PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE
ESCUELA DE INGENIERÍA

UNDERSTANDING THE EFFECTS OF MICROWAVE HEATING AND LONG-TERM AGING ON THE RECOVERED BITUMEN

MATÍAS ANDRÉS FERNÁNDEZ GONZÁLEZ

Thesis submitted to the Office of Research and Graduate Studies
in partial fulfillment of the requirements for the Degree of
Master of Science in Engineering

Advisor:
ÁLVARO GONZÁLEZ VACCAREZZA

Santiago de Chile, December, 2020

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Try to reach the sky with your feet on the ground

ACKNOWLEDGEMENTS

I would like to thank to my family for their unconditional support during my life, specially to my mother Pamela González for her love, support and sacrifice, understanding and constant encouragement while I prepared this thesis.

I would like to express my gratitude and deep appreciation to Professor Álvaro González, my supervisor, who has provided assistance, advice, and encouragement without which this research would not have been possible. I have learned a lot from you during my studies.

I really appreciate the financial support received from Technische Universität Dresden, which gave me the opportunity to do an internship at the Institute of Urban and Pavement Engineering of Dresden. In addition, I am very grateful to Dr. Sabine Leischner and Dr. Gustavo Canon for their advice and support for this research. I would also like to thanks to René Schubert, Matthias Bisse and Mrinali Rochnali for their assistance during the experimental work.

Finally, many thanks to my friends who helped me in different ways and shared with me beautiful moments during my university period. Specially to my dear friend Ruben Tobar for his continuous support and friendship through the years.

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ABSTRACT

Asphalt mixture is one of the most common surface materials used for pavement construction, which provides good mechanical performance, economy, and construction advantages. Nevertheless, asphalt pavements have been exposed to more severe conditions due to increased traffic circulation and more extreme environmental conditions caused by climate change. Bitumen aging is one of the most important factors affecting its service life causing cracking of the pavements. Cracking occurs as result of the oxidation of the hydrocarbon compounds of bitumen. Self-healing of cracks in asphalt pavements by external microwave heating is a promising technology to build more durable asphalt pavements. Nevertheless, previous studies have shown that microwave heating technology at high temperatures could also damage the bitumen of the asphalt mixture, which is an unwanted effect of this crack-healing technique. This study aims to quantify the effects of microwave heating damage on the rheological and chemical properties of recovered aged bitumen. With this purpose, Stone Mastic Asphalt specimens were exposed to different cycles of microwave heating and long-term aging controlled in oven. The effects of microwave heating damage on the rheological and chemical properties of recovered aged bitumen were quantified through a frequency sweep test and Fourier Transform Infrared Spectrometry analysis, respectively. The results of recovered aged bitumen by microwave were compared with those obtained by normal long-term aging process. The main results indicate that microwave heating has no significant effect on the aging performance of G* and δ for aged asphalt mixtures. However, the rheological properties of bitumen show minor changes with microwave heating for newer asphalt mixtures. A strong relationship with the chemical and rheological results can be observed, which demonstrates that both properties can be potentially used as good indicators for assessing bitumen aging level. Overall, this study confirms that microwave heating is a sustainable alternative for maintenance of asphalt pavements, without severely affecting the rheological and chemical properties of bitumen.

Keywords: Asphalt pavements; Stone Mastic Asphalt; Aged bitumen; Self-healing asphalt; Microwave heating technology; Rheological and chemical properties.

RESUMEN

El asfalto es el material más utilizados en la construcción de pavimentos, ya que proporciona un buen desempeño mecánico, economía y ventajas en la construcción. Sin embargo, en los últimos años los pavimentos de asfalto han estado expuestos a condiciones más severas debido al aumento de la circulación del tráfico y a las condiciones ambientales más extremas causadas por el cambio climático. El envejecimiento del betún es uno de los factores más importantes que afectan a su vida útil causando el agrietamiento de los pavimentos. El agrietamiento se produce como resultado de la oxidación de los compuestos de hidrocarburos del betún. La auto-reparación de las grietas en los pavimentos de asfalto mediante el calentamiento externo por microondas es una tecnología prometedora para construir pavimentos de asfalto más duraderos. No obstante, estudios anteriores han demostrado que la tecnología de calentamiento por microondas a altas temperaturas también podría dañar el betún de la mezcla asfáltica, lo cual es un efecto no deseado de esta técnica de auto-reparación de grietas. Este estudio tiene por objeto cuantificar los efectos del daño causado por el calentamiento por microondas en las propiedades reológicas y químicas del betún envejecido recuperado. Con este propósito, los especímenes de *Stone Mastic Asphalt* fueron expuestos a diferentes ciclos de calentamiento por microondas y de envejecimiento a largo plazo. Los efectos de los daños causados por el calentamiento por microondas en las propiedades reológicas y químicas del betún envejecido recuperado se cuantificaron mediante una prueba de barrido de frecuencia y un análisis de espectrometría de infrarrojos por transformada de Fourier, respectivamente. Los principales resultados indican que el calentamiento por microondas no tiene un efecto significativo en el rendimiento de envejecimiento de G^* y δ para las mezclas asfálticas más envejecidas. Sin embargo, las propiedades reológicas del betún muestran cambios menores con el calentamiento por microondas para mezclas asfálticas más nuevas. Se puede observar una fuerte relación con los resultados químicos y reológicos, lo que demuestra que ambas propiedades pueden utilizarse potencialmente como buenos indicadores para evaluar el nivel de envejecimiento del betún. En general, este estudio confirma que el calentamiento por microondas es una alternativa sostenible para el mantenimiento de los pavimentos de asfalto, sin afectar gravemente a las propiedades reológicas y químicas del betún.

Palabras clave: Pavimentos asfálticos; *Stone Mastic Asphalt*; Asfalto envejecido; Asfalto auto-reparable; Tecnología de calentamiento por microondas; Propiedades reológicas y químicas.

STRUCTURE OF THE THESIS

The thesis document is organized in the following chapters:

1. **Introduction:** This introductory chapter presents a general background review to understand the problem under study. In addition, problem statement, proposed hypothesis, research objectives, and methodology of the thesis.

2. **Literature review:** This chapter presents the state of the art on the durability of asphalt pavements and on the new preventive maintenance work strategies. In addition, the chapter presents a literature review on bitumen aging and currents methods of evaluation.

3. **Journal Article:** Chapter 3 presents an article, submitted to the Journal of Cleaner Production, which presents my study of the Effects of microwave heating and long-term aging on the chemical and rheological properties of recovered bitumen.

4. **Conclusions and recommendations:** This chapter presents the conclusions of this research and recommendations for future research.

1. INTRODUCTION

1.1 Background

Asphalt mixture is one of the most common surface materials used for pavement construction, which provides good mechanical performance, economy, and construction advantages (González et al., 2018a). Despite its good properties as a road material, asphalt mixture deteriorates over time, due to increased traffic circulation and more extreme environmental conditions caused by climate change (Rochlani et al., 2019). Cracking is one of the most common forms of damage and it is caused by repetitive traffic loading and environmental factors that trigger bitumen aging (Y. Kim, Little, Asce, Lytton, & Asce, 2003). The aging of bitumen is one of the most important factors determining the lifetime of asphalt pavement. The phenomenon of bitumen aging mainly consists of an oxidation process and polymeric reaction, which modifies the microstructure of bitumen (Tauste et al., 2018). The process of aging involves changes in chemical and rheological properties that usually make bituminous materials harder and more brittle, thus increasing risk of cracking (Lu, Talon, & Redelius, 2008)

In order to maintain the desired performance of asphalt pavements during their service life, it is necessary to perform conservation and maintenance operations, which imply expensive investments, delay of traffic flow, and environmental pollution (J. Norambuena-Contreras, Serpell, Valdés Vidal, González, & Schlangen, 2016). The problem of preservation, maintenance and rehabilitation work is that its carried out over a long period of operation, triggering environmental pollution and delay of traffic flow and the final results may not be achieved as expected (Shuyin Wu, Yang, Yang, Zhu, & Liu, 2018). These consequences have necessitated the search for sustainable new alternatives to reduce maintenance, and this comes mutually with the intentions to reduce impacts to the environment caused by maintenance treatments (Zulu et al., 2020).

In recent studies, microwave radiation heating has been proposed as a new method of preventive maintenance of asphalt pavements (Gallego et al., 2013; J. Norambuena-Contreras, Gonzalez, Concha, Gonzalez-Torre, & Schlangen, 2018; J. Norambuena-Contreras et al., 2016; Jose Norambuena-Contreras & Gonzalez-Torre, 2017). Asphalt mixtures have the potential to restore stiffness and strength by closing the micro-cracks caused in the material as a result of traffic loads and severe environmental condition (Yalçın et al., 2018). Microwave power offers a new solution to healing asphalt pavements, a phenomenon known as self-healing of asphalt pavements. The development of self-healing asphalt and its use in road paving is an innovation that could potentially increase road lifespan between 40 to 80 years (Schangen & Tobakovic, 2015), which not only reduces the use of extra resources, but also reduces maintenance cost, and the greenhouse gas emissions (Chung et al., 2015).

1.2 Problem Statement

The self-healing of asphalt mixture is a temperature dependent phenomenon, and it is necessary to heat the bitumen for a sufficient time to reach an adequate viscosity change for healing (Quantao Liu, Schlangen, Van De Ven, et al., 2012). Previous research has reported that the self-healing of asphalt mixtures by microwave heating can be achieved with a heating time of 40 seconds (Jose Norambuena-Contreras & Gonzalez-Torre, 2017). Norambuena-Contreras and Garcia (J. Norambuena-Contreras & Garcia, 2016) evaluated the surface temperature of dense asphalt mixtures with different percentages of metallic fibers for various heating times, observing that samples with 8% fibers reached 135ºC after 120 seconds of heating. However, when the temperature is too high, it may decrease the healing level due to drainage of the bitumen under gravity. Bitumen also tends to suffer more serious aging at higher temperatures (Tang et al., 2016), and the oxidation process of its components can accelerate significantly, which could potentially decrease the durability of the mixtures. Thus, microwave heating can age the bitumen in the asphalt mixture, which is an unwanted effect of the crack-healing technique.

The influence of temperature on bitumen by effect of the microwave heating was investigated for the first time by Norambuena-Contreras and Garcia (2016). To do this, authors carried out thermogravimetric analysis on virgin bitumen combined with microwave heating tests on asphalt mixture samples in a range of fibers amounts before and after several heating cycles. The main results proved that the temperature of the binder under microwave heating can be higher than the flash point temperature of bitumen, and consequently microwave heating may damage the chemical structure of the binder used into the self-healing asphalt mixtures. This result has not been tested on mixtures without fibers.

Additionally, Wu et al. (2018) investigated the aging effect of microwave heating on the physical properties of bitumen. In this investigation, the bitumen was heated to a target temperature of 150ºC and cooled down to room temperature (25ºC). The researchers measured the penetration, ductility and softening point of the bitumen after, one, three, and five microwave-heating cycles, which were used to evaluate the aging. The results showed that after the five cycles of microwave heating, a reduction of 3.87% in penetration value, 9.19% increase of softening point and 25.93% decrease of ductility were reported. They found no clearly negative effect of microwave heating and concluded that this method causes slight aging on the bitumen. Nevertheless, these physical properties are an empirical measurement that cannot effectively describe viscoelastic characteristics of bitumen and fails to correlate well with asphalt mixture performance (Airey, 2002). Moreover, Wu et al. (2018) did not analyze the chemical variation of the functional groups of the bitumen, which are good indicators to evaluate the aging effect (Ge et al., 2019). Therefore, a further analysis by rheological and chemical parameter is required for the evaluation of the microwave heating on the aging bitumen.

The study of the bitumen rheology is adopted in most of the studies about bitumen aging (Cheng et al., 2020; Gao et al., 2018; Zhang et al., 2018a). The advantage of rheological indices is that some of them have been proven to be more associated with pavement performance than the physical properties of the bitumen (Zhang et al., 2018a).

This performance enables characterizing bitumen at a certain temperature, which is related to both the constitution (chemical composition) and structure (physical layout) of the molecules in the material. The rheological analysis is commonly carried out using a Dynamic Shear Rheometer (DSR) and is usually focused on the evolution of Complex modulus (G*) and the Phase angle (δ) under different temperatures or frequencies (Tauste et al., 2018). These results can be complemented with chemical analysis by FTIR test, which provides the most effective method to confirm the oxidation aging of bitumen (Villegas-villegas, Loria-salazar, Rica, Rica, & Rica, 2015).

1.3 Hypothesis

Microwave heating is a promising alternative for preventive maintenance of asphalt pavements because the increase in the functional group carbonyl and sulfoxide does not affect more than 30% of the complex module and 5% of the phase angle of the bitumen.

1.4 Research Objectives

1.4.1 General Objective

Evaluate the effect of microwave heating and long-term aging on the chemical and rheological properties of recovered bitumen.

1.4.2 Specific Objectives

(1) Evaluate the rheological effect of bitumen using the complex modulus (G*) and phase angle parameters (δ) based on frequency sweep test after microwave heating and long-term aging cycles.

(2) Determine the change in molecular composition of bitumen using Fourier Transform Infrared Spectroscopy (FTIR) after microwave heating and long-term aging cycles.

1.5 Scope of the research

This is a research initiative that intends to evaluate the effect of microwave heating and long-term aging on the chemical and rheological properties of recovered bitumen that have not been clearly evaluated in the past. To achieve this, a comprehensive laboratory study was conducted using a conventional microwave oven of 900W and 2.45GHz for microwave heating and a conventional heating oven for long-term aging of the samples.

In both phases, the specimens were manufactured with a bitumen 50/70 pen, however with a different aging mode. In addition, in both phases the specimens were manufactured without metallic fibers.

1.6 Methodology

This research was done in two phases, where the bitumen used was treated under two different modes of aging: (1) *Mode I:* fresh bitumen used for the SMA manufacturing under method 1 was aged using hot air and UV light to simulate a long-term aging of 6 years of service life. In total, using this aged bitumen 8 SMA test specimens were prepared and tested. (2) *Mode II:* bitumen within SMA cores only reproduce the short-term aging conditions during pavement construction. In total, 8 SMA test specimens were evaluated under this mode. Phase I includes the chemical and rheological tests performed on the bitumen aged with *Mode I*. In Phase 2, the same tests were performed with the difference that the bitumen aged in *Mode II* was used.

Initially, several Stone Mastic Asphalt (SMA) test specimens were manufactured at a mixing temperature of 165ºC through two methods: (1) conventional SUPERPAVE preparation under laboratory conditions, and (2) preparation in asphalt plant, which was then placed and compacted on a test track, where several cores were drilled out. To study the aging effect on the bitumen under two different methods, the specimens were exposed to various cycles of microwave heating and long-term aging. The heating time on the microwave was set to 40 seconds following the recommendations given by Norambuena-Contreras and Gonzalez-Torre (Jose Norambuena-Contreras & Gonzalez-Torre, 2017). The microwave heating was repeated four times with 40s of rest period (i.e. without heating) to improve the heating distribution through the test specimens. The long-term aging procedure was applied in a conventional oven during 72 ± 0.5 hours at 85ºC. Further details of this procedure will be explained in the following section.

In both phases, the aged bitumen was separated from the aggregates (bitumen extraction) using a dissolution of trichloroethylene according to the standard EN 12697-4 (British Standard Institution., 2005), in order to perform the frequency sweep and FTIR tests. Finally, the rheological and the chemical changes after the microwave and long-term aging are analyzed. The proposed experimental plan is presented in the Figure 1.1.

