Diplomarbeit

Evaluierung des Alterungsverhaltens von Biogenen Bindemitteln und Bitumen mittels chemischer und mechanischer Analyse

ausgeführt zum Zwecke der Erlangung des akademischen Grads
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Diploma Thesis

Evaluating the Ageing Behavior of Bio-binders and Bitumen via Chemical and Mechanical Analysis

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von

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Danksagung

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Erklärung

Ich bestätige, dass für die Fertigstellung dieser Arbeit mit dem Titel „Evaluierung des Alterungsverhaltens von Biogenen Bindemitteln und Bitumen mittels chemischer und mechanischer Analyse“ ChatGPT, ein von OpenAI entwickeltes Sprachmodell für künstliche Intelligenz, verwendet wurde. ChatGPT half bei der Verfeinerung der Formulierungen. Obwohl sich ChatGPT als wertvolles Hilfsmittel zur Unterstützung meiner akademischen Aktivitäten erwiesen hat, bin ich mir bewusst, dass seine Beiträge algorithmisch generiert werden und nicht die Arbeit menschlicher Forscher oder Experten darstellen. Darüber hinaus übernehme ich die volle Verantwortung für den endgültigen Inhalt und die Analyse meiner Abschlussarbeit. Ich erkläre, dass alle Abschnitte meiner Diplomarbeit, einschließlich derjenigen, die durch Interaktionen mit ChatGPT entstanden sind, den von der Technischen Universität Wien geforderten akademischen Standards für Integrität, Zitierung und Originalität entsprechen.

Abstract

Bitumen is a waterproof, viscoelastic, oil-based material that offers a great variety of applications amongst industries due to its one-of-a-kind mechanical and chemical properties. The material is mainly utilized in the field of paving, roofing and waterproofing. The majority (95%) is used in the production of asphalt pavements, which accounts for 100 Mt of yearly production. In an asphalt pavement the bitumen acts as a binders for mineral aggregates, which then forms the asphalt mixture, asphalt concrete or bituminous concrete [1].

It is used because of its great adhesive qualities that help to keep the aggregates connected. However, since bitumen originates from fossil resources, its availability becomes limited. Thus, the research community is looking for renewable "bio" alternatives that can replace these fossil resources. This is a challenging task, since the complex chemical composition of bitumen is the reason for such unique material behavior. Thus, merely partial replacement of up to 50% is a suitable option until now. Furthermore, the addition of bio alternatives brings up a completely new level of material characterization and evaluation of its ageing behavior, which might be different compared to conventional bitumen. Furthermore, the public are facing new environmental standards and regulations that ensure less emissions and save fossil resources from extraction of the resource to, transportation of the material, to production, to consumption until end of use and the disposal of the product [2]. Thus, the question is whether we are gaining sustainability for the price of decreasing durability. Or is there a mix of possible uniting both durability and sustainability.

Therefore, this diploma thesis investigates and characterizes the ageing behavior of bio-based binders via artificial laboratory ageing and subsequent chemical and mechanical analysis. Three different bio-binders were compared to an unmodified base and a reference bitumen. The percentage of bio additive ranges from 10 – 50%. Various laboratory short-term ageing (STA) and long-term ageing (LTA) procedures involving different ageing inducing factors like temperature, light and reactive oxygen species (ROS) were applied on the five binders. Chemical analysis using Fourier Transform Infrared (FTIR) spectroscopy and mechanical analysis using the dynamic shear rheometer (DSR) were applied to evaluate the binders.

Results revealed that the impact of thermal ageing is limited and only one cycle of Pressure Ageing Vessel test (PAV) ageing does not meet the level of other LTA ageing methods like Viennese Binder Ageing (VBA) or light ageing (LA). VBA shows significant ageing for bio-binder 1 and bio-binder 2, while bio-binder 3 is showing sort of resilience to ROS. In terms of light ageing, this study revealed that across several binders light induced ageing depends a lot on the light source (LA1 – LA3). All bio-binder exhibit a lower ageing susceptibility compared to the reference 70/100 binder. Bio-binder 1 shows an interesting rheological behaviour between intermediate and high temperature and performs better at lower temperatures. Bio-binder 2 indicates characteristics that almost end up at the rheological levels of the binder 2. Bio-binder 3 shows a high susceptibility towards light ageing (compared to ROS).

Kurzfassung

Bitumen ist ein wasserabweisendes, viskoelastisches, ölbasierendes Material, das aufgrund seiner einzigartigen mechanischen und chemischen Eigenschaften in zahlreichen Industrien vielseitig einsetzbar ist. Hauptsächlich wird es im Bereich des Straßenbaus, für die Dachabdichtung und der Wasserabdichtung verwendet. Der größte Teil (95 %) wird für die Herstellung von Asphaltbelägen genutzt, was einer jährlichen Produktionsmenge von 100 Millionen Tonnen entspricht. In einem Asphaltbelag fungiert Bitumen als Bindemittel für mineralische Zuschlagstoffe, die dann ein Asphaltmischgut bilden [1].

Bitumen wird wegen seiner hervorragenden adhäsiven Eigenschaften verwendet, die helfen, die Zuschlagstoffe zusammenzuhalten. Da Bitumen jedoch aus fossilen Ressourcen gewonnen, ist die Verfügbarkeit der Ressource limitiert.

Aus diesem Grund sucht die Wissenschaft nach erneuerbaren „Bio"-Alternativen, die diese fossilen Ressourcen ersetzen können. Dies stellt jedoch eine große Herausforderung dar, da die komplexe chemische Zusammensetzung von Bitumen für das einzigartige Materialverhalten verantwortlich ist. Daher ist bislang nur ein teilweiser Ersatz von bis zu 50 % eine geeignete Option. Darüber hinaus bringt die Zugabe von Bio-Alternativen eine völlig neue Dimension der Materialcharakterisierung und der Bewertung des Alterungsverhaltens mit sich, das sich erheblich von herkömmlichem Bitumen unterscheiden könnte.

Zudem stehen die Öffentlichkeit vor neuen Umweltstandards und Vorschriften, die darauf abzielen, Emissionen zu reduzieren und fossile Ressourcen entlang der gesamten Wertschöpfungskette – von der Rohstoffgewinnung über den Transport und die Produktion bis hin zur Nutzung und Entsorgung des Produkts – zu schonen [2]. Daraus ergibt sich die Frage, ob wir Nachhaltigkeit auf Kosten einer verringerten Haltbarkeit erreichen, oder ob es eine Möglichkeit gibt, Haltbarkeit und Nachhaltigkeit zu vereinen.

Diese Diplomarbeit untersucht und charakterisiert daher das Alterungsverhalten biobasierter Bindemittel durch Laboralterung sowie anschließende chemische und mechanische Analysen. Drei verschiedenen Biobindemittel wurden mit ihrem unmodifizierten Grundbindemittel und einem Referenzbitumen verglichen. Der Anteil an Bio-Additiven lag zwischen 10% und 50 %. Dafür wurden Kurzzeitalterungen und Langzeitalterungen durchgeführt, die unterschiedliche Alterungsfaktoren wie Temperatur, Licht und Reaktivgase (ROS) induzieren. Zur Bewertung der Bindemittel wurden die Fourier-Transform-Infrarotspektroskopie (FTIR) für die chemische Analyse und das dynamische Scherrheometer (DSR) für die mechanische Analyse eingesetzt.

Die Ergebnisse zeigen, dass der Einfluss der thermischen Alterung sehr begrenzt ist und ein einziger PAV-Zyklus das Alterungsniveau anderer LTA-Methoden wie VBA oder LA nicht erreicht. Die VBA zeigte eine signifikante Alterung bei Bio-binder 1 und Bio-binder 2, während Bio-binder 3 eine gewisse Widerstandsfähigkeit gegenüber der ROS zeigte. Im Hinblick auf die Lichtalterung zeigt diese Diplomarbeit, dass lichtinduzierte Alterung stark von der Lichtquelle (LA1 – LA3) abhängt. Alle Biobindemittel weisen eine höhere Alterungsanfälligkeit im Vergleich zum Referenzbitumen 70/100 auf.

Bio-binder 1 weist ein interessantes rheologisches Verhalten bei mittleren und hohen Temperaturen auf und das Bindemittel verhält sich besser bei niedrigen Temperaturen. Bio-binder 2 zeigt Eigenschaften, die sehr nahe an die rheologischen Eigenschaften von Bindemittel 2 herankommen. Bio-binder 3 ist stärker anfällig gegenüber der Lichtalterung. Dafür zeigt der Bio-binder 3 eine Resilienz gegenüber den in der VBA induzierten ROS.

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1. Introduction

Bitumen is a material that surrounds our everyday life and yet it is often overlooked unless you take a closer look. The word "bitumen" instantly sounds familiar and still it likely needs to be googled, because it rings a bell and yet a clear connection is missing. When looking up "bitumen" on the search engine of your trust it comes to mind that there is a difference to concrete and asphalt. You might come across that this is a material that seamlessly integrates into our daily lives, often unnoticed despite its vital role in modern infrastructure. Its extensive application in the pavement industry has been a cornerstone of societal progress, enabling the development of versatile and reliable infrastructure that supports our economic and social well-being. Its versatility has led to the infrastructure that we use daily and take for granted. Infrastructure that enables mobility and trade to shape today's global world to the extent we know today. Infrastructure, roads, pavement and bitumen deserve recognition for the wealth and development of societies they enabled. But as the world faces multiple challenges and shifts focus towards sustainability, it needs to be researched whether bitumen will be able to also pave a more sustainable future.

Bitumen is a waterproof, viscoelastic, oil-based material that offers a great variety of applications amongst industries due to its one-of-a-kind mechanical and chemical properties.
The material is known to have been used as hafting material in the antique Syria 180.000 years ago [3]. Its references last from many historic publications such as the bible statements for waterproofing of Noah's arche, ancient medicine trusted its disinfection to the material. All the way to the Egyptians who relied on natural bitumen following their rituals for mummifications [1, 3]. This shows the historic demand that is unbroken even in today's industry, bitumen is a widely used material. By this time, the product is artificially produced by vacuum residue from petroleum distillation. That means it is based on crude oil, a finite resource.

Bitumen is utilized in paving, roofing and waterproofing. 95% of the bitumen used, which in total accounts for 100 Mt of yearly production, are employed for paving. Products like binders for mineral aggregates used for asphalt mixes [1]. It is used because of its adhesive qualities that help to keep the aggregates connected. Many parameters of performance are demanding, such as heating to 180°C during mixing procedure to apply the material. After mixing the binder needs to endure temperatures at around 60°C-80°C and avoid rutting. Furthermore, low temperatures request the material to be soft and ductile enough to prevent breaking at -20°C [1].
These demands make it a versatile material, because it can be designed for certain specifications. However, its origin lies in the faith of crude oil and therefore many studies crave a reduction or even substitution of bitumen. Trading Economics a bitumen price index, lists the price for bitumen at 450 US-dollars per ton, as of December 2024 [4]. As a production derivative of petroleum bitumen price is strongly connected to the petroleum price. In the last year the price for bitumen has fallen by 3% as stated by Trading Economics [4]. That drives motivation to look for comparable components that range far below that price level with similar composition and so there are blends possible that bring in new materials to add to bitumen in the future [2].That can have a sustainability advantage. It leads also to less energy consumption

because these bio additives require less temperature in the bituminous mix. That reduces the costs of paving by 20% and saves emissions in the mixing process [2].

Infrastructure and the construction and maintenance of roads relies on these binders. Meanwhile, the Intergovernmental Panel on Climate Change (IPPC) report (Chapter 10) states that transports accounts for 23% of global greenhouse gas (GHG), equating to 8.7 gigatons of CO_2-equivalent ($GtCO_2e$) as of 2019 [5]. Infrastructure accounts for 79% of all GHG emissions defined, infrastructure—including energy production, buildings, and transport systems [6]. Specifically, the construction industry alone accounts for about 10% of global GHG emissions [6].These numbers underline the urge to conduct research and limit the use of binders that come from fossil fuel. The consciousness and interest for the environment has increased tremendously in the past years. The European Union stresses net zero of emissions by the year 2050. Austria aims to achieve net zero of emissions by 2040 in the national report for climate and sustainability [7].The United Nations Framework Convention on Climate Change (UNFCCC) was installed in 1992 to prevent further degradation on behalf of the climate. Despite the efforts of that committee, the CO_2 emissions from fossil fuels grew by 67% in the period from year 1990 to 2018 [8]. Accordingly, both the public is facing new environmental standards and regulations that ensure less emissions and save resources from extraction of the resource to, transportation of the material, to production, to consumption until end of use and the disposal of the product [2]. Thus, the question is whether we are gaining sustainability for the price of decreasing durability. Or is there a mix of uniting both durability and sustainability? Therefore, this diploma thesis investigates and characterizes the ageing behavior of bio-based binders via artificial laboratory ageing and subsequent chemical and mechanical analysis.

2. Theoretical paradigm

2.1 Bitumen

Bitumen is a product of crude oil distillation in the petroleum refining process. It is a black, sticky material with viscoelastic properties, behaving as a solid or liquid depending on the temperature. Within a range of -25°C to +80°C, bitumen remains durable: at higher temperatures, it resists permanent deformation, while at lower temperatures, it can relax enough to withstand cryogenic or tensile stress without cracking. These characteristics make bitumen ideal for applications such as road construction, sealing, and roofing [9].

Within the distillation process, crude oil is separated into several compartments. The distillation is based upon the fact that the compartments each have their individual boiling point at which they leave the complex and are set free. First heating of the oil is performed at a temperature of 350°C-400°C by an atmospheric distillation column. In this distillation column, the lighter compartments such as gasoline, kerosene, diesel, fuel oils, naphta, gasoline and gas (methane, ethane, propane and butane) are at the top. The heavier compartments remain at the bottom and need to be addressed later. These heavier parts will be processed in the subsequent vacuum distillation where low pressure is exerted to reduce the boiling point so that heavier compartments become more feasible to extract. Lubricating oils and paraffins are set free at this stage. Left behind is the vacuum residue which is a thick and viscous material and sets the base for bitumen [10]. In the straight run distillation the vacuum residue of suitable crude oils fulfills the characteristics of bitumen and is kept as it is. If the resulting bitumen requires higher viscosity the vacuum residue can be treated with higher temperatures between 200°C-300°C to heat up and cause oxidation. This air-blowing process makes the material stiffer and is commonly called oxidized bitumen[10].

2.2 Bio-binders and Extenders

Going from bitumen and transition to bio-binders and extenders in the paving industry is driven by economic, technological and environmental motivations. Talking about ”bio”, “bio-mass” or “bio-binders” there is a large amount of definitions out there and it makes it hard to speak about the same thing. Biomass is a term for all organic material that stems from plants including algae, swine manure, trees and crops. These organic materials hold potential as sustainable alternatives compared to fossil resources and oil-based products [11].

Biomass stores solar energy through photosynthesis saving it in chemical bonds of structural components of biomass. The biomass contains cellulose, hemicellulose, lignin and extractives. All of those are particularly valuable [11]. Lignin has a benefitting influence on heating value due to the complex aromatic structure and rich carbon composition [12]. Biomass contains stored energy, which is of big focus when aiming to replace fossil fuels with renewable resources. The motivation for bio-binder and extenders is driven by multiple factors:

1. Depletion of fossil resources and the limited availability of fossil fuels.
2. Economic motivation as the cost of crude oil has experienced large fluctuations over the last decades.

3. Environmental degradation has caused to consider carbon emissions and enforcing a circular economy to save resources and climate.
4. Regulations and governmental policies are implemented on a global scale to reduce resource depletion and limit carbon emissions. A bio-based circular economy that produces fuels and energy from renewable sources is the target scenario [2].

