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Study of the Effect of Laboratory-Simulated Ageing on the Damage Resistance of Polymer-Modified Bitumens in Intermediate Climates

By

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Abstract

Polymer additives are widely used to improve the performances of road bitumens. However, although their advantages are well recognised, there are still drawbacks and concerns that limit the widening of their usage. One of these concerns is the lack of understanding of their ageing-inhibitor properties.

This work focuses on the study of the effect of laboratory-simulated ageing on the microstructure and the rheological response of different polymer-modified bitumens (PMB). A single base bitumen has been modified with different concentrations of two polymers: an elastomer (Styrene-Butadiene-Styrene – SBS), and a plastomer (Ethyl-Vinyl Acetate – EVA). In the preparation of the SBS modified bitumens, the presence of sulphur as cross-linker has been varied to evaluate the effects of the use of cross-linker on their ageing resistance. The bitumens have been laboratory aged in the RTFO and the PAV. The microstructure of the unaged and aged bitumens has been investigated through fluorescence microscopy and Gel Permeation Chromatography (GPC). On the other hand, the rheological response has been investigated by linear viscoelastic characterisation, the Multiple Stress Creep and Recovery (MSCR) test, and the Linear Amplitude Sweep (LAS) test.

The artificial ageing susceptibility of the SBS modified bitumens depends on the use of sulphur as cross-linker and the polymer concentration. More specifically, the SBS network degrades in the RTFO and the PAV. The degradation of the polymer phase is clearly visible in the fluorescence microscopy, and it is detected in the GPC. The deterioration of the polymer network contributes to mitigating the effects of the PAV-oxidative hardening of the bitumen

phase on the rheological response. The use of cross-linker and the increase in the polymer concentration improve the ageing-inhibitor effect of the SBS.

The EVA polymer shows a low ageing susceptibility and a low affinity with the base bitumen irrespective of the polymer concentration. As a consequence, the rheological response of aged EVA modified bitumens does not seem to show relevant deviations from one of the unmodified bitumens except for the cumulative damage resistance at high polymer concentration.

Besides PMBs, this work includes a section focused on the laboratory–simulated ageing of SBS modified mastics. An unmodified bitumen and different SBS modified bitumens (i.e., different polymer concentrations) have been mixed with a single filler concentration. The mastics have been aged by using multiple cycles of PAV. The rheological response of the mastics has been investigated by the MSCR test. Results show that the variation with ageing of the resistance to the accumulation of permanent deformation of mastics shows a similar trend to one of the corresponding bitumens. The correspondence of the findings between the bitumen and mastic scales appears to be promising and support the approach followed in this work to study PMBs.

Acknowledgements

This thesis has not been developed in the context of a specific project. The work has been generated from the willing to pursue the degree of Doctor of Philosophy in Civil Engineering for the sake of a valid personal and professional development. Therefore, it is with great honour for me to thank the people who contributed to this development.

This thesis has been a witness of several changes that occurred in my life during the years I have spent on its development. As a consequence, I would like to thank the different people I have met during these years who helped me with this work.

I want to thank my advisors, Professor Gordon Airey (University of Nottingham), Professor Massimo Losa (University of Pisa) and Dr Davide Lo Presti (University of Nottingham, and University of Palermo) who gave me valid guidance and support in this work. Besides them, the same gratitude goes to Professor Pietro Leandri, Professor Giovanni Polacco, and Dr Sara Filippi (University of Pisa) for their continuous and valuable contribution to the development of the experimental protocols. Without their contribution, this work could not have been developed.

I want to thank Dr Nick Thom and Dr Emmanuel Chailleux for accepting of being the internal and the external advisor for the evaluation of this work.

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Finally, I want to thank my family for the endless presence, support and encouragement.

Declaration

This thesis has been developed in the road research laboratory of the Department of Civil and Industrial Engineering of the University of Pisa under the continuous supervision and guidance of Professor Gordon Airey and Dr Davide Lo Presti of the Department of Civil Engineering of the University of Nottingham from April 2015 to June 2019. I declare that this work is my own and that has not been submitted for a degree of another university.

Giacomo Cuciniello

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1 Introduction

1.1 Background

In the past few decades, materials and technologies used in road applications have undergone continuous improvements prompted by the increase in transportation demand. The modification of bitumens with polymeric additives (Polymer Modified Bitumens – PMB) represents a successful technology developed for improving the performance of bituminous mixtures (1-5). Two types of polymer are mainly used in bitumen modification: elastomers and plastomers. The elastomers resist deformation by stretching and recovering their shape, while the plastomers resist deformation by forming a 3-D rigid network. Among the elastomers, the Styrene-Butadiene-Styrene (SBS) block copolymer is the most widely used, followed by reclaimed tyre. On the other hand, Ethyl Vinyl Acetate (EVA) and Polyethylene are the plastomers most widely used.

The quality of the modification can be defined as the polymer's capability of improving the properties of the base bitumen when added in small quantities. In particular, polymers aim to stiffen the bitumen at high pavement temperatures, to lower the stiffness at low and intermediate pavement temperatures, and to maintain adequate levels of workability during the production and laying of mixtures. Besides this, other properties such as reducing the moisture susceptibility, increasing the ageing resistance, and being stable in storage are desired.

These properties represent the macroscopic result of complex chemical and thermodynamic interactions that occur at the microscopic level between the polymer and the bitumen. These interactions consist mainly of the polymer swelling in the bitumen phase by absorbing the fractions with the highest affinity while maintaining its structure.

The more the polymer and the bitumen are compatible, the more the polymer is dispersed and enhances the properties of the PMB (6). The complexity of such interactions is mainly due to the large variability in the composition of bitumens and polymers that affects their affinity. Although some of the advantages of polymer modification are clear, there are technical drawbacks and concerns that, besides costs, appear to limit the widening of the use of polymer additives with road bitumens.

One of these aspects is represented by the lack of clarity and consensus on the beneficial effects of polymers on the oxidative ageing mechanism that occurs in road bitumens. The comprehension of the benefits of polymers on the oxidative resistance of PMBs is relevant under several perspectives. Lowering the oxidation of the mixtures in the field can contribute to delivering more lasting pavements. On the other hand, considering the attention to recycling asphalt, polymer modification might result in providing a better Reclaimed Asphalt Pavement (RAP) by reducing the oxidative level of the RAP binder in the mixtures.

However, before identifying the effects of the polymer on the oxidative mechanism of PMBs, clarity needs to be provided on the ageing mechanism occurring in unmodified bitumens.

The study of ageing in road bitumens is not recent and has captured the interest of the industry and academia over the past 60 years (6 - 10). A large part of the research has focused on the compositional changes arising in the bitumen microstructure throughout the progress of ageing, and their effects on the rheological response. Very often, ageing indexes have been developed as the ratios between properties measured at unaged and aged conditions. Devices capable of simulating ageing in laboratories, and ageing-inhibitor additives have been developed from the findings of the research (13, 14).

Two ageing mechanisms are known to occur in road bitumens: the Short-Term Ageing (STA) and the Long-Term Ageing (LTA). The first occurs during plant and paving operations when the bitumen is exposed as a thin film to high temperatures. The second occurs during the service life of the pavement where the bitumen is exposed to environmental factors such as atmospheric oxygen and solar radiation. During the STA, the main changes in the bitumen composition consist of the volatilisation of the light fractions. Whereas, in the case of LTA, oxidation seems to be the leading mechanism with some steric hardening.

The oxidation of bitumens is produced by the diffusion of the atmospheric oxygen through the thin film of bitumen coating the mineral aggregates. The effect is the formation of oxygen-containing carbonyl compounds characterised by strong interactive forces that contribute to the formation of polar functional groups (i.e., asphaltenes). At the microscopic level, this reduces molecular mobility. Macroscopically this results in increasing the stiffness and reducing the strain tolerance of the bitumens with the consequent risk of premature fatigue or low-temperature cracking (8, 15, 16).

Some of the questions that have inspired this work are: “Where do polymers affect this mechanism? At the molecular level? Does that mean that polymer mitigates the formation of carbonyls? Alternatively, at the functional level, where might the polymer contribute to reducing the formation of asphaltenes?” The large variety of polymers and bitumens sources available on the market and the complexity of their interactions do not allow drawing a general conclusion. Nevertheless, the study of oxidative ageing in polymer-modified bitumens has been of considerable interest.

As observed in unmodified bitumens, the study of ageing in PMBs encompasses two approaches: the study of changes in the bitumen microstructure with ageing, and their effects on the mechanical response. The examination of the microstructure has focused on several parameters. Fourier Infrared Spectroscopy (FTIR) has been applied to measure the formation of carbonyls at different levels of ageing. Gel Permeation Chromatography (GPC) has been used to evaluate the variation in the molecular weight distribution of the polymer and the bitumen phases (17-24). Alternative approaches promote the use of the variation in the asphaltenes content as an indicator of the ageing susceptibility of asphalt (25, 26).

Besides compositional methods, also the mechanical characterisation has been contemplated to quantify bitumen oxidation. The majority of the works have aimed to assess the role of the polymers in the oxidative mechanism through the comparison of physical parameters (i.e., penetration, softening point, viscosity, complex modulus and phase angle), of unmodified and polymer modified bitumens under the same level of ageing. The findings from these studies do not seem to converge towards the definition of a unique ageing mechanism that would be in any case, unexpected, since it is polymer-dependent. Nevertheless, general conclusions can be drawn for some polymers.

The SBS copolymer appears to reduce the formation of sulfoxide while producing a negligible effect on the rest of carbonyls (19). Additionally, results from the GPC show that the polymer chain undergoes thermo-oxidative degradation during the short-term and the long-term ageing (18, 20-24). According to the findings from the rheological analysis, such deterioration seems to induce a more viscous response of the PMBs mitigating the hardening of the bitumen phase.

However, the conclusions related to the compositional changes occurring in PMBs with ageing, are likely to be generic and sometimes result as conflicting even when different works focus on the same polymer (e.g., Styrene Butadiene Styrene - SBS). This aspect depends probably on the fact that the study of the interactions between polymer and bitumen is complex. Additionally, the repeatability of chemical test methods is sometimes of concern. As a consequence, it seems that a clear assessment of the benefit of polymer modification on the ageing resistance of PMBs cannot be advocated unless a case by case study is conducted.

1.2 Problem statement

The modification of road bitumens with polymeric additives is a widely used technology to improve the performance of asphalt mixtures. However, although the use of polymers has proven to be successful, there are still shortcomings that limit their usage. One of these limitations is their unclear effect on the ageing susceptibility of PMBs.

Although the problem of ageing in PMBs appears to be complicated, in this research, some of the shortcomings in the existing works have been identified. In the majority of the studies, the Job Mix Formula (JMF) of the PMBs is given in terms of polymer concentration only. No details on the use of cross-linker, stability, level of dispersion of the polymer (morphology) are given. Besides this, in most of the studies, the bitumens are laboratory-aged up to a single cycle of Pressure Ageing Vessel (PAV), and no additional or intermediate ageing exposures are conducted. In the case of PMB, such conditions might not be severe enough to produce significant changes in the microstructures of the PMBs due to their high viscosity at the PAV conditions (27). Additionally, the descriptions of the chemical test protocols lack details.

Aside from this, the Dynamic Mechanical Analysis (DMA) of PMBs is conducted in the linear viscoelastic region where the low strain level used in the tests does not allow considering the stress dependency of polymers, and it may provide an uncertain correlation with mixture performance (28). The strain dependency of polymers is given by the fact that when their chains are extended, glassy or crystalline regions and chain entanglement can produce the distortion of the morphology with a consequent change in the physical response (29-33). Therefore, the effect of the thermo-oxidative degradation of the polymer chain on the physical response of PMB should be determined at strain levels higher than those used in the linear viscoelastic (LVE) characterisation (34-37).

1.3 Scope of the research

This research focuses on the analysis of the mechanism of laboratory-simulated ageing (LSA) in Styrene Butadiene Styrene (SBS), and Ethyl Vinyl Acetate (EVA) modified bitumens. The work considers the variation of the bitumens 'microstructure with ageing and the consequent variations in the rheological response measured at strain levels higher than those of the LVE characterisation.

The scope is to develop a rigorous approach based on the understanding of how the polymer modification considering the polymer type, its concentration, and its compatibility with the base bitumen, can affect the laboratory-ageing resistance of PMBs.

A single base bitumen has been modified with different concentrations of SBS and EVA. The SBS modified bitumens have been prepared by varying the presence of sulphur as cross-linker. The bitumens have been laboratory-aged in the Rolling Thin Film Oven (RTFO) to simulate the STA and long-term aged in the Pressure Aging Vessel (PAV).

The bitumens' microstructure has been studied using Fluorescence Microscopy and Gel Permeation Chromatography (GPC). The first provides information on the level of dispersion of the polymer phase in the bitumen phase at the different levels of ageing. The second is used to investigate the variation in the molecular distribution with ageing.

The rheological response has been measured in the Dynamic Shear Rheometer (DSR) by using the frequency sweep test (UNI EN 14770:2012; AASHTO T 315), the Multiple Stress Creep and Recovery test (MSCR – AASHTO T350), and the Linear Amplitude Sweep test (LAS – AASHTO TP 101-12).

The frequency sweep measures the magnitude of the shear complex modulus |G*| and of the phase angle within the LVE region at different levels of temperature and frequency. The MSCR focuses on the resistance to the accumulation of permanent deformation. At the unaged and RTFO-aged conditions, the stress applied in this test should be capable of producing slippage in the polymer chain. Therefore, the effects of the degradation in the polymer chain on the rheological response can be identified.

On the other hand, the LAS measures the cumulative damage resistance of the bitumens at different levels of laboratory-simulated ageing (LSA) within the intermediate pavement temperatures.

1.4 Research objectives

The objectives identified in this research are given below.

Objective 1

To improve the understanding of the effects the bitumen-polymer compatibility on the laboratory-ageing susceptibility of SBS and EVA modified bitumens.

Objective 2

To identify the effects of laboratory-ageing on the microstructure of SBS and EVA modified bitumens, and to correlate them with the variation in the rheological response measured at strain levels higher than those used in the LVE characterisation.

Objective 3

To understand the effect of multiple levels of laboratory-simulated ageing on rutting and fatigue cracking resistance of bitumens.

1.5 Research Hypothesis

Linear Viscoelastic characterisation of PMBs does not provide a clear description of the effect of oxidation on modified bitumens. The effect of ageing on PMBs within the linear viscoelastic strain range is not indicative of the damage resistance of binder.

1.6 Organisation of the document

The thesis is organised in six major chapters. The content of each chapter is summarised as follows.

- *Chapter 1* – This chapter includes the background information on the topic of the research, and provides the problem statement, the scope of the research, the objective of the research, and the hypothesis on which the experimental plan has been developed.

- *Chapter 2* - This chapter includes the literature review of the research, and it is organised in five major parts. The first part focuses on the current challenges of bituminous materials. The second part focuses on the durability of unmodified bitumens and their mechanism of ageing. The third part introduces the fundaments of the modification of road bitumens with polymeric additives. The fourth part refers to the mechanism of ageing in PMBs, while the fifth part includes the background of the rheological characterisation of unmodified bitumens and PMBs.

- *Chapter 3* – This chapter includes a description of the experimental methodology developed in this research. The experiment comprises two groups of tests, one focused on the study of the microstructure of bitumens, the other on the study of their rheological response.

- *Chapter 4* – This chapter presents the results of the studies conducted on the microstructure of bitumens. The first part of the chapter focuses on the findings from fluorescence microscopy, the second on the findings from the GPC.

- *Chapter 5* – This chapter presents the results from the linear viscoelastic characterisation and the rutting resistance measured through the MSCR test.

- *Chapter 6* – This chapter includes the description of the portion of the experimental pan focused on the cumulative damage resistance of PMBs. The first part of the chapter focuses on the results of the LAS test. The second part includes the results from the time sweep test, which has been used on a sub-set of bitumens to verify the findings from the LAS test.

- *Chapter 7* – This chapter includes the description of the portion of the experimental plan focused on polymer-modified mastics.

- *Chapter 8* – This chapter includes the conclusions and the limitations of the work, and provides recommendation for future works. Aside from the conclusion, this section remarks about the achievements of the research concerning the initial objectives.

2 Literature review

This section includes the findings of a literature review conducted to support the objectives and the hypothesis of this research.

Ageing is a non-load related phenomenon that affects bitumens' chemical composition and occurs in two stages. The first stage includes the exposure of the bitumen as a thin film to high temperatures (150°C to 180°C) during plant and paving operations. This stage is defined as Short-Term Ageing (STA). The second stage refers to the exposure of the bitumen coating the mineral aggregates to environmental factors such as atmospheric oxygen and solar radiation during the service life of the pavements. This stage is defined as Long-Term Ageing (LTA). The capacity of the bitumens to resist loading varies as a consequence of such changes, and a durable bitumen is capable of maintaining its properties with time. Therefore, the study of ageing in bitumen encompasses primarily two approaches: the investigation of the chemical changing of the composition caused by ageing (microscopic level), and the consequent variations in the rheological response (macroscopic level).

In the case of unmodified bitumen, the changes in the chemical composition depend on the crude source and the refining method. In the case of PMBs, three mechanisms affect the chemical composition: bitumen hardening, polymer degradation, and their interaction.

The rheological characterisation of unmodified bitumen can be undertaken within the LVE region or through empirical test methods. On the other hand, the rheological response of PMBs needs to be evaluated within the appropriate range of strain to provide a correct estimation of the polymer contribution.

The conceptual scheme of the literature review on the mechanism of ageing in unmodified bitumen is given in Figure 2-1.

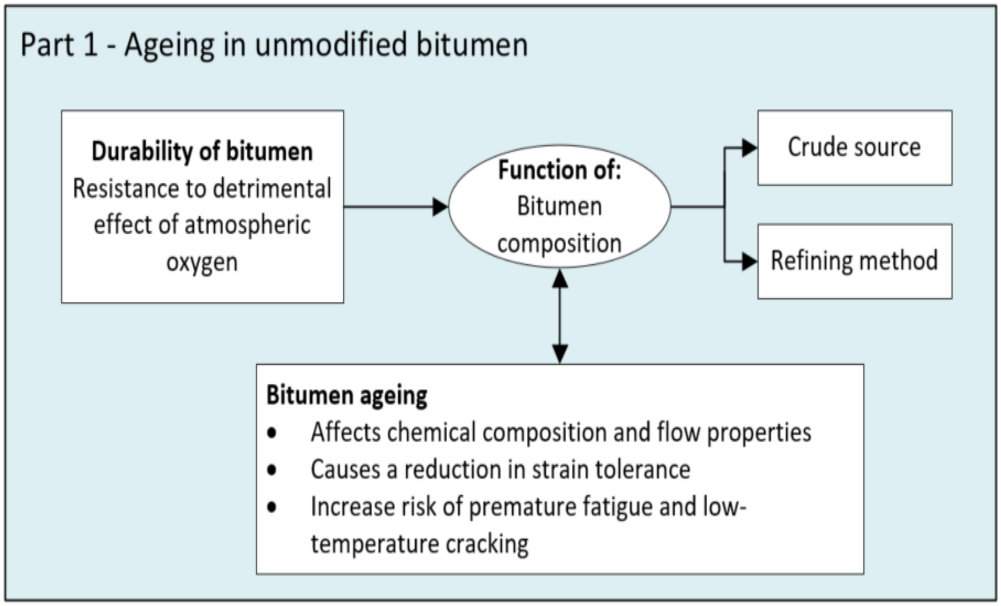


Figure 2-1 – Conceptual scheme of literature review on ageing in unmodified bitumens.

The conceptual scheme of the literature review on the mechanism of ageing in polymer-modified bitumen is given in Figure 2-2. The conceptual scheme of the literature review focused on the rheological characterisation of PMBs is given in Figure 2-3.

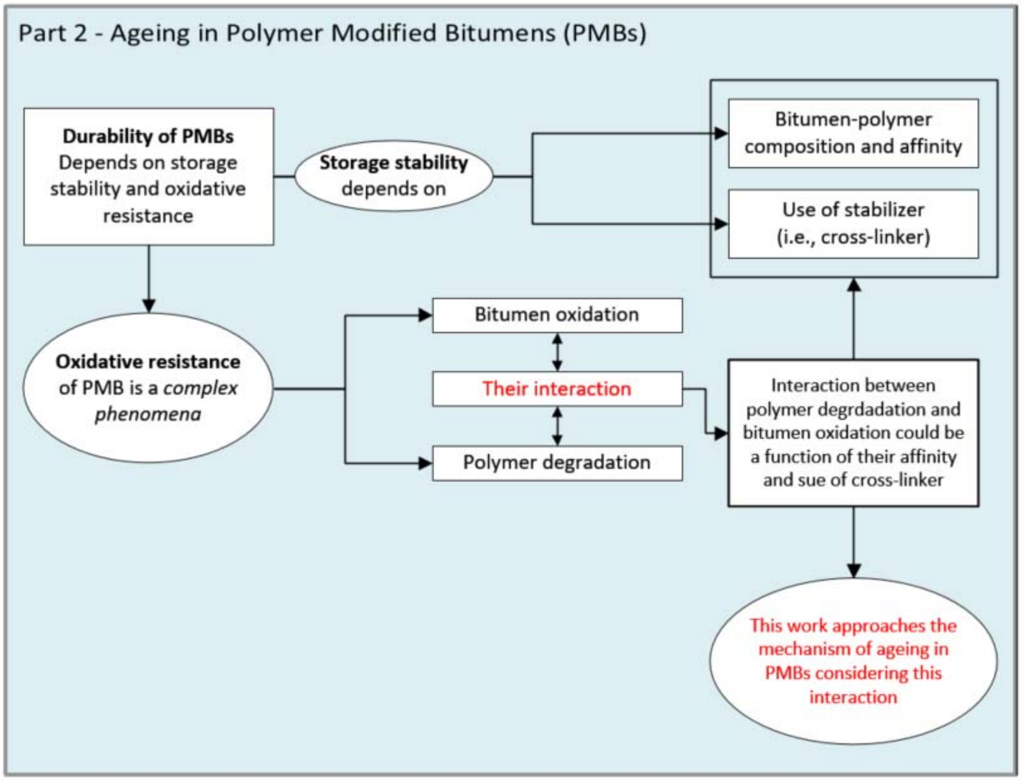


Figure 2-2 - Conceptual scheme of literature review on ageing in PMBs.

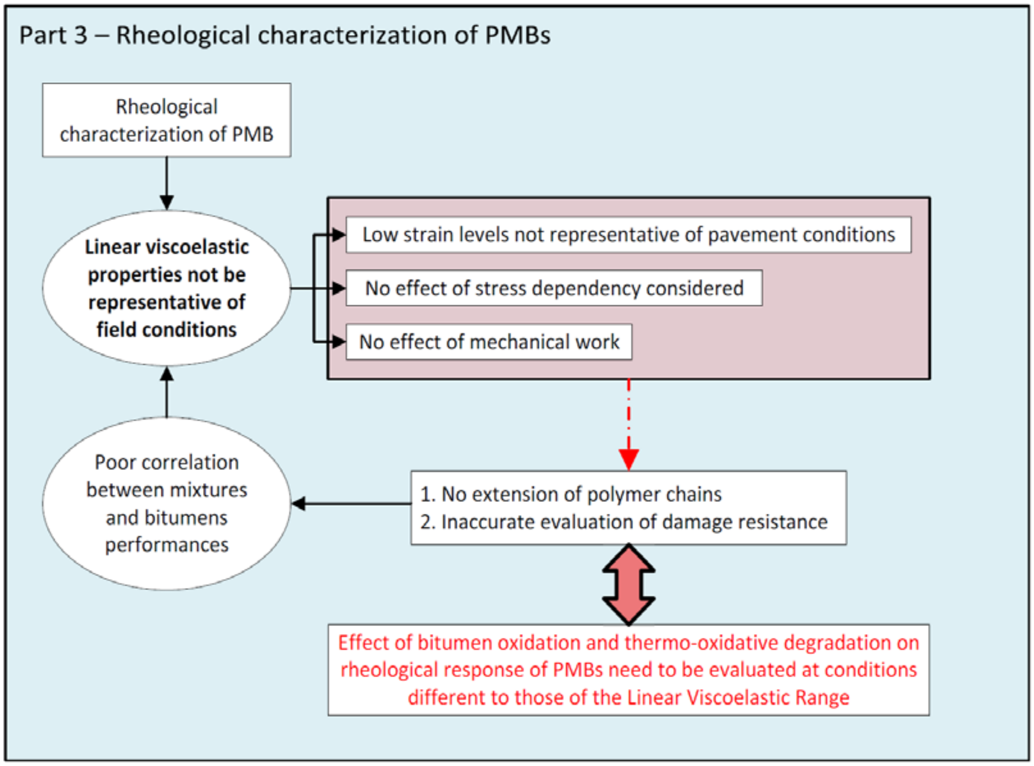


Figure 2-3 – Conceptual scheme of literature review on rheological characterisation of PMBs

The schemes in Figures Figure 2-1, Figure 2-2, and Figure 2-3 are intended to support the understanding of the literature review included in this thesis.

2.1 Bitumen origin and historical usage

This work refers to bitumen or asphalt in the case of binder produced from the distillation of crude oil. In the case of natural bitumen, the work refers to it as natural bitumen or natural asphalt.

Bitumen (or asphalt) has mainly two different origins: natural asphalt that occurs from natural deposits such as lake or rocks, and petroleum bitumen that is manufactured from the distillation of crude oil. The bitumen manufacturing from the crude distillation appeared at the beginning of the 20th century when distillation strategies became available. Before that, the bitumen was available from natural sources located in different parts of the World.

Several natural sources of asphalt are available all over the World.

Based on the available information, it appears that the Dead Sea (Figure 2-4), also called Lake Asphaltite, has been the primary worldwide source of natural asphalt in both the ancient and the modern eras (1). In this sea, asphalt exists in the form of asphaltic limestone where 5% of asphalt is impregnated in porous limestone.

Figure 2-4 - Dead Sea (courtesy of CBN.com)

Besides the Dead Sea, the Trinidad Lake (Figure 2-5) represents one of the largest natural asphalt deposit in the World. This lake includes about 39% asphalt, 33% of emulsified water and 27% of the mineral matter in colloidal form (7).

Figure 2-5 - Trinidad Lake (Trinidad and Tobago), (courtesy of http://www.richard-seaman.com)

Another source of natural asphalt significant for the US market until the beginning of the 20th century was the Bermudez Pitch Lake from Venezuela (Figure 2-6).

Figure 2-6 – Bermudez Pitch Lake – Venezuela

(courtesy of http://www.lakescientist.com)

This lake is composed of 64% of asphalt, 30% of water, 4% of insoluble organic matter and 2% of dispersed mineral matter.

Throughout history, natural bitumen has undergone different types of application, and its usage increased mainly due to its waterproofing qualities. It seems that the earliest record of usage dates back around 180,000 years ago in the El Kowm Basin Syria, where it was applied to stick flint and other tools. Even the Bible cites its usage as well in the waterproofing of the keel of Noah’s ark and the Tower of Babel (7). However, the use of natural asphalt as an engineering material appeared between 3,800 and 3,000 BC, where it was used for masonry and waterproofing in the Euphrates and Indus Valleys (45).

The first application of natural asphalt in road construction dates back to the king of Babylon Nabopolassar between 625 and 604 BC where a mortar constitute of natural bitumen was used in the construction of a foundation which consisted of three layers of burned bricks and the stone slab put on top of them. Afterwards, the usage of natural asphalt in road applications disappeared until the 19th century when new sources of natural bitumen discovered in Europe widened the diffusion of its usage in modern applications including road construction. The first example of asphalt paved road in Europe seems to be Place de La Concorde in Paris in 1834, where panels of asphalt were used to pave the yard.

On the other side of the Atlantic, in the United States of America, the first asphalt roadway was constructed in Newark, New Jersey, in 1870 (Figure 2-7) (46). Then, in 1910, with the advent of vacuum distillation, the use of natural bitumen started diminishing in lieu of the petroleum bitumen distilled from crude oil (henceforward called bitumen) (7).

Figure 2-7 - First paved road in the US (Newark – NJ, 1870)

(courtesy of www.uniquepavingmaterials.com/)

2.2 Bitumen global demand

Although natural bitumen is still used in a few applications, bitumen manufactured from crude is now dominant. In 2015, the Asphalt Institute, jointly with the Eurobitume, published a report entitled “The Bitumen Industry – a Global Perspective” (47). According to this report, the estimation of the current world production of bitumen is approximate 87 Million tonnes per year with a worldwide, diversified demand (Figure 2-8).

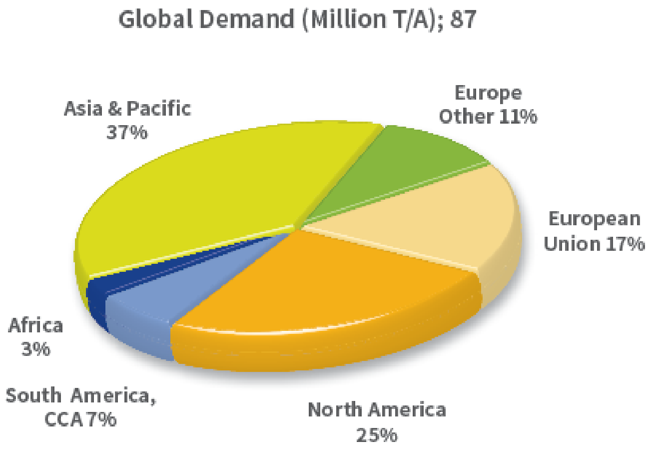


Figure 2-8 - Annual global demand for bitumen from crude refining (47)

The data show that the majority of the demand lies between the Asian (dominated by China), the United States, and the European markets. The African continent with South America remarks for 10% of the demand.

Such demand incorporates about 250 types of application for bituminous products. However, 95% of the applications comprise two fields only: road paving (85%) and roofing (10%). This work considers the use of bitumen in road paving applications.

With the term paving (or pavement) applications is meant the construction of flexible pavements, semi-rigid pavements (Cement stabilized layer + Hot Mix Asphalt), and composite pavements (Concrete + Hot Mix Asphalt) used to build roads, runways, parking lots, lining of water reservoirs, racetracks, and foundation of railway tracks. On the other hand, bitumen in roofing application is used for the production of shingles used in waterproofing applications. In road paving, the bitumen is used as a binder in the production of asphalt mixes (or bituminous mixtures). In this process, the bitumen is generally heated at a temperature of approximately 160°C (in the case of Hot Mix Asphalt - HMA), and it is mixed with mineral aggregates to coat them uniformly. Then, after mixing, the mixture is transported to the construction site where it is compacted to the desired density through apprpriate machinery. Typically, the weight composition of asphalt mixtures comprises 5% of bitumen and 95% of aggregates.

The demand for bitumen as a construction material is linked to the internal Gross Domestic Product (GDP) of a country which is an indicator of its level of development. Besides the GDP, the amount of investment allocated to road infrastructure represents another indicator.

To provide a measure of the worldwide distribution of investment dedicated to road infrastructure, in this work the data from the Office of the Economic and Development of the World Bank (https://data.oecd.org/) related to the year 2015 have been included in Figure 2-9.

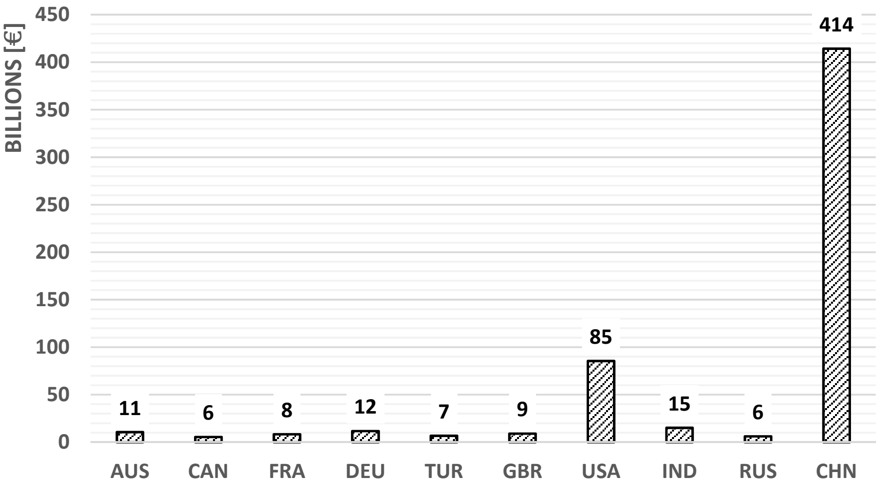


Figure 2-9 - Road infrastructure investment in 2015 (data from https://data.oecd.org/)

The data in Figure 2-9 show that during 2015, the construction of road infrastructure has represented a worldwide business of about 570 billion euros. The most substantial amount of this investment belongs to the Chinese market that, alone, remarks for 72% of the total. Such massive investment is supported by the Chinese demand for bitumen given in Figure 2-8. Besides the massive Chinese road infrastructure market, the US and the Indian markets display an intense activity as well compared with the rest of the European countries. Based on the forecasted data available on the trend of the construction industry for the next 15 years (49), these three countries (China, United States and India), will make 57% of the total amount of investment in construction, which is expected to total an overall amount of 21 trillion of dollars. However, caution needs to be maintained once such type of data is discussed and presented because of the volatility of markets; global crises and wars need to be considered as potential causes capable of reversing the equilibrium and the direction of the investment.

The reason to emphasise the substantial growth expected in the construction market in the next 15 to 20 years lies in the fact that the amount of manufactured bitumen available might not be adequate to cover the global demand. Although bitumen demand seems to represent a sound investment prompted by future investment in the construction industry for the next two decades, the current bitumen production represents only 2.5% of the total refining product (50).

The reason for such a limited production lies in the economy of refined crude products. In other words, the production of bitumen generates a lower revenue compared with other crude products such as transportation fuels. Petroleum refineries are large, capital-intensive manufacturing facilities, characterised by complex and unique schemes (48). Nowadays there are about 660 refineries active in 116 countries producing more than 85 million barrels of crude per day. Each refinery converts crude oils into several co-products, such as liquefied petroleum gases, gasoline, jet fuel, Kerosene (for lighting and heating), diesel fuel, petrochemical feedstock, fuel oil, and bitumen.

The production chain of each refinery depends on its operational characteristics, and these are unique for each refinery. In particular, the operational properties of crude refineries depend on location, vintage, availability of funds for capital, available crude oil in the vicinity, product demand, product quality requirements, environmental regulations, market specifications and product requirements. For instance, in North America, refineries are configured to maximise gasoline production. However, transportation fuels generate higher incomes, while bitumen generates the lowest. For this reason, conventional refining practices do not focus on optimising the quality of its production. As a consequence, the properties of neat bitumens produced as a residue of crude distillation, might not be adequate for the modern traffic and environmental conditions.

This aspect is relevant for the asphalt pavement industry since it represents one of the main reasons for developing the modification of petroleum bitumens with polymeric additives (38).

2.3 Overview of the challenges of bituminous materials

Besides economic and strategic perspectives, the analysis of bitumen demand should include an assessment of the performance required for bituminous materials used in modern road applications. As seen in §2.1, the historical use of natural bitumen was promoted by its waterproofing characteristics. Nowadays, although this property is still valuable, bituminous materials undergo stringent requirements of durability, sustainability, and cost-efficiency (51).

Pavement durability depends on the mechanical response of asphalt mixtures under repeated traffic loading and the effect of atmospheric agents such as temperature, solar radiation, moisture, and atmospheric oxygen. Specifically, asphalt pavements are designed to resist rutting and fatigue cracking. Both distresses are load-related phenomena which depend on the cumulative damage generated by repeated traffic loads.

A more accurate definition of these distresses is given as follows:

- **Rutting** is a load-associated phenomenon that occurs gradually at the surface layer of the pavement structure with increasing numbers of load applications (62). It appears as a longitudinal depression of the pavement surface accompanied by small upheavals to the side (Figure 2-10). Rutting occurs mainly in the range of high pavement temperatures where the mix is soft, and it is produced by the combination of two factors: densification (increase in density with a consequent reduction in air voids), and accumulation of plastic shear deformation that can occur in one or more pavement layers including the subgrade. Accumulation of shear deformation appears to be the leading mechanism.

Figure 2-10 – HMA Rutting.

- **Fatigue cracking** is the result of tensile strain at the bottom of the asphalt layer that results in the generation and propagation of cracks upward to the pavement surface under the effect of repeated traffic heavy loading (63). These cracks become visible on the pavement surface as longitudinal cracks in the wheel path (in the case of low or moderate severity), while resulting in alligator cracking in the case of severe cumulative distress (Figure 2-11). This mechanism is also known as bottom-up fatigue cracking. Besides the bottom-up mechanism, the top-down fatigue cracking phenomenon is produced by the formation of cracks in the pavement surface, which propagate downward under the effect of repeated traffic loading. Cracks at the pavement surface are generated by excessive stress concentration due to heavy loads and high tire inflating pressure. Fatigue cracking occurs at intermediate pavement temperatures.

Figure 2-11 - Severe fatigue cracking (alligator cracking).

However, pavements undergo failure also under the effect of climatic factors (combined with traffic) such as temperature and moisture. In fact, besides the load-related phenomena, there is distress related to excessive low pavement temperature (low-temperature cracking or thermal cracking) and related to moisture-induced damage (stripping or ravelling).

The thermal cracking produces a pattern of transverse cracks spaced longitudinally (Figure 2-12).

Figure 2-12 – Thermal cracking.

This failure mechanism is not associated with traffic loading but rather with the thermal stresses generated by the friction between the asphalt layer, which shrinks at low temperatures, and the underlying unbound layer. The crack is generated in the section where the stress built-up overcomes the strength of the material. The stress build-up is a function of the relaxation properties of the mixtures.

Moisture damage may be defined as the loss of strength and durability of mixtures due to the presence of moisture at the bitumen-aggregate interface (adhesive failure), or within the bitumen (cohesive failure) (63). About the adhesive failure, the loss of bond strength at the interface may be related to the bitumen-aggregate interface or the mastic-aggregate interface (65). Nevertheless, moisture damage in road pavements is caused by the combined effect of water and traffic. One of the most visible effects of water (combined with traffic), on a pavement, is the creation of pot-holes on the pavement surface (Figure 2-13) due to surface ravelling. Hence, water not only affects the mechanical properties of the mixtures (therefore influencing durability), it also has a significant effect on the functional capacities of pavements (such as friction and ride comfort), and therefore on the safety. It is clear that many moisture damage mechanisms can be responsible for the premature failure of pavements, increasing maintenance and rehabilitation costs.

Figure 2-13 – Poth-hole on the pavement surface course caused by debonding.

A durable pavement can be defined as a cost-efficient layered structure capable of lasting the design period without unexpected failure. The successful delivery of a durable pavement comprises the application of different methodologies and technical solutions that can be summarised as follows:

- A reliable pavement design based on realistic traffic assumptions and locally calibrated material properties;
- A very accurate materials selection accompanied by the consistent production of mixtures;
- A well-established construction practice.

Besides a reliable design method and adequate mixture production/placing, the long-term pavement performances depend on the selection of adequate materials which must provide the required mechanical properties.

A safe pavement is capable of providing adequate levels of friction and driving comfort to road users under different environmental conditions. Suitable levels of friction can be achieved through the use of tough and angular aggregates whose grading shall be proportioned to optimise the surface macro-texture and micro-texture.

On the other hand, sustainable production of asphalt mixtures shall limit the use of primary materials such as mineral aggregates from quarry operations and virgin bitumen from crude distillation. Based on this necessity, the asphalt industry promotes the usage of recycled materials (or secondary materials) in new-constructed pavements. These materials derive from the recycling of existing asphalt pavement, ground tyre rubber, glass and shingles. In the United States, the use of recycled pavements (Recycled Asphalt Pavement – RAP) dates back to 1915, but it did not become a common practice until 1970 when the Arab oil embargo boosted the price of bitumen (52). Data from the European Asphalt Pavement Association (EAPA) show that in Europe, several technologies for recycling materials from pavement demolitions are available (53). Recycled pavement can be used in the construction of new Hot Mix Asphalt, Cold Mix Asphalt, Warm Mix Asphalt, unbound layers and hydraulically bound layers. However, the general principle to follow while designing mixtures, including RAP is that these mixtures should perform at least equal to 100% virgin mixtures.

Regarding the use of ground tyre rubber (GTR) recycled from automotive tyres, in 1991 the United States adopted the use of GTR into their federal policy (issuing a law) for the construction of a National Intermodal Transportation System. The act required, starting from 1994, 5% of roads built with federal funds must use pavements constructed using GTR from the recycling of automotive tyres or modified asphalt. By 1997, 20% of roads constructed with federal funds included the use of recycled tyres in the pavements (1). Besides the use of recycled materials, production of asphalt mixtures shall minimise the consumption and carbon dioxide emissions during plant and paving operations. Technologies known as Warm

Mix Asphalt (WMA) have been developed to lower mixing and compaction temperatures based on different mechanisms. The use of WMA allows reducing the production temperatures by 30 to 50°C compared to HMA. Such a reduction enables an energy saving of about 11% (52, 59). The WMA technologies can be classified between water-based processes and processes based on the use of organic additives as waxes and amides. Water-based processes are based on the phenomenon for which once a given volume of water turns to steam at atmospheric pressure, and it is dispersed into hot bitumen it causes a consequent reduction in viscosity that allows adequate levels of coatability of mineral aggregates. The injection of a small amount of water is conducted through foaming processes or the use of a hydrophilic material such as zeolite. On the other hand, the use of organic additives (waxes or amides) shows a decrease in viscosity above the melting point of the wax.

Aside from the concerns related to recycling, carbon emission and fuel consumption, the assessment of the environmental impact of road infrastructures includes the evaluation of noise emission generated by the tyre-pavement interaction. Based on a report issued by the European Environmental Agency “Noise in Europe, 2014” (60), road traffic noise appears to be the most dominant source of the environmental noise. The data collected have shown that about 125 million people are exposed to environmental noise levels higher than 55 dB (A) LDEN (day-evening-night level). The World Health Organization (WHO) through the WHO Centre for Environment and Health has widely documented the detrimental effects of environmental noise on human health.

Consequently, the European Union issued the Directive 2002/49/EC to require the State Members to adopt preventing actions with the scope of reducing the environmental noise generated by road traffic. Therefore, the optimisation of the acoustic performances of road pavement is of concern for road authorities, academia and stakeholders (56-58). The challenges mentioned in this section (e.g., safety, recycling, WMA, noise) represent extensive research areas in the field of pavement engineering. However, the considerations above are not meant to be a comprehensive state of the art, but rather, they aim to convey the message that asphalt mixtures are not designed to be rutting and fatigue resistant only, but they need to be genuinely treated as engineered solutions capable of meeting stringent requirements.

Such challenges are made ambitious and arduous by increased traffic, shortage of resources and primary materials, volatile economies, and ageing of existing infrastructures (especially in developed countries) (50). Moreover, road authorities are requested to optimise investment by constructing safe, durable, and sustainable pavements.

2.4 The use of polymer-modified bitumens (PMB)

Based on the considerations included in §2.3, the construction of durable pavements to minimise maintenance and save costs is of crucial importance. To produce more resistant mixtures, academia and the road industry have developed several technologies capable of improving the mechanical (e.g., rutting resistance, fatigue cracking resistance) and the functional characteristics (e.g., skid resistance, noise emission) of pavements with a close focus on environmental aspects. Before introducing part of these technologies, a brief description of Hot Mix Asphalt needs to be provided.

Hot Mix Asphalt (HMA) is a composite material volumetrically constituted of mineral aggregate, bitumen, (in some cases) additives, and air voids. The weight composition of such mixtures generally includes about 95% of mineral aggregates and 5% of bitumen. Such proportions are to be considered as representative of traditional “dense” mixtures. In the case of “Gap Graded” or “Open Graded” mixtures, such proportions can show variations. The successful production of such mixtures depends on accurate materials selection and an optimised proportion of the constituents defined as mix-design. The term “successful” indicates a mixture capable of meeting the mechanical and functional requirements as per the design specification.

Although the bitumen phase represents a limited portion of the mix, it affects the response of the mixtures. Furthermore, results from mixture testing, finite element modelling and digital image processing have demonstrated that the bitumen phase experiences more considerable strain than the bulk mixture (31 - 33). Such a difference depends on localised rotations of aggregates, on the different stiffness between the bitumen and the aggregates and the lack of uniformity of the bitumen film coating the aggregates. As a consequence, the bitumen phase significantly affects the failure properties of the mixtures.

Bitumens are modified with small quantities of different types of polymers that contribute to improving their performances, and the performances of mixtures.

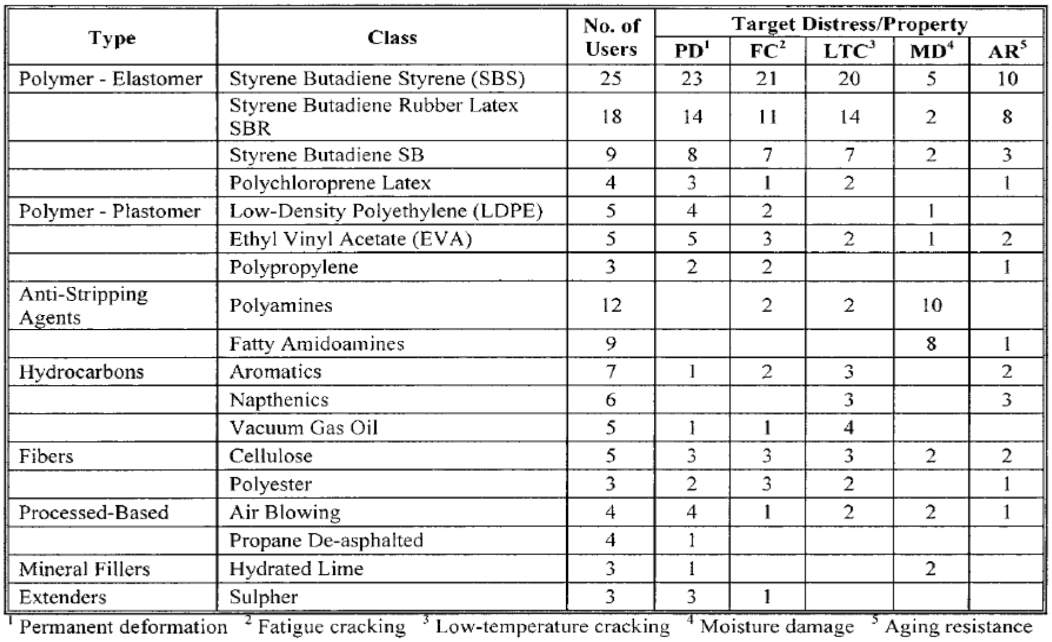
Polymer-modification is widely used to enhance mixture performances in terms of rutting resistance, fatigue cracking resistance, low-temperature-cracking resistance, moisture susceptibility, and ageing resistance.

The understanding of the advantages provided by polymer modification is not recent, and the use of synthetic polymers for binder modification on a large commercial scale dates back to the end of the World War II (1-3). Several polymeric additives are available on the worldwide market. They can be classified as per the chemical composition or as per the target bitumen property. Two types of polymer are mainly used in bitumen applications: the elastomers that resist deformation by stretching and recovering their shape, and the plastomers that resist deformation by forming a 3-D rigid network below their melting point. Among the elastomers, the Styrene-Butadiene-Styrene (SBS) block copolymer appears to be the most widely used followed by reclaimed tyre. On the other side, among the plastomers, Ethyl Vinyl

Acetate (EVA) and Polyethylene are used (4, 54). However, other types of additives are available.

Findings from the National Cooperative Highway Research Programme (NCHRP) Project 9-10 show that in the US market, 15% of the total annual tonnage of asphalt produced is polymer modified (2). Furthermore, many road authorities are planning to increase their use to 25%. The European market shows similar percentages (50).

As mentioned above, PMBs can be used to enhance one or more mixtures properties. For instance, based on the data collected during the NCHRP 9-10 Project (Figure 2-14), the U.S. road authorities declare to use different polymers to target one or more pavement distresses (2).



Type	Class	No. of Users	Target Distress/Property				
			PD[1]	FC[2]	LTC[3]	MD[4]	AR[5]
Polymer - Elastomer	Styrene Butadiene Styrene (SBS)	25	23	21	20	5	10
	Styrene Butadiene Rubber Latex SBR	18	14	11	14	2	8
	Styrene Butadiene SB	9	8	7	7	2	3
	Polychloroprene Latex	4	3	1	2		1
Polymer - Plastomer	Low-Density Polyethylene (LDPE)	5	4	2		1	
	Ethyl Vinyl Acetate (EVA)	5	5	3	2	1	2
	Polypropylene	3	2	2			1
Anti-Stripping Agents	Polyamines	12		2	2	10	
	Fatty Amidoamines	9				8	1
Hydrocarbons	Aromatics	7	1	2	3		2
	Napthenics	6			3		3
	Vacuum Gas Oil	5	1	1	4		
Fibers	Cellulose	5	3	3	3	2	2
	Polyester	3	2	3	2		1
Processed-Based	Air Blowing	4	4	1	2	2	1
	Propane De-asphalted	4	1				
Mineral Fillers	Hydrated Lime	3	1			2	
Extenders	Sulpher	3	3	1			

[1] Permanent deformation [2] Fatigue cracking [3] Low-temperature cracking [4] Moisture damage [5] Aging resistance

Figure 2-14 – Use of different additives to target pavement distresses (NCHRP 9-10 Project).

Elastomeric polymers are widely adopted compared to other types of additive. In particular, SBS copolymer seems to improve the properties of the mixture over a wide range of temperatures. Its usage is extended to improve the performance of mixtures from rutting resistance (high pavement temperature) to low-temperature cracking resistance. However, this does not seem to be surprising since SBS might be considered as the most suitable polymer used for bitumen modification purpose (4). Besides SBS, Styrene Butadiene Rubber (SBR) is used as well.

Plastomers seem to have more limited usage in the U.S. market compared to the elastomers. However, although their use is limited to a few agencies, EVA polymer is the only plastomer adopted for all the scopes considered in the survey. Besides the traditional pavement distresses, additives are used to mitigate the potential of premature ageing. In particular, SBS and SBR are given credit by road authorities to be applied as ageing-inhibitors. The wide range of applications of these additives has been enabled by intense research into their properties conducted by academia and the road industry in the past few decades (1-10).

Nevertheless, although the advantages of PMBs are well accepted, their use is still challenged by open questions, drawbacks and concerns. These limitations are related mainly to cost, storage stability, ageing resistance, and the development of dedicated specifications (3). Concerning the cost, depending on the type of additive, the unitary cost of modified bitumen could increase by 50 to 100% compared to neat asphalt cement with a consequent increase of 10 to 20% in the cost of in-place HMA (2).

The storage stability represents the capability of the two phases constituting the PMB (binder and polymer) of remaining blended without any phase separation (or segregation) during a prolonged time in storage at high temperatures. It is a function of thermodynamics and chemical interactions existing between the polymer and the bitumen phases. Specifically, the storage stability, like other properties, depends on the affinity between the polymer and the bitumen with the polymer having an adequate degree of swelling and solubility in the bitumen phase (6). A more detailed description of the mechanism of modification is given in §2.7.

Besides the limitations related to cost and storage stability, there are concerns about the applicability of the Linear Viscoelastic (LVE) characterisation for the development of dedicated specifications. The Superpave binder specifications (AASHTO MP1) were developed on unmodified bitumens, considering that the pavements would have been designed to maintain the strain levels within the linear regime. One of the main concerns is that the low strain levels considered in the LVE characterisation does not allow consideration of the stress-strain dependency of the response of PMB, and it may provide a weak correlation with mixture performance (2, 8-28).

Besides improving the mechanical response of mixtures, polymers are used as anti-oxidative additives to mitigate the detrimental effects of atmospheric oxygen on the mechanical response of bitumen. However, the effect of polymers on the oxidative mechanisms occurring in PMB remains relatively unclear, and it is polymer-dependent. This work refers to this last consideration and focuses on the effect of polymer modification on the durability of PMB. The term durability is intended as the bitumen resistance to changing its flow properties under the detrimental effects of atmospheric oxygen during the in-service life (8). The evaluation of bitumens' durability is critical to define long-term pavement performance (LTPP) (61).

2.5 Durability of bitumens

In the case of unmodified bitumens, durability can be defined as the capacity to resist changes in flow properties during in-service life (8). On the other hand, once the bitumen is modified with polymers, besides the resistance to changes in the field, the durability includes the storage stability and the polymer-bitumen compatibility (38).

Based on this definition, in the evaluation of long-term pavement performance (LTPP), the bitumen needs to be studied as an ageing material whose chemical and physical properties change over time under environmental effects (90). As recommended in the AASHTO 1993 Pavement Design Guide, the evaluation of LTPP shall consider the combined effect of damage from repeated loading and ageing that affects the flow properties of asphalt (61). The reason behind this is that while ageing the bitumen can become stiffer and less strain tolerant with the consequent risk of premature cracking depending on the climate (15). In cold climates, the embrittlement of the bitumen can contribute to accelerating thermal cracking. While, at intermediate temperatures, the reduction in the strain tolerance of the bitumen can increase the risk of fatigue cracking. Besides cracking, the changing in the chemical composition seems to affect the adhesive bond between bitumen and aggregate as well, increasing the moisture sensitivity of asphalt mixes, increasing the potential of aggregate ravelling in the surface layer (102, 103).

The effect of bitumen ageing on pavement cracking was already observed in extensive work from Sisko and Brunstrum in 1968 (88). Quoting their conclusion:" *Large increases, induced by ageing, in the hardness of the asphalt bitumen (as measured by the complex modulus) are associated with road cracking*".

Afterwards, other authors have focused on the study of the effect of bitumen ageing on the fatigue resistance of bitumens and asphalt mixtures (2, 37, 191-195). Based on the results, it appears that the bitumen has a very significant effect on the fatigue life of mixtures. However, it appears that oxidative ageing has a lower effect on the fatigue life of asphalt mixtures compared to the mix volumetrics, and moreover, it is noticeable that bitumen ageing does not necessarily worsen the fatigue life of mixtures.

In any case, a clear conclusion is unlikely to be drawn due to the difficulty of reproducing the field conditions in laboratory tests. The environment and the traffic provide a simultaneous action on pavements, and such combined effects cannot be currently reproduced on a smaller scale. Furthermore, although laboratory tests are designed to reproduce stress and strain conditions similar to as those the mix is exposed to in the field, the identification and the reproduction of the actual field strain levels at the different scales (i.e., bitumen, mastics, mixtures) are of concern.

Despite these challenges, the study of fatigue cracking resistance of mixtures represents a wide field of interest in research. On the other hand, the focus on the fatigue resistance of the bitumen phase alone is still limited compared to the effort provided at the mixtures scale. This represents a significant shortcoming in the evaluation of the fatigue phenomenon in pavements since the bitumen phase has proven to have an important role in such a mechanism (2).

According to Petersen, a durable bitumen has “*the physical properties necessary to produce the desired initial product performance properties, and that is resistant to change in physical properties during long-term in use environmental ageing*” (8). The resistance of the bitumen to the changes in flow properties depends on its oxidative susceptibility. The more the oxygen interacts with the bitumen molecules, the more the flow properties change over time. In particular, the oxidative susceptibility is related to the level of dispersion of the asphaltene in the other bitumen fractions. The more the asphaltenes are dispersed, the less the bitumen is susceptible to oxidation. These properties depend on the composition of the bitumen, which is a function of the crude oil and the distillation method.

The next sections include a description of the bitumen composition from the elemental analysis to the bitumen fractions.

2.5.1 Chemo-physical properties of crude oil

The chemo-physical properties of bitumen, including the oxidative susceptibility, are a function of the crude source and the refining method.

A parameter widely used to classify different sources is the crude oil density which is a measure of how heavy or how light is crude as a whole (48). Light crudes include a higher proportion of light molecules that are more suitable for the production of gasoline, fuels, and diesel. On the other hand, heavy crudes have a more abundant bitumen residue.

To identify the density of crudes, the American Petroleum Institute (API) adopts the API gravity, which is a measure of the crude density compared with the density of the water at a temperature of about 15.5°C. Water has an API of 10°. A typical light crude has an API of 35°; while a heavy crude has an API of about 25° or lower (i.e., Boscon Venezuelan's API is equal to 10°).

The table (Table 2-1) below shows a scheme widely used in the classification of crude oil based on API gravity and Sulphur content.

Table 2-1 – Crude Oil Classification (48).

Crude Oil Class	Gravity (°API)	Sulphur (wt.%)
Light sweet	35 - 60	0 - 0.5
Light Sour	35 - 60	> 0.5
Medium Medium Sour	26 - 35	0 - 1.1
Medium Sour	26 – 35	> 1.1
Heavy Sweet	10 - 26	0 - 1.1
Heavy Sour	10 – 26	> 1.1

Based on this classification, Table 2-2 shows the characteristics of widely known sources of crude oils based on API° and sulphur content.

Table 2-2 – Classification of Important Crude Oils Sources (48)

Crude Oil	Country of Origin	Crude Oil Class	API°	Sulphur (wt%)
Brent	U.K	Light Sweet	40.0	0.5
West Texas Intermediate	U.S.A		39.8	0.3
Arabian Extra Lt. Report	Saudi Arabia	Light Sour	38.1	1.1
Daqing	China	Medium Medium Sour	33.0	0.1
Forcados Export	Nigeria		29.5	0.2
Arabian Light export	Saudi Arabia	Medium Sour	34.0	1.9
Kuwait Export Blend	Kuwait		30.9	2.5
Marlim Export	Brazil	Heavy Sweet	20.1	0.7
Cano Limon	Colombia		25.2	0.9
Oriente Export	Ecuador	Heavy Sour	25.0	1.4
Maya Heay Export	Mexico		21.3	3.4

An example of different bitumens obtained from different API density crude is given in Figure 2-15.

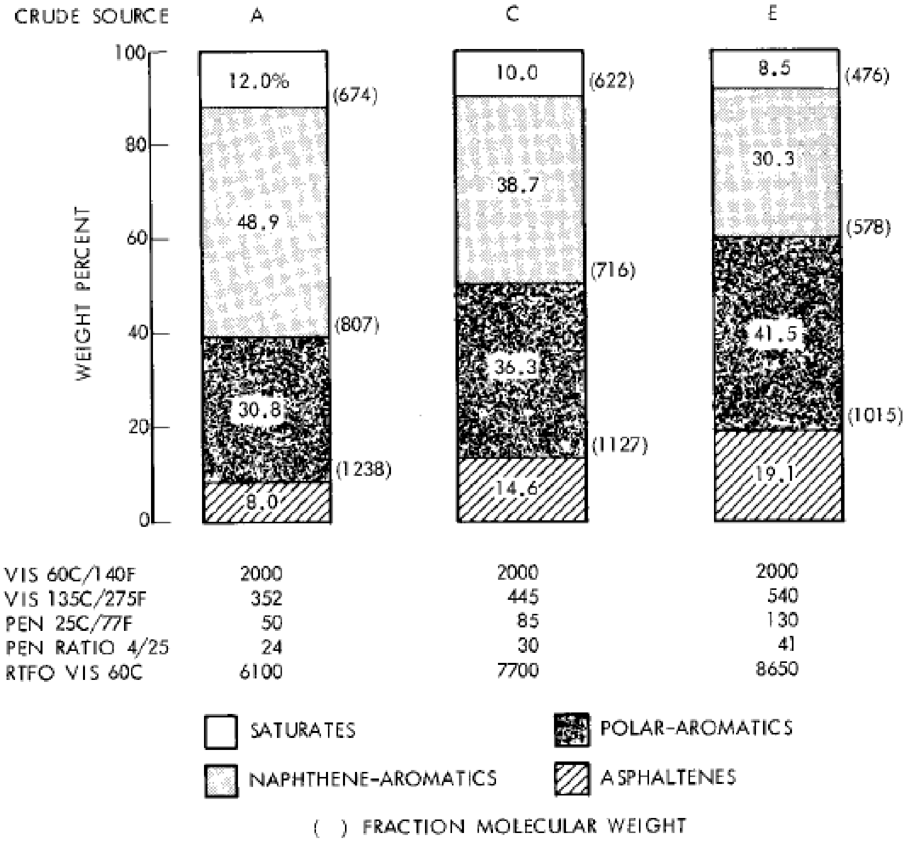


Figure 2-15 – Weight per cent of fractions of bitumen distilled from

different API gravity crude (120).

In this example, Type A includes crudes with API ranging from 30°-34°.

2.5.2 Crude Refining Methods

Besides the crude source, the refining method influences the properties of bitumen. The most common method for manufacturing bitumen from oil is a straight reduction to grade from crude oil or crude blend using atmospheric and vacuum distillation. The atmospheric distillation is used to separate the light fractions, characterised by lower molecular weight (and therefore by a lower boiling point), from the crude components characterised by higher molecular weight (and therefore with a higher boiling point). A scheme of the atmospheric distillation and the vacuum distillation is shown in the figure below (Figure 2-1).

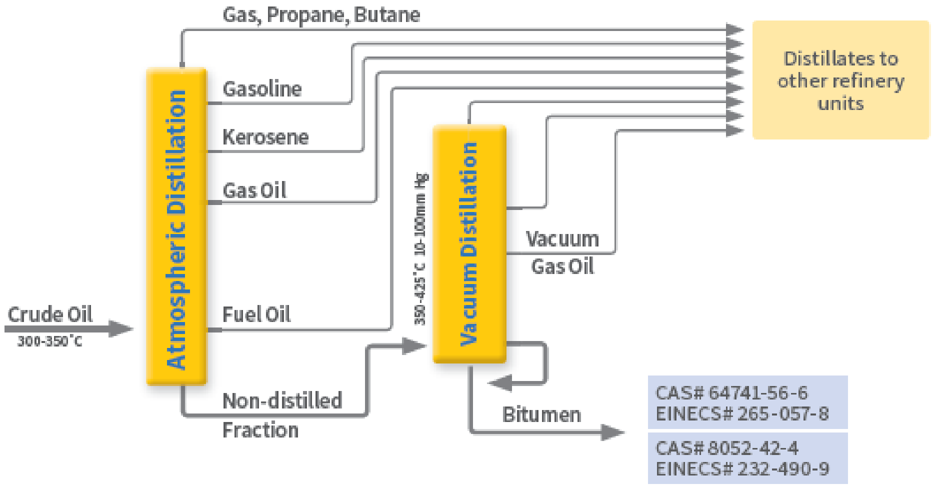


Figure 2-1 – Schematic Diagram of Distillation (47)

To remove residual lighter fractions avoiding any thermal changes in the molecules, the residue of the atmospheric distillation is pumped into a vacuum distillation unit where, at a lower pressure, it is possible to separate any light fraction at lower boiling temperatures. The non-distillable materials produced from the atmospheric residuum under the vacuum distillation process, are defined as asphalt and residues (cutback). Residues can be used for the production of prime coats used as an interlayer in the construction of flexible pavement.

The asphalt can be directly available for road applications, or its properties can be further adjusted based on different refining methods. Several refining methods are available to adjust the properties of asphalt based on the needs.

As a consequence, the final properties of asphalt depend on the type of treatment method conducted.

A brief description of each refining method is given as follows:

- *Air-blown or Air Rectification* – this method is used to obtain minor adjustments of physical properties such as a reduction in penetration or an increase in stiffness. Air-rectified bitumen is used in paving application as unmodified bitumen or for the production of polymer modified bitumen. Other applications can include roofing or industrial use as well.
- *Residual Oil Supercritical Extraction (ROSE)* – in this process the properties of asphalt are modified by the use of solvents such as propane, butane, isobutene, pentane, to separate the asphaltene fraction from the oily fractions (used for producing oils or other lubricants). The hard bitumen remaining (with reduced oily component and high asphaltene fraction) can be blended to produce specification grade bitumen.
- *Vacuum Distillation of thermal Cracked Residuum (or Visbreaking)* – in a visbreaking unit the residue is heated between 440°C-500°C to break the links between the long paraffinic side chains and the aromatic rings that are responsible for viscosity and pouring point of the residue stream. By breaking such linkages, a reduction in viscosity and pouring point are expected. When such a method is used for the production of bitumen, the residue from the visbreaking is subjected to vacuum distillation to remove further light fractions used for other applications. The residue from the vacuum can be used as a blending component for the production of bitumen.

The scheme of the Visbreaking method is shown in Figure 2-2.

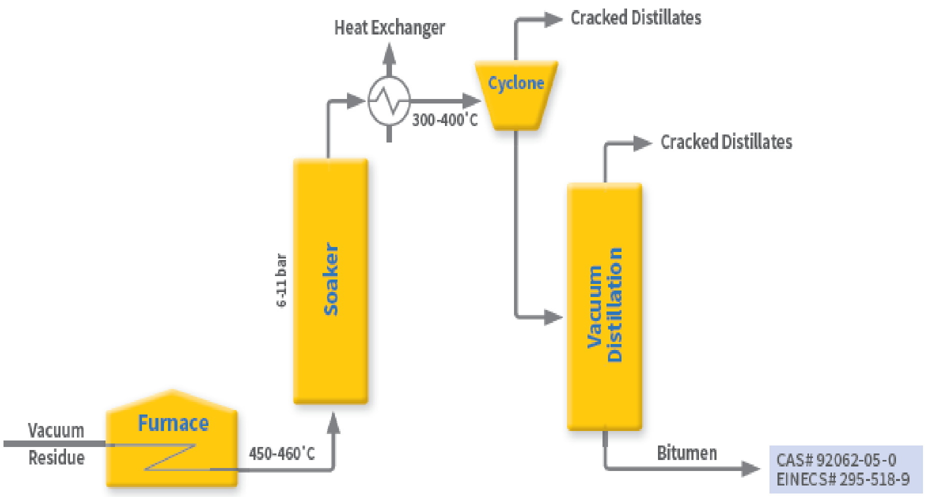


Figure 2-2 – Visbreaking scheme (47)

- *Oxidation* - this method involves the passing of air through bitumen at elevated temperature to change the physical properties. Oxidation produces a shift of the molecular weight distribution towards higher molecular weight components with higher polarity (asphaltene). Oxidised bitumen have lower penetration, higher softening point, and are stiffer.

The scheme of the oxidation method is shown in Figure 2-3.

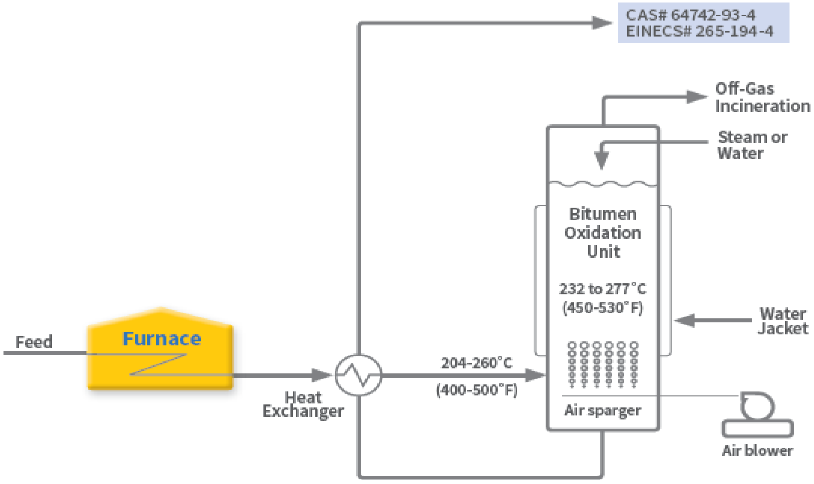


Figure 2-3 – Scheme of oxidation method (47)

2.5.3 Bitumen composition

A true definition of the chemical composition of bitumen is very arduous due to the complex and source-dependent variety of hydrocarbon mixtures included in this material. However, several researchers have attempted to provide a chemical characterisation of bituminous binders that would reflect their field performance.

So far such a characterisation remains unavailable. Nevertheless, the understanding of bitumen composition is of fundamental importance in the study of the mechanism of ageing and polymer modification. For this reason, this section describes the different bitumen constituents starting from the elemental analysis through the bitumen fractions.

2.5.3.1 Elemental composition

Due to origin from crude oil, bitumen is a complex mixture of organic molecules varying from non-polar saturated hydrocarbons (i.e., molecular compounds constituted of Carbon and Hydrogen) known as Saturates, to highly polar condensed aromatic ring systems known as Asphaltenes (8). As a hydrocarbon, the backbone of the bitumen is predominantly composed of Carbon (C) and Hydrogen (H). However, some heteroatoms are present. In chemistry, heteroatoms are those atoms that are not Carbon or Hydrogen that are included in the molecular backbone. Table 2-3 gives an elemental analysis of bitumens.

Table 2-3 – Elemental composition of bitumen (45).

		Heteroatoms			
Carbon (C) (%)	**Hydrogen (H) (%)**	**Sulphur (S) (%)**	**Nitrogen (N) (%)**	**Oxygen (O) (%)**	**Metals (ppm)**
82 – 88	8 – 11	0 - 6	0 – 1.5	0 – 1.0	Trace

Although the amount of heteroatoms is limited compared with the concentration of Carbon and Hydrogen, their concentration affects the polarity and the reactivity of the bitumen molecules and provides a significant contribution to the physical properties of bitumens. The heteroatoms enter the bitumen molecules as functional groups or polar groups that are attached to the carbon atoms. These molecules determine some of the engineering properties of asphalt.

The term functionality indicates the presence of functional groups and determines how the asphalt molecules interact with each other or with the molecules or the surfaces of other materials such as mineral aggregates. For this reason, the presence of heteroatoms affects the bonding between aggregates and bitumen.

The term polarity refers to an unbalanced configuration of the electrochemical forces within the molecule that produces a dipole. Such a dipole has electropositive and electronegative charges like a magnet, and this affects the physical response of the bitumen (87).

Therefore, although the heteroatoms have a lower concentration than C and H, they provide a significant contribution to the engineering properties of bitumen. The amount of heteroatoms varies significantly between different crude sources (8). The reason behind this is that crude oil is the result of an extended period of maturation of numerous organic compounds that occurs under variable conditions. Therefore, the large variability in bitumen composition as a function of the crude source is not surprising. As shown in Table 2-3, asphalt includes a trace of metal as well. The most common metals are vanadium, nickel, iron, magnesium and calcium and may be present and occur as inorganic salts and undergo oxidation as porphyrin structures (105).

However, the elemental analysis might not reveal an exhaustive description of the bitumen composition to such an extent as to determine its paving-related properties. Besides atoms, the types of molecular structures and the molecular bonds present are essential to understanding the relationship between chemical composition and physical properties, including the oxidative susceptibility.

Before describing the molecular composition of asphalt, some details on the properties of the atoms are provided. The valence is the number of electrons that an atom can share to form chemical bonding. This property is critical since it provides information on the number of bonding that can be formed with oxygen. The valence of the atom constituting asphalt is given in Table 2-4.

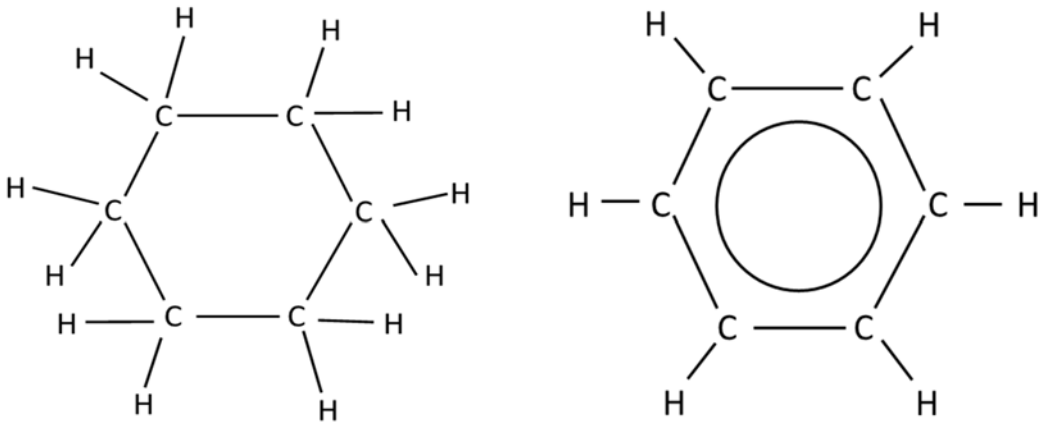
Table 2-4 – Valence of the atoms constituting bitumen (105).

		Heteroatoms		
Carbon (C)	**Hydrogen (H)**	**Sulphur (S)**	**Nitrogen (N)**	**Oxygen (O)**
4	1	2, 4 or 6	3, 5	2

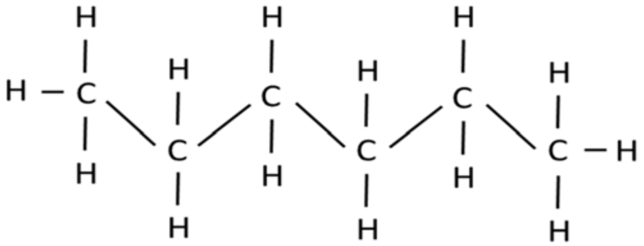
The Sulphur and the Nitrogen have different levels of valence depending on the bonding they create with the Oxygen. The valence of metal is not reported since it is dependent on the oxidation state.

2.5.3.2 Molecular composition

The bitumen molecular composition consists of a mixture of a variety of high-boiling-point hydrocarbons. The molecular structure depends on the bonding between Carbon and Hydrogen. In the case of bitumen, there are three major hydrocarbon compounds: aliphatic compounds, aromatic compounds, and naphthenic compounds (106).



(a) - Naphthenic (b) - Aromatic



(c) – Aliphatic

Figure 2-16 – Molecular compounds in bitumen.

In Naphthenic compounds, carbon atoms are linked by simple or complex saturated rings (Figure 2-16 - a). However, the majority of bitumen molecules comprise aliphatic and aromatic compounds. Aliphatic compounds (Figure 2-16 - c) do not have double bonds, and the carbon atoms are linked in straight or branched structures. The bond angle is approximately 109° (i.e., tetrahedral). This type of molecule is very flexible.

On the other hand, aromatic compounds are characterised by stable six-carbon rings with alternate double bonds (Figure 2-16 - b). These molecules are more rigid and are planar in shape. Besides the molecular compounds shown in Figure 2-16, the bitumen composition appears to include small quantities of nonhydrocarbon base materials such as organic acids, bases, and metallic or non-metallic heterocyclic components (107).

However, a precise chemical characterisation of the bitumen becomes difficult and somehow undetermined due to the presence of a large variety of molecular structures and molecular chemical reactivity (106). The large variability in the molecular composition of bitumens is well represented in a recent study of Wang et al. that is based on molecular simulations (180). Results show that in crude-refined bitumens 105-106 different types of molecules exist.

For this reason, the analysis of bitumen composition has moved toward methodologies that identify different groups of molecules as per their size, polarity, and solubility in solvents with different polarity. Masson and Polomark consider bitumen as a natural polymer with low molecular weight and degree of polymerisation approximately 10 (119). However, caution must be taken once comparing bitumen properties to that of polymers, especially once it comes to viscoelastic properties. The Strategic Highway Research Program tried to define asphalt based on Molecular Weight Distribution (MWD) and polarity (108). This definition is given as follows: "A*sphalt is a relatively homogeneous randomly distributed collection of molecules differing in polarity and molecular size*".

Bitumen molecules form a vast spectrum of molecular weight. Such spectrum ranges from low molecular weight oils (MW: 240 – 800 g/mol) to polycyclic and polyaromatics structures with high molecular weight divided into cyclano-aromatics, polar aromatics (MW: 800-2400 g/mol) and highly condensed polar asphaltenes also containing heteroatoms and heavy metals.

However, the values in the literature depend on the test method (6, 7). Besides the identification of a wide interval of molecular weights, a broad spectrum of molecular polarities can be identified as well. In this regard, the bitumen composition varies from low polar light oils (consisting of alkano-cyclanes) through intermediate polar compounds (e.g., cyclanoaromatic and polyaromatic compounds) to highly polar aromatic compounds constituting the asphaltene phase (6).

In the case of low-polar molecules, the majority of the molecular bonds consist of non-polar interactions based on Lifshitz-Van deer Walls forces where no electron exchange occurs. Such bonds are defined as secondary bonds, and their strength is sensitive to the inverse of the molecular distance to the power of 6. For this reason, the oily component of the bitumen is susceptible to the temperature.

On the other hand, in high-polar compounds, the majority of the molecular interactions depend on polar bonds based on the Lewis acid-base interactions. In this case, the acid represents the electron-donor, and the base the electron-acceptor. This type of molecular bond is defined as a primary bond, and these types of interactions are one or two orders of magnitude stronger than the secondary. For this reason, asphaltenes are less sensitive to temperature (109, 110).

The difference in bond strength between primary and secondary bonds is of fundamental importance for the understanding of the mechanism of bitumen ageing. The result of the oxidative process is the formation of molecular compounds polar in nature characterised by strong interactive molecular bonds. The higher strength of such interactions, characterised by the presence of primary bonds, reduces the molecular mobility of the bitumen with a consequent reduction in strain tolerance.

Nevertheless, the approach based on the chemical characterisation of bitumen (including the elemental and the molecular analyses), for understanding the mechanical response still does not provide a solution to correlating bitumen composition and paving performance. The reason behind this is represented by the large variability of the molecular compounds present in the various sources of bitumen all over the world (7, 8, 17).

In light of this complexity, the molecular compounds in the bitumen are separated into groups of molecules, characterised by similar properties, defined as bitumen fractions that do not represent distinct chemical species. Such type of fractionation, although less rigorous than the elemental and molecular analysis, allows identifying groups of molecules whose characteristics and proportion represent accurate indicators for understanding the flow properties bitumen. Furthermore, when studying ageing, the compositional changes occurring in bitumen with oxidation are often expressed in terms of changes in the proportion of these fractions.

2.5.3.3 Separation techniques

The definition of the current procedure for bitumen separation has gone through two centuries of experiments where different technologies and experimental set-ups of the same technology have been developed, discussed and compared.

Bitumen molecules can be grouped into two fractions: the oily (or maltene) fraction, and the asphaltenes fraction. The first is composed by light low polar molecules; while the second is composed by heavy polar molecules. Such fractions are not mutually soluble and must coexist in a homogeneous mixture whose properties deviate from those of a true solution. The interaction among the different fractions depends on their compatibility (most important is the level of dispersion of the asphaltene). The higher is the compatibility among different components; the more favourable are the properties of asphalt, including durability (12).

The asphaltene fraction was obtained in 1836 when Baussingault separated through distillation asphalt into two components at 230°C: 85% by weight of petrolene (or oily) and a 15% of solid fraction he defined as asphaltenes (117). A few decades later, the maltene phase was identified by Richardson (118). Afterwards, different separation methods were developed.

According to Petersen (8), the separation methods can be classified into three major groups based on the procedure followed: partitioning with partial solvent, selective adsorption-desorption, and chemical precipitations methods (Rostler analysis). Besides such methods, also the Gel Permeation Chromatography (GPC) need to be mentioned despite they provide a separation based on molecular size only and do not contribute to identifying a defined chemical composition.

The selective adsorption-desorption technique has encountered the most extensive usage, and although different experimental set-ups were available, the configuration proposed by Corbett became the one used as a reference (111). In particular, such a method is defined as adsorption-desorption selective chromatography, and it is currently known as Saturates Aromatics Resins Asphaltenes (SARA) analysis. This method is based on the separation of the asphalt fractions by using solvents with different polarity. The asphaltene (A) phase is insoluble to n-epthane paraffinic non-polar solvent, and they are initially separated from the maltene phase that remains dissolved in the paraffinic solvent. Then, due to the development of chromatography, the maltene phase can be desolved in Saturates (S), Aromatics (A) and Resins (R) by using solvents with different polarities. The polarity, the molecular weight and the aromaticity of the bitumen fractions increases from the saturate to the asphaltenes. A typical scheme of the selective adsorption-desorption chromatography is given in Figure 2-17.

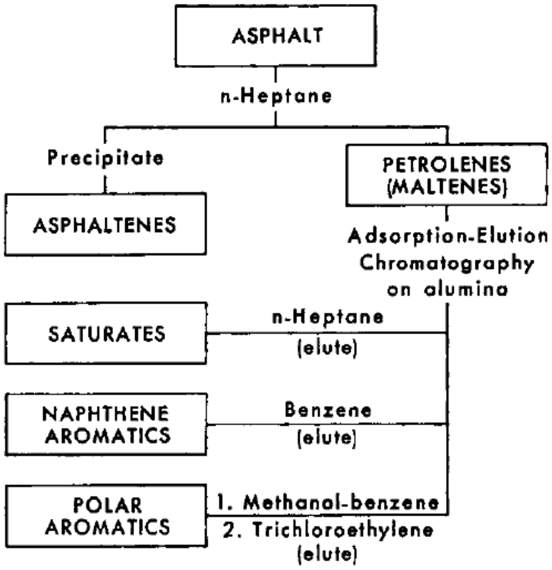


Figure 2-17 – Typical scheme of adsorption-desorption chromatography (8).

Initially, Corbett did not use the definition of aromatics and resins but rather naphthene aromatics and polar aromatics, respectively. However, although nowadays the experimental scheme has remained unvaried concerning the Corbett method, different solvents and experimental set-up have been adopted for safety and convenience purposes. The current reference method is represented by the ASTM D 4124 – "*Standard test method for Separation of Asphalt into Four Fractions*". The scheme of the separation method is given in Figure 2-18.

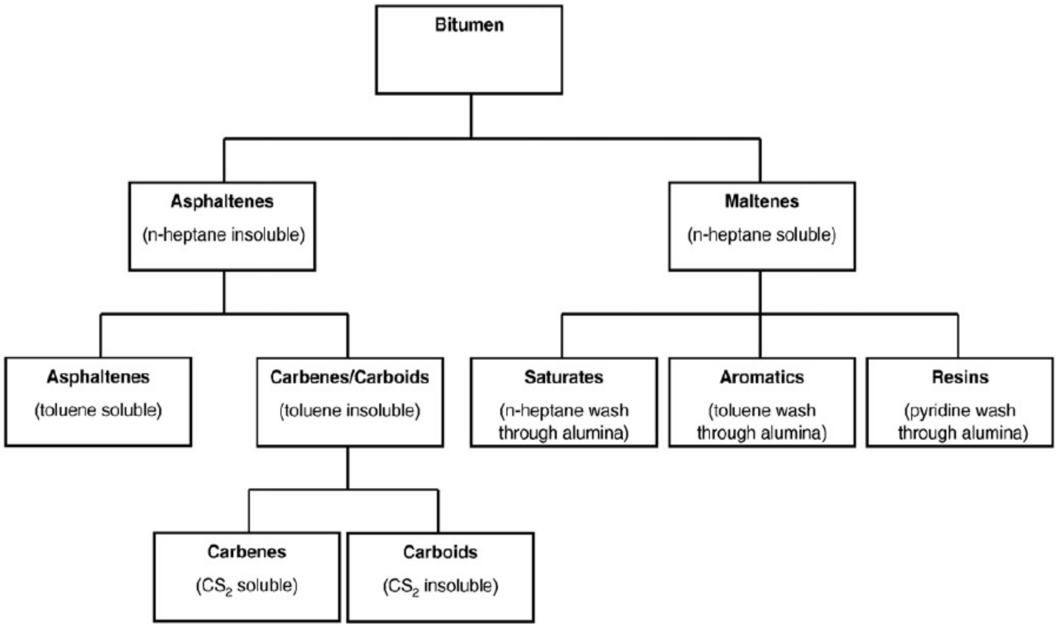


Figure 2-18 – Separation of bitumen into fractions (7).

The separation of bitumen into fractions identifies two main groups of molecules depending on their solubility in n-epthane solvent: asphaltene (n-epthane insoluble) and maltene (n-epthane soluble).

For the sake of definition, asphaltene can be defined as the asphalt fraction insoluble to n-epthane but soluble in toluene. After the separation of the asphaltene, the maltene phase is passed through a chromatographic column CG-20 grade alumina. Here, saturates are firstly separated using n-epthane as eluant. Then, toluene and methanol are used to separate the aromatics. Finally, trichloroethylene is used to separate the resins (7). Alternative set-up configurations such as the thin layer liquid on silica gel and flame ionisation detector (IATROSCAN) are also available and used mainly for bitumen fractionation (116).

2.5.3.4 SARA fractions

Aside from the development of the different methods of bitumen separation, it is crucial to understand that the bitumen fractions play a fundamental role in the mechanisms of ageing and the polymer modification process.

On the one hand, the chemical oxidative processes occurring in the field exposure affect the bitumen fractions with a transition towards the formation of asphaltene. On the other, polymers may have more affinity with some bitumen components while showing a lower affinity with others. For this reason, a detailed description of the different fractions and a discussion on their effect on the bitumen flow properties needs to be provided.

The study of the bitumen fractions has been undertaken by several authors focusing on the chemical composition of each fraction and its contribution to the bitumen physical properties (87, 112, 115, 120, 186, 232). Before describing the chemical and physical properties of each fraction, it is worth mentioning that different bitumens are composed of different weight proportions of each fraction. This difference is a function of the crude source (§ 2.5.1) and the refining method. Bitumens having different fractional proportions show different physical properties such as temperature susceptibility, viscosity and other rheological parameters.

Due to the large variability of the crude sources available all over the world, the definition of precise ranges of fraction weight content in the different bitumens becomes exceptionally complex. Besides this, bitumen represents the results of a refining method, therefore also differences in refining might produce bitumens (from the same crude) with a different composition. However, some typical ranges can be provided (Figure 2-19).

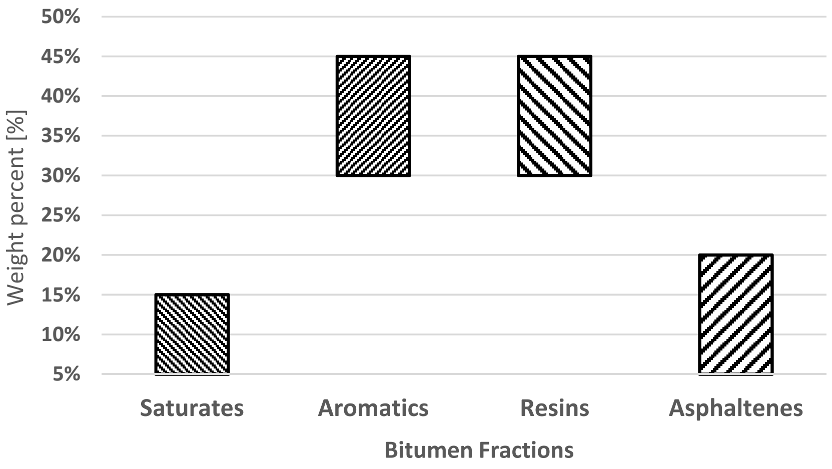


Figure 2-19 – Typical range of bitumen fraction weight per cent (111).

According to the data, the typical weight distribution of a paving grade bitumen is constituted of:

- Saturates from 5% to 15%;
- Aromatics and Resins from 30% to 45%;
- Asphaltenes from 5% to 20%.

However, these data are meant to be indicative of typical paving grade bitumen.

Indicative values of the chemical properties (i.e., H/C ratio, elemental analysis, average molar mass) and solvent used in the ASTM analysis of each SARA fraction are given in Table 2-5.

Table 2-5 – Typical values of chemical proportions of SARA fractions (111-116, 163, 186).

	H/C [1]	C [%]	H [%]	O [%]	N [%]	S [%]	M_n [g/mol]	Solvent
Bitumen	1.5	80-88	8-12	0-2	0-2	0-9	600-1,500	-
Saturates	1.9	78-74	12-14	<0.1	<0.1	<0.1	470-880	n-Epthane
Aromatics	1.5	80-86	9-13	0.2	0.4	0-4	570-980	Toluene/toluene methanol 50/50
Resins	1.4	67-88	9-12	0.3-2	0.2-1	0.4-5	780-1,400	Trichloroethylene
Asphaltenes	1.1	78-88	7-9	0.3-5	0.6-4	0.3-11	800-3,500	n-Epthane insoluble

Several detailed definitions and descriptions of bitumen fractions are available in the literature. In this document, a detailed description of each fraction is provided merging the information collected from selected references (45, 6, 7, 8, 188) and including data from Figure 2-19 and in Table 2-5.

Furthermore, Figure 2-20 provides images of the bitumen fractions. It appears that the saturates are a colourless liquid at room temperature. The aromatic fraction is liquid at room temperature as well, but it shows a yellow to red colour. Then, the black colour of the bitumen seems to be given by the resins that are solid black at room temperature. As shown in Figure 2-21, the asphaltene fraction is constituted of small black particles that, as the resin fraction, contribute to the black colour of asphalt.

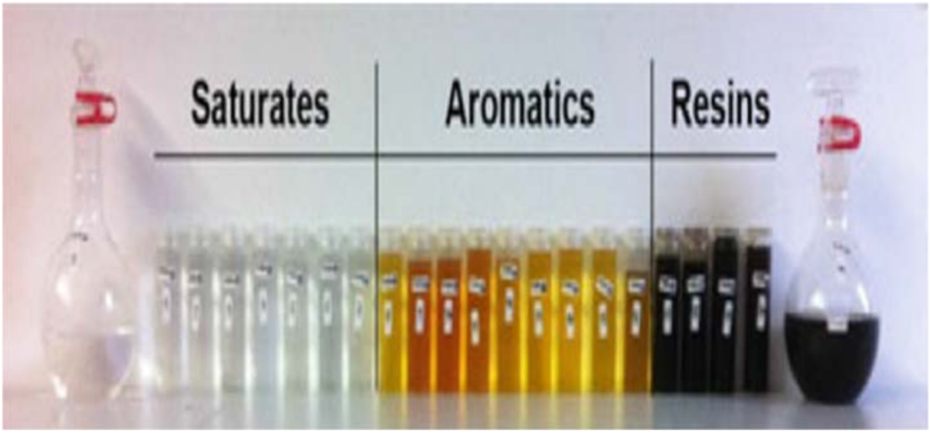


Figure 2-20 – Saturates, Aromatics and Resins (187).

Figure 2-21 – Asphaltene (189)

The description of the bitumen fractions is given from the less complex to the more complex.

Saturates

This fraction is constituted of the simplest molecules included in asphalt. They comprise some straight chain and branched alkanes, as well as cycloalkane (naphthenic) non-polar hydrocarbons without double bonds. Cycloalkanes contain one or more rings, which may have several alkyl side chains. At room temperature they are at the liquid state due to a Glass Transition Temperature (Tg) around of -70°C that is 40°C below the Tg of the parent bitumen.

Their H/C ratio is around two, which indicates that the molecules contain a majority of Hydrogen atoms. They represent the lightest fraction among bitumen components with an average molecular weight of 600 g/mol. Saturates are non-polar and contain just a few (or absent) heteroatoms. Saturates crystallise upon cooling and the aliphatic structure of their molecules provide asphalt with flexibility.

Aromatics (or naphthene aromatics)

Aromatics represent the major constituents of the bitumen together with the resins. They are more viscous than the saturates due to a higher Tg, which is around -20°C that is close to the parent bitumen. Aromatics are typical in petroleum products, and their carbon backbone contains alkyl chains and cycloalkane rings, along with lightly (or often absent) aromatic rings. Sometimes, they are classified as mono-, di-, and tri-aromatics depending on the number of aromatic rings present in the molecule. Although higher than the saturates fraction, the content of heteroatoms is still limited. Their average molecular weight is around 800 g/mol. When their polarity and molecular weight increase, they become resins or asphaltenes. Aromatics tend to increase bitumen viscosity and provide it with more elasticity.

Resins (or polar aromatics)

Resins represent a transition between the asphaltenes and the traditional polar aromatics. However, a clear distinction between resins and asphaltenes has not been defined yet. Structurally, resins can be defined as the part of the asphaltene that is soluble in n-epthane. The average molecular structure of the resins is given in Figure 2-22.

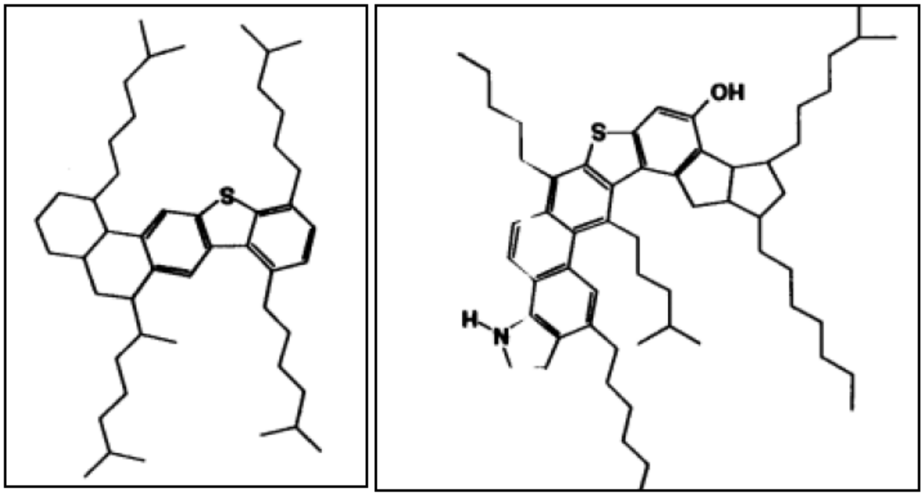


Figure 2-22 – Average molecular structure of resins (196)

Resins are polar and comprise polar aromatic molecules containing heteroatoms such as Nitrogen, Oxygen and Sulphur. Their Hydrogen to Carbon ration is higher than asphaltene, and it appears to vary between 1.38 and 1.69. Resins form a black solid at room temperature, and it is unclear whether they show a glass transition as observed in saturates and naphthene aromatics. Their molecular structure resembles one of the asphaltenes; however, it appears that they contain less aromatic rings (2 to 4 units) and have a lower molecular weight (<1,100 g/mol). The resins have a peptization function of the asphaltene, therefore although they belong to the oily part, their degree of aromaticity cause them to be more adsorbed by the asphaltenes rather than by the other oily components. This function depends on the compatibility between the fractions, and it favourites the dispersion of the asphaltenes in the oily medium rather than their absorption. The physical properties of the bitumen, including durability, are a function of the adequate level of dispersion of the asphaltenes in the maltenes fraction.

