

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**EVALUATING THE EFFECT OF SBS MODIFIED
BITUMEN PREPARATION PARAMETERS ON
THE CHARACTERISATION OF BITUMEN**



by
Derya KAYA ÖZDEMİR

September, 2019
İZMİR

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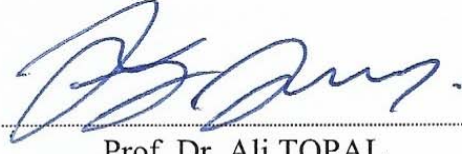
**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Doctor of
Philosophy in Civil Engineering, Transportation Program**

**by
Derya KAYA ÖZDEMİR**

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İZMİR**

Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “EVALUATING THE EFFECT OF SBS MODIFIED BITUMEN PREPARATION PARAMETERS ON THE CHARACTERISATION OF BITUMEN” completed by DERYA KAYA ÖZDEMİR under supervision of PROF.DR. ALİ TOPAL and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.



Prof. Dr. Ali TOPAL

Supervisor



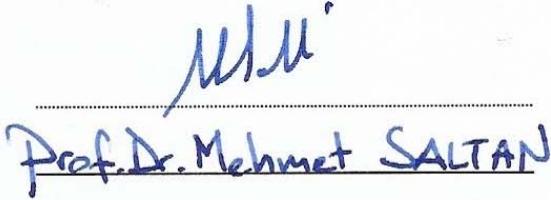
Prof. Dr. Burak ŞENGÖZ

Thesis Committee Member

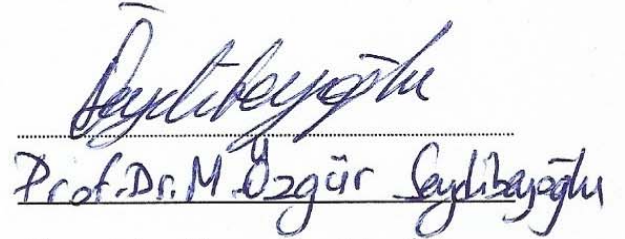


Assist. Prof. Dr. Mehmet Zübeyir ÜNLÜ

Thesis Committee Member



Examining Committee Member



Examining Committee Member



Prof. Dr. Kadriye ERTEKİN

Director

Graduate School of Natural and Applied Sciences

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Derya KAYA ÖZDEMİR

EVALUATING THE EFFECT OF SBS MODIFIED BITUMEN PREPARATION PARAMETERS ON THE CHARACTERISATION OF BITUMEN

ABSTRACT

Increment in the volume of traffic and vehicle loads caused by developing technology with environmental effects cause deterioration in asphalt pavements. Bitumen modification with various polymer additives is a prerequisite for enhancing the long term behavior of the pavement and improving its mechanical properties. In Turkey, Styrene-Butadiene-Styrene (SBS) is the most commonly used elastomeric polymer additive in polymer modified bitumen (PMB).

Modification of bitumen by different modifiers, causes the morphological, rheological and chemical characterisation differences related to the following three main factors: the type of the polymer, bitumen components and blending conditions such as the temperature, shearing rates and duration of mixing. Blending conditions, can be evaluated in relation with the polymer dispersion, phase separation and most importantly the aging of the bitumen. Among the blending conditions the duration of mixing and shearing rates among the blending conditions were chosen as key parameters. A mixing speed of 1000 rpm was selected to represent a low shear rate and 3000 rpm for a high shear rate, whereas two mixing durations were chosen, 15 and 45 minutes to represent nominal minimum and maximum mixing times. Different PMB samples were produced with the combination of selected key under the constant mixing temperature, aiming to evaluate the characterisation alters. Structural and microstructural characterisation, thermal characterisation as well as the rheological characterisation were investigated on the prepared samples. Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Force Microscopy (AFM) were employed for structural and microstructural characteristics; Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA) for thermal characteristics; Optical Microscopy (OM) and Confocal Laser Scanning Microscopy (CLSM) for morphological characteristics and two different rheometer for rheological

characteristics. Consequently, mixing polymer with bitumen under longer duration or higher shear rates caused the bitumen to be oxidised, since it directly affects the interaction of the oxygen with the bitumen.

Keywords: Polymer modified bitumen, SBS, aging, characterisation, blending conditions, key parameters



SBS MODİFİYE BİTÜM HAZIRLAMA PARAMETRELERİNİN BİTÜM KARAKTERİZASYONU ÜZERİNE ETKİLERİNİN DEĞERLENDİRİLMESİ

ÖZ

Nüfus artışı ve teknolojik gelişmelere bağlı olarak trafik hacminde ve taşıt yüklerindeki artışlar ile olumsuz iklim ve çevresel faktörler asfalt kaplamalarda bozulmalara neden olmaktadır. Son yıllarda asfalt kaplamaların uzun dönem performansını iyileştirmek ve mekanik özelliklerini geliştirmek için çeşitli polimer katkıları ile bitümün modifiye edilmesi gündeme gelmiş ve başarılı sonuçlar elde edilmiştir. Ülkemizde polimer modifiye bitüm (PMB) üretiminde en yaygın olarak kullanılan katkı maddesi elastomerik polimerler grubundan Styrene-Butadiene-Styrene (SBS)'dir.

Bitümün farklı polimerler ile modifikasyonu, aşağıdaki üç faktörle ilgili morfolojik, reolojik ve kimyasal karakterizasyon farklılıklarına neden olur: polimerin tipi, bitüm bileşenleri ve sıcaklık, kesme oranları veya karışım süreleri gibi karışım koşulları. Anahtar parametreler olarak adlandırılabilen karışım koşulları, polimer dispersiyonu, faz ayrılması ve en önemlisi bitümün yaşlanması üzerinde etkilidir. Bu tez çalışması kapsamında, karıştırma süresi ve karıştırma hızı (kayma hızı) anahtar parametreler olarak seçilmiştir. Düşük kesme hızını temsil etmek için 1000 rpm'lik ve yüksek kesme hızı için 3000 rpm'lik karıştırma hızları seçilirken, iki karıştırma süresi, minimum ve maksimum karıştırma zamanlarını temsil etmek için, 15 dakika ve 45 dakika olarak belirlenmiştir. Karakterizasyon değişikliklerini değerlendirmek için, karışım sıcaklığı sabit alınıp söz konusu anahtar parametrelerin kombinasyonları kullanılarak farklı PMB örnekleri üretilmiş ve hazırlanan numuneler üzerinde yapısal ve mikroyapısal, termal ve reolojik karakterizasyon incelemeleri yapılmıştır. Yapısal ve mikroyapısal karakterizasyon için Fourier Dönüşümü Kızılötesi Spektroskopisi (FTIR) ve Atomik Kuvvet Mikroskobu (AFM); termal karakterizasyon için (MDSC) ve Termogravimetrik Analiz Cihazı (TGA); morfolojik karakterizasyon için Optik Mikroskop (OM) ve Konfokal Lazer Tarama Mikroskobu (CLSM) ve reolojik karakterizasyon için iki farklı reometre kullanılmıştır. Sonuç olarak, polimerin bitüm ile daha uzun süre karıştırılması veya daha yüksek kayma

hızlarının kullanılması, oksijenin bitüm ile olan etkileşimini doğrudan etkileyerek bitümün okside olmasına neden olmuştur.

Anahtar Kelimeler: Polimer modifiye bitüm, SBS, yaşlanma, karakterizasyon, karışım koşulları, anahtar parametreler



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CHAPTER ONE

INTRODUCTION

Bitumen is a viscous liquid or semi-solid form of petroleum, which is made with hydrocarbons. It can be found naturally or obtained by the distillation of petroleum. The term of asphaltum, which is derived from Ancient Greek term “asphaltos”, was used until 20th century instead of bitumen or asphalt (Herbert, 1920). Although, bitumen can be used in roofing isolation systems or waterproofing products, the primary use (70%) of bitumen is as a highway material in paving industry (Sörensen & Wichert, 2009).

Bitumen is a soft and fluid material in hot weathers, also hard and brittle in cold weather conditions which is a disadvantage in some cases (Whiteoak, 1990). Therefore, polymer addition became to be a solution to bring the desired properties in bitumen. Polymer modified bitumen (PMB) has different physical, mechanical, chemical or thermal properties depending on the polymer or polymers used in the blend. Over the years, researchers developed several polymer modifiers, which can be used in the asphalt industry. Styrene butadiene styrene (SBS), is a thermoplastic polymer and used in 1965 for the first time, and it is the most common polymer used both in Turkey and the world. SBS copolymer, which is composed of styrene and butadiene triblock chains with a biphasic morphology of rigid polystyrene (PS) domains (dispersed phase) in the flexible polybutadiene (PB) matrix (continuous phase), yielded several advantages to bitumen such as; relatively good compatibility, resistance to hot and cold weather, improved resistance to permanent damages etc. (Chen, Liao, & Shiah, 2002; Lu & Isacsson, 1997).

1.1 Aim of the Study

Modification of bitumen by different modifiers, causes the morphological, rheological and chemical characterisation differences related to the following three factors: the type of the polymer, bitumen components and blending conditions such as the temperature, shearing rates or duration of mixing. Blending conditions, which can

be evaluated in relation with the polymer dispersion, phase separation and most importantly the aging of the bitumen. Mixing polymer with bitumen under longer duration or higher rate of shear causes the bitumen to be oxidised, since it directly affects the interaction of the oxygen with the bitumen. The influences of key parameters on the characteristics of PMB, have been an interesting topic for researcher through the years (Cortizo et al., 2004; Fawcett & McNally, 2003; García-Morales et al., 2007; Larsen et al., 2009; Ortega et al., 2016; Pérez-Lepe et al., 2003; Schaur et al., 2017). However, there is less study conducted on the SBS modified bitumen samples investigating the effects of mixing duration and shearing rates with regards to aging occurrence and the consequences of it on the properties of the final blend. This thesis attempts to cover some of the knowledge gaps in the literature, by assessing the influences of SBS modified bitumen' mixing conditions, with considering the aging effects on the rheological, physical, chemical and structural characteristics.

1.2 Scope of the Study

In this dissertation, mixing duration and shearing rates among the blending conditions were chosen as key parameters. A mixing speed of 1000 rpm was selected to represent a low shear rate and 3000 rpm for a high shear rate, whereas two mixing durations were chosen, 15 minutes and 45 min to represent nominal minimum and maximum mixing times. Different PMB samples were produced under the combination of these key parameters by taking the mixing temperature constant, in order to evaluate the characterisation alters. Moreover, samples were subjected to long term aging to obtain correlation of aging with the mixing conditions.

Structural and microstructural characterisation, thermal characterisation as well as the rheological characterisation were investigated on the prepared samples. Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Force Microscopy (AFM) were employed for structural and microstructural characteristics; Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA) for thermal characteristics; Optical Microscopy (OM) and Confocal Laser Scanning Microscopy (CLSM) for morphological characteristics and two different rheometer for rheological

characteristics. The experimental investigations were conducted in two different laboratories, which are located in Dokuz Eylul University/Turkey and University of Warwick/ England.



CHAPTER TWO

LITERATURE REVIEW

In this chapter, literature reviews and the previous studies on the chemical compositions of bitumen, durability of bitumen, modification types, polymer modified bitumen production methods and characterisation of the polymer modified bitumen were addressed.

2.1 Chemical Composition of the Bitumen

Bitumen is defined as “A hydrocarbon material of natural or puyrogenous origin, gaseous, liquid, semi-solid, or solid which is completely soluble in carbon disulphide” according to the American Society for Testing and Materials (ASTM). There are two types of bitumen, which can be used in the road construction; asphalt and tar. Asphalt is a black to dark brown solid or semi-solid cementitious material which gradually liquefies when heated, in which the predominating constituents are bitumen, all of which occur in the solid or semi-solid form in nature or are obtained by refining petroleum or which are combinations of the bitumens mentioned with each other or with petroleum or derivatives thereof. Asphalt can naturally be occurred as bitumen (native asphalt), lake asphalt and rock asphalt (Speight, 2000). However, it can also arise from tar sand or petroleum extractions. In 1859, crude oil became to be used as a highway material by obtaining the bitumen from distillation of the petroleum.

Bitumen is mostly used as an asphalt binder, while it can be used inside the roofing materials, water tightening etc. (Redelius & Soenen, 2015). Bitumen is a complex mixture of various organic molecules and mainly composed of hydrocarbons, but also it includes sulphur, nitrogen and oxygen, or some metals like; vanadium, nickel and iron (Romberg et al., 1959; Traxler, 1936; Traxler & Coombs, 1936). As Read, Whiteoak and Hunter stated in 2003, the basic analysis of bitumen produced from a variety of crude oils shows that the majority of bitumen contains the following elements: (Read et al., 2003)

- Carbon 82-88 %
- Hydrogen 8-11%
- Sulphur 0-6%
- Oxygen 0-1.5%
- Nitrogen 0-1%
- Nickel (ppm) 10-139
- Vanadium (ppm) 7-1590
- Iron (ppm) 5-147
- Manganese (ppm) 0.1-3.7
- Calcium (ppm) 1-335
- Magnesium (ppm) 1-134
- Sodium (ppm) 6-159

Bitumen is a viscoelastic multiphase material (Behzadfar & Hatzikiriakos, 2013), which has a viscous liquid and elastic solid characteristics, when undergoing deformation (Shaw & MacKnight, 2018). Van der Poel was the initiatory researcher, who studied the linear viscoelasticity of the bitumen, while Heukolem and Klomp followed him by improving nonlinear multivariable models (Heukelom & Klomp, 1964; Van der Poel, 1954).

Bitumen has a thermoplastic behaviour, which can be clarified with being liquid when heated, but solid at room temperature. It softens as the temperature increases and hardens as the temperature decreases. At high temperatures (above 70°C) bitumen behaves like Newtonian liquids, which can be explained with the decreasing viscosity by increasing temperature and viscoelastic behaviour at room temperature (Redelius, 2006).

Bitumen occurs from asphaltenes and maltenes, which consists of saturates, aromatics, and resins (SARA). Saturates contain nonpolar hydrocarbons like paraffins and naphthenes (PIN), while aromatics comprise polarisable hydrocarbons. On the other hand, resins and asphaltenes are non-hydrocarbon constituents of bitumen (Bissada et al., 2016).

Chemical composition of asphalt binder is directly related to the properties of the crude oil and processing conditions (Kök & Gul, 2013). Moreover, physical and chemical properties of the final blend is related with the SARA fractions of the bitumen (Cuadri et al., 2011).

It is possible to separate abovementioned 4 components by the following methods; solvent extraction, chromatography, adsorption with adsorbed finely divided solids and removal of adsorbed solution with filtration and the molecular distillation used in together with one of the above techniques (Read et al., 2003). The aim of the SARA separation methods is generally based on the differences of solubility, polarity and affinity of the constitution of the bitumen. It should be considered that, posterior fraction distribution can vary depending on the lab conditions or method used for the same sample. Figure 2.1 shows the extraction of bitumen's components with petroleum fractionation method (Speight, 2004), based on ASTM D4124-09.

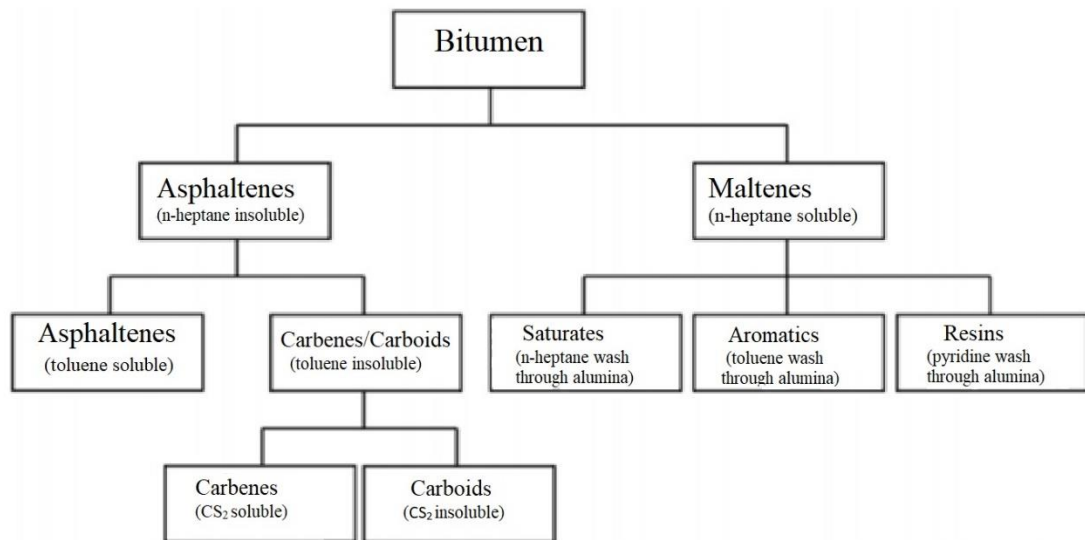


Figure 2.1 Petroleum fractionation method and bitumen's components (Speight, 2004)

SARA analysis is generally done by using chromatography methods with the help of polar stationary phases like activated silica gel or aluminium oxide etc. There are different kinds of chromatographies used in SARA analyses as follow;

Thin Layer Chromatography (TLC)

Thin Layer Chromatography is generally combined with flame ionization detection (FID) in order to become semiautomated and can be employed with a commercial system named Iatroscan (Masson et al., 2001). This method is carried out with all oils on alumina or silica rods as a stationary phase and pursued by evaporating the solvents from the solution. At the end of this process, FID is used to obtain the amount of fractional zone (Boysen & Schabron, 2013). It has advantages such as; it does not require deasphaltenation and the amount of the solvent needed is not too much. On the other hand it has some disadvantages like; poverty of obtaining correct results on repeat analyses and inefficacy with asphaltene fraction (Masson et al., 2001).

“Iatrogramme” is the output graph of this method, which generally demonstrates four signals corresponding saturates, aromatics, resins A and resins B, respectively. It is remarkable that, asphaltenes cannot be safely obtained by this method. Figure 2.2 shows a typical iatrogramme of bitumen.

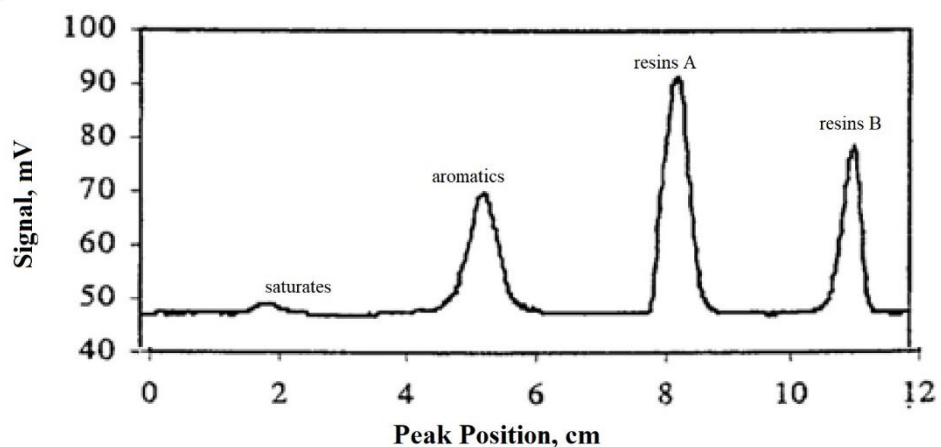


Figure 2.2 Typical iatrogram for bitumen (Masson et al., 2001)

High Performance Liquid Chromatography (HPLC)

HPLC can be semiautomated or automated methods with amino, cyano or alumina columns (Boysen & Schabron, 2013; Grizzle & Sablotny, 1986). These methods are semi-quantitative since, they do not provide accurately separated saturates, aromatics, resins and asphaltenes. Refractive Index (RI) is utilized to detect the fractions because; all the components of bitumen have different RI value, but RI detector does not allow altering the solvent, since it has to be calibrated after changing the solvent. Furthermore, it is not convenient for paving grade bitumen, because it is not possible to desorb the most polar component of bitumen, which will foul the column of the system (Grizzle & Sablotny, 1986).

Flash Chromatography

Although Liquid Chromatography (LC) is capable of obtaining big amount of bitumen fractions, it is relatively a difficult method. However, Thin Layer Chromatography (TLC) combined with Iatroscan is a very practical method but does not allow further evaluation due to the destructiveness of the method (Corbett, 1969). Flash chromatography is developed with taking the advantages of both LC and TLC methods. The setup and the flowchart of this method, which is rapid and useful for sizeable quantities, is presented in Figure 2.3 (Raki et al., 2000). It separates the maltenes into saturates, aromatics and resins based on the Iatroscan. It requires 25% less solvents compared to LC and takes only 45 minutes which makes it more economical and practical.

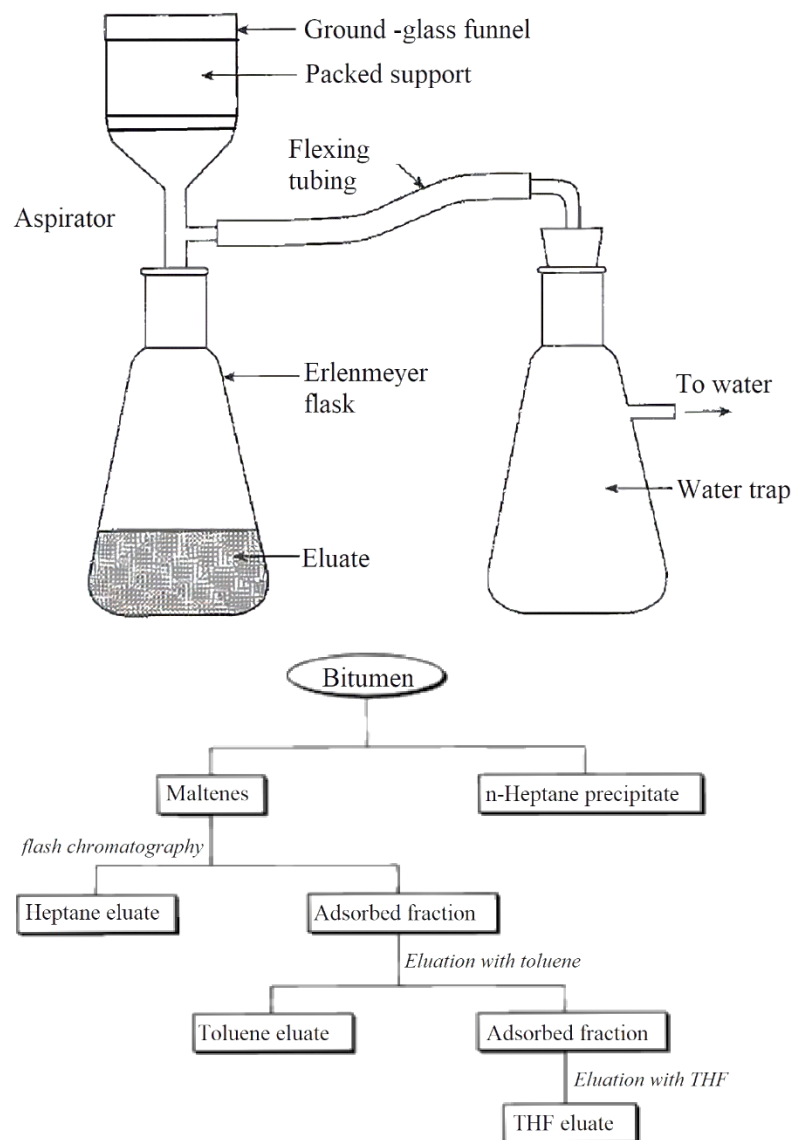


Figure 2.3 The setup and flowchart of Flash Chromatography method (Raki et al., 2000)

Gravimetric Adsorption Chromatography

Gravimetric Adsorption Chromatography is the first technique, that was used in order to separate the bitumen's fractions. This method is based on the precipitation of asphaltenes by alkane solvent, n-pentane, n-hexane or n-heptane, since asphaltene fraction is permanently absorbed into the stationary phase (Jewell et al., 1974; Jewell et al., 1972). After removing the asphaltene fraction from the bitumen, maltenes are separated into saturates, aromatics and resins fractions by liquid chromatography

(Boysen & Schabron, 2013). This method is graphically represented in Figure 2.4 (Bissada et al., 2016).

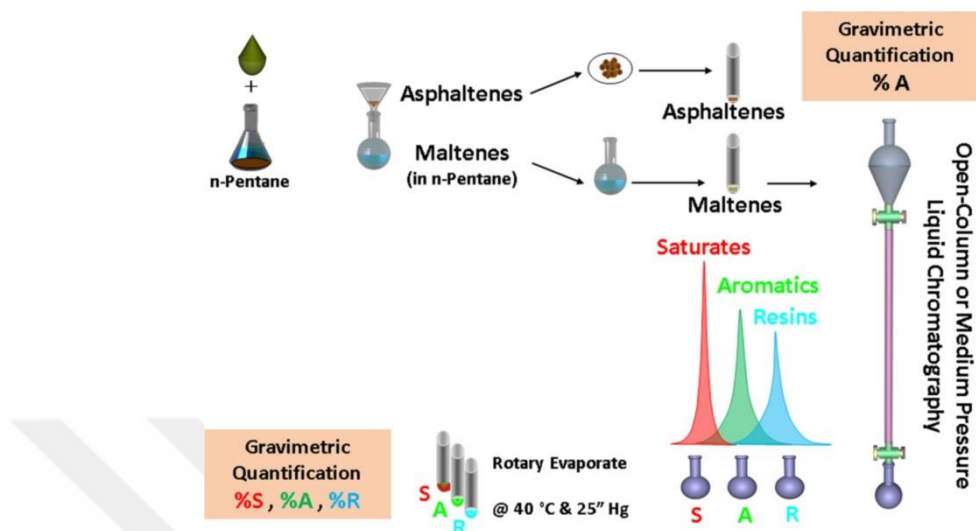


Figure 2.4 Gravimetric Adsorption Chromatography of SARA (Bissada et al., 2016)

Automated Solubility Separation of Asphaltenes

This method depends on the solubility characteristics of the fraction by using HPLC system, but not chromatography. Polytetrafluoroethylene (PTFE) filled column with the excess of heptane is used to precipitate asphaltenes (Schabron & Rovani Jr, 2008; Schabron et al., 2010). By the help of this system, it is possible to elute asphaltene from bituminous samples. Evaporative Light Scattering Detector (ELSD) is used in order to detect the volatile losses in maltenes, but unfortunately it does not allow determining the sub fraction of the losses occurred.

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS)

FT-ICR MS can be used for separating the fractions of crude oil and bitumen. It provides to obtain molecular composition and distribution of highly complex hydrocarbon mixtures (Klein et al., 2006; Shi et al., 2010). Each element composition corresponds to a peak in the mass spectrum obtained by FT-ICR MS, which allows to assign the fractions accurately (Liu et al., 2010). Figure 2.5 gives an example of mass spectrum belongs to Venezuela crude oil obtained by FT-ICR in Liu et al.'s study.

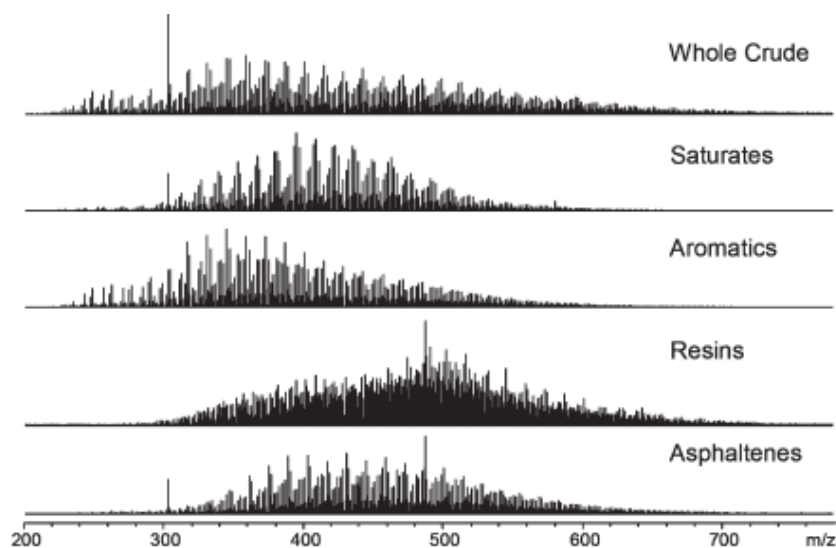


Figure 2.5 FT-ICR mass spectrum of Venezuela crude oil (Liu et al., 2010)

2.2 Fractions of Bitumen

Traditionally, bitumen consists of two broad chemical groups of asphaltenes and maltenes, where saturates, aromatics and resins are the subgroups of the maltenes. These 4 hydrocarbon type constitutions are classified depending on the properties of solubility, polarity and molecular weight (Speight, 2014).

2.2.1 Saturates

Saturates composed of straight and branched chain aliphatic hydrocarbons along with cycloaliphatic compounds. Saturates are viscous oily components with non-polarity properties. Saturated hydrocarbons, in other words saturates, contain paraffin or alkenes. They have the lowest molecular weights (between 470-880 g/mol) with the average number of carbon atoms of 40-60 among the bitumen's fractions (Liang et al., 2000), and also their Hydrogen/Carbon ratio (H/C) is approximately 2 (Lesueur, 2009). Saturates constitutes 5-20% of bitumen (Read et al., 2003).

The amount of saturates fraction is very important for the rheological properties of bitumen. The increase in the amount of saturates, results in much negative or relatively positive characteristics. For example; bitumen with higher saturates content causes a lower elastic and viscous behaviour, which lead to be less resistant to the plastic

deformation. However, it is well known that lower saturates content gains resistance against fatigue cracking (Hermadi et al., 2012). Additionally, it is proven that, the amount of saturates decreases with the aging (Zhao & Machel, 2012). Figure 2.6 shows different saturates structures.

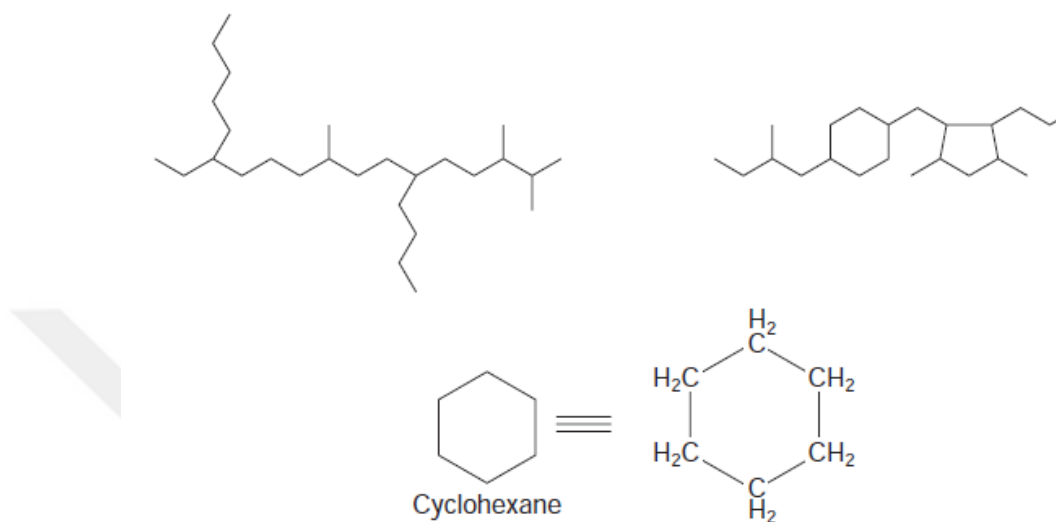


Figure 2.6 Different saturate structures (Read et al., 2003)

2.2.2 Aromatics

Aromatic fraction is dark-brown viscous liquid with having 700-1100 g/mol of molecular weight, which is higher than saturates, but lower than resins and asphaltenes. They composed of non-polar carbon chains attached to unsaturated ring systems. H/C ratio can vary from 1.5 to 1.7 (Liang et al., 2000). Aromatics form 40-65% of the total bitumen, which means they are the main fractions of the bitumen (Read et al., 2003). They have the lowest molecular weight among the other fractions of bitumen therefore; they are the first fractions to volatilize. The hardening of the bitumen after ageing, can be related with losing of aromatic content, which provides liquid properties to the bitumen (Peralta et al., 2014). Chemical structures of different aromatic fractions can be seen in Figure 2.7.

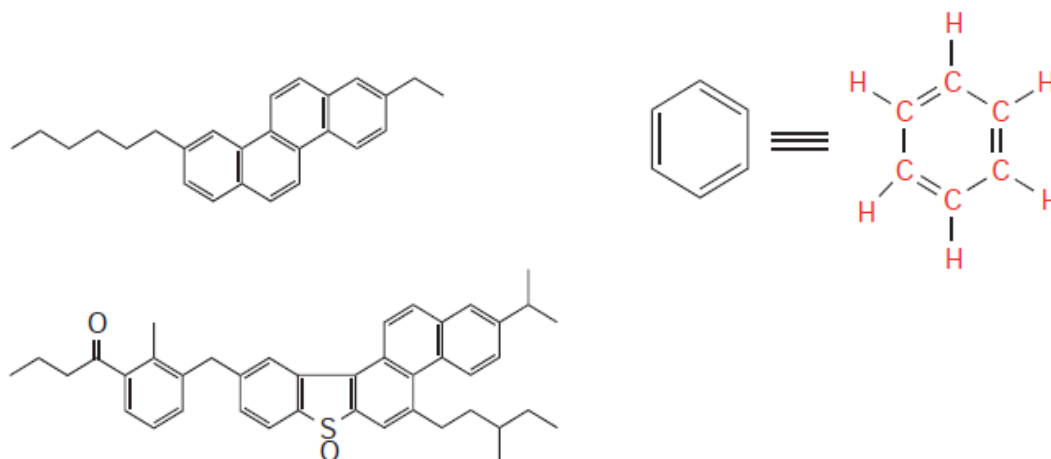


Figure 2.7 Chemical structure of aromatics (Read et al., 2003)

2.2.3 Resins

Resins consist of hydrogen and carbon atoms, but also they have little amount of oxygen, sulphur and nitrogen atoms. Resins can be solid or semi-solid and they are polar, strongly adhesive and soluble in n-heptane. The molecular weight of resins is between 1100 and 2800 g/mol and H/C ratio is 1.4-1.7 (Liang et al., 2000). Proportion of resin fraction in bitumen is very important to determine the solution (sol) or gelatinous (gel) characteristics of the bitumen (Read et al., 2003).

2.2.4 Asphaltenes

Asphaltene fractions of bitumen are the most polar constituents with having the highest molecular weight (Speight, 2004). They are black or brown amorphous solids, with having no definite melting point or no distillability and they remain in the residual fuels during the production of bitumen (Speight, 2004). They are insoluble in n-heptane unlike the other fractions of bitumen. Their molecular weights, H/C ratio and particle size can vary from 800 to 3500 g/mol (depending on vapour pressure osmometric measurements), 0.98 to 1.6 and 2-5 nm, respectively (Lesueur, 2009; Read et al., 2003). Asphaltenes, which consist of condensed aromatic rings bounded by alkyl chains involving different functional groups, are soluble in light aromatics and insoluble in low molecular weight paraffin (Strausz et al., 1992). The amount of oxygen, nitrogen and sulphur in asphaltene fraction is crucial for the properties of

bitumen, since they bring polar properties such as stability etc. (Jada & Salou, 2002). Besides, the amount of oxygen is crucial for the rheological behaviour of bituminous mixtures. For example, higher asphaltene fraction results in harder, more viscous bitumen with a lower penetration, higher softening point and viscosity. Asphaltene fractions form, 5-25% of the total bitumen. Figure 2.8 represents the chemical structure of an asphaltene.

