples. The organic radical content increases during thermal ageing (see Figure 17, left). The impact of ageing temperature was studied in air at 60, 80, and 110 °C for 3 days (see Chapter 9.1.1, Figure 21). The results show that organic radical formation is dependent on the ageing temperature.

4.4.3. Infrared spectroscopy (IR)

The infrared spectroscopic ageing assessment is based on the ageing index, which is the sum of the carbonyl and sulfoxide indices (A_{CO}+A_{SO}). The evaluation of 7 different binders in 3 different ageing states (unaged, STA, and LTA) is shown in Figure 18. Ageing induces carbonyl and

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sulfoxide formation in all samples, with no significant dependencies on the PEN grade, crude oil origin, refinery, and the presence of SBS in the mixture.

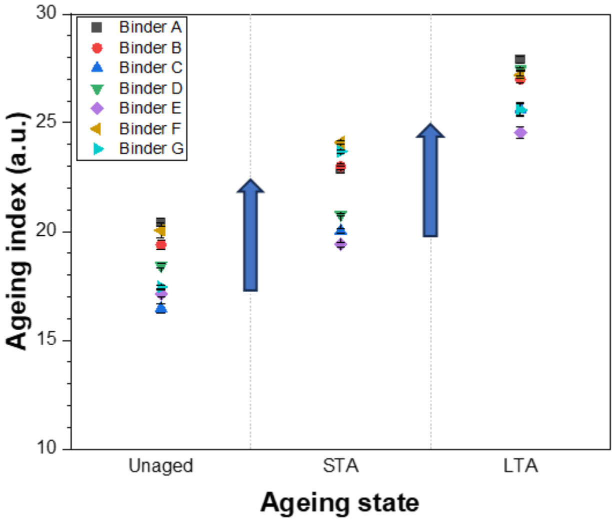

Figure 18. Ageing index based on infrared spectroscopy (sum of carbonyls and sulfoxides) of 7 different binders in 3 ageing states: Unaged, STA-, and LTA.

4.4.4. Fluorescence spectroscopy (FS)

Figure 19 represents how STA and LTA impact the fluorescence properties. Therein, the fluorescence intensity decreased during both procedures. The fluorescence maximum shifts to lower wavelengths (blue shift) during STA and then to higher wavelengths (redshift) during LTA. Both results validate that the observable trends represent (sample-independent) characteristic features of bitumen ageing. The possibilities for quantitative evaluation, problems in the interpretation, and general remarks on this technique are discussed in the publications.

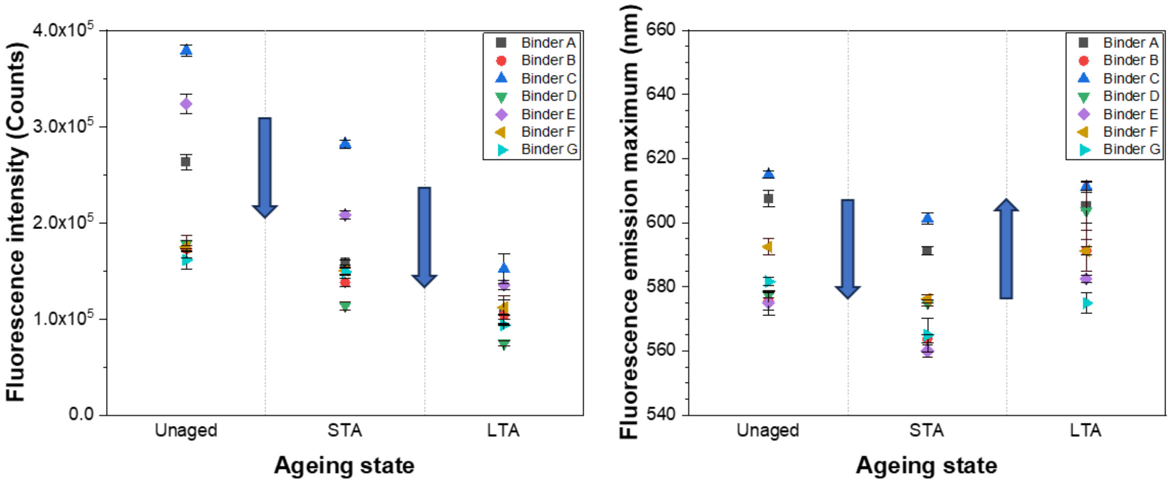

Figure 19. Fluorescence intensity (left) and emission maximum (right) of 7 different binders in 3 ageing states: Unaged, STA-, and LTA.

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4.5. Summary of spectroscopy-based semi-quantitative parameters

Table 5. Semi-quantitative parameters derived from spectroscopic analysis of bitumen.

Spectroscopic technique	Parameter	Potential information
HSQC NMR	Structural information	Aromaticity, aliphaticity
	Polymer content	Amount of SBS, degradation of SBS subunits
EPR	Organic radical content	Thermal history of the sample
	Vanadyl content	Origin of the sample
Infrared	CO index	Oxygen incorporation, carbonyl distribution
	SO index	Oxygen incorporation, sulfoxide distribution
	Ageing index	Total oxygen incorporation
	Aromaticity	Origin, formation/degradation of aromatic structures
	Aromatic ratio	Growth of polycyclic aromatic systems
	Branching index	Cleavage of aromatic side chains
	SBS content	Relative amount of polystyrene and polybutadiene units, degradation processes
Fluorescence	Maximum intensity	Number of the dominant aromatic fluorophores
	Overall intensity	Total number of aromatic fluorophores
	Emission maximum	Growth of polycyclic aromatic systems

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5. References

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6. Publications

6.1. Summary of Scientific Publications

6.1.1. Multi-spectroscopic characterization of bitumen and its polarity-based fractions

In this investigation, structural and chemical peculiarities of bitumen were analysed using nuclear magnetic resonance (NMR) techniques combined with infrared/fluorescence spectroscopy and elemental analysis. The bitumen sample was separated into saturates, aromatics, resins, and asphaltenes. Elemental analysis shed light on variations in heteroatom content and hydrogen-carbon ratio among the fractions. Fluorescence spectroscopy revealed an increase in the aromatic system size with polarity. Combining heteronuclear single quantum coherence (HSQC) and elemental analysis allowed the evaluation of the length and degree of branching of the aliphatic side chains. Heteronuclear multiple bond coherence (HMBC) spectroscopy confirmed the presence of carboxylic esters and amides within the resins. Hydroxyl and amino groups were detected with ^{31}P NMR after derivatisation, uncovering minor amounts of aliphatic alcohols, amides, and carboxylic acids in the resins and asphaltenes. Diffusion-ordered spectroscopy (DOSY) yielded estimations of average molecular sizes and weights. Both increased from the saturates to the asphaltenes. This study introduced novel analytic approaches (application of 2D NMR, size evaluation by NMR, determination of alcohols and acids by derivatisation) and showed how to combine them with established analytical techniques.

