EXPERIMENTAL CHARACTERIZATION OF CHEMICAL AND PHYSICAL PERFORMANCE OF EPOXY MODIFIED BITUMEN

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EXPERIMENTAL CHARACTERIZATION OF CHEMICAL AND PHYSICAL PERFORMANCE OF EPOXY MODIFIED BITUMEN

THESIS

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by

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Summary

The increasing traffic load has led to the use of polymer modifiers in bituminous mixes in order to improve the performance and the durability of the pavement structures. Epoxy is a thermoset material which ensures enhanced fatigue performance and improved mechanical characteristics when used to modify bituminous materials. However, unlike conventional modification techniques, a series of experimental methods have to be conducted to evaluate the chemical- related phenomena occurring during the binder production and their effects on the performance of the epoxy modified bitumen. For this reason in this thesis, the utilization of epoxy modifiers was investigated at binder level.

Initially, the chemical hardening (curing) process of epoxy modified bitumens (EMBs) was investigated by means of Fourier Transform Infrared (FT-IR) spectrometer and Dynamic Shear Rheometer (DSR). Different combinations of hardening conditions for three epoxy modification levels were studied. Properties, such as modulus and viscosity, were utilized to determine the workability of EMB. At the same time, by using the FT-IR spectrometer, the functional groups of EMBs during the chemical reactions were identified for the understanding of polymerization in the epoxy components.

Additionally, the DSR device was utilized to determine the fatigue and tensile strength of EMBs. It was found that, with increasing the content of epoxy modifier, the fatigue life and tensile strength were increased significantly compared to an unmodified binder.

Finally, the age hardening (aging) of EMBs was evaluated at different time intervals. For the simulation of short-term aging on EMBs, a short-term oven aging method (STOA) was used. For long-term aging, simulations were performed in a pressure aging vessel (PAV) under constant pressure and temperature. The results of chemical characterization and rheological properties of the aged EMBs were obtained by using DSR and FT-IR and were compared to the unmodified bitumen.

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Introduction

In this chapter, the main objectives of this research are given. The research questions generated as well as the framework in which this thesis was performed, are presented. The experimental techniques used during this research and the methodology to answer the research objectives are shortly described. An overview of the whole report is finally provided.

1.1. INTRODUCTION

Bitumen is the most widely used binder in pavement engineering. Nowadays, the changing climatic conditions combined with the increase of traffic loads make the use of various chemical additives, named modifiers, such as plastomers and thermoplastic elastomers, an alternative solution for long lasting binders. Distress phenomena, such as rutting and low temperature cracking, are addressed satisfactorily with modified binders [1, 2]. Despite the fact that several types of modifiers ensure enhanced performance, they lack to establish durable and sustainable pavements as long-term solutions. Currently, a new modifier, namely epoxy resin, is used to further improve the properties of bitumen and promises enhanced resistance to physico-chemical degradation, improved fatigue life and excellent adhesive characteristics [3, 4, 5]. Based on these advantages, epoxy modifiers were utilized in the bituminous mixes for orthotropic steel decks, tunnels and intersections subjected to heavy traffic loads [6].

The successful implementation of this technology in open-graded surfacing mixes in New Zealand, increased strongly the interest of using epoxy modifiers [7]. However, before application, the understanding and assessment of the chemical (curing) and age hardening (aging) of epoxy modified bitumen (EMB) is of great importance. Therefore, this research emphasizes on addressing the unknown chemical-related processes that take place in epoxy modified bitumen. The available time after the mix production to complete the construction is limited, because of the nature of the modifier. Other than the thermoplastic modifiers, epoxy resins are thermosets and become solid after the completion of certain chemical reactions [8]. Different time intervals were used to evaluate the chemical and age hardening that take place with this particular modifier.

1.2. THESIS FRAMEWORK

This thesis was performed as part of a large project to implement epoxy asphalt concrete (EpoxAC) mixes in the Dutch industry. This research has been focused on how the epoxy modifier affects the binder properties at micro-scale. Particularly, beside the ultimate goal of this research which was the development of a durable binder with improved mechanical characteristics, this research targets to identify the influential factors related to chemical and age hardening of EMB. Three modification levels of epoxy modifier were utilized and mixed with virgin 70/100 penetration grade. Different conditions of temperature and time were used as hardening conditions. As a reference, the unmodified binder was also evaluated in the same testing series.

1.2.1. RESEARCH OBJECTIVES

The research objectives of this thesis attempt to give clear answers to the following statements.

- The critical hardening conditions of EMBs should be understood completely, to have full control of all application related operations.
- The performance evaluation of EMB compared to unmodified bitumen is needed.
- The possible material degradation should be simulated for short- and long-term.

1.2.2. METHODOLOGY

For the investigation of the aforementioned research objectives appropriate experimental tests were performed. The experiments were divided into two main phases. In total, 231 tests were performed in the facilities of Delft University of Technology. Firstly, the critical chemical hardening was evaluated. The functional groups related to chemical hardening were identified and demonstrated by means of FT-IR spectrometer. DSR frequency sweep tests and time sweep tests for assessing the viscosity and modulus evolution were performed for different conditions as well. In the second phase, the performance before and after aging was determined. For the simulation of age hardening (aging), samples were placed in an oven for certain time intervals and in the pressure aging vessel, and they were tested in DSR and FT-IR. An overview of the thesis structure is depicted in **Figure 1.1**.

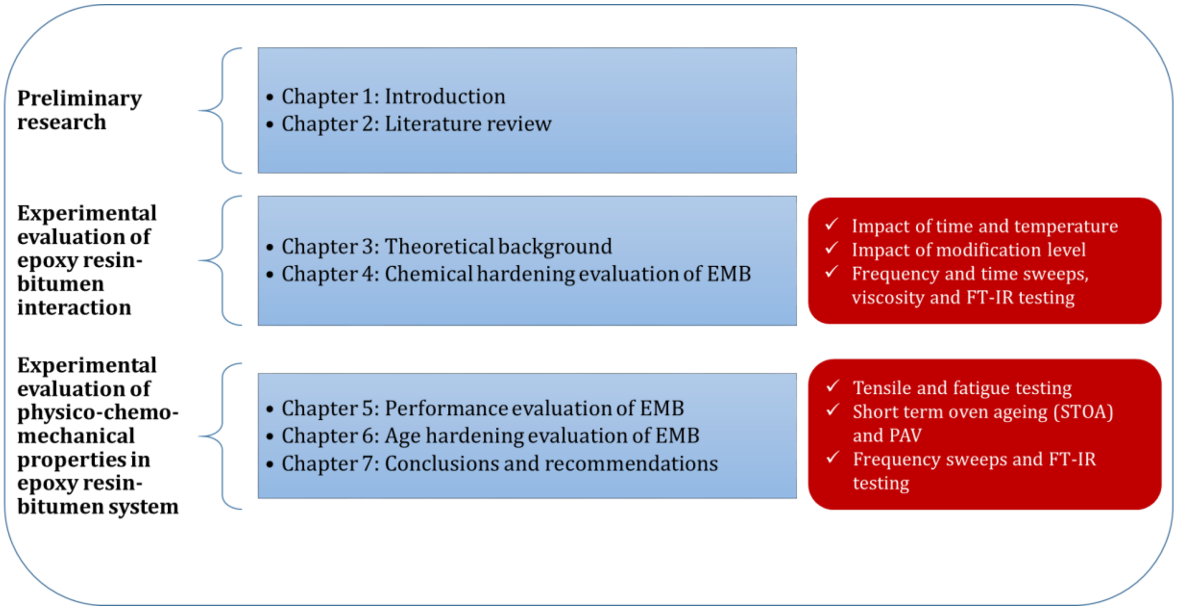


Figure 1. 1: Overview of the thesis

1.3. THESIS OUTLINE

In the first Chapter, the objectives and the framework in which this thesis was performed are given. In the second Chapter, a literature review of bitumen and polymeric modifiers is described. A short history of epoxy resin and its applications are given. The alternative modification of bitumen with epoxy resins, its molecular crosslinking and the production consequences are analyzed in the same Chapter. The description of the tests performed with

DSR and FT-IR spectroscopy is given in the third Chapter. In the following Chapter four, the main chemo-mechanical properties related to the curing process, which were obtained from various tests are presented and discussed. From the previous chapter, the critical conditions of curing were identified and used in Chapter five, to compare the performance of EMBs with the conventional bitumen. In Chapter six, short- and long-term aging were investigated and the results are discussed. Finally, the main conclusions and recommendations are presented in Chapter seven.

2

Literature Review

In this Chapter, the importance and the advantages of polymeric modification in bituminous binders is discussed. The utilization of epoxy resin as modifier in bitumen is introduced, presenting also an overview of the existing applications of this technology.

2.1. INTRODUCTION

Bitumen is one of the oldest materials used in civil engineering [8]. Thousands of years ago bitumen was applied and its improved performance regarding the adhesion strength, waterproofing and preservative properties has been reported by many researches. Its outstanding advantage compared to other materials lies in the exploitation of bitumen as a binder material in pavement constructions [9].

Bitumen was already known from ancient times, found initially in the Salt Sea. The use of this bitumen was eventually succeeded, after special treatment, with surface discharge from the bottom of the sea. Other well-known deposits of natural bitumen were found in Trinidad Lake and Venezuela. Another formation of asphalt is the rock type, such as limestones enriched with bitumen, which is called tar sand. This type of rock can be found in Alberta in Canada, and East Venezuela. Due to the high cost of recovery of bitumen from rock types, only the natural bitumen lakes are widely used for pavement purposes [9]. Another type of bitumen, which is mainly used from the 1900s in the USA is the artificial bitumen or refined bitumen produced as a by-product of refining crude oil [8]. From that time onwards the world consumption of bitumen increased rapidly and used predominantly in the pavement industry (85% of the whole consumption) [10]. According to CEN EN 12597 (2000), bitumen is defined as :

> *"An involatile, adhesive and waterproofing material derived from crude petroleum or present in natural asphalt, which is completely or almost completely soluble in toluene and very viscous or almost solid at ambient temperatures".*

The previous definition is used in the European pavement industry, whereas the word asphalt is defined as a mix of mineral aggregates and bitumen. In contrast to European terminology American specifications ASTM D 8 (2013) use the term asphalt for bitumen. To prevent confusion in this thesis the European terminology was followed. According to the American specifications binder is the bitumen without any modifier included.

The procedure that is followed for the production of high-quality bitumen from crude oil sources is described in the sub-Chapter 2.2. It is a fact that the refinery processes and the attempt of their effective control are among the obstacles for high-quality bitumen [11]. In addition, increased traffic load and insufficient maintenance made the demand for more durable and less susceptible pavements urgent. One very promising alternative was the use of various modifiers in bituminous mixes. An overview of the most commonly used and their chemical composition is described in the next sub-Chapter 2.3.2. In the sub-Chapter 2.4. the application of epoxy resins as bitumen modifiers and their use until now are given. Their chemical composition differs from the conventional modifiers. The improved performance of the new technology is also briefly presented.

2.2. BITUMEN DISTILLATION

The refined bitumen used today is a by-product of fractional distillation of crude oil. The crude oil was created millions of years ago from organic parts deposited in very thick layers together with rocks at the bottom of the oceans. A combination of pressure, radiation and temperature between the waterborne rocks and the presence of salt in the deep oceans turned the organic matter into hydrocarbons [9]. After millions of years, crude oil raised to the surface through rock pores or formed underground reservoirs in impermeable rock formations. The composition of the organic material and the conditions under which the crude oil was created affect also the final chemical and physical properties. Consequently, crude oil differs from one place to another and varies from black and viscous to tawny and viscoelastic liquid.

Among the oil-producing areas all over the world only a few are suitable for producing bitumen. The bitumen, as a by-product of crude oil (petroleum) is obtained after fractional distillation under high-temperature vacuum conditions. In many cases, the residue is further processed by blowing or oxidation, which is conducted for harder and more viscous bitumen. In this case the product is called oxidized bitumen. The process of bitumen production is given schematically in **Figure 2.1**. The type of bitumen produced is determined by both the origin of the crude oil, the vacuum (10–100 mm Hg) and the temperature conditions (350–400°C) that exist in the distillation column [9].

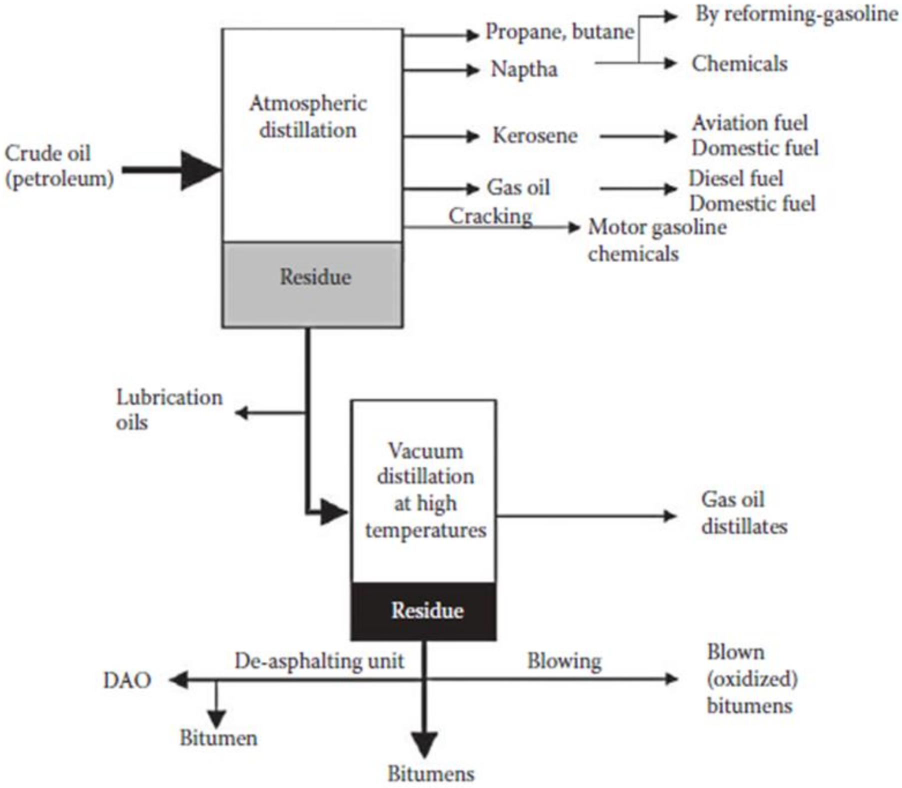


Figure 2. 1: Bitumen as a by-product of the distillation of crude oil **[9]**

2.3. BITUMEN MODIFICATION

One of the solutions applied to improve the properties of bitumen was the modification by incorporating different types of polymers. Among these polymers are ; plastomers, such as polyethylene (PE), polypropylene (PP), ethylene-vinyl acetate (EVA), ethylene-butyl acrylate (EBA), as well as thermoplastic elastomers, styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS) and styrene-ethylene/butylene-styrene (SEBS) [12, 13], resulting in high stiffness at high temperatures, high cracking resistance at low temperatures, lower moisture susceptibility and longer fatigue life [14, 15, 16]. Furthermore, some modifiers provide improved binder/aggregate adhesion bonding.

More recently, most of the research is focused on durability, recyclability and environmental aspects for the development of environmentally friendly products with enhanced durability [17]. However, individual constituents of paving materials affect the final performance and their trustworthiness. By increasing the content of polymer, phase inversion may occur in some polymer modified bitumen (PMB). In this case, the polymer phase is the dominant phase and leads to incompatibility with the conventional bitumen [18]. According to previous studies, the ideal mix composition contains two interlocked continuous phases showing an overall improved performance with respect to mechanical properties and cost-efficiency [19].

However, due to the fact that PMBs can present drawbacks related to low aging resistance and limited improvement in mechanical properties, alternative solutions have been proposed [17]. Epoxy modification was considered as an alternative. Epoxy modifiers which belong to thermoset elastomers, despite its high cost promise all the aforementioned improved properties of PMBs. In addition, these modifiers are more resistant to oxidative degradation at ambient temperatures [4]. These additional properties can improve the low skid-resistance in the final mix and protect against crack initiation due to aging.

For all type of modifiers, the chemical structure and reactivity with bitumen are of paramount importance because they determine the final compatibility with the bitumen [20]. For each type of reactive modifier, one needs to understand and predict potential effects in the lifecycle of the new blend and its influence in the final mix. One of the biggest obstacles in the application of modifiers at large scale is the rather high initial cost compared to unmodified binders. It is not always beneficial to choose the use of modifiers as a solution, and a preliminary study should be always done. Taking into account the estimated content of applied modifier and the traffic demands of the road, the right decision should be taken. At the moment, it is estimated that the percentage of PMB consumption is less than 20% annually in most European countries and the percentage of polymer modifier, such as SBS is 3,5% by weight in the final mix [21, 22].

2.3.1. HISTORICAL DEVELOPMENT

The utilization of different materials as modifiers, such as rubber, is not a new idea [23]. An example of such modifier was neoprene latex used in North America after the mid-50s [1]. Successively, plastomers before the 1960s and thermoplastic elastomers in 1965 were produced commercially initially for various purposes [24, 17]. It was first in roofing technologies that PMBs were applied and shortly after that in the paving industry. More specifically, due to the oil crises in 70s road construction with PMB started to be applied on a larger scale [25]. Independent researches showed that the use of PMBs could increase the permanent deformation resistance at high temperatures [26].

The necessity of thin layers for road industry during the 80s, with less material and more resistance, led to a more systematic exploitation of PMB, as thinner layers with PMB promised similar behavior with thicker unmodified layers [25]. In 1982 and 1983 several studies investigated the morphology and the use of bitumen modified with PE, as well as the occurred problems of its phase separation [27, 28]. The initial high-cost was reported in 1984 and claimed to be outweighed by the effects of the reduced thickness (less material used) and longer life. It was not before 1987 that the Strategic Highway Research Program (SHRP) in the USA made a clear distinction between unmodified and modified bitumen [29, 30]. At the beginning of the 20th century researchers investigated not only the mechanical but also the rheological behavior of PMBs to figure out the potential usability [31, 32]. The results of these studies ensure better elastic recovery, higher cracking resistance at low temperature and prevention of rutting [33, 34, 35]. Because some disadvantages were reported by utilizing polymers after 2000 many investigations focused to overcome these difficulties. Among the main difficulties reported, were the phase separation and the understanding of mechanisms related to failure. Different theories exist until today for the structure of PMB [36]. Among the solutions investigated to eliminate the disadvantages of PMB were sulfur vulcanization, adding of antioxidants, hydrophobic clay minerals and functionalization [37, 38, 39, 40].

The demand to reduce maintenance costs and increase the long life performance of bituminous materials initiated in the 1960s the idea of epoxy modified bitumen, originally developed by Shell Oil [41]. The idea was based on the use of a thermoset, namely epoxy, mixed with a hardener prior to the curing process. Thermosets had been already used in a wide range of consumer items, advanced composites for printed circuit boards, jet engine coals and ducts, aerospace structural components and high-performance sports equipment. The use of a thermoset as a surface coating was something new at this time and the idea was based on the exploitation of the good adhesive properties of epoxy [42]. The first applications of epoxy resin in pavement industry were on orthotropic steel bridges. One of the popular applications still in service is the San Mateo-Hayward Bridge surfaced with epoxy asphalt in 1967 [4]. The reported potential benefits of high fatigue resistance and rutting resistance, accelerated the involvement of epoxy modifiers in paving materials [41].

2.3.2. COMMON MODIFIERS

2.3.2.1. PLASTOMERS

One of the earliest types of plastomers, polyolefines, was used for bitumen modification. The structure of polyolefin contains polyethylene or polypropylene (**Figure 2.2).** The polyolefin is the dispersed phase, with the bitumen forming the continuous phase [43]. The interlocked continuous phases are ideal for low cost polyolefin modification in bitumen resulting in improved rutting resistance. Nevertheless, polyolefin materials cannot significantly improve the elasticity of the final blend and their compatibility with bitumen is rather poor due to the non-polar nature [17, 44].

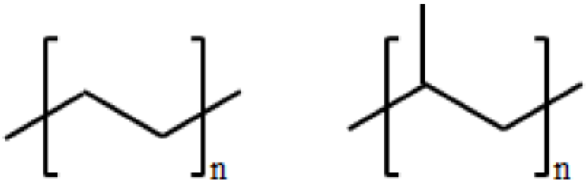


Figure 2. 2: Structure of polyethylene and polypropylene **[17]**

Other types of plastomers used are ethylene-vinyl acetate (EVA) (**Figure 2.3**) and ethylene-butyl acrylate EBA, both presenting enhanced resistance to rutting. The presence of polar acetate groups disrupts the crystalline microstructure, decreases the crystallization degree and increases the polarity of the polymer, eliminating in parallel the storage stability [17]. Increasing the vinyl acetate content leads to a biphasic microstructure with a crystalline phase and a vinyl acetate amorphous phase [8]. After EVA or EBA copolymers are added to the bitumen, the light components swell. Similar to polyolefines, two interlocked continuous phases improve the toughness, the rigidity of the network and the resistance to deformation. The problem of elastic recovery due to the nature of EVA and EBA still remains a disadvantage, as well as the glass transition temperature which depends on the content of the copolymer [45, 17].

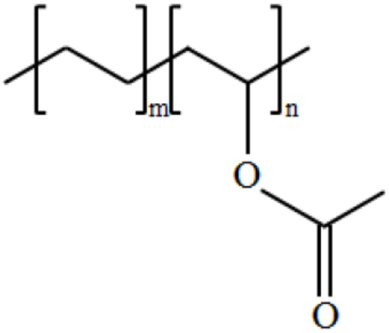


Figure 2. 3: Structure of ethylene-vinyl acetate (EVA) **[17]**

2.3.2.2. THERMOPLASTIC ELASTOMERS

Thermoplastic elastomers are another effective modification alternative. Among the most commonly used are SBS and SIS copolymers which have a similar chemical structure. Another type is the styrene-ethylene/butylene-styrene (SEBS) which results in low elasticity in the final mix and has a comparatively high cost. SBS and SIS show improved elastic response as well as temperature resistance but are less resistant to heat, ultraviolet and oxidation than conventional bitumen. According to the structure of these copolymers, SBS is composed of styrene-butadiene-styrene triblock chains with a biphasic morphology of rigid polystyrene domains in the flexible polybutadiene matrix [44]. The chemical bonds of polystyrene and polybutadiene can immobilize in the matrix as depicted in **Figure 2.4**. The structure of SIS copolymers shows similar behavior as the SBS.

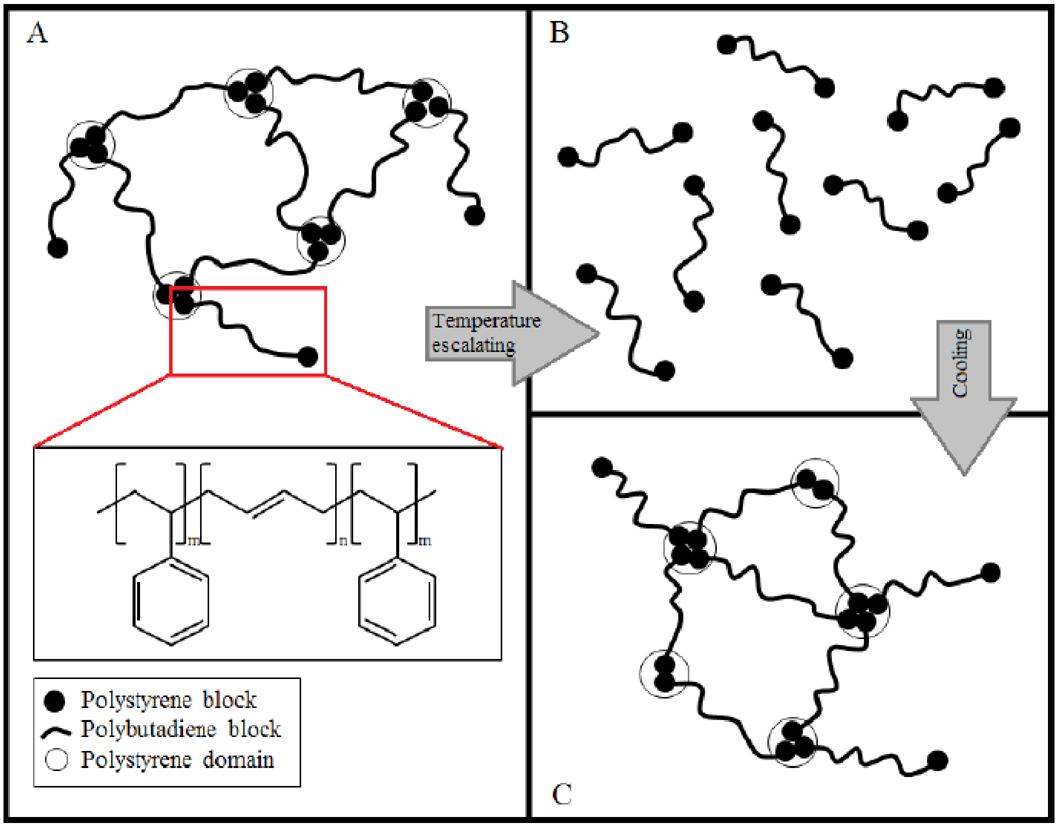


Figure 2. 4: Structure of styrene-butadiene-styrene and schematic of reversible crosslinking **[17]**

With respect to their properties, polystyrene blocks are glassy and contribute to the strength whereas polybutadiene provides the elasticity in bitumen [46]. In addition, the incompatibility of polybutadiene and polystyrene makes the crosslinking of polybutadienes possible as uniform domains governed by intermolecular forces. The crosslinking can be reformed and the related properties can be restored after cooling of bitumen, a fact that makes it popular as bitumen modifier, also because of the potential for recycling [47].

After adding the modifier, several interactions between bitumen and copolymer take place. These interactions are stronger than those between polybutadiene domains, and they enhance the compatibility with bitumen [48]. Moreover, an increase of the copolymer content leads to phase inversion in the PMB and two main sub-phases are observed: swollen polybutadiene matrix and pure polystyrene domains. The increased complex modulus is a result of the copolymer phase which creates a rubbery network in PMBs. This type of copolymers show storage instability, low heat, oxidation and ultraviolet resistance compared to bitumen, because of the presence of double bonds in the polybutadiene blocks [49]. Attempts to tackle the aging susceptibility of SBS and SIS by using high vinyl content SBS copolymers proved to be insufficient.