Bio-binders and extenders can be classified into three different groups. The use of bio-based alternatives in bitumen applications varies depending on the degree of substitution and the purpose of the material. These alternatives are categorized into three groups based on the level of replacement:

1. **Full Binder Replacement**: This approach involves completely replacing conventional bitumen with materials derived entirely from renewable resources. It achieves a 100% substitution, offering a sustainable alternative to traditional oil-based binders [13, 14].
2. **Extenders**: Extenders are blended with base bitumen to reduce the overall proportion of oil-based components. They can substitute between 25% and 75% of the bitumen, striking a balance between sustainability and traditional performance [13, 14].
3. **Additives**: Additives are used in smaller proportions, typically replacing 10% or less of the conventional bitumen. These are designed to enhance specific properties of the binder while maintaining compatibility with traditional materials [13, 14].

By incorporating these bio-based solutions, it becomes possible to design the level of sustainability and performance to meet various application requirements, paving a road towards more resource-efficient practices [13, 14].

Based on these different types of bio-binders and extenders, the question arises which types of bio-binders and extenders are available and what they are made of. The work by Penki et al. [11] from 2021 shows an overview of different bio-binders. A promising alternative to conventional bitumen, offering a more sustainable and eco-friendly way to build roads. They are made from renewable resources like waste oils, plant residues, and animal byproducts. These materials improve the performance of bitumen while reducing the environmental impact. Bio-binders can be derived from wood plants and agricultural products, herbaceous plants/grasses, aquatic plants and waste biomass [11]. Here are some of the most promising bio-binders and what makes them stand out:

Bio-oil from waste cooking oil (WCO), a byproduct of biodiesel production, is processed through alkaline catalysis and chemical polymerization [15]. This bio-oil is effective in improving the fatigue resistance of bituminous binders. It can act as both a modifier for conventional bitumen and a rejuvenator for aged bitumen. By incorporating WCO-based bio-oil, the durability of pavements can be extended, addressing issues of material degradation while offering an environmentally friendly recycling solution [2].

Lignin-based bio-binders, a major byproduct of the paper and pulp industry, is extracted from black liquor, a waste stream generated during the paper manufacturing process. When used as a binder, lignin-based bio-oil significantly reduces the formation of carbonyl compounds and minimizes the presence of aromatics, which are linked to bitumen aging. Notably, lignin-based bio-binders show improved aging resistance without undergoing chemical reactions when blended with conventional bitumen. This stability makes lignin an ideal candidate for bio-bitumen production [2].

Bio-binder from animal waste, particularly swine manure, can be converted into bio-oil through pyrolysis, a thermochemical process. Swine-manure-derived bio-binders are notable for their ability to enhance low-temperature performance. They improve crack resistance under freezing conditions, making them particularly suitable for regions that experience extreme temperature variations. When the bio-oil is added to conventional bitumen, however, the review states that there is a negative impact on water stability. It also lowers the fatigue performance and low temperature crack resistance [2].The issue can be solved by adding another binder. Palm kernel oil derived from bio-oil by esterification. This is interesting because it shows the complexity of the bio-binder. They only perform in the right way when they passed specific treatment method [2].

Biochar, produced through the pyrolysis of organic materials such as coconut shells, rice husks, and other agricultural residues, is a carbon-rich substance. When added to bitumen, biochar improves critical performance properties, including viscosity, ageing resistance, and thermal stability. The highly porous structure enhances the interaction between the bitumen matrix and aggregates, leading to better resistance to permanent deformation and thermal cracking [2].

Palm kernel oil-derived polyol is produced through esterification and condensation processes. This bio-binder shares similar thermal and chemical properties with conventional bitumen but offers enhanced flow resistance and durability. This oil is consistent in performance under varying temperatures makes it a reliable option for improving the flexibility and resistance of bituminous pavements [2].
Looking at the advantages of bio-binder, McKendry states the central motivation for developing a fossil fuel free economy. Burning fossil fuels uses old biomass and converts it into new CO_2, which supports the greenhouse effect. New biomass are ideally produced so they reach maximum biomass growth per year and area, low energy input to produce, low financial cost, free of contaminants and low nutrient demand [11].

Performance booster is a strong term, but many bio-binders contribute to a positive effect upon the asphalt mix and enhance performance parameters. Less cracking in higher and lower temperatures is a popular aim in paving industry. The benefit of a modified material is that for a crumb rubber asphalt in addition of epoxidized soybean oil (ESO) and a polyester fiber (PF) less cracking occurs in lower temperatures [16].

There are also certain disadvantages and challenges when working with bio-binders. Processing requirements, these materials require thermal treatment, vegetable oils require extensive modification to be up at the level of mechanical desires which will be further addressed in the following paragraphs [17].Figure 1 depicts three paths to enhance binder performance. It mentions transesterification, epoxidation and acrylation. Transesterification reduces viscosity of the oil, which makes them more compatible as a fluxing agent. Epoxidation and acrylation lead to better interaction with asphalt binder [17]. Epoxidation is a big term as it includes various steps that help improve the performance of the oil. Carboxylic acid and hydrogen peroxide generating peroxycarboxylic acid also giving the name for multiple epoxy products derived from that procedure. As a catalysator inorganic acid like a phosphoric acid is used and finally peroxycarboxylic acid reacts with double C bond in an unsaturated fatty acid which then leads to epoxy vegetable oil [17].

The big advantage is that compared to regular vegetable oil, the incorporation of epoxy groups significantly increases the polarity of vegetable oil. This makes the oil more thermally stable and resistant to oxidation. This enhancement improves the compatibility of epoxy-modified vegetable oils with asphaltenes, which also exhibit high polarity within asphalt components, thereby facilitating better dispersion of asphaltenes. Moreover, epoxy vegetable oils contribute to simultaneously adjusting the composition of the four primary components of asphalt [17, 18].

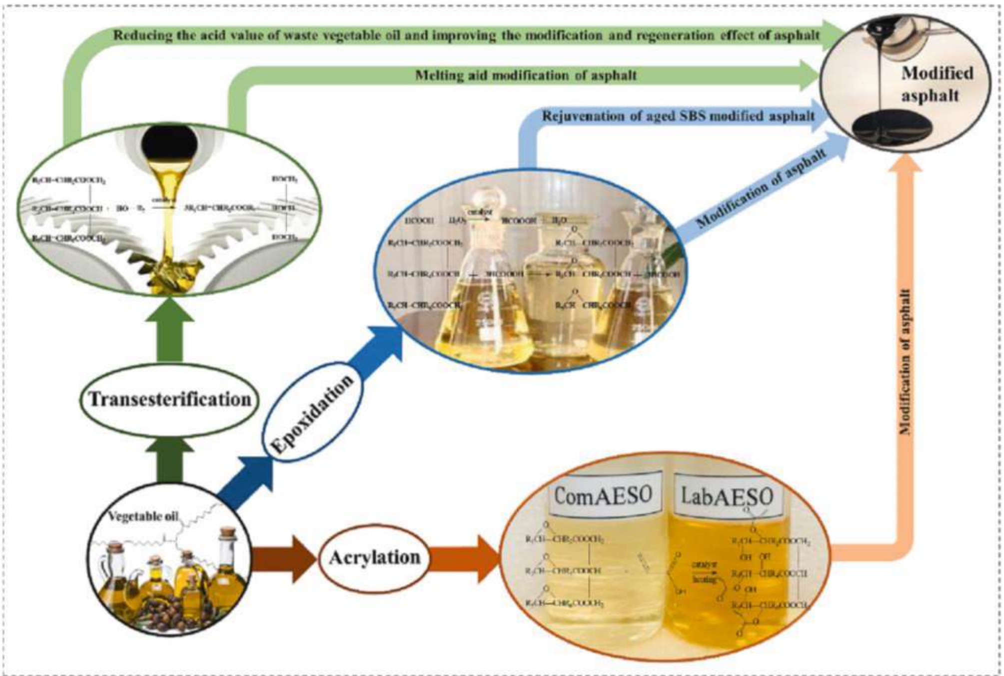

Figure 1:Asphalt modification and rejuvenation [17]

In terms of endurance or long-term performance, it is a big advantage when a material exhibits a high ageing resistance: Lignin has a complex aromatic structure that is resistant to oxidative ageing. Esterification is the simplest of all modifications involving lignin hydroxyl groups [2].

Advantageously to the petroleum-based modifiers, oils of bio-origin are reported to be successful in supplying the light oil components and therefore restoring the physical properties of bituminous binders subjected to aging processes, while presenting lower flammability and volatility [17, 19, 20].

Regarding economic assessment, costs will likely increase because the treatment of bio-binders pushes the price in production and makes it hard to rise on scalability. Oils from plants are certainly below the cost of bitumen per ton. However, additional treatment will also increase the costs. There is performance variation, so there is always a missing consistency, depending on where the source is and where the material comes from. Within the physical, chemical, and morphological properties, there are variations depending on the source, quality and type of oil. The process state is also an indicator to the fatty acids that are included in the oil [17, 21, 22].

The sensitivity of certain bio-oils can be high due to the content of polyunsaturated fatty acids. They are mentioned as a critical factor destabilizing the oil. This especially comes to attention when these biomaterials are applied to bitumen due to their drying or non-drying nature [17, 21, 23].

Another challenge is the effect on the mixture when combining additives or extenders to the bitumen. How does the bitumen incorporate the new material and what are challenges on a physical, mechanical, rheological, chemical and morphological scale [21]?

Crops that substantially grow for producing fuels oils and bitumen, raise strong concern towards water depletion, water pollution and energy consumption. Water consumption has a strong influence. When using fossil fuels all energy and water are already inserted in the resource. Over the past 20 years technological developments led to lower costs and higher conversion efficiency for biomaterials. Thermically usage of biomass allows to relocate energy from bio waste materials [11]. Bitumen is a distinctive substance that marginalizes many favorable properties that certainly make it challenging to replace. Bio-binders are renewable and biodegradable but need to be treated thermically so that they are more durable and withstanding. However, over the past few years various studies have faced broad range of sources for bio-binder [24].

All in all, these bio-binders offer a promising, sustainable alternative to petroleum-based material. The dependency on non-renewable resources is declining. Alongside less non-renewable resources being depleted, the environment is harmed less. Bio-binders derived from various biomass sources offer significant advantages over conventional bitumen. They can enhance key properties such as fatigue resistance, aging durability, and low-temperature crack performance while reducing the environmental footprint of road construction materials. By leveraging these sustainable resources, bio-bitumen contributes to circular economy principles and represents a step forward in the development of eco-friendly infrastructure solutions. As stated above, the technological development drives promising synergies. That is worth diving into further research, because they could radically improve in a short time and be the drivers of the future. It is also of great interest, how these bio-binders behave under the influence of ageing. Will they degrade faster than conventional binders or will they remain stable are questions that need to be addressed.

2.3 Ageing and Laboratory Ageing Methods

Evaluating the ageing behavior of a material is a crucial aspect to determine the long-term quality and lifetime. However, since field ageing takes a long time, an artificial shortcut is of desire: laboratory ageing. These ageing methods are an experimental representation of what is happening in the field but will consume much less time.

They are divided into short-term (STA) and long-term ageing (LTA). STA simulates the ageing during the processing of bitumen e.g. during mixing, laying and compaction of an asphalt pavement. During this period, the bitumen is heated up to 160-200°C, which oxidizes the bitumen and leads to a loss in volatile compounds. Laboratory STA methods are also performed prior to LTA methods.

In the case of this diploma thesis, where five different LTA methods were deployed, the respective STA states were required. Thus, the first LTA method, called the Viennese Binder Ageing (VBA) method and the second, third and fourth LTA method, classified as light ageing methods start with a STA method called PreVBA. The fifth LTA method, called the Pressure Ageing Vessel test (PAV) method is conducted on a sample that was short-term aged in the Rolling Thin Film Oven Test (RTFOT). The theoretical background of the two STA methods, PreVBA and RTFOT, as well as the different LTA methods (VBA, light ageing and PAV) are described below.

2.4 Laboratory Short Term Ageing

2.4.1 Rolling Thin Film Oven Test (RTFOT)

RTFOT stands for the Rolling Thin Film Oven Test as shown in Figure 2 and is a method used for short-term ageing (STA) of bitumen as stated in EN 12607-1. The Rolling Thin Film Oven operates at 163 °C as the target temperature for 75 minutes of STA. 8 glasses containing 35 g of sample material are inserted into a rotating oven. The RTFOT inserts compressed air into the oven while operating. The rotation inside the RTFOT is an improvement towards the Thin Film Oven Test (TFOT) where no rotation of the bitumen glass was carried out. The problem here is that the constant position of bitumen causes a vertical ageing profile within the material. That was improved by the RTFOT and enables homogenic ageing among the entire bitumen sample [9].

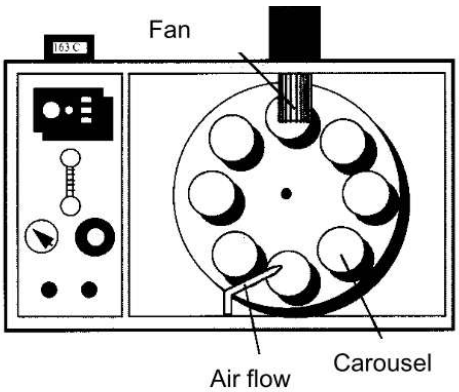

Figure 2: Rolling Thin Film Oven [25]

2.4.2 PreVBA

PreVBA is the second method to conduct STA using an oven at 163 °C for 65 minutes. It simulates the ageing of bitumen during the mixing procedure. The driving parameter for ageing is temperature (same as for RTFOT). 8 g of the bitumen are placed on the aluminum tray. The diameter of the aluminum tray measures 14 cm. The tray is inserted into the oven for the bitumen to liquify and distribute across the entire area of the aluminum tray. After 15 minutes the bitumen tray is taken out for a short time of swirling to ensure the formation of an even sample surface that underwent the same degree of STA.

2.5 Long-Term Ageing (LTA)

Long-term ageing in the field occurs after the bituminous product is completed and when it is exposed to environmental ageing inducing factors like light, reactive gases from the troposphere, elevated temperatures of up to 80° and rain or moisture. These parameters are included in the different LTA methods applied in this diploma thesis (besides the implementation of rain or moisture, which is currently under development).

2.5.1 Pressure Ageing Vessel Test (PAV)

Pressure Ageing Vessel test (PAV) is a standardized procedure for long-term ageing (LTA) as stated in EN 14769. The PAV involves pressure and temperature for ageing and is the most common method for laboratory long-term ageing. An RTFOT aged binder is used for PAV ageing. This is done to mimic conditions in the field [26].
For PAV-ageing, 50 g of the material is required for one tray. Accordingly, the material is filled into aluminum trays and stacked up in a testing rack that fits in the PAV vessel as shown in Figure 3**.** The vessel is heated up and once the temperature stabilize at 100°C, pressure is enforced. This is achieved by filling compressed air into the pressure ageing vessel. 2,1 MPa of pressure are inserted for PAV ageing. A consistent monitoring of the temperature of 100°C is required. The test runs for 20 hours. After completion pressure is slowly being released. The sample rack is removed from the vessel and samples are poured into an aluminum container and the test is completed [27].