6.1.2. How infrared and fluorescence spectroscopy can shed new light on the characterization of bitumen and its ageing processes

This study combined chromatography and spectroscopy to characterise thermally-induced ageing processes in bitumen. Ageing was employed with standardised procedures for short-term ageing (thin-film oven test (TFOT)) and long-term ageing (LTA) (TFOT+pressure ageing vessel (PAV)). The binder was separated into the SARA fractions and subjected to analysis using infrared (IR) and fluorescence spectroscopy. The gravimetric analysis showed that mainly molecules from the aromatics fraction are oxidised and polarity-shifted to the resins and asphaltenes. The content of saturates remained constant while the shares of resins and asphaltenes increased. IR spectroscopy showed the formation of ketones and sulfoxides during oxidative ageing. Quinolones and carboxylic acids, already present in the unaged fractions, decreased during ageing in the resins and asphaltenes. Fluorescence spectroscopy provided insights into abundant aromatic structures and the impact of ageing on specific molecular classes. All ageing procedures led to decreases in aromatic content. The fluorescence emission maximum shifted to higher emission wavelengths during LTA, initiated by growing aromatic system sizes. Polarity-based shifts were also observed by fluorescence spectroscopy, confirming molecular migration from the aromatics to the resins and asphaltenes. Solid-state measurements of the resins revealed characteristic signals of porphyrins and their alterations during ageing. This investigation contributes to the understanding of the chemical ageing of bitumen by evaluating the effects of thermal ageing and extending the possibilities of infrared and fluorescence spectroscopic analysis.

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6.1.3. The impact of field ageing on molecular structure and chemistry of bitumen

This investigation examined the impact of ageing during production, transportation, mixing and paving, as well as after a 5-year exposure on a test field, by analysing the chemical alterations within bitumen and its polarity-based fractions. Elemental analysis revealed a twofold increase in oxygen content at the binder level and the molecular exchange of structures containing nitrogen, oxygen, and sulfur between the fractions. Two-dimensional NMR and fluorescence spectroscopic analysis indicated an increase in the size of aromatic systems through aromatization and/or dehydrogenative polymerization reactions. Fluorescence and infrared spectroscopy confirmed that the content of nitrogen-containing structures (amides and porphyrins) decreases also during field ageing. After selective derivatisation, the evolution of minor oxidation products was monitored using ^{31}P NMR spectroscopy. Field ageing induced the formation of aliphatic carboxylic acids and alcohols. This study seeks to enhance our comprehension of field ageing processes in bitumen and offer novel insights into utilising and combining analytical approaches for a comprehensive assessment of bitumen ageing.

6.1.4. Photo-induced ageing processes in bitumen

The impact of UV and visible light on the surface chemistry of bituminous materials was analysed in this investigation. Surface processes were simulated by ageing thin-layered (sub-μm) specimens. Qualitative and quantitative information on chemical modifications was obtained using infrared, fluorescence, and nuclear magnetic resonance spectroscopy. The findings highlighted the indispensability of oxygen for photo-induced molecular changes. Light ageing initiated the formation of a unique set of oxidation products comprising sulfoxides, various carbonyl species, and aliphatic alcohols. Simultaneously, the number of fluorescent aromatic molecules diminished while the average size of aromatic systems increased due to concurrent photo-induced degradation, condensation, and aromatization reactions. The ageing rates depended on the binder's origin and the light source. The developed/adapted experimental setup facilitated a stepwise comprehension of the molecular processes associated with light-induced ageing. This knowledge is essential to develop more effective strategies to mitigate the impact of solar radiation on bituminous infrastructure in the future.

6.1.5. Unraveling the molecular processes in polymer-modified bitumen

This study delved into crucial aspects of the chemical structure and its evolution during laboratory and field ageing experiments in unmodified and styrene-butadiene-styrene (SBS) modified bitumen. Heteronuclear single-quantum coherence NMR was used to explore the ongoing molecular changes in the binder and the polymer. The analysis revealed that olefinic and allylic groups of the polymer were oxidised during field ageing, a phenomenon absent in thermal ageing. Thermochemical ageing (introducing NO_2 and O_3 as reactive gases) induced similar reactions as field ageing in the polymer. Diffusion-ordered spectroscopy demonstrated a decrease in the average molecular size of polymers during field ageing, which was attributed to SBS degradation in the polybutadiene phase. A similar polymer degradation was only possible by extending the ageing time in the laboratory. However, the extension of the ageing time in the ageing reactors affected the molecules of the bitumen phase more than in the field due to differences in evaporation, degradation, oxidation and condensation reactions. These investigations demonstrate the usefulness of spectroscopic methods to study polymer-modified samples and show the strengths and weaknesses of standardised and novel ageing procedures in simulating field ageing.

6.2. Multi-spectroscopic characterization of bitumen and its polarity-based fractions

This chapter was published by S. Werkovits, M. Bacher, J. Theiner, T. Rosenau, and H. Grothe in Construction and Building Materials, 2022, Volume 352, 128992,
https://doi.org/10.1016/j.conbuildmat.2022.128992

Abstract

Bitumen contains a complex mixture of molecules, ranging from simple linear alkanes to complex polyaromatic systems. Used in road construction, those structures are permanently influenced by atmospheric processes, which result in oxidation, degradation, loss of volatiles and structural rearrangements. In order to understand those molecular changes, a profound description of the unaltered system is needed. In this study, structural and chemical peculiarities of bitumen and its polarity-based fractions were analysed using nuclear magnetic resonance (NMR) techniques in combination with infrared/fluorescence spectroscopy and elemental analysis. The bitumen sample was separated into saturates, aromatics, resins and asphaltenes. Elemental analysis provided insights into variations of heteroatom content and hydrogen-carbon ratio among the fractions. Fluorescence spectroscopy showed an increase in the aromatic condensation degree with rising polarity. The combination of heteronuclear single quantum coherence (HSQC) and elemental analysis facilitated the assessment of length and branching extent of aliphatic side chains, throughout the fractions. Another 2D NMR technique, heteronuclear multiple bond coherence (HMBC) found evidence for minor contributions of carboxylic esters or amides within the resins. Hydroxyl and amino groups were analysed by ^{31}P NMR after derivatization, revealing minor amounts of alcohols, amides and carboxylic acids in the most polar fractions. Additionally, diffusion ordered spectroscopy was carried out to obtain estimations on average molecular sizes and weights. Applying in-depth NMR analysis to bitumen and combining it with complementary analytical techniques, this study provides a unique basis for future ageing studies and demonstrates how multi-spectroscopy can give new insights into bitumen structure and chemistry.

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6.3. How infrared and fluorescence spectroscopy can shed new light on the characterization of bitumen and its ageing processes

This chapter was published by S. Werkovits, K. Hofer, T.R. Schöberl, B. Hofko and H. Grothe in *Road Materials and Pavement Design*, 2023, https://doi.org/10.1080/14680629.2023.2191730

Abstract

A combination of chromatography and spectroscopy was applied to characterize the chemical peculiarities of bitumen and analyse thermally induced ageing processes. Therefore, a bitumen sample was short-term and long-term aged followed by a polarity-based fractionation. Subsequently, the fractions and the base binder were analysed by infrared (IR) and fluorescence spectroscopy. IR provided the possibility to track the fate of carboxylic acids and quinolones and the evolution of ketones and sulfoxides during oxidative ageing. Information on abundant aromatic structures and the effect of ageing on certain molecular classes was obtained with fluorescence spectroscopy. It was shown that shifts to higher emission wavelengths correlate to the polarity of the fractions and the ageing state. Solid-state measurements of the resins revealed characteristic signals of porphyrins and how they are affected during ageing. Here we evaluate the impact of different ageing conditions with the perspective to improve the understanding of complex chemical ageing in bitumen.