2.3.2.3. THERMOSET ELASTOMERS

One of the most popular thermosets is epoxy resin which is utilized in various applications with different hardening agents. One of the major differences with thermoplastics and plastomers is that thermosets cannot be reshaped and softened by reapplication of heat and pressure [42]. Moreover, the previous two categories are processed in molten stage and their polymer chains remain discrete after moulding. On the contrary, thermosets follow a different process which is distinguished in three main phases. The first phase is called resole in which the thermoset remains fusible and soluble. After that, they come into a nearly insoluble phase and remain however thermoplastic. One of the most important processes is the irreversible crosslinking of the material in the final stage. This takes place under specific heat and pressure conditions for a specific time period, during moulding of the product. Thus, thermosets build a final structure of a three-dimensional network of tightly crosslinked polymer chains (**Figure 2.5**) [42].

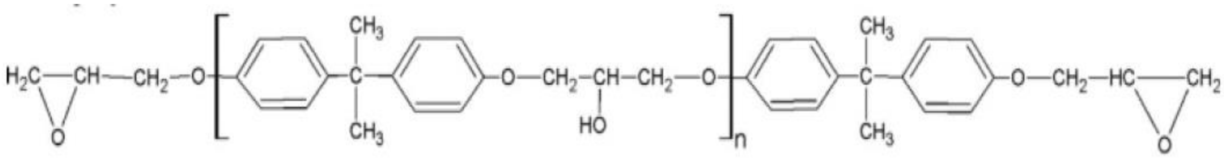


Figure 2. 5: Structure of a crosslinked epoxy resin **[50]**

One of the crucial aspects for the understanding of thermosets is to make clear the mechanisms of the formation of the crosslinked network. Different researches have been utilizing chromatography analysis, Fourier Transform Infrared (FT-IR) spectroscopy, Differential Scanning Calorimetry (DSC) and the rheological properties of the resin to identify the processes involved and the rheological changes in the nature of thermosets.

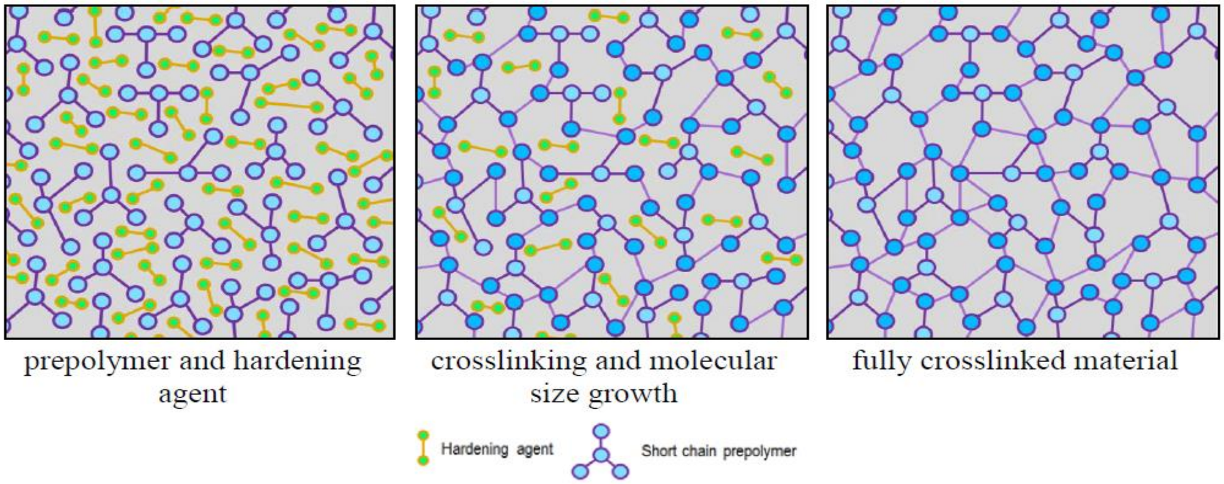


Figure 2. 6: Schematic representation of thermoset curing **[51]**

The formation of the crosslinking network, from the unreacted monomers until the development of small branched molecules, is described through the chemical hardening or curing process. Simultaneously, the molecular size growth is observed with the crosslinking of monomers. This process is accelerated with increasing temperature as the reactants are multi-functional and the crosslinks are formed among the polymer chains in all directions. There is a limit point in the chemical process in which the flow ceases and the whole system gels, known as gel point or gelation. The matrix becomes solid and the composites are fixed in a path across the sample. Providing an additional amount of heat is essential to reach an appropriate level of stiffness. This final step is also known as the post-curing step, after which a cured, cross-linked polymer is created. The different steps of this process are given schematically in **Figure 2.6**.

The changes that take place during the structural development can be observed as significant changes in rheological properties. The resin is the basic component of the thermoset combined usually with a hardening agent and a suitable solvent. During the chemical hardening, the resin changes from liquid state to gel and finally to solid [42]. The knowledge of these parameters is crucial for the paving industry in terms of controlling the material workability. The time window from production to transportation and construction of the road is also important with regards to low-temperature behavior of the blend, when cooling after placement. Consequently, the identification of the gel point after which the material turns into its solid state is important to employ this material effectively and economically. The development of modulus and viscosity are following the laws of non-Newtonian fluids. The main characteristic of this type of fluids, is the dependence in reaction time. Among the influential factors are the activation energy, the reaction order as well as the extent of hardening reaction until the gel point [51]. In addition to this, the polymerization rate depends highly on the temperature under isothermal conditions.

2.4. EPOXY MODIFIED BITUMEN

2.4.1. BITUMINOUS BINDER

Epoxy bitumen is commercially available from different suppliers usually in two parts, an epoxy resin and a blend of bitumen with a hardener. These two parts are mixed together to produce the epoxy modifier and the specific ratio differs according to the supplier and the application. Epoxy modifiers belong to the category of thermosets, thus the understanding of the chemical properties is of paramount importance especially for paving application.

Although an epoxy modifier is seen as a promising solution compared to common modifiers the manufacturing in practice (plant, transport, paving, compaction) faces difficulties because of possible accelerated or delayed chemical hardening. Efficient chemical hardening is important for a sufficient modulus and viscosity to open the road on time. Not only the aforementioned possible limitation but also the changes of production plants to allow proportional in-line feeding of epoxy modifiers into the pug-mill should be considered [51]. Therefore, a specific range of temperatures, mixing and compaction time should be given to fully control the production based on this time window.

For economic reasons, the epoxy modifier replaces part of bitumen. Thus, the modified blend is characterized as quasi-thermoset. The formulation of the epoxy part follows a slow acid-curing chemistry and relatively high temperatures (100-150°C) are necessary to be handled and applied easily [41]. Quasi-thermosets, however, need more time to form a crosslinked network through the polymerization process, because bitumen molecules interrupt the crosslinking. Once it has reached its gel point, it is considered cured and turns into a flexible rubbery consistency rather than a brittle glass. This rubbery material is guarantees an increased longevity and durability [51].

The epoxy resin is responsible for the improved properties of bitumen, however, phase separation can take place when bitumen and epoxy mixed together [52]. Epoxy resins consist of a linear chain molecule with a reactive epoxy group at each end of the chain which is known as epoxide [53]. The hardening agent or hardener is the second part, which reacts with the epoxide groups of epoxy to produce covalent bonds. Based on the type of hardener, epoxy modifiers are classified as amine- or acid-type [51]. Most commonly used are acids and anhydride acids which also improve the compatibility of bitumen and epoxy. Both types of EMBs are used as binders in dense- and open-graded bituminous mixes.

2.4.2. DENSE-GRADED BITUMINOUS MIXES

From the very first application of EMB on bridge decks until today many researchers tried to prove the long-lasting material performance. The first EMB was developed by Shell Oil company in the 1960s and it was not before 1967 that it was used as surfacing in San Mateo-Hayward Bridge, which is in-service until today. Other well-known bridges such as Westgate Bridge in Australia (1978) and Erskine Bridge in Scotland (1994) were also high deflection bridge decks constructed with this binder [4]. However, for the EMBs various applications are possible than in steel decks. EMBs were used in airfield and port pavements in the late 1950s. The first EMB was placed in 1959 at American Air Force and until the mid-1960s, 20 airfields in the USA used EMB as a thin overlay. The resistance to jet blast effects made EMB also suitable for aircraft parking and refuelling areas [4].

Thin dense-graded overlays of EMB were also used on concrete bridge decks because of their waterproofing and skid resistance properties. The most popular application is the San Francisco-Oakland Bay Bridge which was built in 1976 with 27,000 vehicles per lane every day [4]. Another application of EMB is in chip seals with stone size of approximately 10mm. These are applied prior to paving, on orthotropic steel decks before the installation of the deck system on the bridge. This method was used in the replacement of Golden Gate Bridge in the USA in 1986. In many cases, thin dense-graded waterproof layers were applied in orthotropic steel decks, such as the Ben Franklin Bridge in Philadelphia in 1984. Moreover, epoxy bond coats are used between the deck and dense-graded epoxy asphalt, especially in China after 2000 [4]. Finally, dense-graded concrete asphalts used EMB as a binder in 1986 in Staffordshire in U.K. This application promised better fatigue performance, in trafficked roads of metropolitan areas of Staffordshire [4]. EMB is also reported to have been used at intersections of heavy duty roads and in tunnels [51].

2.4.3. OPEN-GRADED BITUMINOUS MIXES

A special application is that of porous asphalt concrete, whose main characteristic is the high percentage of air voids. The choice of open-graded surfacing mixes reduces hydroplaning, it also results in pavement defects. EMB in open-graded surface material was first used in the late 1960s in San-Francisco-Oakland Bay Bridge. It resulted in improved skid- and wear-resistance and strongly improved durability with regards aging- and moisture-susceptibility. In 2006, the Organization for Economic Co-operation and Development (OECD) started a project in which agencies from New Zealand, Europe and USA participated. The aim of this project was the utilization of EMB as a binder for surfacings. The research was funded by the NZ Transport Agency and focused on open-graded bituminous mixes. The results from the research predicted a lifetime of 30 years instead of about 10 years until that time. Full-scale trials in the Canterbury Accelerated Testing Indoor Facility and Main North Road in Christchurch in 2007 were combined with success. The potential benefits of mixing of bitumen with EMB have been proved with only limitations related to the handling time from production plant to field operations [41].

2.4.4. HIGH PERFORMANCE

Previous research reported the potential benefits of epoxy modified bitumen which is summarized in the following list [4, 53, 54]

- EMB are more resistant to low temperature cracking due to their higher tensile strength and flexibility, something that was proved experimentally,

- They are less susceptible to distress phenomena such as fatigue cracking, rutting and oxidation; these make them an ideal choice for long-life surfaces with increased durability,
- They are stiff at service temperatures with a great load spreading ability,
- They perform ideally as adhesive materials and present increased resistance to surface abrasion from tyre action, preventing also ravelling,
- Water-induced damage, bitumen bleeding, fuel spillage and blast from jet-type aircrafts were also reported to be almost totally eliminated,
- It can be applied, after minor modifications, with conventional paving equipment.

2.5. CONCLUSIONS

From the current literature review, it can be concluded that large efforts have been made from the invention of bitumen until now to improve its properties. The various solutions suggested over the decades did not manage to address completely the experienced problems. Until recently, where EMB was suggested as an ideal long-life paving solution, the main interest was in polymer modification. It is suggested from the literature that EMB performs ideally, but there are some issues related to the production, that should be further investigated. During this research, these uncertainties related to the curing process will be investigated at binder level of EMB through laboratory testing. Finally, the excellent properties reported in various international reports will be validated in this thesis.

3

Theoretical Background

In this Chapter, the theoretical background of the two main devices used in this research, namely the Dynamic Shear Rheometer (DSR) and the Fourier Transform Infrared (FT-IR) spectrometer, is provided. The description of the main tests performed in DSR is given. Accordingly, the operating system of the FT-IR spectrometer is described and the processing of the results is thoroughly explained. This Chapter represents the introduction for the experimental part in which the various hardening processes were investigated. Performing the tests based on these testing conditions, the following chapters illustrate, compare and discuss extensively the results.

3.1 INTRODUCTION

The utilization of EMB seems outstanding compared to previous trials of bitumen modification. This high performance should be compared with unmodified bitumen through laboratory and field testing. However, from the literature review, it was concluded that some parameters need further clarification. With regards the in-plant material production, the modification of production facilities was reported to be limited. Plant modifications, such as additional storage tanks and a metering system to allow in-line blending of the epoxy components are required. From previous research, it has been reported that no further changes are required to lay the mix besides that of a well-scheduled planning of material production, storage and transport [55].

An important issue that makes the physico-chemical understanding more complex is the mixing of the epoxy components with bitumen. The final product should be economically optimized. The rather high initial cost of epoxy can be reduced by dilution of epoxy modifier with bitumen. Even low epoxy modification levels in bitumen will result in improved performance. A cost-benefit analysis conducted in New Zealand for an open-graded bituminous mix, where epoxy modifier was mixed with bitumen, proved to give about 2.5 times lower Present Worth of Costs compared to unmodified binders [55]. This means that the expected long-term material performance can outbalance the high initial cost of this modification technology. In this chapter, the theoretical technical details of the DSR and FT-IR device and the different tests performed are described.

3.2. DYNAMIC SHEAR RHEOMETER (DSR)

3.2.1. BASIC PRINCIPLES

The DSR device was used according to European Standard EN14770:2012 [56] for the measurement of the elastic and viscous nature of bituminous binders for a range of temperatures and frequencies in the viscoelastic region. This type of test is based on the oscillation of the upper of two parallel plates and in between a sandwiched sample is placed. The sample is subjected to sinusoidal torque or sinusoidal angular displacement of constant angular frequency. The rheological properties are extracted as the result of the applied torque converted into shear stresses or strains [57]. This method is applicable not only to unaged but also to recovered, cured or aged bituminous binders.

The amplitudes of these data can be used to measure the complex modulus and the phase angle of the bituminous binders in a range of temperatures and frequencies. The ratio of shear stress over shear strain varies at different temperatures and applied frequencies of oscillation. Mainly two different types of test conditions are applied in a DSR device, namely a stress-controlled and a strain controlled. For each type of test one of the two parameters is kept constant.

To fulfil the linearity requirements of the viscoelastic range it is important to understand the stress-strain behaviour and apply the proper conditions to model afterwards the data in practical problems [58]. The selection of stress or strain sweeps is limited by a stress/strain range beyond which the complex modulus reduces to 95% of its zero stress/strain value [59]. The linearity investigation is selected with strain sweep tests at selected temperatures and a specified frequency to ensure a modulus within the linear viscoelastic (LVE) limits [57]. The stress and strain used for testing should be controlled with a tolerance of ±20% according to the following equations of the specification [1-2]

$$\gamma = 12/(G^*)^{0.29} \tag{1}$$

$$\tau = 0.12/(G^*)^{0.71} \tag{2}$$

where,

γ=shear strain (%)
τ=shear stress (MPa)
G^* = complex modulus (MPa)

It is specified that the gap between the two parallel plates should remain constant and undisturbed during the execution of tests. To achieve this, the device sets a zero gap before placing the sample, as well as the moment of inertia for the upper oscillating plate. The parallel plates diameter, as well as the gap, differ at different temperatures. A temperature controlled chamber, heating and cooling devices are used to ensure isolation and arrangement of the test temperature with an accuracy of ±0.1 ^{o}C.

The two main geometries used widely in pavement research are plates with 25mm and 8mm diameter [60]. The 8 mm diameter plates are used for the measurement of complex modulus under temperatures lower than 20^{o}C with a constant gap of 2mm in a range of 100KPa to 10MPa, whereas the 25 mm diameter plates are used with a 1mm gap for the measurement of rheological properties at higher temperatures in a range 1KPa to 100KPa. Other diameters of plates can also be used under the condition that compliance effects of the device do not affect the results [56]. The selection of the appropriate plate at intermediate temperatures is up to the researcher’s experience and the compliance of the geometry with the rheological measurements [61].

During the test execution, the upper plate is oscillating sinusoidally to a selected range of frequencies under a constant temperature while the base plate is fixed. The movement is performed in a radial line between three points. This is demonstrated in **Figure 3.1**, where a fixed point A is moving to B and then reverses its direction moving back to A and continuing to C in an equal curving distance when finally returns back to point A. The described oscillation corresponds to a responding strain over stress measurement determined by applying a torque in the compacted bituminous sample. The calculation of the shear stress and strain are given according to formulas [3] and [4]. They are dependent on the radius of the plates and they are calculated in the outer part of the plate [57, 62]

$$\tau = \frac{2T}{\pi r^3} \tag{3}$$

where,
τ = shear stress (Pa)
T=torque ($N \cdot m$)
r= radius of plates (m)
and

$$\gamma = \frac{\theta r}{h} \tag{4}$$

where,
γ=shear strain (%)
θ=deflection angle (^{o})
h=gap width between the parallel plates (m)

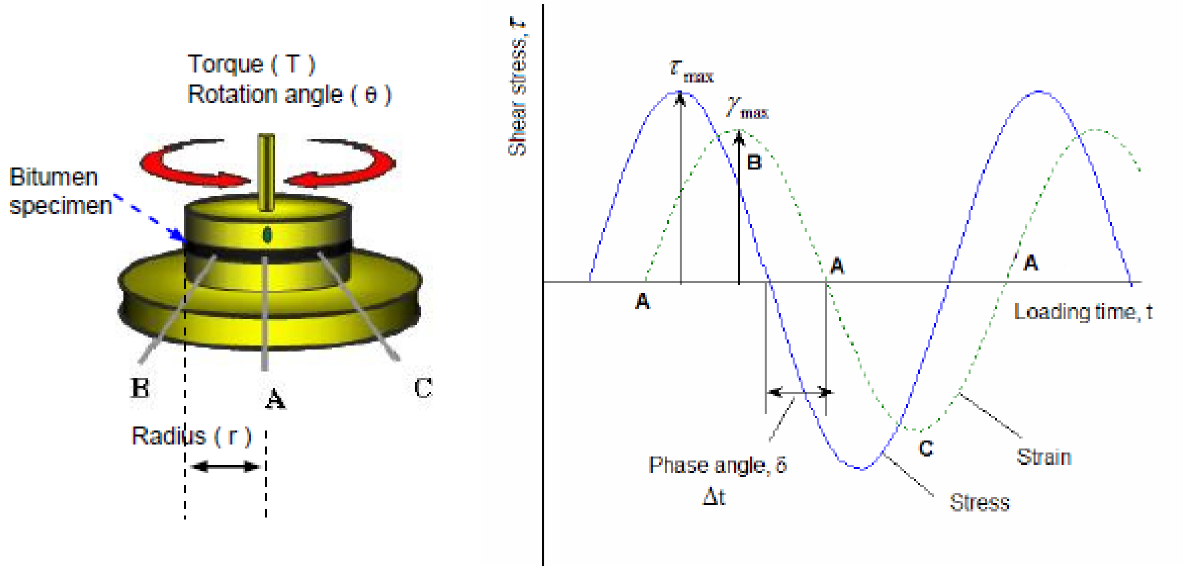


Figure 3. 1: Applied sinusoidal strain and sinusoidal stress response **[62]**

The main function of a DSR device is to address the nature of the material varying from viscous to elastic for bituminous binders in the different temperatures and loading rates. The primary response lies in the complex modulus which is noted as G^{*} and depends on the frequency. It results as the ratio between the amplitudes of stress and strain given by [5]. The complex modulus is given schematically by the absolute stress and strain values expressed as amplitudes in **Figure 3.1**.

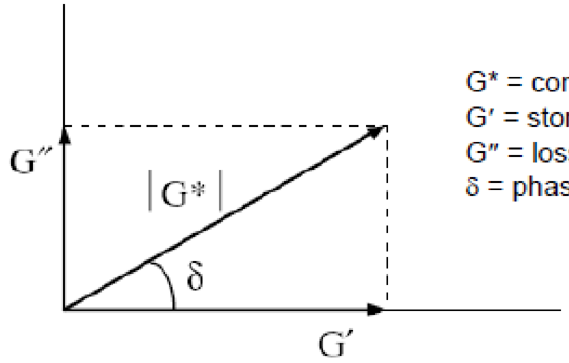
$$G^*(f)=\frac{\tau_{\max}-\tau_{\min}}{\gamma_{\max}-\gamma_{\min}} \qquad [5]$$

where,
f=frequency (Hz)

In the same **Figure 3.1**, the response of the applied shear strain to the resulting shear stress is expressed through the phase angle δ and is given by expression [6]. At the time that this distance is minimized corresponding to a phase angle of 0° the material behaves as an elastic solid, whereas for a phase lag of 90° the material's behavior is of a viscous liquid [62]. This is one of the important parameters for the characterization of the viscoelastic behavior of the material.

$$\delta = f \cdot \Delta t \qquad [6]$$

where,
δ=phase angle (^{o})
f=frequency (Hz)
Δt=phase lag between stress and strain signal



G* = complex shear modulus
G′ = storage modulus (elastic component)
G″ = loss modulus (viscous component)
δ = phase angle (tan δ = G″/ G′)

Figure 3. 2: Relationship among complex, storage and loss modulus, and phase angle **[62]**

Apart from the complex modulus, other dynamic parameters of paramount importance are the storage or elastic modulus G', the loss modulus G'' and the loss tangent tanδ. These parameters are given by equations [7-10] and presented schematically in **Figure 3.2**.

$$G'(f)=G^*(f)\cdot\cos\delta \qquad [7]$$

$$G''(f)=G^*(f)\cdot\sin\delta \qquad [8]$$

$$G^*=G'+iG''=\sqrt{(G')^2+(G'')^2} \qquad [9]$$

$$\tan\delta = \frac{G''}{G'} \qquad [10]$$

The storage modulus represents the in-phase component of the complex modulus, whereas the loss modulus represents the out-of-phase component of the modulus. The total deformation resistance under load is represented by the contribution of both. The phase angle is the relative contribution to the total response of an in- and out-of-phase component and provides information for the visco-elastic behavior of the binder [62].

3.2.2. FREQUENCY SWEEP

A very useful type of test that can be performed in a DSR device is a frequency sweep test over a range of frequencies and temperatures. A commonly used frequency range is from 0.1 to 10 Hz, whereas higher frequencies result in inconsistencies if the linear viscoelastic range has not been chosen properly. The test is usually performed from low temperatures of -10 to high temperatures of 60°C, however, this range can be modified according to the main area that the research is focusing on and the possibilities of the DSR device.

The steps that are being followed include heating and preparation of the sample by pouring of the material in silicon moulds of specific geometry and thickness. To become sufficiently fluid the binder is heated in an oven for a minimum required time. Alternatively, the material after preheating can be poured in small drops in a silicone paper and then stored in a refrigerator. By this way, the material can be easily trimmed in the desired shape for the placement in the DSR device. The DSR device should be connected to a proper software, provided by the supplier of the device in which temperature control, stress control and tolerance are given as an input for a frequency sweep. The machine gives the choice of alternating automatically between the tested temperatures starting from the lower one. The stress level should be chosen accordingly to the material and its shear complex modulus and differs for each temperature. This should be determined first with a strain sweep test and is up to operator's experience to choose it in a suitable way. According to Superpave specifications as mentioned above, two types of plates are used: an 8mm diameter plate for temperatures up to 20°C and a 25mm diameter plate for higher temperatures. Setting a zero gap, measuring the moment of inertia and keeping a constant temperature are upon the requirements of the test procedure. Finally, after cleaning the plates with a suitable solvent, such as dichloromethane, using a cloth or paper the sample is being placed. At this stage it is important that the sample covers the whole measuring plate otherwise it should be removed and be re-prepared. The last step is the trimming of the material that excess from the predefined geometry with a hot knife or blade and the machine is ready for the execution of the test.

Two important aspects that should be taken into account are:

- The determination of the equilibration time, which is the time needed for a bituminous binder to reach thermal equilibrium in the chamber.
- The machine could have automatically gap compensation with changing temperature which is necessary to correct the gap and keep it constant in case of expansion at high temperatures [56].

One of the analytical techniques for the parameters of bituminous binders involves the construction of master curves. This enables the presentation of the complex shear modulus and phase angle at any frequency and temperature based on the time-temperature superposition principle. The data extracted from isothermal plots can be used to predict for every frequency and temperature condition the complex modulus and the phase angle with a continuous curve known as master curve. The technique is rather easy and is based on the horizontal shifting of the isothermal curves along the frequency axis at a single reference temperature.

To obtain these shifting factors for each temperature several solutions have been given ranging from trial and error to graphical and analytical. Some of the most popular ones are the Williams-Landel-Ferry (WLF) equation and the Arhennius function which are shortly described by [11-12] respectively [57, 62].

WLF equation

$$\log a_t = \frac{-C_1(T - T_{ref})}{C_2 + T - T_{ref}} \qquad [11]$$

where,

a_t = shift factor

T=temperature K

T_{ref} =reference temperature K

C_1, C_2 = coeffiecients

Arhennius function

$$\log a_t = \frac{\Delta H_\alpha}{2.303 \cdot R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \qquad [12]$$

where,

a_t = shift factor

ΔH_α = activation energy,typically 250 kJ/mol

R=gas constant (8.314 J/mol/°K)

T =temperature K

T_{ref} =reference temperature K

With regards the two mentioned methods for the construction of master curves, it has been reported that for polymers above the glass transition temperature T_g the shift factor is approximated sufficiently by the WLF equation, whereas the opposite holds for polymers below the glass transition temperature [63]. Another difference between the two methods of analysis is the range of the testing temperatures, where Arhennius function is preferred for lower temperatures. The coefficients C_1 and C_2 of the WLF equation can be found through minimization of the sum error between two different reference temperatures. The main advantage of the WLF method lies in the fact that the reference temperature is not necessarily one of the testing temperatures.

3.2.3. TIME SWEEP FOR MODULUS EVOLUTION

As discussed previously, thermosets experience viscosity evolution and thus the determination of their gel point is important. For the category of EMBs, the modulus evolution after the material gelation is of paramount importance as well. The moment that the curve of modulus stabilizes after a specific time at a constant temperature (isothermal conditions) is a rough indicator for the completion of the chemical hardening.