Asphaltenes

Although they represent a limited portion (from 5% to 20%) of the whole bitumen composition, the asphaltene fraction has an essential influence on the physical and chemical properties of crude oils and, therefore, of bitumens. Asphaltenes are believed to control the bitumen viscosity and to be the part of bitumen that interacts with mineral aggregates and fillers. In particular, their polar nature contributes to building-up the adhesive bond between aggregates and bitumen. On the other hand, the study of their chemical interaction with mineral filler has highlighted that this fraction is adsorbed on the filler surface with a consequent changing in the mechanical response and the thermo-volumetric properties of the bituminous mastic (189). Due to their importance, they have attracted a broad focus. The description included in this document aims to be as comprehensive as possible, although there are uncertainties that still affect the understanding of this fraction.

Asphaltenes are black-brown solid highly-polar complex amorphous materials, and they do not show any relevant transition within the range of the traditional investigation temperatures (< 200°C). They are the most polar bitumen component with the highest molecular weight (800 – 3500 g/mol) measured by Vapor Pressure Osmometry. However, the molecular weight has shown to vary of six orders of magnitude depending on the technique used. A precise chemical characterisation of asphaltenes is still under an intense debate with additional chemical species that are progressively identified with the development and the application of modern analysis methods of crude oils (i.e., mass spectrometry, Nuclear Magnetic Resonance) (230).

The lack of consensus on a well-accepted chemical definition has brought researchers to define asphaltenes (and the other bitumens function groups), as a function of their solubility in solvents. Their definition is given as solubility class that is not intended as molecular solubility but as “not generating precipitate”. In this sense, asphaltenes result insoluble in n-epthane but soluble in toluene.

An example of asphaltenes average molecular structure is given in Figure 2-23.

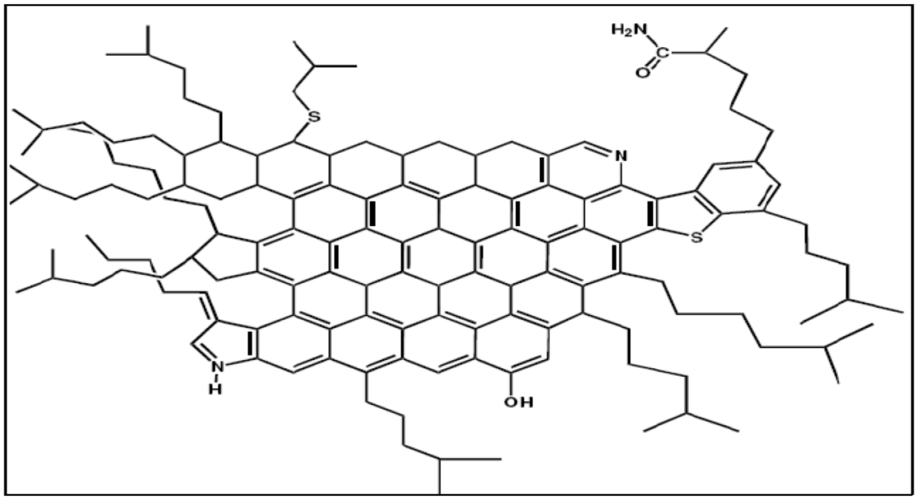


Figure 2-23 – Asphaltenes average molecular structure (196).

The molecules of asphaltenes differ from the molecules characteristic of the other fractions because of the higher presence of condensed aromatic rings, polar groups, metals (in the complex form of porphyrins) and heteroatoms (i.e., Sulphur, Vanadium and Nickel). Lesueur reported that the different molecular structure is primarily given by the presence of fused aromatic rings (7). A more detailed description of the chemical constitution and properties of asphaltenes would be out the scope of this document. However, a very rigorous discussion on their properties can be found in an independent report of Mullins (230).

The chemical approach in studying bitumen has fascinated researchers for decades. The ambition of issuing technical specifications of bitumen based on chemical properties has been widely pursued, and it still represents an on-going work. In particular, asphaltenes and their proportion are believed to affect some of the bitumen properties such as viscosity, and softening point, and in more recent works also the viscoelastic parameters such as the shear complex modulus (G*) and the phase angle (δ) (12, 197-198).

However, as concluded by Petersen (12), the asphaltenes content per se does not provide a sufficient correlation with flow properties. The reason behind this is the presence and the position of polar groups that affect the relationship between the proportion of the bitumen fractions and the flow properties such as shear rate dependency and temperature susceptibility. As a consequence, the development of chemical-based bitumen specifications reliable in predicting mechanical performances appears to be not possible. Asphalt is chemically very complex. Although such a concept appears to be clear, here follow some of the conclusions from the authors referenced above:

Goodrich J.L. et al., (17) – "*In the authors' technical opinion, it is unlikely that the field performance of all, or even most, asphalts can be characterized in terms of operationally defined fractions that exist only as artifacts of a test procedure. Physical and rheological tests have been shown to correlate well with road performance on numerous test roads. These performance-related tests remain the most reliable guide to asphalt quality*".

Hatting M.M., (197) – "*Asphaltene content alone does not provide sufficient data for the evaluation of the quality of an asphalt; it must be used in conjunction with the molecular mass distribution, i.e., the size and amount of the large molecular size material present, to give an indication of the road performance that can be expected from a particular asphalt*".

Therefore, ascribing the flow properties to bitumen fraction considered as independent entities appears to be misleading. If a correlation between the bitumen composition and its physical properties needs to be developed, constitutive properties need to account for the interactions between the asphalt components and not for the components alone. Thus, the bitumen has to be considered as a structure composed of interacting parts (or fractions) whose individual chemical composition, weight proportion and mutual affinity affect the physical (and rheological) response of the whole bitumen.

Besides the physical response, such types of interactions become very important once durability is considered. In particular, according to several noteworthy authors, a balanced bitumen fractional composition, a balanced chemical composition of each fraction, sufficient levels of compatibility among the different fractions, and an adequate dispersion of the asphaltenes in the maltene phase, contribute to a durable asphalt (8, 87, 12, 120-124).

The possibility of separating the bitumen into less complex (although still complex) chemical groups allowed the development of different models of the bitumen structure that attempt to describe how such fractions interact with each other. However, a unique model has not been identified. The model that has met the broadest acceptance is the colloidal model.

2.5.3.5 Fluorescence approach

Fluorescence microscopy is typically used with PMBs to study the morphology of the bitumen-rich-phase and the polymer-rich phase (199). However, a more recent approach has focused on the study of the microstructure of bitumens based on the identification of different fluorescence species by using fluorescence spectroscopy (231). The asphaltenes, the resins, and the aromatics are the bitumen fractions capable of fluorescence. The saturates do not provide fluorescence due to their chemical nature. The asphaltenes show a limited fluorescent capability. On the other hand, aromatics yield the highest fluorescent behaviours that is about 200 times higher than resins. These findings should be kept into consideration while discussing results of fluorescence microscopy in PMBs.

2.5.3.6 Colloidal structure of the bitumen

As highlighted in the previous sections, bitumen is constituted of a vast spectrum of molecules with different polarity and a molecular weight that need to coexist. Such variability has lead researchers to separate the bitumen into multiple chemical groups that do not seem to represent distinct chemical species. These groups of molecules, defined as fractions, need to coexist in a homogeneous structure whose properties affect the physical response of bitumen. The higher the compatibility among such groups, the more desirable are the properties of bitumen, including the durability.

The number and the type of identifiable fractions depend on the separation method used. However, asphalt seems to be constituted of two main groups of hydrocarbons with different solubility, polarity and molecular weight: an oily low-polar fraction, and the asphaltene polar fraction. The properties of this biphasic structure deviate from a true suspension and seem to be proper that of a colloid (8). Colloidal systems have been widely investigated by academia and industry in a wide range of problems, including the study of suspension and interfaces. The large variety of approaches followed, and the large variety of materials to which the colloidal behaviour have been applied does not allow formulating a single definition (110).

The definition of a colloidal system that appears reasonably applicable to bitumens is found in Meyers (110) :"*a state of subdivision of matter in which the particle (or molecular) size of the basic unit involved varies from just larger than that of ''true'' molecular solutions to that of coarse suspensions—that is, between 10 and 10,000 nm*". In a general sense, a colloidal structure deviates from a true suspension and a true solution, and it is represented by two phases of which, one is dispersed (solid-like micelles), and the other one represents the dispersing matrix.

The colloidal structure of the bitumen was initially proposed by Rosinger (114). However, the first description of the bitumen structure as a colloid was attributed to Nellensteyn (113). According to the colloidal theory, bitumens are mainly composed the solid-like asphaltene micelles (that constitute the dispersed part) and the surrounding liquid-like environment that is constituted of the maltene part (saturates + aromatics). The solid-like micelles are formed by the aggregation of large and complex hydrocarbon asphaltenes and are stabilised by the polar resins which provide a flocculating/peptizing action. That is, although resins are included in the oily medium, their polarity is higher than the polarity of saturates and aromatics.

For this reason, the resins are also absorbed by the asphaltene fraction and form an interphase between the asphaltenes and the surrounding oily medium. In other words, the resins prevent the asphaltenes from being absorbed in the oily medium. Finally, the maltenic medium represents the continuous liquid-like phase, and it is mainly constituted of low polar, and low molecular weight saturates and aromatics (6, 85, 87, and 109).

The first analytical description of such a model was given at the beginning of the 1940s, and, based on the characteristics of the colloidal structure, “sol” bitumens and “gel” bitumens were identified (68). The “sol” bitumens are characterised by a high content of maltenes giving a high dissolving ability with enhanced molecular mobility of the micelles (Figure 2-24). This structure is characterised by higher flexibility. On the other hand, the bitumens characterized by a gel-type structure (Figure 2-25), show a lower maltene content which results in a higher level of interaction between the micelles (asphaltenes) that form aggregate structures until a low maltene content and dissolving ability result in micelle aggregation until a continuous stable network is formed (6, 7).

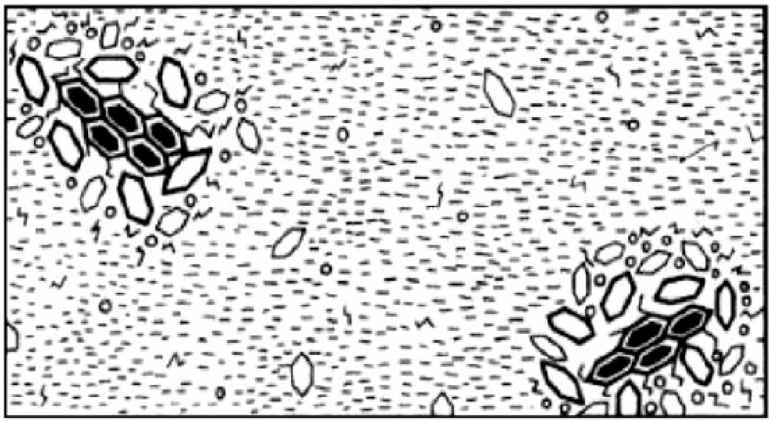


Figure 2-24 – Sol-type bitumen structure (7)

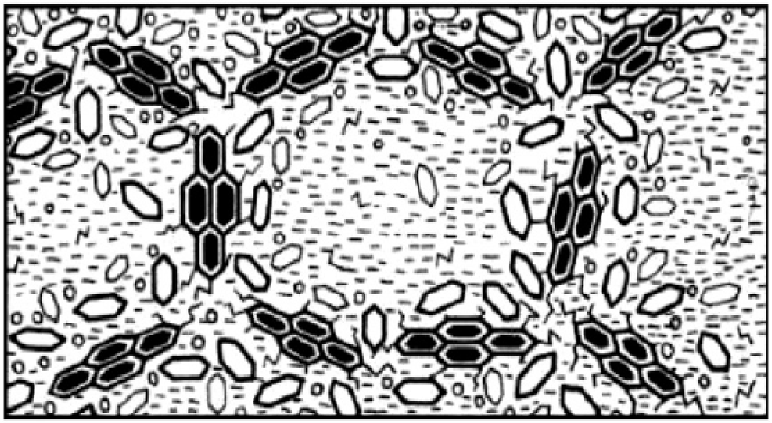


Figure 2-25 - Gel-type bitumen structure (7)

The formation of a structured network in the gel bitumens is thought to give rise to its non-Newtonian behaviour. Although the sol and gel structures have been described separately, the majority of paving bitumens shows an intermediate structure (sol-gel bitumens) with the coexistence of sol-type micelles in a gel structure. The type of structure (more sol or more gel) that is formed depends on the equilibrium between the bitumen components. That is, the colloidal structure that is formed depends on the bitumen constituents and their proportions. For instance, the difference between a hard bitumen and a soft bitumen from the same crude source depends on asphaltenes and aromatics proportions, with the saturates and the aromatics having a negligible role (69). Depending on the proportion of the constituents, the system evolves towards an equilibrium (or stable) configuration that might not correspond to the configuration that provides the best flow properties. The more the configuration deviates from the optimum, the more the bitumens can display low durability. To understand whether a bitumen is more “gel-type” or “sol-type”, Gaestel et al developed a colloidal (or instability) index (I_C) also known as Gaestel Index that is calculated by Equation (2-1) (70).

$$I_c = \frac{X_{Asphaltene} + X_{flocculant}}{X_{surfactant}} \tag{2-1}$$

Where:

- $X_{Asphaltene}$ – is the weight fraction of the asphaltenes;
- $X_{flocculant}$ – is the weight fraction of the maltenes generating the flocculation of the asphaltenes;
- $X_{surfactant}$ - is the weight fraction of the peptizing agents like molecules that behave as a surfactant for the dispersion of the asphaltenes.

In terms of SARA fractions, the flocculant fractions would be a mix of saturates and aromatics; while the surfactant portion would be constituted of aromatics and resins (Equation (2-2).

$$I_c = \frac{X_{Asphaltene} + X_{Saturates}}{X_{Aromatics} + X_{Resins}} \tag{2-2}$$

Typically, the colloidal Index ranges from 0.5 and 2.7, with the more sol-type bitumens having I_C<0.7 and the more gel-type bitumens having I_C>1.2 (7).

Due to its dependency on the functional composition of bitumens, the Gaestel Index has been proposed by several authors as an index to quantify the changes with ageing in the bitumen microstructure (71, 85, 87).

However, although the use of the colloidal system has encountered extensive usage over the decades to model bitumen structures, there are still several inconsistencies between this model and the rheological response of bitumens. For this reason, although it is widely considered, its applicability is still debated.

2.6 The mechanism of ageing in unmodified bitumens

Two ageing mechanisms occur in bitumens, short- term ageing, and long-term ageing (15, 17, 27, 62, 123). The first occurs at high temperatures during plant and paving operations. In this range of temperatures, volatilisation of the light bitumen fractions (maltenes phase) represents the leading ageing mechanism. Besides volatilisation, some oxidation and the absorption of the light fractions in the mineral aggregates occur as well.

The long-term ageing (or field ageing) occurs during the pavement service life where a thin film of asphalt is exposed to environmental factors such as atmospheric oxygen, moisture, and solar radiation. In 1936, Traxler (74), identified 15 factors that contribute to the field ageing of bitumen. However, oxidation and steric hardening are considered as the primary long-term ageing mechanisms that contribute to reducing the durability of pavements (11, 24).

The list of the factors identified by Traxler is given in Table 2-6. It is worth mentioning that some of these factors have not been found in experimental evidence.

Table 2-6 – Factors affecting bitumen ageing as identified by Traxler (74).

	Affected by					**Occurs**	
Factors	Time	Heat	Oxygen	Sunlight	β and γ rays	At the surface	bulk
Oxidation (in dark)	x	x	x			x	
Photo Oxidation (direct light)	x	x	x	x		x	
Volatilisation	x	x				x	

	Affected by					Occurs	
Factors	Time	Heat	Oxygen	Sunlight	β and γ rays	At the surface	bulk
Photo-oxidation (reflect light)	x	x	x	x		x	
Photo-chemical (direct light)	x	x		x		x	
Photo-chemical (reflect light)	x	x		x		x	x
Polymerization	x	x				x	x
Steric or Physical	x					x	x
Exudation of soils	x	x				x	
Changes by nuclear energy	x	x			x	x	x
Action by water	x	x	x	x		x	
Absorption by solid	x	x				x	x
Absorption of components at a solid surface	x	x				x	
Chemical reactions	x	x				x	x
Microbiological deterioration	x	x	x			x	x

2.6.1 Oxidation of unmodified bitumens

Bitumen oxidation is generated by the infiltration of oxygen throughout the interconnected air voids of asphalt mixes and by its subsequent diffusion through a thin film of bitumen that coats the mineral aggregates (16, 77). The effect of oxidation on the flow properties depends on the ageing susceptibility of the bitumen that depends on its composition.

A durable bitumen provides adequate initial flow properties and resists chemical and physical changes caused by oxidation during the pavement life. The resistance to oxidation depends on the functional composition of bitumen (equilibrium among Saturates, Aromatics, Resins and Asphaltenes), and specifically, it is a function of the level of dispersion of the asphaltenes in the maltene phase. The more the asphaltenes are dispersed, the lower is the ageing susceptibility. However, a well-balanced proportion among the bitumen fractions and balanced chemical composition of each fraction are desirable conditions for a durable bitumen (11, 80-82).

Due to their origin, bitumens are hydrocarbons and are constituted by a majority of carbon and hydrogen atoms. In hydrocarbons, oxidation occurs through the formation of carbonyl compounds whose concentration increases with oxygen uptake (84). The formation of carbonyl compounds results in the formation of strongly interacting functional groups containing oxygen characterised by stronger interaction forces that affect the flow properties, including viscosity. Petersen (11, 145) identified four polar functional groups containing oxygen formed during bitumen oxidation: ketones, anhydride, carboxylic acid, and sulfoxides (Figure 2-26).

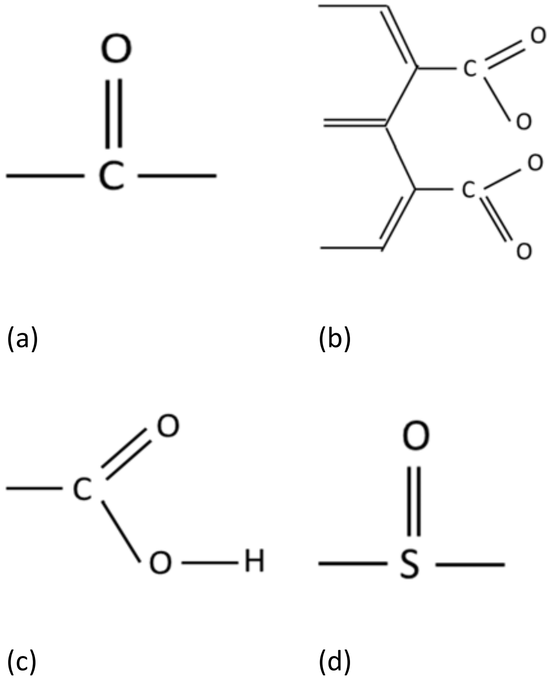


Figure 2-26 – Carbonyl groups identified by Petersen (11)

a) Ketone; b) Anhydride; c) Carboxylic acid; d) Sulfoxide

Ketones and sulfoxides represent the majority of the functional groups generated since they have the highest content of hydrocarbon types sensitive to air oxidation. Sulfoxides form at the beginning for a short time, while the formation of ketones, carboxylic acid and anhydride occurs with time with oxygen uptake and causes the growth in carbonyl content (84). A linear correlation was observed between the amount of oxygen uptake and the formation of carbonyl compounds. The coefficients of this correlation depend on the distribution of the three C=O functionalities and are affected by temperature and bitumen composition. For instance, the formation of one ketone requires one atom of oxygen and a single carbonyl bond is formed. The increase of Carbonyl double bond content has been used to quantify the amount of oxidation occurring with time in modified and unmodified asphalt bitumen (18-22).

Therefore, the main effect of oxidation at the molecular level is the transition of asphalt components from non-polar (maltenes phase) to more polar components (asphaltenes) characterised by higher molecular weight and stronger interacting polar bonds (85-87) (Figure 2-27). The saturates are stable during oxidation, while the concentration of polar aromatic and naphthenic aromatic decrease. Simplistically, both the aromatic components are assumed to be converted to asphaltene (86).

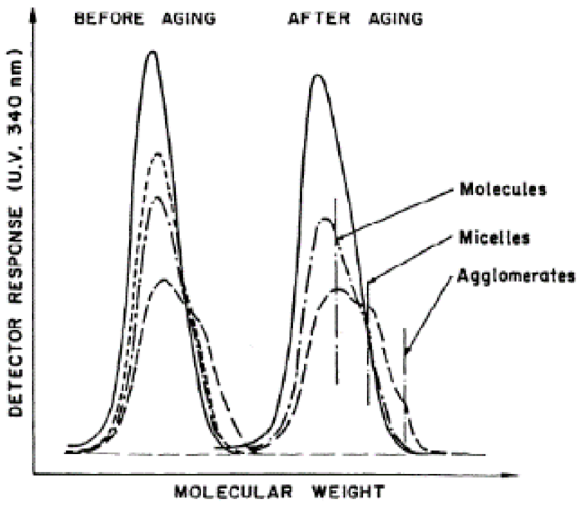


Figure 2-27 - Bitumen molecular weight distribution before and after ageing (86).

In the maltenes phase, molecular bonds are characterised by weak associations, the Lifshitz - Van deer Waals force whose strength depends on the atomic distance, and it is sensitive to temperature. On the other side, the asphaltenes, which are characterised by highly condensed rings and chemical functional groups containing nitrogen and oxygen, are polar and are linked by strong interaction forces making them prone to associating in conglomerates. Therefore, besides the increase in molecular weight, the increase in the asphaltenes enhances the molecular strength of the bitumen with a reduction in the molecular mobility. At the macroscopic level, this makes the bitumen less capable of flowing under shear stress with a consequent increase in cracking susceptibility. Thus, from a chemical point of view, the bitumen’s hardening depends on the development of stronger molecular interactions that produce agglomerate and reduce the mobility of the system (11). The decrease in molecular mobility tends to stiffen the bitumen making it more viscous (86, 88, 89). Bitumens that are susceptible to ageing show higher agglomerates formation and therefore, lower durability.

Besides bitumen properties, several external factors affect the oxidative process. Some of these factors depend on the characteristics of the asphalt mixture, such as interconnected air voids, bitumen film thickness, and layer thickness. Others depend on environmental conditions such as air temperature, solar radiation, and moisture level. In 1958, Fink showed that in most of the oxidative processes, the rate of oxidation doubles with each 10°C of temperature increase (79). For this reason, it appears that the bitumens' ageing becomes critical in hot climates where the surface of asphalt pavements is exposed to high temperatures and solar radiation.

The effect of oxidation on the flow properties of unmodified bitumen is well understood and has been widely documented by researchers (11, 12, 24). Oxidative ageing is proved to harden asphalt bitumen by reducing the penetration and increasing softening point and viscosity (24, 69, 87, 120).

Extensive work has also been done to evaluate the effect of short-term and long-term ageing on the viscoelastic properties of asphalt bitumen. Results have shown that oxidation stiffens the bitumen with a reduction of the phase angle and temperature susceptibility (19, 24, 121, 122).

2.6.2 Steric hardening

Steric hardening (or molecular structuring) is a reversible phenomenon that produces thixotropic effects on the flow properties of asphalt without altering the chemical composition. Structuring is a slow process that may go on for several years at ambient temperature. It is promoted by aggregate surfaces (as in pavement mixtures), where it is difficult to measure its effects.

Aggregate surface promotes molecular structuring and immobilisation of asphalt molecules in the proximity of the aggregate surface. It is known that thixotropy seems to depend on a hydrodynamic interaction among components in a suspension as a colloid system. Depending on the orientation of the particles suspended, this effect might produce a thinning effect or thickening effects.

Brown et al (73) attributed steric hardening to the formation of an internal structure in the asphaltene phase. The formation of this structure seems to cause the segregation of asphaltenes from the maltene phase (72). Traxler and Schweyer (74), studied the effect of steric hardening regarding the degree of complex flow and observed an increase in shear rate sensitivity while measuring viscosity. This aspect highlights that once binders undergo oxidative ageing, their behaviour might become non-Newtonian. Davis and Petersen (83) have shown that steric hardening and oxidation seem to be interrelated, and oxidation promotes molecular structuring.

Unfortunately, steric hardening is a reversible phenomenon that is destroyed by recovering asphalt from mixtures, and for this reason, it did not get enough emphasis.

2.6.3 The rheological response of aged unmodified bitumens

The chemical composition and the microstructure of bitumen have been widely used to support the changes in the rheological response of aged bitumens. As discussed in §2.6.1, oxidative ageing is a chemical process that stiffens the bitumens and reduces their strain tolerance. However, understanding the magnitude of these changes in the rheological (or physical) response becomes critical for predicting long-term performance.

The evaluation of the effects of ageing on rheological response consists mainly of providing ageing indexes measured as the ratio between the same properties at unaged versus aged condition (e.g., viscosity index). The more these indexes are close to unity, and the less the bitumen is susceptible to ageing.

The parameters mainly used to calculate the ageing indexes are as follows:

- Empirical parameters (i.e., penetration, softening point);
- Viscosity;
- Viscoelastic shear complex (G*) modulus and phase angle (δ);
- Different viscoelastic properties.

The changes in the rheological response of unmodified bitumens are given in Table 2-7 (12, 18,21, 24, 54, 69, 74, 75, 85-88, 120-122, 129, 141, 144-146, 158, 203).

Table 2-7 – Typical trend of empirical and viscoelastic parameters of unmodified bitumens with ageing.

Parameter	Typical trend with oxidative ageing
Penetration	Decreases
Softening point	Increases
Viscosity (different types)	Increases
Complex Shear Modulus (G*)	Increases
Phase angle (δ)	Decreases
Temperature susceptibility	Decreases

The table aims at highlighting the possibility of identifying a general trend of changes in the physical response with the ageing of unmodified bitumens. The trends of the empirical and viscoelastic functions included in Table 2-7 are solidly supported by the collected literature and are physically sound with the hardening effects of oxidation on the bitumens flow properties.

The parameters in Table 2-7 have been used through the decades to measure the physical response of bitumens as a function of the technologies available.

The measures of bitumen consistency (i.e., penetration and softening point) and viscosity were adopted between the 1920s to the 1980s. More recently, viscoelastic parameters became more popular.

2.6.3.1 Effects of ageing on Penetration and Softening point

Penetration and softening point have been (and still are) widely used as empirical parameters to measure the consistency of bitumens respectively at intermediate (Penetration at 25°C) and high temperature (Softening point). Oxidative hardening has been demonstrated to reduce the penetration and to increase the softening point (20, 21, 23, 24, 54, 141). Although the two parameters have an empirical base and may be less meaningful once applied to PMBs, they are representative of the hardening effect of ageing on bitumen consistency.

2.6.3.2 Effects of ageing on viscosity

A considerable portion of the research conducted includes viscosity as the primary physical property to measure the effects of ageing on the flow properties of bitumens. In the opinion of the author, there are several reasons for this:

- Viscosity is an engineering property that measures the flow properties of fluids;
- At the time of the development of bitumen compositional test methods, viscosity was widely used (with consistency) in road research laboratories to measure the physical response of bitumens;
- Viscosity seems to correlate with the asphaltene content.

The increase in viscosity is caused by the changes in the microstructure of bitumens. As discussed in §2.6.1, the carbonyls formed with oxidation are characterised by stronger interactive polar forces which contribute to enhancing the strength of the molecular bonds with a consequent increase in the resistance to flow. Therefore, the viscosity increases with the increase in the polarity and the strength of the molecular bonds.

Besides the changes at the molecular levels, the formation of asphaltenes has been widely used to correlate compositional changes with the increase in viscosity (12, 87, 106). Asphaltenes represent the most complicated species with the highest polarity and the highest tendency to interact and associate. There are pieces of evidence on the correlation between viscosity and the content of asphaltenes.

However, the increase in viscosity with ageing is disproportionate when compared to mild variation in the bitumen components. Therefore, there is reason to believe that viscosity is not dependent on the asphaltene fraction only, but rather, it depends more on the proportions and the interactions between the SARA fractions (87). Based on this, even a mild change in the proportion of the bitumen components can cause a more evident change in viscosity.

This conclusion is that, at least at present, developing a bitumen chemical-based specification representative of performances is very arduous. The presence of functional groups, their proportion, and their interactions affect the flow properties of bitumens to such an extent that even a moderate change in their proportion results in evident changes in the flow properties. The reason for this might depend on the presence of the heteroatoms that affect the polarity of molecules.

The SARA fractions are not considered as truly distinct chemical species. Therefore their molecular composition remains partially undetailed. This lack of details does not allow having comprehensive information on the composition of the SARA fractions, including their constituting atoms and molecules. Therefore, the same fraction (e.g., asphaltene) of two different bitumens might contribute with different polarity, and consequently with different flow properties.

Nevertheless, researchers have tried to develop models that correlate flow properties such as viscosity with the carbonyl content in order to develop a predictive model (84, 87, 149, 150). According to this model, the logarithm of viscosity varies linearly with the peak of the carbonyl area, according to Eq.(2-3).

$$\ln \eta = \ln m + HS \cdot CA \qquad (2\text{-}3)$$

Where:

- η - is the binder viscosity;
- m - is an asphalt-dependent constant;
- *HS* - is the hardening susceptibility that is unique for each binder, and it is independent of the oxidation temperature below 212 °F, but it depends on pressure;
- *CA* - is the peak of the carbonyl area.

Liu et al (84) identified that the rate of oxidation in asphalt is significantly dependent on asphalt, air temperature, and oxygen pressure.

Combining Eq.(2-3) with the findings from the kinetic studies, an equation that evaluates the variation of viscosity with time (and oxidation) has been developed (Eq.(2-4)).

$$\eta = m \cdot \exp\left[\left(CA_0 + AP^{\alpha} e^{-E/RT} t\right) HS\right] \qquad (2\text{-}4)$$

Where:

- CA_0 - is the initial jump in carbonyl content that varies with pressure but not with temperature;
- *A* - and α are asphalt dependent constants;
- *E* - is the asphalt dependent activation energy.

Mirza and Witzack developed the Global Aging System (GAS) model to predict the effects of ageing on long-term pavement performance (147). The model is currently adopted in the Mechanistic-Empirical Pavement Design Guide (MEPDG) (148).

The GAS model accounts the effect of the mixture ageing on the viscosity of asphalt bitumen. Three ageing conditions are considered:

- Unaged bitumen;

- Short-term aged bitumen (after storage, mixing, laying and compaction);
- Long-term aged bitumen (ageing under the effect of oxidation and other environmental factors).

Figure 2-28 shows the qualitative effect of ageing on then bitumen viscosity as per the GAS model.

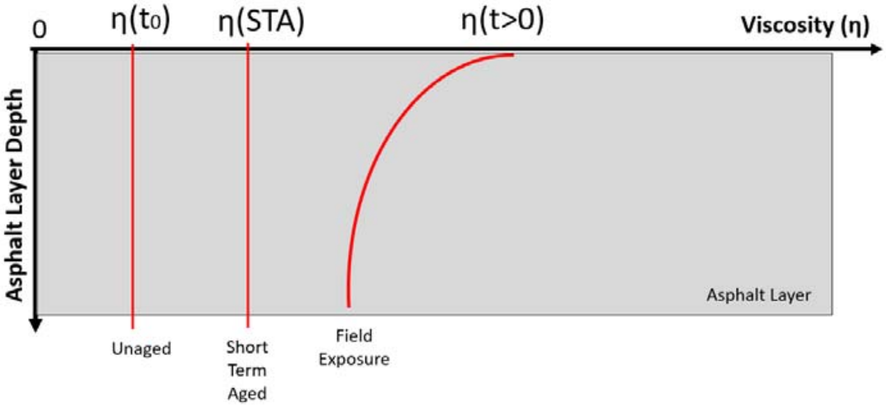


Figure 2-28 – Qualitative variation of bitumen viscosity versus bituminous layer depth at different levels of ageing provided by the GAS model.

The horizontal axis of the figure shows the values of viscosity at different levels of ageing (i.e., unaged, short-term aged, and after field exposure). The vertical axis represents the depth of the asphalt layer. According to this model, the viscosity of bitumens increases with ageing. In the case of short term-ageing, viscosity increases uniformly throughout the pavement structure. On the other hand, during the field exposure, the viscosity increases with the layer depth with the bitumen localised at the surface experiencing more considerable variation. The effect of the pavement depth on the variation of bitumen properties with filed exposure has been shown by other authors (20). The equations of the models are not included for the sake of brevity. However, they are discussed in (147, 148).

The GAS model was developed empirically from field-aged mixtures only, and no laboratory-simulated ageing methods were used. Data (capillarity viscosity) from more than 70 unmodified bitumen from all over the world were collected through an extensive literature review. Whenever viscosity measurements were not available, their value was estimated from measures of consistency through Penetration and Softening Point.

The model predicts the variation of viscosity with time as a function of the pavement depth. Furthermore, it allows considering the effects of bitumen and mixes air voids.

However, the model limitations are discussed as follows:

- It does not apply to polymer-modified bitumen;
- It was developed on regression equations only, and no fundamental constitutive bitumen properties were considered (e.g., functional composition);
- It was developed on capillarity viscosity values and, once viscosity was not available, it was estimated from empirical equations;
- No fundamental viscoelastic properties such as complex modulus or phase angle are considered in the model;
- Results used in the regression analysis were measured from cores taken from the surface, and the consistency values were related to a typical pavement depth of 0.25 inches;
- The effects of ageing on capillarity viscosity does not necessarily reflect the effect of ageing on damage resistance of bitumen.

2.6.3.3 Effects of ageing on the viscoelastic properties

The use of dynamic shear loading to characterise the viscoelastic properties of bitumen became popular during the ’80s and ’90s once rheology was introduced into the specifications (108). The main viscoelastic parameters measured are the Complex Shear Modulus (G*) and the phase angle (δ). As detailed in §2.10.1, the first represents the capacity of resisting to loads, while the second is a measure of the internal dissipative mechanisms of the material.

The |G*| increases with ageing (i.e., the material becomes stiffer). While the phase angle decreases, showing reduced viscous effects (i.e., lower energy loss) under repeated loading cycles.

The study of the effect of oxidative ageing on the viscoelastic response of bitumens (and mixtures) has considered several parameters intending to identify the one capable of controlling the phenomena. Besides the measure of stiffness and phase angle, indicators such as the Zero Shear Viscosity (ZSV), William-Landel-Ferry (WLF) equation parameters, temperature susceptibility, and Activation Energy, have been investigated (45, 121, 156, 157, 158,). In a work of Chailleux et al, the parameter C_2 of the WLF equation has shown to increase with ageing highlighting the loss in thermal dependence of the material (203). Besides this, Ruan et al have shown that in unmodified bitumens, the Activation Energy increases with ageing presumably due to an increase in the interactions between different bitumen components (121). What looks interesting is different PMBs (i.e., SB, SBS, SBR) show an opposite behaviour with the Activation energy decreasing with ageing perhaps due to the degradation occurring in the polymer chains

In the SHRP Programme, the viscous modulus ($G^* \times \sin\delta$) has been selected to control the cracking at intermediate temperatures; while the rut factor ($G^*/\sin\delta$) has been selected to control rutting. It is well known that the first is measured at the PAV-aged conditions, while the second at the RTFO aged conditions. Unfortunately, none of the parameters has resulted in being appropriate to capture the physical impact of the increase in stiffness and the decrease of the phase angle.

The need for the identification of bitumen rheological parameters to control ageing-induced cracking is not recent. The findings from an investigation on ravelling conducted by Khandal in Pennsylvania in the early 1970s identified the ductility of binders at 15°C (1 cm /min) as the controlling factor for surface cracking. Significant surface distress was noted once ductility was below 3 cm (159). Subsequently, Glover, Anderson and Rowe, starting from the work of Khandal, developed and verified a rheological parameter measured in dynamic shear oscillation to control ageing-induced damage. This parameter appears to agree with field data (158) and has been named as the Glover-Rowe parameter or Glover Rowe cross-over modulus given by Eq.(2-7).

$$G^*_{(c)} = \frac{G^*(\cos\delta)^2}{\sin\delta} \tag{2-5}$$

Where the significance of the terms is well-known, and the G* and the phase angle are measured in the linear region at 15°C and 0.005 rad/sec. The proposed specification limits are:

- $G^*_{(c)} = 180kPa$ – Damage onset;
- $G^*_{(c)} = 450kPa$ Significant cracking.

The applicability of this parameter to PMBs remains unknown.

Based on what discussed in this section, some considerations can be raised as follows.

The response of viscoelastic materials under oscillatory loading depends on the stiffness and on how dissipative the material is under dynamic loading. Therefore, considering stiffness alone may not be representative of the full response of the material. Oxidative ageing is responsible for stiffening the material and for decreasing the viscous response (lower dissipation of strain energy under loading). Coupling these two effects to deliver an indicator that controls ageing induced damage is very challenging. For this reason, despite the considerable effort expended (and still in progress), the use of linear viscoelastic parameters to control ageing induced damage in bitumens still lacks consensus.

This consideration is not meant to criticise the work conducted so far. On the contrary, it highlights that the studies conducted (§2.6.3), have contributed to the understanding of the effects of ageing on the viscoelastic response of unmodified bitumens (and PMBs), but unfortunately, the findings and the conclusions refer mainly to “increase with ageing” or “decrease with ageing”, and quantitative long-term performance assessment remains absent. Perhaps, this critical shortcoming depends on the lack of ability of linear viscoelastic characterisation to control long-term pavement performance.

Nevertheless, as seen as with viscosity, the variation in the viscoelastic response is supported by the changes in the microstructure of the bitumen. Therefore, although it is unlikely to be capable of controlling the long-term pavement performances, linear viscoelastic characterisation can be considered as “phenomenological” in nature. In particular, the phase angle (δ) measured at different temperatures and frequencies is representative of the Molecular Weight Distribution (MWD) of bitumens (151, 152, and 154). Such a correlation derives from the work conducted on dispersed polymer solutions considering bitumens as a low molecular-weight polymer having a continuous MWD. Specifically, for each (bitumen) molecule, the molecular weight (MW) is proportional to the relaxation frequency (ω_i), which is the loading frequency below which that molecule relaxes and stops contributing to the modulus. At that frequency, unrelaxed molecules are to some extent diluted into relaxed molecules. The relaxation frequency decreases with the increase of the molecular weight with the lighter molecules relaxing under the increase in the loading frequency (151). In this scenario, the phase angle at a specific frequency (and temperature) becomes proportional to the fraction of relaxed molecules.

Supported by this theoretical background, Themeli and co-workers have developed the δ-method, which provides the average molecular weight of unmodified bitumen by using DSR measurements (152, 154). The advantage of this type of approach lies in the possibility of deriving the molecular weight distribution of bitumens without using chromatographic methods. For example, in the work of Jimenez and co-workers, it has been used to determine the effect of rejuvenators on the MWD of bitumen extracted by mixtures prepared with high RAP content (155).

Besides the weight of molecules, the polarity and the carbonyl content have been used to model the rheological response (153, 160).

The complex shear modulus (G*) is predicted as a function of the carbonyl content through a logistic model (Eq. (2-7) in 160).

$$G^* = \frac{G_g^*}{[1 + e^{-\beta(Carbonyl-\gamma)}]} \tag{2-6}$$

Where:

- G_g^* is the glassy modulus (1 GPa);
- $Carbonyl$ is the carbonyl content in the absorption unit;
- β describes the shape of the curve;
- γ is a correlation constant.

According to the model, modulus grows with the growth of carbonyls. Therefore it is representative of the stiffening effect of oxidative ageing.

This section has included a detailed discussion of the effects of ageing on the rheological response of unmodified bitumens measured through different methods. As per the points discussed, two main points deserve to be highlighted:

- It appears that a rheological indicator that adequately controls the effects of ageing on the field performances of bitumens has not yet been identified.

- Phenomenological equations between the bitumen composition (i.e., carbonyl content, molecular weight) and the Viscosity (η) and the viscoelastic shear modulus (G*) and phase angle (δ) can be developed.

2.7 Polymer Modified Bitumens

2.7.1 Need for polymer modification

The modification of road bitumens with polymeric additives has expanded since World War 2 (3), and currently represents one of the most successful technologies developed for improving the performance of asphalt mixtures. The need for such improvements has been prompted by transportation demand (volume and load), which has shown rapid growth in the past few decades (1-4).

Besides this, the requirements to which asphalt mixtures are subjected have changed from those traditionally considered in the past. Aside from the traditional requirements such as rutting and fatigue cracking resistance, nowadays asphalt mixtures represent truly engineered materials that take on challenging requirements of durability, sustainability, eco-efficiency and recyclability. For instance, besides an adequate load resistance, these mixtures have to be produced at lower temperatures, need to include recycled materials without worsening their performances, and are required to be still usable at the end of their design life representing a recycled product and not a waste (§2.4). The purpose of meeting such requirements has prompted academia and industry to develop different types of polymeric (and non-polymeric) additives that aim to meet specific requirements depending on the characteristics to be improved (1-4, 6-10, 66, 28). This work focuses on polymeric additives.

The quality of the modification represents the capability of the polymer to improve the performance of the bitumen when added in small quantities. Specifically, polymer modification aims to stiffen the bitumen and to increase its elasticity at high pavement temperatures; to decrease the temperature susceptibility; to maintain sufficient levels of workability during mix production and laying, and to provide lower levels of stiffness at intermediate and low pavement temperatures. Furthermore, properties such as storage stability, reduced moisture susceptibility and sufficient ageing resistance need to be investigated (8). The more the polymer is capable of swelling while maintaining its structure, the more the response of the bitumen improves.

However, the mechanical properties need to be considered as the visible results of thermodynamics and chemical interactions occurring between the bitumen and the polymer. A clear description of the mechanism of modification at the microstructural level is provided by the works of Polacco et al, and Lesueur (6, 7).

The ideal bitumen modification occurs once the mechanical response of the polymer becomes dominant. This condition occurs under the Phase Inversion (PI) that represents the condition under at the polymer becomes the continuous phase (matrix) with the bitumen being the dispersed phase. An example of a well-dispersed polymer (SBS) phase is given in Figure 2-29.

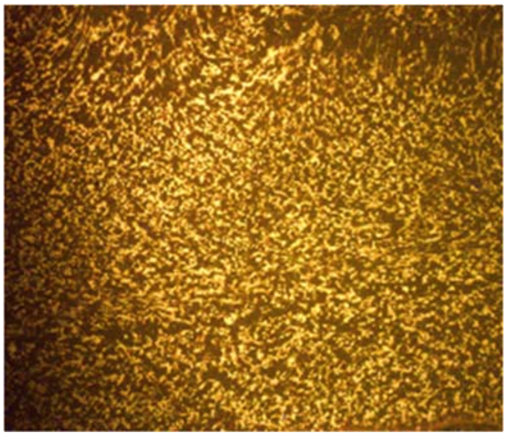


Figure 2-29 – Example of polymer (SBS) dispersion

In this case, the mechanical response of the PMB is markedly dependent on the polymer. The PI occurs under sufficient levels of affinity between the polymer and the bitumen, and proper blending operations (i.e., blending temperature, blending time, applied shear, use of cross-linker).

During blending, the polymer swells within the bituminous phase by absorbing the bitumen fractions with which it shows high affinity. Polymers have a different interaction with the different SARA fractions (§2.5.3.4) depending on their polarity. The different levels of affinity between the polymer and the bitumen fractions lead to the formation of a biphasic structure whose phases are defined as a bitumen-rich phase and a polymer-rich phase. The first includes the bitumen fractions that show a low affinity. Generally, this fraction includes the asphaltenes.

The second fraction consists of those molecules that have a higher affinity with the polymer. The equilibrium between these two phases can be achieved under a determined degree of relative solubility and swelling. In the case of a limited degree of swelling, the polymer remains segregated within the bitumen rich-phase, and the properties of the PMB do not differ significantly from the unmodified bitumen.

On the other hand, once adequate levels of swelling occur, the polymer phase shows a dispersed structure throughout the bitumen with a strong influence on the mechanical response. However, the condition of excessive levels of dispersion is not necessarily desirable. In this case, the polymer would be completely soluble into the bitumen phase with the chains somehow dissolved, and the structure ultimately be lost. The mechanical response obtained under such a configuration would correspond to an increase in viscosity without any of the other advantages expected from polymer modification. In this case, it would behave as a reinforcement particle only.

Therefore, the ideal condition would be of the polymer having adequate swelling without losing its structure. In the case of low affinity and inadequate levels of swelling the polymer modified bitumen evolves toward a biphasic system where the two phases are not compatible and display a significant tendency to macroscopic segregation due to a difference in density. This aspect is critical for the durability of PMBs, which, besides oxidative-resistant need to be stable at storage (38).

2.7.2 Polymers

Before describing the polymeric additives with the most extensive usage in road applications, some general information on polymers needs to be provided (3, 94).

A polymer can be defined as "*A substance composed of molecules which have long sequences of one or more species of atoms or groups of atoms linked to each other by primary, usually covalent, bonds*" (94). The word substance highlights that the words polymer and macromolecules can be used interchangeably to indicate that a polymer is representative of a group of molecules (macromolecules) also known as monomers that are distributed along defined schemes to form the polymer chains.

Depending on the combination of the different molecules, polymers have different architectures, skeletal structures and, consequently, properties. Concerning the skeletal structures, polymers display different configurations depending on how the molecules are organised in chains and junctions. In the case of *linear polymers*, the skeleton of the macromolecule can be represented by a linear chain between two points. In the *ring polymer* (or cyclic) there are no chain-ends, and the properties differ from the linear. In the case of *branch polymers,* branch chains are connected through branching points to the main chain. These polymers are characterised by the number and the size of the chains. *Network polymers* are those forming a 3-dimensional structure where the chains are interconnected to each other by a sequence of junctions, points and chains. Such polymers are said to be cross-linked.

Besides the skeleton structure, polymers are classified according to the number of species of monomer that compose the repeat unit. Once the repeat unit is composed of a single species of monomer, the polymer is defined as “Homopolymer” (Figure 2-30). On the other hand, when the repeat unit is composed of two or more monomer species, the polymer is defined as copolymer (Figure 2-31), or block copolymer (Figure 2-32) when the repeated unit consists of blocks of repeating groups of monomer.

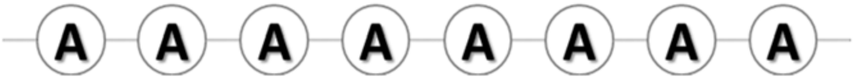


Figure 2-30 – Homopolymer structure

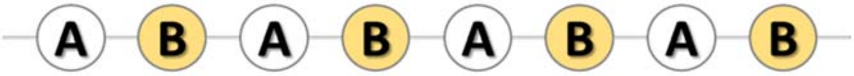


Figure 2-31 – Copolymer structure

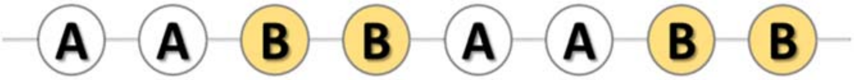


Figure 2-32 – Block copolymer structure

Besides the constitutive classifications of polymers, these macromolecules are also classified according to their reaction to temperature. In this case, polymers are classified into *thermoplastic* and *thermosetting* (Figure 2-33).

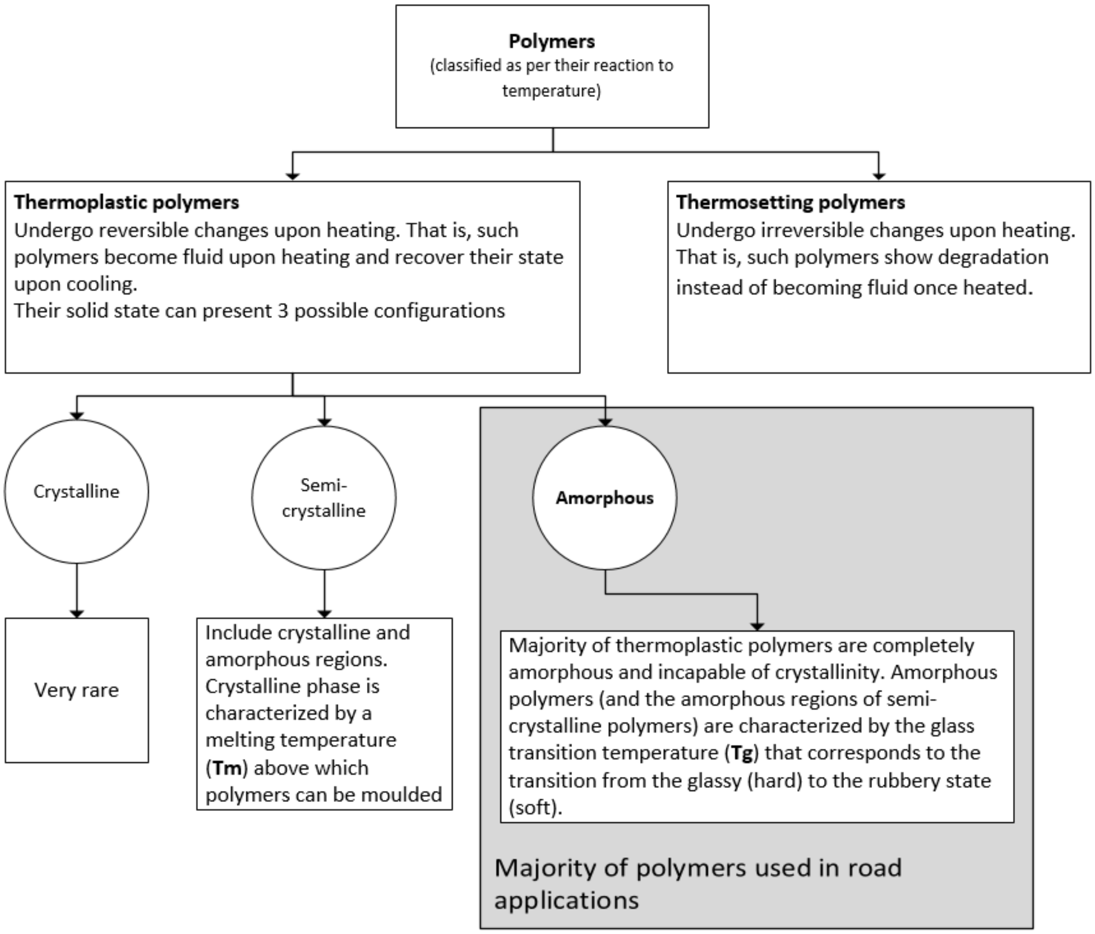


Figure 2-33 – Polymer classification as per reaction to temperature (94)

The majority of the polymers used in road applications are classified as thermoplastic amorphous. As explained in Figure 2-33, in the amorphous polymers, the glass transition temperature (T_g) represents the threshold between the glassy state and the rubbery state. This property is significant since the two fields (glassy and rubbery) display remarkable differences in molecular mobility, and thus, in terms of shear resistance.

In the glassy state (below T_g), the polymer chains remain frozen in their configuration and molecules are unable to move. On the other hand, in the rubbery state (above the T_g), polymer chains are capable of displaying multiple configurations enabled by the molecular mobility that increases with the temperature. Therefore, in the glassy region, the polymer does not seem to deform under loading, and this can be defined as the *hard domain*.

On the other hand, in the rubbery region, the polymer chains are capable of deforming and recovering their shape (*soft domain*). A more detailed characterisation of polymers would be out of the scope of this document which focuses on polymers as bitumen additives. Therefore, besides the constitutive classification that is more of concern for polymers technologists, in road application polymers are mainly distinguished depending on the effect they provide on modified bitumens.

Based on this classification, two types of polymer are identified: the elastomers that resist deformation by stretching and recovering their shape, and the plastomers that resist deformation by forming a 3-D rigid network.

Thermoplastic elastomers have found successful application in bitumen modification due to their capacity of recovering their shape once the load is removed [3]. Generally, these are block copolymers obtained by joining soft and hard segments in a three-block sequence *hard-soft-hard* (6). Soft segments are higher in number compared to hard. Both the segments are in the amorphous state, and as shown in Figure 2-33, their soft or hard state depends on the operative temperature. In the case of road applications, the hard segment is below the glass transition temperature, while the soft segment is above.

Quantitatively soft segments are predominant, and the absent solubility between the soft and the hard segments leads to the formation of a biphasic structure consisting of a small domain of hard segments dispersed in a continuous soft matrix (Figure 2-34).

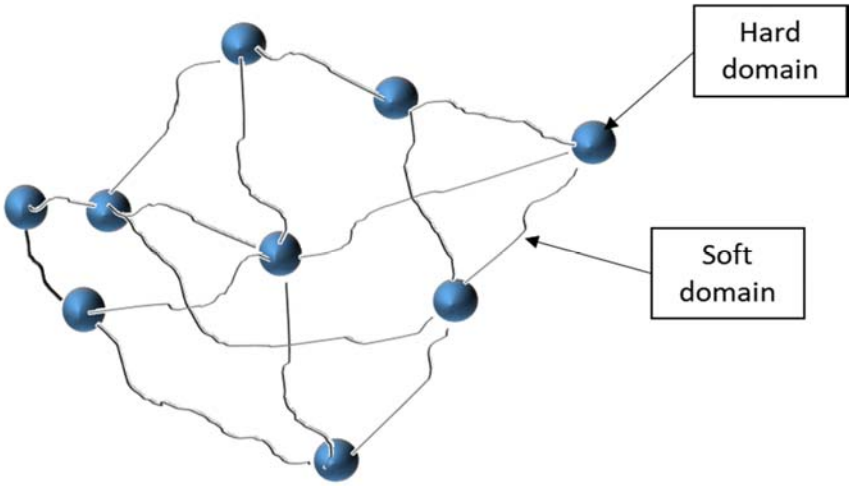


Figure 2-34 – Conceptual scheme of polymers biphasic structure constituted of soft and hard domains

The soft domains are linked to hard domains on both sides, and this configuration generates a physical network capable of elastomeric behaviour. During modification, the polymer swells in the bitumen phase by absorbing the bitumen fractions to which it has higher affinity. Based on the concept of the polymer network, and of its capability of showing elastomeric behaviour, the ideal condition would be that the soft (elastic) matrix would swell by absorbing the bitumen molecules, with the hard domain swelling just slightly (Figure 2-35).

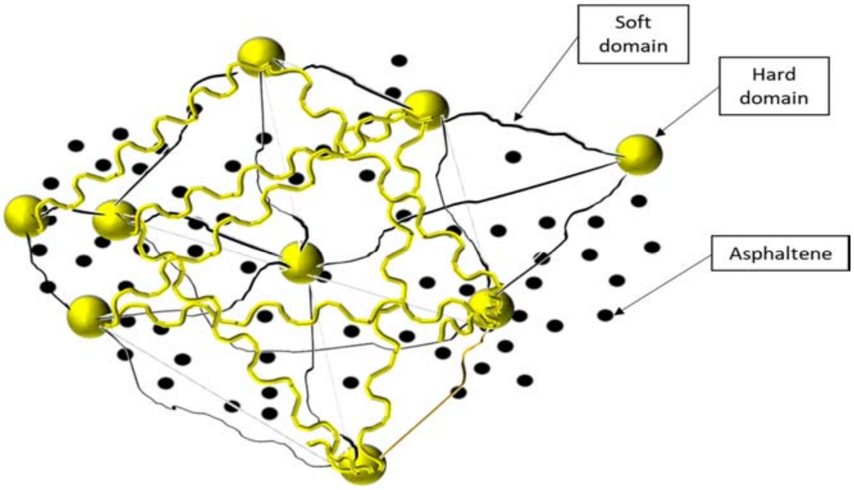


Figure 2-35 – Conceptual scheme of polymer phase swelling in the bitumen phase

In this way, the polymer structure would be conserved in the bitumen phase with the polymer being capable of providing the elastomeric response showing elastic recovery and resistance to the accumulation of permanent deformations (6).

In the thermoplastic elastomers used in the paving industry, the hard domains are very often constituted of Styrene blocks whose glass transition temperature is approximately 100°C. Styrene blocks are combined with different types of soft segments depending on the polymer that is produced (e.g., Butadiene, Isoprene, Ethylene, Butene).

In the case of thermoplastic plastomers, Ethyl Vinyl Acetate (EVA) is the most widely used. EVA has a molecular structure that is entirely different from SBS or the other thermoplastic elastomers. In this case, the ethylene and the vinyl-acetate repeating units are randomly distributed along the backbone of the macromolecule. Despite this, the repulsive forces between the two monomers and the presence of homo-sequences of ethylene units lead to the formation of a structure similar to the one shown in Figure 2-34.

In this structure, the hard domains are formed by crystalline or semi-crystalline poly (ethylene)-rich zones. Therefore, as seen with thermoplastic elastomers (TPE), the considerations related to the formation of a polymer network formed by the swelling of the polymer in the bitumen phase (Figure 2-35) are applicable also in this case (6).

Among the thermoplastic elastomers, the Styrene-Butadiene-Styrene (SBS) block copolymer appears to be the most widely used followed by reclaimed tyre. On the other side, among the thermoplastic plastomers, Ethyl Vinyl Acetate (EVA) and Polyethylene are used (4, 54).

In their work, Zhu et al., (3), provide a list of the principal polymer additives used in road applications giving some insights into their advantages and disadvantages.

Table 2-8 – Principal polymer additives used in bitumen modification (3)

Categories	Examples	Advantages	Disadvantages
Plastomers	Polyethylene (PE)	Good high-temperature properties. Relatively low cost.	Limited improvement in elasticity. Phase separation.
	Polypropylene (PP)		
	Ethyl Vinyl Acetate (EVA)	Improved storage stability. Increased Rutting resistance.	Limited enhancement in elastic recovery and low-temperature properties.
	Ethylene Butyl Acrylate (EBA)		
Elastomers	Styrene Butadiene Styrene (SBS)	Increased stiffness. Reduced temperature sensitivity. Improved elastic response.	Compatibility problems depending on bitumen source. Low resistance to heat, oxidation and ultraviolet. Relatively high cost.
	Styrene Isoprene Styrene (SIS)		
	Styrene Ethylene Butylene Styrene (SEBS)	High resistance to heat, oxidation and ultraviolet	Storage instability problems. Relatively reduced elasticity. High cost.

Besides industrial polymers, recycled tyre rubbers such as Styrene-Butadiene-Rubber (SBR), and Natural Rubber are widely used (1). As shown in Table 2-8, the majority of the disadvantages of using polymer additives seem to be related to cost and compatibility (including storage stability). The aspect of compatibility has been discussed earlier in this paragraph. The considerations reported suggest that the problem of compatibility derives from the complex nature of both polymers and bitumen and the large variability in their composition.

Concerning the cost implications, it appears evident that introducing industrial polymers in neat bitumens increases the cost of materials and the processes involved in their usage. However, these considerations have to be brought under the perspective of cost-effectiveness and not of cost only. That is, "*What is the advantage of using polymer additives in bituminous mixtures?*" The benefit of using polymer is the improvement of the rheological response of the bitumen in the mix.

Several studies based on Accelerated Pavement Testing (APT) and full-scale sections have highlighted the benefits of using polymers in delivering performing, lasting, and cost-efficient pavements (95-101). In terms of performance, polymer modification is proven to improve fatigue resistance, rutting resistance and low temperature cracking resistance (96, 97, 100, and 101) of HMA layers. The enhanced pavement life is a consequence of improved performance. Cost efficiency is based on a study conducted by the Asphalt institute that asserted through Life Cycle Cost Analysis that the use of Polymer Modified Asphalt (PMA) allows a cost-saving between 4.5% and 14.5% compared to unmodified mixtures (98). Besides this a work by Timm et al., (99), highlighted that Heavy Polymer Modified Mixtures allow a reduction in the average thickness of HMA. However, once the cost-efficiency of polymer modification is evaluated, the need of polymer concentrations to achieve adequate performance has to be taken into account.

Nevertheless, the use of polymers additives with road bitumens still shows limitations and drawbacks that still limit the widening of their usage. Among these limits, the concerns of durability and ageing resistance are critical.

2.7.3 Use of cross-linking agents in polymer modification

Superior performances of PMBs are achieved under satisfactory quality of modification which is the result of thermodynamic and chemical interactions (§2.7.1). PMBs are materials whose equilibrium depends on the compatibility of the phases. In the case of prolonged exposure at high temperatures (e.g., 150°C-175°C), the two phases can undergo separation due to low compatibility. As a consequence, the storage stability a fundamental property of PMBs that affects their performance, including durability. An unstable PMB is not durable.

The stability of the polymer system is critical in the case of elastomers whose effects on the bitumen response are correlated to the capability of the polymer in forming a networked structure in the bitumen phase (cross-linking). For example, SBS copolymer, although it is widely used, seems to be susceptible to separation once exposed to high temperatures.

One of the methods used to induce the formation of a polymer network has been the use of cross-linking agents. Several studies show the advantages of cross-linkers on the performance of PMBs (6, 178, and 182).

Sulphur has been used and investigated as a cross-linker for the modification of bitumens, mainly when SBS is used (168, 179-182). When added as a cross-linker during mixing, sulphur cross-links the polymer molecules promoting the polymer networking, and links through chemical bonds (i.e., sulphide and disulphide) the polymer to the bitumen (improving the stability) (179). More specifically, sulphur seems to react with the alkene moieties in the SBS, creating chemical bonding with the bitumen molecules with consequent enhancement of stability (182).

The applicability of sulphur to PMBs has generally been investigated under the perspective of storage stability to develop appropriate procedures for their production. However, its effects on the rheological properties and the oxidative resistance of PMBs remain relatively unclear

(178, 180). Concerning the oxidative resistance, the amount of work conducted appears to be too limited to draw a general conclusion (35, 168, 180, and 185). For this reason, in this work, the oxidative resistance of SBS/sulphur modified bitumens has been carefully investigated.

2.8 Thermo-oxidative degradation of polymers

One of the methods followed by researchers in studying oxidative ageing in PMB is to evaluate the degradation of the polymer alone, and then to highlight the differences compared to the degradation of the polymer phase occurring in PMB. For this reason, a brief description of the degradation mechanism occurring in polymers needs to be given.

The polymer chain reacts with oxygen causing the deterioration of the polymer backbone with a consequent reduction in the molecular weight. Although the term polymer degradation is well accepted and widely used, ASTM defines polymer thermal decomposition as the process where large chemical species change caused by heat (240).

However, besides heat, thermal decomposition of polymers may also proceed by an oxidative process where the decomposition is accelerated by oxidants (e.g., air and oxygen), and the presence of oxygen decreases the decomposition temperature. For this reason, the evaluation of a precise decomposition rate becomes quite difficult (130).

Several studies (131-138) have shown that the thermal decomposition of polymers is affected by the presence of oxygen. Additionally, in the case of thermoplastic polymers (e.g., SBS), besides oxygen, other factors that as molecular weight, weak linkages before thermal damage, and radicals affect polymer decomposition. The presence of oxygen also affects the kinetics of the reaction. Therefore, the prediction of the kinetics of oxidation developed for neat bitumen becomes more complicated for polymer-modified bitumen (84).

Four main chemical mechanisms have identified in polymer decomposition (130):

- Random-chain scission – chain scission occurs apparently in random locations of the polymer chain.
- End-chain scission – individual monomer units are removed at the chain-end.
- Chain stripping – atoms or groups not part of the polymer chain (or backbone) are cleaved.
- Cross-linking bonds are created between polymer chains.

More than one of these mechanisms occur during polymer decomposition. For this reason, the chemical reaction occurring during polymer decomposition can be grouped into two main groups:

- The main chain reaction that involves a decrease in the molecular weight with the volatile formation and cross-linking, and
- Side chain or substituent reaction that involves the elimination and the cyclisation of the side chain of the polymer.

In thermoplastic polymers such as SBS, widely used in road application, the most common reaction mechanism is the breaking of bonds in the main polymer chain. This break may occur randomly in the chain or at the end of the chain. The random chain mechanism generates both monomers and oligomers (polymer with 10 or fewer monomer units) while the end chain mechanism generates the formation of a monomer and the process is known as unzipping. The creation of small units from the decomposition of the polymer chain causes a reduction in the molecular weight. This reduction has been widely observed during ageing polymer-modified bitumen. Cross-linking is another reaction that occurs and involves the creation of bonding between adjacent polymer chains (generally it occurs after some stripping).

Polymer decomposition includes four main steps: initiation, propagation, branching, and termination steps (130).

Initiation represents the first phase in the decomposition of a polymer. There are two types of initiation: random chain scission and end chain scission. The first involves the breaking of the bonds at random locations within the polymer chain while the second comprises the breaking of a single unit or a small group of units at the end of the polymer chain. However, in both cases, free radicals are produced.

The second step is the *propagation*; in this case, three different mechanisms seem to be observed: intramolecular H transfer, intermolecular H transfer and the third that includes unzipping, depropagation, and depolymerisation. In the first mechanism, a single atom of hydrogen is transferred within a single polymer chain with the formation of a radical and unsaturated polymer (a chemical compound containing carbon-carbon double bonds). The second reaction includes the transfer of a hydrogen atom from between two different polymer chains. In this case, the polymer becomes a radical that breaks up into unsaturated polymer and radical. In the third mechanism of propagation, no exchange of hydrogen atoms is observed while the reverse of polymerisation occurs (unzipping, depolymerisation).

Three main *termination* reactions are common: unimolecular termination, recombination, and disproportionation. The first mechanism is not possible since a radical cannot be removed from a polymer radical without the addition or the subtraction of at least one hydrogen atom while still satisfying the valence requirements of the atom. Recombination represents the reverse of the random chain scission, and it is generally likely to occur. In the third mechanism, a hydrogen atom transfers from one radical to another. The hydrogen donor forms a double bond, and the acceptor is fully saturated. If this reaction occurs immediately after an initiation reaction, no unzipping or other propagation reaction occurs, and the polymer decomposition is a random process of bond scissions.

Based on the results included in the studies discussed above, it appears that the degradation of the polymer occurs predominantly within a range of temperature characteristic of production and placing of HMA mixtures. However, the effect of oxidation below 70°C, which is more applicable for a pavement, should be considered in the study of the effect of polymer degradation on properties of long-term aged polymer-modified bitumen.

2.9 The mechanism of ageing in PMBs

One of the advantages required of polymer modification is to increase the durability of asphalt mixtures. However, although there are several benefits recognised for polymers, the increase in durability, intended as enhanced oxidative (ageing) resistance, still does not receive full consensus.

The mechanism of ageing in polymer-modified bitumen is a complex phenomenon that does not allow drawing of general conclusions such as observed in unmodified bitumen. Advocating a unique mechanism might not be appropriate due to the large variability in the composition of bitumens and polymers. The variability of the bitumen composition is intrinsic of the bitumen itself as a secondary product of crude distillation. It has been widely shown that the different bitumen fractions (SARA) interact diversely with atmospheric oxygen. The variability in polymer composition leans on the fact that polymers are industrially manufactured products pursuing different scopes and functions, and thus, they are constituted of different elements (i.e., atoms, molecules, monomers). Therefore, different polymers have different interactions with oxygen and with the other factors that cause degradation. In light of this, the mechanism of ageing in PMBs could be identified as a function of the polymer considered. In any case, even such an approach is unlikely to be straightforward due to the complex polymer-bitumen interactions.

The reason behind the complexity of the ageing phenomena is that the bitumen phase and the polymer phase seem to undergo different ageing mechanisms, and each phase affects the ageing mechanism of the other. The bitumen phase undergoes oxidation (§2.6.1), while the polymer phase undergoes thermo-oxidative degradation with the polymer chain being damaged by heat and oxygen (19, 20, 24, 121, 129). It appears evident that the response of aged PMBs depends on the interactions of such mechanisms.

Furthermore, considering oxidative ageing as a unique contribution to the changing of the modified bitumen properties while in-service, represents an oversimplification of the long-term mechanisms that occur in PMB. Besides oxidation, the effect of the stability of the bitumen-polymer system has to be considered on the long-term performances and, recent studies have highlighted that also the Ultra-Violets rays (UV) contribute (38, 125, 169, and 170). However, before combining all these factors, each mechanism still needs to be studied through a stand-alone (i.e., factor by factor) approach to avoid premature excessive complexity.

Despite the complexity of the problem, the mechanism of ageing in PMBs has captured the attention and the work of a large number of researchers. However, in the works conducted, there are several limitations in the approaches followed.

Such limitations are have been discussed by various authors (3, 27, 126 - 128), and refer to:

- First, the traditional laboratory methods used to simulate STA and LTA in the laboratory (i.e., TFOT, RTFO and PAV), were calibrated on unmodified bitumens (27, 128). As a consequence, they may not provide the same expected effect on PMBs, and their applicability may not be representative of real conditions (126-127).

- Second, field testing lacks reproducibility due to the presence of uncontrollable factors and requires long experimental time to achieve relevant variations in the response.

Consequently, the conclusions related to the anti-oxidative performances of PMBs are sometimes contradictory and the results unclear. Besides the limitations of the ageing protocols followed (i.e., laboratory, or real scale), this work considers another limitation in the works conducted so far, the rheological characterisation (34, 35). In the majority of the work analysed, the ageing indexes, intended as the ratio of a measured property at unaged condition versus the same aged-property, are evaluated through empirical properties (i.e., penetration), viscosity, or linear viscoelastic properties. As it is widely discussed in §2.10.2 and §2.10.3, empirical test methods and linear viscoelastic characterisation may not be representative of the field response of PMBs. Therefore, the conclusions drawn supported by these results are not convincing and do not find a clear correspondence with the field performance of pavements.

The considerations above are meant to identify the difficulties and the main shortcomings in the assessment of the durability of PMBs to support the need for future research on this topic. However, the findings from the works analysed help to detail and enhance the understanding of what has been simplistically defined to as "degradation of the polymer phase, oxidation of the bitumen phase, and their interaction".

2.9.1 Introduction to the conducted research

If the understanding of the effect of "time" on the response of asphalt mixtures dates back to the 30's prompted by the application of compositional test methods (i.e., fractionation methods) (74), the oxidative resistance of PMBs attracted its deserved interest in the beginning of the 80's (3, 122). The reason for this is that the use of polymer additives in road application started to become popular two decades after the end of the Second World War (1) prompted by the advantages discussed in §2.7.1.

As anticipated in §2.8, the bitumen phase and the polymer phase undergo different ageing mechanisms: bitumen oxidation, and polymer degradation. The two mechanisms have been studied separately. As widely discussed in §2.6.1, the study of oxidative hardening of bitumens has been (and still is) of considerable interest in research. On the other hand, the thermo-oxidative resistance of polymers has been and still is of substantial interest for the polymer industry.

However, in PMBs, the two mechanisms co-occur. In other words, the bitumen does not oxidise alone, and the polymer does not degrade alone. Isolating the two mechanisms is quite tricky. For this reason, the changes in the composition of PMBs with ageing have been studied through the comparison between the changes occurring in unmodified bitumens and those occurring in the same bitumens once the polymer is introduced. The oxidative mechanism of bitumen has been studied at different scales, from the molecular scale level to the mechanical response level. Therefore, the effect of polymers can be observed from the molecular level (i.e., the formation of carbonyl compounds or sulfoxide) to the mechanical response (e.g., change in the viscoelastic properties). This concept is outlined in Figure 2-36.

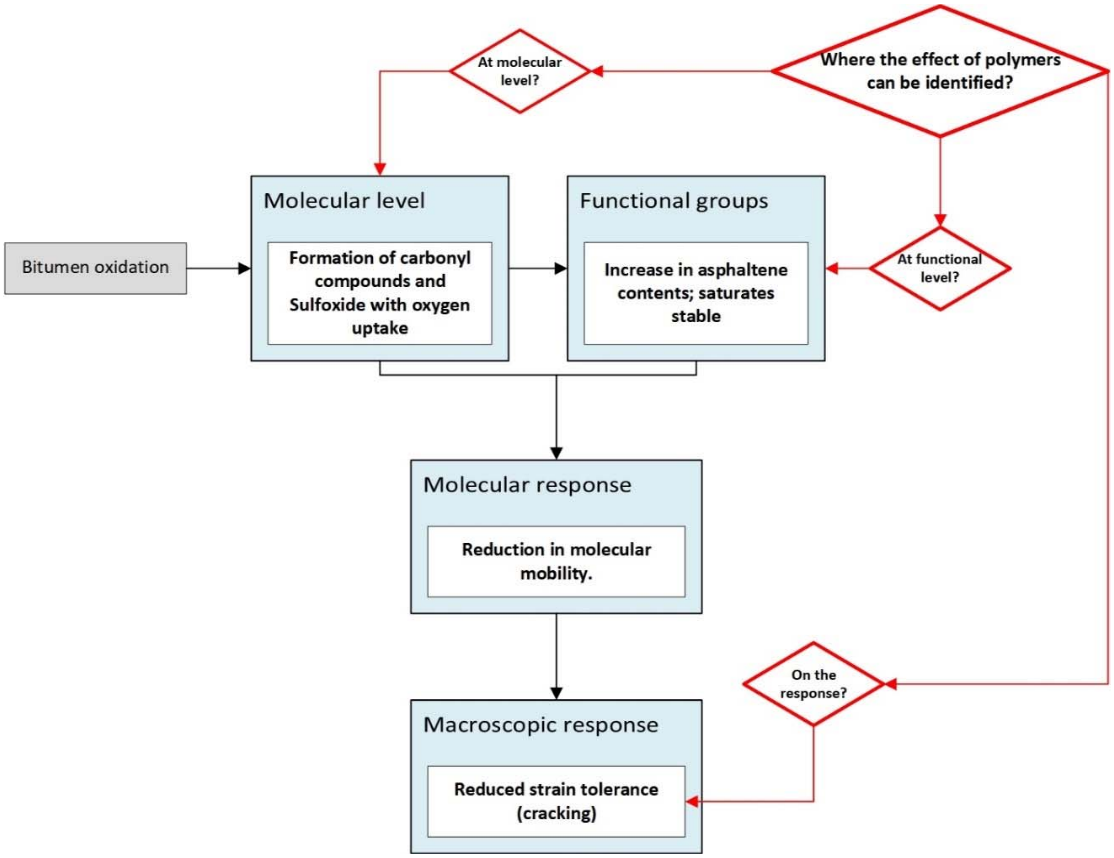


Figure 2-36 – Understanding the effect of polymers on oxidative ageing of bitumens.

Bitumen oxidation is a chemical phenomenon caused by atmospheric oxygen. The formation of carbonyls and sulfoxides with oxygen uptake produces the formation of heavier functional groups (i.e., asphaltenes) characterised by stronger molecular interactions. The increased bond strength reduces the molecular mobility stiffening the bitumen and reducing the strain tolerance. The understanding of the role of polymers in this mechanism requires identification of where the polymer produces an effect. Does it have anti-oxidative properties, reducing the formation of carbonyls and sulfoxides? Does it mitigate the formation of asphaltenes through the interactions with the other bitumens functional groups? Alternatively, does its decomposition soften somehow the mechanical response of the PMBs? Several works have tried to respond to these questions.

However, as mentioned previously (§1.1, §2.8), the identification of a unique mechanism applicable to different polymers may not be advocated due to the differences in their composition and due to the complexity of the polymer-bitumen interactions.

Despite this, the effects of the major polymers on the oxidation of bitumens at molecular, functional and mechanical levels have been investigated. According to the NCHRP 9-10 Project (2), in the United States, the road authorities use polymer modification to improve the ageing resistance of bitumens. The polymers used are mainly the SBS, Styrene Butadiene Rubber (SBR) and EVA. On the other hand, SBS is widely used in the European market (4, 50). The following sections include the relevant findings on the oxidative resistance of PMBs modified with SBS and EVA. It is worth mentioning that due to its extensive usage in comparison with other polymers, SBS has been subjected to a large number of studies and investigations in comparison with the other polymers. As a consequence, the sections, including the results of EVA, refer to a synthesis of the important studies available.

2.9.2 Effects of ageing on the composition of SBS modified-bitumens

Although SBS copolymers are widely used in polymer modification, their effects as ageing-inhibitor additives are not well defined. Despite this, numerous road authorities use SBS to enhance the ageing resistance of bitumens (2).

As discussed above, the effects of polymers on bitumen oxidation can be studied considering the changes (with ageing) in the molecular composition, in the functional groups and the mechanical response.

The first includes the study of the effects of SBS on the formation of carbonyls and sulfoxides with oxygen uptake. Various authors have compared the growth in carbonyl compounds (using FTIR) in unmodified, and SBS modified bitumens to evaluate the anti-oxidative effects of the polymer (18, 19, 20, 22, 54, 141, 142, 177). Negulescu and co-workers (22) used infrared spectroscopy (FTIR) to evaluate the sensitivity to oxidation of SBS modified bitumen at different levels of PAV ageing. As the PAV exposure rises, a substantial increase in carbonyl content was observed with the polymer acting as an oxidative-inhibitor agent. Therefore, the increase in carbonyl compounds observed in the bitumen-polymer system is caused mainly by the degradation of the polymer backbone with the bitumen phase being to some extent protected. The researchers observed that, in the case of SBS, the degradation of the polymer backbone is due to the reaction between the allyl group (CH_2) adjacent to the C=C double bond within the polybutadiene segment that readily reacts with oxygen at a temperature higher than 100°C increasing the content of carbonyl species (Figure 2-37).

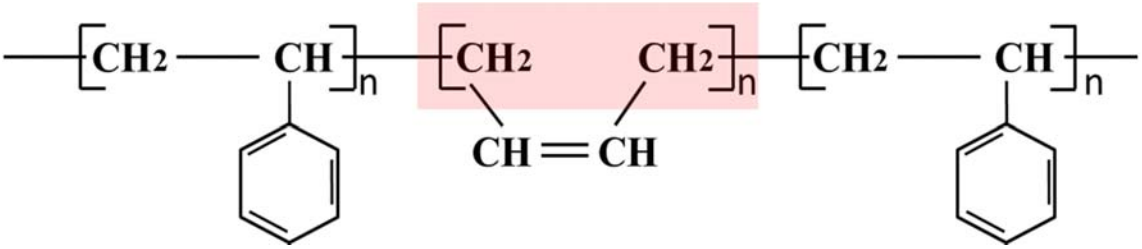


Figure 2-37 - Allyl group of SBS copolymer.

Liu and Isacsson (18, 19) observed that SBS has an anti-oxidative effect in sulfoxides formation. In other words, the polymer reduces the formation of sulfoxides. While the effects on the formation of carbonyls were dependent on the polymer and its concentration. Similar conclusion seems to be drawn by Tabatabei, who observed a lower increase in carbonyl groups in the bitumen phase for SBS modified bitumen after PAV (141). The SBS mitigates the formation of carbonyls and sulfoxides in the bitumen phase, acting as an anti-oxidant agent. The polymer interacts with the oxygen in place of the bitumen molecules. The main consequence of this interaction is the degradation of the polymer backbone that, as discussed in §2.8, occurs randomly or in the terminal portion of the polymer chain.

Researchers have documented that the oxidative susceptibility of SBS copolymer depends on the existence of unsaturated double bond in the Polybutadiene segment (20, 22, 137, 138, and 144). The existence of the double bonds of Polybutadiene segment (Figure 2-37), makes the SBS copolymer sensitive to light, heat, and oxidation.

For the sake of completeness, before continuing the discussion on oxidative degradation, it is worth mentioning that the UV-susceptibility of SBS modified bitumens is gaining attention. It is believed that UV light has a significant role in the degradation of the polymer backbone. For this reason, there are recent works that adopt the use of weathering machines that are capable of laboratory simulation of the combined effect of UV radiation and oxidation (125, 169, and 170).

Like Butadiene Rubber, SBS is prone to yellowing crosslinking and hardening, especially under ultraviolet irradiation which impacts its performance. In their experiment, Xu et al (137), conditioned SBS polymer at 30°C for 3 minutes and then heated it to 120°C at 5°C/min and then thermally oxidised it for 2 hours at 120°C. The reaction was monitored with FTIR, and the infrared spectrum was recorded every three minutes. The authors concluded that the thermal oxidation of SBS mainly occurs on butadiene blocks, while styrene does not show any relevant changing. However, although the polymer chain undergoes degradation, the size of the remaining segments remains sufficient to retain the expected rheological properties. These same conclusions were confirmed by using the GPC technique.

Cortizo et al conducted an interesting study with the scope of identifying the differences in the oxidative mechanisms of different SBS copolymers (i.e., having different architectures) once they are oxidised alone (pure polymer degradation) versus their oxidation in the bitumen phase (23). The polymers were introduced into a rotating flask submerged in an oil bath at a temperature of 180°C for different time exposures, while the PMBs were aged in the RTFO and the PAV. Pure polymer degradation and the ageing of the polymer phase in PMBs show some interesting differences. In the first case, cross-linked products are mainly formed, that is the polymer alone tends to cross-link. In the second case, free radical reactions produce chain scission and radical addition to some bitumen components.

A study based on infrared microscopy conducted by Mouillet et al has shown that the polymer rate (the presence of polymer as measured by the microscope), increases with ageing in the bitumen phase while it decreases in the polymer phase (177). Therefore, it appears that the smaller polymer fragments (originated by the degradation of the backbone) tend to be homogenised in the bitumen phase. It has been hypothesised that the fragmentation of the polymer backbone is linked to the oxidation of the alkene in the polybutadiene block.

Based on the evidence provided, it appears that the SBS copolymer is sensitive to oxidation because of the presence of the double carbon bonds in the Allyl group of the Polybutadiene segment (Figure 2-37) that appears to be prone to interaction with the oxygen instead of the bitumen (phase) molecules. Therefore, if the anti-oxidative effect is considered under the perspective of mitigating the formation of carbonyls and sulfoxides in the bitumen phase, the SBS results in being a sacrificial antioxidant agent. The term “sacrificial” is meant to indicate that the interaction with the oxygen (at >100°C) causes the cleavage of the polymer chain. Such a degradation (or decomposition) reduces the effect of the polymer on the expected rheological response in proportion to the level of degradation achieved by the polymer. The more the polymer fragments are “damaged”, the less the polymer maintains its properties. The degradation of the polymer chains is observed through Gel Permeation Chromatography as well. Those authors that have used such method have observed in aged SBS modified bitumens a reduction of the peak intensity in correspondence to the retention time interval of the polymer phase (17, 18, 20, 23, and 24). An example is given in Figure 2-38.

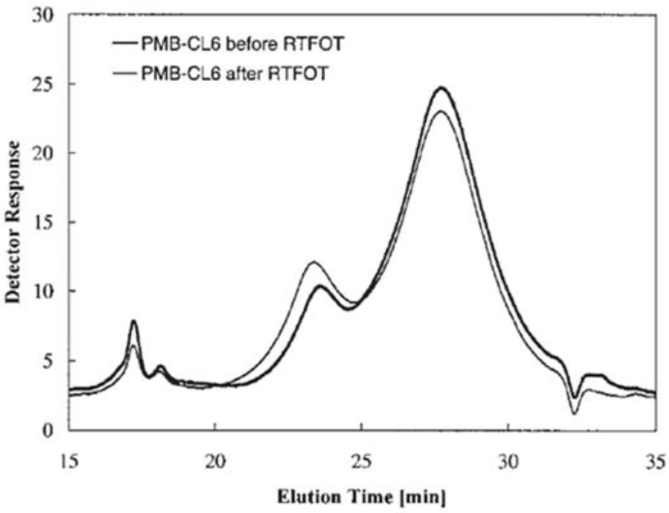


Figure 2-38 – Chromatograph of SBS modified bitumens before and after RTFO ageing (18).

Although the GPC provides gravimetric information only (it refers to the size of molecules only), the observed reduction in the peak intensity in the polymer phase is significant since the mass is a relevant property of polymers (94). This analysis allows concluding that the polymer phase is damaged. The challenge is to define the extent of damage and how much the damage affects the rheological response.

Besides the study of the formation of carbonyls and the MWD, the study of the changes in the microstructure of PMBs has been conducted in more recent years by using powerful microscope technologies such as Atomic Force Microscopy (AFM) (125, 171). These studies include the variation of the bitumen microstructure with ageing by studying the different types of structure displayed by the surface of samples. An example of the variation in the structures with weathering-time exposure of a Performance Grade (PG) 76-22 bitumen is given in Figure 2-39 (125).

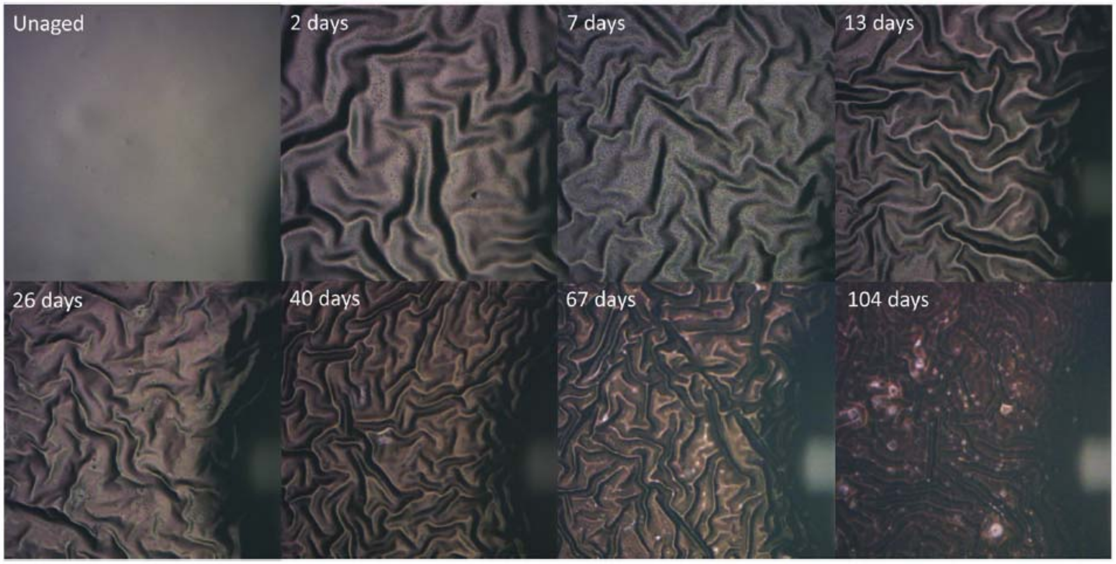


Figure 2-39 – Changes in the microstructure of a PG 76-22 bitumen at different weathering exposure times measured using the AFM (125).

At present, these results are at the early stage and require further investigation.

The uncertainty of the level of damage occurring in the polymer backbone is behind the lack of consensus (and clarity) on the anti-oxidative effects of SBS used in PMBs (1-3, 18-23, 142, 143, and 168).

Some supporting considerations to this statement are given below.

1. The anti-oxidative effect of SBS on the formation of carbonyl and sulfoxide is a sacrificial process where the polymer chain undergoes damage (or decomposition). Therefore, the fact that the polymer mitigates the formation of such polar molecular compounds is not necessarily an advantage, but the level of degradation which the polymer chain undergoes needs to be considered.

2. However, measuring the damage level of the residual (after ageing) polymer backbone is very complex, especially if compositional test methods (i.e., FTIR, GPC) are used. Therefore, there might be some cases where the polymer backbone, although

degraded, is still capable of performing as expected. In this case, the effects of SBS can be considered beneficial. On the other hand, if the effects of the polymer (or of the residue of its backbone) are not as expected, the effect of SBS on the oxidative resistance is of concern.

3. Rheological test methods can be used to evaluate the integrity of the polymer chain. From this perspective, it is clear that the rheological characterisation needs to be conducted within a strain-domain representative of the bitumen phase in mixtures. The strain levels used need to be sufficient to mobilise the polymer backbone introducing slippages in the chains. Under this condition, the effects of the polymer (and of its degradation) on the rheological response can be identified.

4. Oxidation is very sensitive to temperature. The majority of the test methods used in the laboratory represent accelerated procedures where higher temperatures (sometimes unrealistically high) temperatures are used to expedite the degradation. The use of such high temperatures, although representative of the short term ageing, may not be representative of the oxidative field conditions.

As mentioned at the beginning of §2.8, the study of the effect of “time” on PMBs is more recent than that conducted on unmodified bitumens. Therefore, the effects of ageing on the PMBs fractions (Saturates, Aromatics, Resins, and Asphaltenes) are not well documented. However, besides studies of the formation of carbonyls, there are works that use asphaltene formation to define rational ageing indicators (22, 25, 26).

As discussed in §2.6.1, oxidative ageing modifies the proportions of the bitumens’ functional groups inducing an increase in heavy and polar components (i.e., asphaltenes). The saturates fraction remains stable at ageing. Resins and aromatics decrease to form asphaltenes. Such a scheme “simplistically” describes the changes in the proportions in the bitumen components. The term simplistically is used since it is unclear which components are truly transformed in asphaltenes. Therefore, it is assumed that both transform in asphaltenes.

As reported in §2.7, while blending at high temperatures, the polymer swells into the bitumen phase by absorbing the light oily fraction. As a consequence, the presence of polymer affects the distribution of the SARA components. Nevertheless, the works referenced in this document conclude that the asphaltene portion increases despite the presence of the SBS polymer. Following the approach discussed at the beginning of this section, which is to compare the changing occurring in unmodified bitumens with those observed once the polymer is included, it can be concluded that the changes in the asphaltene portion might not be indicative of the effects of SBS on the oxidative mechanism in PMBs.

In this section, several works on the effects of the SBS modification on the changes in the composition of PMBs with oxidative ageing have been discussed. There are precise pieces of evidence that the Polybutadiene segment of the SBS chains undergoes degradation due to the combined effect of temperature and oxygen. Such degradation releases free radicals. Part of the radicals cross-links, while the other part links with some bitumen components. The degradation of the polymer chain seems to retard the bitumen oxidation reducing its contribution to the rheological response. The presence of damage in the polymer chain identified through the FTIR and the GPC, however, makes identifying its extent arduous. The effectiveness of the remaining polymer needs to be evaluated through dedicated rheological test methods.

2.9.3 Rheological characterisation of aged SBS modified bitumens

As introduced in §2.8, the investigation of the effects of polymers on the ageing mechanism of PMBs includes the comparative analysis of the same mechanism (e.g., the formation of carbonyls) occurring in bitumens in the presence and the absence of the polymer. The same approach has been followed in the investigation of the rheological response.

The effects of ageing on the physical response of unmodified bitumens are reported in Table 2-7, which is here reported to ease the description of the effects of SBS.

Table 2-9 – Table 2-7 (bis).

Parameter	Change in response with ageing
Penetration	Decreases
Softening point	Increases
Viscosity (different types)	Increases
Complex Shear Modulus (G*)	Increases
Phase angle (δ)	Decreases
Temperature susceptibility	Decreases

In the case of PMBs, besides the parameters reported in Table 2-9, ductility has been measured as well.

The applicability of the empirical test methods may not be appropriate to highlight the real effects of polymers in PMBs. However, several works have considered the effects of SBS on the retained penetration and the variation of the softening point with ageing (20, 21, 23, 24, 141, 161, and 162). As observed in unmodified bitumens, penetration at 25°C increases with ageing in SBS modified bitumens as well. On the other hand, ductility and softening points increase with RTFO and PAV ageing. Therefore, the consistency of SBS modified bitumens increases as observed in neat bitumens. However, besides considerations in terms of relative comparison as “increase” or “decrease”, the traditional empirical methods do not enable further and more detailed considerations.

Bitumen viscosity has been a parameter widely investigated to evaluate the effects of ageing on flow properties. In the case of unmodified bitumens, viscosity increases with ageing due to the changes in the microstructure that reduce molecular mobility. In the case of SBS modified bitumens, viscosity increases with ageing as well. However, the changes in the viscosity are not as marked as those observed in control unmodified bitumens. The limited gain in viscosity with ageing seems to be due to the degradation of the polymer chains that compensates for the hardening of the bitumen phase (122, 164).

Furthermore, based on the work of Cortizo et al, SBS architecture affects the increase in viscosity with ageing (23). That is, SBS copolymers with similar molecular weights but with different structures, undergo different thermo-oxidative degradations providing a different effect on the viscosity. However, the applicability of the viscosity as an indicator of the oxidative resistance of PMBs is of concern. That is, the viscous effect that mitigates the increase in the viscosity might not be indicative of higher oxidative resistance (164).