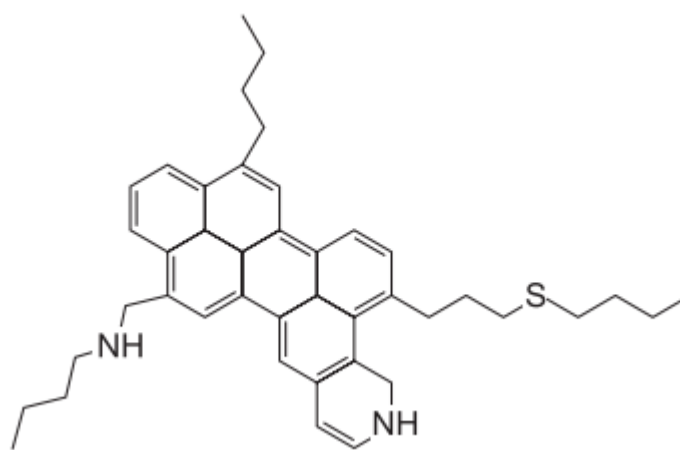


Figure 2.8 Chemical structure of an asphaltene (Read et al., 2003)

2.3 Bitumen as Colloid System

Bitumen is typically considered as a colloidal system composed of high molecular weight asphaltene micelles, distributed or dispersed in maltenes (Girdler, 1965).

For the first time in 1920s, Nellensteyn theorised a colloidal structure for bituminous materials depending on the observation of Tyndall effect. The Tyndall effect means that, the light of different wavelengths diffuses or does not disperse, depending on the size of the substances they are facing (Hirsch et al., 2006). Kist supported Nellensteyn hypothesis about the highly absorbent carbon nature of the core of asphaltene, on the other hand, Sack and Trillat exempted the entity of graphitic structures in bitumen depending on the diffraction evidence. Pfeiffer and Saal were the first researchers, who used the term “micelle” and developed a model for asphaltene/maltene/resin complex (Barth, 1962). SHRP has put forward another model, that attempts to explain the correlation between composition and performance.

There are no separate boundaries in the SHRP model between the agglomerates of the more polar molecules and the solvent.

Bituminous materials can be separated in three categories: sol (viscous), gel (elastic) and sol-gel (viscoelastic). Sol type bitumen behaves like a Newtonian fluid, which can be explained with the independency of the viscosity value from the shear stress. On the contrary, gel type bitumen has an elastic behaviour, that means the material has deformation with adequate forces, but returns its initial shape after forces are removed. Finally, the sol-gel type bitumen has almost complete elastic behaviour after relatively slight deformations (Barth, 1962; Bonemazzi & Giavarini, 1999; Pfeiffer, 1936). Figure 2.9 presents the pictorial view of Sol type (A) and Gel Type (B) bitumen (Read et al., 2003).

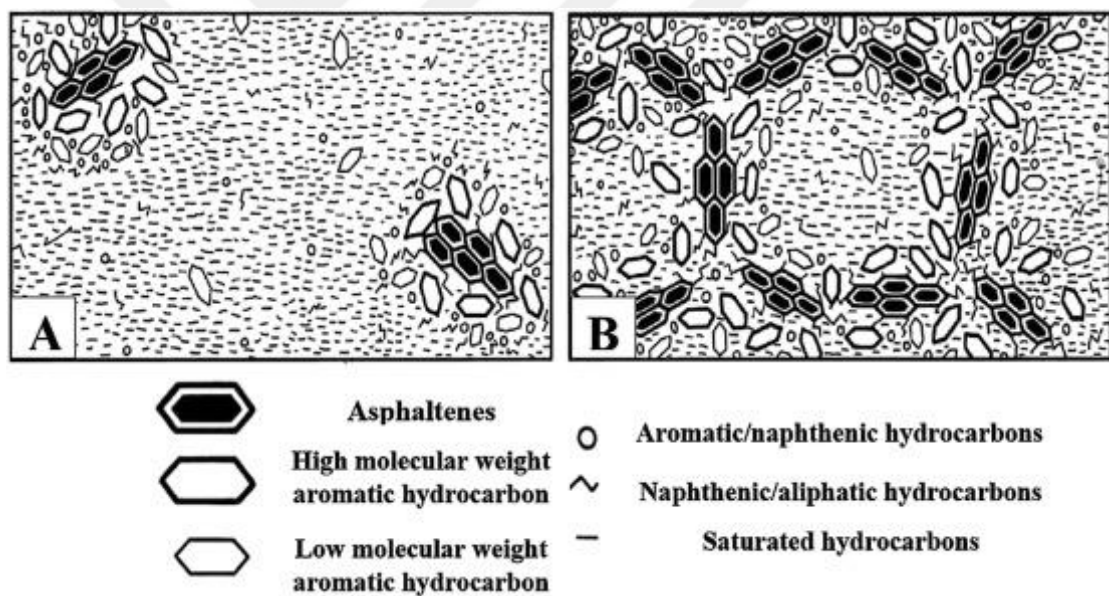


Figure 2.9 Sol type (A) and Gel type (B) bitumen (Read et al., 2003)

As can be seen in Figure 2.9, bitumen with the type of sol, has sufficient quantities of resins and aromatics of adequate solvating capacity, where the asphaltenes are fully dispersed or peptised, and the resulting micelles have good mobility within the bitumen. On the other hand, bitumen with the type of gel has insufficient quantities of aromatic, resin fractions or solvating capacity, where the micelles can be associated

(Read et al., 2003). Table 2.1 summarizes the properties of sol, gel and sol-gel types of bitumen.

Table 2.1 The properties of sol, gel and sol-gel types of bitumen

Sol Type	Gel Type	Sol-Gel Type
Asphaltenes are fully separated	Asphaltenes are discrete	Still bound, but not closely
Viscous fluid	Strongly bound in 3D	Elastic when load applied
No elasticity	Elastic, in-elastic, permanent deformation	In nature viscoelastic

Determination of the bitumen types and its colloidal structure depends on the colloidal instability index, penetration index, resins/asphaltenes ratio, plastic flow index and relaxation half time (Gaestel et al., 1971; Lin et al., 1991; Pfeiffer, 1936). Aggregation and salvation of asphaltenes are influential on the colloidal behaviour by changing the viscosity of the system. The gel character of the bitumen decreases with the increase of the temperature. The viscosity of the maltene component of bitumen rises by increasing molecular weight and the degree of interaction between the molecules (Read et al., 2003).

2.4 Durability of the Bitumen

Durability is defined as the property that permits a pavement to withstand the detrimental effects of air moisture and the temperature. Durability in civil engineering means the capability of a material to resist the conditions by the time. Generally, durability behaviour of bituminous materials can be explained with the increase of viscosity and becoming more stiff and brittle.

Durability is produced by several mechanisms. These are oxidation, volatilization, polymerization, thixotropy, synerisis and separation, which are explained as follows:

- **Oxidation:** Oxidation can be summarised with the reaction of oxygen and bitumen. Occurrence of this mechanism can be explained as follows; aging causes hardening of the surface, which creates surface cracks and enables oxygen to diffuse from these cracks which creates oxidation. Oxidation penetrates up to 15 mm below the surface layer (Martínez & Caicedo, 2005). Aromatics, resins and asphaltene fractions are effected by the oxidation, but not the saturates according to Corbett and Mertz's study, conducted in 1975 (Corbett & Merz, 1975). The amount of aromatics is reduced by aging since they turned into resins and then asphaltenes due to the oxidation. As a result, it is possible to say that oxidation decreases the amount of aromatics and resins fraction, however this is other way around for the asphaltene fraction (Lesueur, 2009).
- **Volatilization:** Volatilization is the reason of the temperature increase during production, storage, transportation and the laying phases. It can be linked with the short term aging. Volatilization starts above 150°C with the evaporation of aromatics fraction (Read et al., 2003). Similar to the oxidation, volatilization decreases the amount of the aromatics but increases the amount of resins approximately between 1 and 4 by wt% (Farcas, 1996). Moreover, viscosity is affected from the volatilization, it increases from 150 to 400 % (Bell, 1989; Christensen & Anderson, 1992).
- **Polymerization:** Polymerization is another mechanism that can be occurred because of aging. The progress of polymerization can be explained as follows; after aging, monomers of bitumen can be combined together in a chemical reaction and become to form polymer chains. These chains induces progressive hardening (Aghazadeh Dokandari, 2012).
- **Thixotropy:** Thixotropy is explained as “decreasing viscosity of a material with the time of shearing and then increasing, when the force inducing the flow is removed” in the polymer technology dictionary (Whelan & Whelan, 1994).

Thixotropy, in other words, is steric hardening and can be destroyed by heating or working the material.

- **Syneresis:** Syneresis can be classified as an exudation reaction. By aging, oily liquids of bitumen leeks to the surface. Syneresis causes hardening of the bitumen, since the thin oily constituents of the bitumen is evaporated by this mechanism.
- **Separation:** Separation can be defined as the absorption of the oily constituents, asphaltenes or resins, by aggregates. Similarly, bitumen becomes to harder with the separation due to the decrease of the oily fractions.

Hardening of the bitumen occurs under different circumstances such as; storage, mixing, transportation and laying or service life. Bitumen is in a bulk form throughout the storage period. However, it becomes to be a thin film at a high temperature, during the mixing, storage, transporting or laying periods. At the end, bitumen is a thin film at low temperature for the rest of the periods, which is called as its service life (Read et al., 2003). Aging index (AI) can be defined as the ratio of performance parameters such as viscosity, stiffness or penetration values etc. of aged asphalt to unaged asphalt (Zhang et al., 2018). Film thickness is a crucial parameter for aging index and described in Figure 2.10 (Griffin et al., 1955).

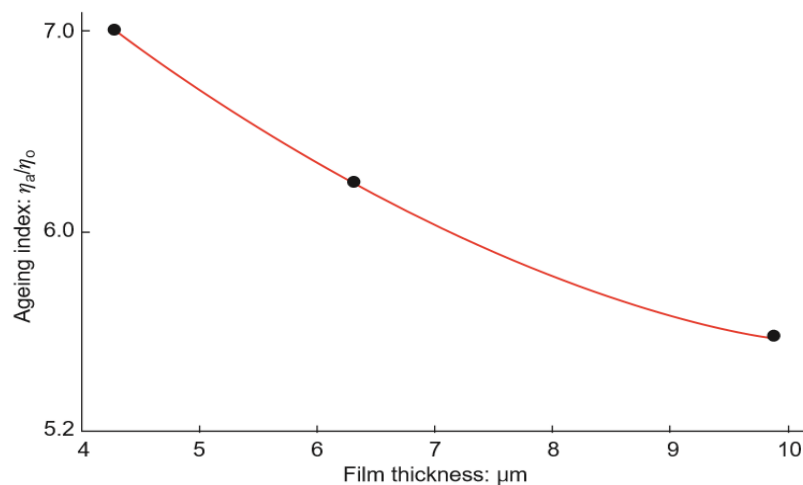


Figure 2.10 Changing of aging index with the film thickness (Griffin et al., 1955)

Based on the graph, it is possible to say that, aging index decreases with the increasing film thicknesses. Therefore, aging, which happens during different production stages, has different influences on the characteristics of final product, depending on the film thicknesses. Figure 2.11 presents the aging of the bitumen during mixing, storage, transportation, laying or service life (Read et al., 2003).

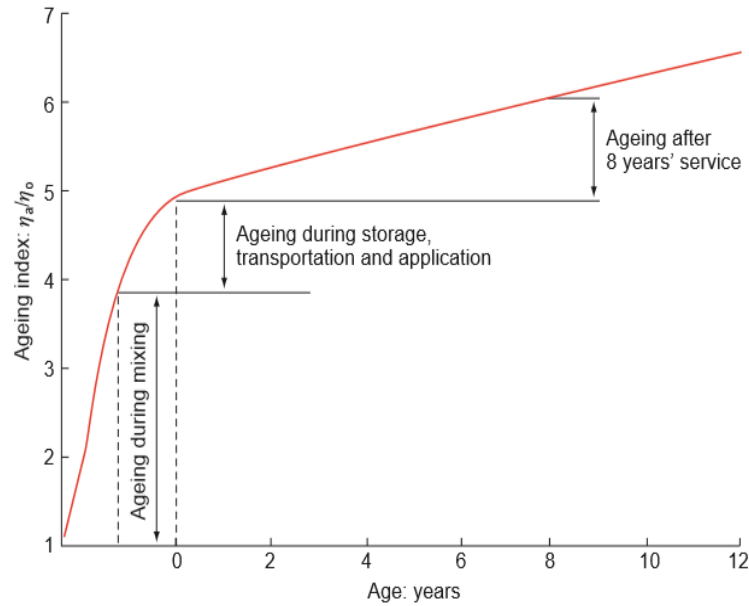


Figure 2.11 Aging of bitumen during mixing, storage, and transportation, laying or service life (Read et al., 2003)

As can be seen on Figure 2.11, bitumen hardening mainly occurs during mixing, storage, transportation and laying periods, which is named as short term aging. On the other hand, it will continue during its service life as well and that is called the long term aging. Short term aging can be simulated with Thin Film Oven Test (TFOT) or Rolling Thin Film Oven Test (RTFOT) while long term aging is simulated with Pressure Aging Vessel (PAV) within laboratory conditions.

2.5 Types of Modification

Basically, modification can be described as, enhancing the bitumen by different modifiers to have less cost of asphalt manufacturing, increase the temperature susceptibility, overcome the lack of good quality neat bitumen etc. (Becker et al., 2001). Some advantages of bitumen modification are: (Alataş & Yilmaz, 2013; Gorkem & Sengoz, 2009; Isacsson & Zeng, 1998; Polacco et al., 2006; Ponniah & Kennepohl, 1996; Tayfur et al., 2007; Von Quintus et al., 2007).

- Increasing the stiffness value at high temperature
- Increasing cracking resistance at low temperature
- Enhancing the moisture resistance
- Increasing aggregate durability
- Reduction of the maintenance costs
- Improving the resistance against aging and oxidation
- Rejuvenating the oxidized/aged bitumen
- Preventing the stripping and bleeding of bitumen
- Increasing the application areas of bitumen
- Reducing the viscosity, in order to ensure proper mixing and compression at low temperatures
- Reducing the thickness of pavement's layers and producing the thinner wear courses
- Minimising the absorption

Rutting, fatigue cracking, thermal cracking and water damages are some kinds of deformation, which can be occurred during pavement's service life, and they reduce its quality. Rutting can be explained as the surface depression in the wheel path and it is one of the major distresses. Rutting is occurred at high temperatures, due to the compaction and mix design problems such as; subgrade settlement, densification of HMA etc. Rutting is not only related to bitumen itself, but also with the mixture and the structure of it (Anderson & McGennis, 1994). Fatigue cracking, also named as alligator cracks, because of their special shape, is existed as longitudinal and

interconnected cracks, due to the repeated loads (Hunter et al., 2015). Seasonal and day-night thermal variations, causes thermal cracking, which is also known as the low temperature cracking. Thermal cracking is uniformly spaced cracks and oriented orthogonally to the road direction and effects the driving quality, since it changes the roughness of the surface (Hunter et al., 2015; Polacco et al., 2006). All these failures are related to the viscoelasticity of the bitumen. Therefore, it is possible to say that, in some cases, modification has been the solution to overcome abovementioned problems by changing the characteristics of the bitumen.

Modification can be applied by two methods depending on the characteristics of the additive: modification of asphalt mixture or modification of bitumen.

2.5.1 Asphalt Mixture Modification

Asphalt modification is carried out, by adding the additives into the aggregate-bitumen mixtures. The adding the modifiers to the appropriate gradation of aggregate and neat bitumen then continues during the mixing process commences modification. Natural filler additive materials are the common types of additives which are proper for asphalt mixtures.

2.5.2 Bitumen Modification

In this method, modifiers used for modification should be completely or partially soluble in the bitumen. Additive is dissolved with the absorption by bitumen and forms a reticulated structure. Modification process is begun during mixing and continues through the mixing of the bitumen with aggregates. Once the asphalt mixture is produced, modification process is completed. Most of it is polymer based and some of it is warm mix asphalt additives, such as organic and chemical, synthetic and natural zeolite, which are the examples of modifiers that can be used for bitumen modification.

2.5.2.1 Modification of Bitumen with Polymers

PMB is obtained by the modification of bitumen with different types of polymers by chemical reactions or mechanical mixing (Lu, 1997). The types of polymer should be determined depending on the desired properties of the final product. SBS, EVA, Polypropylene (PP), ethylene-butyl acrylate (EBA) are some examples of the polymers, which can be used with bitumen. Interestingly, none of these polymers were developed for bituminous materials, but several advantages of these materials were obtained when they are used with bitumen.

The logic behind the modification is that, polymer used for modification is swollen by the light fractions of bitumen like aromatics and saturates. Once the modification is done the final product, also known as PMB, has different properties from the bitumen itself. However, it depends on the amount and the type of the polymer, manufacturing condition and the characteristics of the bitumen (Alataş & Yilmaz, 2013; Becker et al., 2003; Chen, Liao, & Tsai, 2002; Gorkem & Sengoz, 2009; Isacsson & Zeng, 1998; Larsen et al., 2009; Lu, 1997; Panda & Mazumdar, 1999; Polacco et al., 2005; Polacco et al., 2006; Ponniah & Kennepohl, 1996; Sengoz et al., 2009; Tayfur et al., 2007; Von Quintus et al., 2007).

There are several types of polymers, which are used with bituminous materials. Widely used polymers can be categorised into two groups as thermoplastic elastomers and plastomers. Table 2.2 presents the most common polymers used in the asphalt industry, with the advantages and disadvantages.

Table 2.2 Most common polymers used in asphalt industry with the advantages and disadvantages (Airey, 2002a; Bahia et al., 2001; Becker et al., 2003; Becker, Mendez, & Rodríguez, 2001; Chen et al., 2002; Gonzalez et al., 2004; Isacsson & Lu, 1995; Lu, 1997; Panda & Mazumdar, 1999; Pérez-Lepe et al., 2003; Pérez-Lepe, et al., 2006; Polacco et al., 2005; Polacco et al., 2006; Sengoz & Isikyakar, 2008a; Sengoz et al., 2009)

Category	Polymer	Advantages	Disadvantages
Plastomers	Polyethylene (PE)	Enhanced the high temperature properties	Inadequate improvement in elasticity
	Polypropylene (PP)	Reasonably low cost	Phase separation difficulties
	Ethylene-vinyl acetate (EVA)	Improved storage stability	Insufficient enhancement in elastic recovery
	Ethylene-butyl acrylate (EBA)	Increased rutting resistance	Limited improvement in low temperature characteristics
Thermoplastic Elastomers	Styrene-Butadiene-Styrene (SBS)	Improved stiffness	Compatibility problems in some cases
	Styrene-isoprene-styrene (SIS)	• Reduced temperature susceptibility • Enhanced elastic behaviour	• Reduced resistance to oxidation and aging • Relatively High cost
	Styrene-ethylene/butylene-styrene (SEBS)	High resistance to oxidation and aging	• Storage instability problems • Reduced elasticity • High cost

2.5.2.1.1 Modification with Plastomers. Plastomers are one of the oldest modifiers used as polymers in the asphalt industry, they began to be produced before 1960 (Utracki, 1995). They increase the viscosity of the mixture however, they cannot increase the elasticity of the bitumen sufficiently (Hoban, 1987). Modifying bitumen with plastomers provides increased rigidity and good resistance to deformation, under traffic load (Zhu et al., 2014).

Among the plastomers, Polyolefin is the primary polymer used as modifiers. High-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), are some polyolefin materials. Having relatively low cost could be the reason for the presence of these materials (Attaelmanan et al., 2011; Gonzalez et al., 2004; Polacco et al., 2005; Yeh et al., 2005). Polyolefin type polymers are swollen by the light fractions of the bitumen (Pérez-Lepe et al., 2006).

Polyethylene (PE) and Polypropylene (PP) are the first polymers coming to mind among plastomers however, they do not interfuse entirely with the bitumen depending on their non-polar nature. Furthermore, these types of plastomers' tendency to crystallization causes the decrease on the interaction between asphalt and polymer. Today, PE and PP are used for the production of impermeable membranes since, the insufficient storage stability properties of these materials, inhibit the usage within the asphalt industry (Pérez-Lepe et al., 2006) .

Ethylene vinyl acetate (EVA) and ethylene butyl acrylate (EBA) are the example of plastomers which can be used in the paving industry, due to the increase on the polarity of the polyolefin and the decrease on the crystallization ability by the insertion of some polar groups (Airey, 2002a; Fawcett & McNally, 2000; García-Morales et al., 2006; García-Morales et al., 2004; García-Morales et al., 2007; Gonzalez et al., 2004; Hussein et al., 2005; Isacsson & Lu, 1999). Abovementioned properties of EBA and EVA yield an increase on the compatibility with the bitumen. However, there still some limitation to use them as a very common asphalt modifier because, it cannot improve the elastic recovery of the bitumen, due to the plastic nature of themselves (Becker et al., 2001; Isacsson & Lu, 1995).

2.5.2.1.2 Modification of Bitumen with Elastomers. Elastomeric types of polymers are more common to use with bitumen, compared to plastomeric polymers. Elastomers can be divided into two main categories, which are rubber based elastomers such as; natural and synthetic rubber or rubber crumb and thermoplastic elastomers like block copolymers of butadiene and styrene (Pyshyev et al., 2016). Rubber based elastomers provides improved flexibility, extensibility, elasticity at low temperatures, enhanced thermal cracking, permanent deformation resistance and durability. Nevertheless, they have poor dispersion in bitumen therefore, special mixing procedures are required in order to have homogenous PMB samples.

Thermoplastic elastomers obtain strength and elasticity from a physical molecular crosslinking into a three-dimensional network. Utilization of thermoplastic elastomers for modification, yields an enhanced elastic recovery of the bitumen. Elastomer modified bitumen may have sufficient elastic properties at low temperatures and high resistance to permanent deformation at high temperatures (Shim-Ton et al., 1980). Styrene butadiene styrene (SBS) and Styrene-Isoprene-Styrene (SIS) are the most common block copolymers among the thermoplastic elastomers. Although thermoplastic elastomers are extremely popular within the asphalt industry, there are some disadvantages, which should be considered before their usage as a modifier, such as their high cost or tendency to oxidation. There are several ways in order to overcome the disadvantages of thermoplastic elastomers and one of them is the utilization of functionalized thermoplastic copolymers, such as Styrene-Ethylene/Butylene-Styrene (SEBS) grafted with maleic anhydride. Functionalization yields an increased compatibility between the components of the bitumen and copolymers however, it also increases the cost.

2.6 Styrene-Butadiene-Styrene Copolymer as a Modifier

Styrene-Butadiene-Styrene (SBS) is an elastomeric type of polymer additive that can be combined with thermoplastic materials like bitumen. It is one of the most commonly used copolymer in the PMB production, since it improves temperature cracking resistance at low temperature and rutting resistance at high temperatures in

the meantime (Collins et al., 1991; Lu & Isacsson, 2000; Sengoz & Isikyakar, 2008b; Zhu et al., 2014). SBS copolymers are composed of styrene and butadiene triblock chains with a biphasic morphology of rigid polystyrene (PS) domains (dispersed phase), in the flexible polybutadiene (PB) matrix (continuous phase). Figure 2.12 shows the schematic illustrations of SBS copolymers, consisting of different amount of PS and PB (Schaer et al., 2017).

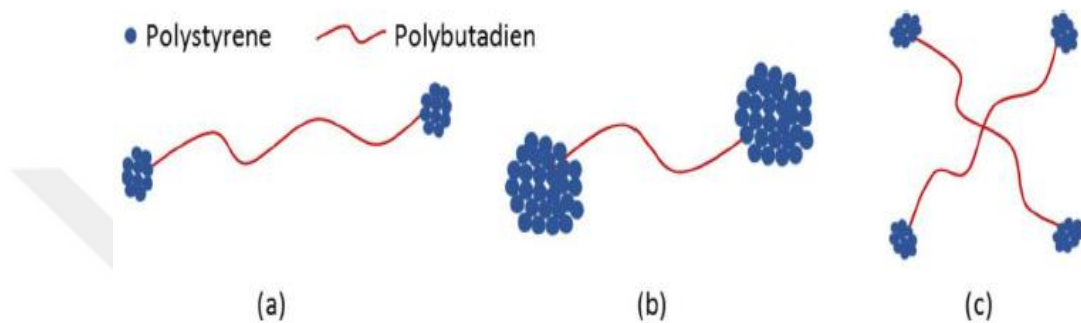


Figure 2.12 Schematic illustrations of SBS polymers consisting of different amount of PS and PB (Schaer et al., 2017)

SBS (polybutadiene segment) absorbs the maltenes and swells up to between 9 to 10 times of its original volume. PB blocks are swollen by saturates, where the PS blocks are swollen by aromatics, due to the similar solubility parameters (Hernández et al., 2006; Liang et al., 2015; Masson et al., 2003). The swollen polymer becomes mobile under the influence of shearing (mixing) and disperses in the bitumen. By mixing SBS with bitumen, the polystyrene (PS) end-blocks become physically cross-linked, forming a three-dimensional network, where the polybutadiene (PB) mid-blocks provide the material's elasticity. Figure 2.13 presents the mechanism of modification of the bitumen by SBS copolymer (Bull & Vonk, 1984).

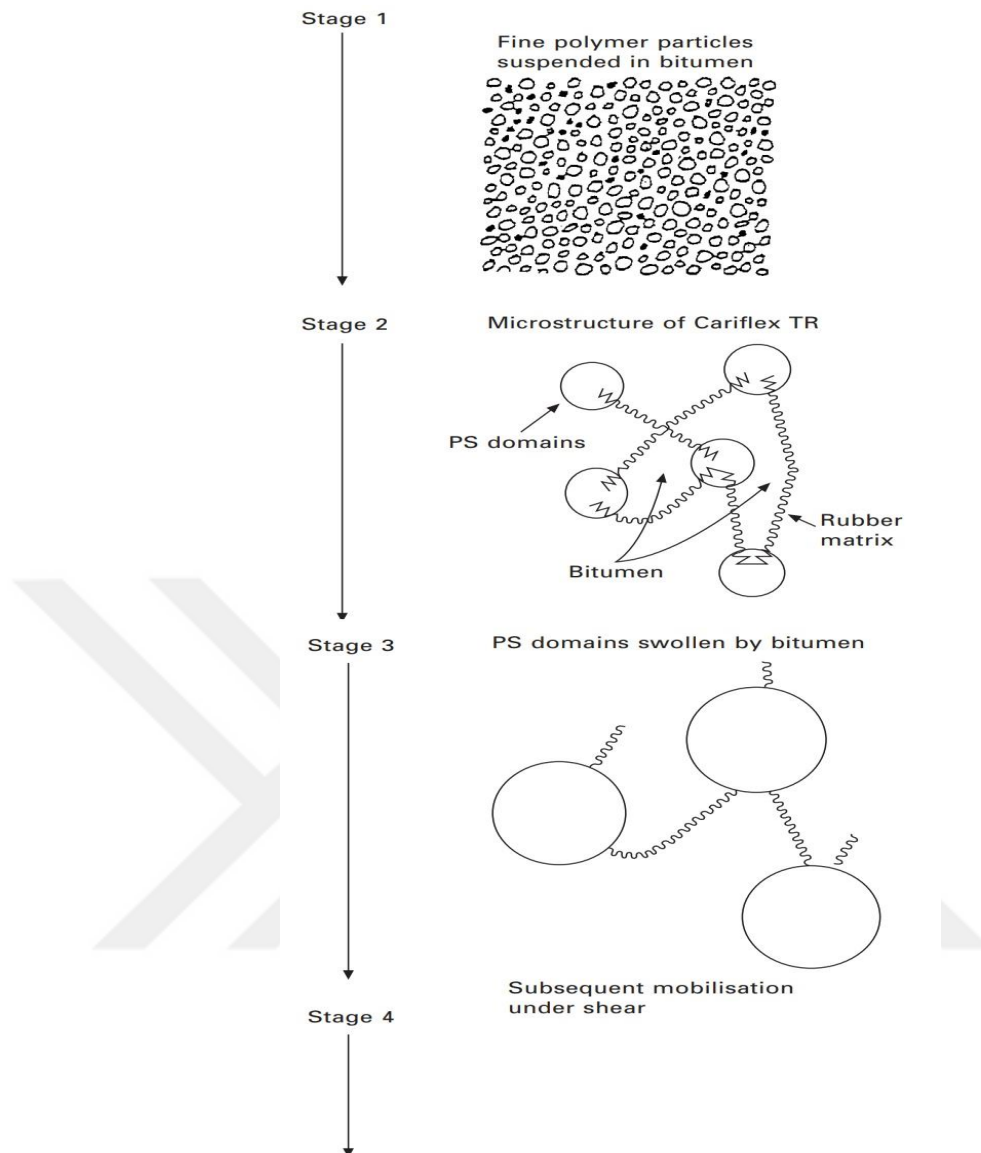


Figure 2.13 Stage-wise dispersion of SBS (Shell Cariflex TR1184)

Vonk and Bull evaluated the phase morphology of the SBS modified bitumen and revealed the influences of SBS and the bitumen on the final product. The major findings of this study was: (Vonk & Bull, 1989)

- The composition of the bitumen is predominant on the blend characteristics
- The properties of the blend are affected mostly by the continuous phase (bitumen)
- Once the molecular weights of the bitumen and polymer is similar, a single network can be formed

- High aromaticity or low molecular weight of the bitumen provides a blend with a low softening point

High asphaltene content may decrease the compatibility between polymer and the bitumen. On the other hand, the aromaticity of the maltenes, needs to fall between certain values, to reach an acceptable compatibility. Maltenes/asphaltenes ratio is also an important parameter during the production of modified asphalt, via styrene and butadiene processing (García & Nájera, 2016). High aromatics content can cause the dissolution of polystyrene blocks, which reduces the benefits of SBS addition.

2.7 Polymer Modified Bitumen Manufacturing Key Parameters

Manufacturing conditions can be investigated in several groups such as; mixing temperature, duration of mixing, shearing rate (mixing speed) and mixer properties. These manufacturing conditions are the key parameters, since they act an important role on the properties of the final product. These key parameters and their effects have always been an interesting topic for the researchers, because they may have some consequences like aging of the sample, degradation of the polymer or sometimes less absorption of the polymer by bitumen etc. In the literature, there are many intensive studies revealing the influences of the mixing conditions on thermal, structural, morphological or rheological characteristics of the sample. Some studies emphasize that, the importance of manufacturing key parameters, were given in this section.

Lepe et. al. investigated the influences of the processing conditions on the rheological properties of PMB samples. They used different type of mixer, in order to reveal the consequences of high energy mixing. As a result, they claimed that, although it is required for stabilization and dispersion of polymer into the bitumen, high energy mixing also has some disadvantages like oxidation, increase in steady state viscosity and linear viscoelastic functions (Pérez-Lepe et al., 2003).

Another study was done in Canada by Gingras et al. They examined the effects of process parameters, which are temperature, rotor speed, dispersed phase content and

bitumen grade, on the droplet size in bitumen emulsion. They obtained that, average droplet size is decreased with the increment of rotor speed, but it is increased with the decrement of temperature, bitumen grade or concentration. As a conclusion, they exhibited the process parameters' influences for the sample (Gingras et al., 2005).

Alfonso et. al studied the mixing temperature of bitumen with MDI-PEG (Polyethylene-Glycol functionalised with polymeric MDI). Atomic Force Microscopy (AFM), Thermogravimetric studies (TGA) and thin layer chromatography (TLC-FID) were employed to highlight the effects of mixing temperature on the reaction, between the polymer and bitumen fractions. They determined that, increased mixing temperature provides 3D polymer-bitumen network and reaction ability, however, it also causes polymer degradation (Martín-Alfonso et al., 2009).

Haddadi et. al investigated the importance of the mixing condition and duration on the performance of bitumen, modified with different amount of EVA additive. They measured the penetration value by increasing the mixing duration up to four hours, for each sample. As a result, they deduced that, penetration value was decreased by the duration and at the end, after four hours, it became a constant value. Additionally, they did the same investigations for softening point and obtained the similar results. Therefore, they determined mixing duration as four hours for the speed of 300 rpm (Haddadi et al., 2008).

Contreras et al. studied the effects of mixing and aging on the self-healing and mechanical characteristics of asphalt mixtures. They used different aging time and mixing methods, while producing the asphalt mixtures including polymeric capsules. As a result, they did not observe significant changes on the flexural strength by altering the aging time. For that reason, they did not recommend to heat the capsules over 20°C prior to mixing process (Norambuena-Contreras et al., 2018).

Dogan and Bayramli conducted a study about the processing temperature of the PMB samples containing three different types of polymers; LDPE, EVA and SBS. They chose 2 different mixing temperatures (150°C and 180°C) and compared the

morphological, mechanical, rheological and thermal conductivity of the final products. Consequently, they determined that, processing temperature had a little influence on the characteristics of the samples (Dogan & Bayramli, 2009).

Another study was carried out in Texas, United States by Dessouky et al. to reveal the effects of processing temperature and duration on the rheological properties of the bitumen. Samples produced at low temperature, induced less aging as expected, because high temperatures cause oxidation for bituminous samples. However, viscosity and creep stiffness values of the samples did not yield any significant changes, by altering the mixing temperature. On the other hand, mixing duration slightly effected by viscosity, creep stiffness and the complex modulus (Dessouky et al., 2011).

Key parameters are not only important at mixing stage, but also crucial during sample preparation process. In the literature, many studies were conducted to exhibit the importance of the key parameters for sample preparation. For instance, Liu et al observed different morphological images under confocal laser scanning microscopy (CLSM) by altering the duration of curing for EVA modified bitumen. Initially, PMB samples have more homogenous morphologies, by increasing time, but after a specific duration, morphologies became to be phase separated. Additionally, they employed SEM for further morphological characterisation, to evaluate the effects of the curing time and the results agreed well with the results of CLSM (Liu et al., 2017).

Larsen et al. completed a similar study by investigating the effects of manufacturing conditions on the microstructural and rheological characteristics of the SBS modified bitumen. They used different mixing temperatures and shearing rates as key parameters and employed rotational viscosity, fluorescence microscopy, size exclusion chromatography and FTIR spectroscopy. Consequently, they observed that, key parameters effected the dispersion of SBS into bitumen and, higher shearing rate and temperature causes the degradation of SBS within the PMB sample. Moreover, they concluded that, all key parameters are interdependent of each other and dependent to polymer type and molecular weight or bitumen characteristics (Larsen et al., 2009).

Different study, which was done by Navarro et al., presented the influences of processing conditions, mixing temperature, shear rates and processing device, on the rheological characteristics of crumb tire rubber modified bitumen. As a result, they observed that higher mixing temperatures yielded an increase of dissolved/dispersed rubber. However, they did not obtain significant changes with different processing device. They associated this result with the insufficient (low) mixing temperature to break up the cross-linked network of the rubber (Navarro et al., 2007).