The procedure of the time sweep test does not differ significantly from a frequency sweep. Usually, the test is performed at a frequency of 10 Hz and/or a temperature which simulates the mixing or curing temperature for thermosets. It is crucial also in this test to identify the applied stress based on a strain sweep to perform the test in the linear viscoelastic range. The applied stress is highly dependent on the chosen temperature. The steps followed are exactly the same as the frequency sweep test until the beginning of the test, apart from the software settings. For this test a constant frequency, in contrast with frequency sweep, is used in combination with a stress level. The temperature is set within a tolerance of ±0.1°C and the duration of the test, as well as the number of oscillations, is given by the input for the time intervals. More specifically, an oscillation is applied in the sample at predefined time intervals and parameters, such as shear modulus, phase angle and viscosity are determined. The number of time intervals prescribes the total duration of the test. There is also the choice to terminate the test after a specific time is passed or to terminate it after a predefined value is reached, such as an upper or lower limit of the modulus.

Two parameters that should be carefully chosen for this test to capture all the changes, is the adequate duration as well as the time intervals of this test. The chemical hardening will be completed after a specific time. This time could be identified by plotting the modulus over time and the observation of a plateau value. The increasing rate of the modulus and the duration until the stabilization of the modulus are the two most useful parameters extracted from this test. Characteristic plots of such figures are given in the next chapter.

3.2.4. TIME SWEEP FOR VISCOSITY EVOLUTION

The viscosity of the binder is of major importance for production of the final asphalt mix. In terms of rheology, bituminous binders belong to complex liquids whose viscosity depends on temperature change, the shear rate and the test duration [64]. The term viscosity of bitumen, which is a material property defined as the internal friction between particles when one bitumen layer moves relative to another. The higher the viscosity is the lower the temperature of unmodified bitumen is [64]. The combination of temperature and viscosity is used for mixing with aggregate and pavement compaction. However, the linear relationship of viscosity with temperature does not hold for thermosets. Thermosets follow a different trend of viscosity evolution and they do not remain constant at a specific temperature as the formation of crosslinking occurs.

The principle of viscosity measurement was formulated by Isaac Newton, known as Newton's law and expressed by [13].

$$\tau = \eta \cdot \frac{d\gamma}{dt} \qquad [13]$$

where,

τ=shear stress (Pa)

η=dynamic viscosity ($\mathrm{Pa \cdot s}$ or $\mathrm{N \cdot s/m^2}$)

$d\gamma/dt$=shear rate ($\mathrm{s^{-1}}$)

There are several definitions of viscosity related to different types of measurement. The dynamic viscosity measured with Cannon-Manning vacuum capillary, cone and plate method and Brookfield rotary viscometer, is a measure of liquid flow resistance. It is referred as liquid viscosity in the European standard EN 12596: 2014 [65]. Moreover, it is measured either in Pa·s or in Poise (P), (1 Pa·s=10P), and it is the ratio of shear stress and shear rate. Another commonly used type of viscosity is the kinematic viscosity measured with BS/IP/RF viscometer, given by the ratio of dynamic viscosity and liquid density. It is a measure of flow resistance under gravity according to EN 12595:2007 [66]. The relation between dynamic and kinematic viscosity is given as

$$v = \frac{\eta}{\rho} \qquad [14]$$

where,

v=kinematic viscosity ($\frac{\mathrm{m^2}}{\mathrm{s}}$)

η=dynamic viscosity ($\frac{\mathrm{N \cdot s}}{\mathrm{m^2}}$)

ρ= density ($\frac{\mathrm{N \cdot s^2}}{\mathrm{m^4}}$)

According to the specifications, there are different types of testing methods at the commonly used temperatures of 60 and 135^{o}C. These temperatures correspond respectively to service at high temperatures and pumping processes [64]. The most frequently used methods are given in the following list.

- Kinematic viscosity testing with BS/IP/RF viscometer EN 12595,
- Dynamic viscosity testing with Cannon-Manning vacuum capillary EN 12596,
- Dynamic viscosity testing with Rheometer by cone and plate method EN 13702,
- Dynamic viscosity testing with Brookfield rotary viscometer EN 13302.

From the previous methods, the Brookfield, and the cone and plate methods are used widely in paving applications. The Brookfield viscometer according to EN13302: 2010 [67] uses a rotating spindle and calculates the resistance under a constant speed of rotation translated eventually into dynamic viscosity. Different diameters of spindles are used with a specific torque and the measurements are given in a digital readout [64]. A cone upper shaft viscosity measurement could be performed in a DSR device, similar to the **Figure 3.3**. According to EN 13702: 2003 [68], the test involves the determination of torque for a fixed shear rate. Using a known rate and torque with a cone factor based on the cone geometry, the viscosity is calculated as

$$\eta = \frac{A \cdot M_d}{\gamma} \quad [15]$$

where,

A=cone factor (m^{-3})
M_d=torque ($N \cdot m$)
γ=shear rate (s^{-1})

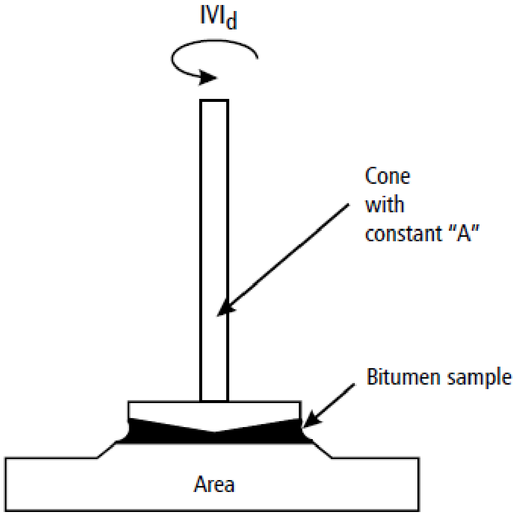


Figure 3. 3: Testing configuration with a sample during the cone and plate viscosity method **[64]**

In a DSR device, the gap between the conical vertex with the bottom flat plate is prefixed at 0.049 mm. The zero-gap should be set only after the assurance of the testing temperature because if the gap is too small possible thermal expansion of the cone may damage the bottom flat plate. A problem can be experienced at temperatures above 100°C, where also the sample should be placed carefully to avoid flowing of the bituminous binder. Proper quantity of the sample can prevent the aforementioned flowing issue. A detailed mathematical interpretation of the geometry with cone and plate method is used to select the appropriate shear rate. Usually, a 1° cone is used in a DSR device and mathematical formulas for the relationships between the torque, the cone angle and the radius can be used to calculate comparable shear rate with other test methods.

$$\tau = \frac{\mathrm{T}}{2/3 \cdot \pi \cdot r^3} \qquad [16]$$

$$\gamma = \frac{\omega}{\sin\theta} \qquad [17]$$

where,

T=torque (dyne $\cdot$ cm)

r=cone radius (cm)

ω=cone speed (rad/sec)

θ=cone angle($^\circ$)

For instance, using the relationships of shear stress and shear rate [16-17], a rotation of 10 RPM in a Brookfield viscometer is equal to 1.047 rad/sec and results in a shear rate of approximately 58.70 s^{-1}. For bitumen, the viscosity with cone and plate is given as the mean of two measurements. However, thermosets develop their viscosity while chemical hardening takes place. These types of binders are categorized as time-dependent non-Newtonian, which means that they are highly dependent on time with a constant shear rate [69]. Changes in viscosity, are crucial for the pot life and the production exhibit over time. In particular, the determination of pot life is crucial for a workable mix. According to European and American specifications, there are defined limits of dynamic viscosity upon delivery and before compaction which suppliers should comply with. In contrast with other binders, viscosity tests for EMBs should be performed for a specific duration to be able to follow the viscosity evolution. Thus, the viscosity with the cone and plate method is performed for an arranged duration with a constant shear rate at a specific temperature inside the climatic chamber of the DSR device. The cone rotates and records the viscosity measurements after specific time intervals, which should be short enough to observe the change in viscosity due to the chemical hardening. Finally, the viscosity results are plotted against time to observe the viscosity increase of thermosets.

3.2.5. TIME SWEEP FOR FATIGUE

The fatigue performance of bitumen is related to its complex molecular structure [70]. The term fatigue to a pavement structure implies to a failure mode resulted from repeated traffic loading [57]. Various types of fatigue tests have been proposed over the years. Based on crack growth laws, brittle failure is observed after the passage of specific time and fatigue cracking is considered as one of the major failures in pavement structures [71].

DSR fatigue test is used to estimate the fatigue performance of the examined binder. The fatigue test is mostly a cyclic load application, either stress or strain controlled. It estimates the contribution of binder to the initiation and development of fatigue damage [62]. The repeated traffic load imposes fatigue in mixes. For a decent DSR fatigue test, a high enough initial modulus is required to ensure initiation of fatigue damage and avoid flow phenomena [72]. The steps for the preparation of the DSR test are similar to previous tests with the only difference being the way of termination of the test. After an appropriate plate geometry and a stress level have been chosen for the testing temperature, the test initiates until a minimum value of modulus is reached and the test stops. The software which is connected to a DSR device usually gives two options for this minimum value, namely as a specific value or as a percentage of the initial modulus. The user also predefines the time intervals after which a value of the modulus is recorded, as well as the applied stress or strain level. Moreover, the total duration of the test can be translated in a number of cycles depending on the specific frequency at which the test was performed.

The fatigue life of material can be determined as the number of repeated applications at different stress or strain levels. Usually, three replicas at three different stress or strain levels are performed to have an acceptable repeatability to create a fatigue line. The number of cycles is based on the assumption that crack initiation is related to the 90% reduction of the initial modulus for stress control or 50% reduction for the strain control fatigue test [70]. Moreover, the initial modulus has been chosen between 60 to 200 MPa to ensure a real fatigue response. The temperature and frequency should be set properly to avoid flow instability in the periphery of the sample [57, 72]. The aforementioned issue eliminates the edge fracture and the compliance error between the plates based on the gap. In addition, it is possible to use the dissipated energy ratio as a fatigue parameter.

To analyze the results of a fatigue test, one should be really aware of the interpolation that it is used. The results can be approximated by a straight line on a logarithmic horizontal axis for the number of cycles and a logarithmic vertical axis for the applied stress. It is obvious that for higher stress levels shorter fatigue life is expected and vice versa. In a fatigue life representation, the points represent the experimental data and the lines are based on interpolation and represent predictions. The closer the coefficient of determination is equal to 1, the better the lines fit to the tested behavior. The fatigue performance of different modification levels of the same binder or a comparison with other binders can be done based on the slope of the fatigue line. The optimal goal of the fatigue life of binder is the correlation with the fatigue performance of the final mix.

3.2.6. TENSILE STRENGTH

Tensile properties are important because they are related to the fatigue life and crack initiation in binders. The tensile test is used to provide tensile failure properties of bitumen at low in-service temperatures [57]. Two methods to carry out a direct tensile test in bituminous blends are with a Universal Testing Machine (UTM) or with a DSR. The first method, according to Superpave standard procedure TP3, is widely used because ensures cracking in the middle of specimen. A suitable effective length and cross-section provide cracking in the middle. A dog-bone-shaped specimen is contained in a silicone rubber mould and pulled in tension at a low temperature. The specimen is subject to displacement until rupture occurs [57]. Normally, a pneumatic loading actuator is used in combination with a temperature cabinet and displacement transducers to perform the test, and lower loading displacement rates are used at low temperatures to capture a broader picture regarding the tensile properties [62].

The use of a DSR device to determine the tensile properties can be done with small cylindrical columns if the possibility of performing tensile tests with that DSR is available. One of the drawbacks is the non-conical geometry of the specimen, something that might not ensure cracking in the middle of specimen. Nevertheless, with a proper selection of the displacement rate at a certain temperature and with a suitable preparation of the small columns good repeatability can be obtained.

Figure 3. 4: Silicon mould and metal rings (left) and storage of the specimens (right)

For the preparation of the small columns, a special silicone or a Teflon mould with metal screws is used (**Figure 3.4**). The mould is made based on the dimensions presented in **Figure 3.5**, where the metal rings are placed and tightened. After heating both the mould and the bitumen at 150°C for half an hour the material is poured into the mould with a metal spoon and is slightly overfilled. After filling all the specimens the mould is again placed in the oven for 5 minutes at the same temperature to allow possible air voids to escape and ensure a homogeneous column. The mould is then cooled down for an hour at ambient temperature and eventually stored in a refrigerator at -10°C for two hours. After that the specimens are demoulded and the excess of the material from the rings is removed with a hot knife. Finally, the rings are cleaned with a solvent like dichloromethane and after visual inspection, they are stored in a fridge in fine sand or silicone rubber to avoid bending of the column [73].

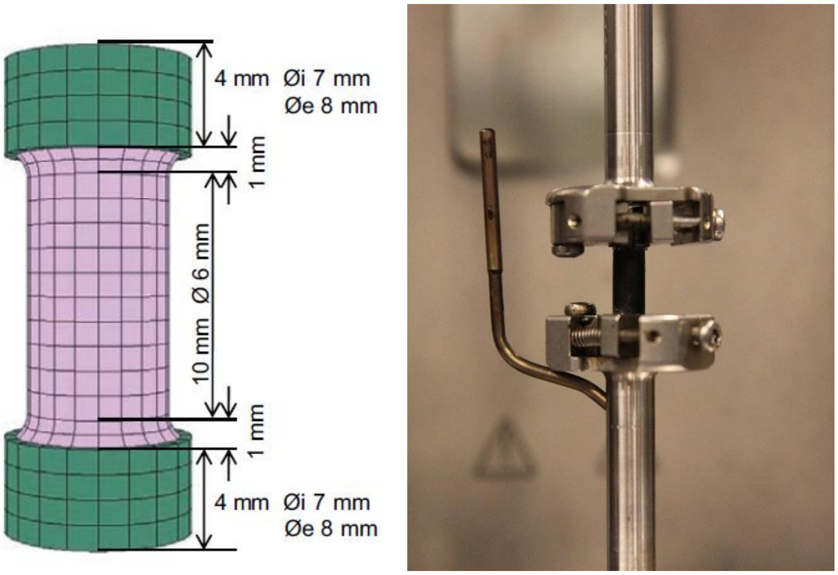


Figure 3. 5: Geometry of column specimen (left) and close view of specimen in DSR (right) **[73]**

The stainless steel rings are used to ensure that the adhesion between the ring and the binder is strong enough to avoid failure in the ring area [73]. These rings are clamped in an upper loading shaft of a DSR device and in the bottom fixed shaft. These special shafts are used for this purpose instead of parallel plates. This test configuration is shown in **Figure 3.5** where the clamps and the column specimen is depicted. The diameter of the bitumen is increased near the rings to minimize the possibility of failure near the rings due to high corner stresses. Once the sample is placed in the clamps of the DSR device the displacement rate is set accordingly. The geometry of the column is set also in the connected software to the DSR device. The DSR device has some limitations with regards maximum load and maximum displacement. The test can be performed till a maximum elongation of approximately 5 cm, at low temperatures, due to the limited length of the climatic chamber.

For the aforementioned methods of tensile tests the repeatability of three replicas should be acceptable (CV<15%). For analyzing the tensile properties, the peak load and the maximum displacement are recorded and plotted in a displacement versus load graph. The stress and strain are calculated based on the maximum load. This maximum force occurs either on failure or at the yield force. Relationships [18-19] allow the calculation of the previous properties and are dependent on the effective geometry.

$$\sigma(t) = \frac{P}{A} \tag{18}$$

$$\varepsilon = \frac{\Delta l}{L_e} \cdot 100\% \tag{19}$$

where,

$\sigma(t)$=time dependent stress (MPa)

ε=strain (%)

P= applied axial force (N)

A= cross sectional area of specimen (mm^2)

Δl= change in length (mm)

L_e = effective length (mm)

From the previous relationships, it is important to compare not only the tensile strength but also the strain, which is an indicator of the ductility of the binder.

3.3. FOURIER TRANSFORM INFRARED (FT-IR) SPECTROSCOPY

3.3.1. BASIC PRINCIPLES

Infrared spectroscopy is used to identify the functional chemical groups that are part of materials characterization and characterize the chemical composition. Fourier Transform Infrared (FT-IR) spectroscopy is often used to follow the aging process of all categories of binders. Specifically for EMBs FT-IR can also be used during the chemical hardening of the epoxy resin in the EMB. Over the years different methods of analyzing the data have been proposed varying from quantitative to qualitative studies.

Different types of spectrometers are used for different research fields. In pavement engineering, the data generation needs to be reliable, repeatable and reproducible to consider the measurements trustworthy [73]. Due to the complex nature of bitumen and the inhomogeneity that might occur in modified binders as well as in a mastic, a standardized technique should be followed. The common method used for bituminous binders includes the use of attenuated total reflectance (ATR), which is used for qualitative and quantitative analysis of the data with acceptable reliability of the information [74]. The experience of the user, in terms of mixing the blends and handling the samples, the type of the device and its adjustments play also a crucial role in obtaining reliable results.

A more close observation of FT-IR spectroscopy allows the understanding of the device operation. In particular, the operation is based on the absorption of the infrared radiation of chemical bonds, as the interaction of the infrared light with the bonds in the material [73]. An infrared beam is charged in binder and activates bonds in its molecules, which start to vibrate at specific frequencies. These absorbed frequencies can be isolated and analyzed afterwards. The spectrum that infrared radiation belongs to is part of the electromagnetic spectrum and varies in a range between 10^{-3} and 10^{-6} m [75].

It was also proved from other researches that the velocity of propagation in a vacuum is constant for all regions of the electromagnetic spectrum, known as velocity of light. This propagation can be interpreted as a wave with its velocity resulting as a product of the wavelength and the frequency. The definition of the wavelength is given as the difference between two successive peaks, and the frequency of a wave is defined as the number of cycles per second [73]. Based on Bohr's equation [20] the energy of an infrared photon is

$$E = h \cdot v = \frac{h \cdot c}{\lambda} = h \cdot c \cdot \overline{v} \qquad [20]$$

where,

E=photon energy (J)

h= Planck's constant ($6{,}626 \cdot 10^{-34}$Js)

v= frequency (cycles/s)

c= velocity of light ($2.997925 \cdot 10^{8}$)

λ=wavelength (m)

$\overline{v}$=wave number (cm^{-1})

This photon energy is proportional to frequency and wave number. The wave number is most commonly measured in centimeter. The chemical characterization of a material using the previous information is defined by this bond energy between the components of the binder. The change of the bond or structure in molecular level is depicted by the infrared absorptions during vibration, which are related to a specific frequency for each bond. The rotation and vibrations of the atoms are the consequence of the infrared absorption and are crucial for identifying the type of functional groups. These vibrations can be either stretching of the atoms in a molecule or bending by means of a change in angle between two bonds [73].

Another important issue for the understanding of infrared spectroscopy is the simulation of the vibration under a specific frequency for each functional group. It is affected by the stiffness of the bond and the masses of the atoms at the end of each bond and is unique for each group. Usually, a diatomic harmonic oscillator is simulated with two masses connected by a spring, resulting in a potential energy based on Hooke's law and divided into different energy levels based on quantum mechanics. The aforementioned simulation is only valid for the lowest energy levels. For other energy levels phenomena (i.e., vibration coupling, overtones bands, etc.) the interpretation is more complicated [73].

The two general modes used for performing measurements using an FT-IR spectrometer are with transmittance of the beam through the sample and reflection of the beam within the sample. In the first method, the radiation is sent through the sample and specific wavelengths are absorbed. The use of an ATR add-in in an spectrometer is mostly used for bituminous binders. The principle is based on the total reflection, as a radiation enters a crystal and reflects off the internal surface in contact with the sample. The reflection can be multiple or at least one depending on the crystal. The two types of crystals are given in **Figure 3.6**. The beam is reflected by the sample and also internally in the crystal in case of multiple reflections. The wave is capable to penetrate only a few μm in the sample, and the prism is manufactured in such a way to ensure the total reflectance of the beam. Crystals of diamond and germanium have refractive indices which are larger than the testing materials to provide internal reflectance. The sample absorbs specific frequencies and the beam loses energy at this particular frequency for each functional group. The radiation after reflection is collected by a detector connected to a software which can demonstrate in a plot the wave number against absorbance or transmittance after leaving the crystal [73].

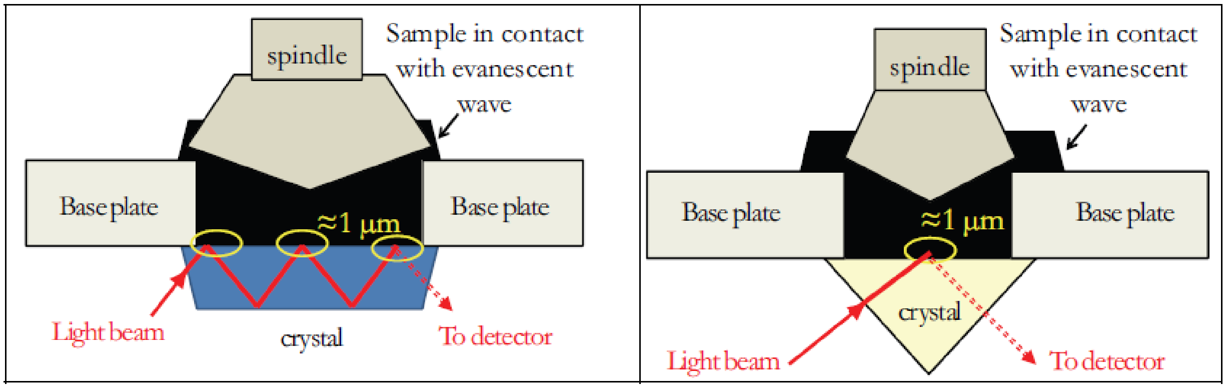


Figure 3. 6: FTIR-ATR spectrometer with multiple (left) and one reflection (right) **[73]**

The steps needed to record the spectrum include firstly a background check of the device to avoid influences of sand, other chemicals or water that are used for the cleaning of the crystal. After that, the settings for the device are given as input in the software. The device may include a heating unit for the sample or not. After the background check, the sample is split into small quantities and placed with a clean lancet on the base plate. Prior to the reflectance, a constant force of 130N is applied and ensures proper and direct contact with the crystal. This enables the penetration depth of the light beam in the sample. Afterwards, the sample is scanned and the mean of 20 scans with a resolution of 4 cm^{-1} is given. This set of scans gives the absorbance or transmittance in relation to the wavenumber. The absorbance and transmittance are related to the intensity of the light beam entering the sample and transmitted by it [21-22]

$$A = \log_{10} \frac{1}{T} \qquad [21]$$

$$A = \log I_O - \log I = \log \frac{I_O}{I} = -\log T \qquad [22]$$

where,

A=absorbance (cm)
T=transmittance (%)
I_O=intensity of light beam entering the sample
I=intensity of light beam transmitted by the sample

For reproducibility of results, five replicas per sample are analyzed to minimize the mean error. The important spectrum for bitumen is between wavenumbers 600 and 4000 cm^{-1} because the crucial functional groups of bitumen are in this middle infrared zone. The FT-IR device of Perkin Elmer with an ATR fixture was used in this research. The functional groups that are important for the curing and aging process are given before the presentation and interpretation of the results in the next chapters. From the two existed methods of analysis of the results, quantitative and qualitative, the first is preferred. To eliminate the errors between replicas a specific reference technique should be used for quantitative analysis. This reference technique, as analyzed thoroughly in the related subchapter, is based on constant peak areas or a baseline between predefined points. This method makes the data independent of the concentration of the specimen. Also, a comparison of different areas and peaks with a semi-quantitative analysis is used. The methodology of ratios of areas where one functional group is assumed constant, is well-known in the literature. The ratio of absorbance is assumed to be constant for samples of the same binder. The area of absorbance can be compared for variable functional groups of different materials or of the same binder under different hardening conditions [73].

3.3.2. SEMI-QUANTITATIVE ANALYSIS

This technique is used as a reference for comparison between different binders, with different modification levels, but also at different stages of chemical processes for the same material. This analysis exploits the peak ratio and area ratio evaluation. The area ratio eliminates the interference between vibrations of similar type. A band of a functional group is more reliable than a single peak because it includes the total contribution of the neighbouring groups [73]. It is also important in the processing of the data to avoid the influence of the film thickness and path length of the light beam. Consequently, a generalized technique of factors from ratios between different areas was invented. The denominator is assumed to remain constant for different chemical processes, such as aging. The denominator is defined as the sum of specific areas of bands for functional groups that are not affected by this process. The aging process has been extensively investigated for bitumen as it is related to service life performance. However, for other chemical processes, such as chemical hardening of EMB, the crucial areas have not yet been identified. For this process the analysis based on peak heights is preferred.

Aging is extensively analyzed in sixth Chapter. An introduction to the concept of aging indices will be given here. According to various independent researches [62, 73] it has been concluded that the band areas around 1700 cm^{-1} and 1030 cm^{-1} are crucial for the aging process of bitumen and are related to carbonyl and sulfoxide bonds respectively. Thus, the change of these bonds can be used as an indicator. Other areas such as ethylene groups (1460 cm^{-1}) and methylene (1375 cm^{-1}) are remaining constant and the sum of them is used to define the denominator. The nominator is the area near carbonyls (CO) or sulfoxides (SO) and it is believed that their ratio to the sum of constant areas are two aging indices.

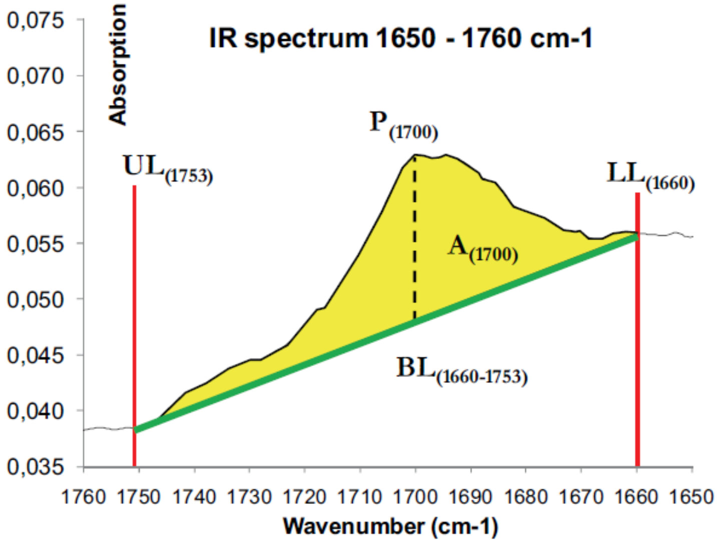


Figure 3. 7: Band area and peak value with its baseline and limits for carbonyl group **[73]**

It is important to set properly the range of bands around the examined functional group. A baseline is introduced for this reason and is defined by fixed limits or vertical borders, corresponding to specific wavenumbers [73]. **Figure 3.7** shows the identification of the baseline plotted with a green colour and the vertical limits plotted with a red colour. Setting of the limits is important for the studied functional groups and should be identical for all the measurements for a fair comparison. The selection of these limits is based either on the literature or on the fact that the defined areas should be rather unilateral. It has been reported that for very narrow bands both positive and negative areas can be acceptable. Herein, fixed limits and different methods of computation are used [73].