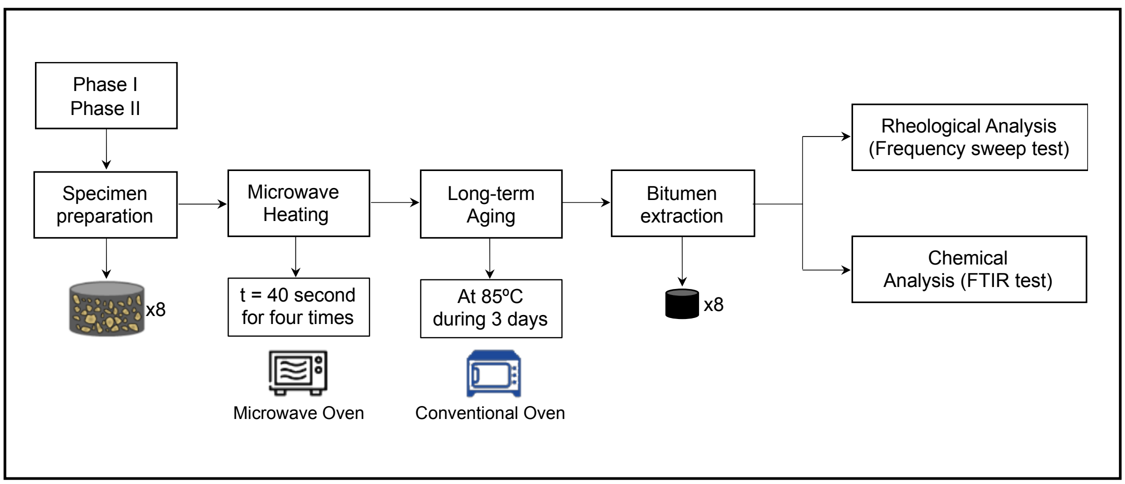

Figure 1.1. Schematic diagram of the experimental plan in this research work.

2. LITERATURE REVIEW

2.1 Durability of asphalt pavements

Road infrastructure is essential for the development of a country, providing mobility, economic growth, access to goods and services, and promoting social equality (Lizasoain-Arteaga, Indacoechea-Vega, Pascual-Muñoz, & Castro-Fresno, 2019). Pavements are the main load carrying structure in a road, and asphalt is the most common material used for pavements as a result of its good mechanical, economical, and construction advantages (González, Norambuena-Contreras, Storey, & Schlangen, 2018a). For example, in the United States 94% of pavements are surfaced with asphalt, while in the European Union more than 90% of the road network is surfaced with asphalt (EAPA, 2019). Despite its good properties as a pavement material, asphalt, as other pavements materials, deteriorates with time, being cracking the most common distress. This condition is mainly caused by repetitive traffic loading and environmental factors that trigger bitumen aging. In recent years, pavement structures have been deteriorating at a high rate, which has led to a rapid decrease in pavement durability (Rochlani et al., 2019).

The durability of pavements decreases due to a series of variables, such as aggregate characteristics, rheological properties of bitumen, type of mixture and environmental and traffic effects after construction (Hicks, 1991). However, the most important issue associated with durability reduction is the aging of bitumen (Zhang, Chen, Xu, & Shi, 2018a). The phenomenon of aging bitumen consists mainly of the loss of its volatile components, along with an oxidation process and polymer reactions that produce changes in its chemical composition (Tauste, Moreno-Navarro, Sol-Sánchez, & Rubio-Gámez, 2018). The oxidation process could be considered the principal mechanism of aging. This mechanism is the irreversible chemical reaction controlled by thermal reaction between oxygen molecules and the bitumen components, which modifies its chemical features (Sirin, Paul, & Kassem, 2018; Tauste et al., 2018). Consequently, the chemical changes of the bitumen have an impact on the rheological properties with an increase in the viscosity and the stiffness of the bitumen (Lesueur, Teixeira, Lázaro, Andaluz, & Ruiz, 2016). In addition, asphalt mixtures become excessively hard and brittle and thus susceptible to disintegration, fatigue and low temperatures cracking (Sirin et al., 2018).

As a result, maintenance is necessary in order to achieve a high-performing, safe, and cost-effective pavement network for users. Preventive strategies are the most important work during the operation stage of the roads, because they enhances the overall condition of the network and simplifies later decisions about resource distribution (Flintsch & Bryce, 2014). Figure 2.1 shows different maintenance thresholds according to the life cycle of a pavement structure:

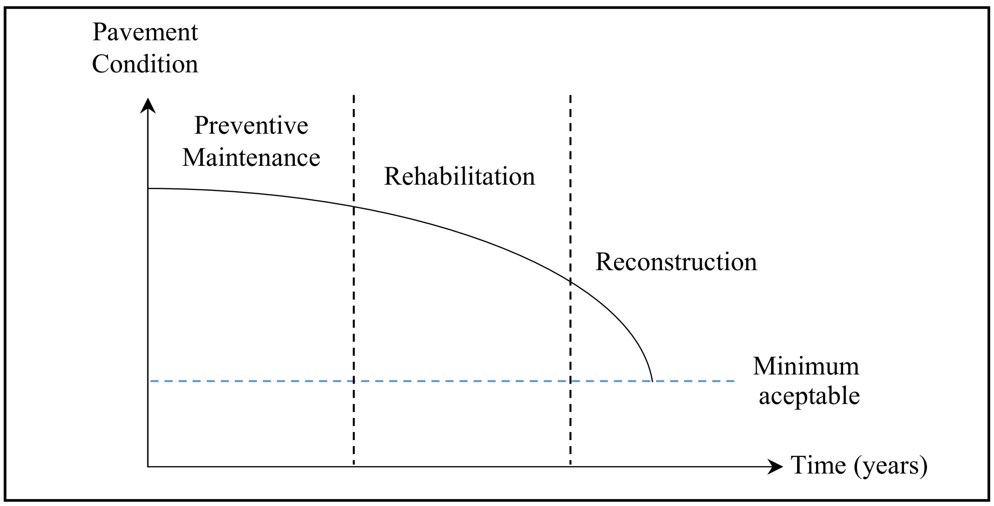

Figure 2.1. Concepts of life cycle assessment for a pavement

Adapted from (Zaniewski & Mamlouk, 1999)

Preventive work focuses mainly on the surface layer and seeks to prevent road deterioration, reducing the harmful effects of aging and the deterioration of the surface layer of the pavement, thus increasing the durability of the asphalt pavement. The most common treatments are crack, slurry, and chip seal applications (Chehovits & Galehouse, 2010). On the other hand, maintenance strategies are used to repair elements in order to improve the functional and/or structural capacity of the asphalt pavement. When accelerated deterioration takes place, rehabilitation work is required, with the aim to recover the structural capacity of the pavement. In general, if proactive preservation treatments are not used, asphalt pavements will deteriorate rapidly and will require rehabilitation with structural coatings much earlier than estimated (Zaniewski & Mamlouk, 1999).

The problem of preservation, maintenance and rehabilitation work is that its carried out over a long period of operation, triggering environmental pollution and delay of traffic flow and the final results may not be achieved as expected (Shuyin Wu, Yang, Yang, Zhu, & Liu, 2018). Also, the maintenance activities consume a lot amount of energy, cost financially, and nonrenewable recourses (Dinis-Almeida & Afonso, 2015). The economic impacts are considerable, for example in 2015, the United States expended US$ 3.3 billion into the development and maintenance of roads networks and in the European Union expenditure was around US$ 14.8 billion (Yalçın, Norambuena-Contreras, García, & Yilmaz, 2018). When deterioration occurs in asphalt pavements, multiple improvement works can be carried out to ensure the serviceability. For example, the use of additives, such as antioxidants and rejuvenators has become a common practice, with the aim to extend the pavements life, by increasing the performance and resistance of the asphalt. However, although additives can extend the service life, this method is based on extending maintenance and repairing work for only a few years (Yalçın et al., 2018). These consequences have necessitated the search for sustainable new alternatives to reduce maintenance, and this comes mutually with the intentions to reduce impacts to the environment caused by maintenance treatments (Zulu, Singh, & Shaba, 2020).

2.2 Self-healing of asphalt pavements

As previously mentioned, maintenance works have a great economic and environmental impacts. In last years, the development of self-healing asphalt and its use in asphalt pavements is a promising technology to build more durable asphalt pavements and reduce the maintenance and preservations works (Schangen & Tobakovic, 2015).

Self-heling can be defined as the ability of a material to repair the damage occurred in its service life, either automatically or activated by external stimuli (Ayar, Moreno-Navarro, & Rubio-Gámez, 2016). Some materials have this intrinsic capability, as in the case of the asphalt mixtures (Norambuena-Contreras & Concha, 2016; Schangen &

Tobakovic, 2015). Asphalt mixtures have the potential to restore stiffness and strength by closing the micro-cracks caused in the material as a result of traffic loads and severe environmental condition (Yalçın et al., 2018).

The healing capability of the asphalt mixtures is mainly due to the intrinsic viscoelastic and thermoplastic properties of the bitumen when it is exposed to temperature variation. When exposed to temperatures between 30ºC and 70°C, the bitumen in asphalt mixtures reduces its viscosity and begins to flow through micro-cracks (Ayar et al., 2016), in a motion similar to capillary flow (García, 2012). When pavement cools down to lower temperatures, the bitumen that sealed the crack increases its viscosity, healing or recovering the mechanical properties of the mixture (Gallego, Del Val, Contreras, & Páez, 2013). That happens only when asphalt pavement is subjected to rest periods, i.e., when asphalt roads are not exposed to traffic loads (Norambuena-Contreras & Garcia, 2016). Otherwise, traffic loads could open the cracks even more. Also, this natural healing capability is limited to the repair of microcracks, since macrocracks do not close unless external forces are applied to press the cracked surface together (Jones & Dutta, 2010).

Currently, investigations regarding the self-healing asphalt mixtures have been classified as a new method of preventive maintenance of asphalt pavements (Ayar et al., 2016). The development of self-healing asphalt could decrease maintenance cost and eventually reduce greenhouse gas emission (Chung, Lee, Park, Yoo, & Hong, 2015). Furthermore, the use of recycled materials such as fibers and metal shavings has become a common practice with the aim of: (1) improving the thermal conductivity and homogenization of the heating in the mixtures, and (2) developing asphalt pavements that are environmentally sustainable (González, Norambuena-Contreras, Storey, & Schlangen, 2018b). As a preventive maintenance technique, it is expected that its application will be carried out periodically every certain year to reduce the damages that occurred during the long-term aging of the asphalt pavements. In this context, a recent study published by Rodríguez-Alloza et al. (Rodríguez-Alloza et al., 2019) in 2019 have established that self-healing roads could prevent a considerable amount of emissions and costs over the global road network. In short, 16% lower emissions and 32% lower costs compared to a conventional road over the lifecycle.

2.3 Self-healing by means of external heating and capsules

The healing capability of asphalt mixtures is a temperature-dependent phenomenon (Tang et al., 2016) with the temperature as the dominant factor influencing the healing process. An increase in the temperature of the pavement not only increase the self-healing rate but also shortens the total time needed for full healing (Liu, 2012). This process is very slow at room temperature at typical 25ºC, but begins at temperatures between 30ºC and 70ºC (Ayar et al., 2016). It has been shown that the use of external energy can enhance the self-healing capability by increasing its temperature (Menozzi, Garcia, Partl, Tebaldi, & Schuetz, 2015). Currently, two external heating technologies for self-healing asphalt pavements have been reported: (1) Electromagnetic induction heating and (2) Microwave heating. Additionally, rejuvenator microcapsules have been used as a method of self-healing of asphalt mixture (Ayar et al., 2016).

2.3.1 Electromagnetic induction heating

Electromagnetic induction heating is one of the most widely used methods for improving the self-healing capability of asphalt pavements. Nowadays, it is even considered as a preventive maintenance technique. (Quantao Liu, Schlangen, van de Ven, et al., 2012). When this method is used, electrically conductive and magnetically susceptible particles must be included in the bituminous materials (Ayar et al., 2016), which is the reason some researchers have developed asphalt mixtures with the addition of metallic fibers to increase the electrical conductivity of the mixtures (Xu et al. 2018). With this method, an induction heating device generates alternate electromagnetic fields that affect the ferrous particles in the mixture, achieving an increase of temperature by the Joule principle (Norambuena-Contreras & Garcia, 2016). At the same time, thermal energy is diffused into the asphalt mixture, increasing the temperature of the bitumen (Liu, Garcia, Schlangen, & Ven, 2011) and generating the self-healing process. One of the most important limitations of this technique is that the mixtures require metallic fibers in order to generate an increase in temperature of the mixture, otherwise without this, the magnetic induction does not have the capacity to heat and change the viscosity of the bitumen.

2.3.2 Microwave heating

Microwave power also offers a new solution to healing asphalt pavement cracks. Bituminous mixtures were found to readily absorb microwave power at 2.45 GHz to depths of 12 cm, without overheating the surface layer of the asphalt pavement (Bosisio, Spooner, & Granger, 1974). With this technique, asphalt pavements are exposed to alternating electromagnetic fields, affecting the water and bitumen in the mixture and specifically the aggregates, as they have a great capacity to absorb heat. The microwave radiation causes them to create electromagnetic waves that change the orientation of the polar molecules of the mixture, generating internal friction and an increase in the temperature of the pavement (Norambuena-Contreras & Concha, 2016). The use of metallic fibers with this technology is optional, as heating occurs equally with or without fibers. The benefit of modifying the mixtures with these ferrous particles is that the distribution of the heating in the mixture is improved, because they can reflect the microwave radiation and accelerate the temperature increase (González et al., 2018b).

Norambuena-Contreras & Garcia (2016) have studied the healing effect of microwave and induction heating for asphalt mixtures and found that self-healing of cracks with microwave heating is more efficient than electromagnetic induction heating. Microwave heating increases the temperature of the bitumen and the aggregates; induction heating does not; so, it requires metallic fibers. In both cases, the temperature reached by the bitumen is much higher when microwave heating is used. Sun et al., (2017) compared the strength restored in asphalt mixtures with fibres heated by microwave and induction, concluding that the self-healing performance of microwave- heated samples was slightly better than induction-heated samples after nine self-healing cycles.

On the other hand, González et al., (2018a) studied the use of reclaimed asphalt pavement (RAP) and metallic fibers to measure self-healing ability. The results showed that with this method, it is possible to recover approximately 50% of the original strength. In general, the addition of RAP to asphalt mixtures resulted in a decrease in self-healing capability, while the fiber content increased this capability. From this research, a very interesting behaviour was observed in control specimens (without metallic fibers), as they can also seal their cracks by microwave heating. The preliminary explanation is that the aggregates used in the investigation contain metals, which can absorb heat when heated by microwave radiation. Therefore, the authors predicted that even existing asphalt pavements could be healed by microwave heating if the aggregates contain metals. This could be a major advance in asphalt pavement rehabilitation in many parts of the world.

2.3.3 Rejuvenator microcapsules

An additional technology has been developed to accelerate the self-healing asphalt. The rejuvenator agents capsules have been introduced in asphalt mixtures with the goal to restore the original bitumen properties. This technique is based on micro-cracks beginning to form within the pavement system but finding a capsule in their propagation path (Yalçın et al., 2018). Then the capsules break, and the rejuvenator is released. This technique has the potential to extend the life service of the pavements, but presents one disadvantage: the inability to reuse the capsules after they are cracked (Yalçın et al., 2018), enabling a one-time use only.

2.4 Rheology of bitumen

The rheology of bitumen can be defined as the fundamental measurements associated with the flow and deformation characteristics of the material (Yusoff, Shaw, & Airey, 2011). In addition, it is used to investigate the aging of bitumen. The rheological properties of bitumen are measured using conventional tests including softening point, viscosity, elastic recovery, storage stability (penetration point, softening point), flash point and tests after thin film oven aging (softening point, viscosity, elastic recovery). However, these measurements are insufficient to properly describe the rheology of the bitumen, for which the use of viscoelastic properties are needed.

The performance of asphalt pavement strongly depends on the viscoelastic response of the bitumen to changes in climate and traffic loading when undergoing deformation. A dynamic Shear Rheometer (DSR) apparatus is used to characterize the performance of the linear viscoelastic properties of the bitumen in a wide range of frequency and temperatures

(Tetteh, 2018). The DSR test enables measurement of flow properties (such as shear viscosity from flow tests) and dynamic material properties (such as complex modulus and phase angle). During the DSR test, the samples are subjected to an oscillatory torque, which induces a sinusoidal angular rotation (Profile, 2018). When sinusoidal stress is applied to viscoelastic material, a sinusoidal strain response is produced. These responses are characterized by a delay between the applied stress and the resulting strain, defined as a phase angle (δ) (Gao, Wang, You, Rosli, & Hasan, 2018). Figure 2.2 shows the typical behavior of a bituminous material when exposed to sinusoidal loads.