Ortega et al. compared the effects of shearing rates on PMB samples in their study. They employed two types of mixer: high shear (16000-18000 rpm) and low shear (800-1000 rpm), to manufacture the samples. Microstructural characteristics and rheological characteristics were investigated by AFM and oscillatory rheometer. Consequently, they clarified low shear mixing as “poor mixing condition” depending on the investigations (Ortega et al., 2015).

Fang et al. studied the effects of processing parameters (mixing temperature and duration) of waste polyethylene modified bitumen on high temperature storage stability, thermal and morphological characteristics of the sample. TGA, DSC and fluorescence microscopy were employed for the investigations. In this study, it was found that, phase segregation changed with the mixing duration, if the mixing temperature was not high enough. Moreover, morphologies of the samples were directly affected with the key parameters. Homogeneity of the polymer phase into the bitumen phase, increased with the increasing mixing duration. However, after a specific value, PMB polymer in the PMB became to agglomerate. On the other hand, this study validated that, key parameters had a little influence on the thermal characteristics of the sample. Additionally, they suggested the optimum key parameters of the blend (Fang et al., 2014).

Dehouche, Kaci and Mouillet, considered the effects of five different manufacturing shearing rates from 750 rpm to 4500 rpm, on the morphological and physical properties of PMB samples, by employing Wide Angle X-Ray scattering (WAXS), AFM, DSC and FTIR. Significance of the manufacturing conditions was

demonstrated by WAXS result, because, samples showed intercalated structures up to 2000 rpm. However, beyond 3000 rpm the behaviour of the sample changed into exfoliated structure. Moreover, height and the number of aromatic sheets in the bitumen was decreased with the accelerated shear rates, which can be associated with the oxidation. Based on the AFM results, they announced that, the amount of bee like structures were increased with the increasing shearing rates. On the other hand, crystalline index value was decreased for higher shearing rates (Dehouche et al., 2016).

2.8 Characterisation of PMB

Characterisation in materials science can be explained as the process of materials' structural, chemical, thermal, physical, morphological etc. properties investigation (Sam et al., 2009). Material characterisations have been examined for centuries. Nowadays, it is possible to study, not only micro and also macro characteristics of the materials, with the help of developing technology.

For bituminous materials most common characterisations techniques can be investigated in four groups which are; physical, rheological, chemical and structural (Yu et al., 2011). Penetration, ductility and the softening points are the examples of bitumen's physical characteristics. Viscosity, rutting resistance, fatigue behaviours, Zero Shear viscosity (ZSV) etc. are the properties of bitumen that can be addressed by the means of the rheological characterisation. On the other hand, there are many techniques and devices like, Thin Layer Chromatography-Flame Ionization Detector (TLC-FID), High Pressure Gel Permeation Chromatography (HP-GPC), Size-Exclusion Chromatography (SEC) etc. Structural characterisation can be determined as one of the most popular characterisation techniques for the researchers, since it is utilised for ages. FTIR, NMR, AFM can be employed for the structural characterisation.

In this thesis, the influences of the manufacturing conditions on the material properties, were analysed by the means of structural, rheological, morphological and thermal characterisations. Therefore, in this section, previous studies in the literature

on structural, rheological, morphological and thermal characterisation were presented with the techniques and general information.

2.8.1 Structural Characterisation

In this sub section, the structural characteristics of bitumen is analysed by FTIR spectroscopy and AFM investigations. FTIR spectroscopy enables to evaluate the chemical characteristics, while AFM assesses the microstructural properties of the sample. More information about the investigation of the structural characteristics by FTIR spectroscopy and AFM are given in this chapter.

2.8.1.1 Structural Characterisation by Fourier Transform Infrared (FTIR)

Infrared Spectroscopy has been one of the most important analytical techniques for scientists in recent years. The advantage of infrared is the fact that, it allows inspection in almost every case and for every sample. Liquids, solutions, powders, films, fibers are just a few of the samples that can be examined using this technique. The greatest developments in infrared systems have been the result of the introduction of Fourier-conversion spectrometers. In these methods, called Fourier Transform Infrared (FTIR), it is aimed to reduce the time, required to obtain data by using the interferometry and improved mathematical Fourier-transform.

Bituminous materials have become the subject of even greater curiosity for scientists, especially with the development of FTIR techniques, which are possible to conduct infrared investigation. It is possible to validate the aromaticity, aliphaticity and oxygenation rate of the bituminous sample, with reliable results (Doumenq et al., 1991; Ganz & Kalkreuth, 1990).

Spectrum obtained by FTIR gives the absorbance bands which allows for the investigations of functional and structural indexes of the samples. It is important to evaluate the areas instead of the height of the absorbance band, since it is more reliable

to consider similar vibrations. Table 2.3 presents the different assignment of the main absorption bands with corresponding wavenumbers (Larsen et al., 2009).

Table 2.3 Different assignments of the main absorption bands with the corresponding wavenumbers (Larsen et al., 2009)

Wavenumber (cm ⁻¹)	Assignations
2924, 2853	C=H alifatic
1735	C=O
1690	C=O conjugated
1603	C=C aromatic
1460	C H of (CH ₂) _n (aliphatic index)
1376	C—H of CH ₃
1031	S=O sulfoxide
721	C—H aromatic
968	C—H trans disubstituted —CH=CH— (butadiene block)
748	C—H aromatic monosubstitued (styrene block)
690	C—H aromatic monosubstitued (styrene block)

Lamontagne et al. developed a formula to investigate the change of the chemical structure of bitumen, depending on the results of FTIR spectroscopy. Based on their study, with the absorbance values of carbonyl, sulfoxide and butadiene group, it is possible to evaluate the carbonyl, sulfoxide and SBS indices, by using the Equation 2.1 to 2.3 (Wu et al., 2009).

$$I_{C=O} = \frac{\text{Area of the carbonyl centered around } 1700 \text{ cm}^{(-1)}}{\text{Area of the spectral bonds between } 2000 \text{ and } 600 \text{ cm}^{(-1)}} \quad (2.1)$$

$$I_{S=O} = \frac{\text{Area of the sulfoxide centered around } 1030 \text{ cm}^{(-1)}}{\text{Area of the spectral bonds between } 2000 \text{ and } 600 \text{ cm}^{(-1)}} \quad (2.2)$$

$$I_{SBS} = \frac{\text{Area of the butadiene centered around } 968 \text{ cm}^{(-1)}}{\text{Area of the spectral bonds between } 2000 \text{ and } 600 \text{ cm}^{(-1)}} \quad (2.3)$$

Bitumen aging is a complex series of chemical reactions, which include molecular level oxidation and intermolecular level structuring (Bell et al., 1994). Aging influences may be investigated by FTIR spectroscopy since the chemical structure of

the bitumen changes, after the aging process (Lamontagne et al., 2001; Wu et al., 2009). The presence of highly polar and interacting oxygen functional groups, like carbonyl group (C=O), is increased by oxidation. Therefore, many studies have been conducted to reveal the aging effects on the structural characteristics of bituminous materials by investigating the carbonyl group.

Zhang et al studied the influences of TFOT aging, UV aging and PAV aging by considering the carbonyl group indices. According to their study, sample with PAV aging, yielded the highest carbonyl index, while TFOT had the lowest, as expected (Zhang et al., 2018).

Larsen et al. investigated the aging effects of the mixing conditions on the structural characteristics of the sample. They examined two different SBS modified samples, one mixed for 90mins while the other for 150 mins. They compared the absorbance values, which correspond to carbonyl group and butadiene blocks, to reveal the aging effects of longer mixing. Moreover, they could be able to conclude the degradation of SBS, after mixing at higher temperature and shearing rate depending on the FTIR investigations (Larsen et al., 2009).

2.8.1.2 Micro Structural Characterisation by Atomic Force Microscopy (AFM)

AFM is one of the most common approaches in order to characterise the bituminous mixtures, in terms of morphologies. It is capable of measuring topographic features at the nanometer-scale or even at atomic-scale resolution. Moreover, AFM enables to understand bitumen's micro mechanical behaviour, such as phase separation, micro friction, micro abrasion etc. (Hou et al., 2017). Moreover, previous researches clarified that, microscale properties of the samples are directly related with the macro scale properties (Al-Rub et al., 2010; Mahboob Kanafi et al., 2015). Different phases in bitumen, yields different properties into bitumen, such as stiffness, adhesive behaviour etc. (Allen et al., 2014; Lyne et al., 2013; Yu et al., 2013). Therefore, it is possible to say that, AFM can be used to predict the performance of the asphalt. Additionally, one of the most determinant preferences of AFM, over the other microscopes is that,

sample preparation techniques of AFM is relatively simple and it operates under ambient conditions.

Bitumen fractions have different morphological images under AFM. Morphological images belongs to bitumen surface, occurred from multiple micron-size domains. The typical characterized morphology of the neat bitumen consists of catana phase, peri-phase and para-phase (Figure 2.14) (Masson et al., 2006). De Moraes reported that, Peri-phase, which surrounds the bee structures is stiff, while hard Para phase is softer and more viscous among the other phases (De Moraes et al., 2010; Fischer et al., 2014). Therefore, it can be expected that, aging will affect the microstructure and phase distribution of material due to the changes on sample's stiffness and viscosity after the aging. Previous studies revealed influences of aging on the phase dispersion, clustering and materialization, which are visible under AFM (Allen et al., 2012).

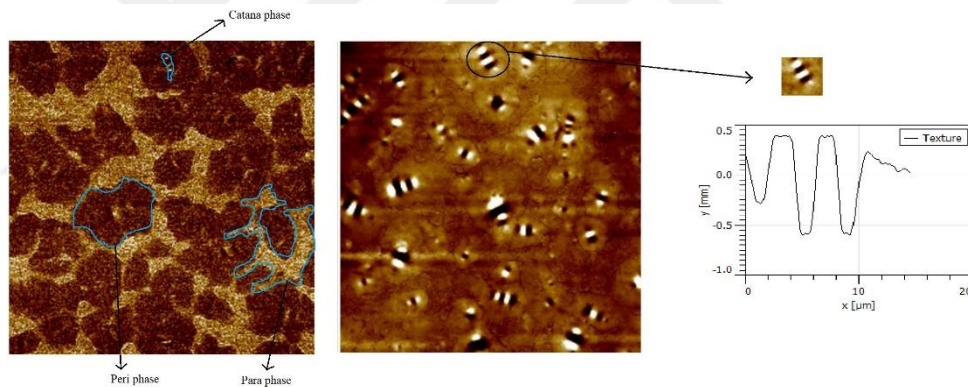


Figure 2.14 Phases and bee structures of bitumen

Bee structure, showing variable black and white striped stands, characterises areas of higher and lower stiffness than the surrounding area, which can be explained as the result of wrinkling of very thin surface films on the order of 10 nm thick (Hung & Fini, 2015; Ortega et al., 2016), has always been a dispute by researchers. Some researchers attributed bee structure to asphaltene (Dembinski et al., 2017; Loeber et al., 1998; Masson et al., 2006), while the rest believed that this bee-like structures are related with the paraffin crystallization (Fischer et al., 2014; Schmets et al., 2010; Soenen et al., 2014). For the first time, Loeber et al. evaluated the bitumen morphology, by AFM

and they concluded that, bee-like structures represent the asphaltene content of the bitumen (Loeber et al., 1998).

Wu et al. studied the influences of SBS modification in terms of morphology by AFM. The authors concluded that, SBS modification changed the bee-structure appearance of the samples. Moreover, they investigated the aging effects on the morphology and found that, aging increases the amount of bee-structure for both neat bitumen and the PMB samples (Wu et al., 2009). De Moraes et al. attributed bee structure to paraffin wax content, by using DSC and AFM in their study (De Moraes et al., 2010). An important study to clarify the reason of the bee structure appearance was done in USA, by Pauli et al. They separated the all components of the bitumen (Saturates, aromatics, resins and asphaltenes) with different solvents and techniques. Flowingly, they extracted the wax content from the saturates and evaluate the differences in the morphology with and without waxes. Based on the results, they reported that samples without waxes, did not show the bee structures. Concordantly, they observed more bee structures in the morphology, by the increment of the wax content. Moreover, they alluded that, the presence of bee structures in the asphaltene free samples, was the evidence of disassociation of bee structures, with asphaltenes (Pauli et al., 2011). Similar results were obtained by Laurell Lyne et al. They found that, samples with higher wax content has more bee structures (Lyne et al., 2013).

Aging has crucial importance on the microstructure and phase dispersion of the bituminous sample. The molecular structure depends on the aging, because of some chemical changing and degradation after oxidation (Wang & Liu, 2017; Zhang et al., 2011). Based on this point of view, it can be conceivable that, influences of mixing conditions, which will cause aging can be evaluated by AFM. Dehouche et al investigated the mixing rates' effects on the morphologies, obtained under AFM and discovered that, the increment of shearing rates, causes not only the increment of bee-like structures, but also it enlarges the contrast difference, between the dispersed phase and the matrix (Dehouche et al., 2016).

2.8.2 Rheological Characterisation

Rheology is defined as the branch of physics that deals with the deformation and flow of matter, especially the non-Newtonian flow of liquids and the plastic flow of the solids. Rheometer is a device, which is employed to investigate the rheological characteristics of the bitumen at different temperatures or frequencies (Schowalter, 1978).

Complex modulus (G^*) is defined as the ratio of maximum shear stress to maximum strain, and provides a measure of the total resistance to deformation, when the bitumen is subjected to shear loading. Phase angle (δ) is the phase difference between the shear stress and strain in an oscillatory test at different temperatures. This value corresponds 0° for purely elastic materials, while 90° for purely viscous materials. Therefore, it is possible to say that, higher phase angle validates more viscous material (Airey, 2011).

Complex modulus (G^*) and phase angle (δ) values are directly related with the viscoelastic properties of the sample. Therefore, it is known that, either modification or aging of the sample, effects the rheological behaviour of the sample.

By using abovementioned two values (complex modulus (G^*) and phase angle (δ)), master curves, black diagrams, Cole-Cole plots, Zero Shear Viscosity (ZSV), Multiple Stress and Recovery (MSCR) values etc., can be investigated to evaluate the rheological properties of the bitumen. Moreover, aging characteristics of the binder might be obtained by rheological investigations because, bitumen becomes to be stiffer and have different rheological properties after aging.

2.8.2.1 Rutting parameter

Rutting is the best known permanent deformation occurred, due to the surface depression in the wheel path. Rutting, which is happened due to the high temperature and heavy vehicle, with high traffic volume, decreases the driving comfort (Radhakrishnan et al., 2018; Wang & Zhang, 2014). Rutting susceptibility of asphalt

is related to the binder's characteristics, which is a crucial property, since it effects the service life behaviours of the pavement. Therefore, measuring and evaluating the rutting properties of the bitumen is necessary to have proper asphalt binder with the desired properties.

The Superpave rutting parameter ($G^*/\sin(\delta)$), is suggested in 1993 by American Strategic Highway Research Program (SHRP), in order to evaluate the rutting susceptibility of the bitumen (Anderson & Kennedy, 1993). This formula of rutting parameter is proposed for neat bitumen, which has less strain recovery ability compared to modified bitumen. Shenoy suggested new rutting parameter formula $G^*/(1-(1/\tan\delta\sin\delta))$, which is more suitable for modified bitumen, because it considers the nonrecoverable response of the bitumen (Gibson et al., 2012). However, researchers recently observed that, rutting parameters yielded in the laboratory do not correlate well with the fields' result. Therefore, new parameters such as zero shear viscosity (ZSV), multiple stress and recovery (MSCR) are developed to investigate the rutting behaviour of the bituminous sample.

Short term or long term aging improves the rutting resistance of the sample by causing the increased stiffness (Bahia & Anderson, 1995). Similarly, modification of the binder enhances the rutting resistance of the sample. For instance, modification of bitumen by polyefin, EVA or SBS copolymer, yields the increased rutting resistance (Zhu et al., 2014).

2.8.2.2 Fatigue Resistance

Fatigue cracking is an asphalt pavement distress, which is observed by the failure of the surface, due to the repeated traffic loads. Fatigue potential of the binder is evaluated with the fatigue factors, which can be obtained by $G^*\cdot\sin(\delta)$. The higher the $G^*\cdot\sin(\delta)$ value yields, the more fatigue cracking susceptibility of the bitumen. It should be considered that, fatigue resistance of the sample can be investigated on the sample, which are subjected to aging, since fatigue cracking is observed after repeated loads. Asphalt binder becomes stiffer and more cracking susceptible after aging.

2.8.2.3 Performance Grade (PG) Classification

Penetration and viscosity grading of the bituminous samples provide insufficient characteristics, since these methods do not consider the rheological properties of the sample. Therefore, in the SUPERPAVE method, researcher developed a new grading system named performance grade (PG), which considers the performance of the binder in different temperature conditions. Involving traffic load combination, climatic conditions and aging concerns are some of the advantages of PG classification over the other grading systems.

PG specifies two different temperatures corresponding to minimum and maximum temperatures, which can be experienced during the service life. The maximum temperature is obtained as the average seven-day maximum pavement temperature ($^{\circ}\text{C}$), while the minimum one is the temperature ($^{\circ}\text{C}$), which the pavement would possibly encounter in cold weather conditions. An example, bitumen named PG 64-22 validates that, this bitumen is convenient to a region, where the maximum seven-day average temperature is 64°C and the minimum pavement temperature is 22°C . PG value of the sample depends on the modification and aging characteristics of the sample. Therefore, it is possible to change it into the desired values by modifiers.

Performance Grade (PG) upper limit value of the PMB samples can be defined at laboratory conditions, by determining the maximum temperature, at which $G^*/\sin(\delta)$ value is less than 1kPa for unaged samples and 2.2 kPa for aged samples. The frequency of 10 rad/s was selected regarding the criteria of Strategic Highway Research Program (SHRP) (Dehouche et al., 2016), which simulates the vehicles at the speed of 100 km/h.

2.8.2.4 Master Curves

Master curves allow for the generation of a continuous rheological parameter curve by shifting the values for complex modulus at different temperatures based on a reference temperature. These curves yield information about materials behaviour on a

time and frequency scale larger than that measurable under normal laboratory conditions (Liang et al., 2015). The principle in order to create a master curve, is to correlate the equilibrium between time and temperature, known as the time-temperature superposition principle (TTSP). According to TTSP, bitumen's viscoelastic properties measured at two different temperatures will be same if the measurement frequency is properly shifted (Soleimani, 2009).

The applicability of time-temperature superposition principles to bituminous materials, has been discussed in the previous studies and it was determined that, they can characterise the rheological behaviour of PMBs, reasonably well, due to the linear viscoelastic properties of the bitumen (Ferry, 1980; Partal et al., 1999; Polacco et al., 2003). The most critical point in generating master curves is the calculation of the horizontal shifting factors (α_T). Because, it defines the temperature dependency of the material. There are several approaches used to model the complex modulus and phase angle master curves. Among these approaches the Arrhenius and Williams–Landel–Ferry equations are the most popular ones (Di Benedetto et al., 2011). The Williams–Landel–Ferry equation (WLF) is widely used as a function of temperature, to designate the shift factors (Anderson et al., 1994);

$$\log(\alpha_T) = \frac{-c_1(T - T_r)}{c_2 + (T - T_r)} \quad (3.4)$$

Where,

α_T : the shift factor at temperature (T), relative to the reference temperature (T_{ref})

T_{ref} : the reference temperature, in (°C), which is a characteristic parameter for each asphalt binder

Researchers found that, C_1 and C_2 constant values are determined in between 19 and 92, according to the characteristics of the bitumen. However, it is also clarified that, temperature for below T_{ref} can be determined by using Arrhenius-like equation. The horizontal shifting factor (α_T) was determined, by using an Arrhenius-like equation, which yields information about the temperature susceptibility of the sample as follows:

$$\alpha_T = \exp \left[\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (3.5)$$

Where,

E_a : activation energy

R : universal gas constant

T : current temperature and

T_0 : reference temperature.

The activation energy, governed by the molecular properties of the polymer, such as; molecular weight, tacticity and the level of chain branching in the polymer, are related with the temperature susceptibility (Ait-Kadi et al., 1996; Di Benedetto et al., 2011; Ferry, 1980; Garcia-Morales et al., 2004; Liang et al., 2015).

2.8.2.5 Black Diagrams

Black diagrams are created from plots of complex modulus versus phase angle, for values obtained at different temperatures and these can be used to differentiate between thermo-rheological simple and complex materials (Airey, 2002b; McKee et al., 2005). The properties of black diagram instruct the time-temperature characteristics of bitumen. Smooth curve of the black diagram means that, the sample is time temperature equivalent, while disjointed one, specifies the breakdown of TTSP, the existence of high wax content and asphaltene fraction or the presence of polymer modification (Lesueur et al., 1996). Therefore, it is possible to say that aging or polymerisation characteristics of the sample can be investigated by evaluating the black diagrams of the sample. Previous studies have showed that, polymer modification provides increased complex moduli, with decreased phase angle at high temperature. On the other hand, bituminous materials lose their elastic properties at high temperatures (Mturi et al., 2010).

2.8.2.6 Cole-Cole Plots

Cole-Cole plots show the correlation between G'' (loss modulus) and G' (storage modulus) or η'' (imaginary dynamic viscosity) and η' (dynamic viscosity) as a function of the frequency for the applied load and test temperature (Mturi et al., 2014). Cole–Cole plots are the most effective method to assess the extent of the compatibility, between polymer and bitumen in polymer modified bitumen blends. For example, when evaluating the SBS modified bitumen it was observed that, swelling and interactions among PS domain, PB segments and the bitumen components, greatly affect the extent of the compatibility and thus the form of Cole-Cole plots (Liang et al., 2015).

2.8.2.7 Zero Shear Viscosity

The zero shear viscosity (ZSV) of a bituminous binder is used as an alternative performance indicator of resistance to permanent deformation of the asphalt pavements (Phillips & Robertus, 1996; Sybilski, 1996). Based on the previous studies, it has been proved that, rutting parameters observed at the lab conditions, are not corresponding the actual performance of the pavement in the fields. For this reason, researchers lean to use ZSV, which can be described as the asymptotic viscosity value in the 1st Newtonian region, where the viscosity value has the highest value to investigate the rutting performance (Biro et al., 2009; De Visscher & Vanelstraete, 2004; Gungor & Saglik, 2012).

Bitumen has both elastic solid and viscous liquid behaviour depending on the change in temperature and the loading time. The design of the asphalt pavement depends on the assumption that, as wheel loading occurs, an asphalt mixture moves into the linear viscoelastic region, the relevant viscosity of the binder is considered independent of the shear loading time. However, based on the temperatures specified in the rutting criteria for asphalt pavement, bitumen leans towards non-Newtonian behaviour, and the viscosity values of the sample change with the loading time. This

phenomenon reveals the importance of zero shear viscosity, since it is independent of loading time at a specific temperature (Liao & Chen, 2011).

2.8.3 Morphological Characterisation

2.8.3.1 Optical Microscopy

Fluorescence microscopy is used to study heterogeneous surfaces, where the components have different responses to UV excitation. Oily fractions of the bitumen (like aromatics) have fluorescence properties, however resins and asphaltenes have no fluorescence responses under UV light (Lambert, 2005; Skoog & Leary, 1996). Neat bitumen itself has little emission, due to the fact that, all components are well mixed therefore, it cannot be observed under OM (Loeber et al., 1996). However, it is possible to investigate the PMB samples under Optical Microscopy (OM), because the volume of aromatic component of the bitumen will increase by modification. Moreover, it is not possible to use OM for aged samples, neat bitumen or even PMB, since aging decreases the aromatics content, and increases the resin and asphaltene content, which don't have fluorescence properties (Liu et al., 2005; Pilat & Krol, 2008; Sengoz & Isikyakar, 2008a; Sengoz et al., 2009; Xiao et al., 2005; Yang & Yin, 2012).

SBS modified bitumen, which is one of the most common PMB, has two different phases; polymer rich phase and the bitumen phase (Brûlé et al., 1988; Wegan & Bredahl Nielsen, 2000). The polymer rich phase appears white or yellow, since it has higher fluorescence to UV, while bitumen phase exhibits dark brown or black (Airey, 1999; Dony & Durrieu, 1990; Kraus, 1982). As abovementioned, the maltenes are absorbed by SBS and swollen up 9-10 times of its original volume, which makes the sample more visible under OM.

Fluorescence microscopy has been one of the most popular tool to investigate the morphological characterisation of PMB samples. Depending on the different coloured appearance of two phases (bitumen and polymer), it is easy to study the homogeneity and the dispersion of polymer into bitumen (Brûlé et al., 1988).

Sengoz and Isikyakar investigated the influences of polymer content on the dispersion of the polymer phase into bitumen phase with the help of optical microscopy. They concluded that, bitumen is in a continuous phase, when less than 5% SBS is used, however, over 5% SBS becomes a continuous phase, while bitumen is the dispersed one. As a result of this study, they recommended the usage of 5% SBS in order to have two twisted continuous phases (Sengoz & Isikyakar, 2008a).

The conditions of PMB manufacturing process have some influences on the morphological images of PMB samples. A study has been conducted in Argentina to reveal the effects of different mixing conditions (duration, shearing rate and temperature) on PMB morphological characteristics. As a result, higher shearing rates and temperature causes the decomposition of SBS and the dispersion of maltenic phase (Larsen et al., 2009).

Sample preparation methods for OM surveys are crucial, because morphological characteristics depend on the temperature, presence of pressure, heating time or cooling rate etc. Soenen, Lu and Redelius considered the effects of different sample preparation methods on the final morphology of the PMB samples. Drop method, freeze fracture method and thin film method are the different approaches used in this study. According to their findings; drop method is the simplest method, however; it is affected by stir and shear forces used during the manufacturing process. Freeze fracture method requires specific cooling steps to investigate the structure of the sample. On the other hand, thin film method is the most common sample preparation technique, since it allows to use demanded temperature during melting process of the sample, prepared for the OM investigations. Furthermore, the temperature should be constant for each sample, in order to have equal thermal history, which effects the morphological properties (Soenen et al., 2008).

2.8.3.2 Confocal Laser Scanning Microscopy (CLSM)

CLSM is qualified of considering extremely localized fluorescence emissions and enables a thorough study of bitumen scale of asphalt observation (Handle et al., 2014). That capability of CLSM, allows to handle the microstructure of the bitumen (Bearsley et al., 2004; Forbes et al., 2001; Handle et al., 2012).

CLSM has many advantages, such as; enhanced signal strength, narrower focus, and its scanning procedure allows for a better spatial resolution. Moreover, the sample preparation method for CLSM is trivial. Fluorescence spectroscopy provides an integrated spectrum, that is not capable of visualising spatial distributions (Bearsley et al., 2004; Handle et al., 2016; Handle et al., 2012). Moreover, one of the biggest advantages of CLSM is that, it can be used to study the aging properties of PMB samples, by measuring the different fluorescence emission behaviour of the bitumen components. Additionally, it is possible to investigate polymer dispersion, compatibility and network formation by CLSM based on the interaction between the polymer and bitumen (Collins et al., 1991; Forbes et al., 2001; Handle et al., 2012; Lee et al., 1997; Newman, 1998; Rozeveld et al., 1997; Takamura & Heckmann, 1999).

CLSM allows to investigate 2D or 3D morphologies. Asphaltene phase can be observed with 2D images however, 3D images also allows to evaluate the size, shape and the asphaltene structures. Bearsley et al. studied different bitumen samples and showed that, they had different asphaltene fractions, which in turn produced various morphologies depending on the source of the bitumen (Bearsley et al., 2004).

Forbes et al. studied the microstructure of polymer modified bitumen emulsions, by CLSM. They were adopted latex additives as a polymer and assessed the polymer dispersion and binder structure, depending on the addition method. Moreover, they were compared the homogeneity of the polymer dispersion in emulsions and hot binders by CLSM. As a result, they found that, hot polymer modified binders have more homogenous polymer dispersion (Forbes et al., 2001).

Another study to investigate the wax content in bitumen with CLSM, was done by Lu, Langton and Redelius on different sourced bitumen. It was clarified that, having different wax content causes, different CLSM images. Additionally, they concluded that, sample preparation method, effects the observance of wax content in the bitumen therefore, having the equal sample preparation conditions is crucial for CLSM observation (Lu et al., 2005).

Previous studies have showed that, aging behaviour of bituminous materials can be characterised by CLSM. Maltenic fractions of the bitumen has fluorescence centres although, asphaltene doesn't have and this phenomenon was proven in Handle et al.'s study, where they evaluated the fluorescence capabilities of the different fractions under the same detection and excitation wavelength. Furthermore, they aimed to evaluate the aging effects on the bitumen by CLSM, since oxidation effects the fractions' distribution. As a result, they clarified that asphaltene amount is increased after aging (Handle et al., 2014).

2.8.4 Thermal characterisation

2.8.4.1 Differential Scanning Microscopy (DSC)

DSC or MDSC is employed to characterise the physical/chemical properties, depending on the heat exchange such as T_g , heat capacity, chemical reactions or phase transition, like crystallization and melting (Soenen et al., 2014). Glass Transition Temperature (T_g) is a distinctive feature of the polymeric materials. It is always lower than the melting point and it gives the temperature of materials after, which it has viscous behaviour. Bitumen has 4 different T_g corresponding the T_g 's of saturates, aromatics, resins and asphaltene fractions. Therefore, PMB samples should have more than 4 T_g , depending on the polymer used for modification. Moreover, in some situations new T_g '(s) can arise/arises, from a phase of mixed compositions, which occurred by branching and cross linking between polymer and bitumen.

Modulated DSC (MDSC) is used in order to study the thermal behaviour of the polymer modified bitumen samples, as it is useful in the detection of overlapping T_g 's (Reading et al., 1994). The distinct advantage of MDSC is that, it applies two simultaneous heating rates to the sample, a linear heating rate provides the total heat flow rate similar to standard or conventional DSC, but at the same time, a sinusoidal (modulated) heating rate provides a route to determine a fraction of the total heat flow. This fraction of the total heat flow is termed the reversing heat flow or the heat capacity component of the total heat flow. Heat flow that does not respond to the changing heating rate is then obtained by subtracting the reversing signal from the total signal and is called the non-reversing heat flow or the kinetic (time dependent) component (Gill et al., 1993).

For PMB samples, it is another challenge to determine the T_g occurred, because of the polymer. For example, for SBS modified bitumen, polymer and bitumen should be evaluated separately. A study about thermal characterisation of SBS polymer was conducted by Masson Perc and Delgado in 2004. They employed MDSC instead of DSC to evaluate the overlapped T_g of the SBS samples. Polybutadiene has a T_g around -92°C , while PS has a T_g around -60 and 125°C , which is not easy to determine, since it is a broad range. Therefore, they also used DMA to obtain the new T_g occurred, because of PS in SBS. Moreover, they distributed SBS into PB, PB rich and PS rich phases and they determined the T_g values for this phases as -94°C , -25°C and 68°C respectively (Masson et al., 2005).

It has been always an interesting study for researchers, to evaluate the interaction between the components of bitumen by DSC or MDSC. Soenen et al., investigated the different crude origins' T_g values by considering the wax content and as a result, they found that, wax content directly effects the thermal characteristics of the bitumen. Another study was done to evaluate the influences of the wax content on the thermal properties of bitumen and asphalt concrete. They used bitumen samples from different sources, including the different amount of wax content. As a result, they concluded that, wax content and type, alter the melting point, crystallization properties of the sample by using MDSC (Edwards, 2009). Another similar study about the

investigation of wax content indicated that, exothermic and endothermic peak profiles obtained by DSC can provide the information about, the type of wax (Edwards & Redelius, 2003).

Ageing evaluation can be done by DSC, since it allows to assess the asphaltene fractions among the bitumen components. Masson, Collins and Polomark explore the steric hardening and the ordering of asphaltene in bitumen, by employing the MDSC. As a result they found that, the more the endotherm, the more the asphaltene presence, which caused the steric hardening of bitumen (Masson et al., 2005). Moreover, MDSC provides to evaluate the microstructure of the bitumen, by evaluating the thermal behaviour. In that study, T_g 's of the saturates, aromatics, resins and asphaltene were found as around -60, -20, 20 and 60°C. Additionally, they linked the endotherms with the aromatics, while exotherms with the resins and asphaltene (Masson & Polomark, 2001).

2.8.4.2 Thermogravimetric Analyse (TGA)

Thermal gravimetric analysis is an experimental technique, which is useful for measuring the thermal stability of a material and extrapolate its maximum operating temperature above, which degradation starts to take place (Hatakeyama & Quinn, 1999). The thermal characterisation of bitumen is a very difficult investigation, because of the complex fractions of the bitumen (Yoon et al., 2009). In the literature, it can be found that, bitumen displays three major mass losses, first one because of the volatilization of light fractions (saturates and non-polar aromatics), second one depending on the decompositions of resins and asphaltene and the last one due to the asphaltene (Zhang et al., 2011).

The distribution of the SARA fractions, directly effects the thermal properties of the bitumen, which can be investigated by TGA. Firoozifar et al studied the influences of asphaltene fractions on the thermal behaviours of the bitumen. They used three different types of bitumen, with different asphaltene content and as a result, they concluded that, with the increase in asphaltene content, thermal stability was

decreased, which means asphaltene caused the decrease on the decomposition temperature. However, after initial decomposition temperature, it became the contrary; bitumen sample with higher asphaltene content decomposed slower, compared to the sample with lower asphaltene content. It was determined that, the amount of asphaltene has positive influences on the aging resistance, after it was started (Firoozifar et al., 2011).

Benbouzid and Hafsi were revealed the aging effects on the thermal characteristics, by evaluating the pure and oxidised bitumen under TGA. According to the experiments, oxidised bitumen has two stages, while the pure bitumen has only one. They asserted that, the occurrence of second stage is related with the decreased thermal stability, caused by the aging (Benbouzid & Hafsi, 2008).

Naskar, Chaki and Reddy investigated the modification effects on the thermal behaviour of the bitumen. They used different amount of waste plastics as a modifier to obtain the polymerization effects. Based on the result, they released that, polymerization with waste plastics, enhanced the thermal properties of the bitumen, which depends on the amount of the polymer (Naskar et al., 2010). Another study was conducted in China to reveal the blending conditions' effects on the thermal properties of the bitumen. They used different mixing durations and temperatures as blending conditions and evaluated the thermal stabilities of the produced samples. As a result, they published that, modification preparation process has little effect on the thermal characteristics of the polyethylene modified bitumen (Fang et al., 2014).

CHAPTER THREE

EXPERIMENTAL STUDIES

In this chapter, materials, procedure of the PMB production, aging methodology, properties of equipment and programmes used in structural, rheological, morphological and thermal characterisation investigation was presented.

3.1 Materials

3.1.1 Bitumen

The neat bitumen with penetration grade within the range of 50/70, was used as the base bitumen, obtained from Aliaga/Izmir oil terminal of the Turkish Petroleum Refinery Corporation. SARA analyses and conventional test results of the neat bitumen are given in Table 3.1 and 3.2, respectively.