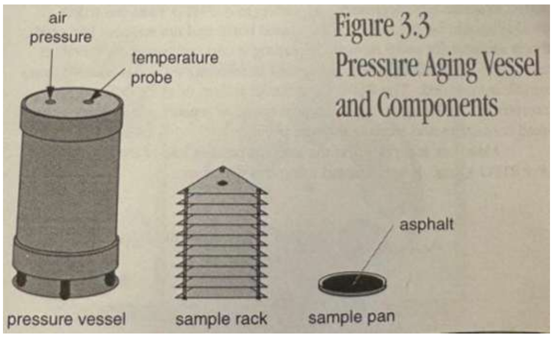

Figure 3: Scheme of PAV ageing[25]

2.5.2 Viennese Binder Ageing (VBA)

Viennese Binder Ageing is an alternative ageing method (Figure 4). It incorporates atmospheric parameters like reactive gases, temperature, light and humidity within the ageing method. Introduced by Mirwald et. al (2020), it intends to perform a more realistic simulation of the

chemical reactions within the troposphere involving ozone (O_3) and nitrogen oxides (NO_x) as the driving ageing inducing factor. In certain combinations there are presumably various degrees of accelerated ageing [28]. The ageing cell consists of 2 stainless steel compartments that are locked by 4 steel clamps. The vessel can be filled with up to 4 aluminum trays at the same time. The top tray is covered with a lid as all three lower trays are covered by a tray above them. A heating cuff ensures an ageing temperature of 80°C ±1 °C with a steady ROS intake of 4g per m^3 of ozone and 25 ppm nitrogen oxides within the cell and the ageing process takes place for 3 days. Figure 4 illustrates the driving parameters for this ageing method. Comparing this method to other long-term ageing methods as more complex due to more parameters that can be altered. Yet considering more parameters that occur in the field already and that have not been addressed by previous LTAs. Within the troposphere as well as on the pavement surface, there are multiple gases with potential to contribute to chemical ageing. With the right concentration they are likely to cause oxidation [29].
The VBA is carried out with a steady ROS intake [30]. After three days of the ageing the heating cuff is turned off, insulation material removed, ozone generator turned off and the cell is left untouched for 1 hour so the ozone can vanish through the ventilation system. Ozone is known for its harmful effect on respirational organs so attention to safety is strongly recommended [29].

Figure 4:scheme of the Viennese Binder Ageing [28]

2.5.3 Light Ageing Methods

The sun's radiation is the source of life as it delivers photochemical energy to the Earth, enriching planetary life. The energy served as radiation is very powerful in the optimal dose. It can also degrade planetary life when intensity is too strong. Consequently, radiation and its wavelength are substantial for longevity of life. In conditions of low temperature at 10°C and little radiation exposure an organic material may be durable and long-lasting. In case these conditions change, i.e. temperature and radiation increase, the ageing of this material is likely to accelerate. Consequently, the time this material can serve its purposes decreases. This explains the interest in understanding more about radiation and its influence on ageing. Radiation leads to photochemical reactions including oxidation and the degradation of the material can be expected, leading to lower life expectancy due to harder and more brittle material behavior. Within the construction of roads, roofing and buildings, bitumen and its performance are crucial and therefore a deeper understanding of the light-ageing is substantial. Light ageing is a relatively new field in bitumen ageing. There are several studies that state the driving influence of heat and light. Yet ,there are still many questions that need to be addressed [29].

The sun's radiation emits up to 5700 K of radiation. However, not all the sun's radiation is emitted to the Earth´s surface. Certain wavelengths of the spectrum are absorbed and reflected by atmosphere [31]. As stated in literature, specific parts of the wavelength spectrum influence ageing to the highest degree including ultraviolet (UV)-light, visible (VIS)-light and infrared (IR)-light as the main drivers [32]. UV-light can be separated into UV-C (100 nm-280 nm), UV-B (280 nm-320 nm) and UV-A (320 nm-400 nm). UV-C light is completely neutralized by the earth's atmosphere, leaving UV-B and UV-A as the ones that strike the earth's surface. The work by Mirwald et al. 2022 claims that the proportion of all radiation hitting the earth's surface is crucial and that only 5% of UV-B and UV-A reach the pavement surface. VIS-light contributes 43% and IR-light 52% of the total radiation by the sun (1367 W/m^2). The radiation peaks at wavelengths of 550 nm – 580 nm within the range of VIS-light [32, 33].

That insight is taken into account, and this study focuses on (UV)-light as well as (VIS)-light for the light sources. To grasp a deeper understanding of how different amounts of solar radiation per area (cm^2) affect the degree of ageing various lamps with different power and spectra were used for testing. This should help us answer the question whether there is a correlation between the lamps power and the degree of ageing.

The light-ageing setup used in the diploma thesis is shown schematically in Figure 5. The distance between the lamp and the bitumen tray is kept at 20 cm. The temperature of the heating plate is set to 80 °C. An insolation and protection box is placed around the heating plate to ensure constant temperature during the three days of ageing. The cardboard box measuring 72 cm of height, 55 cm of width and 55 cm of depth. The three setups only differ in the choice of the lamps. The rest of the setup was kept the same and the distance and temperature were checked before the start. After 3 days of ageing the aluminum tray with the bitumen is taken out and heated for 5 minutes in the PreVBA oven. Then, the bitumen sample was stirred for homogenization and collected for further testing

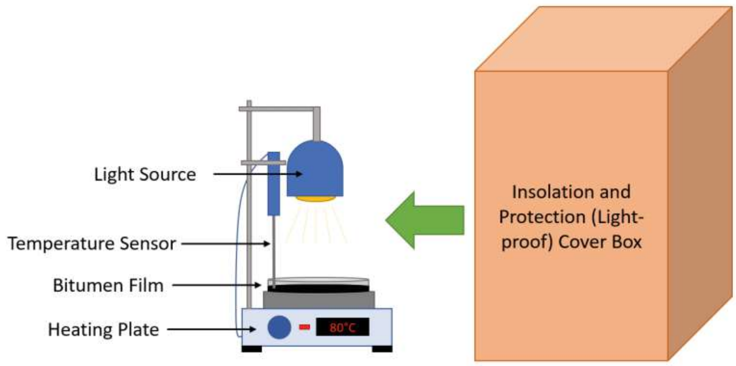

Figure 5:schematic drawing of light ageing setup used in the thesis

2.6 Testing and Analysis Methods

2.6.1 Attenuated Total Reflection (ATR) Fourier Transformation Infrared Spectroscopy (FTIR)

Fourier Transformation Infrared (FTIR) spectroscopy is a chemical method to analyze the samples characteristics in regard to its infrared active functional groups. In the laboratory, the Attenuated Total Reflectance Fourier (ATR) mode is used. The classical transmission mode is sending the radiation through the entire sample which allows a scan of the entire depth of the material, if it is transparent. Using the transmission mode, the preparation of a transparent (therefore very thin) bitumen film is complex. Thus, ATR-FTIR is utilized. ATR-FTIR as shown in Figure 6 represents faster sample preparation and better repeatability as fewer mistakes can occur. However, this method only takes a scan of the surface of the material, so a significant amount of focus needs to be put on homogenization of the samples. ATR-FTIR spectroscopy identifies infrared active chemical moieties in a material by analyzing how molecules interact with infrared radiation. When infrared responding molecules are exposed to this radiation, their dipole moment changes, causing them to rotate or vibrate. Radiation not absorbed by the molecules is detected and represented in a graph of absorption versus wavenumbers (cm^{-1}), which are the inverse of wavelengths. This technique effectively characterizes chemical properties, making it useful for analyzing bitumen samples and observing changes in binders and biocomponents through different aging stages (unaged, short-term aged, and long-term aged) [9].

→Wavenumber = total electromagnetic waves within a centimeter

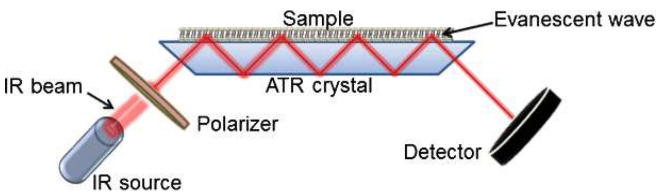

Figure 6: schematic construction of ATR-FTIR[34]

2.6.2 DSR

In the field of bitumen performance, time and temperature are both crucial to the behavior of the material since it exhibits its viscoelastic reaction to loading. That’s why the ideal test of that material should include both those factors. The testing that can take these factors into account is known as dynamic shear rheometer (DSR), which is capable to measure the mechanical behavior of bitumen [25].

There are two types of rheometers. One is operating with controlled strain and controlled stress. Strain-controlled devices will sinusoidally vary strain and measure the magnitude and phase of the resulting stress. A stress-controlled device will sinusoidally vary stress and measure the phase and magnitude of the resulting strain [25].

The viscoelastic properties can be quantified into the complex shear modulus (G*) and the phase angle (δ). The complex shear modulus (G*) accounts for the resistance against deformation under repeating shear stress. That separates into the elastic part which means recoverable and the viscous part that is non recoverable. The phase angle (δ) represents the degree of viscoelasticity. Various temperatures and frequencies can be used while applying oscillating shear strain at the devices used in the diploma thesis (MCR 302 from Anton Paar) [25].

Figure 7 and Figure 8 illustrate the schematic overview of the DSR. For proceeding with the DSR, the bitumen sample is filled into a silicone mold (also referred to as rubber mold), just high enough, so the surface of the bitumen droplet outstands a bit above the ring. The measurement is started and the DSR tightens two plates. The lower plate is fixed, and the upper plate can oscillate. The oscillating plate turns clockwise for one turn followed by a turn anticlockwise. By doing so, a sinusoidal loading and reaction is created that is recorded by the DSR, concluding into the complex shear modulus and phase angle. When applying shear strain to a viscoelastic material it takes certain time so the resulting stress occurs, that time lag is stated as the phase angle [25].

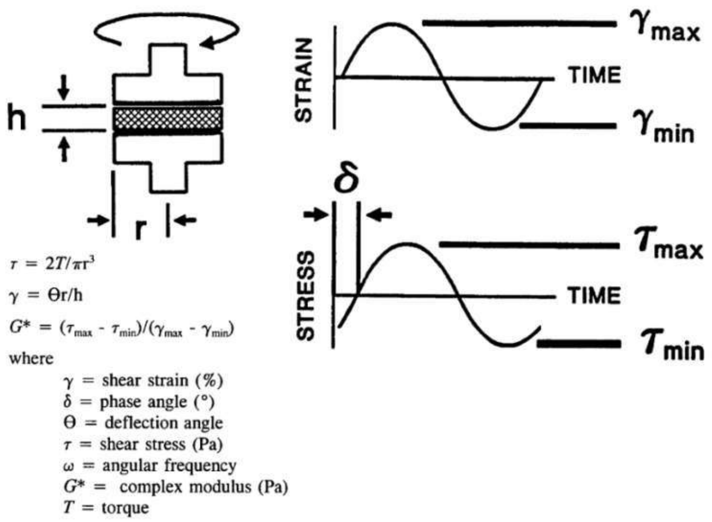

Figure 7: schematic overview of DSR [35]

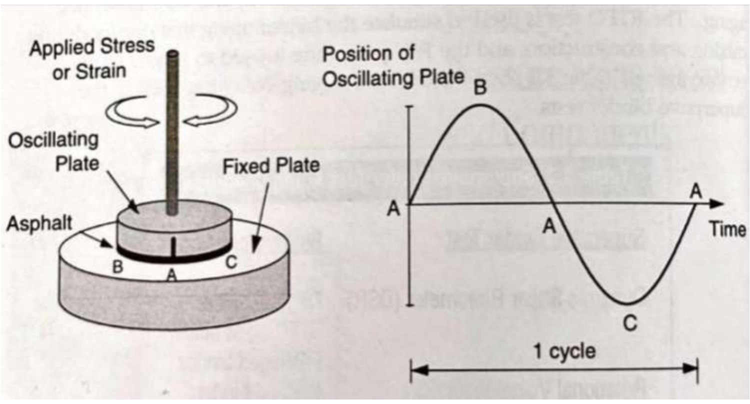

Figure 8: schematic overview of DSR source [36]

3. Materials and Methods

This chapter aims to explain the procedure that led to generating all the results for this study. It is also striving to present a better understanding of the handling of the material. Thirdly, it will give an overview of the lab work, and which methods were used to what extent.

3.1 Materials and Sample Handling

To have a reference and a comprehensive dataset, multiple binders and bio-binders that were aged and analyzed. This diploma thesis included two unmodified binders derived from fossil fuels and three bio-binder.

The unmodified binders were labeled as binder 1 and binder 2. Binder 1 is a conventional binder with a needle pen grading of 84 [1/10 mm] that is typically used in central Europe and serves as a reference binder to compare the data. Binder 2 is a stiffer binder with a needle pen grading of 12 [1/10 mm] that also originates from the crude oil refinement process and serves as the main component for the bio-binder. All bio-binders contain a certain percentage of binder 2 plus bio additives in the range of 10 – 50 %. These binders are labeled as bio-binder 1, bio-binder 2 and bio-binder 3.

Thus, this diploma thesis investigates the following five binders:

- Binder 1 (unmodified reference binder)
- Binder 2, (unmodified base binder for the bio-binders)
- Bio-binder 1, bio-binder 2 and bio-binder 3

All binders were analyzed for chemical and mechanical properties as described in the following chapters.

All five binders were aged in STA (PreVBA and RTFOT) and LTA (PAV, VBA, LA1, LA2 and LA3), which will be explained in the following chapters. An overview of the samples aged in this thesis is given in Table 1.

Table 1: Binder Matrix

Binder 1 unaged	Binder 2 unaged	Bio-binder 1 unaged	Bio-binder 2 unaged	Bio-binder 3 unaged
Binder 1 PreVBA	Binder 2 PreVBA	Biob. 1 PreVBA	Biob. 2 PreVBA	Biob. 3 PreVBA
Binder 1 RTFOT	Binder 2RTFOT	Biob.1 RTFOT	Biob. 2RTFOT	Biob. 3 RTFOT
Binder 1 PAV	Binder 2 PAV	Bio-binder 1 PAV	Bio-binder 2 PAV	Bio-binder 3 PAV
Binder 1 VBA	Binder 2 VBA	Bio-binder 1 VBA	Bio-binder 2 VBA	Bio-binder 3 VBA
Binder 1 LA1	Binder 2 LA1	Bio-binder 1 LA1	Bio-binder 2 LA1	Bio-binder 3 LA1
Binder 1 LA2	Binder 2 LA2	Bio-binder 1 LA2	Bio-binder 2 LA2	Bio-binder 3 LA2
Binder 1 LA3	Binder 2 LA3	Bio-binder 1 LA3	Bio-binder 2 LA3	Bio-binder 3 LA3

Proper handling of the material is crucial to ensure repeatability and high-quality results. This process involves several steps: treating viscoelastic materials, extracting them from storage containers, appropriately storing the containers once opened, and preparing the materials to achieve the optimal condition for testing. All samples were stored in darkness to avoid too much influence of light causing light induced ageing. Homogeneity and the evenly distributed sample

are a big challenge so that measuring the representative conditions of the sample, instead of measuring the surface that differs from the bulk of the sample. All these aspects are just a few listings of what establishes a representative sample or data set. That's why all materials were handled with great care, following consistent procedures to maintain temperature control, homogeneity, heating duration, and storage conditions. To preserve the integrity of the materials, they were kept away from direct sunlight and laboratory lighting, covered to protect them from any incidental light exposure.
Excessive heating was avoided to prevent the formation of oxidized products. During the mixing process, samples were heated to temperatures between 100°C and 130°C. For samples that had previously undergone aging, higher temperatures were employed to facilitate effective mixing. By sticking to these handling practices, it can be ensured that the materials remained consistent and reliable throughout the testing process, thereby achieving dependable and high-quality results.

3.2 Ageing Experiments

3.2.1 Rolling Thin Film Oven Test (RTFOT)

All RTFOT ageing (see Figure 9) was carried out according to EN 12607-1.

Figure 9: Rolling Thin Film Oven(left) and Binder after the RTFOT (right)

3.2.2 PreVBA

PreVBA is another method to conduct short-term ageing inside the laboratory using an oven at 163°C for 65 minutes. The PreVBA oven as shown in Figure 10 is preheated around 20 minutes prior to heat up to target temperature. The binder can is opened, and 8 g of the bitumen are taken with a spoon or a knife and are placed on the aluminum tray. The tray is weighted on a scale to ensure the exact weight. When the 8 g are achieved, the tray is inserted into the oven for the bitumen to liquify and distribute across the entire area of the aluminum tray. After 15 minutes the bitumen plate is taken out by hand for a short time of swirling. That avoids oxidation of the surface only and ensures homogenic ageing of the bitumen. After completing, the PreVBA bitumen is then filled into a closed aluminum container, labelled and stored for further analysis.