Therefore, the measure of viscosity provides the first insight into the combined effects of bitumen hardening and SBS degradation with the latter seeming to mitigate the former. Considering this scenario, it appears that the changes occurring in the polymer phase and in the bitumen phase provide opposite effects on the flow properties. Although this consideration is based on the viscosity, the viscoelastic characterization of aged SBS modified bitumens has led, in some cases, to similar conclusions.

The study of the complex shear modulus and the phase angle of aged PMBs started in the late ‘80s once the application of rheology DMA to road bitumens became popular. A valuable approach to the problem is followed in the PhD work of Airey (24, 45) and the study of Cotte and Such (129). This approach considers the PMBs (in this case SBS and EVA), as a biphasic system constituted of a bitumen-rich phase and a polymer-rich phase (§2.7). The two phases undergo different ageing mechanisms.

The bitumen-rich phase does not deviate from the age-hardening shown by unmodified bitumens.

On the other hand, the ageing of the polymer-rich phase is linked to the breakdown of the molecular structure of the SBS copolymer that leads to the formation of a polymer substructure with lower molecular weight. This transformation results in increased viscous behaviour in the time-temperature domain dominated by the polymer.

The differences in the ageing of the two phases have been evaluated through black diagrams that represent the norm of the complex modulus versus the phase angle conducted at different temperatures. The polymer-rich phase controls the response at high temperature (40°C in the work of Airey). In this domain, a more viscous (dissipative) behaviour is observed with ageing, in comparison with a more elastic (storage) behaviour shown by the unmodified bitumens.

On the other hand, in the range of temperatures below 40°C, the ageing in the bitumen-rich phase is more dominant and the ageing in this phase does not deviate from the ageing mechanism observed in the unmodified bitumens that, besides stiffening, shows a reduction in the phase angle. This mechanism is reasonable because the effects of SBS on the mechanical response are more visible in the range of high pavement temperatures where the polymer network is expected to maintain sufficient levels of stiffness and elasticity. Therefore, if the polymer undergoes degradation, the response of the PMBs in the range of high temperatures (low frequency) is affected by the loss in integrity of the polymer backbone. The magnitude of the range of temperature is a function of the polymer.

The time-temperature dependency of the mechanical response of aged SBS modified bitumens has been discussed in the works of Lu and Isacsson (18, 19). Their conclusions are aligned with those drawn by Airey and Cotte & Such. By studying SBS modified bitumens after RTFO ageing, degradation of the polymer backbone was observed, and this was more evident at higher polymer concentration (i.e., 6% SBS). Moreover, they concluded that the application of ageing indexes based on the complex shear modulus and phase angle might not apply to PMBs due to their time-temperature dependency. That is, the two parameters show different trends with ageing depending on the time-temperature domain considered.

The works discussed above were throughout the ‘90s. In the subsequent decades, several authors have focused on the mechanisms occurring in SBS modified bitumens, by including their rheological response, by following different approaches (20 -22, 34-37, 121, 143, 165-167).

These works include different test methods to measure the rheological response of SBS modified bitumens. Ruan et al investigated the effect of long oxidative exposure (i.e., 6 months at 60°C) on different PMBs, including SBS modified bitumens (121). Besides the analysis of the changes in the bitumen stiffness, the researchers evaluated the changes in the temperature susceptibility and the activation energy measured as parameters of the master-curve. Oxidative ageing seems to reduce the temperature susceptibility of unmodified bitumens and PMBs. On the other hand, the changes in the activation energy seem to be affected by the presence of the SBS. Under ageing, unmodified bitumens show an increase in the activation energy, while in the case of SBS modified bitumens, the activation energy is lower in aged PMBs.

In the work of Negulescu et al, besides the traditional linear viscoelastic parameters, the effect of ageing on the cross-over temperature (Tc) (measured at 10 rad/sec) was measured

(22). The results show that SBS modification increases the cross-over temperature (as expected), and oxidative ageing produces an increase in Tc as well.

However, the works analysed do indicate the presence of a unique ageing mechanism and do not draw any definite conclusion on the benefits of SBS as an anti-oxidative additive.

However, there is a consensus on concluding that the polymer backbone undergoes thermo-oxidative degradation with the polymer losing its structure. Such degradation has been considered, in some cases, as beneficial since it provides a viscous effect that helps in compensating for the bitumen hardening, thus retaining the rheological properties with time (20, 21).

Several authors claim that polymer degradation is expected to occur at an early stage in the pavement life or once the PMB is exposed to high temperatures during storage and construction. In their work, Lu et al studied the effect of ageing in SBS modified bitumens used in the construction of porous asphalt pavements (20, 21). It was found that the decomposition of the polymer occurs during production and early in the pavement life. Moreover, their results show that polymer-modified bitumen aged uniformly throughout the pavement thickness in the first two years (under the same air voids); then the bitumen in the top layer aged more. The study of Urquhart (165), investigated the effects of thermal storage on the chemical composition, the physical properties and field performance of PMBs containing two percentages of SBS (3.5% and 6.0%). Results show that after a prolonged period of storage at 180°C, the SBS polymer breaks into smaller fragments. In the case of PMB with 6% SBS, the effect of polymer degradation resulted in a reduction of conventional bitumen properties as consistency, stiffness at 25°C and elastic recovery with the increase of storage time.

On the other hand, 3.5% SBS PMB showed a different trend. Even though the polymer in both PMBs was degrading during storage, there was no change in the wheel tracking performance of mixtures for storage periods up to five days. However, results on mixture performance show that polymer degradation does not necessarily worsen road performances.

As previously mentioned, the results of the rheological characterisation conducted in the LVE region are unlikely to provide a definite conclusion. This characterisation may not be representative of actual bitumen performance related to durability. Despite this, the works that provide a performance-based characterisation of aged PMBs (including SBS modified bitumens) are still limited (34-37).

Hintz et al investigated the effects of laboratory-simulated ageing on the fatigue resistance of PMBs (including SBS) using the Linear Amplitude Sweep (LAS) test (37). Results show that the effect of ageing on the cumulative damage resistance of bitumens depends on the level of strain to which the bitumen is exposed. It seems that ageing provides a dual effect. On the one hand, it increases the capacity of the material to maintain integrity with damage. On the other, it reduces the strain tolerance. The combination of these two effects influences the fatigue resistance of bitumens as a function of the strain level considered. In the case of high low strain levels, ageing seems to be beneficial to the fatigue resistance. On the other hand, at higher strain levels, oxidative ageing worsens the performances. The range of strain at which these trends are observed depends on the bitumen.

Other authors have focused on the effects of ageing on the rutting resistance using the MSCR test (20, 34-36, 168). In this test, the effects of the polymer phase, especially in the case of elastomers, is visible in the strain recovery. Results have shown that the strain recovery decreases with ageing due to the degradation of the polymer backbone. On the other hand, the effects of ageing on non-recoverable compliance are a function of different parameters such as the polymer concentration.

The content discussed in this section leads to the following considerations:

1. The application of empirical test methods (i.e., Penetration and Softening point) to aged SBS modified bitumens (and general PMBs) is not representative of the effects of the polymer on the oxidative mechanisms of PMBs. The bitumens analysed in the works show an increase in consistency with ageing, as shown by unmodified bitumens.
2. The SBS modification seems to mitigate the increase in viscosity produced by oxidative ageing. However, the applicability of viscosity to calculate representative ageing indexes is of concern since the reduced increase in viscosity is due to the thermal degradation of the polymer backbone that might contribute to retaining the viscosity without necessarily acting as an anti-oxidative additive.
3. The linear viscoelastic characterisation highlights the time-temperature dependency of the effects of ageing on the complex shear modulus and phase angle. In the high-temperature domain, the degradation of the polymer backbone causes a more viscous (under cyclic loading) response in aged SBS modified bitumens than in unmodified bitumens. In the intermediate and low-temperature domain, the bitumen-rich phase of PMBs controls the response and SBS modified bitumens age similarly to unmodified bitumens. Therefore, the calculation of ageing indexes based on linear viscoelastic parameters should account for time-temperature effects to be representative of aged SBS modified bitumens. Besides this, as discussed in §2.6.3.3, there is a lack of a parameter representative of the effects on the PMBs' durability under the simultaneous changes in the phase angle and complex shear modulus occurring with ageing.
4. The degradation of the polymer chain is recognised by rheological test methods, and there are several pieces of evidence that this occurs at an early stage in the pavement

life. However, LVE characterisation cannot provide an explicit and conclusive finding on the effect of SBS on the durability of PMBs. Performance test methods that operate at higher strain levels and a higher number of cycles might help. However, their application is still limited.

2.9.4 Ageing in EVA modified bitumens

As anticipated in §2.9, the study of the effect of ageing on EVA modified bitumens has not received the same focus to as SBS. However, this shortcoming is not related to ageing only, the rheological characterisation and the understanding of bitumen-EVA interactions are unlikely to be completely understood (9). In the majority of the works conducted, the EVA polymer was studied with to other polymers, while a dedicated study as those undertaken with SBS is missing (24, 34, 129, 164, 173-177). However, results from the research conducted show that ageing provides similar effects on the rheological response of EVA modified bitumens to those observed with SBS.

Airey and Brown followed the same testing protocol as the one used with SBS (24). The results from empirical test methods on aged EVA modified bitumens, do not show substantial deviation from the mechanism observed in unmodified bitumens.

The findings from the DMA have been analysed considering the response of the PMB within different temperature ranges. As observed in the SBS, in the ranges of temperatures where the polymer-rich phase is dominant, the changes of rheological response are affected by the degradation of the polymer phase. In this work, the chemical changes occurring in the polymer-rich phase were conducted through Differential Scanning Calorimetry (DSC). The polymer phase undergoes ageing by changes observed in its semi-crystalline region where the polymer melts and recrystallise.

A detailed study on the composition of unaged and aged EVA modified bitumens was conducted by Mouillet et al (177). Their study includes (besides the physical characterisation), the use of the infrared microscope and the FTIR. The first provides the changes in the nodular micromorphology (Figure 2-40).

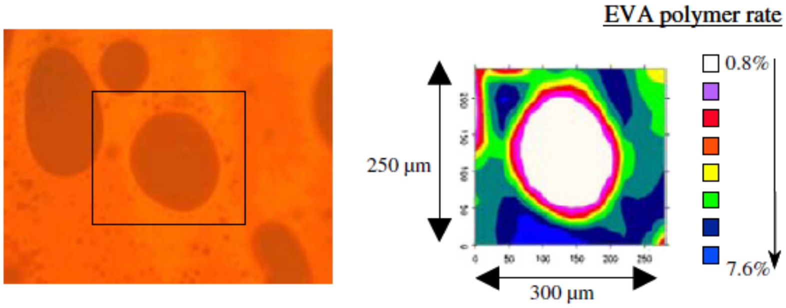


Figure 2-40 – Example of nodular micromorphology EVA modified bitumens (177).

This analysis focuses on the level of swelling of the polymer phase into the bitumen phase and its variation after RTFO + PAV exposure. After the laboratory simulated ageing, the polymer is observed to de-swell, with its level of dispersion throughout the bitumen phase that diminishes. This mechanism is observed through the comparison of the polymer concentration in the polymer phase (identified concerning the wave number interval) and in the bitumen phase (same concept). The “de-swelling” is displayed through a reduction in the polymer concentration from the bitumen phase (where it is dispersed) that leads to an increase of EVA concentration in the polymeric phase.

The partial “de-swelling” of the polymer might be due to the increase in the asphaltene content, and a decrease in the aromatics (occurring in the microstructure of the bitumen), that leads to reduced compatibility between the EVA chains and the bitumen molecules. The effects of aromatics and asphaltenes on the compatibility between bitumen and EVA chains were studied by Lu and co-workers (176). Higher storage stability in the case of bitumens with high aromatic and low asphaltene content was observed. Therefore, the final remarks related to the reason for the “de-swelling” of the EVA polymer with ageing appear reasonable. Besides the infrared microscopy, the work of Mouillet et al included the spectral analysis of the aged bitumens using the FTIR. In this case, the trends of the carbonyl and sulfoxides indexes increase with ageing. Besides the variation in the carbonyls and sulfoxide contents, the level of aromaticity in the bitumen and the polymer phases were measured. The aromaticity in the polymer phase results in increasing, while in the bitumen phase, the opposite occurs. This mechanism provides supportive insights into the loss of compatibility between the EVA chain and the bitumen molecules. The higher aromaticity of the chemical species in the polymer phase reduces the compatibility with the EVA chains. Therefore, the reduced compatibility of these chemical species leads to their expulsion to the bitumen phase. This “migration” leads to the “de-swelling” of the EVA.

The authors hypothesised a similar conclusion to that of Airey and Brown, where the reduced swelling of the polymer might be due to the crystallisation of the polyethylene phase. However, this conclusion resulted in being less plausible due to the thermal history of the samples.

Other authors (129, 173-175), have been focused on the rheological properties of the EVA modified bitumens, including ageing as one of the parameters considered. The relevant findings that have surfaced from these works are mainly related to the interaction between the polymer and the bitumen and remark as follows:

- The dispersion of the EVA in the bitumen phase depends on the polymer content and the affinity between the EVA and the base bitumen. Higher polymer concentrations provide a wider dispersion.

- The rheological properties of the EVA modified bitumens depend on the capability of the polymer of influencing the response. Such a capability improves with the dispersion and the affinity with the base bitumen.
- The rheological response of aged EVA modified bitumens does not deviate significantly from that of unmodified bitumens. Aged bitumens show an increased stiffness and a reduced phase angle.

The interactions between the EVA and the base bitumen depend on their compatibility. The more they compatible, the more the polymer is capable of swelling by absorbing the most compatible species. Oxidative ageing does not seem to produce pure degradation. What is more convincing to occur is a de-swelling with the polymer phase that reduces its dispersion. Such a de-swelling might be caused by the increase in aromaticity of some of the chemical species included in the bitumen that was initially absorbed by the polymer, and are subsequently expelled due to the reduced compatibility.

The rheological characterisation does not highlight any relevant changes compared to those observed in the SBS (under the same test methods).

However, besides the findings discussed a comparison with the magnitude of the works conducted on the SBS polymer highlights that there is much room for improving the understanding of the effects of EVA on the properties of PMBs (including the oxidative resistance).

2.10 Rheological characterisation of bitumens

Rheology has been defined as “the study of flow and deformation of materials” (91). The application of rheology to road bitumens has been conducted over the decades to determine the properties representative of their mechanical response under different conditions. In road applications, bitumens are exposed to a range of temperatures that varies from – 50°C to 180°C. During plant and paving operations, bitumens are exposed to temperatures varying from 140°C to 180°C. In the field, the range of pavements temperature can vary from -50°C to (about) 80°C depending on local conditions. Determining a single parameter that is representative of the mechanical response of bitumens under such different conditions, might not be that accurate. Furthermore, the outcomes of the materials characterisation are a function of the level of knowledge and the available measuring techniques.

The characterisation of road bitumens started more than one century ago, and throughout the decades, the testing methods have undergone continuous enhancements. At the beginning of the 19th century, in the absence of test methods, bitumens were inspected through tactile methods or by chewing. It is evident that such an approach provided a qualitative assessment of "consistency".

Afterwards, the Penetration and Softening point tests were introduced (7). Although introduced more than one century ago, these tests are still used in local specifications. Nowadays, rheological measurements are conducted through advanced pieces of equipment as rheometers that allow the materials characterisation over a wide range of temperature and loading. Although appealing, a detailed dissertation on the advancement of material testing in bitumen technology is out of the scope of this thesis. What has to be kept in mind is that the characterisation of bitumens (as with other materials used in engineering applications) should aim at measuring fundamental engineering properties (i.e., stiffness, strength, elasticity, and others). These properties are usually (and maybe simplistically) defined as "design properties".

This concept is critical in the field of application of this thesis that is based on a fundamental question:" *Can the same rheological indicators characterise unmodified and polymer-*

modified bitumen bitumens?" In other words, it is essential to understand whether the properties selected for unmodified bitumens to control the pavement distresses (§2.3) apply to PMBs as well. In particular, this thesis focuses on the assessment of the effect of oxidative ageing on the mechanical response. Therefore, the purpose is to understand whether the rheological indicators used to evaluate the effect of ageing on unmodified bitumens can be applied to PMBs as well.

Before discussing this, the fundamental bases applicable to the response of unmodified bitumens and polymer-modified bitumens are discussed in the following sections.

2.10.1 Viscoelastic materials

Several authors have approached the problem of viscoelasticity. This work refers mainly to two authors that provide a very rigorous and fundamental approach to the description of the theory of viscoelasticity: John D. Ferry (92) and Roderick Lakes (90).

In viscoelastic materials, the relation between stress and strain is a function of time. More specifically, the constitutive equations show deviations from the two ideal mechanical models developed in the 17th century: the Elastic Solid ("*Theory of Elasticity*", Robert Hooke – 1678); the Viscous Liquid ("De Principia", Sir Isaac Newton – 1687).

The elastic solid and the viscous liquid represent the categorisation of the ideal solid and the ideal liquid (Figure 2-41).

Elastic solid $\tau = G \cdot \gamma$ (2-7)

Viscous fluid $\tau = \eta \cdot \frac{d\gamma}{dt}$ (2-8)

Figure 2-41 – Elastic Solid, spring – Equation (2-7); Viscous Fluid, Dashpot – Equation (2-8).

The mechanical response of the elastic solid is represented by Equation (2-7) where:

- τ is the shear stress [F/L^2];
- G is the stiffness modulus (Shear Stiffness) [F/L^2];
- γ is the shear strain [1];

As shown in Equation (2-7), the stress is proportional to the strain applied, but it is independent of the strain rate. Additionally, the strain is recoverable, and there is no time lag between the stress removal and the strain recovery. That is, the strain is produced and recovered instantaneously.

The mechanical response of purely viscous (or Newtonian) liquids is described by Equation (2-8) where:

- τ is the shear stress [F/L^2]
- η is the viscosity [(F/L^2)*time]
- $\frac{d\gamma}{dt}$ is the shear strain rate [rad/sec];

In the purely viscous (or Newtonian) fluid, the stress is proportional to the strain rate, but it is independent of the strain itself. The coefficient of proportion is the viscosity (η) that represents the resistance to the accumulation of permanent flow in a fluid. The viscous flow is non-recoverable. In the case of pure Newtonian behaviour, viscosity is independent of the strain rate. Two types of deviations from the Newtonian behaviour can be displayed by fluids that can be pseudo-plastic or dilatant (Figure 2-42).

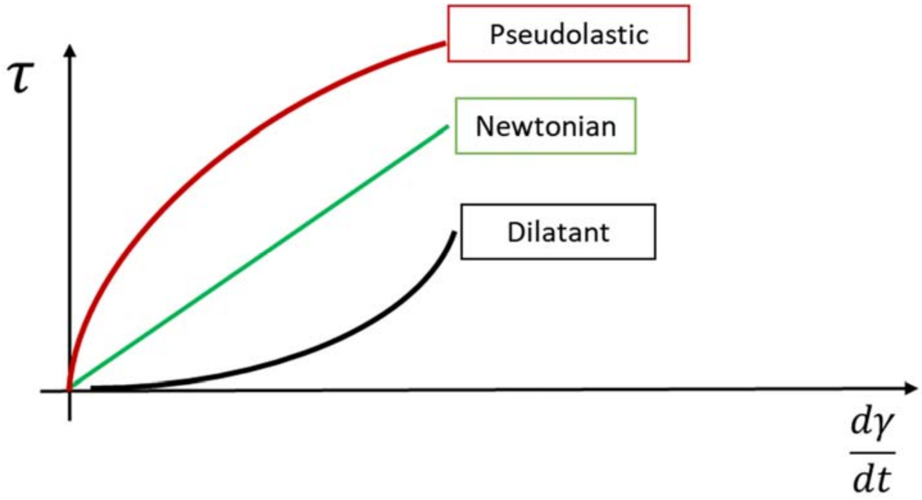


Figure 2-42 – Deviations from Newtonian behaviour.

In Pseudo-plastic fluids, the viscosity increases with the increase of the strain rate, while in dilatant fluids, the viscosity decreases. The deviations from the pure Newtonian behaviour are functions of hydrodynamic interactions between the fluid particles. These interactions depend on the intensity of the shear rate and the magnitude of the particles' interactions.

The shear strain (and strain rate) are provided in this representation because they are the well-applicable when studying viscoelastic bodies since they can be applied to liquid-like and solid-like bodies. Furthermore, the application of this type of strain produces variations in the shape of the body without any change in volume.

Besides the elastic solid and the viscous fluid, there is a third fundamental behaviour defined as plastic behaviour for which, the strain is time-independent, and it is completely unrecoverable.

The elastic solid and the viscous fluid represent ideal mechanical categorisation of materials. However, many solids approach elastic behaviour under infinitesimal strain, and many liquids approach Newtonian behaviour under infinitesimal strain rate.

Since these are idealisations, real solids and liquids show two types of deviation from such behaviours:

1. In the case of application of finite strain, the stress and strain relation becomes non-Hookean (e.g., yield tension exceeded in a solid). In the case of application of finite strain rate, many fluids as polymeric solutions exhibit marked non-Newtonian behaviour (Figure 2-42).
2. Even in the application of infinitesimal strain and strain rate, the response of the materials can combine solid-like and liquid-like characteristics. Solid-like materials (imperfect solid bodies) show creep under constant stress and show stress relaxation under a constant strain. On the other hand, fluid-like materials while flowing under constant stress may store some energy instead of dissipating in heat the overall energy content. Additionally, once subjected to sinusoidal loading, stress and strain show a time lag, that is, they are not in phase (i.e., elastic solid) nor out of phase (i.e., viscous fluid). Therefore, under sinusoidal applied loading, they show energy storage and dissipation.

Materials that show the second type of deviation are defined as *viscoelastic*. Therefore, viscoelastic materials are those materials whose relations between stress and strain are a function of time. In the case of infinitesimal strain and strain rate, and stress-strain-time relations explicated by 1st order differential equations with constant coefficient, the materials are *linear viscoelastic.*

Sinusoidal cyclic loading has been widely used in the characterisation of viscoelastic materials (including bitumens), due to their practical applicability. Additionally, in the case of creep tests, the application of instantaneous strain (or stress) remains somehow conceptual since it is affected by several practical limitations. Besides the instantaneous strain (recovered or applied), also the measure viscoelastic strain, that is recoverable if a "sufficient" long time e is provided, has several practical repercussions. That is, complete recovery or relaxation are challenging to achieve.

2.10.1.1 Time-temperature equivalency

Viscoelastic materials have been described as materials whose stress-strain relations deviate from purely elastic and purely viscous behaviours as a function of the loading time. Besides loading time, the test temperature affects their response. More specifically, between the glassy-like region to the rubbery-like region, the effects of the temperature on the viscoelastic response are impressive with the retardation and relaxation times rapidly decreasing with the temperature increasing (92).

As per their definition, viscoelastic materials show stress-relaxation under a constant applied strain. The stress relaxation is a function of molecular rearrangement processes. The faster the molecules are capable of rearranging, the more rapidly the stress is relaxed. Therefore, the nature of the viscoelastic spectra arises from the tendency of the molecules to restore the configuration with the highest level of entropy available. Entropy (or conformational entropy) can be defined as the availability of a system to display different configurations. The capability of the molecules to rearrange depends on their mobility (i.e., Brownian motion), and the temperature is a measure of the molecular mobility.

If the molecular processes contributing to viscoelasticity are equally affected by a temperature rise (or decrease), the relaxation function can be given by the following form.

$$E(t, T) = E(\xi, T_0) \tag{2-9}$$

Where:

- E – is the relaxation modulus;
- t – is time;

- $T-$ is temperature;
- T_0 – is the reference temperature that can be arbitrarily selected;
- $\xi-$ is defined as the reduced time that is calculated by Equation (2-10).

$$\xi=\frac{t}{\alpha_T(T)} \tag{2-10}$$

Where $\alpha_T(T)$ is defined as shift factor and it is a function of the material and the selected reference temperature ($\alpha_T=0\ if\ T=T_{ref};\ \alpha_T>0\ if\ T<T_{ref};\ \alpha_T<0\ if\ T>T_{ref}$). The temperature dependence of the shift factor should be determined experimentally. There are different forms of shift factor available. Detailed discussions on the different forms available are provided in the work of Yusoff et al (202) and Rowe et al (204).

In this case, relaxation times should have the same temperature dependence. Materials that obey to this principle are defined as thermorheologically simple for which the time-temperature superposition (TTSP) principle is applicable (90).

Thus a change in temperature from T to T_0 corresponds in a shift in the domain of frequency that can be calculated by Equation (2-11).

$$f_{rid}=\alpha_{T_0}(T)\cdot f \tag{2-11}$$

Where f_{rid} is defined as reduced frequency.

This superposition allows the horizontal shift of experimental curves obtained at different temperatures to a single composite curve related to a reference temperature arbitrarily selected. This curve is defined as master curve and merges the domains of temperature and frequency (or time) into the domain of frequency (reduced frequency) alone.

The applicability of TTSP principle can be verified through three different criteria (92):

1. The shape of the master curve should match the shapes of the adjacent curve into the tolerance limits;
2. The same values of α_T should superimpose (when possible) all the viscoelastic functions;
3. The temperature dependence of the shift factor must have a reasonable form consistent with experience.

Whenever the validity of one of these criteria is not verified, the TTSP breaks down.

Materials constituted of multiple phases having different temperature susceptibilities of their viscoelastic response are not thermorheologically simple. For instance, crystalline polymers and composite materials do not meet the TTSP, while several amorphous polymers appear to be thermorheologically simple.

Moreover, if part of the material undergoes phase transformation (e.g., melting or freezing) within the test temperature interval, such material not thermorheologically simple (90). This consideration is critical once applied to PMBs.

There are several concerns on the applicability of the TTSP to heavily modified bitumens (high polymer content – e.g., 6%), to bitumens having a high asphaltenes content, and to bitumens with a high wax content (45). In these types of bitumen, the microstructure is heterogeneous and shows the coexistence of different phases, materials, and molecular bonds. For this reason, the applicability of the TTSP needs to be carefully investigated.

2.10.1.2 Linear viscoelastic response under oscillatory loading

This section details the linear viscoelastic response of road bitumens subjected to oscillatory loading. In the case of bitumens, sinusoidal stresses and strains are applied, in the range of intermediate and high temperatures through the dynamic shear rheometer (DSR - Figure 2-43).

Figure 2-43 – Dynamic Shear Rheometer (DSR – Anton Paar® Physica Modular Compact Rheometer 301).

The DSR is widely used in different fields (e.g., polymer, milk and chocolate industry). The DSR is used to conduct the dynamic mechanical analysis of the bitumens by applying different types of loading at different temperatures. In the case of Linear Viscoelastic (LVE) characterisation, the DSR is used in the parallel plates geometry configuration (Figure 2-44).

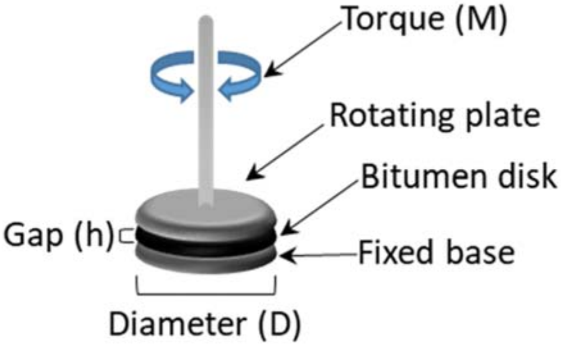


Figure 2-44 – Scheme of DSR parallel plate geometry.

The top plate is connected to the measuring system, and it applies to the sample a torque (M) capable of providing the required shear strain and shear stress. On the other hand, the bottom plate (base) is fixed and does not rotate.

As seen in Figure 2-44, the plate configuration is characterised by the plate diameter (D) and the gap (h). The test can be conducted in controlled-stress mode or controlled-strain mode.

In the case of bitumens, tests are conducted at controlled temperature and level of sample ageing. Once pure torque is applied (as assumed in the DSR testing), the (shear) stress and (shear) strain vary with the distance from the centre, as shown in Figure 2-45.

(a) (b)

Figure 2-45 – Stress (a) and Strain (b) distributions in a circular plain section subjected to pure torque.

The maximum stress and strain are found to be at the edge of the sample and are calculated by Equations (2-12) and (2-13).

Maximum shear stress
$$\tau_{max} = \frac{16 \cdot M}{\pi \cdot D^3} \tag{2-12}$$

Maximum shear strain
$$\gamma_{max} = \frac{\theta \cdot D}{2 \cdot h} \tag{2-13}$$

The significance of the symbols in Equations (2-12) and (2-13) is given in Figure 2-44.

Oscillatory stress and strain histories are represented by sinusoid functions (Figure 2-46).

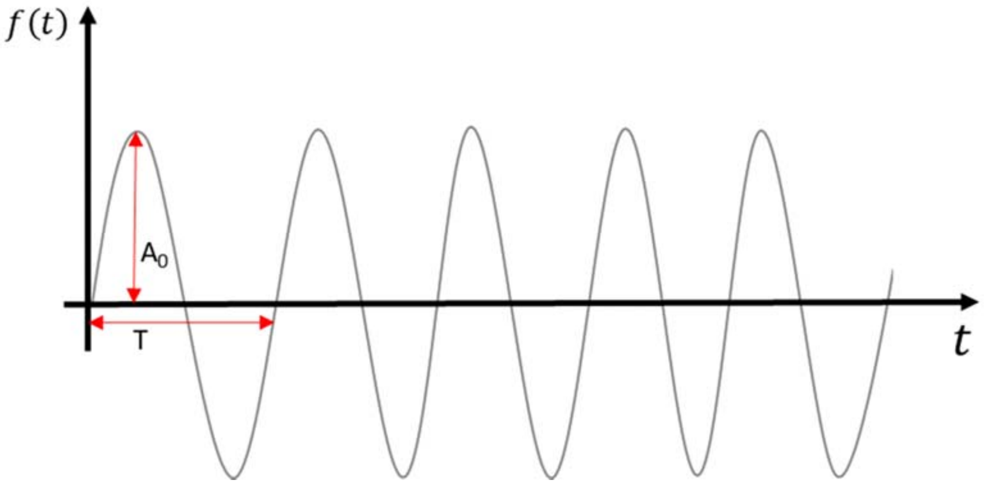


Figure 2-46 – Sinusoidal function.

The parameters characteristic of a sinusoidal function are:

- A_0 – signal amplitude;
- T – period (time interval between two consecutive identical phases of the signal);
- $f = \frac{1}{T}$ - frequency [Hz];
- $\omega = 2\pi f$ – Angular frequency [rad/sec].

As mentioned in §2.10.1, viscoelastic materials subjected to sinusoidal oscillatory loading show energy dissipation during loading. Because of this dissipation of energy, the stress and the strain sinusoidal are out of phase, that is, there is a time lag between stress and strain (90). A schematic representation of this phenomena in the case of sinusoidal applied strain is given in Figure 2-47.

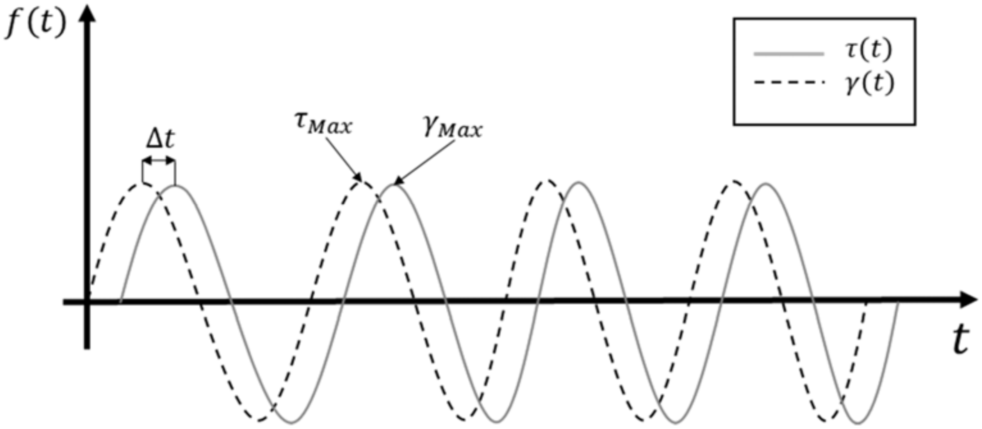


Figure 2-47 – Time lag (Δt) between stress and strain sinusoids

Equations (2-14) and (2-15) represent the variation of the intensities of the stress and the strain during a strain-controlled test conducted in the linear viscoelastic domain.

Stress $$\tau(t) = \tau_0 \cdot \sin(\omega t + \delta) \qquad (2\text{-}14)$$

Strain $$\gamma(t) = \gamma_0 \cdot \sin(\omega t) \qquad (2\text{-}15)$$

Where:

- τ_0 – is the amplitude of the stress sinusoid [F/L^2];
- γ_0 – is the amplitude of the strain sinusoid [rad];
- ω – is the angular frequency of the two sinusoids [rad/sec];
- t – is time [sec].
- δ – is the phase lag between the stress and the strain that is a function of energy stored and dissipated energy during the loading cycle. The phase (or phase angle) is calculated as a function of the time lag between the stress and the strain by Equation (2-16).

$$\delta = \omega \cdot \Delta t \qquad (2\text{-}16)$$

The significance of the parameters has been clarified above. The higher the time lag between the strain and the stress sinusoids, the higher is δ. As a consequence, the phase angle is a measure of the internal damping of the material. In the case of the elastic solid, the stress and strain are in phase, and the phase angle is equal to 0°. In this case, no energy is dissipated, but it is used for full strain recovery. In purely viscous fluids, the phase angle is equal to 90°, which indicates complete dissipative behaviour. In the case of viscoelastic materials (as bitumens) the value of δ ranges from 0° and 90° depending on temperature, loading frequency and ageing.

The complex notation is used once there is the need for representing oscillatory quantities where the phase has to be highlighted. Therefore, the dynamic stiffness can be written in complex notation as given by Equation (2-17).

$$G^*(\omega) = \frac{\tau^*(\omega)}{\gamma^*(\omega)} = \frac{\tau_0}{\gamma_0} \cdot e^{i\delta} \qquad (2\text{-}17)$$

In viscoelastic materials, the dynamic shear stiffness determined through sinusoidal oscillatory loading is defined as Complex Shear Modulus or Complex Modulus (G*). As a complex number, the Complex Modulus is composed of a real part and an imaginary part, as shown in Equation (2-18).

$$G^*(\omega) = G'(\omega) + iG^{"}(\omega) \qquad (2\text{-}18)$$

Where:

- G^* - is the Complex Shear Modulus;
- G' - is the in-phase component of the Complex Modulus defined as Storage Modulus;
- $G^{"}$ - is the out of phase component the Complex Modulus defined as Loss Modulus;
- i - is the imaginary unit ($\sqrt{-1}$)

Complex numbers can be represented as a vector (Figure 2-48).

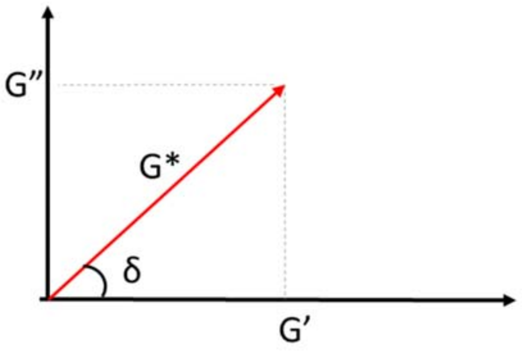


Figure 2-48 – Vector of Complex Shear Modulus

The norm of the complex modulus that is defined as Dynamic Modulus, and it is calculated by Equation (2-19).

$$|G^*| = \frac{\tau_{max}}{\gamma_{max}} = \sqrt{(G')^2 + (G")^2} \qquad \text{(2-19)}$$

While the ratio between the Viscous Modulus and the Elastic Modulus is defined as the Loss Tangent (of the phase angle) and it is calculated by Equation (2-20).

$$\tan\delta = \frac{G"}{G'} \qquad \text{(2-20)}$$

The two components of the complex modulus can be calculated as a function of the complex modulus (G*) and the phase angle (δ) by Equation (2-21) and (2-22).

$$G' = |G^*| \cdot \cos\delta \qquad \text{(2-21)}$$

$$G" = |G^*| \cdot \sin\delta \qquad \text{(2-22)}$$

The values of Phase Angle calculated as per Equation (2-16) and of Loss Tangent given by Equation (2-20), describe the amount of energy stored and dissipated during a loading cycle. The higher the phase angle, the larger is the dissipated energy. The Storage Modulus describes the amount of energy stored in each loading cycle, while the Loss Modulus describes the amount of energy dissipated. Storage Modulus, Loss Modulus, and Loss Tangent are a function of the loading frequency, the test temperature, and ageing.

As a consequence, in linear viscoelastic materials, the stiffness is represented by two fundamental parameters: the Complex (Shear) Modulus (G*), and the phase angle (δ). The first quantifies the overall capacity of resisting to loads. While the second is a measure of the internal friction of the material in terms of stored and dissipated energy during the loading cycles.

2.10.1.3 Representation of viscoelastic parameters

In pavement engineering applications the magnitude of the shear complex modulus (|G*|) and phase angle (δ) represent the response of bitumens under sinusoidal loading. However, there are different methods of presenting the norm of G* and the phase angle. Some of the methods are discussed below (45).

Isochronal plots

An isochronal plot is an equation or a curve on a graph that represents the variation of a viscoelastic function (i.e., |G*|, δ) at constant frequency or loading time. In the case of DSR measurements, an example of such representation may be given by the value of the phase angle measured at a fixed frequency under different temperatures.

Isothermal plots

An isothermal plot is an equation or a curve on a graph that represents the variation of a viscoelastic function (i.e., |G*|, δ) at a fixed temperature within a range of different frequencies. In the case of DSR measurements, a clear example of an isothermal plot is given by the variation of |G*| at different loading frequencies.

An example is given in Figure 2-49.

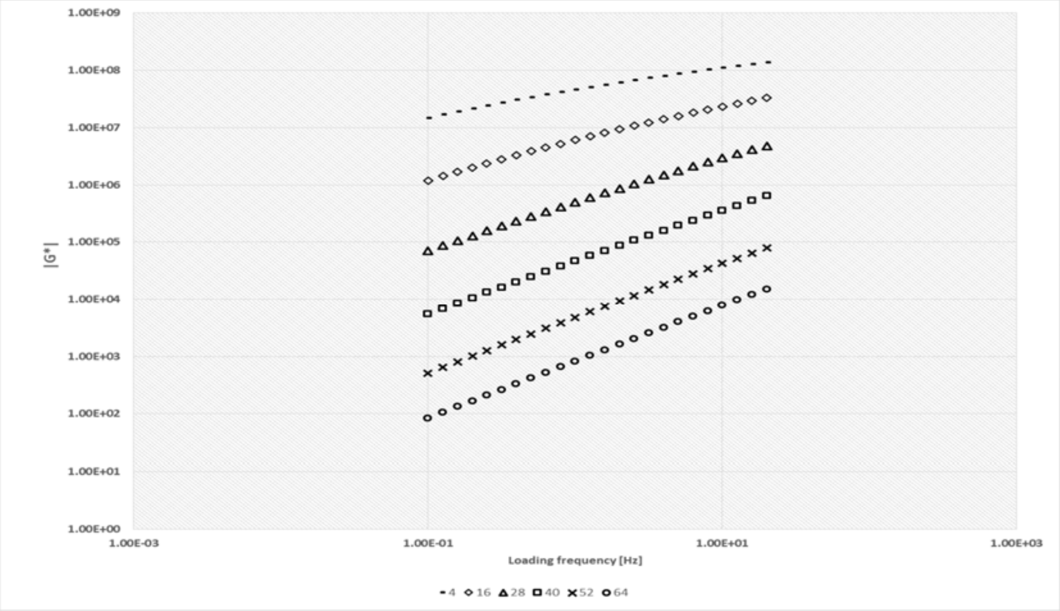


Figure 2-49 – Example of the isothermal plot from a frequency sweep test in DSR

Master curves

Due to the time-dependency of the viscoelastic response of bitumens (i.e., |G*| and δ), it is often convenient plotting the viscoelastic response over a wide range of frequency to gather a complete spectrum of the response. This curve represents the master curve of the viscoelastic function considered. The master curve is developed by conducting oscillatory measurements at different temperatures (over the same range of frequency) and combining the isotherms measured into a unique curve through the definition of a shift factor. This type of data manipulation can be conducted under the applicability of the time-temperature superposition principle (§2.10.1.1). The applicability of the TTSP raises concerns in the case of bitumens that show a complex structure. Examples of complex structures are heavily modified bitumens, bitumens with high wax content, with high asphaltene content or bitumens showing extensive oxidative levels (45).

Black diagrams

A black diagram is the representation of the variation of |G*| versus the phase angle (δ). Loading frequency and test temperature are not considered in this representation. It is essential to mention that a smooth black diagram highlights a satisfactory time-temperature equivalency; while a disjoined curve indicates the non-applicability of the TTSP. The latter can occur in the types of bitumen where the TTSP breaks down discussed in §2.10.1.1. One of the advantages of using black diagrams to plot LVE data is given by the fact that there is no need to conduct any TTSP manipulation of the data to gather comprehensive information on the viscoelastic response of bitumens.

Cole-Cole diagrams

A Cole-Cole diagram is the chart representative of the Loss modulus (G”) versus the Storage modulus (G’). The diagram represents the status of the balance between the dissipative and the storage character of the response under oscillatory loading without incorporating the effects of time (or frequency) and temperature.

2.10.1.4 Energy Storage and Dissipation

In linear viscoelastic materials, the stress and strain relations are given by Equations (2-14) and (2-15). Such equations represent the parametric equations of the elliptical Lissajous curve [91]. The elliptical shape of the stress and strain curve is typical of linear viscoelastic materials where the sinusoids of the stress and the strain are out of phase. In purely elastic solids (δ=0°), the ellipse collapses into a strain line. In purely viscous fluids, the ellipse converges in a circle (δ=90°). The ellipses of linear viscoelastic materials (0<δ<90°) range between these two different shapes (Figure 2-50).

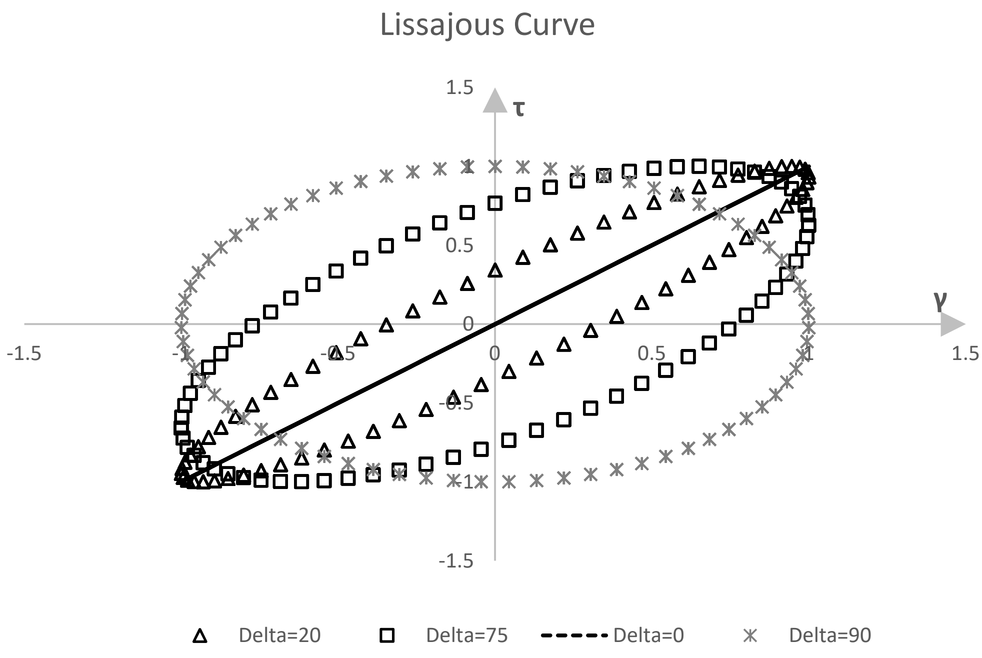


Figure 2-50 – Lissajous curves

A detailed interpretation of the Lissajous curves would be very important for the understanding of the response of linear viscoelastic materials under oscillatory loading. However, and in-depth interpretation may be not required considering the context of this work that focuses on the mechanisms of energy dissipations on which the Superpave Performance Grading criteria are based. Premised this, Lissajous curves have been introduced since the areas within the ellipse represents the energy per unit of volume dissipated the materials per cycle. The stored energy considered over a full cycle is equal to zero because the material returns to its original configuration. Therefore, to find the stored energy, it is necessary to integrate the equation of the dissipated energy over a quarter of cycle ($\pi/2$) as shown by Equation (2-23).

$$W = \int_0^{\pi/2\omega} \tau \cdot \frac{d\gamma}{dt} dt = \cdots$$

$$= \tau_{max} \cdot \gamma_{max} \cdot \left[\frac{\cos\delta}{2} + \frac{\pi \cdot \sin\delta}{4}\right] \tag{2-23}$$

In such equation:

- $\tau_{max} \cdot \gamma_{max} \cdot \left[\frac{\cos\delta}{2}\right]$ is the stored energy calculated over a quarter of cycle;
- $\tau_{max} \cdot \gamma_{max} \cdot \left[\frac{\pi \cdot \sin\delta}{4}\right]$ is the dissipated energy that vanishes once δ is equal to 0.

Combining Equations (2-21) and (2-23) the equation of the stored energy calculated over a quarter of the cycle is given in Equation (2-24).

$$W_s = \int_0^{\gamma_{max}} G'\gamma d\gamma = \frac{1}{2} G' {\gamma_{max}}^2 \tag{2-24}$$

As shown, the stored energy during the oscillation is proportional to the Storage Modulus (G').

The dissipated energy is proportional to the area within the ellipse. Therefore, the dissipated energy over a quarter of the cycle is proportional to one-quarter of the whole area.

$$W_d = \frac{1}{4} \int_0^{2\pi/\omega} \tau \cdot \frac{d\gamma}{dt} dt = \frac{\pi}{4} G" \gamma_{max}^2 \tag{2-25}$$

As shown in the equation above, the dissipated energy is proportional to the Loss Modulus (G").

Therefore, once external work is applied to the system, part of the applied energy is stored, while another part is dissipated in heat. The ration between the dissipated energy and the stored energy is proportional to the loss tangent given in Equation (2-26).

$$\frac{W_d}{W_s} = \frac{\pi}{2}\tan\delta = \frac{\pi}{2}\cdot\frac{G''}{G'} \qquad (2\text{-}26)$$

As a consequence, the loss tangent (and the phase angle) is a measure of the internal resistance of the materials and provides information on the tendency of the material to dissipate energy under oscillatory loading. Such a characteristic is significant, and it has been used in the definition of the criteria to control rutting and fatigue cracking of bitumens during the Strategic Highway Research Programme (SHRP) (66), and used in the AASHTO MP 1.

2.10.1.5 Superpave Performance Grading (PG)

As anticipated above, the theory of linear viscoelasticity discussed in the previous section has been applied to unmodified road bitumens for the definition of performance-based criteria to the rutting and the fatigue cracking resistance of road bitumens (§2.3).

The criteria were developed on unmodified bitumens, considering the following assumptions (2):

- Road pavements were designed to keep the strain level of the bitumen phase within the linear region (low strain levels);
- The bitumens investigated in the SHRP Programme show relatively a low strain dependency;
- The mechanical response of the bitumens is independent of film thickness and sample geometry.

The linear range can be defined as the strain interval where the measured stiffness is independent of the strain (or stress) applied. In the use of the DSR, the linear range is practically defined as the strain interval where the complex modulus ranges between the G* interpolated at 0 strain level (G_0^*) and the strain level at which G* is equal to 0.95 G_0^* (205, 234). A qualitative representation of the range of linearity is given in Figure 2-51.

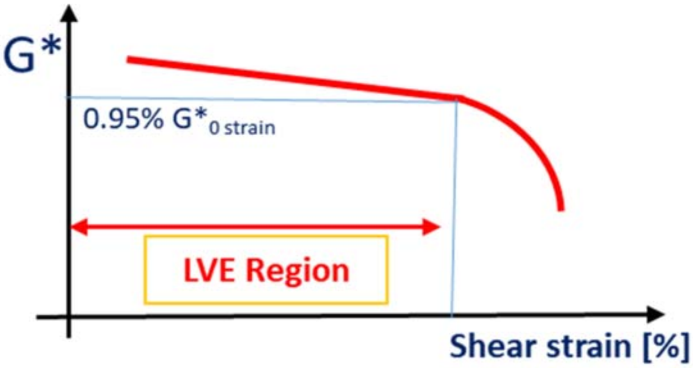


Figure 2-51 – Strain interval of linear viscoelastic response

In the SHRP programme, the definition of the limits of linearity of the bitumens investigated was undertaken as a function of the shear stiffness. The equations of the linear thresholds for the values of strain and stress applied are given below (33).

Strain limit of linearity

$$\gamma_{linear} = \frac{12}{(G^*)^{0.29}} \tag{2-27}$$

Stress limit of linearity

$$\tau_{linear} = \frac{0.12}{(G^*)^{0.71}} \tag{2-28}$$

The criteria used to control the bitumen resistance to rutting and fatigue cracking, are based on the limitation of the dissipated energy (Wd – Equation (2-25)) over the loading cycle. A schematic description of the theoretical development of the criteria is described as follows (66).

1. The application of external forces to a thermodynamic system (as the application of shear stress to road bitumens) coincides with the application of mechanical energy dQ. According to the first principle of thermodynamics, the energy cannot be

created nor destroyed, but it can be transformed. In this case, part of the applied energy dQ is stored, while another part is dissipated according to Equation (2-29).

$$dQ = dU + dW \tag{2-29}$$

Where:

- dQ is the mechanical energy applied to the system;
- dU is the part of the energy that is stored and recovered (Elasticity);
- dW is the part of the energy that is dissipated.

2. The definition of the criteria was based on the limitation of the dissipated energy (dW). Two main mechanisms cause the dissipation of energy: the accumulation of permanent deformation (viscous flow), and the formation of new surfaces (cracking). The second mechanism requires higher energy levels. In linear viscoelastic materials, the dissipated energy over an entire oscillation is given by Equation (2-30).

$$W_d = \int_0^{2\pi/\omega} \tau \cdot \frac{d\gamma}{dt} dt \tag{2-30}$$

3. Therefore, to limit the accumulation of permanent deformation and cracking, the dissipated energy shall be limited as much as possible. Two different formulations of the dissipated energy are given in the case of rutting (viscous flow) a fatigue cracking (cracking).
4. In the case of rutting, the pavement is exposed to high pavement temperature, and it is assumed that all the dissipated energy contributes to viscous flow only and no cracking occurs. Besides this, rutting is considered as a stress-controlled phenomenon, and consequently, the dissipated energy is given as a function of τ_{max} (Equation (2-31).

$$W_d = \pi \cdot {\tau_{max}}^2 \cdot \frac{1}{G^*/_{\sin\delta}} \tag{2-31}$$

Where:

- $G^*/_{\sin\delta}$ is the “rut factor” which represents viscoelastic parameter, measured in the linear region that is used to control rutting. Since the dissipated energy shall be minimised, the value of the rut factor shall be maximised.

HMA rutting is more likely to occur at an early stage in the pavement life where the bitumen is less oxidised (therefore it is softer), than after a prolonged field exposure where it becomes harder. For this reason, the AASHTO M 320 (236) prescribes to control the rut factor under the unaged condition and on the RTFO residue (after short term ageing). The specifications are given in Table 2-10 and shall be satisfied at the PG high pavement temperature (236).

Table 2-10 – Superpave PG grading at high pavement temperature.

Ageing Level	Applied Strain	Specification
Unaged	12%	$\left(G^*/_{\sin\delta}\right) \geq 1.00kPa$
RTFO	10%	$\left(G^*/_{\sin\delta}\right) \geq 2.20kPa$

5. In the case of fatigue cracking, it is assumed that at intermediate temperatures the dissipated energy contributes to the formation of cracks only, and no viscous flow occurs. Furthermore, fatigue cracking is considered as a strain related phenomenon that occurs in thin asphalt pavements. The formulation of the dissipated energy of linear viscoelastic materials under strain-controlled phenomenon is given by Equation (2-32).

$$W_d = \pi \cdot \gamma_{max}^2 \cdot G^* \cdot sin\,\delta \qquad (2\text{-}32)$$

Where:

- $G^* \cdot sin\,\delta$ is the viscous modulus (G''- Equation (2-22)) that is the viscoelastic parameter measured in the linear region considered to control fatigue cracking. According to Equation (2-32), to minimise the dissipated energy it is, necessary to minimise the viscous modulus.

Fatigue cracking occurs late in the pavement life (unless it is premature), therefore according to the AASHTO M 320 (236), the viscous modulus is controlled on the PAV residue. The specifications are given in Table 2-11 and have to be satisfied at the PG intermediate pavement temperature (236).

Table 2-11 – Superpave PG grading at intermediate pavement temperature.

Ageing Level	Applied Strain	Specification
PAV	1%	$(G^* \cdot sin\,\delta) \leq 5.0\ MPa$

The items discussed in this section show the principles of linear viscoelasticity applied to road bitumens for the definition of performance-based criteria. As aforementioned, one of the primary assumption considered in the development of such specifications is that the bitumen response remains in the linear region since pavements are designed to provide a sufficient bearing capacity. As discussed in the following section, it appears that the strains estimated in the bitumen phase of pavements approach levels that are significantly higher than those considered in the linear region. If such an effect might not be that relevant for unmodified bitumens, which show a limited strain susceptibility, in the case of PMBs such effect might cause noticeable consequences due to their non-linear response under loads. Therefore, the application of linear viscoelasticity in the definition of performance criteria of PMB is of concern. The next section introduces the limitations of the Superpave grading method applied to polymer-modified bitumens.

2.10.2 Rheological characterisation of PMBs

The definition of the Superpave testing protocol of bitumens was mainly focused on unmodified binders. Therefore, several properties of PMBs were neglected or did not receive an adequate focus (2, 38 – Ch. 2, pp.38-39).

The properties that were not accurately considered are:

- **Storage Stability** – PMBs are multiphase materials that can show problems of low compatibility leading to phase separation during storage at high temperatures.
- **Shear Rate Dependency of Viscosity** – PMBs can show non-Newtonian behaviour at mixing and compaction temperatures with consequent problems of reduced workability.
- **Strain Dependency of Rheological Response** – PMBs may show non-linear behaviour under stress and the strain levels experienced in pavements. Therefore, relying on LVE properties to estimate the contribution of binders to pavement performances can be misleading.
- **Effect of Mechanical Work** – Asphalt binders show Damage accumulation under repeated loading. The measure of the rheological response after a few cycles may not allow an evaluation of resistance to damage accumulation and the potential beneficial effects of polymer it.
- **Loading-rate dependency and time-temperature equivalency –** Modified binder may show loading frequency-dependency due to modification of the microstructure at different traffic speed., A direct measure of loading rate dependency is needed to estimate the contribution of bitumens on pavement performance

This work aims to evaluate the effect of ageing on the mechanical response of PMBs trying to overcome part of these shortcomings. In particular, the shortcomings tackled are the strain dependency of the rheological response and the effect of mechanical work. Before detailing the limitations of the LVE characterisation applied to PMBs, some considerations on the strain level experienced by the bitumen phase in mixtures, and on the sources of non-linearity in the response of PMB need to be discussed.

2.10.2.1 Non-linear response of PMBs

The understanding of the role of the bitumen phase in the response of mixtures requires the definition of the strain level to which it is exposed. The sentence “role of the bitumen phase in the response of mixtures” means the possibility of predicting (or investigating) the response of mixtures through the analysis response of the bitumen phase only. This aspect is relevant when polymer modified bitumens are considered due to their possible non-linear response. The strain level of the bitumen phase in mixtures has been investigated by various authors adopting different methodologies: Finite Element Modelling (FEM), Imaging Analysis and material testing (29, 31-39).

Results from these studies highlight that the majority of the bulk strain of mixtures is experienced by the bitumen phase rather than the aggregate phase, due to a large difference in stiffness between the two phases. Furthermore, the strain distribution within the binder is complex and far from being uniform. Localised high strain levels are caused by a lack of uniformity of the thickness of the bitumen film coating the aggregates and by localised aggregate rotations (31-33). Results from the FEM analyses highlight that the strain distribution within the binder phase is wide and depends on the ratio of the stiffness of the bitumen versus the aggregates, and the binder distribution in the mixture skeleton (39). Combining the results of imaging analysis and FEM, Bahia et al observed that, due to the reasons above, the strain level in the bitumen phase could be realistically assumed to be between 10 to 100 times the strains in the bulk mixture (29). This conclusion is in agreement with a work of Airey et al (33) focused on the study the strain distribution in the mixture scale, the bitumen scale, and the polymer network scale. Results show that the range of linearity of the bitumen scale is two orders of magnitudes larger than the mixture scale (0.01% strain in the mixture versus 1% strain in the bitumen). While the range of linearity of the polymer network is four orders of magnitude larger the range in mixtures (0.01% versus 100%). In other words, this means that the bitumen and the polymer phases can undergo non-linearity even at small strain levels in mixtures. In the majority of the cases, the strain levels achieved by PMBs goes beyond their linear limits.

Although the test methods used might show some limitations (e.g., limited resolution of the images), the authors concluded that the differences in the strain levels between the mix bulk and the bitumen are realistic, and that because of such localised strain concentrations, the bitumen can develop considerable strain even once the strain in the mix are small. If this aspect might not be that relevant for unmodified bitumens, the response of PMBs could be primarily affected. When the formers are extended, the molecules flow past one other without changing the morphology, and the response remains linear. In the latters, the strain (and stress) dependency derives from the fact that when the polymer chains are extended, glassy or crystalline regions and chain entanglement can produce the distortion of the morphology with a consequent change in their physical response (28). For this reason, the strains developed go beyond the linear limits for the majority of the PMBs investigated. The strain sensitivity of PMBs is a function of the type of additive, stiffness, temperature and frequency (29). One of the “macroscopic” consequence on the mechanical response might be represented by thixotropic effects with the stiffness decreasing under repeated loading (29).

The introductory part of this section mentions the possibility of predicting (or investigating) the response of the mixtures through the analysis of the response of the bitumen phase. The concepts discussed allow raising the conclusion that the strain limits of the Linear Viscoelastic characterisation may not be appropriate for PMBs due to their inability of highlighting the strain (and stress) dependency of the response of these materials.

2.10.3 Limitation of LVE characterisation of PMBs

The applicability to PMBs of the Superpave binder testing protocol has been widely investigated and, as highlighted in §2.10.2, various shortcomings were identified (2, 28-30, 40-42). The simplifications considered in the development of the PG grading method reduce its applicability to the majority of the bitumen additives (2). In other words, the application of the Superpave testing protocols to PMBs is unlikely to provide an adequate understanding of the role of the bitumen in the response of the mixtures. Furthermore, in the NCHRP 9-10 project, it was observed that although binders can show a similar linear viscoelastic response, the non-linear behaviour and the damage resistance varies significantly (2).

The majority of PMBs result being non-linear and susceptible to mechanical work. Furthermore, PMBs show high sensitivity to traffic speed, traffic volume, and stress and strain depending on the pavement structure (2, 41, and 42). These shortcomings derive mainly from two aspects. On the one hand, the reduced strain levels considered in the LVE characterisation do not allow determining the stress dependency of polymers. On the other, the limited number of loading cycles used to determine G^* and δ do not allow accounting for thixotropic effect or the effect of mechanical work that is very important to control the fatigue cracking resistance (28, 29). The strain dependency and the fatigue cracking resistance are very sensitive to the composition of binders, type of additives, ageing, temperature, heating rate, and the interaction of all these factors (29).

As detailed in §2.10.1.5, in the Superpave Performance the indicators selected to control the rutting resistance and the fatigue cracking resistance are measured in the linear region and are based on limiting the dissipated energy over the loading cycle. These criteria were developed on unmodified bitumens assuming that in the field the binder phase in mixtures would have experienced low strain levels because of well-designed pavements. The general shortcomings of this approach have been discussed in detail in §2.10.2.1.

The limitations of each parameter (i.e., rut factor in Equation (2-31)), and the viscous modulus in Equation (2-32) are given as follows.

2.10.3.1 Use of $G^*/sin\,\delta$ to control the rutting resistance of PMBs.

The basis and the assumptions of the applicability of the $G^*/\sin\delta$ factor to control rutting is given in §2.10.1.5.

The limitations of this approach are discussed as follows (2, 28, and 38).

- In the case of rutting, the whole dissipated energy is lost in viscous flow (damage) once it could be dissipated in more than one form. In viscoelastic materials, a significant part of energy could be dissipated in damping, which depends on the delayed elasticity proper of viscoelastic materials, and that is not necessarily damage. The use of cyclic loading with the complete reverse in strain or stress does not allow highlighting the difference between damping and viscous flow.
- Rutting occurs because of repeated creep, and there is no reversible loading. Therefore, reversible cycling loading might not be appropriate to rate bitumen contribution to the rutting resistance of mixtures.
- The strain domain of the bitumen phase in the mixture is larger than the strain level at which the bitumens are subjected in the DSR (i.e., 12% at unaged conditions, 10% at RTFO aged conditions). The low strain levels used in the linear region does not allow taking into

account the effect of the non-linearity in the response of PMBs that can show stress (or strain) dependency.

- The rut factor (i.e., $G^{*}/\sin\delta$) shows a weak correlation with mixture performances.

These considerations contribute to raising the concerns on the use of viscoelastic parameters to evaluate the effect of ageing on the rheological response of PMBs in the range of high pavement temperatures. Therefore, the MSCR test was developed to control the resistance to accumulating permanent deformation of PMBs.

In this work, the effect of laboratory-simulated ageing on the resistance to accumulating permanent deformation was conducted through the MSCR test method as per the AASHTO T350 test procedure (237). The details on the MSCR test are given in §3.3.7.

2.10.3.2 Use of (Viscous Modulus) to control fatigue cracking resistance of PMBs.

The basis of the applicability of the $G^{*} \times \sin\delta$ factor to fatigue cracking are discussed in §2.10.1.5.

Fatigue cracking in asphalt mixes is a complex load-related phenomenon. Some researchers believe that it is a mixture-related problem. Some others believe it is a structural problem of thin pavement; therefore, it is in the design of the pavement. However, there is consensus on considering that fatigue initiates and propagates in the bitumen phase of mixtures. The limitations of considering the viscous modulus for controlling the fatigue cracking resistance of bitumens are discussed as follows (2, 38, 40-43).

- The lack of ability of the viscous modulus in controlling fatigue cracking resistance depends on the fact that it is measured within the linear viscoelastic region at low strain levels. It is unlikely that it can provide information about the resistance under repeated loading and on the variation in the bitumen properties with damage accumulation.

- The use of a single strain level (i.e., 1%) does not allow considering the effect of the pavement structure.
- Linear strain levels may not be representative of the strain domain, which the bitumen phase undergoes in pavements (and mixtures). Furthermore, testing in the linear domain does not allow considering the non-linear response of PMBs under loading.
- Reduced number of loading cycles does not account for thixotropic effects and the energy dissipation in damage (i.e., microcracks).

The use of the viscous modulus to control fatigue cracking resistance of PMBs has been widely challenged since the late ’90s. To summarise the points discussed in the above paragraph, the main reason for which this parameter lacks utility is that the low strain levels and the reduced number of cycles used in the test do not allow measuring the damage resistance of bitumens. Therefore, dedicated bitumen test methods based on the concept of cumulative damage resistance have been developed (41, 42).

In this work, the effects of laboratory-simulated ageing on the cumulative damage resistance of PMBs have been evaluated through the Linear Amplitude Sweep (LAS) test method as per the AASHTO TP 101-12 Procedure (238). The details on the LAS test are given in §3.3.8.

2.10.4 Theoretical background of the MSCR test

The limitations of the rut factor $G^*/\sin\delta$ to control the rutting resistance of PMBs have been discussed in §2.10.3.1. The MSCR test was explicitly developed for PMBs with the scope of providing performance-based specifications blind to modification, representative of mixtures performances, and that represents a replacement for the Superpave binders’ high-temperature grade (2, 28).

Rutting can be defined as the excessive accumulation of permanent deformation in the wheel path under repeated heavy loading. It depends mainly on two mechanisms: densification and shearing deformation of one or multiple pavement layers (207). The first occurs in the case of insufficient compaction, while the second occurs in the case of well-compacted mixtures that have other deficiencies in the volumetrics. Such distress is, therefore, a load-related phenomenon that occurs at “macroscopic” levels of mixtures (bulk) strain. So, considering what discussed in §2.10.2, when rutting occurs, the bitumen phase is likely to approach the non-linear region, and in the PMBs can show a marked strain sensitivity in the response.

Creep and recovery tests allow controlling the stress (and the resulting strain) applied. The test was developed in such a way that the stress applied to the bitumen in the DSR would simulate the mixture conditions. The details of the development of the MSCR test are included in the work of D’Angelo et al., (28). However, the non-recoverable compliance (J_{nr}) was selected as a bitumen indicator that correlates well with the mixtures response. The stress level proposed was of 3.2 kPa for both unmodified and polymer-modified bitumens. In the first case, unmodified bitumens can start showing some shear-thinning after this value. In the second case, many of the PMBs considered start showing slippage in the polymer chain above this level. Alternative stress levels for PMBs and unmodified bitumens are under discussion.

This work focuses on long-term ageing, and the use of a test focused on controlling rutting may be of concern since rutting is expected at an early stage in the pavement life where oxidation may be still limited. However, the MSCR test has not been considered for grading purpose. This test has been adopted since it was explicitly developed for PMBs to fulfil part the limitations of the LVE characterisation. Specifically, it is believed that the stress levels used in the test allow highlighting the effects of the bitumen PAV-oxidative hardening and the polymer degradation on the rheological response of PMBs.

2.10.5 Theoretical background of the LAS test

Section 2.5 includes a reference to the AASHTO 1993 Pavement Design Guide (61) that highlights the importance of combining the effects of ageing and traffic loads to determine the Long Term Pavement Performances (LTPP) of asphalt pavements. A schematic representation of this concept is given in Figure 2-52.

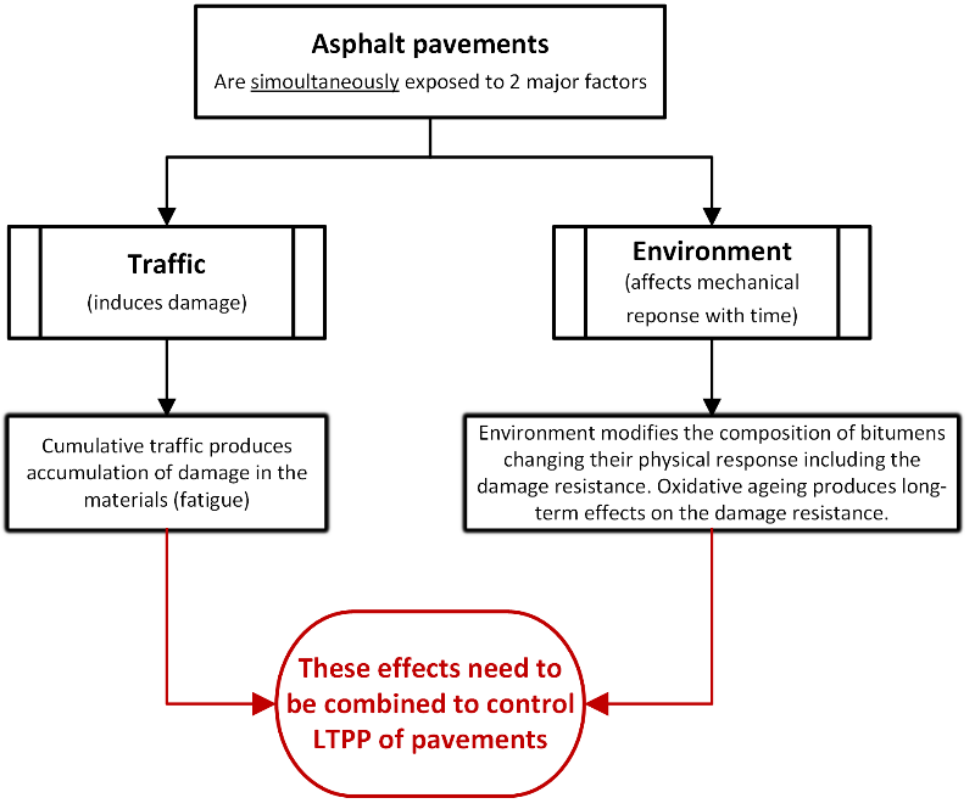


Figure 2-52 – Conceptual scheme of the combination of traffic and oxidative ageing on LTPP

The objectives of this work have been somehow inspired and prompted by this concept that is here included to explain the part of the experimental method included in this section. Before describing the LAS test, a more specific focus on investigating the combined effects of oxidative ageing and cumulative damage resistance is needed. To do so, a clear definition of damage should be initially provided.

Damage can be defined as the “*Deterioration of internal microstructure of material (breaking of molecular bonding) with a consequent worsening of mechanical response due to the accumulation of micro-cracks and defects. Specifically, damage can be seen as a reduction in the stiffness of materials”* (41).

Oxidative ageing has been observed to produce changes towards stronger molecular bonds in the microstructure of bitumens with a consequent increase in stiffness. Therefore, it appears that damage and oxidative ageing produce opposite effects on the stiffness of bitumens (and mixtures).

Based on this, a fundamental question can be raised:” *Even though oxidative ageing cause the stiffness of bitumen increasing*, *can ageing be considered as damage?”* If the analysis of the rheological response would be limited to the complex modulus in the LVE conditions, the evaluation of the effect of ageing might be misleading. Although the stiffness increases (and the damping decreases), aged pavements are more susceptible to damage (e.g., low temperature cracking, fatigue cracking, ravelling).

Therefore, the investigation of the effect of oxidative ageing on the long-term pavement performance should focus on how the bitumen oxidative ageing affects the resistance to cumulative damage. To achieve this, it is necessary to characterise bitumens within a stress-strain interval where the strain tolerance can be measured. The LVE characterisation is unlikely to provide such type of information since the strains applied are reduced and might not be representative of the conditions of the pavements. Additionally, in the case of PMBs, linear viscoelastic properties (e.g., similar PG grade) may not be indicative of the mechanical response of the corresponding mixtures (2). Therefore, there is a need to consider the damage characterisation of aged bitumens.

2.10.5.1 Damage characterisation

This section includes the theoretical background of damage characterisation. The content has been mainly developed considering the book "*Modelling of Asphalt Concrete"* (Chapter 7), by Professor Richard Kim and other authors. The literature review of this topic has not been organised in more detail since this work does not focus on the principles of damage characterisation. Notwithstanding, it uses its principles and findings to investigate the effects of laboratory-simulated ageing on the long-term performances of PMBs.

Different types of experiment are available to characterise the cumulative damage resistance of different materials. One of these is represented by comparing "undamaged" material properties determined at low strain levels, with "damaged" properties obtained through destructive test methods (38). One of the precursors of this approach has been Dr Richard Schapery in the field of composite materials (208). These concepts were subsequently applied to the study of fatigue cracking resistance of asphalt mixtures by Dr Richard Kim, Dr Robert Lytton, and Dr Dallas Little (38).

Damage initiation and propagation reduce the stiffness of materials. In the case of linear elastic materials, the stress is proportional to the strain according to Equation (2-33).

$$\sigma = E \cdot \varepsilon \tag{2-33}$$

Where:

- σ – is the stress applied;
- ε – is the resulting strain;
- E – is the stiffness of the material (Modulus).

When damage occurs, the same form of Equation (2-33) can be used by introducing the function $C(S_m)$ that indicates the changes in stiffness due to damage that expressed by the parameter (S_m) (Equation (2-34)).

$$\sigma = C(S_m) \cdot E \cdot \varepsilon \tag{2-34}$$

For several viscoelastic materials, time-dependent problems can be simplified into a linearly elastic solution by the use of pseudo strain and pseudo stress variables. Therefore, Equation (2-33) applicable to elastic materials, is applied to viscoelastic materials (Equation (2-35)), in terms of pseudo strain (ε^R) and reference modulus (E_R).

$$\sigma = E_R \cdot \varepsilon^R \tag{2-35}$$

The pseudo strain is defined as follows:

$$\varepsilon_R = \frac{1}{E_R} \int E(t-\tau) \frac{\delta\varepsilon}{\delta\tau} d\tau \tag{2-36}$$

Where:

- E_R – is the reference modulus and has the same dimension of a relaxation modulus (usually taken as a unit);
- $E(t)$ – is the relaxation modulus;
- t – is time.

The same form adopted for elastic materials can be used for damaged viscoelastic by referring to pseudo strain and reference modulus (Equation (2-37)).

$$\sigma = C(S_m) \cdot E_R \cdot \varepsilon^R \tag{2-37}$$

The function $C(S_m)$ can be defined as pseudo-stiffness and represents the loss of stiffness solely due to the loss of material integrity caused by crack propagation. The work of potential theory based on continuum damage mechanics developed by Schapery is used to evaluate $C(S_m)$ with the damage growth (208).

According to this theory, a body showing various sparse defects can be reformulated in a continuous body with weakened effective properties (220). Damage is quantified as per an internal state variable/s (S_m) involved in the mechanisms of thermodynamically irreversible processes. Under undamaged conditions, the value of C is equal to 1 (no damage occurs). Afterwards, once micro cracks start to propagate, C decreases and approaches to zero. In the case, uniaxial loads C depends on a single parameter (S_m) (210, 214, 219).

To understand the thermodynamic processes, it is necessary referring to the internal state energy of materials and the work produced by external loads.

In elastic materials, when a load is applied in the absence of damage and thermal processes, the internal energy is given by the Helmotz free energy potential and the Gibbs free energy potential. In these conditions, the internal energy can be defined as strain energy (W), and it is equal to the algebraic sum of the work done by the system of external forces.

In the work of potential theory, W is considered as the internal state variable involved in irreversible thermodynamic processes. In the absence of damage, the total strain energy is stored by the system to be released to recover the initial configuration upon the loading removal. This process is fully reversible since all the energy is stored in deformation, and it is used to recover the initial conditions.

When damage occurs, part of the strain energy is dissipated, and the system is unable to recover the original configuration. The dissipation of energy makes this process irreversible. The damage accumulation rate can be expressed by the variation of the strain energy with the damage intensity according to Equation (2-38).

$$\frac{dD}{dt} = -\frac{dW}{dD} \tag{2-38}$$

Where:

- $\frac{dD}{dt}$ – is the damage (D) accumulation rate;
- $\frac{dW}{dD}$ – is the variation of the strain energy with damage intensity.

The form of the strain energy used depends on the configuration of the external loads used in the experiment (e.g., monotonic, oscillatory).

Equation (2-38) does not apply to materials by using the elastic-viscoelastic correspondence principle since the force needed to produce damage, and the associated resistance, are both rate dependent.

However, experimental pieces of evidence have shown the damage accumulation law follows the same type of relationship as the Paris' Law, valid for the crack-propagation in other types of materials (209 – Equation (2-39)).

$$\frac{dD}{dt} = \left(-\frac{dW}{dD}\right)^{\alpha} \tag{2-39}$$

Where:

- The significance of the left-hand side and right-hand side of the equation is the same as those given for Equation (2-38);
- α – is the exponent determining the energy release rate that is determined under undamaged conditions.

Damage characterisation experiments are designed to solve Equation (2-39) through numerical methods. The forms used to explicit the damage (D), the energy release rate, and the strain energy (W) are functions of the loading configuration used.

The analytical framework used to define the experiment is based on the strain decomposition principle proposed by Schapery (211). According to this principle, the whole deformation measured during an experiment can be decomposed into two parts (Equation (2-40)).

$$\varepsilon_{total} = \varepsilon_{ve} + \varepsilon_{vp} \tag{2-40}$$

Where:

- ε_{total} – is the total strain measured during the experiment;
- ε_{ve} – is the viscoelastic strain that includes the undamaged strain measured in linear condition (LVE) and the strain due to microcracks;
- ε_{vp} – is the viscoplastic strain that includes irreversible plastic strain.

The approach proposed by Schapery for measuring the three components is based on a stepwise method that starts from the LVE conditions, followed by more severe conditions of strain levels, test temperatures, and loading frequency.

The stepwise approach followed to decompose the total strain (Equation (2-40)) includes different analytical approaches:

- In the case of the linear component of the viscoelastic strain (ε_{ve}), the elastic-viscoelastic correspondence principle is applied;
- In the case of the strain component due to micro-cracks of the viscoelastic strain (ε_{ve}) is analysed through the work of potential theory based on continuum damage mechanics.
- The permanent strains achieved under the most severe conditions (ε_{vp}) are modelled by the viscoplastic strain model (38).

An experimental method can focus on both the viscoelastic and the viscoplastic parts of strain or the viscoelastic strain only. In the first case, the step-wise method is defined as

Viscoelastoplastic Continuum Damage (VEPCD) approach; while in the second, it is defined as the Viscoelastic Continuum Damage (VECD) approach.

A conceptual scheme of the different steps is given in Figure 2-53.

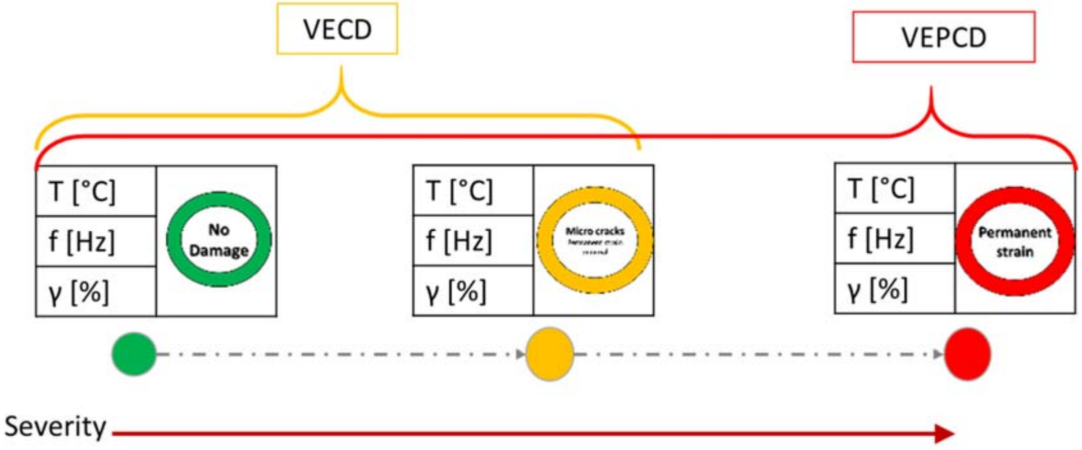


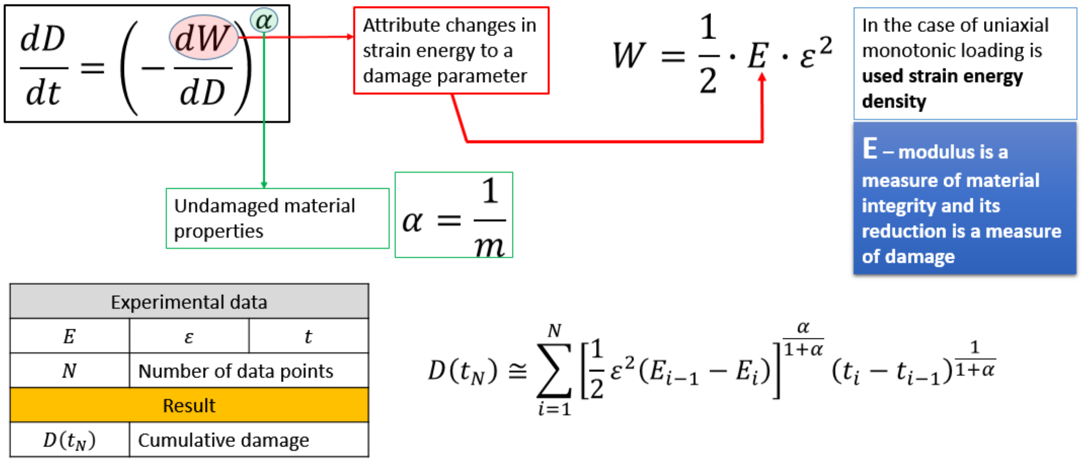
Figure 2-53 – Conceptual scheme of VEPCD and VECD methods.

The advantages of the applicability of the VECD theory to the study of the fatigue cracking resistance of asphalt mixtures has brought to the development of numerous VECD models (41, 215). Results show that the parameters derived from these models provide a reliable prediction of the damage evolution in asphalt mixtures irrespective of the mode of loading and test temperature.

2.10.5.2 VECD theory in asphalt mixtures and bitumens

Fatigue cracking of flexible pavements is a complex and wide diffused phenomenon, and it has received considerable interest from pavement engineers. Initially, fatigue cracking occurs as a series of small isolated micro-cracks that under repeated loading grow and interconnect developing the characteristic chicken and alligator crack patterns (214). Traditional test methods are based on the evaluation of the reduction in the dynamic modulus under repeated cyclic loading. However, this approach raises several concerns since the response depends on the mode of loading and additional effects as ageing, resting periods, temperature and rate of loading are not easy to take into account (214, 215). The application of the VECD approach has represented a valuable tool for a more detailed and comprehensive understanding of the mechanism of fatigue cracking in asphalt.

The application of the VECD theory to the study of fatigue cracking resistance of asphalt mixtures was initially perpetrated by the application of uniaxial tensile monotonic loading (212) (Figure 2-54).



$$\frac{dD}{dt} = \left(-\frac{dW}{dD}\right)^{\alpha}$$

$$W = \frac{1}{2} \cdot E \cdot \varepsilon^2$$

$$\alpha = \frac{1}{m}$$

$$D(t_N) \cong \sum_{i=1}^{N} \left[\frac{1}{2}\varepsilon^2 (E_{i-1} - E_i)\right]^{\frac{\alpha}{1+\alpha}} (t_i - t_{i-1})^{\frac{1}{1+\alpha}}$$

Experimental data		
E	ε	t
N	Number of data points	
Result		
$D(t_N)$	Cumulative damage	

Figure 2-54 – VECD theory applied in the case of monotonic tensile loading.

The parameter α represents the damage accumulation rate, and it is an undamaged material property. α represents the reverse of the slope of the creep compliance versus time power law (m). This parameter is determined within the linear viscoelastic region. In the case of monotonic loading, the strain energy is a function of the strain energy density given by Equation (2-41).

$$W = \frac{1}{2} \cdot E \cdot \varepsilon^2 \qquad (2\text{-}41)$$

Where:

- W – is the strain energy that is the area under the stress-strain curve;
- E – is the stiffness of the material;

- ε^2 – is the square of the applied strain.

In the case of damage, a reduction in the strain energy depends on the decrease in the modulus caused by a loss in material integrity.

The growth of the damage intensity is given by Equation (2-42) obtained by fitting Equation (2-39) with the experimental data.

$$D(t_N) \cong \sum_{i=1}^{N} \left[\frac{1}{2}\varepsilon^2(E_{i-1} - E_i)\right]^{\frac{\alpha}{1+\alpha}} (t_i - t_{i-1})^{\frac{1}{1+\alpha}} \tag{2-42}$$

Where:

- $D(t_N)$ – is the cumulative damage at the end of N-time intervals (N);
- t_i – represents the i-time interval.

However, although monotonic tensile loading are applicable, fatigue cracking is produced by load repetitions. Therefore, a large number of studies on the fatigue cracking resistance of mixtures has been conducted by using cyclic loading — specifically, flexural repeated loading for mixtures (215).

Viscoelastic materials under cyclic loading show energy dissipation due to delayed elasticity (damping). Although it is associated with energy dissipation, damping is a function of molecular mobility, and it is not associated with damage (2, 90). The dissipated energy over a loading cycle is given by Equation (2-2), and it is here reported in terms of axial strain (valid for mixtures) for the sake of clarity.

$$W_d = \pi \cdot \varepsilon_o^2 \cdot |E^*| \cdot \sin\delta \tag{2-43}$$

Where:

- ε_0 – is the applied strain at each loading cycle;
- $|E^*| \cdot \sin\delta$ – is the viscous component of the complex modulus (loss modulus).

The form of the equation adopted is valid for strain-controlled conditions. The dissipated energy over a loading cycle is proportional to the loss modulus. Although it is not related to damage, the changes in the dissipated energy (W_d) are used to quantify damage accumulation during cyclic loading (2).

In the case of shear loading (applicable to bitumens), the form of the dissipated strain energy for damage characterisation under cyclic loading was developed by Kim and co-workers (213). The equation is given below.

$$W_d = \pi \cdot I_D \cdot \gamma_{max}^2 \cdot |G^*| \cdot \sin \delta \tag{2-44}$$

Where:

$$I_D = \frac{|G^*|_{initial}}{1\ MPa} \tag{2-45}$$

- $|G^*|_{initial}$ – is the initial undamaged shear modulus;
- γ_{max} – maximum expected shear strain for a given pavement structure.

The dissipated energy is proportional to the viscous component of the complex shear modulus ($|G^*| \cdot \sin \delta$). Therefore, the variation of W_d caused by damage is a function of the loss in material integrity expressed by the reduction in $|G^*| \cdot \sin \delta$ over the loading cycles. As seen in the case of monotonic loading, the experimental data are used to fit Equation (2-39) to obtain the cumulative damage ($D(t_N)$) at the end of the N-loading cycles (Equation (2-46)).

$$D(t_N) \cong \sum_{i=1}^{N} [\pi \cdot I_D \cdot \gamma_0^2 (|G^*|\, sin\, \delta_{i-1} - |G^*|\, sin\, \delta_i)]^{\frac{\alpha}{1+\alpha}} (t_i - t_{i-1})^{\frac{1}{1+\alpha}} \tag{2-46}$$

Where:

- I_D – represents the initial undamaged complex modulus;
- γ_0 – is the applied shear strain;
- α – is an undamaged material property determined within the linear region that indicates the damage accumulation rate.

The variation of the viscous modulus with damage can be obtained by fitting the model given in Equation (2-47).

$$|G^*| \cdot \sin\delta = C_0 - C_1(D)^{C_2} \tag{2-47}$$

Where:

- D – is the cumulative damage after the loading cycles considered;
- C_0, C_1, C_2 – are regression coefficients used to fit the model.

Substituting Equation (2-47) into Equation (2-44), and undertaking the derivative versus D Equation (2-48) is obtained.

$$\frac{dW}{dD} = -\pi \cdot I_D \cdot C_1 \cdot C_2 \cdot (D)^{C_2-1} \cdot (\gamma_{max})^2 \tag{2-48}$$

Combining Equation (2-39) with Equation (2-48) gives a closed-form solution to calculate the number of load repetition (N_f) that bring the damage parameter (D) to failure.

$$N_f = \frac{f\left(D_f\right)^k}{k(\pi I_D C_1 C_2)^\alpha}(\gamma_{max})^{-2\alpha} \tag{2-49}$$

Where:

- N_f – is the number of loading cycles to failure;
- f – is the loading frequency;
- D_f – is the damage accumulation at failure.

The equation can be simplified by grouping the parameters into two terms A and B.

$$A = \frac{f\left(D_f\right)^k}{k(\pi I_D C_1 C_2)^\alpha} \tag{2-50}$$

$$B = 2\alpha \tag{2-51}$$

Equation (2-49) achieves the form

$$N_f = A(\gamma_{max})^{-B} \tag{2-52}$$

That is typical of the fatigue life of asphalt mixtures developed by Monismith and co-workers (217). According to Equation (2-52), the fatigue life of asphalt materials is a function of A and B that (as discussed), represent material properties, and it is a function of the applied strain level (γ_{max}). Equation (2-52) is applicable to road bitumens as well (2).

The graphical representation of this relationship is known as a Wholer curve (218), and an example is given in (Figure 2-55)

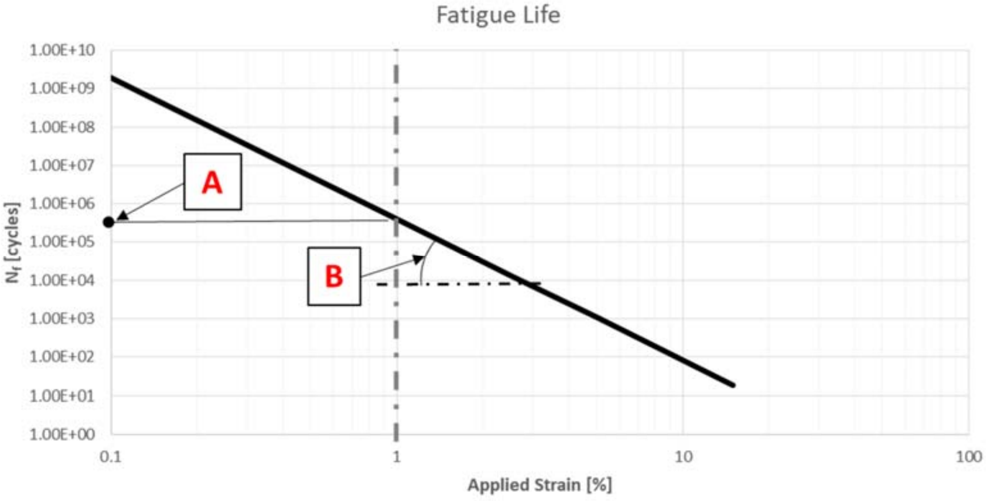


Figure 2-55 – Fatigue law of bitumen as the number of cycles (N_f) versus the applied strain.

The definition of a fatigue law requires to conduct multiple tests by varying the level of strain (or stress) applied and by measuring the number of cycles to failure.

The definition of failure depends on the level of reduction of the modulus concerning its initial value. Usually, failure is considered once the stiffness achieves 50% of its initial value (2, 214). It can be understood that this kind of experimental processes can be time-sensitive providing lengthy tests in the case of performing materials. The advantage of applying the VECD to such tests comes from the possibility of gathering information on a large variety of conditions from a single subset of parameters.

The application of VECD theory to the fatigue cracking resistance of asphalt materials was initially developed on asphalt mixtures. Subsequently, it was applied to road bitumens. The theoretical background discussed for mixtures under shear loading applies to bitumens as well. Details on the development of damage characterisation methods applied to bitumens are well discussed in the works of Johnson and Hintz (41, 42).

The development of a binder fatigue test based on the damage characterisation was prompted by the needs of defining performance-based criteria for PMBs since the application of the intermediate temperature PG criteria has been unlikely to be successful (§2.10.3.2). During the NCHRP 9-10 Project, the Time-Sweep test was developed to study the fatigue cracking resistance of bitumens in the DSR (2). The test consists of the application of repeated oscillatory loading under stress-controlled or strain-controlled conditions until damage occurs. The details of the development of this test and its limitations are discussed in (2, 41, and 42). However, besides some geometrical effects related to the sample geometry in the DSR, testing based on repeated loading to study fatigue cracking can become time-sensitive. However, one of the advantages is given by the fact that the number of cycles to failure can be directly measured.

To overcome the excessive length of the repeated cycling loading test, accelerated damage tests for bitumens have been investigated. Accelerated procedures increase the loading energy provided by the DSR by increasing the stress applied or the strain applied with the scope of accelerating damage. Martono and Bahia have proposed a stress-sweep test where the stress applied increases over the loading cycles upon the same frequency (216).

Unfortunately, the test was unlikely to be accurate in ranking the bitumens with mixtures results (41).

Besides cyclic loading, the application of a constant shear strain rate in the DSR was investigated to examine the relations between cyclic and monotonic loading in the damage accumulation of bitumens. The Binder Yield Energy test (BYET) considers the area beneath the stress and strain curve defined as Yield Energy as the parameter indicative of the damage resistance of bitumens (Figure 2-56).

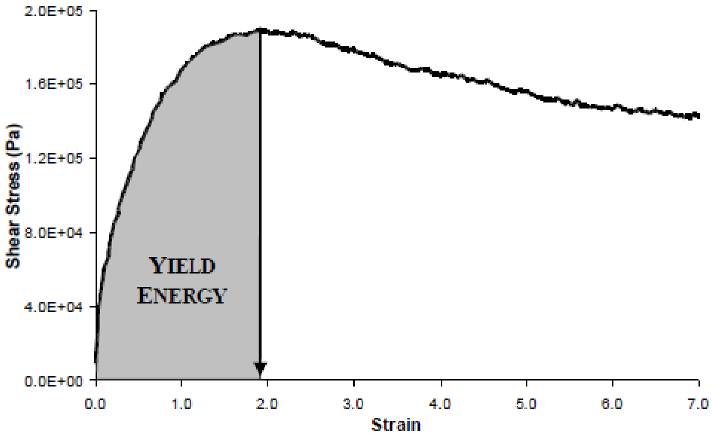


Figure 2-56 – Yield Energy from BYET test (41)

Although the initial correlations with the accelerated fatigue testing on mixtures resulted as promising, the correlation between the Yield Energy and the fatigue resistance through the VECD theory resulted as challenging.

