DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

INVESTIGATION OF THE PERFORMANCE OF ELASTOMERIC POLYMER MODIFIED BITUMEN USING WARM MIX TECHNOLOGIES

by
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December, 2014
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INVESTIGATION OF THE PERFORMANCE OF ELASTOMERIC POLYMER MODIFIED BITUMEN USING WARM MIX TECHNOLOGIES

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M.Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"INVESTIGATION OF THE PERFORMANCE OF ELASTOMERIC POLYMER MODIFIED BITUMEN USING WARM MIX TECHNOLOGIES"** completed by **SAYED FARHAD RIJA** under supervision of **PROF. DR. BURAK ŞENGÖZ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

In recent years, warm mix asphalt is extensively used in hot mix asphalt industry for reducing energy requirements and emissions by lowering mixing and compaction temperatures of bitumen. There are many benefits behind the use of warm mix asphalt technologies, comprising longer paving seasons and hauling distances, earlier traffic opening, reduced binder aging and reduced cracking. In addition, the use of polymer modified bitumen has become a very important part of pavement construction due to its superior performance including less aging, enhanced rutting resistance and lower fatigue cracking properties.

This study presents an experimental evaluation of polymer modified bitumen, involving warm mix asphalt additives. In scope of the study, base bitumen has been modified with three different concentrations (4 percent, 5 percent and 6 percent) of Styrene Butadiene Styrene copolymer. The polymer modified bitumen has been mixed with 3 percent organic and 2 percent chemical warm mix asphalt additives at identified production temperatures and periods. The prepared polymer modified bitumen samples involving warm mix asphalt additives have been subjected to conventional and rheological bitumen tests. Mixing and compaction temperature ranges of each bitumen sample have been determined using viscosity test results. The upper critical temperatures used in Performance Grading (PG) system have been determined for each bitumen sample using $G^*/\sin\delta$ results from Dynamic Shear Rheometer test. The effects of loading and temperature on the performance of the samples have been evaluated using $G^*/\sin\delta$ results from low (0.01Hz) and high frequency (10Hz) loadings at 4 different temperatures (50°C-80°C). Rutting performance of polymer modified bitumen samples involving warm mix asphalt additives have been evaluated using Zero Shear Viscosity results from Creep Test.

Keywords: Polymer modified bitumen, SBS, warm mix asphalt technology, organic WMA additive, chemical WMA additive, rheology, rutting performance.

ILIK KARIŞIM ASFALT TEKNOLOJİSİ İÇEREN ELASTOMERİK POLİMER MODİFİYE BİTÜMÜN PERFORMANSININ İNCELENMESİ

ÖZ

Son yıllarda, sıcak karışım asfalt sanayisinde, karıştırma ve sıkıştırma sıcaklıklarını düşürerek enerji ihtiyacı ve emisyonların azaltılması için ılık karışım asfalt yaygın bir biçimde kullanılmaktadır. Ilık karışım asfalt teknolojileri kullanımı, daha uzun taşıma ve serme mesafeleri, daha kısa trafiğe açılma süresi, bağlayıcı yaşlanması ve çatlakların azaltılması gibi birçok faydayı da beraberinde getirmektedir. Buna ek olarak, polimer modifiye bitüm, yaşlanma ve tekerlek izlerine karşı gösterdiği direnç, yorulma çatlaklarını engelleme özelliği ve diğer üstün performansları nedeniyle yol inşaatı sektörünün çok önemli bir parçası haline gelmiştir.

Bu çalışma, ılık karışım asfalt katkı maddeleri içeren SBS polimer modifiye bitümlerin performansı ile ilgili deneysel bir değerlendirme sunmaktadır. Çalışma kapsamında saf bitüm, Styrene Butadiene Styrene kopolimerin üç farklı konsentrasyonu (yüzde 4- yüzde 5 ve yüzde 6) ile modifiye edilmiştir. Hazırlanan polimer modifiye bitüm numuneleri yüzde 3 organik ve yüzde 2 kimyasal ılık karışım asfalt katkılarıyla tespit edilen üretim süre ve sıcaklıkları altında karıştırılmıştır. Söz konusu ılık karışım asfalt katkıları içeren polimer modifiye bitüm örnekleri üzerinde geleneksel ve reolojik bitüm deneyleri uygulanmıştır. Viskozite deneyi sonuçları kullanılarak tüm numuneler için karıştırma ve sıkıştırma sıcaklıkları belirlenmiştir. Dinamik kayma reometresi deneyleri sonucunda elde edilen $G^*/\sin\delta$ değerleri kullanılarak tüm numuneler için Performans Sınıflandırma (PG) sisteminde kullanılan üst sınıf sıcaklıkları tespit edilmiştir. Bununla birlikte düşük (0,01Hz) ve yüksek (10Hz) frekans ve 4 farklı sıcaklık (50°C-80°C) altında $G^*/\sin\delta$ sonuçları değerlendirilerek sıcaklık ve yüklemenin performans üzerindeki etkileri ortaya konulmuştur. Ayrıca sünme deneyi neticesinde elde edilen sıfır kesme viskozite değerleri kullanılarak, ılık karışım asfalt katkıları içeren polimer modifiye bitüm numünelerin tekerlek izine karşı dirençleri araştırılmıştır.

Anahtar kelimeler: Polimer modifiye bitüm, SBS, ılık karışım asfalt teknolojisi, organik WMA katkısı, kimyasal WMA katkısı, reoloji, tekerlek izine karşı direnç.

CONTENTS

LIST OF FIGURES

Pages

LIST OF TABLES

CHAPTER ONE

INTRODUCTION

In order to reduce energy consumption and limit the production of emissions and to reduce its effects on human health and the environment, the paving industry should fulfil its part in controlling those produced by the hot mix asphalt (HMA) production facilities. HMA plants, regardless of their manufacturing technique (drum or batch) emit between 56,000 lbs. /yr. and 83,000 lbs. /yr., depending on their fuel type (natural gas, oil etc.) (United States Environmental Policy Act [USEPA], 2000). These emissions contain substances which involves a wide part of air contaminants, smog formation and visibility degradation.

Polymer modified bitumen (PMB) has been developed by the asphalt industry to fulfill the needs for making better pavements that show better performance under loads due to high traffic applications as well as high temperature conditions of the climate. Polymer modifications are becoming important factors in paving industry due to their proven effects such as better resistance to rutting, fatigue damage, stripping, and thermal cracking in asphalt pavements (Wekumbura et al., 2007; Punith, 2005; Chen et al., 2002). Yet, according to Newcomb (2006) and Illinois DOT (2005) because of the high viscosity of modified bitumen there could be some difficulties in workability of PMB. As a solution for this problem in order to attain the desired density at site we could increase the production and placement temperatures at site which in turn brings concerns about the continuous exposure of workers to high temperatures during paving operations which may yield significant health problems; health issues that will arise from high level of emissions; thermally degradation of the polymer and decrease in its potential performance and higher economical cost due to the increased fuel consumption.

Amongst the polymer modifiers, styrene butadiene styrene (SBS) originally developed by Shell Chemical Co. is widely used in the majority of the asphalt binder industry and probably the most appropriate polymer for bitumen modification (Lavin, 2003; Becker et al., 2001). SBS creates a three dimensional network within base bitumen phase, resulting in excellent bonding strength to aggregates which leads to a durable and long lasting pavement (Kim, 2003; Adedeji et al., 1996).

Warm mix asphalt (WMA) represents technologies that allow considerable reduction of mixing and compaction temperatures of asphalt mixes using additives. The temperature reduction of 19 ~ 56°C (35 ~ 100°F) is the key idea behind WMA. In addition to reduction in fuel consumption and emissions in plants, there are many other promising advantages of using the WMA technologies including, but no limited to, longer paving seasons, longer hauling distances, earlier traffic opening, reduced bitumen aging, and reduced cracking (Hurley & Prowell, 2005a; 2005b; 2006; Gandhi, 2008). In order to obtain strength and durability that is equivalent to/or better than HMA, a common way is the use of additives which lower the production temperature by either lowering the viscosity and/or expanding the volume of the bitumen at a given temperature which helps the aggregates get completely coated in bitumen at temperatures lower than the conventional (Kim, 2010). Organic, chemical and foaming WMA additives are currently used within WMA technology.

The main purpose behind this study is to use the established industry standards of using styrene butadiene styrene (SBS) modified bitumen samples and combine them with relatively new WMA technology in order to create a more sustainable and eco-friendly asphalt paving process. This process is aimed to reduce concerns about the continuous exposure of workers to high temperatures during paving operations, decrease health issues that will arise from high levels of toxic fumes and provide a lower economical cost due to decreased fuel consumption and yet have durable and long lasting pavements.

Recommended contents of two different WMA additives (Organic WMA additive at concentration of 3% by weight of the PMB and chemical WMA additive at concentration of 2% by weight of the PMB) have been mixed with three different contents (4%, 5% and 6% by weight of bitumen) of SBS polymer. The effects of adding WMA additives into PMB have been acquired through conventional bitumen tests (viscosity, penetration and softening point tests before and after RTFO aging, storage stability) and rheological test methods (dynamic shear rheometer test and zero shear viscosity test). The results have been compared with base bitumen and PMB samples.

CHAPTER TWO
MODIFICATION

This chapter is aimed to provide general information regarding the purpose of modification and materials and polymers used in the process.

2.1 Reason Behind Modification

Modification is described as the process of adding specific proportions of different types of additives into bitumen or asphalt aiming to improve the performance of the pavement (Malkoç, 2002).

Bitumen is a viscoelastic material and shows rheological behaviors. Bitumen is meanwhile a thermoplastic material and its consistency changes while heated. This feature could be indicated as one of the main reasons behind using bitumen as a binding material in pavements.

The viscoelastic character of the bitumen is also reflected in the same manner in bituminous hot mix asphalt mixtures. Viscoelastic materials exhibit rather elastic behavior and high resistance under high loading rates (fast vehicles). In contrast they exhibit rather viscous behavior and lower resistance under low loading rates (slow or stationary vehicles). In moderate traffic loading rates, bituminous mixtures exhibit both viscous and elastic behavior (Hunter, 1994).

Due to the thermoplastic properties, bitumen demonstrates low mechanical strength at high temperatures while showing high strength at lower temperatures. The deformation of the bituminous pavement layers largely depend on these properties of the bitumen and the mixture.

In recent years, researches have revealed that the addition of some polymers and other additives affect the rheological behaviors of bitumen by improving its properties and bestowing superior performance. Therefore, the main purpose behind addition of polymers to the bitumen is to change its viscoelastic behavior and in particular to reduce its sensitivity to temperature without damaging its low temperature performance (Choquet, 1994).

The main reason to modify bitumen and bituminous mixture could be summarized as follows.

1- To obtain more flexible mixtures at low service temperatures and reduce permanent deformations,
2- To obtain higher stiffness at high service temperatures, and reduce rutting and shoving,
3- To obtain surfaces with high skid resistance,
4- To increase the stability and strength of mixtures,
5- To increase fatigue resistance of mixtures,
6- To rejuvenate aged bituminous binders,
7- To make low-quality aggregates usable,
8- To increase the adhesion between bitumen and aggregate by forming thicker bitumen films around aggregates and reduce stripping,
9- To reduce bleeding,
10- To provide resistance against fuel spills,
11- To reduce structural thickness of pavements,
12- To hold over the formation of cracks,
13- To increase the field of application,
14- To minimize absorption,
15- To improve the performance of the pavement,
16- To ensure long term cost-effectivity of the pavement,
17- To ensure proper mixing and compaction by reducing the viscosity at low temperatures,

2.2 Modification Methods

There are varieties of additives that could be used in modification methods. The methods used include bitumen and asphalt modification. The details of these methods are discussed below.

2.2.1 Bitumen Modification

Additives used in this method are the kinds that are completely or partially soluble in bitumen. In this method the modifier dissolves in bitumen and forms a reticulated structure. Modification is completed by mixing the blend of bitumen and modifier with aggregates of the specified gradation. This group includes polymer based and chemical and organic based warm mix asphalt additives. Modifiers and general purposes of their usage are listed in Table 2.1.

2.2.1.1 Modification of Bitumen by Extender

Extenders modified bitumen is divided into two groups based on the amount of sulfur used in modification. A small amount of application serves to dilute the bitumen. An excess amount of application increases the workability of the mixture and becomes workable enough to be laid with paver only and without the use of roller for compaction and still resistant to deformations during its service life The amount of extender that reacts with bitumen is based on temperature and the composition of the bitumen (Whiteoak, 2004).

Because of its low viscosity at temperatures around 160°C, bitumen makes the mixture easily handled. As the mixture cools down, the mineral filler partially fills the pores and gaps in in the material and raises the strength of mixture by increasing the friction between aggregates (Whiteoak, 2004).

Table 2.1 General classification of modifications (Gorkem, 2014)

Type	Generic example		General purpose of use
Extender	Sulfur lignin		Increase stiffness
Rubber	Natural latex Synthetic latex Reclaimed rubber Polyethylene		Decrease HMA stiffness at low temperatures to resist thermal cracking, Rutting resistance, Improving cohesion of mixture
Polymer	Elastomer	SBS	High temperature performance, Surface treatment and isolation, Improving cohesion of mixture, HMA rutting resistance, Crack filling
	Plastomer	EVA EBA	
Fiber	*Natural:* Asbestos Rock wool *Manufactured:* Polypropylene Polyester Fiberglass		Increase stiffness
Oxidant	Manganese salts		Increase stiffness
Warm mix asphalt additives	Organic	Sasobit® Asphaltan® A Asphaltan® B Licomont® BS 100	Decrease viscosity, Decrease mixing and compaction temperatures, Increase workability
	Chemical	Evo Therm® Rediset® WMX Cecabase® RT	
	Foaming by water injection	WAM-Foam LEA® Double Barrel Green	

The behavior and properties of a mixture modified by sulfur which is an extender, is time dependent. In the first instance, the Marshall stability of the sulfur-modified mixtures is lower than that of the unmodified mixtures although 7 to 21 days later the Marshall stability of the modified mixture rises about twice that of the unmodified mixture. The most valid explanation for the situation is that the crystallization process of the mineral fillers slows down as a result of interaction with bitumen (Whiteoak, 2004).

2.2.1.2 Modification of Bitumen by Rubber

Polybutadiene, polyisoprene, natural rubber, butyl rubber, chloroprene, irregular styrene butadiene rubber, and so on are the examples used with bitumen and the principal effect is to increase viscosity (Gorkem, 2014).

In some cases, vulcanized (cross-linked) rubber is used. These materials obtained from used vehicle tires are often mixed with bituminous mixtures at high temperatures (Gorkem, 2014).

In addition to the mixtures used for road construction, rubber can be mixed with aggregate and bitumen and can be used for football or children playground and achieve elastic surfaces (Guru, Tekeli, Cubuk et al., 2005).

2.2.1.3 Modification of Bitumen with Organo-Manganese Compounds

In order to facilitate quick distribution of organo-manganese in material, it is first mixed with a catalyst. It is believed that manganese accelerates the formation of stable and high resistant metal complexes. These complexes reinforce the strength of bituminous mixtures by linking bitumen molecules (Gorkem, 2014).

Use of organo metallic manganese additives with limestone and basalt aggregates show a 90% increase in resistance of aggregates against stripping. They are more effective used with limestone than basalt (Guru, 2004).

2.2.1.4 Modification of Bitumen by Polymers

Polymer modification of bitumen has progressively become regular in designing optimally performing pavements, mostly in the United States, Canada, Europe and

Australia (Yildirim, 2007). Polymer modification of bitumen and specific polymers used in polymer modification is widely discussed in the coming chapters.

2.2.2 Asphalt Modification

In this method, additives are added to bitumen-aggregate mixture during production. Such modifications are mostly applied on bitumen mixtures prepared with natural filler additive materials. Modifying additives used in asphalt modifications and their classifications are given in Table 2.2.

Table 2.2 General classification of asphalt modifying agents (Gorkem, 2014)

<table>
<tr><th>Type</th><th colspan="2">Generic example</th><th>General purpose of use</th></tr>
<tr><td>Mineral fillers</td><td colspan="2">Mineral Filler
- Stone dust
- Lime
- Portland cement
- Fly ash
Black carbon</td><td>Stiffness</td></tr>
<tr><td>Antioxidants</td><td colspan="2">Lead compounds
Carbon
Calcium salts</td><td>Softening</td></tr>
<tr><td>Anti-stripping agents</td><td colspan="2">Lime</td><td>Anti-stripping</td></tr>
<tr><td>Warm mix asphalt additives</td><td>foaming</td><td>Advera WMA®
Aspha-Min®</td><td>Decrease viscosity,
Decrease mixing and compaction temperatures,
Increase workability</td></tr>
</table>

2.2.3 Warm Mix Asphalt Applications

Warm mix asphalt (WMA), which reduces the production temperatures (mixing and compaction) while maintaining the advantages of hot mix asphalt (HMA), is becoming an attractive paving material. Based on the direct and indirect advantages of this technology, warm mix asphalt additives have gained a place within both bitumen and asphalt modifications. The details of this technology will be discussed in the coming chapters.

CHAPTER THREE
POLYMERS

This chapter is intended to provide extensive information regarding polymers used within bitumen modification and their types and applications.

3.1 Types and Applications of Polymers

As already discussed in previous chapters, a variety of additives are used in bitumen modification. One of the methods that can significantly improve asphalt quality is the addition of polymers.

The term "polymer" merely refers to very large molecules made by many chemically reacting small molecules (monomers) to produce long chains. The sequence and chemical structure of the monomers from which the polymer is made, its molecular weight and molecular weight distribution define the physical properties of a specific polymer (Becker, Mendez & Rodriguez, 2001).

The properties of polymer modified bitumen depend on various parameters such as:

- Polymer characteristics
- Asphalt characteristics
- Mixing conditions
- Compatibility of polymer with bitumen

Polymer modified bitumen is used as a substitute for asphalt in many paving and maintenance applications, including hot mix, cold mix, chip seals, hot and cold crack filling, patching, recycling and slurry seal to offer improvement in rutting resistance, fatigue damage, thermal cracking, stripping and temperature susceptibility (Becker, Mendez & Rodriguez, 2001).

Some paving techniques such as micro-surfacing and use of emulsion chip seals on high traffic roads that were previously not viable, have become customary with the use of polymer modified bitumen (Becker, Mendez & Rodriguez, 2001).

Lewandowski (1994) summarizes the main reasons to modify bitumen with polymers as:

- To obtain softer blends at low service temperatures and reduce cracking
- To reach stiffer blends at high temperatures and reduce rutting
- To reduce viscosity at layout temperatures
- To increase the stability and the strength of mixtures
- To improve the abrasion resistance of blends
- To improve fatigue resistance of blends
- To improve oxidation and aging resistance
- To reduce structural thickness of pavements
- To reduce life costs of pavements

Many polymers are used to modify bitumen and each has their own related physical properties. Table 3.1 presents a summary of these polymers and their general purpose of uses.

3.1.1 Elastomers

Styrenic block copolymers also termed thermoplastic rubbers or thermoplastic elastomers may be produced by a sequential operation of successive polymerization of Styrene-butadiene-styrene (SBS) or styrene-isoprene-styrene (SIS). Alternatively, a di-block precursor can be produced by successive polymerization of styrene and mid-block monomer, followed by a reaction with a coupling agent. Thus, not only linear copolymers but also multi-armed copolymers can be produced; these are often referred to as radial or branched copolymers (Read & Whiteoak, 2003, p.67).

Thermoplastic elastomers derive their strength and elastic from a physical cross-linking of the molecules into a three-dimensional network. This is achieved by the agglomeration of the polystyrene end-blocks into separate domains, providing the physical cross-links for a three-dimensional polybutadiene or polyisoprene rubbery matrix. It is the polystyrene end-blocks that impart strength to the polymer and the mid-block that gives the material its exceptional elasticity (Read & Whiteoak, 2003, pp.68-69).

When the polymer is added to the hot bitumen, the bitumen immediately starts to penetrate the polymer particles causing the styrene domains of the polymer to become solvated and swollen. Once this has occurred, the level of shear exerted on the swollen particle is critical if a satisfactory dispersion is to be achieved within a realistic blending time. Thus, medium or, preferably, high shear mixers are required to adequately disperse thermoplastic elastomers into the bitumen (Read & Whiteoak, 2003, p.69).

Today, SBS, despite its low aging resistance, is probably the most appropriate polymer for asphalt modification (Giavarini, Santarelli, Braga, 1993).

Table 3.1 Common polymers used in bitumen modification (Isikyakar, 2009)

Polymer	**Common Name**	**Uses**
SBS Copolymer	Thermoplastic Rubber (Elastomer)	Low temperature performance, High temperature performance, Surface treatment and isolation, Hot Mix Asphalt (HMA), Crack filling
EVA® Copolymer EBA Copolymer	Thermoplastics (Plastomer)	High temperature performance, Surface treatment and isolation, Improving cohesion of mixture, HMA rutting resistance, Crack filling
Polyethylene (PE)	Thermoplastic Rubber	Rutting resistance
SBR		Low temperature performance, Rutting resistance Crack filling Better Aggregate Adhesion
Natural Rubber	Rubber	Crack Filling Better aggregate adhesion
Epoxy Resins	Thermoset	Rutting resistance, Hot Mix Asphalt (HMA), High skid resistance

3.1.2 Plastomers

Plastomer type polymers increase the viscosity of the mixture at ambient temperature when mixed with bitumen. However they do not increase the elasticity of bitumen notably. They result decomposition when heated and a rough distribution when cooled (Hoban, 1987).

Ethylene-vinyl acetate (EVA) copolymer is an irregular shaped thermoplastic material produced by copolymerization of ethylene and vinyl acetate. The properties of copolymer vary as the content of vinyl acetate increases (Gorkem, 2014). Overall characteristics of the EVA copolymer are controlled by their molecular weight and the ratio of vinyl acetate.

EVA copolymers can be easily dispersed in bitumen and provide a good compatibility. A degree of decomposition may occur during storage. Thus modified product must be thoroughly mixed before use (Gorkem, 2014).

The addition of EVA to the bitumen mix is not only used to improve the performance of pavement. It is also used in significant quantities in cold weather applications. EVA improves the workability of mixture because of its sensitivity against shear force (Woolley, 1986) and ability to be used with softer bitumen.

3.1.3 Thermosetting

International Union of Pure and Applied Chemistry (IUPAC) define a thermosetting resin as a petrochemical in a soft solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing. Curing can be induced by the action of heat or suitable radiation, or both. A cured thermosetting resin is called a thermoset. Curing can be induced by the action of heat or suitable radiation or both. A cured thermosetting polymer is called a thermoset (McNaught & Wilkinson, 2004).