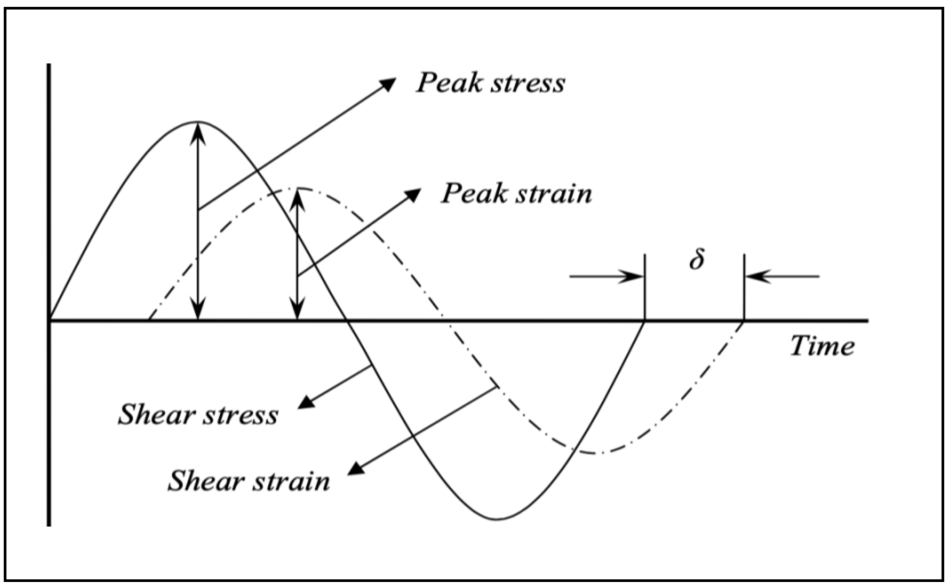

Figure 2.2. Sinusoidal response of bitumen (J. Wu, 2009a)

If δ equals 90°, bitumen can be considered to be purely viscous in nature, whereas δ of 0° corresponds to a purely elastic behavior. Between these two extremes, the material behavior can be considered to be viscoelastic. In addition, another response of interest in dynamic testing is the complex modulus *(G^*),* defined as the ratio of maximum (shear) stress to maximum strain when subjected to shear loading. This modulus directly represents the rigidity of the bitumen (Yusoff et al., 2011).

2.5 Bitumen aging

The aging of bitumen is one of the most important factors determining the lifetime of asphalt pavement. The process of aging involves changes in chemical and rheological properties that usually make bituminous materials harder and more brittle, thus increasing risk of cracking (Lu, Talon, & Redelius, 2008). Changes in the rheological properties of the bitumen result from changes in chemical composition during construction and during the period of service life (Sirin et al., 2018).

In general, the aging of asphalt mixtures is divided in two phases: (1) short-term and (2) long-term. The first phase occurs through the production of asphalt mixtures at very high temperatures. During this stage, a very thin film of asphalt is exposed to air at elevated temperatures, leading to a significant change in the rheological properties of the bitumen. Such changes presents as high viscosity and increased stiffness (Roberts, Kandhal, Brown, Lee, & Kennedy, 1996). The second phase takes place when asphalt is exposed to environmental conditions such as low-temperatures, UV radiation, moisture, etc. The effect of long-term aging is associated with an increase in viscosity and stiffness of the asphalt mixture (Lopez-Montero, Teresa; Miró, 2015).

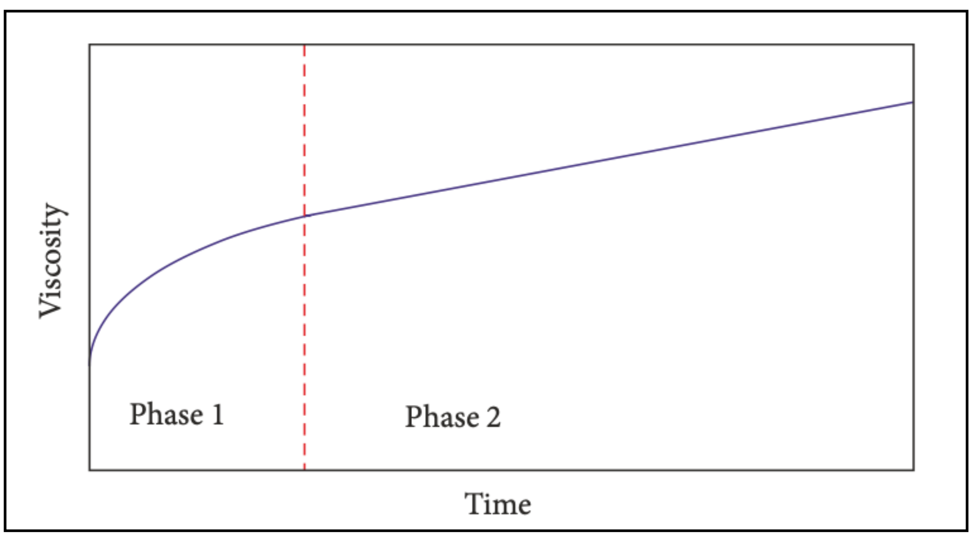

Figure 2.3. Effect of short-long term aging on bitumen viscosity (Glover et al., 2014).

Figure 2.3 illustrates the viscosity behavior of bitumen during the production phase with a higher level of viscosity and the service phase with a linear increase at a lower constant rate. In general, the viscoelastic properties of the bitumen change at a lower rate for aged materials (Yuhong Wang, Wen, Zhao, Chong, & Wong, 2014).

2.5.1 Aging Mechanism

The main aging mechanism is irreversible, characterized by chemical changes of the bitumen, which in turn have an impact on the rheological properties. The processes contributing to this type of aging include oxidation, loss of volatile components and exudation (Lu & Isacsson, 2002). Together, these three chemical processes lead to a hardening of the mixture caused by the aging of the bitumen, which becomes hard and brittle (Hunter, Self, & Read, 2015; Sirin et al., 2018).

The oxidation process could be considered the main reason for bitumen aging. This mechanism is the irreversible chemical reaction between oxygen molecules and the bitumen components resulting in significant alterations of the microstructure of the bitumen (Sirin et al., 2018). This phenomenon occurs not only in mixing and construction stages, but also through the service life of pavement. During the oxidation process, the functional chemical groups, such as the carbonyl group (C═O) and sulfoxide group (S═O), increase the overall polarity of the bitumen, which causes agglomeration among molecules resulting from increased chemo-physical association (Hunter et al., 2015). As a result, the chemical changes reduce the viscoelastic properties of the bitumen, making bitumen stiffer until it becomes a brittle material that reduces its adhesion to aggregates (Miró, Martínez, Moreno-Navarro, & del Carmen Rubio-Gámez, 2015). In addition, additional factors such as the void content of the mixture, the depth of the different layers of the road, and the bitumen content, or the presence of cracking in the mixture could all affect the amount of bitumen exposed and, therefore, the amount of bitumen that is potentially ages (Tauste et al., 2018).

The mechanism of volatilization occurs when at high temperatures, lighter molecular weight bitumen can vaporize and escape into the atmosphere. The oxidation and volatilization occurs at a slow rate at room temperature, but their effects are accelerated when the bitumen is exposed to high temperatures, such as during the mixing and construction stages (Sirin et al., 2018; Tauste et al., 2018). The final chemical mechanism is the exudation of oily ingredients from the bitumen and absorption by the surrounding mineral aggregates that reduces the percentage of these oily components in the bitumen. This in turn makes the bitumen less flexible and more viscous (Heneash, 2013).

The hardening of the bitumen mainly manifests as a variation of physical properties of the bitumen. For example, the penetration grade decrease and the softening point and viscosity increase (Heneash, 2013), may be attributed to molecular structuring, i.e., the reorganization of bitumen molecules (Lu & Isacsson, 2002) in order to achieve an optimum thermodynamically stable state (Heneash, 2013).

2.5.2 Laboratory accelerated aging methods

Several laboratory methods have been used to emulate the aging phenomenon of the bitumen and asphalt mixture during the different phases of their production process as well as during the service life of the materials. These often involve increasing the temperature and/or the pressure of oxygen as a way to generate severe aging conditions (Tauste et al., 2018). Treatment of asphalt or tests related to aging of asphalt materials can be broadly divided into two categories, namely, tests performed on bitumen and tests performed on asphalt mixtures. These could also be divided according to short-term and long-term aging bitumen.

The most commonly used standard tests for simulation of asphalt mixture aging are the thin film oven test (TFOT) and the rolling thin film oven test (RTFOT). The second test is a significant modification of the TFOT, because the bitumen is not agitated or rotated during that test. The TFOT aims to simulate the hardening that a bituminous binder undergoes during the mixing, transporting, and compacting processes (short-term aging) (Southern, 2015). The RTFOT test consists of rotating eight cylindrical glass containers, each containing 35g of bitumen, on a vertically rotating rack while hot air is blown over the sample to be aged. During the test, the bitumen is continuously slid around the walls of the cylindrical container, in relatively thin 1.25 mm films, at a temperature of 163ºC for 75 min. The vertical circular carriage rotates at a speed of 15 revolutions/min. The effects of heat and air are determined on the basis of the change in mass (expressed as a percentage) or the change in characteristics of the bituminous binders characteristics before and after the period in the oven (Shalaby, 2002; Sirin et al., 2018).

In order to simulate several years of field aging (long-term aging), the pressure aging vessel (PAV) has been developed. In this process, RTFOT aged asphalt is subjected to 100ºC for 20 hours under an air pressure of 2.1 MPa to reproduce field aging effects (Tauste et al., 2018). Typically this test simulates aging of 8–10 years of pavement service life according to USA standards (Sirin et al., 2018).

On the other hand, the current practice to simulate the aging of the asphalt mixtures is recommended by the American Association of State Highway and Transportation Officials (AASHTO). This method consists of curing asphalt mixtures for a few hours for short-term and several days for long-term aging, respectively (Sirin et al., 2018). In this method, compacted asphalt mixture specimens are subjected to short-term aging at 135°C for four hours. The long-term aging simulation is performed at 85 ± 3°C for 120 ± 0.5 hours (Elwardany, Yousefi Rad, Castorena, & Kim, 2017) to represent the effect of aging over a period of between 5 and 10 years of service (Tauste et al., 2018).

Researchers have adjusted this procedure to simulate different years of long-term aging. Bell, Wieder, & Fellin, (1994) suggested conditioning the compacted specimen for 2 days at 85ºC or 1 day at 100ºC to simulate long-term aging of new pavements (1 to 3 years old). Mixtures were needed to condition for a longer time (4 to 8 days for 85 ºC or 2 to 4 days for 100 ºC) to predict aging of 9-10 years of field aging. However, the authors suggested avoiding the higher temperature of 100ºC, since conditioning the mixtures at this temperature could cause damage to the specimens.

2.5.3 Bitumen aging indicators

2.5.3.1 Master curves

In recent years a number of researchers have developed master curves to characterize the rheological properties of the aging of bitumen (Cheng, Yu, Zhao, Wu, & Zhang, 2020; Gao et al., 2018; Zapién-Castillo, Rivera-Armenta, Chávez-Cinco, Salazar-Cruz, & Mendoza-Martínez, 2016; Zhang et al., 2018a). In master curves, a viscoelastic parameter such as the complex modulus G* and the phase angle δ are presented of a wide range of a frequency and loading times in one graph. The time–temperature superposition principle (TTSP) is used to construct master curves from linear viscoelastic data by shifting measurement at different temperature in order to obtain a continuous curve at a reference temperature (Asgharzadeh, Tabatabaee, Naderi, & Partl, 2015). The TTSP relates the frequency and temperature and makes it possible to get the same rheological behavior in different experimental conditions (Chailleux, Ramond, Such, & De La Roche, 2006). Rheological properties, determined at high temperature and high frequency, can also be found at low temperature and low frequency.

To construct a master curve, small strain data should be collected for a wide range of temperatures and frequencies using a DRS test. Master curves are produced using a reference temperature (T_R) that is arbitrarily chosen. It is necessary to shift, parallel to the axis of the abscissa, each isotherm (T) in relation to the reference isotherm (T_R) until the curves merge into a single, smooth function (master curve) (Asgharzadeh et al., 2015). The method for shifting isotherms consist of using a shift factor $\alpha(T)$. The shift factor represents the amount of shifting required at each temperature to be shifted to the defined T_R and can be accurately described using a Williams-Landel-Ferry (WLF) equation (Dondi et al., 2014) as follows:

$$\log \alpha(T) = -\frac{C_1(T - T_R)}{C_2 + (T - T_R)} \quad (2)$$

where $\alpha(T)$ is the shift factor, T is the initial temperature, T_R is the reference temperature and C_1, C_2 constant of the equation. The values of these constants were obtained in an iterative process until an exact superposition of the isotherms displaced to the master curve was achieved.

As previously discussed, the master curves G* and δ were plotted as a function of reduced frequency (f_r) at the defining temperature on a log-log scale and semi-log scale respectively. The f_r is function of the shift factor log α(T) and the frequency (f) and is calculated using the follow equation (Booshehrian, Mogawer, & Bonaquist, 2013):

$$f_r = f \cdot 10^{\log \alpha(T)} \tag{3}$$

In Figure 2.4 a typical graph of a master curve is presented. When aging occurs in the bitumen, the complex modulus increases as the bitumen becomes harder and when the phase angle decreases, the bitumen becomes more elastic. Therefore, the aging of bitumen can be observed when G^* master curve moves upwards and when δ master curve moves down (Zhang et al., 2018a).

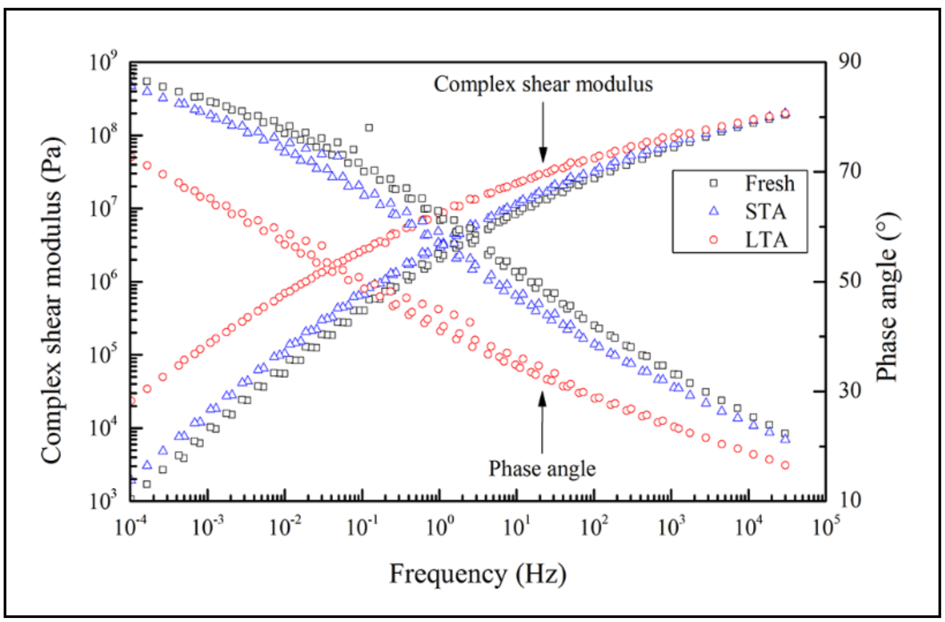

Figure 2.4. Master curves of G* and δ of different bitumens

(Jing, Varveri, Liu, Scarpas, & Erkens, 2019).

2.5.3.2 Rheological aging index

The aging of bituminous materials is commonly expressed by means of an aging index (AI) (J. Wu, 2009a). After any aging acceleration treatment, samples are usually studied to quantify changes in the asphalt binder/mixture properties before and after the aging treatment (Sirin et al., 2018). The following equation shows a generic form of the AI:

$$AI = \frac{P_{Aged}}{P_{Unaged}} \quad (1)$$

Where P_{Unaged} means some chemical, physical or rheological property such as carbonyl and sulfoxide groups areas, weight loss, viscosity, penetration, ductility, tensile strength and stiffness modulus and phase angle. All of them measured on the unaged bituminous material. P_{Aged} could be the same chemical, physical or rheological property, but measured after the materials have been aged (J. Wu, 2009a).