Figure 10: PreVBA oven

Figure 11 shows the binder 1 and binder 2 after the PreVBA. They show differences in the distribution of bitumen. Binder 1 on the left shows a homogenic distribution across the entire area of the tray. Binder 2 on the right side illustrates a higher stiffness and lower elasticity therefore sticking. The temperature was not high enough so that this binder could not liquify entirely. The standardized 163°C based on EN 12607-1 did not affect binder 2 as much as the reference binder. Figure 12 shows bio-binder 1 after STA and it comes to sight the binder distributed evenly over the area of the aluminum tray based on the 163°C of the oven.

Figure 11: Binder 1 short aged after PreVBA, binder 2 short aged after PreVBA

Figure 12: Bio-binder 1 short-term aged after PreVBA (left), bio-binder 2 short-term aged after PreVBA (right)

3.2.3 Pressure Ageing Vessel (PAV)

The Pressure Ageing Vessel (Figure 13) is a standardized procedure for long-term ageing. All PAV-aging in this thesis was carried out as stated in EN 14769.

Figure 13: PAV Vessel in the laboratory

3.2.4 Viennese Binder Ageing (VBA)

When conducting a VBA a PreVBA is performed to ensure STA state of the material. After completing the PreVBA, the aluminum tray is inserted into the VBA cell. The vessel is shown on the right side in Figure 14 and can be filled up to 4 aluminum trays at the same time. Via a heating cuff, there is 80°C conveyed in the cell and the ageing takes place for 3 days. The VBA is carried out with a steady ROS intake of 4g per m^3 of ozone and 25 ppm nitrogen oxides. While the VBA is running a constant temperature check is performed to guarantee 80°C over the course of the experiment [29, 30].

Figure 14: VBA stack of 4 aluminum trays (left) VBA vessel (right)

After three days of the ageing, the heating cuff is turned off, insulation material removed, ozone generator turned off and the cell is left untouched for 1 hour so the ozone be washed and removed through the ventilation system. For all the experiments conducted there was no light emitted into the VBA, nor humidity involved. The result after the three days of VBA ageing can be seen in Figure 15. For some samples, an interesting texture of the samples is noticed. The sample is heated again in the oven for 5 minutes with a fixed temperature of 163 °C. This ensures that the sample can be transferred in a viscous matter into the aluminum can. It is now ready to be labeled and added into the data system. Further analysis will take place later.

Figure 15: Bio-binder 2 after VBA

3.2.5 Light ageing Methods

In this study, there are three different setups for the light ageing. The labeling "Light ageing 1" (LA1), "Light ageing 2" (LA2) and "Light ageing 3" (LA3) is kept simple to avoid confusion as shown in Table 1. All light-aged samples were short-term aged with PreVBA prior to long-term ageing. After the long-term ageing, homogenization is also performed after three days of ageing. The samples are put back in the oven for 5 minutes to heat up and liquify at 163°C. To grasp a deeper understanding how different amounts of solar radiation per area (cm^2) affect the degree of ageing various lamps with different power were used for testing. This intended to answer questions related to whether there is a correlation between a stronger lamp, higher watt and higher ageing levels or whether there are more parameters involved that need to be considered for light-ageing.

The light-ageing was set up in a cardboard box located in the laboratory at room temperature and atmospheric pressure. The three setups only differ in the choice of the lamps. The rest of the setup was kept the same and the distance and temperature were checked before the start. The distance between the lamp and the bitumen tray is kept at 20 cm. The temperature of the heating tower is set to 80 °C. The cable for the mobile thermometer was kept inside the box.

Table 2: Light ageing lamps shows the specification of the lamps and their solar intensity was measured with a Solarenergy Meter SLX-300 where the sensor had a distance of 20 cm to the bitumen. The same distance which also was used for the light ageing from lamp to bitumen.

Table 2: Light ageing lamps

setup	specification	solar intensity [W/m^2]
Light ageing 1 (LA1)	50-Watt lamp metal halide lamp	1999
Light ageing 2 (LA2)	25-Watt lamp LED	192 [2]
Light ageing 3 (LA3)	50-Watt LED + 25-Watt LED	465 + 192 = 550

3.2.6 Light ageing 1 (LA1)

At the beginning of an LA1 experiment, the STA binder is placed inside the insolation box, on top of the heating plate. Then the heating controller is set to 80°C and the heating plate is turned on and set to 80 °C. The lamp for LA1 is a metal halide lamp (also called metal halogen lamp). These lamps are designed to generate a higher light output in lumen. That's why they are used in stadiums, concert stages to ensure bright vision and in terrariums to meet living conditions of higher temperatures. Metal halide lamps range from 80 to 100 lumens per watt and those in special applications range even higher. LEDs are extremely efficient and often achieve 100 to 150 lumens per watt. Lumens per watt (lm/W) is a standard and widely used unit in lighting to measure the efficacy of a light source [37]. The documentation of the lamp states the following technical details wave spectra as illustrated in Figure 16 and Figure 17**.**

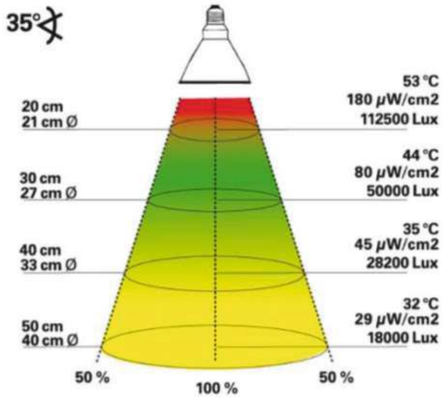

Figure 16: 50-Watt Halogen lamp light spectrum

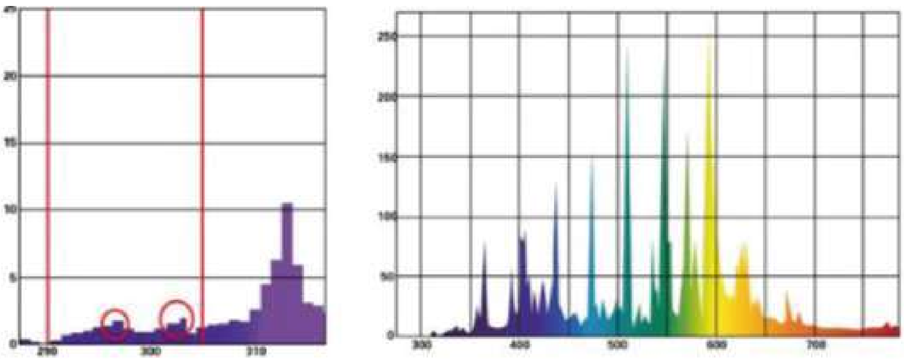

Figure 17: 50-Watt Halogen lamp wavelength spectrum

The lamp from LA1 produces a lot of heat as well. For ignition and operation, high current induced by a transformation is necessary. The running current produces heat, which will add to the heating plate within the light ageing cell. The 50-Watt light bulb is set into place and turned on. Directly after that the tray with short-term aged bitumen was placed inside the light-ageing box for three days. Figure 18 visualizes the setup for LA1 ageing of bio-binder 3. It was important to verify 80 °C regularly, because the combination of lamp and heating plate caused an increase in temperature. This was manually corrected by decreasing the temperature of the heating plate by 1 or 2 degrees. After aging, the binder was taken out and put into the oven with 163°C for 5 minutes. This is done to match the VBA procedure and to liquify the binder so it can be transferred into a storage container.

Once the binder is filled in the storage container, it again was left in the oven for 5 minutes and hand-stirred afterwards for homogenization. At this point the ageing is completed, and the binder is labelled (e.g. "Binder 1 LA1").

3.2.7 Light ageing 2 (LA2)

In LA2, the 50-Watt lamp was replaced by a 25-Watt lamp. The thought behind this is the testing with lower power and different lamp spectrum to clarify how a change of intensity affects the ageing.

3.2.8 Light ageing 3 (LA3)

For LA3 two LED-lamps of 25W and 50W run the light ageing simultaneously as shown in

Figure 18.

Figure 18: LA3 25W and 50 W lamp and Binder 1 after 3 days of light ageing

3.3 Analysis Methods

3.3.1 Attenuated Total Reflection (ATR) Fourier Transformation Infrared Spectroscopy (FTIR)

For Fourier Transformation Infrared (FTIR) spectroscopy, roughly 0.5 g of binder or bio-binder material is heated to 120-130 °C in a metal spoon. With a digital thermometer the bitumen is hand stirred to homogenize and carefully the material reaches a liquidlike state. Now the thermometer is swung to form small droplets with a diameter of 1-2 mm. These droplets are placed on silicon paper. As an example, bio-binder 1 after VBA ageing, is shown in Figure 19, which highlights the difficulty to prepare heavily aged binders for ATR-FTIR spectroscopy due to their high viscosity. While the reference bitumen starts to liquify at around 120 °C, long-term aged bitumen and bio-binders started to liquify at around 150- 180 °C. The recovered droplets are then covered with a lid and directly transferred to the ATR.

Figure 19: Bio-binder 1 after VBA – after preparation for ATR-FTIR spectroscopy

Figure 20 shows the FTIR spectrometer used in the diploma thesis. Before the samples are applied on the ATR crystal, a background spectrum is recorded of the clean ATR crystal. Then the sample droplet is carefully placed on the ATR diamond. The lever is used to press the sample droplet onto the crystal to ensure sufficient contact between crystal and sample. For the testing of one binder sample, 16 spectra are recorded to ensure a sufficient amount of spectra are obtained to ensure repeatability of the material and testing routine. After finishing one measurement the bitumen droplet is removed from the crystal and the surface is cleaned with limonene and isopropanol. Then the procedure can be repeated with the next bitumen droplet.
The spectrometer records 4 times 4 spectra that are the baseline for FTIR testing. The device is linked to the OPUS software that visualizes the measurement. The FTIR curve can be normalized to balance out uncertainties of the measurement.

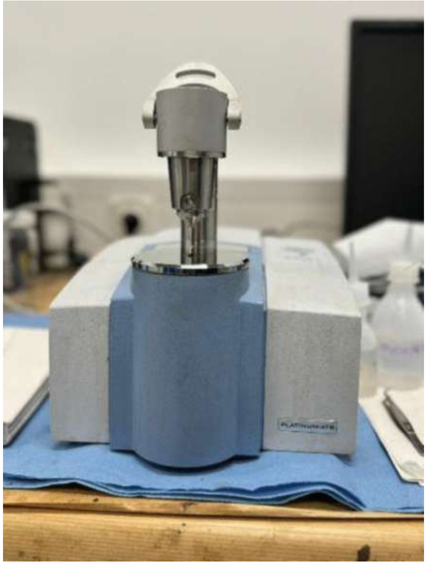

Figure 20: ATR-FTIR in the laboratory

Then the wavenumbers can be analyzed, and they illustrate the presence of several groups such as carbonyls, aromatics or sulfoxides, which can be found in the follow wavenumber domains:

- Carbonyls (AI_{CO}): 1660 – 1800 cm^{-1}
- Sulfoxides (AI_{SO}): 1079 – 984 cm^{-1}

From these boundaries it is possible to identify groups that add or that are degraded during ageing. By mathematical deductions it is possible to introduce an "FTIR Ageing Index" as shown in Figure 21 to quantify the change presented by the FTIR and to compare it with the ageing of other binders or other ageing methods. It should be noted that beside the two functional groups (carbonyls and sulfoxides) there is also a region called the "polarity region" that increases in intensity during ageing. Thus, it was added to the FTIR ageing index calculation. The spectra were recorded and visualized in the software OPUS. The best representative out of the 16 spectra obtained per binder was chosen for plotting using the software package Origin Pro.

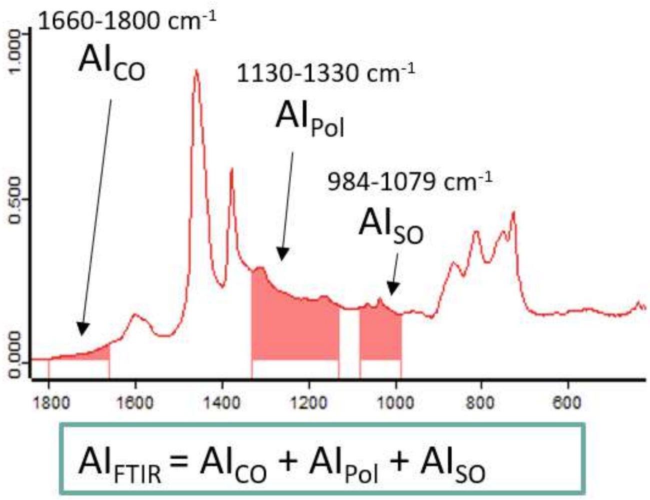

Figure 21: Integration of carbonyls, polarity region and sulfoxides to form the AI_{FTIR}

3.3.2 Dynamic Shear Rheometer (DSR)

The dynamic shear rheometer (DSR) is shown in Figure 22. The device measures the viscoelastic behavior of the binders. The viscoelastic properties can be quantified into the complex shear modulus and the phase angle. During this diploma thesis, the 25 mm geometry was used for the DSR measurements.. The binder sample was prepared 24 hours before the start of the DSR measurement. 2-4 grams of bitumen were heated on a metal spoon in order to liquify the material. The following parameters were used for all binders investigated in the diploma thesis:

Temperature range: 40 – 82 °C [40/46/52/58/64/70/76/82]

Frequency range: 0.1 – 40 Hz [0.1/ 0.3/ 1/ 1.592/ 3/ 5/ 8/ 10/ 20/ 30/ 40]

The device concludes the measurement into several parameters of raw data including the complex shear modulus and phase angle.

Figure 22: DSR in the lab

3.3.3 Chemo-mechanical correlation (CMC)

In order to conclude results from spectroscopy and rheology from all different binders in their various ageing states, the chemo-mechanical correlation (CMC) was employed in this thesis. This correlation brings both schools of engineering and chemistry into a correlation and provides a link between chemical composition and its effect on mechanical behavior. Since the bio-binder results were new, a relative representative of the CMC was selected for their evaluation. This implies that for the complex shear modulus a ratio between aged and unaged was set up (|G*|aged/|G*|unaged) and for FTIR ageing index, the difference between the integrated area from the aged and unaged FTIR spectra (FTIR aged – FTIR unaged) was selected.

A respective example of a CMC is shown in Figure 23. Since the DSR produces a lot of different complex shear modulus values at various temperatures and frequencies and the results are plotted in a 2D representation, one specific DSR value was selected that represents the ageing trends accordingly. Therefore, the complex shear modulus data at 1.59Hz and 46°C was selected and plotted with the FTIR ageing index to create the CMC.

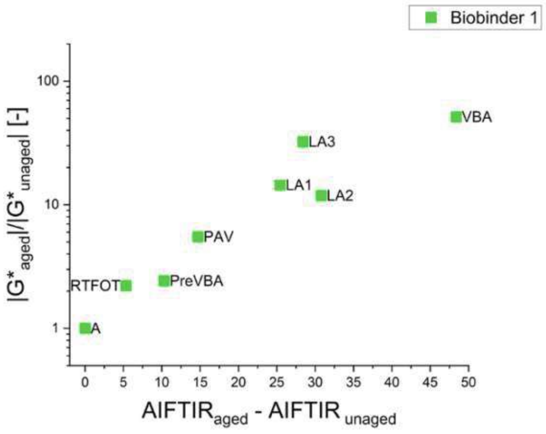

Figure 23:Introduction to CMC

4. Results and Discussion

This chapter of the thesis will present the results obtained from the chemical and mechanical analysis of the unaged, short-term-aged (STA) or long-term-aged (LTA) binders. Analysis includes the FTIR spectroscopy, DSR and the combination of both methods into the chemo-mechanical correlation. In addition, there is also a comparison of all unaged, PAV-aged, VBA-aged and light-aged binders.