6.4. The impact of field ageing on molecular structure and chemistry of bitumen

This chapter was published by S. Werkovits, M. Bacher, J. Mirwald, J. Theiner, T. Rosenau, B. Hofko and H. Grothe in *Fuel*, 2023, Volume 343, 127904,
https://doi.org/10.1016/j.fuel.2023.127904

Abstract

Bitumen is an important construction material applied as sealing material in roofing membranes and as binding material in roads. Due to its organic nature, it is prone to environmentally induced changes on the molecular up to the macroscopic-mechanical level, resulting in a limited service life. Various methods (spectroscopic and chromatographic) have been applied to elucidate specific aspects of ongoing chemical processes. However, a systematic analysis covering multiple molecular modifications is missing. In this study, the impact of ageing during construction and paving and after 5-years on a test field was analyzed by looking at the chemical changes within bitumen and its polarity-based fractions. Elemental analysis showed doubling of oxygen content on the binder level and molecular exchange of nitrogen, oxygen, and sulfur containing structures between the fractions. The combined use of 2-dimensional nuclear magnetic resonance (NMR) and fluorescence spectroscopy indicated the growth of aromatic system sizes by aromatization and/or dehydrogenative polymerization reactions. Fluorescence and infrared spectroscopy demonstrated the ageing sensitivity of nitrogen containing molecular classes such as amides and porphyrins. Finally, in-depth analysis of the specific nature and fate of hydroxyl groups with ^{31}P NMR spectroscopy after derivatization, revealed increasing amounts of aliphatic carboxylic acids and alcohols with ageing. The outcome of this study aims at improving the understanding of ageing processes in bitumen and at showing new ways to use and combine analytical approaches for proper assessment of bitumen ageing.

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6.5. Photo-induced ageing processes in bitumen

This chapter was submitted by S. Werkovits, M. Bacher, J. Mirwald, T. Rosenau, B. Hofko and H. Grothe to Construction and Building Materials, submission date: 15.02.2024.

Abstract

Asphalt roads and waterproofing membranes on roofs are exposed to sunlight, which induces irreversible changes in those materials. The underlying chemical processes initially affect the surface but later on impact the bulk chemistry and the mechanical properties. Bitumen, the binding and sealing material, is particularly susceptible to such influences. However, the molecular processes that initiate material deterioration are still poorly explored. Here, we show that ultraviolet and visible light cause the formation of a unique set of oxidation products and alter aromatic structures on the bituminous surface. Qualitative and quantitative information is obtained using infrared, fluorescence and NMR spectroscopy. Bulk ageing studies have shown a shift from the aromatics to the resins and asphaltenes fractions, potentially influencing colloidal stability. The evaluation of surface processes was facilitated in ageing studies with thin sub-µm specimens. We find that the presence of oxygen is essential for molecular changes to occur. The formation of carboxylic acids, esters and aliphatic alcohols, coupled with degradation and restructuring of aromatic systems demonstrates the unique nature of light ageing. This is due to a nuanced interplay between oxidation, degradation, condensation and aromatization reactions. Ageing rates depend on the origin of the binder and the light source, showing an asymptotic growth with time. All results considered, this study is unique and enabled us to decipher critical molecular processes during photochemical ageing. In this regard, we hope to develop more effective strategies for mitigating and preventing the adverse impact of solar radiation on bituminous infrastructure in the future.

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6.6. Unraveling the ageing processes in polymer-modified bitumen

This chapter was submitted by S. Werkovits, K. Primerano, M. Bacher, T. Rosenau, B. Hofko and H. Grothe to *Fuel*, submission date: 05.03.2024.

Abstract

Polymers play a crucial role in modifying the mechanical and rheological properties of bituminous construction materials. The selection of polymer type and quantity depends on several factors, such as application area, climate, and the origin of the bituminous binder. One of the most employed polymers, particularly in road engineering, is styrene-butadiene-styrene (SBS). However, long-term interaction of the SBS composite mixture with solar radiation and atmosphere can result in material degradation. Despite its prevalent use, the specific contribution of the polymer in these degradation processes remains insufficiently understood. To address this gap in knowledge, we analyzed the impact of different ageing procedures (thermal, chemical, and field ageing) on the chemistry of the bitumen-SBS mixture. A comparative analysis with unmodified bitumen samples helped in elucidating the complex mechanisms. Evaluation of oxidation products reveals that the presence of SBS has no discernible impact on the oxidation kinetics. Two-dimensional nuclear magnetic resonance spectroscopy indicates reactions of olefinic and allylic SBS groups during field ageing, while aromatic SBS structures remain unaffected. Diffusion-ordered spectroscopy unveils a decrease in the average molecular size of the polymer during field ageing, indicative of degradation processes. Multiple ageing cycles are required to replicate this trend in the laboratory. However, the extension of laboratory ageing time affects bitumen chemistry more severely than field ageing, showing the necessity for improved artificial ageing methodology. This study demonstrates the utility of spectroscopy in assessing ageing mechanisms in bitumen and bitumen-polymer blends, with a particular emphasis on the comparison of laboratory and field ageing procedures.

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7. Summary and Discussion

This work aimed to widen the understanding of bitumen characterisation and the chemical processes initiating material degradation and failure. As outlined, the conceptual design was mainly based on spectroscopic techniques. Therefore, it was necessary to test the applicability, informative value, and ageing sensitivity of the employed methods.

The ^{1}H NMR spectra of bitumen showed broad (overlapping) bands and interfering solvent signals, which made qualitative and quantitative analysis difficult. HSQC NMR was employed to solve these problems. The preliminary study showed that this technique facilitates the assessment of aromatic methyl and aromatic methylene groups and allows the detection and quantification of polymer subunits. The quantitative evaluation of the structural elements (aromatic/aliphatic groups and aliphatics attached to aromatic molecules) showed high similarities among all samples. EPR spectroscopy provided an entirely different perspective on the chemical system. The presence of vanadyls and organic radicals was confirmed. Due to the geographical variability of vanadium concentration in crude oil and bitumen, this method might be a promising tool for origin determination [1, 2]. Infrared spectroscopy helped to evaluate the initial contents of carbonyl, sulfoxide, aromatic, and aliphatic groups. When comparing different unaged binders, sulfoxide content and aromaticity had the highest variability. Fluorescence spectroscopy provided unique information on the quantity and average size of aromatic systems. Considering all fluorescence parameters, bitumen samples were distinguishable, which could be applied as an additional method to determine the crude oil source.

DOSY NMR showed that the molecular radius of the SARA fractions increases steadily from the saturates to the asphaltenes, with relatively small steps between the SAR fractions and a larger one between resins and asphaltenes. The significant increase in size was attributed to the agglomeration processes of the asphaltenes in the concentration range under investigation. Polymer and bitumen molecular sizes were determined in PMBs, showcasing their simultaneous measurability and substantial differences in size. Insights into minor oxidation products were obtained with ^{31}P NMR spectroscopy using a derivatisation approach. This provided the spectral resolution of NMR spectroscopy, facilitating the differentiation of aliphatic and aromatic alcohols/carboxylic acids (which is not possible with IR spectroscopy). Quantification showed that aliphatic alcohols (no phenols) and carboxylic acids are present in the resins and asphaltenes. HMBC NMR was employed to obtain information on quaternary carbon atoms in carbonyls and polycyclic aromatic systems. The share of quaternary aromatic carbons increased from saturates to asphaltenes. Carbonyl structures (amides or carboxylic acids) were detected in the resins. Fluorescence studies of the SARA fractions facilitated the assessment of the distribution of aromatic compounds and the extent of polycondensation. The aromatic system size increases from saturates to asphaltenes, ranging from 1-3 aromatic rings to 5-7 condensed aromatic rings in polyaromatic structures. Additionally, porphyrin structures were measured and semi-quantitatively evaluated with fluorescence spectroscopy. This was only possible by measuring the resins fraction in the solid state. The problem with fluorescence measurements in solution is that the primary relaxation process of porphyrinic structures with oxyvanadium (VO^{+2}) as a central ion is radiationless [3]. EPR experiments showed that organic radicals and vanadyls occurred predominantly in the resins and asphaltenes (organic radicals in the aromatics in traces). Although vanadyl porphyrins were measured in the asphaltenes (EPR and UV/VIS spectroscopy), this fraction did not exhibit the characteristic porphyrin fluorescence pattern. This observation can be explained by the association of porphyrins with other molecular

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structures and agglomerates in the asphaltenes fraction. These interactions severely impact the electronic structure of porphyrin moieties, resulting in an increased probability of non-radiative relaxation processes [3].