Epoxy resins are used in a variety of special applications in pavements such as airport and bridge surfacing. Blended with asphalts, the bitumen displays the behavior of thermosetting resins rather than those of asphalts (Giavarini, Santarelli & Braga, 1993). Asphalt pavements designed using epoxy modified bitumen (EMB) doesn't exhibit viscous flow, exhibit resistance against chemical attack and are less temperature susceptible. They exhibit higher cracking resistance and better adhesion (Giavarini, Santarelli & Braga, 1993).

Epoxy modified bitumen (EMB) could be used for construction of antiskid surfaces that are rough enough and have high micro texture. Antiskid surfacing is an ultra-thin layer applied on the pavement and runway surfaces. It was mainly used for airport runways in the Netherlands. Antiskid surfaces may get slippery because of snow, ice, water and rubber deposits. Therefore the surface texture of antiskid layer should be rough enough and should have a high micro texture. The antiskid surfacing should also be capable to survive from high strains, because heavy loading will cause temporary deformation on the surface if flexible pavement structure is used. The bitumen used for the antiskid purpose should have high tensile strength and sufficient adhesion to bond the aggregates (Xiao, Ven, Molenaar & Wub, 2013).

CHAPTER FOUR
WARM MIX ASPHALT

One of the key sources of pollution stemming from industries related to transportation infrastructures (i.e. road construction), resides in the manufacturing, spreading, and conservation of asphalt mixes. A cleaner production of bituminous mixes needs lowering the manufacturing temperature of these mixes without weakening or reducing their level of mechanical performance.

Warm Mix Asphalt (WMA) is a technology that allows 20°C to 55°C lowering of the production and paving temperature compared to typical HMA. The WMA temperature reduction is the result of recently developed technologies that involve the use of organic additives, chemical additives, and water-based or water-containing foaming processes (Zaumanis, 2010). Even though these technologies are quite different, they all target the same goals, namely, lower bitumen viscosity, better mat workability, and improved workability and emissions conditions.

The reduction of temperature enables various benefits over HMA such as reducing emissions; better working conditions because of the absence of harmful gases; lower energy consumption in mix production; quicker turnover to traffic and longer hauling distances (Zaumanis, 2010; Chowdhury & Button, 2008).

4.1 Warm Mix Asphalt Technology

The world focus on the development of WMA technologies may be traced back to two distinctive events: the 1992 United Nations' discussions on the environment and the 1996 Germany's consideration to review asphalt fumes exposure limits. The United Nations' discussions resulted in the 1997 Kyoto Accord, which formalized a commitment by the signatory states to reduce greenhouse gas emission to the 1990 levels, while the Germany's review of asphalt fumes exposure limits lead to the formation of a partnership forum (The German BITUMEN Forum) to discuss these considerations. Reduction of mixing and placement temperatures became the obvious answer and triggered the development of WMA concepts and technologies (Croteau & Tessier, 2008, p.3).

The first trials were performed in Germany and Norway between 1995 and 1999. The first application on a public road was performed in Germany in 1999 using the Aspha-min$^{®}$ zeolite system (Croteau & Tessier, 2008).

For the first time in 1956, asphalt with bitumen foamed by steam was produced by Prof. Ladis Csanyi at Iowa State University, US (Sargand, Figueroa, Edwards, & Al-Rawashdeh, 2009). This process consisted of injecting steam into hot bitumen to reduce the mixing temperature. In 1968, Mobil Oil Australia used cold water instead of steam to foam hot bitumen. This amplified the practicality of the foaming process. Then, foaming technology started to spread out different countries such as Australia, US and Europe (Sargand, Figueroa, Edwards, & Al-Rawashdeh, 2009).

In 2002, the use of Warm Asphalt Mixes with Foam (WAM-Foam) to produce asphalt mixtures at lower operation temperatures was introduced in 2002 by Koenders (Sargand, Figueroa, Edwards, & Al-Rawashdeh, 2009).

Zeolite was used as an additive material to the asphalt mixture by Barthel in 2004 to increase the workability of the mix at lower temperatures (Sargand, Figueroa, Edwards, & Al-Rawashdeh, 2009).

For the last twenty years, the utilization of waxes as viscosity modifiers have been introduced by scientists. Before that,Waxes were used for efficient workability of asphalt, not for lowering the temperature purpose (Oylumluoglu, 2012).

In 2005, two reports were published by the National Center for Asphalt Technology (NCAT) about the use of Sasobit and Aspha-min as additives to the asphalt mixture to produce warm mix asphalt. In 2006, another report was published by NCAT on the use of Evotherm in warm mix asphalt (Sargand, Figueroa, Edwards, & Al-Rawashdeh, 2009).

In conjunction with developing modern WMA technologies, laboratory studies have been performed to show potential benefits of Warm Mix Asphalt and to evaluate the performance compared to traditional Hot Mix Asphalt (Oylumluoglu, 2012).

HMA is produced at temperatures ranging from 138°C to 160°C. This high temperature is used to decrease the viscosity of bitumen and dry the aggregates in order to cover them by bitumen. However; in warm mix asphalt, temperature and viscosity are decreased by adding chemicals or wax as lubricants in mixing processes. The additives are simply an adhesion agent, which may play a significant role in Warm Mix Asphalt Technology. The workability of the bitumen is increased by reduction of the viscosity of bitumen as result of the mixing of the additives (Oylumluoglu, 2012).

Decreasing asphalt production emissions and lowering compaction emissions in the plant are the most important benefits of utilization of warm mix asphalt. Lowering of mixing and compaction temperatures reduce energy consumption because of saving fuel. A comparison between the warm mix and hot mix asphalt technologies in terms of emission of compaction fumes is shown in the Figure 4.1.

Figure 4.1 Comparison between the warm mix and hot mix asphalt technologies in terms of emission of compaction fumes (Warm mix on the left, hot mix on the right), (Pavement interactive, 2010)

4.1.1 Classification of Warm Mix Asphalt Technology

The WMA technologies can be classified in a number of ways. One way is by the degree of temperature reduction. A classification by various application temperatures for asphaltic concrete, from cold mix to hot mix is shown in Figure 4.2 (D'Angelo, Harm, Bartoszek, Baumgardner, Corrigan, Cowsert, Harman, Jamshidi, Jones, Newcomb, Prowell, Sines, & Yeaton, 2008). The ranges of production temperatures in Figure 4.2 define four types of asphaltic concrete that are:

- Cold Mix Asphalt (0° C-30° C)
- Half Warm Mix Asphalt (65°C-100°C)
- Warm Mix Asphalt (100° C-140°C)
- Hot Mix Asphalt (above 140°C)

The range of production temperatures within warm mix asphalt is wide, from mixes that are 20 to 30°C (36 to 54°F) below HMA to temperatures slightly above 100°C (212°F). Warm mix asphalt mixes are parted from half-warm asphalt mixtures by the resulting mix temperature. The mix is considered a half-warm mix if the resulting temperature of the mix at the plant is less than 100°C (212°F) (D'Angelo et al., 2008).

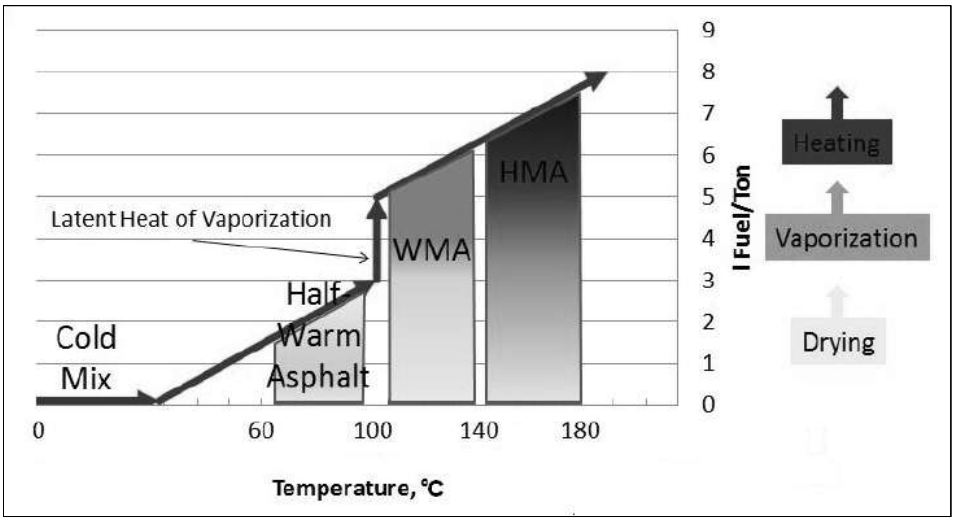


Figure 4.2 Classification of WMA asphalt technology by temperature ranges (D'Angelo et al., 2008)

WMA technologies have the potential to notably reduce the temperature and still not affect the performance of the asphalt in a negative manner. WMA could also be classified by the type of the technologies used to reduce temperature. A more descriptive discussion of the process is allowed by this type of classification. The present WMA production technologies can be categorized in the following three groups and all of the existing products use at least one of these technologies or may be a combination of them as well (Zaumanis & Haritonovs, 2010):

- Foaming technologies
- Organic or wax technologies
- Chemical additives

Table 4.1 presents a summary of the most widely used products available on the market along with their descriptions. The reported region of the use of the corresponding products from the literature is also listed. All the reposts does not show the same production temperatures values and this difference in the reports may be caused by different factors, such as type and the amount of the used additives, humidity of materials, mix design method, climatic conditions, materials used, etc. So the most commonly reported data or data supported by the production company are listed first and the data from different research after. The amount of WMA additive usually depends on the materials, their proportion and especially on the grade and type of bitumen used (Zaumanis, 2010).

Additives constitute a significant portion in evaluation of Warm Mix Asphalt. The following two different ways could be listed as the methods of adding additives in the plant based on the asphalt plant production system (Oylumluoglu, 2012).

- The dry method
- The wet method

Additive is added directly in the mixing chamber in the dry method while in the wet method; the additive is mixed with bitumen homogenously and then mixed together with the aggregates in the mixing chamber (Oylumluoglu, 2012).

Table 4.1 Summary of some of WMA products and technologies available (Zaumanis, 2010)

Product	Company	Description	Use Reported In	Additive	Production Temperature [Or Reduction Ranges]
ORGANIC					
Sasobit®	Sasol	Fischer-Tropsch wax	US, EU, Worldwide	2.5-3.0% of bitumen weight in Germany 1-1.5% of bitumen weight in US	130-150°C, [varies]
Asphaltan® A **Romonta® N**	Romonta GmbH	Montan Wax for mastic asphalt	Germany	1.5-2.0% of bitumen weight	Varies, [20°C]
Asphaltan® B	Romonta GmbH	Rafined Montan wax with fatty acide amide for rolled asphalt	Germany	2.0-4.0%, 2.5%by mixture weight	Varies, [20-30°C]
CHEMICAL					
Evotherm® ET	Mead-Westvaco	Chemical bitumen emulsion	US, France, worldwide	Delivered in form of bitumen emulsion	85-115°C, [varies]
Evotherm ® DAT	Mead-Westvaco	Chemical package plus water	US, France, worldwide	30% by weight of binder	85-115°C, [varies]
Rediset® WMX	Akzo Nobel	Cationic surfactants and organic additive	US, Norway	1.5-2% of bitumen weight	126°C, [varies]
REVIX®	Mathy-Ergon	Surface-active agents, waxes, processing aids, polymers	US	Not specified	-,[15-26°C]
FOAMING TECHNOLOGY					
WAM-Foam®	Shell Bitumen and Kolo Veidekke	Foaming process using two binder grades	US, Norway	Antistripping agents could be added to soften binder	100-120°C
Advera®	PQ Corporation	Water containing using Zeolite	US	0.25% of mixture weight	-, [20-30°C]
Aspha-Min®	Eurovia	Water containing Zeolite	US, France, Germany	0.3% by mixture weight	-, [20-30°C, varies]

4.1.1.1 Organic Warm Mix Asphalt Additives

Organic or wax additives are used to attain the temperature reduction by reducing viscosity of binder. The processes show a decrease of viscosity above the melting point of the wax and as a result produce asphalt mixes at lower temperatures. They tend to increase the stiffness of the binder they are combined into after crystallization.

Sasobit® is an example of the organic additives. It is a by-product from the synthetic petrol production process called Fischer-Tropsch Process. Fischer-Tropsch waxes are long-chain aliphatic hydrocarbon waxes produced as a result of coal gasification. With a melting range between 85°C and 115°C, Sasobit® shows high viscosity at lower temperatures, and low viscosity at higher temperatures. It is known as an "asphalt flow improver" since it lowers the viscosity of the binder at mixing and compaction temperatures. With a lower bitumen viscosity, the working temperatures can be decreased by 18°C - 54°C (Hurley & Prowell, 2005). At service temperatures, Sasobit forms a lattice structure in the asphalt binder that gives the mixture stability (Zaumanis, 2010). A sample of Sasobit® is shown in Figure 4.3.

Figure 4.3 Sasobit sample

Since Sasobit® is delivered in a pellet form; it may be added into the asphalt plant by many different methods. The favored method requires a specially built feeder with a blower that connects directly to the drum. Sasobit® pellets may also be added to the existing RAP system or mixed directly into the asphalt bitumen tanks in a molten state (Middleton & Forfylow, 2009).

The use of Sasobit® content used in this study is based on the research made by O'Sullivan & Wall (2009) whom concluded that in order to achieve maximum effectiveness; the Sasobit® should be added at a rate of 3.0% by weight of bitumen.

4.1.1.2 Chemical Warm Mix Asphalt Additives

Chemical additives are the third type of most commonly used WMA technologies. Warm mix asphalt systems involving the use of chemical additives or surfactants are not too much relying on the reduction of the binder viscosity, but rather the improvement of the coating capability of the binder at a lower mixing temperature (Croteau & Tessier, 2008). A variety of chemical packages are used for different products which usually include a combination of surfactants, emulsification agents, polymers and additives to improve coating, workability and compaction of mixture, as well as antistripping agents (Zaumanis, 2010). The WMA systems using this approach are relatively new and their development is promising. Temperature reduction is provided without addition of water.

Rediset® WMX (developed by Akzo Nobel) is a good example of chemical additives which not only lowers mixing and compaction temperatures but also provides superior compaction, improves the moisture resistance properties of the mix, and maintains the performance properties of the binder. Its combination includes both organic additive and a kind of cationic surfactant (Chowdhury & Button, 2008). Prowell & Hurley (2007) stated that the surfactants simply increase the coating ability of the aggregate with the bitumen by "active adhesion." and the other constituents play role in reducing the viscosity of the bitumen. There is no need for additional anti-striping agent in the mixture since Rediset® provides better coating to the aggregate. Rediset® can be blended with bitumen or can be added to the mixture right after the addition of bitumen. If it is directly blended with bitumen at the refinery, it does not require any modification at the plant.

Chowdhury & Button (2008) recommend Rediset® at a rate of 1.5-2.0% by weight of bitumen which is supposed to allow 15-30°C temperature reduction compared to HMA. A sample of Rediset® is shown in Figure 4.4.

Figure 4.4 Rediset sample

4.1.1.3 Foaming Warm Mix Asphalt Additives

Foaming processes is based on the reality that when a given volume of water turns to steam at atmospheric pressure, it expands by a factor of 1,673. Water is added in small amounts into the hot bitumen in foaming technology. When the water is dispersed into hot asphalt binder and turns into steam, there is a resulting expansion of the binder and corresponding reduction in the mix viscosity (Middleton & Forfylow, 2009). Some adhesion problems could be experienced in using of water and thus, anti-stripping additives can be used to minimize moisture susceptibility and to provide chemical adhesion between bitumen and aggregate surfaces.

There are two commonly used foaming techniques available up to the date. These are called direct and indirect foaming methods.

In the direct method of foaming a small controlled amount of water is injected to hot bitumen via foaming nozzles. This results in a large but temporary increase in the effective volume of the binder which helps coating at lower temperatures. Some vapor remains in the bitumen during compaction reducing effective viscosity and facilitating compaction. On cooling the binder reverts to normal, as the amount of water is insignificant. This technique can enable a temperature reduction of the asphalt mix of about 20 to 40°C (European Asphalt Pavement Association [EAPA], 2014).

The indirect foaming technique uses a mineral as the source of foaming water. Hydrophilic minerals from the zeolite family are commonly used. They contain about 20 percent of crystalline water, which is released above 100°C. A controlled foaming effect is created by the release of water, which can provide an improved workability for a 6- to 7-hour period, or until the temperature drops below 100°C. The foaming results in an improved workability of the mix which can subsequently allow a decrease in the mix temperature by approximately 30°C with equivalent compaction performance (EAPA, 2014).

One of the reportedly common foaming practices in Norway is WAM-Foam which does not use any additive material. Two binder grades one nominally soft, and one nominally hard is maintained. The soft and hard binders are blended in-line to produce the desired binder grade. Typically the soft binder has a viscosity grade of 1500 centistokes at 60°C (V1500) and the hard one is a 70/100 Pen, or approximately a PG 58/64-22. The aggregate first heated to approximately 130°C and then coated with the soft binder which is typically 20 to 30 percent of the total binder. Then the hard binder is foamed into the mixture by adding cold water at a rate of 2 to 5 percent by mass of the hard binder at approximately 180°C (356°F). The resulting binder grade for 20 percent of a V1500 and 80 percent of a 70/100 Pen binder would be a 70/100 Pen binder, non-aged. Coating the coarse aggregate with the soft binder acts to satisfy the asphalt absorption of the coarse aggregate that may not otherwise occur with a stiffer binder at low temperature (Prowell, 2007).

Adding an additive which contains a particular amount of water is another foaming technology method. A pre-moistened additive releases its moisture when added to the hot mixture. This acts as the same system of injection method. Released steam results in more lubricant mix and correspondingly increases the workability. Many additives such as Advera® and Aspha-min® (both are synthetic zeolites) have been developed on the basis of this theory. Water is absorbed and maintained by Zeolites since they are minerals with micro-porous structure (D'Angelo et al., 2008).

4.2 Advantages of Warm Mix Asphalt Technology

Many advantages were consistently acknowledged as driving the development of WMA in Europe (D'Angelo et al., 2008):

- Environmental aspects and sustainable development concerns, or "green construction," especially reduction in CO_2 emissions as a result of reduction in consumption of energy.

- Improvement in field compaction. Paving seasons are extended and the possibility for longer haul distances are facilitated by improvements in the compactability of WMA mixes.

- Welfare of workers, particularly with gussasphalt or mastic asphalt, which is produced at much higher temperatures than HMA.

4.2.1 Environmental Benefits

One pillar of sustainable development is environmental protection. Reduction in the use of natural resources (fuel) and the production of CO_2 is an important part of sustainable development. Reduction of CO_2 emissions is assigned as part of the European Union’s ratification of the Kyoto Protocol.

Reduced plant emissions are indicated in a number of suppliers’ presentation data’s from Norway, Belgium, and France. At temperatures below 80°C (176°F), there are virtually no emissions of bitumen; even at about 150°C (302°F), emissions are only about 1 mg/h. Significant emissions were recorded at 180°C (356 °F) (D’Angelo et al., 2008). Table 4.2 presents the ranges in reductions in plant emissions in some countries.

Table 4.2 Reported reductions in plant emissions with WMA (D’Angelo et al., 2008)

Emissions	**Norway**	**Italy**	**Netherlands**	**France**
CO_2	31.5%	30-40%	15-30%	23%
SO_2	-	35%	-	18%
VOC	-	50%	-	19%
CO	28.5%	10-30%	-	-
NO_X	61.5%	60-70%	-	18%
DUST	54.0%	25-55%	-	-

4.2.2 Paving Benefits

Several paving-related benefits of warm mix asphalt technologies have been reported and discussed to the date. Some of them are presented as follows:

- Improved workability because of lower bitumen viscosity at paving temperature;
- Improved compaction possibility, as a result of the reduction in viscosity of binder;
- Ability to pave in cooler temperatures and still obtain density. The drop in temperature with time is less significant and allows longer time for paving and compaction. This is because the difference with the ambient temperature is smaller for WMA than for Hot Mix Asphalt (HMA);

- Lower paving temperature improves the working conditions for workers, which means enhanced productivity and improved quality;
- Possibility to pave at lower temperature allows longer hauling distances;
- Reduced time of pavement cooling because of lower initial temperature;
- Reduction of emissions of fumes and odor provides less inconvenience to public near production and work sites.
- Ability to incorporate higher percentages of RAP;

4.2.3 Fuel and Energy Savings

Economic aspects of using warm mix asphalt technology could be listed as follows:

- Decrease in energy costs because of reduced energy consumption;
- Less wear on asphalt plant due to reduced temperature.

Burner fuel savings with warm mix asphalt technology typically range from 20 to 35 percent as indicated by fuel savings reports. These levels could be higher if burner tuning was completed to allow the burner to run at lower settings. Fuel savings could be higher and possibly 50 percent more with processes where the aggregates or a portion of the aggregates are not heated above the boiling point of water.

CHAPTER FIVE
POLYMER MODIFIED WARM MIX ASPHALT TECHNOLOGY

As mentioned in the previous chapters, WMA denotes technologies that allow considerable reduction of mixing and compaction temperatures of bitumen and mixes using varieties of processes and additives. It was also stated that besides reduction in fuel consumption and emissions in plants, there are many other promising advantages of using warm mix asphalt technologies including, but not limited to, longer paving seasons, longer hauling distances, earlier traffic opening, reduced binder aging, and reduced cracking (Hurley & Prowell 2005*a*, 2005*b*, 2006; Gandhi & Amirkhanian, 2007).

Again as stated in previous chapters, PMB due to its superior performances including less aging, better rutting resistance, and lower fatigue cracking properties, has become a very important part of road construction (Wekumbura et al. , 2007; Yildirim, 2007).

Most of the time, due to the higher viscosity properties than the conventional HMA, those produced with PMB are mixed and compacted at higher temperatures. HMA including PMB additives which is prepared with lower mixing and compaction temperatures might cause several problems, such as inadequate volumetric properties (i.e., high air voids) and poor short-term and long-term performance. In addition, the higher temperature for the mixture requires more energy consumption and produces more environmental issues like excessive carbon dioxide emission or odor problems (Zubeck et al., 2003).

Optimum mixing and compaction temperatures of the PMB mixes are expected to decrease and be comparable to those of conventional mixtures if the warm mix asphalt technologies are incorporated into the PMB mixes. Thus, investigating the properties and performance of incorporating warm mix processes and additives into PMB binders has become a popular subject lately.

Kim, Lee & Amirkhanian (2010) have made an experimental evaluation for the performance properties of PMB binders using two of the available warm mix processes (i.e., Aspha-min® and Sasobit®). After short and then long- term aging the warm PMB binders and carrying superpave binder tests on them, Kim et al. (2010) state that (1) the addition of the WMA additives into the PMB binders showed positive effects on increasing rutting resistance at high temperature; (2) the PMB binders containing the additives were observed to be less resistant to fatigue cracking at intermediate temperatures compared to the control PMB binders; and (3) the addition of wax additive represented a possible lower resistance on low temperature cracking.