Table 3.1 Properties of neat bitumen

Test	Specification	Results	Specification Limits
Penetration (25°C; 0.1 mm)	ASTM D5-97 EN 1426	55	50-70
Softening Point (°C)	ASTM D36-95 EN 1427	49.1	46-54
Viscosity at 135°C, (Pa.s)	ASTM D4402-06	0.413	-
Thin Film Oven Test (TFOT) (165°C; 5h.)	ASTM D1754/D1754M-09 TS EN 12607-2	-	-
Change of Mass (%)	-	0,04	0,5 (max)
Retained Penetration after RTFOT (%)	ASTM D5/D5M-13 TS EN 1426	25	-
Softening point rise after TFOT (°C)	ASTM D36/D36M-12 TS EN 1427	54	48 (min)
Ductility (25°C; cm)	ASTM D113-07 TS EN 13589	100	-
Specific Gravity	ASTM D70-09e1 TS EN 15326	1,03	-
Flash Point (°C)	ASTM D92-12b TS 123 EN 22592	+260	230 (min)

Table 3.2 SARA analyses of neat bitumen

Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)
8.76	66.37	9.84	15.03

3.1.2 Thermoplastic Elastomer (SBS)

SBS copolymer (grade D1192), which is presented in Figure 3.1, was purchased from Kraton® polymers, The Netherlands. Gel Permeation Chromatography (GPC) analysis was performed in order to determine the average molecular weights and molecular weight distribution by using tetrahydrofuran (THF) as the eluent ($1\text{mL}\cdot\text{min}^{-1}$), for the SBS copolymer. Table 3.3 presents the GPC molecular weight results, obtained for the SBS block copolymers relative to polystyrene standards.



Figure 3.1 SBS Copolymer (Personal archive, 2019)

Table 3.3 Molecular weight results ($\times 10^5$) for SBS copolymer (D1192)

M_p (g/mol)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_{z+1} (g/mol)	M_v (g/mol)	PD
1.62	1.52	1.65	1.81	2.05	1.78	1.09

3.2 Methodology

3.2.1 Preparation of PMB Samples

Polymer modified bitumen samples were obtained by altering the mixing duration and shearing rate at the constant temperature ($175\pm 5^\circ\text{C}$). Mixing speeds were chosen as 1000 and 3000 rpm to represent the low and high shearing rates respectively,

whereas the mixing durations were chosen as 15 minutes for minimum and 45 minutes for maximum. SBS content was determined as 5%, a standard value based on the Republic of Turkey General Directorate of Highway Technical Specification. Table 3.4 gives information about the sample names in terms of mixing conditions and aging characteristics of each PMB samples and neat bitumen, used in this study.

Table 3.4 Mixing conditions and aging characteristics of each PMB samples and neat bitumen

Sample Name	Shearing Rate (rpm)	Mixing duration (min.)	Aging characteristic
1000-15-UA	1000	15	unaged
1000-45-UA	1000	45	unaged
3000-15-UA	3000	15	unaged
3000-45-UA	3000	45	unaged
1000-15-A	1000	15	aged
1000-45-A	1000	45	aged
3000-15-A	3000	15	aged
3000-45-A	3000	45	aged
%5-Aged*	3000	45	aged
NB-UA	NEAT BITUMEN		unaged
NB-A	NEAT BITUMEN		aged

* Due to time and equipment constraints, in some cases, only 3000-45-A was able to be investigated to assess the effects of aging during the modification on the long term performance of the samples. In these cases, this sample was named as %5-Aged to prevent any confusion.

3.2.2 Aging Procedures

Aging of bitumen samples are occurred during different stages such as processing, mixing or during its service life. Mixing by higher shearing rates or longer duration lead the bitumen to be oxidised. Aging mainly contains two components. First component is mainly associated with the loss of volatilization in asphalt, during the construction and mixing phase, also called short term aging, and the second component, which is associated with gradual oxidation of the in-place material in the field, called long term aging (Bell, 1989). It is possible to simulate short term and long term aging in the laboratory by using RTFO and PAV respectively.

RTFO Test: 35 grams of neat bitumen is located in a cylindrical specific glassy bottle, which is then placed in a carousel inside the RTFOT device. The oven is heated to 163°C and the carousel continues rotating for 85 minutes at 15 rpm rate. The carousel rotation continuously exposures new bitumen to the heat, where air is blown by a compressor (Bell, 1989). Both AASHTO and ASTM standarts (AASHTO T240, ASTM D2872) adopt this test. Figure 3.2 represents the RTFO device used in this study. Additionally, RTFO test is the first step of long term aging. Samples that will be subjected to PAV to simulate long term aging in laboratory should be aged by using RTFO test.



Figure 3.2 Rolling Thin Film Oven Test (RTFOT) device (Personal archive, 2019)

PAV: Heat and pressure are the conditions applied to bitumen sample to simulate aging, during the service life of the pavement. Bitumen sample residue of RTFOT, which has been subjected to short-term aging, is taken by PAV. Test procedure contains placing sample inside a steel pan and heated inside pressurized (305 psi) vessel to apply aging. This test has been adopted by AASHTO and the details can be found in AASHTO R 28. PAV device, which was used in this study, was located in the Karadeniz Technical University, Trabzon and presented in Figure3.3.



Figure 3.3 Pressure Aging Vessel (PAV) (Personal archive, 2019)

3.2.3 Experimental Plan

In this section, all the properties of devices and the procedures of test methods used in this thesis, to evaluate the effects of mixing condition on structural, rheological, morphological and thermal characterisation were discussed.

3.2.3.1 Structural Characterisation

Testing procedures of FTIR and AFM were examined for characterising the structural properties of the samples were as follows:

- **FTIR Spectroscopy**

Fourier transform infrared spectroscopy (FTIR) measurements were taken using a Bruker Alpha spectrometer, equipped with an attenuated total reflectance (ATR) crystal. Neat bitumen and PMB samples were dissolved in carbon disulphide with 5 wt% concentration, and then dropped onto KBR disks and dried for FTIR analyses. Spectra were recorded using the OPUS analysis software in the range of 400 – 6000 cm^{-1} at r.t. The resolution was set to 2 cm^{-1} and averaged over 16 scans to acquire each spectrum. Background scans were taken and subtracted from sample spectra, to remove atmospheric contributions. FTIR spectroscopy, which was located in the Characterisation Lab of International Institute for Nanocomposites Manufacturing

(IINM) Building, owned by Warwick Manufacturing Group (University of Warwick-England), is given in Figure 3.4.



Figure 3.4 FTIR Spectroscopy (Personal archive, 2019)

- **AFM**

AFM (Nanoscope III, Bruker, Santa Barbara, CA, USA), presented in Figure 3.5, was employed in order to measure topography and the phase properties of neat bitumen and PMB samples, by using tapping mode attached rectangular V shaped cantilevers (OTR8, Bruker), with a nominal spring constant of 0.57 N/m. All images were acquired at room temperature under normal pressure, with a scan rate of 0.70 Hz and a resolution of 512 * 512 lines. AFM, used in this study, was supplied by the Physics Department of the University of Warwick, England.



Figure 3.5 Atomic Force Microscopy (Personal archive, 2019)

3.2.3.2 Rheological Characterisation

Rheological characterisation studies were carried out using two different rheometers, one in Dokuz Eylul University and the other in the University of Warwick. The differences between these two devices were their heating principles. One of them is heating the sample with water, which is called Malvern Dynamic Shear Rheometer (DSR), while the other one heating with the air (oven) is called Haake Oscillatory Rheometer. In order to prevent the denomination confusion, rheometer with heating principle is named oscillatory rheometer (OR) and the other one abbreviated as DSR. Master curves, cole-cole plots, black diagrams were obtained with the OR and zero shear viscosity (ZSV), Performance Grade (PG) classification of the samples were determined with DSR.

- **Oscillation Rheometer (OR)**

Rheological tests were performed on a stress-controlled rheometer, Thermo-HAAKE Mars III, Germany, with parallel disk geometry (25mm in diameter with 1 mm gap), by using frequency sweep (0.01-100 rad/sec) and temperature sweep (40, 50, 60, 70, 80°C). The OR, represented in Figure 3.6, was connected to a computer, to collect and store data, by using rheology software—HAAKE RheoWin 3. During the experiment, heating was provided with an air convection oven set. The value of the stress was chosen as 10Pa, since all samples were within linear viscoelastic range, under this stress level. In order to elucidate the effect of the mixing conditions on the rheological behaviour, heating of the samples was avoided at the sample preparation stage. Proper amount of samples (approximately 10 g) were taken and reformed into a disk with 25 mm of diameter using a mold and pressed by applying pressure during the absence of any heating source. This rheometer was located in the Characterisation Lab of International Institute for Nanocomposites Manufacturing (IINM) Building, owned by Warwick Manufacturing Group (University of Warwick-England).



Figure 3.6 Oscillation rheometer (Thermo-HAAKE Mars) (Personal archive, 2019)

- **Dynamic Shear Rheometer rheometer (DSR)**

Malvern Dynamic Shear Rheometer (DSR) Asphalt Rheometer was developed by Malvern Instruments®, for the rest of the rheological characterisation evaluations. Smooth plate-and-plate geometry of 25 mm in diameter with 1 mm gap, was used for unaged samples and 8 mm in diameter, with 2 mm gap, was used for aged materials. Frequency sweep tests (0.01, 0.1, 1 and 10 Hz) have been performed to investigate the rheological characterisation of unaged PMB samples at different temperature (50, 60, 70 and 80°C). DSR, used in this study for ZSV and fatigue cracking investigations, was located in the Mehmet Uluçaylı Ulaştırma Lab., Dokuz Eylul University, Turkey (Figure 3.7).



Figure 3.7 DSR (Malvern) (Personal archive, 2019)

3.2.3.3 Morphological Characterisation

Morphological characterisation can be investigated by different methods depending on the phase dispersion or fluorescence properties of the samples. In the scope of this thesis, confocal laser scanning microscopy (CLSM) and optical microscopy (OM) were conducted, in order to characterise the morphological properties of the samples.

- **Optical Microscopy**

Nikon (Eclipse 12400) optical microscopy, presented in Figure 3.8, was employed to observe the PMB morphologies, with an adapted digital Nikon Coolpix 4500 camera. Images were taken with a $\times 10$ to $\times 40$ magnification by using Blue Filter and analysed with ImageJ program. Obtained images were processed by Image J programme. The distribution of the SBS phases within the bitumen phases and the effects of aging related to the mixing conditions were analysed. Optical Microscopy was supplied by the Institute of Advanced Study based in Millburn house, The University of Warwick, England.



Figure 3.8 Optical Microscopy (Personal archive, 2019)

- **Confocal Laser Scanning Microscopy (CLSM)**

Confocal Laser Scanning Microscopy (CLSM) is based on a conventional optical microscope, Fluorescent Optical Microscopy, but instead of a lamp, a laser beam is focused onto the sample. CLSM has many advantages; such as enhanced signal strength, the narrower focus, and the scanning procedure allowing a better spatial resolution, moreover sample preparation method for CLSM is considerably easy.

The morphology of the neat bitumen and the PMB samples were observed with a HORIBA Lab Ram CLSM (Tokyo - Japan) (Figure 3.9). Spectrometer at 488 nm excitation and a 600 l/mm grating. All spectrum were collected using a $\times 50$ long working distance objective at 1% and are normalised for acquisition time. Fluorescence maps were collected over a 500 x 500 μm at a step size of 5 μm region selected at random. The fluorescence intensities were collected between 600-650 nm. DuoScan mirrors were used for collection, at laser power of 3.5 % using a $\times 5$ objective. CLSM, used in this thesis was supplied by the Institute of Advanced Study based in Millburn house, The University of Warwick, England.

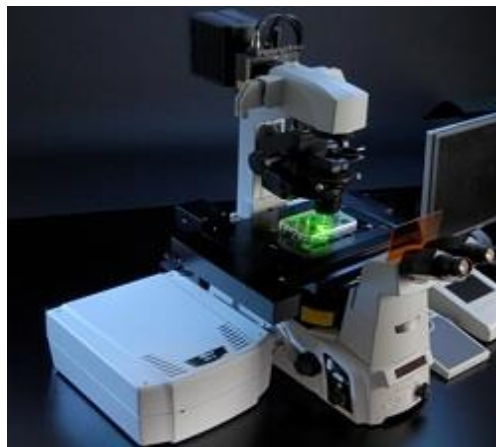


Figure 3.9 Confocal Laser Scanning Microscopy (CLSM) (Personal archive, 2019)

3.2.3.4 Thermal Characterisation

Thermal characteristics of the samples were examined by TGA, and modulated DSC. Testing procedures and the properties of the equipments were given below.

- **TGA**

A Mettler Toledo TGA1-STARe system, as shown in Figure 3.10, was employed to analyse the thermal stability of the samples under oxidative conditions. The samples were placed into 70 μL alumina pans and heated from room temperature to 800°C, at a constant heating rate of 10°C/min. Two kinds of graphs are typically represented in relation to the thermal gravimetric measurements; TGA and the derivative of TGA, which is called the differential thermogravimetric thermograms (DTA). By using TGA curve, the initial decomposition temperature (T_d), at which 5% of the weight loss of the sample occurs can be determined, as well as T_{10} wt% and T_{50} wt% (10% and 50% weight loss, respectively). The temperature at which the maximum weight loss rate occurs (T_{max}), was determined from the peak value of the DTA thermograms, as well as the onset temperature (T_{onset}), which is determined by the intersection of the tangent of the peak, with the baseline. TGA, used in this thesis was located in the Characterisation Lab of International Institute for Nanocomposites Manufacturing (IINM) Building, owned by Warwick Manufacturing Group (University of Warwick-England).



Figure 3.10 Thermogravimetric Analyser (TGA) (Personal archive, 2019)

- **Modulated DSC**

Modulated DSC (MDSC) was employed in order to reveal the thermal behaviour of the PMB samples, because it prevents the underestimation of the overlapping T_g's (Reading et al., 1994). Superiority of MDSC is that, it applies two simultaneous heating rates to the sample. The linear heating rate provides the total heat flow rate similar to the standard DSC, but at the same time, the sinusoidal (modulated) heating rate provides to determine the fraction of the total heat flow. This fraction of the total heat flow is named reversing heat flow or the heat capacity component of the total heat flow. Heat flow that does not respond to the changing heating rate is obtained by subtracting the Reversing signal from the total signal and called the nonreversing heat flow or the kinetic (time dependent) component (Gill et al., 1993). DSC tests were performed using METTLER DSC using 5-10 mg of samples, in the 40ul aluminium pans, under a nitrogen flow of 50ml/min. The picture of the MDSC, which was located in the Characterisation Lab of International Institute for Nanocomposites Manufacturing (IINM) Building, owned by Warwick Manufacturing Group (University of Warwick-England), is given in Figure 3.11. MDSC heating and cooling curves were obtained at a rate of 3 °C/min with a modulation period of 60 s and an amplitude of 0.47 °C.



Figure 3.11 Modulated Differential Scanning Calorimetry (MDSC) (Personal archive, 2019)

All samples were subjected to the following thermal programs: (i) First heating: -100 to 150 °C (after rapid cooling from the annealing temperature). Rapid cooling is an exponential cooling rate fastest at the beginning of cooling. About 15 min is required for cooling, so that the average cooling rate is about 15°C/min. The first heating provides results for the annealed samples. (ii) Second heating: -50 to 150 °C (after rapid cooling from the 150 °C). This step provides results for unannealed samples. (iii) Cooling from 150 to -50°C. Heat flow curves and the first derivative heat flow curves of the samples, belong to second heating, were investigated in order to obtain the Tg's and the heat capacities. Figure 3.12 summarizes the MDSC method used in this study.

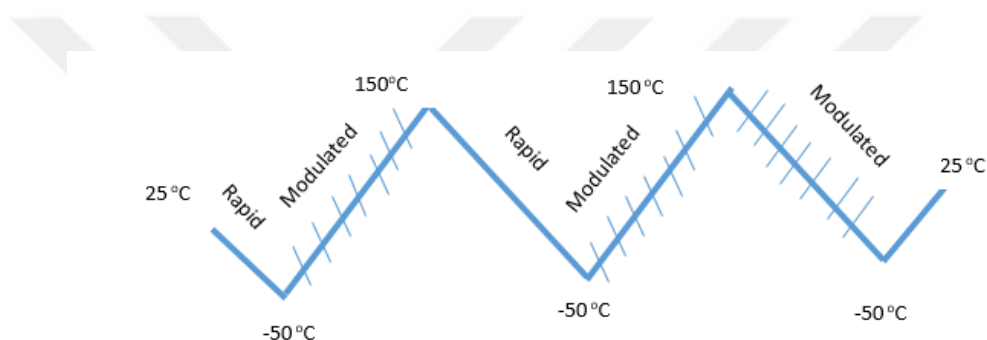


Figure 3.12 MDSC Method used in this study

CHAPTER FOUR

RESULTS AND DISCUSSION

In this chapter, all the results obtained from experiments and investigations were given with the discussion. Structural, rheological, morphological and thermal characterisation of the samples were done based on the results.

4.1 Structural Characterisation Results

Neat bitumen and PMB samples, produced by using different mixing conditions, were structurally characterised depending on the results of FTIR spectroscopy and AFM.

4.1.1 FTIR Spectroscopy Results

Absorption values at different wavelengths were investigated the possible impacts of mixing conditions of the PMB. Figure 4.1 presents the FTIR spectra of SBS, neat bitumen and the PMB samples.

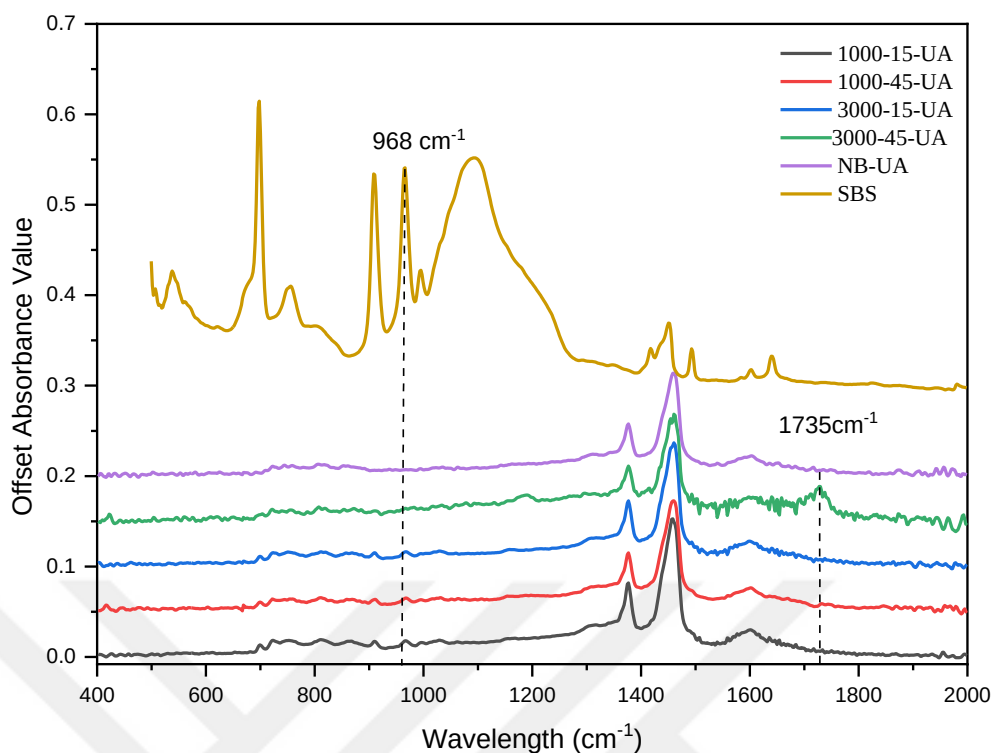


Figure 4.1 FTIR spectra of PMB samples

The absorbance values for peaks at 968cm^{-1} , 1030cm^{-1} , 1608cm^{-1} , 1690cm^{-1} and 1735cm^{-1} , which are associated with butadiene, sulfoxide, aromatics, conjugated carbonyl and carbonyl groups respectively, are listed in Table 4.1.

Table 4.1 Absorbance values of the samples corresponding to different wavelengths

Sample Name	C=O (1735) Carbonyl	CH=CH(trans) (968) Butadiene	S=O (1030) Sulphoxide	C=C (1603) Aromatics	C=O (1690) Carbonyl Conjugated
NB-UA	0.0072	0.0070	0.0093	0.0224	0.0084
1000-15-UA	0.0055	0.0176	0.0165	0.0296	0.0097
1000-45-UA	0.0081	0.0150	0.0174	0.0262	0.0115
3000-15-UA	0.0078	0.0163	0.0172	0.0271	0.0127
3000-45-UA	0.0369	0.0139	0.0184	0.0254	0.0247

The absorbance value, which corresponds 1735 cm^{-1} , is associated with the carbonyl content of the sample. Carbonyls are products of oxidative aging therefore

they increase by aging (Lamontagne, 2001). Besides, previous studies have shown that, absorbance values corresponding to carbonyl and Sulfoxide groups increase by the increase in mixing time and rate (Larsen et al., 2009). Absorbance value corresponding to 1603 cm^{-1} is related with the aromatic content of the sample. An increase in the absorbance value of aromatic group is occurred with SBS modification, as the SBS ejected the maltenes phase of the bitumen and swollen as stated in the previous literature (Brûlé et al., 1988). In contrast, with increasing shear rate and mixing time, the aromatics index (AI) of the SBS modified bitumen samples decreased, which is associated with a decrease in the aromatic content as a consequence of aging (Ouyang et al., 2006). The more severe the oxidation reaction carried out, the more carbonyl and sulfoxide groups are formed. From this study, the SBS modified bitumen sample 3000-45-UA had the highest Carbonyl group among all samples, while the 1000-15-UA sample had the lowest, as expected. The absorbance value corresponding to Carbonyl and sulfoxide group were increased with the increasing mixing time and shear rate. This can be explained as, the more severe the oxidation reaction aging, the more carbonyl and sulfoxide groups are formed (Larsen et al., 2009; Lucena et al., 2004; Wu et al., 2009; Zhu et al., 2018). The peak at around 968 cm^{-1} , was detectable in the spectra of the SBS modified bitumen, which is derived from the stretching vibration of chain segments in the butadiene phase of the SBS (Larsen et al., 2009). Moreover, the 3000-45-UA sample had the lowest intensity peak at 968 cm^{-1} , whereas the 1000-15-UA sample had the most intense. This observation can be explained by aging also, because of a reduction in butadiene segment, due to the degradation of SBS (Liu et al., 2011). In order to highlight the aging effects of varying mixing conditions, SBS modified bitumen samples and neat bitumen were subjected to long term aging and studied by FTIR, as can be seen on Figure 4.2.

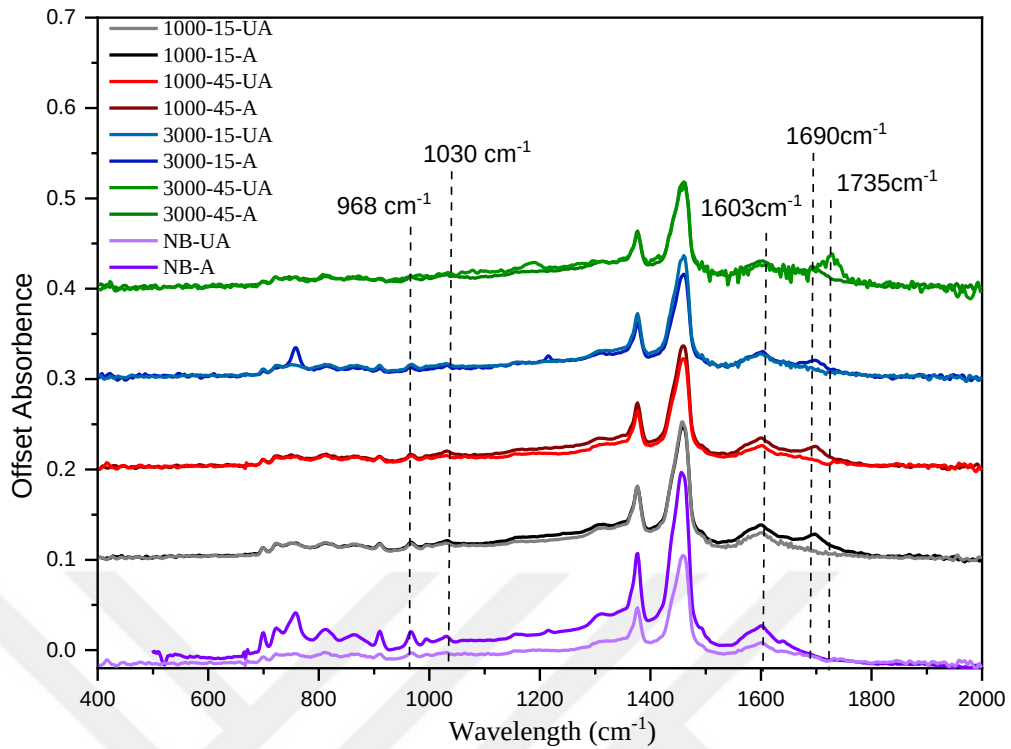


Figure 4.2 FTIR spectra of the PMB samples

As can be seen from Figure 4.2, the observations made for the different chemical groups of aged samples, were similar to that made for the unaged samples with the exception of the 3000-45-UA sample. Long term aged SBS modified bitumen samples had more intense carbonyl (1735 cm^{-1} - 1690 cm^{-1}) and sulfoxide (1030 cm^{-1}) absorption bands compared to the unaged SBS modified bitumen, due to the oxidation. Moreover, the absorbance value for the peak at 968 cm^{-1} is decreased, since the butadiene segment of the SBS phase was degraded, as a result of the aging. The decrease in the intensity of the carbonyl group band for the 3000-45-A sample may originate, with the destruction of the C=O bonds, within the sample during long term aging. For the neat bitumen sample the spectrum of the aged sample was much more intense than that recorded for the SBS modified sample, since the addition of SBS to neat bitumen, resulted in increased resistance to aging.

4.1.2 AFM Results

The morphological investigation of the PMB samples and neat bitumen, were conducted by AFM, where 2D and 3D images were observed and presented in Figure 4.3 and 4.4. Figure 4.3 shows the dark phase, light phase and phase contrast of the sample. Dark phase, which appears black to brown, is associated with the stiff components (resins and asphaltenes) of the bitumen, while the light phase, which appears yellow to light brown, is with the soft components (aromatics and saturates). The increase in phase separation of these two phases can be interpreted as the differences between rigidity and composition of the samples. The contrast of these two phases is increased by aging (Rebelo et al., 2014).

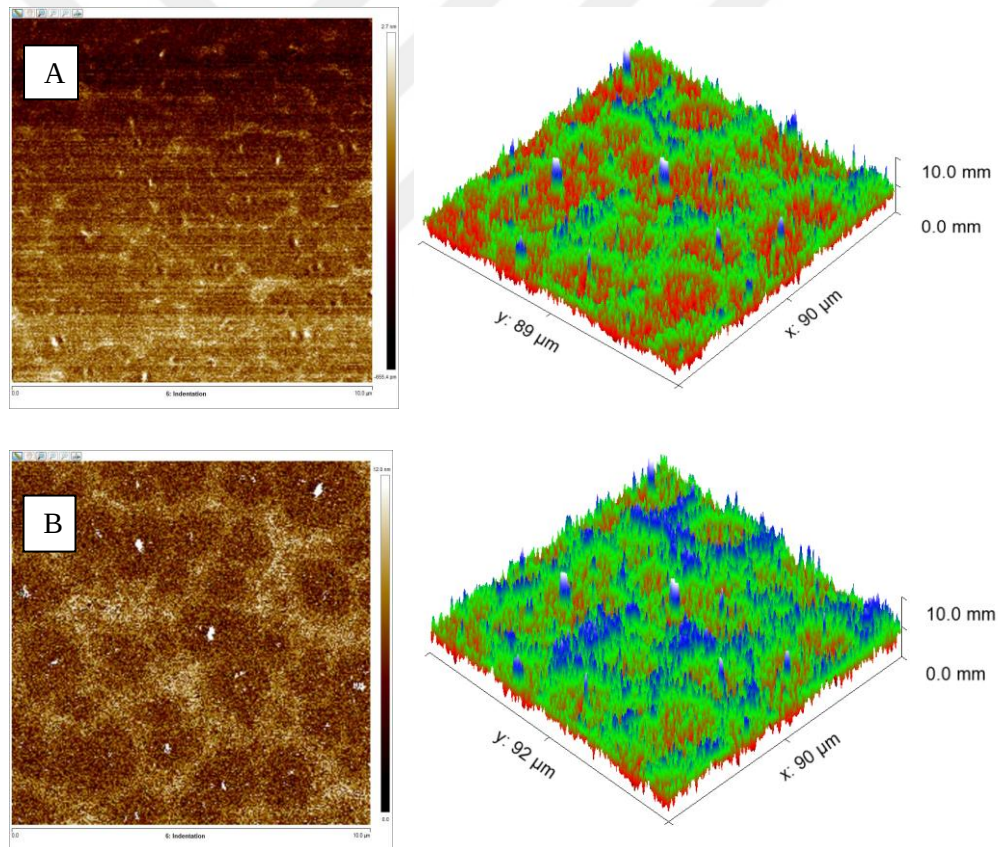


Figure 4.3 The phase contrast images of all the samples (A) NB, (B) 1000-15-UA, (C) 1000-45-UA, (D) 3000-15-UA, (E) 3000-45-UA

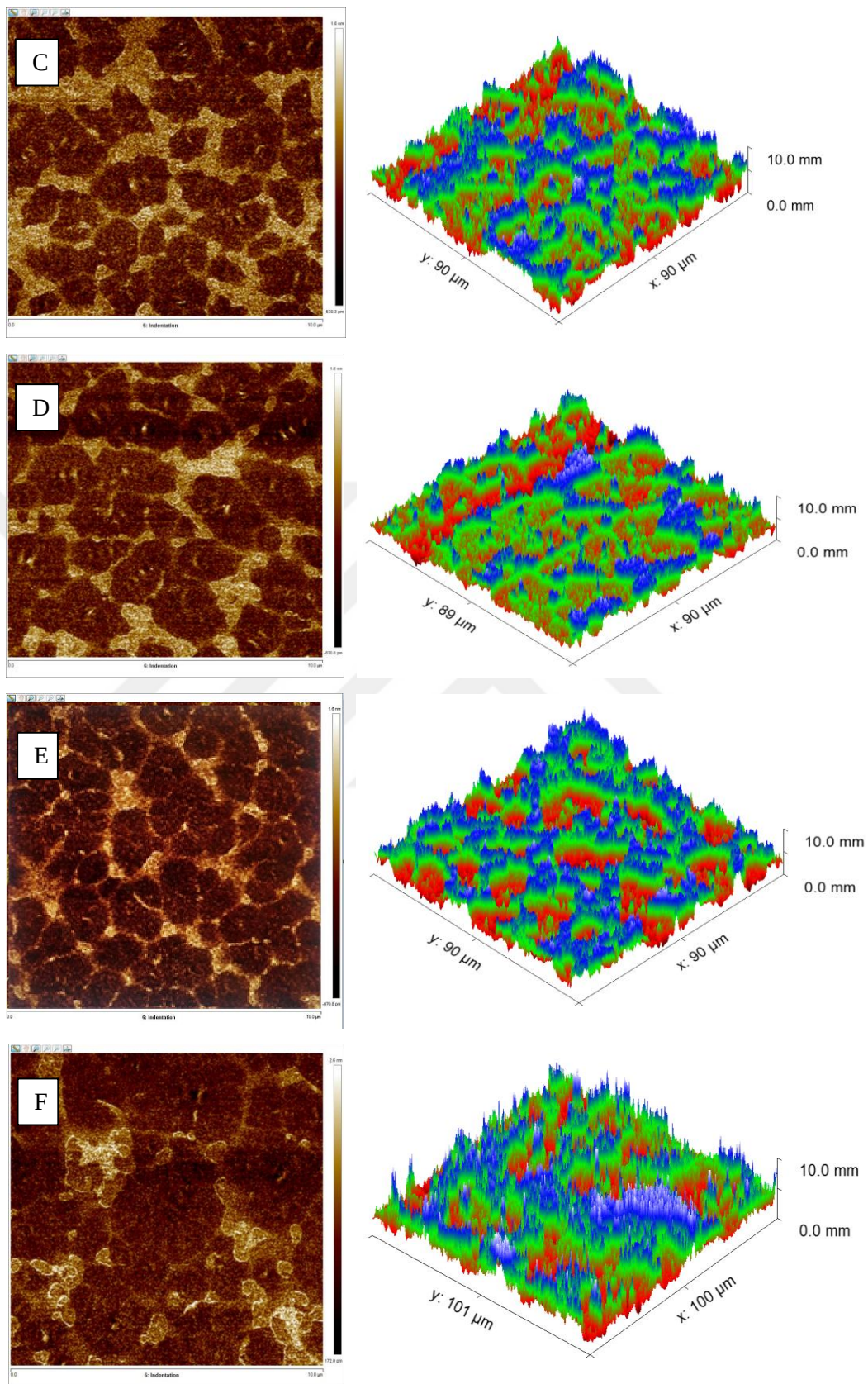


Figure 4.3 continues

From the 2D phase contrast images (on the left hand side of Figure 4.3), two separate phases can be observed, firstly the homogenous matrix and second the dispersed components in that matrix. The volume of the dark phase became to increase and phase contrast became to be more visible by the increment of mixing duration and the shearing rate. Clearly, the long term aged PMB sample (F) had the largest area of dark phases, indicating having the most asphaltene content. Since the concentration of SBS in PMB sample was constant, it can be said that, mixing conditions have a significant effect on the stiffness of the sample.

Based on the evaluation of 3D images, the variation of phases can be clearly seen in 3000-45-UA and 1000-45-UA. This fact can be explained with the hardening of the bitumen depending on the extent of aging and degradation. In this instance, it can be attributed to longer mixing time results in aging of the SBS modified bitumen.

Morphological images obtained by the height vales of the bitumens' surfaces, and the topographic properties of the samples were evaluated and presented in Figure 4.4. Based on the results, either SBS modification or using different mixing conditions caused some differences on the topographic images such as: physical appearance, distribution or amount of bee-like structures (Hofko et al., 2016; Magonov et al., 2017; Pauli et al., 2011). Amount of the bee structures belongs to each sample were analysed and the results are found as 36, 29, 33, 33, 30 and 31 for NB, 1000-15-UA, 1000-45-UA, 3000-15-UA, 3000-45-UA and %5-A, respectively. Therefore, it is possible to say that, although polymer modification decreases the amount of the bee structures, mixing conditions and long term aging did not cause a significant change. However, based on the topographic images, it is possible to say that, modification of the bitumen with polymers yielded an increase on the length and distinction of bee-like structures. In order to evaluate this phenomenon, length and the magnitude of the bee structures for each samples were obtained by Gwyddion, which is an analysing program for AFM based images, and given in Figure 4.5 a and b.