One of advantages of the rheological indices is that some of them have been proved to be more associated with pavement performance. The use of rutting factor ($G^*/sin\ \delta$) and fatigue factor ($G^*sin\ \delta$) developed by The Strategic Highway Research Program (SHRP) in the 1990's, prove to be efficient indicators for pavement rutting and fatigue behaviors respectively and are commonly used to classify asphalt binder grade in SHRP specification. Moreover, complex modulus G* and phase angle (δ) are typically used to evaluate the aging behavior of the bitumen. These two parameters can roughly reflect stiffness or viscoelastic balance of bitumen (Zhang et al., 2018a).

2.5.3.3 Carbonyl and sulfoxide group index

It is acknowledged that the primary cause of aging in asphalt mixtures during its service time is oxidation by oxygen from air (Zhang, Chen, Xu, & Shi, 2018b). This irreversible chemical reaction is responsible for the chemical and physical aging of the bitumen. During the aging process, carbonyl (C═O) and sulfoxide (S═O) compounds increase in the overall polarity of the bitumen, which in turn will influence bitumen rheology (Lu &

Isacsson, 2002). The chemical changes in the chemical bonds of the bitumen can be analyzed using Fourier Transform Infrared Spectroscopy (FTIR) (Jing et al., 2019).

In the FTIR test, the energy from the infrared light source with wavenumbers from 600 to 4000 cm^{-1} is transformed into vibrational energy in the molecules of bitumen. This vibrational energy that presents a series of absorption bonds, which are recorded as absorbance against the wavenumber (J. Wu, 2009a). Peaks in the spectral data can be used to detect the functional chemical groups in the bitumen (Y. R. Kim et al., 2017). A typically infrared spectrogram is shown in Figure 2.5:

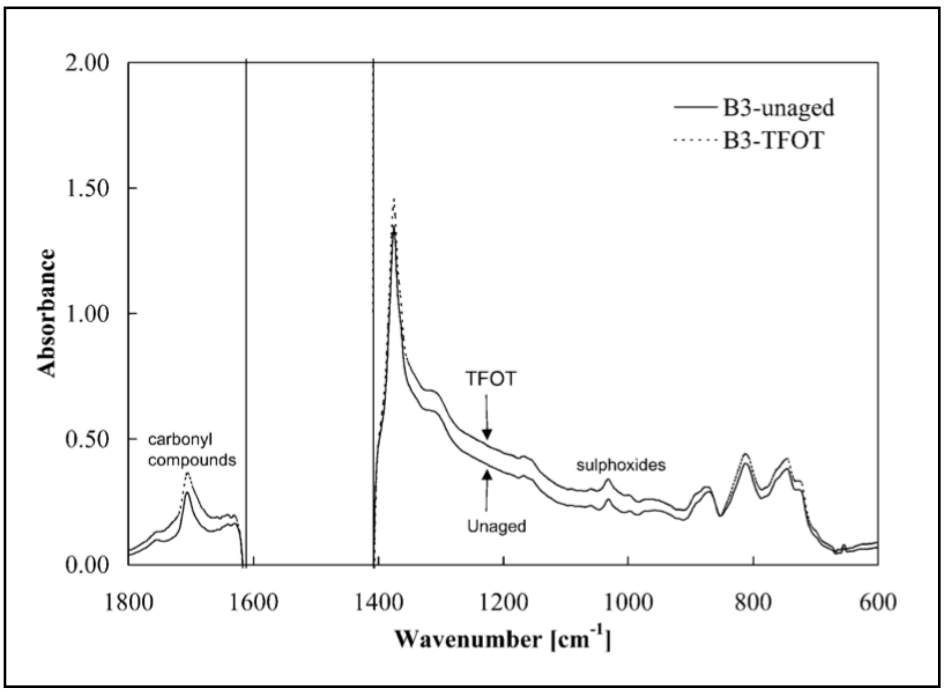

Figure 2.5. Effect of aging on bitumen FTIR spectrogram

(Lu & Isacsson, 2002).

Special attention was paid to the results with wavenumbers ranging from 600 to 2000 cm^{-1} which covers the regions for the main oxidative aging products (J. Wu, 2009b). Bands around 1700 cm^{-1} proved to be a stretching vibration of carbonyl group C═O, and bands around 1030 cm^{-1} were an effect of sulfoxide group S═O vibration (Ge et al., 2019).

In order to evaluate the aging of bitumen, carbonyl index ($I_{C=O}$) and sulfoxide index ($I_{S=O}$) were proposed (Cheng et al., 2020). The index of these functional groups can be computed by the peak area of their bands and divided by the sum of the all bands in wavenumbers range 600 - 2000 cm^{-1} (Jing et al., 2019). The relative ratios of the areas of C═O and S═O is computed by the following equations (Cheng et al., 2020; Zeng, Wu, Wen, & Chen, 2015; Zhang et al., 2018b):

$$I_{C=O} = \frac{A_{1700}}{\sum A} \tag{2}$$

$$I_{S=O} = \frac{A_{1030}}{\sum A} \tag{3}$$

$$\sum A = A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} \tag{4}$$

where A_{1030} represent the area of sulfoxide peaks, A_{1700} the area of carbonyl peaks and $\sum A$ the sum of areas of all bands in wavenumber range of 600 - 2000 cm^{-1}. When the $I_{C=O}$ and $I_{S=O}$ increases, the more serious aging degree of the bitumen is (J. Wu, 2009b).

3. EFFECTS OF MICROWAVE HEATING AND LONG-TERM AGING ON THE RHEOLOGICAL AND CHEMICAL PROPERTIES OF RECOVERED BITUMEN

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3.1 Abstract

In recent years, asphalt pavements have been exposed to more severe conditions due to increased traffic circulation and more extreme environmental conditions caused by climate change. Bitumen aging is one of the most important factors affecting its service life causing cracking of the pavements. Cracking occurs as result of the oxidation of the hydrocarbon compounds of bitumen. Self-healing of cracks in asphalt pavements by external microwave heating is a promising technology to build more durable asphalt pavements. Nevertheless, previous studies have shown that microwave heating technology at high temperatures could also damage the bitumen of the asphalt mixture, which is an unwanted effect of this crack-healing technique. This study aims to quantify the effects of microwave heating damage on the rheological and chemical properties of recovered aged bitumen. With this purpose, Stone Mastic Asphalt specimens were exposed to different cycles of microwave heating and long-term aging controlled in oven. The effects of microwave heating damage on the rheological and chemical properties of recovered aged bitumen were quantified through a frequency sweep test and Fourier Transform Infrared Spectrometry analysis, respectively. The results of recovered aged bitumen by microwave were compared with those obtained by normal long-term aging process. The main results indicate that microwave heating has no significant effect on the aging performance of G* and δ for aged asphalt mixtures. However, the rheological properties of bitumen show minor changes with microwave heating for newer asphalt mixtures. A strong relationship with the chemical and rheological results can be observed, which demonstrates that both properties can be potentially used as good indicators for assessing bitumen aging level. Overall, this study confirms that microwave heating is a

sustainable alternative for maintenance of asphalt pavements, without severely affecting the rheological and chemical properties of bitumen.

Keywords: Asphalt pavements; Stone Mastic Asphalt; Aged bitumen; Self-healing asphalt; Microwave heating technology; Rheological and chemical properties.

3.2 Introduction

Road infrastructure is essential for the development of a country, providing mobility, economic growth, access to goods and services, and promoting social equality (Lizasoain-Arteaga et al., 2019). Asphalt mixture is a composite material which includes virgin aggregates, bitumen (a temperature-responsive polymer) and air (Dondi et al., 2014). This material is the most commonly used for pavement road construction because it provides good mechanical performance, economy, and construction advantages (González et al., 2018a). Despite its good properties as a road material, asphalt mixture deteriorates over time, being cracking one of the most common forms of damage (Y. Kim, Little, Asce, Lytton, & Asce, 2003). Cracking is mainly caused by repetitive traffic loading and environmental factors that trigger bitumen aging (Rochlani et al., 2019). The phenomenon of bitumen aging mainly consists of an oxidation process and polymeric reaction, which modifies the microstructure of bitumen (Tauste et al., 2018). The irreversible oxidation process is controlled by thermal reaction between oxygen molecules and the bitumen components, which alters its chemical features (Sirin et al., 2018; Tauste et al., 2018). This type of aging occurs during the service life of the pavement and it is known as long-term aging (Shaopeng Wu, Pang, Liu, & Zhu, 2010). During the oxidation process, the functional chemical groups of the bitumen, such as the carbonyl (C=O) and sulfoxide (S=O) groups, increase the overall polarity of the bitumen, which causes agglomeration among molecules due to increased chemo-physical association (Hunter et al., 2015). As a result, the chemical changes reduce the viscoelastic properties of the bitumen, making bitumen stiffer until it becomes a brittle material and reduces its adhesion to aggregates (Miró et al., 2015). The stiff brittle bitumen causes the asphalt mixture to crack, which in turn reduces the pavement capability to withstand repeated traffic loads and shortens the pavement life (Sandoval, Thenoux, & Molenaar, 2017).

In order to maintain the desired performance of asphalt pavements during their service life, it is necessary to perform conservation and maintenance operations, which imply expensive investments, delay of traffic flow, and environmental pollution (J. Norambuena-Contreras, Serpell, Valdés Vidal, González, & Schlangen, 2016). Several preservation and maintenance construction techniques can be carried out to ensure the serviceability of asphalt pavements. For example, crack sealing and filling to prevent water infiltration (Vargas-Nordcbeck & Jalali, 2020) and the use of additives, such as antioxidants and rejuvenators with the aim to extend the lifespan of pavements, has become a common practice in the asphalt industry, consequently increasing the performance and resistance of asphalt. Although these techniques can prolong the asphalt pavement service life, they are based on extending maintenance and repair work for only a few years (Yalçın et al., 2018). These consequences have necessitated the search for sustainable new alternatives to reduce maintenance, and this comes mutually with the intentions to reduce impacts to the environment caused by maintenance treatments (Zulu et al., 2020).

In recent studies, microwave radiation heating has been proposed as a new method of preventive maintenance of asphalt pavements (Gallego et al., 2013; J. Norambuena-Contreras, Gonzalez, Concha, Gonzalez-Torre, & Schlangen, 2018; J. Norambuena-Contreras et al., 2016; Jose Norambuena-Contreras & Gonzalez-Torre, 2017). Microwave power offers a new solution to healing asphalt pavements, a phenomenon known as self-healing of asphalt pavements. Self-healing asphalt aims to develop a sustainable asphalt pavement by using self-healing technology, such as the external microwave heating to stimulate and improve the healing capacity of asphalt so that damage can be self-repaired to extend the service life of roads (S. Xu, Liu, Tabaković, & Schlangen, 2020). Asphalt mixtures were found to readily absorb microwave power at 2.45 GHz to depths down to 12 cm, without overheating the surface layer of the asphalt pavement (Bosisio et al., 1974). To improve the electrical conductivity and thermal distribution of the asphalt mixtures with self-healing properties, metallic waste or steel wool fibers must be added to the asphalt matrix (Gonzalez, Norambuena-contreras, Storey, & Schlangen, 2018; González et al., 2018b; J. Norambuena-Contreras, Gonzalez, et al., 2018; J. Norambuena-Contreras et al., 2016; Jose Norambuena-Contreras & Gonzalez-Torre, 2017). However, Gonzalez et al. (González et al., 2018a) found that asphalt mixtures without metallic additives are also capable of healing their cracks by microwave heating; therefore, existing asphalt pavements could also be crack-healed through microwave heating.

The healing capability of the asphalt mixtures is mainly due to the intrinsic viscoelastic and thermoplastic properties of bitumen when it is exposed to temperature variation. When exposed to temperatures between 30ºC and 70°C, the bitumen in asphalt mixtures reduces its viscosity and begins to flow through micro-cracks (Ayar et al., 2016) in a motion similar to capillary flow (García, 2012). When pavement cools to lower temperatures, the bitumen that sealed the crack increases its viscosity, healing or recovering the mechanical properties of the mixture (Gallego et al., 2013). Hence, the bitumen plays an important role in the healing performance of asphalt mixtures.

Recent studies regarding self-healing of bituminous materials have been classified as environmentally sustainable strategies in the construction engineering field (Ayar et al., 2016; Gonzalez-Torre & Norambuena-Contreras, 2020; Jose Norambuena-Contreras et al., 2020; Shu et al., 2020). The development of self-healing asphalt and its use in road paving is an innovation that could potentially increase road lifespan between 40 to 80 years (Schangen & Tobakovic, 2015), which not only reduces the use of extra resources, but also reduces maintenance cost, and the greenhouse gas emissions (Chung et al., 2015). As a preventive maintenance technique, it is expected that its application will be carried out periodically every certain year to reduce the damages that occurred during the long-term aging of the asphalt pavements. In this context, a recent study published by Rodríguez-Alloza et al. (2019) have established that self-healing roads could prevent a considerable amount of emissions and costs over the global road network. In short, 16% lower emissions and 32% lower costs compared to a conventional road over the lifecycle.

The self-healing of asphalt mixture is a temperature dependent phenomenon, and it is necessary to heat the bitumen for a sufficient time to reach an adequate viscosity change for healing (Quantao Liu, Schlangen, Van De Ven, et al., 2012). Previous research has reported that the self-healing of asphalt mixtures by microwave heating can be achieved with a heating time of 40 seconds (Jose Norambuena-Contreras & Gonzalez-Torre, 2017). Norambuena-Contreras and Garcia (2016) evaluated the surface temperature of dense asphalt mixtures with different percentages of metallic fibers for various heating times, observing that samples with 8% fibers reached 135ºC after 120 seconds of heating. However, when the temperature is too high, it may decrease the healing level due to drainage of the bitumen under gravity.

Bitumen also tends to suffer more serious aging damage at higher temperatures (Tang et al., 2016) and the oxidation process of its components can significantly accelerate, which could potentially decrease the durability of the mixtures. Additionally, temperature significantly influences the kinetics of aging, with those effects related to the bitumen. In general terms, the rate of oxidation doubles with each 10ºC rise in temperature above 100ºC (Hunter et al., 2015). Thus, microwave heating can age the bitumen in the asphalt mixture, which is an unwanted effect of the crack-healing technique. The influence of temperature on bitumen by effect of the microwave heating was investigated for the first time by Norambuena-Contreras and Garcia (2016). To do this, authors carried out thermogravimetric analysis on virgin bitumen combined with microwave heating tests on asphalt mixture samples in a range of fibers amounts before and after several heating cycles. The main results proved that the temperature of the binder under microwave heating can be higher than the flash point temperature of bitumen, and consequently microwave heating may damage the chemical structure of the binder used into the self-healing asphalt mixtures. However, this result has not been tested on mixtures without fibers, although recently González et al. (2019) found good promising crack-healing results on mixtures without fibers. Moreover, rheological and chemical tests have not been performed to evaluate bitumen aging on this type of mixtures.

Additionally, Wu et. al. (2018) investigated the effect of microwave heating on the physical properties of a bitumen 60/70 pen. The bitumen was heated to a target temperature of 150ºC and cooled down to room temperature near 25ºC. The researchers measured the penetration, ductility, and softening point of the bitumen after one, three, and five microwave-heating cycles to evaluate the bitumen aging. The results showed, after five cycles of microwave heating, a reduction of 3.87% in penetration value, 9.19% increase of softening point, and 25.93% decrease of ductility. They found no clearly negative effect of microwave heating and concluded that the microwave heating causes slight aging in the bitumen. Nonetheless, these physical properties are an empirical measurement that cannot effectively describe viscoelastic characteristics of bitumen and additionally fail to correlate well with asphalt mixture performance (Airey, 2002). Moreover, Wu et al. (2018) did not analyze the chemical variation of the functional groups of the bitumen, which is a useful indicator for evaluating the aging effect (Ge et al., 2019). Therefore, a further analysis by rheological and chemical parameters is required for the evaluation of microwave heating on aging bitumen.