Kim (2010) has made an extensive performance evaluation of SBS modified asphalt binders and mixtures combined with WMA technology. Two WMA technologies, micro water (Aspha-min®) and synthetic wax (Sasobit®) based, have been used to evaluate their effectiveness in SBS modified asphalt mixtures along with binders. The four major areas of research included the binder analysis (including Superpave binder performance and surface topography); compaction condition study; oxidative aging analysis and mixture performance analysis.

He states that the WMA additives improved the binder properties especially at higher temperatures namely viscosity and rutting and the inclusion of these materials did not adversely affect the engineering properties of the mixtures. Atomic Force Microscopy (AFM) was utilized to obtain the various surface images that showed the strong correlations with especially aging process. The compaction condition study showed that WMA mixtures had better compaction behavior under lower temperatures and gyrations and also the other volumetric results indicated the comparability with the HMA mixtures. The oxidative aging results showed that the asphalt mixtures aged in the oven had a higher level of aging than the binder by itself aged in the rolling thin film oven (RTFO) (Kim, 2010).

Kok et al. (2013) have performed investigations on rheological properties of SBS modified bitumen using organic warm mix additives. After performing dynamic shear rheometer test (DSR) on different binders prepared with a combination of different concentrations of SBS and organic additive (SBS at concentration of 2%, 3% and 4% and organic WMA additive at concentrations of 2%, 3% and 4%) and investigating and comparing the rutting parameter $G^*/\sin\delta$ and phase angle δ values of the combination, Kok et al. (2013) state that (1) 4% SBS + 4% organic WMA additive combination shows superior performance in terms of rutting resistance; (2) 3% SBS + 3% organic WMA additive combination shows better resistance against rutting than 67% of the combinations; (3) addition of organic WMA additive helps in increasing the elastic behavior of the combinations. He finally states that the addition of organic WMA additive which is known to decrease the viscosity of the mixture, helps in increasing the performance of SBS modified bitumen as well.

CHAPTER SIX
RHEOLOGY

6.1 Fundamental Rheological Terms

6.1.1 Introduction

Rheology is the science which describes the deformation of a body under the application of stresses. “Bodies” in this context can be solids, liquids, or gases. The word comes from the Greek “rheos” that means to flow.

Rheometry describes measuring methods and devices used to determine rheological properties.

Application of an external force on a body produces displacement between the particles relative to each other. We call this displacement as strain and the type and magnitude of the strain are characteristic properties of the material.

Shear Stress, Shear Rate, and Viscosity are the constituents leading to an understanding of Rheology (US Ink, 1995).

The simplest model to explain rheological properties is the parallel plate model presented in Figure 6.1. The top plate, which has a surface area A [m^2], is moved by a force F [N= Kg.m/s^2] at a speed v [m/s]. The bottom plate remains at rest. The distance between the plates, to which the material adheres, is described by h [m]. Now, thinnest elements of the liquid will be displaced between the plates. This laminar flow is of fundamental importance for rheological investigations (Rheotec, n.d.).

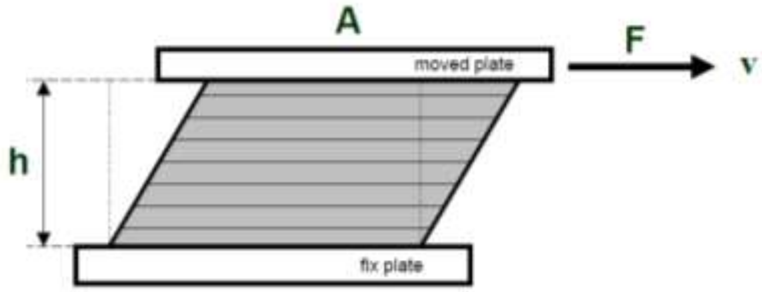


Figure 6.1 Parallel plate model (Rheotec, n.d.)

Shear Stress	$\tau = F/A$	in Pa	(6.1)
Shear rate	$\dot{\gamma} = v/h$	in s^{-1}	(6.2)
Viscosity	$\eta = \tau/\dot{\gamma}$	in Pa.s	(6.3)
Strain	$\gamma = dx/h$	dimensionless	(6.4)

6.1.2 Definitions

6.1.2.1 Shear Stress

As shown in Figure 6.1, a force F applied laterally to an area A being the interface between the upper plate and the liquid underneath, leads to a flow in the liquid layer. The velocity of the movement at a given force is controlled by the internal force of the liquid. The Shear stress is defined as:

$$\text{Shear stress } \tau = \frac{\text{Force F}}{\text{Area A}} = \frac{\text{N (Newton)}}{\text{m}^2} = Pa \tag{6.5}$$

6.1.2.2 Shear Rate

As shown in Figure 6.1, the shear stress τ causes the liquid to flow in a special pattern. At the upper boundary, a maximum flow speed v_{max} is established, while the lowermost layer remains at rest. The shear rate is defined as:

$$\text{Shear rate } \dot{\gamma} = \frac{dv}{dh} \tag{6.6}$$

In the formula above dv is velocity differential between adjacent velocity layers and dh is thickness differential of the flow layers. When the flow is laminar the velocity differential between adjacent layers of like thickness is constant (dv=const., dh= const.). The differential thus is resembled as follows (Rheotec, n.d.):

$$\text{Shear rate } \dot{\gamma} = \frac{\text{Velocity v}}{\text{Distance h}} = \frac{m/s}{m} = s^{-1} \tag{6.7}$$

The symbol D is also used instead of $\dot{\gamma}$ in literature.

6.1.2.3 Dynamic Viscosity

Viscosity is used to describe toughness of a material. Dynamic viscosity is defined as:

$$\text{Dynamic viscosity } \eta = \frac{\text{Shear stress } \tau}{\text{Shear rate } \dot{\gamma}} = \frac{\text{Pa}}{\text{s}^{-1}} = Pa.s \tag{6.8}$$

The unit Pa.s (or mPa.s) is used for the viscosity. It should be noted that the previously used units of “centiPoise” (cP) for the dynamic viscosity η are interchangeable with (mPa.s) (Schramm, 2000).

$$1\text{mPa.s} = 1\text{cP} \tag{6.9}$$

Typical viscosity values for some materials are given in Table 6.1 (Schramm, 2000):

Table 6.1 Typical viscosity values at 20°C (mPa.s)

Petrol	0.65	Coffee cream	≈10
Water	1.0	Honey	≈10^4
Mercury	1.5	Polymer melts	≈10^3-10^6
Grape juice	2 - 5	Bitumen	≈10^8
Blood (at 37°C)	4 - 25	Glass	≈10^{23}

6.1.2.4 Kinematic Viscosity

When Newtonian liquids are tested using capillary viscometers such as Ubbelohde or Cannon Fenske, kinematic viscosity υ concept is used instead of dynamic viscosity η. The density of the sample is one other additional parameter in the kinematic viscosity. Kinematic viscosity υ and dynamic viscosity η are linked (Schramm, 2000):

$$\text{Kinematic viscosity } \upsilon = \frac{\text{Dynamic viscosity } \eta}{\text{Density } \rho} = \frac{\text{mm}^2}{\text{s}} \tag{6.10}$$

Old unit: cSt (centistokes) = mm^2/s

6.1.3 Factors Which Effect the Viscosity

There are many parameters that affect the flow and strain behavior of a material. Some of them are listed as follows (Rheotec, n.d.):

- Physical and chemical properties of substance
- Temperature
- Shear rate
- Time
- Pressure

6.2 Load-Time-Temperature Dependent Flow Behavior

This section is intended to explain flow and strain behavior of materials depending on load, time and temperature parameters.

6.2.1 Load-Dependent Flow Behavior

The relation between shear stress τ and shear rate$\dot{\gamma}$ is used to characterize the flow behavior of materials. For the graphic representation, a $\dot{\gamma} - \tau$ diagram is often used. Irrespective of whether $\dot{\gamma}$ or τ were given for the measurement, most often, the shear stress is shown on the ordinate and the abscissa the shear rate. The diagrams shown in Figures 6.2 to 6.3 are referred to as flow and viscosity curves.

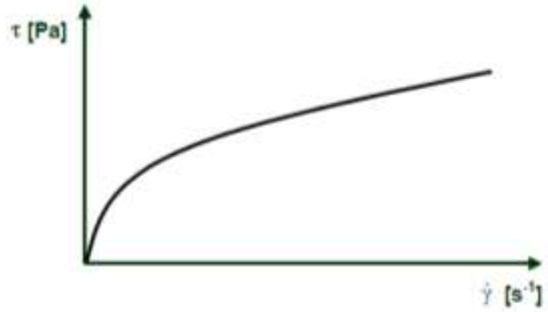


Figure 6.2 Flow curve

In order to produces the viscosity functions or viscosity curve, the viscosity is plotted over the shear rate or shear stress.

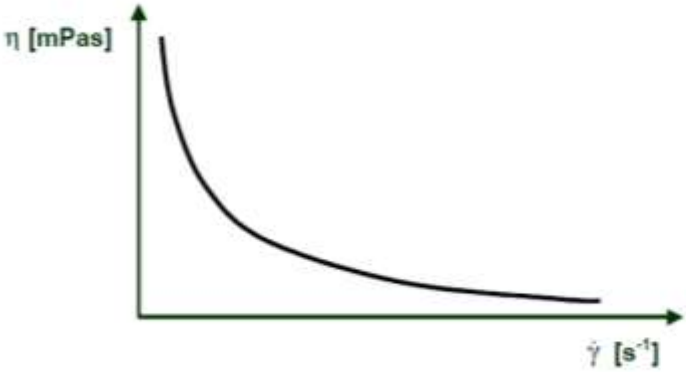


Figure 6.3 Viscosity curve

When the measurement is done via a viscometer or rheometer the result is always a flow curve. However, the viscosity curve could be worked out from the measured values (Rheotec, n.d.).

6.2.2.1 Newtonian Flow Behavior

If the shear gradient $\dot{\gamma}$ of viscous flow in a material is proportional to the applied shear stress τ on it, it is named as Newtonian material. The flow function of a Newtonian material is a straight line which starts from origin of the coordinate system and runs through it at an angle α. This relation between shear stress and shear gradient is defined by Newton's law of viscosity.

$$\eta = \frac{\tau}{\dot{\gamma}} = \text{Const.} \tag{6.11}$$

η is the material constant of the dynamic shear viscosity.

The viscosity function of the Newtonian materials is a straight line which runs parallel to the abscissa. Water, mineral oil, sugar solution, bitumen are examples of Newtonian materials (Rheotec, n.d.). Flow and viscosity curves of Newtonian materials are presented in Figure 6.4.

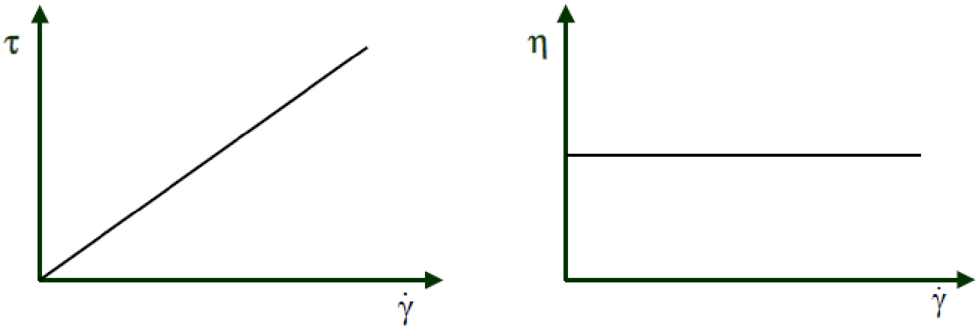


Figure 6.4 Flow and viscosity curves of Newtonian materials

6.2.1.2 Pseudoplasticity

Fluids which become thinner as the shear rate surges are called "pseudoplastic" (Schramm, 2000). A pseudoplastic or structurally viscous material can be pumped through pipelines with lesser effort at the same flow velocity (Rheotec, n.d.). According to Ostwald-de Waele, the mathematical expression for pseudoplastic material is:

$$\tau = \mathrm{K}.\dot{\gamma}^{n} \tag{6.12}$$

Where n<1 for pseudoplastic materials

Converted into a viscosity function:

$$\eta = \frac{\tau}{\dot{\gamma}} = \mathrm{K}.\dot{\gamma}^{n-1} \tag{6.13}$$

A flow and viscosity curve for a typical pseudoplastic material is presented in Figure 6.5.

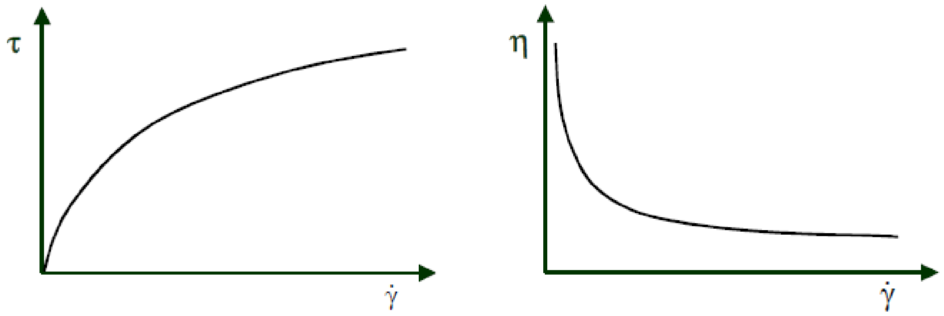


Figure 6.5 Flow and viscosity curves of Pseudoplastic materials

Suspensions, dispersions, paints, lacquers, creams, lotions and gels are examples of pseudoplastic material.

6.2.1.3 Dilatancy

Dilatant materials show an increase in viscosity as the shear rate grows. This behavior could cause concerns in technological process. Dilatant behavior found rather seldom. According to Ostwald-de Waele, the mathematical expression for dilatant material is:

$$\tau = \mathrm{K}.\dot{\gamma}^{n}\ , where\ n > 1 \tag{6.14}$$

When we change it to a viscosity function:

$$\eta = \frac{\tau}{\dot{\gamma}} = K.\dot{\gamma}^{n+1} \tag{6.15}$$

A flow and viscosity curve for a typical Dilatant material is presented in Figure 6.6.

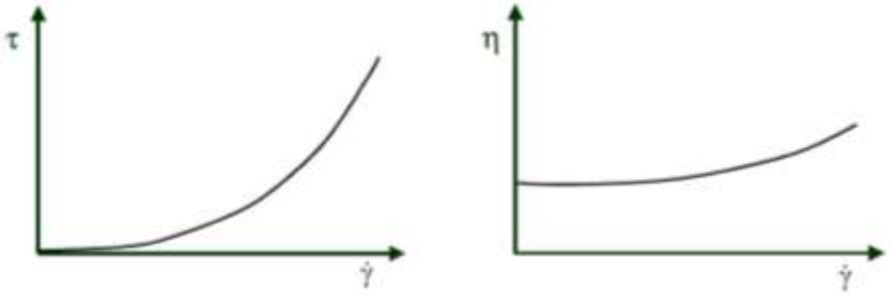


Figure 6.6 Flow and viscosity curves of Dilatant materials

Concentrated corn starch dispersions, wet sand, several ceramic suspensions, several surfactant solutions are example of dilatant materials (Rheotec, n.d.).

6.2.1.4 Plasticity and Yield Point

Plastic fluids belong to both groups of liquids and solids. They are mostly dispersions which at rest can develop an intermolecular/interparticle network of binding forces (polar forces, van der Waals forces, etc.). These forces prevent positional change of volume elements and give the substance a solid view (Schramm, 2000). If an eternal force which is smaller than the internal forces (bonding forces) acts on the material, the resulting strain is reversible, as with solids. However, if the external forces exceed the internal bonding forces of the network, the material will start flowing, the solid turns into a liquid (Rheotec, n.d.). Yield point τ_0 could be defined as follows:

The maximum shear stress τ ate shear rate $\dot{\gamma} = 0s^{-1}$

Thus, if $F_{external} < F_{internal}$, the material does not flow
$F_{external} > F_{internal}$, the material starts to flow

In plastic liquids the flow curves do not start in the origin of the coordinate system, but run on the ordinate axis until the yield point is reached, then they converge from the ordinate. There are a number of mathematical equations to express the flow curves of plastic liquids depending on the actual material.

Mathematical expression developed by Bingham:

$$\tau = \mathrm{f_B} + \eta_\mathrm{B}.\dot{\gamma}\text{ , where } \mathrm{f_B} = \text{yield point according to Bingham} \qquad (6.16)$$

Mathematical expression developed by Casson:

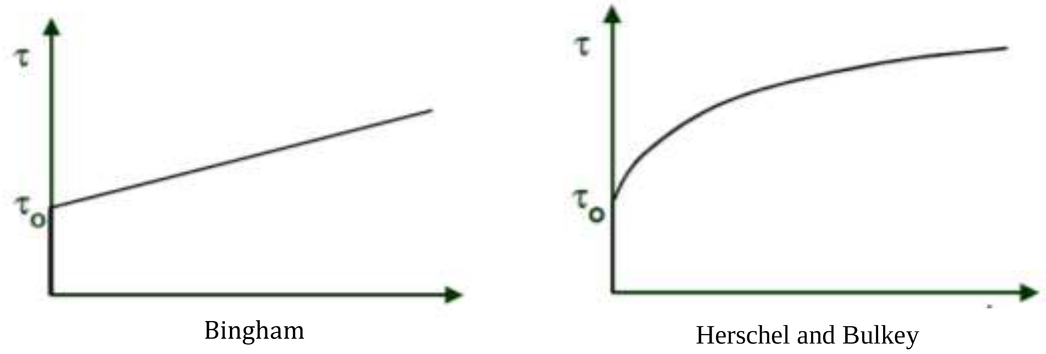
$$\sqrt{\tau} = \sqrt{\mathrm{f_C}} + \sqrt{\eta_\mathrm{C}.\dot{\gamma}}\text{ , where } \mathrm{f_C} = \text{yield point according to CASSON} \quad (6.17)$$

Mathematical expression developed by Herschel and Bulkey:

$$\tau = \mathrm{f_H} + \mathrm{m}.\dot{\gamma}^{p} \qquad (6.18)$$

Where, $\mathrm{f_H} = $ yield point according to Herschel and Bulkey
Where, $p < 1$ for pseudoplastic and $p > 1$ for dilatant materials

Flow curves of materials with a yield point are presented in Figure 6.7.



Bingham

Herschel and Bulkey

Figure 6.7 Flow curves of materials with a yield point

Toothpaste, PVC paste, emulsion paint, lipstick, fats, printing ink and butter are examples of materials with a yield point.

6.2.2Time-Dependent Flow Behavior

6.2.2.1 Thixotropy

A material is called thixotropic that not only dilutes when subjected to a sufficient shear rate, but also returns to its original viscosity after a material-specific period of rest. Thixotropy is a property seen in non-Newtonian liquids, they return to their original viscosity only with a delay after the shear force ceased to act. In addition, these materials often also have a yield point (Rheotec, n.d.). Figures 6.8 presents viscosity-time curve of a thixotropic material.

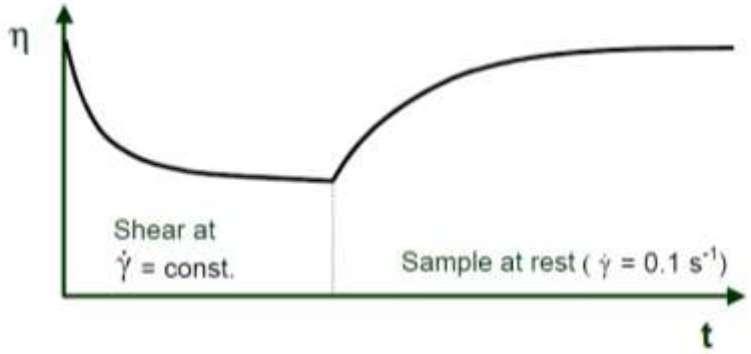


Figure 6.8 Viscosity-time curve of a thixotropic material

It is easy to see the two transitional areas in the curve above. A gel is quickly altered into a sol at a constant shear force. During the period of rest the material-specific structures are re-established. Some examples of thixotropic materials are tomato ketchups, paints, cosmetics, pastes and other foodstuff.

6.2.2.2 Rheopexy

They are usually called rheopective liquids, in short. Rheopective materials show an increase in viscosity related to the duration of shear. When these liquids are allowed to rest they recover the original viscosity level. Rheopexy and Thixotropy are opposite flow properties. Thixotropy is a very common behavior for many liquids whereas true rheopexy is very rare indeed (Schramm, 2000). Several latex dispersions, several casting slips and several surfactant solutions are could be given as examples of Rheopective materials. Viscosity-time curve of a Rheopective material is presented in Figure 6.9.

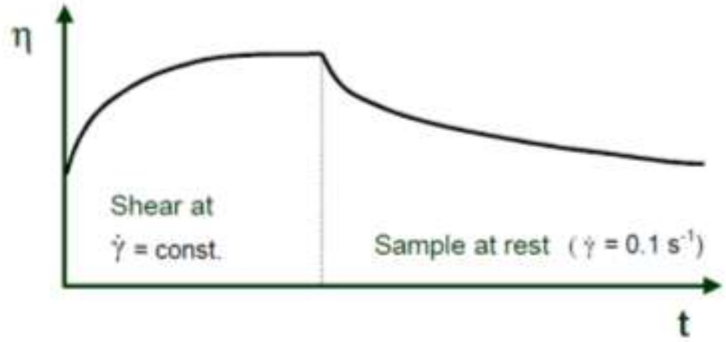


Figure 6.9 Viscosity-time curve of a Rheopective material

6.2.3 Temperature-Dependent Flow Behavior

As stated above, the viscosity of a material is also a function of temperature. That’s why it is important in viscosity measurements to have an accurate temperature control and indication.

The viscosity-temperature of a material is found at a constant shear rate. In most materials, a rise in temperature causes a viscosity decreases. In ideally viscous materials, this phenomenon can be explained with the help of the Arrhenius equation (Rheotec, n.d.):

$$\eta = A.\, e^{B/T} \tag{6.19}$$

Where, T is the temperature in Kelvin and A, B are material constants. A typical viscosity-temperature curve is presented in Figure 6.10

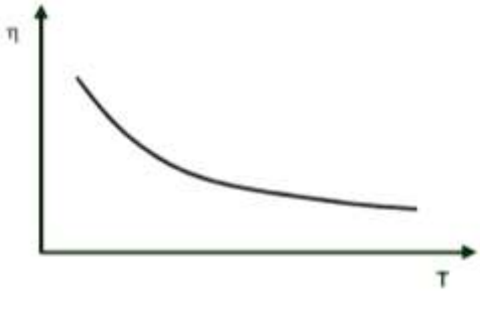


Figure 6.10 Viscosity-temperature curve

6.3 Flow Behavior of Viscoelastic and Elastic Materials

6.3.1 Flow Behavior of Viscoelastic Materials

A material which shows both viscous and elastic properties is called Viscoelastic. Considering their physical differences, viscoelastic materials could be divided into groups of viscoelastic liquids and viscoelastic solids. The elastic portion of viscoelastic liquids is described by Hooke's law, which is also known as the spring model, the viscous model by Newton's damper model (Rheotec, n.d.).