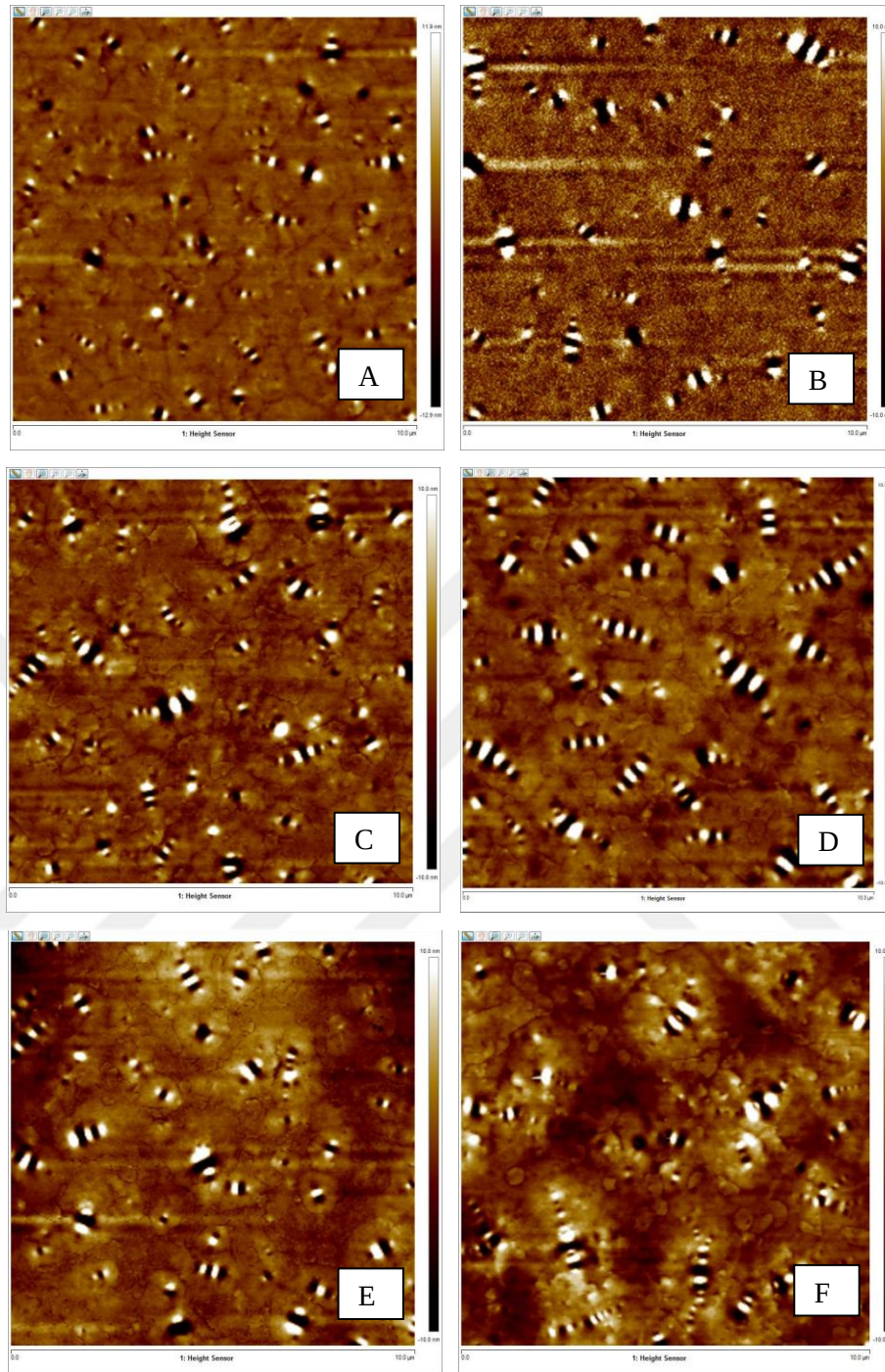


Figure 4.4 Topographic images and bee structures of all the samples (A) NB, (B) 1000-15-UA, (C) 1000-45-UA, (D) 3000-15-UA, (E) 3000-45-UA, (F) %5-A

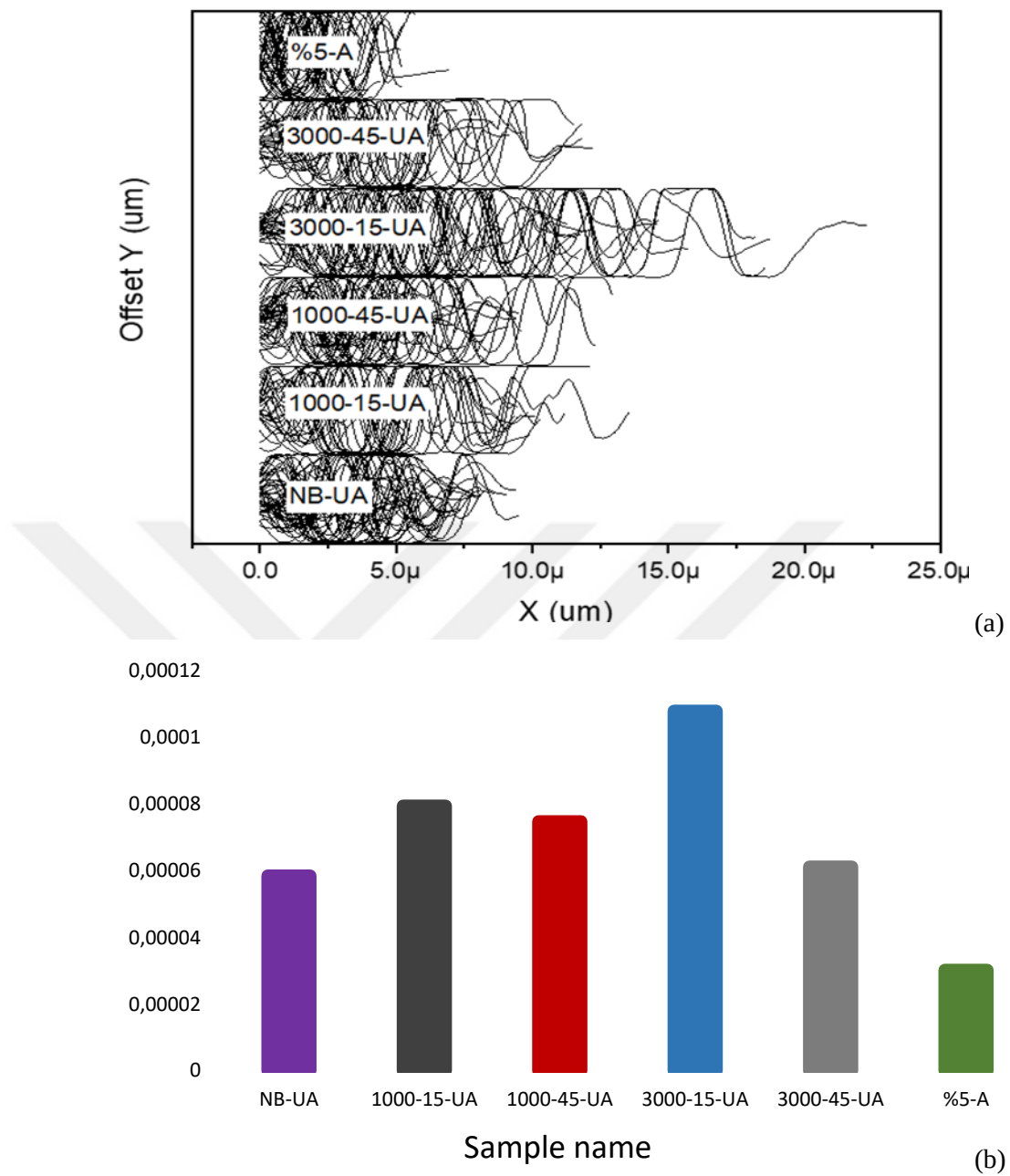


Figure 4.5 Bee structure properties of all sample (a) Length and magnitude of the all bee structures (b) Average length of bee structure for each samples

Based on the results, SBS modification had some effects on the length of the bee like structures. 3000-15-UA had the longest bee structures among the samples, therefore, it can be concluded that, 3000 rpm and 15 min provide the optimum mixing conditions in order to have the benefits of SBS copolymer. Due to the fact that 3000-15-UA has longer bee structures than 1000-15-UA, it may be assumed that, the SBS do not absorb the oily components of the bitumen under 1000 rpm, due to the

inadequate mixing conditions. However, this idea should be validated by further investigations. Aging influences were observed by the decreasing length of the bee structure, with the fact that %5-A had the shortest bee structures. Concurrently, 3000-45-UA and 1000-45-UA had shorter bee structures, when compared with 3000-15-UA and 1000-15-UA. This results might be clarified with the aging effects of longer mixing duration.

4.2 Rheological Characterisation Results

Rheological investigations were conducted by two different rheometers, Oscillation rheometer (OR) and Dynamic shear Rheometer (DSR). Master curves, black diagrams, cole- cole plots investigations and determination of performance grade were accomplished by OR while, fatigue cracking and zero shear viscosity experiments were performed by DSR. All the results were given within this section.

4.2.1 Master Curves

The horizontal shifting factor (aT) was determined by the Arrhenius-like equation (Equation 3.5) to yield the information about the temperature susceptibility of the sample. The activation energy is governed by the molecular properties of the polymer, such as molecular weight, tacticity, and the level of chain branching in the polymer, all related to the temperature susceptibility (Ait-Kadi et al., 1996; Di Benedetto et al., 2011; Ferry, 1980; Garcia-Morales et al., 2004; Liang, et al., 2015).

In this study, a reference temperature of 60 °C was selected, since the rheological experiments were conducted over the range of 40 °C, 50 °C, 60 °C, 70 °C and 80°C. The complex modulus versus frequency plots at different temperatures, were shifted in order to obtain a linear curve with the lowest standard deviation. Figure 4.6 shows the master curves of the neat bitumen (NB), the unaged PMB samples and the long-term aged PMB samples, in order to extract the effects of aging on the viscoelastic behaviour of the PMB samples.

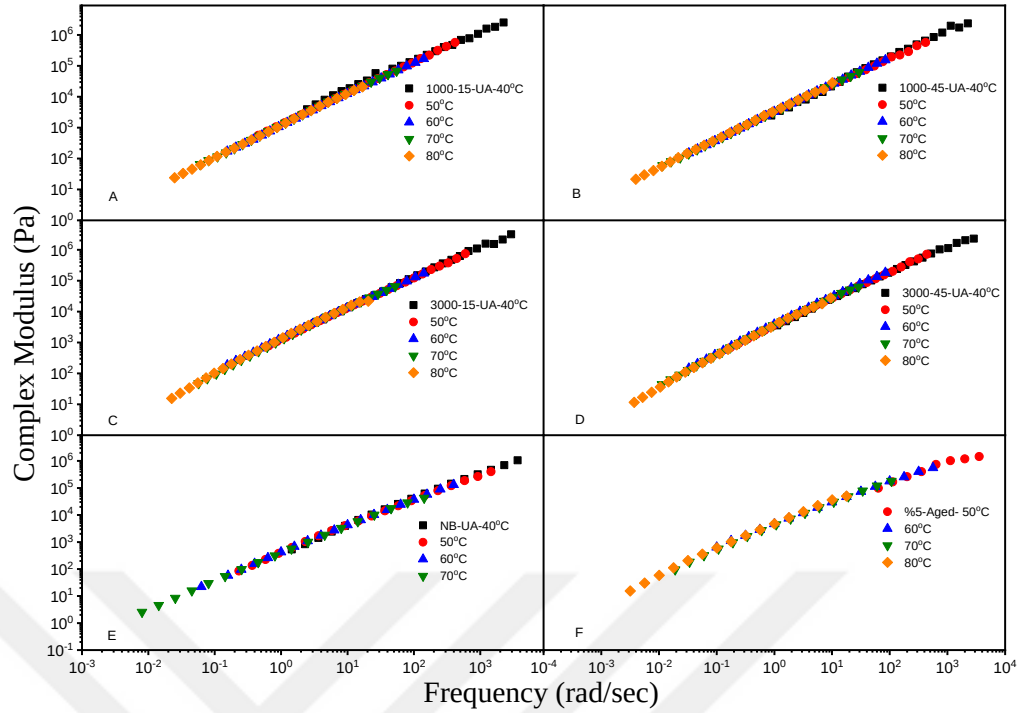


Figure 4.6 Master curves for SBS-bitumen blends produced at A) 1000 rpm and 15 min., B) at 1000 rpm and 45 min., C) at 3000 rpm and 15 min., D) at 3000 rpm and 45 min., E) NB and F) for long term aged sample

If $\log(\alpha_T)$ is plotted as a function of temperature, by using the corresponding Kelvin (K) values for temperature ($^{\circ}\text{C}$) used in the experiment, the activation energy of the each SBS modified bitumen, can be obtained by using the following equations, with the slope (s) and intercept (i) values of a linear curve (Liang et al., 2015).

$$E_a = 2.303R_s \quad (4.1)$$

$$E_a = 2.303RT_0 \quad (4.2)$$

The values used for the calculation of the activation energy for each sample and neat bitumen were obtained from Figure 4.7.

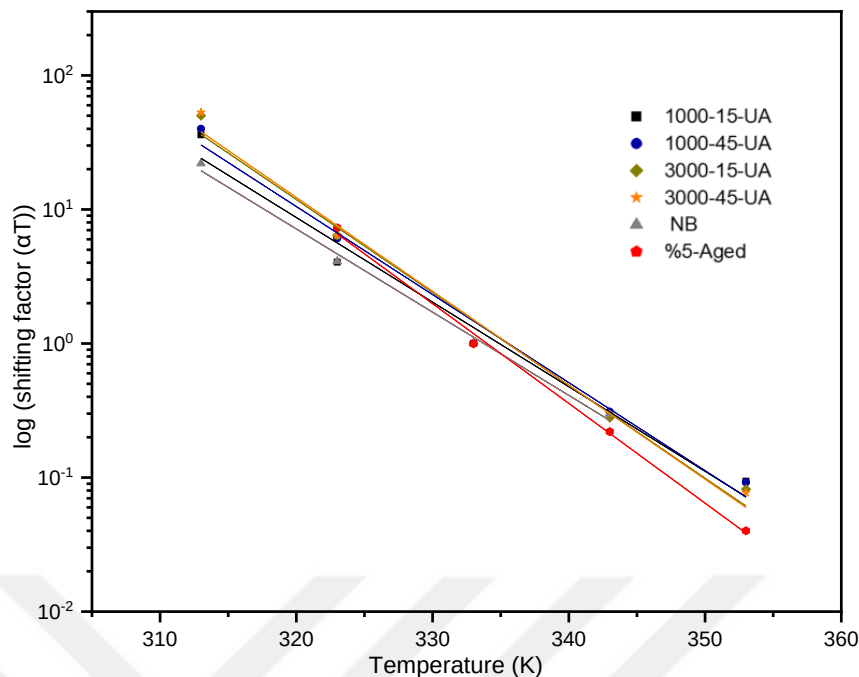


Figure 4.7 Plot of shift factor as a function of temperature

It is generally accepted that aging increases polymer chain stiffness and consequently the activation flow energy (Daga & Wagner, 2006). Similar statement can clearly be made by the plots presented in Figure 4.7. Neat bitumen had the lowest slope value followed by unaged and then the long-term aged samples, respectively. Moreover, the SBS-bitumen samples produced using the higher shearing rate and longer mixing time yielded the higher slope values. The activation energies for flow for all samples were calculated and are listed in Table 4.2. It can be seen from this data that neat bitumen has the lowest activation energy, whereas the more aged PMB samples have higher activation energy, due to higher chain stiffness.

Table 4.2 Values for the activation energy for flow calculated from shift factors

	Sample Name					
	1000-15	1000-45	3000-15	3000-45	NB	5%-Aged
Activation Energy E_a (KJ/mol)	120.8	125.8	128.6	134.1	118.7	142.5

4.2.2 Black Diagrams

The black diagrams for the SBS modified bitumen samples produced under different mixing conditions are shown in Figure 4.8.

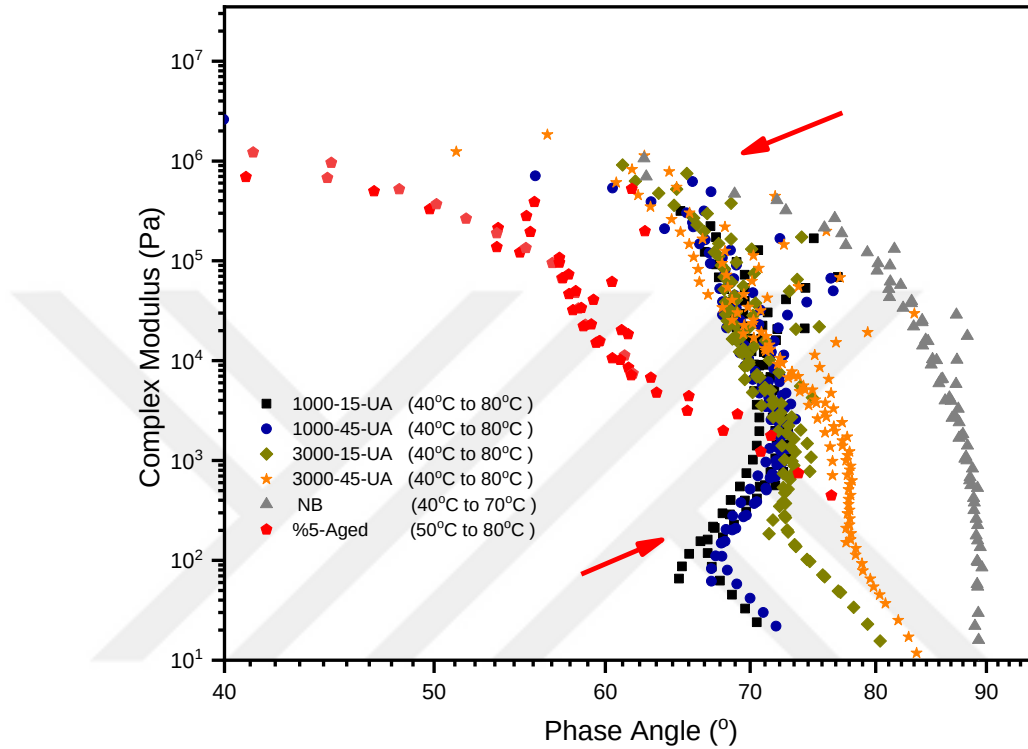


Figure 4.8 Black diagrams (i.e. complex modulus vs phase angle) for SBS modified bitumen produced using different mixing conditions

It can be seen from Figure 4.8 that, neat bitumen has the highest phase angle values for each temperature attributed to the more viscous behaviour of this material. Moreover, neat bitumen has a smoother continuous curve in comparison with the SBS modified bitumen samples, which can be explained with the thermo-rheological simplicity of unmodified bitumen (Mturi et al., 2014). Additionally, higher phase angle values corresponding to the same complex modulus values, were obtained, by increasing both the shearing rate and the mixing time. The elasticity of the SBS modified bitumen samples, changed with the variation in mixing conditions, which is associated with the aging. The phase angle values decreased for the same complex modulus value due to aging at low temperatures, while at high temperatures the phase angle values tend to approach 90° . This behaviour is derived from the gel-like structure

of the bitumen (Mturi et al., 2014). The SBS modified bitumen samples display more viscous behaviour at high temperatures but exhibit elastic behaviour at low temperature with increasing shear rate and mixing time and. This is related to the influence of mixing conditions on aging characteristics of the samples. The black diagram for the long term aged sample was more horizontal having both the lowest phase angle value at high temperatures and the highest value at low temperatures among all samples studied, confirming the relationship between effects of aging and mixing conditions.

4.2.3 Cole-Cole Plots

Figure 4.9 shows the Cole-Cole plots for the SBS modified bitumen samples (reference temperature 60°C), and reveal the effects of different mixing conditions (aging) on the absorption of SBS by the bitumen. As can be seen from the shape of the curves, it can be concluded that, the same shear rates and mixing times result in similar compatibility between blend components.

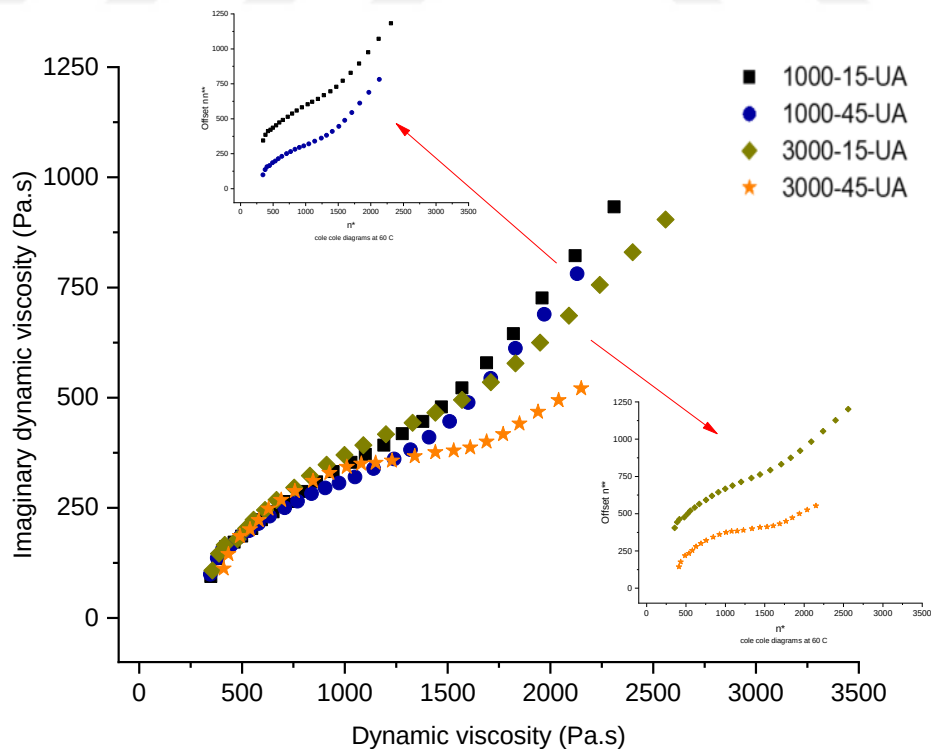


Figure 4.9 Cole-Cole plots for SBS modified bitumen samples produced under different mixing conditions

4.2.4 Determination of the 'Performance Grade'

Figure 4.10 shows the plots of $G^*/\sin(\delta)$ as a function of temperature for SBS modified and neat bitumen samples.

As can be seen from Figure 4.10, the $G^*/\sin(\delta)$ value decreased with increasing temperature for all samples, as expected. PG value for neat bitumen was obtained as 70, while it was 82 for both unaged and long term aged samples. For the unaged SBS modified bitumen samples, different mixing conditions did not result in a significant change in the PG temperature. Although it is possible to conclude that, the temperature corresponding to 1 kPa on the $G^*/\sin(\delta)$ axis increased with higher shear rates and longer mixing times, as a consequence of increased oxidation during the modification process. The long term aged SBS modified bitumen had the highest $T_{G^*/\sin\delta (10 \text{ rad/s})}$ value corresponding 1 kPa, demonstrating the effect of aging on the viscoelastic behaviour of SBS modified bitumen. The results are summarized in Table 4.3 for all samples. The effect of both SBS addition to neat bitumen and aging can be seen to result in increased $G^*/\sin(\delta)$ at any given temperature.

Table 4.3 SHRP PG criteria determined at different mixing conditions for PMB and NB samples

	Sample Name					
	1000-15	1000-45	3000-15	3000-45	NB	5% SBS-Aged
$T_{G^*/\sin\delta (10 \text{ rad/s})}$ corresponding 1 kPa	81.9	82.9	82.7	83.52	69.93	-
$T_{G^*/\sin\delta (10 \text{ rad/s})}$ corresponding 2.2 kPa	-	-	-	-	-	83.1

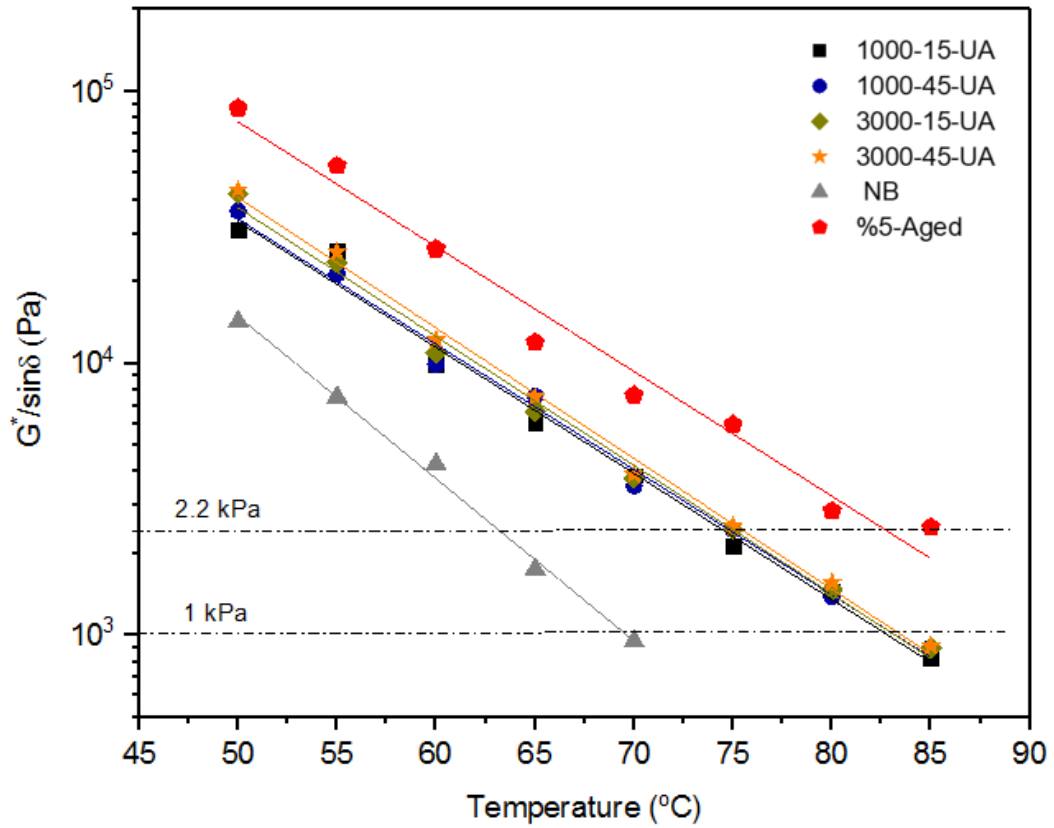


Figure 4.10 Plot of $G^*/\sin(\delta)$ as a function of temperature showing the PG values for neat bitumen, SBS modified bitumen and the long term aged SBS modified bitumen samples

4.2.5 Fatigue Cracking Test Results

Figure 4.11 is presented in order to investigate the mixing conditions effects on the fatigue cracking resistance. The decrease in fatigue-cracking parameter is clearly seen by increasing temperature, which is due to the bitumen's viscoelastic behaviour. Moreover, it can be said that, samples produced, with the same duration, yield similar fatigue behaviour more than the samples produced with the same shearing rates in. Samples produced by longer mixing duration provided higher fatigue parameter, this can be associated with being stiffer due to the aging.

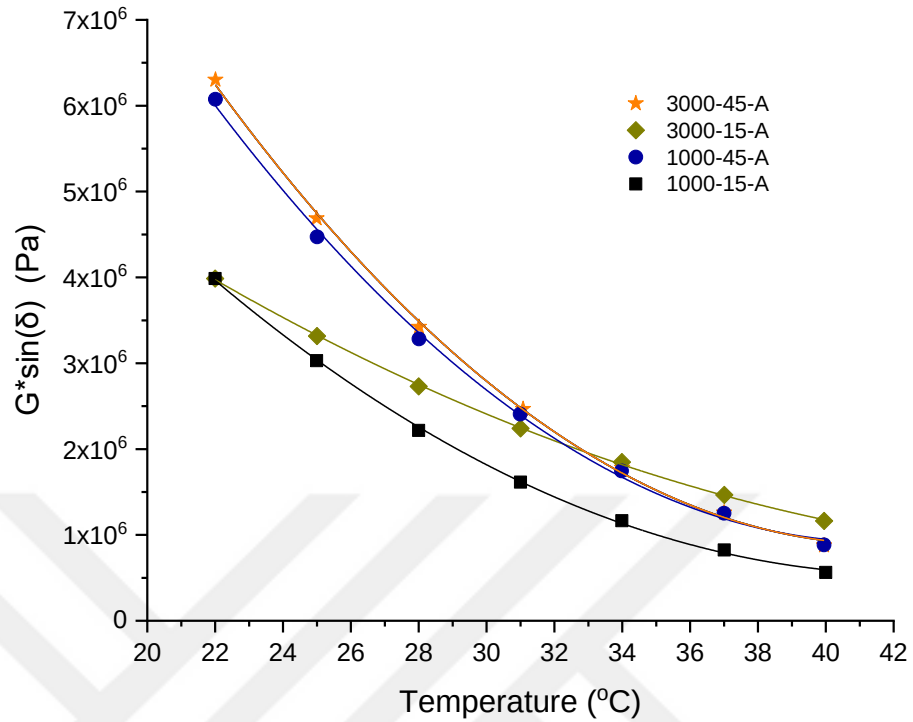


Figure 4.11 $G^*\sin(\delta)$ values for PMB samples at different temperature

4.2.6 Zero Shear Viscosity Test Results (ZSV)

A higher ZSV value indicates higher resistance to permanent deformation under long-term loading. Figure 4.12 illustrates the ZSV results of all unaged and long term aged samples.

As illustrated in Figure 4.12 SBS modified bitumen samples have higher ZSV results compared to neat bitumen for both unaged and aged samples. On the other hand, aging yielded higher ZSV value. Mixing conditions have slightly changed the results and higher ZSV values were obtained by higher shearing rates and longer durations. ZSV results are in compatible with the previous result and support to aging effect of higher shearing rates and longer duration of mixing.

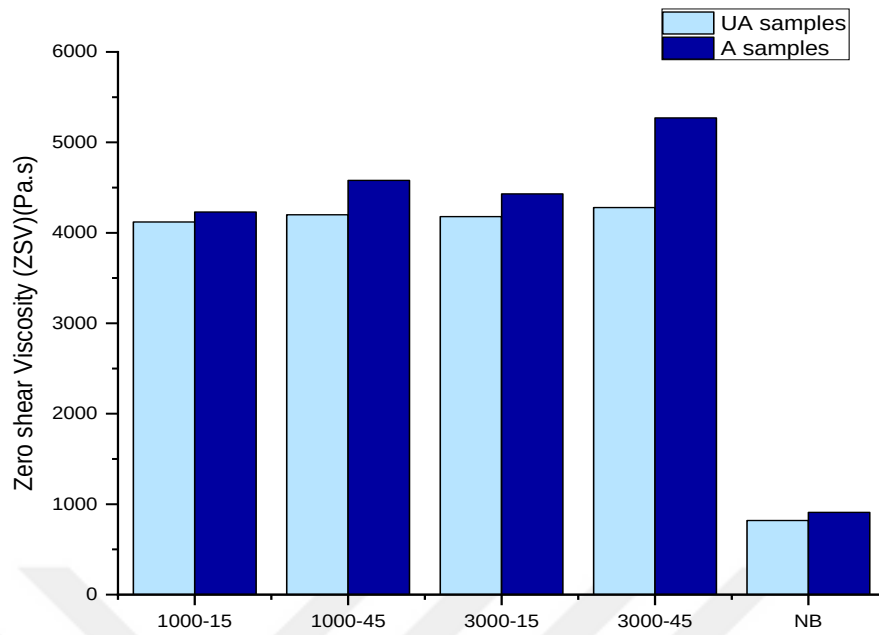


Figure 4.12 ZSV values for all the tested bitumen samples

4.3 Morphological Results

Morphological characterisation of neat and PMB samples were conducted by using Optical Microscopy and Confocal Laser Scanning Microscopy. All the morphological images were given with the discussion.

4.3.1 Optical Microscopy Results

Optical microscopy is incapable of investigating the fluorescence intensities of the samples; therefore, only unaged PMB samples were examined by OM in order to observe the extent of SBS dispersion and bitumen phases separately. The morphological images of the unaged PMB samples were taken with 40× of magnification by using a Blue Filter which can be seen in Figures 4.13 to 4.21. Ten different specimen of each sample were prepared and analysed under OM.