However, the important role of bitumens on the fatigue cracking mixtures highlights the need for an accelerated testing procedure for bitumens, capable of defining their number of loading to failure (N_f). In order to pursue this, the researchers of the University of Wisconsin-Madison, have developed the Linear Amplitude Sweep test (LAS), that represents an accelerated damage test for bitumens that includes an initial part conducted in the LVE region, and a second portion of the test where damage is induced by increasing the strain applied (41-43). The VECD theory applies to the test results, and the LAS appears to be promising for the development of dedicated specification of fatigue cracking resistance in road bitumens (221).

In this work, the LAS test has been used to evaluate the effect of laboratory simulated ageing on the cumulative damage resistance of PMBs, measured through the VECD theory. The details of the LAS test are given in § 3.3.8.

3 Materials and methods

3.1 Introduction to the development of the experimental method

The experimental method developed in this works originates from some of the shortcomings identified in Section 2 to provide more clear insights on the effects of polymer modification on the ageing resistance of PMBs.

Two polymers (i.e., radial SBS, EVA) were mixed with one base bitumen using different concentrations. The SBS was selected as representative of an elastomer widely used in bitumen modification. The EVA was selected as a plastomer. Besides this, based on the background information available (§2.9), the first polymer could be considered representative of a polymer susceptible to ageing, while the second as a polymer with low susceptibility.

The bitumens were laboratory short-term and long-term aged by using the traditional methods of the RTFO (STA) and the PAV (LTA).

Two test protocols were adopted. One focuses on the changes in the microstructure of PMBs with ageing (compositional test protocol). The other investigates the effects of ageing on the rheological response of PMBs measured within the LVE region and at higher strain levels (rheological test protocol).

Before introducing the details of the experimental method, it is worth mentioning that besides PMBs, the work includes a dedicated experimental procedure on laboratory aged polymer-modified mastics whose details are included in Section 7.

The test methods adopted in each test protocol are given in Table 3-1.

Table 3-1 – Test methods used in the work

Test method	**Standard**	**Reason for using**
Rolling Thin Film Oven (RTFO)	UNI EN 12607-1	Laboratory simulation of the STA
Pressure Ageing Vessel (PAV)	AASHTO R28	Laboratory simulation of the LTA
Compositional test protocol		
Fluorescence microscopy	Internal method	Evaluation of the effects of ageing on the morphology of PMBs.
Gel Permeation Chromatography (GPC)	Internal method	Evaluation of the effects of ageing on the MWD of PMBs.
Rheological test protocol		
Frequency Sweep test	UNI EN 14770-12 AASHTO T315	Evaluation of the effects of ageing on the Shear Complex Modulus (G*) and the Phase Angle (δ) measured at different temperatures and frequencies.
Rheological test protocol		
Multiple Stress Creep and Recovery (MSCR) test	AASHTO T 315 AASHTO M 322	Evaluation of the effect of ageing on the resistance to the accumulation of permanent deformation of bitumens. Specifically, the outcomes of the test are the Non-Recoverable Compliance (J_{nr}) and the Average Percent Recovery (R) measured at different levels of ageing.
Linear Amplitude Sweep (LAS) test	AASHTO TP 101-12	Evaluation of the effect of ageing on the cumulative damage resistance of PMBs.

The next sections include a detailed description of the materials and the test methods.

3.2 Materials

Ten types of bitumen were prepared by combining one base bitumen (Penetration grade – Pen 70/100) with a radial SBS copolymer (polystyrene content 29-31%), and a plastomer EVA (28% by weight vinyl acetate). In the case of SBS modified bitumens sulphur (S) was used as a cross-linker.

The bitumens are given in Table 3-2.

Table 3-2 – Bitumens used in the experiments

Bitumen	**Base bitumen**	**Polymer concentration (w/w) [%]**	**Sulphur [%]**
Pen 70-100 (Pen)	-	0	-
Pen/S	Pen 70-100	0	0.1
SBS 2/S		2% SBS	0.1
SBS 4/S		4% SBS	0.1
SBS 6/S		6% SBS	0.1
SBS 4		4% SBS	-
SBS 6		6% SBS	-
EVA 2		2% EVA	-
EVA 4		4% EVA	-
EVA 6		6% EVA	-

Five SBS modified bitumens were prepared by varying the presence of the polymer and the sulphur as a cross-linker. In this case, the concentration of sulphur is 0.1% by weight of the blend bitumen + polymer. It is worth mentioning that the cross-linked SBS modified bitumens have a different cross-link density since they have different cross-linker versus SBS weight ratios. The cross-link density decreases with the increase of the polymer content. The job-mix formula of the PMBs was initially discussed with the polymer supplier to target stability, and the cross-link density was not considered as an experimental factor. Future developments of the work can consider investigating the same effect under a constant cross-link density.

An additional bitumen modified with sulphur (0.1% sulphur by weight of the bitumen) was prepared to highlight any potential effects of sulphur. Images of the raw materials used are given in Figure 3-1.

(a) (b)

(c) (d)

Figure 3-1 – Pictures of raw materials used in the experiment: a) base bitumen (Pen 70-100); b) SBS copolymer; c) EVA copolymer; d) sulphur.

3.3 Methods

3.3.1 Preparation of polymer modified bitumens

The polymer-modified bitumens were prepared by using a Silverson® high-shear mixer (Figure 3-2). In the case of SBS modified bitumen the sample prepration was inituially discussed with the supplier. In the case of EVA, it was derived from experience from previous projects.

Figure 3-2 – Silverson® high-shear mixer

In the case of SBS modified bitumens with sulphur (i.e., SBS 2/S, SBS 4/S, and SBS 6/S), the base bitumen was heated to 180°C, and then the polymer was added. After 1 hour blending at 180°C with a shear rate of 5,000 RPM, the sulphur was added to the blend that was kept under rotation for additional two hours at 180°C with a shear rate of about 2,800 RPM. In the case of SBS modified bitumens (i.e., SBS 4, and SBS 6) the same procedure was used as for cross-linked SBS modified bitumens without adding sulphur. In the case of the SBS modified bitumens, the storage stability was measured on the SBS 6/S and the SBS 6 bitumens according to the ASTM D7173 standard. Details about the stability test are given in §3.3.2.

For the Pen/S modified bitumen the process was the same as those above with the difference that no polymer was added but only sulphur after 1 hour at 180°C (5,000 RPM). After the addition of sulphur, the blend was kept under rotation for an additional two hours at 180°C with a shear rate of about 2,800 RPM.

Finally, for the EVA modified bitumens (i.e., EVA 2, EVA 4, and EVA 6), the base bitumen was brought to 180°C, then EVA was added, and the blend was kept under rotation at 2,000 RPM for 2 hours at 180°C.

3.3.2 Storage stability test (ASTM D7173 - Tuben Test)

The storage stability test was conducted on the SBS 6/S and SBS 6 bitumens (Table 3-2) as per the ASTM D7173 test procedure (241).

According to the procedure, after blending the modified bitumen is poured into aluminium tubes. The tubes are placed into an oven at a temperature of 163 ± 5°C for 48 ± 1 hours held in a vertical position by a supporting rack (Figure 3-3).

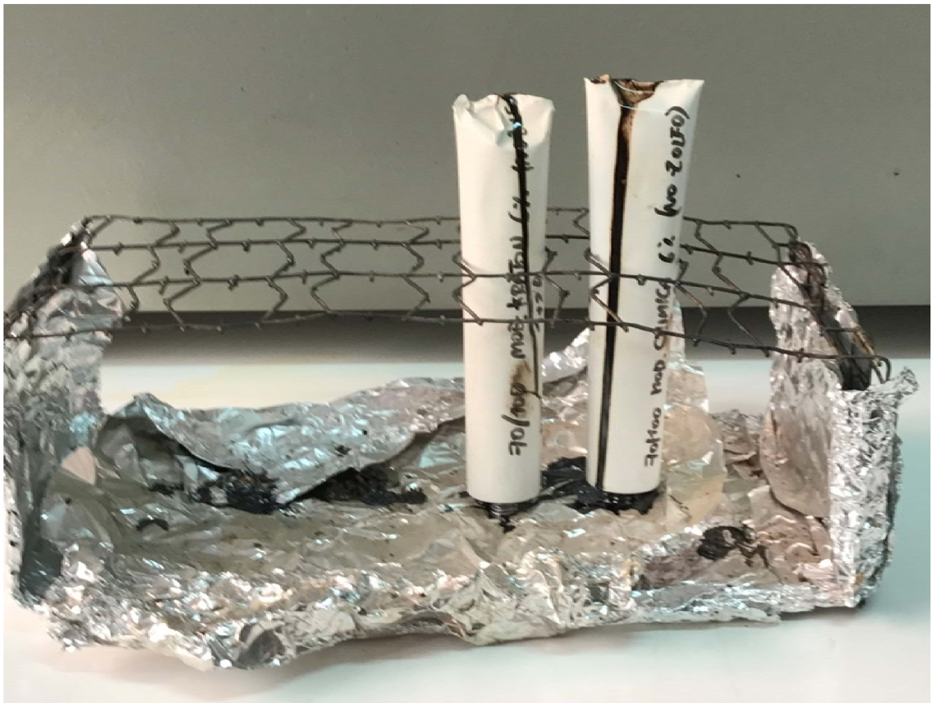


Figure 3-3 – Tubes in a vertical position in a supporting rack

After the oven conditioning, the tubes are placed into a freezer for 4 hours at a temperature of -18°C to solidify the sample. Afterwards, the tubes are cut in three parts of approximately equal length (Figure 3-4). The part in the middle is discarded, while the top and the bottom portions are placed into an oven at 163 ± 5°C for a sufficient time to remove the remaining parts of the metallic tubes (Figure 3-5).

Figure 3-4 – Cutting of tube sample after solidification.

Figure 3-5 – Top and bottom part of the tube placed into the oven after solidification.

After the removal of the remaining part, the samples are stirred and are ready for evaluation. The tendency to separation is measured by measuring the softening point of the top and the bottom parts (ASTM D36) or by measuring the shear complex modulus and phase angle in the DSR (ASTM D7175). In this test, both methods were used.

In the case of the DSR measurements, the values of the G* of the bitumen at the top and the bottom were compared by using Equation (3-1)

$$R\ [\%] = \frac{\left|G^*_{Top} - G^*_{Bottom}\right|}{G^*_{Top}} * 100 \leq 20\% \tag{3-1}$$

Where:

- G^*_{Top} is the complex shear modulus of the bitumen in the top side of the tube measured at 76°C (10 rad/sec);
- G^*_{Bottom} is the complex shear modulus of the bitumen in the bottom side of the tube measured at 76°C (10 rad/sec).

This criterion has been developed through the findings of the NCHRP 9-10 Project, and it is currently applied in the State of Qatar to check the storage stability of PMBs.

Besides rheological test methods, fluorescence microscopy has been used to evaluate the morphology of the bitumen contained within the top and the bottom parts of the tube.

3.3.3 Laboratory-simulated ageing (LSA) methods

The bitumens were short-term aged by using the RTFO as per the UNI EN 12607-1 and long-term aged by using multiple cycles of PAV as per the AASHTO R 28 (242).

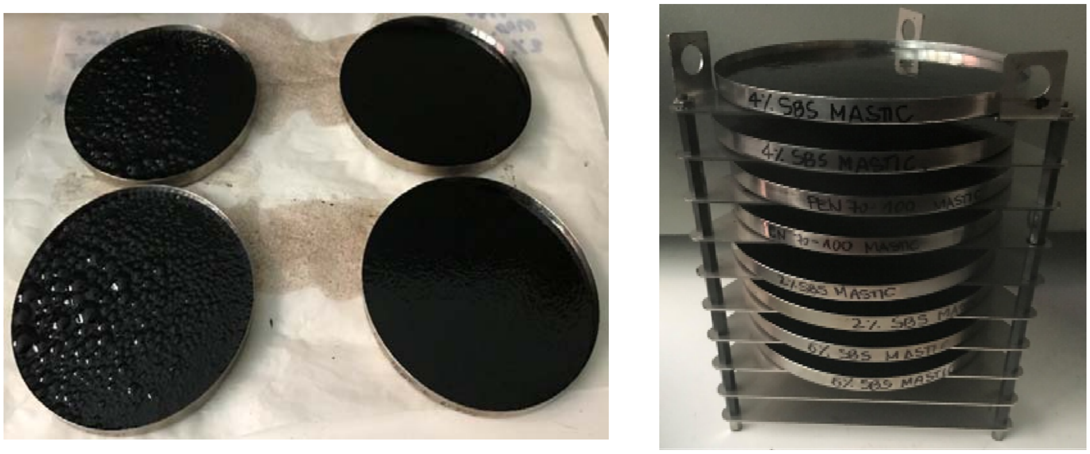
(a) (b)

Figure 3-6 – a) RTFO apparatus; b) PAV apparatus.

A brief description of each ageing method is given below.

In the case of the RTFO, 35 ± 0.5 g of bitumen are poured in a glass cylindrical bottle. A total of 8 bottles can be allocated into the RTFO oven. As shown in Figure 3-6 (a), the bottles are allocated into a circular steel bottle retainer in a horizontal position. Once the bottle positioning has been completed, the bottles are made rotating at 15 ± 0.2 rotations/min for 75 minutes (UNI EN 12607-1) at a temperature of 163°C. Meanwhile rotating the bitumen contained into the bottle is exposed to an airflow of 4000 ± 200 mL/min. The test is conducted to expose a thin film of semi-solid bitumen to airflow and heat.

The PAV ageing is conducted on RTFO-aged bitumens. In this case, a sample of 50 ± 0.5 g of bitumen is poured into a metallic plate whose internal diameter is equal to 145 mm and an internal height of 9.5 mm. The plates are located horizontally inside the PAV apparatus through a steel rack. Examples of PAV plates and the horizontal rack are given in Figure 3-7.



(a) (b)

Figure 3-7 – a) PAV plate; b) PAV plates allocated on a horizontal rack.

The target of the sample preparation is to have a fixed thickness of the film of bitumen in the plate. According to the geometry and the weight of the sample, and considering the specific gravity of the bitumen approximately equal to 1.03 g/cm^3, the sample thickness is approximate 3.2 mm. This clarification is included because oxidation is a diffusion process that depends on the thickness of the sample.

According to the AASHTO R 28, the samples shall be exposed to an air pressure of 2.1 ± 0.1 MPa for 20 hours ± 10 minutes at a test temperature selected based on the climatic region. Besides the reference PAV exposure of 20 hours, in this experiment, additional PAV times were included: 0.5 PAV (10 hours); 2 PAV (40 hours); 4 PAV (80 hours).

Although the bitumens used show sensible differences in polymer content (and therefore in stiffness), the same PAV temperature of 100°C was used for all the bitumens. After the PAV ageing, the bitumens are subjected to vacuum degassing at a temperature of 170°C for 45 minutes to remove the entrapped oxygen.

The laboratory-simulated ageing levels for each bitumen are given in Table 3-3

Table 3-3 – Laboratory-simulated ageing levels of the bitumens.

Bitumen	Unaged	RTFO	0.5 PAV	1 PAV	2 PAV	4 PAV
Pen	V	V	V	V	V	V
Pen/S	V	V	-	V	V	V
SBS 2/S	V	V	V	V	V	V
SBS 4/S	V	V	V	V	V	V
SBS 6/S	V	V	V	V	V	V
SBS 4	V	V	-	V	V	V
SBS 6	V	V	-	V	V	V
EVA 2	V	V	-	V	V	-
EVA 4	V	V	-	V	V	-
EVA 6	V	V	-	V	V	-

3.3.4 Fluorescence microscopy

Fluorescence microscopy has been used to investigate heterogeneous surfaces where the component have different Ultraviolet (UV) excitation responses. In the case of PMBs, this method has been applied to investigate the morphology of the bitumens that represents the partition between the polymer-rich phase and the bitumen-rich phase, with the polymer-rich phase having a higher UV susceptibility (199).

Unless it is subjected to computational imaging analysis methods, the morphology provides a qualitative description of the level of the polymer dispersion in the bitumen phase. Although the term “qualitative” may be unlikely to be “rigorous enough”, the study of the polymer dispersion provides significant insight into the compatibility, the potential effects of cross-linkers, and the quality of the modification. Furthermore, with a certain extent of caution, the morphology can be correlated with the rheological response (34, 199). Caution should be taken since, besides the compatibility between the polymer and the bitumen, phase, the dispersion shown by the polymer phase at the time of observation depends on the thermal history of the sample, and the sample preparation. The details of the latter are given in the next section.

3.3.4.1 Sample preparation

The samples were prepared from stripes of bitumen kept at room temperatures (Figure 3-8).

Figure 3-8 – Stripes of bitumen at room temperature

Three small stripes approximately 10 mm x 50 mm x 2 mm were cut at room temperature from the large irregular stripes (Figure 3-8). The small stripes were refrigerated for 10 hours at low temperatures to freeze the morphology. Then, once these stripes are solid and brittle, they are cut in three parts as so as not to affect the morphology (Figure 3-9).

Figure 3-9 – Parts of bitumen stripes after being cut at low temperature

The surface corresponding to the cut is attached to the glass for microscopy observation (Figure 3-10).

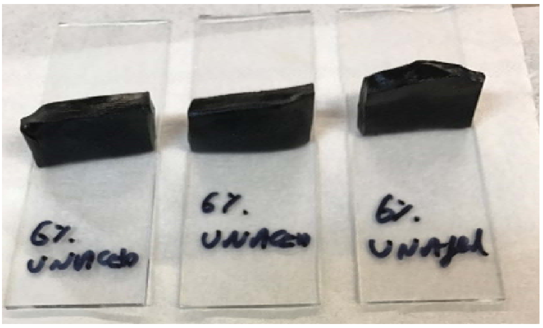


Figure 3-10 – Microscopy samples.

To obtain representative images of the morphology, nine surfaces per bitumen were prepared. Using the cut face allows obtaining the bulk morphology that has not been affected by contact with any surface during the preparation.

3.3.4.2 Test method

A Leica® DM LB fluorescence microscope was used to capture images of the PMB morphology at 10 x magnification. The microscope is connected to a camera that allows gathering pictures of the various samples.

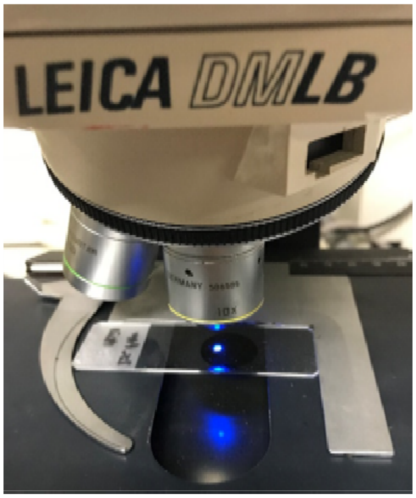


Figure 3-11 – Leica DM LB Microscope

The materials used in this test are given in Table 3-4.

Table 3-4 – Materials observed with fluorescence microscopy

Bitumen	Unaged	RTFO	0.5 PAV	1 PAV	2 PAV	4 PAV
SBS 2/S	V	V	V	V	V	-
SBS 4/S	V	V	V	V	V	-
SBS 6/S	V	V	V	V	V	-
SBS 4	V	V	-	V	V	-
SBS 6	V	V	-	V	V	-
EVA 2	V	V	-	V	V	-
EVA 4	V	V	-	V	V	-
EVA 6	V	V	-	V	V	-

Fluorescence microscopy was not used with the Pen and the Pen/S bitumens since these bitumens are not polymer-modified and do not show any polymer-rich phase (or bitumen-rich phase).

3.3.5 Gel Permeation Chromatography (GPC)

3.3.5.1 Principles

In §2.5.3 of this document, the applicability of compositional test methods to road bitumens has been discussed. Among the considerations provided, what appears to be clear is that a precise molecular (or elemental) composition of bitumens has not been identified. The reason behind this is the large variability in the molecular species present in this material. Therefore, the composition of bitumens is conducted in terms of groups of molecules with similar properties such as polarity and molecular weight (SARA fractions). Once the polarity is discounted, the molecular weight can be considered to identify different groups of molecules. The analysis of the molecular weight distribution of road bitumens has been successfully used in the investigation of oxidative ageing. To pursue this, Gel Permeation Chromatography (GPC) or size-exclusion chromatography has been widely used. These methods are based on the susceptibility of the bitumen fractions to organic solvents. A small sample of bitumen (in the order of 10 to 15 mg per sample), is dissolved in a solvent (Figure 3-12).

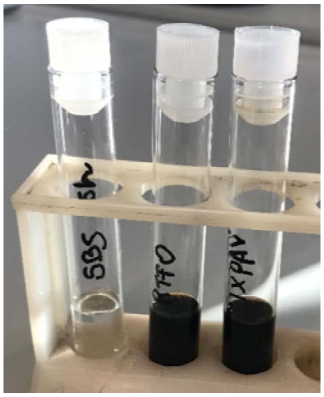


Figure 3-12 – Preparation of GPC sample

Afterwards, this solution is filtered to eliminate residual gross particles, and it is injected into a system of one or multiple columns depending on the equipment and test used.

Such column/s is/are filled with a reticulated polymeric porous packing constituted of spheres whose surfaces show pores with different sizes. During the test, a constant flow rate of the same solvent used to dissolve the bitumen is injected through a pump in the column and passes through the porous packing. The temperature is kept constant. The polymeric material constituting the porous packing does not dissolve in the solvent used.

The solution of bitumen + solvent is injected in the column, avoiding any disruption of the solvent flow (e.g., interruption or overflow due to injection). It is assumed that there are not interface interactions between the bitumen and the spheres (i.e., adhesion, absorption) and that the molecules pass through this packing as a function of their size only (stationary condition). Large molecules pass through the packing faster since they do not interact with the pores. The smaller the molecules are, the longer they take to pass through the porous packing since they are more “entrapped” in the pores. At the final part of the columns system, a concentration detector is installed that emits a signal at each time the molecules are detected. A schematic representation of this system is given in Figure 3-13.

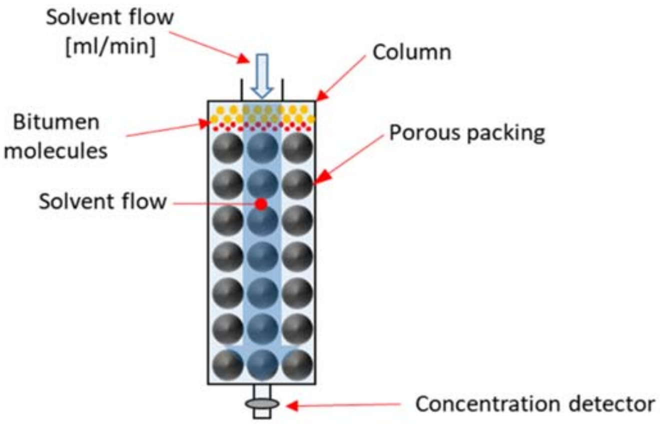


Figure 3-13 – Scheme of GPC column

As mentioned above, the detector emits a signal any time a group of molecules are detected (i.e., retention time). The curve retention time versus the intensity of the signal emitted is defined as a chromatogram and represents the raw data from the GPC test.

The larger molecules (heavier fractions) have a lower interaction with the pores in the column. Therefore, they flow through the porous packing faster than the smaller molecules (lighter fraction). As a consequence, the heavier fractions are detected at lower retention time than the lighter fraction. A schematic representation of this mechanism is given in Figure 3-14.

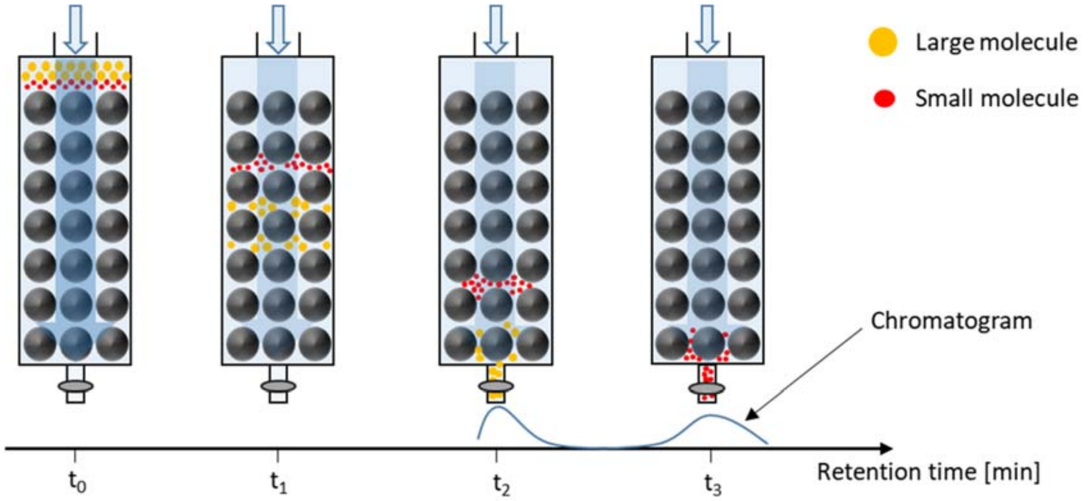


Figure 3-14 – Scheme of the GPC test method

The interaction between the bitumen molecules and the porous packing depends exclusively on the size of the molecules. Therefore, this method refers to size-exclusion chromatography. Since no information on polarity is provided, the molecules are classified as per their molecular weight only. For this reason, the results are provided and discussed in terms of light fractions or heavy fractions, while no SARA fraction can be identified. However, based on the differences between the bitumen fractions discussed in §2.5.3.4, it is more likely to have the aphaltene fractions (or agglomerates of asphaltenes - 232) in the heavy fractions (i.e., lower retention time), and the other fractions (resins, aromatics and saturates) at higher retention times.

3.3.5.2 Test method

The chromatograms of the bitumen samples were measured from solution in Tetrahydrofuran (THF) (10 mg/mL) by using a Gel Permeation Chromatography (GPC) apparatus Perkin Elmer 200 Series (Figure 3-15).

Figure 3-15 – Perkin Elmer Series 200 Apparatus

The apparatus is equipped with two columns in series: a Resipore column, 3µm, 300x7.5 mm from Agilent operating in the range of weight average molecular weight (M_w) up to 500.000 Da; and a Phenogel column, 5 µm 50 Å, 300x7.5 mm, from Phenomenex (M_w from 100 to 3000 Da).

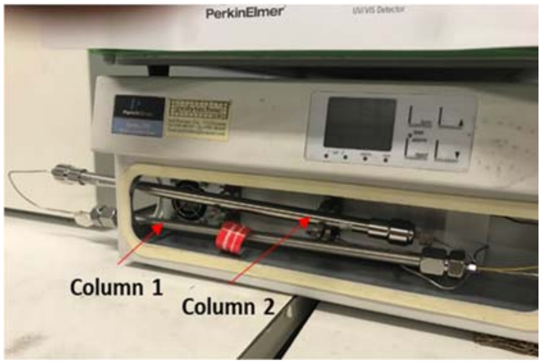


Figure 3-16 – GPC columns

The system is maintained at 40°C by a Peltier column oven Perkin Elmer 200 Series and using a Flexar UV/VIS Perkin Elmer as a detector. The volume of solution injected was 15 µL. The flow rate of the solvent was 1 mL/min. Samples containing SBS and sulphur were filtered before injection using a 0.45 µm PTFE filter (Figure 3-17). Filtering the solution before its injection in the column represents a practice conducted to prevent the column from clogging.

(a) (b)

Figure 3-17 – a) PTFE Filter; b) filtering bitumen sample.

After filtering the sample is injected into the columns.

The materials used in this test are given in Table 3-5.

Table 3-5 – Materials used in the GPC test

Bitumen	**Unaged**	**RTFO**	**0.5 PAV**	**1 PAV**	**2 PAV**	**4 PAV**
Pen	V	V	-	V	V	V
Pen/S	V	V	-	V	V	V
SBS 2/S	V	V	-	V	V	V
SBS 4/S	V	V	-	V	V	V
SBS 6/S	V	V	-	V	V	V
SBS 4	V	V	-	V	V	V
SBS 6	V	V	-	V	V	V
Polymer						
SBS copolymer	V	-	-	-	-	-

Two replicates were tested for each material.

3.3.5.3 Data analysis

This section includes the general details of the analysis conducted on the raw chromatogram to calculate the ageing indexes function of the bitumens' compositions. Additional considerations on the analysis are given in the section related to the results.

The chromatogram from the GPC device needs to be considered as the raw data from this test. By the numerical analysis of such curves, different types of parameters can be extracted from the raw chromatogram (Figure 3-18).

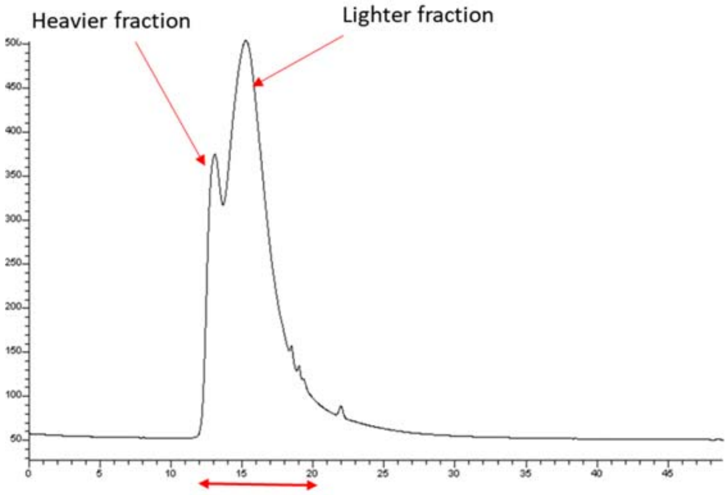


Figure 3-18 – Example of the raw chromatogram of unmodified bitumen.

The ageing index indicative of the changes in the bitumen and PMB microstructures was calculated by using the area beneath the curves of the heavy and the light fractions in the chromatograms. To calculate the two areas, the curves need to be isolated. The identification of each of the two curves includes four main steps:

1. Identification of the retention time interval characteristic of whole bitumen molecular weight interval (process of GPC Raw Data - Figure 3-19).

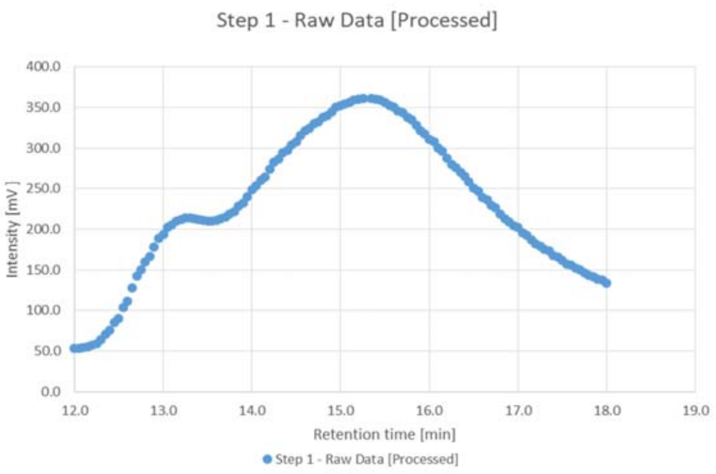
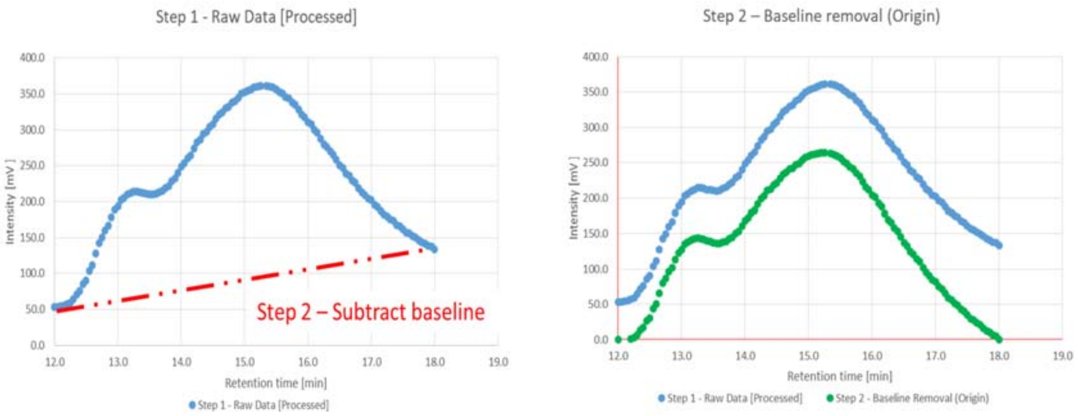


Figure 3-19 – Step 1 GPC analysis

2. Baseline removal of the raw chromatogram (Figure 3-20)



(a) (b)

Figure 3-20 – a) definition of the chromatogram baseline; b) green curve represents the chromatogram after the removal of the baseline

3. Removal of negative values that might be present at the two extreme abscissae of the curve.
4. Deconvolution of the bimodal curve of the bitumen. In this work, Origin® Software (Version 9.1) was used to process the deconvolution of the bimodal curve.

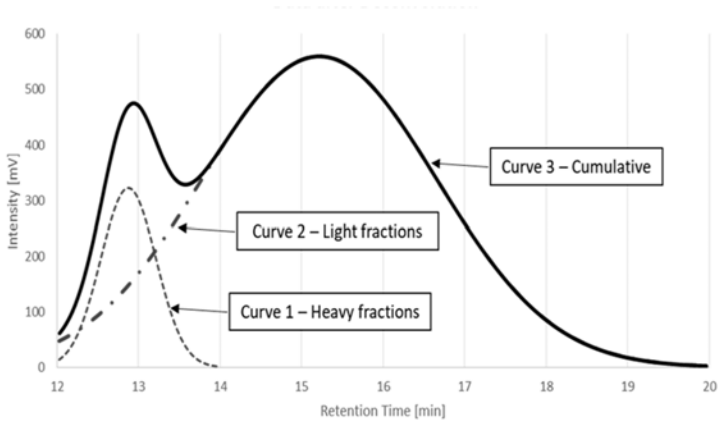


Figure 3-21 – Results of deconvolution of the bimodal curve of bitumen conducted with Origin® Software.

> After the deconvolution, the bimodal curve is decomposed into two curves representative of the heavy fractions (Curve 1 - Figure 3-21) and the light fractions (Curve 2 - Figure 3-21).

Once the two curves were obtained, the ageing indexes were calculated using the following equations:

The weight percentage of the heavy fraction (R_H)

$$R_H = \frac{\int Curve_1}{\int Curve_1 + \int Curve_2} \tag{3-2}$$

The weight percentage of the light fraction (R_L)

$$R_L = 1 - R_H \tag{3-3}$$

The variation of these indexes at the different levels of ageing was considered as representative of the changes occurring in the microstructure of bitumens.

The same analysis method was used for unmodified bitumens and SBS modified bitumens. However, in the first case, the two fractions (light and heavy) are constituted of bitumen molecules only. While in the case of PMB, the two fractions include polymer molecules as well. Further details of this aspect are discussed in the results of the experiment (Section 4.3).

To conclude, it is worth mentioning that this analysis method represents an internal procedure, including mathematical aspects widely applied to GPC results. However, additional details on deconvolution of GPC chromatograms can be found in Bartels et al (200), and Jenning et al (201).

3.3.6 Frequency Sweep test

3.3.6.1 Principles

The frequency sweep test is a DMA method conducted within the linear viscoelastic region under strain controlled or stress controlled conditions (§2.10). The results of this test are isothermal plots of viscoelastic functions as dynamic shear modulus (|G*|) and phase angle (δ). Under the applicability of the TTSP, the results of this test are used to develop the master curves of the viscoelastic functions that are represented over a wide range of (reduced) frequencies.

To do so, the material is tested within a narrow range of frequencies at different test temperatures. In the case of thermorheologically simple materials, the data obtained at the different temperatures, are shifted to a reference temperature through a shift factor $\alpha_T(T)$ representative of the temperature dependency of the material. The concept of temperature dependency is indicative of the material relaxation with the temperature that is a function of the molecular mobility.

The temperature shift is conducted in the domain of frequencies where each test frequency is associated with a reduced frequency according to Equation (3-4).

$$f_{rid} = \alpha_T(T) \cdot f \qquad (3\text{-}4)$$

Where:

- f_{rid} is the reduced frequency [Hz];

- f is the test frequency [Hz];
- $\alpha_T(T)$ is the shift factor.

The final result is a unique master curve developed in the domain of the reduced frequency. An example of phase angle master curve is given in Figure 3-22.

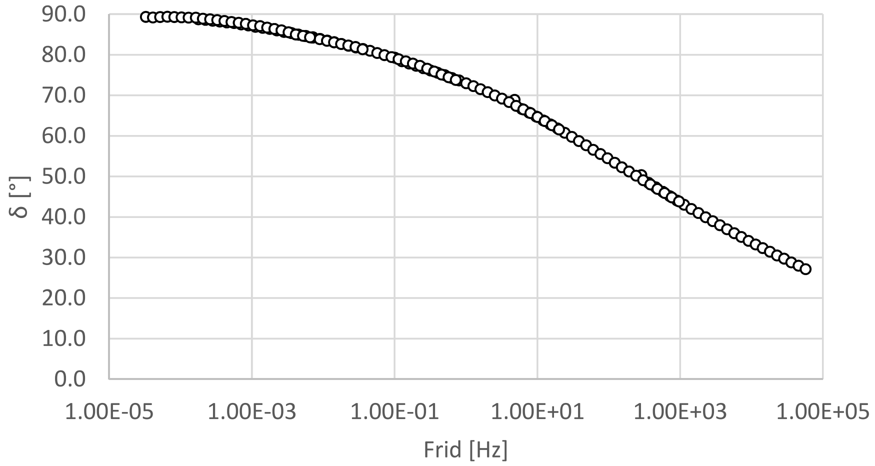


Figure 3-22 – Example of phase angle master curve.

As mentioned above in this section, the shift factor represents a measure of the temperature dependency of the materials. However, the applicability of TTSP implies that the shape of the master curve matches the shapes of the measured curve within the tolerance of the experiment. However, as discussed in §2.10.1.1, the TTSP can be applied under the condition that the relaxation spectra show similar temperature susceptibility.

The TTSP breaks down in the case of heavily modified bitumens and highly oxidised bitumens. Based on this consideration, the bitumens and the ageing levels considered in the frequency sweep test are given in Table 3-6.

Table 3-6 – Bitumens used in the frequency sweep test

Bitumen	Unaged	RTFO	0.5 PAV	1 PAV	2 PAV
Pen	V	V	V	V	V
SBS 2/S	V	V	V	V	V
SBS 4/S	V	V	V	V	V
SBS 6/S	V	V	V	V	V
EVA 2	V	V	-	V	V
EVA 4	V	V	-	V	V
EVA 6	V	V	-	V	V

The experiment includes heavily modified bitumens with a polymer concentration up to 6% of the polymer and relatively extended PAV exposure up to 40 hours. Therefore, there might be cases where the applicability of the TTSP may be of concern.

3.3.6.2 Test method

The test was conducted as per the UNI EN 14770-2012 (233). The test temperatures are given in Table 3-7.

Table 3-7 – Frequency sweep test temperatures

Testing Temperatures [°C]					
4	16	28	40	52	64

Twenty-four values of loading frequency following a logarithmic ramp scale from 0.1 Hz to 20 Hz were used. As per the reference standard, before conducting the test, the equilibrium temperature and the linear strain interval were determined for each bitumen at each level of ageing. The equilibrium time can be defined as the time necessary to homogenise the temperature in the test specimen. The DMA was conducted by using two different DSR geometries. Within the range 4°C to 40°C, the 8 mm plate was used, the 25 mm plate was used between 40°C and 64°C. At the overlapping temperature, the effect of the geometry was controlled according to the UNI EN 14770:2012.

Furthermore, the linearity and the equilibrium time were conducted for both the geometries as recommended in the standard. In the case of the frequency sweep, three samples were tested for each combination (bitumen – ageing level). In other cases, two samples were used.

3.3.6.3 Analysis of data

This analysis aims to provide the effects of laboratory simulated ageing on the variation of the complex dynamic modulus (|G*|) and of the phase angle (δ) of the PMBs included in Table 3-6. Although master curves are widely used, their development depends on the applicability of the TTSP. Aware of the possibility that some of the bitumens (and aged bitumens - Table 3-6) might have shown thermorehological non-simplicity, the data were analysed avoiding any TTSP manipulation.

The applicability of the TTSP was defined by following two different criteria. The first was based on the evaluation of the qualitative trend of the black diagram of the bitumens at the different levels of ageing. As discussed in §2.10.1.3, a smooth black diagram is representative of thermorheologically simple material. While the second criteria consisted of developing the phase angle master curves by using the shift factors calculated from the corresponding |G*| isotherms. In the case of thermorheologically simple materials, the phase angle master curves should have shown an adequate smoothness and matching with the shifted curves.

The isothermal curves of |G*| were shifted to the reference temperature (of 40°C) to develop the complex modulus master curve. The William-Landel and Ferry (WLF) equation was used to calculate the shift factors at different temperatures. Then the G* data were fitted by using the Christensen-Anderson Marasteanu (CAM) modified model (206).

However, since the majority of the bitumens do not seem to meet the TTSP, the linear viscoelastic data have been presented in terms of black diagrams and Cole-Cole diagrams that do not need time-temperature manipulation of data.

For the sake of completeness, the WLF equation and the CAM model are described as follows.

The form of the WLF equation is given by Equation (3-5).

$$\log \alpha_T(T) = -\frac{C_1\left(T - T_{Ref}\right)}{C_2 + \left(T - T_{Ref}\right)} \tag{3-5}$$

The significance of the parameters in the WLF equation is given in Table 3-8.

Table 3-8 – Significance of the WLF equation parameters

α_T	Its value is a function of temperature and material.
C_1	It is an empirical parameter function of the free volume.
C_2	This parameter is a function of the free volume and represents an indicator of the thermal dependency of the material. Chailleux and co-workers have shown that this parameter increases with ageing (203).
T_{ref}	It is the reference temperature to which the experimental curves are shifted. In this work, a reference temperature of 40°C was used.
T	It is the testing temperature

The form of the modified CAM model of the norm of the complex modulus with the reduce frequency is given by Equation (3-6).

$$|G^*| = G_e + \frac{G_g - G_e}{\left[1 + \left(\frac{f_c}{f'}\right)\right]^{\frac{m_e}{k}}} \tag{3-6}$$

The parameters of the |G*| model are discussed in Table 3-9 (206).

Table 3-9 – Significance of the modified CAM model of for |G*|

|G*|	It is the norm of the **Complex Modulus**. It represents the stiffness of the bitumen under sinusoidal applied shear loading.
G_e	Is the **Equilibrium Complex Modulus** which represents the value of the complex modulus for $\lim_{f\to 0}\lvert G^*\rvert$. This is the horizontal asymptote at low frequencies.
G_g	Is the **Glassy Modulus** which represents the value of the complex modulus for f→∞. This is the horizontal asymptote in the region of high frequencies. Its value is set to 1 Gpa that refers to the stiffness of crystalline (or semi-crystalline) polymers within the glassy region.
f_c	This is a location parameter with the dimensions of frequency.

f’	This is the cross-over frequency where the storage modulus (G’) and the loss modulus (G”) show the same value, or where the damping factor ($\tan\delta = 1$).
m_e	This is a shape parameter of the curve. It provides somehow information on the temperature susceptibility of the bitumen within a certain range of frequency.
k	This is a shape parameter.

A schematic illustration of the of the formulation of the model for complex modulus is take from the work of Zheng and co-workers (206) and reported in Figure 3-23.

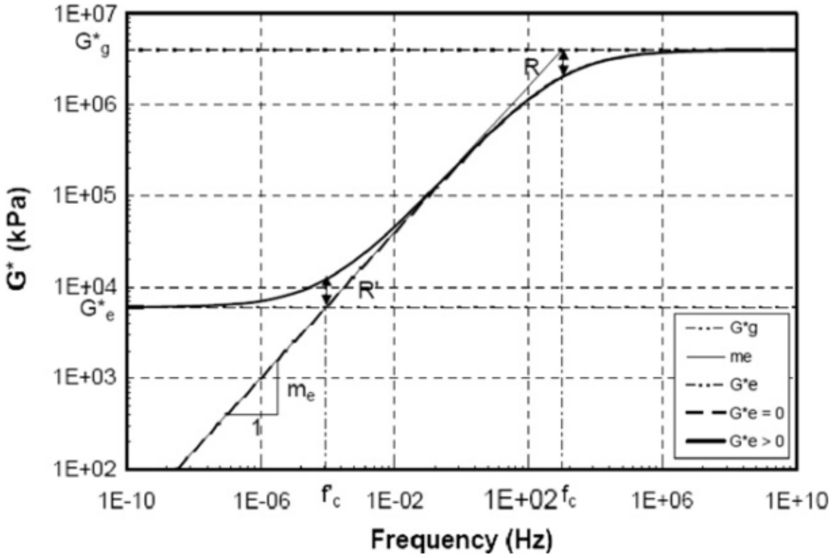


Figure 3-23 – Schematic illustration of |G*| model according to modified CAM model (206).

The parameter R is a rheological index representative of the width of the relaxation spectrum. Accurately, it represents the distance between G_g^* and $G^*(f_c)$ that in the case of bitumens is expressed by Equation (3-7).

$$R = \frac{m_e}{k \cdot \log 2} \tag{3-7}$$

This parameter is an indicator of the transition from the elastic behaviour to viscous behaviour. The higher is the value of R, the more gradual is the transition.

3.3.7 Multiple Stress Creep and Recovery (MSCR) test

3.3.7.1 Test method and data analysis

The MSCR test was conducted as per the AASHTO T-350 test method (237). The test is conducted in the DSR by using the parallel plate geometry with 25 mm plate diameter. The procedure is conducted under stress-controlled conditions applying a total of 30 loading creep and recovery cycles. Each cycle is of 10 seconds, of which 1 second of creep loading and 9 seconds of recovery. An example of the variation of strain versus time is given in Figure 3-24.

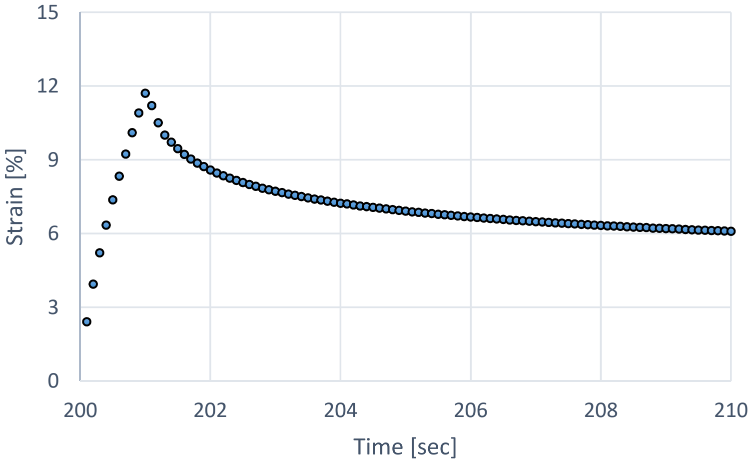


Figure 3-24 – Strain versus time within a single loading cycle in the MSCR test.

Two stress levels are applied: 0.1 kPa for the initial 20 cycles, and 3.2 kPa for the final 10 cycles. The initial ten cycles at 0.1 kPa are used for stabilisation purpose and are not considered in the analysis.

The analysis of the strain at each loading cycle is conducted by considering the Burgers micromechanical model that is a combination of a Maxwell and Kelvin-Voight models (Figure 3-25).

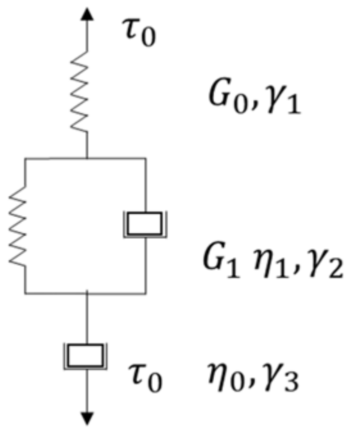


Figure 3-25 – Scheme of Burger's model.

The Maxwell model is represented by the spring (i.e.,G_0, γ_1) and the viscous dashpot (i.e.,η_0, γ_3) in series. On the other hand, the Kelvin-Voight model is represented by the remaining spring and dashpot in parallel. According to this representation, the variation of the strain versus time in each loading cycle is given in Equation (3-8).

$$\varepsilon(t) = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \frac{\tau_0}{G_0} + \frac{\tau_0}{G_1}\left(1 - e^{-\frac{t}{\tau}}\right) + \frac{\tau_0}{\eta_0} \cdot t \tag{3-8}$$

Where:

- $\varepsilon(t)$ is the whole strain at the (t);
- ε_1 is the elastic portion of the strain (it is instantaneous and fully recoverable);
- ε_2 is the viscoelastic portion of the strain (delayed – elastic strain) that is recoverable with time;
- ε_3 is the viscous portion of the strain that is non-recoverable and it is considered as responsible for the accumulation of permanent deformation.

If the applied stress normalizes the strain components in Equation (3 8), the Equation of the strain can be written in terms of compliance (Equation (3-9)).

$$J(t) = J_e + J_{de}(t) + J_{nr}(t) \tag{3-9}$$

Where:

- J_e is the elastic compliance;
- $J_{de}(t)$ is the delayed-elastic component of the compliance;
- $J_{nr}(t)$ is the non-recoverable compliance that is the parameter considered in the specifications.

The non-recoverable compliance (J_{nr}) and the average percent recovery (R) are calculated in each loading cycle. The portions of the strain used to calculate the test parameters at each loading cycle are represented in Figure 3-26.

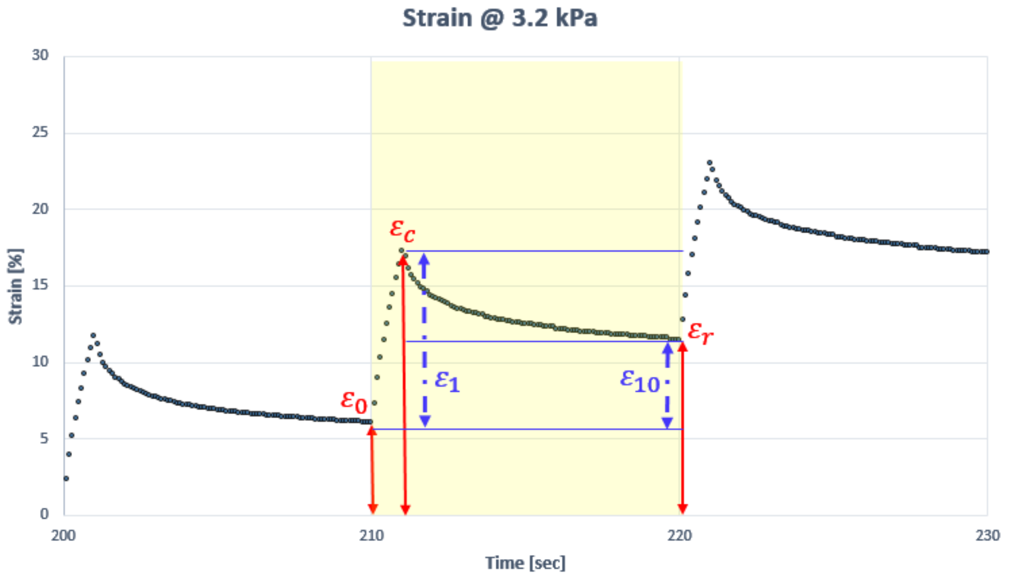


Figure 3-26 – Portions of the strain used to calculate J_{nr} and R.

The definitions of the terms in Figure 3-26 are given in Table 3-10.

Table 3-10 – Definition of the terms given Figure 3-26

ε_0	Strain value at the beginning of the creep portion of the n-cycle	
ε_c	Strain value at the end of the creep portion of the n-cycle	
ε_r	Strain value at the end of the recovery portion of the n-cycle	
ε_1	$\varepsilon_1 = \varepsilon_c - \varepsilon_0$	Adjusted strain at the beginning of the creep portion of the n-cycle
ε_{10}	$\varepsilon_{10} = \varepsilon_r - \varepsilon_0$	Adjusted strain at the end of the creep portion of the n-cycle

Considering the definition of the terms given in Table 3-10, the non-recoverable compliance is calculated at the n-loading cycle by Equation (3-10), while average percent recovery R is calculated at each loading cycle by Equation (3-11).

$$J_{nr}^{n}(kPa^{-1}) = \frac{\varepsilon_r^n - \varepsilon_0^n}{\tau_0} \tag{3-10}$$

$$R(\%) = \frac{\varepsilon_c^n - \varepsilon_r^n}{\varepsilon_c^n - \varepsilon_0^n} \tag{3-11}$$

The average values of J_{nr} and R are calculated for each stress level (i.e., 0.1 and 3.2 kPa) according to Equations (3-12) and (3-13) for the non-recoverable compliance;

$$J_{nr0.1}(kPa^{-1}) = \frac{\sum_{n=1}^{10} J_{nr0.1}^{n}}{10} \tag{3-12}$$

$$J_{nr3.2}(kPa^{-1}) = \frac{\sum_{n=1}^{10} J_{nr3.2}^{n}}{10} \tag{3-13}$$

Moreover, according to Equations (3-14) and (3-15) for the average percent recovery R.

$$R_{0.1}(\%) = \frac{\sum_{n=1}^{10} R_{0.1}}{10} \tag{3-14}$$

$$R_{3.2}(\%) = \frac{\sum_{n=1}^{10} R_{3.2}}{10} \tag{3-15}$$

The stress sensitivity of the bitumens is calculated by Equation (3-16).

$$J_{nr-diff}(\%) = \frac{[J_{nr3.2} - J_{nr0.1}] \times 100}{J_{nr0.1}} \tag{3-16}$$

The stress sensitivity is expressed as the ratio between the differences in the J_{nr} at the two stress levels versus the Jnr at the lowest stress level considered in the test.

The specifications of the MSCR test are given in the AASHTO M 332 (235). The standard identifies four traffic designation as a function of the number of Equivalent Standard Axle Loads (ESAL) and the traffic speed. Bitumen are classified for each designation as per the J_{nr} at 3.2 kPa measured at the high PG grade temperature on the RTFO residue (Table 3-11).

Table 3-11 – Traffic designation AASHTO M332

Traffic designation AASHTO M 332		**$J_{nr3.2}$ max [kPa^{-1}]**
Standard (S)	ESAL < 10^7(speed >70 km/h)	4.5
Heavy traffic (H)	10^7 < ESAL < 3 x 10^7 (speed >20 and <70 km/h)	2.0
Very Heavy traffic (V)	ESAL > 3 x 10^7 (speed <20 km/h)	1.0
Extreme (E)*	ESAL > 3 x 10^7 (speed <20 km/h)	0.5

*E-grade includes port and to plazas with extreme standing heavy traffic

Besides, the J_{nr} at 3.2 kPa a maximum value of 75% for the $J_{nr-diff}$ of is recommended at all the traffic designations to avoid excessive stress dependency of PMBs. The average percent recovery (R) is not used for grading purpose, and there are no specification limits. However, according to AASHTO TP 70, R can be used to identify the presence of elastomers in the PMBs.

As mentioned in §2.10.4, in this work, the MSCR has not been used for grading purpose, but to study the effects of the thermo-oxidative process occurring in the PAV on the rheological response of PMBs trying to distinguish the contribution of the polymer phase and the bitumen phase. Specifically, two rheological indicators have been considered:

- The J_{nr} at 3.2 kPa ($J_{nr3.2}$) has been considered as representative of the response of the resistance to the accumulation of permanent deformation of the whole system bitumen + polymer.
- The average percent recovery R at 3.2 kPa ($R_{3.2}$) has been considered as an indicator of the efficiency of the polymer network. Although the relations between bitumen elasticity and mixture performance are not fully understood, the use of average percent recovery (%R) as a quality indicator of the polymer efficiency and mixture durability can be advocated (189, 190). The elasticity of rubber can be defined as the capacity to complete large deformation recover. This property is a function of molecular requirements such as the flexibility of polymer chains and the presence of a structured network. In the case of PMBs, the formation of this network depends on several factors such as the polymer concentration, the blending process, the use of stabilising cross-linkers, and the affinity between polymer and bitumen. Therefore, the capacity of this network to resist the effect of thermo-oxidative ageing processes could be evaluated through its capacity of maintaining the strain recovery at different levels of ageing.

The bitumen used in this test are given in Table 3-12.

Table 3-12 – Bitumens used in the MSCR test

Bitumen	Unaged	RTFO	0.5 PAV	1 PAV	2 PAV	4 PAV
Pen	V	V	V	V	V	V
Pen/S	V	V	-	V	V	V
SBS 2/S	V	V	V	V	V	V
SBS 4/S	V	V	V	V	V	V
SBS 6/S	V	V	V	V	V	V
SBS 4	V	V	V	V	V	V
SBS 6	V	V	V	V	V	V
EVA 2	V	V	-	V	V	-
EVA 4	V	V	-	V	V	-
EVA 6	V	V	-	V	V	-

Three replicates were tested for each material.

3.3.7.2 Definition of MSCR test temperature

According to the AASHTO M 332, the MSCR test is conducted at the high PG grade temperature. Such temperature is determined by measuring the shear complex modulus and the phase angle on the unaged bitumen and the RTFO residue.

In this work, the MSCR test temperature was selected according to the continuous grade temperature criteria, that is the temperature at which the $G^*/\sin\delta$ measured on the RTFO residue is equal to 2.2 kPa. Therefore, the MSCR test temperatures were determined on the RTFO residue and then maintained constant to highlight the effects of the PAV only avoiding any possible confounding effect. In some measure, this is representative of the field conditions. That is, the bitumen is selected as per its high-temperature properties determined after the short-term ageing. Then, as per the criterion adopted, it is possible to highlight how these properties (measured at the same temperature) vary with the oxidative ageing simulated in the PAV.

3.3.8 Linear Amplitude Sweep (LAS) test

3.3.8.1 Test method

The LAS test was conducted as per the AASHTO TP 101 – 12 (239). The test is conducted in the DSR by using the 8 mm parallel plate geometry.

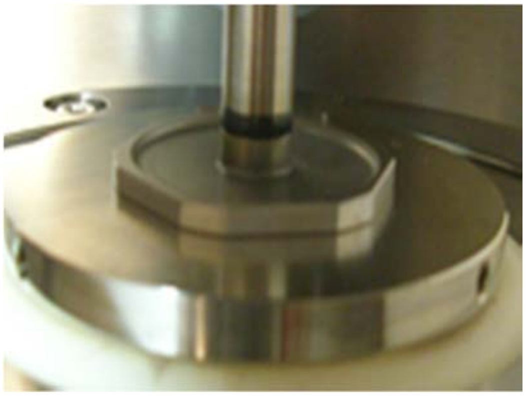


Figure 3-27 – DSR 8 mm parallel plate

The test method includes two parts. The first aims to determine the undamaged linear viscoelastic properties. The second part represents the “destructive” part of the test where damage is induced by increasing the strain level applied at the different loading cycles.

In Equation (2-39), the parameter α represents the damage accumulation rate that is determined within the linear viscoelastic region.

In the case of the LAS test, α is determined through a frequency sweep test whose characteristics are given in Table 3-13.

Table 3-13 – Frequency sweep in LAS test

Frequency [Hz]	Log ramp [0.1÷30]
Strain level [%]	0.1

After the frequency sweep, the strain sweep portion of the test is applied to induced damage. The strain applied is linearly increased over the loading cycles (Figure 3-28).

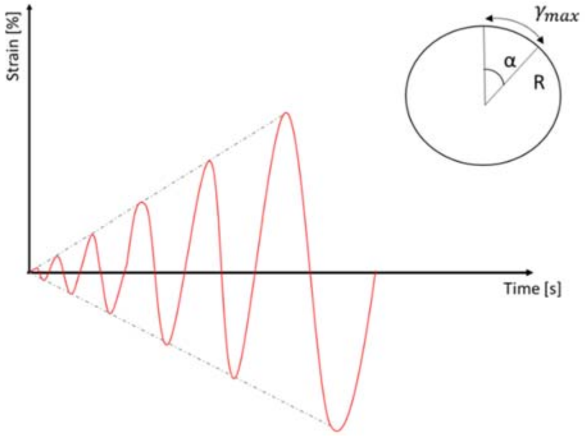


Figure 3-28 – Sketch of linearly-increasing shear strain during the LAS test

The strain considered is measured at the edge of the sample where based on the section (circular), the maximum level is achieved. The test frequency, the strain levels and the number of loading cycles are given in Table 3-14.

Table 3-14 – Strain sweep in LAS test

Frequency [Hz]	10
Strain level [%]	Linear ramp [0.1÷30]
Cycles [1]	3,100

During the strain-sweep portion, the damage is induced by increasing the strain. The mechanism is supposed to be cohesive crack propagation with loading (43). An example of the top surface of the sample after the LAS test is given in Figure 3-29.

Figure 3-29 – Example of sample top surface after the LAS test

(cohesive cracks propagating from edge to the centre)

Cohesive cracks seem to initiate at the edge of the sample (where the strain level achieves the maximum), and then they propagate towards the centre under loading (Figure 3-30).

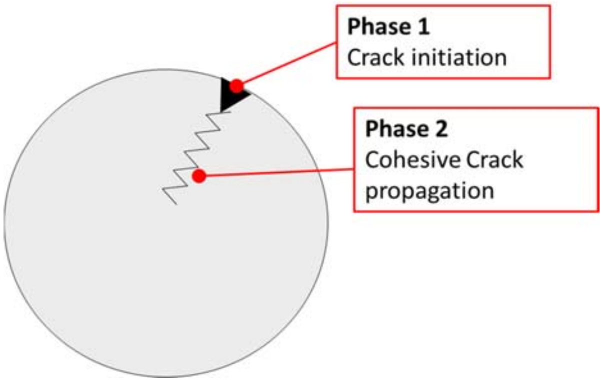


Figure 3-30 – Sketch of crack initiation and crack propagation during LAS test

As discussed in §2.10.5.1, in the VECD theory, the damage is seen as the loss in the material integrity with the consequent reduction in stiffness and strength. In viscoelastic materials, damage induces changes in the dissipated strain energy (Equation (2-44)) that is proportional to the viscous modulus$|G^*|\sin\delta$. Therefore, in the LAS test the cohesive crack propagations causes a reduction in the viscous shear modulus with consequent changes in the dissipated strain exergy. An example of the variation of the viscous modulus with the applied strain is given in Figure 3-31.

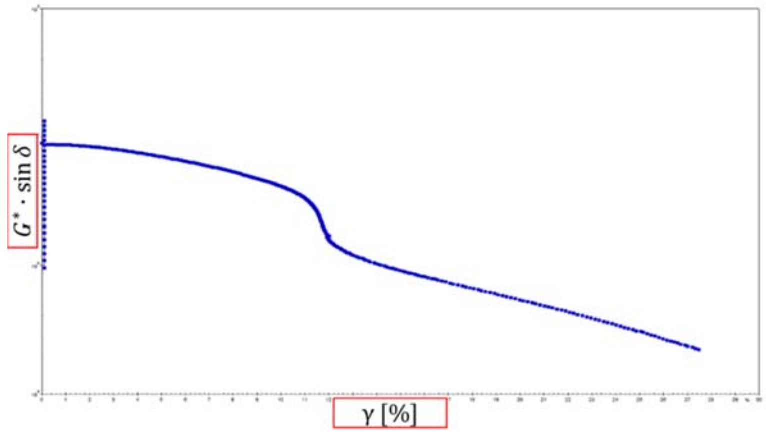


Figure 3-31 – Example of the variation of the viscous modulus during strain sweep

The viscous modulus undergoes a reduction throughout the whole strain interval. However, around a strain of 11%, the bitumen shows a marked reduction within a limited number of loading cycles. It is known the stiffness of viscoelastic materials under cyclic loading undergoes a reduction due to different contributions as thixotropy (time-dependent shear thinning phenomena), increase in temperature due to internal viscous effects, damage (222, 223). Therefore, the reduction in the viscous modulus with strain does not entirely depend on the damage. However, the sharp reduction in stiffness around of 11% allows thinking that damage has started in that zone. The materials used in this test are given in Table 3-15.

Table 3-15 – Materials used in the LAS test

Bitumen	Unaged	RTFO	0.5 PAV	1 PAV	2 PAV	4 PAV
Pen	V	V	-	V	V	V
Pen/S	V	V	-	V	V	V
SBS 2/S	V	V	-	V	V	V
SBS 4/S	V	V	-	V	V	V
SBS 6/S	V	V	-	V	V	V
EVA 2	V	V	-	V	V	-
EVA 4	V	V	-	V	V	-
EVA 6	V	V	-	V	V	-

A minimum of three samples were tested for each combination bitumen – ageing level. Replicates are acceptable once they show a variation lower than 15%.

3.3.8.2 Analysis of data

The LAS test data were analysed according to the VECD theory included in the AASHTO TP 101-12 (239). The main scope of the data analysis is to solve Equation (2-39) by using the experimental data and to define the Number of cycles to failure (N_f) given by Equation (2-52) that is here reported.

$$N_f = A(\gamma_{max})^B \tag{2-52}$$

The forms and the significance of the terms in Equation (2-52) applied to the LAS test as per the AASHTO TP 101 – 12 are given in Table 3-16.

Table 3-16 – Significance and forms of Equation (2-52) applied

to the LAS test as per the AASHTO TP 101 -12 (239).

$A = \frac{f(D_f)^k}{k(\pi C_1 C_2)^\alpha}$	The coefficient A35 represents the value of the Wholer curve at a strain level of 1% (Figure 2-55). It depends on the material integrity versus the damage curve (e.g., Figure 4 73), and the criterion selected as a failure (37).
$D_f = \left(\frac{0.35}{C_1}\right)^{1/C_2}$	That is the damage intensity corresponding to a reduction of 35% of the initial complex shear viscous modulus ($\lvert G^*\rvert \sin\delta_{residual} = 0.65 \cdot \lvert G^*\rvert \sin\delta_{initial}$).
C_1, C_2	See Equation (3-20) and (3-21)
f	Is the loading frequency during the amplitude sweep portion of the test (10 Hz);
$k = 1 + (1 - C_2);$	Test parameter.
$\alpha = \frac{1}{m}$	Is the inverse of the slope of the isotherm (of the storage modulus) obtained in the frequency sweep test (Figure 3-32). It is the exponent that determines the energy release rate (Equation (2-39)).
$B = -2\alpha$	It is the slope of the Wholer curve (Figure 2-55), and it is a function of the parameter α, which depends on the time-temperature dependency of the material. A decrease in the time-

	temperature dependency of the material corresponds to a decrease in B.
γ_{max}	Is the maximum strain level expected in the bitumen phase for a given pavement structure.

Considering the failure criterion as a reduction of 35% in the viscous modulus, Equation (2-52) can be written as Equation (3-17).

$$N_f = A_{35}(\gamma_{max})^{-B} \tag{3-17}$$

However, other levels of damage at failure could be considered by maintaining the same forms of the equation and modifying the Equation of D_f (Table 3-16) only. An example of the fatigue law Figure 2-55.

The steps of the data analysis are given below.

Step 1 – Calculate the parameter α

The parameter α is calculated from the frequency sweep data. Specifically, α represents the inverse of the slope (m) of the isotherm of the logarithm of the storage modulus versus the logarithms of the frequency (Figure 3-32).

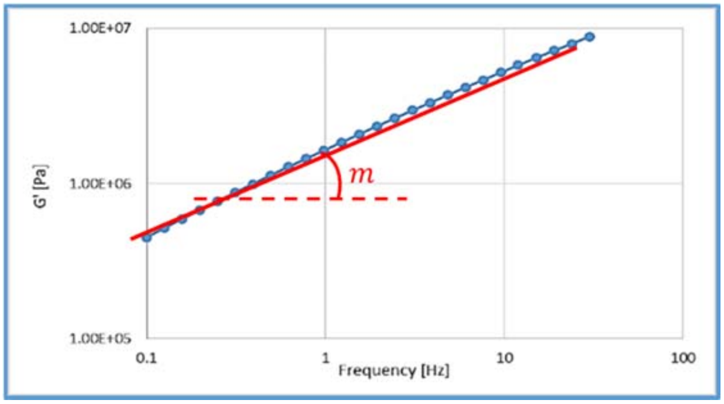


Figure 3-32 – Isotherm of the log storage modulus (G’) versus the log (frequency)

The Storage modulus represents the in-phase component of the complex modulus calculated at the test temperature for each frequency by Equation (2-21).

The parameter α is calculated by Equation (3-18).

$$\alpha = \frac{1}{m} \tag{3-18}$$

Where m represents the slope of the isotherm curve log (G’) versus log (f). Therefore α is a measure of the time-temperature dependency of the materials. Being the parameter B (Table 3-16) function of the parameter α only, it is a function of the time-temperature dependency of the material.

Step 2 – Calculate the Damage Accumulation D(t)

The damage accumulation is calculated through Equation (3-19) by using the data from the strain-sweep test.

$$D(t_N) \cong \sum_{i=1}^{N} [\pi \cdot \gamma_0^2 (C_{i-1} - C_i)]^{\frac{\alpha}{1+\alpha}} (t_i - t_{i-1})^{\frac{1}{1+\alpha}} \tag{3-19}$$

Where:

- $C = \frac{|G^*| \sin \delta_i}{|G^*| \sin \delta_{initial}}$ – that represents the variation of the viscous modulus with damage expressed as the ration between G” at the i-cycle versus the G” at the initial conditions;
- γ_0 – is the strain applied at the i-cycle (Table 3-14);
- t – is the time;
- $\alpha -$ Equation (3-18).

The form used to calculate the cumulative damage over the loading cycles in the LAS test is similar to as Equation (2-46) developed by Kim and co-workers (213) valid for the damage characterisation of asphalt mixtures under cyclic loading.

Step 3 – Fit empirical equation C(t) versus D(t).

The values of D(t) are used to fit the empirical model given by Equation (3-20).

$$C(t) = C_0 - C_1\big(D(t)\big)^{C_2} \tag{3-20}$$

Where:

- C_0 – is the initial value of C (C_0=1);
- C_1, C_2 – are the curve-fit coefficient derived from the linearization of the power-law form (Equation (3-20)) in the form suggested by Hintz and co-workers (43) given in Equation (3-21).

$$\log\big(C_0 - C(t)\big) = \log C_1 + C_2 \log\big(D(t)\big) \tag{3-21}$$

Step 4 – Calculate the number of loading to failure (N_f)

The fatigue damage parameter is given in Equation (3-18) is calculated by using the parameters A_{35} (Table 3-16) and the parameter B (Equation (3-18)) that are derived from the operations described in the steps above, and by considering a certain strain level in the bitumen. According to the researchers of the University of Wisconsin - Madison, two strain levels can be considered: 2.5% for thick pavements, and 5% for weak pavements (37, 43, 221). The evaluation of the strain levels in the bitumen phase from the bearing capacity of the pavements originates from the considerations included in §2.10.2.1 by assuming a factor of 50 between the strain in the mix phase and the strain in the bitumen phase. Therefore, if the mix undergoes a strain equal to 500 micro-strains, the bitumen phase could experience an average strain of 2.5%.

3.3.8.3 Definition of LAS test temperatures

Fatigue cracking of asphalt mixtures occurs within the range of intermediate pavement temperatures. In the case of the LAS test, it is recommended to conduct the test at the intermediate PG grade temperature (221).

The intermediate grade temperature is calculated by Equation (3-22) (108).

$$PG_{IT} = \frac{PG_{HT} + PG_{LT}}{2} - 4°C \tag{3-22}$$

Where:

- PG_{IT} – is the intermediate (PG) temperature;
- PG_{HT} – is the Performance grade high temperature determined according to the AASHTO M 320 (236);
- PG_{LT} – is the Performance grade low temperature determined according to the AAHTO M 320 (236).

In this work, the performance grade low temperature was determined according to the equivalent method based on DSR measurements reported in the SHRP Report 367-A (108). Different performance grade bitumens have different PG_{IT} temperatures. The average PG_{IT} temperature was calculated from the PG_{IT} temperature of each bitumen.

Besides the evaluation of the intermediate grade temperatures, an alternative method to define the LAS test temperature was investigated. The method can be summarised in the following steps:

- Four different provinces from the Italian territory were selected to be representative of intermediate climatic region (Figure 3-33).

Figure 3-33 – Italian climatic region considered to define LAS test temperature

For each province, the parameters included in the model were withdrawn from the climatic data available at (http://www.centrometeo.com).

Table 3-17 – Climatic and geographic data used to calculated LAS test temperature.

(Max. T)	Annual maximum air temperature (Average from the past ten years)
(Min. T)	Annual minimum air temperature (Average from the past ten years)
(Avg. T)	Annual average air temperature (Average from the past ten years)
Latitude	Latitude of the location

- The climatic and geographic data were used in the Bell2 model (224) to estimate the annual average temperature in the centre of a base course layer located to a depth of 14.5 cm. The average value from the four provinces was considered.

The value obtained was compared with the average temperature obtained from the PG_{IT} temperatures of the bitumens, and the higher value was selected. Results are given in section 6.1.

3.3.9 Time Sweep (TS) test

The time sweep test was used for the comparative purpose of the LAS test results on a limited subset of bitumens. If the LAS is an accelerated test method that induces damage by increasing the strain applied, the time sweep test represents a repeated loading cycle method where cumulative damage occurs by the load repetitions.

As discussed in §2.10.5.2, the TS test was developed with the scope of delivering performance-based criteria of the fatigue cracking resistance of PMBs. The test consists of the repeated application of loading under stress or strain controlled condition at a determined loading frequency and test temperature. Therefore, the test allows monitoring continuously the reduction in stiffness with loading. The TS was conducted under strain-controlled conditions. The data were analysed by monitoring the stress versus the strain curves, and the reduction of 35% of the initial viscous modulus (G" – Equation (2-22)) was considered as the failure criterion (in compliance with the LAS test).

The loading frequency and the strain levels adopted are given in Table 3-18.

Table 3-18 – Test condition of TS test.

f [Hz]	10			
γ [%]	1.0	2.5	6.5	11

The strain levels were selected upon the results of the LAS test. The same test temperature used in the LAS test was adopted. The materials used in this test are given in Table 3-19.

Table 3-19 – Materials used in the TS test.

Bitumen	Unaged	1 PAV	2 PAV
SBS 2/S	V	V	V

Two replicates were tested for each material.

4 Chemo-physical properties

This section includes the results of the storage stability, fluorescence microscopy and GPC described in Section 3.

4.1 Results of storage stability (ASTM D 7173 - Tuben Test)

The storage stability was evaluated on the SBS modified bitumen, considering the highest polymer concentration (i.e., 6% SBS).

The Tuben test was performed on the modified bitumens with and without the presence of sulphur as cross-linker (i.e., SBS 6/S and SBS 6). The polymer stability was evaluated by Equation (3-1) that is here reported for completeness.

$$R\ [\%] = \frac{\left|G^*_{Top} - G^*_{Bottom}\right|}{G^*_{Top}} * 100 \leq 20\%$$

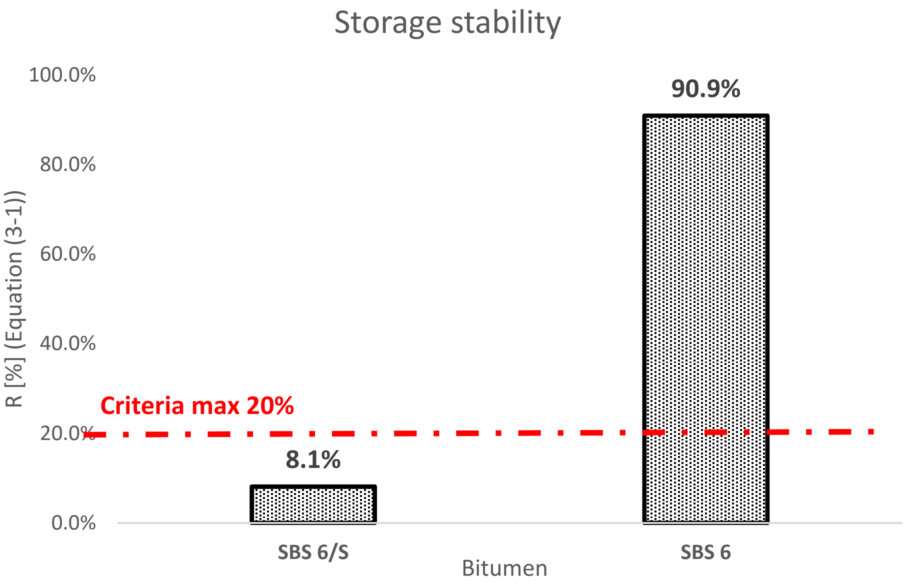
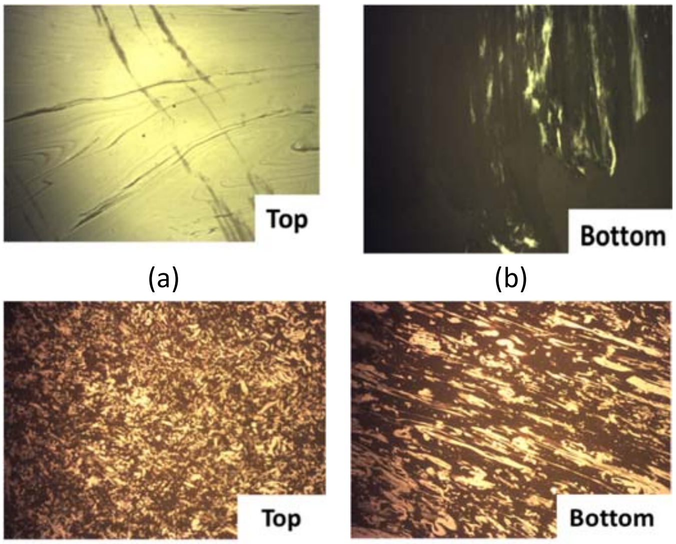


Figure 4-1 – Results from storage stability test according to Equation (3-1)

In the case of cross-linked SBS modified bitumens (i.e., SBS 6/S), the ratio R (Equation (3-1)) is well below the limit provided by the specification. That is, the bitumen portions in the top part of the tube and the bottom part of the tube show a relatively limited difference in the value of G*. On the other hand, in the absence of sulphur, the bitumen in the top part of the shows a higher stiffness. Therefore, in the first case, the polymer phase seems to be well distributed between the top part and the bottom part of the tube. While, in the second, the polymer seems to be more concentrated in the top of the bitumen.

This difference highlights that the presence of sulphur improves the stability between polymer and bitumen with the polymer phase that does not undergo separation even after 48 hours at 163°C.

Besides the rheological characterisation of the top and the bottom parts of the tube, the fluorescence microscopy was used to observe the polymer-bitumen separation of the SBS 6 bitumen (Figure 4-2).



(a) (b)

(c) (d)

Figure 4-2 - Images of Morphology (10x magnification) of SBS 6 after ASTM D 7173 Test

(a – PMB in the top part of the tube; b – PMB in the bottom part of the tube); SBS 6/S after ASTM D 7173 Test (c – PMB in the top part of the tube; d – PMB in the bottom part of the tube).

The images show that in the case of SBS 6 bitumen due to the phase separation, the SBS phase moves to the top part of the tube where a higher polymer concentration is shown. On the other hand, the SBS 6/S bitumen shows higher stability with the morphology of the PMB in the top and the bottom parts of the tube being very similar. These results are in agreement with other research published on the advantages of using sulphur as a cross-linking agent with PMBs (178, 225, and 226).

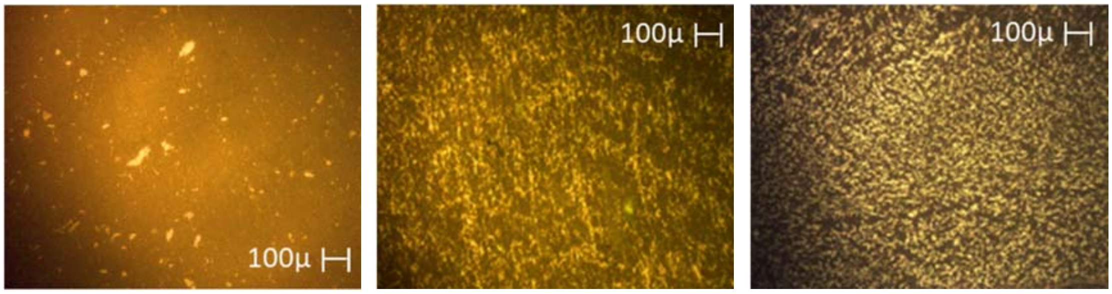
4.2 Results of fluorescence microscopy

This section includes the results of fluorescence microscopy of the PMBs at the different levels of ageing. Results are organised for SBS modified bitumens and EVA modified bitumens.

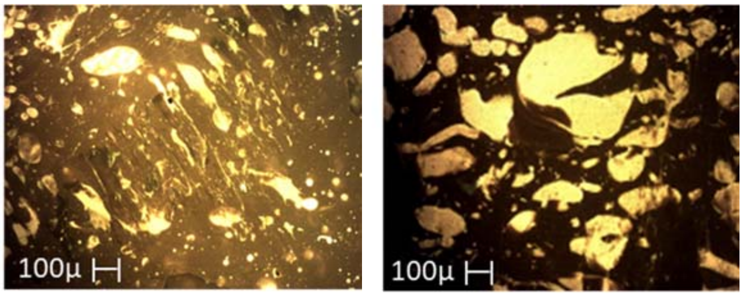
4.2.1 Morphology of SBS modified bitumens

In the case of the SBS modified bitumens, the fluorescence microscopy was used to evaluate the effects of the laboratory-simulated ageing on the level of dispersion of the SBS phase into the bitumen phase. Furthermore, the comparative analysis of the morphologies of the cross-linked SBS modified bitumens (i.e., SBS + sulphur) and the uncross-linked (i.e., SBS no sulphur), has been conducted to evaluate the effects of sulphur on the changes in the SBS morphology with ageing.

The morphologies of the SBS modified bitumens at the unaged conditions are given as reference in Figure 4-3.



a) SBS 2/S b) SBS 4/S c) SBS 6/S



d) SBS 4 e) – SBS 6

Figure 4-3 – Morphologies of SBS modified bitumens at unaged conditions (a, b, c – cross-linked SBS respectively at 2%, 4% and 6% SBS); (d, e – uncross-linked at 4% and 6% SBS).

Considering that all the samples for fluorescence microscopy were prepared with the same procedure, it seems to be clear that the morphology of the SBS modified bitumens depends on the polymer concentration and the use of sulphur as cross-linker.

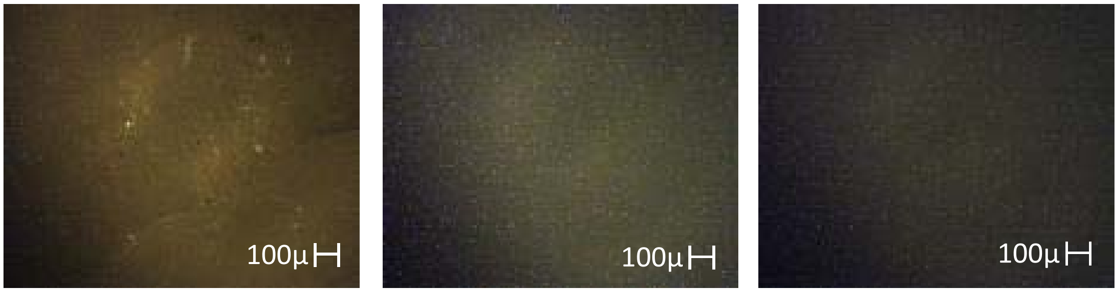
In the case of cross-linked SBS, the morphology of the SBS depends on the polymer concentration, specifically:

- At 2% SBS (Figure 4-3 - a), the polymer is not capable of forming a visible interconnected network, and the particles remain dispersed within the bituminous phase;
- While at 4% and 6% SBS, the polymer forms a structured network throughout the bituminous phase becoming, apparently, the dominant phase (Figure 4-3 – b, c). The formation of this network is more evident at 6% SBS. Such a network is constituted of elongated interconnected branches. Such a shape could reveal an adequate level of affinity with the base bitumen since it is likely to have a high specific surface. In other words, its seems that the polymer "*wants to interact with the bitumen offering the highest surface available per unit of volume*". On the other hand this shape provides a higher polymer surface exposed to the oxygen diffusion.

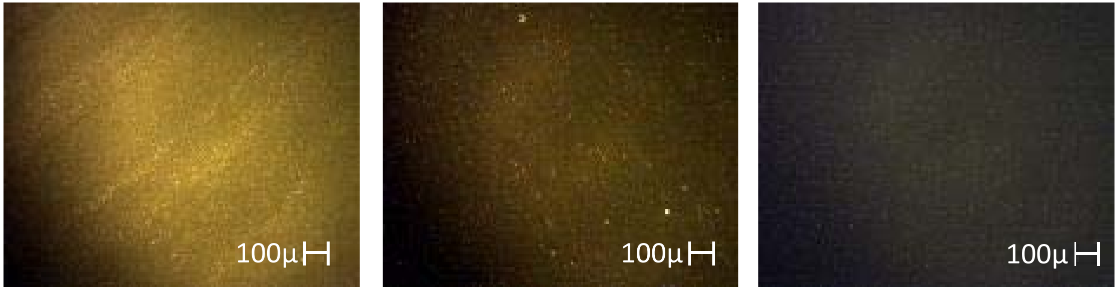
In the case of uncross-linked SBS modified bitumens (Figure 4-3 – d, e), under the same polymer concentrations, the polymer phase achieves a lower dispersion remaining more separated from the bitumen phase. In this case, the polymer does not seem to become the dispersing phase (or dominant phase), but rather it remains the dispersed phase. This aspect might be indicative of low affinity.

Therefore, the use of sulphur as cross-linker seems to enhance the polymer dispersion. The reason behind this is that sulphur cross-links the chains of the SBS copolymer, increasing its level of reticulation.

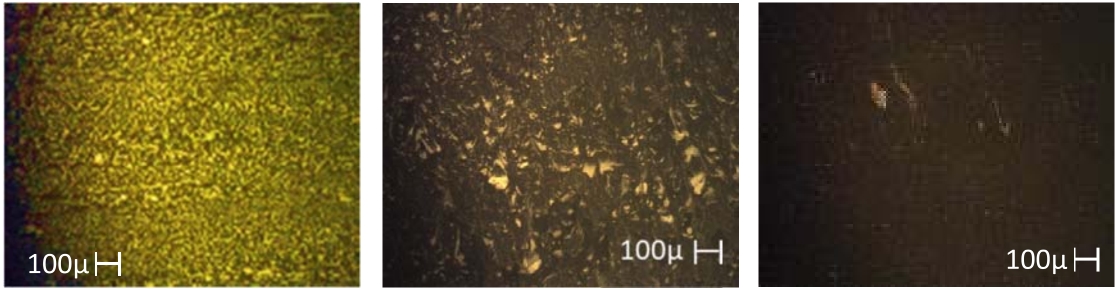
The residual morphologies of the SBS modified bitumens at the different levels of laboratory-simulated ageing are given in Figure 4-4.



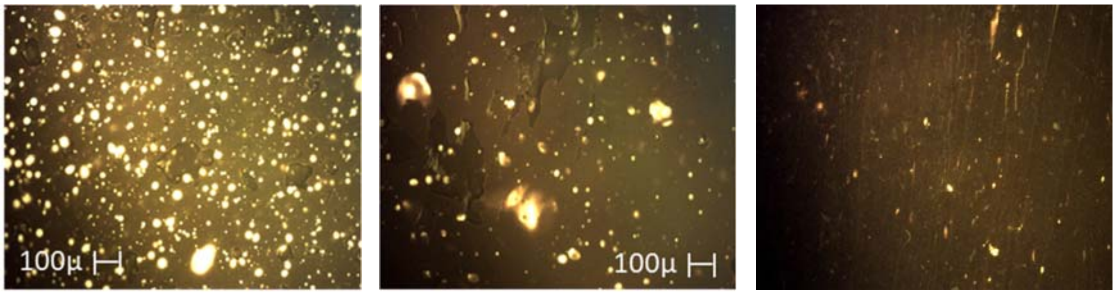
a) SBS 2/S - RTFO   b) SBS 2/S -PAV   c) SBS 2/S -2 PAV



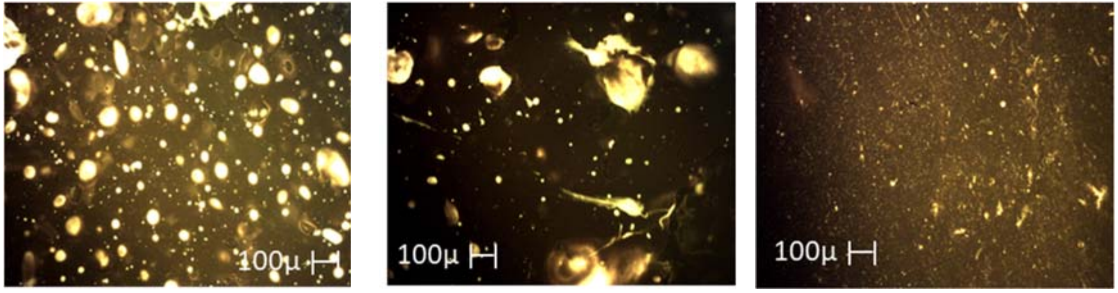
d) SBS 4/S - RTFO   e) SBS 4/S - 1PAV   f) SBS 4/S – 2PAV



g) SBS 6/S - RTFO   h) SBS 6/S - 1PAV   i) SBS 6/S – 2PAV



j) SBS 4 - RTFO k) SBS 4 – 1PAV l) SBS 4 – 2PAV



m) SBS 6 - RTFO n) SBS 6 – 1PAV o) SBS 6 – 2PAV

Figure 4-4 – Residual morphologies of SBS modified bitumens after RTFO, 1 PAV and 2 PAV cycles;

(A to i – cross-linked SBS modified bitumens); (j to o – uncross-linked SBS modified bitumens)

The effect of laboratory-simulated ageing on the morphology of the SBS modified bitumen depends on the polymer concentration and the use of cross-linker. At 2% SBS (Figure 4-4 – a, b, c), the polymer completely degrades after the RTFO ageing. Comparing Figure 4-3 (a) and Figure 4-4 (a), it is noted that the fluorescence of the polymer particles is sensitively reduced after the RTFO. Therefore, in the absence of formation of a structured network (as it occurs at 2% cross-linked SBS), the majority of the polymer particles dispersed throughout the bitumen phase disappears during the RTFO-ageing.

The morphology of the SBS 4/S bitumen after RTFO (Figure 4-4 - d) is different from the morphology shown at the unaged conditions (Figure 4-3 - b). After RTFO, the branched structure dissolves in thin particles widely dispersed in the bitumen phase. Then, the polymer phase disappears already after a single PAV cycle (Figure 4-4 – d).

In the case of the SBS 6/S bitumen, the morphology after RTFO (Figure 4-4 - g) does not show any relevant variation compared to the unaged conditions (Figure 4-3 - c). However, this aspect does not allow concluding that at high polymer concentration, the polymer network is not sensitive to the RTFO-ageing. At such high polymer concentration, the viscosity of the bitumen at the RTFO temperature (163°C) might be as such as high to prevent the bitumen from forming a thin film accessible to oxygen and heat during the test. Aware of this aspect, the viscosity of the bitumen at 163°C was measured at low shear rate. The bitumen viscosity resulted in being of 1.4 Pa*s, which seems to be as such as high to support the hypothesis aforementioned.

Nonetheless, as per the images in Figure 4-4 (h, i), it is clear that the thermo-oxidative processes in the PAV cause the degradation of the SBS network that loses it structure and degenerates in dispersed disconnected particles. It is well known that SBS shows reactivity with oxygen due to the presence of unsaturated C=C double bonds in the Polybutadiene blocks (20, 22, 137, 138, and 144). Although the polymer degrades with oxidation, the polymer phase is still visible in the morphology after 1 cycle of PAV ageing (Figure 4-4 - h). However, at 6% SBS concentration, the effect of the PAV ageing might be mitigated by the higher viscosity (and therefore lower permeability to oxygen) of the bitumen at the PAV temperature.

The variation of the morphology of the uncross-linked SBS modified bitumens with laboratory-simulated ageing (Figure 4-4 – j to o) shows that besides storage stability and polymer dispersion, the use of cross-linker affects the laboratory-ageing susceptibility of the polymer phase in the bitumen phase. The polymer phase of the SBS 4 bitumen at unaged conditions (Figure 4-3 – d) does not form a structured network. The polymer phase remains dispersed in the bitumen phase as disconnected particles of various irregular shapes. After the RTFO - ageing (Figure 4-4 - j), the polymer particles are widely dispersed in the bitumen phase as small spheres. The polymer phase seems to be more visible compared to the analogue ageing level of the SBS 4/S bitumen (Figure 4-4 - d). The reason behind this might depend on the quality of the image, or, as a hypothesis, on the fact the in the case of uncross-linked polymer the SBS phase is separated from the bitumen phase and has a significantly different (and higher) fluorescence. In the PAV, the dispersion of the polymer particles is reduced into small sparse fragments of polymer barely visible in the microscope (Figure 4-4 – k, l).