6.3.1.1 Viscoelastic Liquids

The difference between a viscous and a viscoelastic liquid when they are stirred by a rotor in a pot is shown in the Figure 6.11. While the viscous liquid as the result of centrifugal forces is thrown outwards and upwards against the wall of the pot, the viscoelastic liquid is drawn up the rotor shaft against the force of gravity. This phenomenon of masses "creeping up" a rotating shaft due to the acting normal forces is called the Weissenberg effect. It can be seen typically when mixing flour and water to make bread- or cake dough (Schramm, 2000).

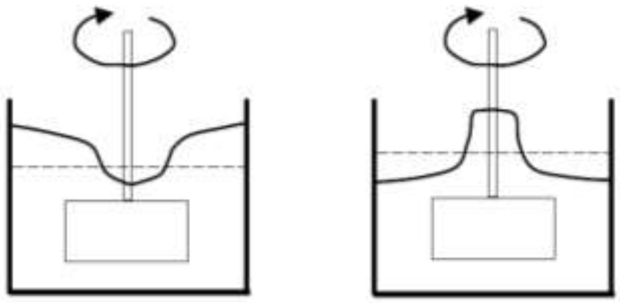


Figure 6.11 Flow behaviors of a viscous and a viscoelastic liquid (Rheotec, n.d.)

A viscoelastic liquid can be described using the model in Figure 6.12, where damper and spring are arranged in series which is also called Maxwell model. A force applied on a viscoelastic material deforms the spring, but the damper reacts with a delay. If the force is stopped, the spring will return immediately while the damper remains displaced, so that the material remains partly strained and there is no full restoration of shape. Elastic portion is described by the amount that the spring returns while, the viscous portion is explained with the amount of the remaining strain (damper). Gels and silicone rubber compounds are examples of viscoelastic liquids.

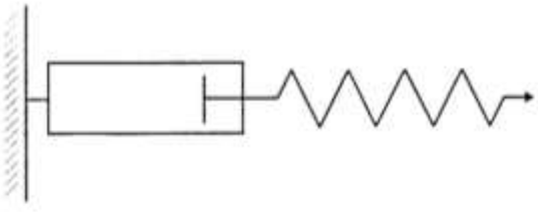


Figure 6.12 Maxwell model

6.3.1.2 Viscoelastic Solids

The model to describe viscoelastic solids is again a combination of spring and damper models. In contrast to viscoelastic liquids, however, the two elements are connected in parallel, as in the Kelvin-Voigt model as shown in Figure 6.13. If a force is applied on a viscoelastic solid a delayed strain will occur, because the damper impedes the displacement of the spring. If the force is stopped, the body will fully return to its original shape (but again delayed by the damper). That means that there is a full restoration of shape. A viscoelastic solid is characterized in that it has the ability of reversible strain (Rheotec, n.d.).

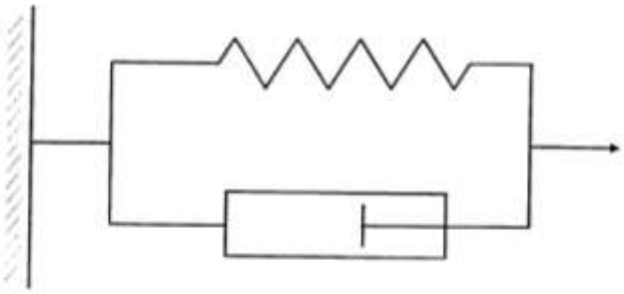


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Figure 6.13 Kelvin-Voigt model

6.3.2 Flow Behavior of Elastic Materials

6.3.2.1 Strain

In order to illustrate the strain γ we will investigate the cube in Figure 6.14 as the volume element. The bottom face of the volume element is fixed. The upper face of the volume will be displaced at an amount of s in case of the application of a force F.

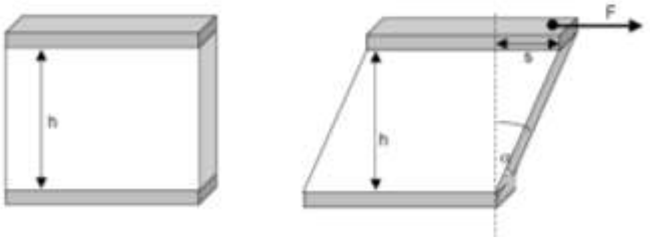


Figure 6.14 Unloaded and loaded volume elements (Rheotec, n.d.)

The mathematical expression for strain is:

$$\tan\alpha = \frac{s}{h} = \gamma \tag{6.20}$$

Strain is a dimensionless parameter. The symbol used for shear rate ($\dot{\gamma}$) is derived from that for the strain (γ). A change in strain $d\gamma$ during a period of time dt is defined as shear rate. Therefore, $\dot{\gamma}$ is the derivative of strain γ with respect to time t. that is to say, the shear rate can be considered to be the strain rate.

6.3.2.2 Shear Modulus

In absolute elastic materials, the ratio of shear stress τ and resulting strain γ is constant. The material stiffness is explained by this material-specific parameter and is defined as the shear modulus G.

$$\text{Shear modulus G} = \frac{Shear\ stress\ \tau}{Strain\ \gamma} = \frac{Pa}{1} = \text{pa} \tag{6.21}$$

6.4 Rheometry

If the calculated values are established on the basic physical units of force$[\mathrm{N}]$, length $[\mathrm{m}]$and time$[\mathrm{s}]$, Viscometers or rheometers used to determine the rheological properties are called absolute viscometers.

$$\text{dynamic viscosity}\ \eta = [\mathrm{N/m^2}] \cdot [\mathrm{s}] = \ \mathrm{force/length^2 \cdot time} = \ [\mathrm{Pa}] \cdot [\mathrm{s}]$$

In order to determine the viscosity depending on the rotational speed (shear rate), time and temperature, viscometers are used as the measuring device.

Rheometers are devices which are additionally able to determine the viscous and viscoelastic properties of the materials depending on the force (shear stress) in both rotation/creep test and oscillation test.

Considering the Newtonian relation $\eta = \tau/\dot{\gamma}$, the viscosity η can be determined using either of two different measuring methods (Rheotec, n.d.).

6.4.1 Tests at Controlled Shear Rate (CSR Mode)

In this measuring method shear rate assigned and shear stress measured accordingly. The dynamic viscosity η is calculated from the shear stress τ and shear rate $\dot{\gamma}$ (Schramm, 2000).

6.4.4.1 Viscosity-Time Test

A constant shear rate is exerted for an exact time period (Figure 6.15). The shear stress is calculated as a time function. The viscosity determined in accordance to the viscosity equation is obtained in relation to time (Figure 6.16). In practice this test is used in stability investigations, to study hardening reactions and with thixotropic materials (Rheotec, n.d.).

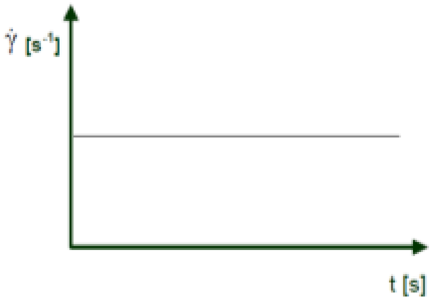
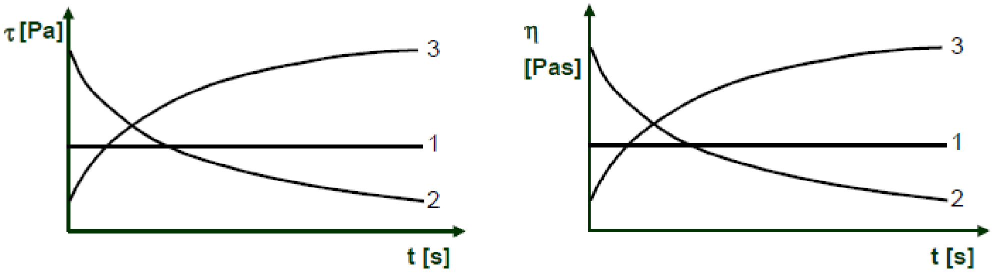


Figure 6.15 Shear rate-time diagram (conditions: shear rate = const., temperature = const.)



1- Material with a viscosity which does not change over time (i.e. calibration oil)
2- Material with a viscosity which decreases over time (i.e. ketchup)
3- Material with a viscosity which increases over time (i.e. hardening lacquer)

Figure 6.16 Results of the viscosity-time tests

6.4.1.2 Viscosity-Temperature Test

A temperature ramp is preset at a constant shear rate (Figure 6.17), and the viscosity is calculated in relation to temperature (Figure 6.18). While investigating temperature-dependent hardening or melting reactions in practice, we conduct this test (Rheotec, n.d.).

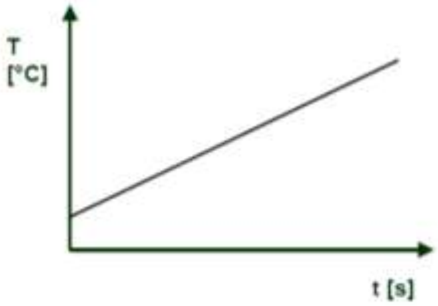
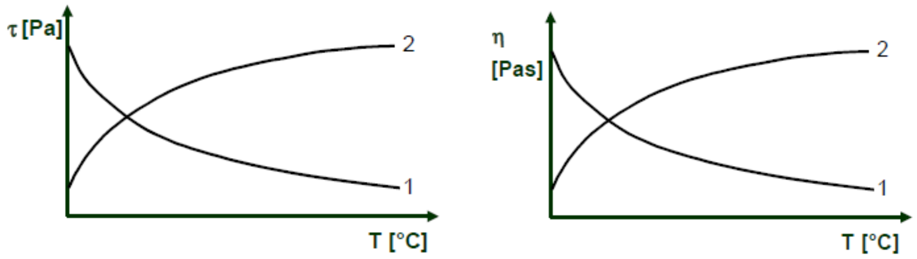


Figure 6.17 Temperature-time diagram (conditions: shear rate = const., variable temperature)



1- Material with a viscosity which decreases as the temperature rises (i.e. chocolate)
2- Material with a viscosity which increases as the temperature rises (i.e. hardening lacquer)

Figure 6.18 Results of the viscosity-temperature tests

6.4.1.3 Flow and Viscosity Curves

A shear rate-time profile is preset at a constant temperature (Figure 6.19). The shear stress is calculated for each shear rate value and the corresponding viscosity is obtained from those measuring results (Figure 6.20) (Rheotec, n.d.).

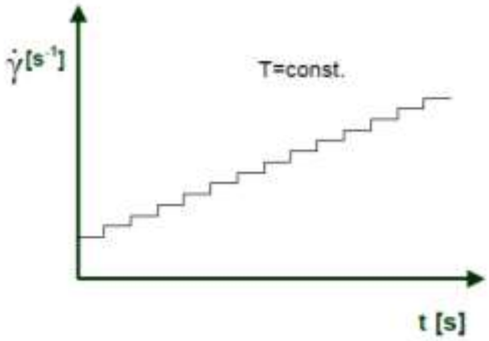
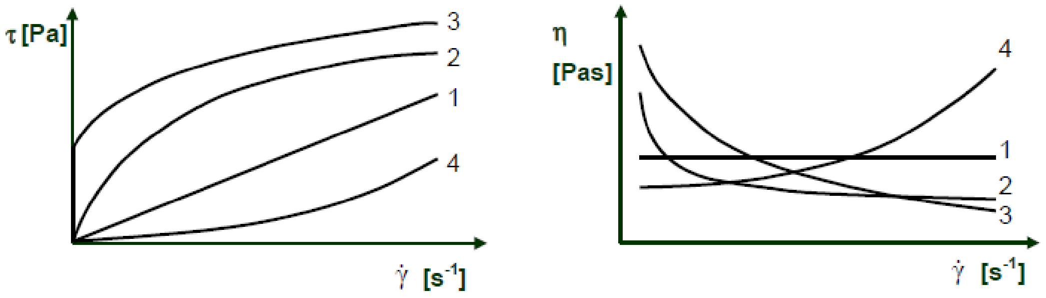


Figure 6.19 Shear rate-time profile (conditions: variable shear rate, temperature = const.)

Materials with ideally viscous behavior such as water have a constant viscosity value (Newtonian materials). In pseudoplastic materials the viscosity decreases as the shear rate rises (“shear thinning”). In contrast, dilatant materials the viscosity increases as the shear rate rises (“shear thickening”).



1- NEWTONIAN material
2- Pseudoplastic material
3- Plastic material
4- Dilatant material

Figure 6.20 Flow and viscosity curves of materials with different rheological behavior

It is frequent to plot the flow and viscosity curves in a way that the viscosity values are shown at both rising and falling shear rate as presented in Figures 6.21 and 6.22. There is often a section with constant shear rate between the two sections of the curve (up ramp, down ramp).

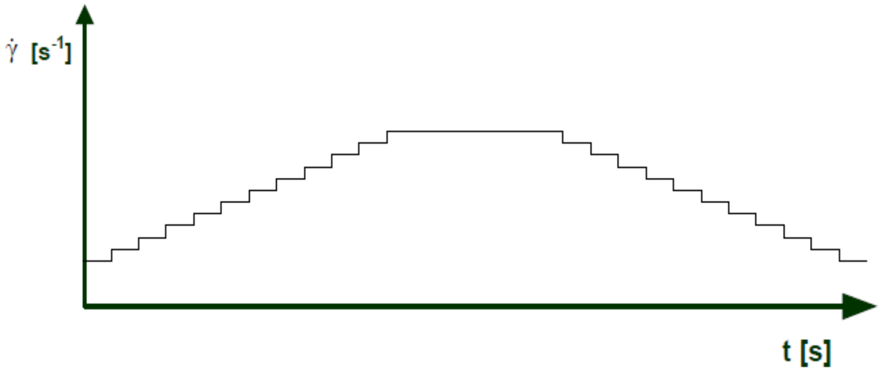


Figure 6.21 Rising and falling shear rate

The results of the calculations also allow information about time-dependent flow behavior to be derived along with the load-dependent flow behavior (pseudoplasticity, dilatancy). The area between the up and down curves is often used as a measure for time-dependent flow properties in practice. A large area is shown between two curves in the diagram by materials which require a long time after maximum shear to resume their structure (hysteresis area).

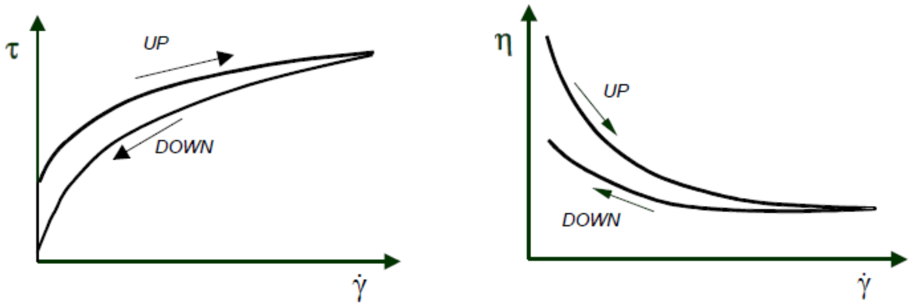


Figure 6.22 Flow and viscosity curve of a pseudoplastic and thixotropic material

Pseudoplasticity and Thixotropy are two rheological properties which exist fully independent of each other. They should not be mistaken.

6.4.2 Tests at Controlled Shear Stress (CSS Mode)

In this measuring method, Torque/Shear stress is assigned and strain/strain rate is measured accordingly. The dynamic viscosity η is calculated from the shear stress τ and shear rate $\dot{\gamma}$ (Schramm, 2000).

6.4.2.1 Viscosity-Time Test

The material under investigation is subjected to a constant shear stress τ for an exact period of time as shown in Figure 6.23. The achieved shear rate $\dot{\gamma}$ is calculated as a time function. The viscosity determined in accordance to the viscosity equation is obtained as a function of time as presented in Figure 6.24. This test is applied in practice when studying hardening reactions (Rheotec, n.d.).

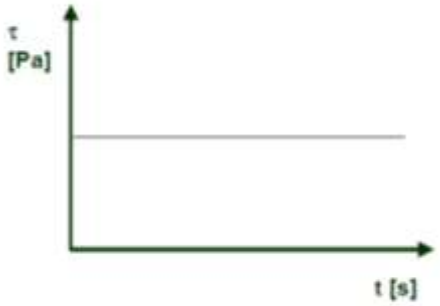
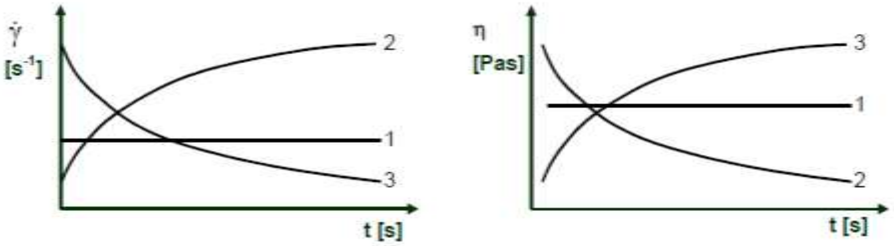


Figure 6.23 Constant shear stress-time diagram (conditions: shear stress and temperature = const.)



1- Material with a viscosity which does not change over time (i.e. calibration oil)
2- Material with a viscosity which decreases over time (i.e. ketchup)
3- Material with a viscosity which increases over time (i.e. hardening lacquer)

Figure 6.24 Results of the viscosity time test

6.4.2.2 Viscosity-Temperature Test

A temperature ramp is preset at a constant shear stress as presented in Figure 6.25 and the viscosity is calculated in relation to temperature as presented in Figure 6.26. In practice, this test is conducted in order to inspect temperature dependent hardening or melting reactions (Rheotec, n.d.).

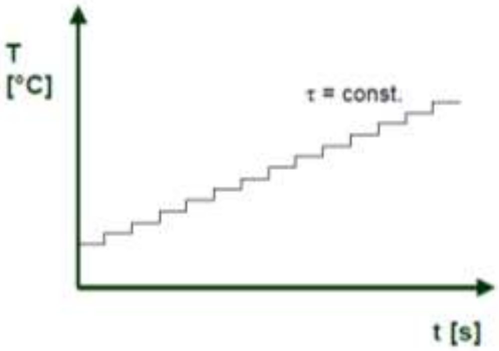
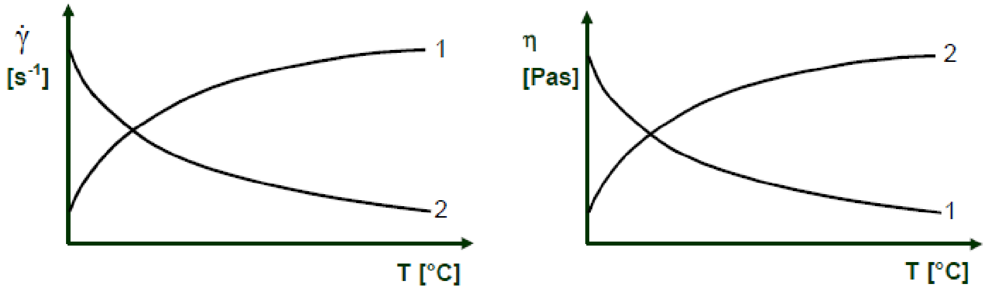


Figure 6.25 Temperature ramp (conditions: shear stress = const., variable temperature)



1- Material with a viscosity which decreases as the temperature rises (i.e. chocolate)
2- Material with a viscosity which increases as the temperature rises (i.e. jellying starch)

Figure 6.26 Results of viscosity-temperature test (Rheotec, n.d.)

6.4.2.3 Flow and Viscosity Curves

A shear stress-time profile is appointed at a constant temperature as presented in Figure 6.27. The shear rate is measured for each shear stress value and from the measured result the corresponding viscosity values are calculated as shown in Figure 6.28.

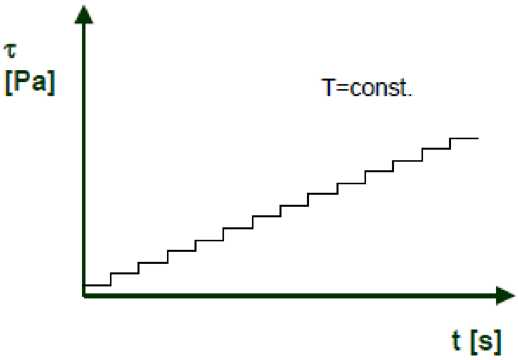
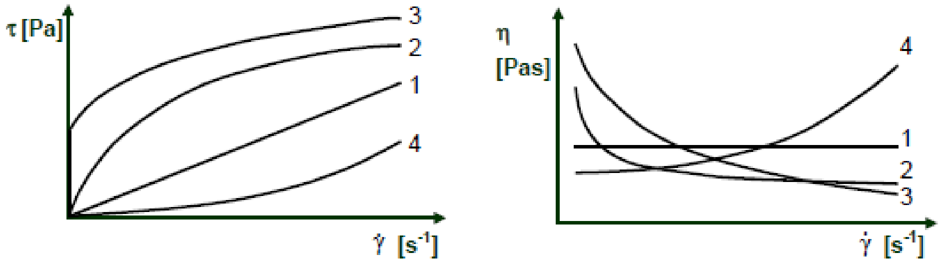


Figure 6.27 Shear stress-time profile (conditions: variable shear stress, temperature = const.)

Newtonian materials such as water have a constant viscosity value. As the shear stress rises, the viscosity decreases in pseudoplastic materials. In contrast, in the viscosity increases in dilatant materials as the shear stress rises.



1- NEWTONIAN material
2- Pseudoplastic material
3- Plastic material
4- Dilatant material

Figure 6.28 Flow and viscosity curves of materials with different rheological properties

In order to determine the yield point in a metrological manner, the shear stress test is the only measuring method used. The material starts to flow only when the exerted shear stress exceeds the network bonding forces and a measurable shear rate is obtained. The flow curve does not pass the origin of the coordinate system for materials that show a yield point, but shows a certain translation on the Y axis. In order to obtain a shear rate in the plastic material an additional shear rate is required.

Flow and viscosity curves are also often plotted such that the viscosity values are shown at both rising and falling shear stress in controlled shear stress tests as shown in Figure 6.29 and 6.30. There is often a section between the two sections of the curve (up ramp, down ramp) where the shear rate is kept constant (Rheotec, n.d.).