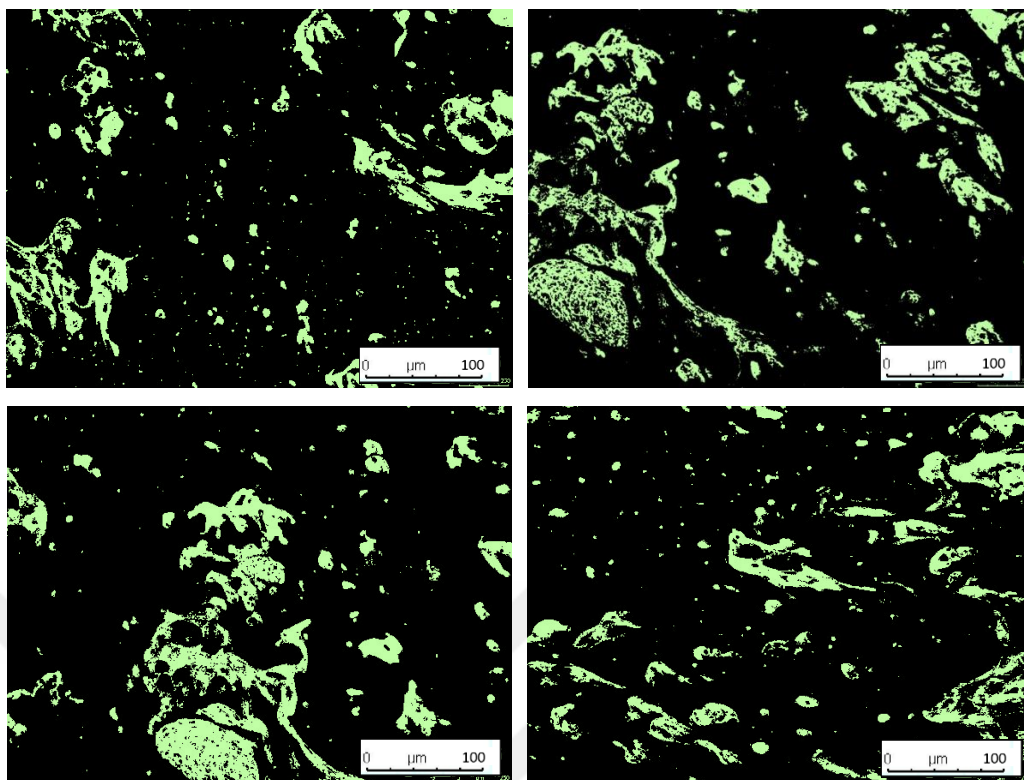


Figure 4.13 Representative OM images taken at $\times 40$, showing the morphology of 1000-15-UA

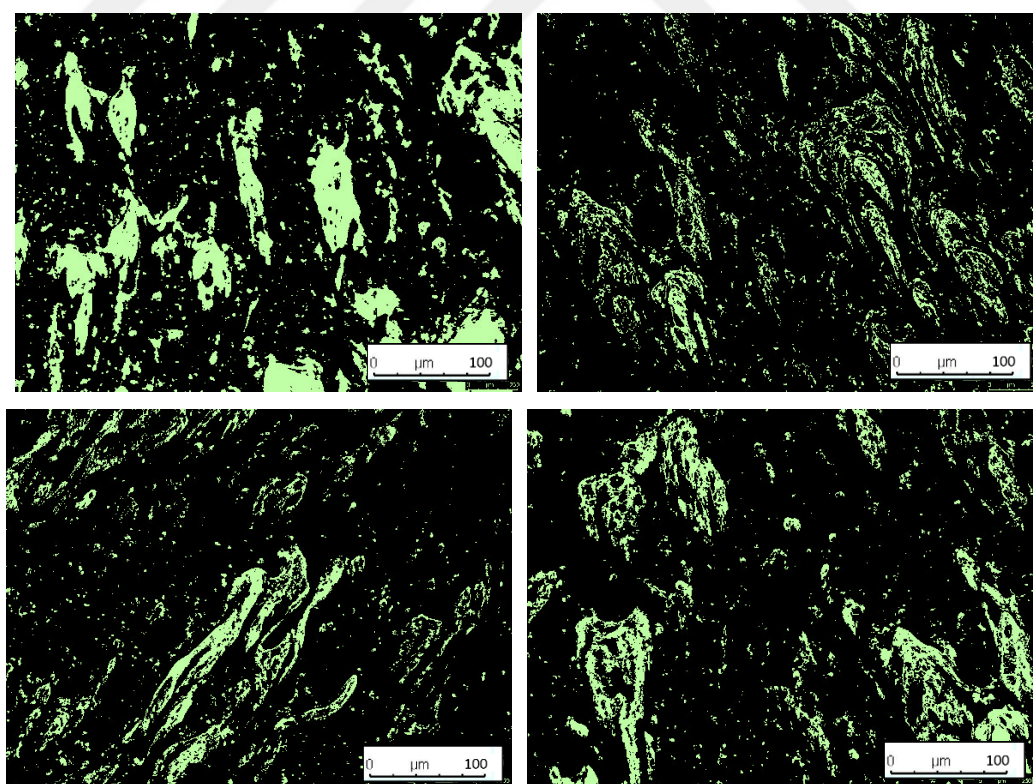


Figure 4.14 Representative OM images taken at $\times 40$, showing the morphology of 1000-45-UA

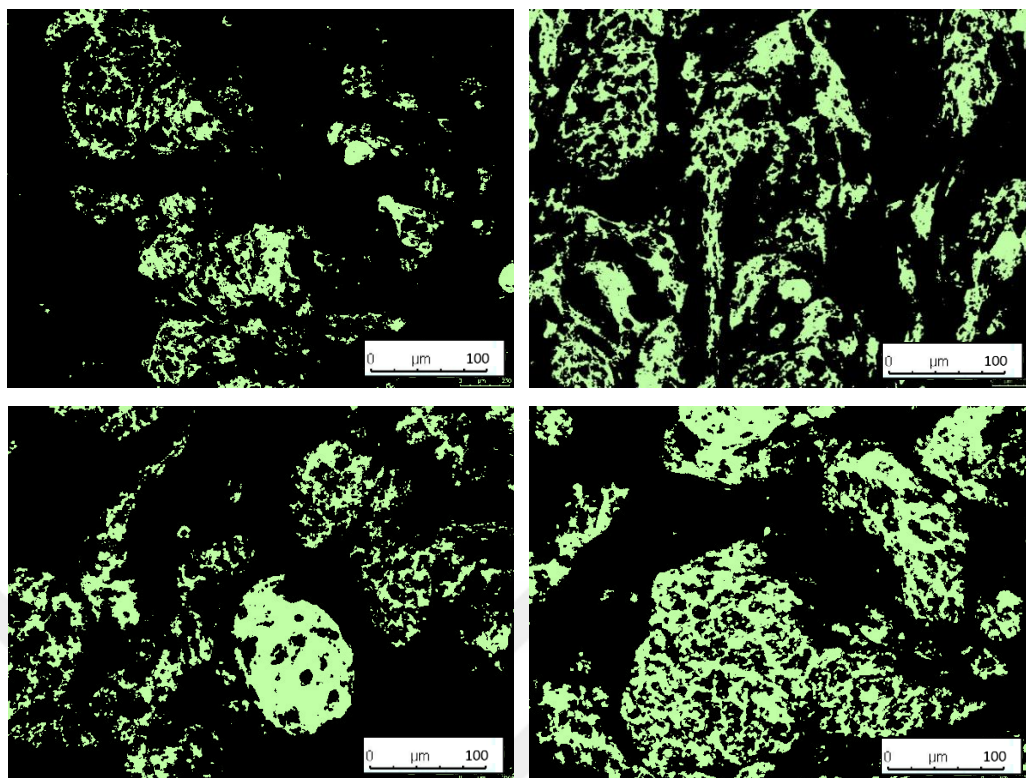


Figure 4.15 Representative OM images taken at $\times 40$, showing the morphology of 3000-15-UA

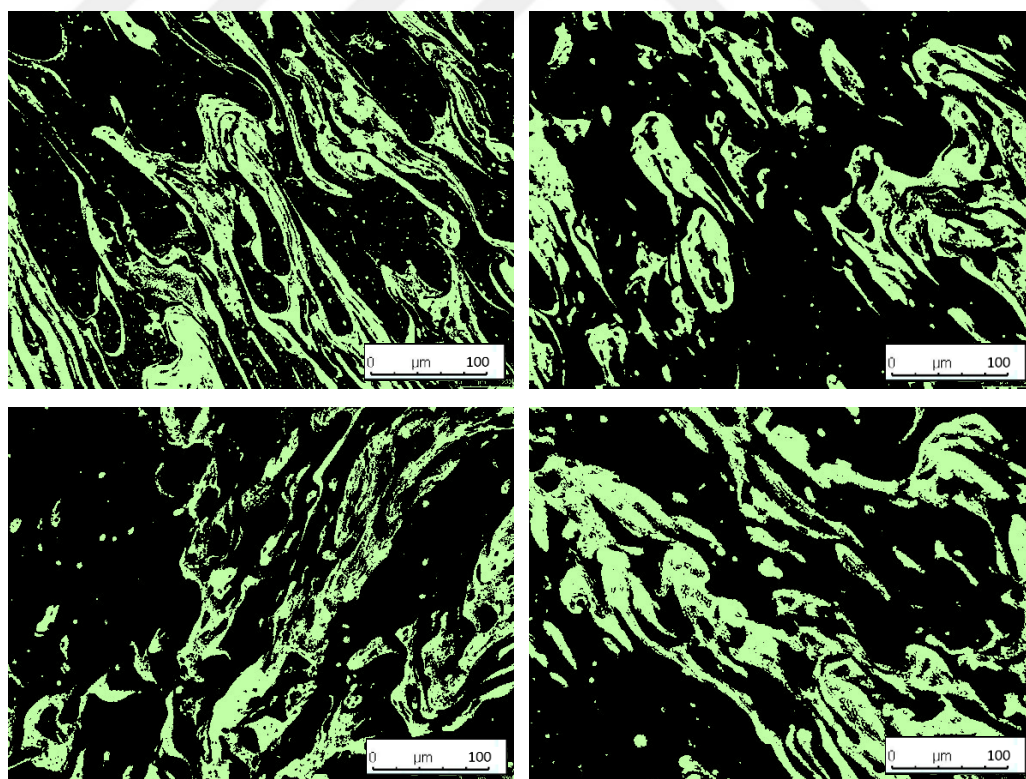


Figure 4.16 Representative OM images taken at $\times 40$, showing the morphology of 3000-45-UA

As can be seen from the captured images, significant changes in morphology are obtained for the different mixing times and shear rates. The SBS copolymer (green colour) is much better dispersed and distributed in the bitumen phase, when the blend was mixed for 45 min compared to 15 min duration and for both shearing rates (1000 rpm and 3000 rpm). Conversely, when the difference in shearing rate was taken into account (at constant mixing time for either 15 min or 45 min), the size of the fluorescence phase increased and is associated with the absorption of bitumen by the SBS. On this basis, it is possible to conclude that the longer the mixing time the more homogeneous SBS phase is obtained, whereas for higher shearing rates increased the absorption of the asphaltenes by SBS results. Figure 4.17 shows the morphologies of each unaged PMB taken at $\times 200$ in order to examine the inclusion of the asphaltenes inside the SBS copolymer phase.

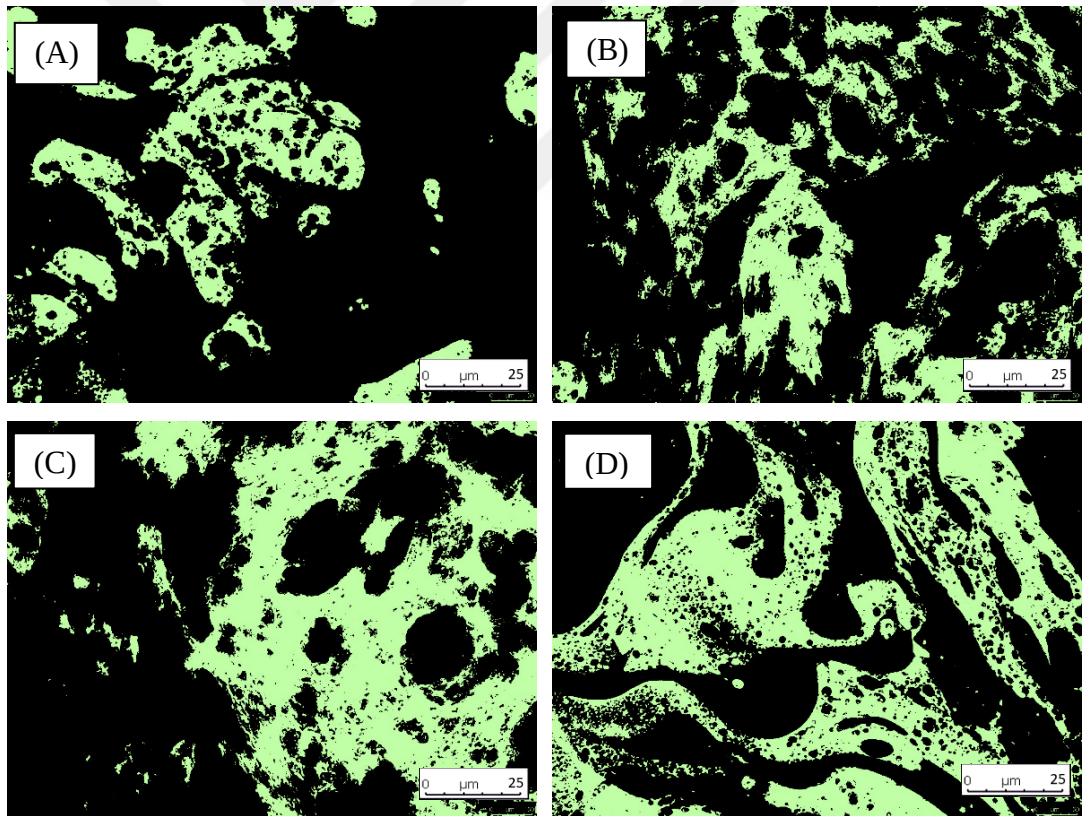


Figure 4.17 OM images taken at $\times 200$ (A) 1000-15-UA, (B) 1000-45-UA, (C) 3000-15-UA and (D) 3000-45-UA

By comparing the ratio of the green area (SBS rich phase) to the black area (bitumen rich phase), it can be observed that the greater the shearing rate and mixing time the

greater the absorbance of SBS, since the SBS phase (green) is more dominant with increasing mixing time and shearing rate. ImageJ software was employed to determine the ratio of both phases and the results were presented in Table 4.4 and Figure 4.18.

Table 4.4 Distribution of SBS and bitumen phases in PMB samples

Sample Name	SBS dispersion in PMB (%)	Bitumen dispersion in PMB (%)
1000-15-UA	18.77	81.23
1000-45-UA	31.19	68.81
3000-15-UA	34.66	65.34
3000-45-UA	40.06	59.94

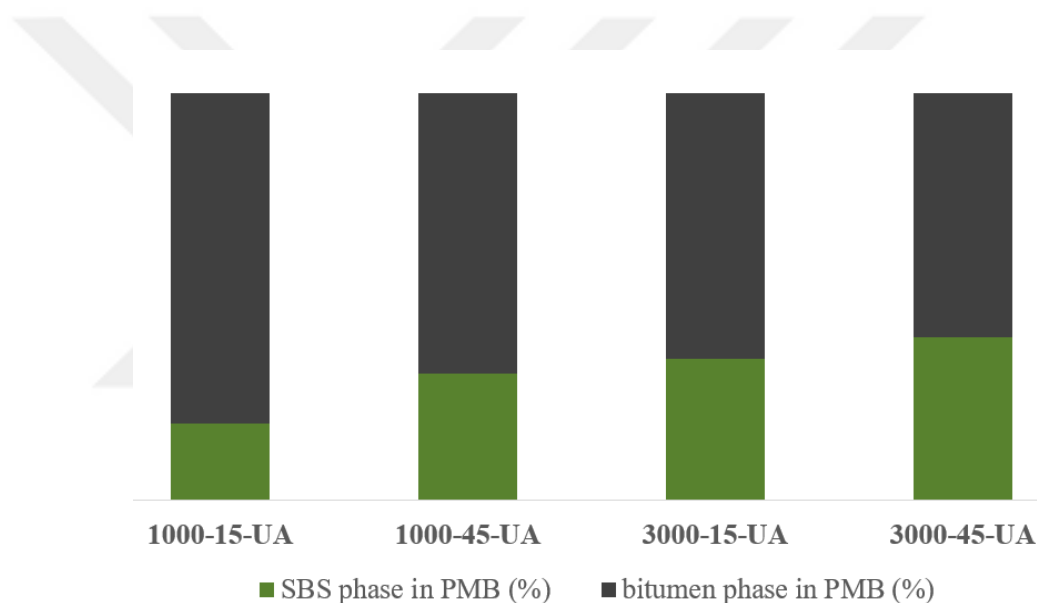


Figure 4.18 Relative ratio and distribution of SBS and bitumen phases in PMB samples

Based on the data, with increasing mixing time and/or shear rate, the extent of SBS dispersion increases in the blend, however the major phase is always bitumen phase. The swelling ratio of SBS for all PMB samples can be calculated by dividing the final level of SBS dispersion (%) by the initial SBS rate (5% by weight). Consequently, the swelling ratios for the various blends are 3.75, 6.23, 6.93, and 8.01 for 1000-15-UA, 1000-45-UA, 3000-15-UA and 3000-45-UA, respectively. Clearly, the production of the PMB using a combination of 1000 rpm and 15 min mixing time was not effective to promote SBS interaction with the asphaltenes fraction and swell. Increasing the mixing time to 45 min was more effective and the SBS phase was much more swollen.

For the PMB samples, produced with 1000rpm 45min and 3000rpm-15min shearing rate is more influential compared with the mixing time, since 3000-15-UA had a greater SBS phase in the blend. However, a combination of 3000rpm and 45 min mixing time resulted in the highest level of SBS swelling by asphaltenes, ~60%.

4.3.2 Confocal Laser Scanning Microscopy Results

Both mixing time and shear rate are critical in controlling the extent of bitumen modification, since both parameters influence the level of SBS dispersion in the bitumen matrix and the aging properties of the PMB blend formed. As presented in Figure 4.19, CLSM was used to assess the aging effects of mixing conditions on PMB morphology of both neat and modified bitumen with the corresponding 3D colour maps of fluorescence intensities.

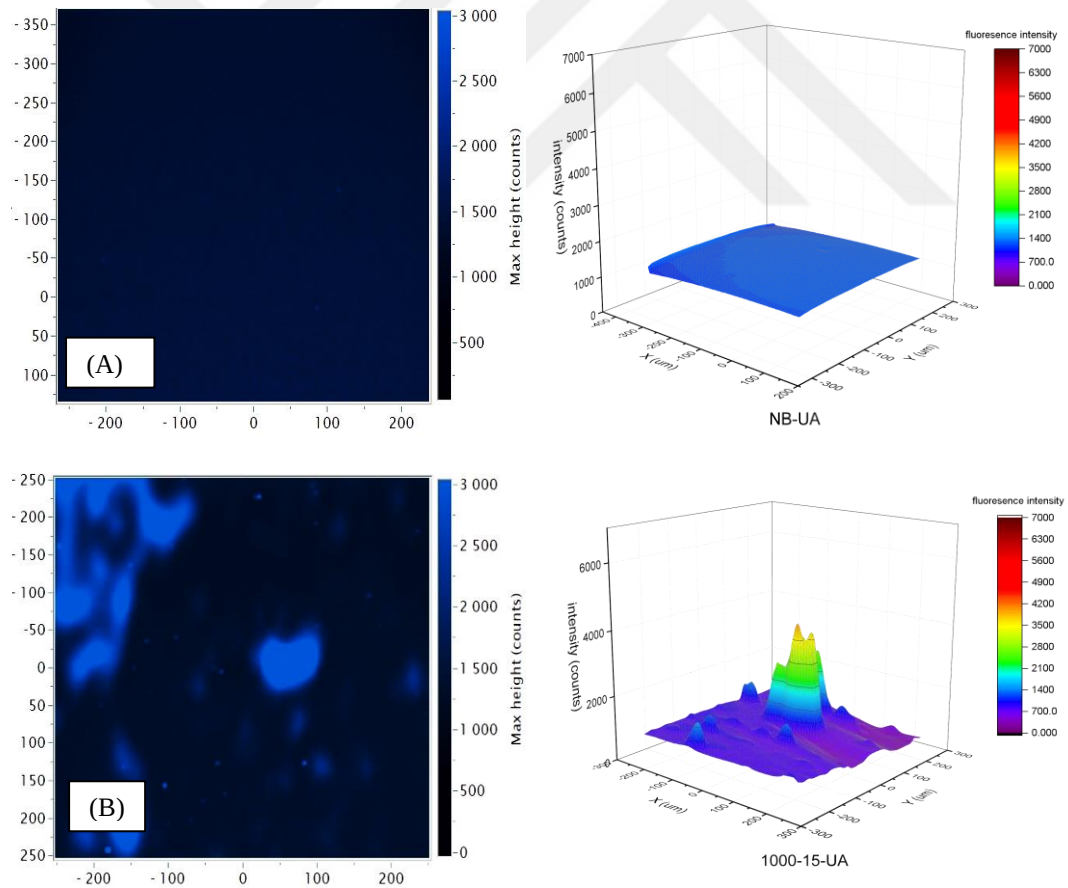


Figure 4.19 CLSM images and corresponding 3D colour maps of fluorescence intensity of SBS based PMB samples, (A) NB, (B) 1000-15-UA, (C) 1000-45-UA, (D) 3000-15-UA and (E) 3000-45-UA.

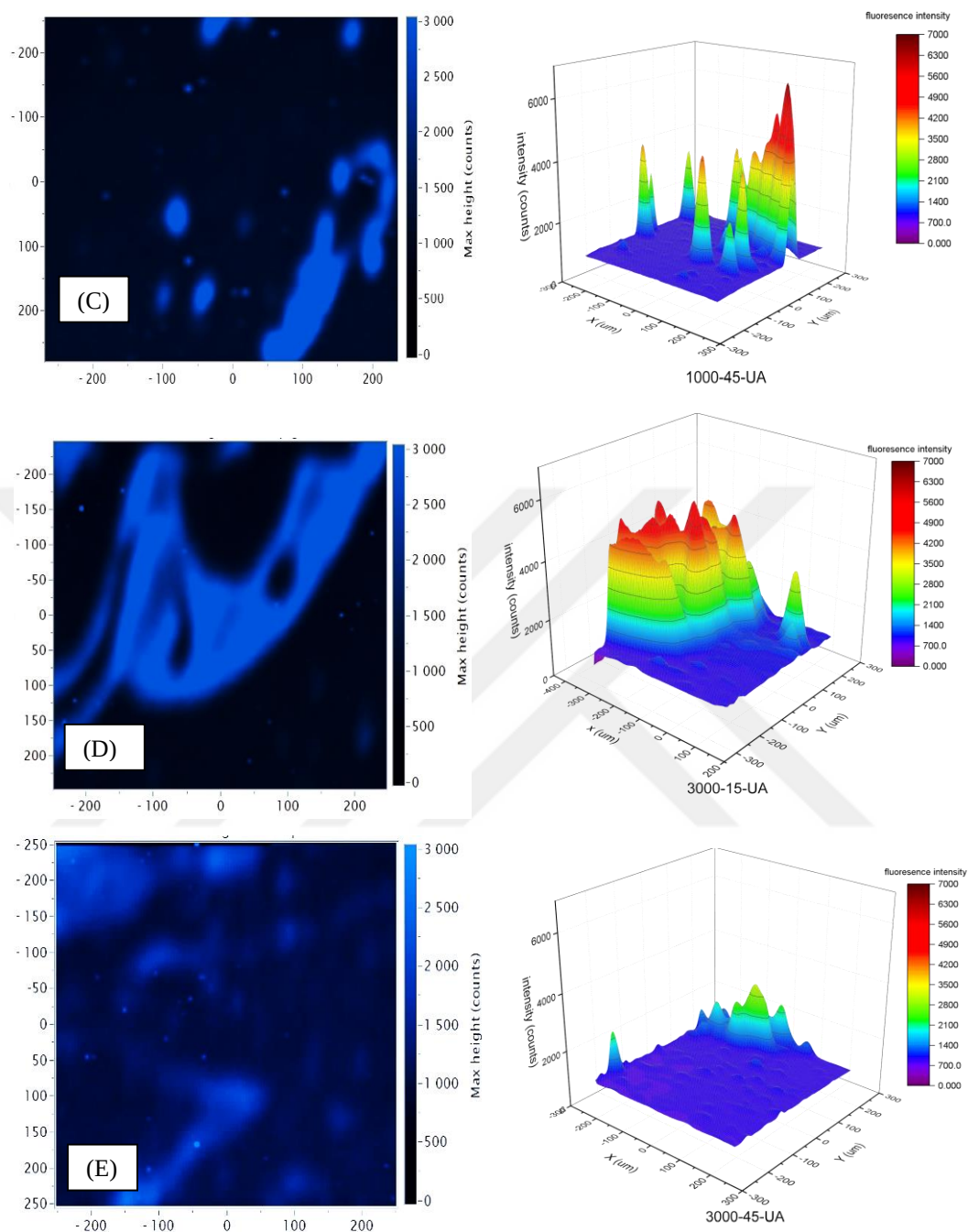


Figure 4.19 continues

As can be seen in Figure 4.19, (A) for neat bitumen, no morphological features are observed. However, while the resin and asphaltene fractions of bitumen do not fluoresce the, saturates and aromatic fractions do. These fractions are homogenously dispersed and a uniform fluorescence intensity, between 1200 and 1300 counts is measured, since all the components were well mixed at the surface of the bitumen

(SARA) and not locally. In contrast, modification of neat bitumen with SBS or altering the mixing conditions (time and/or shear rate) during the production of the PMBs, results in a change of phase morphology as seen from the change in fluorescence properties of the PMB samples, see Figures 4.19 (B) through (E). As the SBS is added to the bitumen local regions of inhomogeneous dispersion, can be seen with corresponding local increases in fluorescence intensities associated with SBS. Although the SBS phase for all PMB samples had significantly high fluorescence, the bitumen phases were less intense (800-900 count), due to the absorption of the fluorescence fractions of the bitumen (aromatics and saturates) by the styrene (PS) and butadiene (PB) phases of SBS. For the PMB samples, 1000-15-UA had the least SBS phase detected, in line with the OM results. 1000-45-UA and 3000-15-UA had the higher fluorescence intensities, compared to other samples. 3000-45-UA had the lowest intensities even though it had greater SBS phase compared to 1000-15-UA considering the morphology images in Figure 4.19. Aging effects through the application of higher shearing rates or longer mixing times could explain this behaviour, but this hypothesis should be clarified by further investigation. Therefore, the PMB samples were subjected to long-term aging, by using a pressure aging vessel (PAV, 100° C at 2.10MPa for 20 hours) to simulate aging, during service life of a pavement and in order to observe any exaggerated aging effects on the fluorescence intensities from CLSM experiments, see Figure 4.20.

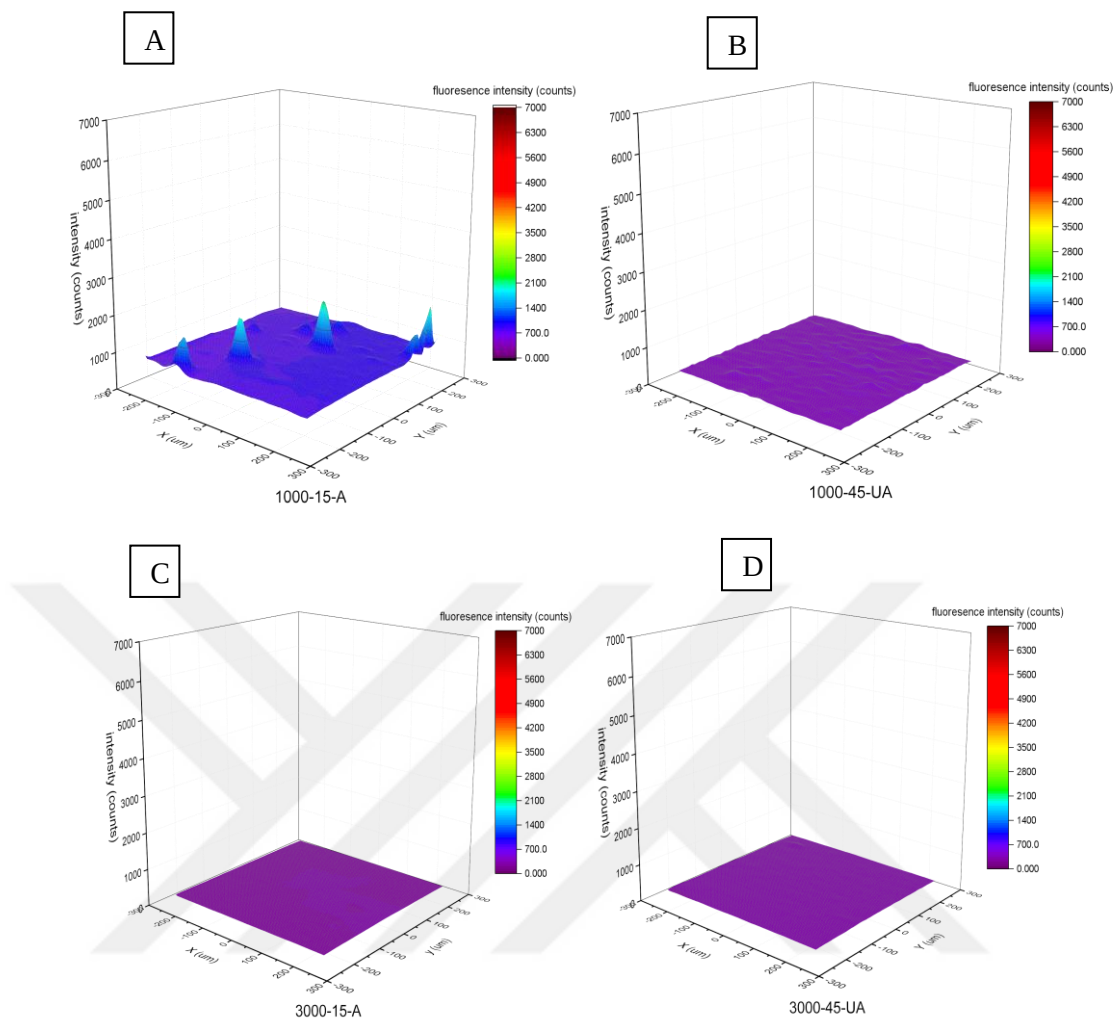


Figure 4.20 3D colour maps of fluorescence intensity for the PAV aged PMB samples (A) 1000-15-A, (B) 1000-45-A, (C) 3000-15-A and (D) 3000-45-A

As can be seen from the 3D colour maps of all four samples in Figure 4.20, PAV aging resulted in decreased fluorescence intensities for the bitumen phase compared with the unaged samples. Interestingly, the 1000-15-A had the highest fluorescence among all aged samples. Given the PAV methodology does not include a mixing component, it may be assumed that the SBS copolymer interacted poorly, with the bitumen, highlighting the importance of shear rate and mixing on the properties of SBS modified bitumen. However, more extensive experiments are required to support this hypothesis.

4.4 Thermal Characterisation Results

Thermal characterisation and the behaviour of neat and PMB samples were inquired by TGA and Modulated DSC are given in this section.

4.4.1 TGA Results

Figure 4.21 and 4.22 show the TGA and DTA curves for un-aged neat bitumen, SBS and SBS modified bitumen, respectively. From these curves the onset degradation temperature (T_i), maximum decomposition temperature (T_{max}) and the yield of charred residue were determined, as presented in Table 4.5.

Table 4.5 TGA/DTG results for unaged SBS, neat bitumen and SBS modified bitumen

Samples	T_i (°C)	T_{10} wt% (°C)	T_{50} wt% (°C)	T_{max} (°C)	Residue at 800 °C (wt%)
NB-UA	266.7	374.2	447.8	453.8	13.3
1000-15-UA	279.7	378.8	449.0	448.2	12.5
1000-45-UA	283.5	360.8	437.5	445.7	9.5
3000-15-UA	260.3	349.2	433.8	445.0	11.9
3000-45-UA	207.0	355.3	437.7	446.2	12.1
SBS	283.5	399.5	448.5	450.0	3.7

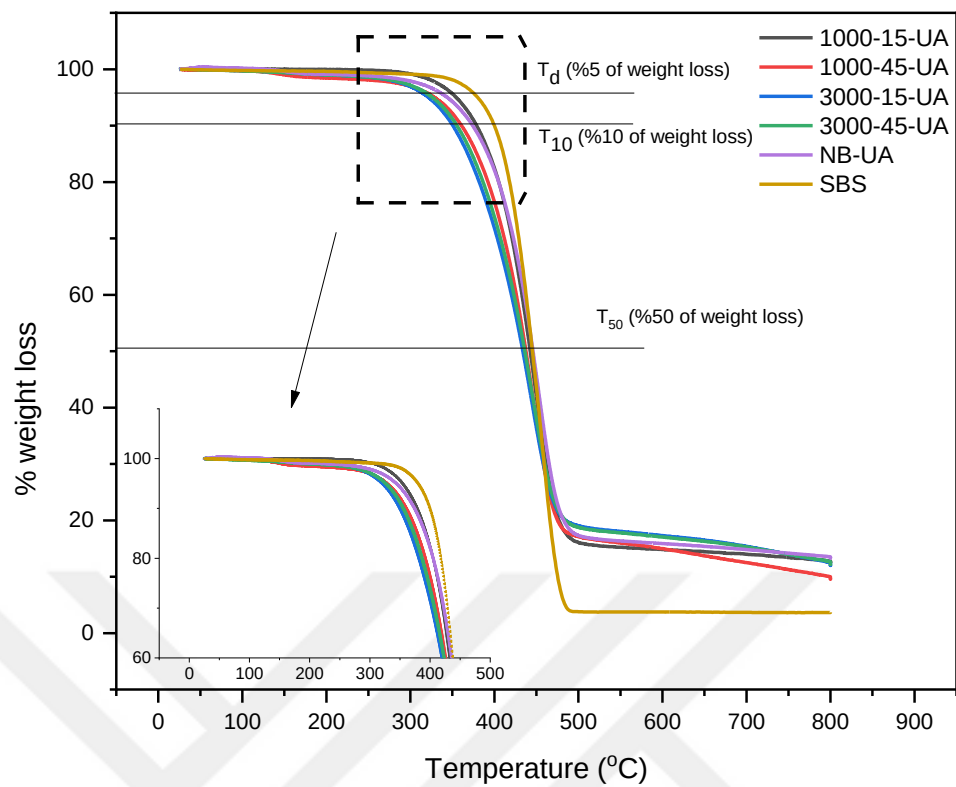


Figure 4.21 TGA graphs of PMB samples

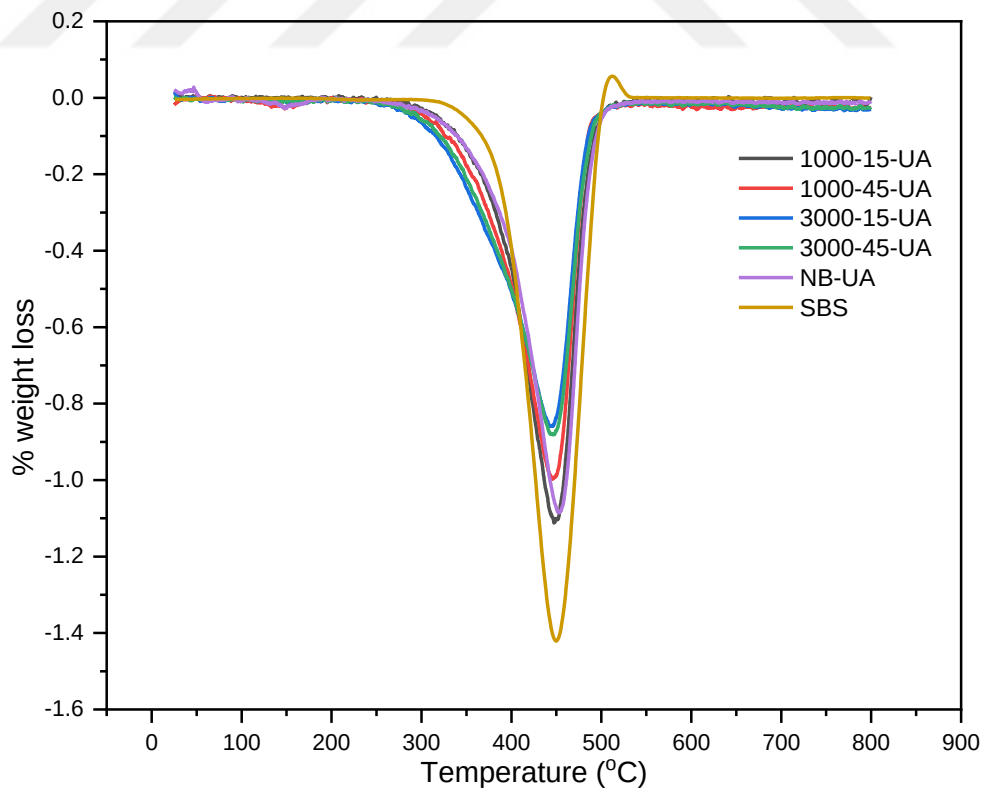


Figure 4.22 DTA graphs of PMB samples

At 800°C, SBS had the lowest char residue at 3.7 wt%, while neat bitumen had the highest at 13.3 wt% and for the SBS modified bitumen samples values were between them. It would appear that, addition of SBS enhanced the thermal stability of the neat bitumen (Naskar et al., 2010). The 1000-15-UA sample had a higher residue content, in comparison with 1000-45-UA, which is due to insufficient mixing time and limited dispersion of the bitumen components. This blend behaved more like neat bitumen. Interestingly, T_i increased for these blends, before decreasing below that for both unaged neat bitumen and SBS alone, when the shear rate was increased to 3000 rpm, where again the residual char content was constant at about 12 wt% as a consequence of oxidative cross-linking during mixing. The effect of varying mixing conditions (i.e. mixing time and shear rate) on the performance of SBS modified bitumen was also investigated, by performing TGA experiments on long term aged (simulated) samples (Figure 4.23 and 4.24).