The effect of sulphur is visible in the case of 6% SBS as well. If in the case of cross-linked SBS the RTFO produces negligible effects on the morphology compared to the unaged conditions (i.e., SBS 6/S - Figure 4-4 – g), in the absence of the cross-linker the polymer phase undergoes degradation with the polymer becoming dispersed as disconnected spheres of various size (Figure 4-4 - m). It seems that once the polymer does not form a reticulated network has a lower resistance to the thermal processes occurring in the RTFO. However, the effect of viscosity at the RTFO temperature might be considered. That is, in the case of an uncross-linked polymer, the viscosity of the bitumen at the RTFO temperature is lower than the cross-linked with the RTFO being more effective in damaging the polymer network. The effects of the PAV on the polymer dispersion (Figure 4-4 – n, o), are the same as those observed at 4% SBS (Figure 4-4 – k, l).

The variation of the morphologies of the SBS modified bitumens has been qualitatively discussed in terms of polymer degradation. This interpretation is plausible and is in agreement with the existing literature.

However, results could be alternatively analysed in terms of polymer de-swelling. In other words, if during blending the polymer swells in the bitumen phase by absorbing the most compatible bitumen fractions, during ageing the aromaticity of these fractions can be altered to make them migrating to the bitumen-rich phase and causing the polymer morphology to reduce significantly and almost to disappear. The changes with ageing in the chemical composition of the bitumen fractions absorbed by the polymer during swelling have been discussed by Mouillet et al in a work focused on the ageing of EVA modified bitumens (177). Besides this, recent approaches based on fluorescence have highlighted the differences in the fluorescence response among the different bitumen fractions (§2.5.3.5). The aromatics seem to have the highest fluorescence compared to asphaltenes (almost negligible fluorescent response) and resins.

Considering the findings of Mouillet et al (177) and those of Handle et al (231), the hypothesis of the de-swelling of SBS during ageing might be raised. That is, during blending the polymer swells initially by absorbing compatible and fluorescent fractions. Thus, at unaged conditions, the morphology is well visible through a contrast between the asphaltenes (less compatible, not absorbed and less fluorescent), and the polymer swollen (presumably) by the aromatics, which has a marked fluorescence. Then, once ageing occurs, the aromatics change their structure and leave the polymer phase, which is de-swollen and, alone, might not show the same contrast in fluorescence with the other components of the PMBs. In this way, the morphology observed at unaged conditions disappears.

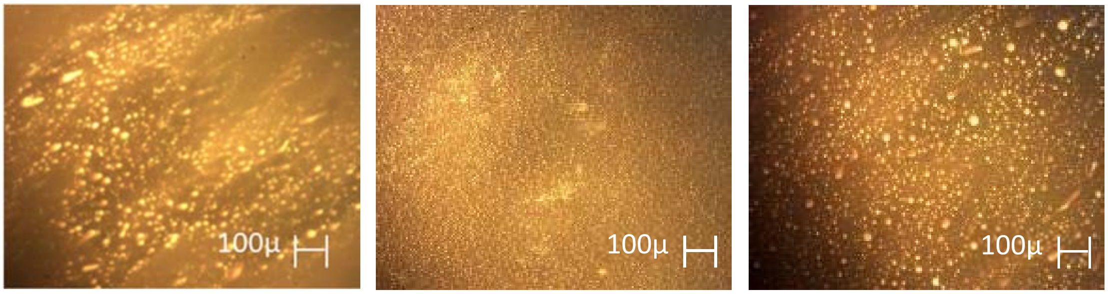
The de-swelling theory could sound reasonable as well. However, there are some shortcomings that contribute to raising some concerns on the applicability of this hypothesis. For example, the effect of the polymer concentration remains unclear. The morphology of the SBS/2S bitumen has undergone sensible reduction after the RTFO, while higher concentrations have resulted in being more resistant (i.e., 6% SBS). Besides polymer concentration, crosslinked and un-crosslinked SBS show different de-swelling mechanisms with the former being more resistant than the latter. What is the effect of the crosslinker on the changes in the aromaticity of the bitumen components that leave the polymer phase, causing a reduction in its volume? These examples highlight how challenging (and at the same time fascinating) this problem is.

Nevertheless, fluorescence microscopy allows a qualitative interpretation of results and does not allow the precise identification of fluorescent species. Therefore, such hypothesis needs a further and more rigorous investigation to be supported (including, for instance, rheological pieces of evidence).

For this reason, in this work the hypothesis of polymer degradation is considered as more reasonable.

4.2.2 Morphology of EVA modified bitumens

In the case of EVA modified bitumens, the fluorescence microscopy was used to evaluate the effects of laboratory-simulated ageing n the polymer dispersion in the bitumen phase. The morphologies of the EVA modified bitumens at unaged conditions are given as reference in Figure 4-5.

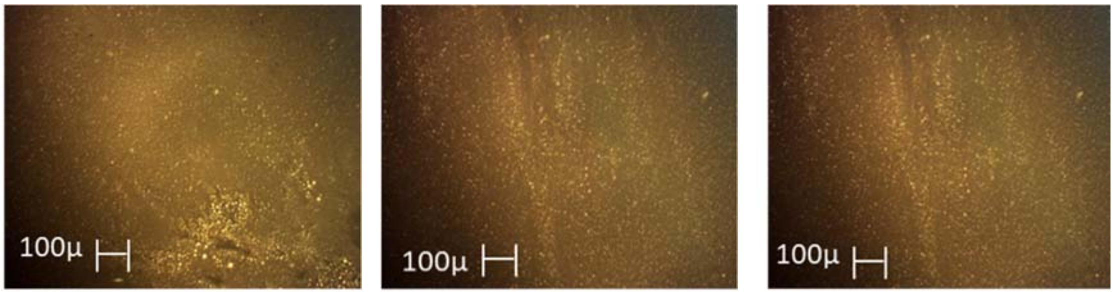


a) EVA 2 b) EVA 4 c) EVA 6

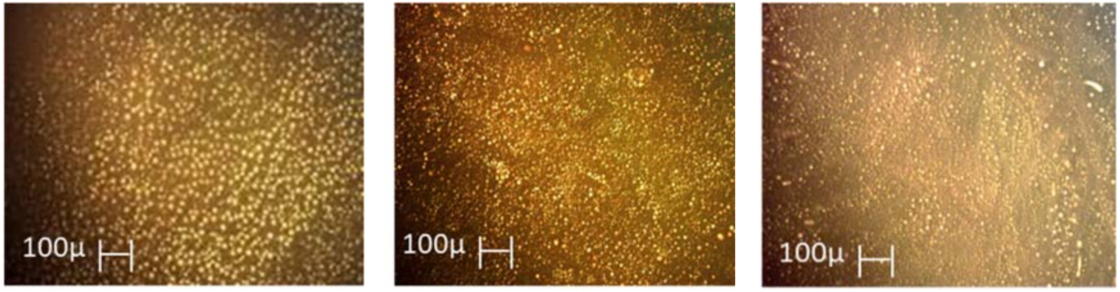
Figure 4-5 – Morphology of EVA modified bitumens at unaged conditions

(a – 2% EVA; b – 4% EVA; c – 6% EVA).

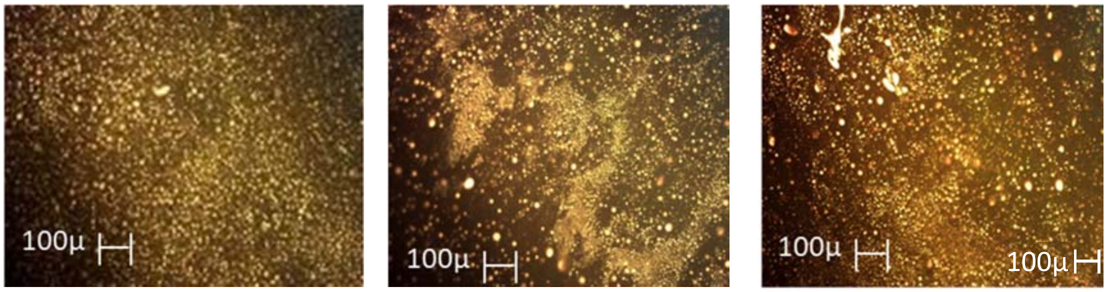
The EVA (Figure 4-5 – a, b, c) remains dispersed within the bituminous phase as disconnected spherical droplets irrespective of the polymer concentration. However, at 2% EVA (Figure 4-5 – a), such droplets do not have the same dispersion as the other two levels. This aspect is not necessarily related to the polymer concentration, but rather, it may depend on a different thermal history of the bitumen after modification. The spherical shape of the droplets indicates somehow low compatibility with the base bitumen since the sphere is the shape with the lowest specific surface. In other words, this shape minimises the interface, and thus the interactions, between the two phases. In light of this, the polymer and the bitumen phases, although coexisting, remain separated without forming any network. Besides this, the spherical shape of the polymer might reduce the surface of the polymer exposed to the oxygen diffusion during oxidation. However, the lack of formation of an actual polymer network well correlates with the mechanical response of EVA modified bitumen in which the polymer behaves as a reinforcement only without necessarily increase the elasticity of the bitumen. The residual morphologies of the EVA modified bitumens at the different levels of laboratory-simulated ageing are given in Figure 4-6.



a) EVA 2 - RTFO b) EVA 2 -PAV c) EVA 2 -2 PAV



d) EVA 4 - RTFO e) EVA 4 - 1PAV f) EVA 4 – 2PAV



g) EVA 6 - RTFO h) EVA 6 - 1PAV i) EVA 6 – 2PAV

Figure 4-6 – Morphology of aged EVA modified bitumens (a, b, c – 2% EVA; d, e, f – 4% EVA; g, h, i – 6% EVA).

The morphology of the EVA modified bitumens does not seem to be significantly affected by both the RTFO and the PAV ageing. At 2%, polymer concentration (Figure 4-6 – a, b, c) the polymer particles are dispersed as small spherical droplets distributed within the bituminous phase in all the levels of ageing. Such conformation does not seem to differ significantly from the unaged conditions. The low susceptibility of the morphology to the PAV and the RTFO allows thinking that the differences between the unaged and the aged conditions (including RTFO and PAV) depend on the difference in thermal history between the bitumens. That is, aged bitumens have been exposed for a longer time to high temperature, and the polymer has achieved a different shape and dispersion.

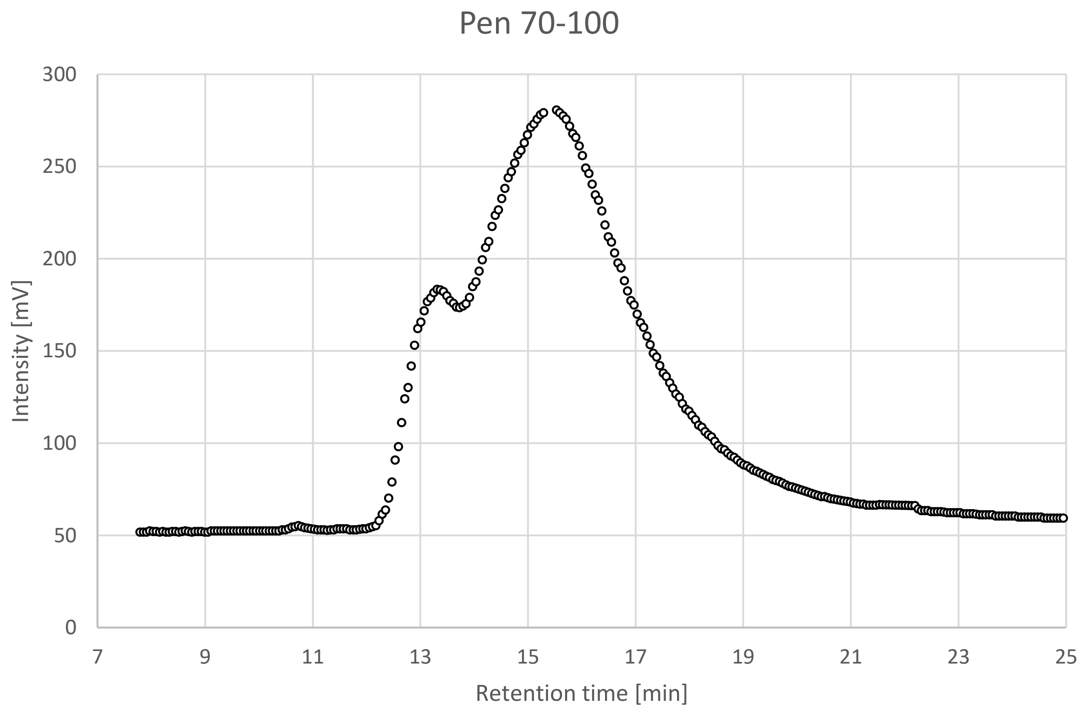
Also at 4% and 6%, polymer concentration (Figure 4-6 – d to i), the morphology constituted of sparsely dispersed particles does not vary with ageing. The reduced sensitivity of this polymer to oxidation might be due to the absence of unsaturated bonds in the chain, which makes the polymer less prone to react with the oxygen molecules during the PAV.

In this case, the low PAV-susceptibility of EVA does not provide any support for referring to polymer de-swelling.

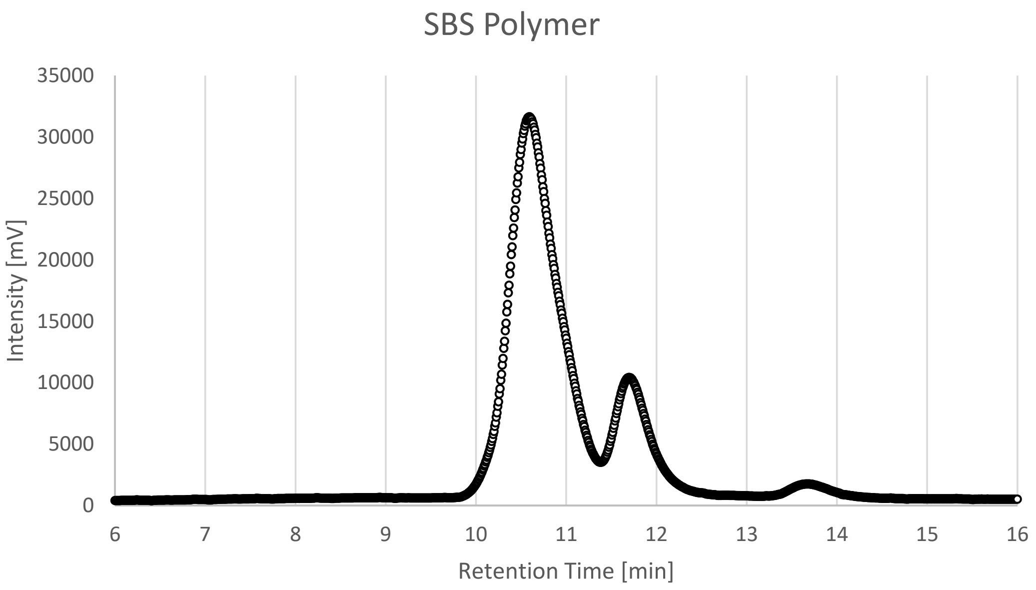
4.3 Results of GPC

The GPC has been used to evaluate the variation in the MWD of SBS modified bitumens at different levels of laboratory simulated ageing.

Before testing the PMBs, the base bitumen and the SBS copolymer were tested separately to identify their retention time interval. The polymer resulted in a retention time interval between 10 and 12 minutes, while the neat bitumen was found between 12 and 20 minutes (Figure 4-7).



(a)



(b)

Figure 4-7 - (a) Chromatogram of Pen bitumen at unaged conditions;

(b) Chromatogram of SBS copolymer

The chromatogram of the Pen bitumen shows two peaks, one related to the heavy fractions, and another related to the lighter (Figure 4-7 - a). The GPC allows the identification of molecules only as a function of their size. Therefore, the molecular compounds included in each fraction cannot be precisely identified. However, the first peak is likely to be representative of the asphaltenes, while the second of the maltenes (i.e., resins, aromatics, and saturates). This picture represents what is typically considered in bitumens chromatography. An alternative interpretation of the peaks “content” is given by Le Guern et al (232). According to their work, it appears that the knowledge of the asphaltene content alone might not be exhaustive for the definition of the colloidal structure of bitumen, which needs to consider, besides asphaltenes as dispersed as single micelles, the presence of agglomerates of asphaltenes found in the intermicellar environment (saturates and aromatics).

In traditional Size Exclusion Chromatography (SEC), the agglomerates are identified in correspondence (retention time) of isolated micelles since their weak bonds are broken within the time interval of the chromatography. To highlight molecular associations, the authors have used the high-speed SEC (HS-SEC), in which the dissociation of molecules occurs more rapidly preserving (to some extent) the agglomerates bonds.

This discussion has been included to highlight that the complexity of the analysis of the bitumen composition extends much beyond the molecular size. Therefore, the analysis of the light and heavy fractions need to be conducted considering this limitation. However, for the scope of this work, the analysis of the chromatograms focuses to the identification of the molar mass (of light and heavy fractions) whose variation is, in any case, representative of the changes in the microstructure of bitumens. On the other hand, it has to be recognised that the work of Le Guern et al points out that the heavy fraction might be composed by agglomerates of asphaltenes rather than single micelles (232). More accurate analyses can be considered for future works.

In the case of PMBs, partial overlapping of the signals (i.e., pure polymer, pure bitumen) was observed because a portion of the polymer chain undergoes thermo-oxidative degradation during blending, STA or LTA with a consequent weight reduction. This overlap indicates that GPC cannot entirely separate base bitumen and SBS polymer.

In the subsequent analysis, the results of the GPC refer to the portion of chromatogram comprised between 12 and 20 minutes. In the case of Pen and Pen/S bitumen, this portion is representative of the whole microstructure of the bitumen.

In the case of SBS modified bitumens, this portion may include both bitumen and polymer molecules. Therefore, this portion can be defined as the ‘bitumen-rich phase’. The polymer phase (10-12 minutes) was not considered because it is not visible in the chromatograms of the PMB/S bitumens. The reason for this is that the use of sulphur as a cross-linker promotes the reticulation of the polymer in the bitumen. At a high level of reticulation, the THF cannot dissolve the polymer phase, which remains in the filter used before injecting the solution into the column. Although this solvent is capable of dissolving several polar and non-polar chemical compounds, in this case, it seems to show some limitations. It other words, the high level of reticulation achieved by the combination of SBS and sulphur can lead to the formation of chemical structures characterised by low solubility in THF.

Two significant effects appear to occur to the Molecular Weight Distribution (MWD) of the unmodified bitumens during laboratory-simulated ageing. The first is the volatilisation of the light fractions during the RTFO; while the second seems to be a relative increase in the heavier fractions during the PAV oxidation.

As shown by Equations (3-2) and (3-3) that refer to Figure 3-21, the weight proportion of each fraction depends on the ratio between the area representative of the fraction considered versus the cumulative area. In this regard, the loss in the light fractions during the RTFO is defined as ‘Volatilization of the light fractions’. While the changes in the MWD during the PAV ageing is defined as ‘PAV oxidative hardening’.

On the other hand, once PMBs are exposed to laboratory-simulated ageing, the polymer phase undergoes thermo-oxidative degradation. In the case of SBS modified bitumen, this mechanism should correspond to the scission of the SBS chains with a consequent reduction in their molecular weight (22, 23). In particular, researchers have observed that the chain scission occurs due to the reaction between the allyl group (CH_2) adjacent to the C=C double bond within the polybutadiene segment that readily reacts with oxygen (Figure 2-37). The higher sensitivity of the polybutadiene segment to oxidation, heat and solar radiation is well known (137, 138).

The more the polymer chains are exposed to thermo-oxidative processes, the more their molecular weight (MW) is reduced, and the fragments of the polymer chains can be detected at retention times characteristic of the bitumen fractions. At low oxidative levels, the fragments of the polymer have retention times comparable to that of the heavy fractions (increase in R_H – Equation (3-2)), while at higher oxidative levels they undergo a further degradation and have retention times comparable to that of the light fractions (increase in R_L – Equation (3-3)). This mechanism is defined as 'polymer degradation' and is visible in the three chromatograms related to the SBS 2/S bitumen within the unaged condition, after 1 PAV and after 2 PAV (Figure 4-8).

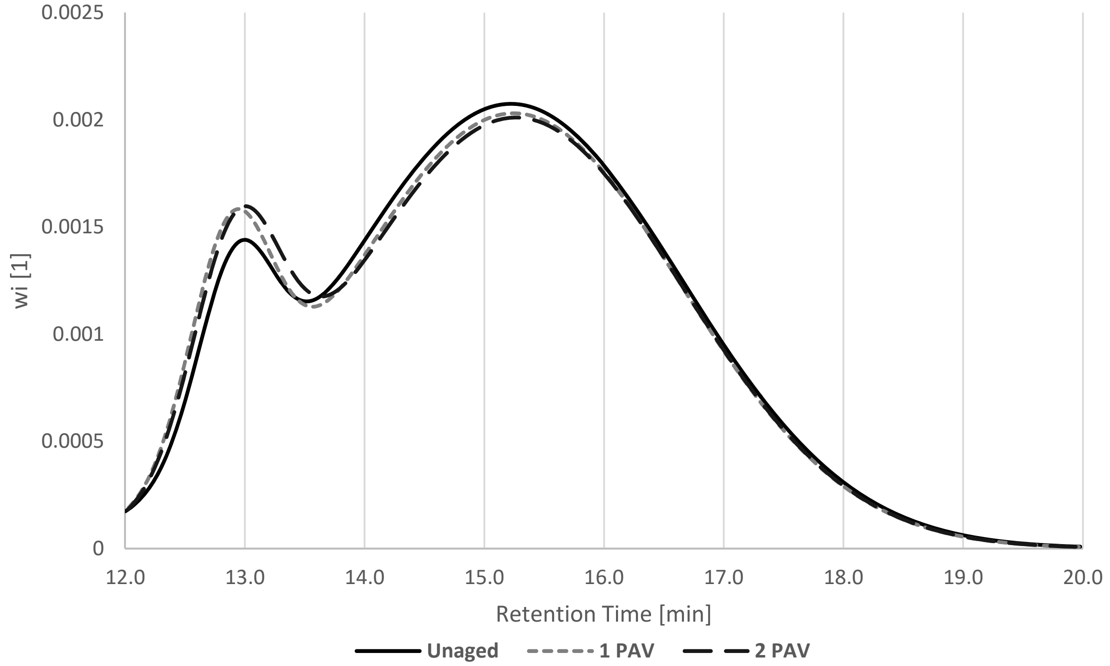


Figure 4-8 – Chromatograms of SBS 2/S bitumen at the unaged condition and after one and two cycles of PAV.

The portion of the chromatogram between 12 and ~13.5 minutes increases with ageing and shifts to lower retention times (higher molecular weight) with ageing. On the other hand, the portion of the chromatogram approximately between 14 and 16 minutes shows a slight shift downward and towards higher retention times (lower molecular weight). Therefore, this fraction does not seem to undergo significant structuring. As a consequence, the increase in the 12 to 13.5 minutes portion might depend on the polymer fragments formed during the RTFO and the PAV oxidation. It is worth mentioning that the degradation of the polymer network is visible in the fluorescence microscopy, where the SBS loses its dispersion throughout ageing (Figure 4-4).

Once the mechanisms that seem to occur at the molecular level have been described, the expected findings from the GPC test are organised in 'Investigated Areas' whose content is summarised in Table 4-1.

Table 4-1 – GPC test investigated areas.

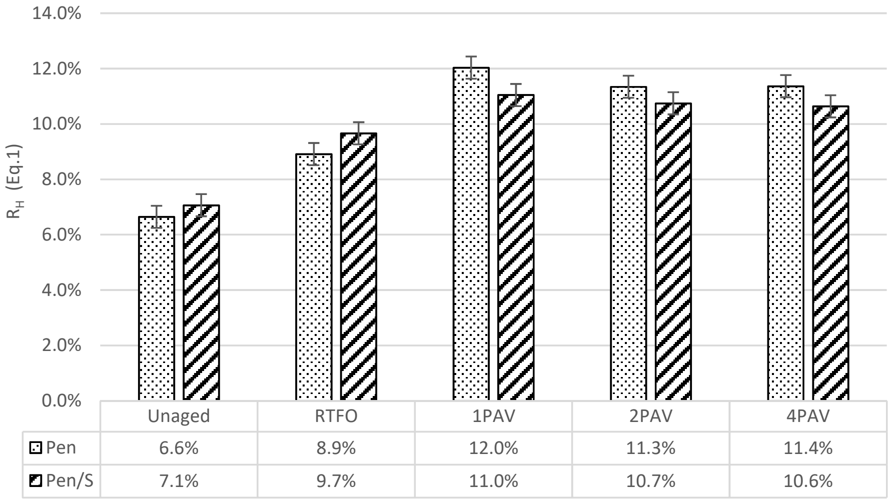
Investigated areas	**Compared bitumens**		**Focus on**
Area 1	Pen	Pen/S	Isolate the effect of 0.1% of sulphur on the variation in the bitumen composition at different levels of Laboratory-Simulated Ageing (LSA).
Area 2	Pen	SBS 2/S	Effect of SBS copolymer modification with the use of cross-linker on the variation in the bitumen-rich phase composition at different levels of LSA.
		SBS 4/S	
		SBS 6/S	
Area 3	SBS 4/S	SBS 4	Comparing the effects of LSA between SBS modified bitumens prepared with sulphur as a cross-linker and SBS modified bitumens without cross-linker.
	SBS 6/S	SBS 6	

4.3.1 Results of Investigated Areas

A detailed discussion of the results is given in the following sections organised as per Investigated Areas. However, it is worth mentioning that the proposed mechanism of the changes in the MWD of bitumens with ageing (in particular for PMB/S) represents a plausible interpretation of the results developed at this stage of the research that might need additional verification.

4.3.1.1 Investigated Area 1

The results of the *Investigated Area 1* are given in Figure 4-9.



	Unaged	RTFO	1PAV	2PAV	4PAV
⊡ Pen	6.6%	8.9%	12.0%	11.3%	11.4%
▨ Pen/S	7.1%	9.7%	11.0%	10.7%	10.6%

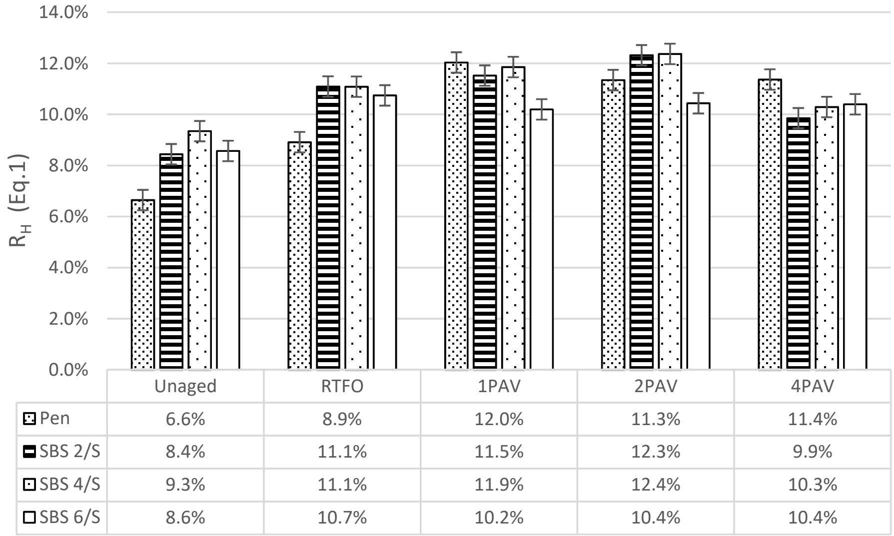
Figure 4-9 - Values of R_H of the Pen and the Pen/S bitumens at different levels of LSA.

In the case of the base bitumen (Pen), the concentration of the heavy fraction (given as per the value of R_H) increases during both the RTFO and the first cycle of PAV. In the RTFO, such an increase might depend on the volatilisation of the lighter fractions, while during the first cycle of PAV it depends on the PAV-oxidative hardening. At higher oxidative levels (i.e., 2 PAV, 4 PAV), the R_H values tend to reduce although remain within the test variability (±0.4%).

Results of the Pen/S bitumen show a similar trend as the Pen bitumen, but sulphur mitigates, to some extent, the formation of the heavy bitumen molecules. The R_H values after one cycle of PAV of the Pen and the Pen/S bitumens differ by 1%. However, the mitigated oxidative kinetics of the Pen/S bitumen might depend on the blending process (3 hours at 180°C). During this stage, part of the oxidative products might be formed causing a subsequent lower PAV oxidative susceptibility. Nevertheless, the evaluation of the effects of the bitumen-sulphur interactions on the oxidation will be considered for future investigations.

4.3.1.2 Investigated Area 2

The results of the *Investigated Area 2* are given in Figure 4-10.



	Unaged	RTFO	1PAV	2PAV	4PAV
▩ Pen	6.6%	8.9%	12.0%	11.3%	11.4%
▤ SBS 2/S	8.4%	11.1%	11.5%	12.3%	9.9%
⬚ SBS 4/S	9.3%	11.1%	11.9%	12.4%	10.3%
□ SBS 6/S	8.6%	10.7%	10.2%	10.4%	10.4%

Figure 4-10 - Values of R_H of the Pen and the PMB/S bitumens at different levels of LSA

In this case, the Pen bitumen has been included as a reference and shows the lowest R_H value at the unaged condition (Figure 4-10). The higher values of R_H for the PMB/S bitumens compared to the Pen at the unaged condition, may depend on the 'Polymer Degradation' that occurs during blending. It is true that some changes in the molecular distribution might have occurred during blending, but the magnitude of the differences (+ 1.8% for SBS 2/S bitumen and +2.7% for SBS 4/S bitumen) suggests the presence of polymer fragments. This aspect is supported by the slightly higher R_H value of the Pen/S bitumen (Figure 4-9), that although having a similar thermal history (3 hours at 180°C) shows an increase of +0.5% concerning the Pen bitumen at the unaged conditions. In the RTFO, the increase in the R_H value is slightly dependent on the polymer concentration, due to the simultaneous effect of the 'Volatilization of the light fractions' and 'Polymer degradation'. The variation of the R_H values with PAV ageing depends on the polymer concentration. A discussion on the variation of the R_H values with laboratory-ageing of the PMB/S bitumens is given below.

SBS 2/S and SBS 4/S bitumens

The increase in the portion of the heavy fractions of the bitumen-rich phase occurs within two cycles of PAV with the R_H values achieving the maximum values at 2 PAV ageing. Therefore, the variation of R_H takes longer before it becomes stable or, as seen in this case, to decrease. Based on this point, it seems that the SBS cross-linked by the sulphur results in a delay in the growth of the heavy fractions. However, the reduction of heavier compounds might also be due to some asphaltenes being retained in the filter together with the polymer network. This hypothesis depends on the possible inability of the THF solvent to dissolve the chemical compounds formed during the PAV (§4.3).

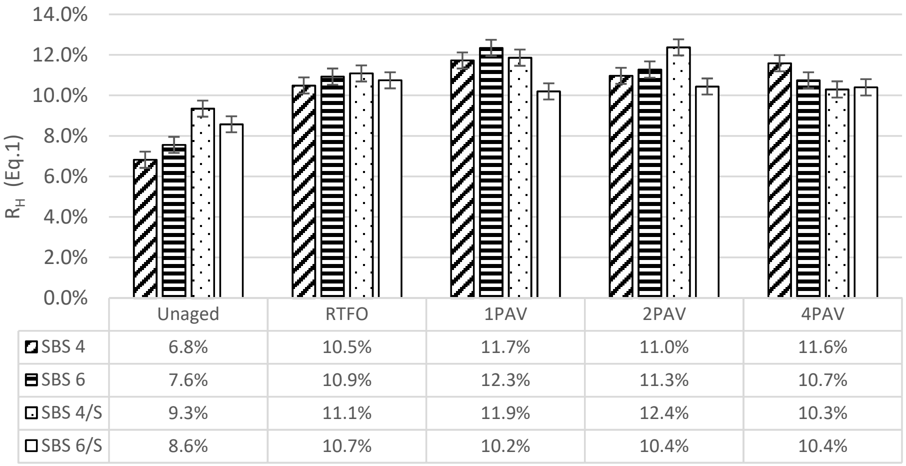
The growth in the R_H values could depend on the combined effect of 'Polymer degradation' and 'PAV-oxidative hardening'. However, these two contributions cannot be recorded separately in the GPC since this test only provides information on the molecular weight. The mechanism of 'Polymer degradation' contributes to understanding the reduction in R_H at 4 PAV ageing. That is, after four PAV cycles, the polymer chains are no longer detected within the interval of the heavy fractions, but instead, they are detected in the interval of the light fractions with a consequent reduction in the proportion of the heavy fractions (Equation (3-2)). An alternative explanation of the results at 4 PAV is that, at such high oxidative levels, the polarity of the bitumen molecules could increase their affinity, and thus solubility, with the THF solvent (§4.3). In other words, the solvent could be more capable of dissolving the heavy fractions causing a decrease in their proportion. If this is the case, the GPC might show some limitations when used at high oxidative levels.

SBS 6/S bitumen

The variation of the R_H remains within the test variability. The low PAV-susceptibility of R_H might depend on the high consistency of the modified bitumen at the PAV temperature (100°C) which could prevent the oxygen from diffusing throughout the layer of bitumen in the PAV pan as discussed in Anderson & Bonaquist (27). Nevertheless, images from fluorescence microscopy show that the polymer network undergoes degradation during the PAV exposure (Figure 4-4 – h, i).

4.3.1.3 Investigated Area 3

The results of the Investigated Area 3 are given in Figure 4-11



	Unaged	RTFO	1PAV	2PAV	4PAV
▨ SBS 4	6.8%	10.5%	11.7%	11.0%	11.6%
☰ SBS 6	7.6%	10.9%	12.3%	11.3%	10.7%
⊡ SBS 4/S	9.3%	11.1%	11.9%	12.4%	10.3%
☐ SBS 6/S	8.6%	10.7%	10.2%	10.4%	10.4%

Figure 4-11 - Values of R_H at different levels of LSA of bitumens SBS 4, SBS 6, SBS 4/S, SBS 6/S.

The combination of the sulphur (*Investigated Area 1*) and the SBS copolymer produces more relevant effects than the two constituents in isolation. These effects depend on the polymer concentration. Although it is difficult to identify whether this is the effect of the sulphur or the polymer, what appears to be clear is that the two additives (SBS and sulphur) alone do not achieve the results of their combination. Therefore, the polymer type alone might not be indicative of anti-oxidative properties, and other factors such as stability and morphology must be taken into account. However, a detailed discussion of each polymer concentration is given below.

SBS 4/S bitumen

The R_H value achieves the maximum after two cycles of PAV and then starts to decrease. The contribution of the polymer to this mechanism has been clarified in Investigated Area 2.

SBS 4 bitumen

The maximum R_H value is achieved after one cycle of PAV and then becomes stable, as observed in the unmodified bitumens.

SBS 6/S bitumen

The PAV susceptibility of the R_H values is negligible.

SBS 6 bitumen

R_H value is susceptible to RTFO and PAV. The R_H value shows an increase in the portion of the heavy fractions between the Unaged to the 1 PAV aged conditions and a subsequent decrease between 1 PAV and 4 PAV aged conditions.

5 Linear viscoelasticity and rutting resistance

This chapter includes the results of the linear viscoelastic characterisation and the MSCR test.

5.1 Linear viscoelastic characterisation

This work challenges the applicability of the LVE characterisation to identify the effects of laboratory-ageing on the response of PMBs.

However, the findings from the frequency sweep test allow raising considerations on the relation between the changes in the microstructure and the viscoelastic response with laboratory-simulated ageing. They are not oriented to estimate expected performance. The phase angle is the viscoelastic function selected to highlight this relation.

The analysis of the LVE data focuses on the equilibrium between the loss modulus and the storage modulus to highlight the effects of ageing on the viscoelastic response in terms of energy storage and dissipation. Results are presented by black diagrams and Cole-Cole diagrams. The firsts are used to highlight the changes in the phase angle within the time-temperature testing interval. The seconds are used to highlight the variation with ageing in G’ and G” in the range of low-intermediate temperatures (i.e., 4, 16, and 28°C) of two SBS modified bitumens (i.e., SBS 2/S and SBS 4/S). The phase angle is representative of the molecular weight distribution of bitumens (and polymers) and provides insight into the effect of the polymer on the linear viscoelastic response (§2.6.3.3). However, the variation is stiffness with ageing is presented as well.

5.1.1 Pen 70-100 bitumen

As discussed in section 3.3.6, the black diagrams and δ master curves have been used as indicators of the applicability of the TTSP to bitumens. Figure 5-1 shows the black diagram of the Pen bitumen at unaged and 2PAV-aged conditions.

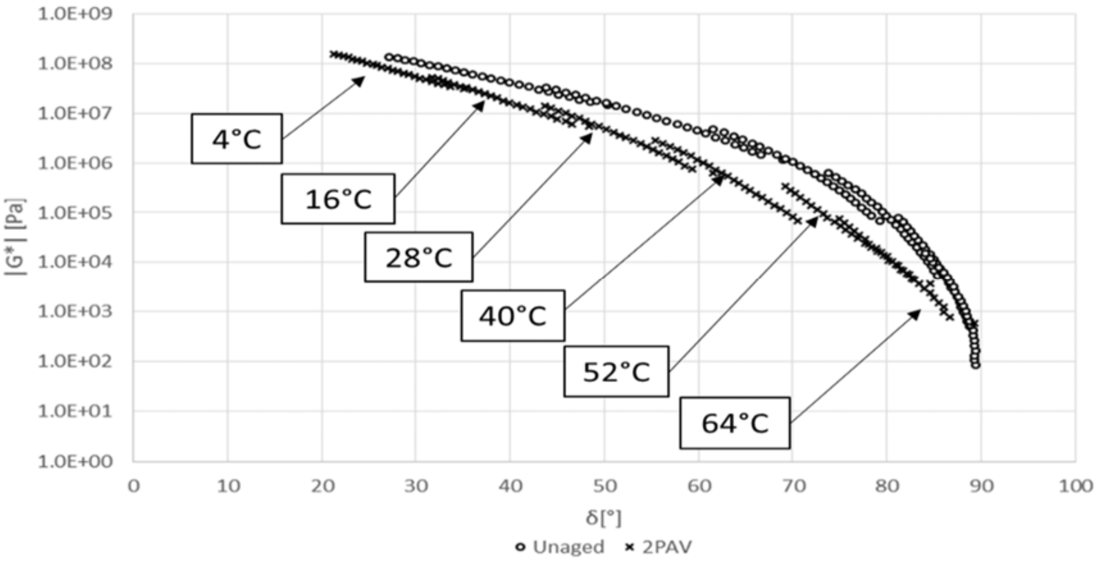


Figure 5-1 – Black diagram of Pen bitumen at Unaged and 2PAV-aged conditions.

The curves are representative of the absence of ageing and the highest level of ageing used in this part of the experiment (2PAV).

The curve related to the unaged conditions shows a satisfactory smooth trend with the isotherms that do not show discontinuities or jumps. The phase angle increases as the stiffness decreases; therefore, the bitumen becomes softer and more viscous by increasing the temperature.

On the other hand, the curve of the data measured at 2PAV-aged condition shows a discontinuity between 40°c and 52°C. The lack of smoothness might depend on the change in the DSR geometry since the compliance of the device affects the accuracy of the results. At 40°C data from the 8 mm plate were used; while at 52°C data from the 25 mm plate were used. In the case of the unaged bitumen, the transition between the two geometries is smoother, and there are no jumps. Therefore, the effect of geometry becomes more evident with PAV-ageing. This is one hypothesis.

The alternative reason might be claiming that at 2PAV, the bitumen is highly oxidised and it may become thermorheologically non-simple. Therefore, at higher temperatures, the curves are less prone to match a unique composite curve. However, if this would be the case, the loss in smoothness would be observed within the same geometry. That is, if the discontinuities depend on the material (and temperature), the fragmentation of the isotherms would appear between 52°C and 64°C (d=25 mm) as well. Results do not show this. Therefore the hypothesis of the geometry gains value, but it has to be verified.

The UNI EN 14770:2012 standard requires to control the effect of geometry at the overlapping temperature (40°C). The criteria proposed are given in the form of Equations (5-1) and (5-2). The first is valid for the complex shear modulus, while the second is valid for the phase angle.

$$\frac{G^*_{g1} - G^*_{g2}}{Average(G^*_{g1}; G^*_{g2})} \leq 15\% \tag{5-1}$$

$$\delta_{g1} - \left(\frac{\delta_{g1} + \delta_{g2}}{2}\right) \leq 3° \tag{5-2}$$

The significance of the terms is clear (g1 – geometry 1; g2 – geometry 2). Such conditions need to be verified at each frequency for the temperature considered. The results of this check are given in Table 5-1.

Table 5-1 – Check of DSR geometries in frequency sweep test.

	Unaged		**RTFO**		**05PAV**		**1PAV**		**2PAV**	
f [Hz]	**G***	**δ**	**G***	**δ**	**G***	**δ**	**G***	**δ**	**G***	**δ**
0.1	18%	1.1	15%	0.1	31%	0.7	23%	1.6	47%	4.0
0.126	15%	0.4	14%	0.5	30%	1.5	22%	1.1	45%	3.7
0.159	15%	0.4	13%	0.5	30%	1.6	21%	1.2	44%	3.7
0.2	15%	0.4	13%	0.4	29%	1.6	21%	1.1	43%	3.6
0.251	15%	0.4	13%	0.4	29%	1.6	21%	1.1	42%	3.6
0.316	15%	0.4	13%	0.4	28%	1.6	20%	1.1	42%	3.6
0.398	15%	0.4	13%	0.5	28%	1.6	20%	1.1	41%	3.5

0.502	15%	0.4	13%	0.5	28%	1.5	20%	1.0	40%	3.5
0.631	15%	0.4	13%	0.5	27%	1.5	19%	1.1	40%	3.5
0.795	15%	0.4	13%	0.5	27%	1.6	19%	1.1	39%	3.4
1	14%	0.3	12%	0.4	27%	1.6	19%	1.1	38%	3.4
1.26	14%	0.4	13%	1.0	26%	1.6	19%	1.1	37%	3.3
1.59	14%	0.4	12%	0.5	26%	1.5	19%	1.1	37%	3.3
2	14%	0.5	12%	0.4	25%	1.5	18%	1.1	36%	3.3
2.52	14%	0.4	12%	0.4	25%	1.6	18%	1.1	35%	3.3
3.17	14%	0.5	12%	0.4	25%	1.6	18%	1.0	34%	3.3
3.99	14%	0.5	12%	0.5	24%	1.6	18%	1.1	34%	3.3
5.02	14%	0.5	12%	0.5	24%	1.7	17%	1.2	33%	3.3
6.32	14%	0.5	12%	0.5	23%	1.6	17%	1.2	32%	3.3
7.96	14%	0.6	12%	0.5	23%	1.7	17%	1.2	32%	3.3
10	14%	0.7	11%	0.6	23%	1.7	17%	1.2	31%	3.4
12.6	14%	0.8	11%	0.5	22%	1.8	16%	1.2	30%	3.5
15.9	14%	0.8	11%	0.6	22%	1.8	16%	1.2	30%	3.5
20	14%	0.9	11%	0.5	21%	2.0	16%	1.2	29%	3.6

The effects of the DSR geometry increase with the level of LSA. At the unaged and the RTFO aged conditions, Equations (5-1) and (5-2) are satisfied (except at 1 frequency at unaged). In the case of PAV aged bitumens (i.e., 10 h, 20 h, and 40h), the DSR geometry shows a higher effect with the 2PAV-ageing conditions being the most affected. Therefore, the concerns related to the smoothness of the black diagram between 40°C and 52° may depend on the sample geometry, and the bitumen meets the TTSP, although it is highly oxidised. To support this, the black diagram developed with the isotherm at 40°C measured with the 25mm plate is given in Figure 5-2.

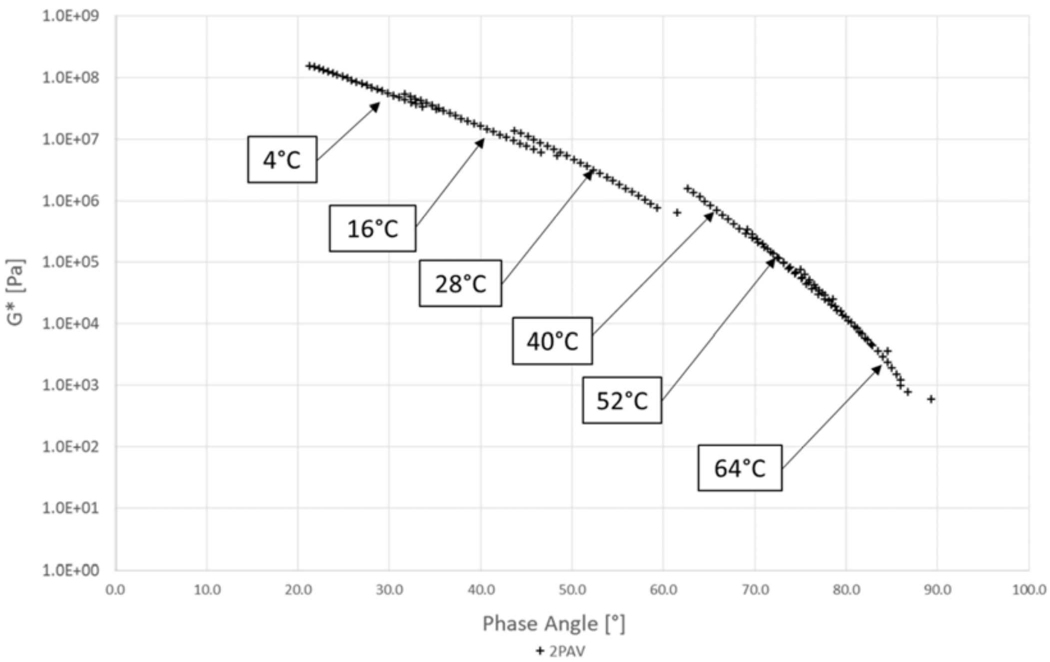


Figure 5-2 - Black diagram of Pen bitumen at 2PAV-aged conditions.

The discontinuity in the diagram is now given at 40°C with the isotherms providing two smooth curves (one per geometry). Therefore, the discontinuity in the black diagram at 2PAV-age bitumen depends on the changes in the DSR geometry. Aware of the effects of the sample geometries on the results, the frequency sweep has been conducted verifying Equations (5-1) and (5-2) in each test. According to the standards, the test should be repeated once one of the two criteria is not verified. However, it was observed that in the case of heavy modified bitumens and highly oxidised bitumens, the conditions of the sample geometry given in equations (5-1) and (5-2) were not verified even upon the usage of multiple samples.

As a consequence, the DSR geometry was considered as affecting the accuracy of the test method. However, the magnitude of its effects was assumed to be acceptable. It is understood that the overlapping temperature might have been varied. However, for the sake of consistency, the same temperature was adopted for all the bitumens. In the data presented, the isotherm at 40°C measured with the 8 mm plate is considered since the DSR was observed to operate in a range of more adequate compliance than at 25 mm.

Aside from their qualitative trend, black diagrams show that laboratory-simulated ageing increases the elastic (storage) component of the complex shear modulus. This is visible by observing that at the same level of |G*|, the curve 2PAV displays a lower phase angle (Figure 5-1).

Figure 5-3 shows the phase angle master curves of the Pen bitumen at unaged and 2PAV-aged conditions calculated by using the values of α_T obtained from the |G*| (at the same respectively ageing conditions).

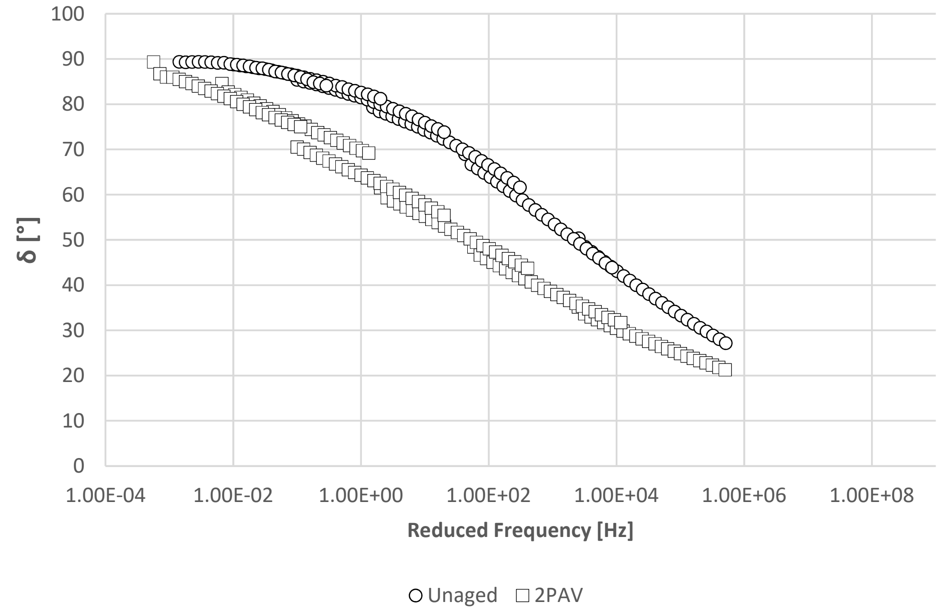


Figure 5-3 – Phase angle master curve of Pen bitumen at unaged and 2PAV aged conditions obtained with shift factor calculated from |G*| values.

The curve related to the unaged conditions shows a smooth trend without any discontinuity. The curve at 2PAV shows a jump in correspondence of low reduced frequency (52°C and 64°C). As discussed above, this effect might depend on the change in DSR geometry. However, although the smoothness of the curves is affected by the DSR geometry, in the black diagrams (Figure 5-1) and the phase master curves (Figure 5-3) the matching of the isotherms appears to be satisfactory. Therefore, the applicability of the TTSP can be advocated, and the master curves can be developed.

The dynamic master curve of the complex shear modulus modelled with the modified CAM model (Equation ((3-6)) are given in Figure 5-4.

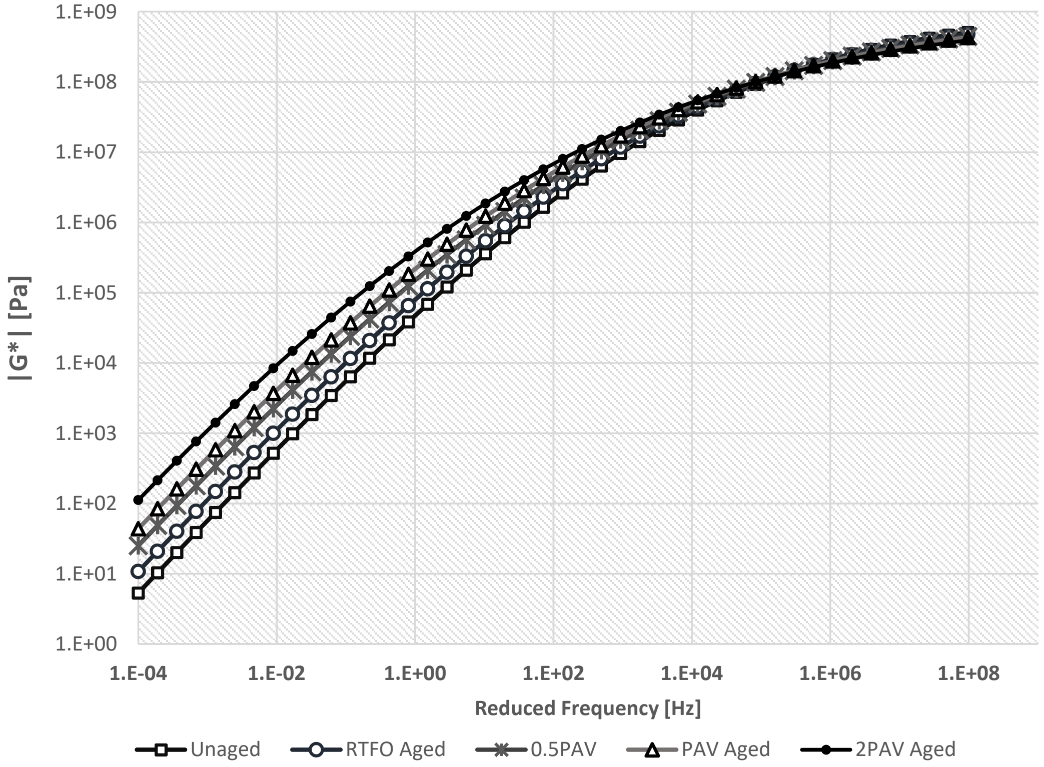


Figure 5-4 - |G*| Master curve of Pen bitumen fitted with the modified CAM model.

The changes in the microstructure of the bitumens produced by LSA case an increase in the stiffness. The more the bitumen is aged, the more the stiffness increases. This result is not surprising, and it is supported by several other works (Table 2-7).

The variation of the phase angle at the different levels of ageing is represented by the master curve calculated by using the shift factor from |G*| values (Figure 5-5).

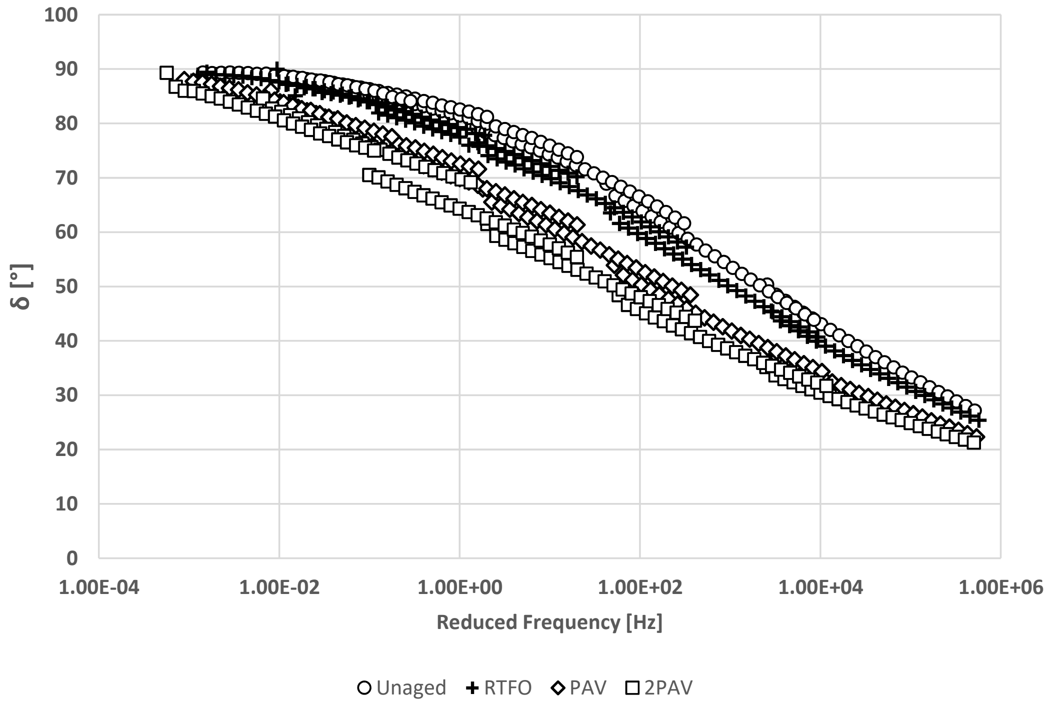


Figure 5-5 – Phase angle master curve of the Pen bitumen at unaged, RTFO-aged, 1PAV and 2PAV aged conditions.

The smoothness of the master curves reduces with LSA, probably due to the increase in the effect of the DSR geometry on the rheological response. However, the matching of the isotherms can be considered as acceptable. The phase angle decreases with ageing within the range of reduced frequency considered. This aspect confirms what was observed in the black diagram in Figure 5-1. This behaviour is not surprising, and it is confirmed by several other works (Table 2-7).

The phase angle is considered as the viscoelastic function that can be correlated with the molecular weight distribution of polymers and bitumens by considering the relation between the molecular mass and the relaxation time (154). Results of the GPC of the Pen bitumen are given in (Figure 5-6).

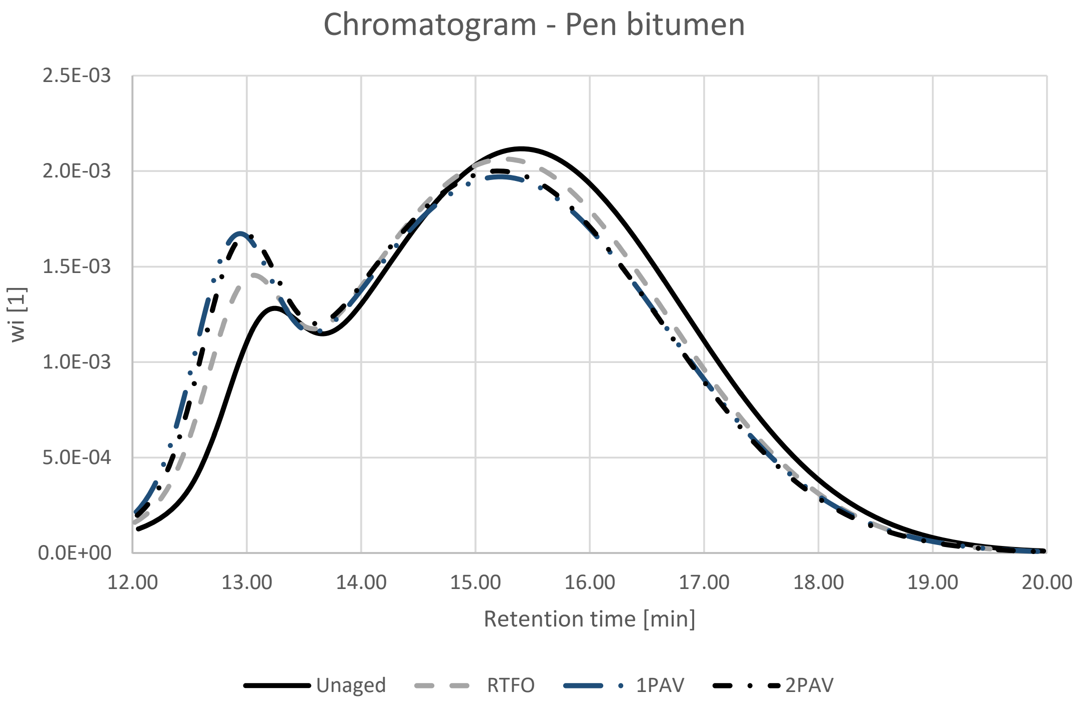


Figure 5-6 – Chromatogram Pen bitumen at unaged, RTFO-aged, 1PAV and 2PAV aged conditions.

The chromatogram of the bitumen shifts towards lower retention times with ageing (heavier molecules). This result is expected since, as discussed in §2.6.1, oxidative ageing is expected to increase the heavier fractions (i.e., asphaltenes). The variation in the phase angle towards lower values highlights that the material becomes more prone to store energy under cyclic loading. This result is corroborated by the GPC that shows an increase in heavy fractions (and probably more polar) with ageing. Although it is difficult to identify a precise correlation between the bitumen fractions and the variation in the viscoelastic response (solid-like or liquid-like), what can be reasonably concluded combining the LVE and the GPC data is that an increase in the heavy fractions seems to produce a more elastic behaviour under cyclic loading. Unfortunately, GPC is a gravimetric method that does not provide any information on the type of molecular bonds that could have an important effect on this mechanism.

The use of FTIR or the SARA analysis might provide additional information respectively on the type of the actual molecular bonds and the polarity of the molecules present. This additional information can contribute to gathering a more precise understanding between the microstructure of the bitumen and the nature of the viscoelastic response.

5.1.2 SBS modified bitumens

Figure 5-7 shows the black diagrams of the SBS modified bitumens and the Pen bitumen at the unaged conditions.

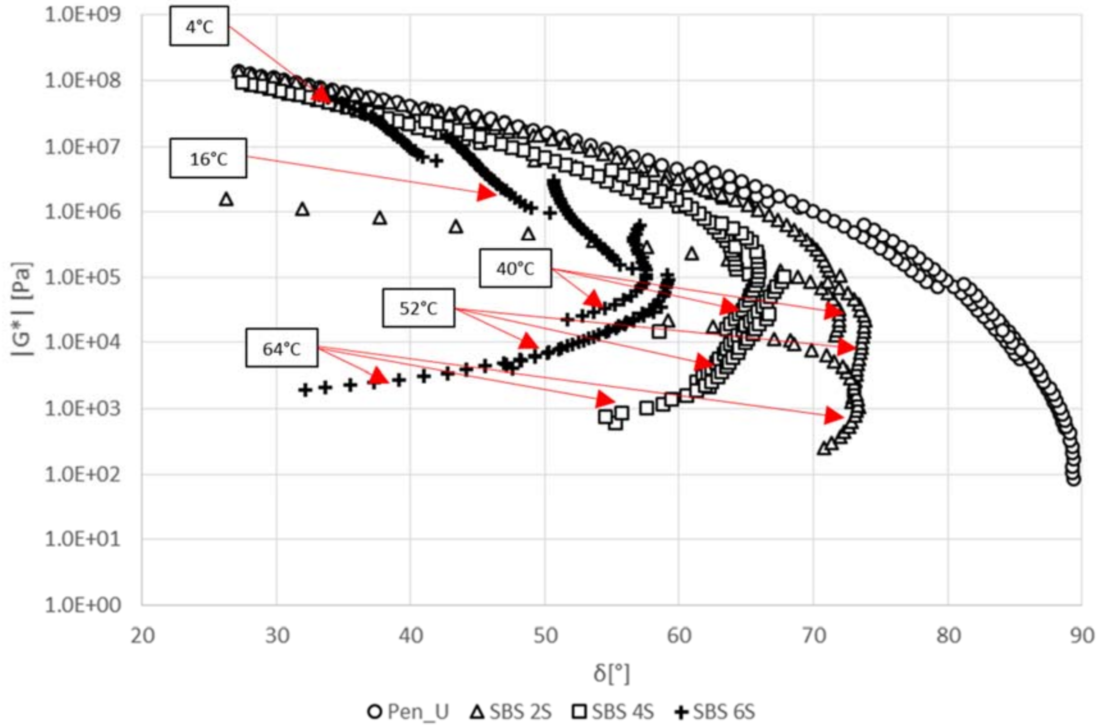
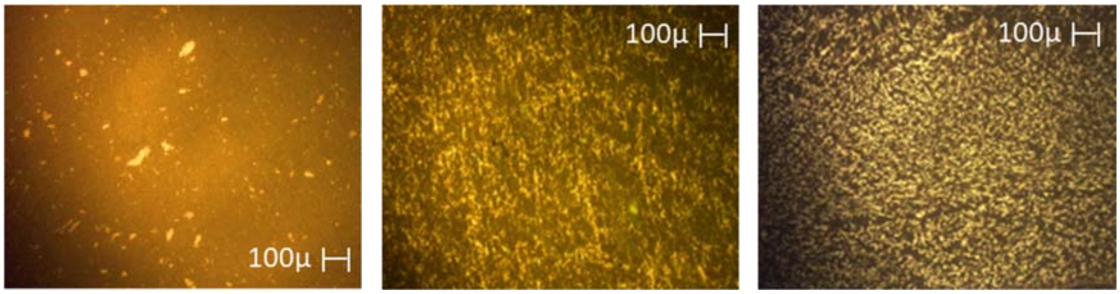


Figure 5-7 – Black diagram of Pen, SBS 2S, SBS 4S, and SBS 6S bitumens at unaged conditions.

The SBS modified bitumens show a different trend compared to the Pen bitumen. In the latter, the phase angle increases with the modulus decreasing, which indicates a more viscous behaviour (typical of unmodified bitumens). In the former, in the range of high temperatures (i.e., 40°C, 52°C, and 64°C) where the dynamic shear modulus decreases, the phase angle of the PMBs decreases with the loading frequency. The higher is the polymer concentration, and the lower are the values of the phase angle measured. In the case of SBS 6/S and SBS 4/S bitumens, the black diagrams display a curve towards lower phase angle values. The SBS is prone to form a polymer network that resists loading at a higher temperature where the bitumen does not provide sufficient levels of stiffness and elasticity. The pattern of the black diagram of the SBS modified bitumens shows precisely the effect of the polymer that, proportionally to its concentration, produces a decrease in the phase angle (and an increase in stiffness) within the range of the high temperatures. Figure 5-8 can provide a qualitative idea of the polymer network.



a) SBS 2/S b) SBS 4/S c) SBS 6/S

Figure 5-8 – Morphology of the cross-linked SBS modified bitumens at unaged conditions (a – 2% SBS; b – 4% SBS; c – 6% SBS).

It seems that the more the polymer is dispersed and dominant in the bitumen phase, the more the black diagram deviates from the condition of unmodified bitumens.

However, besides the effects of modification on the phase angle, the black diagrams in Figure 5-7 make clear that the applicability of the TTSP in the SBS modified bitumens might not be expected. This is well clear in the SBS 6/S bitumen where a smooth curve is far to be observed. In the case of lower concentration (i.e., 2% and 4%), the black diagrams reduce in smoothness in the range of high temperature where the polymer has a higher effect on the viscoelastic response (i.e., 40°C, 52°C, 64°C). Moreover, the diagram shows a lack of smoothness at the same DSR geometry. If the SBS 6S shows disconnected isotherms already at low temperature (i.e., 4°C and 16° - Figure 5-7), the SBS 2/S and SBS 4/S start showing disjunction at 40°C where the 8 mm plate is still used. However, the analysis is not meant to focus in detail on the applicability of the TTSP. In the case of the Pen bitumen, a discussion was included since the data were presented in terms of master curves. Therefore the applicability of the TTSP was somehow to be proven. In the case of the SBS modified bitumens, the use of the black diagrams allows discussing the frequency sweep results without any time-temperature manipulation. Therefore, although the TTSP might be applied to the SBS 2/S and the SBS 4/S bitumens, for consistency with the SBS 6/S bitumens, where master curves cannot be developed (at least at the unaged condition), and the LVE data presented as black diagrams and isotherms of stiffness (|G*|).

Data analysis is conducted for each SBS concentration.

5.1.2.1 SBS 2/S bitumen

The black diagrams of the SBS 2/S at unaged and 2PAV-aged conditions are given in Figure 5-9.

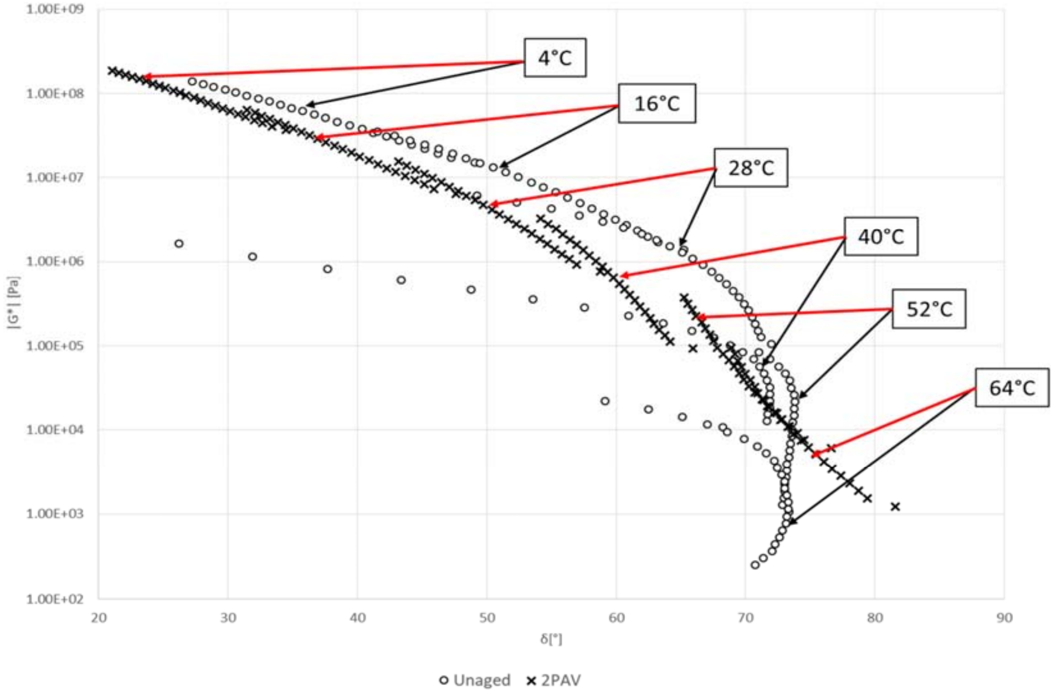


Figure 5-9 – Black diagram of SBS 2/S bitumen at unaged and 2PAV-aged conditions.

The unaged and the 2PAV-aged conditions are considered to discuss the rheological responses corresponding to the initial and final microstructural configurations.

At unaged conditions, the isotherms at higher temperatures (i.e., 40°C, 52°C, 64°C), show that the phase angle tends to a plateau (~73°), and starts decreasing in the final part of the isotherm at 64°C. In this range, the modulus decreases.

On the other hand, at 2PAV-ageing conditions, the curves within the same temperature interval show the reverse trend with the phase angle increasing while the modulus decreases. Comparing the isotherms at 64°C, it appears that under the same frequency, the 2PAV-aged condition has a higher phase angle than the unaged condition. Figure 5-1 shows that in the case of unmodified bitumens, what occurs is the adverse behaviour with the phase angle decreasing with ageing. Therefore, in the range of high temperature, the degradation of the polymer chain causes a more viscous response of the PMB under cyclic loading.

The region of the lower temperatures does not show relevant deviation from the behaviour of the Pen bitumen (Figure 5-1), with the phase angle that decreases with ageing. The Cole-Cole diagram (Figure 5-10) provides similar rheological information of black diagram.

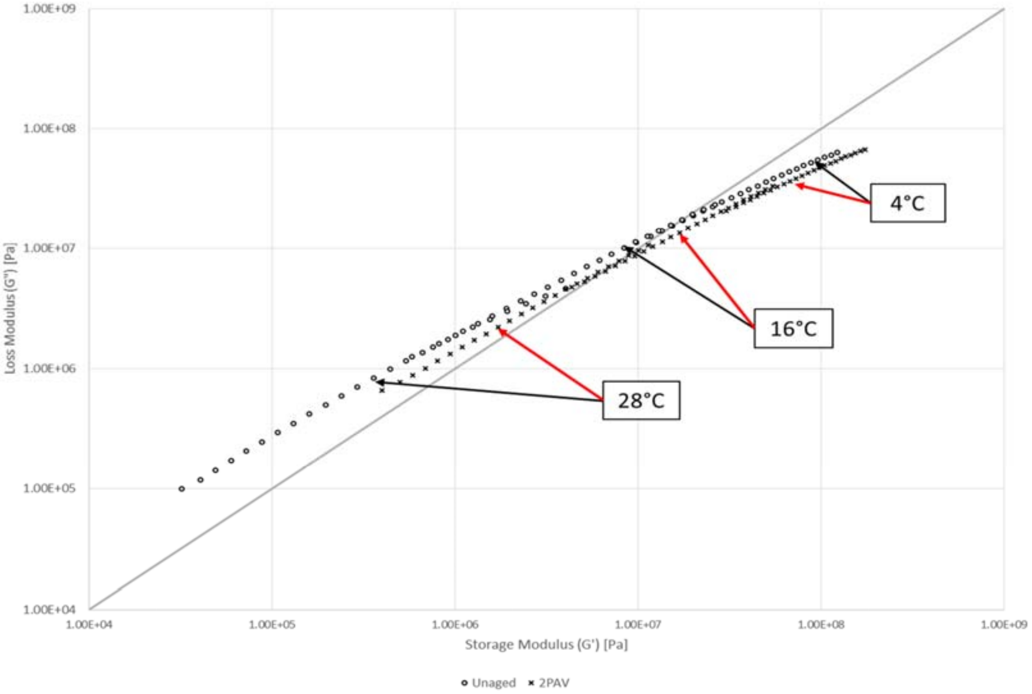
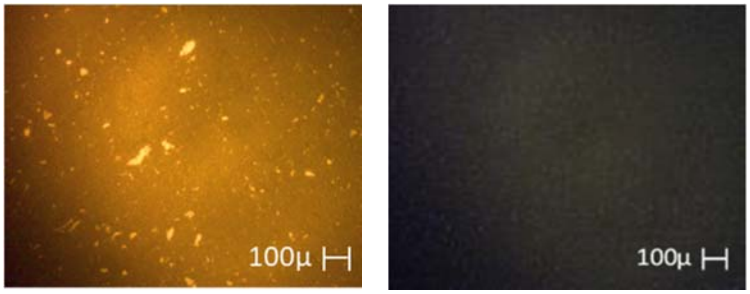


Figure 5-10 – Cole-Cole diagram SBS 2/S bitumen at unaged and 2PAV-aged conditions.

In the intermediate-low temperature region, the curve shifts towards the upper-left side of the diagram showing a more pronounced elastic behaviour with ageing.

These aspects are in agreement with the literature included in §2.9.3, where it is mentioned that the polymer-rich phase and the bitumen-rich phase undergo different ageing mechanisms. The bitumen-rich phase ages as unmodified bitumens showing an increase in the elastic response under cyclic loading. While the polymer-rich phase becomes more viscous. This result is supported by other works (24, 129).

The phase angle is a measure of the equilibrium between storage and dissipation of strain energy, which is fundamental for the characterisation of viscoelastic materials. The variation of the phase angle is an expression of the structural changes in the materials. However, the changes in the microstructure during the RTFO and the PAV have been observed by both the fluorescence microscopy (Figure 5-11) and the GPC (Figure 4-10).



(a) (b)

Figure 5-11 – Morphology of the SBS 2S bitumen at unaged (a) and 2PAV-aged (b) conditions.

The dispersion of the polymer-rich phase reduces with ageing (§4.2.1).

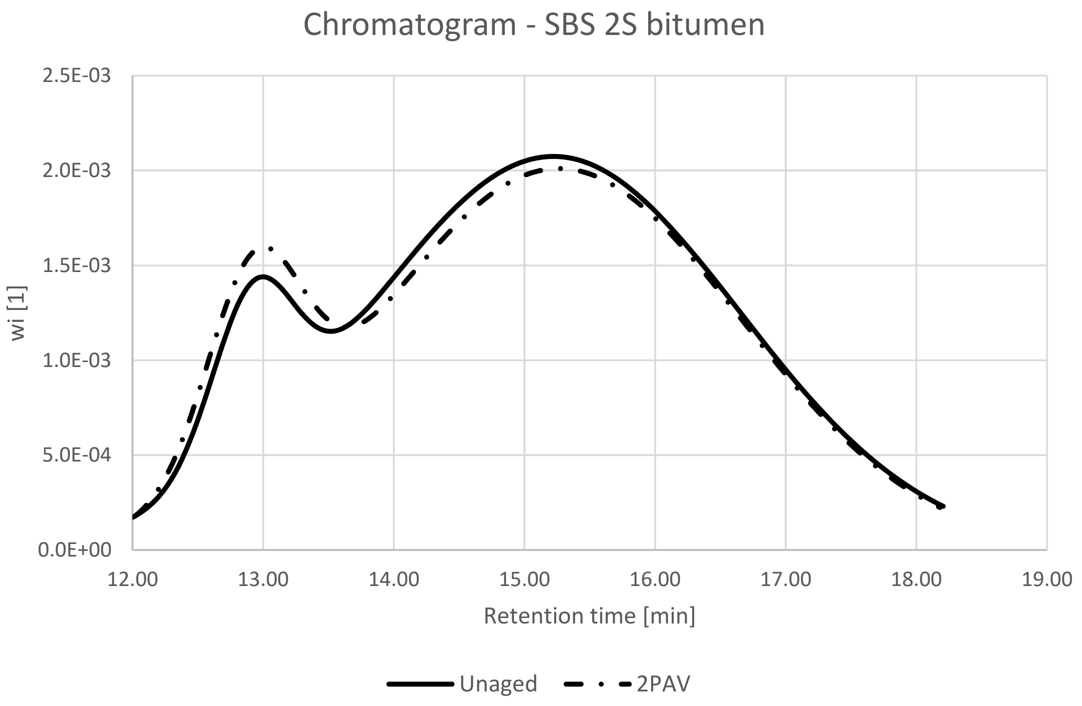


Figure 5-12 – Chromatogram SBS 2S bitumen at unaged and 2PAV aged conditions

The chromatogram of the bitumen shifts towards lower retention time with ageing (heavier molecules) (§4.3).

The changes in the microstructure of the PMB cause a variation in stiffness as well. Isotherms of |G*| at 4°C and 64°C are given respectively in Figure 5-13 and Figure 5-14.

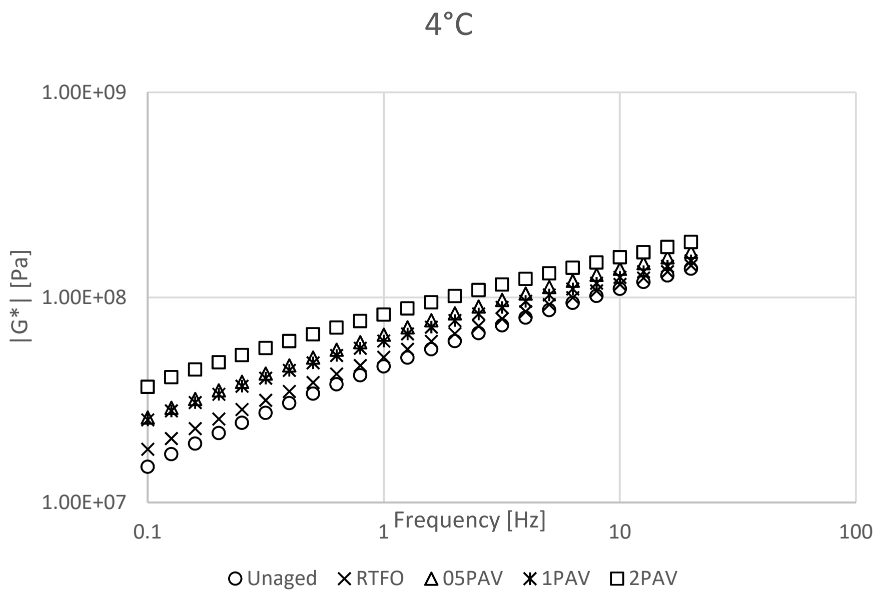


Figure 5-13 – Isotherms @4°C of |G*| of SBS 2S bitumen at different levels of ageing

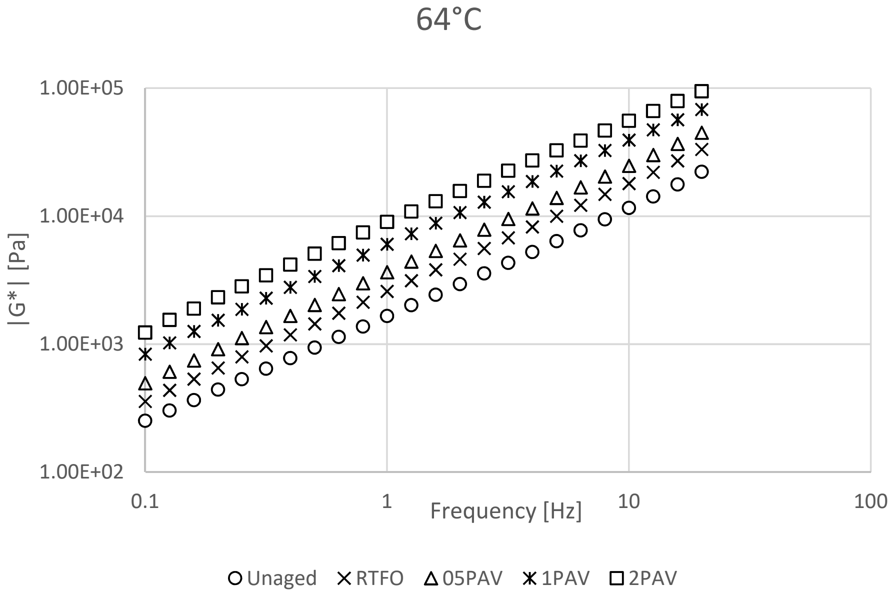


Figure 5-14 - Isotherms @64°C of |G*| of SBS 2S bitumen at different levels of ageing

As shown in Figure 5-13 and Figure 5-14 |G*| increases with ageing at both the temperature intervals where the bitumen phase (4°C) and the polymer phase (64°) control the rheological response. At higher temperature, the increase in stiffness caused by ageing appears to be more visible. There is a reason to think that at very low temperature, the effect of ageing is less visible because, within this range, the temperature has a higher effect on stiffness compared to the changes in the molecular composition occurring with LSA. This consideration applies to the other bitumens as well.

5.1.2.2 SBS 4/S bitumen

The black diagrams of the SBS 4/S at unaged and 2PAV-aged conditions are given in Figure 5-15.

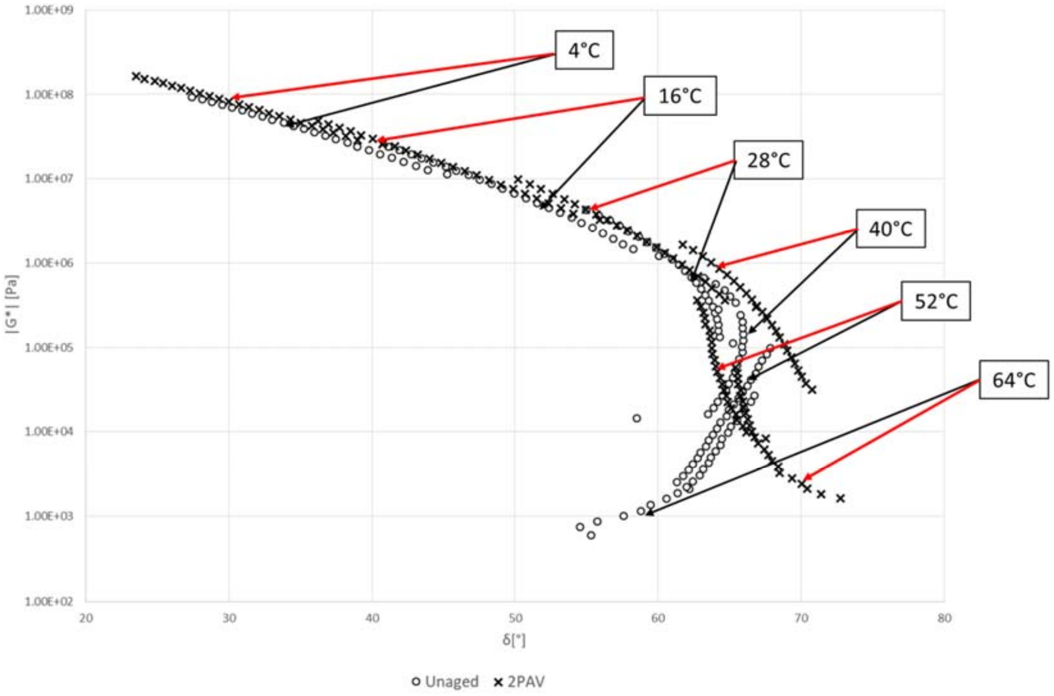


Figure 5-15 - Black diagram of SBS 4/S bitumen at unaged and 2PAV-aged conditions.

The rheological responses corresponding to the initial (unaged) and final (2PAV-aged) configurations of the microstructure are discussed.

In the region of the intermediate – low temperatures (i.e., 4°C, 16°C, and 28°C), the two curves show a similar trend with a reduced difference in phase angle under the same level of stiffness (~4°±1.4° per frequency – in the case of SBS 2S it was 14°±3°). The trend of the phase angle within this region allows considering that LSA does not produce relevant changes in the microstructure of the bitumen phase capable of modifying the nature of the viscoelastic response significantly. The Cole-Cole diagram at intermediate and low temperatures confirm the reduced changes in the viscoelastic response with ageing in this region (Figure 5-16).

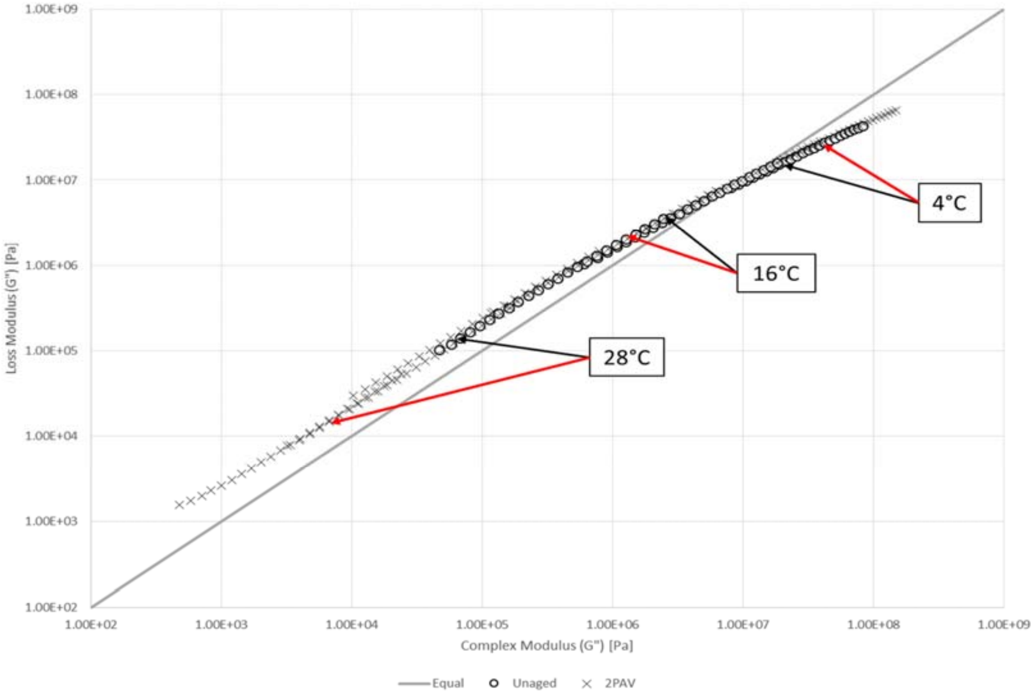


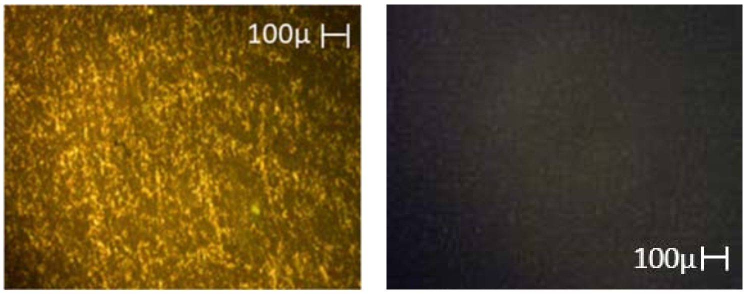
Figure 5-16 - Black diagram of SBS 4/S bitumen at unaged and 2PAV-aged conditions.

The logarithmic scale used in the axis might not be appropriate to highlight a reduced variation in the two curves. However, a numerical analysis of the results undertaken within the intermediate-low temperature region shows that the loss tangent $(\frac{G''}{G'})$ reduces as an average of 13% between the unaged and the 2PAV-aged conditions. In the case of the Pen bitumen, such reduction was of 45%, while for the SBS 2/S bitumen of 22%. As a consequence, the conclusion of mild reduction in microstructure shown by low variation of phase angle seems to be supported.

On the other hand, in the range of high temperature (i.e., 40°C, 52°C, and 64°C), the rheological response varies with ageing. At unaged conditions, the black diagram turns towards lower phase angle values displaying a more elastic response (effect of the polymer) (Figure 5-15). At 2PAV-aged conditions, as observed in the SBS 2S bitumen, the chart tends towards higher phase angle values. The degradation of the polymer network causes an increase in viscous response. However, if in the case of 2% SBS this trend was observed at 52°C and 64°C, at 4% SBS it is already shown by a part of the frequencies at 40°C.

The analysis of the black diagrams within the two temperature intervals (i.e., 4°C - 28°C and 40°C – 64°C) provide the basis for some considerations.

The fluorescence microscopy (Figure 5-17) and the GPC (Figure 5-18) show that the microstructure of the SBS 4S bitumen has changed with ageing.



(a) (b)

Figure 5-17 – Morphology of SBS 4S bitumen at unaged (a) and 2PAV-aged (b) conditions

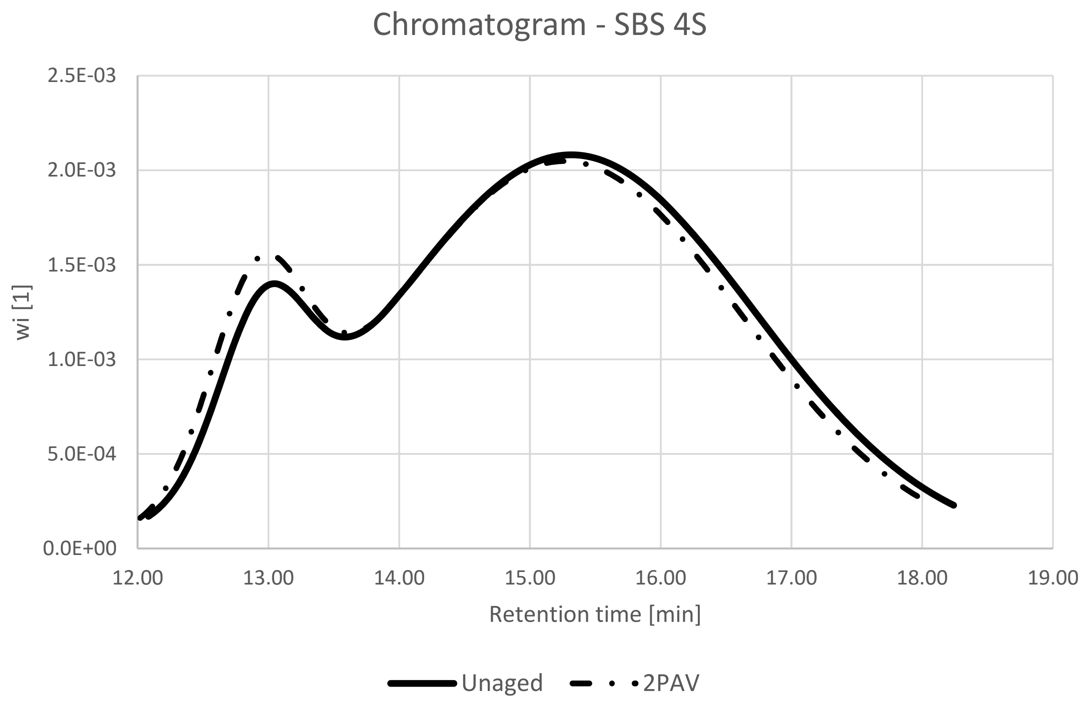


Figure 5-18 – Chromatogram SBS 4S bitumen at unaged and 2PAV aged conditions

The polymer dispersion reduces with ageing (Figure 5-17) and the chromatogram shifts towards lower retention time with ageing (Figure 5-18). Therefore, considering that the microstructure of the PMB varies with LSA, and considering that the effects of LSA are more evident in the higher temperature range (i.e., 40°C – 64°C) where the polymer controls the response, it can be concluded that in the LSA interval considered (i.e., unaged to 2PAV aged), the microstructural changes are more localised in the polymer-rich phase. That is, the polymer-rich phase undergoes degradation and mitigates the PAV-oxidative hardening of the bitumen-rich whose rheological response is less affected by laboratory-simulated ageing.

This consideration is well supported by the analysis of phase angle, the analysis of morphology (§4.2.1) and the variation in the MWD (§4.3).

The effects of SBS degradation are more evident at 4% than at 2%. At 2% SBS, the rheological response varies with ageing also in the intermediate-low temperature interval where the bitumen-rich phase has higher control (Figure 5-9). Therefore, despite the presence of the polymer, the bitumen-rich phase changes its rheological response with ageing. It is clear that the capacity of the SBS of acting as ageing-inhibitor depends on its concentration. There is a reason to believe that, besides the concentration, the polymer dispersion and the use of a cross-linker have an effect as well.

The increase in stiffness with ageing is shown by the isotherms at 4°C and 64°C given respectively in Figure 5-19 and Figure 5-20.