The commonly used semi-quantitative ways to analyze the data are :

- Method A: Peak Calculation
- Method B: Area calculation [74]

The first method is based on the intersection of the vertical line between the peak value of the curve given by the spectrum with the baseline. The limits of the band are based on the functional group and the resulting distance is known as absorbance intensity. For the second method, various possibilities can be used, which are based on the setting of the limits of the band. The limits of the bands can be slightly adjusted to avoid negative areas, and the area can be a result of integration or not. Finally, the accuracy of each method should be acceptable in terms of statistical error expressed as coefficient of variation between the same replicas [73].

3.4. CONCLUSIONS

The description of the operation and use of a DSR and an FT-IR test, as well as the methods for analyzing the results, are the main outcomes of this chapter. The understanding of the various testing methods is considered fundamental to perform the experimental part correctly and with the right reliability. This chapter is also very important for the proper selection of the testing parameters and the post-processing of the results. The presentation of the results presented in the next three chapters is based on this theoretical background.

4

Chemical Hardening Evaluation of EMB

The material preparation of the epoxy modified bitumen (EMB) in the laboratory is discussed in this chapter. Different epoxy modification levels, hardening temperature and time conditions were selected to assess the influence of them on the chemical hardening of EMBs. The results obtained from frequency and time sweeps, and FT-IR analysis, are presented and discussed in this chapter. Understanding of these results will be used for the selection of a critical combination of chemical hardening conditions.

4.1. MATERIAL AND PREPARATION

4.1.1. MATERIALS

Epoxy modifier was prepared and mixed with fresh bitumen. The modifier consists of two parts; the first part (Part A) is named a dual-epoxy-resin and is the product of bisphenol-A and epichlorohydrin, and the second part (Part B) is a homogeneous blend of bitumen and hardener without any organic filler. Part A does not contain any softening agent or other inorganic materials in its composition. The two parts were provided by ChemCo Systems Co., San Francisco, USA. The exact composition of part B is a proprietary secret. The weight ratio and mixing conditions of two parts were given by the supplier. The properties of individual constituents are given in **Appendix A**.

Due to the fact that this study aims to implement the epoxy modification technology in the Netherlands and taking into account the economic aspects, a 70/100 penetration grade bitumen was selected. This type of bitumen is used mostly for open-graded bituminous mixes in Dutch roads. Bitumen was reported to give improved properties when modified with the epoxy. To find an optimal blend composition, different modification levels were investigated. It was reported that addition of a even small amount of the modifier to bitumen could be sufficient for long-life performance [52].

4.1.2. PREPARATION METHOD

For the EMB preparation, part A and B should be mixed together prior to the bitumen modification. According to the supplier, these parts are mixed together at a weight ratio of 20:80 for the production of modifier. Prior to mixing, part A and B were placed in ovens for 1 hour at 85 and 110^{o} C, respectively. Components preheating allow easy pumping and mixing for 1 minute. The homogeneity of the blend is important to guarantee repeatable experimental results and enable the formation of an equally distributed network in the whole mass. Afterwards, the modifier was mixed with the already preheated bitumen at 120^{o}C for 1 minute. The content of modifier in the final blend was varied to evaluate its impact. Three different modification levels were investigated; 20:80, 35:65 and 50:50, where the ratio stands for modifier: virgin bitumen. Two different temperatures were utilized, 100 and 130^{o}C. After the preparation, the chemical hardening of EMBs was studied after three different hardening time intervals of respectively 2, 5 and 8 hours. Using two different temperatures for three different modification levels and three different hardening times, means that 18 different combinations had to be tested. After completion of the hardening procedure, the samples were poured into silicon paper in small drops and in silicon moulds for DSR columns. When using the silicon moulds the air voids were carefully removed by heating the specimen after placement in the mould. In addition, unhardened specimens were produced and tested. All the samples were placed in a refrigerator at -10^{o}C to prevent any further reaction that could take place otherwise.

At this stage, it should be mentioned that the material behaved as a quasi-thermoset during the experiments. This means that the material could be poured after completion of hardening conditions even in the most extreme case of 130 °C for 8 hours. This allowed the workability of the material in the lab and prevented the laboratory equipment for damage. Damage could happen in case the material became a hard solid in the testing device. In previous research, it was mentioned that this modifier, without mixing with fresh bitumen, is rubbery when it is completely cured and not a glassy material [4]. Taking into account various combinations both the temperature-time influence and the modification level were investigated. The selected temperatures and times were based on recommendations of the supplier. The goal is to identify the critical combination of hardening conditions and evaluate further the behavior of EMBs. **Figure 4.1** illustrates schematically the different steps of the material preparation.

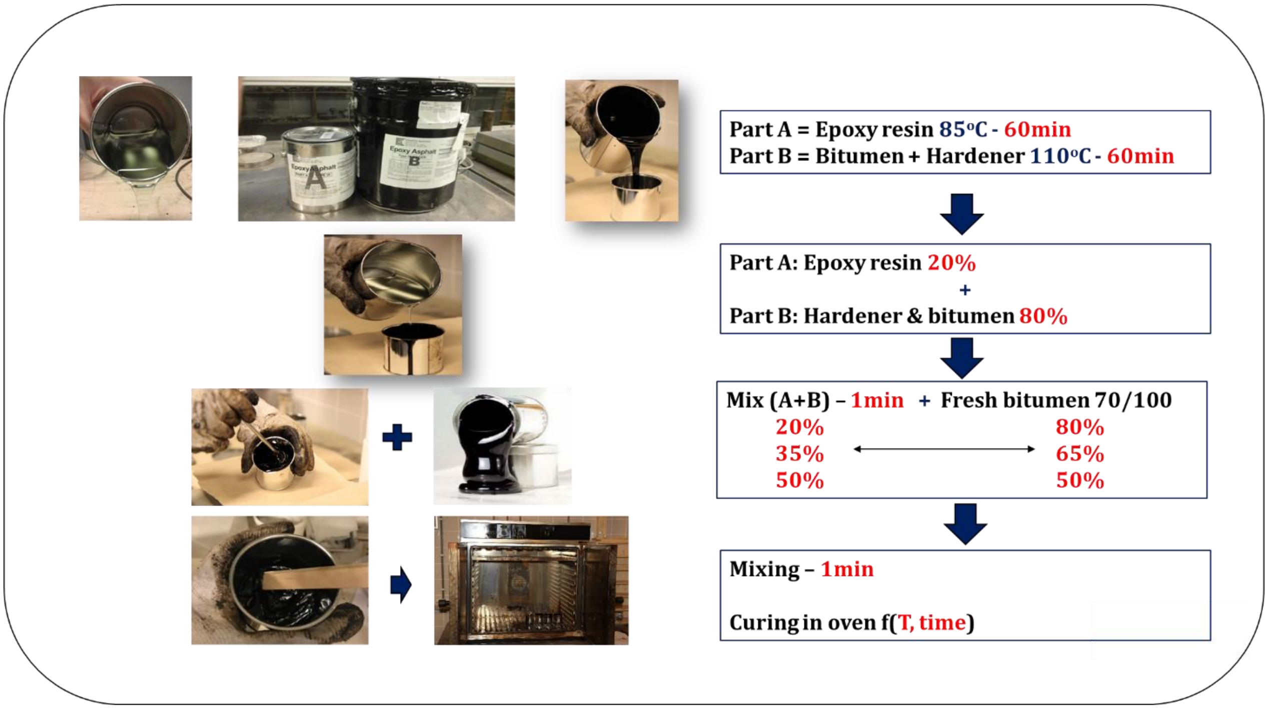


Figure 4. 1: Manufacturing process of EMB

4.2. EXPERIMENTAL METHODS

For the evaluation of the different combinations, frequency sweep tests were initially performed in an Anton Paar MCR 502 DSR device. Based on the standard procedure of EN14770: 2012, appropriate stress levels were selected to fulfill the requirements of a linear viscoelastic range. Two plate geometries were used, an 8mm diameter set of parallel plates from -10 to 20°C and a 25mm diameter set from 30 to 60°C. The gaps were set respectively to 2 and 1 mm and the frequency range varied from 0.01 to 10 Hz. After performing the tests, master curves were constructed with a reference temperature of 30°C to compare the different curing combinations and modification levels. After that, material for each combination was placed directly in the ATR crystal pedestal of a Perkin-Elmer 100 FTIR device. The material was pressed with a constant force of about 130N to ensure proper contact to the surface, and the spectra were analyzed based on the absorbance intensity method of peak difference. The FT-IR spectra collected for all the samples was in the wavenumber range from 600 cm^{-1} to 4000 cm^{-1}.

From the master curves and FT-IR analyses, the most crucial temperature between the two examined temperatures for the investigation of chemical hardening was selected. Additional tests were performed for this temperature.

Firstly, a time sweep test at 130°C and a frequency of 10Hz was performed to investigate the modulus evolution of EMB. The test was performed for uncured specimens with a 25mm diameter plate for all modification levels for 3 hours. The stress level was chosen accordingly to ensure linear viscoelastic range requirements. The same test was conducted at 60°C for 2,5 days to simulate the development of the crosslinking network after cooling of the binder upon delivery. The results of this test are given in **Appendix B**. The last test of this task was to study the viscosity evolution at the chosen curing temperature. This was conducted with a cone of 1° and a plate of 25mm diameter for 3 hours. The increase of the viscosity for the three modification levels was observed to determine the limitations that may occur. The shear rate of $60s^{-1}$ was selected according to the theoretical background presented previously and according to EN 13702: 2003.

4.3. RESULTS AND DISCUSSION

4.3.1. MASTER CURVES

The results for the different hardening conditions were analyzed based on the time-temperature superposition principle at the reference temperature of 30°C. The results are given below per EMB modification level to observe initially the influence of conditions. A comparison of the different modification levels is also needed. Thus, it is useful to demonstrate the results in a cumulative graph per EMB and afterwards to isolate specific reduced frequencies. The selected frequencies are realistic values calculated for a normal traffic flow, based on a vehicle average speed of 80 km/h. The phase angle is also an important parameter for the evaluation of the curing process which gives information on the ratio between elastic and viscous response. From this first series of tests, a rough estimation of the curing time and temperature was obtained. It is important to conclude to a critical combination of curing conditions in which an easy and reliable application can be expected in the field. After that, viscosity and modulus evolution for EMB will give a clear overview for the curing completion and the network formation.

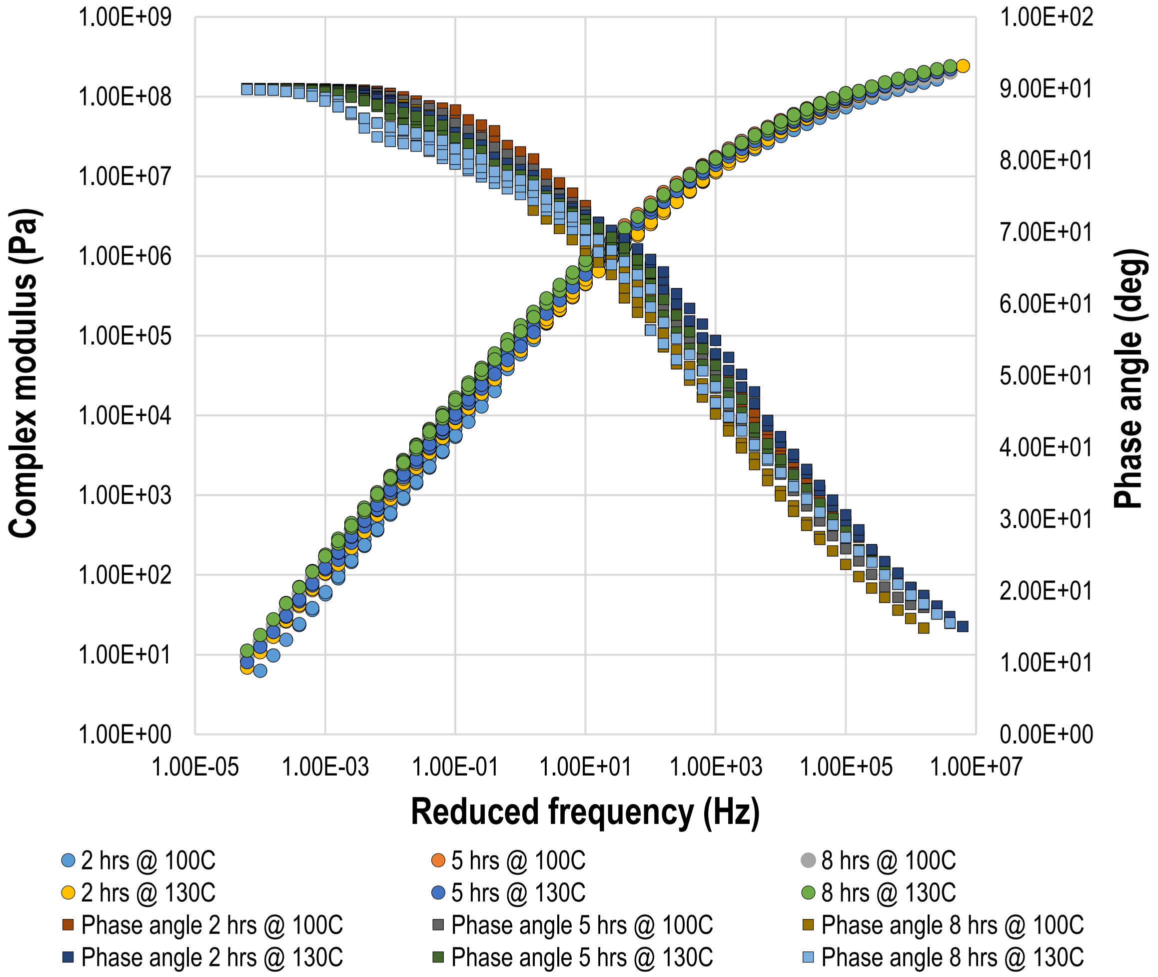


Figure 4. 2: Master curve of EMB 20% for different conditions at a reference temperature 30^{o}C

From the master curve in **Figure 4.2**, where both complex shear modulus and phase angle are depicted for two temperatures and three times, it is observed that the higher temperature of 130^{o}C gives higher complex modulus and lower phase angle values. This means that the network formation happens more easily since the chemical reactions are accelerated at higher temperatures. The lower phase angle means that the material is more elastic when high temperature is utilized. With regards the curing times of EMB with a modification level of 20%, the longer the curing is, the higher the modulus is. The complex modulus is still increasing and the crosslinking has not been fully completed. At low modification levels, epoxy molecules need more time to link with each other. The effect of the curing time is not clear at intermediate frequencies from this graph and the observation of characteristic frequencies will be useful for comparison.

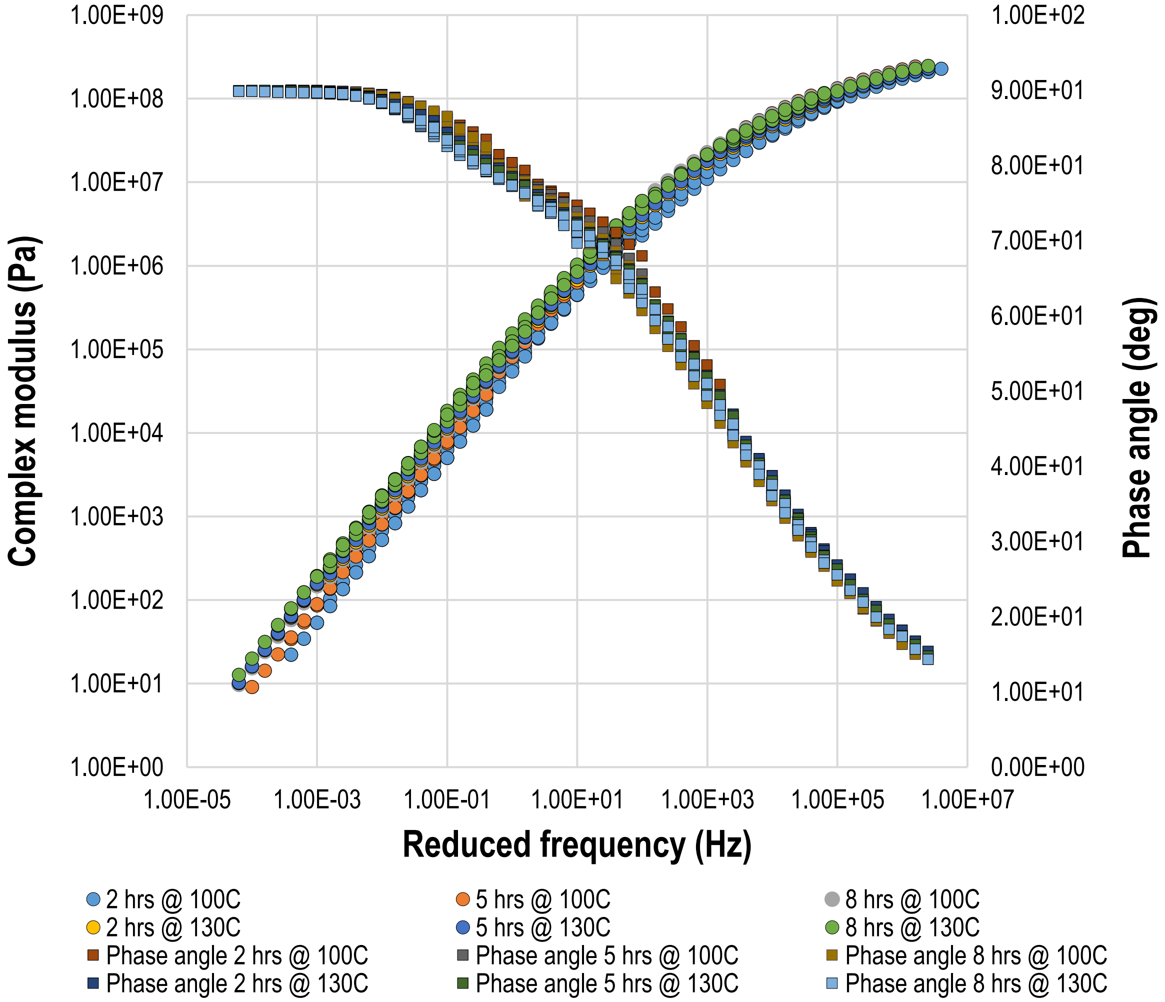


Figure 4. 3: Master curve of EMB 35% for different conditions at a reference temperature 30^{o}C

When the modification level is increased to 35%, the slope of the phase angle remains similar to EMB 20% (**Figure 4.3**). The differences of complex modulus between different curing times are more obvious at low frequencies with a curing temperature of 100^{o}C, whereas a curing time of 5 and 8 hours at 130^{o}C gives similar results. This means, firstly, that the higher temperature gives steady complex modulus after 5 hours and secondly at low curing temperature more time is needed to stabilize the modulus. The phase angle is higher at a curing temperature of 100^{o}C giving a more viscous response than the temperature of 130^{o}C. Thus, the temperature is an important parameter for EMBs application. Upon application, proper truck isolation is essential to keep and ensure the transportation temperature constant. By adding more epoxy, the network formation is accelerated since the mechanical properties stabilized from 5 to 8 hours at 130^{o}C.

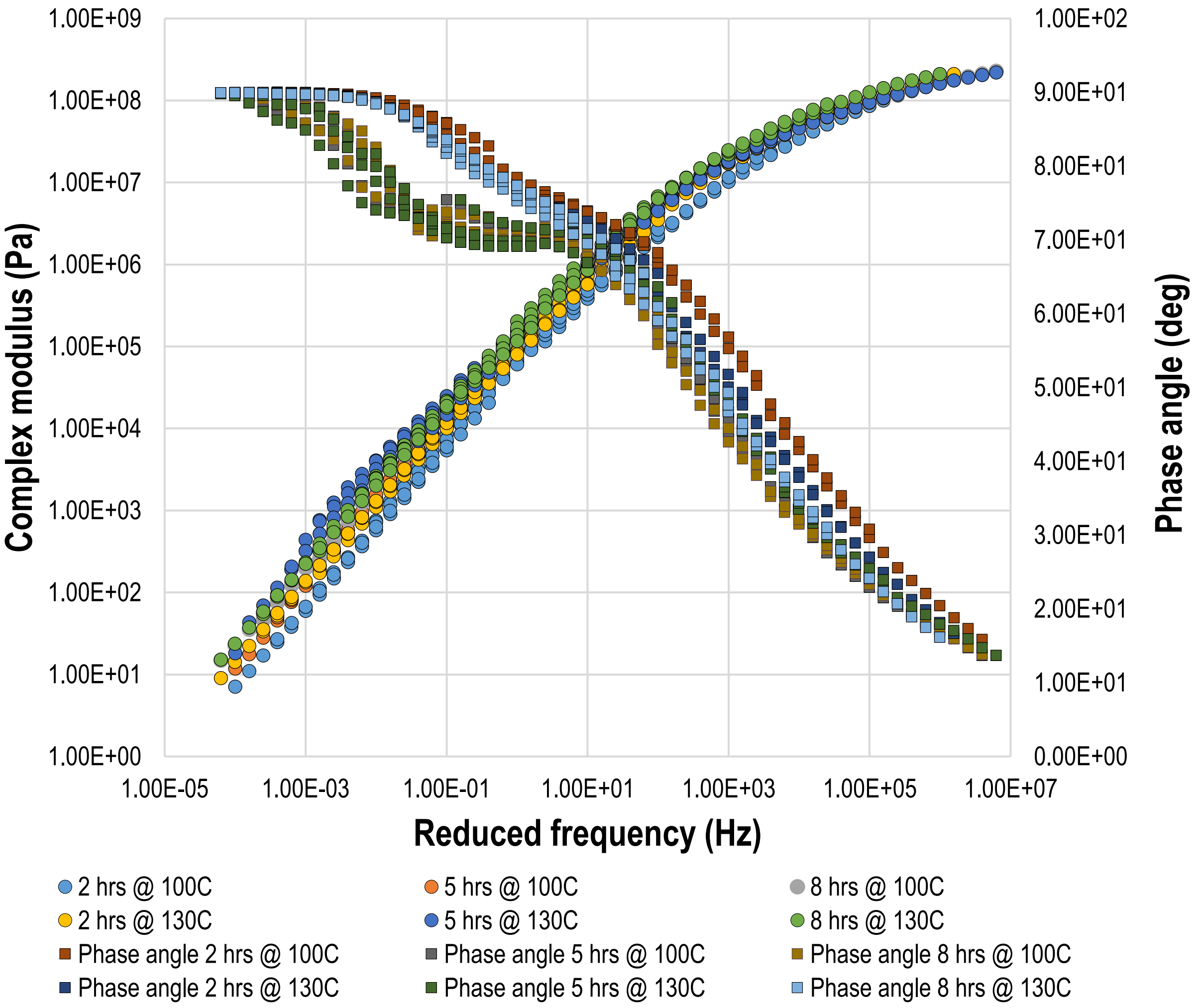
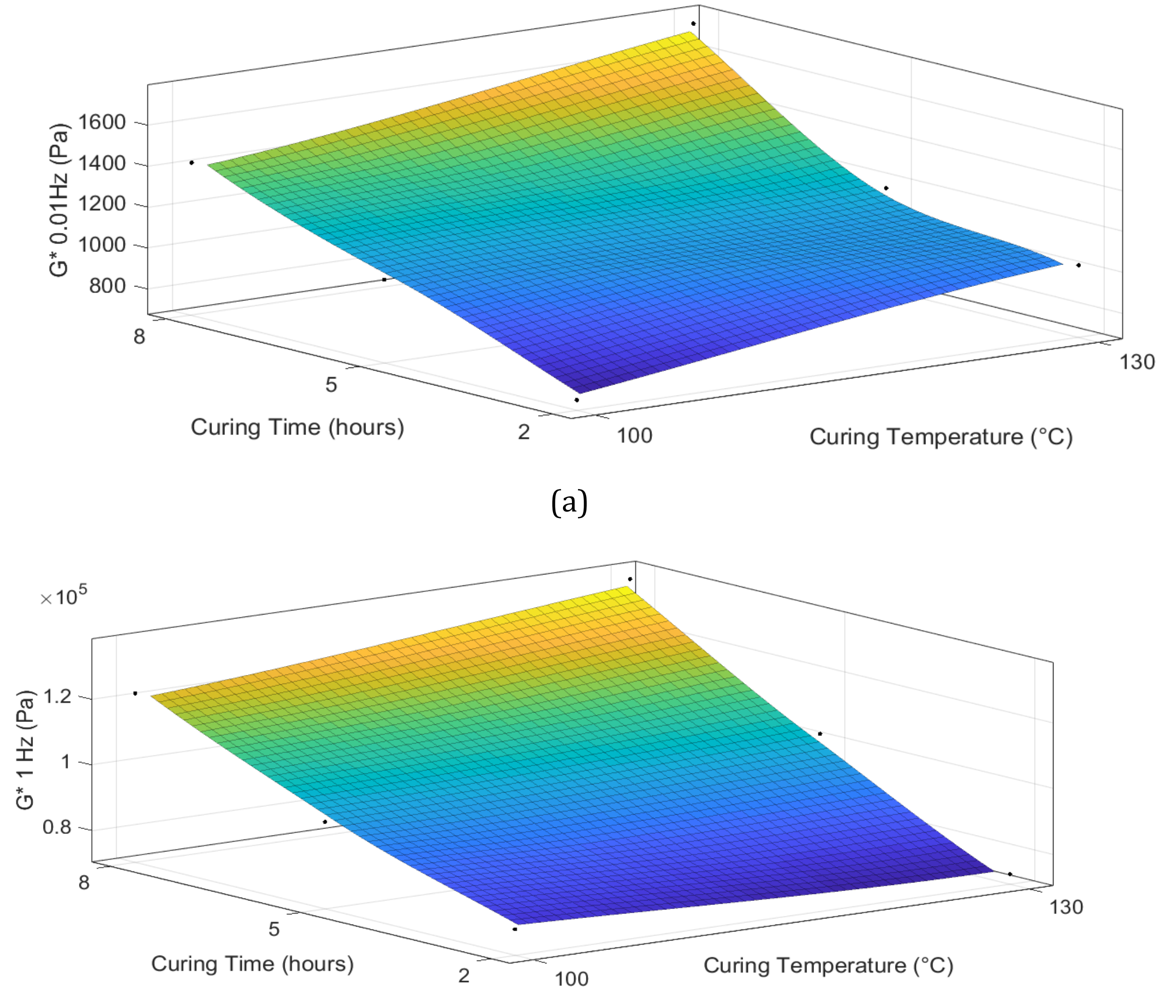


Figure 4. 4: Master curve of EMB 50% for different conditions at a reference temperature 30°C

The modification level of 50% was also investigated. The fact that for reduced frequencies between 0.01 and 1 Hz the phase angle does not follow a decreasing trend of viscoelastic material could be explained by the high percentage of modifier in the blend (**Figure 4.4**). The material behaves more rubbery when the curing process has been completed, due to the dominance of modifier in EMB 50%. Moreover, a stabilization of complex modulus is observed at this percentage for both curing temperatures from 5 to 8 hours. A reasonable explanation to this is that the chemical hardening is completed after 5 hours for both temperatures. Perhaps, a shorter curing time between 2 and 5 hours will give the same modulus. A comparison between the modification levels will be done by isolating the frequencies of 0.01 and 1 Hz, which are believed to simulate realistic traffic conditions.