The ageing sensitivity of parameters derived from HSQC, EPR, IR, and FS was examined by studies in standardised ageing reactors (RTFOT and PAV). It was found that the carbonyl and sulfoxide content increased in all samples. Furthermore, as shown by Pipintakos et al. [1, 2], the organic radical content increased, while the vanadyl content remained constant during thermal ageing. Additionally, we found that organic radical formation is temperature-dependent. The higher the ageing temperature, the more organic radicals were produced. The number of aromatic compounds decreased during STA and LTA, while the aromatic system size decreased during STA and increased again during LTA. No significant changes were observed in overall structural parameters (e.g., aromaticity, based on HSQC). Detailed studies on thermal ageing (see Chapter 6.3) showed that the content of porphyrin-and quinolone-containing molecules decreases in the resins, which was attributed to association reactions with asphaltenes and specific degradation processes. In order to monitor molecular shifts of fluorophoric groups between the SARA fractions, we introduced difference fluorescence excitation-emission maps (FEEMs). Therein, the FEEMs of the SARA fractions were recorded before and after ageing. After normalising and subtracting both spectra, a difference plot was created, which confirmed that small aromatic structures vanish in the saturates and aromatics and reappear in the resins and asphaltenes. The spectral position indicates that molecules from the aromatics were shifted, which agrees with the typical pattern (mass loss of aromatics, mass increase in resins and asphaltenes) of the SARA fractionation.

A thorough characterisation of field ageing was required to facilitate the evaluation of laboratory ageing methods. The analysis of heteroatom-containing compounds with elemental analysis showed that the oxygen content almost doubled (due to oxidation) in 5 years. The oxygen content decreased in saturates and aromatics but increased significantly in the resins and asphaltenes, indicating the impact of oxidation on molecular polarity (polarity-based shifts). Total nitrogen and sulfur content remained constant, proving that no such structures were lost (e.g., evaporation) or added during the process. Nitrogen-containing compounds were initially found in aromatics, resins and asphaltenes, and sulfur-containing compounds were present in all SARA fractions. Field ageing led to a decrease in nitrogen compounds in the AR fractions and sulfur compounds in the SAR fraction. Changes in the contents of both molecular classes indicate a redistribution in the material. Aliphatic sulfides are oxidised to sulfoxides, while nitrogen functionalities are either part of a molecule with reactive centres (benzylic carbon, sulfides) or interact more frequently with the increased number of oxidised molecules in the bitumen matrix. Both processes would induce a shift towards fractions with higher polarity.

The main oxidation products during field ageing were carbonyls and sulfoxides. Besides that, aliphatic alcohols and carboxylic acids emerged (minor oxidation products) and were detected in the aromatics (only alcohols), resins and asphaltenes. Field ageing produced higher amounts of sulfoxides than the laboratory simulations (VBA and PAV). The main reason is the dependency between sulfoxide formation and ageing temperature. The instability of sulfoxides increases with temperature, resulting in thermal decomposition processes, which counteract the formation processes [4-6]. This general limitation of accurate sulfoxide simulation is difficult to overcome because high temperatures are needed to accelerate the carbonyl formation. A problem of sulfoxide determination via FTIR is the spectral overlap with oxygen-containing functionalities. Detailed evaluation of the sulfoxide signal showed the presence of several band maxima, hinting

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at multiple contributing structures (vibrational modes from ketones, carboxylic acids, and alcohols [7]).

The quinolone (amide) containing structures in the resins decreased during field ageing (similar to the thermal ageing studies). The accumulation of quinolones in the asphaltenes could be indirectly traced by elemental analysis (shift of nitrogen towards higher polarities) and by assessing the carbonyl region in the FTIR spectra. However, the spectral overlaps with the emerging ketones made a conclusive detection of amides difficult. Also, the content of fluorescent porphyrins decreased. Due to molecular associations, a shift of these structures towards the asphaltenes is expected. Intermolecular interactions impact the fluorescence behaviour of the porphyrins, making them non-detectable in the asphaltenes. Although quinolones have been tentatively reported in the literature [8], caution has to be taken. The similarities in degradation behaviour and general low nitrogen content suggest that porphyrin structures alone might explain the observed phenomena. Naturally occurring porphyrins can contain carboxylic acids or acetyl groups. If they are attached to the pyrrole rings, their expected/and reported wavenumber is shifted towards 1700-1683 cm^{-1} and 1665-1658 cm^{-1}, which would agree with the observed IR bands in the resins fraction, currently attributed to quinolone structures [9].

Another important class of molecules in bitumen are aromatic compounds. Petersen et al. proposed the emergence of aromatic structures during ageing [10, 11]. Therefore, two aspects of aromatic systems have been analysed in detail: the total amount of aromatic compounds and the aromatic system size. Fluorescence spectroscopy has shown that fluorescent molecules (aromatic compounds in bitumen) are lost during all applied ageing procedures. Long-term ageing simulations in the laboratory (PAV and VBA) induced extensive decreases that exceeded the losses induced by field ageing. Since the main difference lies in the ageing temperature, a possible explanation for this phenomenon could be the increased evaporation of aromatic fluorophores. Although PAV ageing is carried out at higher temperatures than VBA ageing, the loss of aromatic groups is lower due to the high pressure in the PAV reactor, which prevents the evaporation of volatile compounds. Besides evaporation, oxidation and degradation reactions impact the fluorescence intensity. The observed decrease in fluorescence intensity during LTA is probably a combination of these factors. NMR spectroscopy extended the analysis by measuring the relative contents of all aromatic compounds (also non-fluorescent). Aromatic signal intensity decreased during field ageing, while the influence of STA and PAV ageing (thermal ageing methods) was negligible. Evaporation-induced losses (during STA) did not impact the aromatic/aliphatic ratio, which suggests that the volatile compounds align with the average molecules in bitumen (are neither extremely aliphatic nor aromatic). The decrease in field-aged samples (lower temperatures) indicates that the evaporation alone cannot explain aromaticity losses. A limitation of ^{1}H NMR and HSQC NMR spectroscopy in evaluating aromatic structures is their mutual blindness for quaternary carbons. Figure 20 compares different aromatic structures: benzene, terphenyl, and chrysene. The bigger the aromatic system size (chrysene vs benzene) and the higher the number of aromatic substituents (biphenyl, terphenyl), the fewer carbon-hydrogen bonds and methyl/methylene groups in α position are possible. Thus, NMR signal intensity is dependent not only on the total number of aromatic rings but also on the molecular architecture. In this example, all structures contain 18 carbon atoms in aromatic systems. However, the number of C-H bonds drops from 18 to 14 (terphenyl) and 12 (chrysene), while the number of quaternary carbons ($C_{quart.}$) increases from 0 to 4 and 6. These considerations are also crucial for ageing processes, as, e.g., dehydrogenative coupling

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reactions of aromatic groups (e.g., formation of biphenyls, terphenyls) reduce the number of CH groups and the aromatic NMR signal intensity.