The study of bitumen rheological properties is adopted in most of the studies about bitumen aging (Cheng et al., 2020; Gao et al., 2018; Zhang et al., 2018a). The advantage of these properties is that some of them have been proven to be associated with pavement performance (Zhang et al., 2018a). This performance enables characterizing bitumen at a certain temperature, which is related to both the constitution (chemical composition) and structure (physical layout) of the molecules in the bituminous material. The rheological analysis on bitumen samples is commonly carried out using a Dynamic Shear Rheometer (DSR) and is usually focused on the evolution of the complex modulus and phase angle under different temperatures or frequencies (Tauste et al., 2018). These results can be complemented with chemical analysis by Fourier Transform Infrared (FTIR) spectroscopy, which provides the most effective method to confirm the oxidation aging of bitumen (Villegas-villegas et al., 2015).

This study aims to understand the aging of bitumen in asphalt mixtures exposed to microwave heating and long-term aging. To achieve this goal, a comprehensive laboratory study was conducted using a conventional microwave oven to evaluate the microwave heating effects and a conventional heating oven to simulate the long-term aging. Rheological characterization was carried out with a DSR by the values of the complex modulus and the phase angle based on the frequency sweep test. FTIR tests were conducted to analyze the change in molecular composition of the aged bitumen analyzing different bitumen samples exposed to microwave heating and long-term aging cycles. In brief, this study further details the mechanism of bitumen aging caused by microwave heating.

3.3 Materials and experimental methods

3.3.1 Materials and manufacturing of specimens

A Stone Mastic Asphalt (SMA) with a maximum grain size of 11 mm (SMA 11S) was used. The SMA is composed of a strong coarse aggregate skeleton with the grain size distribution shown in Figure 3.1. The used virgin bitumen was classified as 50/70 penetration grade, which is widely used in pavement engineering applications in Germany.

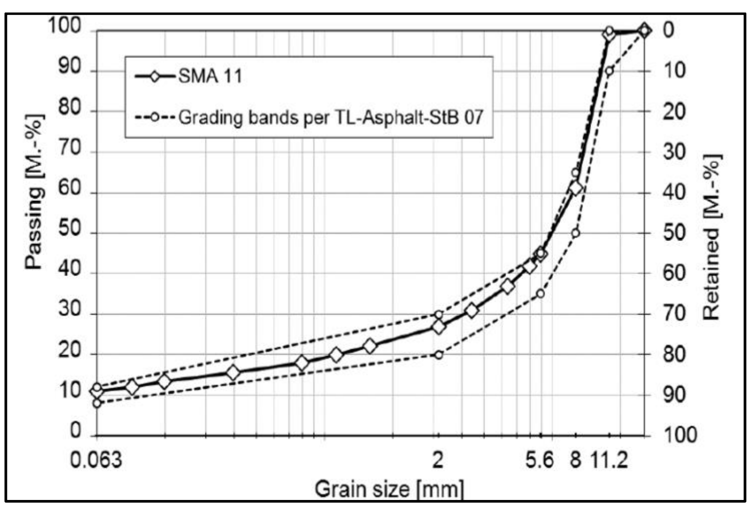

Figure 3.1. Grain size distribution of reference SMA 11S mixture used.

Several SMA test specimens were manufactured at a mixing temperature of 165ºC through two methods: 1) conventional SUPERPAVE preparation under laboratory conditions, and 2) preparation in asphalt plant. To do latter, SMA was industrially produced in a batch type plant in Geilenkirchen (Germany) at 165ºC. Afterwards, SMA was transported to the test track of the institute of highway engineering at RWTH Aachen University (25 km distance) where it was laid down and compacted. Finally, several cores were drilled out from the track and delivered to TU Dresden for testing. Table 3.1 shows the volumetric properties of the SMA.

Table 3.1. Conventional properties of the reference SMA 11S mixture.

Bitumen content [%-v]	Bulk density [kg/m^3]	Void ratio [%-v]	Compaction grade [%]
6.9	2436	2.1	100.9

3.3.2 Aging modes of the bitumen samples

In this research, the bitumen material used was treated under two different aging modes: (1) *Mode I:* bitumen used for the SMA manufacturing under method 1 was aged using hot air and UV light to simulate a long-term aging of 6 years of service life. In total, using this aged bitumen 8 SMA test specimens were prepared and tested. (2) *Mode II:* bitumen within SMA cores only reproduce the short-term aging conditions during pavement construction. In total, 8 SMA test specimens were evaluated under this mode. In addition, Phase I includes the chemical and rheological tests performed on the bitumen aged with *Mode I*. In Phase 2, the same tests were performed with the difference that the bitumen aged in *Mode II* was used.

In both phases, the aged bitumen was separated from the aggregates using a dissolution of trichloroethylene according to the standard EN 12697-4 (British Standard Institution., 2005). Also, to contrast the rheological and chemical results of the bituminous samples exposed to microwave and long-term aging, the reference bitumen was aged using the Pressure Aging Vessel (PAV) method (EN 14769, 2012).

3.3.3 Microwave heating and long-term aging cycles

To study the aging effect on the bitumen under two different methods, the specimens were exposed to various cycles of microwave heating and long-term aging. The microwave heating was applied on the test specimens using a 900 W microwave oven with a working frequency of 2.45 GHz. The room temperature during the test was approximately 20ºC, and the initial temperature of the specimens was measured in five points of the surface with a laser thermometer resulting an average temperature of 22ºC. The test specimens were placed in the center of the microwave oven on an insulator material base and were heated for 40s following the recommendations given by Norambuena-Contreras and Gonzalez-Torre (Jose Norambuena-Contreras & Gonzalez-Torre, 2017). The microwave heating was repeated four times with 40s of rest period (i.e. without heating) to improve the heating distribution through the test specimens. The heating time was found suitable for microwave healing, because the measured surface temperature distribution was found similar to that obtained in previous research (González et al., 2018a; J. Norambuena-Contreras & Garcia, 2016). After microwave heating, the average surface temperature on the test specimens was 70ºC.

After aging by microwave heating, the long-term aging procedure was made on the same test specimens based on the current recommended practice from AASHTO R30 (Y. R. Kim et al., 2017) for aging (5 – 10 years of aging in the field) of compacted asphalt mixtures. In this study, long-term aging was modified following the recommendations given by Elwardany et al. (Elwardany et al., 2017) in order to simulate a period of time related to the application of microwave heating in the field, which it is expected will be applied every 3 – 5 years during maintenance activities. Hence, the test specimens were conditioned in a conventional oven at 85ºC ± 3°C during 72 ± 0.5 hours to simulate the long-term aging of a mixture in the field for a period over 3 – 5 years.

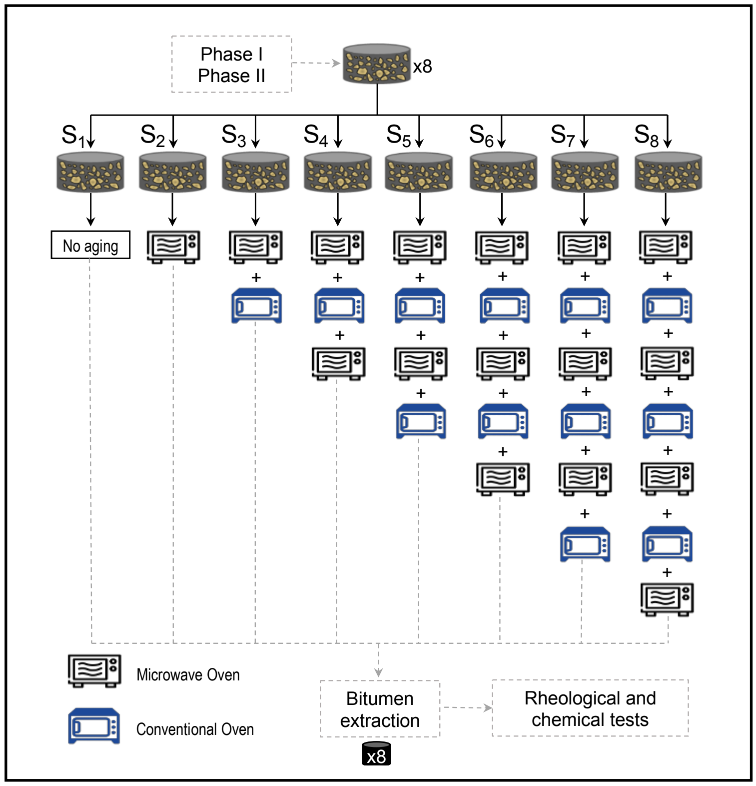

Figure 3.2. Test plan for microwave heating plus long-term aging cycle.

The test specimens were exposed to 8 different stages of microwave heating plus long-term aging (S_1 - S_8 in Figure 3.2) to compare the potential degree of aging that bitumen could have on its rheological and chemical properties. Figure 3.2 summarizes the experimental procedures for the microwave heating plus the long-term aging in conventional oven. In this Figure, specimen S_1 represents the control sample which was not exposed to any microwave heating or long-term aging cycle. However, specimen S_8 went through all cycles, i.e., it was exposed to four microwave heating and three long-term aging cycles, Figure 3.2. Once the experimental plan was completed, bitumen samples were recovered from the SMA test specimens consistent with Phase II to then perform the rheological and chemical tests.

3.3.4 Rheological properties of bitumen by DSR tests

In this study, a Dynamic Shear Rheometer or DSR (Anton Paar MCR 502 Modular Compact Rheometer) was used to perform frequency sweep tests. The data of rheological parameters were generated using a frequency sweep test under small strain conditions to ensure response within linear viscoelastic range. The linear viscoelastic (LVE) range was denoted by the strain value in which the dynamic shear modulus equates to 95% of the initial value (ASTM-D7175-15, 2017). During the test, the frequency varied from 50 Hz to 0.5 Hz testing the recovered bitumen sample at 10 different temperatures (-20, -10, 0, 10, 20, 30, 40, 50, 60 and 70ºC). The plates used in the DSR were 8 mm diameter parallel plate geometry for low and intermediate temperatures in the range of -20ºC to 30ºC and 25 mm diameter parallel geometry for higher temperatures in a range of 30ºC to 70ºC. The gaps were 2 mm and 1 mm, respectively.

It is known that researchers have developed master curves to characterize the rheological properties of bitumen (Cheng et al., 2020; Gao et al., 2018; Zapién-Castillo et al., 2016; Zhang et al., 2018a). Thus, time and temperature dependency are the two primary factors to consider when describing the rheological behavior of bitumen in the LVE range (Asgharzadeh et al., 2015). The time-temperature superposition principle (TTPS) is used to construct master curves from LVE data by shifting measurement at different temperatures in order to obtain a continuous curve at the reference temperature (Chailleux et al., 2006). The TTPS relates the frequency and temperature and makes it possible to obtain the same rheological behavior in different experimental conditions (Chailleux et al., 2006). The rheological properties of bitumen are normally presented in the form of both the complex modulus (G^*) and phase angle (δ) master curves. G^* is defined as the ratio of maximum (shear) stress to maximum strain when subjected to shear loading and δ is the phase difference between stress and strain in harmonic oscillation (Gao et al., 2018). The rheological properties G^* and δ are based on a time and frequency sweep test using the DSR. Master curves enable researchers to evaluate the microwave heating effect on the aging bitumen with changes in the values of these rheological properties.

Based on the time-temperature superposition principle and frequency sweep test results, G* and δ master curves were determined. To create the master curve, a reference temperature of 30ºC was used, and the data collected from frequency sweeps at all other temperatures are shifted to the reference temperature by shift factors. The shift factors represent the amount of shifting required at each temperature to be shifted to a defining temperature and can be accurately described using a Williams-Landel-Ferry (WLF) equation (Dondi et al., 2014) as follows:

$$\log\alpha(T) = -\frac{C_1(T - T_R)}{C_2 + (T - T_R)} \quad (1)$$

where $\alpha(T)$ is the shifting factor relative to the reference temperature, T is the initial temperature (ºC), T_R is the arbitrarily chosen reference temperature (ºC), and C_1 , C_2 are fitting constants. The values of these constants were obtained in an iterative process until an exact superposition of the isotherms displaced to the master curve was achieved.

Master curves for G* and δ were plotted as a function of reduced frequency (f_r) at the defining temperature on a log-log and semi-log scale, respectively. The f_r is function of the shift factor $\log\alpha(T)$ and the frequency (f) and is calculated using the following equation (Booshehrian et al., 2013):

$$f_r = f \cdot 10^{\log\alpha(T)} \quad (2)$$

3.3.5 Quantification of the rheological aging indexes

A common methodology for assessing the aging performance of bitumen is primarily through the measurement of specific parameters before and after aging. These parameters are normally related to the physical, chemical and rheological properties (Cheng et al., 2020). The relationship between a physical, chemical, or rheological property measured on an aged bitumen (P_{Unaged}) respect to an un-aged bitumen (P_{Aged}) is called the aging index (Zhang et al., 2018b, 2018a). The following equation shows a generic form of the aging index (J. Norambuena-Contreras, Yalcin, et al., 2018):

$$AI = \frac{P_{Aged}}{P_{Unaged}} \tag{3}$$

In the present study, the changes in the rheological properties after microwave heating and long-term aging were evaluated by rheological aging indexes. The rheological aging indexes adopted for this research were obtained from the measurement of rheological properties in the frequency sweep test, which were complex modulus index (AI_{G^*}) and phase angle index (AI_{δ}). The following equations show the aging indexes used in this research:

$$AI_{G^*} = \frac{G^*_{Aged}}{G^*_{Unaged}} \tag{4}$$

$$AI_{\delta} = \frac{\delta_{Aged}}{\delta_{Unaged}} \tag{5}$$

where G^*_{Unaged}, δ_{Unaged} are the complex modulus and phase angle of the unaged bitumen, which are represented for the control bitumen sample, i.e., *bitumen 1*. And G^*_{Aged}, δ_{Aged} are the complex modulus and phase angle of the aged recovered bitumen samples, which were exposed to different microwave heating and long-term aging cycles, see Figure 3.2. So, a higher value of AI_{G^*} and lower value of AI_{δ}, means a more serious aging degree, because when the bitumen ages the complex modulus increases and the phase angle decreases (Zhang et al., 2018a).

3.3.6 Chemical properties of bitumen by FTIR tests

Previous research (Zhang et al., 2018b) has shown that the main cause of aging in asphalt mixtures during service time is oxidation by oxygen naturally in the air. As previously mentioned, during the oxidation process, chemical variations that occur refer to the formation of the carbonyl group (C═O) and the sulfoxide group (S═O), which increase the overall polarity of the bitumen (Hunter et al., 2015), affecting its physical and rheological properties (Sirin et al., 2018). Fourier Transform Infrared Spectroscopy

(FTIR) is a successful experimental technique to analyze the changes in the chemical composition of bitumen due to oxidative ageing (Gonzalez-Torre & Norambuena-Contreras, 2020) as a result of detecting the infrared radiation absorption of chemical bonds in the analyzed bitumen sample.

With this in mind, a Nicolet iS5 FTIR spectrometer was used in this study to identify the chemical functional groups of the recovered bitumen after the microwave heating and long-term aging cycles. Each spectrum was scanned 100 times at a resolution of 4 cm^{-1} and recorded in a wavenumber range from 4000 to 600 cm^{-1}. The changes caused by aging can be found at between 2000 – 600 cm^{-1}. These wavenumbers correspond to functional groups related to the oxidation process (Shaopeng Wu et al., 2019). The peaks of the carbonyl and sulfoxide groups can be found in wavenumbers 1700 and 1030 cm^{-1}, respectively (Shaopeng Wu et al., 2019).