The results at a frequency of 0.01 and 1 Hz from the master curves with reference temperature of 30 °C of EMB 20% are compared in a 3D-plot with the x- and y-axis representing the different time intervals and curing temperatures. The z-axis represents the modulus. It is clear from **Figure 4.5** that the complex modulus levels are higher when a longer curing time was applied for both frequencies. The slope of the curved fitting area is slightly positive toward the curing temperature of 130ºC. From this slope, it can be assumed that high curing temperatures enable the development of complex modulus more quickly than the low curing temperatures. Moreover, the increasing trend of complex modulus seems to continue over time for this modification level.

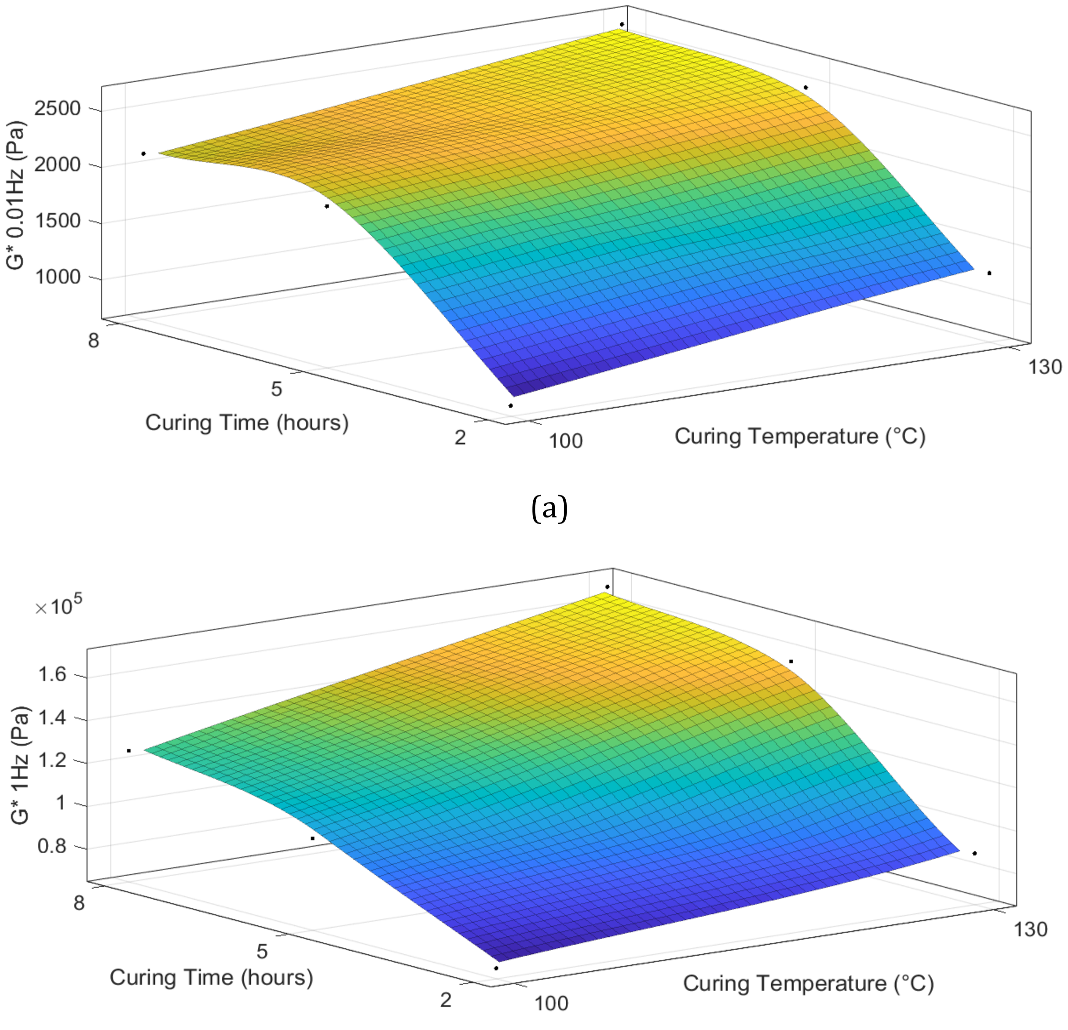


(b)

Figure 4. 5: Complex modulus at (a) 0.01 and (b) 1 Hz versus curing time and temperature for EMB 20%

The main conclusion that can be drawn from **Figure 4.6** is that it can be assumed that around 5 hours is the critical curing time for the modulus evolution of the three investigated curing times. A plateau is reached in the 3D-plot of the modulus versus time and temperature after 5 hours for both frequencies. The plateau is obvious for both temperatures. In addition, the complex modulus of 1 Hz reduced frequency is about 1.4 times higher between the two curing temperatures. The higher values are obtained for the higher temperature.

Additionally, the complex modulus is still increasing from 2 to 5 hours. It is not obvious if there is a shorter curing time that would probably result in the same modulus levels and its stabilization after this time. For the purposes of this research, the curing time around 5 hours is considered as critical curing time and it used to investigate the properties of EMBs in the next Chapter.



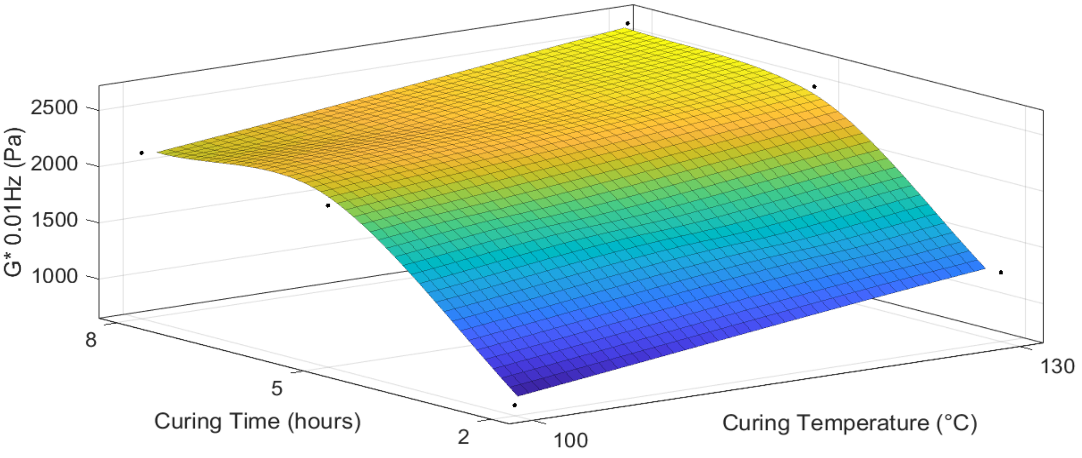
(a)

(b)

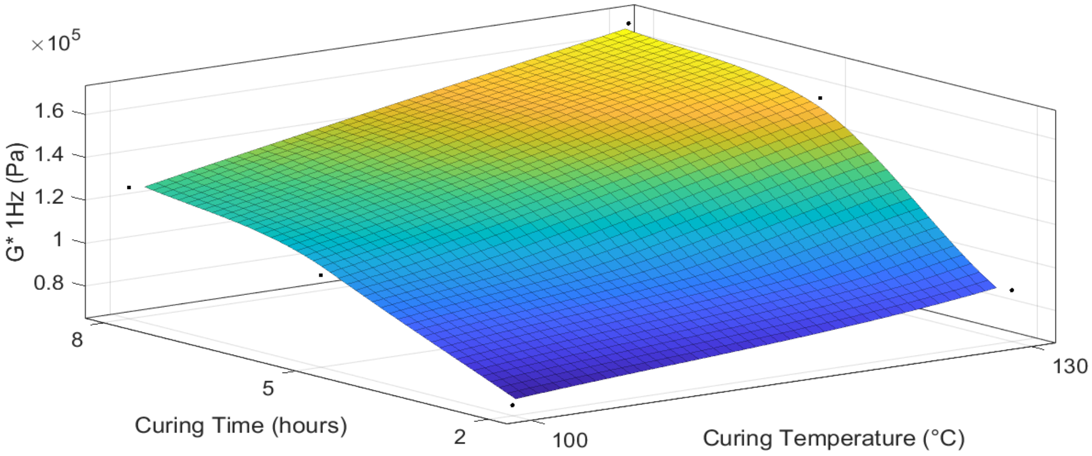
Figure 4. 6: Complex modulus at (a) 0.01 and (b) 1 Hz versus curing time and temperature for EMB 35%

The same trend with EMB 35% holds for EMB 50% as depicted in **Figure 4.7**. A plateau is reached for both frequencies from 5 to 8 hours. Although the two frequencies obtain modulus values of different magnitudes, they follow similar trend. A positive slope of the curved fitted area toward to higher curing temperature justifies once again the acceleration of the modulus evolution when utilizing higher curing temperature. Both EMB 35% and 50%

result in the critical curing time of 5 hours. Since the network formation is accelerated at higher curing temperatures, the combination of 5 hours at 130°C can be assumed to be the critical, an assumption verified with other tests.



(a)



(b)

Figure 4. 7: Complex modulus at (a) 0.01 and (b) 1 Hz versus curing time and temperature for EMB 50%

4.3.2. FTIR ANALYSIS

The first priority in the interpretation of an FT-IR analysis is to identify the crucial functional groups that contribute to the process under investigation. In this case, the curing process is under investigation. A standard reference method (i.e., aging of bitumen) does not yet exist for this process and specific groups will be analyzed. The groups of oxirane (absorbance band at 917 cm-^{1}) and possibly methylene (at 3050 cm-^{1}) are the responsible functional groups for the formation of epoxy resin [76, 77]. The band of methylene is not very useful since its intensity is low and it is also very close to the strong hydroxyls [77]. During the chemical hardening, oxirane reacts with the carbonyl acid group (at 1709 cm-^{1}) resulting in a carbonyl ester (at 1735 cm-^{1}) and hydroxyl group (at 3500 cm-^{1}). Successively, a second chemical reaction takes place for the oxiranes and is resulting in carbonyl ether (at 1040 cm-^{1}) [77]. **Figure 4.8** shows the FT-IR spectra of EMB 20 % recorded at the different hardening times. The processing of the results was conducted based on peak calculation. For this method, a specific baseline with discretized bonds near the examined peak was used and the distance of the governing peak of the spectrum to this baseline was calculated as the absorption intensity [73]. Based on the absorption intensity the results are given in **Figures 4.9** and **4.10**.

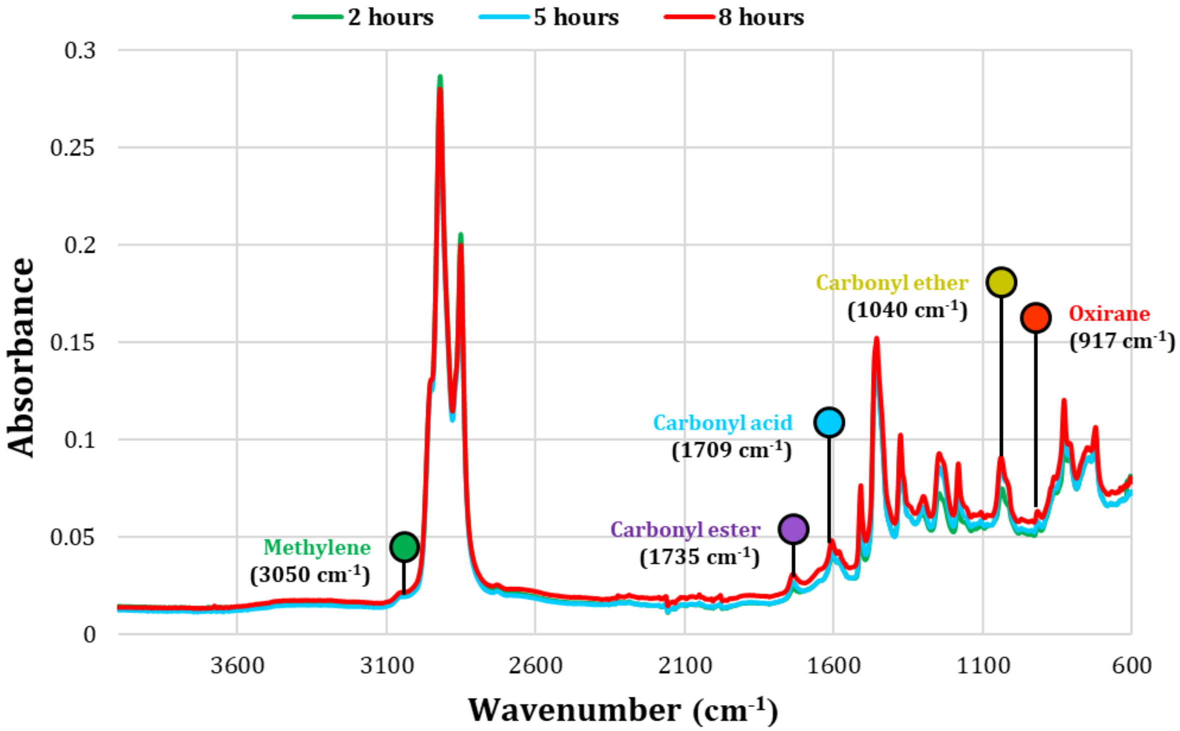


Figure 4. 8: FT-IR spectra at different curing times for EMB 20%

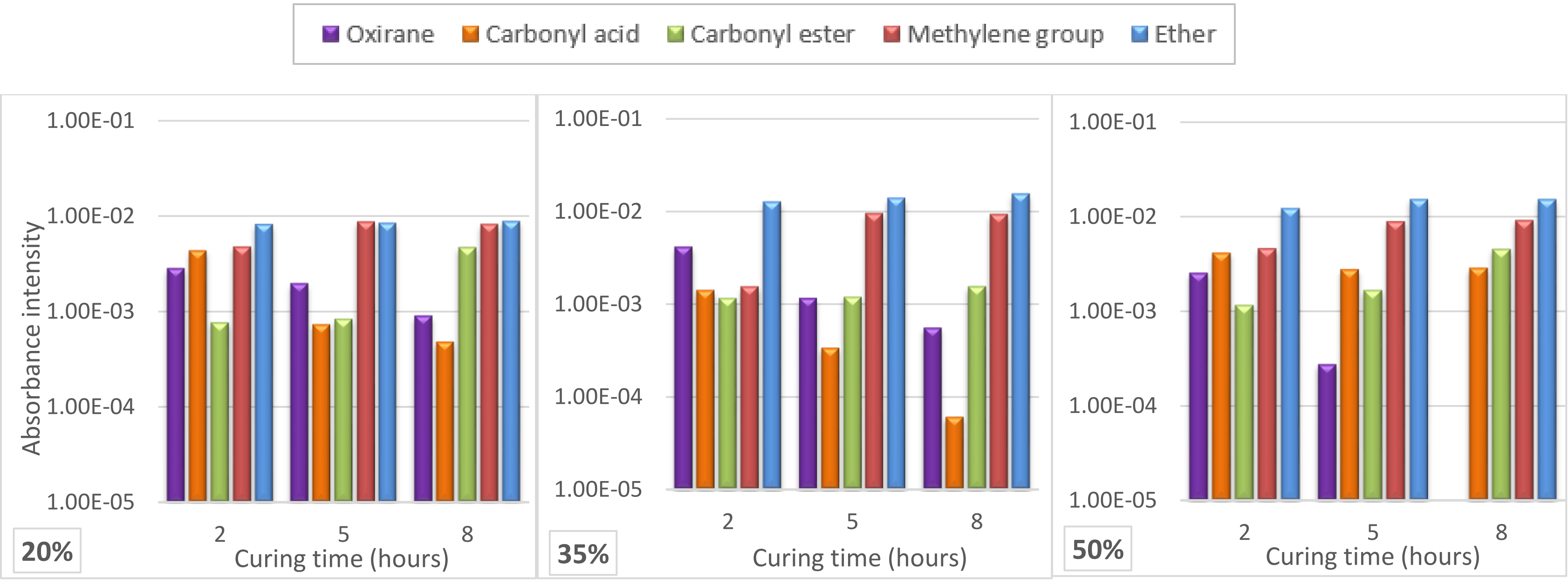


Figure 4. 9 : Functional groups during curing process for all EMBs at 100°C

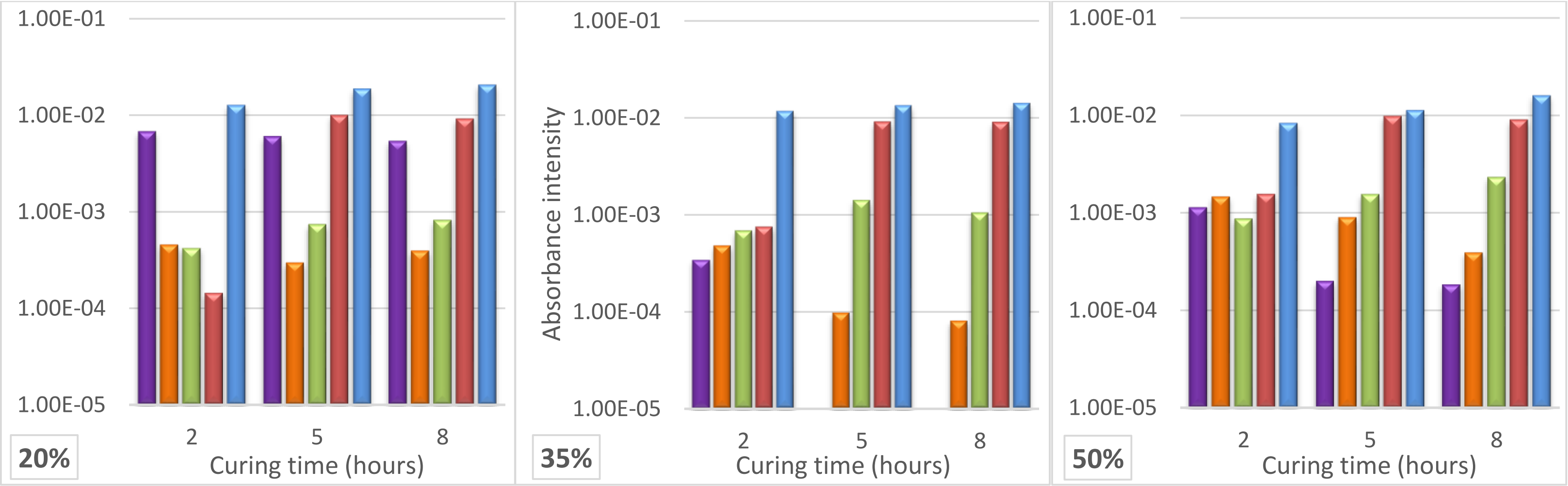


Figure 4. 10 : Functional groups during curing process for all EMBs at 130°C

Regarding the temperature of 100°C, for all modification levels, oxirane reduces with prolonged hardening time. For the modification level of 50% it is almost disappeared after 8 hours, probably due to the higher amount of epoxy modifier included. The network formation is succeeded more easily compared to lower modification levels. The increase of ester initially is a product of esterification. Based on the reduction of carbonyl acid over extended hardening time it can be assumed that the hardener of part B is a carbonyl acid. A second independent reaction of etherification takes place and results to ether, which seems to remain steady at different hardening times. It can be assumed that this reaction is more reactive than esterification, as it reacts completely in a shorter time. Another important observation is the decrease of oxirane from 5 to 8 hours showing that the chemical hardening has not been completed yet. To consider the chemical hardening process completed, both oxirane and methylene group, which are responsible functional groups for the epoxy, should be stabilized between two certain times at 100°C. At the modification level of 50% the produced methylene is stabilized after 5 hours and oxirane has been almost fully reacted after 8 hours.

For the investigated hardening time of 130°C, it is clear that the crosslinking network of epoxy modifier is formed slightly faster at higher modification levels. The crosslinking network is a result of the polymerization of part A with the assistance of part B and is faster at higher modification levels mainly because less bituminous molecules prevent the network evolution. Ester and ether also remained steady after a slight increase from 2 to 5 hours. The oxiranes are stabilized for EMB 20% and 50% from 5 to 8 hours. Additionally, the methylene group remained constant after 5 hours of hardening for all EMBs. Thus, the combination of 5 hours at 130°C was hypothesized as the condition in which EMBs are fully hardened, named critical hardening conditions in this research. The phenomenon of the limited change in methylene group after 5 hours for all EMBs, can be explained by the bond of the epoxy molecules with carbonyl acid to create the crosslinked network. The main conclusion of this FT-IR analysis is that the hardening time around 5 hours and 130°C, which was chosen as the most critical from master curves, is also confirmed by the chemical interpretation of the hardening process. Based on this temperature, viscosity and modulus evolution will be evaluated in the next step.

4.3.3. VISCOSITY EVOLUTION

The control of viscosity during processing of thermosets is critical because the viscosity varies not only with temperature and flow conditions, but also with time because of polymerization reactions. Therefore, a comprehensive understanding of the relationship between the kinetics and rheology is necessary to effectively control the whole process from production to transportation, mixing and compaction and to optimize the material processing. In this study, the time window will be investigated with a viscosity test over a period of 3 hours. The selected temperature from the two previous tests was 130°C, and the viscosity test was performed at this specific temperature for unhardened EMB. Considering that the hardening rate is dependent on the modification level, it is important to observe the influence of the modification on the viscosity evolution.

According to the Superpave Asphalt Binder Specification of the Strategic Highway Research Program (SHRP), the suitable viscosity of the bitumen for compacting the mix should be below 3 Pas at 135°C [60]. This limitation is based on ASTM D 4402 and should provide realistic pumping, mixing and handling temperatures to get complete coating of aggregates. However, others claim that the ideal range of viscosity upon mix delivery is maximum 1 Pas to be capable of pumping it easily and maximum 3 Pas upon compaction [78]. If EMB becomes too hard and exceeds 3 Pas, compacting it would be difficult.

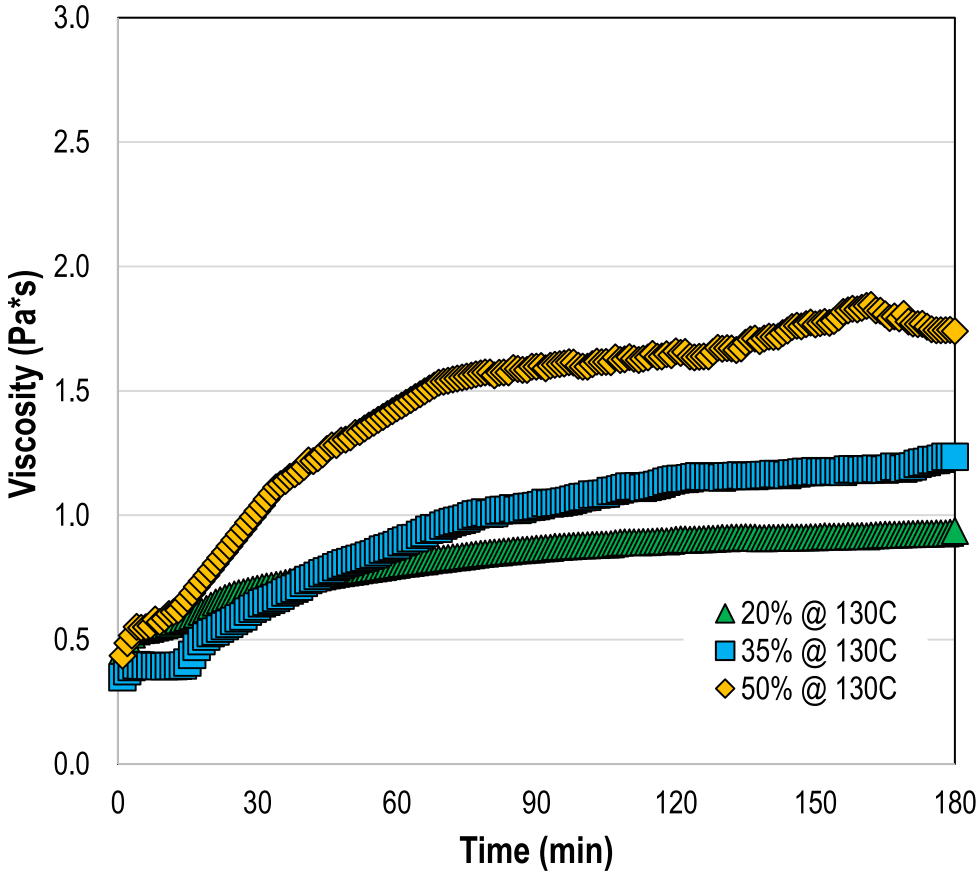


Figure 4. 11: Viscosity evolution for all EMBs at a shear rate 60s^{-1}

Two obstacles during production are that the heat in the trucks should be kept constant in order to estimate a specific pot life under a fixed temperature, and secondly, the curing rate slows down quickly as the temperature decreases when the mixture is transported to the paving site. To address these issues, isolated trucks can ensure a proper temperature and alternatively chemical accelerants could be used. Another solution is the preheating of the material on plants for a specific time prior to transportation.