4.1 Binder 1

Binder 1 is the first of the five binders that was analyzed and it was studied in detail to have a reference binder. Especially in new blends of binders and unknown material compositions it is essential to have a reference binder that is familiar and well analyzed.

4.1.1 FTIR

Looking at the chemical situation, Figure 24 shows the FTIR spectra of binder 1 with the full spectral range (4000–680 cm^{-1}) shown on the left, while the extended fingerprint region (1800–680 cm^{-1}) is highlighted on the right side. The y-axis shows the absorbance [-] of the material and the x-axis presents the wavenumber [cm^{-1}]. The spectra show the unaged, STA (RTFOT and PreVBA) stage and PAV, VBA, LA1, LA2 and LA3 stages for long-term ageing. To enhance visual clarity, a color-coding scheme was applied. Each ageing stage is represented by a distinct color, providing a clear visualization of the changes occurring in the FTIR spectra. For the FTIR, the regions of carbonyl (at 1700 cm^{-1}) and sulfoxide (at 1030 cm^{-1}) will be looked at in more detail because these regions tend to increase upon ageing. They are areas of focus that characterize ageing of the material, so they have considerable importance. When looking at FTIR spectra and their changes during ageing these are the bands that are looked at first. Over the course of ageing, they might change and so does the material. In Figure 24 it is evident that all five LTA ageing methods exhibit a comparable degree of ageing, as indicated by their carbonyl and sulfoxide content.

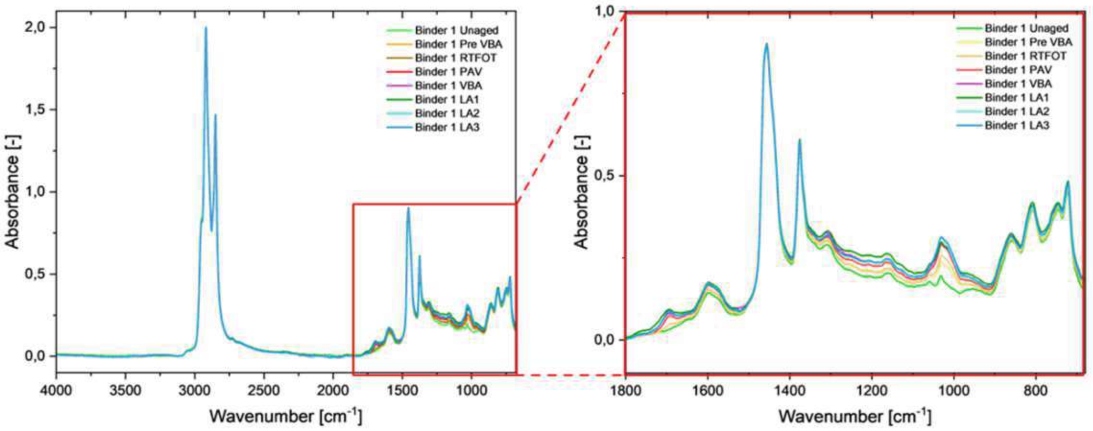

Figure 24: binder 1 FTIR spectra with the full overview (left) and the fingerprint overview (right)

Figure 25 shows the spectra of the unaged and STA binder 1 (left) and the LTA binder 1 (right) in the extended fingerprint area between 1800 cm^{-1} and 680 cm^{-1}. For STA, carbonyls at

1700cm^{-1} and sulfoxides at 1030 cm^{-1} show a slight increase compared to the unaged reference binder (green color code), which is at the lowest level. For LTA, the binder ageing levels can be judged by the formation of carbonyls and sulfoxides. Considering the formation of carbonyls, the LTA binders can be put into the following order: PAV (red) followed by VBA (purple), LA2 (turquoise), LA3 (blue) and LA1 (green), which has the highest absorbance at the carbonyl domain. This indicates that for the reference binder light ageing 1 has achieved the highest level of ageing by the formation of carbonyls. That means that the binder reacts strongly to the parameters set up by light ageing. Light, temperature and the specific characteristics of the lamp (spectrum) amplify the ageing of binder 1 to the highest level. For the sulfoxides at 1030 cm^{-1} it can be observed that the sulfoxide levels for PAV (red), VBA (purple), and LA1 are quite similar, indicating a comparable ageing effect among these methods. However, LA2 and LA3 show a slightly higher sulfoxide content, suggesting that these setups induced a greater amount of sulfoxides. It is interesting to look at the comparison between the light ageing setups.

LA2 stands for a single 25 W LED lamp and LA3 combined two LEDs of (25 W and 50 W) and yet both setups induced the same effect of ageing. The resulting content of oxidized functional groups is identical, suggesting that only a specific amount of photo energy is necessary to reach the maximum level of photoinduced oxidation. The LA1 setup used a 50 W metal halogen lamp that is responsible for an increase in carbonyls, and less in the increase of sulfoxide. Meanwhile LA2 and LA3 are weaker in carbonyls production and stronger in sulfoxides production.

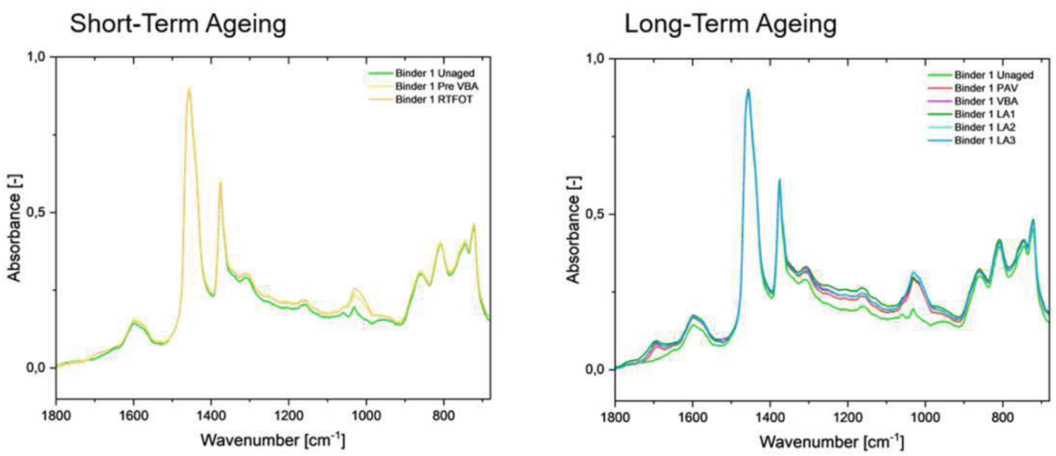

Figure 25: reference binder FTIR spectra with the full overview (left) and the fingerprint overview (right)

4.1.2 DSR

Looking at the rheology of binder 1, Figure 26 shows the complex shear modulus (on the left) and phase angle (on the right). The complex shear modulus states the stiffness of the material and how it changes over temperature. |G*| [Pa] is on the y-axis and the temperature [°C] is presented on the x-axis. The phase angle defines the degree of viscoelasticity of the material over changing temperature. The phase angle (δ) is on the y-axis and the temperature [°C] is presented on the x-axis.

The unaged binder (green) has the lowest stiffness across all the binders. For STA, it is interesting that there is a gap between PreVBA and RTFOT, meaning PreVBA leads to a higher stiffness of the bitumen than RTFOT. One would expect them to cause close to identical ageing to the binder. This is quite important to notice, because the higher ageing of PreVBA causes a head start for LTA methods that start off with PreVBA, like VBA and Light ageing. LTA methods that start off with RTFOT like the PAV-ageing are located at lower level.
The LTA trends are PAV at the lowest, then VBA, then LA2/LA3 and LA1 at the highest level. This is the same trend as observed for the carbonyls from FTIR spectroscopy. Also, it is important to remember that PreVBA has already induced a higher ageing level so LTA that follows the PreVBA has higher ageing level than ageing following RTFOT.
There is a gap between LA1 and the three other LTA of LA2, LA3 and VBA, with LA1 showing significantly higher signs of ageing by a higher complex shear modulus (left diagram) and a lower phase angle (right diagram). This shows that this binder is sensitive to conditions of the LA1 setup.

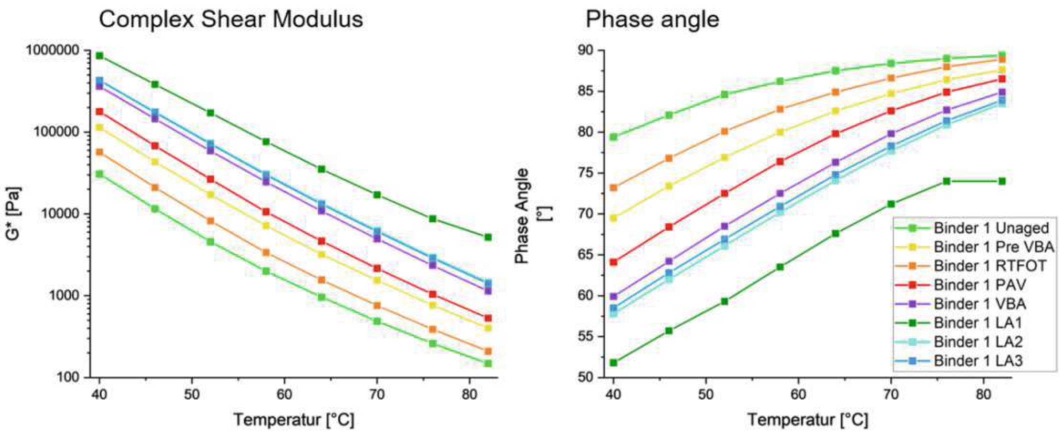

Figure 26:DSR complex shear modulus(left) and phase angle (right)

4.1.3 CMC

Figure 27 shows the chemo-mechanical correlation that sets up a connection between rheology and spectroscopy and how ageing indices and values change during long-term ageing. There is a relative visualization starting at 1 for rheology and 0 for FTIR (which represents the ageing level of the unaged binder).

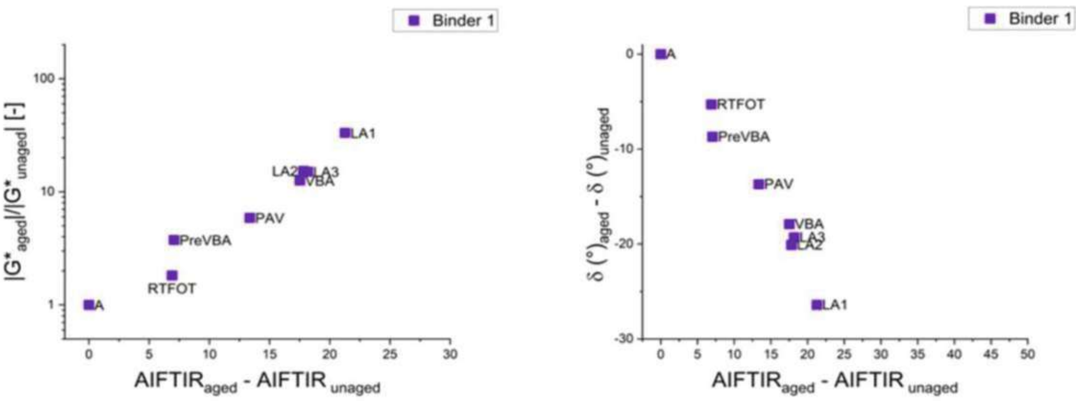

Figure 27: CMC of binder 1

For STA, the difference between RTFOT and PreVBA the difference is visible again. While they are at a relatively similar chemical ageing level, respective differences in rheology are observable. For the LTA methods PAV marks the lowest followed by VBA and LA2/LA3 that range in similar level. LA1 is far out again as chemical analysis stated already. For this binder, the lamp with 50W has produced a higher ageing level than two lamps adding up to 75W. So light intensity does not reach these high results of ageing by itself. LA1 is very high out in terms of complex shear modulus and phase angle which underlines the importance of light influencing ageing on the physical properties of the material.

4.2 Binder 2

Binder 2 is a significantly different binder compared to binder 1 since it is an oxidized and therefore harder binder. Binder 2 was used for blending with the bio additives to produce the bio-binder 1, bio-binder 2 and bio-binder 3 that will be presented in the following chapters. That is the reason why chemical and mechanical properties of this binder 2 are of exceptional interest.

4.2.1 FTIR

Figure 28 shows the FTIR spectra for binder 2, where the chemical characteristics can be seen. The graph illustrates absorbance [-] on the y-axis and wavenumber (cm^{-1}) on the x-axis. The spectrum for unaged binder 2 (green) shows the lowest signs of ageing, with little carbonyl and sulfoxide content. From this state on, all ageing methods increase said band domains.

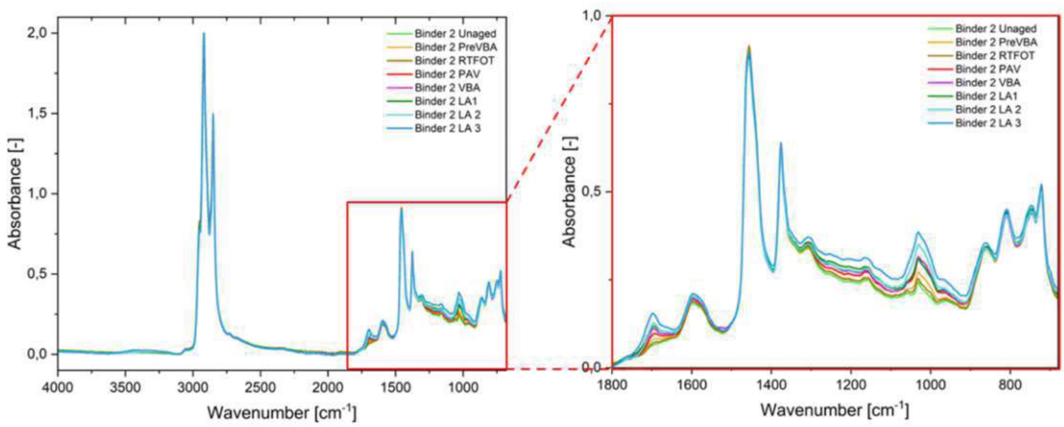

Figure 28:Binder 2 FTIR total overview(left) and focus area (right)

Figure 29 shows the spectra of the unaged and STA binder 2 (left) and the LTA binder 2 (right) in the extended fingerprint area between 1800 cm^{-1} and 680 cm^{-1}. For the STA binders again the difference between RTFOT and PreVBA occurs, with the PreVBA binder showing higher signs of ageing. LTA shows that binder 2 differs from binder 1. The most convenient way to judge the ageing behavior is to separate the formation of carbonyls and sulfoxides. Thus, the LTA binders can be placed in the following order:

- For the carbonyls: PAV < VBA < LA1 < LA2 < LA3.
- For sulfoxides: LA1/VBA/PAV < LA2 < LA3.