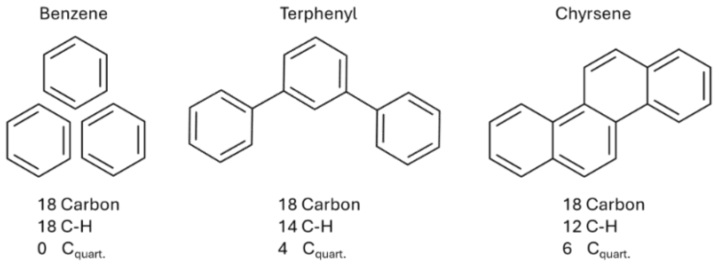

Figure 20. Comparison of benzene, terphenyl, and chrysene

The evolution of aromatic system sizes was analysed with fluorescence spectroscopy. STA induced a shift towards lower wavelengths (blue shift), which indicates a decrease in aromatic system size. However, considering evaporation during STA as the main factor and assuming that preferably small aromatic features (with smaller Stokes shifts) would evaporate (higher vapour pressures due to lower molecular weights and heteroatom content), the average fluorescence emission position was expected to increase. The photophysical reabsorption processes in the material can explain this contradiction. Evaporation reduces the concentration of fluorophores in the mixture, reducing the impact of inner-filter effects. The absence/reduction of reabsorption processes ultimately leads to the observed blue shift. The characteristic red shift during long-term ageing suggests that the increase in conjugation (growing aromatic systems) was significantly higher than in STA and that evaporation became a less important factor. Both LTA methodologies, PAV and VBA, led to growing aromatic system sizes but were insufficient to reach the redshifts of field ageing. The main reasons were competing physico-chemical processes, like evaporation, drastically impacting the resulting average fluorescence emission position. This shows that aromatic transformations depend on many parameters. Therefore, fine-tuning the individual factors is necessary to simulate these processes accurately in the laboratory. Aromatic system size growth was also analysed with infrared spectroscopy. The parameter of aromatic ratio was introduced, which showed that the aromatic system size increases during all ageing procedures (also in STA, avoiding the bias of the photophysical processes). 1xPAV ageing was insufficient to mimic field ageing, while 5xPAV and three days in the VBA cell accurately simulated this process.

The extension of the analysis to PMB samples highlighted that the oxidation pattern was very similar to unmodified samples. This suggests that the polymer does not impact the reactivity of the molecules and does not act as a catalyst. However, by adding polymers to the mixture, changes in those structures also affect the material's overall performance. It was found that the polymer phase changes with ageing. The size determinations of PMB samples with DOSY NMR showed that the polymer decreased to roughly half its starting size. This suggests that the linear triblock copolymer SBS was mainly cleaved in the middle region, which was the PB phase. Simulating the size evolution during field ageing in the laboratory was possible by increasing the time spent in the ageing apparatus. Chemical analysis of the polymers showed that besides cleavage, the amount of double bonds and hydrogens adjacent to the olefinic groups (allylic hydrogens) was reduced during field ageing. The only laboratory method that produced a similar trend was VBA. These results indicate that ROS (VBA, field) and light (field) are the main drivers that initiate reactions at double bonds (e.g., ozonolysis [12, 13], photoaddition [14-16]). However, extending the ageing time or intensifying the oxidation conditions led to additional changes in other regions of the PMB. The impact on bituminous aromatic systems is significantly higher

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during laboratory ageing than in the field. It was particularly interesting that the overall aromaticity (derived by HSQC) did not change in the bitumen phase of the PMB. This was different to unmodified binders, where the aromatic content decreased significantly. One possible explanation is that intermolecular bonding between aromatic bitumen molecules and the polymer reduced the vapour pressure, which reduced the losses of volatile compounds during ageing. On the other hand, the polymer phase could act as a sacrificial lamb, whereby the bitumen phase can only be attacked after the reactive sites in the polymer have been consumed.

Ageing of bituminous construction materials starts on the surface. What has yet to be discussed is the impact of light. In a thorough study, we looked at the reaction products on the surface of light-aged bituminous products. The light had a severe effect on bitumen chemistry, in particular on the formation of carbonyls (much higher compared to the field). The emerging carbonyls could be assigned to ketones, carboxylic esters, and carboxylic acids. There was no impact on the asphaltenes and only limited oxidation rates were observed in the saturates. Thus, aromatics and resins contained the most reactive molecules. Structural elucidation of further oxygen-containing groups proved the emergence of aliphatic alcohols in light-induced ageing. Another molecular group that was severely affected during light ageing were aromatic structures. Intensity losses and substantial wavelength shifts (redshift) suggest that aromatisation, polycondensation, and coupling reactions extended the size of aromatic systems. Interestingly, no such change was observed in the asphaltenes and almost no change was observed in the saturates.

This work focused on the spectral analysis of bitumen and the chemical processes that occur during ageing. The latest techniques were applied, evaluated and adapted for bituminous systems. The possibilities and limitations of the individual techniques and possible combinations with other methods to characterise thermal, photochemical, thermochemical, and field-induced ageing processes were described in detail. The result is a robust and versatile analytical framework that can be used for various samples and a wide range of research questions. The most important results are summarised in Table 6 and compared with the already-known characteristics of the ageing processes.

Table 6. Summary of the main findings of this thesis

Topic	Known	Scientific findings
Oxidation products	• Carbonyl and sulfoxide formation[11, 17-21] • Oxidation kinetics[2, 10, 11, 17, 18, 22] • Alcohols as part of the proposed reaction mechanism[11, 18] • Tentative determination of carboxylic acids [8, 11]	• Quantitative and qualitative determination of minor oxidation products: alcohols and carboxylic acids • Aliphatic alcohols, no aromatic alcohols • Similar oxidation rates for unmodified and polymer-modified binder
N-containing compounds	• Tentative elucidation of quinolones [8] • Porphyrin determination and structural elucidation[23, 24]	• Determination of porphyrin content with FS • Elucidation of resin-carbonyls with NMR (acids or amides) • Decreasing content in the resins due to polarity-based shifts or oxidative quenching phenomena • Quinolones=porphyrins?

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Role of VO^{2+} compounds	• Vanadyl content stays the same during thermal ageing[1, 2] • Vanadyls as central ions of porphyrins[23-25]	• Vanadyls are concentrated in resins and asphaltenes • Vanadyl porphyrin content decreases in the resins with ageing
Aromatic structures	• Aromatic compounds emerge during oxidative and are proposed as part reaction mechanism [11, 18]	• Overall loss of fluorescent aromatic molecules • Increasing aromatic system sizes with ageing • Redistribution from aromatics to resins and asphaltenes – direct insights via difference FEEMs • Multiple contributing factors: Evaporation vs. degradation vs. oxidation vs. condensation
Polymer degradation	• SBS molecules get smaller[26, 27] • Reactions at olefinic positions[26, 28, 29]	• The average size of the polymer is roughly half after 17 years • Reactions mainly in the PB phase • Additional reactive centres within the polymer at allylic positions • Light and/or ROS are required • Aromatic SBS features are non-reactive
Thermal ageing	• Carbonyls and sulfoxides are the main oxidation products[11, 17, 18] • Sulfoxide formation vs decomposition at elevated temperatures [4-6]	• Extension of aromatic systems is not reached with 1xPAV • Redistribution of fluorophores by difference FEEMs • Degradation of porphyrins • No significant changes to the overall molecular parameters • T-dependency of organic radical formation
ROS ageing	• Accelerated ageing at reduced temperatures[30-34]	• Incorporation of NO_2 into the molecular system [35] • Elevated loss of aromatic compounds due to evaporation of volatile compounds in open system
Light ageing	• Direct impact is restricted to the surface[36, 37] • Indirect impact through diffusion processes[37]	• Ester formation during light ageing • Oxidation rates in the fractions during light ageing (Ar>R>S>As) • Almost no change in asphaltenes • Significant changes in aromatic surface structures during light ageing • Resins and aromatics contain the most reactive aromatic structures (R>Ar>S>As)

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8. Conclusion and Outlook

This last Chapter focuses on the stated research questions and gives an outlook on future tasks.