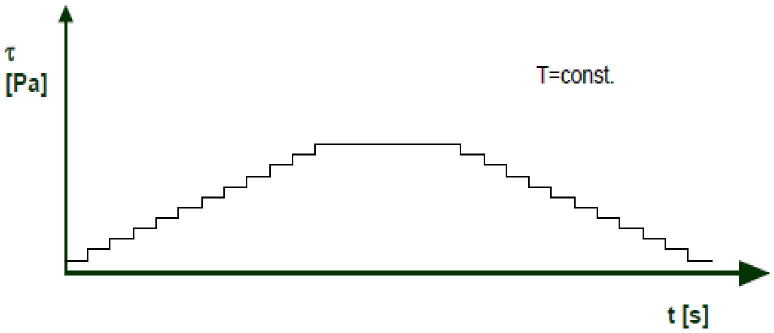


Figure 6.29 Shear stress-time diagram (conditions: Shear stress = variable, Temperature = const.)

The results of the measurements also allow information about load-dependent (pseudoplasticity, dilatancy), and time-dependent (Thixotropy, rheopexy) flow behavior, in addition to the yield point value (If present).

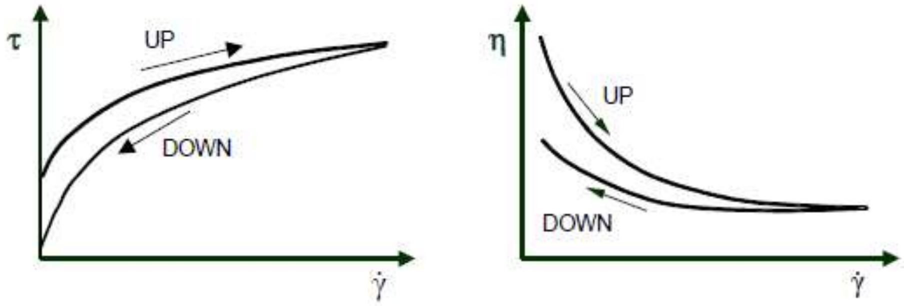


Figure 6.30 Flow and viscosity curve of a pseudoplastic and a thixotropic material

6.4.2.4 Creep and Recovery Test

Most materials are formed by a combination of viscous and elastic components. If we apply a small stress to a viscoelastic material and hold it constant for a long period of time and measure the resultant strain, we will see behavior from elastic components followed shortly by viscoelastic effects. The creep test forms a simple and quick method used to find the viscoelastic properties of the material under investigation. Creep is defined as ‘the slow deformation of a material, usually measured under a constant stress’ (Bohlin Instruments, 1994).

As depicted in Figure 6.31, load is exerted on the mobile part of the measuring instrument with a constant shear stress (τ_x) for an exact time period (t_0-t_2). As a result of this force the sample deforms; i.e. the material starts to creep. After the predetermined time the stress is removed and the material is relieved so that it can recover and the strain is again monitored from (t_2 - t_4).

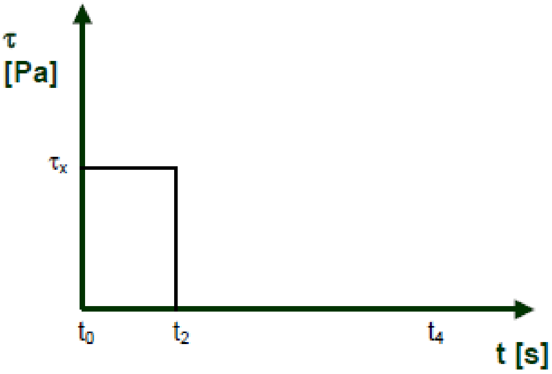


Figure 6.31 Creep and recovery test

6.4.2.4.1 Pure Elastic Materials. The application of a constant shear stress results the strain γ in pure elastic material. The angle of such strain is characterized by the spring modulus of elasticity of the purely elastic solid. The strain is maintained as long as the deforming force keeps acting and the sample will be completely relieved if the force ceases to be exerted as depicted in Figure 6.32. Vulcanize rubber could be given as an example for pure elastic material.

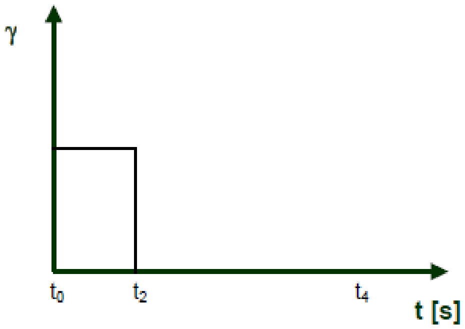


Figure 6.32 Creep and recovery curve for an ideally elastic material

6.4.2.4.2 Pure Viscous Materials. The constant shear stress applied to the material leads to a strain γ which increases linearly over time, i.e. it shows flowing. If the sample is relieved, the strain γ obtained by this moment of time will be maintained as depicted in Figure 6.33. Water serves as an example for pure viscous materials.

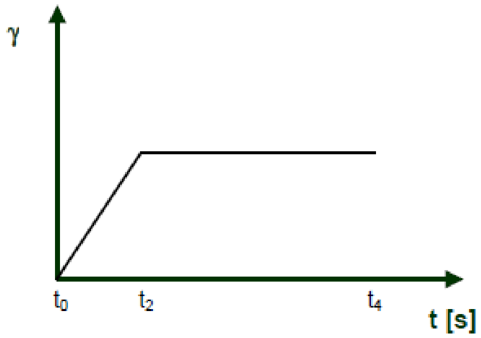
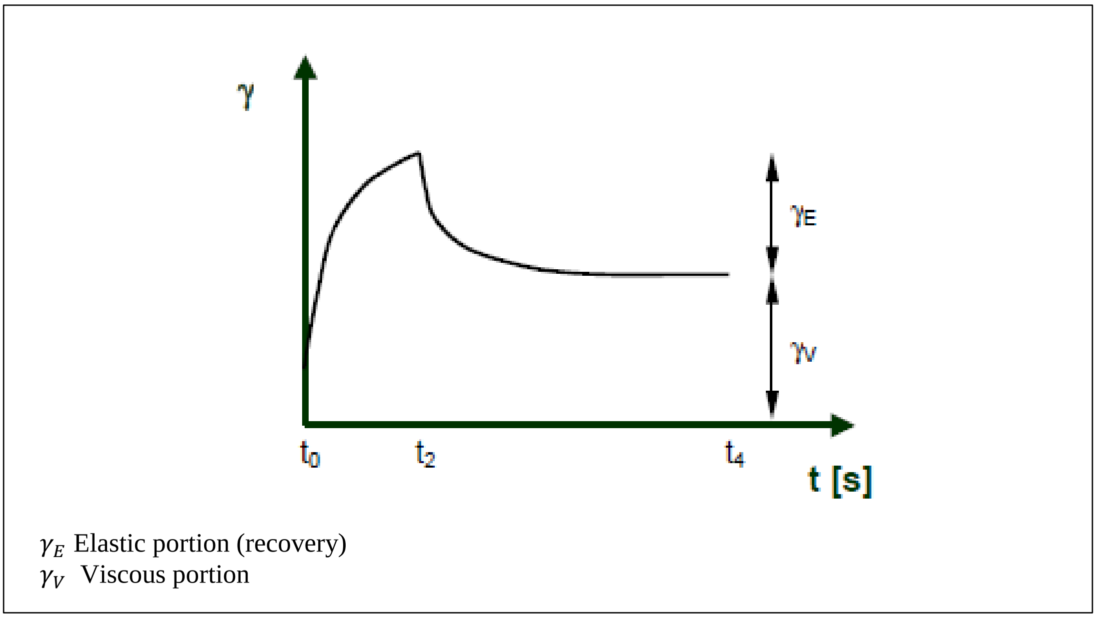


Figure 6.33 Creep and recovery curve for a pure viscous material

6.4.2.4.3 Viscoelastic Liquids and Solids. As depicted in Figure 6.34, viscoelastic liquids show both viscous and elastic strain under the application of shear stress. A partial recovery by the elastic portion γ_E can be detected, but viscous strain portion γ_V remains. A delayed but complete recovery can be observed in viscoelastic solid and γ_V is almost zero.



γ_E Elastic portion (recovery)
γ_V Viscous portion

Figure 6.34 Creep and recovery curve of a viscoelastic liquid

Since the actual change of strain will be dependent upon the applied stress, it is usual to talk about the compliance rather than the strain. The compliance is defined simply as the ratio of the strain to the applied stress and is denoted by the letter J.

$$\text{Compliance } \mathrm{J} = \frac{strain}{stress} \tag{6.22}$$

6.5 Selecting Measuring Geometries

There are three main categories for measuring geometries in rheometry. They are

1- Cone and Plate
2- Parallel Plate
3- Cup and bob

6.5.1 Cone and Plate

The cone and plate depicted in Figure 6.35, is in many cases the ideal measuring system. It could be cleaned simply, needs comparatively little amount of sample in terms of volume and can be used on materials with low viscosities somehow 10 times to that of water (10 mPas) or even lower (Bohlin Instruments, 1994).

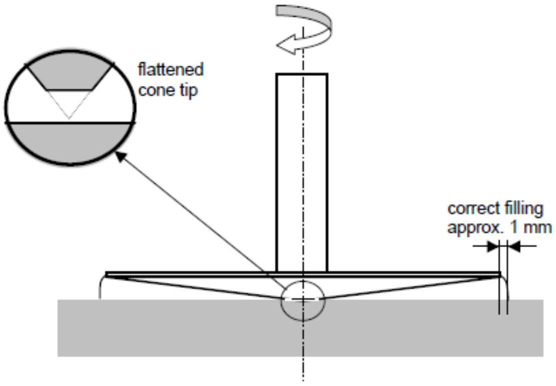


Figure 6.35 Cone and plate measuring system (Rheotec, n.d.)

In order to denote Cone and plate measuring geometries we use cone diameter and angle. For example a CP4/40 denotes a cone 40mm diameter and a cone angle of 4° (Bohlin Instruments, 1994).

Cone tips are often flattened. These types of cones are located such that the theoretical (missing) tip would touch the lower plate. A more strong measuring geometry is produced by truncating the cones (Bohlin Instruments, 1994).

Since strain and shear rate are determined using the angular displacement and the gap it issues that the smaller the cone angle, the greater the error liability in gap setting and hence the results. By using a relatively large angle (4°) it becomes more comfortable to get reproducibility of gap setting. Unluckily, the variation in the shear rate across the gap gets increased as the cone angle gets larger (Bohlin Instruments, 1994).

The shear rate vary by less than 0.5% across the gap for a 4° cone which gives data with around 0.3% error. Although the shear distribution error is small in using smaller cone angle but in the mean while the operator to operator gap settings could introduce errors over 5% even by experience operators and so the larger angle gives a more acceptable error since it is a reproducible error (Bohlin Instruments, 1994).

If the rheometer is fitted with an automatic system for thermal expansion compensation, because of the importance of the gap setting a cone and plate is not recommended in performing temperature sweeps (Bohlin Instruments, 1994).

In order to minimize the errors in using a cone, the one with the largest cone angle and diameter available should be selected and the gap should be at approximately the mid-range temperature of the sweep (Bohlin Instruments, 1994).

If the testing contains particulate material using a cone should be avoided. The particle can 'jam' at the cone apex and result noisy data if the mean particle diameter is not some five to ten times smaller than the gap (Bohlin Instruments, 1994).

It should also be avoided to use a cone in case of testing materials with high concentration of solids because it is prone to being expelled from the gap under high shear rates (Bohlin Instruments, 1994).

6.5.2 Parallel Plate

Just like the cone and plate, as shown in Figure 6.36, the parallel plate system requires a small sample volume and is easy to clean. Another advantage of using parallel plate is being able to take preformed sample discs, which is especially useful while working with polymers. Because of the separation between the plates measured in mm, it is not as sensitive to gap setting. That's why it is ideally suited for testing samples through temperature gradients (Bohlin Instruments, 1994).

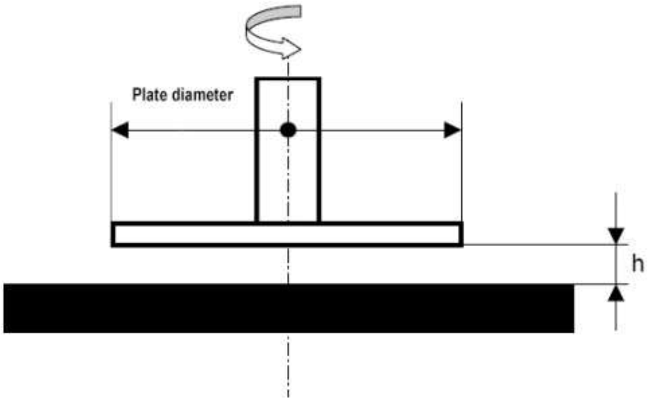


Figure 6.36 Parallel plate measuring system (Rheotec, n.d.)

Parallel plate geometries are denoted by the diameter of the upper plate. For example, a PP40 is a plate with 40mm diameter. The lower plate is either larger than or the same size as the upper plate (Bohlin Instruments, 1994).

The main unfavorable circumstance regarding parallel plates is that the shear rate produced varies across the sample and in most cased the software actually takes the average value for shear rate (Bohlin Instruments, 1994).

It is not recommended to use parallel plates if it is important to test the samples at a known shear rate for critical comparisons (Bohlin Instruments, 1994).

6.5.3 Sample Loading for Cone and Plate and Parallel Plate Measuring Geometries

The gap between the upper and lower elements should be just filled by the sample. It is recommended to put a slight bulge if the sample is feasible to shrink. Using too much or too little sample between the elements produces incorrect torque and thus incorrect data is collected. Figure 6.37 describes sample loading for parallel and cone and plate measuring systems.

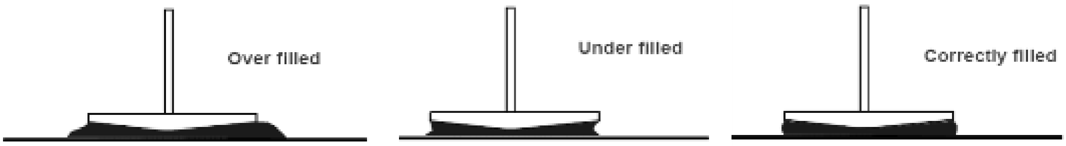


Figure 6.37 Sample loading for Parallel and cone and plate measuring systems

It is advisable to pre-form the sample into a disc of the same diameter with the upper plate especially while using stiff materials. In order to ensure a good contact between the sample and the plates, the sample should be slightly thicker than the required value.

6.5.4 Concentric Cylinder (Cup and Bob)

Depending on instrument design, in the concentric cylinder (also called Couette or Coaxial) geometry, either the inner, outer, or both cylinders may rotate. The test fluid is kept in the annulus between the cylinder surfaces. The most common three geometries used for this tool are listed in Figure 6.38 (Hackley & Ferraris, 2001):

Figure 6.38 Different forms of concentric cylinder type measuring systems

It is useful to use the double-gap configuration for low viscosity fluids, since it increases the total area, and therefore the viscous drag, on the rotating inner cylinder, and in total the accuracy of the of the measurement increases (Hackley & Ferraris, 2001).

In order to reduce the end effects, the cone and hollow cavity configurations espesially designed to be used. The inner cylinder surface is sometimes serrated or otherwise roughenened to prevent slipage. The concentric cylinder geometry is typically used for the analysis of fluid suspensions (Hackley & Ferraris, 2001).

In German institute for standardization (DIN) standards for cone and plate at bottom geometries they are referred to by the diameter of the inner bob. For example a C25 is a “cone and plate at bottom” geometry having a 25mm diameter bob. The diameter of the cup is in proportion to the bob size as defined by the DIN Standard. When it comes to double gap measuring systems, they are usually denoted by the inner and outer diameters i.e. DG 40/50 (Bohlin Instruments, 1994).

Coaxial cylinder measuring geometries need relatively large sample volumes and it is hard to do the cleaning job.

CHAPTER SEVEN
EXPERIMENTAL

This chapter includes test methods, materials and procedures to evaluate the consequences of incorporating WMA technologies into PMB.

7.1 Test Methods

This section includes a brief explanation test methods used to determine the properties of the prepared polymer modified bitumen samples using warm mix technologies. The methods are categorized under two topics of conventional test methods and newly emerged rheological tests.

7.1.1 Conventional Test Methods

7.1.1.1 Penetration Test

Penetration test is one of the oldest asphalt tests. The basic procedure in this test is to measure the penetration of a standard needle into the asphalt binder sample under the following conditions:

Load	= 100 grams
Temperature	= 25° C (77° F)
Time	= 5 seconds

The binder sample is melt and cooled under controlled conditions. The depth of penetration is measured in units of 0.1 mm and reported in penetration units (e.g., if the needle penetrates 8 mm, the asphalt penetration number is 80). Penetration Grading is based on the penetration test (Pavement Interactive, 2007a). A view of standard penetration equipment is presented in Figure 7.1.

Figure 7.1 Standard penetration equipment

AASHTO T 49 and ASTM D 5 standard test methods and procedures should be gone through for further information regarding penetration of bituminous materials.

7.1.1.2 Softening Point Test

The softening point is defined as the temperature at which a bitumen sample can no longer support the weight of a 3.5-g. steel ball. Basically, two horizontal disks of bitumen, cast in shouldered brass rings are heated at a controlled rate in a liquid bath while each supports a steel ball. The softening point is reported as the mean of the temperatures at which the two disks soften enough to allow each ball, enveloped in bitumen, to fall a distance of 25 mm (1.0 inch) (AASHTO, 2000). Figure 7.2 shows the “ring and ball” apparatus, used to evaluate the softening point of the bitumen and Figure 7.3 represents the view of a bitumen sample before and after the softening point test.

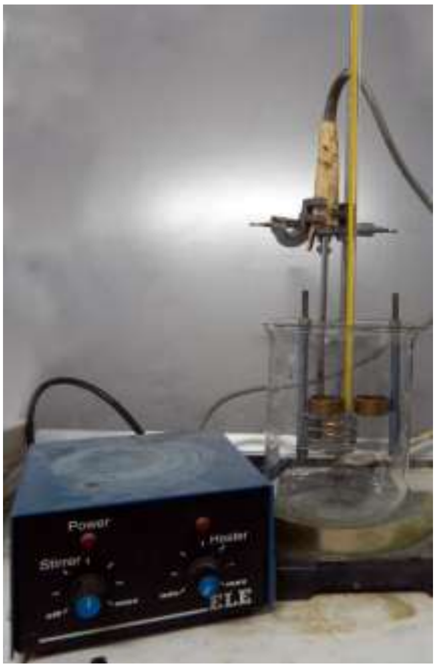


Figure 7.2 The “ring and ball” apparatus

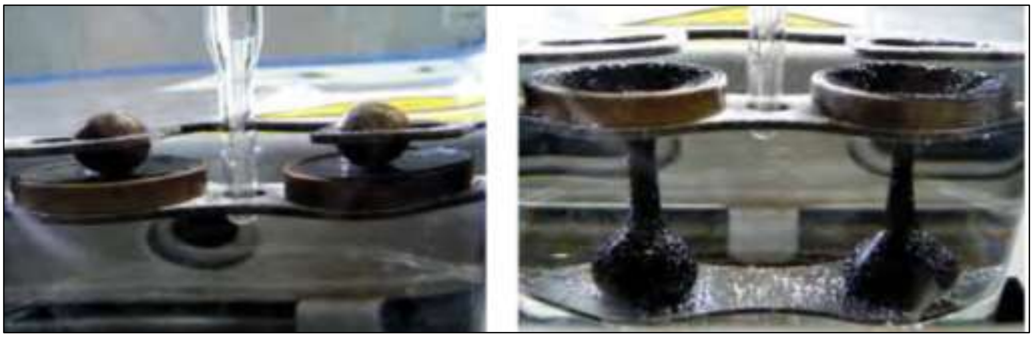


Figure 7.3 View of a bitumen sample before and after the softening point test (ORLEN Asphalt sp.zo.o., 2014)

The softening point is useful in the classification of bitumen, as one element in establishing the uniformity of shipments or sources of supply, and is indicative of the tendency of the material to flow at elevated temperatures encountered in service.

AASHTO T 53 and ASTM D 36 should be gone through for further information regarding Softening Point of Bitumen (Ring-and-Ball Apparatus).

7.1.1.3 Viscosity Test

A viscometer is an instrument used to measure the viscosity of fluids. The Rotational Viscometer (RV) is used in this study to determine the viscosity of base bitumen and the polymer modified bitumen samples prepared using warm mix asphalt technologies. The RV test can be conducted at various temperatures, but since manufacturing and construction temperatures are fairly similar regardless of the environment, the test for Superpave PG asphalt binder specification is always conducted at 275°F (135°C). RV test has been conducted at 135°C and 165°C in this study in order to determine the laboratory mixing and compaction temperatures of the prepared samples and to develop their temperature-viscosity graphs.

The RV test helps ensure that the asphalt binder is sufficiently fluid for pumping and mixing (Roberts et al., 1996).

The basic RV test measures the torque needed to maintain a constant rotational speed (20 RPM) of a cylindrical spindle while submerged in a bitumen binder at a constant temperature. This torque is then converted to a viscosity and displayed automatically by the RV (Pavement Interactive, 2011a). Figure 7.4 shows the major equipment involved.

Figure 7.4 Major RV equipment

The basic procedure to conduct a rotational viscosity test is as follows:

1. Preheat spindle, sample chamber, and viscometer environmental chamber (Thermosel) to the desired temperature (135°C and 165°C in this study).
2. Binder sample is heated to become fluid enough to pour. The sample is stirred with care to not entrap air bubbles.
3. The appropriate amount of sample is poured into the sample chamber. The sample size varies according to the selected spindle and equipment manufacturer (10.5 g in this study).
4. Sample chamber is inserted into RV temperature controller unit and the spindle is carefully lowered into sample.
5. The sample is brought to the desired test temperature within 30 minutes and allowed to equilibrate at test temperature for 10 minutes. The spindle is rotated at 20RPM.
6. Once the sample has reached temperature and equilibrated 3 viscosity readings is taken from RV display, allowing 1 minute between each reading. Viscosity is reported as the average of 3 readings.

AASHTO T 316 and ASTM D 4402 provide further information regarding viscosity determination of asphalt binders using rotational viscometer.

7.1.1.4 Storage Stability Test

One of the major concerns in the production of polymer modified bitumen is the bitumen and polymer incompatibility, which may separate polymer from bitumen sometimes after production. The purpose of the stability test is to check whether modified bitumen is exposed to the risk of polymer separation from bitumen.

A modified bitumen sample placed in an aluminum tube is heated vertically to and held at 180°C for 72 hours. The tube is then left to cool. After cooling, the aluminum coating of the tube is removed and the sample is cut into three roughly equal parts. The central sample part is thrown out. The softening point test is conducted for the upper and lower section of the sample and, potentially, for penetration at 25°C. The result of the stability test is assumed to be the difference between softening point values (or penetration at 25°C) obtained for the upper and lower modified bitumen samples (Blazejowski et. al, 2014). Figure 7.5 describes general view of the filled and sealed tube for the storage stability test.