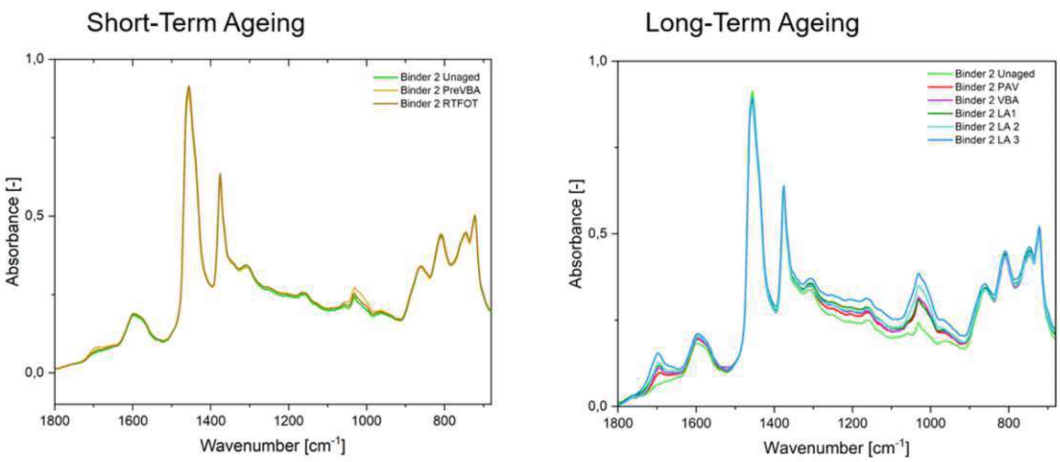

Figure 29:Binder 2 FTIR of STA and LTA

4.2.2 DSR

Figure 30 displays the rheology of Binder 2, where we see that this binder has a very high level of stiffness in all the ageing stages in terms of the complex shear modulus. This is noticeable due to the scale of the y-axis that had to be adjusted to a higher value to visualize the high levels of complex shear modulus.

For STA, the rheology results prove what was observed in the FTIR spectra before: There is a significant gap between PreVBA and RTFOT. For the LTA the trend is as following: PAV < VBA < LA1 < LA2/3. The trends differ from the ones of FTIR – in FTIR larger differences occur between LA2 und LA3. That is not visible in the DSR. VBA and light ageing induce similar ageing as the lines align quite close to each other.

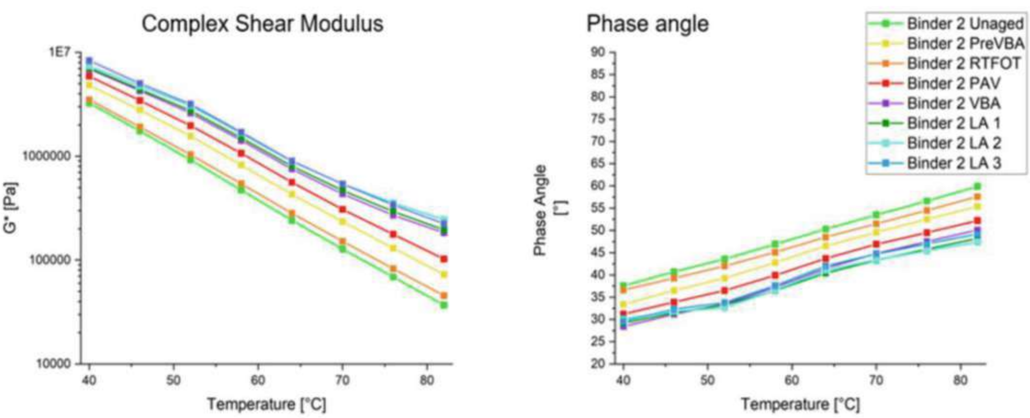

Figure 30:Rheology of Binder 2- CSM (left) and phase angle (right)

4.2.3 CMC

Figure 31 shows the chemo-mechanical correlation of binder 2. The STA methods show the significant difference between PreVBA and RTFOT, that states that the PreVBA caused a higher ageing to binder 2.

The ranking for ageing levels at the LTA starts as the following: PAV < VBA < LA2 < LA1 < LA3. The diagram reaches a flattening and the mechanical levels plateaus, while the chemical levels continues to increase by building up more oxygen containing functional groups. Binder 1´s CMC diagram presented a steeper slope that rose linear without a flattening as shown

previously in Figure 27, so stiffness level increases constantly for binder 1. Binder 2 stiffness level increases only to a certain extent, as this binder started off with higher stiffness in the beginning when looking at the FTIR spectra and DSR diagram.
Comparing binder 2 to the previous binder 1, it can be stated that light intensity has an influence on the degree of ageing. Light ageing has a strong influence on the binders, however, it needs further research to understand whether parameters like wavelength or light intensity have the strongest influence on certain materials.

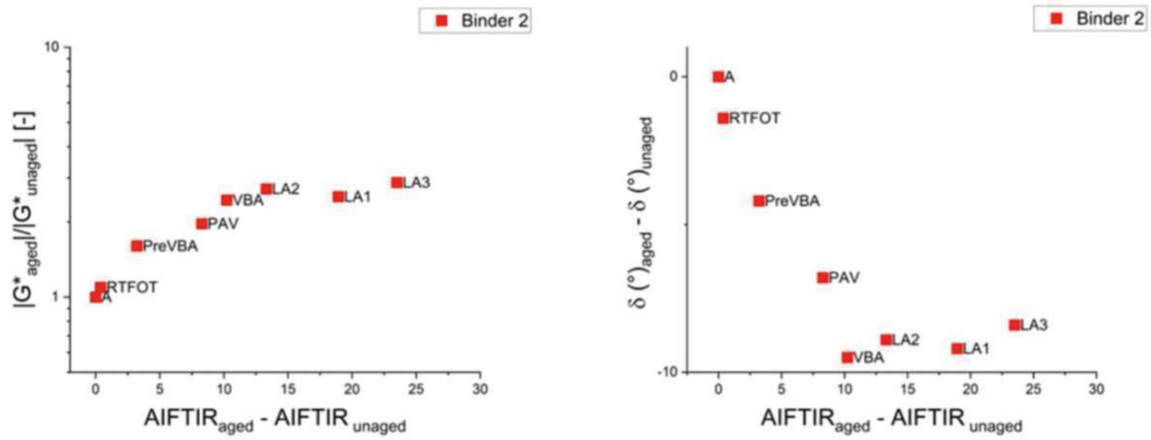

Figure 31:Binder 2 CMC

4.3 Bio-binder 1

This chapter shows the results of the bio-binder, all derived from binder 2. Binder 2 was mixed with additives ranging from 10% to 50%, resulting in bio-binder 1, bio-binder 2, and bio-binder 3. The exact percentages of the additives in each blend are unknown. Each bio-binder contains a unique mix with varying amounts of renewable resources. As a result, significant changes in FTIR, DSR, and CMC measurements are expected.

4.3.1 FTIR

Figure 32 shows a first glimpse of bio-binder 1 chemical properties. It comes to sight that the spectrum has multiple new bands that appear and change during ageing. Thus, the addition of bio-material makes the spectrum more complex.
Bands are added to the spectrum at 1745 cm^{-1},1235 cm^{-1},1160 cm^{-1} and 1100 cm^{-1}. Therefore, it becomes clear why using binder 2 as a reference in regards to its chemical properties (bands in the base binder), as this will be very helpful to recognize the bands originating from the bio additive and how they change upon ageing. The full spectral range (4000–680 cm^{-1}) is shown on the left spectrum, while the expanded fingerprint region (1800–680 cm^{-1}) is highlighted on the right spectrum. The y-axis shows the absorbance [-] of the material and the x-axis presents the wavenumber [cm^{-1}].

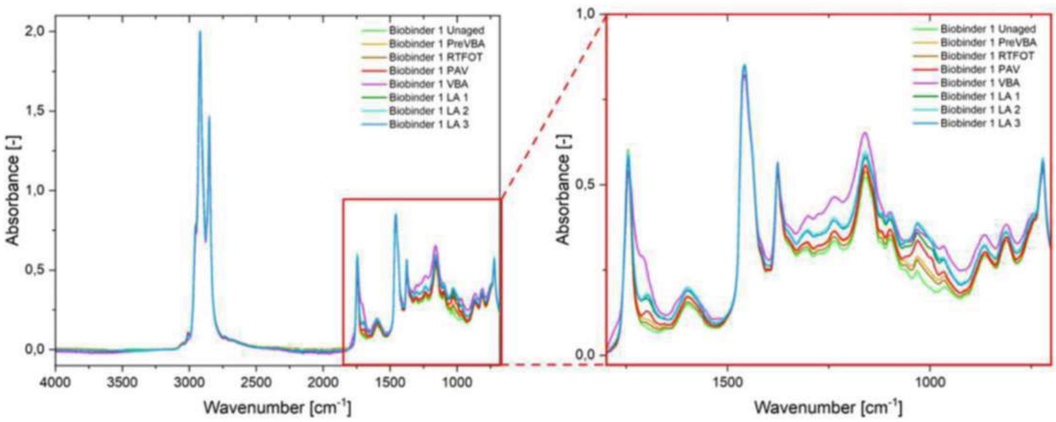

Figure 32:Bio-binder 1 FTIR

The left side Figure 33 shows the spectra of the STA bio-binder 1. Here it is challenging to evaluate the binders ageing state due to the overlapping of the bio-additives bands, which slightly increase with aging, and the increasing bands (carbonyls and sulfoxides) of the bitumen component. It is unclear whether there is an increase in any components of the bio-additive itself. To address this, an aging study of the pure bio-additive would be necessary.

Looking at LTA on the right side of Figure 33, the carbonyls at 1700 cm^{-1} show a few changes. The PAV-aged binder shows the lowest formation of carbonyls, followed by LA1, LA2, and LA3. The VBA binder exhibits the highest absorbance for carbonyls, where a partial overlap occurs with the C=O band at 1745 cm^{-1} due to the bio-additive is observed. This overlap makes the band at 1700 cm^{-1} appear as a shoulder, presenting a challenge for quantitative analysis. To overcome this, the study uses relative values (aged-unaged) in order to visualize these challenging bands within the chemo-mechanical correlation.

For the Carbonyls the order from lowest to highest absorbance is as follows: PAV< LA3/LA1 <LA2/ VBA, where the VBA method was significantly higher than the others. This indicates that the VBA method is relatively harsh, producing more carbonyls compared to the milder oxidation products like sulfoxides. For sulfoxide groups, a different trend is observed. The sulfoxides trend is: PAV < LA1 < VBA < LA2/LA3

Overall, the degradation of the bands originating from the bio-additive is not very strong. This suggests that the bio additive does not degrade or oxidize during LTA methods. Such changes are detected by FTIR spectroscopy. The typical signs of binder aging, such as the formation of carbonyls and sulfoxides, as well as an increase in the fingerprint region between 1330 – 1130 cm^{-1}, remain observable, even when overlapping with bands from the bio additive occurs.

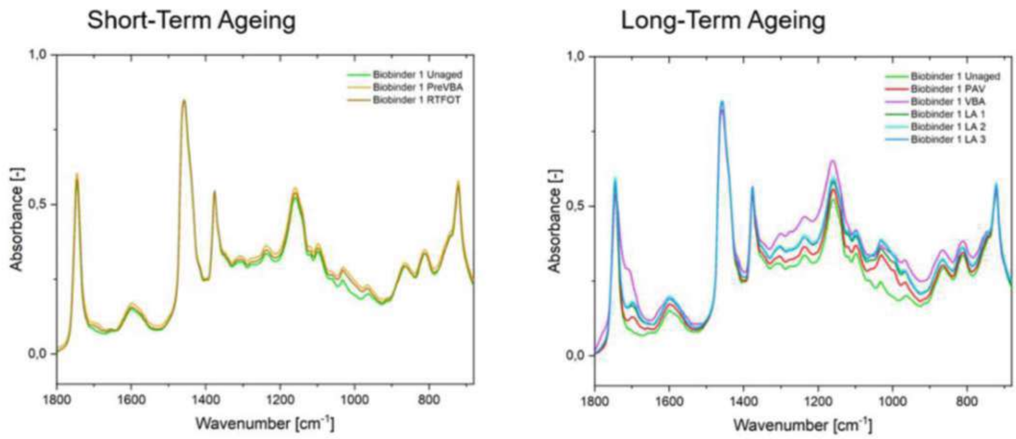

Figure 33:Bio-binder 1 STA and LTA

4.3.2 DSR

Figure 34 shows the rheological properties of bio-binder 1 in the unaged, two different STA and five different LTA stages. The mechanical properties present a ranking that is similar to the chemical results stated above. From lowest to highest it lists as follows: PAV < LA2 < LA1 < LA3 < VBA.

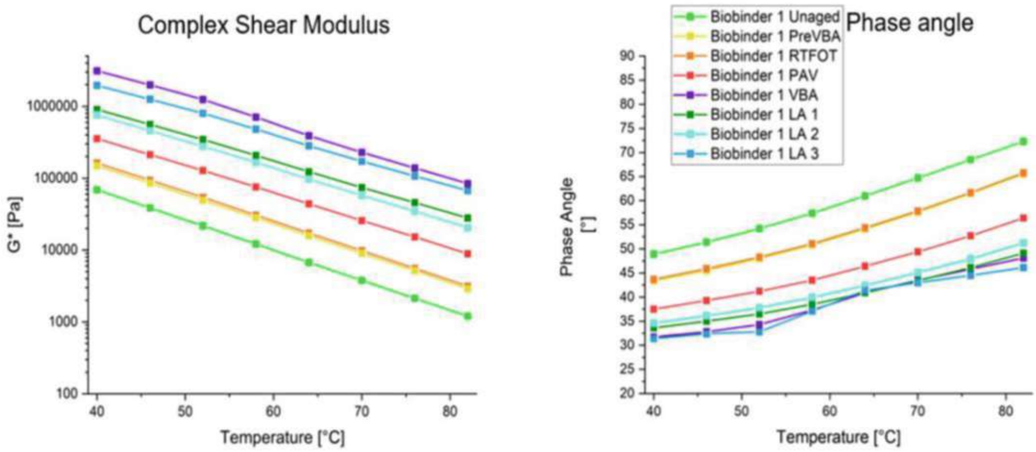

Figure 34: Bio-binder 1 DSR

4.3.3 CMC

The chemo-mechanical correlation of bio-binder 1 also states similar results only LA1 and LA2/LA3 change positions in terms of ageing indices. Furthermore, VBA remains at the highest ageing levels. Therefore, bio-binder 1 has high vulnerability towards VBA ageing and its ROS. PAV ageing has a lower impact on ageing level compared to the other LTA methods. Possibly more cycles of PAV need to be performed in future studies to see how bio-binder 1 performs when exposed to temperature and pressure. The influence of light proves to be significant, but the detailed study of light intensity and quantity of photo energy is recommended based on this study. In this study, LA-setups can not age as strongly as the reactive gases induced by thermochemical ageing by a VBA. Their respective ageing levels are all in a close proximity to each other independent of light source or power.

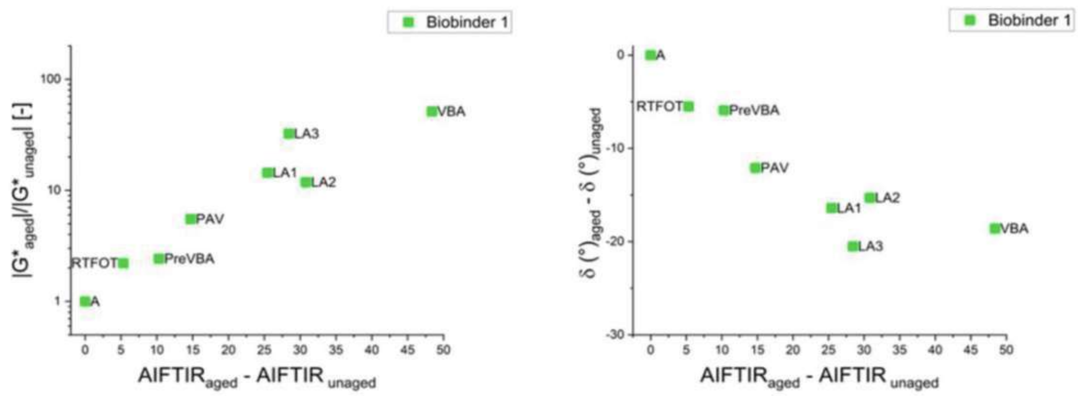

Figure 35: Bio-binder 1 CMC

4.4 Bio-binder 2

Bio-binder 2 is the second bio-based binder based off binder 2 with additives between 10% to 50%. The exact percentage is unknown. The blend is aged in two STA and five LTA stages. The unaged, the STA and LTA stages were all conducted for their chemical and mechanical properties like the previous binders.