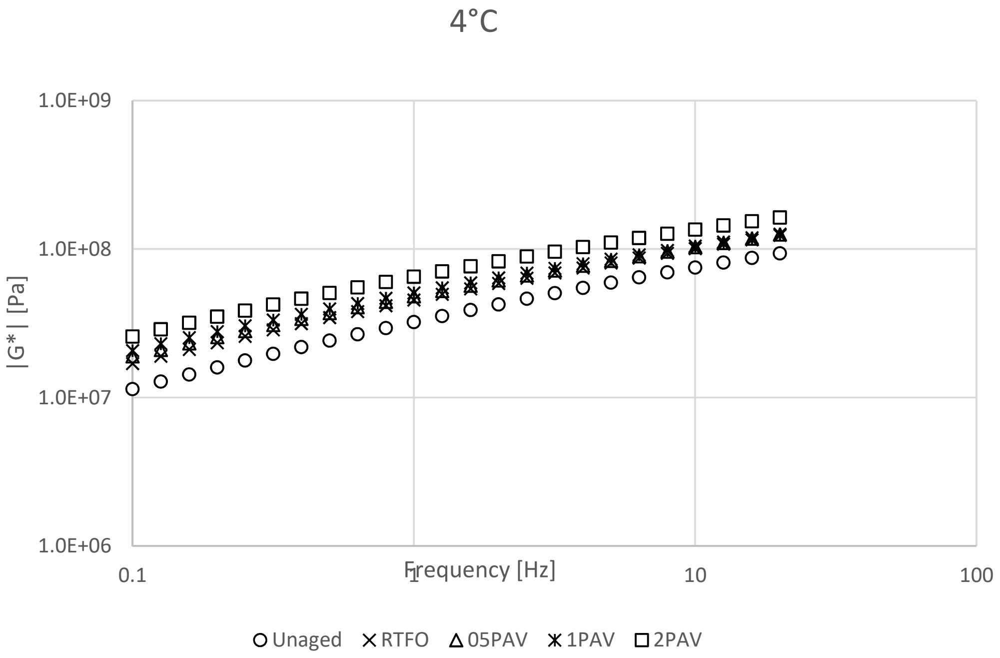


Figure 5-19 - Isotherms @4°C of |G*| of SBS 4S bitumen at different levels of ageing.

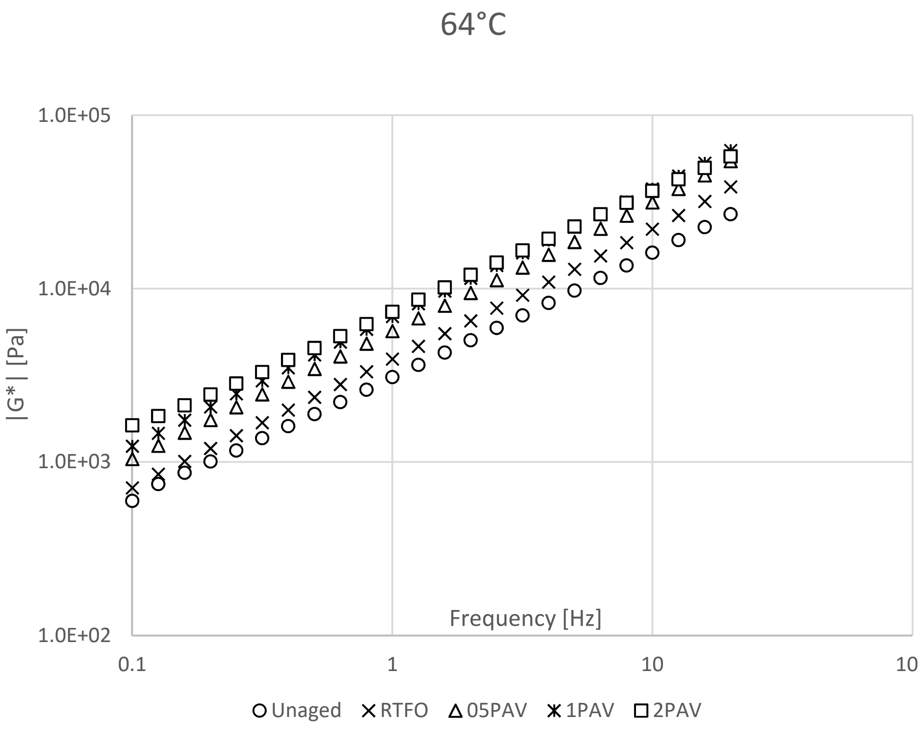


Figure 5-20 - Isotherms @64°C of |G*| of SBS 4S bitumen at different levels of ageing.

5.1.2.3 SBS 6/S bitumen

The black diagrams of the SBS 6/S at unaged and 2PAV-aged conditions are given in Figure 4 23.

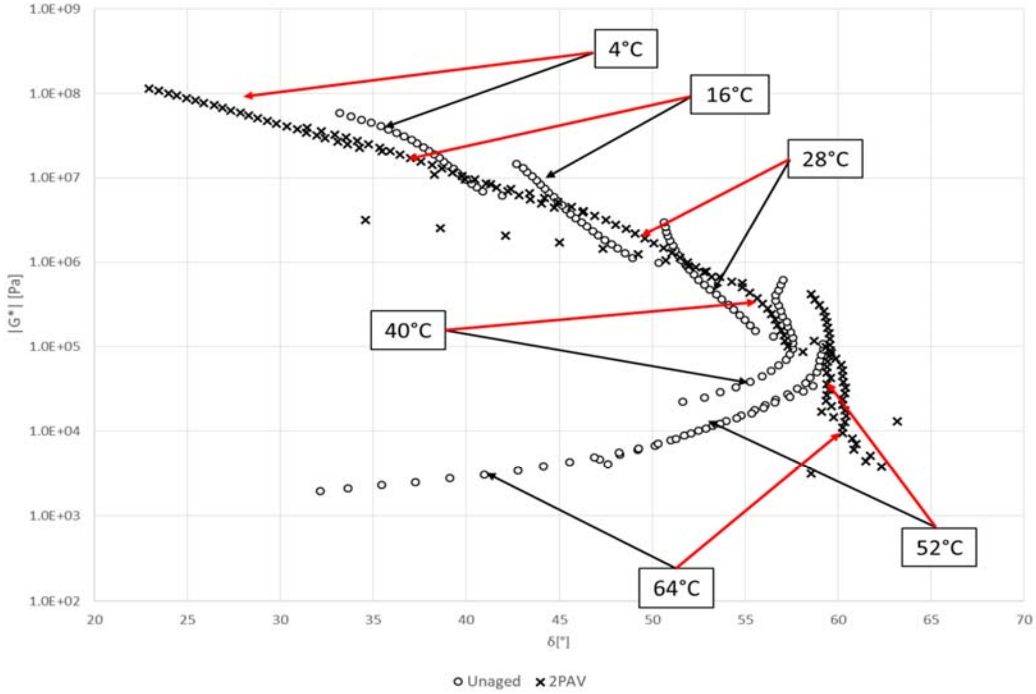


Figure 5-21 – Black diagram of SBS 6S bitumen at unaged and 2PAV-aged conditions.

The black diagram of the unaged bitumen shows that the material is not thermorheologically simple. Between 4°C and 40°C the curve lacks smoothness, and the isotherms are not overlapped. In the range of high temperatures (i.e., 52°C and 64°C), the two isotherms are overlapped, and the phase angle decreases with stiffness.

In the black diagrams of the SBS 2/S and SBS 4/S bitumens, two time-temperature regions were identified. The intermediate-low temperature region (below 28°C) where the rheological response is more controlled by the bitumen-rich phase. And the high-temperature region (above 40°C) where the rheological response is more controlled by the polymer-rich phase.

In the case of the SBS 6/S, the effect of the polymer network is evident even in the range of the lower temperature. It seems that this polymer concentration and the use of the cross-linker, provide the SBS with such a high level of dispersion, swelling, and structuring, to become the dispersing phase with the bitumen being the dispersed one. That is, the phase inversion occurs. The morphology of the bitumen SBS 6S shown in Figure 4-3 (c), supports this hypothesis.

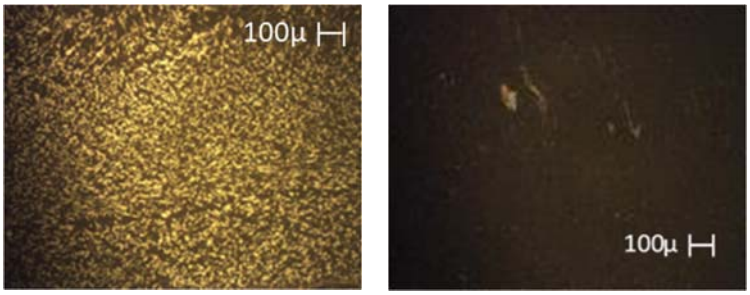
The non-applicability of the TTSP is expected since the high presence of polymer makes the microstructure of the PMB complex.

At 2PAV-aged conditions (Figure 5-21), the curve becomes smooth from 4°C to 40°C and loses the smoothness at higher temperatures (i.e., 52°C, and 64°C). In this case, LSA produces evident effects on the viscoelastic functions of the bitumens. If at the unaged conditions the black diagram highlights a complex structured system (bitumen + polymer), after 2 cycles of PAV the curve between 4°C and 40°C is similar to the one of an unmodified unaged bitumen (Figure 5-1). In this range of temperature, the isotherms do not shift towards lower values of phase angle with ageing, but they seem to rotate counter clock-wise and align along a single curve. On the other hand, the portion of the curve at higher temperature shows that the microstructure of the polymer-rich phase has changed with LSA. After the RTFO and 2 cycles of PAV, the isotherms lose in smoothness and tend towards a plateau (likely the unaged SBS 2S - Figure 5-9). However, in this range, the damage of the polymer network appears evident with the isotherms at 52°C and 64°C that move towards higher phase angles.

The gain in the smoothness of the black diagram between 4°C and 40°C after LSA highlights that polymer structure in the bitumen phase loss in integrity. Therefore, if at the unaged conditions the polymer phase was controlling the viscoelastic response within the entire range of temperature, after the RTFO and 2 cycles of PAV, the polymer undergoes degradation and the bitumen-rich phase gains the control of the rheological response. The black diagram of the 2PAV-aged SBS 6/S bitumen has a similar trend to the SBS 2/S bitumen unaged (Figure 5-9). This comparison highlights that the polymer phase has undergone degradation (therefore the effects of the polymer diminish).

On the other side, it looks like the bitumen-rich phase has been barely affected by LSA. As observed with the SBS 4/S bitumen, the SBS oxidises before the bitumen phase preventing this one from PAV-oxidative hardening.

The changes with LSA in the microstructure have been observed through the fluorescence microscopy (Figure 5-22), and the GPC (Figure 5-23).



(a) (b)

Figure 5-22 - Morphology of SBS 4S bitumen at unaged (a) and 2PAV-aged (b) conditions

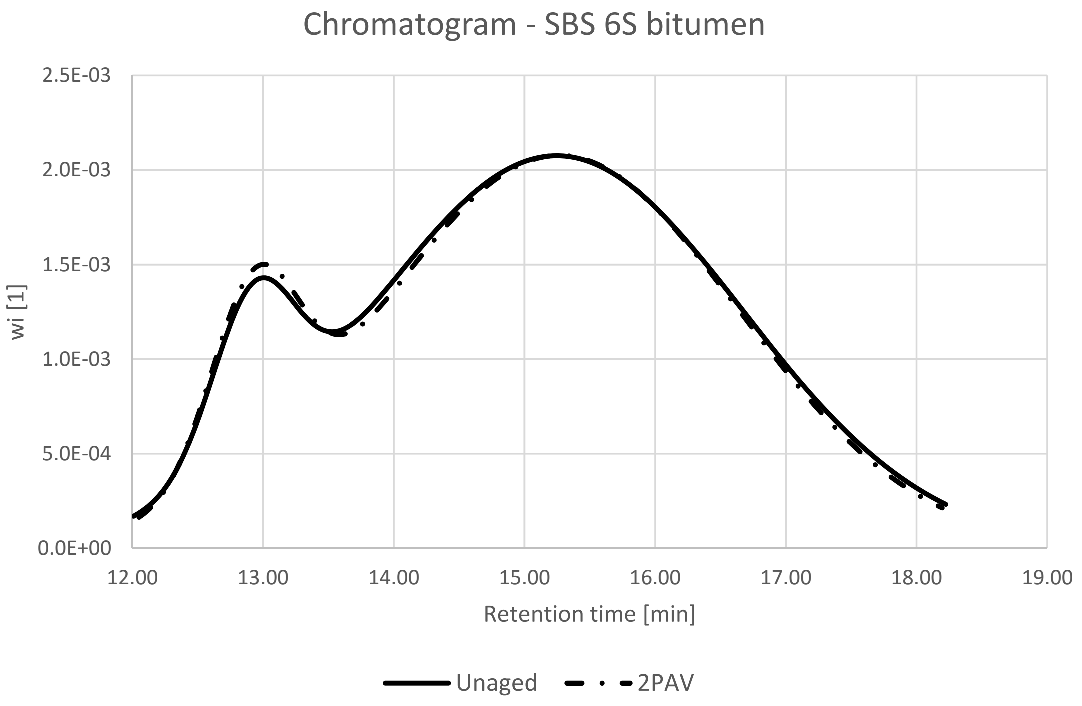


Figure 5-23 - Chromatogram SBS 6S bitumen at unaged and 2PAV aged conditions

Figure 5-22 shows the changes in the morphology with the polymer phase that is reduced after 2 cycles of PAV (§4.2.1). Figure 5-23 shows the changes in the chromatogram with ageing.

However, as discussed in the section of the GPC results (§4.3.1.2), the MWD of the SBS 6/S is unlikely to be susceptible to the PAV (Figure 4-10). It seems that the limited variation in the phase angle values between 4°C and 40°C with LSA (Figure 5-21), is in agreement with the reduced variation in the MWD.

On the other hand, the isotherms at higher temperatures show that the polymer network has lost some integrity with the phase angle that increases at 52 and 64°C. However, such loss in structure does not appear to provide evident effects on the MWD of the polymer phase whose fragments do not produce an evident increase in the heavy fractions.

The isotherms of the |G*| show that stiffness increases with ageing.

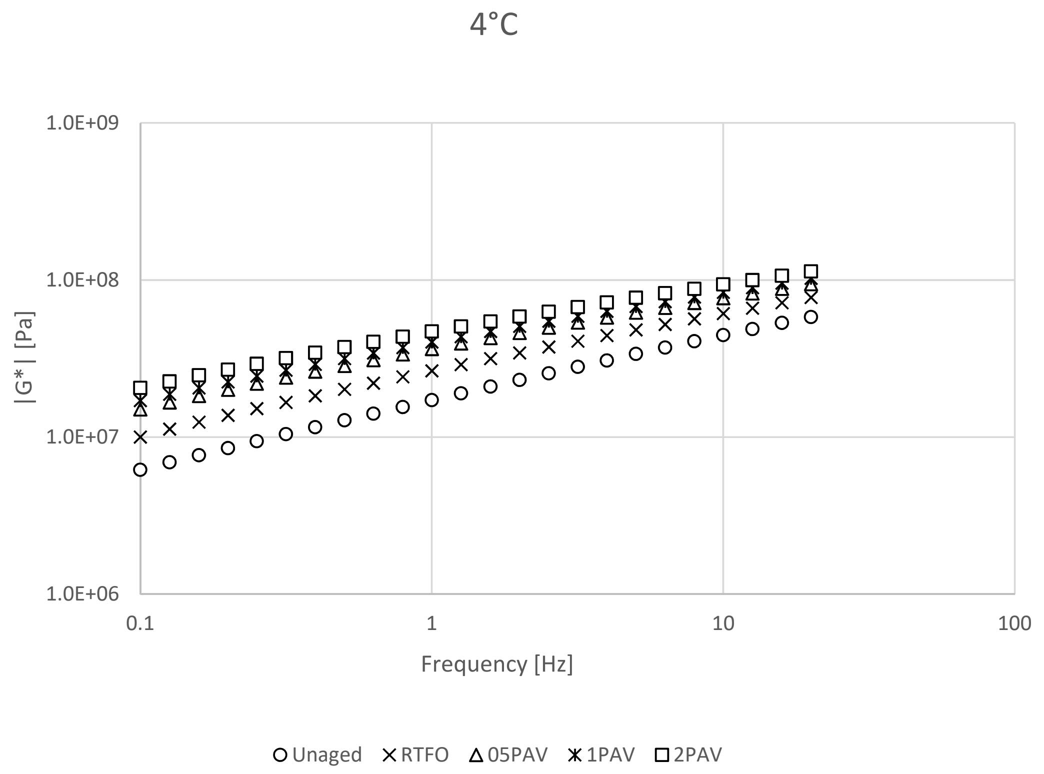


Figure 5-24 - Isotherms @4°C of |G*| of SBS 6S bitumen at different levels of ageing.

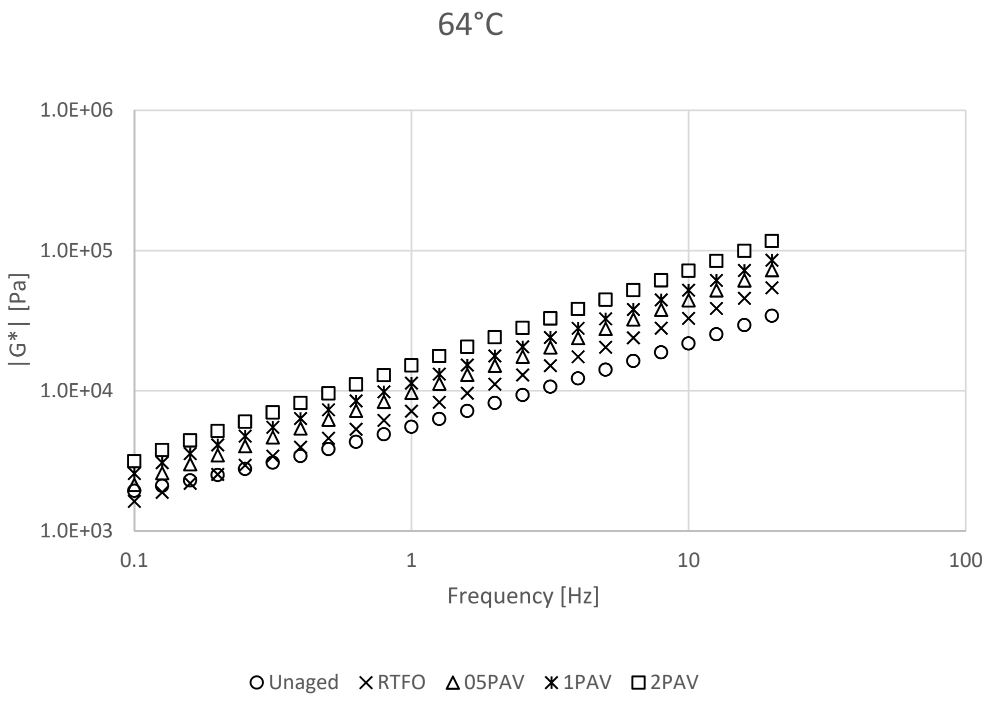


Figure 5-25 - - Isotherms @64°C of |G*| of SBS 6S bitumen at different levels of ageing.

5.1.3 EVA modified bitumens

Figure 5-26 shows the black diagrams of the EVA modified bitumens and of the Pen bitumen at the unaged conditions.

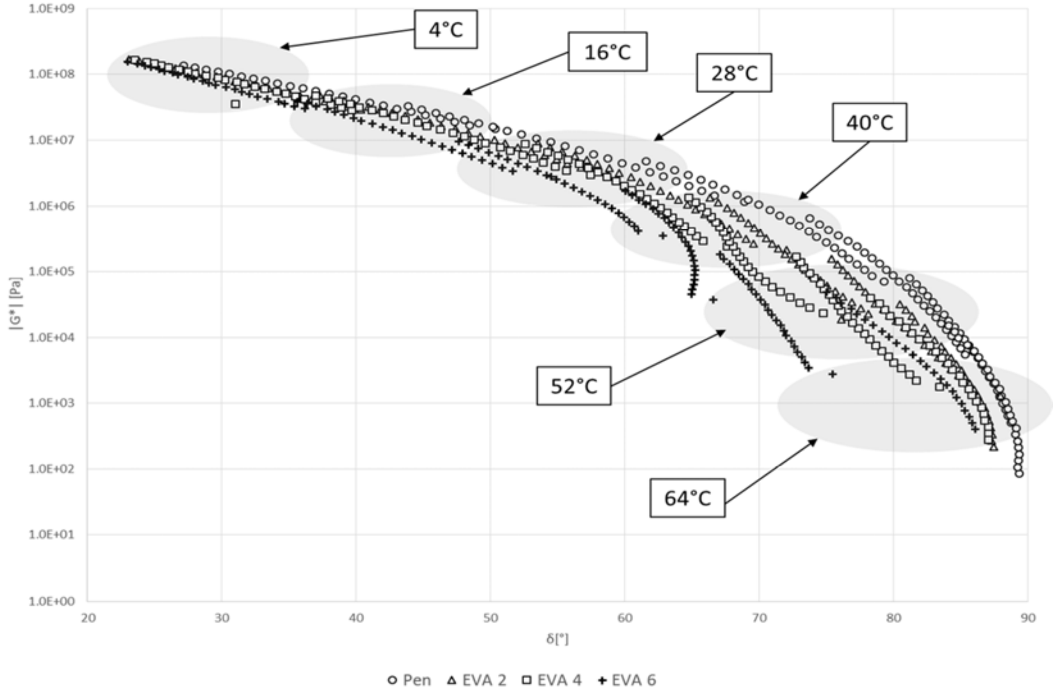


Figure 5-26 - Black diagram of Pen, EVA 2, EVA 4, and EVA 6, at unaged conditions.

In the region of the intermediate-low temperatures (i.e., 4°C, 16°C, and 28°C), the black diagrams of the EVA modified bitumens show a smooth trend similar to the Pen bitumen. The curves of the PMBs show that at the same level of stiffness (|G*|), the phase angle decreases as a function the polymer concentration. Besides this, in this range of temperature, the polymer does not seem to provide a visible effect on the viscoelastic response.

At higher temperatures (i.e., 40°C, 52°C, and 64°C) the EVA perturbs the smoothness of the curves as a function of its concentration. Higher concentrations (i.e., 4%, 6%) cause a waving of the isotherms at 52°C and 64°C. According to the work of Airey (45 – Section 4.4.6), the wavy aspect of the isotherms depends on the different crystalline structures formed by the polymer.

Contrarily to what observed with the SBS modified bitumens (§5.1.2), the EVA does not necessarily increase the elastic response under cyclic loading. The curves of the EVA modified bitumens in Figure 5-26 show that in the high-temperature region (lower stiffness and higher phase angle), the difference in the phase angle between the Pen bitumen and the PMBs is limited. Furthermore, the phase angle increases with temperature (contrarily to the SBS modified bitumens - Figure 5-7). This aspect is not surprising considering the definition of plastomers given in §2.7.2.

As adopted with the SBS modified bitumens, the effect of LSA on the LVE response of the EVA modified bitumens is discussed by referring to the black diagrams and the isotherms of stiffness at the unaged and 2PAV-aged conditions. The results for each polymer concentrations are given in the next sections.

5.1.3.1 EVA 2 bitumen

The black diagrams of the EVA 2 at unaged and 2PAV-aged conditions are given in Figure 5-35.

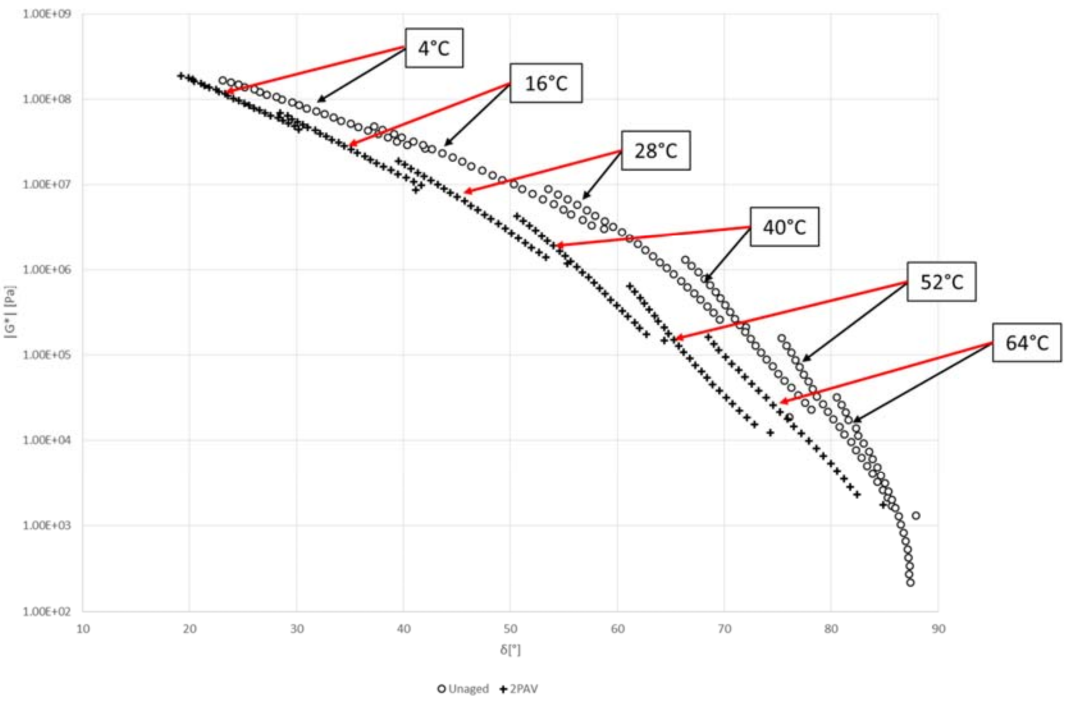
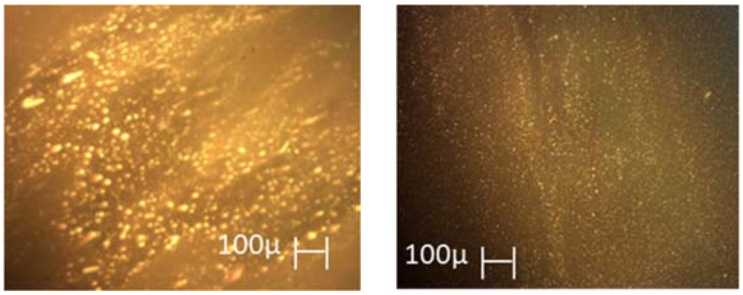


Figure 5-27 - Black diagram of EVA 2 bitumen at unaged and 2PAV-aged conditions.

The curve of the 2PAV-aged bitumen is shifted to the left compared to the unaged. Therefore, laboratory-simulated ageing produces a reduction of the phase angle within the whole temperature interval. This behaviour does not deviate from that observed in unmodified bitumens, where the aged bitumen shows a more-elastic behaviour under cyclic loading (Figure 5-1).

In this case, the polymer does not seem to have a relevant interaction with the bitumen phase. The reason for this might depend on the low affinity between the EVA and the bitumen that was already observed in the analysis of the morphology (spherical dispersed droplets) discussed in §4.2.2 and given in Figure 5-28.



(a) (b)

Figure 5-28 - Morphology of the EVA 2 bitumen at unaged (a) and 2PAV-aged (b) conditions.

It is true that the morphology at the unaged and the 2PAV-aged conditions are different with the latter showing a lower polymer dispersion. However, the EVA is visible in the bitumen phase even after 2 cycles on PAV. Furthermore, as discussed in §4.2.2, the differences between the unaged and the 2PAV-aged conditions are likely to depend on different thermal history.

Combining the results from the frequency sweep with those from the fluorescence microscopy, it appears that the changes in the viscoelastic response due to LSA do not deviate from those of the Pen bitumen. On the other hand, the morphology shows that the EVA dispersion of the polymer phase does not seem to be susceptible to the RTFO and PAV. This is supported by the analysis of the isotherms at high temperatures in Figure 5-27 that show a similar trend at unaged and 2PAV-aged conditions.

These findings support two observations:

- *Observation 1* - In the case of low polymer-bitumen dispersion (and affinity), the polymer-rich phase may not contribute to mitigating (or at least in affecting) the PAV-oxidative hardening of the bitumen-rich phase.
- *Observation 2* - Aside from the low EVA-bitumen affinity, the low laboratory-ageing susceptibility of the EVA could make the bitumen-phase the one being the most

susceptible that prevents the polymer-rich phase from damaging (adversely to that observed with the SBS).

However, the relatively low polymer concentration might be the cause of a low interaction (and low protection) with the bitumen phase. Therefore these two observations should be verified at higher polymer concentrations.

After discussing the combination of the constitutive analysis with the trend of the phase angle, the isotherms of stiffness at the different levels of ageing are given in Figure 5-29 and Figure 5-30.

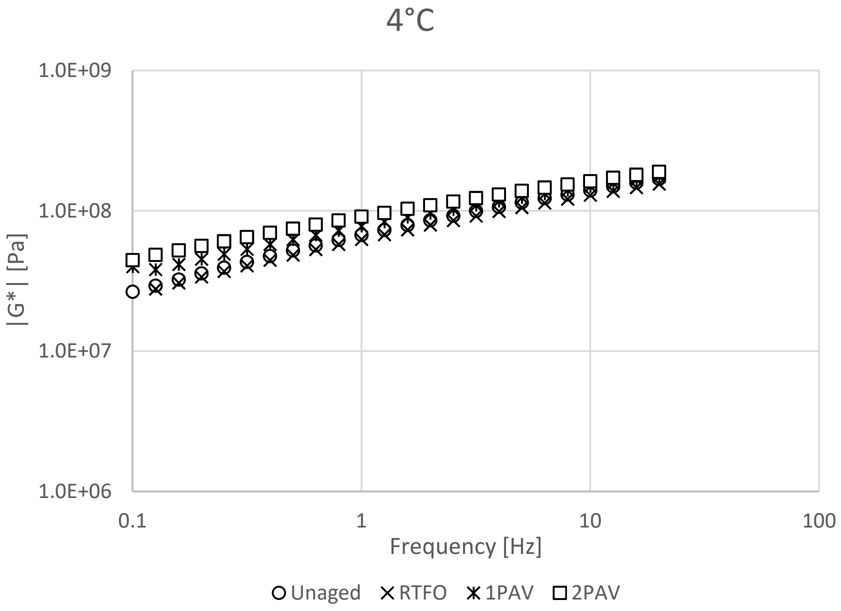


Figure 5-29 - Isotherms @4°C of |G*| of EVA 2 bitumen at different levels of ageing.

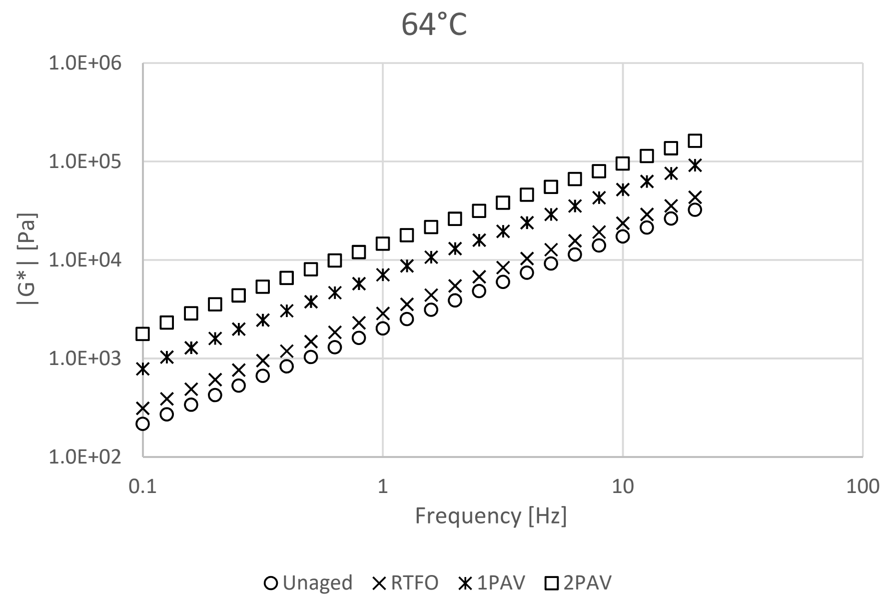


Figure 5-30 - Isotherms @64°C of |G*| of EVA 2 bitumen at different levels of ageing.

As expected, the stiffness increases with ageing and this effect appears to be more visible at higher temperatures.

5.1.3.2 EVA 4 bitumen

The black diagrams of the EVA 4 at unaged and 2PAV-aged conditions are given in Figure 5-31.

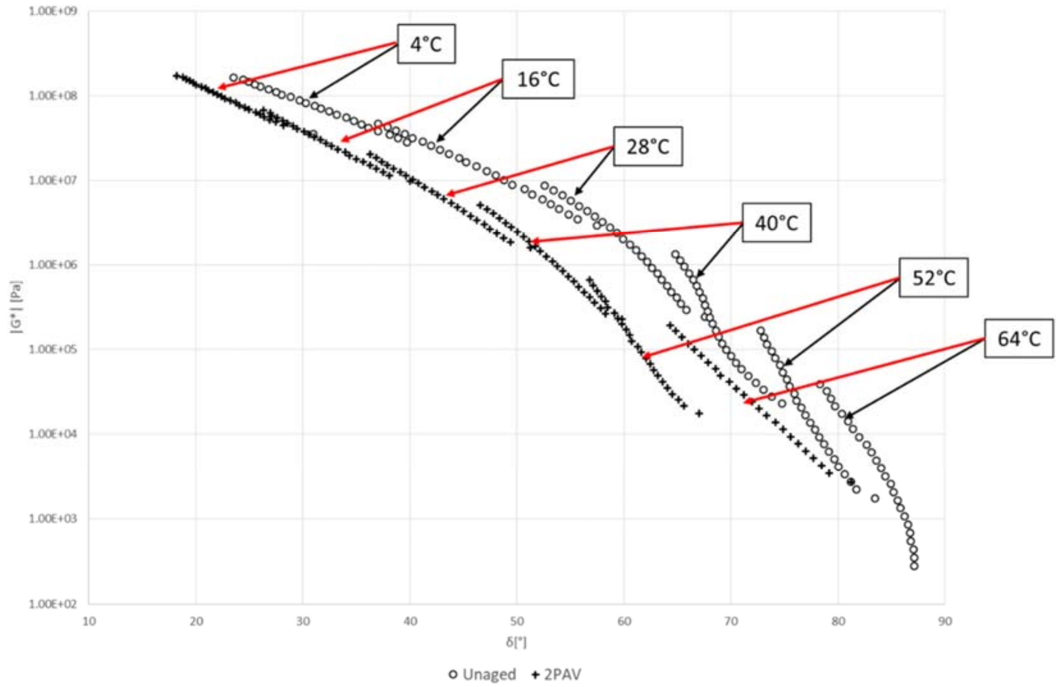
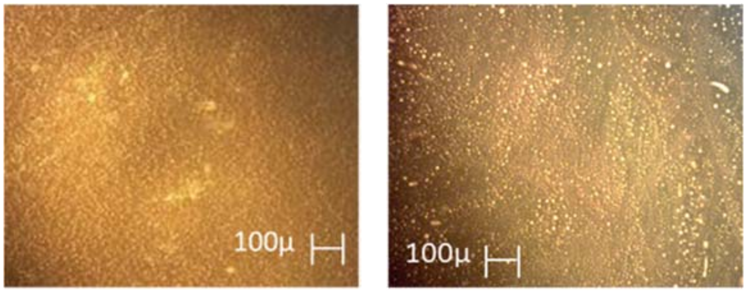


Figure 5-31 - Black diagram of EVA 4 bitumen at unaged and 2PAV-aged conditions

There are not relevant deviations from that observed in the EVA 2 bitumen. The phase angle decreases with ageing showing that in the presence of EVA, the effect of LSA on the LVE response are similar to those observed in the unmodified bitumens.

The isotherms at 52°C and 64°C under unaged and 2PAV-aged conditions show some differences. In the first case, they look like waves, while in the second they show a straighter trend. In section 5.1.3, it was highlighted that the wavy trend of the isotherms in the high-temperature region might depend on the crystalline structures in the polymer phase. Therefore, a change in the shape of the isotherm might indicate a change in the structure of the EVA. However, such consideration needs to be taken more like an observation that might require further investigation.

The morphology of the bitumen at unaged and 2PAV-aged conditions are in Figure 5-32.



(a) (b)

Figure 5-32 - Morphology of the EVA 4 bitumen at unaged (a) and 2PAV-aged (b) conditions.

As discussed in section 4.2.2, the dispersion of the EVA shows a very limited susceptibility to the LSA. Combining the results from the LVE analysis (Figure 5-31) and the morphology (Figure 5-32) the same conclusion drawn for the bitumen EVA 2 (§5.1.3.1) can be somehow replicated here. Therefore, if the Observations 1 & 2 raised for the EVA 2 bitumen might be biased by the relatively low concentration of the polymer, in this case, their validity seems to be supported. That is, the bitumen-rich phase could undergo PAV-oxidative hardening due to the low polymer-bitumen affinity and due to the low LSA-susceptibility of the EVA.

For the sake of completeness, the isotherms of |G*| at different levels of ageing are shown in Figure 5-32 and Figure 5-33.

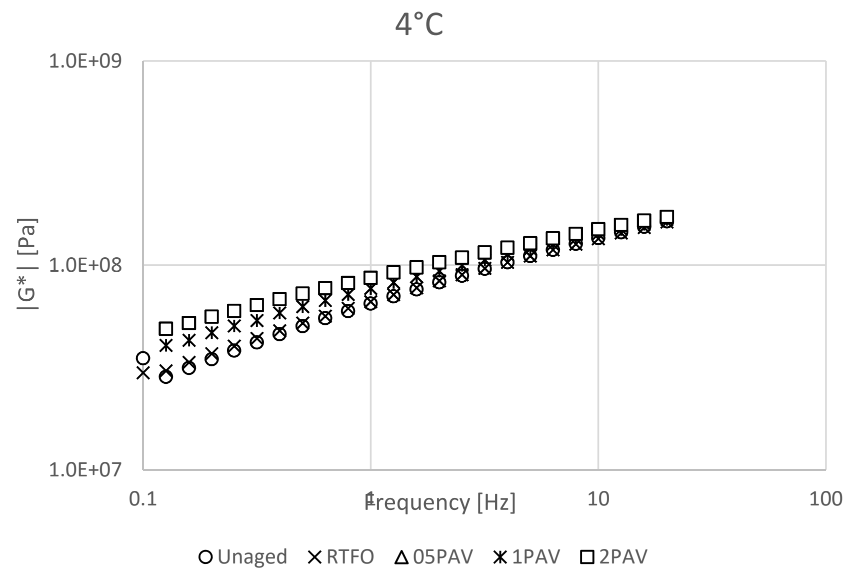


Figure 5-33 - Isotherms @4°C of |G*| of EVA 6 bitumen at different levels of ageing.

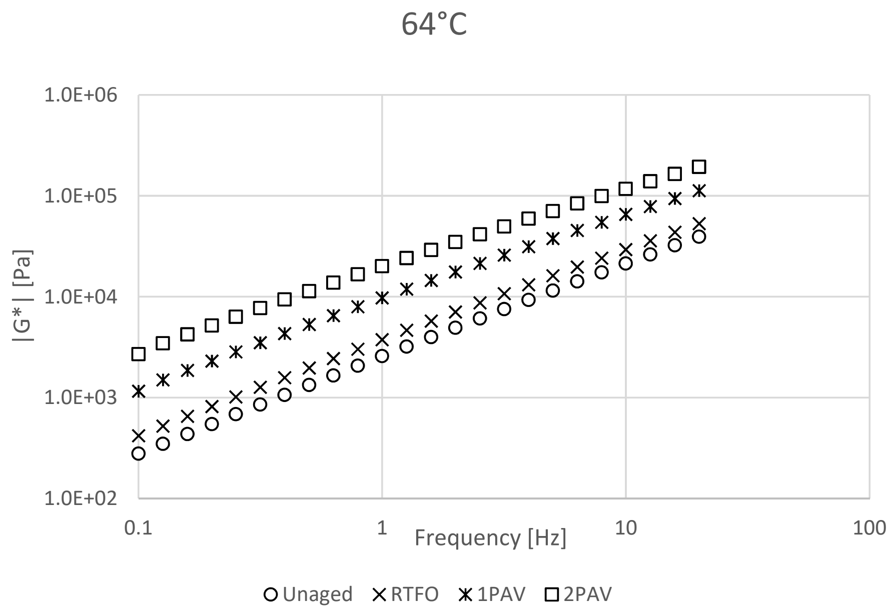


Figure 5-34 - Isotherms @4°C of |G*| of EVA 6 bitumen at different levels of ageing.

As expected, the stiffness increases with ageing and this effect that appears to be more visible at higher temperatures.

5.1.3.3 EVA 6 bitumen

The black diagrams of the EVA 6 at unaged and 2PAV-aged conditions are given in Figure 5-35.

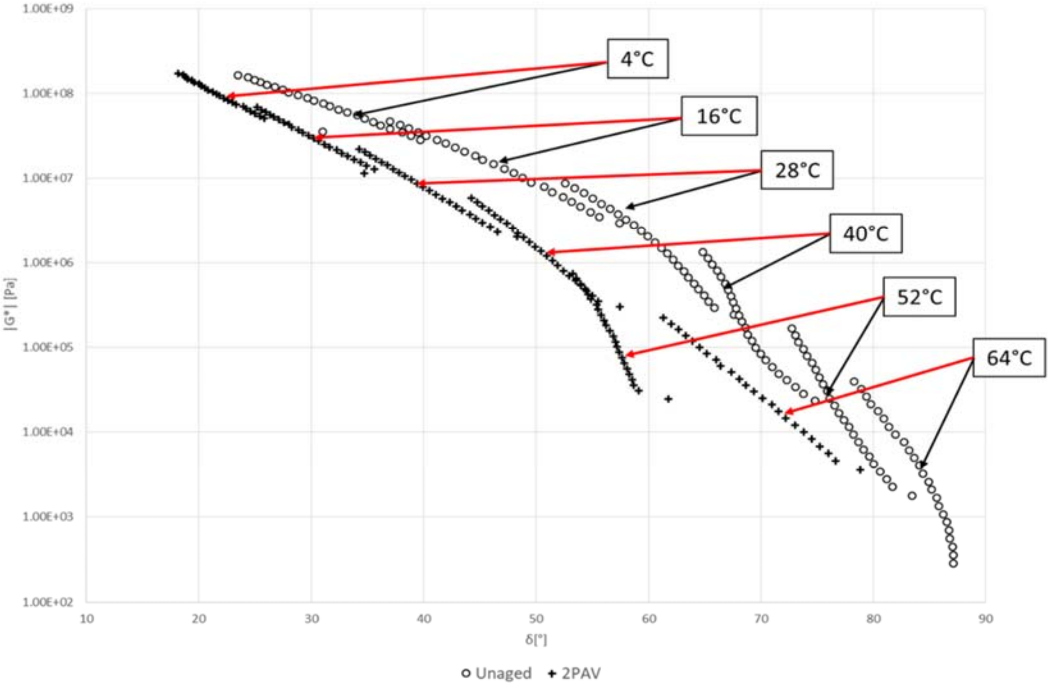
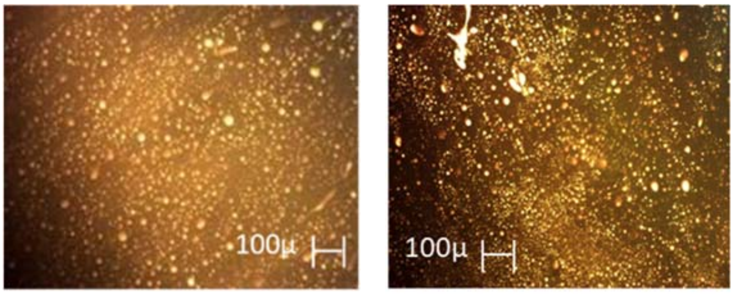


Figure 5-35 - Black diagram of EVA 6 bitumen at unaged and 2PAV-aged conditions.

The curve of the 2PAV-aged bitumen is shifted to the left compared to the unaged. Therefore, laboratory-simulated ageing produces a reduction of the phase angle within the whole temperature interval. This behaviour does not deviate from that observed in the EVA 2 and EVA 4 bitumens. The isotherms at high temperatures (i.e., 40°C, 52°C, and 64°C), vary their shape as observed in the EVA 4.

Following the same scheme adopted for the EVA 2 and EVA 4 bitumens, the images of the morphology at the unaged and 2PAV-aged conditions are given in Figure 5-36



(a) (b)

Figure 5-36 - Morphology of the EVA 6 bitumen at unaged (a) and 2PAV-aged (b) conditions.

Pieces of evidence from the LVE and the morphological analysis show that even in the case of very high polymer concentration, the EVA provides minimal effects on the variation in the rheological LVE response of with LSA of the PMB and, that this polymer has a low oxidative susceptibility.

In light of this, Observation 1 & 2 made for the EVA 2 (§5.1.3.1) polymer can be considered as applicable to this combination bitumen + polymer irrespective of the polymer concentration. The isotherms of |G*| at different levels of ageing are given in Figure 5-37 and Figure 5-38.

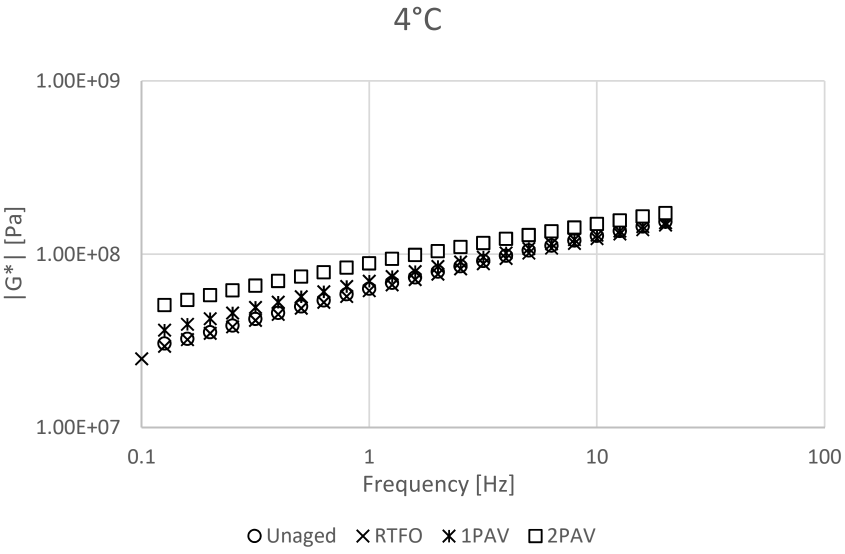


Figure 5-37 - Isotherms @4°C of |G*| of EVA 6 bitumen at different levels of ageing.

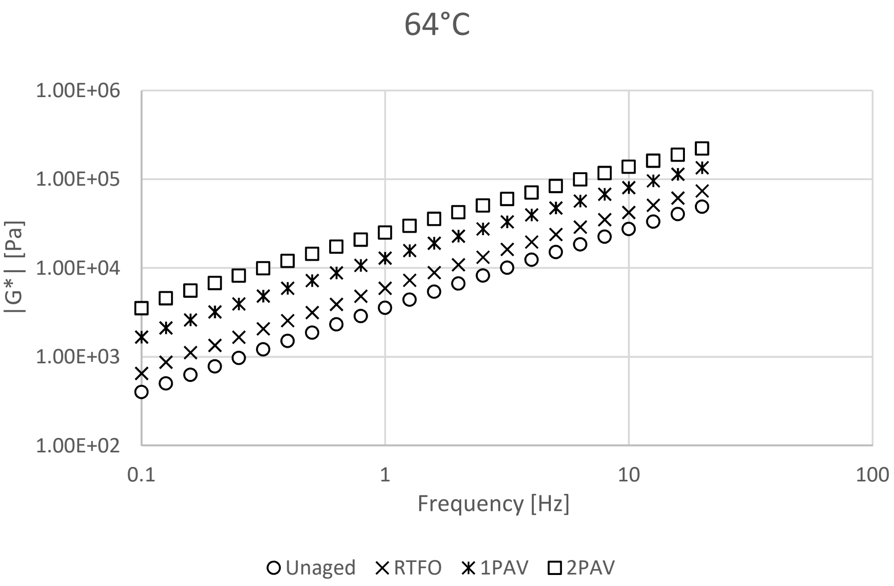


Figure 5-38 - Isotherms @64°C of |G*| of EVA 6 bitumen at different levels of ageing.

The very high polymer concentration does not seem to provide any variation on the increase in stiffness with ageing. Besides, in this case, the increase in stiffness due to LSA is more visible at high temperatures.

5.2 Results of MSCR test

The MSCR test temperatures selected as per the continuous grade temperature criterion (§3.3.7.2) are given in Table 5-2.

Table 5-2 – MSCR test temperatures

Bitumen	MSCR Temperature [°C]
Pen	64
Pen/S	64
SBS 2/S	70
SBS 4/S	75
SBS 4	75
SBS 6/S	87
SBS 6	87
EVA 2	66
EVA 4	70
EVA 6	70

The continuous grade temperature was determined on the SBS modified bitumens including sulphur (i.e., SBS 2/S, SBS 4/S, SBS 6/S) and the base bitumens (Pen). For the remaining bitumens (i.e., SBS 4, SBS 6) the MSCR test temperatures correspond to the ones determined on the PMB/S bitumens with the same polymer concentration. For the bitumen Pen/S, the MSCR temperature corresponds to the one determined on the Pen bitumen. It is worth clarifying that according to AASHTO M 332, the traffic designation should be measured at the Performance Grade temperature and not at the Continuous Grade High Temperature. However, the traffic designation is included to provide a synthetic indicator of the change in the resistance to the accumulation of permanent deformation and not for grading purpose.

Three replicates were used for each bitumen.

Results are organised per SBS modified bitumens and EVA modified bitumens. In the case of SBS, results are corroborated by the findings of the GPC and the fluorescence microscopy. On the other hand, in the case of EVA, results are supported by images of the fluorescence microscopy.

5.2.1 MSCR results of SBS modified bitumens

In this study, the MSCR test was used to provide rheological indicators (i.e., non-recoverable compliance at 3.2 kPa - J_{nr}; and the average percent recovery at 3.2 kPa – R), to evaluate the effect of different-levels of LSA on SBS modified bitumens prepared with and without cross-linker.

Before discussing the results of the J_{nr} and the average percent recovery at different levels of ageing, two examples of the trend of the measured strain versus time in the MSCR test are given. Specifically, the figures below show the variation of the measured strain (at 3.2 kPa) versus time of the unmodified bitumen (Pen - Figure 5-39) and the SBS 6/S modified bitumen (Figure 2).

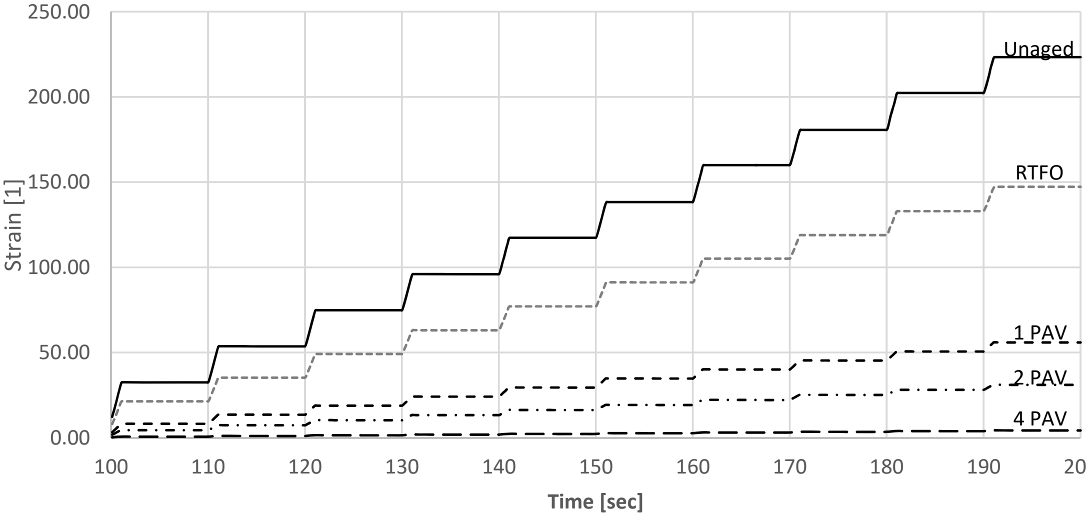


Figure 5-39 - Measured strain at 3.2 kPa versus time Pen bitumen at different levels of ageing

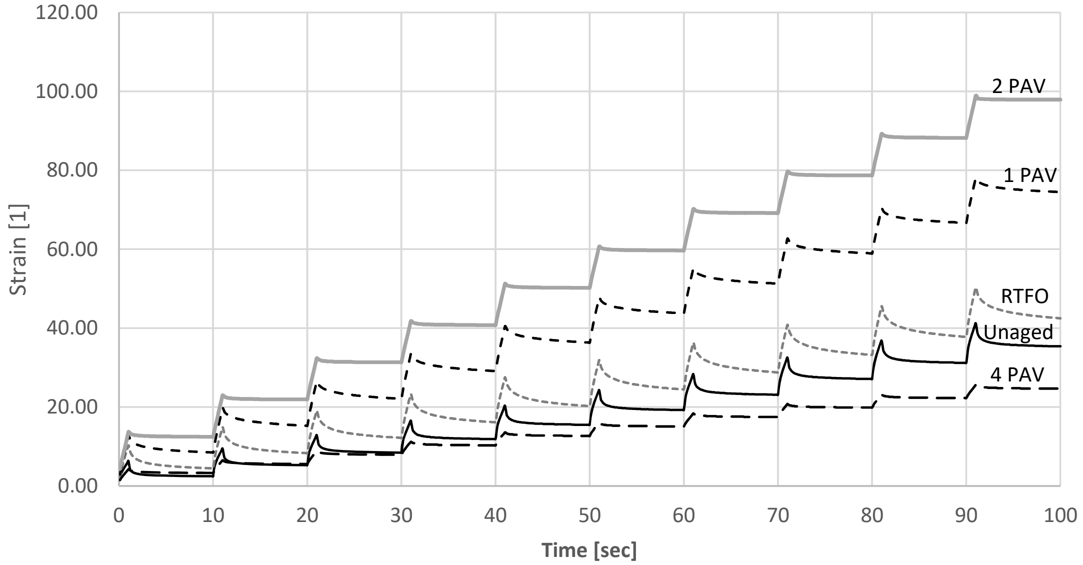
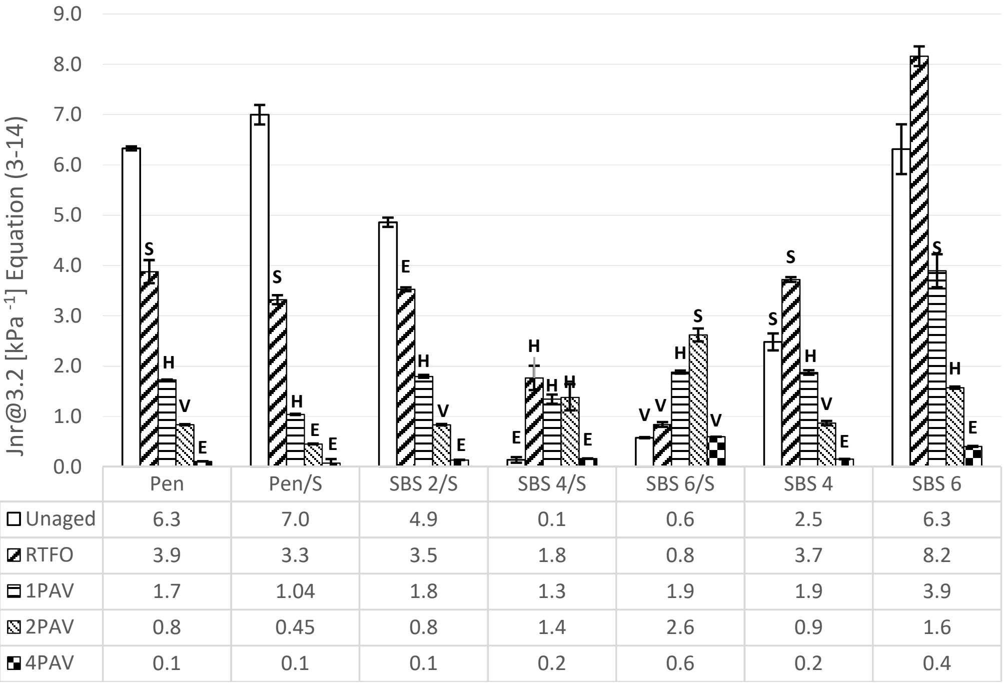


Figure 5-40 - Measured strain at 3.2 kPa versus time SBS 6/S at different levels of ageing

In the case of the unmodified bitumen (Figure 5-39), the accumulated final strain at the end of the loading cycles decreases with ageing with the highest value of final strain at the unaged condition and the lowest after four cycles of PAV. This trend highlights the oxidative hardening of the bitumen occurring in the RTFO and the PAV. On the other hand, the final accumulated strain of the SBS 6/S bitumen (Figure 5-40), shows the opposite trend between the unaged and the 2PAV-aged conditions. In this case, the final strain increases with ageing, indicating that the bitumen is softening in the RTFO and the PAV. Then, after four cycles of PAV, the final strain reduces below the value shown at the unaged condition. The variation of the final strain with ageing depends on the contributions of the polymer and of the bitumen phases at the testing temperatures. This mechanism is detailed in the discussion of the J_{nr} and the R results.

5.2.1.1 Analysis of J_{nr}@3.2 kPa values

The values of the J_{nr} at the stress level of 3.2 kPa are given in Figure 5-41 and discussed as follows.



	Pen	Pen/S	SBS 2/S	SBS 4/S	SBS 6/S	SBS 4	SBS 6
□ Unaged	6.3	7.0	4.9	0.1	0.6	2.5	6.3
▨ RTFO	3.9	3.3	3.5	1.8	0.8	3.7	8.2
☰ 1PAV	1.7	1.04	1.8	1.3	1.9	1.9	3.9
▧ 2PAV	0.8	0.45	0.8	1.4	2.6	0.9	1.6
◘ 4PAV	0.1	0.1	0.1	0.2	0.6	0.2	0.4

Figure 5-41 - J_{nr} @ 3.2 kPa (kPa^{-1}) (AASHTO M 332 traffic Designation: S – Standard ($J_{nr\ max}$ = 4.5 kPa^{-1}); H – Heavy ($J_{nr\ max}$ = 2 kPa^{-1}); V – Very Heavy ($J_{nr\ max}$ = 1 kPa^{-1}); E – Extreme ($J_{nr\ max}$ = 0.5 kPa^{-1}))

Pen and Pen/S bitumen

The Pen and Pen/S bitumen are included in this section for comparative purpose.

The non-recoverable compliance of the Pen bitumen decreases with ageing. This result is not surprising since the stiffening effect of ageing on unmodified bitumen is well known. The use of 0.1% sulphur does not provide a remarkable effect with the J_{nr} showing the same trend (Figure 5-41). To support the results, the outcomes from the MSCR have been overlapped with those from the GPC (Figure 5-42, Figure 5-43).

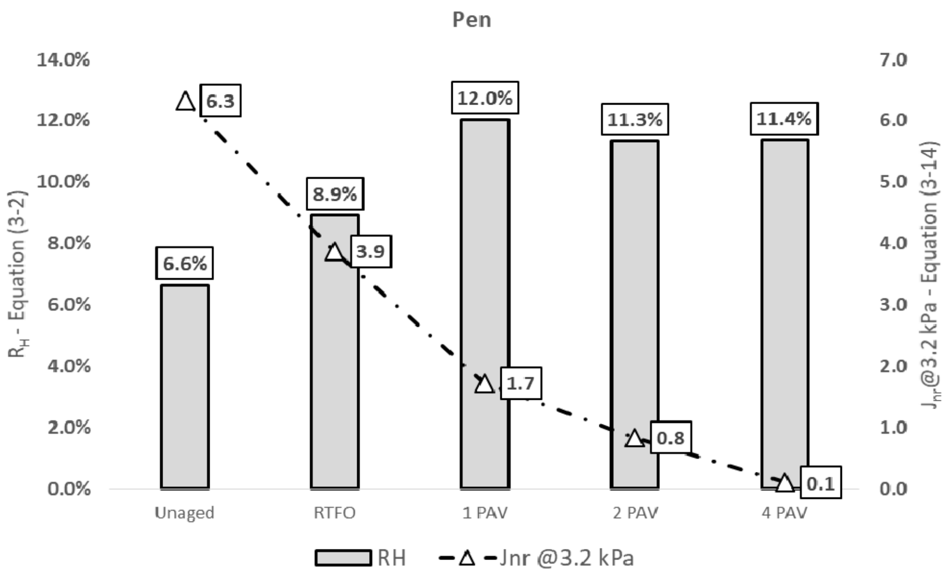


Figure 5-42 – Pen bitumen MSCR test results overlapped with R_H values at different LSA (J_{nr}@3.2kPa (J_{nr} - kPa-1)).

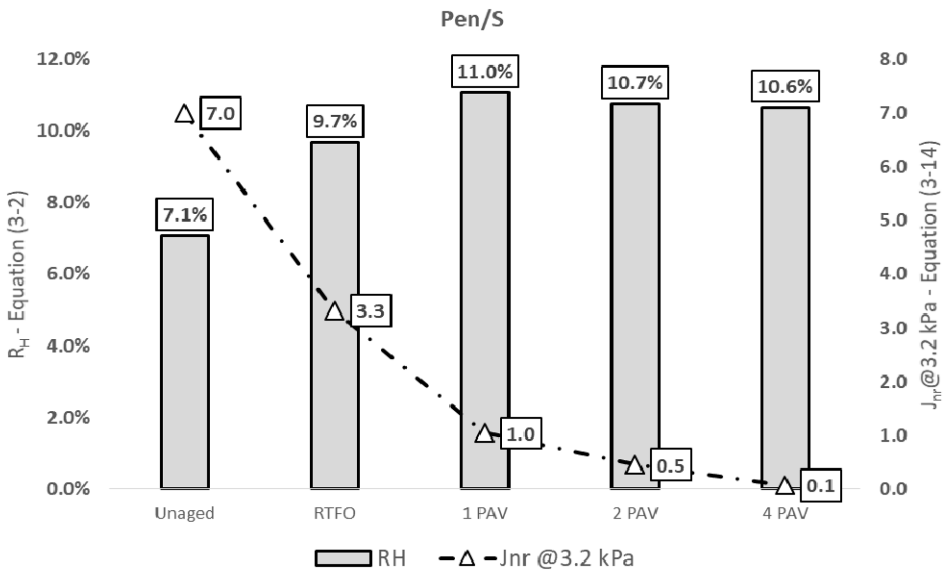


Figure 5-43 – Pen/S bitumen MSCR test results overlapped with R_H values at different LSA (J_{nr}@3.2kPa (J_{nr} - kPa-1)).

Results from the GPC analysis (R_H values Equation (3-2)) show that after the first cycle of PAV, in both bitumens, the portion of the heavy fractions becomes stable. However, the results from the MSCR show that the rheological response still changes even after 1 cycle of PAV. Therefore, although the R_H becomes stable, changes in the polarity and the molecular bonds still occur.

On the other hand, the variation of the J_{nr} value with the ageing of the SBS modified bitumens depends clearly on the polymer concentration and the use of sulphur as cross-linker. A detailed discussion is given below.

SBS 2/S bitumen

The J_{nr} decreases with ageing as seen as on the Pen bitumen. The traffic designation varies from an S-grade at the unaged condition, to an E-grade after 4 cycles of PAV (Figure 5-41). It seems that at such polymer concentration, the polymer phase is not capable of mitigating the effects of the bitumen (phase) hardening on the rheological response. The use of GPC data (Figure 5-44) and images from fluorescence microscopy (Figure 4-3, Figure 4-4) can contribute to detailing this statement.

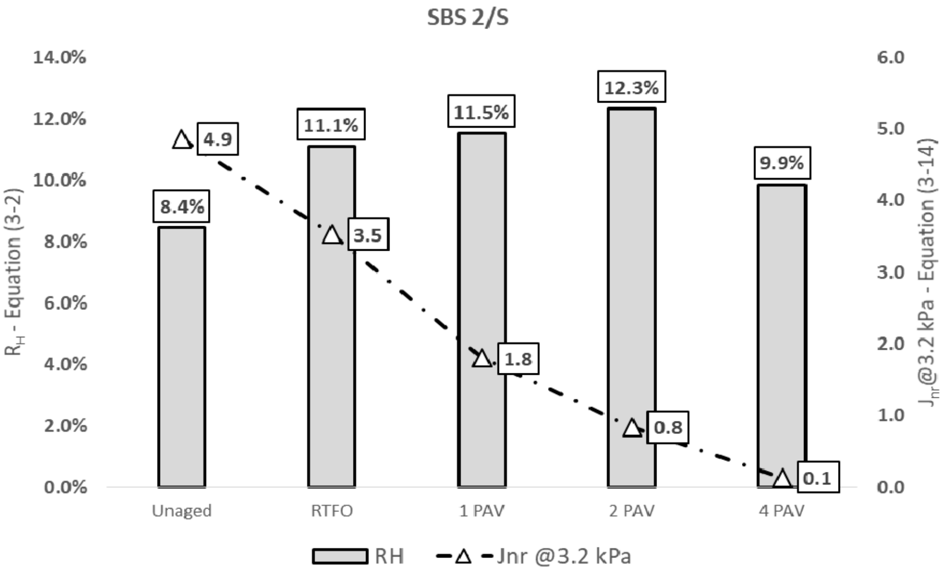


Figure 5-44 – SBS 2/S bitumen MSCR test results overlapped with R_H values at different LSA (J_{nr}@3.2kPa (J_{nr} - kPa-1)).

As discussed in §4.3, the variation of the heavy fractions with ageing in the SBS 2/S bitumen depends on the contribution of the bitumen hardening and of the polymer degradation. However, although the microstructure of the PMB varies in the PAV, the J_{nr} decreases with ageing irrespective of the R_H (Figure 5-44). The inability of the polymer to mitigate the hardening if the bitumen phase in the PAV might depend on the relatively low concentration. As observed in the fluorescence microscope, at 2% weight concentration, the SBS is not capable of forming a dispersed network (Figure 4-3 - a). Under these conditions, once the PMB undergoes ageing, although the presence of the polymer is visible in the GPC, its effects on the rheological response are quite limited. This aspect is, to some extent, in agreement with the morphology (Figure 4-4 – a, b, c), where the polymer particles reduce their fluorescence soon after the RTFO with the polymer phase being not visible in the bitumen phase. Therefore, the presence of the bulk polymer alone (intended to as in terms of mass), may not be sufficient to provide adequate effects as an ageing inhibitor on the rheological response at high pavement temperatures. The formation of a structured network might result in being more effective.

SBS 4/S bitumen

The SBS 4/S represents a stable configuration (defined as 'optimum' polymer content) with the J_{nr} being stable between the RTFO and 2 PAV. Then at 4 PAV, as shown by all the other bitumens, the J_{nr} of the SBS 4/S decreases to very low values (Figure 5-41).

The low variability of the J_{nr} value between the RTFO and the 2 PAV ageing, might depend on the balance between the bitumen hardening and the polymer degradation (observed through the increase in R_H values in Figure 5-45).

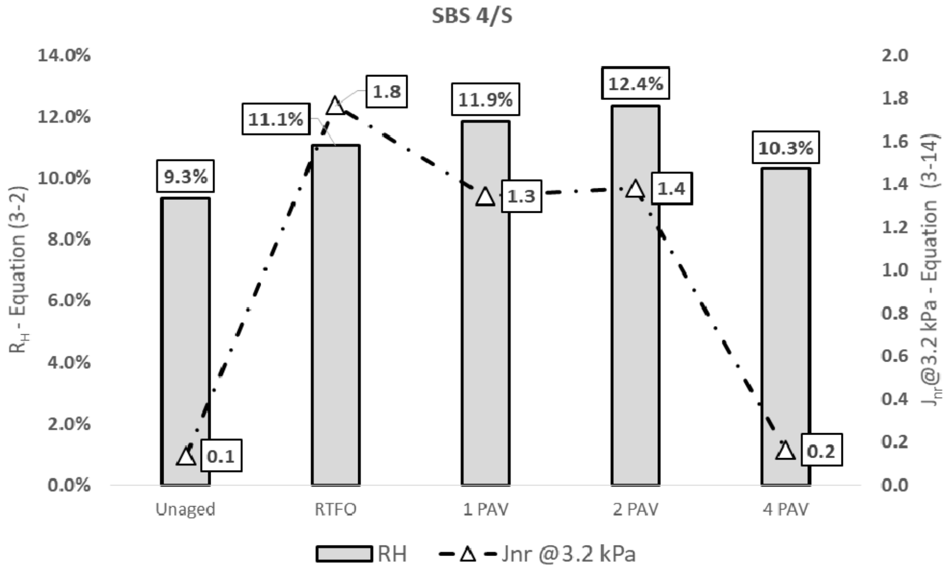


Figure 5-45 - SBS 4/S bitumen MSCR test results overlapped with R_H values at different LSA (J_{nr}@3.2kPa (J_{nr} - kPa-1)).

Therefore, in the case of high polymer concentrations (4% - with the use of the cross-linker), within two cycles of PAV the fragments of the polymer chains, whose weight is similar to the heavy bitumen fractions, are capable of mitigating the PAV-hardening of the bitumen to such an extent of maintaining the J_{nr} value to be almost constant at the MSCR test temperature. Probably, at 2% SBS, the polymer fragments do not have a sufficient concentration to mitigate the bitumen hardening resulting in the J_{nr} values decreasing. Then at 4 PAV, the weight fragments of the polymer chains are reduced due to the thermo-oxidative process occurring in the PAV (R_H decreases from 12.4 to 10.3% - Figure 5-45), and bitumen molecules become dominant with the J_{nr} value decreasing (24). In this case, the images of the morphology at the unaged condition show that the polymer network is well reticulated (Figure 4-3 - b). Therefore, although the dispersion of the polymer phase is reduced during the RTFO and the PAV (Figure 4-4 – d to f), a networked SBS is capable of mitigating the oxidative hardening of the bitumen on the rheological response for more prolonged PAV exposure.

SBS 6/S bitumen

The J_{nr} values increase with ageing between the unaged and the 2 PAV aged conditions (Figure 5-41). This behaviour is counterintuitive since hardening should be expected. However, what might happen in this case, corresponds to what was observed in SBS 4/S modified bitumen with the difference that at very high polymer concentration (6% - with the use of a cross-linker), the polymer fragments are dominant over the bitumen molecules as shown in the J_{nr} values (at 4% there is potentially a balance). That is, the increase in the J_{nr} values might indicate that, although the bitumen phase hardens, the PMB is softening because its response is more controlled by the polymer phase that is degrading in the PAV. Then, as observed in the SBS 4/S binder after four cycles of PAV, the effect of the polymer vanishes because it is highly degraded, and the hardened bitumen dominates the rheological response. Consequently, the J_{nr} value drops. The concept of controlling the rheological response (or dominance) as a function of temperature has been detailed by Airey and Brown (24).

What is interesting is that although the J_{nr} varies with ageing, the GPC data show a limited effect of the PAV on the MWD (Figure 5-46).

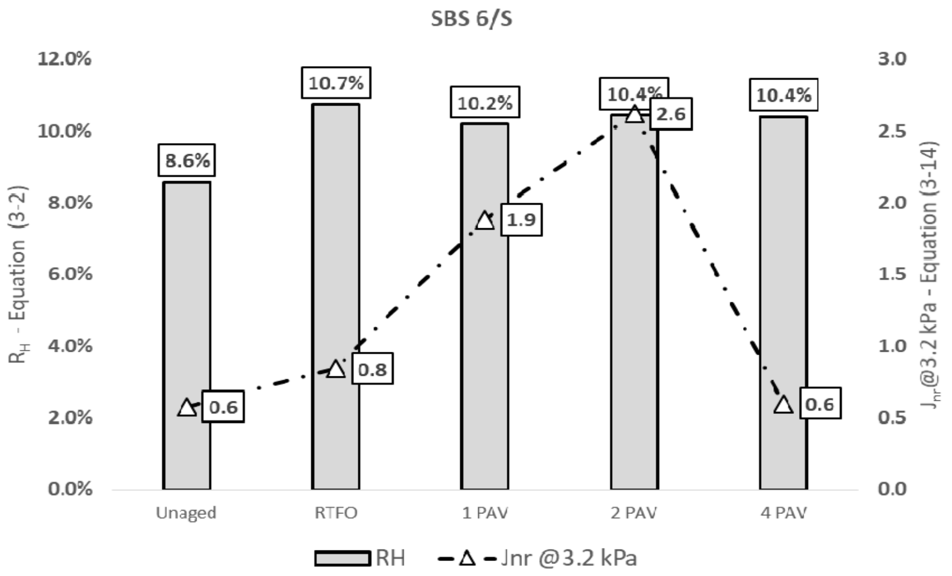


Figure 5-46 - SBS 6/S bitumen MSCR test results overlapped with R_H values at different LSA (J_{nr}@3.2kPa (J_{nr} - kPa-1)).

The RTFO seems to produce an increase in the heavy fractions (RH increases of 2.1% from unaged to RTFO aged) with the PAV producing a negligible effect afterwards. However, the RTFO does not appear to produce significant damage to the polymer chains that maintain the Jnr value still below 1 kPa^{-1} (corresponding to a V-grade). In this case, the change in the R_H might be due to the volatilisation of the light fractions with the polymer chain remaining undamaged. This aspect is confirmed by the morphology (Figure 4-4 – g) and by the value of the average percent recovery (R) in §5.2.1.2.

However, the MSCR – GPC comparison helps to raise some considerations, such as that besides the size of the polymer chains, there are other properties of the polymer that change with ageing even though the weight distribution of the molecules does not vary. Therefore, the effect of the polymer on the MSCR response of PMBs depends on various polymer properties, although the molar mass is one of the most important (94). It appears that these properties begin to degrade in the PAV before the molar mass of the polymer starts changing.

SBS 4 and SBS 6 bitumens

The trend of the J_{nr} values of the SBS 4 and SBS 6 bitumen highlight that the use of sulphur as a cross-linker strongly influences the ageing susceptibility of the PMBs. Both bitumens show an increase in the J_{nr} values between the unaged condition and the RTFO. After the RTFO, the trend throughout the PAV ageing coincides with what was observed in the Pen bitumen (Figure 5-41). Although the SBS is used in the same concentrations of the bitumens modified with sulphur (i.e., 4%, 6%), the rheological response indicates that after the RTFO the polymer phase is degraded, and does not compensate for the hardening of the bitumen phase. In the case of low reticulation (Figure 4-3), the presence of the fragments of the polymer chains at the different levels of ageing (R_H values in Figure 5-47 and Figure 5-48) is not capable of controlling the rheological response with ageing for the same polymer concentration.

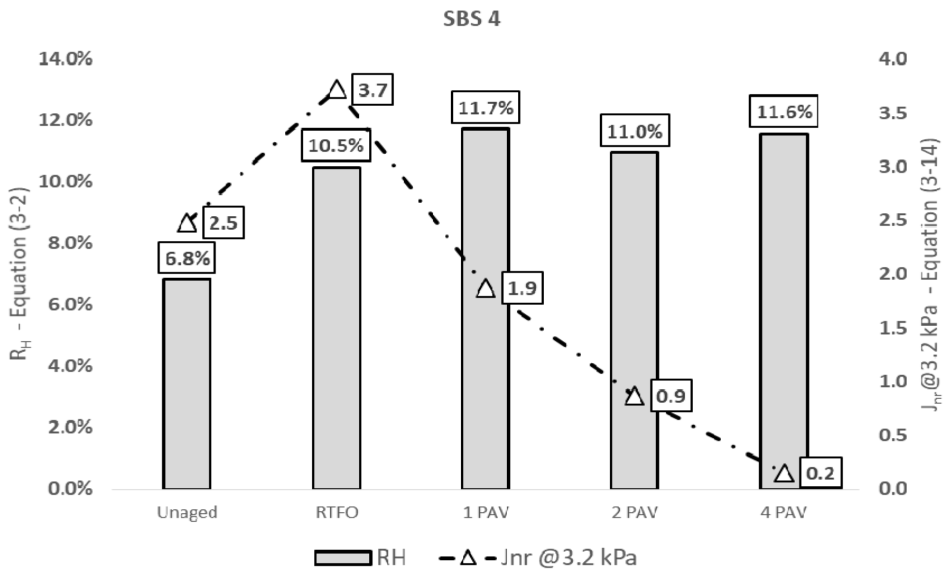


Figure 5-47 - SBS 4 bitumen MSCR test results overlapped with R_H values at different LSA (J_{nr}@3.2kPa (J_{nr} - kPa-1)).

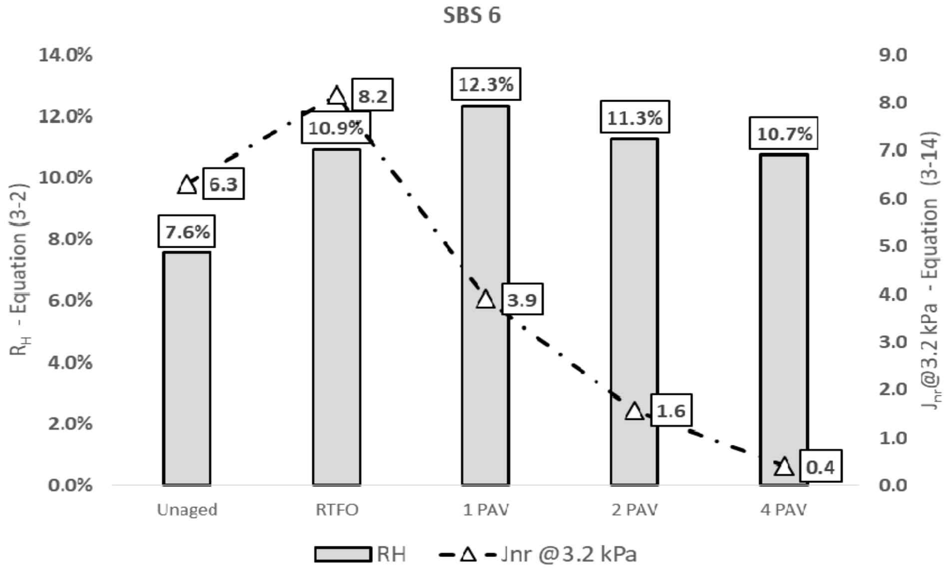


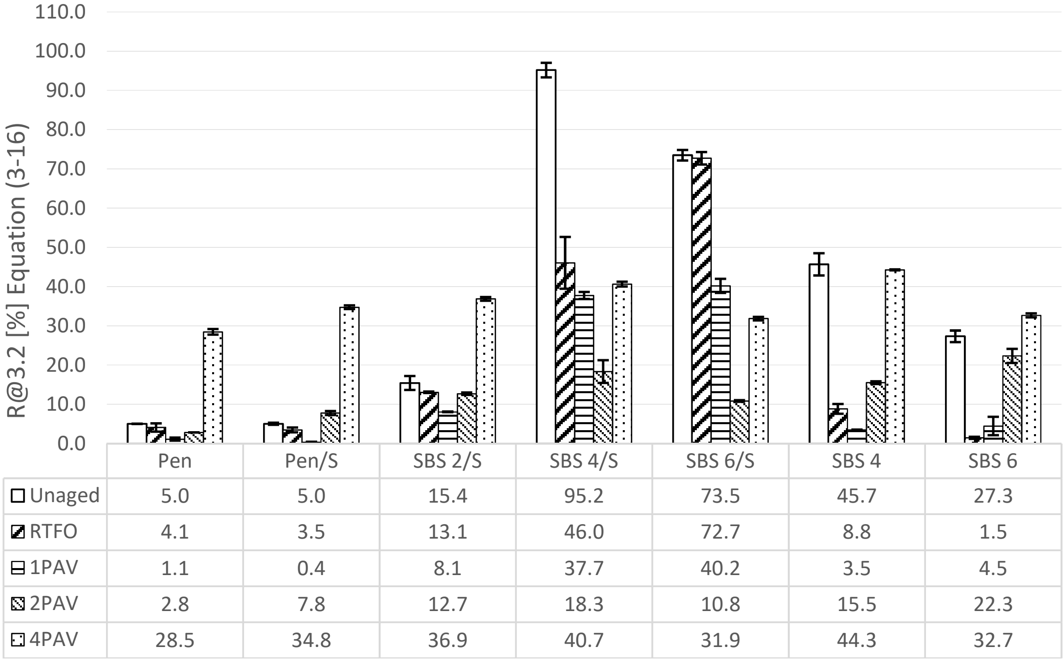
Figure 5-48 - SBS 6 bitumen MSCR test results overlapped with R_H values at different LSA (J_{nr}@3.2kPa (J_{nr} - kPa-1)).

The advantage of using Sulphur in PMBs has been determined by various authors that highlight that the crosslinking effect of sulphur improves polymer stability and enhances the quality of modification (168, 179-182). In this case, results show that the cross-linking effect of sulphur provides the polymer network with a higher oxidative resistance in the PAV with the SBS balancing the hardening of the bitumen phase.

5.2.1.2 Analysis of R@3.2kPa

The average percent recovery is considered as a rheological indicator of the integrity of the polymer network. In the case of elastomers, like SBS, the elastic recovery represents the capacity of recovery the original configuration after the loading removal. This property is a function of the integrity of the polymer network dispersed in the bitumen phase (§2.7.2).

The values of the average percent recovery (R) at 3.2 kPa are given in Figure 5-49.



	Pen	Pen/S	SBS 2/S	SBS 4/S	SBS 6/S	SBS 4	SBS 6
☐ Unaged	5.0	5.0	15.4	95.2	73.5	45.7	27.3
▨ RTFO	4.1	3.5	13.1	46.0	72.7	8.8	1.5
⊟ 1PAV	1.1	0.4	8.1	37.7	40.2	3.5	4.5
▧ 2PAV	2.8	7.8	12.7	18.3	10.8	15.5	22.3
⬚ 4PAV	28.5	34.8	36.9	40.7	31.9	44.3	32.7

Figure 5-49 - R @ 3.2 kPa of Pen, Pen/S and SBS modified bitumens Equation (3-15).

Pen and Pen/S bitumen

No particular considerations need to be made on the percent recovery since these bitumens do not contain the polymer. However, the increase in the percent recovery at 4 PAV (Figure 5-49), may depend on the hardening of the bitumen with the consequent decrease in the strain level of the test particularly in the creep portion (ε_c - Figure 3-26). As discussed for the J_{nr}, also the R values show that although the variations in the light and heavy fractions appear to be reduced (Figure 5-50, Figure 5-51), the rheological response shows clearly visible variations. This confirms what was mentioned above on the importance of the type of molecules besides their size.

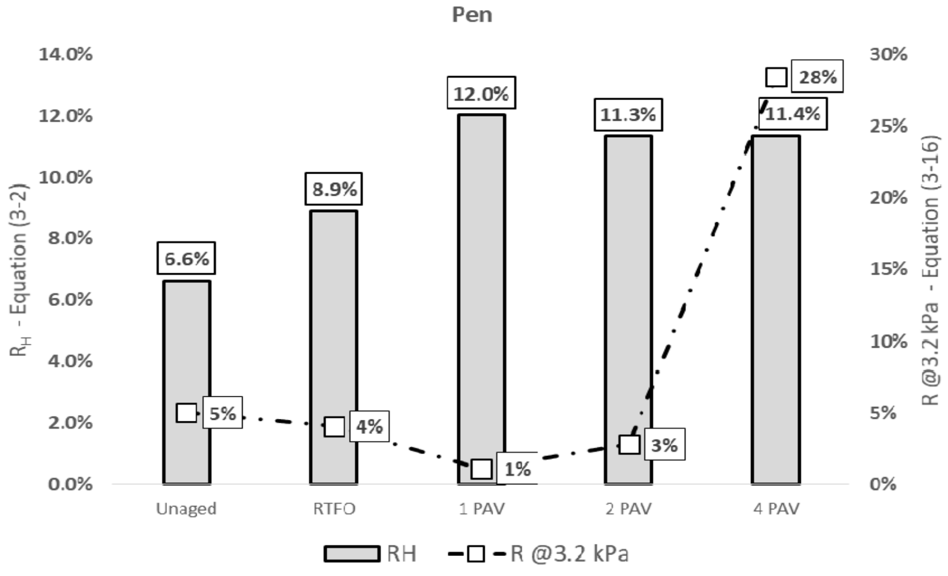


Figure 5-50 - Pen bitumen MSCR test results overlapped with R_H values at different LSA R@3.2kPa (%).

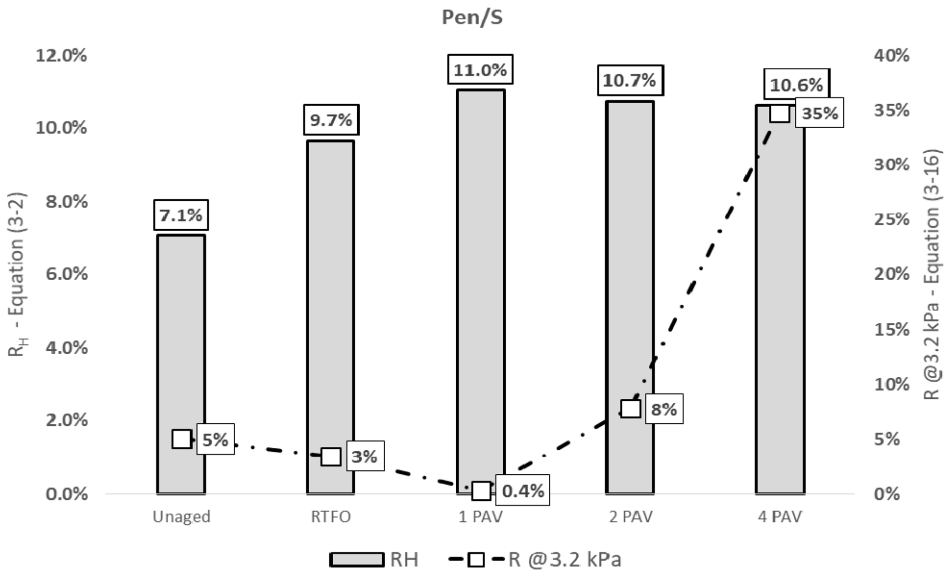


Figure 5-51 - Pen/S bitumen MSCR test results overlapped with R_H values at different LSA R@3.2kPa (%).

SBS 2/S bitumen

As shown in Figure 5-49, the percent recovery of the SBS 2/S shows a relatively reduced variation between the unaged conditions to 2 PAV ageing. Within this ageing interval, the low variation (in R values) is accompanied by a low magnitude of R as well. The reason for this, besides the relatively low polymer concentration, can be found in the low level of polymer reticulation shown in the morphology (Figure 4-3 – a; Figure 4-4 – a, b, c).

Between two and four cycles of PAV, the percent recovery increases up to 37%. The use of the GPC data (Figure 5-52), can support the understanding of these results.

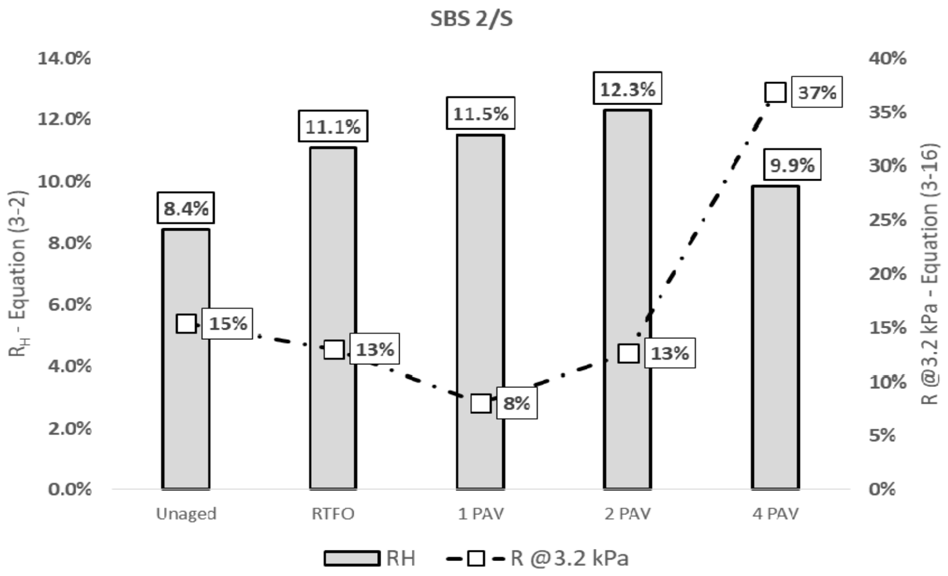


Figure 5-52 – SBS 2/S bitumen MSCR test results overlapped with R_H values at different LSA R@3.2kPa (%).

As discussed in the results of the GPC *Investigated Area 2* (§4.3), between the RTFO ageing and the 2 PAV ageing, the increase in the heavy bitumen fractions is given by the bitumen hardening and the polymer degradation. Therefore, it seems that at the testing temperature (Table 5-2 – 70°C), the polymer fragments (degraded polymer chains), whose weight is similar to the weight of the heavy bitumen fractions, are more dominant on the percent recovery than the bitumen molecules. For this reason, the percent recovery shows relatively low values.

Then, at 4 PAV, once the fragmented polymer chains are further reduced as such as to be detected with the light bitumen fractions (R_H decreases from 12.3% to 9.9% - Figure 5-52), the percent recovery is dominated by the hardened bitumen and increases consequently (as seen with the Pen bitumen). It is worth mentioning that the level of impact on the physical response (referred as 'dominance') between the polymer and the bitumen phase also depends on the testing temperature with polymer’s effect being more relevant at high temperatures (24).

SBS 4/S bitumen

In the SBS 4/S bitumen, the polymer modification produces a remarkable increase in the average percent recovery (R=95% at unaged conditions - Figure 5-49). The quality of the modification is also shown by a dispersed-polymer network visible in the morphology (Figure 4-3). In the RTFO, the polymer network degrades with the value of R that drops to 46%. In the PAV, the residual deterioration of the polymer network is visible after 40 hours of exposure with the value of R decreasing to 18.3% after two PAV cycles (Figure 5-49). The reduced loss in average percent recovery after a single cycle of PAV (-8% - Figure 5-53) is consistent with the trend of the J_{nr} values that show a reduced variation. After four cycles of PAV, the hardening of the bitumen phase produces an increase in the R values as observed in the other bitumens discussed so far (i.e., Pen, Pen/S and SBS 2/S).

The trend of the average percent recovery (Figure 5-49) is representative of the degradation of the polymer chains. The GPC results contribute to corroborate this statement (Figure 5-53).

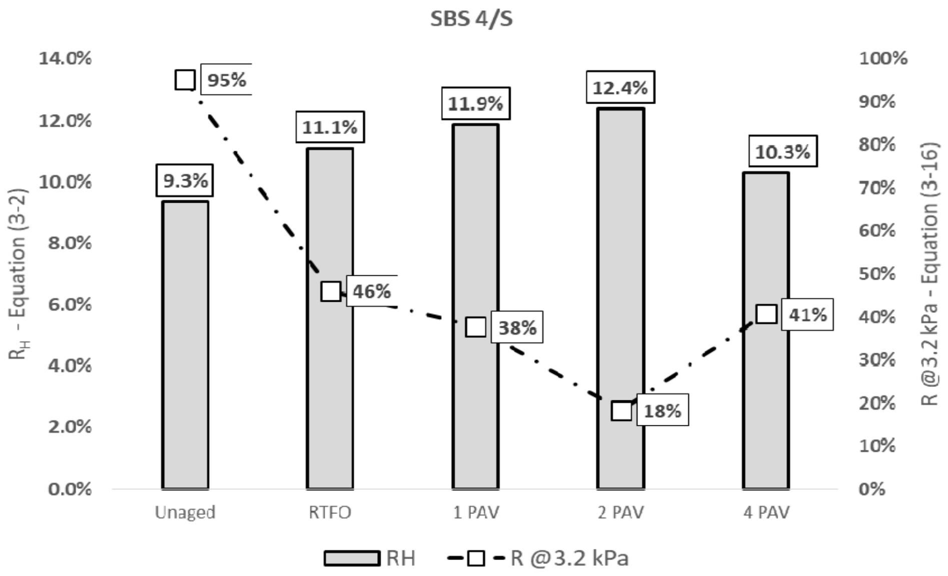


Figure 5-53 - SBS 4/S bitumen MSCR test results overlapped with R_H values at different LSA R@3.2kPa (%).

As shown in Figure 5-53, the decrease in the R values occurs concurrently with the increase in the R_H values that, as mentioned repeatedly, depends on the contribution of the fragments of the polymer chains and the bitumen hardening. Since the hardening of the bitumen should produce an increase in percent recovery, the decrease in R between the unaged to the 2 PAV aged condition highlights that, at the testing temperature (Table 5-2 – 75°C), the polymer chains are dominant on the R values that decrease with the polymer degradation. At 4 PAV, as seen with the J_{nr} values, the hardened bitumen becomes dominant (polymer fragment excessively degraded), and the percent recovery increases.