Figure 7.5 General view of the filled and sealed tube for the storage stability test

7.1.1.5 Rolling Thin Film Oven Test

HMA undergoes significant aging during the manufacturing and placement processes. The Rolling Thin-Film Oven (RTFO) procedure is used to simulate this short term aging of asphalt binders during manufacturing and placement. The RTFOT also provides a quantitative measure of the volatiles lost during the aging process. Figure 7.6 shows a general view of the RTFOT short-term ageing test set.

Figure 7.6 General view of the RTFOT short-term ageing test set

The basic RTFOT procedure takes non-aged asphalt binder samples in cylindrical glass bottles and places these bottles in a rotating carriage within an oven. The carriage rotates within the oven while the 325°F (163°C) temperature ages the samples for 85 minutes.

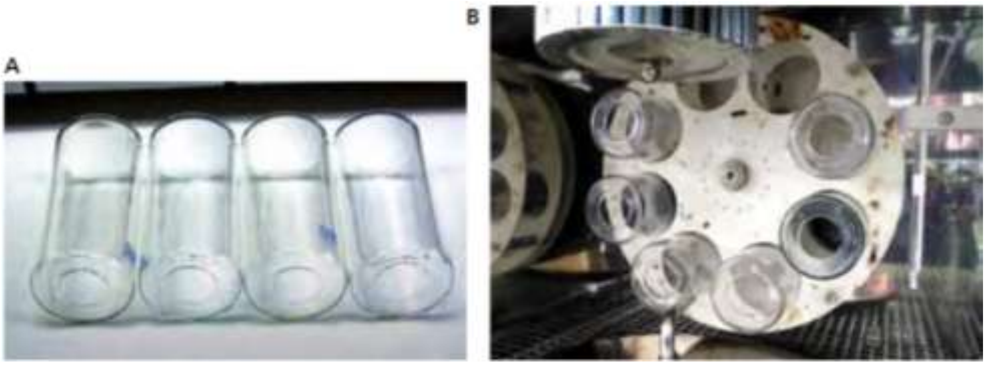


Figure 7.7 View of glass containers from bitumen sample (A) and containers installed in the RTFOT drier (B)

Although many different factors contribute to asphalt binder aging, the key component of concern for the RTFOT is the loss of volatiles. The loss of smaller molecules from the bitumen binder, often termed “volatiles” increases bitumen’s viscosity.

It is recommended to go through AASHTO T 240 and ASTM D 2872 tests for a more extensive understanding of the effects of heat and air on a moving film of bitumen (Rolling Thin-Film Oven Test)

7.1.2 Rheological Test Methods

7.1.2.1 Dynamic Shear Rheometer (DSR) Test

The dynamic shear rheometer (DSR) is used to describe the viscous and elastic behavior of asphalt binders at medium to high temperatures. This characterization is used in the Superpave PG asphalt binder specification.

The basic DSR test uses a thin asphalt binder sample sandwiched between two circular plates. The lower plate is fixed while the upper plate oscillates back and forth across the sample at 10 rad/sec (1.59 Hz) (or any other set frequency) to create a shearing action (Figure 7.8). DSR tests are conducted on non-aged, RTFO aged and PAV aged asphalt binder samples (Pavement Interactive, 2011b).

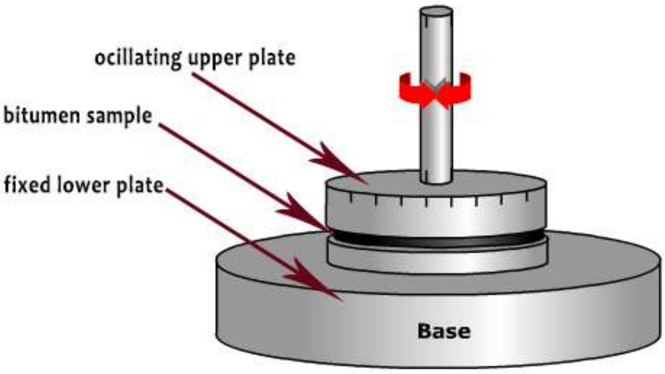


Figure 7.8 DSR mechanism

The DSR measures a specimen’s complex shear modulus (G*) and phase angle (δ). The complex shear modulus (G*) can be considered the sample’s total resistance to deformation when repeatedly sheared, while the phase angle (δ), is the lag between the applied shear stress and the resulting shear strain (Figure 7.9).

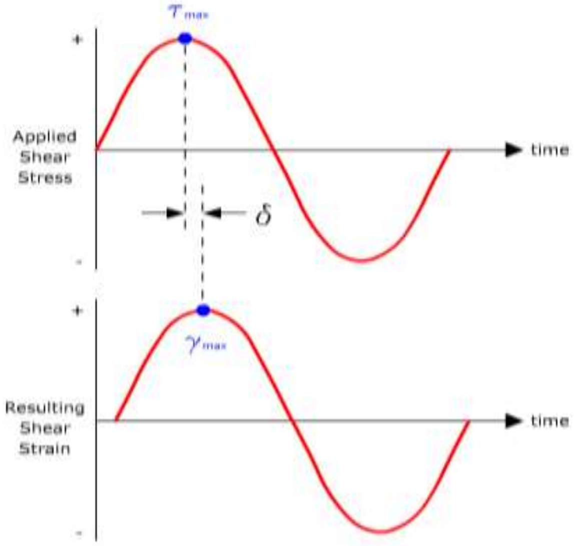


Figure 7.9 DSR curves (Pavement Interactive, 2011b)

The larger the phase angle, the more viscous the material. Phase angle (δ) limiting values are:

Purely elastic material : $\delta = 0$ degrees
Purely viscous material : $\delta = 90$ degrees

G^* and δ are used as predictors of HMA rutting and fatigue cracking. Early in pavement life rutting is the main concern, while later in pavement life fatigue cracking becomes the major concern. $G^*/\sin\delta$ is described as rutting indicating parameter and $G^*\sin\delta$ as fatigue cracking indicating factor. A Summary of the test is as follows:

A small sample of asphalt binder is sandwiched between two plates. The test temperature, specimen size and plate diameter depend upon the type of asphalt binder being tested. Non-aged asphalt binder and RTFO residue are tested at the high temperature specification for a given performance grade (PG) binder using a specimen 1mm thick and 25mm in diameter (Pavement Interactive, 2011b). Figure 7.10 shows major DSR equipment.

Figure 7.10 Major DSR test equipment

Test temperatures greater than 46°C use a sample 1mm thick and 25mm in diameter, while test temperatures between 4°C and 40°C use a sample 2mm thick and 8mm in diameter (Figure 7.11). The test specimen is kept at near constant temperature by heating and cooling a surrounding environmental chamber. The top plate oscillates at 10 rad/sec (1.59 Hz) (or any other frequency set) in a sinusoidal waveform while the equipment measures the maximum applied stress, the resulting maximum strain, and the time lag between them. The software then automatically calculates the complex modulus (G*) and phase angle (δ) (Pavement Interactive, 2011b).

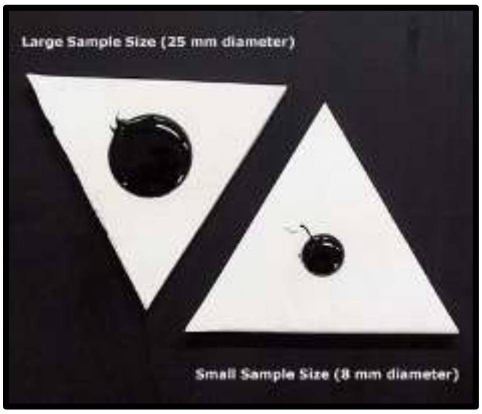


Figure 7.11 DSR sample molds showing the different sizes (Pavement Interactive, 2011b)

The compatibility of the resulting measured parameters is checked with those of the specifications. DSR specifications for performance graded asphalt binders is presented in Table 7.1

Table 7.1 Performance Graded Asphalt Binder DSR specifications (Pavement Interactive, 2011b)

Material value	**Specification**	**HMA Distress of Concern**
Non-aged binder	$G^*/\sin\delta \geq 1.0$ kPa (0.145 psi)	Rutting
RTFO residue	$G^*/\sin\delta \geq 2.2$ kPa (0.319 psi)	Rutting
PAV residue	$G^*\sin\delta \leq 5000$ kPa (725 psi)	Fatigue cracking

Further information regarding the standard dynamic shear rheometer test is provided in AASHTO T 315.

7.1.2.2 Zero Shear Viscosity Test

One of the promising candidates as a European bitumen performance indicator is the zero shear viscosity (ZSV) or the viscosity at zero shear rate. Zero Shear Viscosity (ZSV) is the viscosity measured in shear deformation at a shear rate approaching to zero. This parameter is an indicator for two rutting related binder characteristics:

- The stiffness of the bitumen;
- The binder resistance to permanent deformation under long term loading

Both bitumen characteristics play a crucial role in the prevention of permanent deformation of asphalt pavements. It has been observed by researchers in the recent years, that the SHRP rutting parameter G*/sin δ is not very effective in predicting the rutting performance of bitumen, especially in case of polymer modified bitumen. Zero shear viscosity (ZSV) has been evaluated to be a more appropriate indicator in predicting the rutting behavior of asphalt binders (De Visscher et al., 2004).

Theoretically, ZSV can be determined using a DSR machine by two types of tests (Figure 7.12):

- An oscillation test, in which ZSV is determined as the value to which the complex viscosity approaches at very low oscillation frequency;

- A creep test, in which ZSV is determined as the “steady state viscosity” at low shear stress. Depending on the type of bitumen, a steady state is attained after a short or a very long time period. (De Visscher et al., 2004).

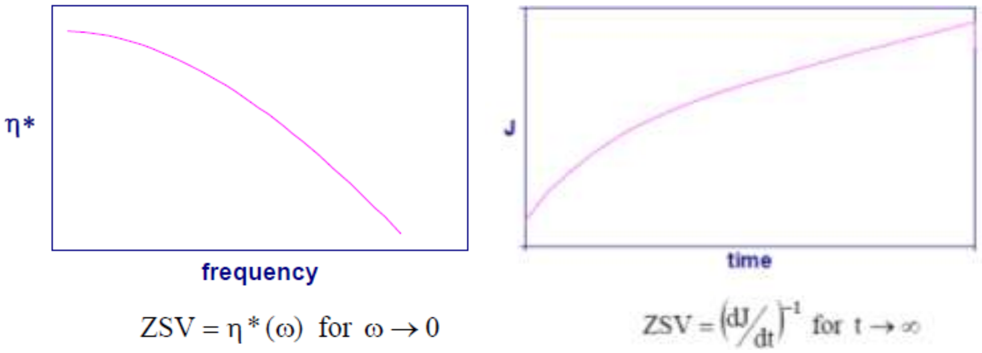


Figure 7.12 Measurement of ZSV in oscillation mode (left) or creep mode (right)

The determination of ZSV in this study is made by the application of Creep Test using DSR machine. Static creep is defined as the slow deformation of a material measured under a constant stress. In the static creep test, a fixed shear stress is applied to the sample and the resultant strain is monitored for a predetermined amount of time. If the stress is applied for a sufficiently long duration of time, the deformation in the binder reaches a constant value, which corresponds to the steady state flow of the binder. The viscosity of the binder at this stage is known as the steady state viscosity or the ZSV.

All of the samples were short-term aged first using a RTFOT procedure. The ZSV of the samples have been predicted by application of creep test at 60°C in accordance to prCEN/TS 15325 European standard. The test geometry for the creep tests consisted of 25mm parallel plates and the gap between the plates was 1mm. The stress level was 10 Pa for base bitumen and 30Pa for the modified bitumen samples and each creep test was continued for 30 minutes.

Since the actual change of strain will be dependent upon the applied stress, it is usual to talk about the compliance rather than the strain. The compliance is defined simply as the ratio of the strain to the applied stress and is denoted by the letter (J).

The time-creep and time-creep compliance graphs are automatically generated by the computer. In the method used for this study, which is selected for standardization by CEN, consists in applying a static stress, characterized by low entity ($\tau = \tau_0 \rightarrow 0$)

and long application time, in order to reach steady state flow (dγ/dt → cost). In this conditions the creep compliance curve almost takes the shape of a straight line and the Zero-Shear Viscosity can be extrapolate, according to the theoretical equation of Burger model, by means of the measure of creep compliance J(t):

$$J(t) = J_0 + J_m.\left(1 - e^{-\frac{1}{\lambda}}\right) + \frac{t}{\eta_0} \tag{7.1}$$

Where, J_0 is the instantaneous compliance, J_m is the viscoelastic compliance, λ is the retardation time and η_0 is the zero shear viscosity. When long loading time is reached only the viscous modulus Jv= t/η0 is increasing. So, according to the theoretical assumptions of this method, the ZSV of a material is represented by the inverse of the average slope that curve J(t) is assuming during the last minutes (e.g. 15 minutes) of the test according to the following equation:

$$ZSV = ZSV = \Delta t/\Delta J = 900/(J_f - J_{15}) \quad [Pa.s] \tag{7.2}$$

Where J_{15} represents the compliance expressed in Pa^{-1} , measured 15 minutes before the load is no longer applied, J_f is the compliance expressed in Pa^{-1} , measured at the end of the test and 900 is the time interval between the two measurements expressed in seconds (Giuliani, F., Merusi, F., Antunes, I., n.d.).

7.2 Materials

Materials presented in this section are consisted of bitumen, SBS polymer modified bitumen, and Sasobit® (organic) and Rediset® WMX (chemical) based warm mix additives.

7.2.1 Bitumen

The properties of the base bitumen with a penetration grade 50/70 were labeled through conventional bitumen tests. Base bitumen was provided by Turkish

Petroleum Refinery Corporation (TÜPRAŞ), Aliaga/Izmir. Table 7.2 summarizes the results and their conformity with the relevant test methods.

Table 7.2 Properties of the base bitumen

Test	**Unit**	**Specification limits**		**Results**	**Specification**
		Min	**Max**		
Penetration (25°C; 100g; 5s)	x0.1 mm	50	70	60	ASTM D5; EN 1426
Softening Point	°C	46	54	48	ASTM D36; EN 1427
Viscosity at (135°C)	Pa.s	-	-	0.463	ASTM D4402
Viscosity at (165°C)	Pa.s	-	-	0.125	ASTM D4402
Thin Film Oven Test (TFOT) (163°C; 5 hr)	-	-	-	-	ASTM D1754; EN 12607-1
Change of Mass	(%)	-	0.5	0.2	
Retained Penetration after TFOT	(%)	50	-	63	ASTM D5 EN 1426
Increase in Softening Point after TFOT	°C	-	9	3.2	TS EN 12607-1
Flash Point	°C	230	-	+260	ASTM D92 EN 22592

7.2.2 Polymers

Polymers were widely discussed in the relevant section of this study. It was stated that amongst the polymer asphalt modifying agents, styrene butadiene styrene (SBS) originally developed by Shell Chemical Co. is widely used in the majority of the asphalt binder industry and probably the most appropriate polymer for asphalt modification (Lavin, 2003; Becker et al., 2001). Kraton® D1192ES is a clear linear block copolymer based on SBS with bound styrene of 30% mass. It is supplied as porous pellets dusted with amorphous silica. It is mostly used for modification of industrial and paving bitumen. It may also be suitable for use in formulating adhesives, sealants and coatings, and in modification of polymers (Kraton®, 2003). Kraton® D1192ES was obtained from EGE ASFALT Maden İnşaat Nakliye San. & Tic. A.Ş. Company. Typical properties of Kraton® D1192ES is listed in Table 7.3. and Figure 7.13 shows Kraton® D1192ES additive in pellets form.

Table 7.3 Typical properties of Kraton® D1192ES

Property	**Test method**	**Units**	**Typical value**
Melt flow rate 200°C/5kg	ISO 1133	g/10min	<1
Specific gravity	ISO 2781	Mg/M^3	0.94
Bulk density	ASTM D1895 method B	Mg/M^3	0.4
Hardness*	ASTM 2240	Shore A (10s)	70
* Measured on compression molded slabs			

Figure 7.13 Kraton® D1192ES

7.2.3 Warm Mix Asphalt Additives

Warm mix asphalt technologies, their classifications and advantages were widely discussed in the relevant chapter. Two type of warm mix additives have been used in this study. One of the additives is Sasobit® which is a good example of the organic WMA additives and the other one Rediset® WMX which takes its position among chemical WMA additives.

Sasobit® concentration in the base bitumen was chosen as 3.0% by weight of bitumen. The utilization of this content is based on a past research made by O'Sullivan and Wall (2009). They concluded that Sasobit® should be added at a rate of 3.0% by mass of bitumen for maximum effectiveness. Sasobit is produced both in flakes and pellets forms, Figure 7.14 shows Sasobit® additive in pellets form.

Figure 7.14 Granular Sasobit®

Rediset® WMX is supplied in bead/pastille form and can be pre-blended into asphalt binder or it could be directly dosed into the mixer at the hot-mix plant. Considering the recommended dosage and method of addition into polymer modified bitumen by AkzoNobel (2011), a content 2.0% by weight of polymer modified bitumen was chosen to be added to the bitumen. A view of granular Rediset® WMX used in this study is shown in Figure 7.15.

Figure 7.15 Granular Rediset® WMX

7.3 Production of Modified Bitumen Samples

The production process of the samples consists of two stages. The first stage was production of SBS modified bitumen samples and the next step was incorporation of organic and chemical warm mix additives into the SBS modified bitumen samples.

7.3.1 Preparation of Polymer Modified Bitumen Samples

Three different concentrations (4%, 5% & 6%) of SBS have been used in this study. The SBS modified bitumen samples have been produced using laboratory type mixer (1300rpm) at a mixing temperature of 180°C and a mixing period of 2 hours. Determination of mixing temperature and period for SBS modified bitumen is based on the past studies made by Sengoz & Isıkyakar (2008). Appropriate amount of base bitumen (500g) in a 500ml graduated beaker has been heated in the stove at 170°C to become fluid enough and then placed under the mixer. SBS pellets have been gradually added to the bitumen and mixing action has been started on the sample and continued for 2 hours at 180± 5°C for each concentration of SBS as shown in Figure 7.16.

Figure 7.16 Production of polymer modified bitumen

7.3.2 Preparation of PMB Samples with Warm Mix Asphalt Technology

No past information has been found in the literature regarding the production temperature and period to incorporate warm mix additives into SBS polymer modified bitumen. A rotational viscometer has been employed to determine the production temperature and periods of SBS polymer modified bitumen containing WMA additives.

7.3.2.1 Organic Warm Mix Asphalt Additives

Appropriate amount of 5% SBS modified bitumen (250g.) in a 250ml. graduated beaker has been heated in the stove to reach 120°C and then placed under the mixer. 3% Organic WMA additive by weight of the modified bitumen was gradually added to the beaker and the mixing action has been started at 125°C. The temperature has been kept constant and the viscosities of the sample have been evaluated using a rotational viscometer for every increment of five minutes. The viscosities have been evaluated for 5 different mixing periods (5, 10, 15, 20 and 25minutes) but no constant viscosity value has been reached. The same procedure has been repeated on another sample but the production temperature has been kept constant at 140°C. It has been identified that the viscosity values of the sample has kept a constant value after being stirred for 15 minutes. Production temperature and period for adding 3% Organic WMA additive into SBS modified bitumen was eventually identified to be 140°C and 15minutes respectively (Table 7.4).

Table 7.4 Results of the viscosity tests on the sample of PMB containing Organic WMA additive

Production period (minutes)	**Viscosity(mPa.s)**	
	125°C	**140°C**
5	1138	1038
10	1125	1063
15	1213	**1088**
20	1338	1088
25	1325	1088

7.3.2.2 Chemical Warm Mix Asphalt Additives

Appropriate amount of 5% SBS modified bitumen (250g.) in a 250ml. graduated beaker has been heated in the stove to reach 150°C and then placed under the mixer. 2% chemical WMA additive by weight of the modified bitumen was gradually added to the beaker and the mixing action has been started at 160°C. The temperature has been kept constant and the viscosities of the sample have been evaluated using a rotational viscometer for every increment of five minutes. The viscosities have been evaluated for 5 different mixing periods (5, 10, 15, 20 and 25minutes). It has been identified that the viscosity values of the sample has kept a constant value after being stirred for 15 minutes. Selection of 160°C as the starting temperature is based on the past studies. Gorkem (2014) identified the production temperature of base bitumen with 2% chemical WMA additive as 150°C. Proper mixing was not achieved in adding 2% chemical WMA additive into SBS modified bitumen at 150°C. Production temperature and period of incorporating 2% chemical WMA additive into SBS modified bitumen was eventually identified to be 160°C and 15minutes respectively. The viscosity results of the sample including 5% SBS and 2% chemical WMA additive are given in Table 7.5.

Table 7.5 Results of the viscosity tests on the sample of PMB containing chemical WMA additive

Production period (minutes)	**Viscosity(mPa.s)**
	160°C
5	1213
10	1238
15	**1288**
20	1288
25	1288

7.4 Results

This section represents the results of the applied tests on 10 samples of bitumen; produced by the combination of polymer modified bitumen including two types of WMA additives. The results have been presented into two groups as conventional bitumen test results and rheological test results.

7.4.1 Conventional Bitumen Test Results

In order to characterize the properties of base bitumen, polymer modified bitumen (PMB) and PMB samples involving organic and chemical WMA additives, penetration test (American Society for Testing and Materials [ASTM] D5-06), softening point test (ASTM D 36-06), viscosity test (ASTM D 4402-06) at 135°C and 165°C, rolling thin film oven test (RTFOT) (ASTM D 2872-12) and penetration and softening point tests after RTFOT were performed. Table 7.6 presents the results of conventional bitumen tests.