Which methods can improve the characterisation of bitumen and its ageing states?

The systematic evaluation of four different spectroscopic methods has shown that they provide unique molecular parameters that profoundly and universally describe various aspects of bitumen chemistry. EPR, IR and FS were sufficiently sensitive to detect alterations due to thermal ageing, while HSQC NMR could not determine any changes. Additional methods were tested in more specific research approaches, resulting in a parameter set that contains oxidation products, degradation/molecular association of fluorophores, growth of aromatic systems, degradation/molecular association of N-containing compounds, increase of organic radical content, assessment of vanadyl content, molecular sizes of bitumen/polymer, quantitative evaluation of polymeric substructures.

How does field ageing compare to conventional and novel laboratory ageing procedures?

Field ageing induces unique changes in bituminous materials initiated by various environmental ageing factors. The harshest laboratory ageing methods mimic the carbonyl formation and aromatic system size growth observed in the field. However, fewer sulfoxides are formed, and the loss of fluorescent molecules is higher in the laboratory due to the elevated temperatures (T-dependent sulfoxide decomposition, evaporation of volatile compounds). The evaluation of PMB samples has shown that extended laboratory ageing can simulate the degradation of the polymers. Cleavage processes in the polybutadiene phase are the fundamental cause of SBS degradation. The additional changes in polymer functionalities were partially simulated with VBA due to reactions induced by NO_2 and O_3 (ROS). Light ageing has yet to be tested on PMBs. The analysis of photo-induced processes in unmodified samples showed a unique set of oxidation products and drastic transformations of the aromatic systems. Secondary oxidation products induced by light might impact the assessment of sulfoxide content (overlapping bands) and contribute to a similar increase in aromatic system size at lower temperatures.

What impact do polymers have on the ageing processes of bituminous products?

The addition of SBS has no impact on the oxidation rates of bituminous molecules. No significant differences are observed regarding fluorescence properties and the emergence of organic radicals. However, field ageing influences aromatic molecules in PMB samples differently than in unmodified samples. The polymer phase acts as a protector of the aromatic molecules, which are preserved either directly (by intermolecular bonds) or indirectly (preferential attack at more reactive polymer sites). Up to now, the impact of ageing-induced changes in the polymer phase (cleavage, side chain reactions), the associations of bituminous molecules to the polymeric structure (swelling), and the intermixing of degraded polymers on the mechanical properties of the construction material has not been evaluated. This, however, is a valuable aim for future investigations.

Outlook

Throughout the experimental work of this thesis, new questions and scientific problems have constantly arisen. These are summarised and discussed in this concluding paragraph. It has been shown that the overall aromatic content decreases during ageing. However, the fundamental reasons for this process and the measured differences between the ageing methods are still not fully understood. As discussed throughout this thesis, four particular mechanisms are imaginable: a)evaporation, b)oxidation, c)condensation, and d)degradation. The elimination of ambiguities in the elucidation of aromatic transformation processes requires the quantification of quaternary aromatic carbons and the detailed evaluation of volatile compounds. A possible way to determine quaternary carbon content is by quantitative ^{13}C- NMR spectroscopy. Evaporation could be assessed by determining the mass loss during laboratory ageing and characterising the emerging VOCs and secondary organic aerosols with mass spectrometric techniques. Mass loss evaluation is only possible in combination with elemental analysis to cover for the mass gain due to the incorporation of oxygen (and NO_2). Determining the chemical characteristics of the VOCs and aerosol particles should provide additional information on the origin of the compounds (from which fraction?) and the specific types of aromatic structures (polycondensed?). Incorporating these considerations in future studies will facilitate a conclusive, unambiguous interpretation of the spectroscopic data already discussed in this thesis.

Other exciting features are organic vanadyl and nickel complexes. Since they contain transition metals, they have been discussed as potential reaction catalysts [11, 38, 39]. However, there was no direct correlation between ageing susceptibility and the total vanadium content. Thus, the chemical functionality might be of greater importance than the total amount. Therefore, future studies should aim at differentiating and quantifying the impact of vanadium in different chemical complexes.

Finally, insights into molecular properties and the developed analytical framework shall be used to progressively adjust the representation of average structures in molecular simulations. Only by constantly improving the correctness of the input parameters can a predictive tool for ageing susceptibility and miscibility with various modifiers and additives be developed. Also, methodologies for quantitative determination of intermolecular associations in agglomeration processes and how they change during ageing should be designed and incorporated. The use of Hansen solubility parameters for the semi-quantitative evaluation of dispersive, polar (dipole-dipole) and hydrogen bonding forces in the material could be a promising approach [40-43]. A link between molecular information and nano-, micro-, and macrostructural information must also be found. The initial questions that drive this scientific approach contain the possibility of linking surface microstructures to bulk structures and how this is affected by molecular size changes, agglomeration processes, and overall molecular transformations that happen during ageing. By searching for correlations between microstructural and mechanical parameters, the fundamental reasons for material failure from the molecular up to the macroscopic level could be coherently described in the future.

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9. Appendix

9.1. Supplementary material

9.1.1. Electron paramagnetic resonance (EPR) spectroscopy. Methodology.

The EPR measurements were performed using a Bruker EMX 10/1 spectrometer (continuous wave (CW) X-band) with an ER4102ST standard rectangular resonant cavity in the TE_{102} mode. About one gram of bitumen was melted (100 °C for 5 minutes in an oven), homogenised (with a spatula), and four drops of each sample were poured onto a silicone mould. The samples were weighed after cooling to room temperature (usually between 50-100 mg). Each sample was glued to the upper end of the EPR capillary and then measured. The SARA fractions were dissolved in HPLC-grade toluene at 1-10 mg/ml concentrations and poured into EPR tubes. The tubes were placed into the EPR cavity, and EPR measurements were performed. The centre field was set to 338 mT, sweep width 100 mT, resolution 2048 points, modulation amplitude 0.1 mT, and modulation frequency 100 kHz. Apart from the saturates, all fractions contained organic radicals. The second contribution in the resins, asphaltenes, and bitumen arises from VO^{2+}-structures. The characteristic splitting pattern is caused by isotropic (8 equidistant signals in the resins because I=7/2) and anisotropic (axial symmetry in asphaltenes, partially overlapping eight parallel and eight perpendicular signals) behaviour of the samples at the given concentration and temperature (room temperature) range.