The results obtained from viscosity tests are presented in **Figure 4.11**. An almost logarithmic increase, after an initial less rapid increase, is followed for all samples. This trend is justified by the bitumen content which initially slows down the network formation. The bitumen mixed with epoxy belongs to a quasi-thermoset. It is obvious that higher modification levels present higher rates of viscosity evolution. The network formation of epoxy molecules is prevented by the presence of more bitumen molecules at lower modification levels. The time window until compaction at 3 Pas is considered an important limit, according to Superpave specifications and is fulfilled for all modification levels. Nevertheless, the lower limit of 1 Pas, which was claimed to ensure pumping and adhesion with the aggregates upon delivery, is also checked. This criterion results in a time window of 30 minutes for EMB 50%, 80 minutes for EMB 35% and more than 3 hours for EMB 20%. It has been reported that the material should neither be too viscous upon delivery to be workable, nor too liquid to stick with the aggregates [79]. The delivery time of 3 hours from production until the in-field paving is considered realistic. The obtained viscosities after 3 hours of chemical hardening at 130^{o}C are 0.94, 1.24 and 1.74 Pas for EMB 20, 35 and 50%, respectively. From the previous sub-tasks, the combination around 5 hours at 130^{o}C was considered as a critical chemical hardening recipe. After viscosity tests, it is shown that the materials perform well as binder related to the compaction limits for viscosity. A plateau of the viscosity evolution is observed from the **Figure 4.11** after 2,5 hours for all EMBs and thus the combination around 5 hours of curing is considered once again the critical. The curing process will be almost completed at this time and the material upon paving will increase its viscosity rapidly as they will cool down while being paved.

4.3.4. MODULUS EVOLUTION

Besides of the viscosity evolution, another important parameter is the modulus evolution. From the master curves, the evolution was observed ifor selected frequencies and hardening times. A more accurate impression of modulus evolution could be obtained via a time sweep test for unhardened EMBs at 130^{o}C. The modulus evolution of these materials continues to increase slightly for several days, and modulus level at which the modulus starts to slow down its increase rate, is considered decisive to open the road to traffic. This limit value differs from site to site, and depends on pavement design and traffic demands.

In **Figure 4.12** it is shown that the modulus reaches its plateau after 140 minutes for all modification levels. An initial rapid increase is observed within the first half hour. The higher the percentage of epoxy used, the higher the obtained modulus recorded after 3 hours of curing. The increasing slope was observed to be more rapid for EMB 50%. These results are of the same magnitude and thus their differences are considered negligible. Finally, the stabilization after 2,5 hours justifies the critical combination of 5 hours as the most crucial from the three examined hardening times.

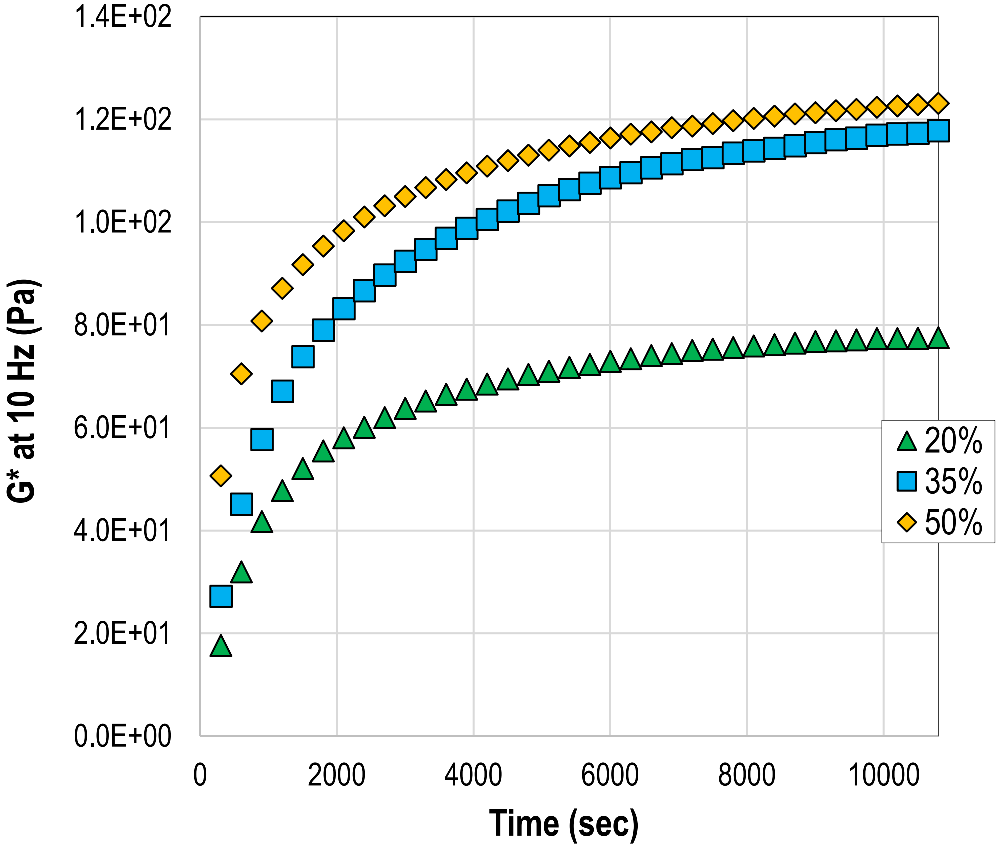


Figure 4. 12: Modulus evolution for all EMBs at 130°C

4.4. CONCLUSIONS

Through this Chapter, the development of the chemical hardening was investigated. 18 different combinations were tested for this purpose. Among the various combinations, the combination around 5 hours at 130°C was considered the most critical. Initially, the stabilization of modulus and phase angle was considerably accelerated with the higher temperature. The same conclusion was verified with FT-IR results. Secondly, from the modulus and viscosity evolution it was concluded that both modulus and viscosity are stabilized and considered workable and secure to be applied after 2,5 hours. This supports also the selected combination as the most critical. Using this critical combination to continue in this research is within the time framework considered reasonable. However, a further investigation from 2,5 to 5 hours is proposed for future research. Based on this critical combination of conditions a comparison of the performance with bitumen will be performed in Chapter 5.

5

Performance Evaluation of EMB

In this chapter, a comparison of three modification levels of EMB with the unmodified bitumen is reported by using the DSR device. Initially, the master curves of the complex shear modulus were evaluated for the EMBs under the critical conditions that have been determined from the experimental tests of the chemical hardening. After that, tensile strength and fatigue properties were investigated by using the same DSR device. Finally, the results of these tests are discussed and compared with the bitumen.

5.1. INTRODUCTION

As it was discussed in the previous Chapter 4, the hardening combination of 5 hours at 130°C was considered as the critical curing condition for EMBs. Based on that, a validation of the high performance of EMB will be attempted in this Chapter. In addition, since modulus evaluation requirement is of great importance for the pavement structure to resist the traffic loads and to provide a guideline for the road authorities to decide the time needed to open the pavement to traffic, the development of viscoelastic properties should be studied. To evaluate the modulus limits, the construction of master curves for all studied materials is an appropriate measurement method. The selection of these master curves with an appropriate reference temperature is also an important issue. Constructing the master curves with a reference temperature of the chosen critical temperature 130°C is considered also crucial to observe clearly the influence of the binders at high temperatures, which are used for the production. It was also hypothesized that fresh bitumen would be used without further conditioning, as no further chemical hardening is needed upon production. On the contrary, in all EMBs the critical curing conditions were applied as the material is subject to chemical hardening. Thus, the construction of master curves, as well as the tensile and fatigue tests were performed for fresh bitumen without further temperature conditioning. A fair comparison of two is done upon placement of the mix. The procedure until this step will differ for the modified and unmodified materials and it is believed that the aforementioned comparison is more realistic. Longevity and tensile strength were evaluated under harsh conditions of low temperature in an attempt to relate the occurred damage with crack initiation. It is well known that crack initiation and propagation is also related to aging. Therefore a simulation of short- and long-term performance will be presented in Chapter 6.

5.2. EXPERIMENTAL METHODS

The frequency sweeps that were already performed before for the investigation of chemical hardening of EMB were used in this task. However, to study the influence of the temperature on the frequency sweeps, the tests were extended from 70 to 130°C. Additionally, for the purpose of comparison, the frequency sweeps were carried out also for the fresh bitumen from -10 to 130°C. The test procedure for performing the frequency sweeps can be found in EN14770:2012 specification which was described in Chapter 3. The frequency range was again set from 0.01 to 10Hz.

According to the method for performing binder fatigue with an 8mm plate-plate geometry described before, the fatigue tests were performed at 0°C by using a DSR device. The fresh bitumen was also tested. The selected frequency was 10 Hz and three stress levels were used, namely 0.4, 0.5 and 0.6 MPa. The execution of the test was done for three replicas per binder and was terminated after the complex modulus value decreased to 10% of the initial value. The gap between the 8mm plates was set to 2mm and the test data was recorded every 20 seconds.

The last test which was performed for the evaluation of EMB performance was the tensile tests with a DSR device. Special columns were manufactured for all EMBs after applying the critical curing combination. The test procedure has been described in Chapter 3. The columns were placed carefully in the set of shafts and the temperature was set to 0^{o}C. A constant displacement controlled loading rate of 0.05 mm/s was used and the values of applied force were recorded every 0.1 seconds to capture the load development. By using the geometry of the small columns, the results were converted to tensile strength for each of the three tested replicas per binder.

5.3. RESULTS AND DISCUSSION

5.3.1. COMPLEX SHEAR MODULUS

To study the influence of temperature on the complex shear modulus of the binder, the master curves of studied materials were compared at a temperature range from -10 to 130^{o}C. **Figure 5.1** provides a comparison between the binders with different modification levels with the unmodified bitumen. From this graph, it is obvious that all EMBs have reached similar complex modulus levels after applying the critical curing condition of 5 hours at 130^{o}C. Slight differences can be observed in the whole range of frequencies. More specifically, for intermediate frequencies from 0.1 to 100000 Hz the low modification levels of 20 and 35% show complex modulus values of the same magnitude but slightly smaller than bitumen. Regarding the EMB 50%, it seems to exceed the complex modulus values of bitumen from 1 to 1000 Hz. This fact verifies that the crosslinking is easily enabled in this specific EMB, whereas it follows similar complex modulus levels with bitumen in the rest frequencies.

The molecular compatibility of bitumen with the modifier is also of paramount importance for this comparison. In fact, the compatibility can be interpreted as follows: the epoxy represents the continuous phase and the bitumen the disperse phase [4]. Both phases are responsible for the complex modulus, with the first developing over time and the second remaining constant. From a design point of view, the values of modulus are acceptable to apply EMBs, however, the design should be first looked into carefully for traffic demand. Eventually, comparing the complex modulus values of EMBs and of unmodified binder did not show significant differences, as bitumen included in the mixes seems to be the governing parameter for this property. Thus, it is similar to the bitumen and that recyclability aspect of EMB is also possible for the future applications.

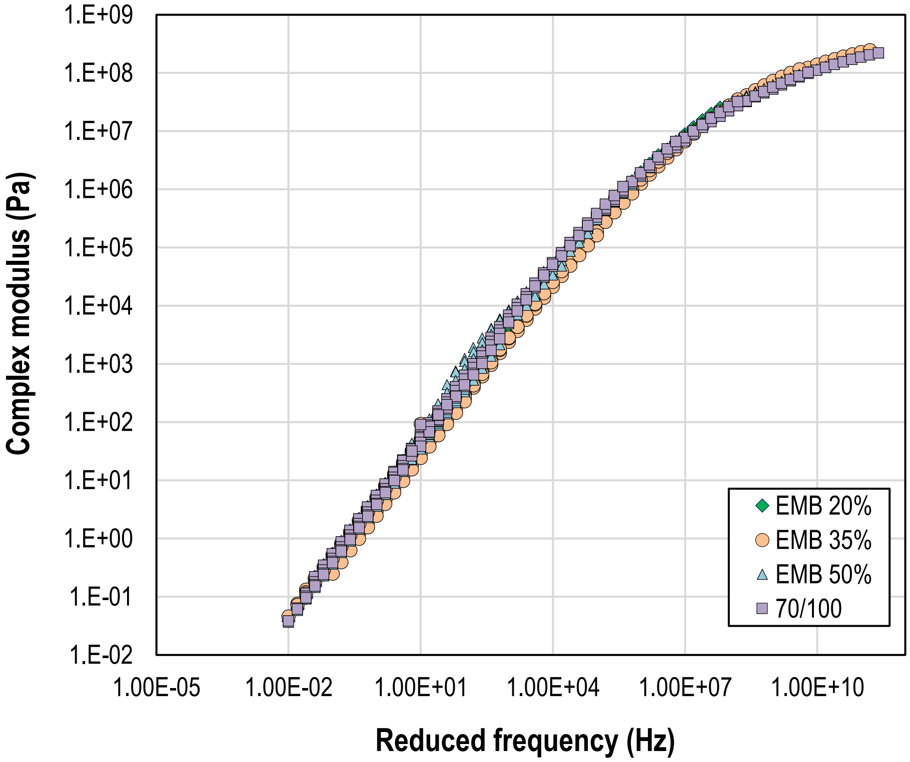


Figure 5. 1: Master curves for all studied materials from -10 to 130°C at a reference temperature 130°C

5.3.2. FATIGUE PERFORMANCE

As has been reported EMB promises extended long-life performance. To evaluate this property which is strictly connected with maintenance needs and costs in long-term application, both EMB and conventional bitumen should be tested. Moreover, fatigue in binder level is translated as brittle failure damage and should be connected with crack initiation in laboratory testing. This type of brittle failure was expected for the tested low temperatures for binder fatigue and was verified as can be observed from by **Figure 5.2**. The repeatability of the results, as well as the regression lines, were acceptable. This is justified by the coefficient of determination given in **Figure 5.3**. The tests were stress-controlled and according to Chapter 3, the results are demonstrated when the maximum load repetitions reach 10% of the initial complex modulus. The initial complex modulus values were at about 100 MPa to avoid flow phenomena. The raw fatigue results for all the tested samples are presented in **Appendix C**.

It was already known that the incorporation of epoxy into bituminous binders results blends of improved properties but limited evidence existed about their long-term performance in binder level. From the fatigue tests presented in **Figure 5.3**, important observations can be extracted.

Figure 5. 2: Fatigue test and crack initiation of the specimen

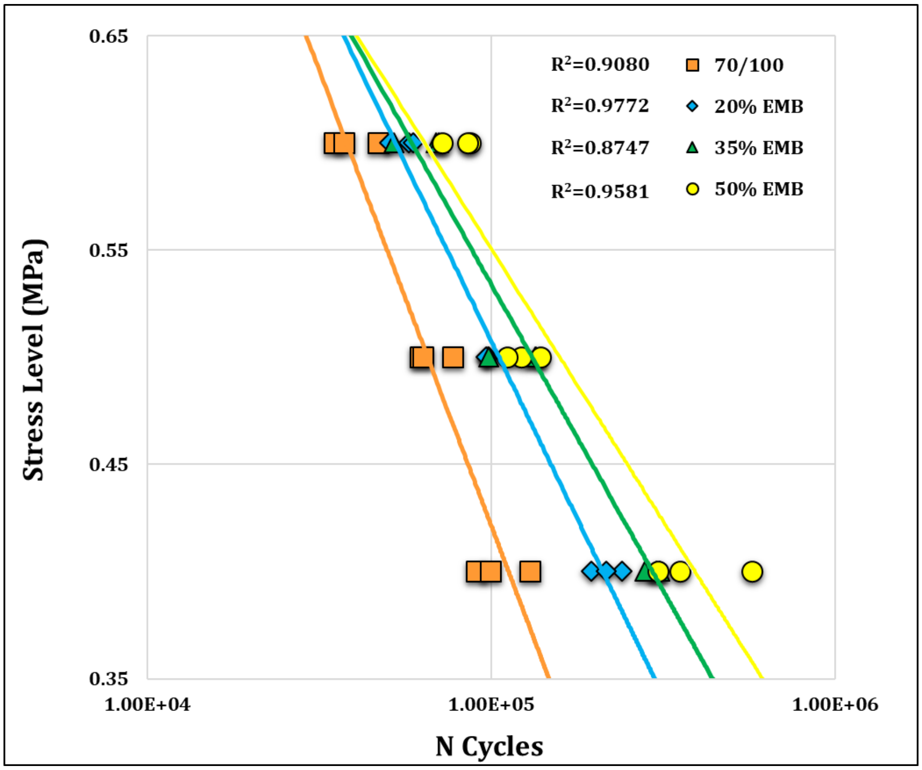


Figure 5. 3: Fatigue curves of studied materials

First of all, the higher the epoxy modification level in bitumen is the higher the resulting fatigue life is. The current results validated the expectations of durability improvement with the epoxy modifier into the bitumen. Secondly, the prediction both at high- and low-stress levels gives better performance compared to the unmodified material. The improvement in fatigue life was even more obvious for lower stress levels. It has been also reported that the improved fatigue performance was beneficial in resisting top-down traffic induced cracking in the final mix [2]. Thus, taking into account the improved durability of epoxy modified bituminous mixes at low temperatures, this type of binders prevent the cracking-type distresses in pavement structures and possibly offering lower maintenance demands.

Another issue that should be taken into account is that fatigue life of pavement is expected to be different, as a result of the rest periods between load applications and the time needed for the crack propagation. The selected stress levels should be reconsidered to simulate the real traffic load. Finally, these results are only a rough estimation of the expected performance of modified binder. Once filler, sand and aggregates are added, they will affect the final mix because of their interaction with the binder.

5.3.3. TENSILE STRENGTH

To evaluate the toughness and ductility of EMBs, the monotonic tensile test can be used as one reliable testing method. The tensile strength calculated on the base of the sample geometric configuration can be used to compare the different samples. The corresponding tensile strain can be computed as the ratio of the elongated length of the sample at the peak force to its initial length. Generally, the tensile strength and the ductility of the sample depend on the extent of hardening reaction, the ratio of the unlinked molecule number to crosslinked molecular number and the chemical structures of EMBs.

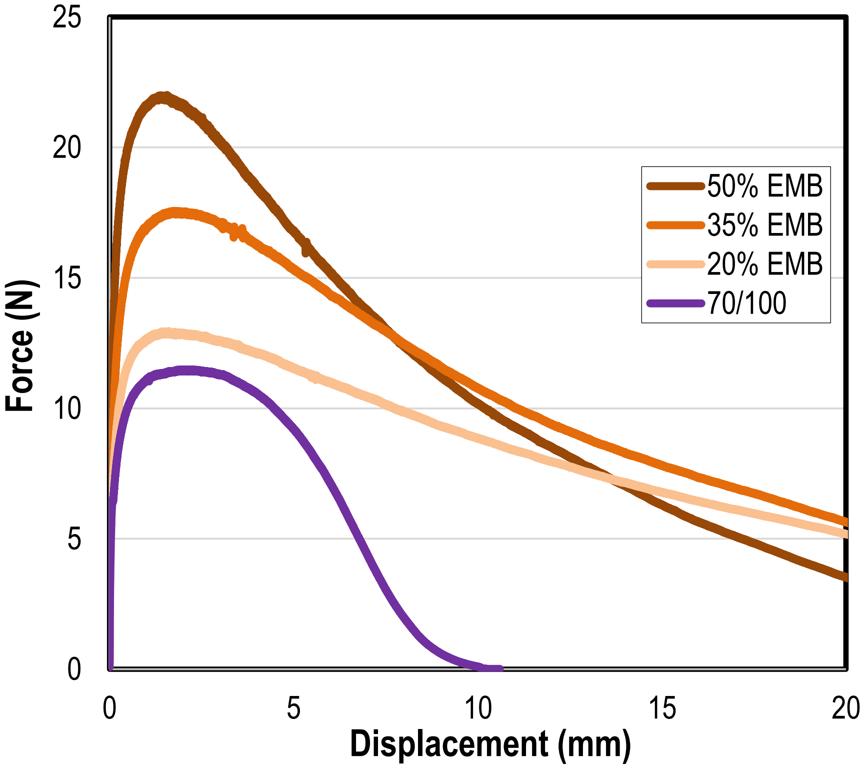


Figure 5. 4: Representative tension curves

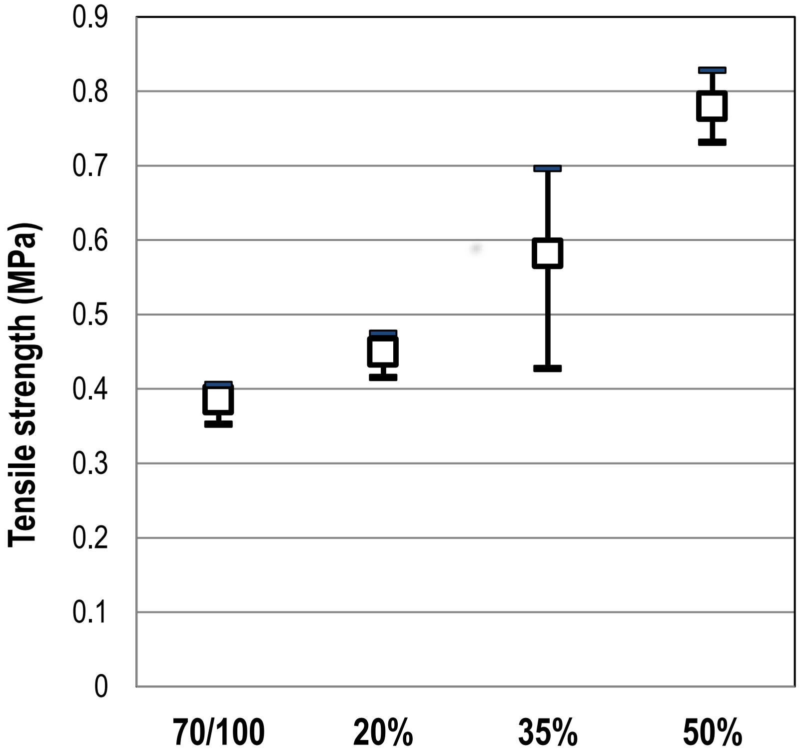


Figure 5. 5: Tensile strength for the studied materials at 0°C with a displacement laoading rate 0.05 mm/s

All the specimens experienced ductile behavior, exhibited higher flexibility characteristics at 0 °C (**Figure 5.4**). EMBs show greater toughness prior to fracture and also higher tensile failure resistant. Overall, EMBs presented significant improvement on the cohesive strength compared to the bitumen something that looks a promising possibility for the application of EMBs also as solution for interlayers such as bond tack coat. Additionally, it was observed that with an increase of epoxy content the tensile strength increased (**Figure 5.5**). Furthermore, the strain of conventional bitumen at the peak load is larger compared with the EMBs, and follows a downward trend for higher modification levels.

5.4. CONCLUSIONS

In this chapter a comparison was made between modified with the unmodified bituminous binders. The complex modulus of EMBs proved to be similar to bitumen. EMBs provide higher tensile strength, fatigue life and flexibility than unmodified materials.

6

Age Hardening Evaluation of EMB

Aging is the main concern of this chapter. Firstly, a short introduction of the different aging stages and the different aging methods is given. After that, the results obtained by DSR and FT-IR with short-term oven aging and long-term aging with a pressure aging vessel are discussed. A comparison of the various time intervals in short and long term aging, is performed for all materials. Finally, aging indices are utilized to evaluate both the material degradation and the influence of oxidation.

6.1. INTRODUCTION

The susceptibility of bituminous materials to damaging effects of aging during their service life leads to brittle failure and makes the material prone to ravelling and cracking [80]. There are different aging mechanisms identified, with the most important being oxidation. Oxidative aging is mainly a diffusion phenomenon, resulted from photo-oxidation and other reactions between bitumen and atmospheric oxygen. Reaction with oxygen changes the chemical properties of bitumen and affects eventually its physical properties [81].

Several parameters influence the aging process, such as heat energy, temperature, the radius of molecules, the polarity and the intermolecular interactions [82]. The oxidation generates a number of various functional groups in the chemical composition of bitumen, such as carbonyls, sulfoxides and carboxylic acids. When benzylic carbons are oxidized, they form carbonyls and carboxylic acids in small amounts, whereas sulfoxides are resulted from the oxidation of sulfides. Because sulfides are more reactive, they have a greater production rate of sulfoxides, which are formed faster than carbonyls [83]. Therefore, the type of bitumen and the crude oil origin influence the amount of oxidation products [81].

Observing these quantities, using a spectrometer, could give an estimation of the aging percentage of the examined binder. This technique is based on the semi-quantitative analysis, expressed by the aging indices and can be related to the affected properties of the binder. Among the influenced properties by aging are the complex modulus and the phase angle. An increase of modulus and a decrease in phase angle are usually observed with aging. Other properties that oxidation influences as well, is the viscosity, the softening point and penetration grade [84].

6.1.2. AGING IN BITUMINOUS BINDERS

The effect of aging can be classified into two major categories, a short- and a long-term aging. The two categories are related to different stages of production or service life of the mixture [85]. Moreover, the consequences of aging could be accompanied with brittle damage of cracking or poor bond with the aggregates and ravelling.

The short-term aging (STA) involves the loss of volatiles and oxidation of the conventional bitumen during the construction phase. The first most significant hardening of the binder takes place in the mixing facility during hot mix asphalt production where heated aggregate and binder are mixed and secondly during storage, transport and compaction. Age hardening of the binder continues, although at a much slower rate, while the hot asphalt mixture is processed through a storage silo, transported to a paving site, laid and compacted. During the STA two main processes accelerate the rate of aging. One is oxidation and another one is volatilization. Oxidation is the reaction of oxygen with the binder, whereas volatilization stands for the evaporation of light bitumen fractions, as a result of high temperatures during production [62].