4.4.1 FTIR

The FTIR spectra of bio-binder 2 are depicted in Figure 36 and additional bands can be seen at 1590 cm^{-1}, 1270 cm^{-1}, 1155 cm^{-1}, 910 cm^{-1}, 780 cm^{-1} and 696 cm^{-1}. The full spectral range (4000–680 cm^{-1}) is shown on the left spectrum, while the expanded fingerprint region (1800 – 680 cm^{-1}) is highlighted on the right spectrum. The y-axis shows the absorbance [-] of the material and the x-axis presents the wavenumber [cm^{-1}].

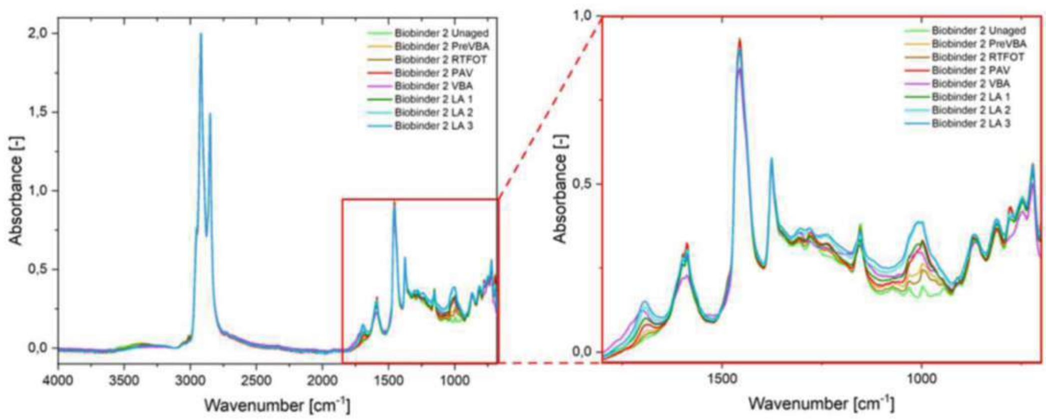

Figure 36:Bio-binder 2 FTIR

Figure 37 shows the extended fingerprint region of the STA (left) and LTA (right) bio-binder 2. The STA binders shows a small difference between RTFOT and PreVBA, with PreVBA showing slightly higher signs of ageing.

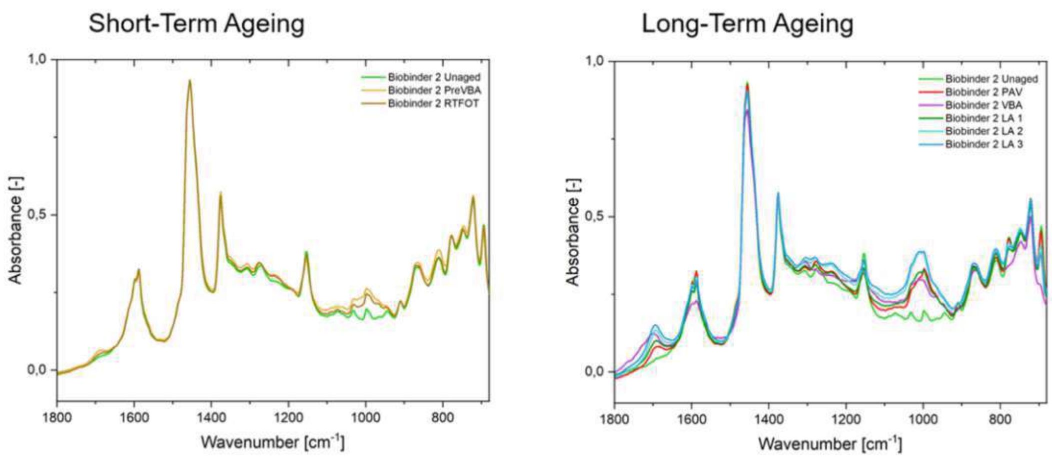

Figure 37:Bio-binder 2 STA and LTA

In the diagram for LTA, there is a lot going on due to the changes in the bio-additive and the changes caused by ageing. Following the ageing trends from previous binders by looking at the order in the carbonyls, the PAV shows the lowest ageing level. Above that there is LA1, then VBA which offers a broad band and ranges right in between the light ageing setups. Then LA2 follows and LA3 reaches the highest degree of ageing amongst all the ageing setups. The trend for sulfoxides states as the following: VBA<PAV<LA1<LA3<LA2. Sulfoxide bands show that VBA has the lowest range, stating that VBA must have been degrading the sulfoxides again during thermochemical ageing. LA3 and LA2 are significantly above the rest of the LTA methods, so the light specific spectrum of the LED has a big impact on bio-binder 2, as far as the chemical components are concerned.

4.4.2 DSR

Looking at the rheology results in Figure 38 in terms of STA there are interesting findings. When looking at the complex shear modulus, it shows that the STA methods reach similar ageing levels as the PAV (as the yellow, orange and red line all reach similar levels). This is surprising that the bio-binder 2 is aged to that level just by using STA methods. Looking at the LTA the ranking is depicted starting from lowest ageing to highest ageing:
PAV < LA1 < LA2 < VBA <LA3.

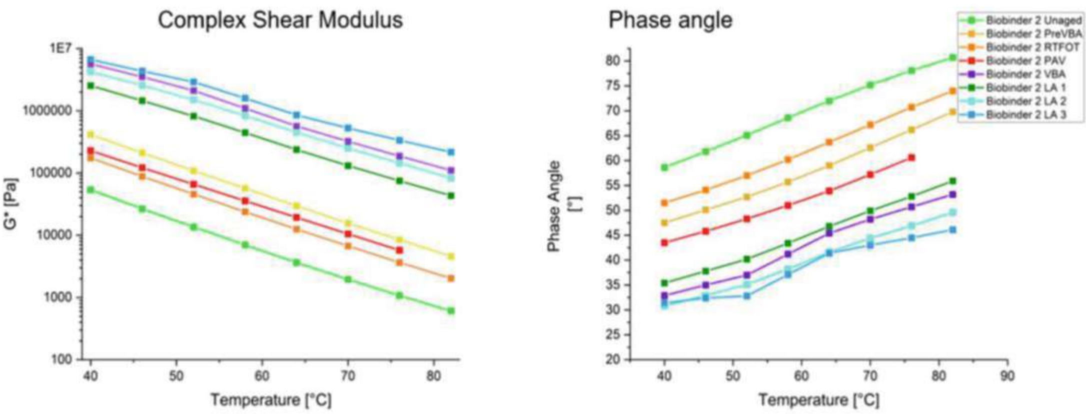

Figure 38:Bio-binder 2 DSR

4.4.3 CMC

Figure 39 combines the results from FTIR spectroscopy and DSR and a similar trend in regard to ageing can be seen for the LTA bio-binder 2:
PAV < LA1 < LA2/3 < VBA.

Bio-binder 2 has a strong ageing vulnerability towards light and ROS induced ageing. Light intensity seems to have a strong influence as the ageing index almost doubled from LA1 (15) to LA3 (27.5).

PAV has a lower impact here again. However, it could be recommended to repeat the PAV ageing again for a second or a third time to clarify its influence upon temperature induced ageing. This evaluation might be more complex, as various increasing and decreasing phenomena are observable in FTIR spectroscopy as stated above, consequently it is difficult to conduct a general comparison to conventional binders.

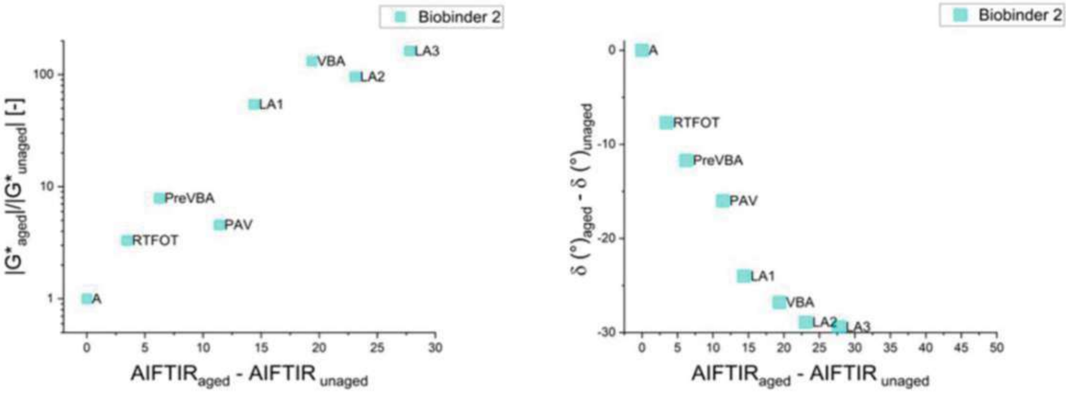

Figure 39:Bio-binder 2 CMC

4.5 Bio-binder 3

4.5.1 FTIR

In Figure 40, the chemical properties of bio-binder 3 are depicted and instantly the amount of changing bands comes to sight at 1800 cm^{-1}, 1735 cm^{-1}, 1695 cm^{-1}, 1240 cm^{-1}, 1140 cm^{-1} -1100 cm^{-1} and 990 cm^{-1}. Amongst all the binders of this study this definitely has the most new bands, especially in the range of carbonyls as 1715-1700 cm^{-1}.

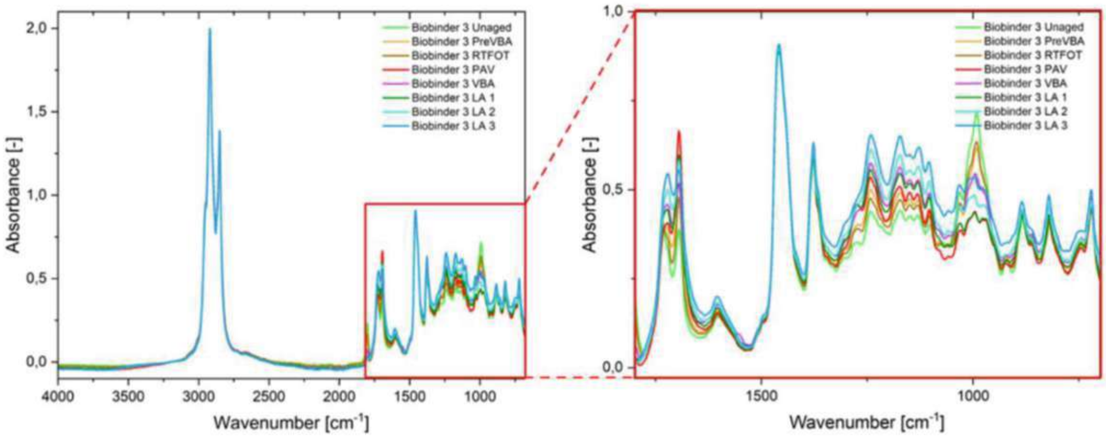

Figure 40:Bio-binder 3 FTIR

Figure 41 shows the extended fingerprint region of the STA (left) and LTA (right) of bio-binder 3. By taking a closer look at the STA where small differences between RTFOT and PreVBA

stand out and also highlight the complexity of ageing such bio-additives. The bands for the bio-additive that came up new are increasing and degrading to some extent.
For LTA, it is very difficult to tell what components are degrading or increasing. But for STA and LTA it could be assumed that the sulfoxides decrease during ageing as the unaged binder has the most sulfoxides. However, a more thorough analysis of this binder and the respective functional group would be needed to come to a meaningful conclusion.

Due to the complex spectrum, the most convenient way to judge the binders ageing behavior is by investigating the absorbance the fingerprint region between 1330 – 1130 cm^{-1}, where the binders ageing level can be put into the following order: PAV < LA1/VBA < LA2 < LA3.

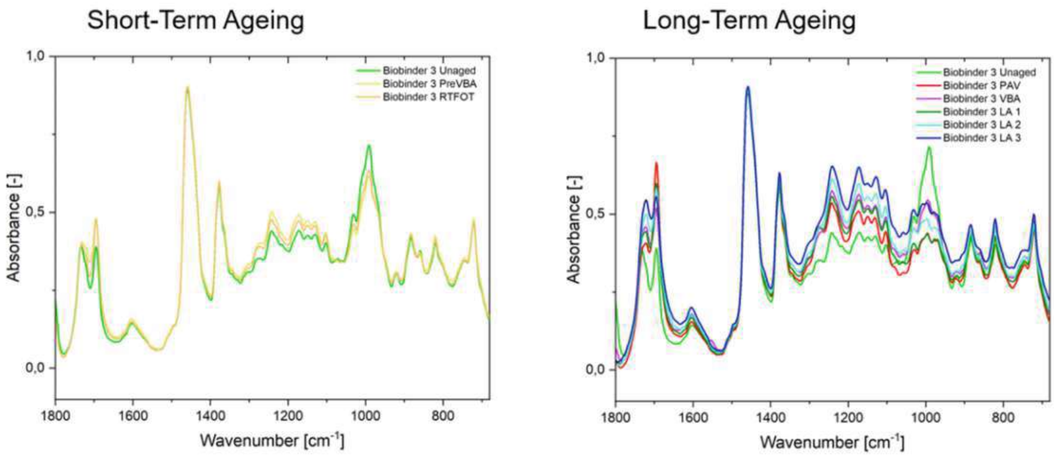

Figure 41:Bio-binder 3 STA and LTA

4.5.2 DSR

In Figure 42 the rheology of bio-binder 3 is depicted and follows a similar trend. Among the ageing methods, PAV exhibits the lowest levels of ageing, followed by VBA and LA1. In contrast, LA2 and LA3 show the highest ageing effects. Between LA2 and LA3 the graph for complex shear modulus drifts apart with increasing temperature. At lower temperatures, their rheological levels are nearly identical, but at higher temperatures, LA3 demonstrates slightly greater stiffness compared to LA2.
PAV< VBA < LA1 < LA2 <LA3 is the ranking from lowest to highest ageing levels.

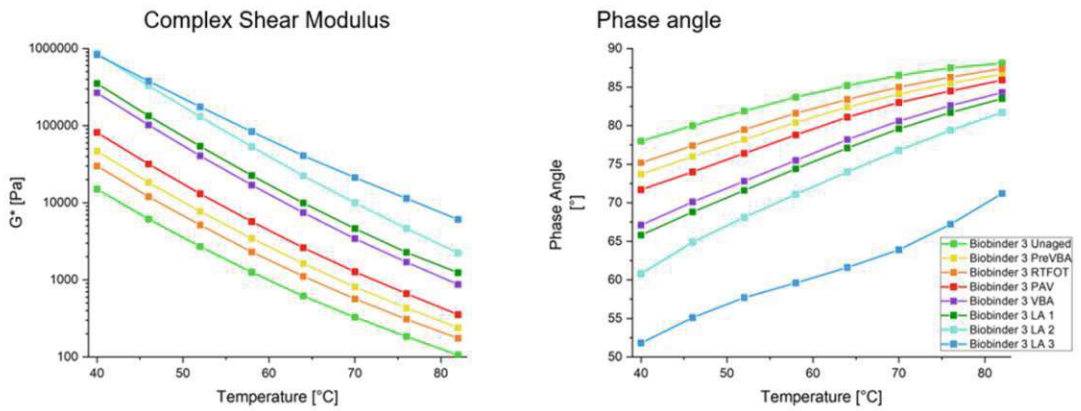

Figure 42:Bio-binder 3 DSR

4.5.3 CMC

In Figure 43 CMC trends follow as: PAV<LA1<VBA<LA2<LA3

This is interesting because in the FTIR and DSR spectra VBA ranged amongst the middle of the LTA setups. Bio-binder 3 ages strongly in LA3 which utilizes a 75-W LED (25 + 50 W LED) lamp. Influence by temperature and pressure is not as strong (PAV). VBA and LA1 have less impact on ageing but they still age the binder to a certain extent, just not as strong as LA3. All in all, also the curve for the CMC flattens out and does not present a steep slope that we received from the previous binders, so there is not a strong increase in stiffness.