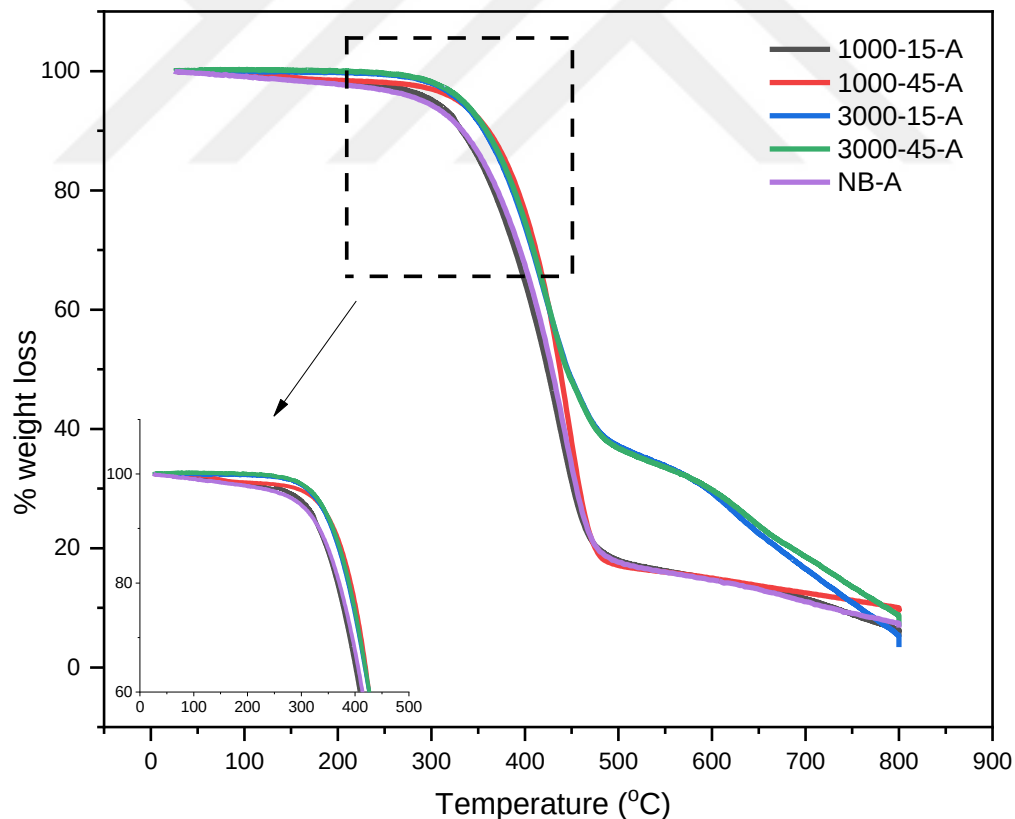


Figure 4.23 TGA graphs of long term aged PMB samples

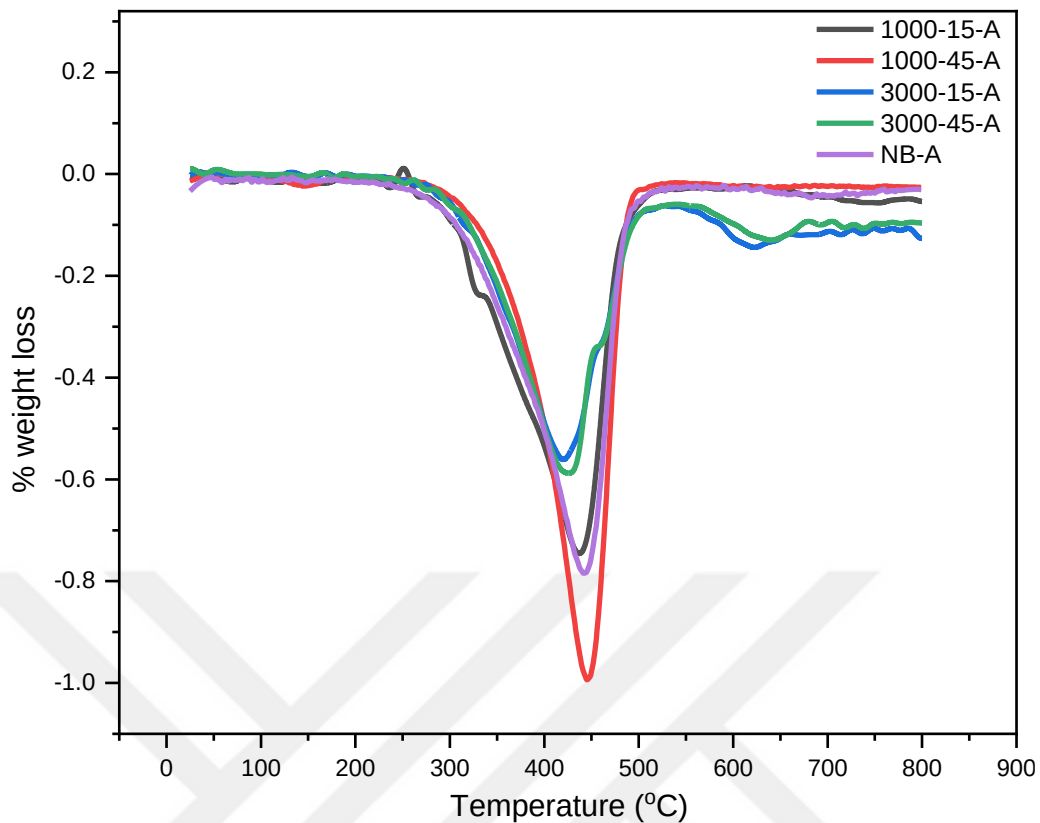


Figure 4.24 DTG graphs of long term aged PMB samples

From both the TGA and DTG curves, it can be seen that by increasing shear rate (irrespective of mixing time) the thermal stability (reduced weight loss) of the SBS modified bitumen was enhanced between about 450°C and 700°C and, thus the blend long term performance. Moreover, when a shear rate of 3000 rpm is employed we see the evolution of a second small degradation process centred at ~610°C for a mixing time of 15 minutes, shifting by 30°C to ~640°C when the mixing time was increased to 45 minutes. Furthermore, the single main degradation process observed for the un-aged samples splits into two, with a shoulder process now positioned at slightly higher temperatures. As seen in Table 4.6, the T_i values for the aged samples are all lower than that for SBS and the residual char at 800°C less than that measured for the un-aged samples. This behaviour can be explained by the combined effects of the application of higher shear rate resulting in increased swelling of the SBS and long term aging initiating the degradation of SBS in the bitumen matrix.

Table 4.6 TGA/DTG results for aged neat bitumen and SBS modified bitumen

Samples	T _i (°C)	T ₁₀ wt% (°C)	T ₅₀ wt% (°C)	T _{max} (°C)	Residue at 800 °C (wt%)
NB-UA	189.7	342.1	431.0	449.5	6.7
1000-15-UA	215.3	341.6	426.1	443.7	5.2
1000-45-UA	274.1	368.2	443.7	448.3	7.5
3000-15-UA	243.5	353.4	451.8	420.0	3.4
3000-45-UA	238.0	359.7	449.9	428.6	7.3

4.4.2 Modulated DSC Results

The DSC signals of the unaged neat bitumen and SBS modified bitumen samples were investigated and the reversing and derivative reversing heat flow curves constructed, see Figure 4.25 and 4.26.

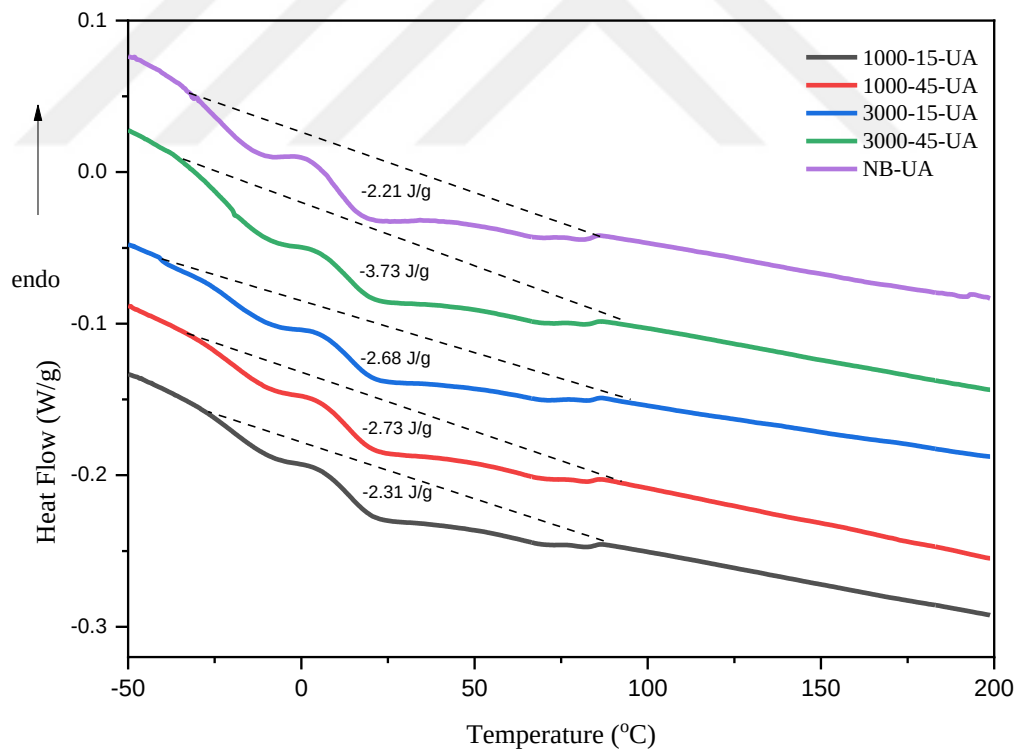


Figure 4.25 Reversing heat flow curves of unaged SBS modified bitumen samples, from MDSC measurements

As can be seen in Figure 4.25, for un-aged samples, the inclusion of 5wt% SBS to the bitumen resulted in an increase in the specific heat capacity (C_p) of bitumen, from -2.21 J/g to -3.73 J/g, the increase in C_p being the greatest when a shear rate of 3000rpm was used. With aging the mobility of the molecules is decreased and therefore more energy is required in order to initiate their mobility (Menapace et al., 2015). The derivatives of the reversing heat flow were calculated in order to determine the T_g values of the blend components, see Figure 4.26.

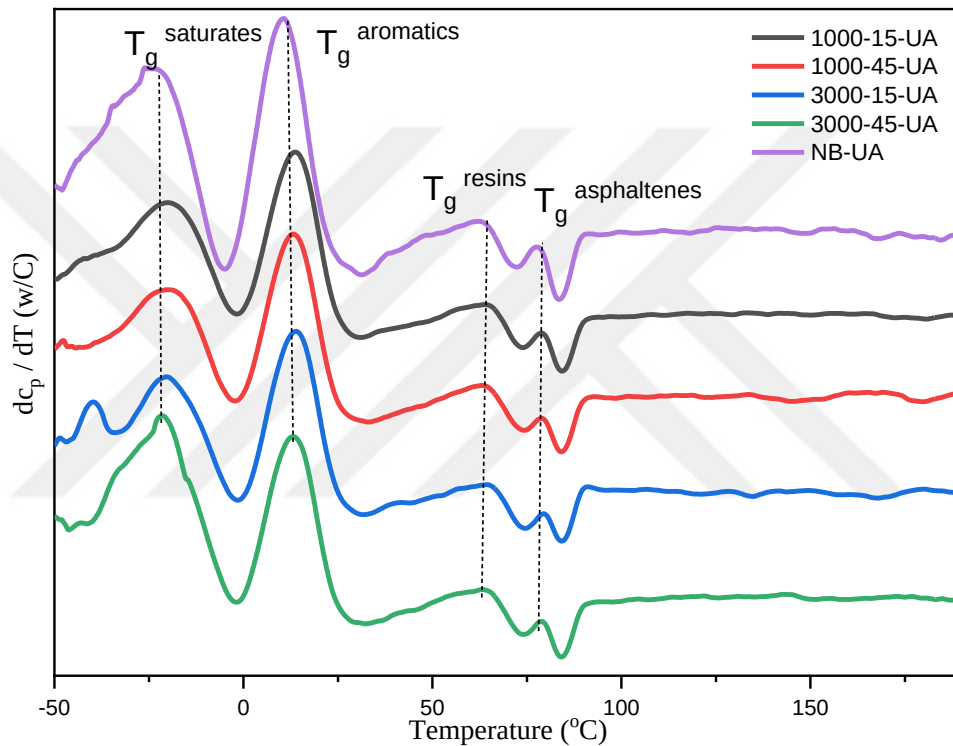


Figure 4.26 Derivative reversing heat flow curves for unaged SBS modified bitumen samples, from MDSC measurements

From Figure 4.26 and for the un-aged samples, four different T_g 's were obtained with maxima at -20°C, 10°C, 60°C and 80°C derived from the bitumen saturates, aromatics, resins and asphaltenes components, respectively. The SBS copolymer had two T_g 's, at -80 °C for the butadiene phase and at 98 °C for the styrene phase. However, in the blends both were dominated by bitumen itself since the SBS weight fraction in the blend was relatively low at 5wt%. The T_g values for each unaged sample were listed in Table 4.7.

Table 4.7 T_g's of unaged SBS modified bitumen samples, from MDSC measurements

Sample Name	T _g ^{saturates}	T _g ^{aromatics}	T _g ^{resins}	T _g ^{asphaltenes}
NB-UA	-25	10.9	62	77.7
1000-15-UA	-20	13.1	64.5	78.5
1000-45-UA	-20.5	12.4	64	78.5
3000-15-UA	-21.5	13	62.8	78.3
3000-45-UA	-25	11.5	62	77.7

In particular, the T_g of the saturates (↑5°C) and aromatics (↑2.2°C) components increased on addition of SBS, reflecting the absorption of these components by the SBS, which is also dependent on the shear rate and mixing time used in the preparation the SBS modified bitumen blends. Ultimately, increasing shear rate and mixing time results in a subsequent decrease in T_g to values similar to un-aged neat bitumen. This behaviour in T_g variability may be associated with the formation of crosslinks, decomposition of SBS or plasticization of SBS by bitumen components. This hypothesis was further investigated by examining the MDSC curves of long term aged neat bitumen and and SBS modified bitumen samples, see Figures 4.27 and 4.28.

It is clear from Figure 4.27 that C_p for aged bitumen is greater than that for unaged bitumen. Likewise, for all aged blends, the C_p values were larger than that for the corresponding unaged samples. Similar trends were observed in that C_p increased with increasing shear rate and mixing time. For the aged samples, the T_g of the saturates phase decreased significantly (↓5°C) and for the aromatics component, T_g also decreased, by 3.4°C, with increasing shear rate and mixing time, see Figure 4.28 and Table 4.8.

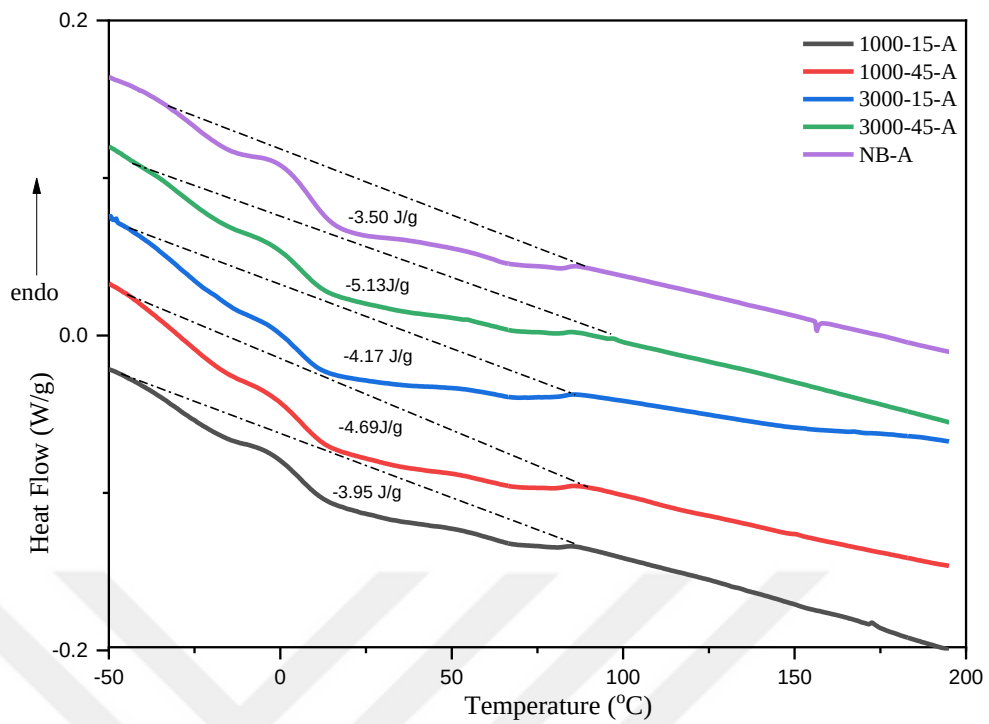


Figure 4.27 Reversing heat flow curves for long term aged SBS modified bitumen samples, from MDSC measurements

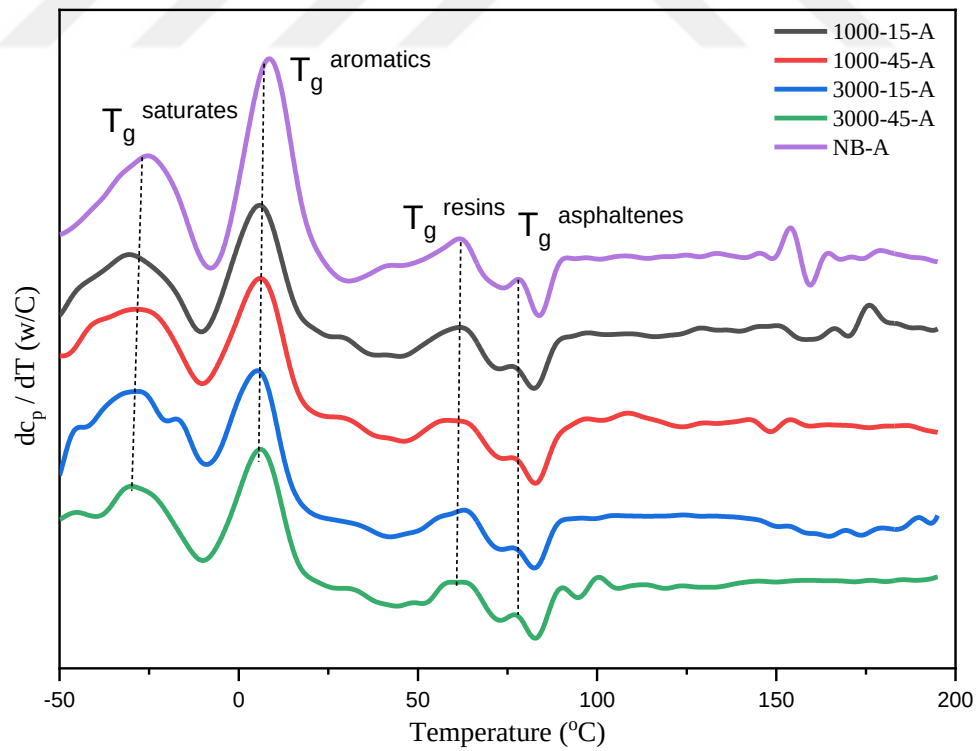


Figure 4.28 Derivative of the reversing heat flow curves for long term aged SBS modified bitumen samples, from MDSC measurements

Table 4.8 T_g's of aged SBS modified bitumen samples, from MDSC measurements

Sample Name	T_g^{saturates}	T_g^{aromaticss}	T_g^{resins}	T_g^{asphaltenes}
NB-A	-25.3	8.5	61.7	76.9
1000-15-A	-30.3	5.8	61.6	76.1
1000-45-A	-28.7	6	61.5	76.5
3000-15-A	-28.5	5.2	62.4	76.1
3000-45-A	-30.5	5.1	60.9	75.8

The application of heat and pressure in simulated long term aging clearly alters the blend structure, by a combination of degradation followed by crosslinking and the formation of new polymeric structures, which is manifest by changes in the T_g values of the bitumen components.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

The effects of mixing conditions, in terms of shear rates and mixing durations, on the structural characteristics, rheological behaviours, morphological characteristics and the thermal properties, were investigated. Based on the results, the major findings of this thesis are as shown below:

Chemical bonds of the samples were affected by not only SBS modification but also by the mixing conditions of the SBS with bitumen. Carbonyl index values, which are related to aging, increased with the increase in mixing time and speed. The aromatics indices are increased by the SBS modification. Nevertheless, with the increase in shearing rate and mixing duration, the Aromatics Index of PMB samples were decreased which is due to the aging effect on the reduction of the aromatic components. The results of the long term aged samples, were revealed the aging effects of the mixing conditions. Based on the microstructural results, which is obtained by AFM, SBS modification and utilization of different mixing conditions, altered topographic and phase images. Dark phase of the PMB samples rises and phase contrast becomes more visible, by the increment of mixing duration and speed. This reason can be clarified with aging occurred, due to the longer mixing durations. Depending on the evaluation of the length of bee structures, it may be assumed that, SBS did not absorb the oily components of the bitumen, under 1000 rpm because of inadequate mixing conditions. Moreover, 3000-45-UA and 1000-45-UA samples depicted shorter bee structures, compared to 3000-15-UA and 1000-45-UA samples. This can be the reason of aging occurred, due to the longer duration of mixing.

Based on the rheological characterisation investigation, higher shear rates and longer mixing durations result in oxidative aging of the SBS modified bitumen. The activation energy for flow of the bituminous sample, is increased with polymer modification. The more aged samples had higher activation energy, again due to increased polymer chain stiffness. From a viscoelastic perspective, the SBS modified bitumen samples, displayed a higher phase angle, compared to neat bitumen

corresponding to the same complex modulus with increasing temperature. This behaviour is associated with increased viscosity at higher temperatures. Moreover, aging of the SBS modified bitumen resulted in a reduction in complex modulus for the same phase angle. Symmetric Cole-Cole plots for the SBS-bitumen blends, prepared using the same shear rates and mixing times, confirmed similar compatibility, between the SBS and bitumen components. The rutting resistance and PG upper critical temperature for neat bitumen, were increased, by the modification with the SBS copolymer. The rheological properties of SBS modified bitumen blends, were affected by processing conditions, employed during their preparation. The longer the mixing time and the higher the shear rate results in increased rutting resistance behaviour. Zero shear viscosity (ZSV) results supported the aforementioned rutting parameters results.

Morphological characteristics of the PMB samples were altered, depending on the mixing time and shear rate applied, confirmed from both OM and CLSM observations. Specifically, the higher shearing rate, the better the dispersion of the SBS phase in the blend, while the longer the mixing time, the more homogeneous the blend is. Based on the observed distribution of SBS and bitumen phases, application of a shear rate of 1000 rpm and a mixing time of 15 min was not effective at producing a homogeneous blend. This was concluded depending on the insufficient swollen volume of SBS in 1000-15-UA, compared to the other samples. Shear rate is more influential, than mixing time in achieving a highly dispersed SBS phase in bitumen. Neat bitumen had a more homogeneously distributed fluorescence intensity, than the PMB samples, since the bitumen components having fluorescence properties (i.e. saturates and aromatics) were homogeneously dispersed in the bitumen phase. In contrast, the PMB samples had inhomogeneous dispersions and variable fluorescence intensities. The bitumen phase of the PMB was less intense, than neat bitumen because, the PS and PB components of SBS absorbed the fluorescence components of the bitumen. An aging effect occurred when a longer mixing duration was used and observed by the decrease in fluorescence intensity values. Besides, long term aging of the PMB samples revealed a decrease in fluorescence intensity. Only, the 1000-15-A sample displayed variable intensity as the SBS copolymer was poorly mixed in the bitumen phase.

Thermal characteristics of the samples were evaluated by TGA and MDSC studies. From TGA studies, addition of SBS, enhanced the thermal stability of the unaged neat bitumen. SBS had the lowest and neat bitumen had the highest residue at the end of the TGA experiments since carbon molecules became to be stronger and more thermally stable after modification. The increasing of shearing rate and mixing duration caused to have higher residual, which can be clarified by cross-linking occurred by aging. Residual char content was shown to be dependant on both shear rate and the mixing duration. Higher residue content results when the applied shear rate and mixing time are not effective at dispersing the bitumen components and SBS. Aging, altered the degradation mechanism of the SBS modified bitumen blends, prepared using the higher shear rate. For all un-aged samples, one degradation process was observed. However, long term aging yielded the second peak for the sample produced by 3000 rpm of shearing rate which can be explained by the increase of SBS's swelling and the degradation of SBS in the blend after aging. The onset of thermal degradation and the residual char content for the aged samples is less than that obtained for the unaged samples, behaviour associated with the increased swelling of SBS by bitumen components when mixed using higher shear rates and the degradation of SBS due to long term aging. TGA results showed that, 1000 rpm of shearing rate and 15 mins of mixing duration were insufficient because the sample named 1000-15-UA behaved more like neat bitumen compared to PMB samples. From MDSC experiments, the specific heat capacity (C_p) of un-aged neat bitumen increased upon SBS modification, and the highest value was measured for the longer mixing duration and the higher shear rate. C_p was shown to increase further, when the samples were aged, due to the reduction in molecular mobility, as aging results in increased crosslinked structures, which hinder molecular dynamics. From the derivatives of the reversing heat flow curves, four different T_g 's were determined for the saturates, aromatics, resins and asphaltene components of bitumen. Ultimately, the T_g 's of the four bitumen components decreased, when a higher mixing rate and longer mixing time was used to prepare the blends, which can be clarified with an effect of aging. Long term aging of SBS modified bitumen, results in oxidative degradation and crosslinking of structures, which results in a decrease in the T_g 's of the bitumen components.

And the followings are recommended:

- There are clear evidences about mixing conditions have an effect on the rheological, morphological, structural and thermal characteristics of the samples. However, further evaluation might be conducted by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-ray Powder Diffraction (XRD) etc.
- Mixing conditions can be evolved by different shearing rates, mixing durations, or even temperature variations.
- Only one type of bitumen having the 50/70 penetration grade was employed, within the scope of this thesis. However, the effects of mixing conditions can bring different results depending on the penetration grade of bitumen. The effects of penetration grades on determining the mixing conditions can be evaluated as a future work.
- In this study only elastomer type, SBS, has been used, but further studies can be implemented for different ratios and modification types such as; plastomers, warm mix additives and reactive elastomeric polymer (RET).
- The effects of mixing conditions on the characteristics of bitumen was evaluated however, it is required to investigate the influences of mixing conditions on the performance of asphalt mixture.

REFERENCES

- Aghazadeh Dokandari, P. (2012). *Effects of warm mix asphalt additives on aging characteristics of bituminous mixtures*. PhD Thesis, Dokuz Eylul University, Izmir.
- Airey, G. D. (1999). Dynamic shear rheometry, fluorescent microscopy, physical and chemical evaluation of polymer modified bitumens. *7th Conference On Asphalt Pavements For Southern Africa*, Capsa. Retrieved August 23, 2019, from <https://rosap.ntl.bts.gov/view/dot/29433>.
- Airey, G. D. (2002a). Rheological evaluation of ethylene vinyl acetate polymer modified bitumens. *Construction and Building Materials*, 16(8), 473-487.
- Airey, G. D. (2002b). Use of black diagrams to identify inconsistencies in rheological data. *Road Materials and Pavement Design*, 3(4), 403-424.
- Airey, G. D. (2011). Factors affecting the rheology of polymer modified bitumen (PMB). In *Polymer modified bitumen* (238-263). Cambridge: Woodhead Publishing.
- Ait-Kadi, A., Brahimi, B., & Bousmina, M. (1996). Polymer blends for enhanced asphalt binders. *Polymer Engineering & Science*, 36(12), 1724-1733.
- Al-Rub, R. K. A., Darabi, M. K., Little, D. N., & Masad, E. A. (2010). A micro-damage healing model that improves prediction of fatigue life in asphalt mixes. *International Journal of Engineering Science*, 48(11), 966-990.
- Alataş, T., & Yilmaz, M. (2013). Effects of different polymers on mechanical properties of bituminous binders and hot mixtures. *Construction and Building Materials*, 42, 161-167.

- Allen, R. G., Little, D. N., & Bhasin, A. (2012). Structural characterization of micromechanical properties in asphalt using atomic force microscopy. *Journal of Materials in Civil Engineering*, 24(10), 1317-1327.
- Allen, R. G., Little, D. N., Bhasin, A., & Glover, C. J. (2014). The effects of chemical composition on asphalt microstructure and their association to pavement performance. *International Journal of Pavement Engineering*, 15(1), 9-22.
- Anderson, D. A., Christensen, D. W., Bahia, H. U., Dongre, R., Sharma, M. G., Antle, C. E., et al. (1994). Binder characterization and evaluation, volume 3: Physical characterization. *Strategic Highway Research Program, National Research Council, Report No. SHRP-A-369*.
- Anderson, D. A., & Kennedy, T. W. (1993). Development of SHRP binder specification. *Journal of the Association of Asphalt Paving Technologists*, 62, 481-507.
- Anderson, R., & McGennis, R. (1994). *Superpave Asphalt Mixture Design Illustrated Level 1 Lab Methods*. Final Report FHWA-SA-94-004, Lexington, KY.
- Attaelmanan, M., Feng, C. P., & Al-Hadidy, A. (2011). Laboratory evaluation of HMA with high density polyethylene as a modifier. *Construction and Building Materials*, 25(5), 2764-2770.
- Bahia, H. U., & Anderson, D. A. (1995). The Pressure Aging Vessel (PAV): a test to simulate rheological changes due to field aging. *Physical Properties of Asphalt Cement Binders*: ASTM International.
- Barth, E. (1962). *Bitumen science and technology*. New York: Gordon and Breach.

- Bearsley, S., Forbes, A., & G. Haverkamp, R. (2004). Direct observation of the asphaltene structure in paving-grade bitumen using confocal laser-scanning microscopy. *Journal of Microscopy*, 215(2), 149-155.
- Becker, M., Muller, A. J., & Rodriguez, Y. (2003). Use of rheological compatibility criteria to study SBS modified asphalts. *Journal of Applied Polymer Science*, 90(7), 1772-1782.
- Becker, Y., Mendez, M. P., & Rodríguez, Y. (2001). Polymer modified asphalt. *Vision Tecnologica*, 9(1), 39-50.
- Behzadfar, E., & Hatzikiriakos, S. G. (2013). Viscoelastic properties and constitutive modelling of bitumen. *Fuel*, 108, 391-399.
- Bell, C. A. (1989). *Summary report on aging of asphalt-aggregate systems*: Strategic Highway Research Program, National Research Council Washington, DC.
- Bell, C. A., Sosnovske, D., & Wieder, J. (1994). *Aging: binder validation*: Strategic Highway Research Program, National Research Council Washington, DC.
- Benbouzid, M., & Hafsi, S. (2008). Thermal and kinetic analyses of pure and oxidized bitumens. *Fuel*, 87(8-9), 1585-1590.
- Biro, S., Gandhi, T., & Amirkhanian, S. (2009). Determination of zero shear viscosity of warm asphalt binders. *Construction and Building Materials*, 23(5), 2080-2086.
- Bissada, K. A., Tan, J., Szymczyk, E., Darnell, M., & Mei, M. (2016). Group-type characterization of crude oil and bitumen. Part I: Enhanced separation and quantification of saturates, aromatics, resins and asphaltenes (SARA). *Organic Geochemistry*, 95, 21-28.

- Bissada, K. A., Tan, J., Szymezyk, E., Darnell, M., & Mei, M. (2016). Group-type characterization of crude oil and bitumen. Part II: Efficient separation and quantification of normal-paraffins iso-paraffins and naphthenes (PIN). *Fuel*, 173, 217-221.
- Bonemazzi, F., & Giavarini, C. (1999). Shifting the bitumen structure from sol to gel. *Journal of Petroleum Science and Engineering*, 22(1-3), 17-24.
- Boysen, R. B., & Schabron, J. F. (2013). The automated asphaltene determinator coupled with saturates, aromatics, and resins separation for petroleum residua characterization. *Energy & Fuels*, 27(8), 4654-4661.
- Brûlé, B., Brion, Y., & Tanguy, A. (1988). Paving asphalt polymer blends: Relationships between composition, structure and properties *Proc Assoc Asphalt Paving Technologists*, 57, 41-64.
- Bull, A., & Vonk, W. (1984). Thermoplastic rubber/bitumen blends for roof and road. *Shell Chemical Technical Manual TR*, 8, 15.
- Chen, J., Liao, M.-C., & Tsai, H. (2002). Evaluation and optimization of the engineering properties of polymer-modified asphalt. *Practical Failure Analysis*, 2(3), 75-83.
- Chen, J., Liao, M., & Shiah, M. (2002). Asphalt modified by styrene-butadiene-styrene triblock copolymer: Morphology and model. *Journal of Materials in Civil Engineering*, 14(3), 224-229.
- Christensen, D. W., & Anderson, D. A. (1992). Interpretation of dynamic mechanical test data for paving grade asphalt cements *Journal of the Association of Asphalt Paving Technologists*, 61, 67-98.

- Collins, J., Bouldin, M., Gelles, R., & Berker, A. (1991). Improved performance of paving asphalts by polymer modification *Journal of the Association of Asphalt Paving Technologists*, 60, 43-79.
- Corbett, L., & Merz, R. (1975). Asphalt binder hardening in the Michigan test road after 18 years of service. *Transportation Research Record*, 544, 27-34.
- Corbett, L. W. (1969). Composition of asphalt based on generic fractionation, using solvent deasphalting, elution-adsorption chromatography, and densimetric characterization. *Analytical Chemistry*, 41(4), 576-579.
- Cortizo, M., Larsen, D., Bianchetto, H., & Alessandrini, J. (2004). Effect of the thermal degradation of SBS copolymers during the ageing of modified asphalts. *Polymer Degradation and Stability*, 86(2), 275-282.
- Cuadri, A., Partal, P., Navarro, F., García-Morales, M., & Gallegos, C. (2011). Bitumen chemical modification by thiourea dioxide. *Fuel*, 90(6), 2294-2300.
- Daga, V. K., & Wagner, N. J. (2006). Linear viscoelastic master curves of neat and laponite-filled poly (ethylene oxide)–water solutions. *Rheologica Acta*, 45(6), 813-824.
- De Moraes, M., Pereira, R., Simão, R., & Leite, L. (2010). High temperature AFM study of CAP 30/45 pen grade bitumen. *Journal of Microscopy*, 239(1), 46-53.
- De Visscher, J., & Vanelstraete, A. (2004). Practical test methods for measuring the zero shear viscosity of bituminous binders. *Materials and Structures*, 37(5), 360-364.
- Dehouche, N., Kaci, M., & Mouillet, V. (2016). The effects of mixing rate on morphology and physical properties of bitumen/organo-modified montmorillonite nanocomposites. *Construction and Building Materials*, 114, 76-86.