Table 7.6 Results of the conventional bitumen tests conducted on base bitumen, PMB samples and PMB samples involving WMA additives

Test	**Specification**	**Base Bitumen**	**4%SBS**	**4%SBS + 3% Organic WMA Add.**	**4%SBS + 2% Chemical WMA Add.**	**5%SBS**	**5%SBS + 3% Organic WMA Add.**	**5%SBS + 2% Chemical WMA Add.**	**6%SBS**	**6%SBS + 3% Organic WMA Add.**	**6%SBS + 2% Chemical WMA Add.**
Penetration (25°C; 100g; 5s), 0.1 mm	ASTM D5-06	60	44	41	40	39	38	37	35	25	25
Softening Point(°C)	ASTM D 36-06	48	57	77	59	74	82	71	74	92	83
Viscosity at (135°C) Pa.s	ASTM D 4402-06	0.463	1.210	0.850	0.930	1.450	1.150	1.290	1.840	1.400	1.380
Viscosity at (165°C), Pa.s	ASTM D 4402-06	0.125	0.380	0.280	0.2625	0.440	0.350	0.400	0.560	0.480	0.490
Penetration Index (PI)		-1.27	0.13	3.41	0.52	2.85	3.91	2.26	2.59	4.15	3.08
Rolling Thin Film Oven Test (RTFOT)	ASTM D 2872-12										
Change of Mass after RTFOT (%)		0.2	0.38	0.19	0.57	0.38	0.38	0.57	0.28	0.29	0.57
Penetration (25°C; 100g; 5s) after RTFOT	ASTM D5-06	38	34	32	31	33	31	25	32	20	21
Retained Penetration after RTFOT (% of Original)		63	78	77	77	85	83	67	91	80	86
Softening Point(°C) after RTFOT	ASTM D 36-06	51.2	64	82	63	76	90	79	81	93	84
Increase in Softening Point after RTFOT		3.2	6	5	4	2	8	8	7	1	1
Storage Stability Test											
Softening Point(°C) Upper segment	ASTM D 36-06	-	63	81	67	75	89	73	79	92	85
Softening Point(°C) Lower segment	ASTM D 36-06	-	64	82	68	75	90	73	80	93	86
Difference (°C)		-	1	1	1	0	1	0	1	1	1

Graphical illustrations of the conventional bitumen test results are presented in Figures 7.17 to 7.19.

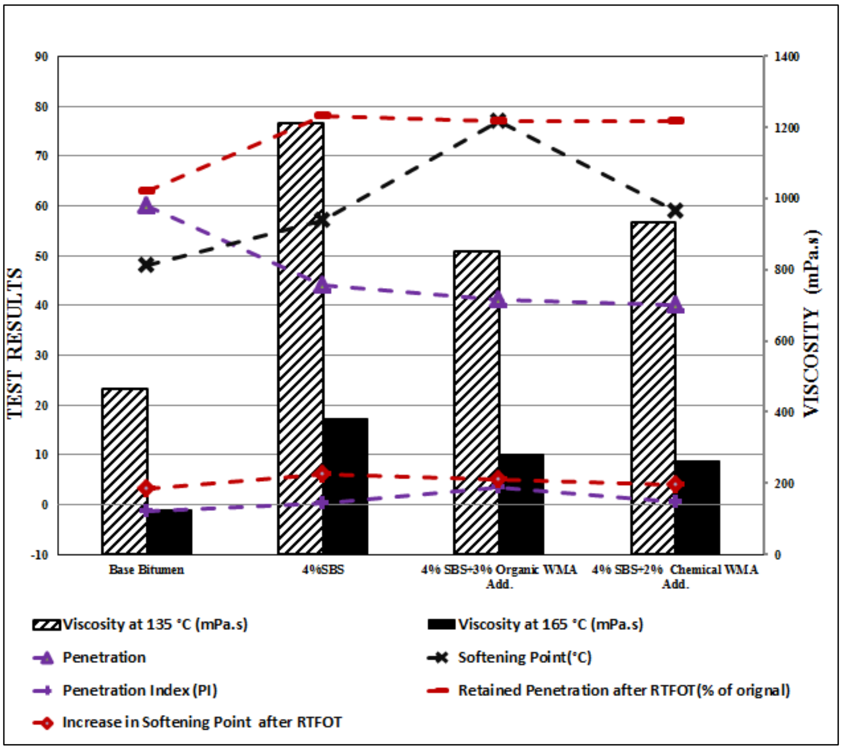


Figure 7.17 Conventional bitumen test results for 4%SBS modified bitumen containing WMA additives

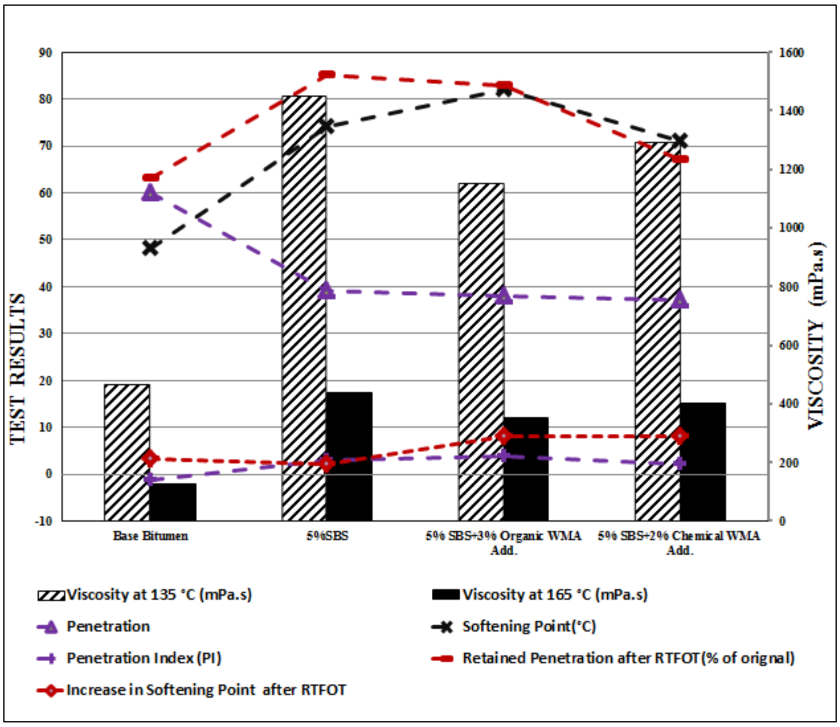


Figure 7.18 Conventional bitumen test results for 5% SBS modified bitumen containing WMA additives

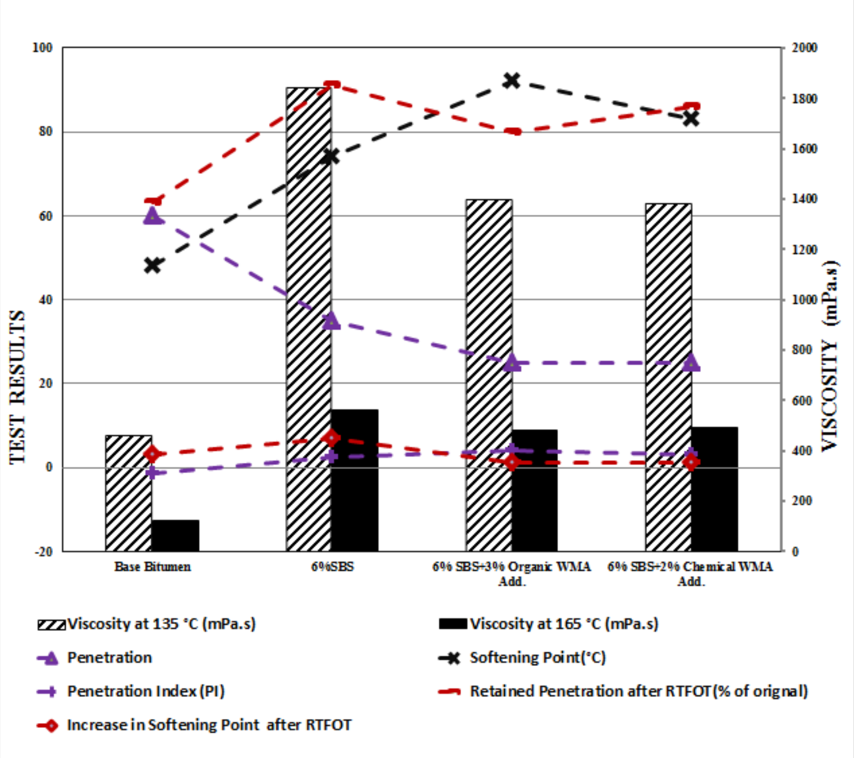


Figure 7.19 Conventional bitumen test results for 6% SBS modified bitumen containing WMA additives

The effects of adding WMA additives on SBS modified bitumen can be explored using Table 7.6 and Figures 7.17 to 7.19. The penetration test is an empirical test which measures the hardness of bitumen at a specified test condition. Softer bitumen will have a higher penetration, while harder bitumen will have a lower penetration. The results indicated that the entire modified bitumen samples depicted a significant decrease in penetration value and increase in softening point temperature as compared to base bitumen. This case is more evident at high concentrations of SBS (%5 & %6). The increase in softening point is favorable since bitumen with higher softening point may be less susceptible to permanent deformation (Sengoz & Isikyakar, 2008). It was also indicated that addition of both organic and chemical additive into SBS modified bitumen decrease the penetration value of the SBS modified bitumen at similar levels. The effects of organic WMA additive in increasing the softening point values are more evident than that of the chemical WMA additives in all concentrations of SBS. Incorporation of chemical WMA additive into 5% SBS modified bitumen slightly decreased the softening point of SBS modified bitumen.

The softening point temperature can be used along with the penetration to determine the temperature susceptibility of bitumen. The Penetration Index is an indicator of the temperature susceptibility of the bitumen. A high PI indicates low temperature susceptibility. Normal asphalt cements have a PI between -2 and +2. Asphalt cements with a PI of more than +2 are of low temperature susceptibility, while those with a PI of less than -2 are of excessively high temperature susceptibility. The results show that all of the modified samples including three different concentrations of SBS and SBS modified bitumen involving organic and chemical WMA additives have a higher PI and thus show lesser temperature susceptibility as compared to base bitumen. It could be also concluded from the results that addition of organic WMA additive significantly lowers SBS modified bitumen samples’ temperature susceptibility.

The most intense bitumen ageing processes take place when bitumen is mixed with hot aggregate in the batching plant’s mixer, during transportation, laying and compaction. Temperature at that time is high and the layer of bitumen on the aggregate is very thin. Under those circumstances the evaporation of light fractions and bitumen oxidation is the fastest and most intense, and bitumen rapidly hardens (aging). The process is referred to as short-term ageing. The hardening of the bitumen is gauged by the mass loss, retained penetration and softening point temperature difference after RTFOT. A slight increase in terms of mass loss could be seen in the entire modified bitumen samples as compared to base bitumen. Addition of chemical WMA additive into SBS modified bitumen samples indicates an identical value in terms of increase in mass loss as compared to base bitumen, all concentrations of SBS modified bitumen and modified bitumen involving organic WMA additives. Chemical WMA additives showed the highest value in terms of mass loss as compared to other samples. Addition of organic WMA additive into SBS modified bitumen samples almost does not show noticed effect in percentage of mass loss on SBS modified samples especially in higher concentrations of SBS. All of the samples showed a better performance in terms of retained penetration as compared to base bitumen. Both of the organic and chemical additives exhibit almost identical values in terms of increase in softening points after RTFOT.

The purpose of storage stability test is to check whether modified bitumen is exposed to the risk of polymer separation from bitumen. Softening point test results on all of the samples taken from the top and bottom of the tube in the storage stability test indicate that the addition of WMA additives do not exhibit any noticeable adverse effect on storage stability of SBS modified bitumen.

All of the SBS modified samples and SBS modified samples involving organic and chemical WMA additives show higher values in terms of viscosity at 135°C and 165°C compared to base bitumen. Involving organic and chemical WMA additives in SBS modified bitumen samples show positive effects in decreasing the viscosity values at 135°C and 165°C for all of the three concentrations of SBS modified bitumen samples. The lowest value in terms of viscosities at 135°C and 165°C was achieved in 4% SBS modified bitumen samples involving both organic and chemical WMA additives as compared to SBS modified samples. However maximum values in terms of decreasing the viscosity of SBS modified samples by involving organic and chemical WMA additives were achieved at 6% SBS modified bitumen samples.

7.4.1.1 Determination of Mixing and Compaction Temperatures

Asphalt Institute Equi-Viscous Method has been implied in determining mixing and compaction temperature ranges of each sample. Viscosity values of each sample at 135°C and 165°C were plotted on semi logarithmic viscosity-temperature charts. Mixing and compaction temperatures for all of the samples are given in Figures 7.20 to 7.23. Acceptable temperature for mixing was chosen as the range matching 0.17±0.02 Pa.s and acceptable temperature for compaction was chosen as the range matching 0.28±0.03 Pa.s. The determined mixing and compaction range temperatures for all of the samples including base bitumen, PMB and PMB samples involving organic and chemical WMA additives are listed in Table 7.7.

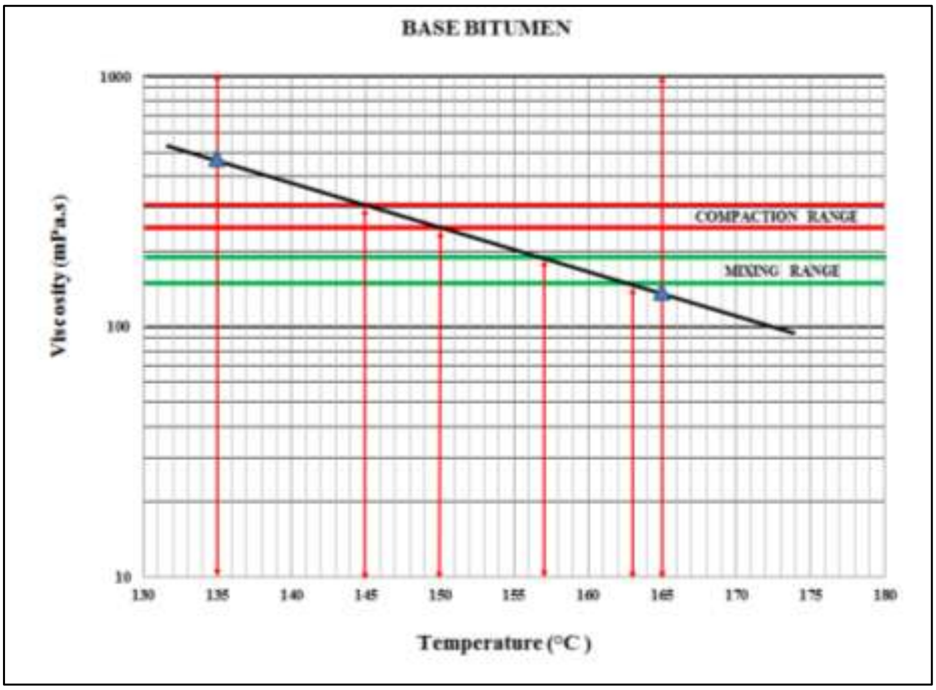


Figure 7.20 Determination of mixing and compaction temperatures for base bitumen

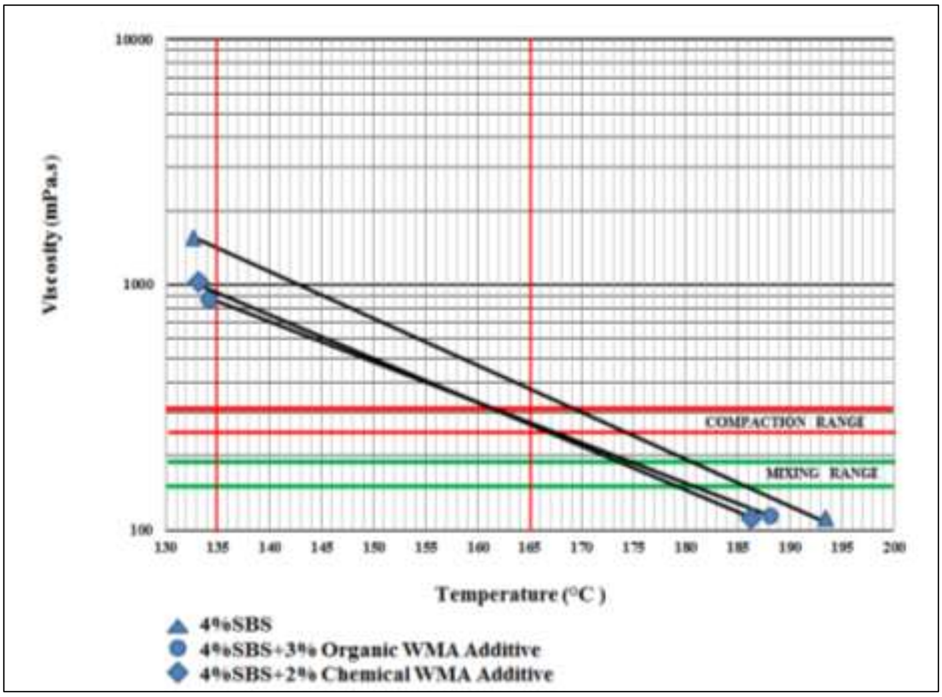


Figure 7.21 Determination of mixing and compaction temperatures for 4% SBS modified bitumen containing WMA additives

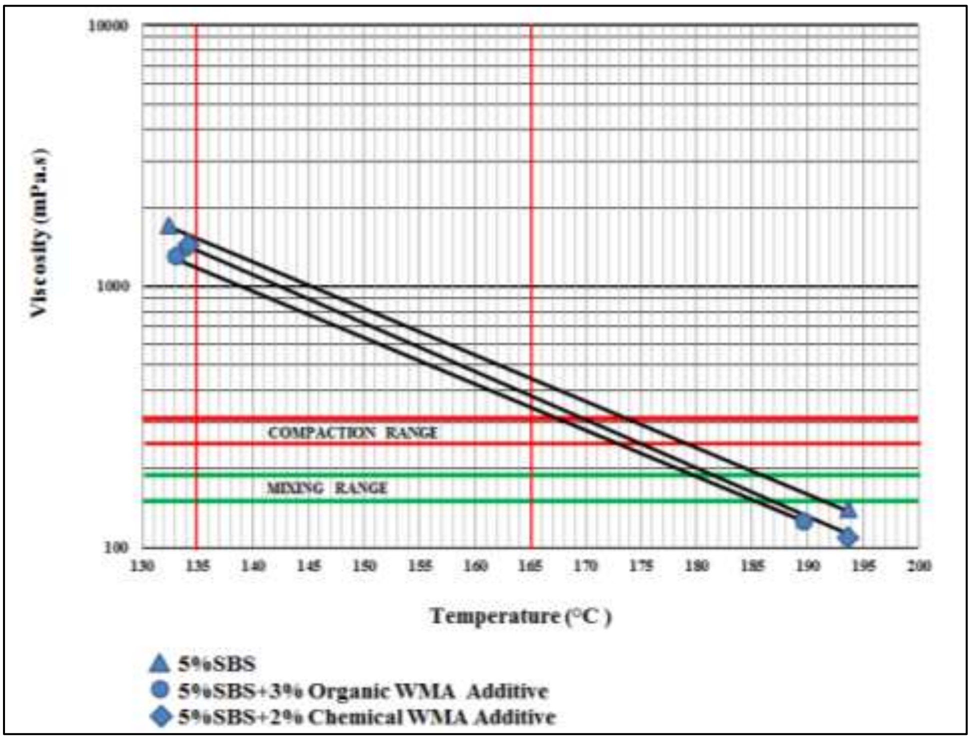


Figure 7.22 Determination of mixing and compaction temperatures for 5% SBS modified bitumen containing WMA additives

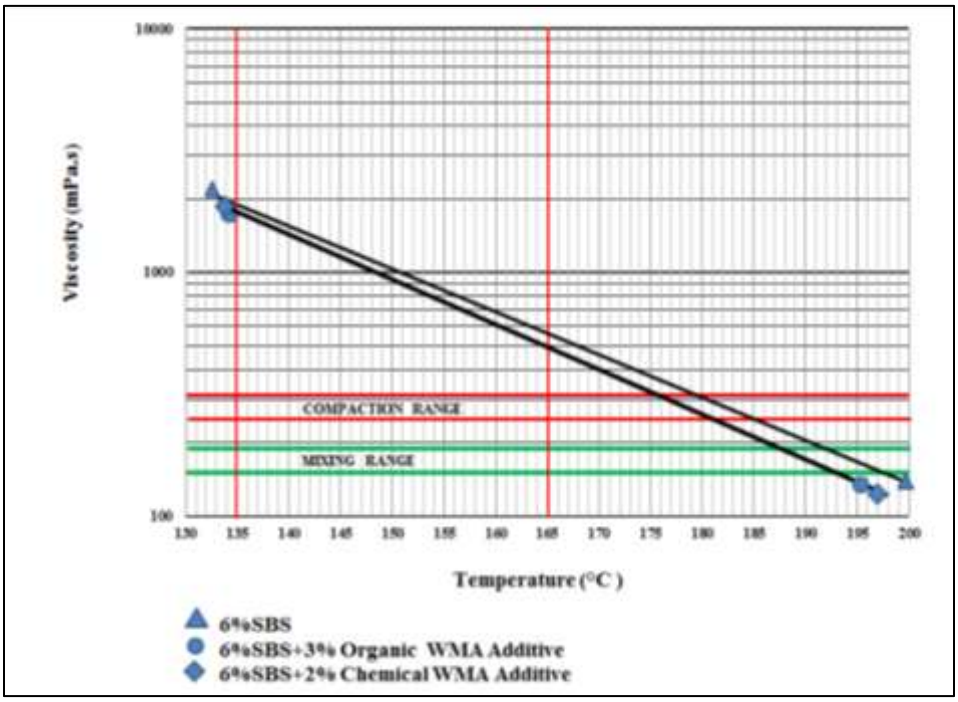


Figure 7.23 Determination of mixing and compaction temperatures for 6% SBS modified bitumen containing WMA additives

Table 7.7 Mixing and compaction temperatures

Percentage of SBS by Weight of Bitumen	**WMA Type**	**Percentage of WMA Additive by Weight of SBS Modified Bitumen**	**Mixing Temp (°C)**	**Compaction Temp. (°C)**
0	-	0	157-163	145-150
4	-	0	181-186	170-174
	Organic WMA Add.	3	175-182	162-168
	Chemical WMA Add.	2	174-180	162-167
5	-	0	186-191	174-179
	Organic WMA Add.	3	180-185	168-173
	Chemical WMA Add.	2	182-187	170-175
6	-	0	192-198	180-185
	Organic WMA Add.	3	188-193	176-181
	Chemical WMA Add.	2	188-193	176-181

As can be seen in Table7.7, modification of base bitumen with SBS significantly increases mixing and compaction ranges of the bitumen. Mixing and compaction temperature ranges of SBS modified bitumen samples increase as the concentration of SBS into base bitumen increases from 4% to 6%. Additions of both chemical and organic WMA additives decrease the mixing and compaction temperatures of the SBS modified bitumen sample in all concentrations of SBS. As seen from the results, there is a decrease of average 5°C in the mixing ranges of the polymer modified bitumen samples containing both organic and chemical WMA additives compared to SBS modified samples. The effects of both organic and chemical WMA additives in reducing compaction ranges decreases from 8°C to 4°C as the percentage of SBS in bitumen increases from 4% to 6%. Both of the tested WMA additives were similar in results from the application temperature point of view.

7.4.2 Rheological Test Results

This section includes the results of rheological tests applied on all of the bitumen samples; produced by the combination of three different concentrations of SBS modified bitumen and organic and chemical WMA additives. The results have been presented into two groups of Dynamic Shear Rheometer (ASTM D7175-05) test results and Zero Shear Viscosity (ZSV) test results.