However, LA3 setup has a stronger influence compared to LA2. So the light source makes a difference on bio-binder 3. This also comes to sight in the DSR diagram, as temperature increases LA3 takes a lead over LA2. VBA lies right in the middle of the light ageing but has stronger influence to ageing of bio-binder 3 than PAV does. PAV reaches little ageing and is very close to the STA methods. More cycles of PAV ageing would be recommended to see if this trend remains stable.

It is also important to keep in mind that the bio additives added new bands into the spectrum and it shows that from unaged to STA to LTA the bands are increasing, but it is difficult to state if the binder 2 component or the additives are ageing. What also comes to vision is that across this FTIR spectra for bio-binder 3 there are decreases of sulfoxides and increase of carbonyls as STA and LTA are carried out. This is something unusual as for conventional binders normally carbonyls and sulfoxides increase during STA and LTA.

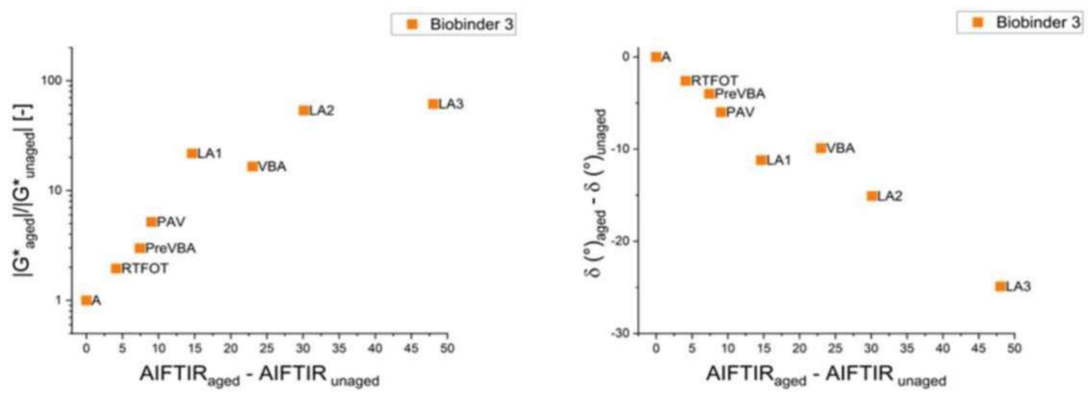

Figure 43:Bio-binder 3 CMC

4.6 LTA Comparison

4.6.1 Impact on Thermal Ageing (PAV)

Figure 44 shows the impact of thermal ageing (PAV) on the five different binders that were analyzed in this diploma thesis.

Looking at the bio-binders it comes to sight that they all demonstrate similar ageing behavior compared to the reference binder 1, as their ageing level is close to each other. Binder 1 and bio-binder 1 reach the highest level of ageing within the PAV ageing. They show high vulnerability towards high temperatures. Binder 2 shows significantly lower aging – however, its initial stiffness is much higher. The circumstance of adding bio-additives shows that ageing susceptibility increases. In terms of FTIR ageing index, the binders all range between 7.5 to 20.

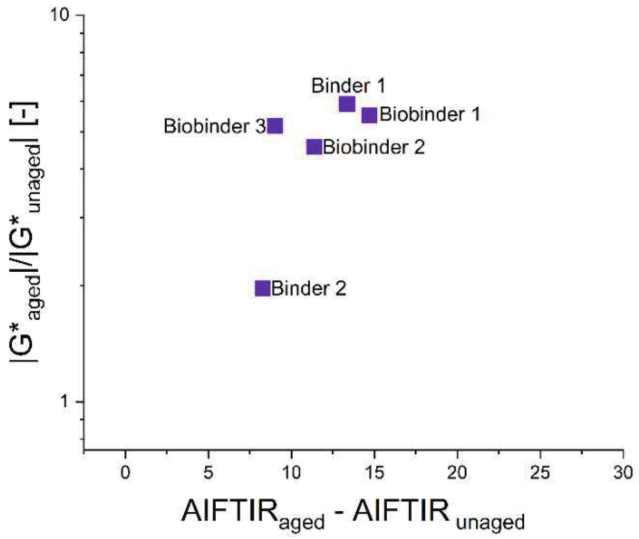

Figure 44: Impact of thermal ageing (PAV)

4.6.2 Impact of Thermochemical Ageing (VBA)

Figure 45 shows the impact of thermochemical ageing (VBA) on the five different binders that were analyzed in this diploma thesis. The scale y-axis had to be adjusted from 10 to 150 because values reached higher levels. There is similar ageing behaviour for bio-binder 3 compared to the reference binder 1. Bio-binder 1 and 2 show significant signs of ageing once they experienced thermochemical ageing. Bio-binder 2 reaches the highest level of ageing due to the VBA, showing high ageing susceptibility towards ROS. The diagram shows that in terms of FTIR ageing index all the binder's range between 15 to 50 which is more than the ageing done by one cycle of PAV. Binder 2 and bio-binder 2 show a big difference in their respective ageing level, which is caused by the addition of the bio additive, which reacts strongly during thermochemical ageing.

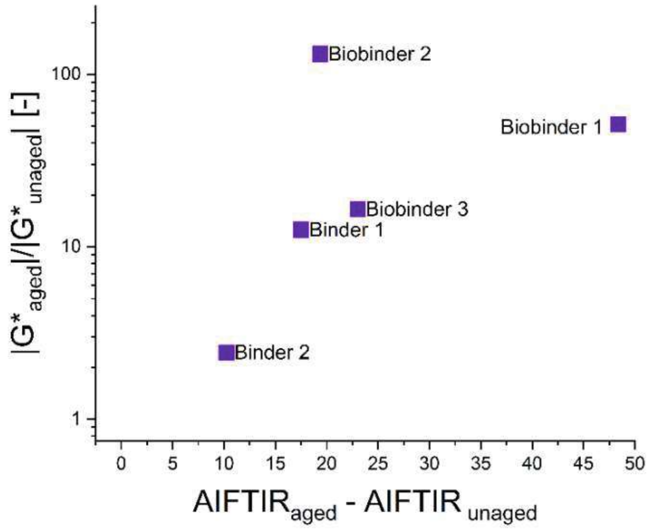

Figure 45: Impact of thermochemical ageing (VBA)

4.6.3 Impact of Photoinduced Ageing (LA1)

Figure 46 shows the impact of light ageing (LA1) on the five different binders that were analyzed in this diploma thesis. The scale y-axis had to be adjusted from 10 to 150 because values reached higher levels. A similar ageing level for all three 3 bio-binders and the reference binder 1 can be observed. Bio-binder 3 shows the lowest signs of ageing and the difference between the three light ageing setups is smaller compared to VBA. However, some differences between bio-binder 1 -3 is observable.

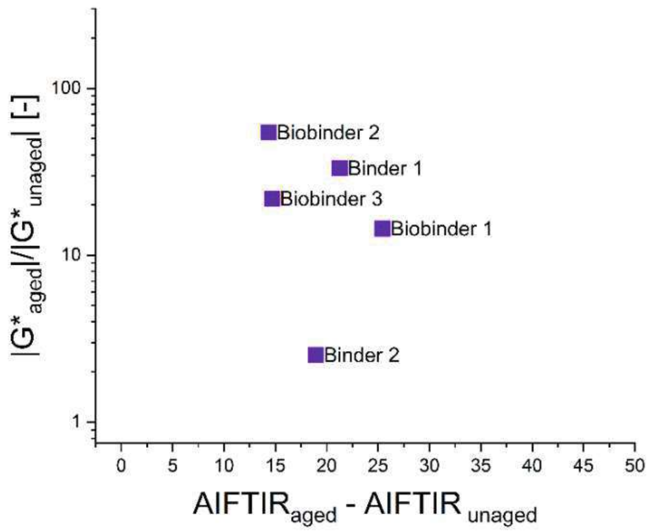

Figure 46: Impact of photoinduced ageing (LA1)

4.6.4 Impact of Photoinduced Ageing (LA2)

Figure 47 shows the impact of light ageing (LA2) on the five different binders that were analyzed in this diploma thesis. Bio-binders aged more than the reference binder 1 (in relative perspective to it is unaged stage). The diagram shows that all the binders experienced high levels of ageing when comparing this diagram to Figure 44 for the PAV ageing. There is still a difference between bio-binder 1, 2 and 3 showing that their bio additives have a significant influence on the binder's ageing behaviour. LA2 offers a greater variety to the bio-binders ageing levels, as in the pervious LTA the binder clustered closer together. With one 25-Watt LED ageing the difference in bio additives make a remarkable difference and all three bio-binders reach high levels of ageing.

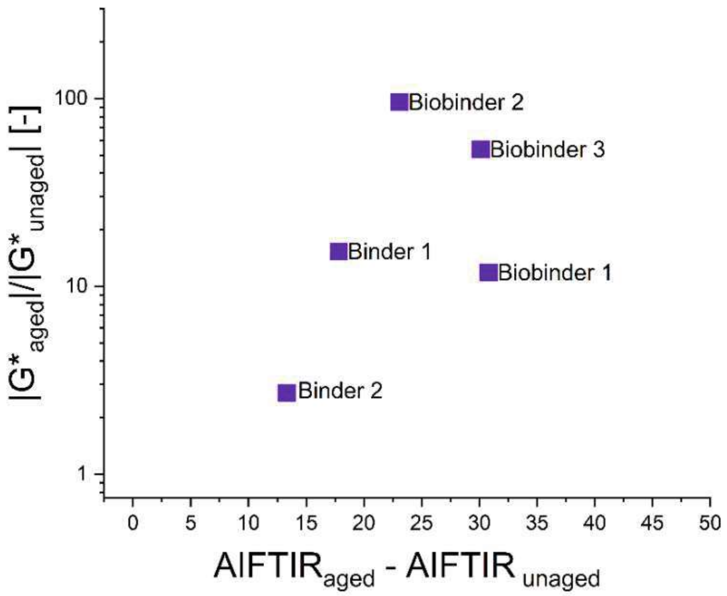

Figure 47: Impact of photoinduced ageing (LA2)

4.6.5 Impact of Photoinduced Ageing (LA3)

Figure 48 shows the impact of light ageing (LA3) on the five different binders that were analyzed in this diploma thesis. Bio-binders are more aged than the reference binder (in relative perspective to its unaged stage). Due to the two LED lamps of LA3 the CMC shows different levels of ageing due to the bio additives that were added to the binder 2. Ageing of the binder increases after bio additives were added. Similar to LA2, LA also offers a great variety to the bio-binders ageing level, as in the previous LTA methods like PAV and LA1 the binder clustered closer together. The diagrams of LA2 in Figure 47 and LA3 in Figure 48 look alike. They show high similarity and with two LED´s ageing at the same time the difference in bio additives make a remarkable difference and all three bio-binders reach high levels of ageing.

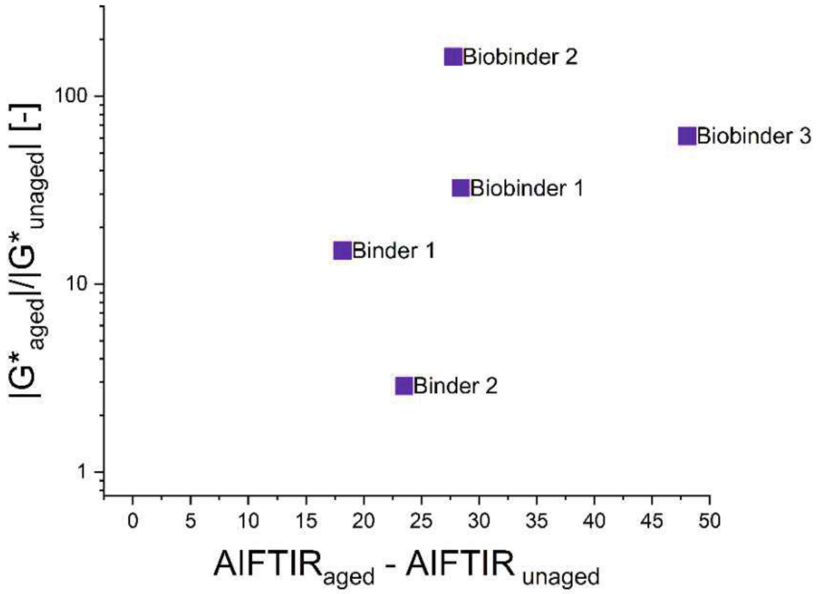

Figure 48: Impact of photoinduced ageing (LA3)

5. Conclusion

This diploma thesis investigated the ageing behavior of different bio-binders and bituminous binders from crude oil origin. While one of the bituminous binders acted as a reference binder, the second binder was used as a base binder for the bio-binders. Bio additives in the range of 10 – 50% were blended to create the three different bio-binders. Various laboratory long-term ageing procedures, involving the exposure to elevated temperatures, sunlight and reactive oxygen species (ROS), were applied to test the respective binders in regard to their ageing susceptibility to these ageing conditions. Chemical and mechanical properties correspond from unaged to STA to LTA were evaluated using Fourier Transform Infrared (FTIR) spectroscopy and the dynamic shear rheometer (DSR). Finally, these two analysis methods were combined into a chemo-mechanical correlation to provide a better understanding of the changes induced by different ageing inducing factors. The respective results lead to the following conclusions:

- For binder 1, LA1 induced the highest ageing, which indicates that the reference binder is strongly affected by photoinduced ageing
- Binder 2 differs from binder 1 and is mostly aged by LA3, the combination of two LED which reached the highest levels in terms of FTIR, DSR and CMC
- Bio-binder 1 exhibited the highest ageing when exposed to thermochemical ageing (VBA). This is visible in the FTIR, DSR and CMC diagrams
- Bio-binder 2 showed the highest ageing induced by LA2 and LA3 for FTIR, whereas in DSR also VBA had the highest influences; CMC LA2 and LA3 have the highest level in terms of ageing
- Bio-binder 3 reached the highest ageing level with LA3 as depicted in the results from FTIR, DSR and in the CMC

A potential outlook for using these binders in the pavement industry would involve evaluating their resilience and weaknesses and considering these factors carefully when determining their applications. For example, all binders showed lower ageing due to thermal influences. In an environment where only thermal influences occur, all the binders could be considered as ageing is limited. Bio-binder 1 could be used in a binder or base layer because that binder degrades strongly under the influence of ROS. The binder and base layer is free of light without reactive gases so any binder that is harmed by light or reactive gases could be used there.. Bio-binder 2 showed high ageing as soon as the binder comes into contact with strong light sources that cause photoinduced ageing. Therefore, it is useful in environments that due not have direct contact with sunlight. Its mechanical properties show that ROS can degrade the mechanical properties, so to make sure environments that include reactive gases like NO_X, ozone, OH-radicals should also be avoided.

Bio-binder 3 also showed resilience to ROS reactive gases, thermochemical ageing (VBA) did not reach high levels of ageing. Bio-binder 3 proved high sensitivity as soon as the samples were exerted to light ageing, where chemical and mechanical analysis showed very high levels of ageing. In terms of specific light sources, as shown in this study, the LA3 showed the highest impact on ageing, meaning that the lamps spectrum has a crucial impact on the binders ageing behavior. This binder should not be used under direct contact with photoinduced radiation for example in a well sunlight isolated area as a base layer for example.

Overall, it can be concluded that the ageing behavior of the investigated bio-binders show complex yet interesting results. Further analysis on the chemical and mechanical level are needed to understand discrepancies between various ageing inducing factors. A complete combination of all ageing inducing factors would also be necessary to come to a conclusion on the ageing behavior in the field. Thus, these results leave a lot of room for further research in the future, that can tackle the potential of bio-binders.

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7. List of Figures

8. List of Tables