To evaluate the aging of bitumen, both a carbonyl index ($I_{C=O}$) and a sulfoxide index ($I_{S=O}$) were determined (Cheng et al., 2020). The indexes of these functional groups can be calculated by the peak area of their bands and divided by the sum of all bands in wavenumbers ranging from 2000 – 600 cm^{-1} (Jing et al., 2019). The relative ratios of the areas of C═O and S═O were calculated by the following equations (Zeng et al., 2015; Zhang et al., 2018a, 2018b):

$$I_{C=O} = \frac{A_{1700}}{\sum A} \tag{6}$$

$$I_{S=O} = \frac{A_{1030}}{\sum A} \tag{7}$$

$$\sum A = A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} \tag{8}$$

where A_{1030} represents the area of sulfoxide peaks, A_{1700} the area of carbonyl peaks, and $\sum A$ the sum of areas of all bands in wavenumber range of 2000 – 600 cm^{-1}. The peak areas were evaluated using numerical integration provided by OriginPro software.

3.3.7 Summary description of the tested bitumen samples

Table 3.2 summarizes the different bitumen samples experimentally analyzed in this study. In addition to the eight bitumen samples, a fresh or virgin bitumen sample and an aged bitumen sample were analyzed for comparison purposes. The bitumen was aged applying the Pressure Aging Vessel (PAV) method.

Table 3.2. Symbology of the bitumen samples tested in this study.

Symbology	Description
Bitumen 1	Bitumen sample recovered from SMA without stages of aging (see Fig. 3.2)
Bitumen 2…8	Bitumen samples recovered from SMA test specimens exposed to different microwave and oven stages of aging (see Fig. 3.2)
Fresh Bitumen	Virgin bitumen sample without any treatment
PAV Bitumen	Bitumen sample aged using the Pressure Aging Vessel (PAV) method

3.4 Results and discussion

3.4.1 Effect of the microwave heating and long-term aging on bitumen from phase I

3.4.1.1 Effect on the rheological properties of bitumen samples from phase I

Figure 3.3 and Figure 3.4 summarize all the results of rheological properties measured for the bitumen samples from Phase I (section 3.3.7) exposed to different cycles of microwave heating and long-term aging. The results of their viscoelastic parameters complex modulus (G*) and phase angle (δ) are presented in master curves at reference temperature of 30ºC. Both master curves for G* and δ were plotted as a function of reduced frequency. In these Figures, the aging of the bitumen samples can be observed in master curves when G* increases and δ decreases (Zhang et al., 2018a).

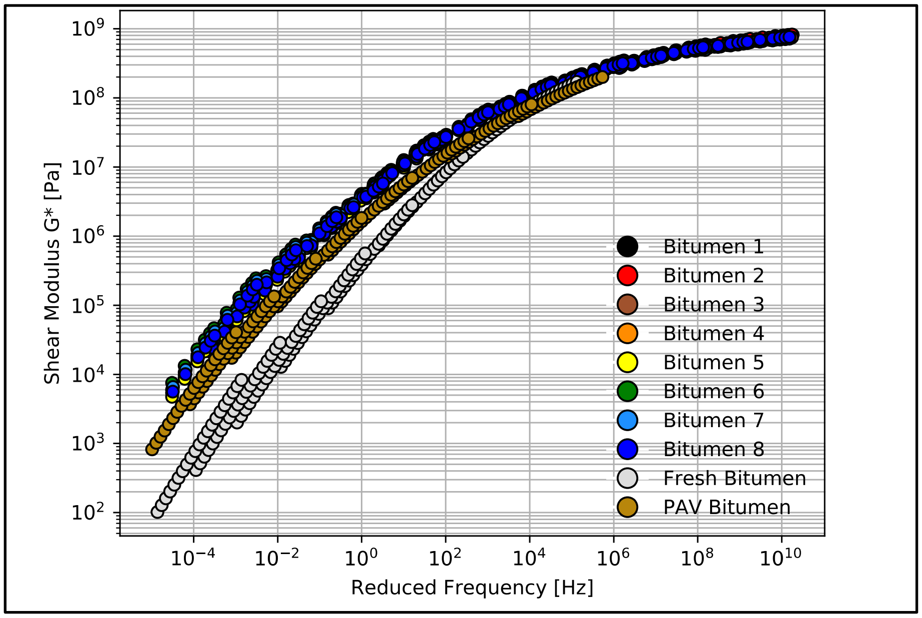

Figure 3.3. Master curves comparison for all bitumen from phase I in terms of G*.

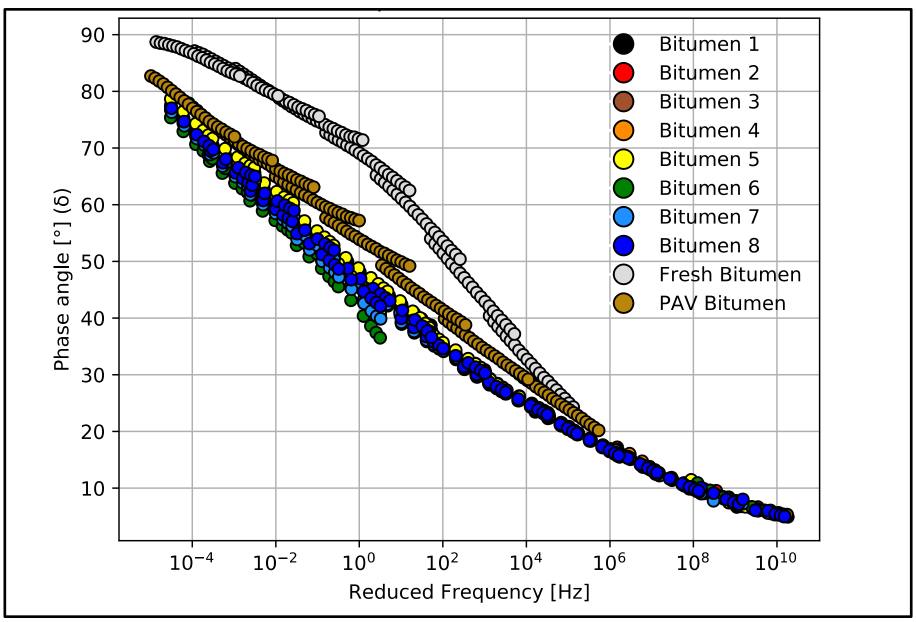

Figure 3.1. Master curves comparison for all bitumen from phase I in terms of δ.

As can be seen in Fig. 3.3 and Fig. 3.4, all the master curves for bitumen 1 to 8 overlap. Hence, no obvious differences can be seen in the variation of G* through the different microwave heating and long-term aging cycles. The overlap tendency shown in Figure 3.3 and 3.4 can be attributed to the fact that once the bitumen or asphalt is aged, the additional aging due to microwave heating has no significant effect on the aging performance of the G* and δ. From low frequency to high frequency, the spacing for the G* master curve of all bitumen is minor in the eight samples. However, at higher frequency, all the samples tend to reach an asymptote at value of 10^6 Pa. Figure 3.4 shows the master curves for the phase angle with an overlap trend between the eight bitumen specimens. No clear effect can be seen in the phase angle through microwave heating and long-term aging cycles.

Additionally, Figure 3.3 and 3.4 show G* and δ master curves for a fresh and a PAV bitumen. From these Figures, it can be observed that the rheological properties at low frequency show that fresh and PAV bitumen have lower values of G* and higher values of δ, which means that fresh and PAV bitumen samples were less aged than the other bitumen samples exposed to the microwave and long-term aging cycles. An interesting phenomenon to be noted considering that all the bitumen samples were exposed to a long-term aging, conditioned in a conventional oven at 85ºC ± 3°C during 72 ± 0.5 hours at different cycles. It would be expected that this method of long-term aging promotes the oxidation process, increasing G* and decreasing δ gradually with the cycles increase, however, this result cannot be seen in the master curves.

Hence, to quantify the effect of the microwave and long-term aging on the rheological properties of bitumen from phase I, the rheological aging indexes (AI) were calculated using two criteria: first, calculated at 20ºC and frequency 10Hz representing the typical design considerations, and the second, calculated at 60ºC and frequency 1Hz, established as the high temperature and low frequency condition that corresponds closely to permanent deformation conditions. Thus, Figure 3.5 and Figure 3.6 present the average results (± one standard deviation error bar) of the rheological aging indexes for the eight bitumen samples at two different criteria, respectively. Average results were calculated using three values. Figure 3.5 shows the aging index of G* and δ for the first criterion. The x-axis shows the identification of the specimen, along with the number of its associated recovered bitumen. For example, for bitumen 1 (which is related to S_1) indicates that there was no microwave heating and no long-term aging cycle (control sample), therefore it has a value of AI_{G^*} and AI_{δ} of 1.0.

In Figure 3.5 no clear effect is observed in the AI_{G^*} because some bitumen samples increase and others decrease the aging index value as the microwave heating increases and the long-term aging cycles extend. The increase of the AI_{G^*} was expected to be gradual, due to the increase in the complex modulus by the oxidation process with the long-term aging procedure. The trend in the AI_{δ} is also variable as microwave cycles and long-term aging increase. There is not a gradual trend as expected. The most important variation of AI_{G^*} can be seen in bitumen 2, which after one microwave heating cycle (S_2) the G* increases in 2% (p-value<0.001, calculated with t-student test and 95% confidence level) in relation to bitumen 1. In the case of AI_{δ}, the most important variation was in bitumen 6, which after three microwave heating and two long-term aging cycles (S_6), the phase angle decreases in 4% (p-value<0.001) in relation to bitumen 1. This result confirms that the effect on the aging performance rheological properties of bitumen samples (G* and δ) was minor.

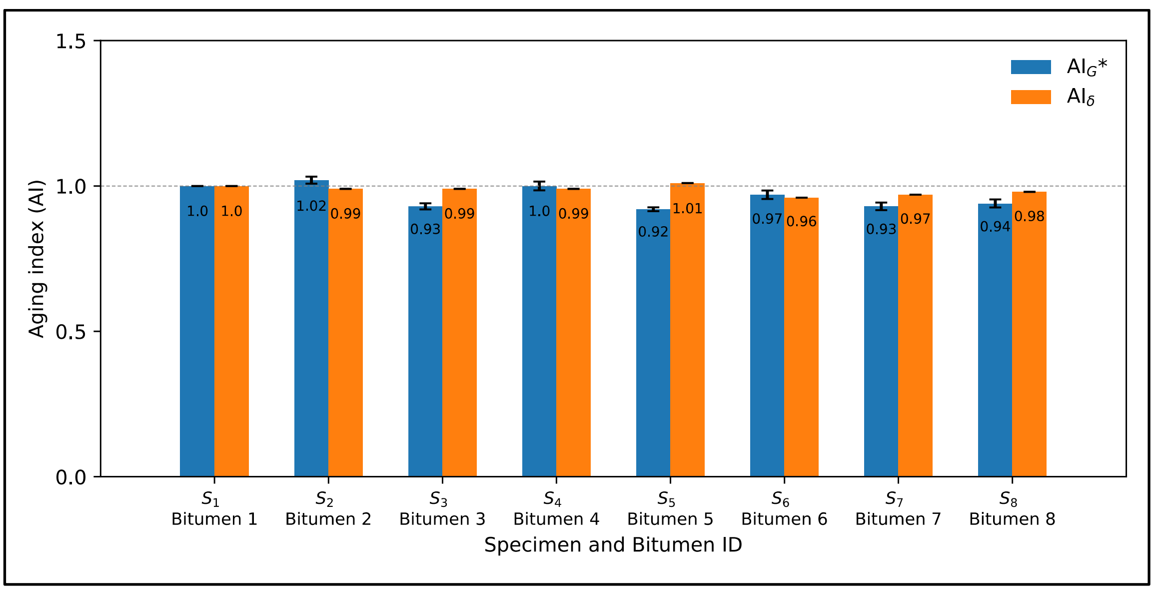

Figure 3.2. Aging indexes using G* and δ for criterion 1 20ºC@10 Hz.

Furthermore, Figure 3.6 shows the aging index of G* and δ for the second criterion. A similar trend to that of the AI_{G^*} and AI_{δ} at 20ºC (see Figure 3.5) can be seen at 60ºC. A variable behavior is noted in the indexes and not a gradual tendency as expected, since as microwave heating and long-term aging cycles increase, the oxidation process also increases, generating a gradual increase for AI_{G^*} and a gradual decrease for AI_δ. An unexpected result of AI_{G^*} can be noted in the bitumen 6 and 7, which relates to the control bitumen the AI_{G^*} with an increase of 31% (p-value<0.001) and 17% (p-value<0.001).

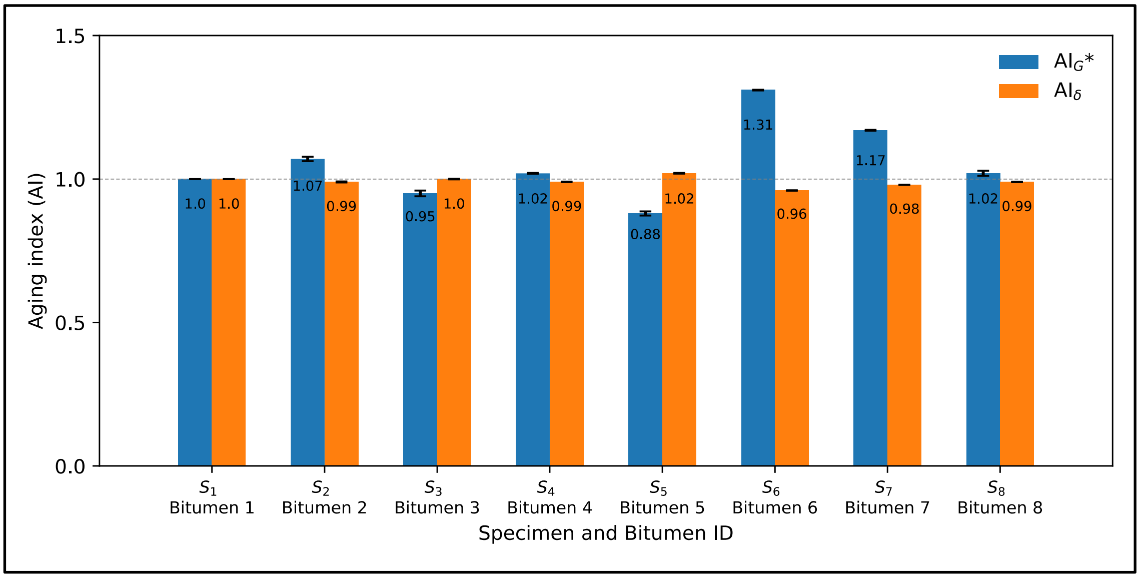

Figure 3.3. Aging indexes using G* and δ for criterion 2 at 60ºC@1 Hz.

3.4.1.2 Effect on the chemical properties of bitumen samples from phase I

Based on DSR results, only bitumen samples 1 and 8 were selected to compare the chemical changes when the bitumen is exposed to microwave heating and long-term aging cycles. Additionally, fresh bitumen 50/70 pen (without any artificial aging treatment) and PAV aged bitumen were analyzed to contrast with bitumen 1 and 8 in terms of FTIR. The FTIR spectra results ranging from 2000 – 600 cm^{-1} wavenumbers, which covers the regions for the main oxidative aging products (J. Wu, 2009b), are shown in Figure 3.7. Inside Figure 3.7 the absorption bands of the C═O and S═O groups of the bitumen were in a wavenumber range centered around 1700 cm^{-1} and 1030 cm^{-1}, respectively. The trend for all the bitumen samples were almost the same. However, as shown by the arrow in Figure 3.7, the FTIR spectra of bitumen 8 (blue line), there were new absorption peaks around 1100 cm^{-1} approximately. These results indicate that a new functional group was generated, which can be attributed to molecular interactions and chemical composition changes of the bitumen under microwave heating and long-term aging cycles. To appreciate the formation of an oxidation product, Figure 3.8 shows a closer view of the carbonyl and sulfoxide peaks framed in Figure 3.7.