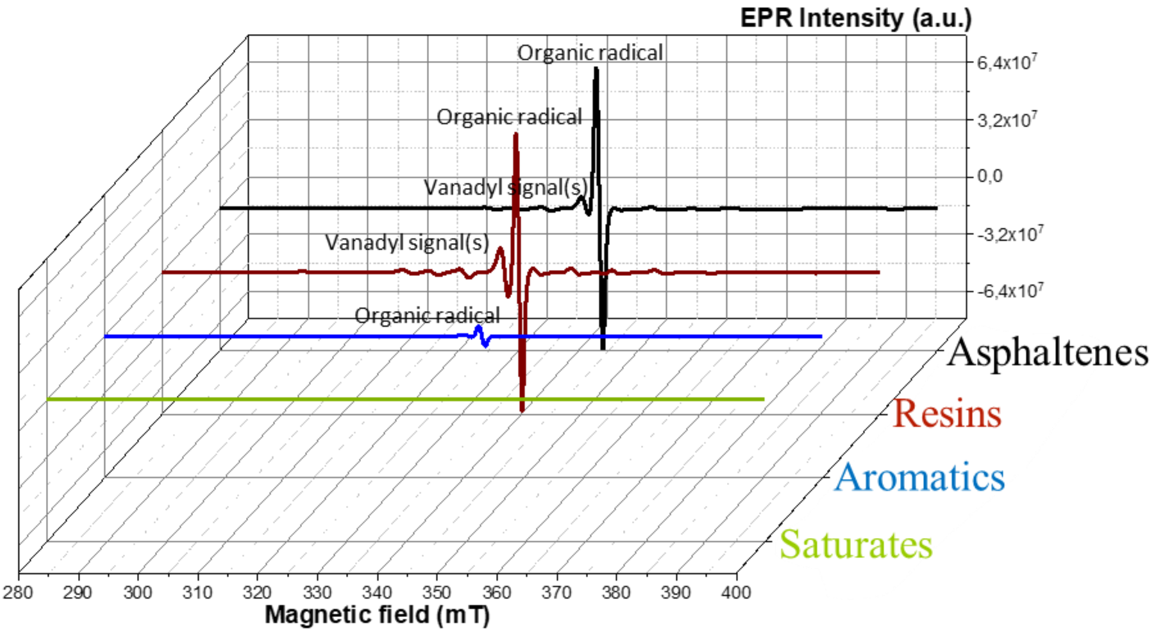

Figure 21. EPR spectra of the SARA fractions.

The bitumen spectra were simulated with Matlab2020b using the EasySpin-5.2.36 module[6]. The total number of spins per g of organic radicals and vanadyls in the samples was evaluated by double integration of the simulated spectra and comparison to external calibrations (using 2,2-diphenyl-1-picrylhydrazyl (DPPH) in toluene).

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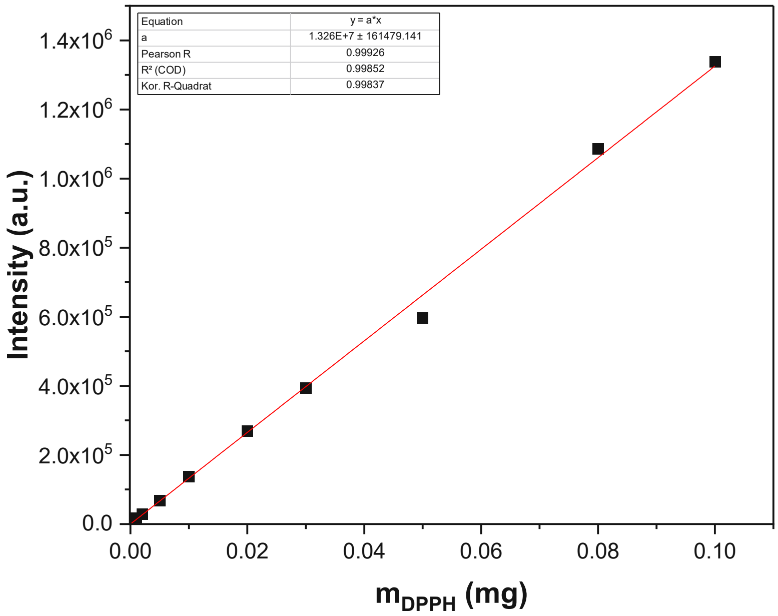

Figure 22. Calibration curve of 2,2-diphenyl-1-picrylhydrazyl (DPPH) in toluene. The intensity refers to the double-integrated EPR spectrum.

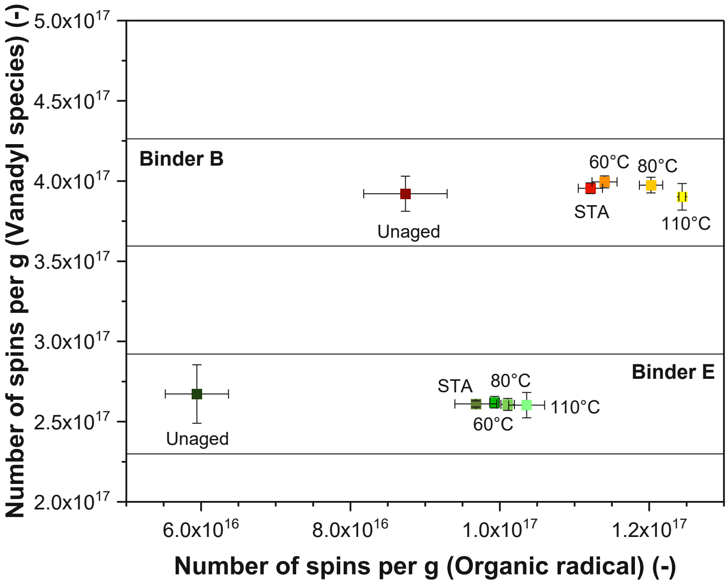

Figure 23. Organic radical and vanadyl content of binder B and binder E. Impact of 60, 80, and 110°C on short-term aged samples. Ageing time: 3 days.

9.1.2. NMR spectroscopy

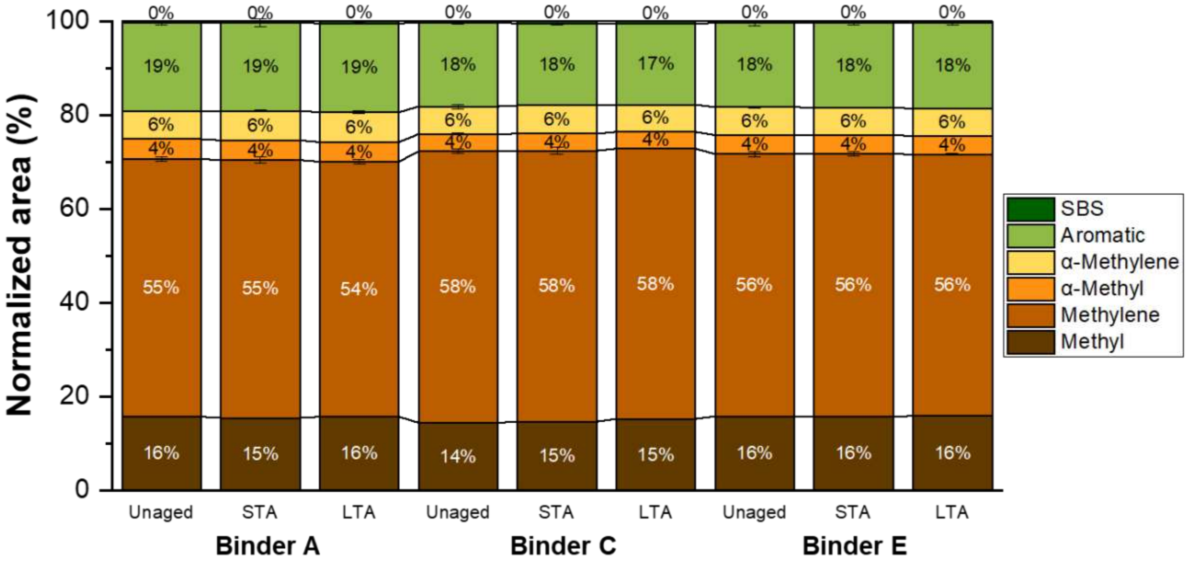

Figure 24. NMR properties of the remaining 3 binders in 3 ageing states. Unaged, STA, and LTA.