SBS 6/S bitumen

As observed in the SBS 4/ bitumen, the polymer modification in the SBS 6/S bitumen increases the percent recovery compared to the unmodified bitumen (Figure 5-49). The SBS 4/S bitumen shows a higher recovery, probably because of the difference in the testing temperature (Table 5-2). The SBS 6/S bitumen maintains almost the same average percent recovery after the RTFO that slightly damages the polymer network. The low effect of the RTFO on the polymer network is shown by the morphology as well (Figure 4-4 - g). The negligible reduction in R between the unaged and the RTFO-aged conditions supports what was mentioned in the comments of the J_{nr} (§5.2.1.1 - SBS 6/S bitumen) regarding the increase in the heavy fraction (R_H). The increase in the R_H values observed in the GPC is more likely to be dependent on the volatilisation of the light fractions (Equation (3-3)) rather than the polymer degradation (Figure 5-54).

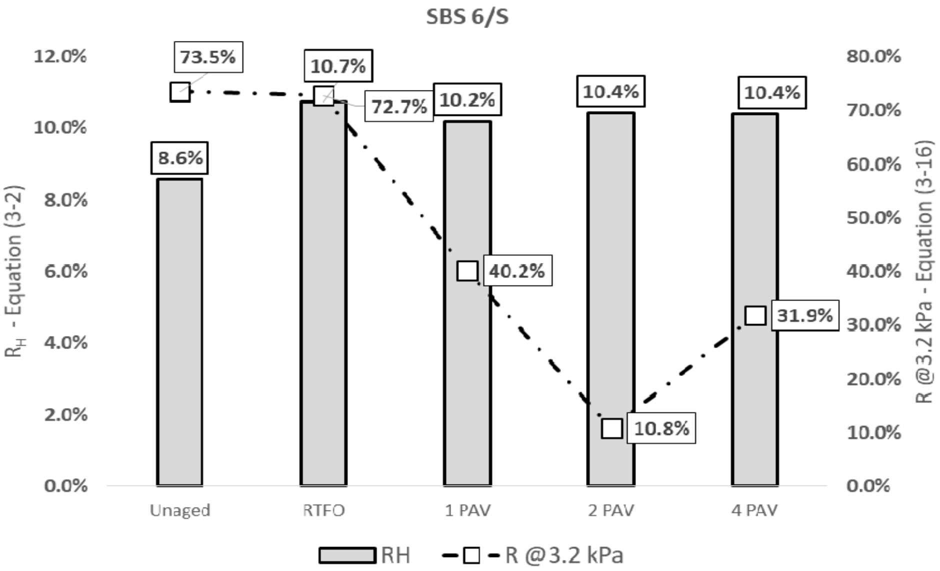


Figure 5-54 - SBS 6/S bitumen MSCR test results overlapped with R_H values at different LSA R@3.2kPa (%).

An increase of 2.1% in the R_H value is accompanied by a reduction of -0.7% in the value of R between the unaged and the RTFO-aged conditions.

On the other hand, the oxidative process in the PAV degrades the polymer network producing a decrease in percent recovery between the RTFO and two cycles of PAV (Figure 5-49 and Figure 5-54). The growth in percent recovery after four cycles of PAV depends on the same mechanism detailed for the SBS 4/S bitumen.

After the RTFO-ageing, the GPC does not provide any relevant information with the percentage of heavy and light fractions remaining almost constant throughout ageing. However, as discussed for the J_{nr} value (§5.2.1.1 - SBS 6/S bitumen), the rheological response shows a significant variation. Therefore, the same considerations on the importance of other polymer properties on their mechanical response, aside from the mass, are applicable in this case.

SBS 4 and SBS 6 bitumens

Results from the average percent recovery of the SBS 4 and SBS 6 modified bitumens confirm that the use of sulphur as a cross-linker affects the oxidative resistance of the polymer network measured in terms of loss in percent recovery (R - Figure 5-49). The majority of the degradation of the polymer network occurs in the RTFO with the values of R dropping below 10% at both concentrations (Figure 5-49). The trends of R with the PAV exposure do not deviate from the trends of the unmodified bitumen. The analysis of the GPC data with the average percent recovery highlights the importance of the effect polymer reticulation (and the use of a cross-linker) on the resistance of the polymer network to the RTFO and the PAV ageing (Figure 4-64, Figure 4-65) again.

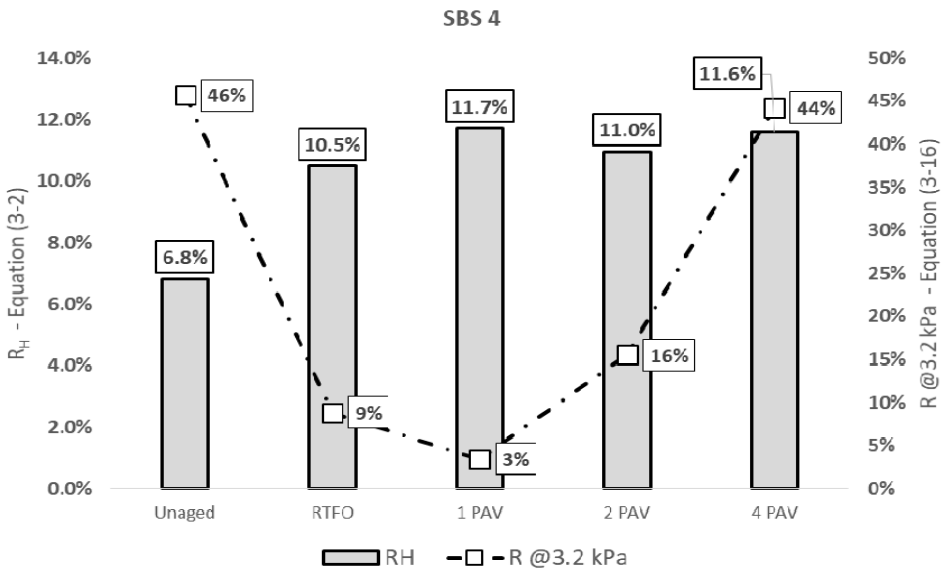


Figure 5-55 - SBS 4 bitumen MSCR test results overlapped with R_H values at different LSA

R@3.2kPa (%).

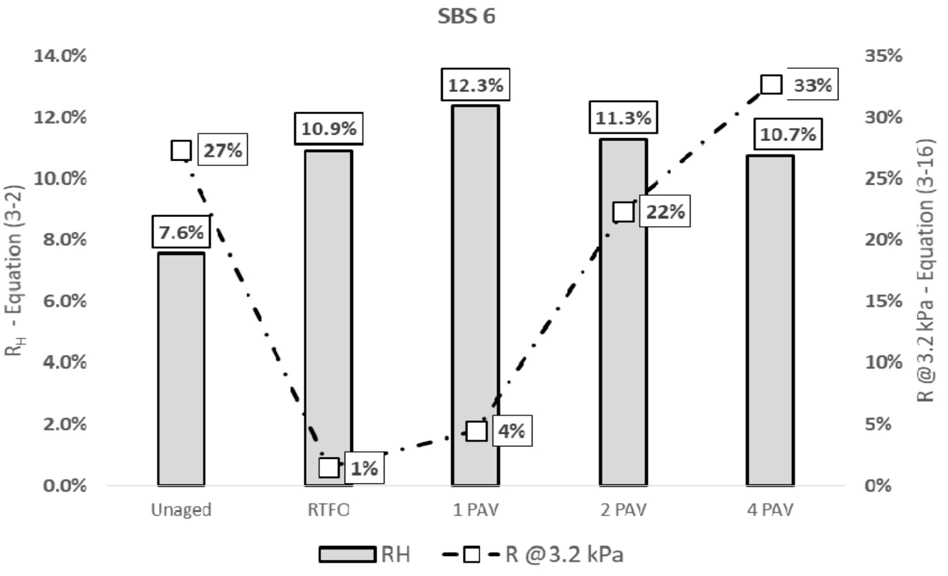


Figure 5-56 - SBS 6 bitumen MSCR test results overlapped with R_H values at different LSA

R@3.2kPa (%).

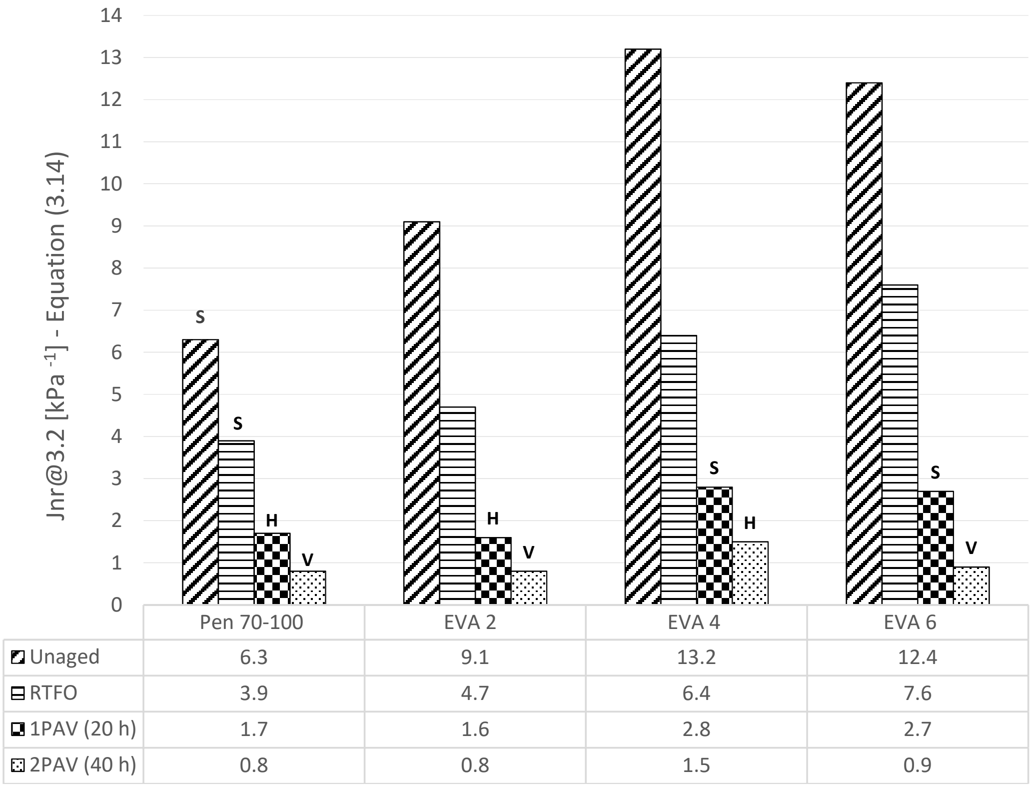
The rheological response indicates that after the RTFO, the polymer phase is degraded and does not provide a relevant effect on the hardening of the PMB. In the case of low reticulation, the presence of the fragments of the polymer chains at the different levels of ageing (R_H values in Figure 5-55, Figure 5-56) is not capable of controlling the rheological response with ageing for the same polymer concentration.

5.2.2 MSCR results of EVA modified bitumens

The MSCR test was conducted on the EVA modified bitumens following the same approach adopted for the SBS modified bitumens. The scope was to identify appropriate rheological indicators of the effects of artificial ageing on their rheological response. However, the EVA is a plastomer, and unlike what is assumed for the SBS, it is not expected to improve the elasticity of the bitumen. Therefore, in this case, the average percent recovery (R – Equation (3-15)), may not be indicative of the integrity of the polymer network. Having this in mind, the MSCR results of the EVA modified bitumens are discussed as follows.

5.2.2.1 Analysis of J_{nr}@3.2 kPa values

The values of the J_{nr} at the stress level of 3.2 kPa are given in Figure 5-57, and discussed as follows.



	Pen 70-100	EVA 2	EVA 4	EVA 6
▨ Unaged	6.3	9.1	13.2	12.4
▤ RTFO	3.9	4.7	6.4	7.6
▦ 1PAV (20 h)	1.7	1.6	2.8	2.7
⛶ 2PAV (40 h)	0.8	0.8	1.5	0.9

Figure 5-57 - J_{nr} @ 3.2 kPa (kPa^{-1}) (AASHTO M 332 traffic Designation: S – Standard ($J_{nr\ max}$ = 4.5 kPa^{-1}); H – Heavy ($J_{nr\ max}$ = 2 kPa^{-1}); V – Very Heavy ($J_{nr\ max}$ = 1 kPa^{-1}); E – Extreme ($J_{nr\ max}$ = 0.5 kPa^{-1})).

The Pen bitumen has been included for reference purpose.

In this case, the variation of the J_{nr} values at the different levels of ageing does not seem to be affected by the polymer or polymer concentration with the J_{nr} values decreasing with ageing (as sees as in the Pen bitumen). Furthermore, the values of the Jnr at the unaged and RTFO aged conditions increase with the polymer content. This aspect may depend on the higher MSCR test temperature adopted in the case of 4% and 6% EVA (Table 5-2). The variation of the J_{nr} values with ageing at all the EVA concentrations allows assuming that the response in the MSCR test is controlled by the bitumen phase that hardens in the PAV. However, the morphologies of EVA remain unvaried from the unaged conditions through to the different levels of ageing (Figure 4-6). This aspect highlights that the polymer dispersion is not affected by the thermo-oxidative processes occurring in the RTFO and the PAV. Such a reduced degradation indicates a low oxidative susceptibility of the polymer. Nevertheless, although the polymer does not deteriorate, it does not seem to provide any remarkable contribution to mitigating the stiffening effect of ageing on the bituminous phase measured as per the J_{nr} values. This aspect may not be surprising considering two aspects.

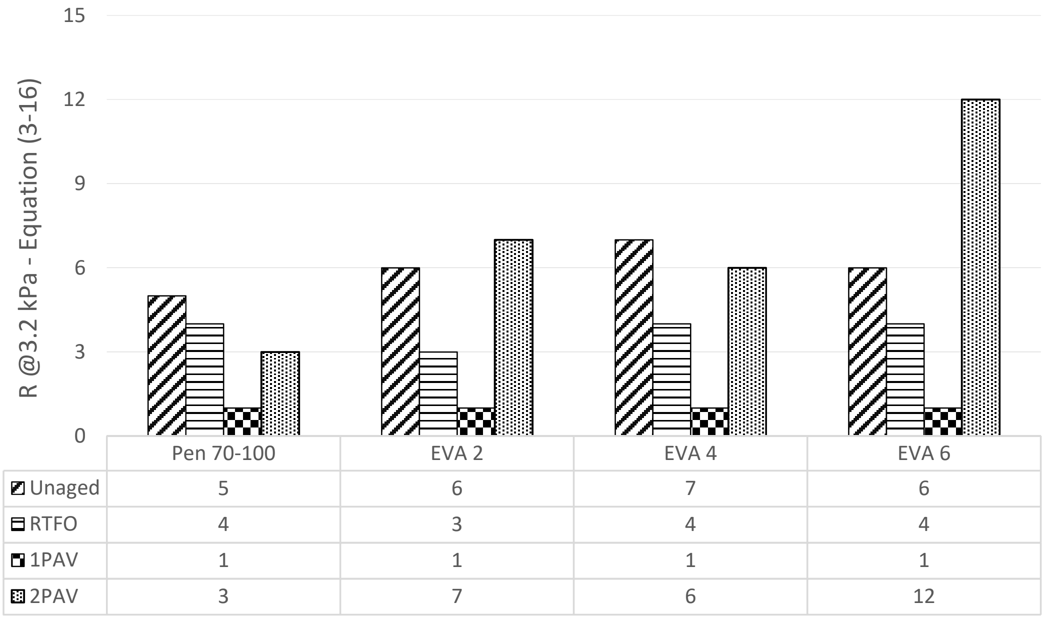
The first depends on the low bitumen-polymer interactions evidenced by fluorescence microscopy (Figure 4-6). That is, the morphology of the polymer phase consists of small dispersed spherical droplets that are indicative of low compatibility.

The second depends on the melting temperature of the EVA polymer used in this work that is of 74°C. Therefore, at the MSCR test temperature (Table 5-2) the consistency of the plastomer is low enough such that although it is not deteriorated, it does not affect the rheological response.

The combinations of these two aspects do allow using the results of the MSCR test to draw any additional (and maybe relevant) consideration on the effects of EVA on the oxidative hardening resistance of PMBs.

5.2.2.2 Analysis of R@3.2kPa

The results of the R at 3.2 kPa are given in Figure 5-58 and are discussed as follows.



	Pen 70-100	EVA 2	EVA 4	EVA 6
▨ Unaged	5	6	7	6
☰ RTFO	4	3	4	4
▚ 1PAV	1	1	1	1
▩ 2PAV	3	7	6	12

Figure 5-58 - R @ 3.2 kPa of Pen, and EVA modified bitumens Equation (3-15).

As expected, the EVA polymer does not produce any relevant increase in the bitumen elasticity irrespective of the polymer concentration. However, at very high oxidative levels (2 PAV aged bitumen), the percent recovery seems to increase. Such a gain in recovery, although limited, could be attributed to the PAV-oxidative hardening of the bitumen phase. As seen as for the J_{nr} values, it can be concluded through the measure of the percent recovery that, although its morphology remains consistent throughout ageing, the EVA polymer does not alter the ageing behaviour of the base bitumen.

6 Cumulative damage resistance

This chapter includes the results of the LAS test and the time sweep test.

6.1 Results of LAS test

The LAS test was used to evaluate the effects of laboratory-simulated ageing on the cumulative damage resistance of the bitumens given in Table 3-15. The data were analysed according to the VECD theory described in §3.3.8.2.

The results of the LAS test are given in terms of fatigue law of the bitumens expressed by Equation (3-17). The terms of the equation are explained in Table 6-1.

$$N_f = A_{35}(\gamma_{max})^B \tag{3-17}$$

Table 6-1 – Significance of the parameters included in the fatigue laws of bitumen calculated as per the VECD theory

$A_{35} = \frac{f(D_f)^k}{k(\pi C_1 C_2)^\alpha}$	The coefficient A_{35} represents the value of the Wholer curve at a strain level of 1% (Figure 2-55). It depends on the material integrity versus the damage curve (e.g., Figure 6-6), and the criterion selected as a failure (37). In this case, the latter has been selected as the loss of 35% of the initial value of viscous modulus (appendices 35).
$B = -2\alpha$	It is the slope of the Wholer curve (Figure 2-55), and it is a function of the parameter α, which depends on the time-temperature dependency of the material (Figure 3-32). A decrease in the time-temperature dependency of the material corresponds to a decrease in B.
γ_{max}	Is the maximum strain level expected in the bitumen phase for a given pavement structure. Two strain levels are considered: 2.5% for strong (or thick) pavements and 5.0% for weak (or thin) pavements.

$\alpha = \frac{1}{m}$	Is the inverse of the slope of the isotherm (of the storage modulus) obtained in the frequency sweep test (Figure 3-32). It is the exponent that determines the energy release rate (Equation (2-39)).
$D_f = \left(\frac{0.35}{C_1}\right)^{1/C_2}$	That is the damage intensity corresponding to a reduction of 35% of the initial complex shear viscous modulus ($\lvert G^* \rvert \sin \delta_{residual} = 0.65 \cdot \lvert G^* \rvert \sin \delta_{initial}$).
f	Is the loading frequency during the amplitude sweep portion of the test (10 Hz);
C_1, C_2	See Equation (3-20) and (3-21)
$k = 1 + (1 - C_2)$	Is a Test parameter.

As discussed in §3.3.8.3, the LAS test temperature was selected by selecting the highest temperature between the average of the intermediate PG temperatures of the bitumens, and the average temperature in an asphalt base course calculated by the Bell2 model in the Italian moderate climate zone. The first temperature resulted in being 28°C, while the second 31°C. Therefore the LAS test was conducted at 31°C for all the bitumens.

6.1.1 Pen and Pen/S bitumens

The fatigue laws of the Pen bitumen at the different levels of ageing are given in Figure 6-1.

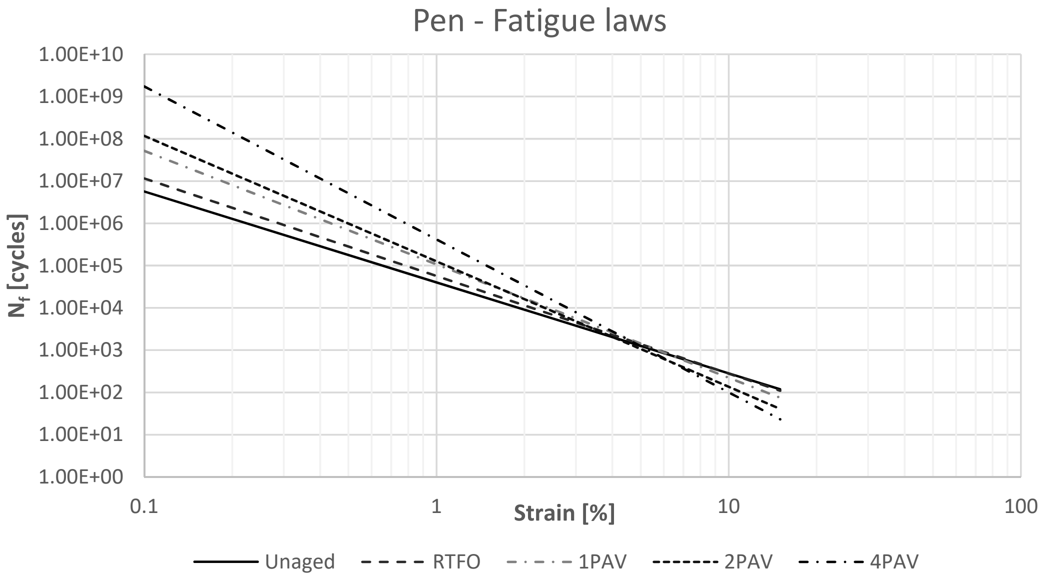


Figure 6-1 – Fatigue laws Pen bitumen at different levels of LSA.

Laboratory-simulated ageing (LSA) increases or reduces the N_f of the bitumens as a function of the strain considered.

In the strain interval below (~) 1%, the number of cycles to failure increases with LSA. The more the strain decreases, the more N_f increases. In this range, the curve at the unaged condition shows the lowest number of cycles to failure that increases as LSA increases (i.e., RTFO, 1PAV, 2PAV, 4PAV).

Between 1% and 10%, the curves converge and reverse with the effect of ageing becoming detrimental. In other words, the curve of each ageing level (i.e., RTFO, 1PAV, 2PAV, 4PAV) intersects the curve of the unaged conditions at a defined strain value. Below such value, the curve of the aged bitumen is above the unaged one. Above such strain, the vice versa occurs. The strain has been qualitatively defined as “pivot strain”, and its value is a function of ageing. The pivot strain related to the ageing levels of the Pen bitumen are given in Figure 6-2

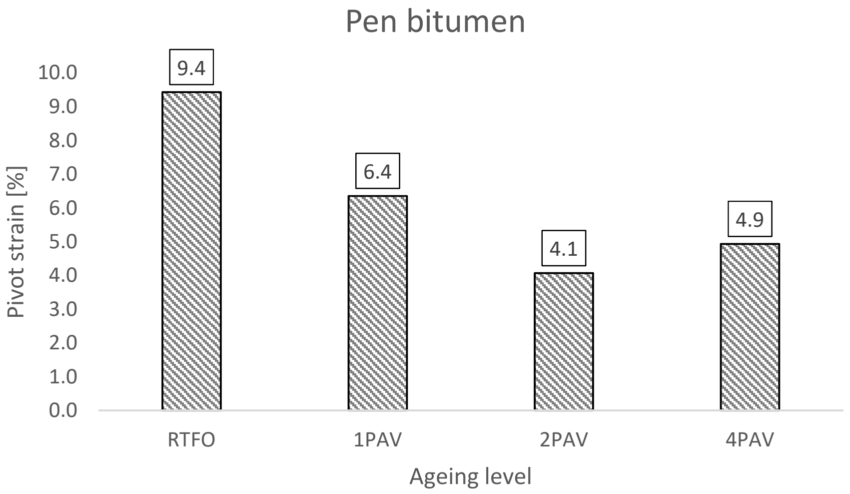
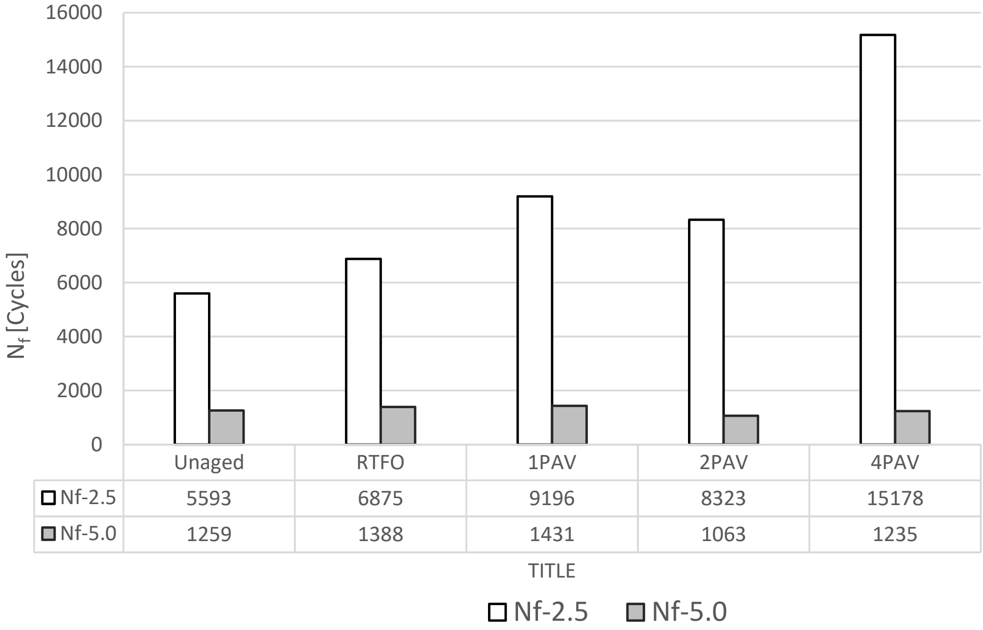


Figure 6-2 – Pivot strains Pen bitumen.

The pivot strain reduces with the increase of LSA.

The number of cycles to failure have been calculated by Equation (3-17), at two strain levels representative of strong (or thick) (2.5%) and weak (or thin) pavements (5.0%). Results are given in Figure 6-3.



	Unaged	RTFO	1PAV	2PAV	4PAV
☐ Nf-2.5	5593	6875	9196	8323	15178
▨ Nf-5.0	1259	1388	1431	1063	1235

Figure 6-3 – Number of cycles to failure (N_f) calculated by Equation (3-17) of the Pen bitumen different levels of LSA at two strain levels: 2.5% (strong pavements) and 5% (weak pavements).

At a strain level of 2.5%, the number of cycles to failure increases with LSA. There seems to be a slight reduction after two cycles of PAV, but this might depend on the accuracy of the experiment. On the other hand, at 5.0%, the high level of strain reduces the effects of LSA with the N_f values distributed in a narrow range.

Therefore, as an opening remark, it can be mentioned that the evaluation of the effects of ageing on the resistance to damage accumulation of bitumen needs to account for the strain level considered. Additionally, the evaluation of the cumulative damage resistance (or fatigue resistance) at a single strain level (i.e., 1%), may not be representative of the actual performance of the bitumen. However, a more detailed discussion on the results from the application of the VECD theory needs to be provided.

As shown in Figure 2-55 the parameter A (in this case A_{35}) represents the intercept of the fatigue law with the y-axis; while the parameter B is the slope of the Wholer curve in the log-log chart. The significance of these parameters is detailed in Table 6-1.

The parameter A_{35} is a function of the variation of the material integrity versus the damage intensity. On the other hand, B is the slope of the fatigue law in the log(Nf)-log(γ) chart, and it is a function of the time-temperature dependency of the material calculated at undamaged conditions. Based on these definitions, the values of A_{35} and B at the different levels of ageing of the Pen bitumen are given respectively in Figure 6-4 and Figure 6-5.

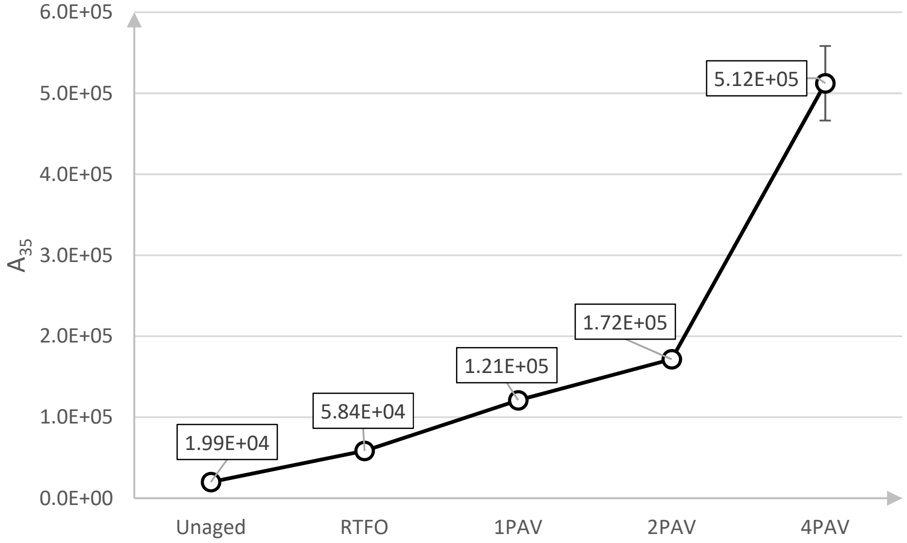


Figure 6-4 – Parameter A_{35} of the Pen bitumen at different levels of LSA.

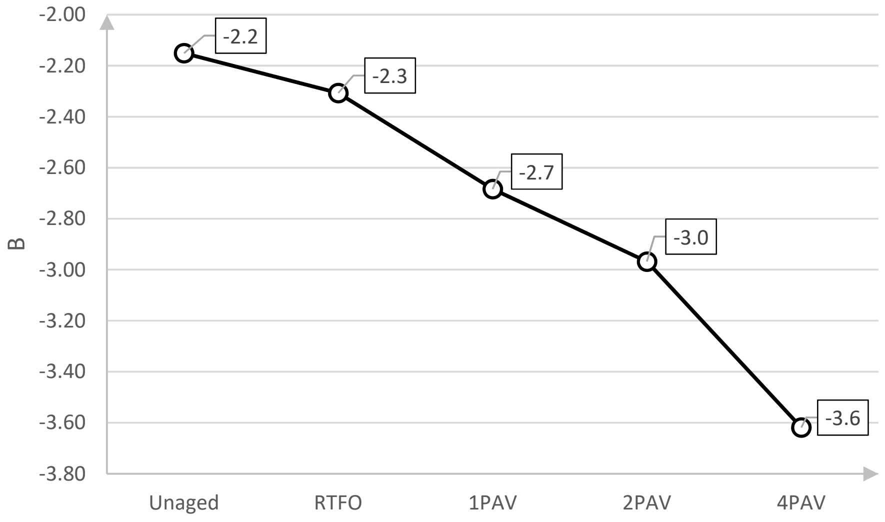


Figure 6-5 - Effect of LSA on the B parameter of Pen bitumen.

The fatigue parameters (A_{35}) and (B) show opposite trends with ageing. A_{35} increases with ageing while B decreases. This behaviour supports the trend of fatigue laws in Figure 6-1. The fatigue laws of the aged bitumens have higher intercepts with the y-axis. The higher the ageing level, the higher is the intercept value. On the other hand, the higher slope of the curve indicates that the material is more susceptible to be damaged with the increase in strain. A further step into the measured bitumen properties needs to be done.

The parameter B comes from data measured in the LVE region where no damage occurs. A reduction in the parameter B depends on the fact that the time-temperature of the material decreases with ageing according to Equation (6-1).

$$B = -2\alpha = -2 \cdot \frac{1}{m} \tag{6-1}$$

The significance of the terms has been clarified in Table 6-1. A reduction in the time-temperature susceptibility of the material indicates a reduction in the m value. As shown by Equation (6-1), B decreases with a decrease in m.

On the other hand, the parameter A_{35} is calculated in the damage zone where the material loses its integrity. The fatigue law parameter is a function of the variation in the material integrity with the damage intensity. The more the material is capable of maintaining its integrity with damage, the higher is the value of A_{35} (§3.3.8.2).

In the analysis of the LAS data, material integrity is a function of the viscous modulus. The parameter A is calculated from the curve that provides the variation of the viscous modulus with the damage intensity (Equations (3-20) & (3-21)). Such a curve is defined as a VECD damage curve. Figure 6-6 shows the VECD damage curves of the Pen bitumen at different levels of LSA.

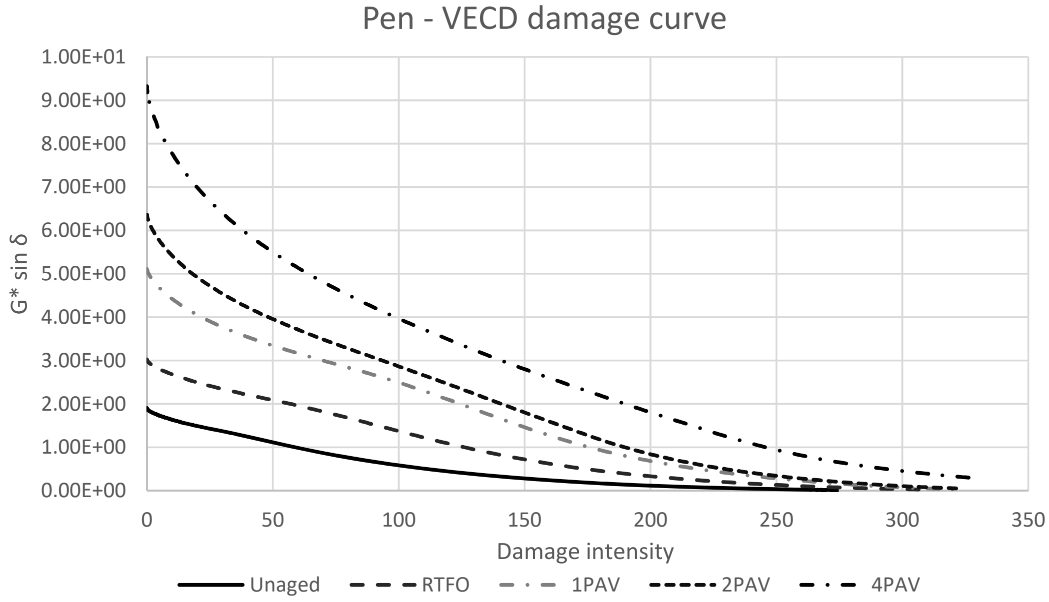


Figure 6-6 – VECD damage curves at different levels of LSA of Pen bitumen.

The curves show that the capacity of the material to maintain its integrity (G”) increases with ageing. In other words, the VECD damage curves shift upward with ageing showing higher values of G” at the same level of damage intensity. Furthermore, the undamaged viscous modulus (@D=0) increases with ageing.

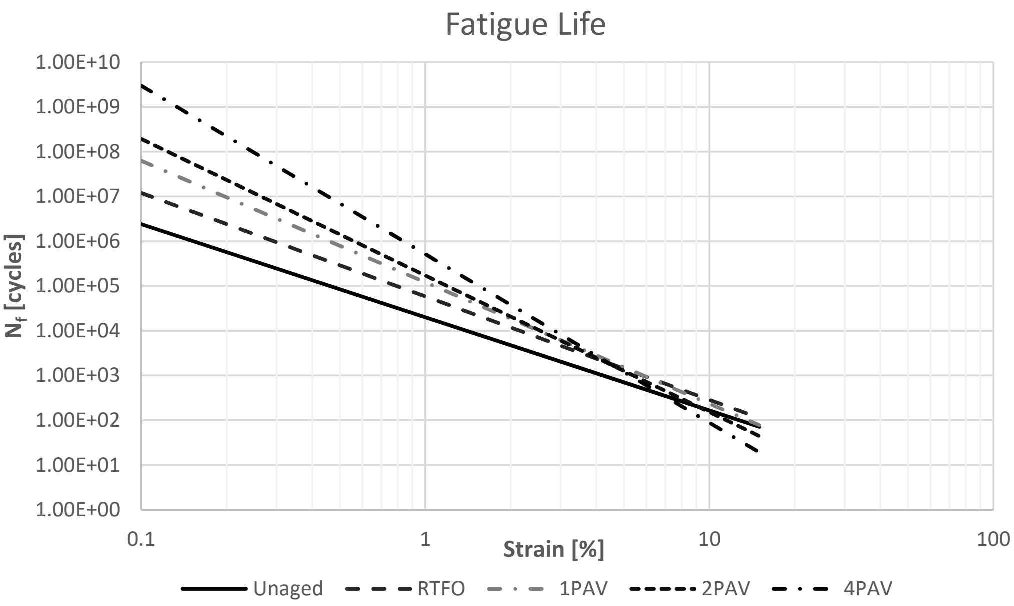
The advantage of using the VECD theory is that A_{35} and B can be determined from a single test set-up.

Therefore the parameters that define the fatigue law of the bitumens show opposite behaviours with ageing. On the one side, the decrease in the time-temperature susceptibility increases the slope of the fatigue law. On the other, the intercept with the y-axis increases since the material seems to be more capable of maintaining its integrity with damage. These two factors need to be combined by considering the strain level applied to determine the effective cumulative damage resistance. Their combination is defined as damage tolerance.

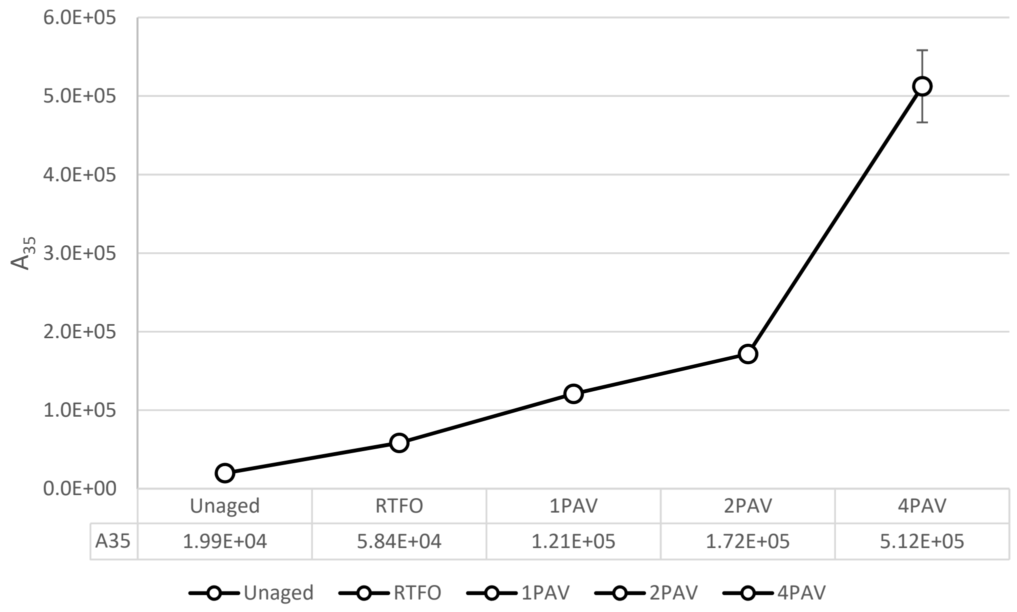
In the case of low strain levels, the capability of maintaining integrity (A_{35}) has a more considerable impact and the number of cycles to failure increase with ageing (Figure 6-1). At higher strain level, the opposite occurs, and ageing contributes to decreasing N_f. Similar results and consideration can be found in a work of Hintz and co-workers (37).

The threshold strain at which the effect of ageing swaps from positive to negative has been defined as pivot strain and, for each bitumen, it is a function of the ageing level (Figure 6-2).

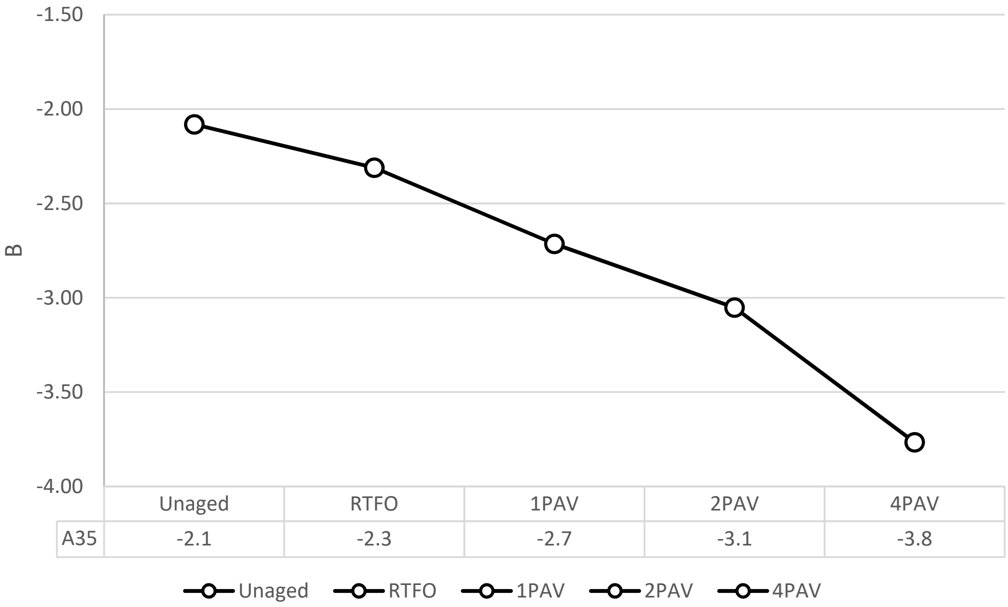
As discussed in the results of the MSCR test, the Pen/S bitumen was prepared to evaluate any confounding effects provided by the presence of sulphur. The same evaluation was done in the case of the LAS test. Results are given in Figure 6-7 (a, b, c, and d).



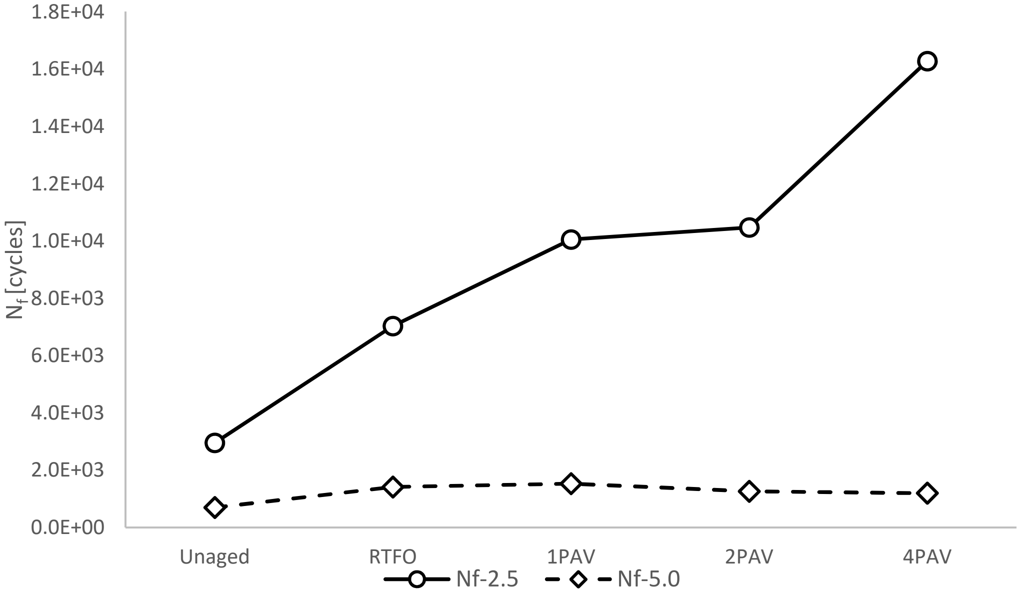
a) Fatigue life



b) Parameter A_{35}



c) Parameter B



d) N_f at 2.5% and 5.0% strain.

Figure 6-7 – LAS test results Pen/S bitumen at different levels of LSA (a – fatigue life; b – parameter A35; c – parameter B; number of cycles to failure at 2.5% and 5.0% strain).

Results show that sulphur does not produce a significant deviation from the Pen bitumen.

6.1.2 Polymer modified bitumens

The mechanism that includes the combination of ageing and VECD damage characterisation has been described in detail for the Pen bitumen. It has been shown that that ageing produces opposite effects on the parameter of the fatigue law given by Equation (3-17). The parameter A_{35} increases with ageing, while the parameter B decreases. The first is beneficial for the cumulative damage resistance, while the second is detrimental. To determine the effective cumulative damage resistance (given by N_f), the two mechanisms need to be combined considering the strain level.

Although this mechanism has been described for the Pen bitumen, it applies to the other bitumens included in this experiment. Therefore, to avoid repetitions in the content, in the case of the PMBs, the discussion of the results focuses on the effects of the polymer on the cumulative damage mechanism rather than on the mechanism itself.

The variations of A_{35} and B of the bitumens investigated with the LAS test are represented in Figure 6-8 and Figure 6-9.

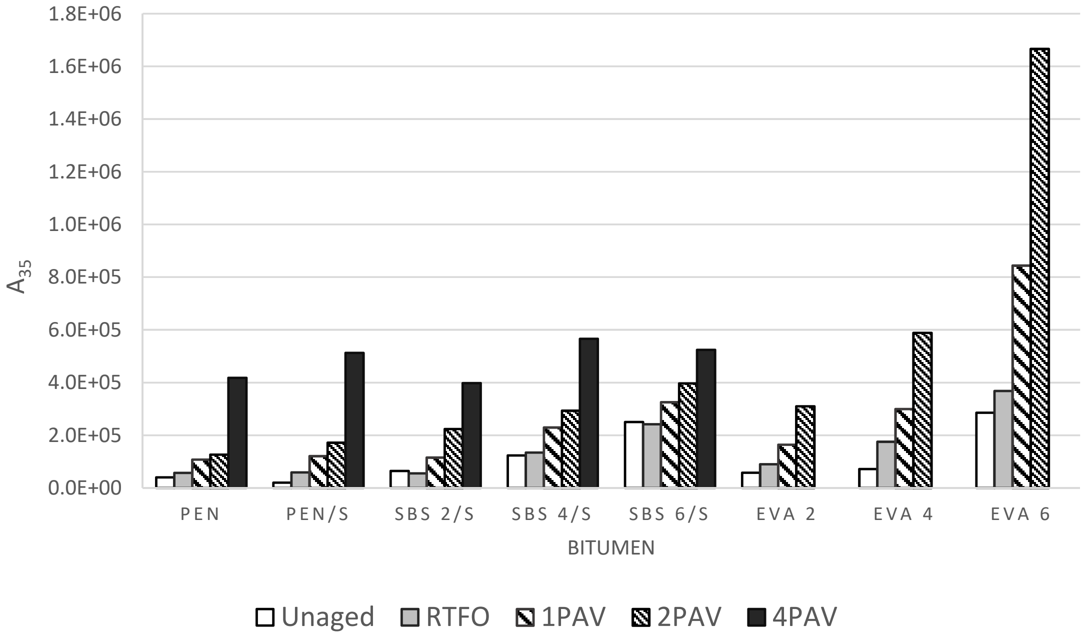


Figure 6-8 – Variation with LSA of A_{35} parameter (Table 6-1) of the bitumens used in this work.

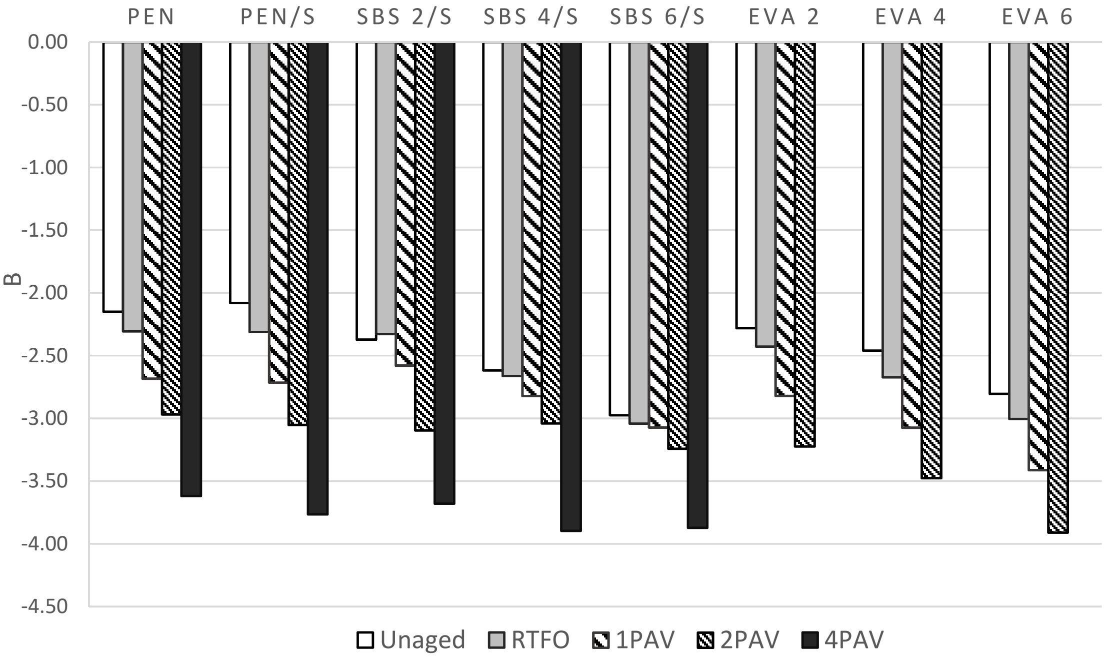


Figure 6-9 – Variation with LSA of B parameter (Table 6-1) of the bitumens used in this work.

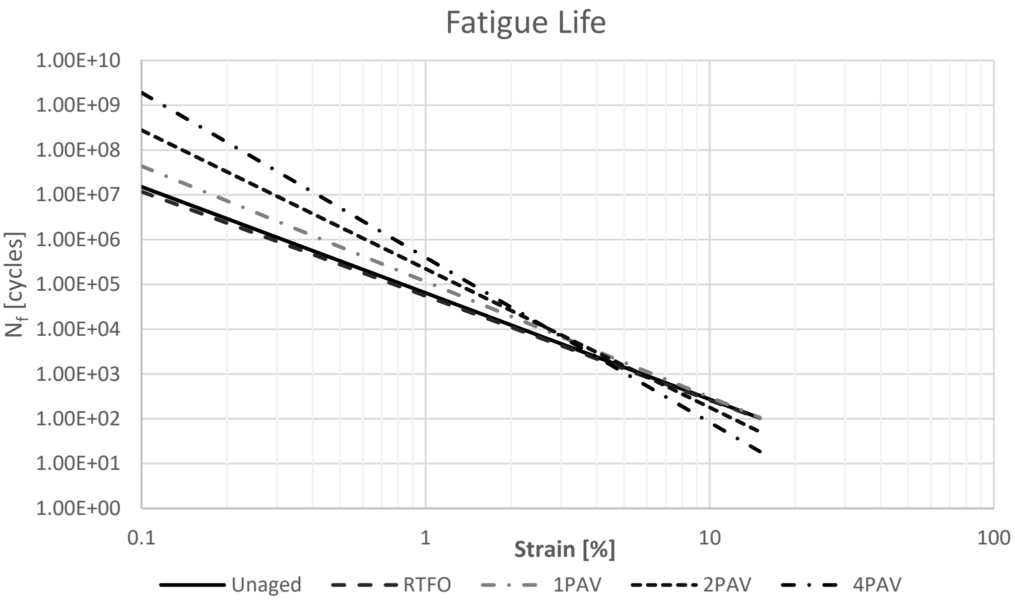
Results show that the parameter A_{35} increases with LSA while the parameter (B) decreases. Therefore, it seems that the polymer modifications here considered do not alter significantly the mechanism described for the Pen bitumen. This result does not mean that polymers do not provide any effects (EVA 6 is a clear example). It could indicate that LSA produces the same physical effects on the cumulative damage resistance of different PMBs, but the polymer modification affects the magnitude of these effects.

A description of the results of the remaining bitumens is given in the following subsections.

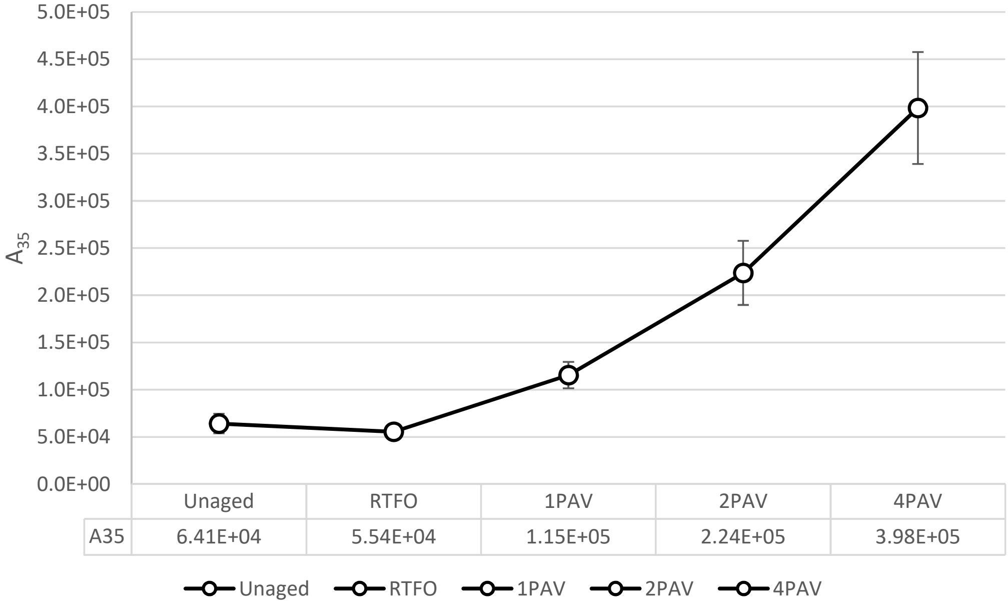
6.1.2.1 Cross-linked SBS modified bitumens

SBS 2/S bitumen

Results of the LAS test of the SBS 2/S bitumen are given in Figure 6-10.

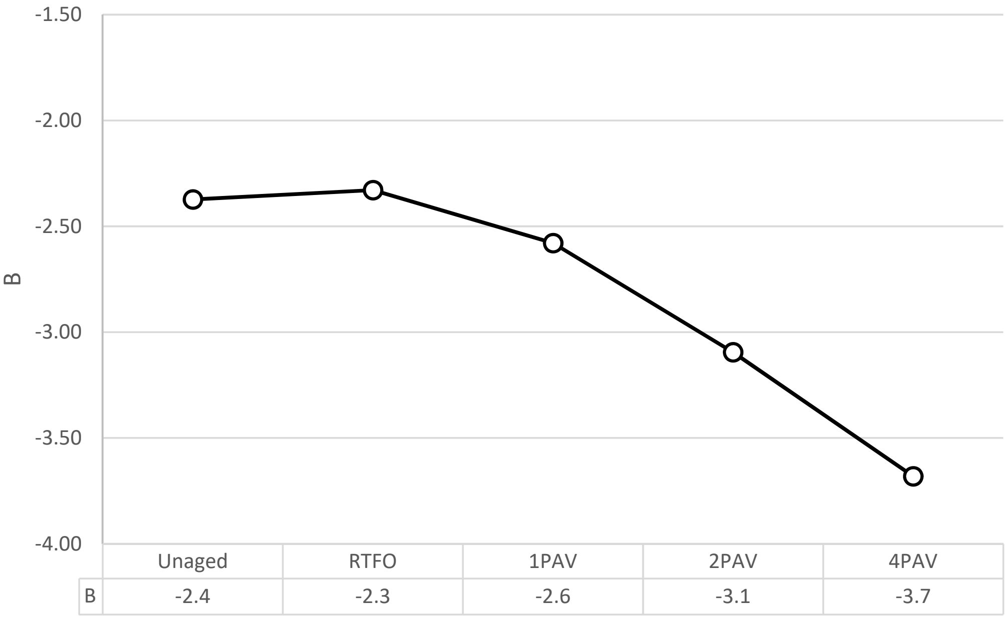


a) Fatigue life

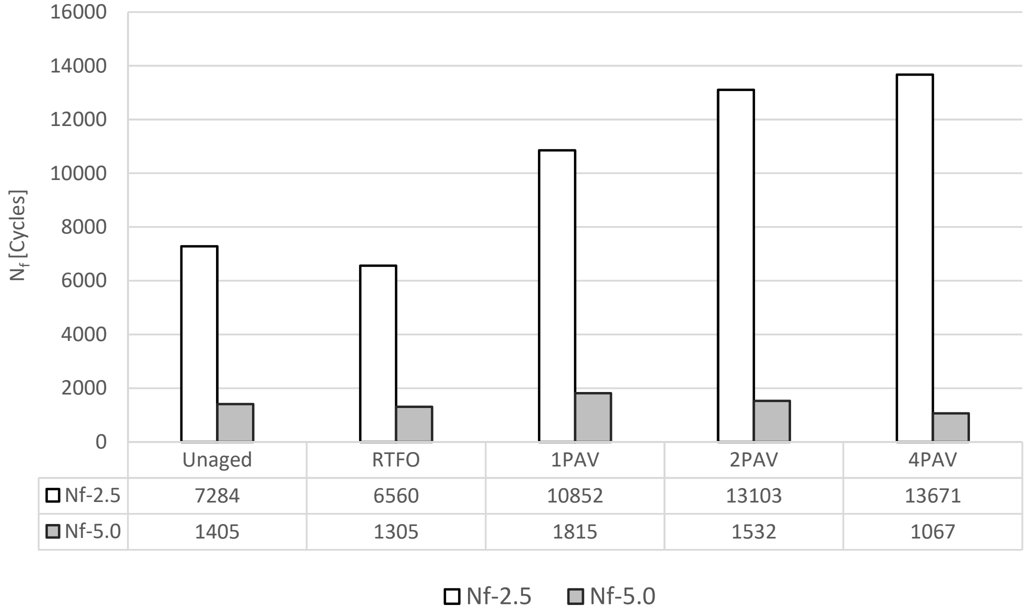


	Unaged	RTFO	1PAV	2PAV	4PAV
A35	6.41E+04	5.54E+04	1.15E+05	2.24E+05	3.98E+05

b) Parameter A_{35}



c) Parameter B



d) N_f at 2.5% and 5.0%.

Figure 6-10 - LAS test results SBS 2/S bitumen at different levels of LSA (a – fatigue life; b – parameter A35; c – parameter B; number of cycles to failure at 2.5% and 5.0% strain).

Results show that a relatively low concentration of SBS does not produce relevant differences from that observed in the Pen bitumen.

SBS 4/S bitumen

The fatigue law of the SBS 4/S bitumen at different levels of LSA is given in Figure 6-11.

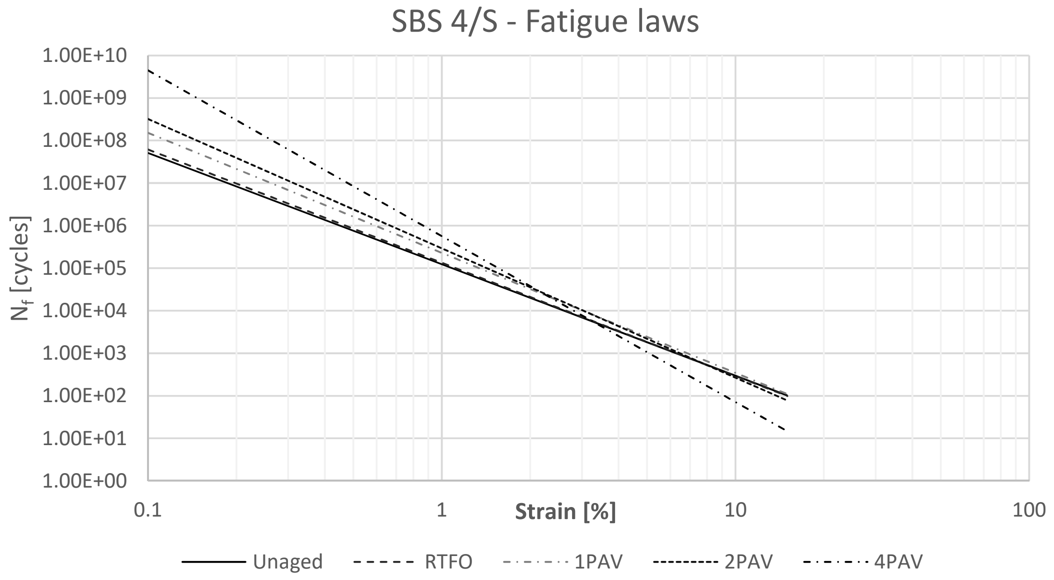


Figure 6-11 - Fatigue law SBS 4/S bitumen at different levels of LSA.

At low strain levels (below 1%) laboratory-simulated ageing produces similar effects to those observed in the Pen bitumen. At higher strain levels (above 4%), only the curve related to 4PAV-ageing deviates from the one related to the unaged condition; while the other curves tend to superimpose each other. In other words, it seems that LSA produces visible effects on N_f only after 4 cycles of PAV. The parameters of the fatigue laws in Figure 6-11 are given in Figure 6-12 and Figure 6-13.

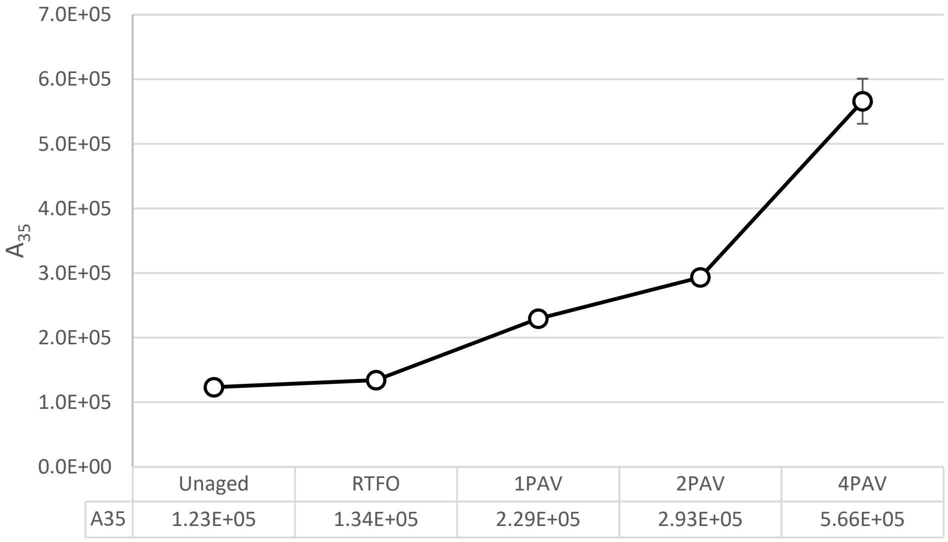


Figure 6-12 - Parameter A_{35} of the SBS 4/S bitumen at different levels of LSA.

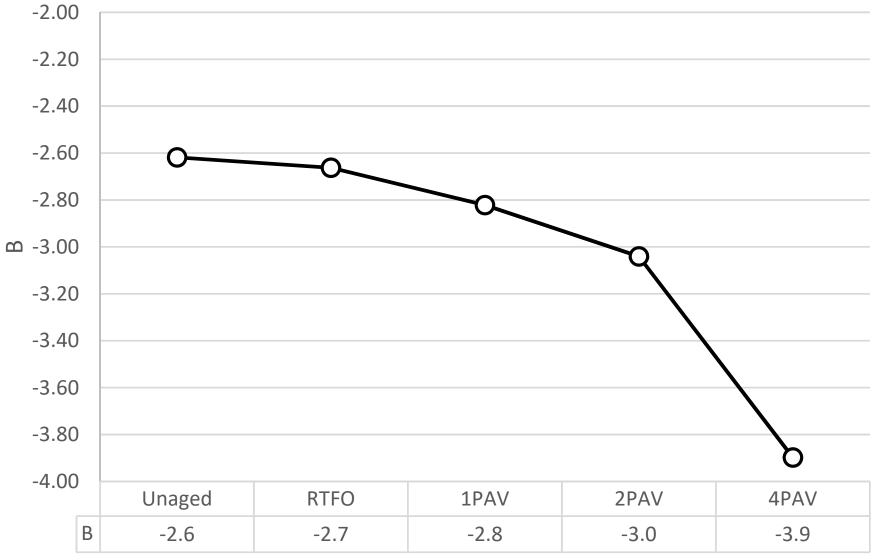


Figure 6-13 - Parameter B of the SBS 4/S bitumen at different levels of LSA.

The parameter A_{35} increases with ageing with a marked increase between 2PAV and 4PAV. (Figure 6-12). On the other hand, the parameter B shows a more visible reduction after 4 cycles of PAV. There is a reason to believe that although the polymer network undergoes degradation in the PAV, its presence is capable of mitigating the effects of ageing on the damage tolerance of the bitumens. The combination of GPC and MSCR results has shown that within two cycles of PAV the polymer is capable of mitigating the hardening of the bitumen.

then, after four cycles its effect diminishes visibly. The trend of the parameter B shows somehow something similar displaying a more marked variation (reduction) after four cycles of PAV. Therefore, it seems that up to two cycles of PAV the SBS is capable of mitigating the effects of hardening on the damage resistance.

Within the 4 cycles of PAV, the fatigue laws of the aged bitumens show a higher number of cycles than the unaged one within the strain interval approximately below 4% (Figure 6-11). At higher strain level, it is difficult to define a clear effect of ageing up to 2PAV with the curves that seem to overlap. At 4PAV, the effect of ageing is evident with the curve showing a lower number of cycles under the same strain. It is possible that after such a PAV exposure, the polymer has lost integrity and its contribution to the damage tolerance might be reduced within the strain interval above 4%.

This effect has been observed by combining the GPC and MSCR results (§5.2.1). In the MSCR, the polymer network was capable of mitigating the effects of the PAV-oxidative hardening of the bitumen phase within 2 cycles of PAV. Then, at 4PAV, its effect reduces. The presence of the polymer was identified through the GPC as well (Figure 5-45).

Although the LAS and the MSCR refer to different damaging mechanisms and are conducted at different temperatures, a similar trend with LSA is found in the rheological response in the two tests. Therefore, it seems that there is a clear relation between the residual structure of the polymer network and the PAV exposure. Such relation is visible through the results of the LAS (and MSCR) where it is shown that the SBS network tends to compensate for the hardening of the bitumen phase at both high and intermediate temperatures.

SBS 6/S bitumen

The fatigue law of the SBS 6/S bitumen at different levels of LSA is given in Figure 6-14.

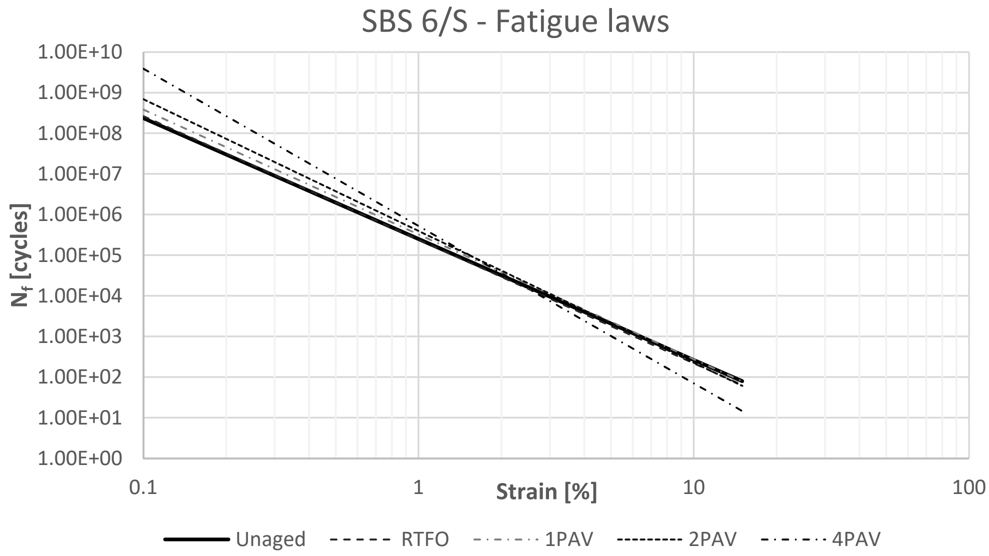


Figure 6-14 - Fatigue law SBS 6/S bitumen at different levels of LSA.

SBS 6/S bitumen shows similar results to as the SBS 4/S. Within the low strain interval (below ~1%) the curves shift towards higher values of N_f with laboratory-ageing. At strain values higher than 3%, it appears that LSA produces visible changes after 4 cycles of PAV.

The parameters of the curves are given in Figure 6-15 and Figure 6-16.

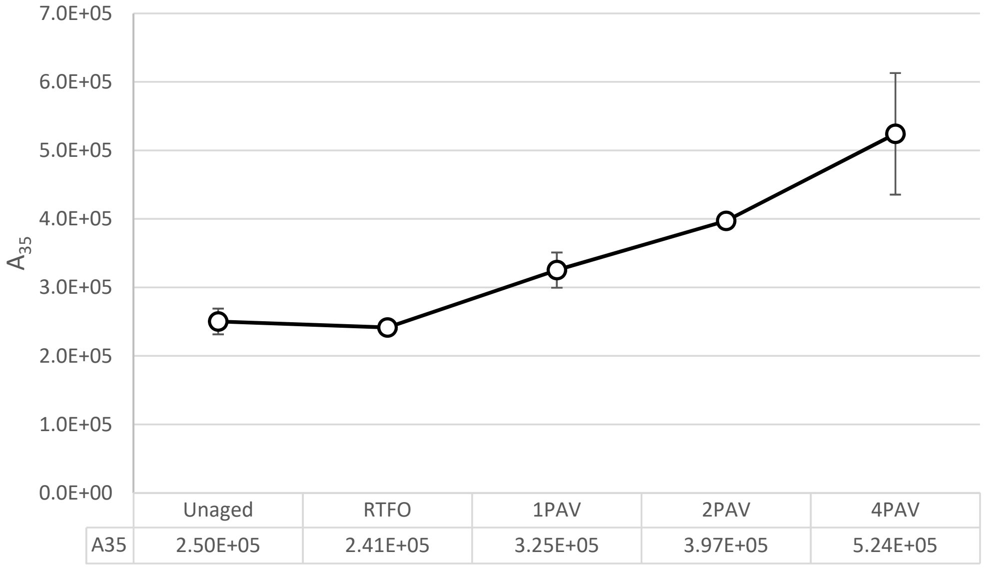


Figure 6-15 - Parameter A_{35} of the SBS 4/S bitumen at different levels of LSA.

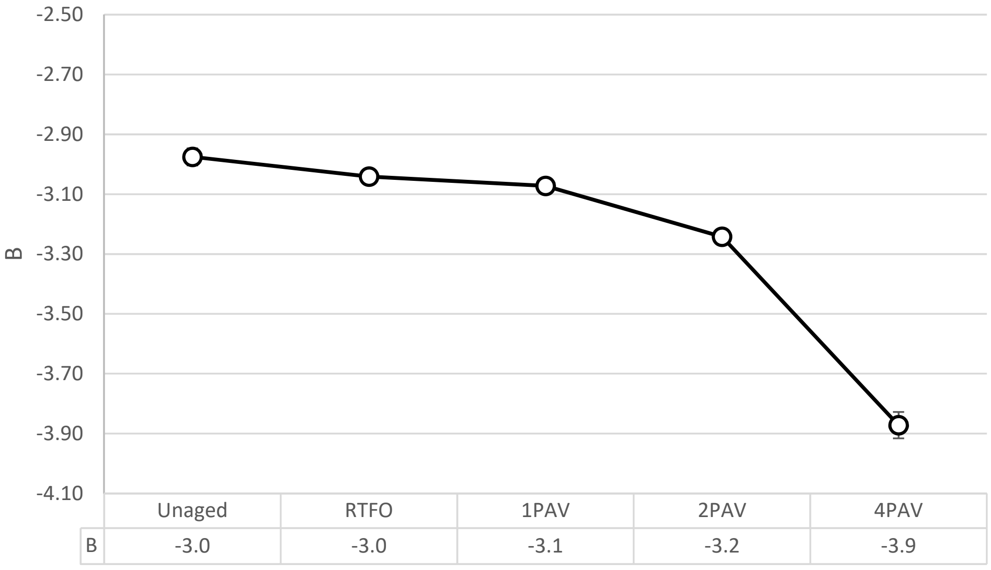


Figure 6-16 - Parameter B of the SBS 6/S bitumen at different levels of LSA.

The variation in the parameters of the fatigue law is more evident after 4 cycles of PAV than at lower PAV exposures. In particular, the magnitude in the changes of B is minimal between the unaged to the 2PAV-aged conditions (Figure 6-16). This aspect might evidence that the changes in the microstructure of this bitumen appear so limited to maintain almost unvaried its time-temperature susceptibility (§3.3.8.3).

The limited changes in the microstructure of this bitumen compared to the other bitumens have been observed in the GPC (§4.3.1.2).

The analysis of the bitumens with 4 and 6% SBS highlights that as long as the polymer network is capable of maintaining a sort of effective structure (or network), the damage propagation seems to be limited. If in the LAS cohesive cracks is the mechanism devoted to damage the bitumen, the presence of the polymer network increases the resistance to crack initiation and propagation. Then, once the bitumens are aged, the effect of the polymer network diminishes as a function of concentration and dispersion with higher concentration providing a higher resistance.

6.1.2.2 Remarks on LAS test results of cross-linked SBS modified bitumens

To understand the effect of SBS concentration on the cumulative damage resistance the numbers of cycles to failure (Equation (3-17)) of the SBS 2/S, SBS 4/S, and SBS 6/S have been compared.

It is worth mentioning that the comparison among different bitumens has been conducted under the same test temperature. This condition does not allow to account for the effects of different stiffness. However, in the assessment of the fatigue life of bituminous materials, materials are tested upon the same temperature to highlight (in this case) the effects of ageing, polymer type, and polymer concentration.

The number of cycles to failure of bitumens have been calculated at strain levels of 2.5% and 5.0%. Results of 2.5% are given in Figure 6-17.

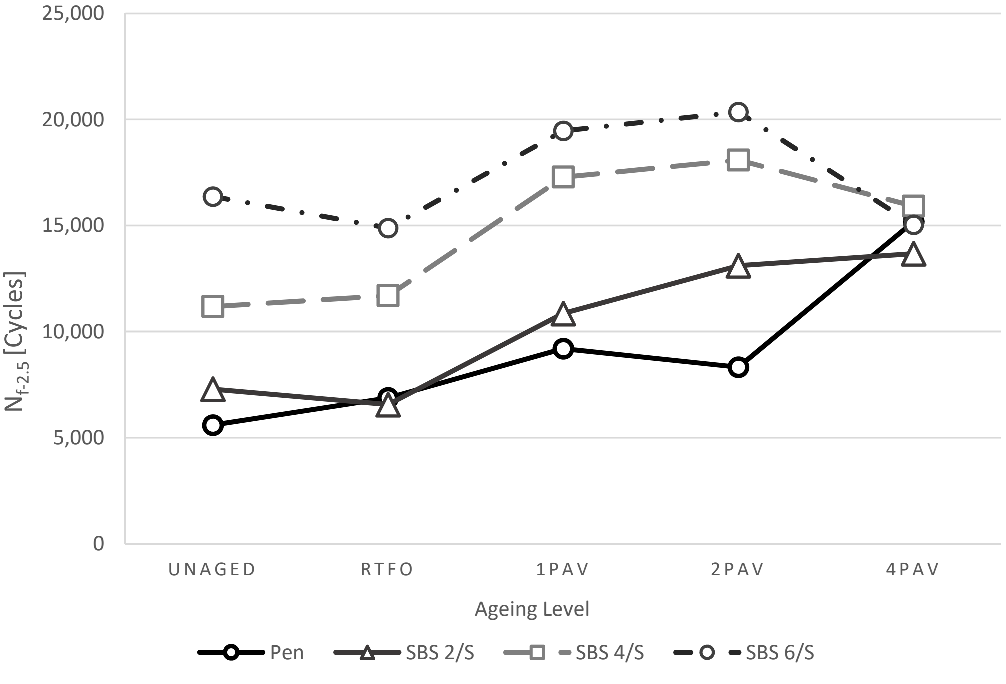


Figure 6-17 – Number of cycles to failure at strain 2.5% of Pen and cross-linked SBS modified bitumens at different levels of LSA.

At unaged conditions, the effect of the polymer is well visible with the number of cycles to failure that increases with the polymer content. Similar results appear between RTFO and 2PAV where, additionally, N_f increases with ageing (except for the Pen bitumen that shows a more limited variation between 1PAV and 2PAV). At 4PAV, the effect of the modification seems to vanish with the bitumens showing similar N_f.

Results of the strain level equal to 5% are given in Figure 6-18.

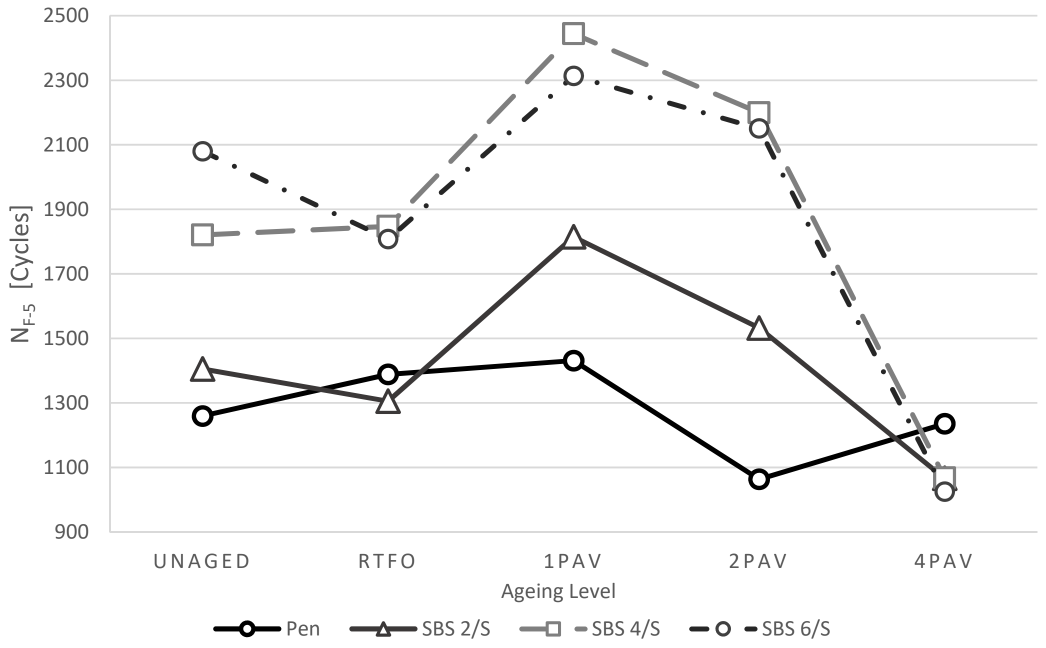


Figure 6-18 - Number of cycles to failure at strain 5% of Pen and cross-linked SBS modified bitumens at different levels of LSA.

The effects of polymer modification are visible in this strain level as well. The variation of N_f at the different levels of ageing depends again on the strain level considered. However, it is clear that increasing the level of strain, the effects of LSA on the cumulative damage resistance starts to be detrimental at lower PAV exposure. Comparing the curves at 2.5% (Figure 6-17) within those in Figure 6-18, it is shown that at the higher strain level the number of cycles to failure decreases between 1PAV and 2PAV; while at the lower strain level, the reduction occurs between 2PAV and 4PAV.

As observed at the strain level of 2.5%, the number of cycles to failure is similar in all the bitumens at 4PAV. This aspect requires some focus.

It appears that once the polymer network is completely damaged, it does not produce any effect of the response, which is assumed to be controlled by the PAV-oxidised bitumen-rich phase. This comment may appear obvious, but it is not like this.

The fact that after 4 cycles of PAV, the unmodified bitumen and the PMBs have the same fatigue life indicate that the bitumen on one side, and the bitumen-rich phase on the other, have undergone similar PAV-oxidative hardening irrespective of the presence and the concentration of the polymer. That is, once the polymer network is damaged the bitumen-rich phase controls the rheological response and the level of ageing it has achieved is similar to the one of the same base bitumen under the same ageing condition.

This aspect is not surprising considering the temperature at which the LAS test is conducted. In the section of the LVE analysis results (§5.1.2.3), it is often mentioned the differences between the temperature interval where the response is more controlled by the polymer-rich phase (higher temperature - approximately 52°C – 64°C), and vice-versa where the response is more controlled by the bitumen-rich phase (lower temperature – approximately 4°C to 28°C). In those sections, results show that in the range of temperatures where the bitumen-rich phase control more the response, the variation of its rheological response with ageing is similar to as one of the unmodified bitumens. This aspect is supported by other authors as Airey (24) and Cotte & Such (129). For this reason, it may be not surprising to observe that, at 31°C once the SBS is degraded, the bitumen-rich phase responds as if it has undergone ageing without the presence of the polymer.

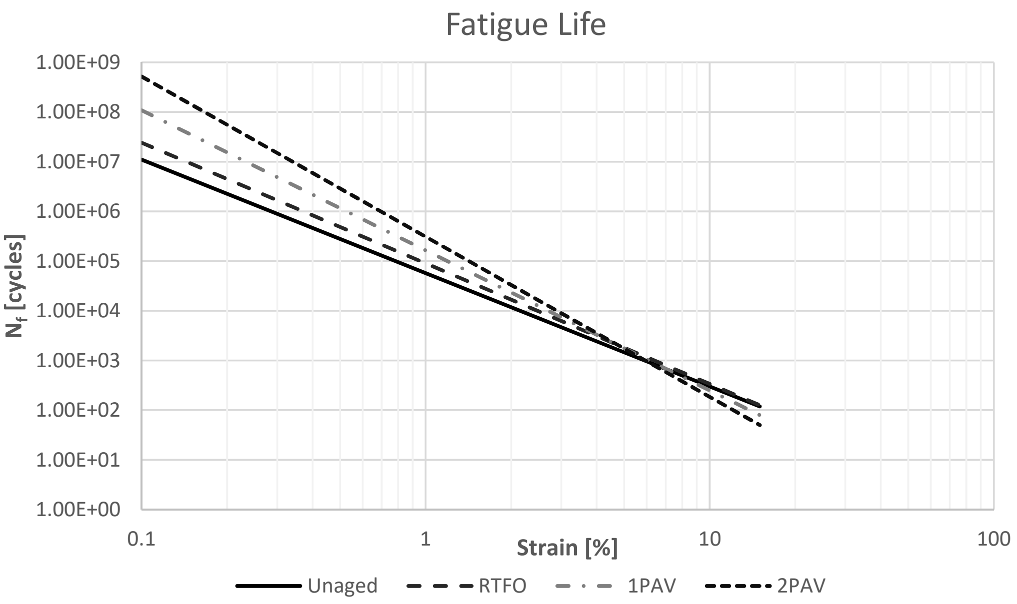
Although results go in this direction, this point of view is not fair regarding the polymer. It is true, that once the polymer has undergone complete damage in the PAV, the cumulative damage resistance of unmodified and polymer-modified bitumens are similar. That is, they undergo similar levels of damage under a similar number of cycles. However, this occurs because ageing and damage are not applied simultaneously. The polymer network is previously damaged in the PAV, and then, the PMB undergoes destructive test method in the DSR. This condition is not representative of the field where the ageing and loading co-occur. Therefore, the cumulative damage after the same field exposure would be different for the Pen and the SBS modified bitumens. However, results are not intended to compare the performances of different bitumens. They have resulted in being significant for the understanding of the effects of LSA on the polymer network and the bitumen-rich phase of cross-linked SBS modified bitumens.

6.1.2.3 EVA modified bitumens

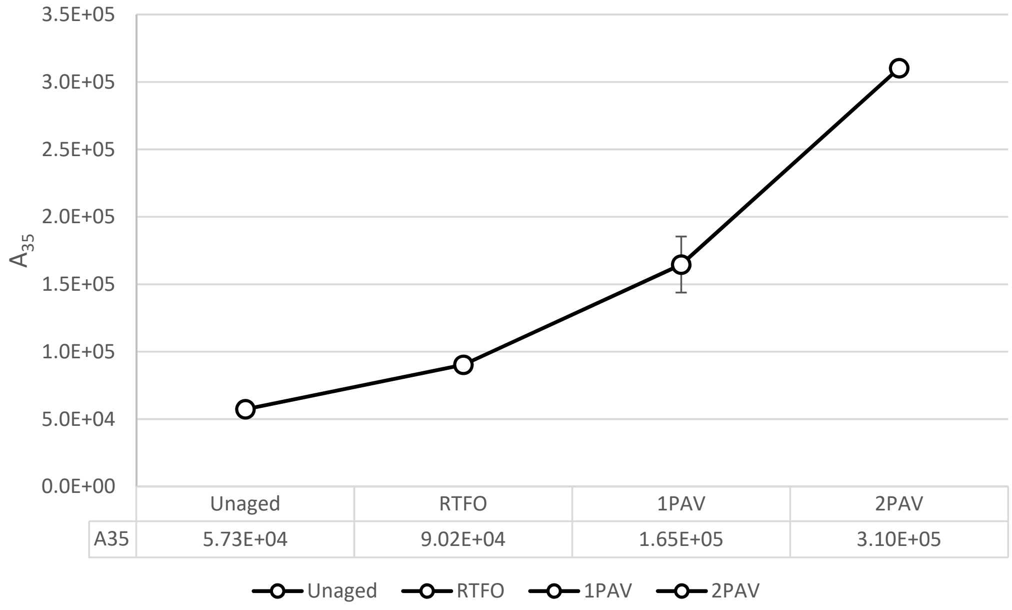
The EVA modified bitumens were aged up to 2 cycles of PAV. Results are given in the following sections.

EVA 2 bitumen

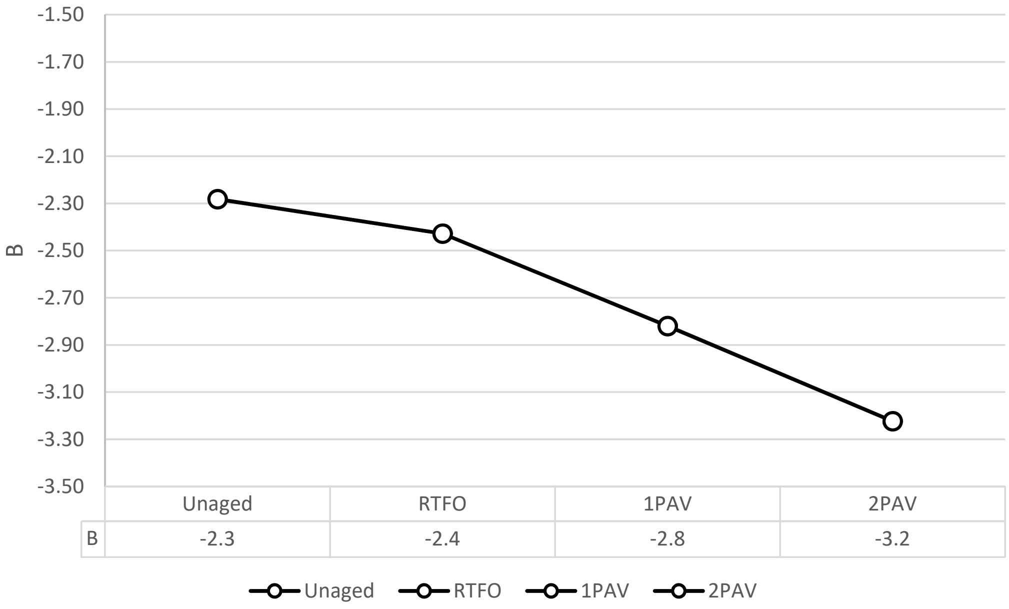
Results of the LAS test of the EVA 2 bitumen are given in Figure 6-19.



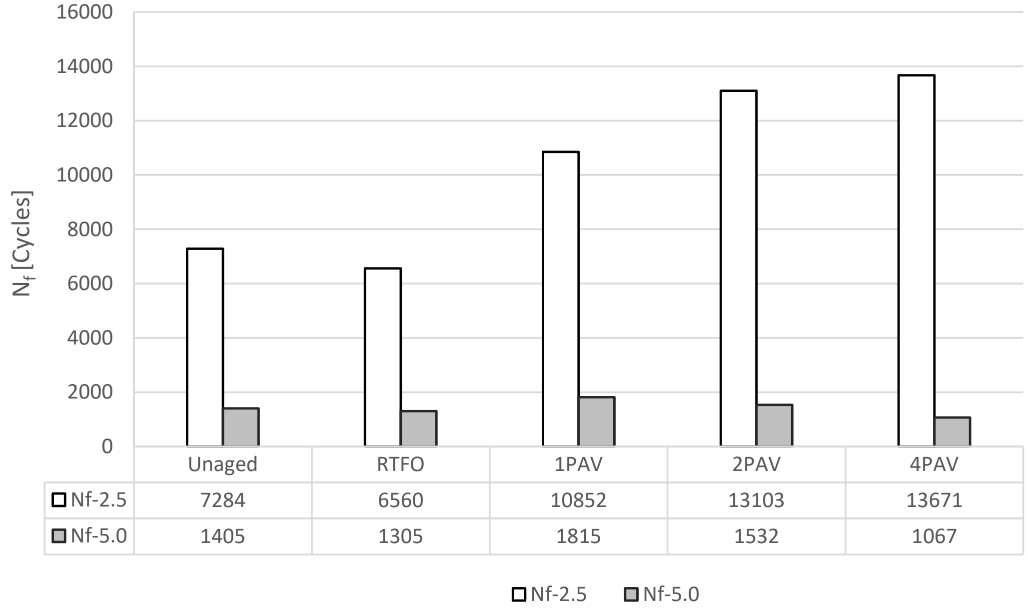
a) Fatigue life



b) Parameter A_{35}



c) Parameter B



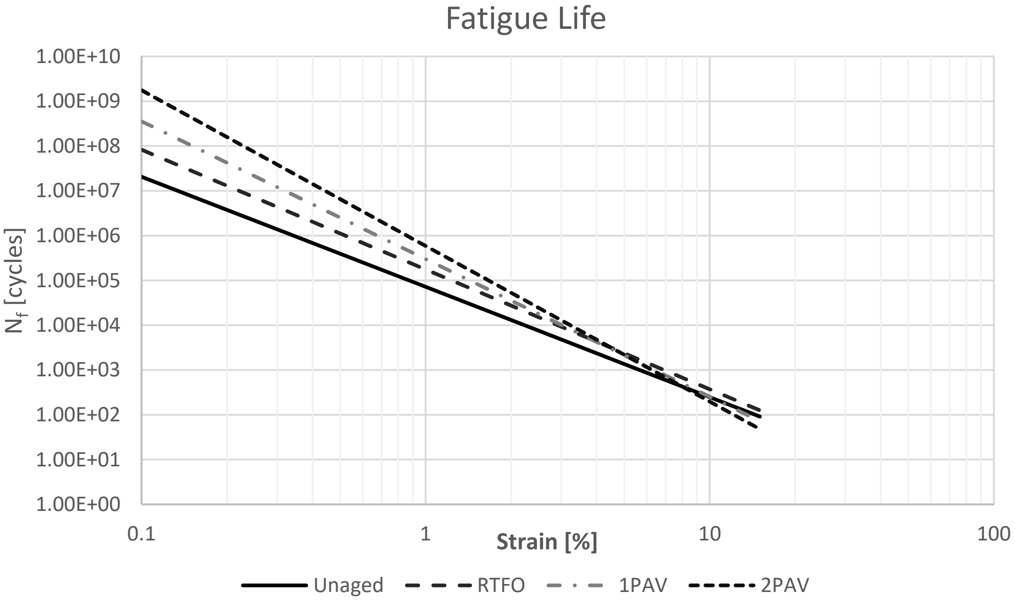
d) N_f at 2.5% and 5.0%.

Figure 6-19 - LAS test results EVA 2 bitumen at different levels of LSA (a – fatigue life; b – parameter A35; c – parameter B; number of cycles to failure at 2.5% and 5.0% strain).