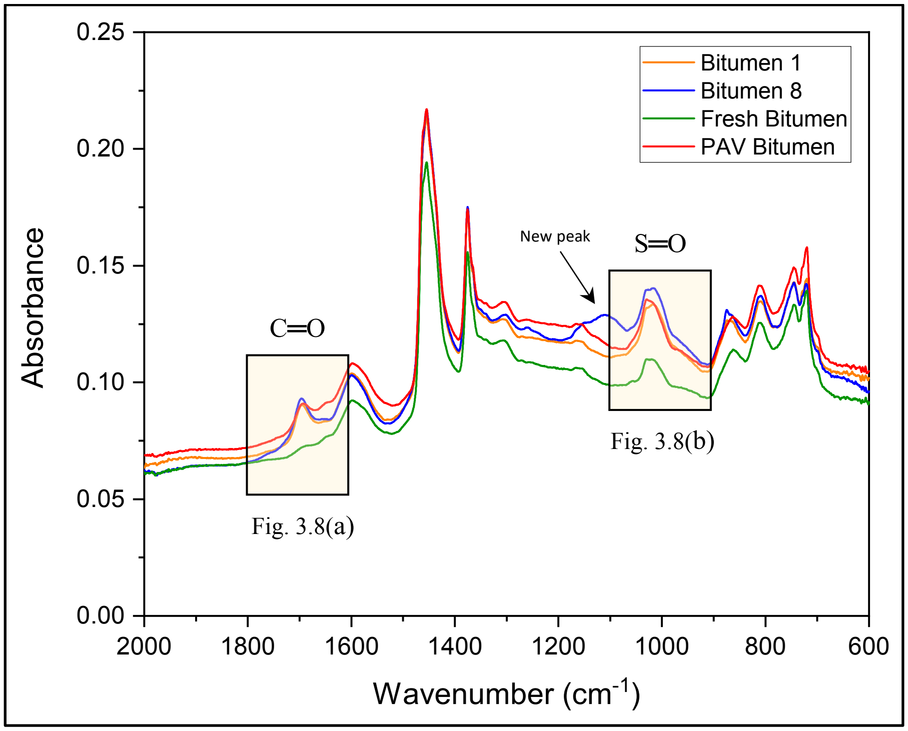

Figure 3.4. FTIR spectra of bitumen samples from phase I in a range 2000 – 600 cm^{-1}.

In Figure 3.8(a) the absorption peaks for the carbonyl group can be seen, where in bitumen samples 1 (S_1) and 8 (S_8) show a similar trend. However, the absorption of bitumen 8 is slightly higher than that of bitumen 1. In addition, at the peak 1700 cm^{-1} the PAV bitumen shows a similar absorption than bitumen 1, but lower absorption than bitumen 8. Moreover, the area amplitude for PAV bitumen is less than bitumen 1 and 8. Fresh bitumen has no peaks of carbonyl group. Likewise, in Figure 3.8(b) the sulfoxides group can be observed in the FTIR spectra, which could occurs because of the thermo-oxidative aging happens during the production and storage of bitumen (S. Wu et al., 2019). Figure 3.8(b) demonstrates that bitumen 1 and the PAV bitumen have a similar tendency in the sulfoxide zone. Additionally, bitumen 8 has a higher absorption in the sulfoxide zone than all bitumen samples. The obtained spectra carbonyl and sulfoxide indexes were calculated with formulas (6) and (7) to quantify the aging degree. Table 3.3 presents the carbonyl index ($I_{C=O}$) and sulfoxide index ($I_{S=O}$) of the different bitumen analyzed. In Table 3.3, it can be observed the carbonyl and sulfoxide indexes as the microwave heating and long-term aging cycles increase. Also, it should be noted that after four microwave heating and three long-term aging cycles, bitumen 8 (S_8) increased slightly the $I_{C=O}$ and the $I_{S=O}$ compared with that of bitumen 1 (S_1). Furthermore, fresh bitumen has the lowest rates, which is consistent with its virgin bitumen condition. PAV bitumen has a lower carbonyl index compared to bitumen 1 and 8, but similar sulfoxide index than bitumen 1 and lower than bitumen 8. These results are consistent with the literature because (1) carbonyl functional group is related with the increase of viscosity by effect of the aging of bitumen, and (2) sulfoxide functional group is usually produced in higher amounts than carbonyl group (Gonzalez-Torre & Norambuena-Contreras, 2020). Thus, the variation of carbonyl and sulfoxide groups represents the oxidation degree and further reflect the aging degree of bitumen. In short, the difference between the carbonyl index values for bitumen 1 (control sample) and bitumen 8 is smaller (0.0021), demonstrating the minor effects of aging on bitumen by effect of microwave heating and long-term aging cycles.

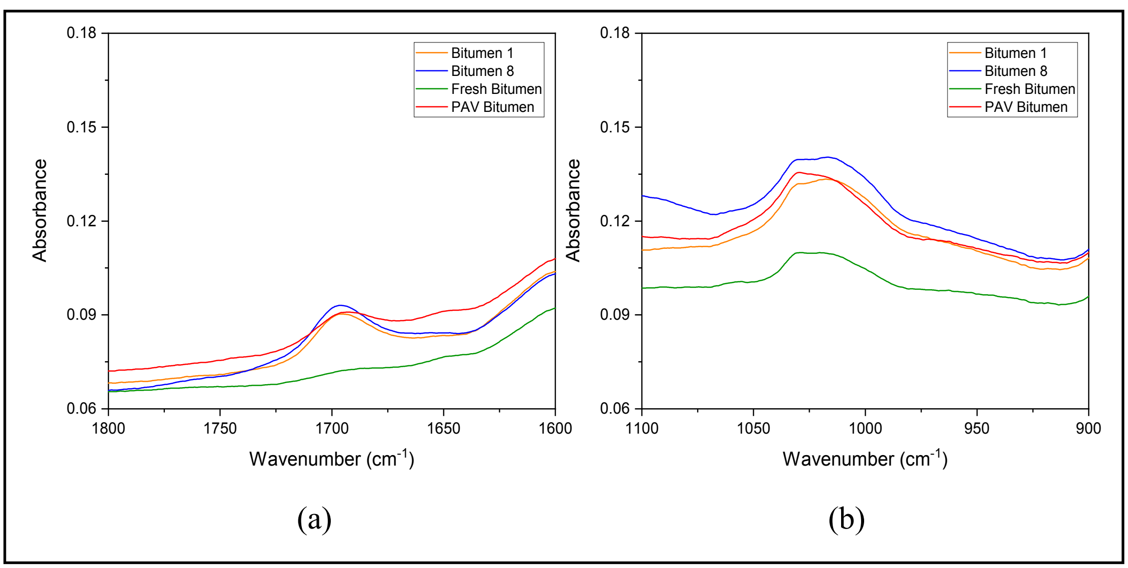

Figure 3.5. FTIR spectra of (a) C═O carbonyl and (b) S═O sulfoxide peaks.

Table 3.3. Carbonyl and sulfoxide indexes for all bitumen samples from phase I.

Bitumen	$I_{C=O}$	$I_{S=O}$
1	0.0345	0.0927
8	0.0366	0.0934
Fresh	0.0034	0.0422
PAV	0.0242	0.0928

3.4.2 Effect of the microwave heating and long-term aging on bitumen from phase II

3.4.2.1 Effect on the rheological properties of bitumen samples from phase II

In phase II a not-so-aged asphalt mixture was compared with phase I. Thus, in this phase and analogously to phase I (discussed in previous section) a comparison of master curves between bitumen 1 and 8 was carried out with the aim of analyzing the specimens most and least exposed to the microwave and long-term aging cycles. The master curves of G* and δ at reference temperature of 30ºC are presented in Figure 3.9 and Figure 3.10, respectively. As shown in Figure 3.9, the difference in the G* master curve for bitumen 8 is narrow compared to that of bitumen 1. There were slight differences after four microwave heating and three long-term aging cycles (S_8) for bitumen 8; the G* range of bitumen 8 was about 205 to 5.30×10^8 Pa and that of the bitumen 1 was 602 to 4.98×10^8 Pa. Besides, Figure 3.10 shows that the δ master curve for bitumen 8 is slightly lower than bitumen 1, which indicates that bitumen 8 could be more aged by effect of the heating aging cycles.

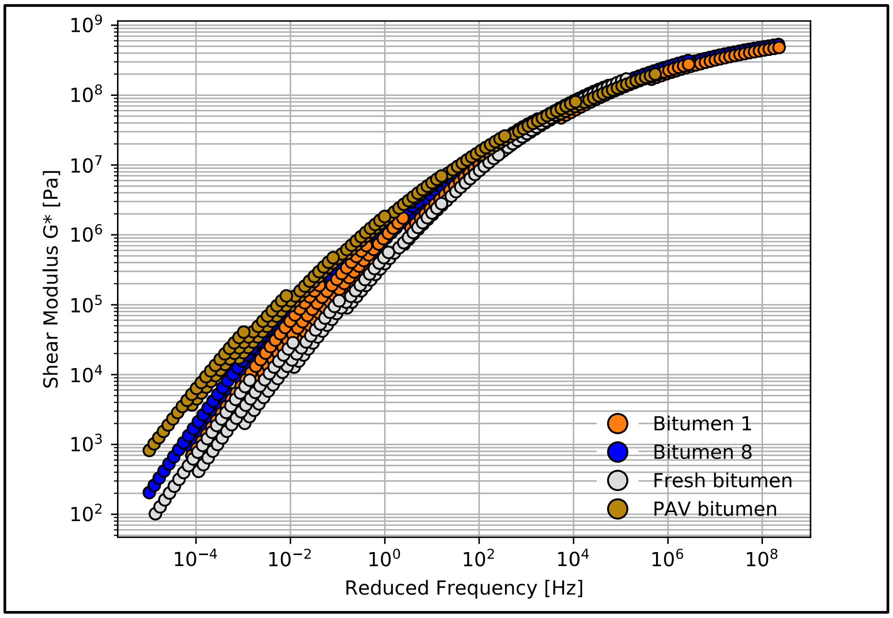

Figure 3.6. Master curves comparison for bitumen 1 and 8 in terms of G*.

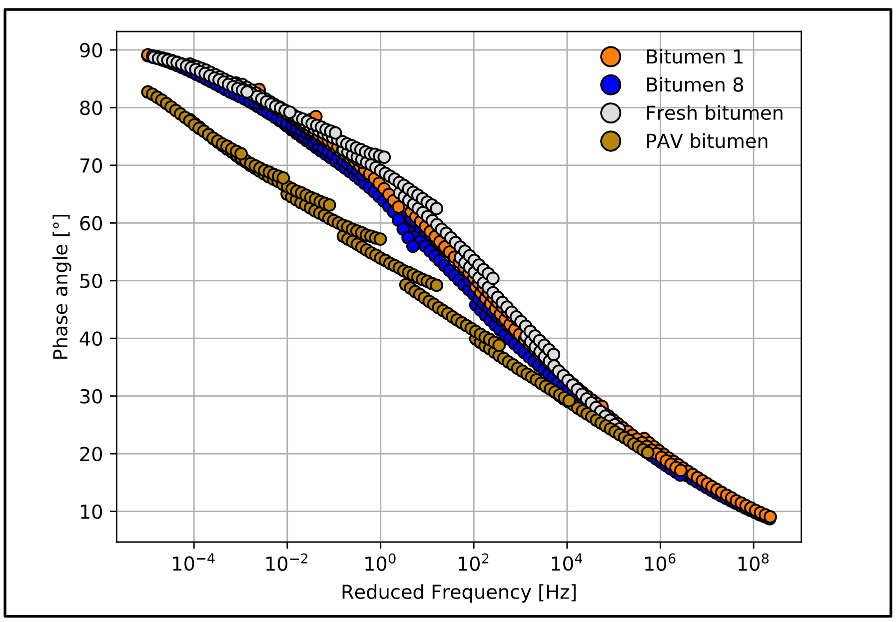

Figure 3.7. Master curves comparison for bitumen 1 and 8 in terms of δ.

Furthermore, fresh and PAV master curves were also drawn inside Figure 3.9 and Figure 3.10, to compare the aging level of the recovered bitumen samples. In Figure 3.9, PAV bitumen is seen as the most aged bitumen, since the master curves present greater values of G*. In contrast, from Figure 3.9 it can be seen that fresh bitumen shows a master curve with lower values of G*. Although bitumen 8 was exposed to four microwave heating and three long-term aging cycles (S_8), the master curve is lower than for PAV bitumen, which shows that the aging cycles may not present as much damage from aging as expected. This conclusion coincides with the observed rheological behavior for the bitumen samples tested in phase I.

Similarly, in Figure 3.10, at lower and intermediate frequency, there is an important difference in the phase angle master curves. PAV has the lower values of δ, which indicates that PAV bitumen has the most important aging in comparison with all bitumen samples. Hence, to quantify the effect of the microwave heating and long-term aging on the rheological properties of bitumen samples 1 and 8 from phase II, the rheological aging indexes (AI) were calculated according to the same criteria as for phase I, i.e., 20ºC@10 Hz and 60ºC@1 Hz, respectively. So, Figure 3.11 shows the aging index of G* and δ for both evaluated criterions.

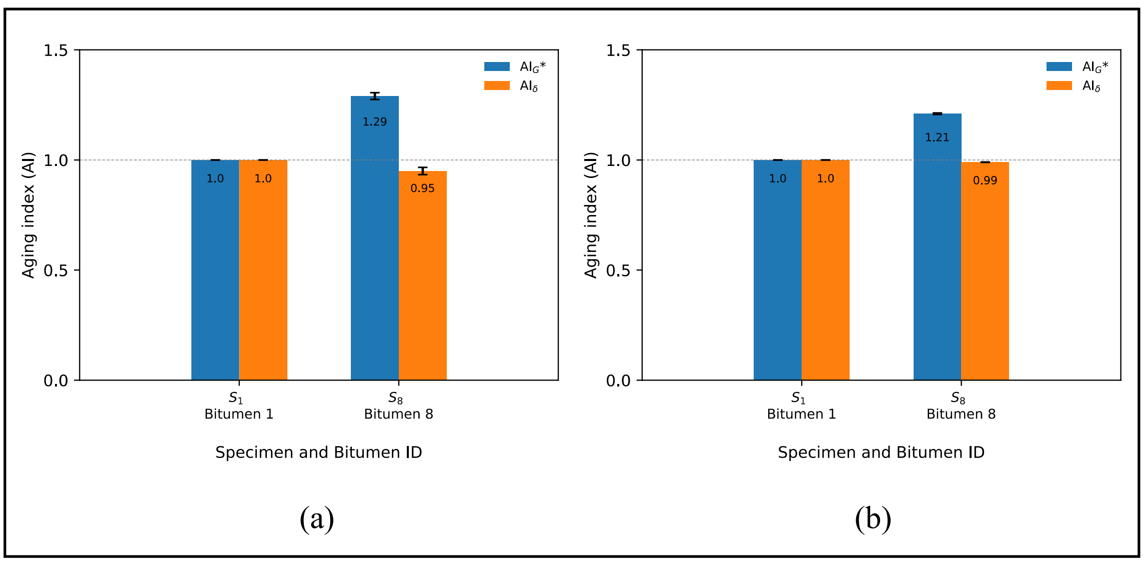

Figure 3.8. Aging indexes for criteria: (a) 20ºC@10Hz and (b) 60ºC@1Hz.

From Figure 3.11, it can be observed that as microwave heating and long-term aging cycles increase, AI_{G^*} increase and AI_{δ} decrease. This result is caused by the oxidation process of the chemical components of the bitumen, which impacts the mechanical properties of the bitumen, becoming the samples more solid-like, as indicated by increased G* and decreased δ. If the aging indexes at 20ºC and 10Hz are compared in Figure 3.11(a), it can be seen that the bitumen 8 increased by 29% (p-value<0.001, calculated with t-student test and 95% confidence level) in relation to bitumen 1. In Figure 3.11(b), the aging index for the bitumen 8 increased in 21% (p-value<0.001) in relation to bitumen 1. For the AI_{δ} at 20ºC and 10Hz, bitumen 8 decreased the aging index by 5% (p-value=0.0015) and at 60ºC and 1Hz the variation of the AI_{δ} is 1% (p-value<0.001), both in relation to the bitumen 1.