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9.1.3. Additional data on the field samples

Table 7. Additional information on the field-aged samples.

Sample	Unmodified sample	Polymer-modified sample
Field ageing period	2012-2017	2005-2022
Analyzed asphalt layer	The top cm of the surface layer	The top cm of the surface layer
Mixture design	Asphalt concrete 11 (maximum nominal aggregate size of 11)	Stone-mastics asphalt
Aggregates	Porphyrite	Steel slag
Filler	Limestone	Limestone
Location	Open area, Vienna, Austria	Austrian state road B1, city bypass Enns, Upper Austria, Austria
Extraction methodology	EN12697-3 (solvent: tetrachlorethylene)	EN12697-3 (solvent: tetrachlorethylene)
Bitumen storage after extraction	In closed metal cans at room temperature (2017-2022)	In closed metal cans at room temperature (2022-2023)
Snow removal	Yes	Yes
Mechanical stress	No	Yes, daily traffic
Average amount of precipitation/a*	668 ± 90 l/m^2	720 ± 125 l/m^2
Average temperature/a*	12.7 ± 0.4 °C	10.4 ± 0.7 °C
Minimum temperature/a*	-8.4 ± 3.1 °C	-11.0 ± 3.5 °C
Maximum temperature/a*	36.9 ± 1.9 °C	34.4 ± 1.3 °C
Average sunshine hours/a*	2077 ± 97 h	1927 ± 87 h
Global radiation/a*	135.2 ± 3.2 W/m^2	135.0 ± 3.9 W/m^2
Global radiation-annual minimum based on monthly averages/a*	31.1 ± 2.6 W/m^2	29.4 ± 3.9 W/m^2
Global radiation-annual maximum based on monthly averages/a*	260.0 ± 17.6 W/m^2	257.2 ± 15.6 W/m^2
Weather station (for calculations)	Vienna (48.1984, 16.3670)	Linz (48.2965, 14.2852) (2005-2009) Enns (48.1957, 14.4509) (2009-2022)

Figure 25. Obtained drill cores of the polymer-modified sample after 17 years in use.

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9.1.4. Branching index and aromaticity determination with IR

Table 8. Branching and aromaticity index of unaged and field-aged SARA fractions.

Sample	Branching index (-)		Aromaticity index (-)	
	Unaged	Field-aged	Unaged	Field-aged
Saturates	0.319±0.001	0.324±0.001	0.042±0.001	0.041±0.001
Aromatics	0.381±0.001	0.376±0.001	0.184±0.005	0.211±0.006
Resins	0.413±0.006	0.399±0.001	0.223±0.005	0.239±0.001
Asphaltenes	0.439±0.008	0.410±0.009	0.322±0.008	0.379±0.004

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9.2. Curriculum vitae

Personal information

Surname, First name: Werkovits, Stefan
Birthday: 03.08.1993
Citizenship: Austria

Education

October 20 – May 24	Doctoral programme in Engineering Sciences, TU Wien, Institute of Materials Chemistry, Physical Chemistry of Atmosphere-Materials-Interactions
April 23	Summer school: Modern Developments in Spectroscopy, Holland Research School of Molecular Chemistry, Netherlands
September 22	Summer school: 1D- and 2D NMR Spectroscopy in Liquids, University of Graz, Austria
October 19 – September 20	Master of Science, TU Wien, Physical and Analytical Chemistry, Technical Chemistry
	Master thesis: *Advanced Characterization of Bitumen using Chromatography and FTIR*
October 14 – June 19	Bachelor of Science, TU Wien, Technical Chemistry
	Bachelor thesis: *Hydrothermal Biomass Conversion Exploration*

Work experience

October 20 – May 24	Project assistant at the research group Physical Chemistry of Atmosphere-Materials-Interactions, TU Wien
April 19 – October 19	Student employee at the Institute of Materials Chemistry, TU Wien
July 18 – August 18	Summer internship at Takeda, Quality control - Microbiology
February 18 – April 18	Student employee at the Institute of Materials Chemistry, TU Wien
July 16 – August 16	Summer internship at Shire, Quality Control – Liquid Chromatography
January 14 – September 14	Temporary soldier at Austrian military – Music corps
July 13 – December 13	National service at Austrian military

9.3. List of publications

Peer-reviewed articles

Werkovits, S., Primerano, K., Bacher, M., Rosenau, T., Hofko, B., & Grothe, H. (2024).
Unraveling the ageing processes in polymer-modified bitumen.
Fuel (under review)

Werkovits, S., Bacher, M., Mirwald, J., Rosenau, T., Hofko, B., & Grothe, H. (2024).
Photo-induced ageing processes in bitumen.
Construction and Building Materials (under review)

Werkovits, S., Bacher, M., Mirwald, J., Theiner, J., Rosenau, T., Hofko, B., & Grothe, H. (2023).
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Werkovits, S., Primerano, K., Schöberl, T. R., Hofko, B., & Grothe, H. (2023).
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Mirwald, J., Werkovits, S., Camargo, I., Maschauer, D., Hofko, B., & Grothe, H. (2020b).
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Construction and Building Materials, *258*, 119577.

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Other articles

Primerano, K., Werkovits, S., Mirwald, J., Grothe, H., & Hofko, B. (2023). Bitumenalterung auf der Spur-Was Sie schon immer über die" Viennese Binder Aging"-Methode wissen wollten, aber bisher nicht zu fragen wagten.

Theses

Werkovits, S. (2020). Advanced characterization of bitumen using chromatography and FTIR spectroscopy. Diploma thesis. TU Wien.

Werkovits, S. (2019). Hydrothermal biomass conversion exploration. Bachelor thesis. TU Wien.

Presentations

Werkovits, S., Primerano, K., Bacher, M., Rosenau, T., Hofko, B., & Grothe, H. (2024). Unraveling the chemical processes within polymer-modified bitumen *International Symposium on Asphalt Pavement (ISAP) 2024. Montreal, Canada.*

Werkovits, S., Primerano, K., Bacher, M., Mirwald, J., Rosenau, T., Hofko, B., & Grothe, H. (2023). Elucidation of the Chemical Processes in Polymer-modified Bitumen. *Asphalt Innovation Symposium 2023. Antwerpen, Belgium. (invited)*

Primerano, K., Werkovits, S., Schönauer, P., Mirwald, J., Grothe, H., & Grothe, H. (2023) Chemical and mechanical analysis of field and laboratory aged bitumen. *European Asphalt Technology Association (EATA) 2023. Danzig, Poland.*

Werkovits, S., Primerano, K., Schöberl, T., Koyun, A. N., & Grothe, H. (2022). How infrared and fluorescence spectroscopy can shed new light on the characterization of bitumen and its polarity-based fractions. *International Symposium on Asphalt Pavement (ISAP)2022. San Jose, Costa Rica.*

Koyun, A. N., Werkovits, S., & Grothe, H. (2022). Structural and chemical analysis of bitumen surface by Surface Probe Microscopy. *International Symposium on Asphalt Pavement (ISAP)* 2022. San Jose, Costa Rica.

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Werkovits, S., Mirwald, J., Koyun, A. N., Hofko, B., & Grothe, H. (2019).
Time dependent studies of bitumen surface with FTIR.
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