The most severe is the second category of long-term aging (LTA). With the definition of LTA, one refers to the oxidation of the bitumen during the service life of the mixture. For the first years of service life (2 to 3 years) the age hardening continues at a slower rate, whereas it decreases further its rate at longer periods. This change in hardening rate makes the understanding of the alteration of properties more complex [62]. Other types of processes that result in the LTA have been reported by different researchers, such as polymerization and separation. These are related mainly to the composition of the binder [62, 85].

The type of the final mix is of paramount importance, due to the significance of the amount of air voids included, which are strictly connected with access to water and oxygen in the whole thickness of layer [62]. Moreover, the performance of the aged binder contributes to its durability. For modified binders this performance is a combined effect of oxidation and polymer degradation and is believed that accelerated simulation of aging may result in extended degradation, something that makes the simulation inadequate [86].

6.1.3. AGING INDICATORS FOR BITUMINOUS BINDERS

For the evaluation of the aging process, some criteria should be established to compare the extent of aging and predict the occurred damages. Initially, fundamental properties were used to quantify the susceptibility of the mixture to aging. Ratios of the value of property obtained after aging to the original value of the binder were used to evaluate the deterioration. Retained penetration, change in temperature of softening point, stiffness, complex shear modulus and mass loss were used to simulate the level of aging. Moreover, the ratio of viscosity of aged binder to the original was used to identify the different stages of aging that take place. A schematic representation of this index with the different stages of service life in **Figure 6.1** gives an impression of the differences between short- and long-term aging [87]. This index is high for conventional bitumen and most of the times is measured at 135°C and 60°C to characterize STA and LTA, respectively [62].

All the aforementioned empirical methods were based on equations obtained from a large number of recovered binders after a passage of some years in service and different mix type, pavement structures and the locations of the recovered binder. Additionally, the atmospheric conditions of rain and temperature variation, UV-radiation angle of the pavement, as well as the temperature isolation during transportation and mixing can affect significantly these properties [62].

As mentioned previously, aging influences the chemical composition of bitumen as well. The focus should be given to the cause of properties changes. Understanding of the chemical composition of the bitumen is necessary to continue to the next step. In short, bitumen consists of asphaltenes, saturates, aromatics and resins, the percentage of each of them affects the aging extent. Based on this concept, the Gaestel Index, was introduced and correlated with age hardening [88]. This index is expressed as the ratio of asphaltenes and saturates to aromatics and resins and it increases after aging. It can be explained as the internal colloidal structure of the binder. The formation of new levels of colloidal structure in the compositional analysis justifies changes in molecular weight, rheological behavior and other physical properties. Moreover, this colloidal structure and its interpretation could be used for an explanation of the LTA and as a prediction of durability performance in the field [88]. An increase of Gaestel Index is mainly due to the increase of polar functional groups (asphaltene content) and a decrease in the polar and non-polar aromatics. Hence, a change in the colloidal structure may reflect the aging sensitivity of different binders and could be used for comparison of them [62].

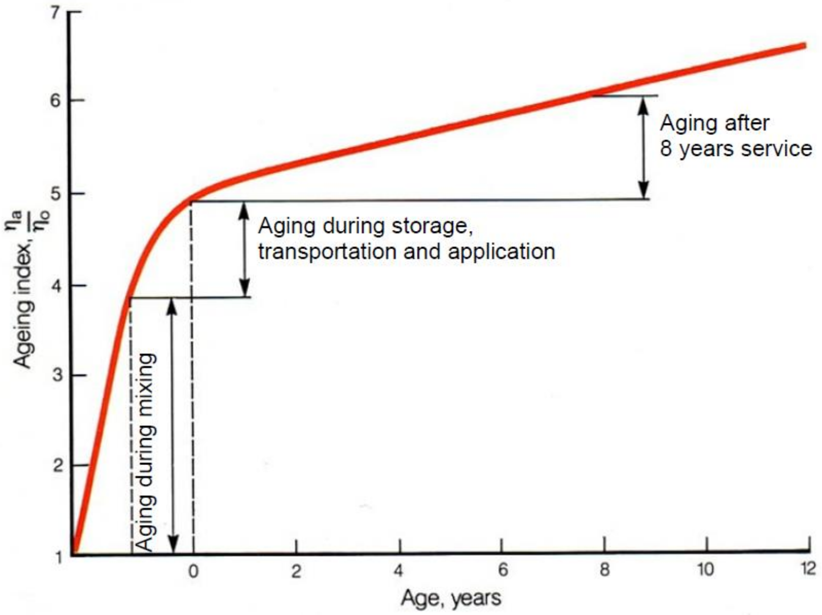


Figure 6. 1: Typical effect of STA and LTA on viscosity ratio **[87]**

Other indicators providing information of the chemical composition of the binder are related to the crucial functional groups of sulfoxides and carbonyls. Different indices have been introduced to indicate the aging degree, from hardening susceptibility which takes into account the logarithm of viscosity with the carbonyl area to peak areas of sulfoxide and carbonyl ratios of obtained with FTIR spectroscopy [89]. Because carbonyls (1700 cm^{-1}) and sulfoxides (1030 cm^{-1}) are the major oxidation products an increase was observed as a function of time. Their sum indicates the relative degree of oxidation in binders expressed by the aging indices. Carbonyl concentration due to oxidation is strongly related to the viscosity increase. Higher amount of carbonyls appear to be formed at the expense of sulfoxides at higher temperatures and carbonyl formation rate decreased with increasing viscosity [90]. It was also important to identify some specific functional groups that remained constant to use them in the attributed changes of sulfoxide and carbonyl groups. Considering the corresponding areas under these bands of wavelength described previously and not fixed peaks sulfoxide and carbonyl indices are given as [73, 91]

$$SI = \frac{A_{1030}}{\sum A} \text{ [23]}$$

$$CI = \frac{A_{1700}}{\sum A} \text{ [24], where}$$

$$\sum A = A_{2953} + A_{2862} + A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724}$$

In this research, the first index as well as the complex modulus ratio obtained for aged binders was used for assessing the aging degree.

6.1.4. AVAILABLE BINDER AGING SIMULATION

To simulate the aging process in binders, both short- and long-term, different techniques have been proposed. In general, these techniques can be categorized into two main groups: the oven tests and the pressure oxidation tests [61]. It should be noted that the contribution of aggregate-binder interaction and the type of filler can influence also the bitumen aging, while bitumen could be absorbed by the aggregate or deteriorate the established adhesive bonding playing an important role for the durability of the mix [61].

The aging occurred during construction, corresponding to STA, is primarily linked to oxidation and loss of volatiles. Two tests have been proposed to simulate the STA, a thin film oven test (TFOT) according to EN12607-2 and a rolling thin film oven test (RTFOT) according to EN12607-1. The first incorporates heat and air on a film of bituminous binder with fixed thickness for 5 hours at 163^{o}C to simulate mainly aging during mixing in the plant, whereas the second utilizes specific amount of binder at the same temperature. RTFOT is conducted for 75 minutes in cylindrical bottles rotating in a device, providing heat and hot air [62]. Other alternatives for STA is the German rotating flask test which takes also into account segregation of the binder, the rotating cylinder aging vessel (RCAT) and finally the short-term oven aging (STOA). STOA can be applied for different time intervals usually using the mixing temperature. For all the above, modified procedures have been proposed to make the simulation more realistic [62].

The field aging during service life takes place at a slower rate as an interaction with the environmental conditions. It was considered, however, important for long-term performance evaluation. Pressure aging vessel (PAV) according to EN14769 and rotating cylinder vessel (RCAT) according to EN15323 are the two main simulations that are performed. For a PAV test, 50 gr of binder is poured into metallic trays and placed on a shelf track, preserving a constant temperature usually at 100^{o}C and a pressure of 2.1 MPa for 20 hours [92]. This ensures good simulation without destroying the integrity of the binder, although it has been criticized by many researchers for inhomogeneous oxygen diffusion [62]. A PAV device, which was also used in this research is presented in **Figure 6.2**.

Figure 6. 2: PAV aging apparatus (left) and metallic tray (right)

The RCAT is a dynamic test which is thought to provide uniform aging simulation of the binder. Another major advantage is that it can simulate both STA and LTA and can produce bigger amounts of aged binder. The procedure usually followed is to place about 500g into a stainless steel cylinder which is rotating. Inside the cylinder constant oxygen flow and temperature of 85°C are preserved for 240h hours. The conditions for STA differ to the flow rate of oxygen, the test duration of 4 hours and the selected temperature which is 163°C [93]. Finally, it is worth mentioning that there is another device for aging called weatherometer, which combines humidity, temperature and UV-radiation [62].

6.2. EXPERIMENTAL METHODS

During this research the STA and LTA of EMB were investigated. The selected simulation protocols that were followed was STOA for the short-term aging and PAV for the long-term. The reasons for the selection of these two methods were based on the availability of the testing equipment and the potential solidification that might occur because of chemical hardening. Moreover, it was believed that chemical hardening takes place in a longer time period after it almost completely reached a stabilization of the modulus and viscosity. Thus, STOA could identify also the changes with extended curing.

Specifically, the used mixing temperature of 130°C for all modification levels was used in STOA for time intervals of 1, 5 and 10 days. During the STOA, uncured blends were placed in ovens with metallic cans and mixed regularly to obtain uniform aging in the whole blend. Similarly, for comparison reasons, the conventional virgin bitumen was simulated also with

STOA. For the long-term aging simulation, the PAV procedure was utilized. The presence of bitumen in EMB kept the blends in a rubber-like phase. A temperature of 100°C and a pressure of 2.1 MPa was applied for 20 hours without prior STA.

All the blends were poured in a silicone paper for the preparation of DSR and FT-IR specimens after the application of the different aging conditions. The frequency sweep tests at the conditions of temperatures varying from -10 to 60°C and frequencies varying from 0.01 to 10 Hz, were performed in the DSR device for samples of different aging conditioning. The temperature of 30°C was chosen as the reference for the construction of master curves. From these master curves, complex modulus values for specific frequency were used as aging indicators. Finally, specimens subjected to the various aging conditions were investigated with FT-IR spectrometer. Based on the area calculation method (see sub-Chapter 6.1.3), the spectrum from 600 to 4000cm^{-1} was analyzed for aging indices.

6.3. RESULTS AND DISCUSSION

6.3.1. COMPLEX SHEAR MODULUS

A first indication for the aging extent of studied materials was examined through the ratio of aged and unaged complex modulus value for a reduced frequency of 1,59 Hz or 10 rad/sec. This was done after the construction of master curves with a reference temperature of 30°C. A first idea for the influence of each aging condition can be given through the observation of the master curves for each binder. For all EMBs, the critical curing combination was selected and used as the unaged situation. That is not the case for pure bitumen in which no prior curing conditioning was performed. Subsequently, the results of aging extent could be compared for all binders per aging condition with the unaged situation. To keep the consistency with the chemical hardening conditions, the temperature of 130°C was used to perform STOA tests. Since clear discrimination of the end of curing process and the beginning of aging is difficult, some further investigations of the influence of these two processes on aging and curing reaction are needed.

From **Figure 6.3** it is obvious that STOA increases slightly the complex modulus and decreases the phase angle compared to the unaged EMB 20%, which makes the binder less susceptible to rutting. In this comparison of these aging conditions chosen for STOA, another mechanism of extended hardening takes place, resulting in increase of modulus. For modified binders, the temperature seems not to cause excess aging even for 10 days. The severe simulation of PAV generates great differences in complex modulus and phase angle, where the results are more observable at intermediate and low frequencies.

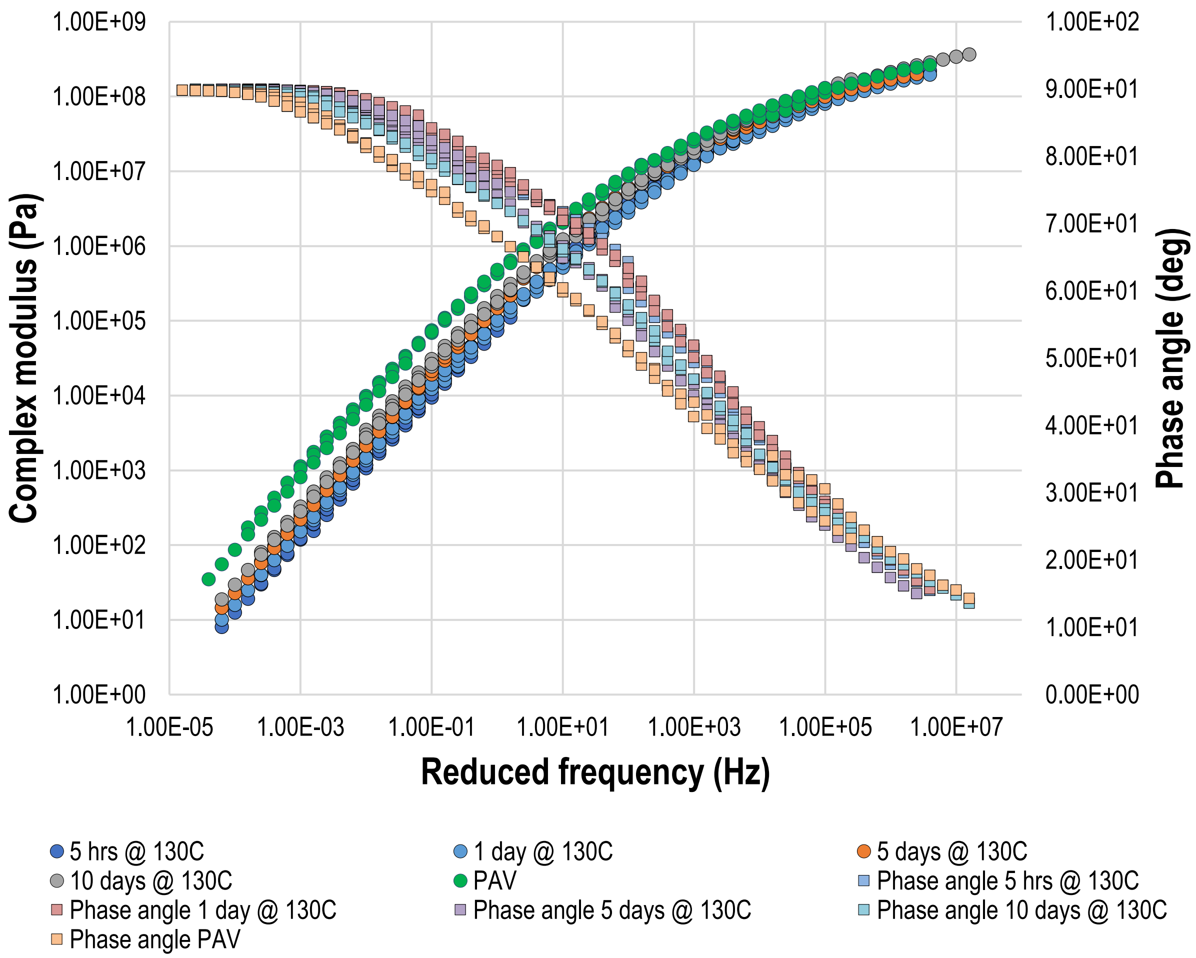


Figure 6. 3: Master curves of EMB 20% for all aging conditions

The EMB 35% followed exactly the same tendency, with an exception between 1 and 5 days (**Figure 6.4**). The increase of complex modulus and accordingly that reduction of phase angle was more apparent than EMB 20%. The chemical hardening has been completed faster for this modification level and age hardening has initiated because of the elevated temperature. The modulus evolution as has been reported previously in Chapter 4 was also more rapid for EMB 35% until it starts to stabilize. PAV once again gave the highest values for complex modulus.

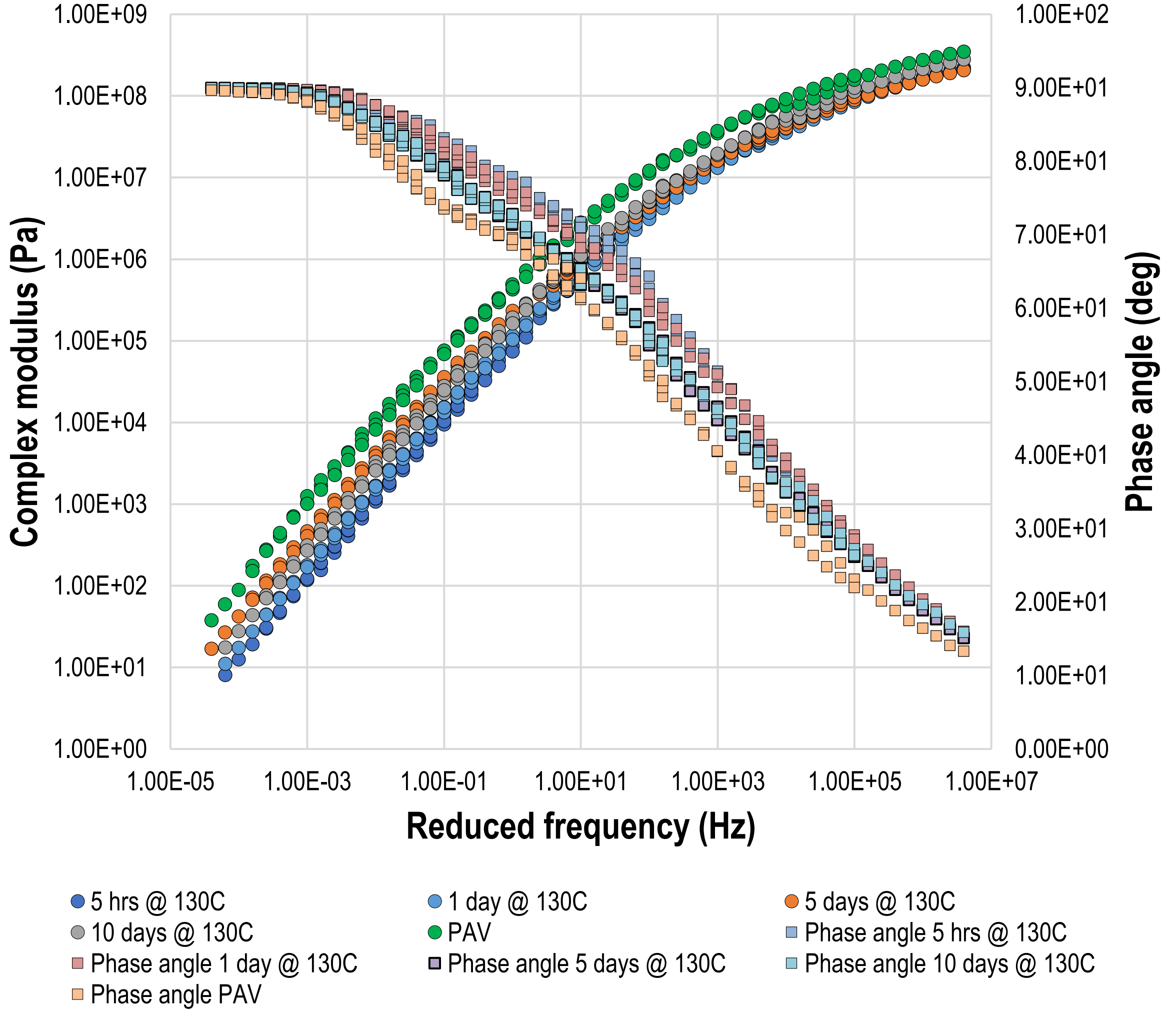


Figure 6. 4: Master curves of EMB 35% for all aging conditions

The maximum modification level of 50% gave the master curves presented in **Figure 6.5**. From this graph, two observations are made; (i) the phase angle values are significantly different compared to lower modification levels and (ii) the complex modulus values after PAV are considerably higher than STOA and unaged EMB 50%. This was not the expected performance of EMB versus oxidation. Explanations of these rather increased complex modulus values, when 50% epoxy was utilized, is that pressure probably affects significantly the modifier and phase separation might occur. Moreover, the thin binder film of PAV may create a non-uniformly hardened material, as has been supported by previous researchers, resulting thus in an inhomogeneous oxygen diffusion [62]. Concerning to STOA there is a jump in complex modulus values from 1 to 5 days. This could be explained by the higher modification level which enables the curing completion more quickly.

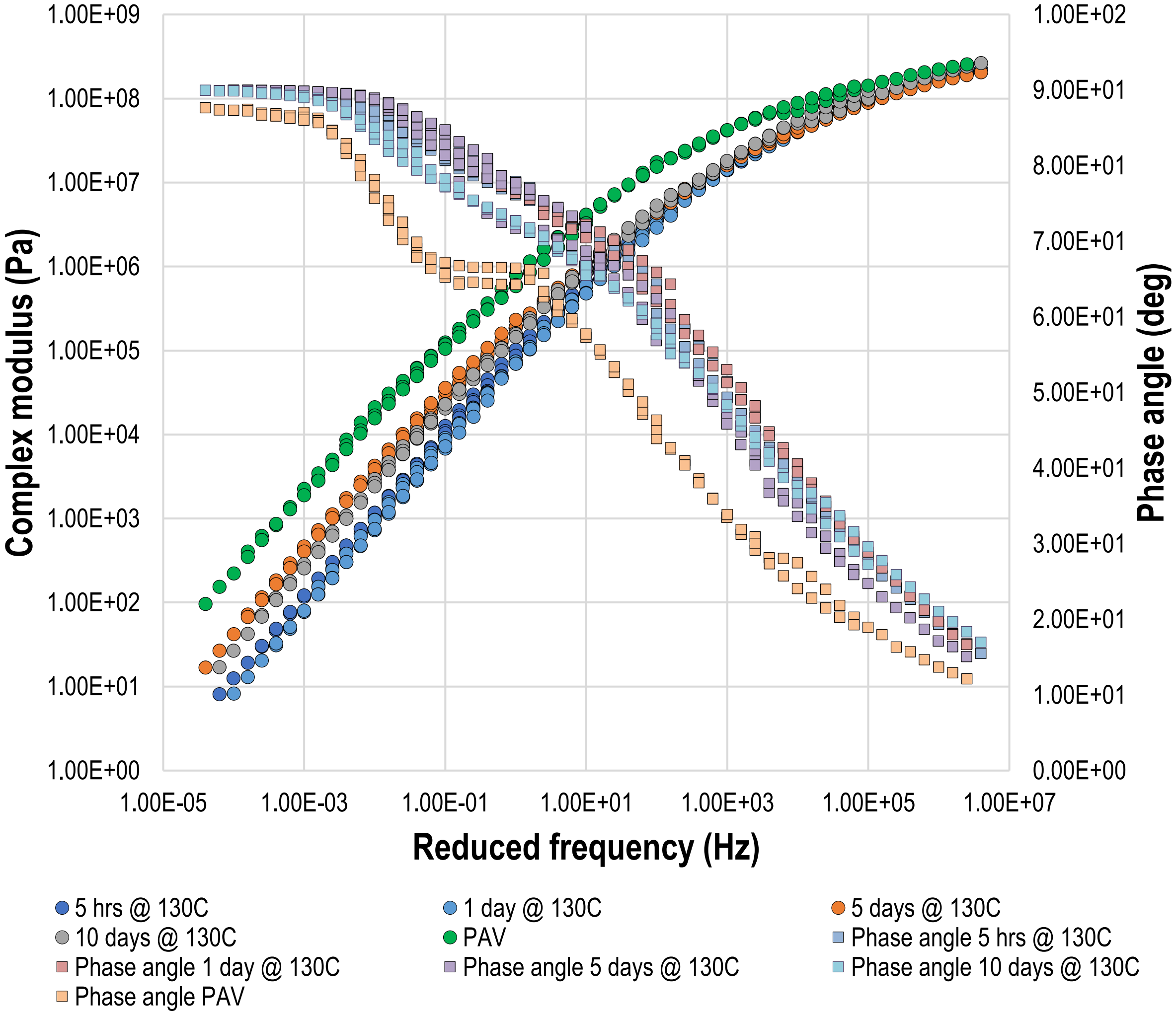


Figure 6. 5: Master curves of EMB 50% for all aging conditions

On the contrary, the pure bitumen seems to give a performance equally applied to STOA (**Figure 6.6**). It should not be forgotten that the increase in complex modulus, especially after 1 day, were attributed to the modulus evolution during chemical hardening for all modified binders. This process does not take place in unmodified bitumen. The complex modulus increase and simultaneously the decrease of phase angle begins after 5 days STOA. PAV simulation for bitumen increases the complex modulus values and shifts the master curves upward, especially at higher testing temperatures.