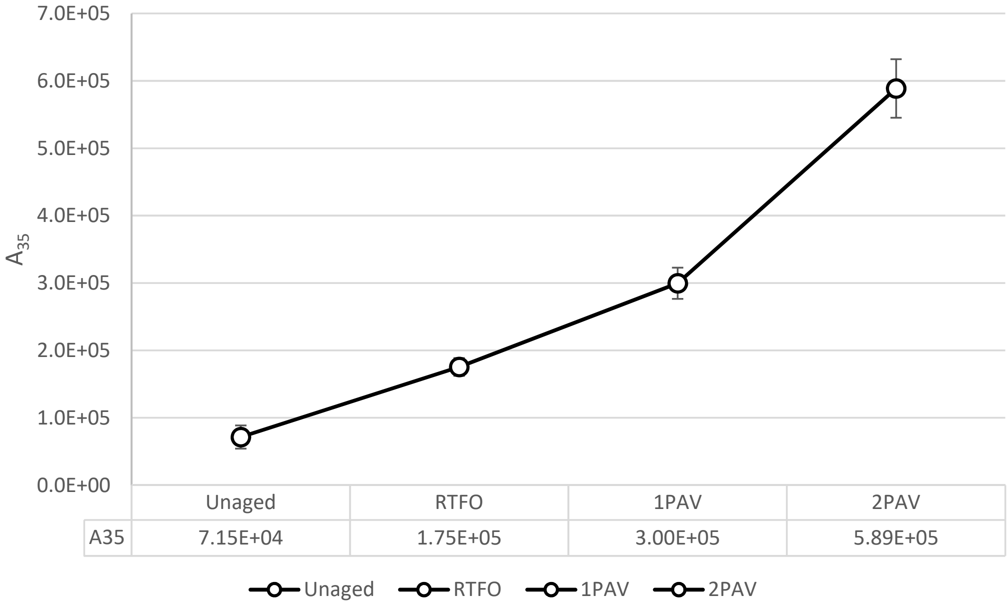
Results show that a relatively low concentration of EVA does not produce relevant differences from that observed in the Pen bitumen. At lower strain level (~<1%) laboratory simulated ageing increases N_f (under the same level of strain). Then, this effect reverses with the strain increasing.

EVA 4 bitumen

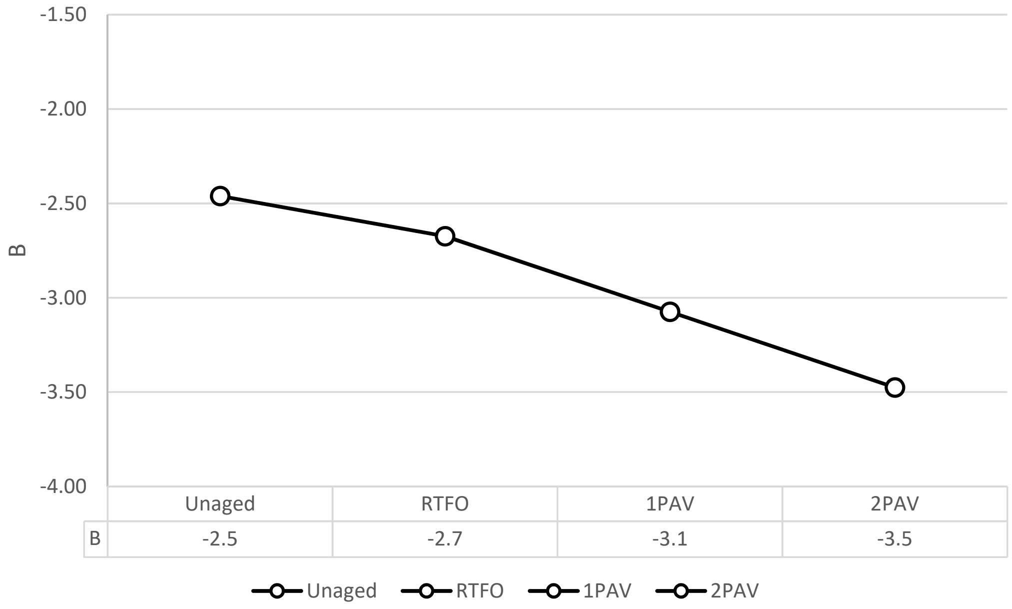
Results of the LAS test of the EVA 4 bitumen are given in Figure 6-20.



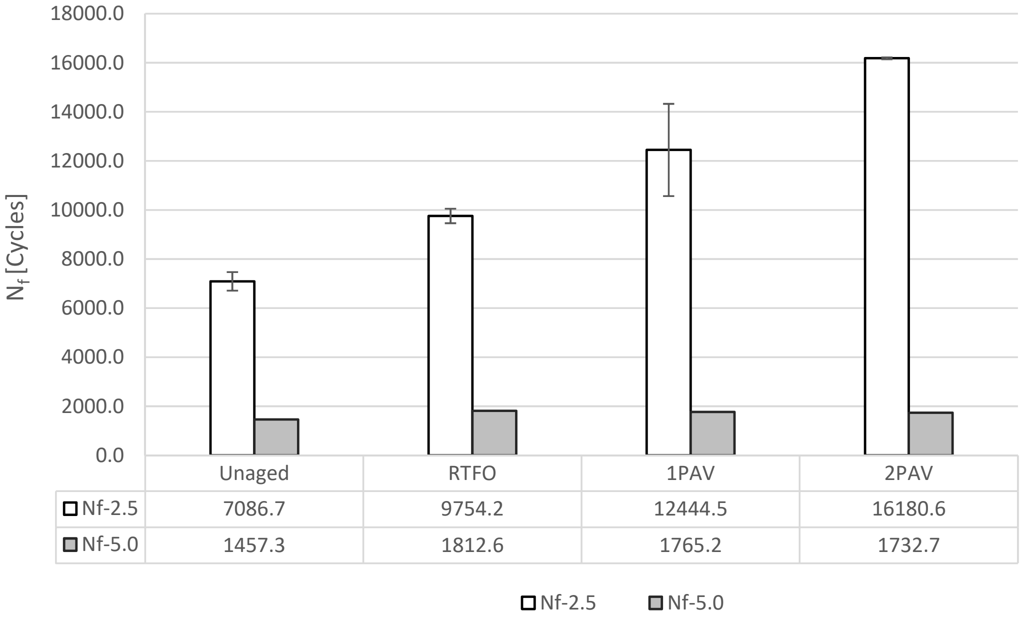
a) Fatigue life



b) Parameter A_{35}



c) Parameter B



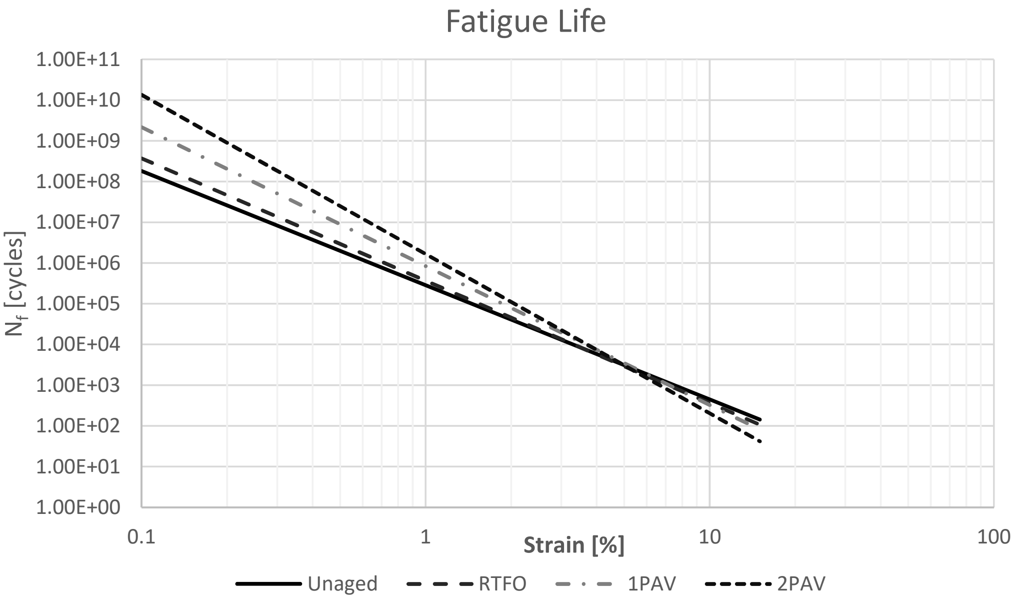
d) N_f at 2.5% and 5.0%.

Figure 6-20 - LAS test results EVA 4 bitumen at different levels of LSA (a – fatigue life; b – parameter A35; c – parameter B; number of cycles to failure at 2.5% and 5.0% strain).

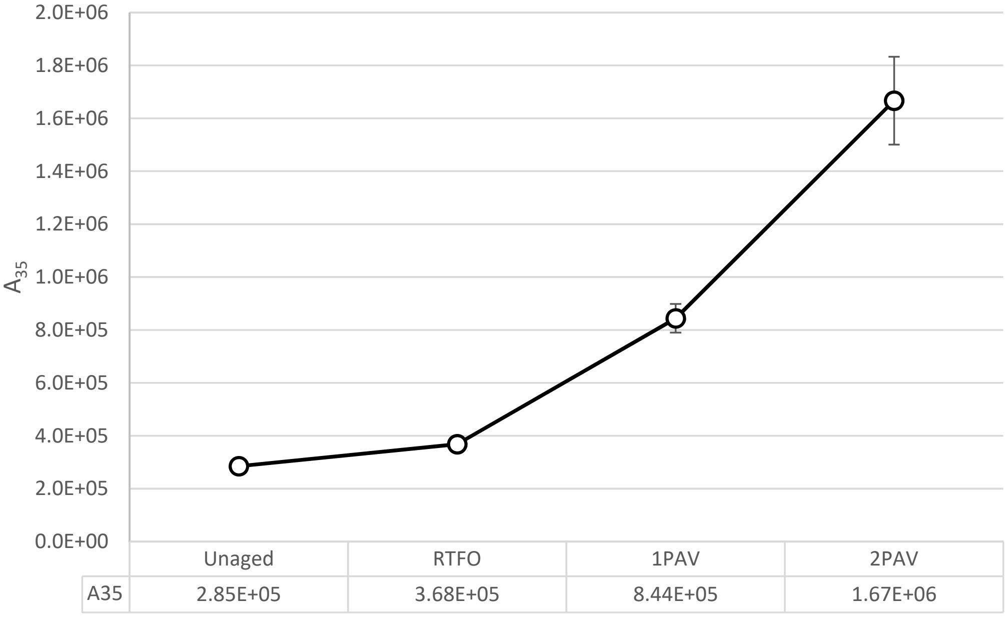
There is not a relevant deviation from that observed in the EVA 2 bitumen.

EVA 6 bitumen

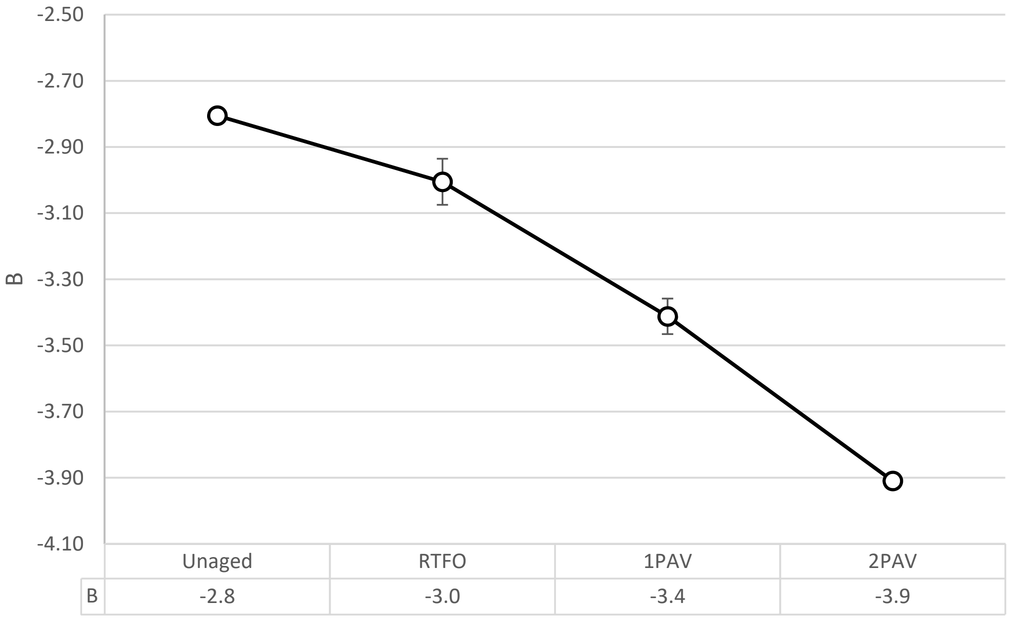
Results of the LAS test of the EVA 6 bitumen are given in Figure 6-21.



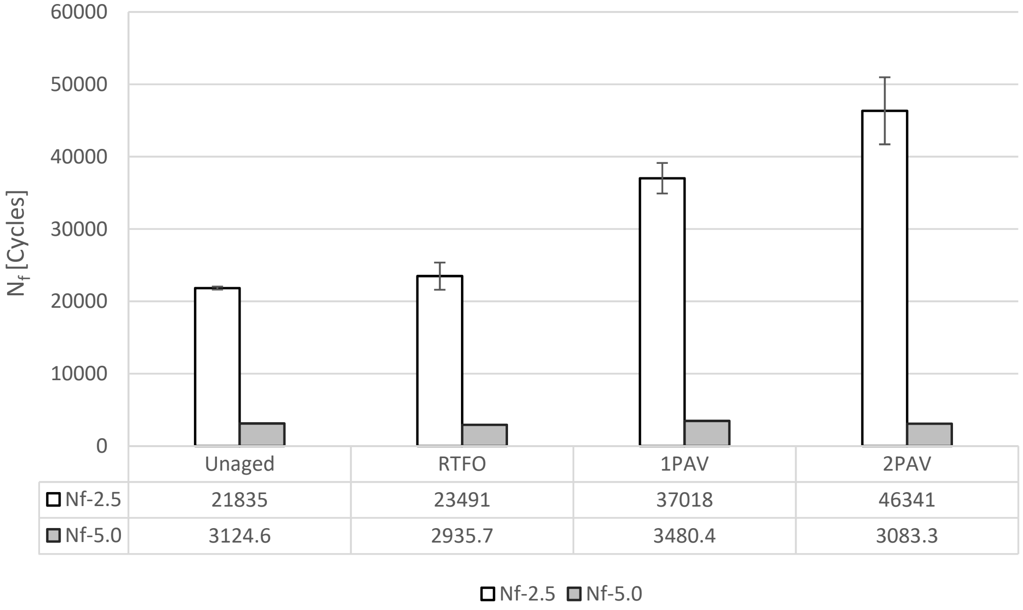
a) Fatigue life



b) Parameter A_{35}



c) Parameter B

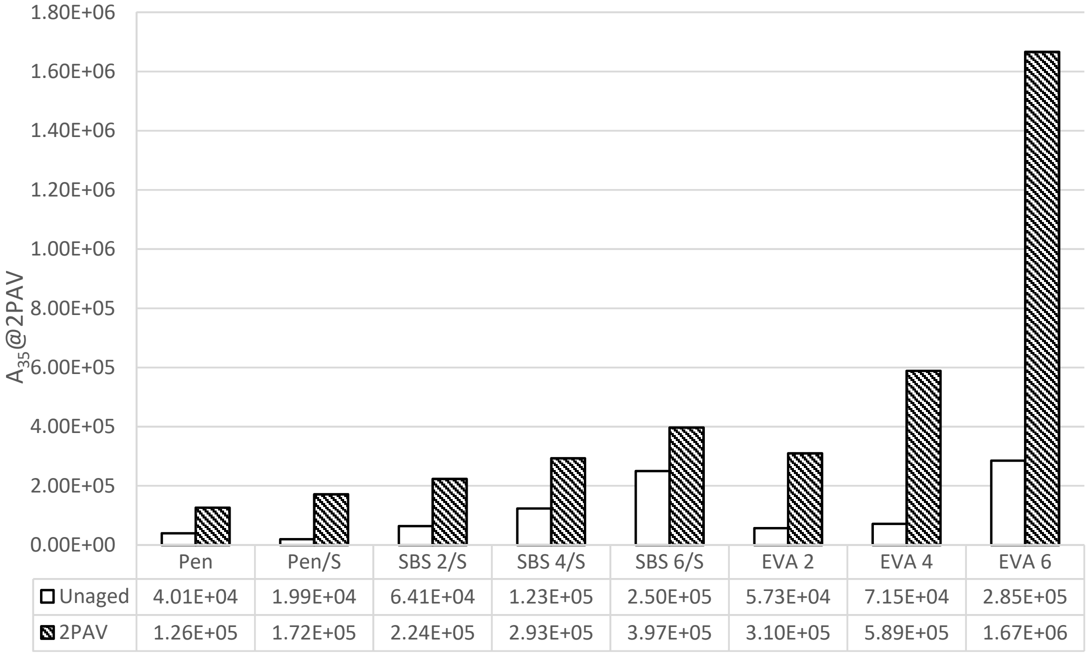


d) N_f at 2.5% and 5.0%.

Figure 6-21 - LAS test results EVA 6 bitumen at different levels of LSA.

The EVA 6 bitumen shows the highest level of material integrity (A_{35}) after 2 cycles of PAV compared to all the bitumens used in the experiment (Figure 6-8). It is interesting to observe that this value is even higher of those of the SBS modified bitumens after 4 cycles of PAV.

The figure below shows the values of the parameter A_{35} at the unaged and 2PAV-aged conditions of the bitumens used in the experiment (Figure 6-22).

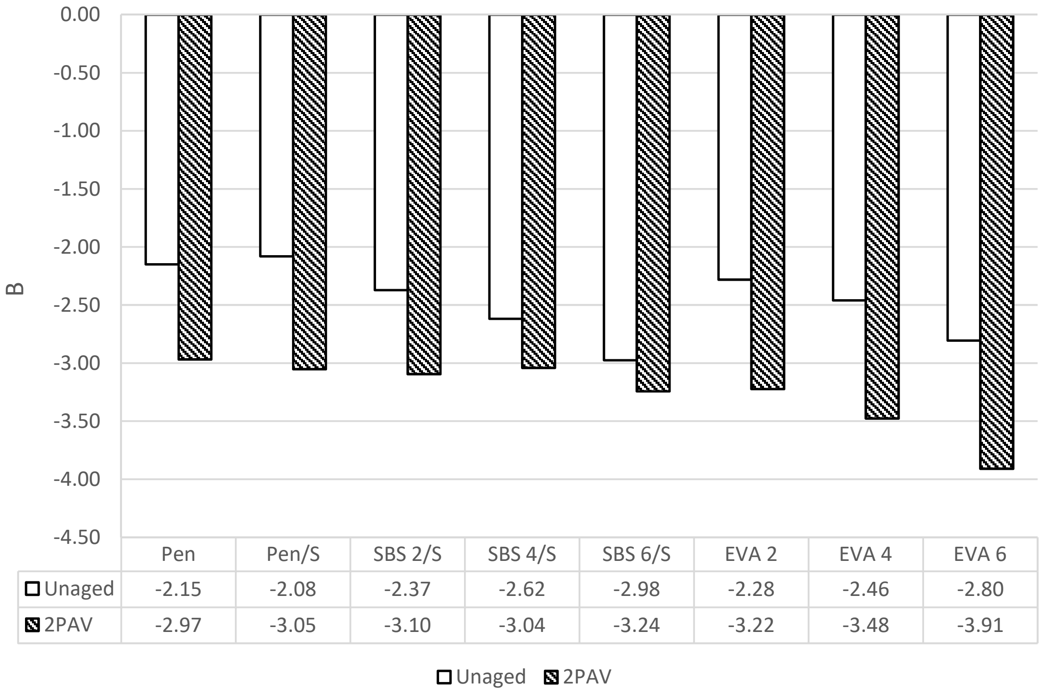


	Pen	Pen/S	SBS 2/S	SBS 4/S	SBS 6/S	EVA 2	EVA 4	EVA 6
□ Unaged	4.01E+04	1.99E+04	6.41E+04	1.23E+05	2.50E+05	5.73E+04	7.15E+04	2.85E+05
▨ 2PAV	1.26E+05	1.72E+05	2.24E+05	2.93E+05	3.97E+05	3.10E+05	5.89E+05	1.67E+06

Figure 6-22 – Fatigue law parameter A_{35} of the bitumens at unaged and 2PAV-aged conditions.

The value of A_{35} of the EVA 6 bitumen at the unaged condition is higher than the others. However, 2 cycles of PAV produce a huge effect on its value that increases on one order of magnitude compared to the unaged condition. As a general comparison, the EVA modified bitumens show a more considerable increase of the fatigue parameter A_{35} than the SBS modified bitumens.

Besides this, the values of the fatigue law parameter B at unaged and 2PAV-aged conditions of the bitumen used in this experiment are given in Figure 6-23.



	Pen	Pen/S	SBS 2/S	SBS 4/S	SBS 6/S	EVA 2	EVA 4	EVA 6
☐ Unaged	-2.15	-2.08	-2.37	-2.62	-2.98	-2.28	-2.46	-2.80
▨ 2PAV	-2.97	-3.05	-3.10	-3.04	-3.24	-3.22	-3.48	-3.91

Figure 6-23 - Fatigue law parameter B of 2PAV aged bitumens.

The EVA 6 bitumen has the lowest value of parameter B after two cycles of PAV and displays the highest LSA susceptibility as well (decrease of 1.11). Besides this, as observed with the parameter A_{35}, the parameters B of the EVA modified bitumens shows a higher LSA susceptibility than those of the SBS.

These results can be explained trying to identify their effects on the number of cycles to failure at 2.5% and 5.0% as with the cross-linked SBS modified bitumens.

6.1.2.4 Remarks on LAS test results of EVA modified bitumens

The number of cycles to failure at 2.5% strain level of the Pen and the EVA modified bitumens at different levels of LSA are given in Figure 6-24.

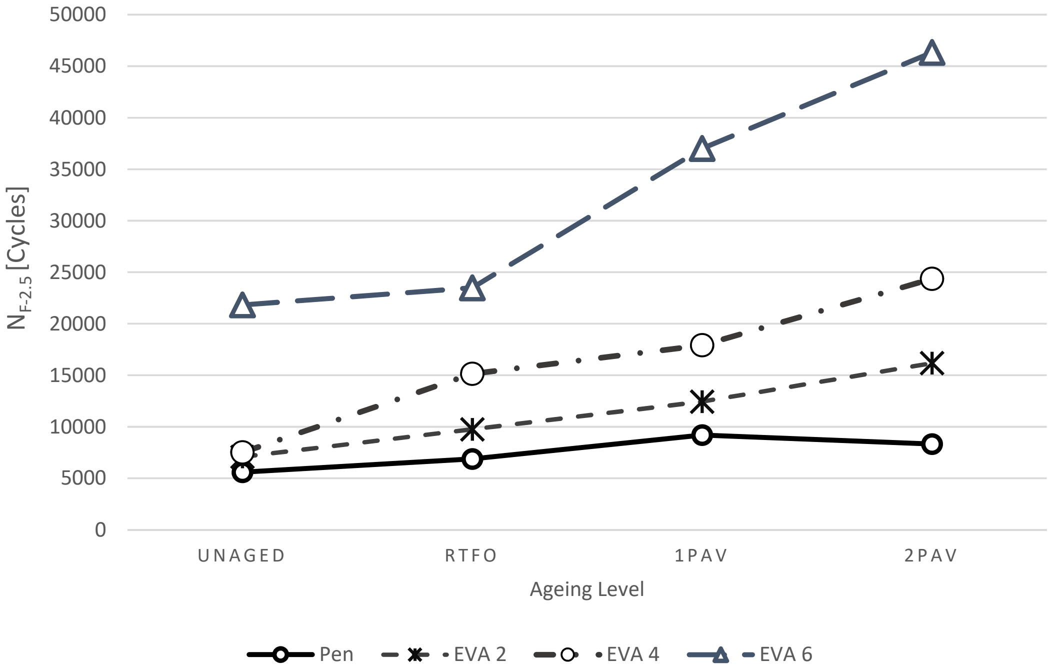


Figure 6-24 - Number of cycles to failure at strain 2.5% of Pen and EVA modified bitumens at different levels of LSA.

At the unaged condition, the EVA modification increases the fatigue life only at very high polymer concentration. The number of cycles to failure of the EVA 2 and EVA bitumens are close to those of the Pen. Considering the results of the SBS modified bitumens (Figure 6-17), the EVA 6 bitumen is the one providing the highest number of cycles to failure.

At the strain level of 2.5%, LSA increases the fatigue life of the bitumens with the number of cycles to failure increasing with ageing. Furthermore, under the same level of ageing, the number of cycles increases with polymer concentration. This trend is maintained up to two cycles of PAV. At this strain level, N_f of the modified bitumens is much larger than the Pen bitumen, with the EVA 6 achieving more than 40,000 cycles to failure.

The SBS modified bitumens show a similar trend, but the differences in N_f among the different polymer concentrations and with the Pen bitumen (Figure 6-17) are more contained. In the case of the SBS, the 4PAV-ageing level represents a turning point where it is believed that the polymer network has undergone extensive damage and N_f decreases close to the value of the unmodified bitumen. In this case, the bitumens were not aged at 4PAV. Therefore, an analogue comparison cannot be made. However, results from the LVE characterisation (§5.1.3) and the fluorescence microscopy (§4.2.2) have shown that the EVA polymer network has a very low PAV-susceptibility. Specifically, the microscope has highlighted that the polymer dispersion remains unvaried with PAV ageing.

On the other hand, the black diagrams show that the bitumen-rich phase ages while the polymer-rich phase doesn't. This aspect might depend on the low PAV-susceptibility of the EVA and the low polymer-bitumen affinity. Therefore, there is a reason to believe that the EVA would resist two additional cycles of PAV and that the bitumen phase would continue to harden in the PAV. For this reason, the trend observed in the EVA bitumen up to 2PAV is believed to continue with the number of cycles increasing with ageing.

If this would be the case, the microstructure of the EVA modified bitumens would evolve towards a highly PAV-hardened bitumen-rich phase and a still integer polymer-rich phase that provides an additional contribution to the bitumen integrity. In other words, the system might evolve towards a "biphasic structure" (due to the low polymer-bitumen affinity) where the highly-hardened bitumen phase is reinforced (or stiffened) by the presence of the polymer. The formation of this system might increase the integrity of the bitumen and its cumulative damage resistance.

However, although the description of this mechanism beyond two cycles of PAV appears reasonable, it remains at the level of hypothesis. Future work might focus on verifying this aspect.

The analysis of the fatigue life at 2.5% strain has allowed to elaborating interesting consideration on the variation in the microstructure of EVA modified bitumens. Results at higher strain levels (5%) are given in Figure 6-25.

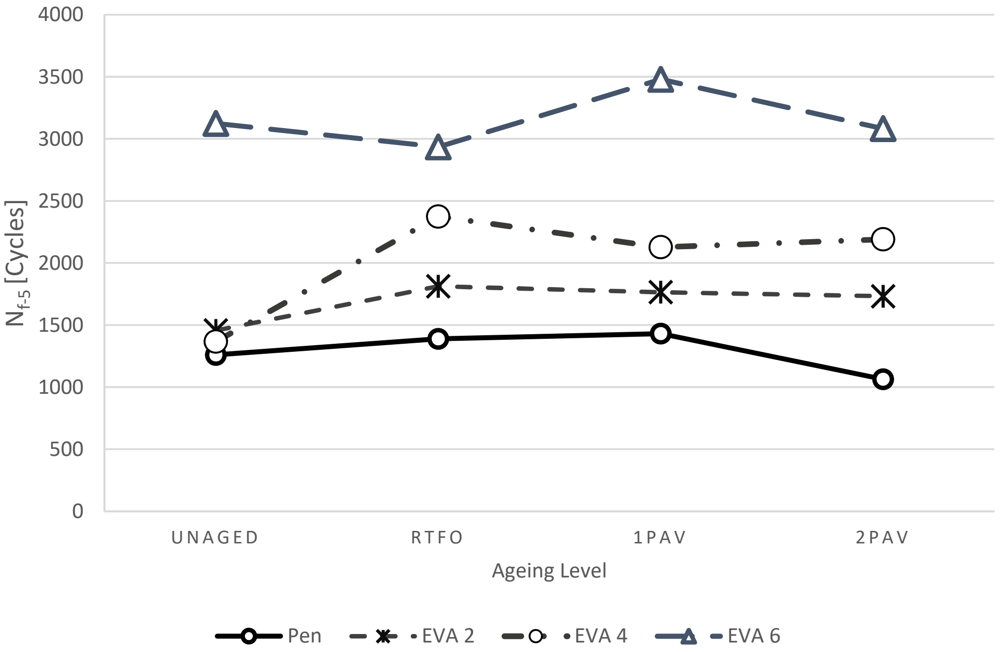


Figure 6-25 - Number of cycles to failure at strain 5.0% of Pen and EVA modified bitumens at different levels of LSA.

The increase in the strain level reduces the number of cycles to failure of the bitumens. As for lower strain levels, at the unaged condition, the polymer modification increases the fatigue life only at very high concentration (i.e., 6% EVA). Considering higher strain levels reduces the effect of ageing on N_f that shows minimal variation for all the bitumens. However, there are no pieces of evidence against that considered at 2.5% strain level regarding the plausible rheological (LAS) response and the evolution of the microstructure of the PMBs at higher PAV exposure.

6.2 Results of Time Sweep test

As discussed in section 3.3.9, the time sweep (TS) and the LAS apply different damage mechanisms. The first induces damage through load repetitions under a unique level of strain amplitude and frequency, while the second by increasing the strain applied.

Besides this, the results of the LAS test have been analysed with the VECD theory for which a body the has cracks and defects can be reformulated as a homogeneous body with reduced properties. This theory was initially applied to asphalt mixtures and after it went to bitumens.

In this work the use of the time–sweep test was initially prompted to verify the results of the LAS test (fatigue laws) in the lower strain region, and then it was adopted into a broader interval (Table 3-18). Specifically, it was considered that the fact that ageing tends to increase the fatigue life of bitumens would have required more focus (although it was observed by other researchers (37). Therefore, the validity of the effectiveness of the VECD theory has been verified with the TS.

In other words, the LAS applies a limited number of cycles of different amplitude. Then according to this theory, it is possible to determine the fatigue life of the material at different strain levels irrespective of the loading pattern and history. The validity of this assumption has been verified running repeated cyclic loading at different strain levels. The TS test was conducted at 31°C to maintain the same conditions used in the LAS test.

It is understood that the TS test as well presents some shortcomings related to some effects of the sample (i.e., edge effect - 41). However, fatigue cracking is caused by load repetitions that reduce the stiffness of the material by inducing damage. In this case, the bitumens were subjected to repeated load (in strain-controlled conditions) and the variation of the modulus with the number cycles was measured.

The results of the LAS and the TS test are compared in terms of ranking and not in terms of the number of loading cycles. That is, the N_f from the LAS are not expected to be equal to those from the TS, but ageing is expected to have the same effect on the number of loading cycles measured by the LAS or by the time-sweep test.

Results of the TS test have been analysed by identifying the number of cycles needed to reduce the viscous modulus by 35% from its initial value. This criterion was adopted to be compliant with the LAS test.

The strain levels used in this test are given in Table 3-18, and the bitumen used has been he SBS 2/S bitumen. Results are given as follows.

6.2.1 SBS 2/S bitumen at 1% strain

The variation of the viscous modulus with the number of cycles is given in Figure 6-26.

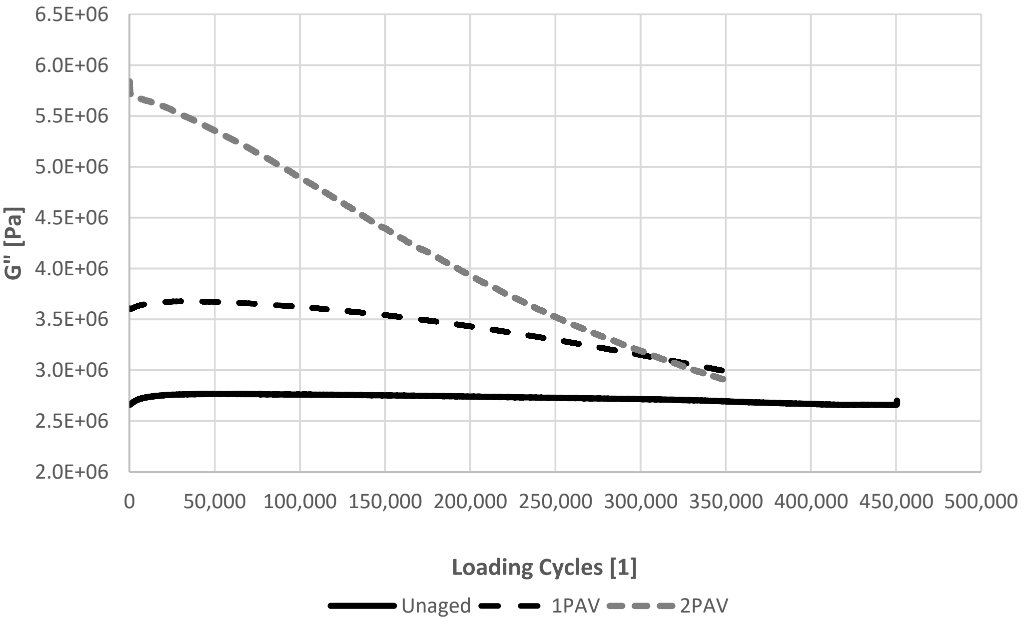


Figure 6-26 – TS test: G” vs loading cycles at 1% strain amplitude.

(SBS 2/S bitumen at unaged, 1PAV and 2PAV ageing conditions).

Ageing increases the initial viscous modulus as a function of the exposure to the PAV. The curve of the 2PAV-aged bitumens starts from a level of stiffness that is about the double of the unaged one. However, at this strain level (and at the temperature of 31°C) the bitumen does not show damage accumulation even after 450,000 cycles (corresponding to ~12.5 hours). The curve related to the PAV aged bitumen shows a reduction in the modulus, but there is no prove of damage after about 10 hours testing. In the case of 2 PAV aged bitumen, it was possible to bring the sample to failure (reduction of 35% of initial G”). Results are given in – TS test: N_f at 1% SBS 2/S bitumen at unaged, PAV and 2PAV aged conditions.

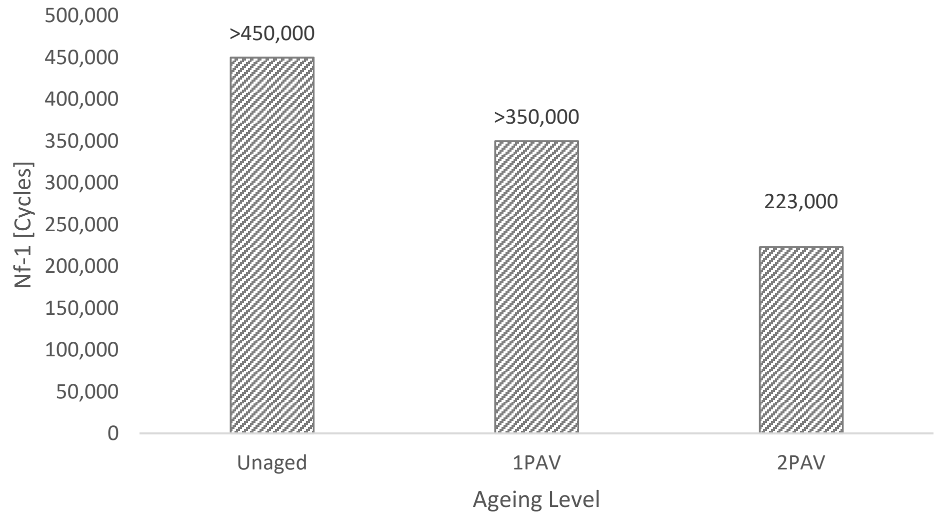


Figure 6-27 – TS test: N_f at 1% SBS 2/S bitumen at unaged, PAV and 2PAV aged conditions.

At 1% strain, the unaged and the 1PAV aged bitumens did not accumulate damage. While, after two cycles of PAV, it was possible to reduce the initial G” of 35% after 223,000 cycles. The fatigue law of the bitumen determined through the LAS test (Figure 6-10), shows the reverse trend where at 1% strain the unaged bitumen has the lowest N_f. Therefore, results from the two test are somehow conflicting. This difference might be in mechanisms of the two tests and in the fact that at this strain level (and this temperature), the validity of the VECD theory could be challenged. In other words, the VECD analysis is based on the assumption that in the bitumen, there are micro-cracks or macro cracks that have initiated or propagated (220). However, the results of the TS test on the unaged bitumen show that the viscous modulus does not change even after a vast number of load repetitions. Therefore, no defects have been provided to reduce the stiffness of the material. One of the possible reasons for the lack of damage caused in the TS test might be the test temperature. Tha is, at 31°C the TS test is not capable of damaging the material when a strin levl of 1% is used. Based on this, there might be a reason to believe that the application of the continuum damage theory to the undamaged region needs some caution.

This comment could be a plausible interpretation of this result.

6.2.2 SBS 2/S bitumen at 2.5% strain amplitude

The variation of the viscous modulus with the number of cycles is given in Figure 6-28.

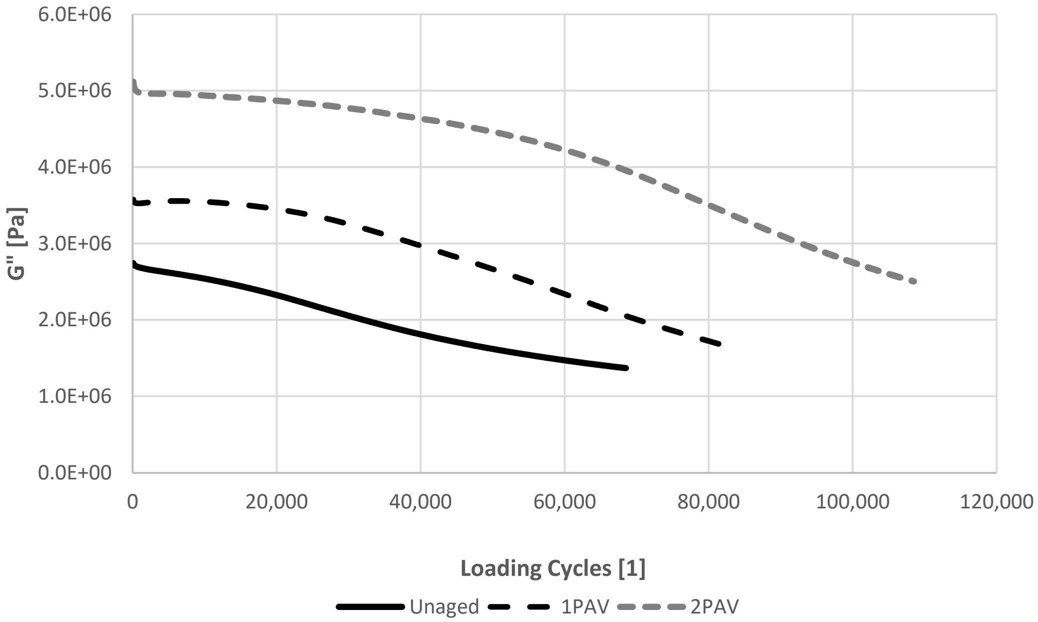


Figure 6-28 - TS test: G” vs loading cycles at 2.5% strain amplitude.

(SBS 2/S bitumen at unaged, 1PAV and 2PAV ageing conditions).

The stiffening effect of ageing is visible. However, in this case, it was possible to induce damage in the samples. Results given below show a comparison between the LAS and the TS tests.

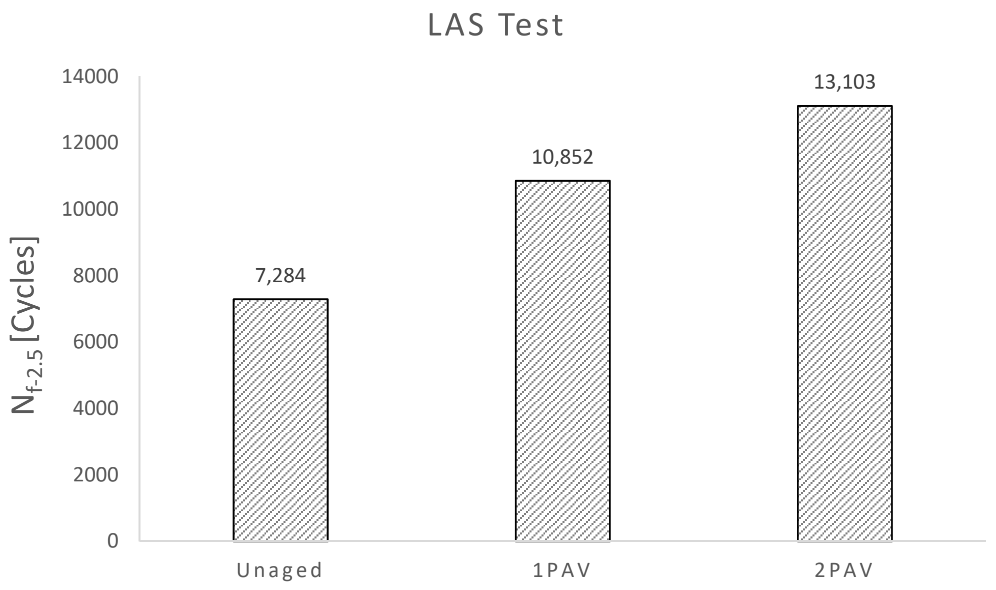


Figure 6-29 – LAS test: N_f at 2.5% SBS 2/S bitumen at unaged, 1PAV and 2PAV ageing conditions.

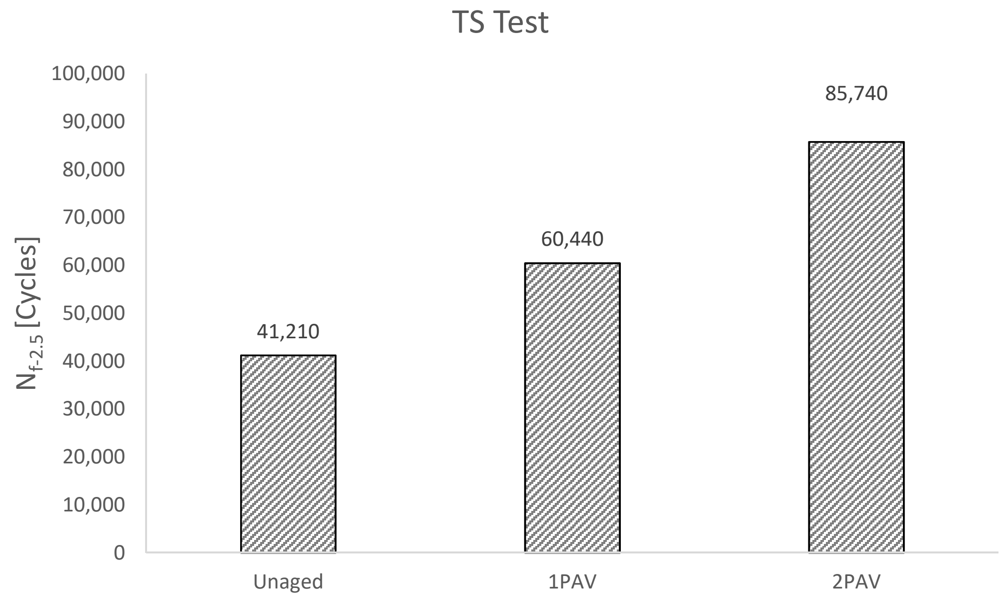


Figure 6-30 - TS test: N_f at 2.5% SBS 2/S bitumen at unaged, 1PAV and 2PAV ageing conditions

Results from the two tests are in agreement at this strain level. LSA produces an increase in the number of cycles to failure. As clarified in §6.2, results need to be compared to highlight the effect of ageing on N_f without expecting the two tests to provide similar N_f.

6.2.3 SBS 2/S bitumen at 6.5% strain amplitude

The variation of the viscous modulus with the number of cycles is given in Figure 6-31.

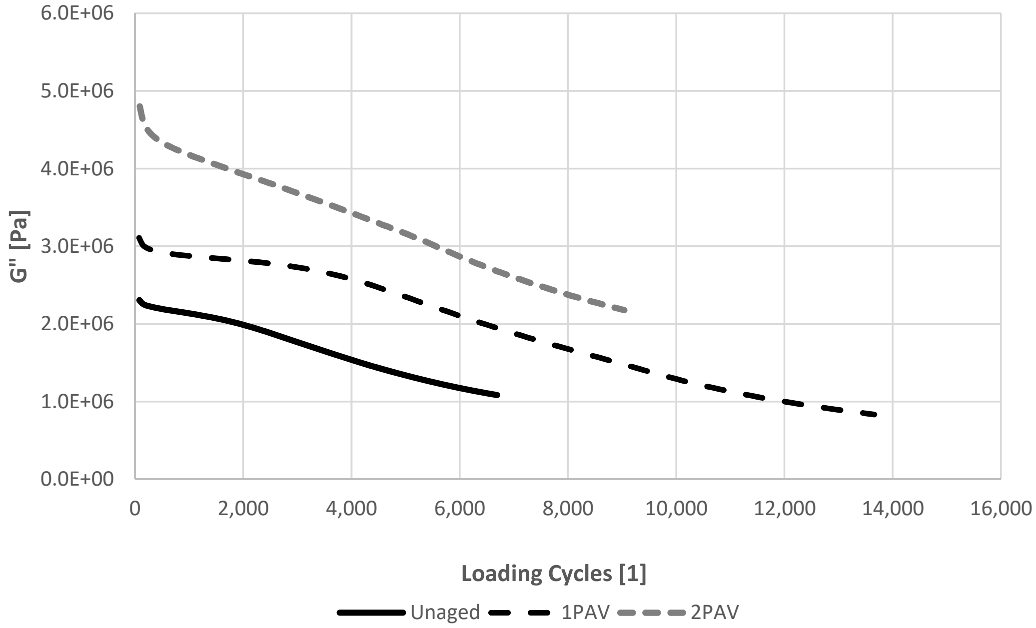


Figure 6-31 – TS test: G” vs loading cycles at 6.5% strain amplitude.

(SBS 2/S bitumen at unaged, 1PAV and 2PAV ageing conditions).

The stiffening effect of ageing is visible. In this case, curves show a sharper reduction in the modulus with the number of cycles. Comparative results between the LAS and the TS test are given below.

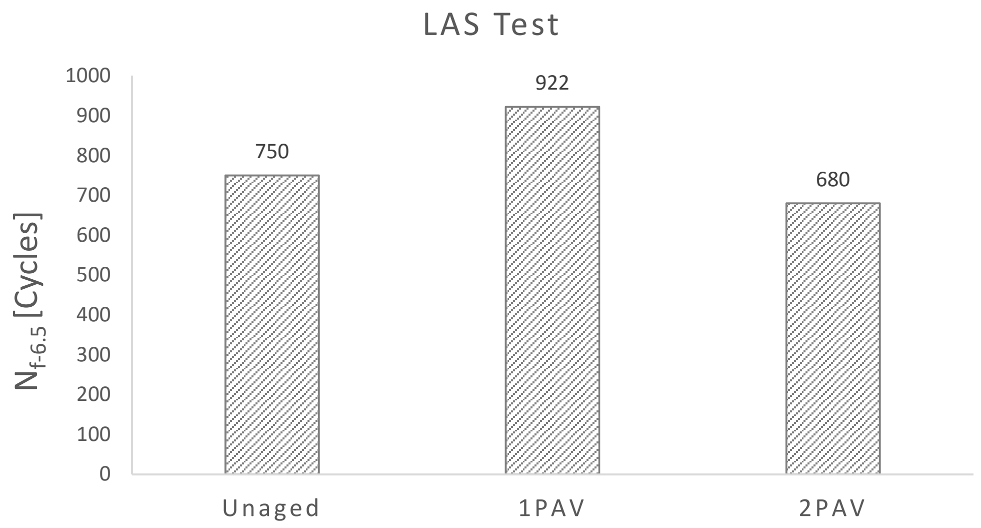


Figure 6-32 - LAS test: N_f at 6.5% SBS 2/S bitumen at unaged, 1PAV and 2PAV ageing conditions.

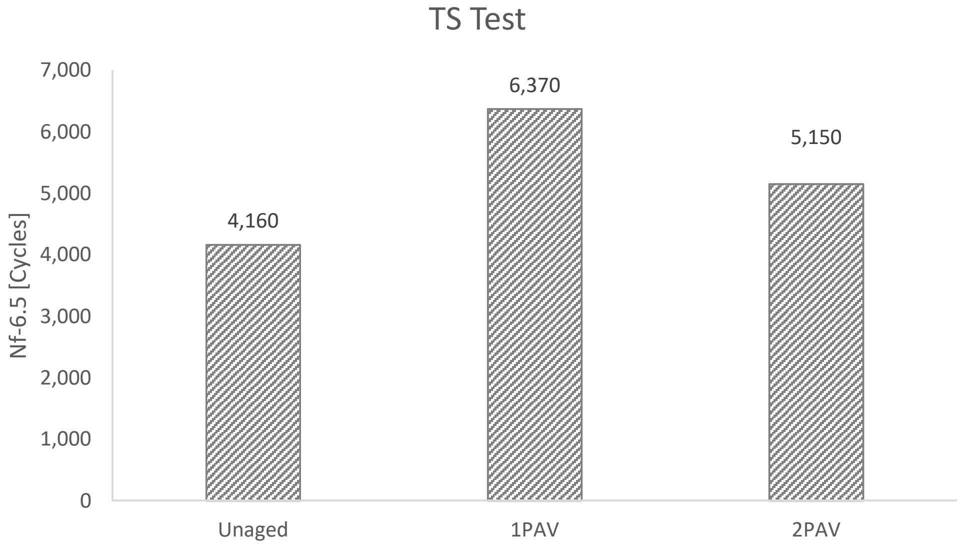


Figure 6-33 - LAS test: Nf at 6.5% SBS 2/S bitumen at unaged, 1PAV and 2PAV ageing conditions.

The LAS test and the TS test show the same trend of the results. For the 1PAV-aged bitumen, the strain of 6.5% belongs to the strain interval, where LSA is beneficial for fatigue life. Then, increasing the PAV exposure (2PAV), LSA becomes detrimental with the N_f that reduces at the same strain level.

6.2.4 SBS 2/S bitumen at 11% strain amplitude

The variation of the viscous modulus with the number of cycles is given in Figure 6-34.

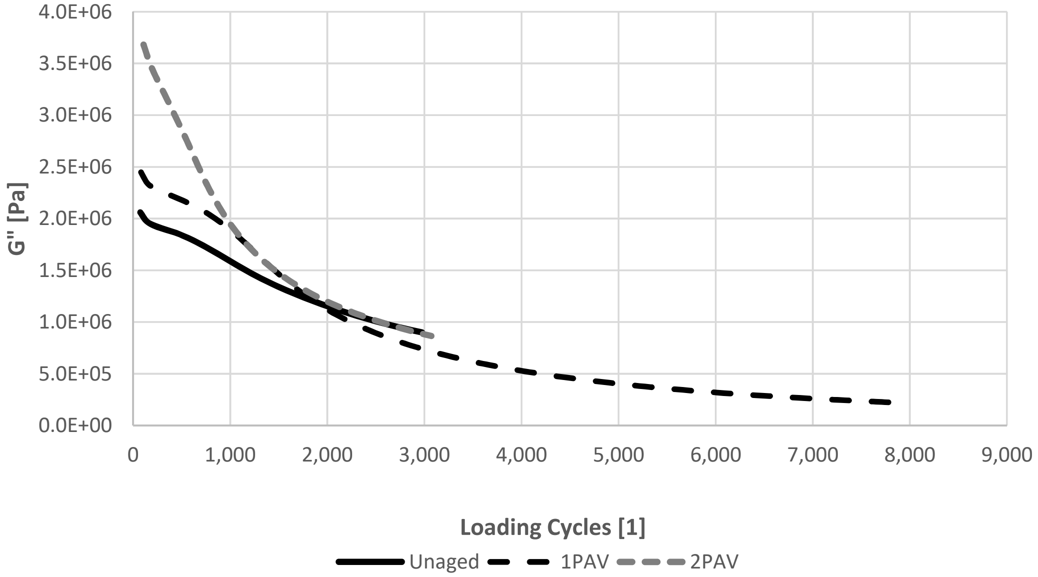


Figure 6-34 - TS test: G” vs loading cycles at 11% strain amplitude.

(SBS 2/S bitumen at unaged, 1PAV and 2PAV ageing conditions).

The stiffening effect of ageing is observed, and the use of a higher strain level reduces the number of cycles to failure. Comparative results between the LAS and the TS tests are given below.

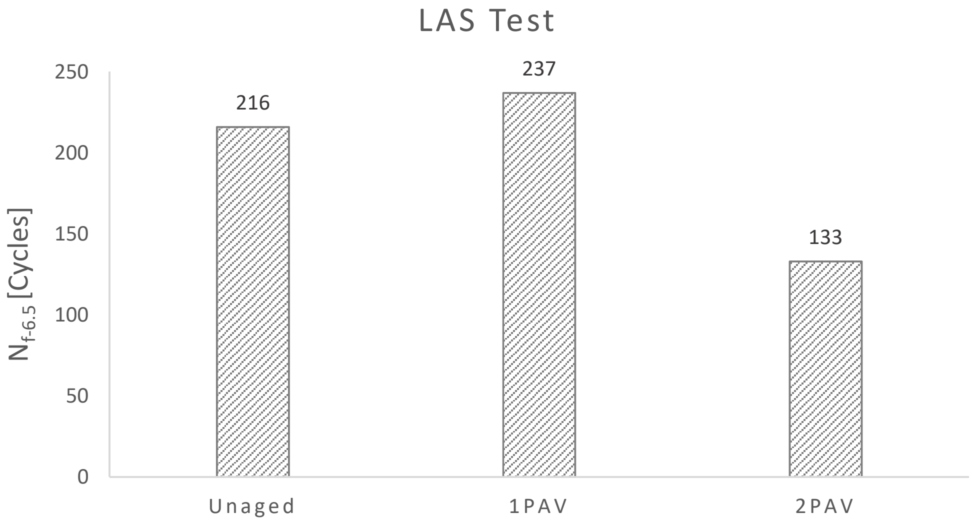


Figure 6-35 - LAS test: N_f at 11% SBS 2/S bitumen at unaged, 1PAV and 2PAV ageing conditions.

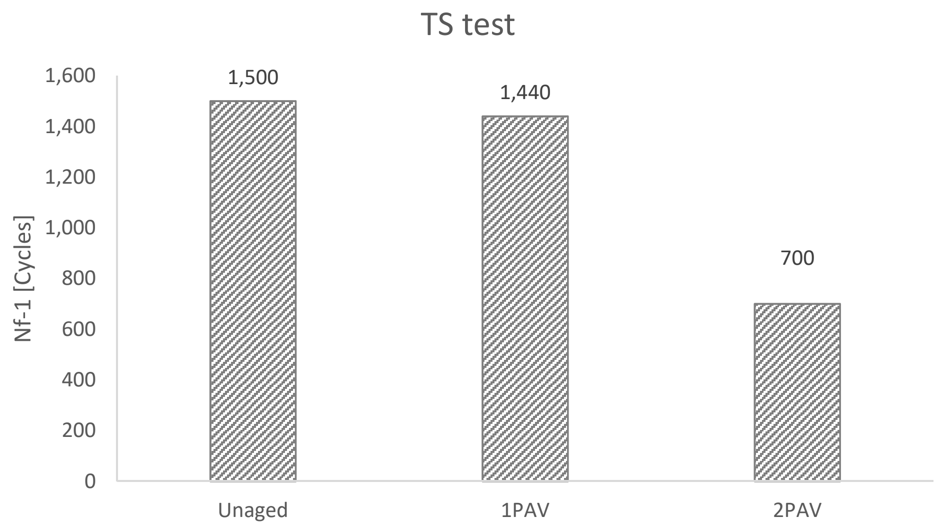


Figure 6-36 - LAS test: N_f at 11% SBS 2/S bitumen at unaged, 1PAV and 2PAV ageing conditions.

The differences in N_f between the unaged and the 1PAV-aged bitumens do not seem to be that relevant in both the tests. At 2PAV ageing, both the tests show a visible reduction in N_f. Therefore, as an overall conclusion, the tests are in agreement at these levels of strain as well.

6.2.5 Remarks

The TS test has been used to verify the LAS test results. The two tests refer to different damage mechanisms, and this difference is visible at the strain level of 1%. The TS induces negligible damage at the unaged and 1PAV-aged conditions. At 2PAV, the test brings the modulus below 35% of its initial value after a relatively large number of cycles. On the other hand, the LAS provides exactly the reverse ranking of the bitumens showing a reverse effect of ageing on the cumulative damage resistance.

This difference could be explained by the fact that the VECD theory applies once the material has some damage. In other words, the LAS test is a destructive test method were damage is induced. Then the application of the VECD theory uses the results from the destructive (and non-destructive) portion of the test to evaluate the cumulative damage resistance within a wide range of strain, including small strains (i.e., 1%), where damage might not occur. This was observed in the TS test where applying repeated loading at 1% strain level does not induce damage at the unaged and 1PAV aged conditions. Therefore, the application of the VECD theory needs caution once damage does not occur.

At higher strain level, the comparison between the two tests can be considered as successful, and the results (with the relative conclusions) from the LAS test can be considered as plausible and verified.

7 Polymer modified mastics

Due to its nature, the bitumen is the part of the asphalt mixtures that is susceptible to STA and LTA. Although the bitumen represents a limited portion in the mix constituents (compared to aggregates), its effect on the behaviour of mixtures is so visible that its rheological response is used to understand and somehow to predict their mechanical response. In light of this, the study of bitumen ageing aims to understand and mitigate the ageing of mixtures. To achieve this, numerous aspects need to be considered. One of them is to understand whether the microstructural changes occurring in the bitumen alone are similar to as those occurring in the bitumen in the mix.

The development of bitumen testing is prompted mainly by the following two needs. The first is related to develop criteria for material selection. The second focuses on the need to replace and (or) reduce (when possible) the testing on mixtures that are more time-consuming. The latter is based on the fact that the response of bitumens needs to be representative of the mixture scale. However, the two scales are so different, that in large part of the cases, bitumen tests need to be supported by mixtures testing.

On the one hand, this is intrinsic of the fact that mixtures include a solid portion that inevitably affects their response. Besides this, it is understood that bitumen does not seem to coat aggregates as a binder, but more as a mastic constituted of bitumen plus filler. On the other hand, there are shortcomings in the bitumen testing that could limit the full applicability of their results to mixtures.

As a consequence, intermediate scales between the bitumen and the mixtures have been (and are) investigated. The mastic scale represents one of these scales. There is a vast number of works focused on the effect of the mastic properties on the response of mixtures (188, 189, 207), and all of them converge on the fact that the bitumen and filler interactions have a significant impact on the mixture properties. Ageing of asphalt mixtures is one of these properties. Therefore the study of mastic ageing could represent a further step towards the understanding of the mechanism of bitumens in mixtures.

7.1 Ageing in bituminous mastics

Bitumen and filler show chemical interactions that affect the composition of bitumens. In particular, during the production of HMA, the mineral filler is responsible for the adsorption of asphaltenes on the surface of particles (189). As a consequence, the distribution of the bitumen fractions is affected by the presence of mineral filler. Being the asphaltenes the fraction most influenced by ageing, this interactions provides significant differences with the ageing of bitumens. Besides this, the ageing mechanism of mastics seems to depend on the factors given in Figure 7-1 (188).

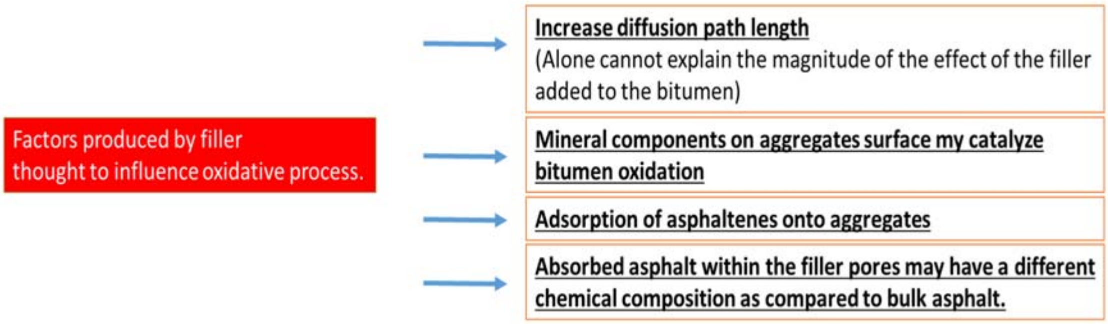


Figure 7-1 – Summary of effects of filler on the ageing of mastics.

The presence of filler increases the length of the diffusion path of oxygen through the film of bitumen. However, the significant effect seems to be provided by the interaction between the filler surface and the bitumen polar component. That is, the formation of asphaltenes might be mitigated since they are somehow entrapped onto the filler surface.

However, the study of ageing in unmodified bitumens is supported by more than a half-century of research. On the other hand, limited research has been done on the ageing of mastics (188). Moreover, if polymers are included in this scenario, it is evident that the problem becomes more complex. Therefore, the study of ageing in polymer modified mastics represent perhaps the logical consequent step to this work.

7.2 Scope of the experiment

The study of aged polymer modified mastics was included to verify whether some of the effects of LSA visible in the bitumen response would have been the same once the filler would have been included. The work does not aim to provide a fundamental understanding of this aspect considering its complexity. The scope is to verify whether the rheological results observed on aged PMBs are visible on mastics as well.

7.3 Materials (Mastics)

7.3.1 Materials and materials preparation

Four mastics were prepared by mixing four different bitumens with one concentration (25% by volume) of a single type of filler. This concentration was used since it results in a dust to binder ratio of 0.84, which is close to the middle of the range (i.e., 0.6 to 1.2) typically used in the specification of HMA mix design. Before the preparation of the mastics, the specific gravity and the Rigden Voids of the filler were measured according to the UNI EN – 1097 (specific gravity) and the UNI EN 1097 – Part 4 (Rigden Voids). The results of the filer characterisation are not included in this document for brevity. The mastics prepared in this work are given in Table 7-1.

Table 7-1 – Polymer modified mastics

Mastic	Job mix formula
Pen_M	Pen + 25% v/v filler
SBS 2/S_M	SBS 2/S + 25% v/v filler
SBS 4/S_M	SBS 4/S + 25% v/v filler
SBS 6/S_M	SBS 6/S + 25% v/v filler

In the preparation of the mastic, the bitumen the filler were mixed in a low shear mixer at 150°C for 30 minutes.

7.3.2 Ageing of polymer modified mastics

The methods traditionally used to simulate in the laboratory the STA and the LTA (i.e., RTFO and the PAV) were specifically developed for unmodified bitumens. Therefore, once they are applied to polymer modified bitumens or even more, to bituminous mastics, the achievement of similar ageing conditions raises several concerns (227). Such shortcomings are mainly related to the high viscosity (consistency) displayed by the mastics compared to the bitumens at the testing conditions.

In their work, Lesueur et al focused on the high viscosity of mastics in the RTFO and propose a simple procedure to reproduce the combination of the RTFO + (20 hours) PAV on bituminous mastics. This procedure consists of ageing the mastic for 25 hours in the PAV (227). Such a procedure was followed in this work.

Besides the concerns related to the high viscosity in the RTFO, another aspect that deserved particular focus was the thickness of the mastics in the PAV pan. Considering the metal pan used in the PAV (145 mm diameter) and the amount of bitumen pored (50 g), the film thickness of the bitumen in the pan is approximate of 3.2 mm. The density of mastics is higher than the density of bitumen, therefore, to achieve the same amount of bitumen and have a similar film thickness, the amount of mastic in the PAV was increased. Based on the concentration of the filler (25% by volume or 84% by weight), and the specific gravity of the filler (2.59 g/cm^3), the amount of mastic in the bitumen pan was of 68.9 g.

Once the shortcomings related to the applicability of the RTFO and the PAV have been somehow tackled, the mastics were PAV-aged (at 100°C 2.07 bars) by using the following time exposures.

Table 7-2 – Mastics PAV time exposures

0 hours	25 hours	65 hours	105 hours
Equivalent bitumen exposures			
Unaged (or after modification in PMB)	RTFO + 1 PAV	RTFO + 3 PAV	RTFO + 5 PAV

Comparing the exposure of mastics with those used for the bitumens (Table 3-3), it is evident that the mastics were aged for a longer time in the PAV. This procedure was followed to make sure that the PAV ageing was severe enough to provide evident changes in the rheological response. Nevertheless, except for 105 hours, the range between 0 hours and 65 hours is compatible with the time range used in the bitumen. Besides this, the comparison between the bitumen and the mastics is undertaken in terms of the trend of results.

7.3.3 Multiple Stress Creep and Recovery (MSCR) test of mastics

The experimental matrix of the MSCR test conducted on mastics is given Table 7-3.

Table 7-3 – Experimental matrix MSCR test conducted on mastics

Mastic	MSCR Temperature [°C]
Pen_M	64
SBS 2/S _M	70
SBS 4/S	75
SBS 6/S	87

The MSCR test temperatures adopted for mastics are those adopted for the bitumens. Besides the traditional stress levels of 0.1 kPa and 3.2 kPa, an additional stress level of 10 kPa (10 creep and recovery cycles) was added for mastics (228, 229) (Figure 7-2).

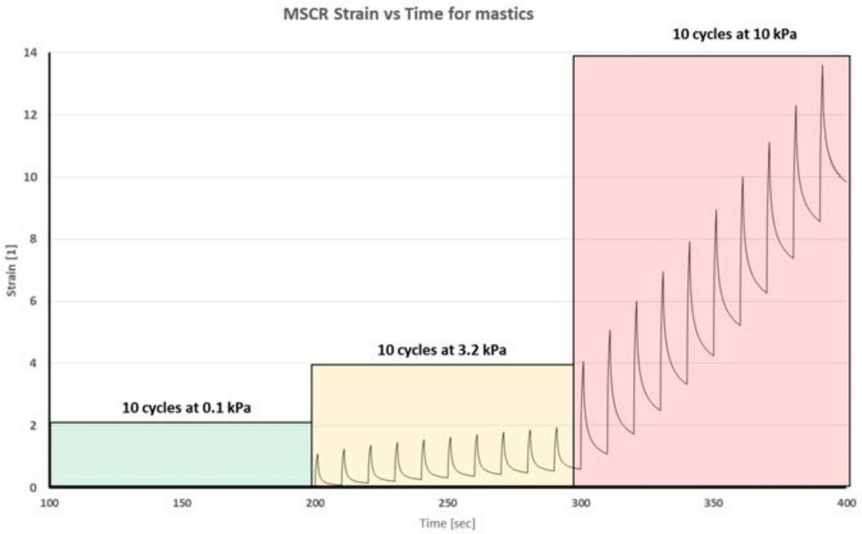
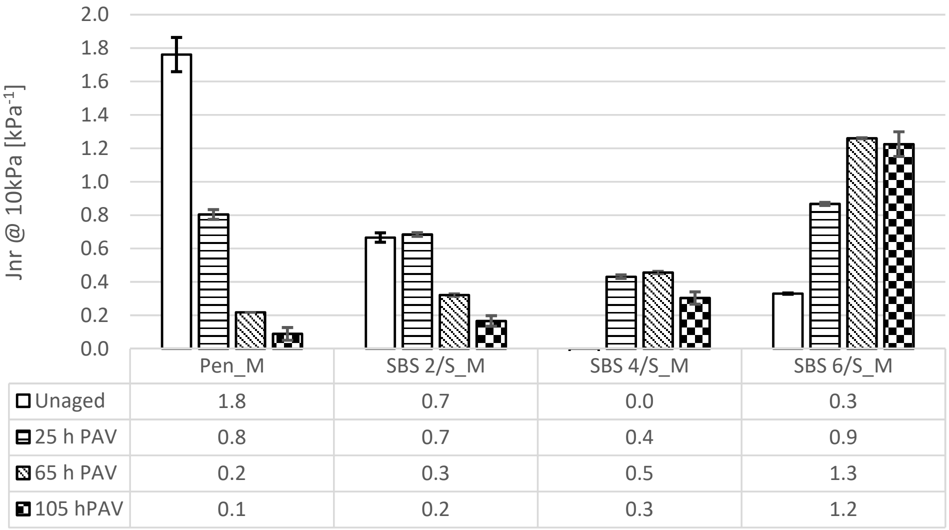


Figure 7-2 – MSCR strain with time for mastics

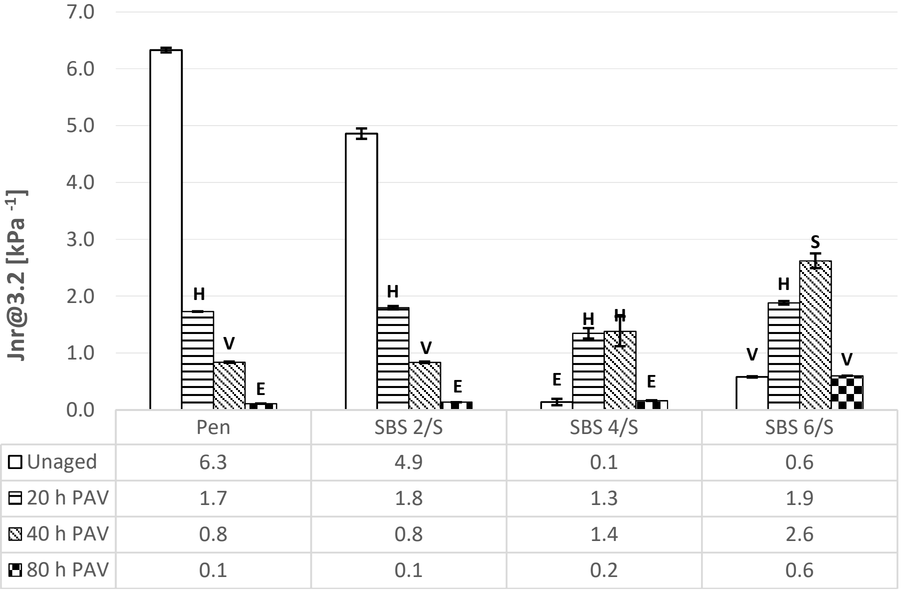
The summary chart of the non-recoverable compliance at 10 kPa is included in Figure 7-3.



	Pen_M	SBS 2/S_M	SBS 4/S_M	SBS 6/S_M
☐ Unaged	1.8	0.7	0.0	0.3
▤ 25 h PAV	0.8	0.7	0.4	0.9
▨ 65 h PAV	0.2	0.3	0.5	1.3
▦ 105 hPAV	0.1	0.2	0.3	1.2

Figure 7-3 – Variation of J_{nr} @ 10kPa of mastics at different PAV time exposures

The variation of the J_{nr} at 3.2 kPa measured on the corresponding bitumens is given in Figure 7-4.



	Pen	SBS 2/S	SBS 4/S	SBS 6/S
☐ Unaged	6.3	4.9	0.1	0.6
▤ 20 h PAV	1.7	1.8	1.3	1.9
▨ 40 h PAV	0.8	0.8	1.4	2.6
▦ 80 h PAV	0.1	0.1	0.2	0.6

Figure 7-4 - Variation of J_{nr} @ 3.2kPa of bitumens at different levels of ageing

The variation with the ageing of the J_{nr} of the mastics is similar to those of the corresponding bitumens. In the case of unmodified bitumen (Pen - Figure 7-4) and mastic (Pen_M - Figure 7-3), the J_{nr} decreases with ageing as a consequence of the bitumen PAV-oxidative hardening.

In the case of polymer-modified mastics, the trend of the results is a function of the polymer concentration. The mastics show a similar trend to as those of the corresponding bitumens (Figure 7-3). In the case of medium-low polymer concentration (SBS 2/S_M), the J_{nr} decreases with the PAV exposure (similarly to as Pen_M). At high polymer concentration (SBS 4/S_M), there is a sort of equilibrium between 25 and 65 hours and then, a decreasing trend after 105 hours is displayed. At very high polymer concentration (SBS 6/S_M) the J_{nr} increases with ageing to become somehow stable at 105 hours. In the case of 2% and 4% SBS, the trend of the mastics is similar to as the trend of the bitumens even at very high oxidative levels.

On the other hand, at very high SBS concentrations (6%) the trends of the bitumen and the mastic are similar within the intermediate exposures. Then, if the J_{nr} of the bitumen (SBS 6/S - Figure 7-4) drops after 4 cycles of PAV, the J_{nr} of the mastic (SBS 6/S_M - Figure 7-3) remains somehow constant. Probably, to observe the same sharp reduction, a more prolonged PAV exposure is needed.

The scope of this part of the experiment was to verify whether the same results observed in the PMBs applied to the corresponding mastics. Although the test conditions used for bitumens differ for those used by mastics, the results seem to be aligned.

8 Conclusions, limitations and recommendation for future works

This work investigates the effects of laboratory-simulated ageing on the microstructure and rheological response of PMBs. Besides PMBs, the experiment includes a subsection where the rheological response of aged polymer-modified mastics has been compared with the one of the related PMBs.

A summary of the significant findings and conclusions of this thesis is given in the following sections.

8.1 Remarks from storage stability

The use of sulphur enhances the storage stability of the SBS modified bitumens (PMB/S). Besides this, the use of the cross-linker improves the level of dispersion of the polymer phase in the bitumen phase providing a more homogeneous structure. These results are supported by the existing literature.

8.2 Conclusions from fluorescence microscopy

- The EVA polymer is not prone to form a networked structure in the bituminous phase, but it remains dispersed as disconnected spherical droplets irrespective of the polymer concentration. The morphology of the EVA modified bitumens does not show a significant ageing susceptibility with the polymer dispersion remaining unaltered with ageing irrespective of the polymer concentration.
- The morphology of the SBS polymer network degrades with ageing as a function of polymer concentration and dispersion. The network resistance seems to increase with polymer concentration and dispersion. However, at very high SBS content (i.e., 6%), the high level of viscosity (and possibly of surface tension) may mitigate the effects of the

RTFO and the PAV ageing. Alternatively to polymer degradation, the de-swelling of SBS could be considered as an interpretation of the variation in morphology with ageing.

- A comparative analysis of the morphology of the SBS and the EVA modified bitumens used in this study highlights that the two polymers have a different ageing susceptibility with the EVA being more resistant than the SBS. However, the ageing susceptibility of the SBS polymer has been remarked by other authors.

8.3 Conclusions from the GPC test

- The polymer phase of the SBS modified bitumens (10-12 minutes) was not visible in the chromatograms, presumably due to the high level of reticulation that does not allow the THF solvent to dissolve this phase.
- The Pen and Pen/S bitumen showed an increase in the portion of the heavy fractions up to 1 cycle of PAV. Afterwards, the portion of heavy fractions appears to remain stable within the test variability. The addition of 0.1% sulphur appears to mitigate the formation of the heavy fractions slightly.
- The results of the GPC on the PMB/S modified binders highlight the fact that the changes in R_H at different levels of ageing depend on the polymer concentration and can be caused by three mechanisms: volatilization of the light fractions during RTFO ageing; polymer degradation (during blending, RTFO and PAV ageing); bitumen oxidative hardening in the PAV. The GPC test is unlikely to isolate the contribution of each mechanism. The first and the third are well-known ageing mechanisms while the second corresponds to the degradation of the polymer chains that reduce their size (and MW) with ageing. The reduction in MW causes an increase in retention time. In the case of the SBS 6/S bitumen, only the effect of the RTFO ageing is visible in the GPC while the PAV ageing has a reduced

effect due (probably) to the high consistency of the bitumen at the PAV temperature (100°C). In the case of the SBS 2/S and SBS 4/S, the three mechanisms are all visible. The degraded polymer fragments are detected in the region of the heavy bitumen fractions between the unaged and 2 PAV aged conditions. Their amount seems to increase with ageing up to 2 PAV. Then, after 4 PAV, the degradation of the polymer chains is so high that they are detected with the light bitumen fractions with a consequent reduction in the proportion of the heavy fractions. At this stage of the research, this mechanism is considered as a hypothesis whose validity finds some uncertainties due to the possible limitations of the THF to dissolve the chemical compounds formed in the PAV.

- In the case of the SBS modified bitumens without cross-linker (i.e., SBS 4, and SBS 6), the variation of the heavy fractions is similar to the one shown for the unmodified bitumens with the microstructure being less resistant to RTFO and PAV ageing than the cross-linked SBS modified bitumens.
- Besides storage stability and a higher polymer dispersion, the use of the cross-linker makes the polymer network more resistant to the effects of laboratory-simulated ageing. Therefore, the SBS concentration alone might not be indicative of the thermo-oxidative resistance of the polymer network in PMBs. The use of cross-linker during polymer modification should be considered.

8.4 Conclusions from the LVE characterisation

- Two portions of the black diagrams have been analysed. The first focuses on the analysis of the isotherms at intermediate and low temperatures (i.e., 4°C, 16°C, and 28°C). The second on the isotherms at high temperatures (i.e., 40°C, 52°C, and 64°C). In the first portion, the rheological response is more controlled by the bitumen-rich phase. While the second more by the polymer rich-phase.

- In the case of Pen bitumen black diagrams and master-curves have been used. Results show that laboratory-simulated ageing makes the material stiffer and more-elastic under cyclic loading. This results is in agreement with the literature on the topic. The microstructural changes observed in the GPC show that the stiffening and the reduction in the viscous response are accompanied by an increase in the heavy (and probably more polar) bitumen fractions.
- In cross-linked SBS modified bitumens, the presence of the polymer network influences the shape of the black diagram and the and its variation with ageing. At unaged conditions, the isotherms show a decrease of the phase angle at high temperatures where the rheological response is more controlled by the polymer-rich phase. The higher is the polymer concentration, and the lower are the phase angle values. At very high polymer concentration (i.e., SBS 6/S), the isotherms show that the PMB has a complex structure even at intermediate and low temperatures.

  Laboratory-simulated ageing (2PAV) produces the degradation of the polymer network and the hardening of the bitumen phase. Their effects are visible in the black diagrams depending on the polymer concentration:

    - **SBS 2/S bitumen**. The isotherms of intermediate-low temperatures show that the phase angle decreases with ageing as observed in the Pen bitumen. In the range of high temperatures, the isotherms tend to higher phase angles than in the unaged condition.

The bitumen-rich phase hardens with ageing, similarly to as the unmodified bitumen becoming more elastic under cyclic loading. The polymer-rich phase becomes more viscous due to the degradation of the polymer network. These results are visible in the Cole-Cole diagram as well. These aspects have been observed by other authors. Stiffness is observed to increase.

- **SBS 4/S bitumen.** The low-intermediate temperatures isotherms do not show relevant variations compared the unaged conditions. At higher temperature, the isotherms tend towards higher phase angles showing more viscous effects. The rheological changes highlight that the bitumen-rich phase does not seem to harden significantly, while the degradation of the polymer network is visible in the region of high temperatures. Comparing these results with those at lower concentration (i.e., SBS 2/S), it seems that at higher polymer concentration (and dispersion), the polymer network degrades and mitigates the hardening of the bitumen-rich phase that does not vary visibly its rheological response (except for becoming stiffer).

- **SBS 6/S bitumen.** The isotherms after two cycles of PAV evidence that the polymer network has been damaged. The shape of the black diagram becomes smooth within 4°C and 40°C with the isotherms that are well connected. Therefore, the structure of the PMB seems to have lost the complexity provided by the presence of the polymer network. Aside from this, no evidence shows that the phase angle is decreased as a consequence of the bitumen phase hardening. Therefore, considering what concluded at lower SBS concentrations, there is a reason to believe that at 6% SBS the bitumen-rich phase has been subjected to a negligible hardening in lieu of the polymer network that has been degraded in the PAV. At higher temperatures, the isotherms show an increase in the phase angle consequent of the degradation of the polymer network. The stiffness is observed to increase.

- In the EVA modified bitumen, the presence of the plastomer does not provide relevant variation in the viscoelastic response of the PMBs compared to the unmodified bitumens. In the intermediate-low temperature region (i.e., 4°C, 16°C, and 28°C), the isotherms shift to lower phase angles as a function of the polymer concentration. The higher is the polymer concentration, and the more elastic is the response under cyclic loading. In the region of high temperatures, the EVA does not provide the same visible effects of the SBS. In this range of temperature, the response of the bitumens becomes more viscous when the stiffness decreases. This behaviour is expected due to the plastomeric nature of the polymer. However, the isotherms at 52°C and 64°C of the EVA 4 and EVA 6 bitumens show some waves that might depend on the presence of different crystalline structures.

  The rheological response of the aged PMBs does not show relevant deviations from the one of the Pen bitumen irrespective of the polymer concentration. The laboratory-aged EVA modified bitumens become stiffer and more elastic under cyclic loading.

  The low effect of the EVA on the ageing susceptibility of the PMBs might depend on two aspects:

  1. The EVA polymer has a low oxidative susceptibility, and therefore, it does not deteriorate with the PAV exposure. As a consequence, the bitumen phase undergoes oxidation as if the polymer would not be present. The low PAV

susceptibility of the EVA polymer has been indicated by the fluorescence microscopy, which shows that the morphology of the EVA polymer does not vary with the PAV.

2. Besides a low PAV-susceptibility, the EVA appears to have low compatibility with the bitumen that is visible in the morphologies. Therefore, if the polymer phase remains separated, it may not be capable of mitigating the hardening of the bitumen phase.

8.5 Conclusions from the MSCR test

- The J_{nr} values of the Pen bitumen decrease with ageing due to the oxidative hardening occurring in the RTFO and the PAV. At high oxidative levels, the bitumen hardening produces an increase in the average percent recovery measured in the DSR. The bitumen modified with Sulphur (Pen/S) shows the same behaviour.
- The rheological response of cross-linked SBS modified bitumens (i.e., SBS 2/S, SBS 4/S, and SBS 6/S) varies with ageing as a function of the polymer concentration. Specifically, the higher the polymer concentration, the more the SBS mitigates the effects of the hardened bitumen phase on the MSCR response. Separate considerations for the different polymer contents are given as follows:
  - At medium-low concentration (2%), the trend of the rheological parameters (J_{nr} and R) does not deviate from those of the unmodified bitumen.
  - At high concentration (4%), the polymer network is damaged in the RTFO and the PAV. Nevertheless, between the RTFO and two cycles of PAV, the SBS phase is capable of balancing the hardening of the bitumen phase with the J_{nr} values showing limited variation. At higher oxidative levels, the polymer network is

  sensibly damaged, and the rheological response is controlled by the hardened bitumen-rich phase. Therefore, the J_{nr} that decreases and the average percent recovery that raises.
  - At very high SBS concentrations (6%), the polymer phase controls the rheological response from the unaged conditions up to two cycles of PAV. The polymer network is damaged in the PAV with the RTFO providing negligible effects. Between the RTFO and two cycles of PAV, the J_{nr} increases with ageing reversely with what is observed in the unmodified bitumen. At higher oxidative levels, the same behaviour of the SBS 4/S bitumen is observed.
  - Results show that the use of the average percent recovery as an indicator of the integrity of the polymer network can be advocated.
- The comparative analysis of MSCR and GPC data of the cross-linked SBS modified bitumens (i.e., PMB/S) helps to raise some considerations. The higher the polymer content, the more the fragments of the polymer chains of a specific size (and molecular weight) are capable of mitigating the oxidative hardening of the bitumen. In the case of 2% and 4% SBS, the correspondence between the size of the fragments of the polymer chains and the MSCR response is visible when comparing the GPC and the MSCR results. In the case of the 6% SBS the GPC findings are not helpful since the limited variation of R_H during PAV ageing does not support the macroscopic changes observed in the rheological response.
- In the SBS modified bitumens without the cross-linker, the effect of the polymer on the rheological response vanishes after the RTFO irrespective of the polymer concentration.

- The comparative results between cross-linked SBS bitumens and un-linked SBS bitumens highlight that the combined use of sulphur and SBS changes the resistance to hardening during artificial ageing of the SBS modified bitumens considered in this work. The available data do not allow the contribution of sulphur to be isolated. However, the cross-linked SBS modified bitumens (SBS + sulphur) are likely to have different resistance to hardening during artificial ageing than un-linked SBS modified bitumens at the same polymer concentration. Therefore, in the study of the anti-oxidative properties of SBS, properties such as polymer stability and level of dispersion (using morphology) should be taken into consideration.

8.6 Conclusions from the LAS test

- Laboratory-simulated ageing of bitumens has been observed to increase their capacity to maintain integrity with damage and to decrease their time-temperature susceptibility. The first effect is given by the increase in stiffness with ageing, and it is visible in the increase of the intercept with the y-axis of the fatigue law (Wholer curve). On the other hand, the second effect increases the magnitude of the slope of the Wholer curve. To estimate the contribution of ageing to the cumulative damage resistance, the two effects need to be combined by considering the maximum strain level experienced by the bitumen phase in mixtures.
- Results of this combination show that for each bitumen, it is possible to define a strain value that represents a threshold for ranking the effects of ageing as positive or negative. Below this strain level, the cumulative damage resistance increases with ageing, while above this range, it decreases. These results have been observed by other authors. Below

a strain of 1%, all the bitumens show an increase in the cumulative damage resistance with ageing.

- Part of the LAS results has been verified using the time sweep test. The TS test induces damage through the application of repeated loading instead of increasing the strain applied. Contrarily to what observed in the LAS test, at the strain of 1%, the time sweep test shows that the cumulative damage resistance decreases with ageing. While at higher strain levels, the two tests allow similar conclusions. Therefore, the applicability of the VECD theory at such a low strain level (for the temperature considered) requires some caution.
- Polymer modification does not alter the mechanism observed but affects the magnitude of the changes observed. Some conclusive considerations can be drawn for each polymer.

    Cross-linked SBS modified bitumens. The fatigue life at a defined strain level increases as a function of the polymer concentration. The higher is the polymer concentration, and the higher is the number of cycles to failure. However, the gain in the cumulative damage resistance is a function of the level of integrity of the polymer network in the bitumen. Between the unaged and 2PAV-aged conditions, SBS modified bitumens have higher fatigue cracking resistance than the unmodified bitumen. Then, after the RTFO and four cycles of PAV, the unmodified bitumen and the PMBs have similar damage resistance. At this level of ageing, the polymer network has undergone extensive damage; as a consequence, there is a reason to believe that at 4PAV-ageing, the rheological response is controlled by the PAV oxidative-hardened bitumen-rich phase. Therefore, it seems that the bitumen-rich phase of the PMBs has undergone the same PAV-oxidative hardening of the plain bitumen irrespective of the presence of the polymer.

- **EVA modified bitumens.** Polymer modification increases the cumulative damage resistance as a function of the polymer concentration. The higher is the polymer concentration, and the higher is the resistance. At 2PAV-ageing, EVA 6 shows the highest material capacity to maintain integrity with damage, and the highest number of cycles to failure at the strain level of 2.5%. The cumulative damage resistance is observed to increase with ageing as a function of the polymer concentration, at the strain of 2.5%; while it has shown a low ageing susceptibility at the strain of 5%. However, at both the strain levels, the PMBs have shown a higher number of cycles to failure compared to the unmodified bitumen. These results are indicative of a low PAV-susceptibility of the polymer network that has also been observed by the fluorescence microscopy and the LVE characterisation.

8.7 Conclusions from tests on polymer-modified mastics

Polymer-modified mastics have been introduced to investigate the effects of the PAV-oxidative ageing on rheological response measured at the mastic scale (§7). SBS modified mastics have been laboratory aged by multiple cycles of PAV and have been tested in the MSCR by including an additional stress level.

The comparative analysis between the results of the SBS modified bitumen and mastics highlights that the laboratory simulated ageing provides the same trend of the rheological results with ageing. Specifically, the unmodified mastic hardens with ageing as observed in the Pen bitumen. While the variation is the response of the SBS modified mastics is a function of the polymer concentration as observed in the related PMBs. Although limited in number, results are promising.

8.8 Achievement of the research

This section includes an overall evaluation of the research versus the objectives that have been proposed and versus the research hypothesis.

8.8.1 Objective 1

The first identified objective has been: *"To provide a more precise understanding of the effects the bitumen-polymer compatibility on the laboratory-ageing susceptibility of SBS and EVA modified bitumens".*

The findings of the research that can demonstrate the fulfilment of Objective 1 are discussed below:

- **SBS modified bitumens.** The research has identified that there is a tremendous difference between the PAV-hardening resistance of cross-linked SBS modified bitumens and uncross-linked SBS modified bitumens.

  In the case of cross-linked SBS modified bitumens, the polymer-bitumen compatibility has been prompted by the presence of sulphur. The cross-linked the polymer has shown a higher level of polymer dispersion and reticulation (Fluorescence microscopy). This type of polymer network has resulted in being more capable of mitigating the RTFO and the PAV-oxidative hardening of the bitumen phase (MSCR, GPC, LAS, and LVE). This capacity seems to depend on the polymer concentration. The higher is the polymer concentration, the more the polymer inhibits the bitumen PAV-oxidative hardening.

In the case of uncross-linked SBS, the dispersion of the polymer network is visibly low, and its effect on the rheological response almost vanishes after the RTFO.

- **EVA modified bitumens.** The EVA polymer adopted in this research has represented an example of polymer with low bitumen compatibility (Fluorescence microscopy), and a low RTFO and PAV susceptibility (Fluorescence microscopy, LVE, and LAS). The low compatibility and the low oxidative susceptibility have brought the polymer phase to remain undamaged, and the bitumen phase to be the one undergoing PAV-oxidative hardening without any mitigating effect of the polymer network.

8.8.2 Objective 2

The second identified objective has been: *"To identify the effects of laboratory-ageing on the microstructure of SBS and EVA modified bitumens, and to correlate them with the variation in the rheological response measured at strain levels higher than those used in the LVE characterisation".*

The findings of the research that can demonstrate the fulfilment of Objective 2 are discussed below:

- The microstructure of the PMBs has been evaluated in terms of morphology (Fluorescence microscopy), and MWD (for unmodified and SBS bitumens only). Both the tests have resulted in being supportive of the rheological responses of the bitumens.
    - In SBS modified bitumens, very detailed analysis has been conducted between the variation in the microstructure (fluorescence microscopy and GPC) and the MSCR test parameters of the SBS modified bitumens. This analysis has highlighted that while the SBS network has sufficient integrity, it is capable of mitigating the PAV-oxidative hardening of the bitumen phase. The same

conclusions have been supported by the LAS test in a different range of temperature and concerning a different damage mechanism.

  - In EVA modified bitumens, the polymer network has resulted in being ageing resistant (fluorescence microscopy). Its effect has not been that visible in the MSCR response since the test is conducted in a range of temperatures that might be very close to the melting temperature of the polymer. However, in the LAS test, the low ageing susceptibility of the polymer has contributed to providing the bitumen with a high capacity of maintaining its integrity under damage.

8.8.3 Objective 3

The third identified objective has been: *“To understand the effect of multiple levels of laboratory-simulated ageing on rutting and fatigue cracking resistance of bitumens”.*

The findings of the research that can demonstrate the fulfilment of Objective 3 are discussed below:

- The rutting resistance has been measured through the MSCR test, while the fatigue cracking resistance has been measured by the LAS test.
- The LAS test conducted on differently-aged bitumens has shown that the strain susceptibility of the cumulative damage resistance varies with ageing.
- In SBS modified bitumens, the use of multiple levels of laboratory ageing has allowed monitoring the degradation of the polymer network whose effects have been visible in the rheological response of the different tests.
  - The MSCR test has shown that the polymer degradation and the bitumen hardening provide an opposite contribution to the response. The first compensates the effects of the second by mitigating the decrease in the J_{nr}

    values. Furthermore, the average percent recovery has been observed as being a valuable rheological indicator of the integrity of the polymer network.
  - The LAS test has shown that the SBS increases the cumulative damage resistance a function of the integrity of the polymer network. At very high levels of PAV exposure, the effect of the SBS vanishes.
- In EVA modified bitumens, the use of multiple levels of ageing has shown the low oxidative resistance of the EVA polymer.
  - The LAS test has shown that the capacity of the material to maintain integrity with damage increases with ageing and that the polymer network is capable of resisting cumulative damage even at high levels of PAV-ageing.

8.9 Limitations of the research

The significant limitations that have been identified in this research are discussed as follows:

- This research is based on artificial ageing methods developed on unmodified bitumens. Their applicability to PMBs is still under discussion.
- The GPC identifies the bitumen and polymer molecules as per their size and not as per their type. Therefore the changes in the microstructure are provided in terms of light and heavy fractions while no information on the polarity of the molecules has been identified. For this reason, there are cases as the SBS 6/S where GPC findings are not helpful since the limited variation of R_H during PAV ageing does not support the macroscopic changes observed in the rheological response.

8.10 Recommendation for future work

Some recommendations for implementing future work are given as follows:

- Measure the changes in the functional groups by infrared spectroscopy and correlate the findings with the rheological results.
- Conduct LVE characterisation on 4PAV-aged SBS modified bitumens.
- Extend the PAV ageing of EVA modified bitumen to four cycles of PAV and conduct the LAS test and LVE characterisation.
- Expand the Time Sweep test experimental matrix to support the findings from the comparison with the LAS test.
- Consider expanding the experimental matrix incorporating additional tests on mastics and mixtures.
- Include field-aged bitumens in the experimental plan.

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