3.4.2.2 Effect on the chemical properties of bitumen samples from phase II

In phase II, the same chemical analyses were made for bitumen 1 and 8 to analyze the chemical composition changes of bitumen in different aging levels by effect of the microwave heating and long-term aging. Thus, fresh bitumen 50/70 pen and PAV-aged bitumen were analyzed to contrast with bitumen 1 and 8 in terms of FTIR discussion. The spectra collected from 2000 – 600 cm^{-1} are shown in Figure 3.12. Figure 3.12 shows that (1) the trend for bitumen 1 and 8 were almost the same, so no new functional groups were generated during the oxidation process with either the microwave and long-term aging cycles, and (2) with the increase of the aging severity the absorption spectra gradually increases. Based on Figure 3.12, peaks at 1030 cm^{-1} that have stretch vibration of the sulfoxide group were observed in all bitumen samples. However, peaks at 1700 cm^{-1} related to the carbonyl group were only observed in the FTIR spectrum of the PAV and bitumen 8. For a better appreciation of the formation of an oxidation product, Figure 3.13 shows a closer view of the carbonyl and sulfoxide peaks framed in Figure 3.12.

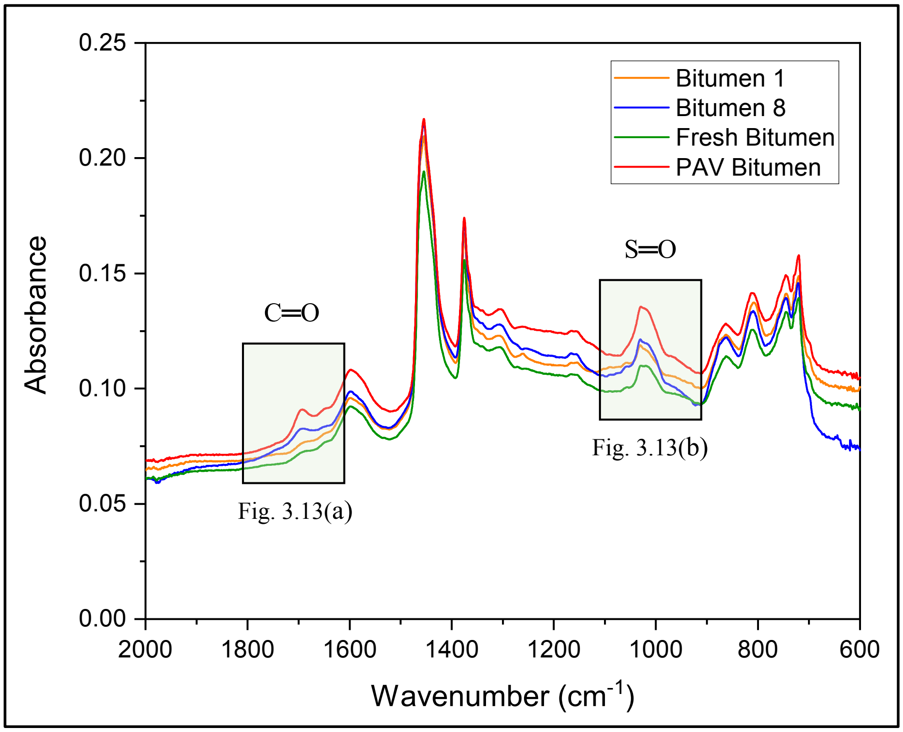

Figure 3.9. FTIR spectra of bitumen samples from phase II in a range 2000 – 600 cm^{1}.

From Figure 3.13(a) it can be observed that the PAV bitumen presents the greater absorption in the carbonyl zone than the other bitumen samples. Moreover, no carbonyl group peaks were observed for bitumen 1 and fresh. In the carbonyl zone, see Figure 3.13(a), bitumen 8 has a slighter increase of absorption than bitumen 1. In contrast, Figure 3.13(b) shows that the peaks of the sulfoxide group were similar to each other for all bitumen samples, while the ratio of the peak area was different. The amplitude for the area increases as the aging level of the bitumen increases. In particular, the amplitude for the area of PAV bitumen was the greatest. In addition to the spectrum observation, the effect of aging was evaluated by the carbonyl and sulfoxide indexes. Table 3.4 presents the carbonyl and sulfoxide indexes for all bitumen from phase II.

After four microwave heating and three long-term aging cycles the $I_{C=O}$ for bitumen 8 reached 0.0109, which is 1.4 times higher than $I_{C=O}$ for bitumen 1. Comparing the results with PAV bitumen samples, it can be seen that $I_{C=O}$ reached 0.0244, which demonstrated that the bitumen aging has a much higher effect than in bitumen 1 and 8. In the case of $I_{S=O}$ bitumen 8 measures 1.2 times higher for bitumen one, and gradually increases as the bitumen aging severity increases, with the PAV bitumen having the greatest index, showing the minor effects of aging on bitumen by effect of microwave heating and long-term aging cycles. This result is consistent with the obtained conclusions for phase I.

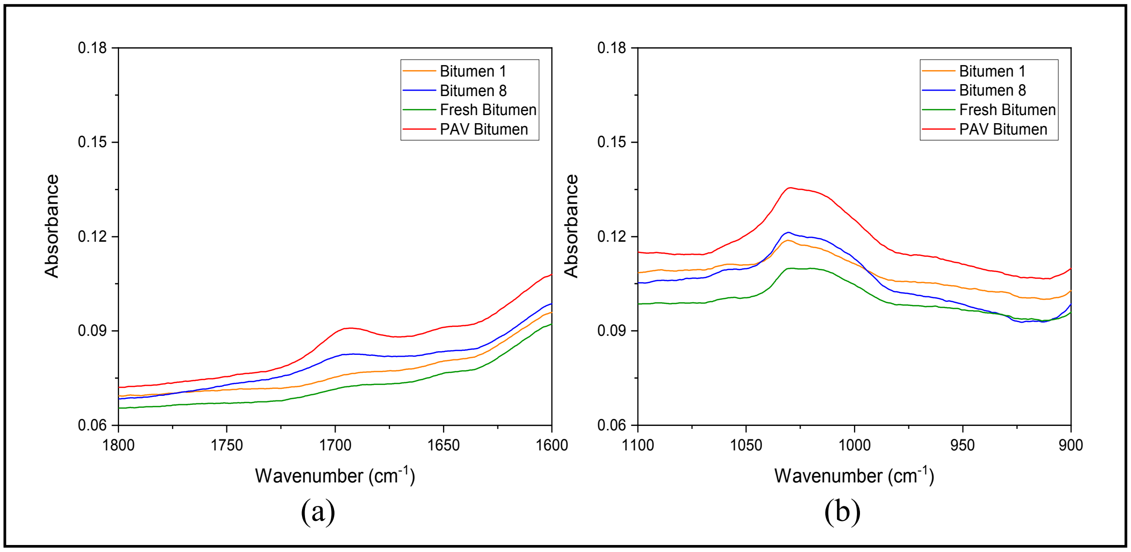

Figure 3.10. FTIR spectra of (a) C═O carbonyl and (b) S═O sulfoxide peaks.

Table 3.4. Carbonyl and sulfoxide indexes for all bitumen samples from phase II.

Bitumen	$I_{C=O}$	$I_{S=O}$
1	0.0078	0.0512
8	0.0109	0.0616
Fresh	0.0034	0.0422
PAV	0.0242	0.1112

3.4.3 Relationship between chemical and rheological results from phase I and II

It is widely recognized that the performance of asphalt mixture is largely dependent on the rheological behavior of bitumen (Yang et al., 2018). At the same time, the rheological properties depend on the chemical changes of the bitumen (Miró et al., 2015). Qin et al. (Qin, Schabron, Boysen, & Farrar, 2014) found a linear relationship between rheological parameters and chemical composition such as FTIR absorbance given by the sum of carbonyl and sulfoxide indexes. In this context, Elwardany et al. (2017) and Ge et al.

(2019) confirm this behavior, where G* increased consistently when the sum of carbonyl index ($I_{C=O}$) and sulfoxide index ($I_{S=O}$) increased. Figure 3.14 presents a relationship between the sum of the carbonyl and sulfoxide indexes ($I_{C=O} + I_{S=O}$) and log G* at 64ºC and 10Hz from obtained results of phase I and II and literature results (Elwardany et al., 2017). As can be seen, as the sum of $I_{C=O}$ and $I_{S=O}$, increases, the log of the complex modulus at 64ºC and 10Hz also increases.

Additionally, Figure 3.14 shows two literature results corresponding to a recovered bitumen from a compacted specimen exposed during a procedure of PAV (3 days at 85ºC and 300 kPa air pressure) and another from an eight-years-old field core (Elwardany et al., 2017), in order to contrast the aging level of the samples in phase I and II. As can be seen, the results of phase I for the bitumen 1 and 8 were very similar to the results of the eight-years-old field core. While the results of the Log G* at 64ºC for phase II are lower than for the bitumen PAV, which simulates a long-term aging of approximately 5 years (Elwardany et al., 2017). Comparing all the results of phases I and II, it can be concluded that the changes in chemical and rheological properties are very low mainly resulting from the viscoelastic properties that change at a lower rate for aged materials (Yuhong Wang et al., 2014). The opposite can be seen in phase II, where the material used is newer, and after different microwave heating and long-term aging cycles the changes are greater.

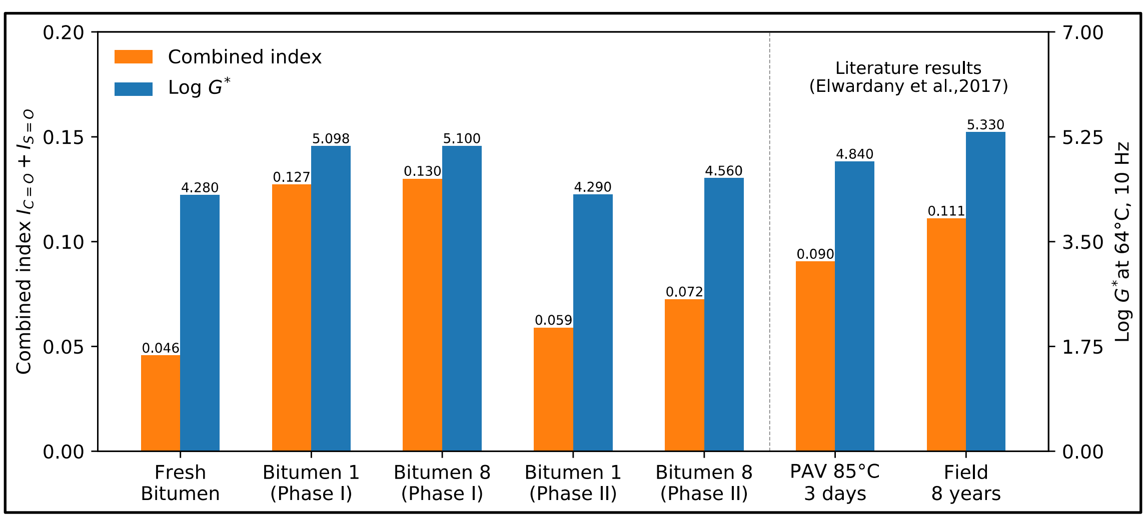

Figure 3.11. Relationship between chemical and rheological results from phase I and II.

From a chemical perspective, the hydrocarbon reaction of the free radical of the bitumen with oxygen is responsible for most of the oxidative aging (Petersen & Glaser, 2011). Aging could be summarized as a process in which the chemical components of the bitumen vary, are consumed and increased. The components move from more non-polar fractions to the more polar fractions as oxygen containing functional groups are formed in the asphalt (Petersen, 2009). As the time of aging increases, the free radical begins to decrease. Initially there is a rapid reaction followed by a slower, constant rate reaction (Petersen & Glaser, 2011). This may be a response to the results obtained in phase I, where the oxidation process does not have a clear behavior. Comparing bitumen 1 and 8 proved that aging reflected in the chemical and rheological properties is low.

3.5 Conclusions

This paper evaluated the aging effect on bitumen exposed to different microwave heating and long-term aging cycles through rheological and chemical parameters. Based on the test results, the following conclusions were drawn:

- In phase I, not clearly effect was observed in G* and δ master curves. Master curves of all bitumen samples overlap; therefore, microwave heating and long-term aging did not present a significant effect on the aging performance of G* and δ for aged asphalt mixtures.

- In phase II, a slight increase of G* and δ master curve for the bitumen 8 in relation to bitumen 1 was noted, indicating that the rheological properties of bitumen showed minor changes with microwave heating and long-term aging cycles for newer asphalt mixtures.

- The aging indexes quantified in phase I showed a variable trend, which would have been expected to increase as cycles increase. In phase II, as the microwave heating and long-term aging cycles increase, the AI_{G^*} increase and the AI_{δ} decrease, which demonstrated that microwave heating and long-term aging influences bitumen aging.

- From FTIR results, as the microwave heating and long-term aging cycles increase, the carbonyl and sulfoxide index increased in both phases. Therefore, bitumen aging influences chemical changes of bitumen, including the formation of carbonyl and sulfoxide compounds. It was found that the chemical changes reduce the viscoelastic properties of the bitumen as shown in DSR tests.

- Overall, this study confirms that microwave heating is a sustainable alternative for maintenance of asphalt pavements, without severely affecting the rheological and chemical properties of bitumen. However, the application of microwaves to a newer pavement can result in minor or moderate aging.

3.6 Acknowledgements

First author thanks for the financial support provided by TU Dresden as part of the Scholarship Program Erasmus+ student mobility for traineeships from partner to program countries. The lead author also thanks to Dr. Frohmut Wellner, chair of the Institute of Urban and Pavement Engineering and Sabine Leischner and Gustavo Canon from TU Dresden for their support in this research, in addition to René Schubert, Matthias Bisse, Mrinali Rochnali for their assistance during the experimental work. Finally, the first author also wants to thank the financial support given by Impulso Inicial foundation from Chile.

4. CONCLUSIONS AND FUTURE WORKS

4.1 Conclusions

This thesis investigated the effects of microwave heating and long-term aging on the chemical and rheological properties of asphalt mixture, using the same base bitumen with two modes of aging. The asphalt mixture specimens were exposed to different levels of microwave heating and long-term aging. The chemical change in molecular composition of bitumen were determined using Fourier Transform Infrared Spectroscopy. The rheological properties of the samples were measured using a Dynamic Shear Rheometer. The tests done on these eight materials in both phases included the strain and frequency sweep test.

Based on the results presented in the third chapter of this thesis, the main objective oriented to the evaluation of the effect of microwave heating and long-term aging on the chemical and rheological properties of recovered bitumen has been fulfilled. This objective was fulfilled from the development of the two specific objectives proposed, being evaluate and determine the chemicals and rheological effects of microwave heating and long-term aging on the recovered bitumen. The use of G* and δ master curves, rheological aging indexes, and Carbonyl and Sulfoxide indexes allowed to corroborate the hypothesis, since microwave heating is a promising alternative for preventive maintenance of asphalt pavements because the increase in the functional group carbonyl and sulfoxide does not affect more than 30% of the complex module and 5% of the phase angle of the bitumen.

The principal conclusions which can be drawn from the experimental work presented in this thesis include:

- Microwave heating and long-term aging has no significant effect on the aging performance of G* and δ for aged asphalt mixtures. However, the rheological properties of bitumen show minor changes with microwave heating and long-term aging cycles for newer asphalt mixtures.

- From chemical point of view, as microwave heating and long-term aging cycles increase, the carbonyl and sulfoxide functional groups increased in both phases. Therefore, bitumen aging influences chemical changes of bitumen, including the formation of carbonyl and sulfoxide compounds.

- It is possible to confirm that changes in molecular composition of the samples vary the viscoelastic properties of the bitumen as shown in DSR tests.

- A strong relationship can be observed with chemical and rheological results, showing that both properties are good indicators to evaluate bitumen aging.

- Overall, this study confirms that microwave heating is a sustainable alternative for maintenance of asphalt pavements, without substantially affecting the chemical and rheological properties of bitumen.

4.2 Future works

It is recommended further analysis for localized aging that may occur at the aggregate-bitumen interface where the aggregate becomes much hotter due to heat absorption by microwave heating. An adhesion analysis and bitumen recovery at the interface zone is recommended for the analysis.

Self-healing of cracks in asphalt pavements by external microwave heating is a promising technology to build more durable asphalt pavements. However, it is recommended further analysis for environmental performance of this technique. Life cycle assessment (LCA) is required for pavements self-healed with microwave heating compared to traditional flexible pavement maintenance technique, particularly in relation to greenhouse gas emissions.

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