- Dembinski, H., Engel, R., Fedynitch, A., Gaisser, T., Riehn, F., & Stanev, T. (2017). Data-driven model of the cosmic-ray flux and mass composition. In *35th International Cosmic Ray Conference*. Retrieved August 19, 2019, from <https://arxiv.org/abs/1711.11432>.
- Dessouky, S., Reyes, C., Ilias, M., Contreras, D., & Papagiannakis, A. (2011). Effect of pre-heating duration and temperature conditioning on the rheological properties of bitumen. *Construction and Building Materials*, 25(6), 2785-2792.
- Di Benedetto, H., Sauzeat, C., Bilodeau, K., Buannic, M., Mangiafico, S., Nguyen, Q., et al. (2011). General overview of the time-temperature superposition principle validity for materials containing bituminous binder. *International Journal of Roads and Airports*, 1(1), 35-52.
- Doğan, M., & Bayramli, E. (2009). Effect of polymer additives and process temperature on the physical properties of bitumen-based composites. *Journal of Applied Polymer Science*, 113(4), 2331-2338.
- Dony, A., & Durrieu, F. (1990). Bitumes et enrobes bitumineux-influence de la nature du bitume sur les propriétés et la stabilité des liants bitumes-polymères. *Bulletin de Liaison des Laboratoires des Ponts et Chaussées*, 168, 57-63.
- Doumenq, P., Guiliano, M., Mille, G., & Kister, J. (1991). Approche méthodologique directe et continue du processus d'oxydation des bitumes par spectroscopie infrarouge à transformée de Fourier. *Analytica Chimica Acta*, 242, 137-141.
- Edwards, Y. (2009). Influence of waxes on bitumen and asphalt concrete mixture performance. *Road Materials and Pavement Design*, 10(2), 313-335.
- Edwards, Y., & Redelius, P. (2003). Rheological effects of waxes in bitumen. *Energy & Fuels*, 17(3), 511-520.

- Fang, C., Liu, P., Yu, R., & Liu, X. (2014). Preparation process to affect stability in waste polyethylene-modified bitumen. *Construction and Building Materials*, 54, 320-325.
- Farcas, F. (1996). *Etude d'une méthode de vieillissement des bitumes sur route*. PhD Thesis, Université Pierre et Marie Curie, Paris.
- Fawcett, A., & McNally, T. (2000). Blends of bitumen with various polyolefins. *Polymer*, 41(14), 5315-5326.
- Fawcett, A., & McNally, T. (2003). Polystyrene and asphaltene micelles within blends with a bitumen of an SBS block copolymer and styrene and butadiene homopolymers. *Colloid and Polymer Science*, 281(3), 203-213.
- Ferry, J. D. (1980). *Viscoelastic properties of polymers*. New York: John Wiley & Sons.
- Firoozifar, S. H., Foroutan, S., & Foroutan, S. (2011). The effect of asphaltene on thermal properties of bitumen. *Chemical Engineering Research and Design*, 89(10), 2044-2048.
- Fischer, H., Dillingh, E., & Hermse, C. (2014). On the microstructure of bituminous binders. *Road Materials and Pavement Design*, 15(1), 1-15.
- Forbes, A., Haverkamp, R. G., Robertson, T., Bryant, J., & Bearsley, S. (2001). Studies of the microstructure of polymer-modified bitumen emulsions using confocal laser scanning microscopy. *Journal of Microscopy*, 204(3), 252-257.
- Gaestel, C., Smadja, R., & Lamminan, K. (1971). Contribution à la connaissance des propriétés des bitumes routiers. *Rev. Gentile. Routes et Aéródromes*, 466, 85-94.

- Ganz, H., & Kalkreuth, W. (1990). The potential of infrared spectroscopy for the classification of kerogen, coal and bitumen. *Erdöl und Kohle*, 43(3), 116-117.
- Garcia-Morales, M., Partal, P., Navarro, F., Martinez-Boza, F., & Gallegos, C. (2004). Linear viscoelasticity of recycled EVA-modified bitumens. *Energy & Fuels*, 18(2), 357-364.
- García-Morales, M., Partal, P., Navarro, F., Martínez-Boza, F., & Gallegos, C. (2006). Process rheokinetics and microstructure of recycled EVA/LDPE-modified bitumen. *Rheologica Acta*, 45(4), 513-524.
- García-Morales, M., Partal, P., Navarro, F., Martínez-Boza, F., Gallegos, C., González, N., et al. (2004). Viscous properties and microstructure of recycled eva modified bitumen. *Fuel*, 83(1), 31-38.
- García-Morales, M., Partal, P., Navarro, F. J., Martínez-Boza, F., Mackley, M. R., & Gallegos, C. (2004). The rheology of recycled EVA/LDPE modified bitumen. *Rheologica Acta*, 43(5), 482-490.
- García-Morales, M., Partal, P., Navarro, F., Martínez-Boza, F., & Gallegos, C. (2007). Processing, rheology, and storage stability of recycled EVA/LDPE modified bitumen. *Polymer Engineering & Science*, 47(2), 181-191.
- García, E. A. G., & Nájera, R. H. (2016). Effect of Stirring Speed in Hot Mixing Process of Modified Asphalt with SBS Copolymer on Polymeric Distribution and its Rheological Properties. *MRS Online Proceedings Library Archive*, 1813. Retrieved August 23, 2019, from <https://www.cambridge.org/core/journals>.
- Gibson, N., Qi, X., Shenoy, A., Al-Khateeb, G., Kutay, M. E., Andriescu, A., et al. (2012). *Performance testing for superpave and structural validation*. Retrieved August 19, 2019, from <https://rosap.ntl.bts.gov/view/dot/25469>.

- Gill, P., Sauerbrunn, S., & Reading, M. (1993). Modulated differential scanning calorimetry. *Journal of Thermal Analysis*, 40(3), 931-939.
- Gingras, J., Tanguy, P., Mariotti, S., & Chaverot, P. (2005). Effect of process parameters on bitumen emulsions. *Chemical Engineering and Processing: Process Intensification*, 44(9), 979-986.
- Girdler, R. (1965). Constitution of asphaltenes and related studies. *Asphalt Paving Technology*, 34, 45-79.
- Gonzalez, O., Munoz, M., Santamaria, A., Garcia-Morales, M., Navarro, F., & Partal, P. (2004). Rheology and stability of bitumen/EVA blends. *European Polymer Journal*, 40(10), 2365-2372.
- Gorkem, C., & Sengoz, B. (2009). Predicting stripping and moisture induced damage of asphalt concrete prepared with polymer modified bitumen and hydrated lime. *Construction and Building Materials*, 23(6), 2227-2236.
- Griffin, R., Miles, T., & Penther, C. (1955). Microfilm durability test for asphalt. *Asphalt Paving Technology*, 24, 31-62.
- Grizzle, P. L., & Sablotny, D. M. (1986). Automated liquid chromatographic compound class group-type separation of crude oils and bitumens using chemically bonded silica-NH₂. *Analytical Chemistry*, 58(12), 2389-2396.
- Gungor, A. G., & Saglik, A. (2012). Evaluation of rutting performance of neat and modified binders using zero shear viscosity. In *5th Eurasphalt & Eurobitume Congress*. Retrieved August 23, 2019, from https://www.researchgate.net/profile/Ahmet_Guengoer.

- Haddadi, S., Ghorbel, E., & Laradi, N. (2008). Effects of the manufacturing process on the performances of the bituminous binders modified with EVA. *Construction and Building Materials*, 22(6), 1212-1219.
- Handle, F., Füssl, J., Neudl, S., Grossegger, D., Eberhardsteiner, L., Hofko, B., et al. (2014). Understanding the microstructure of bitumen: a CLSM and fluorescence approach to model bitumen ageing behavior. In *Proceedings to 12th ISAP International Conference on Asphalt Pavements*. Retrieved August 23, 2019, from <https://www.semanticscholar.org>.
- Handle, F., Füssl, J., Neudl, S., Grossegger, D., Eberhardsteiner, L., Hofko, B., et al. (2016). The bitumen microstructure: a fluorescent approach. *Materials and Structures*, 49(1-2), 167-180.
- Handle, F., Grothe, H., & Neudl, S. (2012). Confocal laser scanning microscopy—observation of the microstructure of bitumen and asphalt concrete. *5th Eurasphalt & Eurobitume Congress, Istanbul*. Retrieved August 23, 2019, from https://publik.tuwien.ac.at/files/PubDat_211706.
- Hatakeyama, T., & Quinn, F. (1999). *Thermal analysis*. New York: Wiley.
- Herbert, A. (1920). 1,357,920. Washington DC: US.Patent and Trademark Office.
- Hermadi, M., Zamhari, K. A., bin A Karim, A. T., Abdullah, M. E., & Lloyd, L. L. (2012). The effect of saturates on rheological and aging characteristics of bitumen. In *Proceedings of World Academy of Science, Engineering and Technology*. Retrieved August 23, 2019, from <https://www.semanticscholar.org>.
- Hernández, G., Medina, E. M., Sánchez, R., & Mendoza, A. M. (2006). Thermomechanical and rheological asphalt modification using styrene–butadiene triblock copolymers with different microstructure. *Energy & Fuels*, 20(6), 2623-2626.

- Heukelom, W., & Klomp, A. (1964). Road design and dynamic loading. *Asphalt Paving Technology*, 33, 92-125.
- Hirsch, R. J., Narurkar, V., & Carruthers, J. (2006). Management of injected hyaluronic acid induced Tyndall effects. *Lasers in Surgery and Medicine: The Official Journal of the American Society for Laser Medicine and Surgery*, 38(3), 202-204.
- Hoban, T. (1987). Modified binders: An underexploited road maintenance tool. *Highways*, 55(1926), 13-19.
- Hofko, B., Eberhardsteiner, L., Füssl, J., Grothe, H., Handle, F., Hospodka, M., et al. (2016). Impact of maltene and asphaltene fraction on mechanical behavior and microstructure of bitumen. *Materials and Structures*, 49(3), 829-841.
- Hou, Y., Wang, L., Wang, D., Guo, M., Liu, P., & Yu, J. (2017). Characterization of bitumen micro-mechanical behaviors using AFM, phase dynamics theory and MD simulation. *Materials*, 10(208), 1-16.
- Hung, A. M., & Fini, E. H. (2015). AFM study of asphalt binder “bee” structures: origin, mechanical fracture, topological evolution, and experimental artifacts. *RSC Advances*, 5(117), 96972-96982.
- Hunter, R. N., Self, A., Read, J., & Hobson, E. (2015). *The shell bitumen handbook*. London, UK: ICE Publishing.
- Hussein, I. A., Iqbal, M. H., & Al-Abdul-Wahhab, H. I. (2005). Influence of M w of LDPE and vinyl acetate content of EVA on the rheology of polymer modified asphalt. *Rheologica Acta*, 45(1), 92-104.
- Isacsson, U., & Lu, X. (1995). Testing and appraisal of polymer modified road bitumens—state of the art. *Materials and Structures*, 28(3), 139-159.

- Isacsson, U., & Lu, X. (1999). Characterization of bitumens modified with SEBS, EVA and EBA polymers. *Journal of Materials Science*, 34(15), 3737-3745.
- Isacsson, U., & Zeng, H. (1998). Low-temperature cracking of polymer-modified asphalt. *Materials and Structures*, 31(1), 58-63.
- Jada, A., & Salou, M. (2002). Effects of the asphaltene and resin contents of the bitumens on the water-bitumen interface properties. *Journal of Petroleum Science and Engineering*, 33(1-3), 185-193.
- Jewell, D., Albaugh, E. W., Davis, B. E., & Ruberto, R. G. (1974). Integration of chromatographic and spectroscopic techniques for the characterization of residual oils. *Industrial & Engineering Chemistry Fundamentals*, 13(3), 278-282.
- Jewell, D., Weber, J., Bunger, J., Plancher, H., & Latham, D. (1972). Ion-exchange, coordination, and adsorption chromatographic separation of heavy-end petroleum distillates. *Analytical Chemistry*, 44(8), 1391-1395.
- Klein, G. C., Angström, A., Rodgers, R. P., & Marshall, A. G. (2006). Use of saturates/aromatics/resins/asphaltenes (SARA) fractionation to determine matrix effects in crude oil analysis by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels*, 20(2), 668-672.
- Kök, M. V., & Gul, K. G. (2013). Combustion characteristics and kinetic analysis of Turkish crude oils and their SARA fractions by DSC. *Journal of Thermal Analysis and Calorimetry*, 114(1), 269-275.
- Kraus, G. (1982). Modification of asphalt by block polymers of butadiene and styrene. *Rubber Chemistry and Technology*, 55(5), 1389-1402.
- Lambert, J. B. (2005). The 2004 Edelstein award address, the deep history of chemistry. *Bulletin for the History of Chemistry*, 30, 1-9.

- Lamontagne, J., Dumas, P., Mouillet, V., & Kister, J. (2001). Comparison by Fourier transform infrared (FTIR) spectroscopy of different ageing techniques: application to road bitumens. *Fuel*, 80(4), 483-488.
- Larsen, D. O., Alessandrini, J. L., Bosch, A., & Cortizo, M. S. (2009). Micro-structural and rheological characteristics of SBS-asphalt blends during their manufacturing. *Construction and Building Materials*, 23(8), 2769-2774.
- Lee, Y., France, L. M., & Hawley, M. C. (1997). The effect of network formation on the rheological properties of SBR modified asphalt binders. *Rubber Chemistry and Technology*, 70(2), 256-263.
- Lesueur, D. (2009). The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Advances in Colloid and Interface Science*, 145(1-2), 42-82.
- Lesueur, D., Gerard, J., Claudy, P., Letoffe, J., Planche, J., & Martin, D. (1996). A structure-related model to describe asphalt linear viscoelasticity. *Journal of Rheology*, 40(5), 813-836.
- Liang, M., Liang, P., Fan, W., Qian, C., Xin, X., Shi, J., et al. (2015). Thermo-rheological behavior and compatibility of modified asphalt with various styrene-butadiene structures in SBS copolymers. *Materials & Design*, 88, 177-185.
- Liang, M., Xin, X., Fan, W., Luo, H., Wang, X., & Xing, B. (2015). Investigation of the rheological properties and storage stability of CR/SBS modified asphalt. *Construction and Building Materials*, 74, 235-240.
- Liang, W., Que, G., Chen, Y., & Liu, C. (2000). Chemical composition and characteristics of residues of chinese crude oils. *Developments in Petroleum Science*, 40, 281-304.

- Liao, M., & Chen, J. (2011). Zero shear viscosity of bitumen-filler mastics. *Journal of Materials in Civil Engineering*, 23(12), 1672-1680.
- Lin, J., Lian, H., Sadeghi, K., & Yen, T. (1991). Asphalt colloidal types differentiated by Korcak distribution. *Fuel*, 70(12), 1439-1444.
- Liu, G., van de Ven, M., Wu, S., Yu, J., & Molenaar, A. (2011). Influence of organo-montmorillonites on fatigue properties of bitumen and mortar. *International Journal of Fatigue*, 33(12), 1574-1582.
- Liu, P., Shi, Q., Chung, K. H., Zhang, Y., Pan, N., Zhao, S., et al. (2010). Molecular characterization of sulfur compounds in Venezuela crude oil and its SARA fractions by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels*, 24(9), 5089-5096.
- Liu, Y., Zhang, J., Chen, R., Cai, J., Xi, Z., & Xie, H. (2017). Ethylene vinyl acetate copolymer modified epoxy asphalt binders: phase separation evolution and mechanical properties. *Construction and Building Materials*, 137, 55-65.
- Liu, Z., Wang, S., & Wang, D. (2005). Morphology and Properties of SBS Modified A sphalt of Different S/B Ratio. *China Plastics Industry*, 33(4), 50-53.
- Loeber, L., Muller, G., Morel, J., & Sutton, O. (1998). Bitumen in colloid science: a chemical, structural and rheological approach. *Fuel*, 77(13), 1443-1450.
- Loeber, L., Sutton, O., Morel, J., Valleton, J. M., & Muller, G. (1996). New direct observations of asphalts and asphalt binders by scanning electron microscopy and atomic force microscopy. *Journal of Microscopy*, 182(1), 32-39.
- Lu, X. (1997). *On polymer modified road bitumens* PhD Thesis, KTH Royal Institute of Technology, Stockholm.

- Lu, X., & Isacsson, U. (1997). *On Polymer Modified Road Bitumens*, Retrieved August 23, 2019, from <https://trid.trb.org/view/567996>.
- Lu, X., & Isacsson, U. (2000). Modification of road bitumens with thermoplastic polymers. *Polymer Testing*, 20(1), 77-86.
- Lu, X., Langton, M., Olofsson, P., & Redelius, P. (2005). Wax morphology in bitumen. *Journal of Materials Science*, 40(8), 1893-1900.
- Lucena, M. C. C., Soares, S. A., & Soares, J. B. (2004). Characterization and thermal behavior of polymer-modified asphalt. *Materials Research*, 7(4), 529-534.
- Lyne, Å. L., Wallqvist, V., & Birgisson, B. (2013). Adhesive surface characteristics of bitumen binders investigated by atomic force microscopy. *Fuel*, 113, 248-256.
- Magonov, S., Alexander, J., Surtchev, M., Hung, A. M., & Fini, E. H. (2017). Compositional mapping of bitumen using local electrostatic force interactions in atomic force microscopy. *Journal of Microscopy*, 265(2), 196-206.
- Mahboob Kanafi, M., Kuosmanen, A., Pellinen, T. K., & Tuononen, A. J. (2015). Macro-and micro-texture evolution of road pavements and correlation with friction. *International Journal of Pavement Engineering*, 16(2), 168-179.
- Martín-Alfonso, M., Partal, P., Navarro, F., García-Morales, M., Bordado, J., & Diogo, A. (2009). Effect of processing temperature on the bitumen/MDI-PEG reactivity. *Fuel Processing Technology*, 90(4), 525-530.
- Martínez, G., & Caicedo, B. (2005). *Efecto de la radiación ultravioleta en el envejecimiento de ligantes y mezclas asfálticas*. Master Thesis, Universidad de los Andes Bogotá, Bogotá.

- Masson, J., Collins, P., & Polomark, G. (2005). Steric hardening and the ordering of asphaltenes in bitumen. *Energy & Fuels*, 19(1), 120-122.
- Masson, J., Collins, P., Robertson, G., Woods, J., & Margeson, J. (2003). Thermodynamics, phase diagrams, and stability of bitumen– polymer blends. *Energy & Fuels*, 17(3), 714-724.
- Masson, J., & Polomark, G. (2001). Bitumen microstructure by modulated differential scanning calorimetry. *Thermochimica Acta*, 374(2), 105-114.
- Masson, J., Price, T., & Collins, P. (2001). Dynamics of bitumen fractions by thin-layer chromatography/flame ionization detection. *Energy & Fuels*, 15(4), 955-960.
- Masson, J. F., Bundalo-Perc, S., & Delgado, A. (2005). Glass transitions and mixed phases in block SBS. *Journal of Polymer Science Part B: Polymer Physics*, 43(3), 276-279.
- Masson, J. F., Leblond, V., & Margeson, J. (2006). Bitumen morphologies by phase-detection atomic force microscopy. *Journal of Microscopy*, 221(1), 17-29.
- McKee, M. G., Unal, S., Wilkes, G. L., & Long, T. E. (2005). Branched polyesters: recent advances in synthesis and performance. *Progress in Polymer Science*, 30(5), 507-539.
- Menapace, I., Masad, E., Bhasin, A., & Little, D. (2015). Microstructural properties of warm mix asphalt before and after laboratory-simulated long-term ageing. *Road Materials and Pavement Design*, 16(1), 2-20.

- Mturi, G., Zoorob, S., & O'Connell, J. (2010). Effect of shear rate on bitumen viscosity measurements—relevance to high temperature processing of bituminous products. In *10th Conference on asphalt pavements in southern Africa, Pretoria, South Africa*. Retrieved August 23, 2019, from http://www.aapaq.org/q/2011st/CAPSA2011/FA6_04_185_1114.
- Mturi, G. A., O'Connell, J., Zoorob, S. E., & De Beer, M. (2014). A study of crumb rubber modified bitumen used in South Africa. *Road Materials and Pavement Design*, 15(4), 774-790.
- Naskar, M., Chaki, T., & Reddy, K. (2010). Effect of waste plastic as modifier on thermal stability and degradation kinetics of bitumen/waste plastics blend. *Thermochimica Acta*, 509(1-2), 128-134.
- Navarro, F., Partal, P., Martínez-Boza, F., & Gallegos, C. (2007). Influence of processing conditions on the rheological behavior of crumb tire rubber-modified bitumen. *Journal of Applied Polymer Science*, 104(3), 1683-1691.
- Newman, J. K. (1998). Dynamic shear rheological properties of polymer-modified asphalt binders. *Journal of Elastomers & Plastics*, 30(3), 245-263.
- Norambuena-Contreras, J., Yalcin, E., Garcia, A., Al-Mansoori, T., Yilmaz, M., & Hudson-Griffiths, R. (2018). Effect of mixing and ageing on the mechanical and self-healing properties of asphalt mixtures containing polymeric capsules. *Construction and Building Materials*, 175, 254-266.
- Ortega, F., Navarro, F., García-Morales, M., & McNally, T. (2015). Thermo-mechanical behaviour and structure of novel bitumen/nanoclay/MDI composites. *Composites Part B: Engineering*, 76, 192-200.

- Ortega, F., Roman, C., Navarro, F., García-Morales, M., & McNally, T. (2016). Physico-chemistry control of the linear viscoelastic behaviour of bitumen/montmorillonite/MDI ternary composites: effect of the modification sequence. *Fuel Processing Technology*, 143, 195-203.
- Ouyang, C., Wang, S., Zhang, Y., & Zhang, Y. (2006). Improving the aging resistance of styrene–butadiene–styrene tri-block copolymer modified asphalt by addition of antioxidants. *Polymer Degradation and Stability*, 91(4), 795-804.
- Panda, M., & Mazumdar, M. (1999). Engineering properties of EVA-modified bitumen binder for paving mixes. *Journal of Materials in Civil Engineering*, 11(2), 131-137.
- Partal, P., Martinez-Boza, F., Conde, B., & Gallegos, C. (1999). Rheological characterisation of synthetic binders and unmodified bitumens. *Fuel*, 78(1), 1-10.
- Pauli, A., Grimes, R., Beemer, A., Turner, T., & Branthaver, J. (2011). Morphology of asphalts, asphalt fractions and model wax-doped asphalts studied by atomic force microscopy. *International Journal of Pavement Engineering*, 12(4), 291-309.
- Peralta, J., Hilliou, L., Silva, H. M., Machado, A. V., & Williams, R. C. (2014). Rheological changes in the bitumen caused by heating and interaction with rubber during asphalt–rubber production. *Rheologica Acta*, 53(2), 143-157.
- Pérez-Lepe, A., Martinez-Boza, F., Gallegos, C., González, O., Muñoz, M., & Santamaria, A. (2003). Influence of the processing conditions on the rheological behaviour of polymer-modified bitumen☆. *Fuel*, 82(11), 1339-1348.
- Pérez-Lepe, A., Martínez-Boza, F., Attané, P., & Gallegos, C. (2006). Destabilization mechanism of polyethylene-modified bitumen. *Journal of Applied Polymer Science*, 100(1), 260-267.

- Pfeiffer, J. (1936). The rheological properties of asphaltic bitumen. *Journal of the Institute of Petroleum Technology*, 22, 414-424.
- Phillips, M., & Robertus, C. (1996). Binder rheology and asphaltic pavement permanent deformation; the zero-shear-viscosity. In *Euroasphalt & Eurobitume Congress*. Retrieved August 23, 2019, from <https://trid.trb.org/view/575022>.
- Pilat, J., & Krol, J. (2008). The Evaluation of Ageing Processes of the Polymer Modified Bitumen by Image Analysis. *Foundations of Civil and Environmental Engineering*(11), 113-122.
- Polacco, G., Berlincioni, S., Biondi, D., Stastna, J., & Zanzotto, L. (2005). Asphalt modification with different polyethylene-based polymers. *European Polymer Journal*, 41(12), 2831-2844.
- Polacco, G., Muscente, A., Biondi, D., & Santini, S. (2006). Effect of composition on the properties of SEBS modified asphalts. *European Polymer Journal*, 42(5), 1113-1121.
- Polacco, G., Stastna, J., Biondi, D., & Zanzotto, L. (2006). Relation between polymer architecture and nonlinear viscoelastic behavior of modified asphalts. *Current Opinion in Colloid & Interface Science*, 11(4), 230-245.
- Polacco, G., Vacin, O. J., Biondi, D., Stastna, J., & Zanzotto, L. (2003). Dynamic master curves of polymer modified asphalt from three different geometries. *Applied Rheology*, 13(3), 118-124.
- Ponniah, J., & Kennepohl, G. (1996). Polymer-modified asphalt pavements in Ontario: performance and cost-effectiveness. *Transportation Research Record*, 1545(1), 151-160.

- Pyshyev, S., Gunka, V., Grytsenko, Y., & Bratychak, M. (2016). Polymer modified bitumen. *Chemistry & Chemical Technology*, 10(4), 631-636.
- Radhakrishnan, V., Sri, M. R., & Reddy, K. S. (2018). Evaluation of asphalt binder rutting parameters. *Construction and Building Materials*, 173, 298-307.
- Raki, L., Masson, J., & Collins, P. (2000). Rapid bulk fractionation of maltenes into saturates, aromatics, and resins by flash chromatography. *Energy & Fuels*, 14(1), 160-163.
- Read, J., Whiteoak, D., & Hunter, R. N. (2003). *The shell bitumen handbook*. London: Thomas Telford.
- Reading, M., Luget, A., & Wilson, R. (1994). Modulated differential scanning calorimetry. *Thermochimica Acta*, 238, 295-307.
- Rebello, L., De Sousa, J., Abreu, A., Baroni, M., Alencar, A., Soares, S., et al. (2014). Aging of asphaltic binders investigated with atomic force microscopy. *Fuel*, 117, 15-25.
- Redelius, P., & Soenen, H. (2015). Relation between bitumen chemistry and performance. *Fuel*, 140, 34-43.
- Redelius, P. G. (2006). The structure of asphaltenes in bitumen. *Road Materials and Pavement Design*, 7(1), 143-162.
- Romberg, J., Nesmith, S., & Traxler, R. (1959). Some Chemical Aspects of the Components of Asphalt. *Journal of Chemical and Engineering Data*, 4(2), 159-161.

- Rozeveld, S. J., Shin, E. E., Bhurke, A., France, L., & Drzal, L. T. (1997). Network morphology of straight and polymer modified asphalt cements. *Microscopy Research and Technique*, 38(5), 529-543.
- Sam, Z., Lin, L., & Ashok, K. (2009). Materials Characterization Techniques. *Taylor & Francis Group Cap*, 7, 177-205.
- Schabron, J. F., & Rovani Jr, J. F. (2008). On-column precipitation and re-dissolution of asphaltenes in petroleum residua. *Fuel*, 87(2), 165-176.
- Schabron, J. F., Rovani Jr, J. F., & Sanderson, M. M. (2010). Asphaltene determinator method for automated on-column precipitation and redissolution of pericondensed aromatic asphaltene components. *Energy & Fuels*, 24(11), 5984-5996.
- Schaur, A., Unterberger, S., & Lackner, R. (2017). Impact of molecular structure of SBS on thermomechanical properties of polymer modified bitumen. *European Polymer Journal*, 96, 256-265.
- Schmets, A., Kringos, N., Pauli, T., Redelius, P., & Scarpas, T. (2010). On the existence of wax-induced phase separation in bitumen. *International Journal of Pavement Engineering*, 11(6), 555-563.
- Schowalter, W. R. (1978). *Mechanics of non-newtonian fluid*. New York: Pergamon.
- Sengoz, B., & Isikyakar, G. (2008a). Analysis of styrene-butadiene-styrene polymer modified bitumen using fluorescent microscopy and conventional test methods. *Journal of Hazardous Materials*, 150(2), 424-432.
- Sengoz, B., & Isikyakar, G. (2008b). Evaluation of the properties and microstructure of SBS and EVA polymer modified bitumen. *Construction and Building Materials*, 22(9), 1897-1905.

- Sengoz, B., Topal, A., & Isikyakar, G. (2009). Morphology and image analysis of polymer modified bitumens. *Construction and Building Materials*, 23(5), 1986-1992.
- Shaw, M. T., & MacKnight, W. J. (2018). *Introduction to polymer viscoelasticity*. New York: John Wiley & Sons.
- Shi, Q., Hou, D., Chung, K. H., Xu, C., Zhao, S., & Zhang, Y. (2010). Characterization of heteroatom compounds in a crude oil and its saturates, aromatics, resins, and asphaltenes (SARA) and non-basic nitrogen fractions analyzed by negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels*, 24(4), 2545-2553.
- Shim-Ton, J., Kennedy, K., Piggott, M., & Woodhams, R. (1980). Low temperature dynamic properties of bitumin-rubber mixtures. *Rubber Chemistry and Technology*, 53(1), 88-106.
- Skoog, D., & Leary, J. (1996). *Instrumentelle Analytik*. Berlin: Springer Verlag.
- Soenen, H., Besamusca, J., Fischer, H. R., Poulikakos, L. D., Planche, J., Das, P. K., et al. (2014). Laboratory investigation of bitumen based on round robin DSC and AFM tests. *Materials and Structures*, 47(7), 1205-1220.
- Soenen, H., Lu, X., & Redelius, P. (2008). The morphology of bitumen-SBS blends by UV microscopy: an evaluation of preparation methods. *Road Materials and Pavement Design*, 9(1), 97-110.
- Soleimani, A. (2009). *Use of dynamic phase angle and complex modulus for the low temperature performance grading of asphalt cements*. Master Thesis, Queen's University, Canada.
- Sörensen, A., & Wichert, B. (2009). *Asphalt and bitumen*. Weinheim: Wiley.

- Speight, J. (2000). Asphalt. In W. E.D. (Ed.), *Kirk-Othmer Encyclopedia of Chemical Technology* (1-33). New York: Wiley & Sons Inc.
- Speight, J. (2004). Petroleum Asphaltenes-Part 1: Asphaltenes, resins and the structure of petroleum. *Oil & Gas Science and Technology*, 59(5), 467-477.
- Speight, J. (2014). *The chemistry and technology of petroleum*. Florida: CRC press.
- Strausz, O. P., Mojelsky, T. W., & Lown, E. M. (1992). The molecular structure of asphaltene: an unfolding story. *Fuel*, 71(12), 1355-1363.
- Sybilski, D. (1996). Zero-shear viscosity of bituminous binder and its relation to bituminous mixture's rutting resistance. *Transportation Research Record*, 1535(1), 15-21.
- Takamura, K., & Heckmann, W. (1999). Polymer network formation in the emulsion residue recovered by forced air drying. In *2nd International Symposium on Asphalt Emulsion Technology*. Retrieved August 23, 2019 from <https://s3.amazonaws.com/academia.edu.documents>.
- Tayfur, S., Ozen, H., & Aksoy, A. (2007). Investigation of rutting performance of asphalt mixtures containing polymer modifiers. *Construction and Building Materials*, 21(2), 328-337.
- Traxler, R. (1936). The Physical Chemistry of Asphaltic Bitumen. *Chemical Reviews*, 19(2), 119-143.
- Traxler, R., & Coombs, C. (1936). The colloidal nature of asphalt as shown by its flow properties. *The Journal of Physical Chemistry*, 40(9), 1133-1147.
- Utracki, L. (1995). History of commercial polymer alloys and blends (from a perspective of the patent literature). *Polymer Engineering & Science*, 35(1), 2-17.

- Van der Poel, C. (1954). Road asphalt. *Journal of Applied Chemistry*, 4(5), 221-236.
- Von Quintus, H. L., Mallela, J., & Buncher, M. (2007). Quantification of effect of polymer-modified asphalt on flexible pavement performance. *Transportation Research Record*, 2001(1), 141-154.
- Vonk, W., & Bull, A. (1989). Phase phenomena and concentration effects in blends of bitumen and cariflex TR. In *Proceedings of the 7th International Roofing Congress*. Retrieved August 23, 2019, <https://www.semanticscholar.org>.
- Wang, C., & Zhang, J. (2014). Evaluation of rutting parameters of asphalt binder based on rheological test. *International Journal of Engineering and Technology*, 6(1), 30.
- Wang, M., & Liu, L. (2017). Investigation of microscale aging behavior of asphalt binders using atomic force microscopy. *Construction and Building Materials*, 135, 411-419.
- Wegan, V., & Bredahl Nielsen, C. (2000). Microstructure of polymer modified binders in bituminous mixtures. In *2nd Euroasphalt& Eorubitume Congress*. Retrieved August 23, 2019, from <https://trid.trb.org/view/673994>.
- Whelan, A., & Whelan, T. (1994). *Polymer technology dictionary*. London: Springer Science & Business Media.
- Whiteoak, B. (1990). *The Shell bitumen handbook*. UK: Shell Bitumen.
- Wu, S., Pang, L., Mo, L., Chen, Y., & Zhu, G. (2009). Influence of aging on the evolution of structure, morphology and rheology of base and SBS modified bitumen. *Construction and Building Materials*, 23(2), 1005-1010.
- Xiao, P., Kang, A., & Liu, B. (2005). Quantitatively analysis on modified asphalt by fluorescent microscope. *Pet Asphalt*, 19(3), 45-48.

- Yang, Q., & Yin, W. (2012). Novel performance measurements of SBS modified asphalt based on microstructure pictures. *Journal of Tongji University. Natural Science*, 40(8), 1176-1179.
- Yeh, P., Nien, Y., Chen, J., Chen, W., & Chen, J. (2005). Thermal and rheological properties of maleated polypropylene modified asphalt. *Polymer Engineering & Science*, 45(8), 1152-1158.
- Yoon, S., Bhatt, S., Lee, W., Lee, H. Y., Jeong, S. Y., Baeg, J., et al. (2009). Separation and characterization of bitumen from Athabasca oil sand. *Korean Journal of Chemical Engineering*, 26(1), 64-71.
- Yu, J.-Y., Feng, Z.-G., & Zhang, H.-L. (2011). Ageing of polymer modified bitumen (PMB). In *Polymer modified bitumen* (264-297). Cambridge: Woodhead Publishing.
- Yu, X., Burnham, N. A., Mallick, R. B., & Tao, M. (2013). A systematic AFM-based method to measure adhesion differences between micron-sized domains in asphalt binders. *Fuel*, 113, 443-447.
- Zhang, H., Chen, Z., Xu, G., & Shi, C. (2018). Physical, rheological and chemical characterization of aging behaviors of thermochromic asphalt binder. *Fuel*, 211, 850-858.
- Zhang, H., Yu, J., Wang, H., & Xue, L. (2011). Investigation of microstructures and ultraviolet aging properties of organo-montmorillonite/SBS modified bitumen. *Materials Chemistry and Physics*, 129(3), 769-776.
- Zhao, Y., & Machel, H. G. (2012). Viscosity and other rheological properties of bitumen from the Upper Devonian Grosmont reservoir, Alberta, Canada. *AAPG Bulletin*, 96(1), 133-153.

Zhu, C., Zhang, H., Xu, G., & Wu, C. (2018). Investigation of the aging behaviors of multi-dimensional nanomaterials modified different bitumens by Fourier transform infrared spectroscopy. *Construction and Building Materials*, 167, 536-542.

Zhu, J., Birgisson, B., & Kringos, N. (2014). Polymer modification of bitumen: Advances and challenges. *European Polymer Journal*, 54, 18-38.