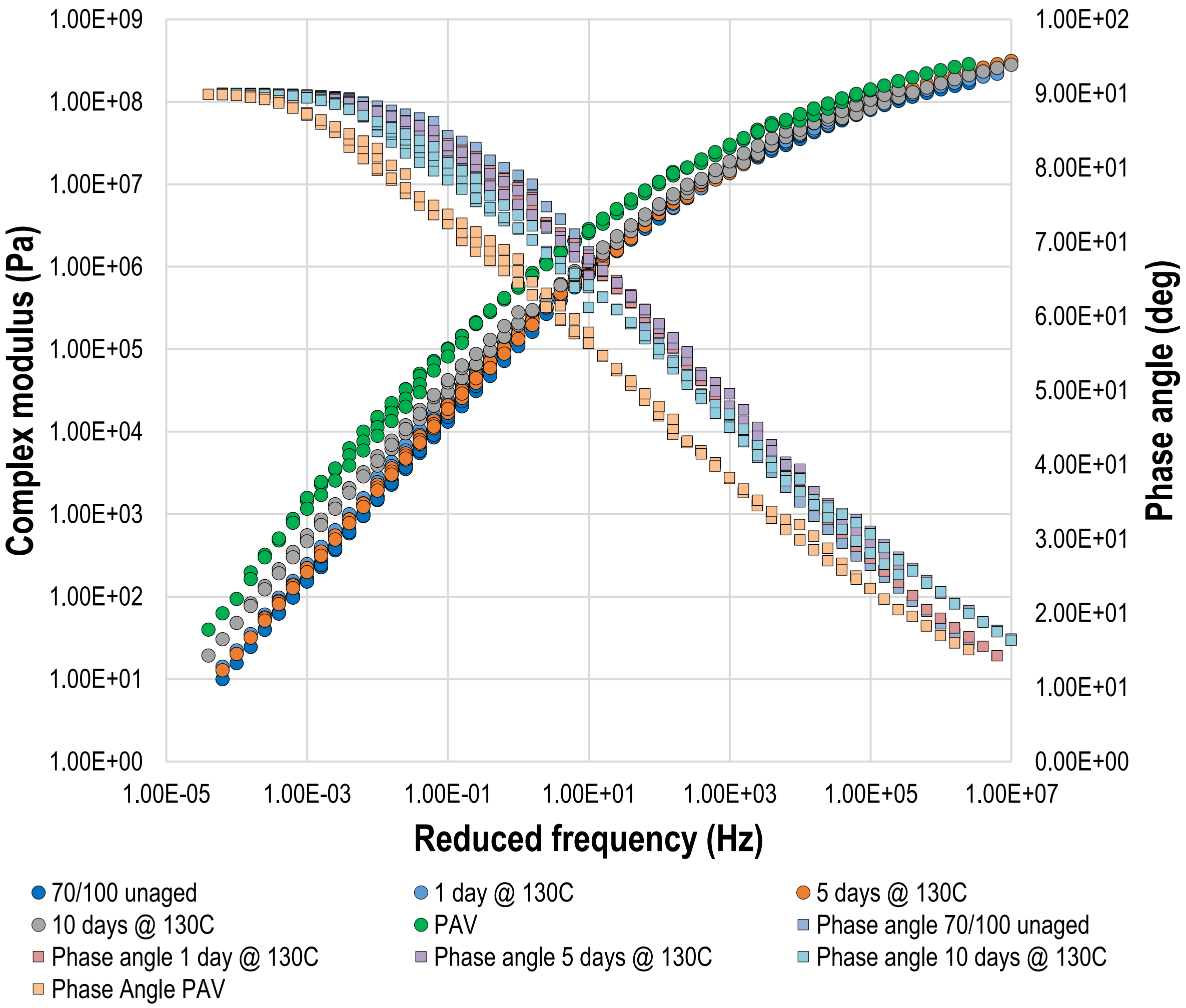


Figure 6. 6: Master curves of bitumen for all aging conditions

A clear comparison of the modulus aging indices at 1,59 Hz is given in **Table 6.1**. From this table, important information can be extracted for the differences of aging in modified and unmodified binders. The first remark is that STOA affects highly all EMBs resulting in higher values than unmodified bitumen. Increasing the content of epoxy modifier increases the modulus aging indicators for all aging conditions. It is believed that the complex modulus should not be considered adequate aging indicator for EMB, because modulus is increased not only by age but also by chemical hardening, and thus keeps developing with STOA. It is reasonable that higher modification level gives higher modulus "aging indicators" (about 2 times). Therefore, STOA includes aging effects, which increase additively the modulus values.

On the other hand, PAV is considered suitable for a modulus aging indicators comparison. The only drawback lies in the principles of simulation based on static diffusion. Thus, PAV affects the EMB considerably when higher amounts of epoxy are present in the blend. This is obvious again for EMB 50%, where the modulus aging indicator is doubled compared to unmodified bitumen. The high value of EMB 50% could be generated as a consequence of the relatively thin film used in PAV, where epoxy molecules are present in a higher content. The most important observation, useful for future aspects of durability evaluation, is the lower complex modulus aging factors obtained after PAV for EMB 20% and 35% compared to bitumen. Lower values mean that there is a maximum epoxy content percentage after which epoxy is dominant and adds up extra hardening. The most severe aging simulation is due to LTA and these results are well-promising for future application when the content of epoxy modifier is lower than 35%. This is also promising from an economical point of view, because of the rather expensive initial cost if high epoxy contents were utilized.

Table 6. 1: Aging indicators of complex modulus obtained through master curves

		Aging indicator G^*_{aged}/G^*_{unaged}			
Type of Aging	**Aging Condition**	**EMB 20%**	**EMB 35%**	**EMB 50%**	**70/100**
STA	STOA - 1 day	1.02	1.10	1.24	1.07
STA	STOA - 5 days	1.46	1.80	2.20	1.17
STA	STOA - 10 days	1.75	1.81	2.69	1.47
LTA	PAV	3.97	3.95	8.28	4.25

6.3.2. FTIR ANALYSIS

FTIR spectroscopy was used to evaluate the aging extent of the examined materials. As mentioned before, carbonyl and sulfoxide indices are utilized for this purpose. However, these groups were also involved in the chemical hardening of EMBs. Although for a fair comparison more suitable groups should be identified, at this point, it was believed that the overall accepted aging indices are sufficient for the first comparison in terms of corresponding functional groups. It was reported that carbonyls played important role in the chemical hardening and thus are considered unsuitable for aging indicators. The contribution of carbonyls to both chemical and age hardening generates fluctuations. For short-term simulation, STOA was used and the borders of chemical and age hardening were not clear. In this research, it was believed that sulfoxide index could be the only index able to be used for comparison with the unmodified binder. Following the semi-quantitative analysis with area calculation method, sulfoxide indices for all materials resulted from a repetition of 5 replicas. This index was calculated for all STA conditions and LTA (**Figure 6.7**).

The results of the sulfoxide index are not in line with the modulus aging indicator, showing that the overall chemical understanding of aging in EMB is more complicated. Probably, other functional groups take place beside the already known in the aging of EMBs. A more suitable indicator equally aging affected in both EMBs and bitumen should be identified. This kind of indicator should not be involved in the chemical hardening and should be affected by aging. After completion of chemical hardening, the material is already in service phase, which means that only LTA phenomena can be investigated. The FTIR characterization of STA is considered difficult to distinguish the two hardening phenomena.

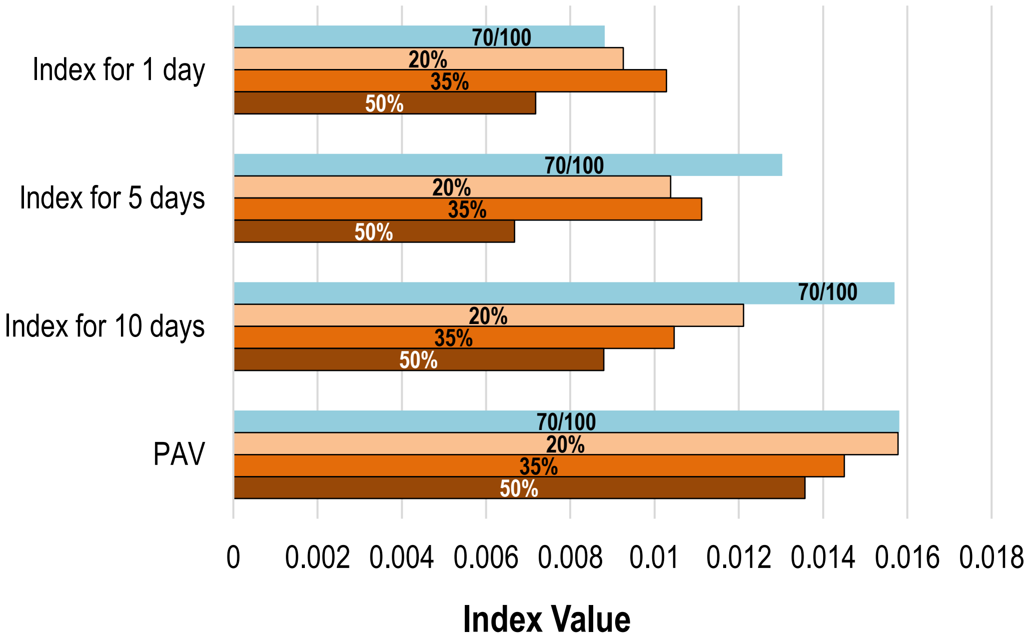


Figure 6. 7: Sulfoxide index per aging condition

The main observation for the sulfoxide index is that all EMBs perform better than unmodified bitumen for STOA after 5 and 10 days. Higher epoxy modification levels give lower indices for all the STOA conditions. Generally, the higher the epoxy content is the lower the index is. For LTA, EMB 50% gives the lower index compared to bitumen. However, EMB 20% and unmodified bitumen obtain similar values and consequently similar aging performance. Based on this index, the long-term performance of EMBs after PAV seems promising. Future research should include a clear discrimination of the chemical groups that participate both in chemical and age hardening. This could be done with the exploration of a new aging index, which should be equally influenced both for EMBs and for the already applied binders.

6.4. CONCLUSIONS

In this Chapter, the influence of aging was investigated both after STA and LTA. It was proved that for STA a new protocol should be built to evaluate EMBs, whereas for LTA the standard simulation of PAV was considered acceptable. It is proposed that for future research an RCAT device should be used for both STA and LTA. Overall, the results of this research show the improved performance after PAV only for EMB 20% and 35%.

7

Conclusions and Recommendations

The main conclusions and recommendations are presented for each process of EMBs. Additional experimental work for the future and suggestions are also proposed.

Chemical hardening

The curing time around 5 hours at 130°C was considered as the most critical. The different modification levels of EMB are considered to have fully cured at these conditions. The time window of 5 hours at 130°C is enough to transfer and in-field place the material with minor modification in the production plant. Shorter time intervals between 2 and 5 hours of curing time should be investigated. Comparing to unmodified bitumen, the obtained modulus values were similar. The glass transition temperature for these materials should be investigated in the future.

All the modification levels of EMB resulted in workable mixes with viscosity values lower than the SHRP limits during the pot life. The lower modification levels followed a more slight increase compared to higher modification. Potential recyclability aspects of the EMBs should be investigated based on their potential re-meltability. The viscosity tests should be performed also with a rotational Brookfield viscometer to validate the results.

Material Performance

The tensile strength increased with the increasing addition of epoxy content. This property improved for all modified binders at 0°C. Direct tensile tests could be performed at higher temperatures of 20°C and at the mastic level. Moreover, the higher the epoxy modification the higher the fatigue prediction at 0°C at binder level. All the EMBs performed better than unmodified bitumen for this property. Fatigue tests should be performed at higher temperatures of 20°C. Finally, tests should be performed to evaluate the permanent deformation of EMBs.

Age hardening

The modulus aging indicator was considered untrustworthy for STA, as the modulus is increased both from chemical and age hardening. For LTA, the EMB 20% and 35% obtained lower values (less aging extent) than unmodified bitumen. The carbonyl index is considered unreliable as carbonyls take place in the chemical hardening of EMBs as well. About the sulfoxide index, the higher modification levels obtained the lower values (less aging extent) after LTA. For the STA it was proved that sulfoxide index gives lower values after 5 and 10 days compared to bitumen. Therefore, a new aging protocol should be built for the STA of EMBs. The Rotating Cylinder Aging Test (RCAT) could be an appropriate simulation method for future work. A new aging indicator should be also introduced for a fair comparison.

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Appendix A

Materials

Table A. 1: Properties of epoxy parts and bitumen **[4]**

Material	Property	Value	Test Method
Epoxy modifier: Part A			
	Viscosity 23° C (Pas)	11-15	ASTM D 445
	Epoxide equivalent weight	182-292	ASTM D 1652
	Color, Gardner, max	4	ASTM D 1544
	Moisture content (% max)	0.05	ASTM D 1744
	Flash point, Cleveland open cup, (° C min)	200	ASTM D 92
	Specific gravity 23° C	1.16-1.17	ASTM D 1475
	Appearance	Transparent	Visual
Epoxy modifier: Part B			
	Viscosity 100° C (Pas)	0.14	Brookfield
	Specific gravity 23° C	0.98-1.02	ASTM D 1475
	Color	Black	Visual
	Acid value (mg KOH/g)	40-60	ASTM D 644
	Flash point, Cleveland open cup, (° C min)	200	ASTM D 92
Bitumen 70/100	Penetration 25° C (pen)	70-100	EN1426
	Softening point (° C)	43-51	EN1427
	Viscosity 135° C (mm^2/s)	385	EN12595
	Flash point, Cleveland open cup, (° C min)	230	EN22592

Appendix B

Time sweep tests

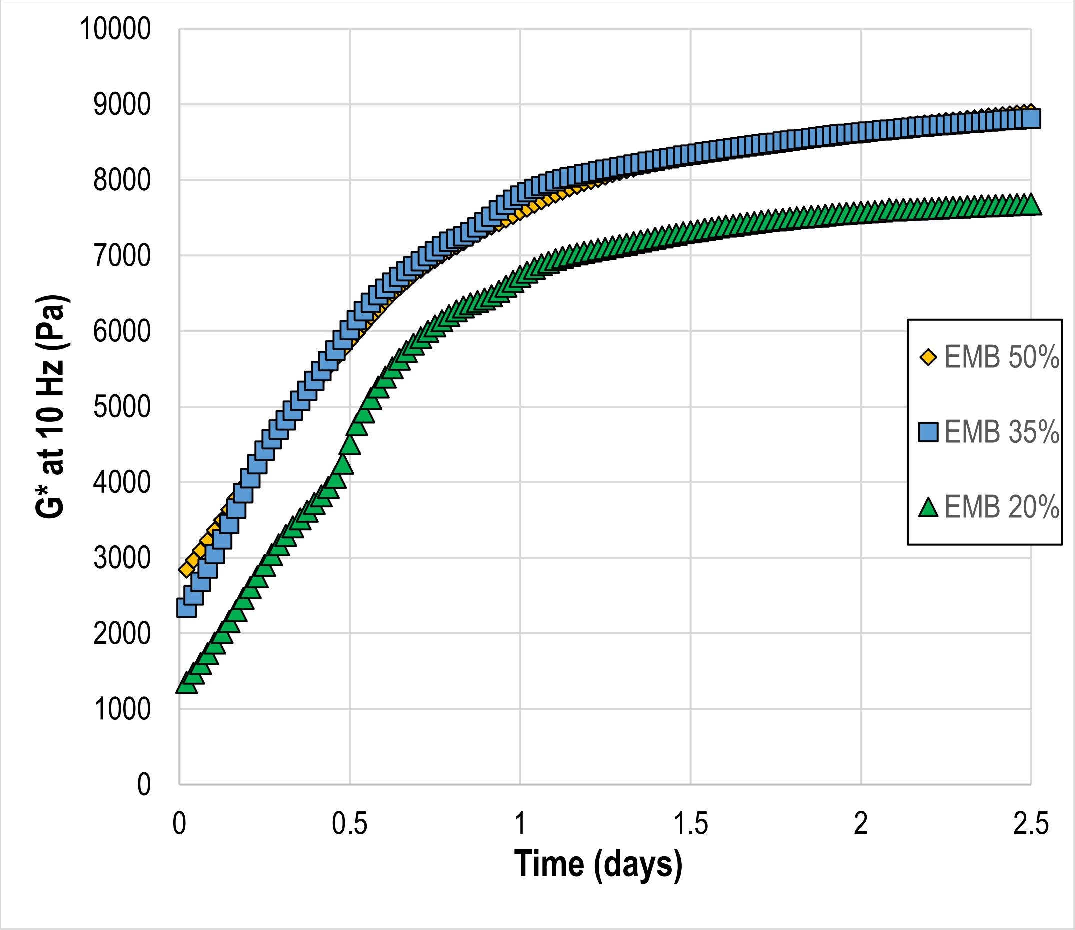

Figure B. 1: Modulus evolution for all EMBs at 60ºC

Appendix C

Fatigue tests

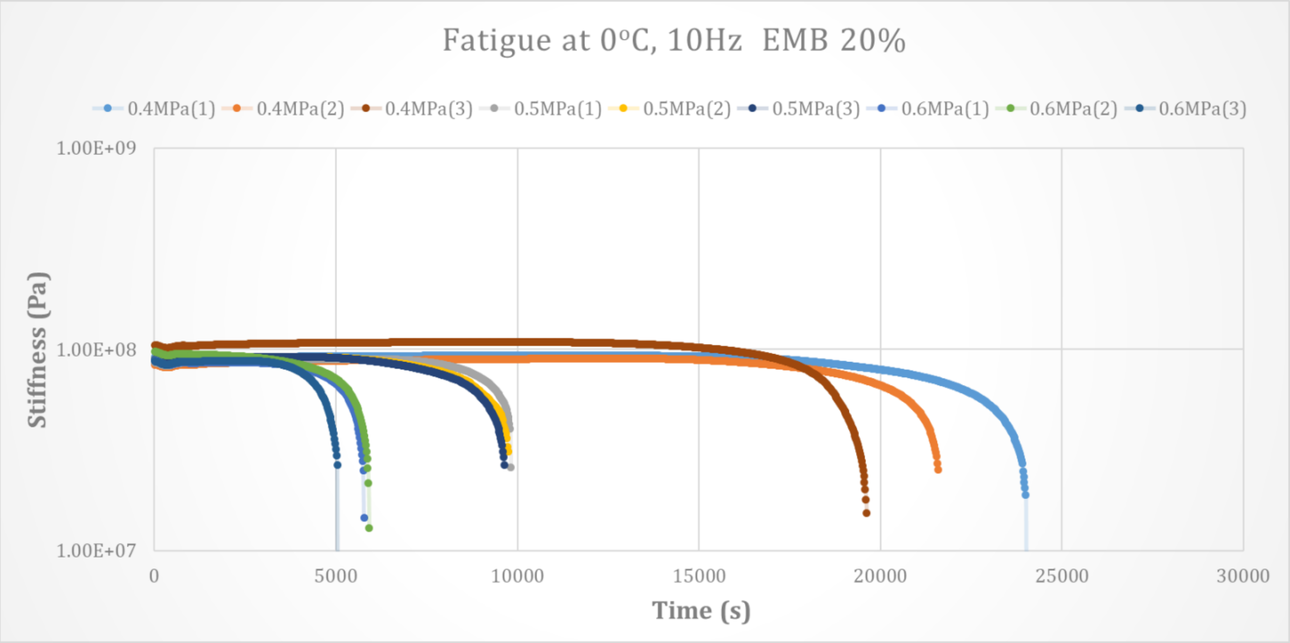

Figure C. 1: Fatigue curves of EMB 20%

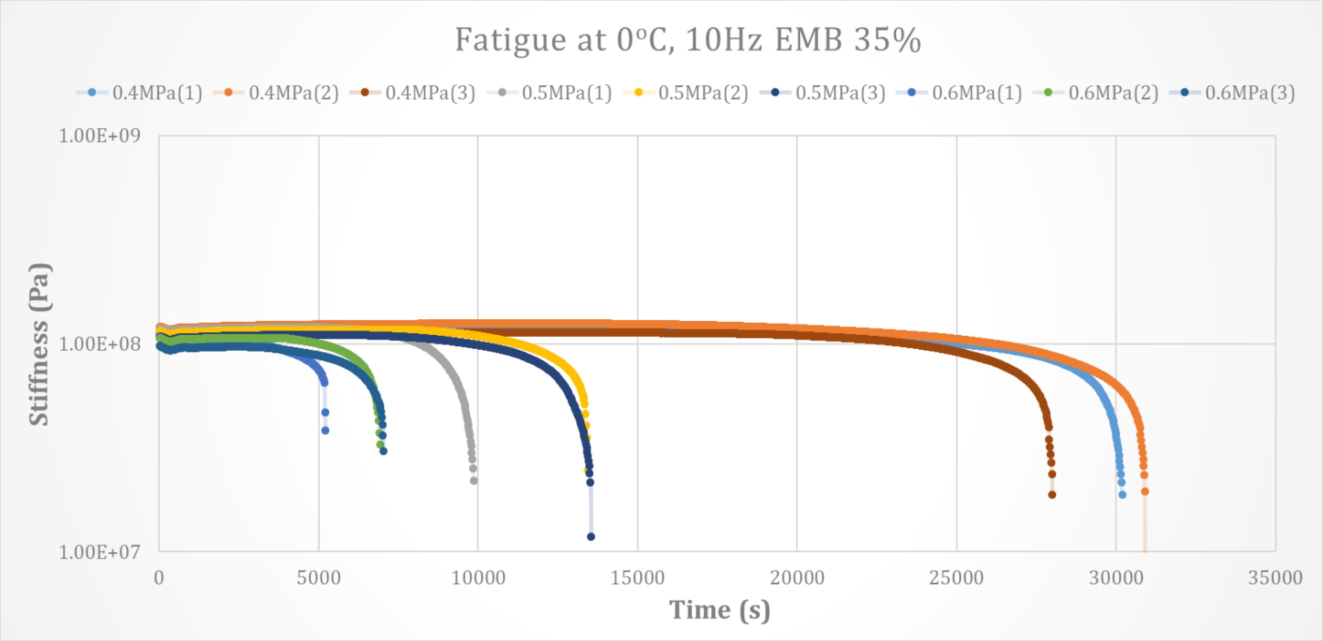

Figure C. 2: Fatigue curves of EMB 35%

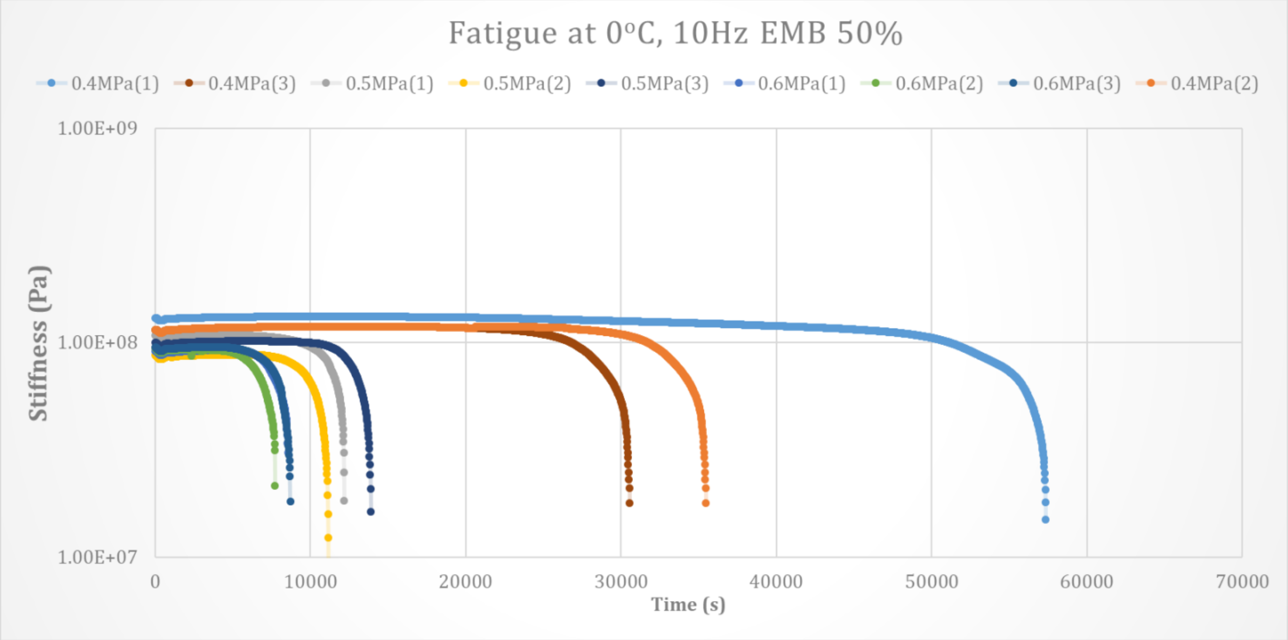

Figure C. 4: Fatigue curves of EMB 50%

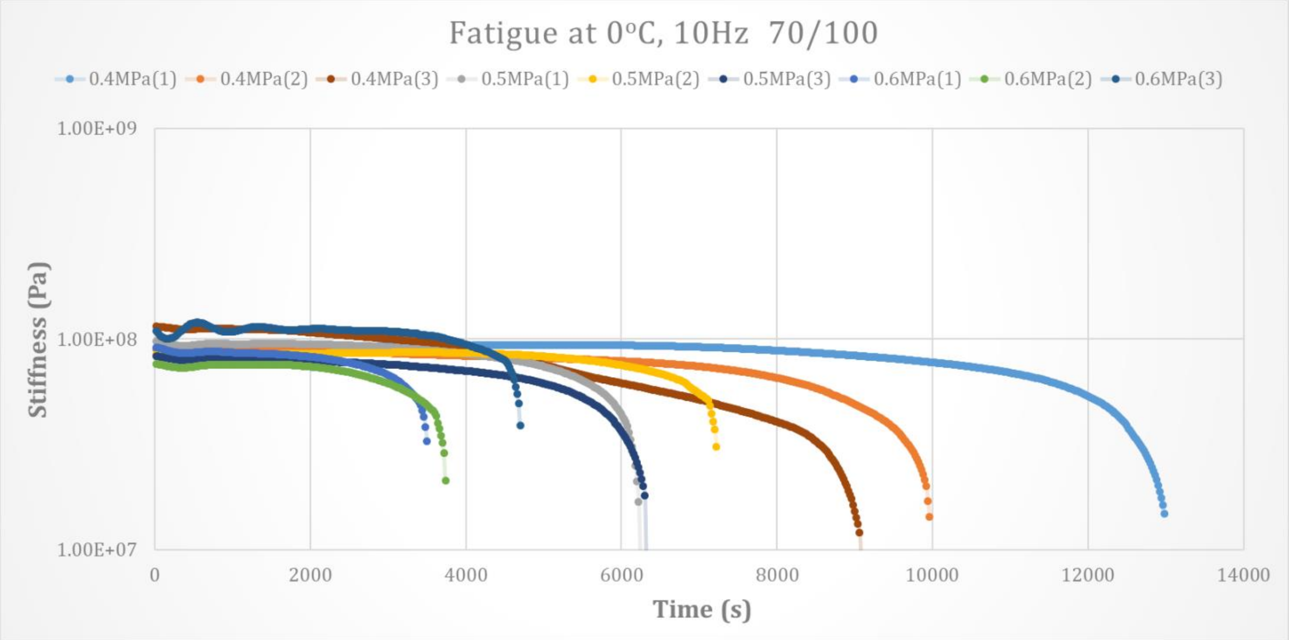

Figure C. 3: Fatigue curves of 70/100

Relevant publications

1. P. Apostolidis, **G. Pipintakos**, X. Liu, M. van de Ven, S. Erkens & A. Scarpas. Epoxy modified bitumen: Chemical hardening and its interpretation. Submitted and accepted for publication in the conference proceeding of *Advances in Materials and Pavement Performance Prediction*, Doha, Qatar, 2018.