7.4.2.1 Dynamic Shear Rheometer (DSR) Test Results

The determination of complex rheological properties of bitumen is currently possible with the use of the Dynamic Shear Rheometer (DSR). Parameters most commonly tested in DSR include the bitumen complex shear modulus (G*) and phase angle (δ), tested in various temperature and frequency ranges.

In order to determine upper critical temperature used in performance grading (PG) system, appropriately formed non-aged and RTFOT aged specimens of base bitumen, SBS modified bitumen and SBS modified bitumen samples containing organic and chemical additives (with dimensions of 25 mm in diameter and 1 mm in height) were subjected to oscillating shear in the DSR at the frequency of 10 rad/s (1.59Hz). The temperature cycles were set to start at 52°C for non-aged and 64°C for RTFOT aged samples an run up in 6°C increments.

The upper critical temperatures (T_{crit}) used in PG system were determined for each sample using the obtained $G^*/\sin\delta$ results and DSR specifications for PG bitumen. In PG system, the upper critical temperature is the temperature at which $G^*/\sin\delta = 1.0$ kPa for non-aged bitumen, and $G^*/\sin\delta = 2.2$ kPa for RTFOT aged bitumen. The upper critical temperatures (T_{crit}) for each sample are presented in Tables 7.8 to 7.11.

In some cases regarding SBS modified bitumen samples involving WMA additives, T_{crit} values of non-aged and aged specimens did not exhibit the same values. Since aging plays a key role in rutting performance of bitumen, it was decided to calculate T_{crit} based on the G*/sinδ results from the aged bitumen specimen in such cases.

It can be concluded from the Tables 7.8 to 7.11 that modification of base bitumen with 4% SBS and 5% SBS increases PG upper critical temperature of the base bitumen (T_{crit}) from 64°C to 76°C. Modification of base bitumen with 6% SBS increases T_{crit} of the bitumen from 64°C to 82°C. Higher T_{crit} means a higher rutting resistance.

As seen in Tables 7.9 to 7.11, addition of organic WMA additive into SBS modified bitumen increases T_{crit} values of bitumen in 4% and 5% SBS concentrations. Addition of organic WMA additive into 6% SBS modified bitumen does not change T_{crit} values of the modified bitumen. Addition of chemical WMA additive into SBS modified bitumen decreases T_{crit} values of modified bitumen in 4% and 6% concentrations of SBS. However, addition of chemical WMA additive into 5% SBS modified bitumen does not change T_{crit} value of the modified bitumen.

It can be concluded that the utilization of SBS into base bitumen improves rutting performance of the base bitumen in terms of T_{crit}. In most cases, the use of organic WMA additive into SBS modified bitumen improves the rutting performance of the SBS modified bitumen in terms of T_{crit} values. However, the use of chemical WMA additive decreases (in most cases) or does not improve the rutting performance of SBS modified bitumen in terms of T_{crit} values.

Table 7.8 Determination of PG upper critical temperature for base bitumen

Sample Type	**Temperature**	**DSR, $G^*/\sin\delta$ (Pa)**		**PG Upper Critical Temp. (°C)**
		Non-aged	**Aged**	
Base Bitumen	52	9117		**64**
	58	3727		
	64	**1641**	**3773**	
	70	776.2	1699	

Table 7.9 Determination of PG upper critical temperatures for 4% SBS modified bitumen samples containing WMA additives

SBS Amount (%) by bitumen weight	**WMA Type**	**WMA Additive (%) by SBS PMB Weight**	**Temperature**	**DSR, $G^*/\sin\delta$ (Pa)**		**PG Upper Critical Temp. (°C)**
				Non-aged	**Aged**	
4	**-**	-	52	23560.0		**76**
			58	10800.0		
			64	4930.0	9613	
			70	2373.0	4596	
			76	**1192.0**	**2313**	
			82	624.20	1212	
	Organic WMA Add.	3	52	43020.0		**82**
			58	20320.0		
			64	9575.0	21750.0	
			70	4602.0	11040.0	
			76	2265.0	5785.0	
			82	**1172.0**	**3112.0**	
			88	614.0	1798.0	
	Chemical WMA Add.	2	52	18830.0		**70**
			58	8969.0		
			64	4280.0	7825.0	
			70	2126.0	**3846.0**	
			76	**1071.0**	1993.0	
			82	581.9	-	

Table 7.10 Determination of PG upper critical temperatures for 5% SBS modified bitumen samples containing WMA additives

SBS Amount (%) by bitumen weight	**WMA Type**	**WMA Additive (%) by SBS PMB Weight**	**Temperature**	**DSR, $G^*/\sin\delta$ (Pa)**		**PG Upper Critical Temp. (°C)**
				Non-aged	**Aged**	
5	**-**	-	52	26330.0		**76**
			58	12750.0		
			64	5969.0	12470.0	
			70	2850.0	6368.0	
			76	**1430.0**	**3424.0**	
			82	756.8	1993.0	
	Organic WMA Add.	3	52	59520.0		**82**
			58	28880.0		
			64	14360.0	27460.0	
			70	7355.0	13880.0	
			76	3956.0	7153.0	
			82	2278.0	**3813.0**	
			88	**1400.0**	2091.0	
	Chemical WMA Add.	2	52	28260.0		**76**
			58	13930.0		
			64	6822.0	8848.0	
			70	3401.0	4569.0	
			76	**1729.0**	**2463.0**	
			82	904.1	1397.0	

Table 7.11 Determination of PG upper critical temperatures for 6% SBS modified bitumen samples containing WMA additives

SBS Amount (%) by bitumen weight	**WMA Type**	**WMA Additive (%) by SBS PMB Weight**	**Temperature**	**DSR, $G^*/\sin\delta$ (Pa)**		**PG Upper Critical Temp. (°C)**
				Non-aged	**Aged**	
6	**-**	-	52	31810.0		**82**
			58	15340.0		
			64	7390.0	15540.0	
			70	3762.0	8175.0	
			76	2050.0	4440.0	
			82	**1220.0**	**2540.0**	
			88	749.8	1568.0	
	Organic WMA Add.	3	52	53130.0		**82**
			58	27230.0		
			64	13560.0	22880.0	
			70	6767.0	12240.0	
			76	3469.0	6576.0	
			82	1906.0	**3654.0**	
			88	**1060.0**	2069.0	
	Chemical WMA Add.	2	52	27490.0		**76**
			58	14460.0		
			64	8060.0	11140.0	
			70	4797.0	5934.0	
			76	3088.0	**3224.0**	
			82	2106.0	1861.0	
			88	**1486.0**	-	

All of the non-aged samples including base bitumen, SBS modified bitumen and SBS modified bitumen involving organic and chemical WMA additives were subjected to oscillating shear in the DSR machine at low (0.01Hz) and high (10Hz) frequency levels at 4 different temperature cycles ranging from 50°C to 80°C with 10°C increment. The variation of the rutting parameter ($G^*/\sin\delta$) of the samples at low and high frequencies are presented in Figures 7.24 to 7.29.

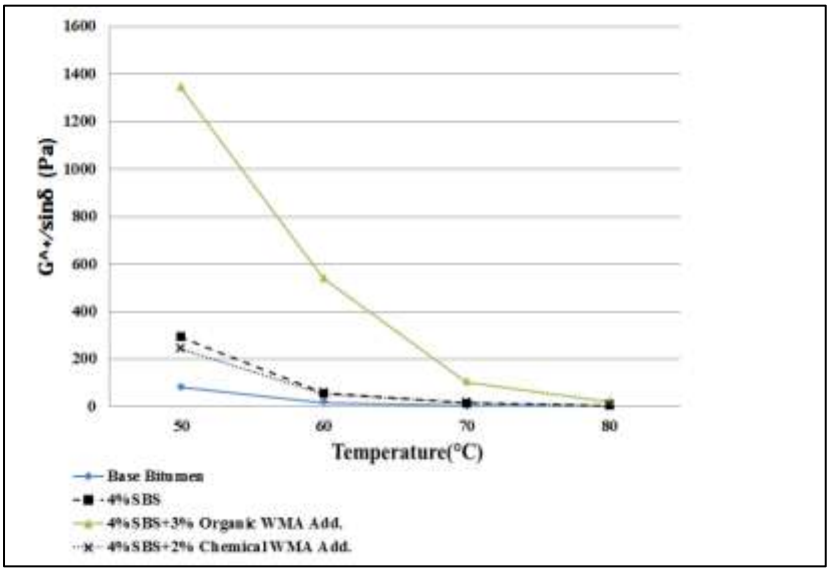


Figure 7.24 $G^*/\sin\delta$ values for 4% SBS modified bitumen and 4% SBS modified bitumen involving organic and chemical WMA additives at 0.01Hz

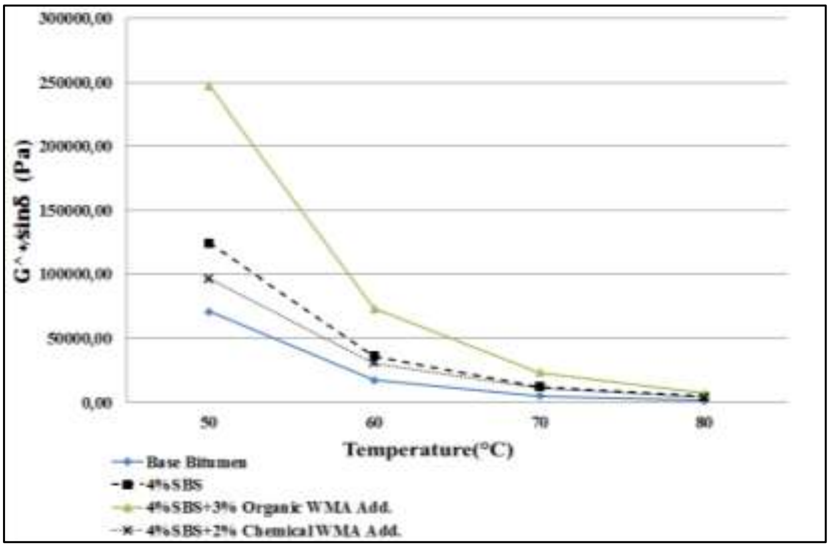


Figure 7.25 $G^*/\sin\delta$ values for 4% SBS modified bitumen and 4% SBS modified bitumen involving organic and chemical WMA additives at 10Hz

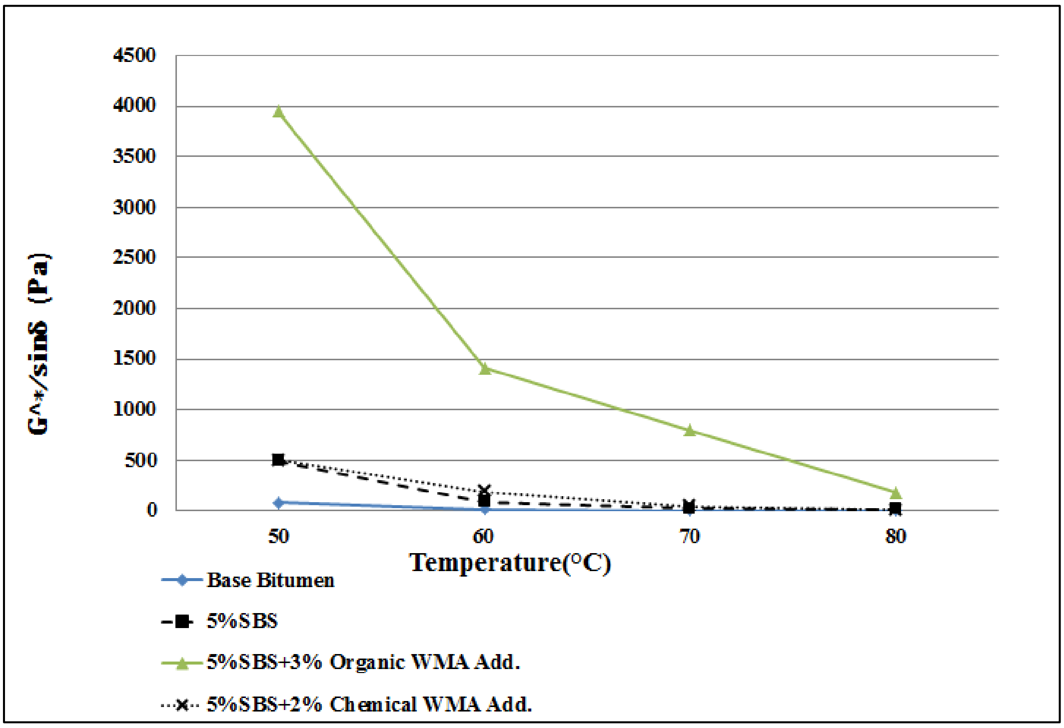


Figure 7.26 G*⁄sinδ values for 5% SBS modified bitumen and 5% SBS modified bitumen involving organic and chemical WMA additives at 0.01Hz

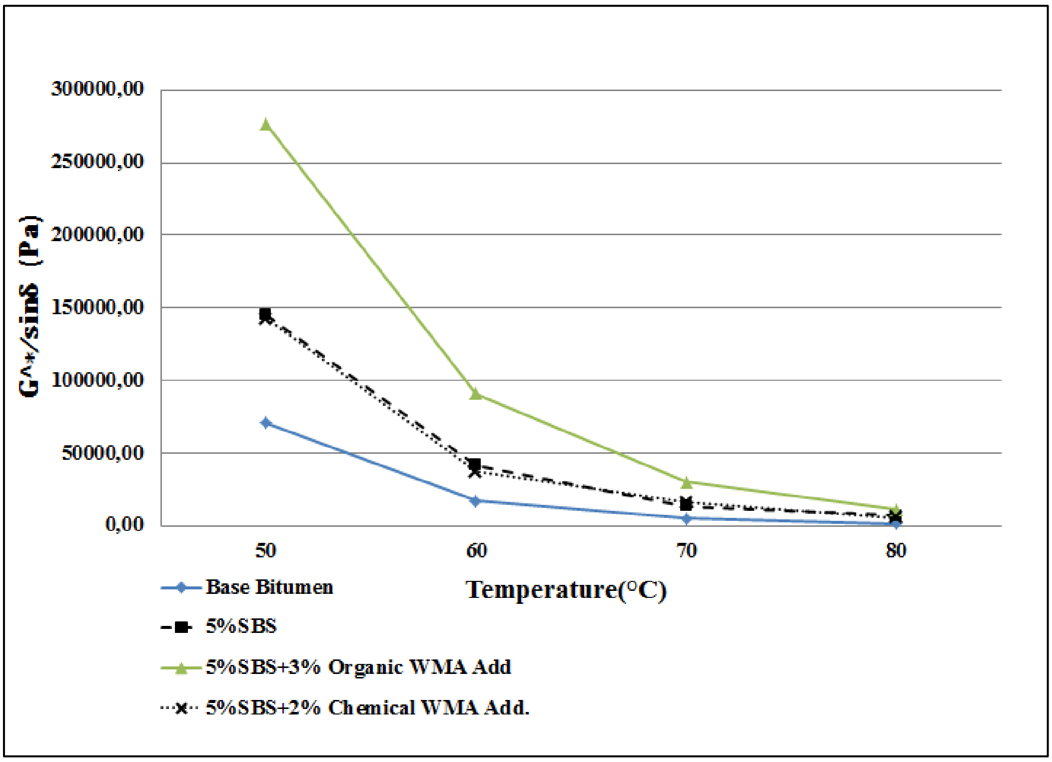


Figure 7.27 G*⁄sinδ values for 5% SBS modified bitumen and 5% SBS modified bitumen involving organic and chemical WMA additives at 10Hz

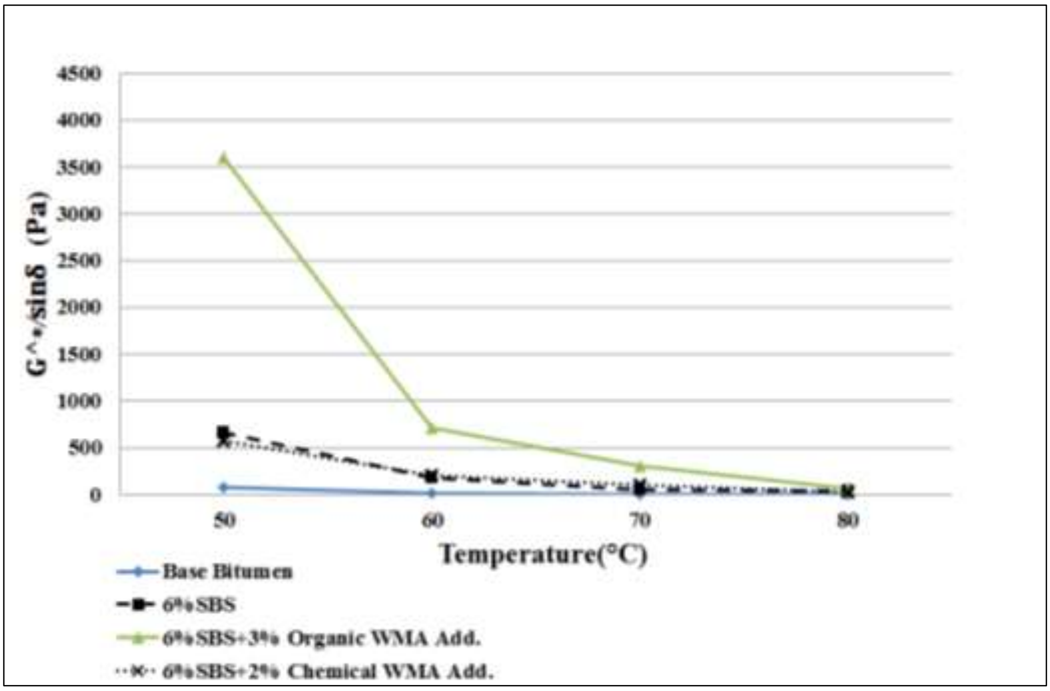


Figure 7.28 G*⁄sinδ values for 6% SBS modified bitumen and 6% SBS modified bitumen involving organic and chemical WMA additives at 0.01Hz

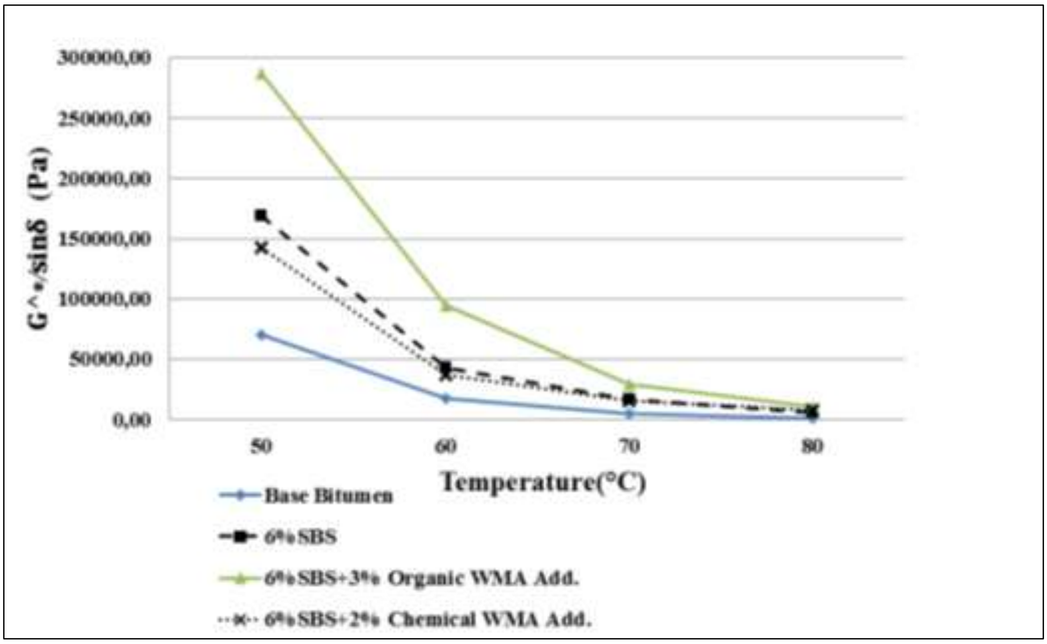


Figure 7.29 G*⁄sinδ values for 6% SBS modified bitumen and 6% SBS modified bitumen involving organic and chemical WMA additives at 10Hz

As presented in Figures 7.24 to 7.29, at both frequencies, G*⁄sinδ values increase in all of the samples as the temperature decreases. An increment in G*⁄sinδ value indicates higher performance against rutting. Besides, G*⁄sinδ values increase with an increase in frequency for all of the bitumen samples. This is due to the rheological behavior of the bitumen samples since bitumen under shorter loading times (high frequency level) exhibit elastic behavior (Sengoz, Topal & Gorkem, 2013).

As can be seen in Figures 7.24 to 7.29 all of the SBS modified bitumen samples depict higher G*⁄sinδ value than the base bitumen samples at both high and low frequencies and at all temperatures. A significant increase in the G*⁄sinδ values can be seen at all of the SBS modified samples containing organic WMA additive at all frequencies and temperatures compared to all other samples. The effects of organic WMA additive in increasing G*⁄sinδ values is more obvious at lower frequencies at all temperature levels. However this case is not valid for SBS modified bitumen involving chemical WMA additive. In most cases at high frequency levels (10 Hz), the utilization of chemical WMA additive decreased G*⁄sinδ values at all concentrations of SBS modified bitumen as presented in Figures 7.25, 7.27 and 7.29. However, there were only two cases in which the G*⁄sinδ value of the SBS modified sample involving chemical WMA additive was slightly larger than that of the SBS modified sample (5% SBS at 70°C and 6% SBS at 80°C). As can be seen in Figures 7.24, 7.26 and 7.28 at low frequency levels, no significant variation is seen with the utilization of chemical WMA additive in SBS modified bitumen specially at high temperature levels.

Consequently, based on the values of G*⁄sinδ which is a rutting performance indicator, it was found that modification of base bitumen with SBS improves the performance of the base bitumen against rutting. Besides, incorporation of organic WMA additives into SBS modified bitumen also significantly increases the performance of the bitumen against rutting. This is because the organic WMA additive is an aliphatic hydrocarbon, which crystallizes in the bitumen at temperatures below 85°C, thereby increases the stiffness of the bitumen. However the effects of incorporating chemical WMA additive into SBS modified samples is less significant in terms of performance against rutting. This may be because the chemical WMA additive is referred to as product package formed by surfactant (Surface Active Agent) and adhesion agents, among other components. Those types of products chemically enhance active adhesion and improve the wetting of aggregates by bitumen without changing considerably the bitumen performance (Capitao, Picado-Santos & Martinho, 2012).

7.4.2.2 Zero Shear Viscosity Test Results

The zero shear viscosity (ZSV) results of all of the bitumen samples including base bitumen, SBS modified bitumen and SBS modified bitumen samples involving organic and chemical WMA additives, determined by the application of Creep Test using DSR machine are illustrated in Figures 7.30 to 7.32.

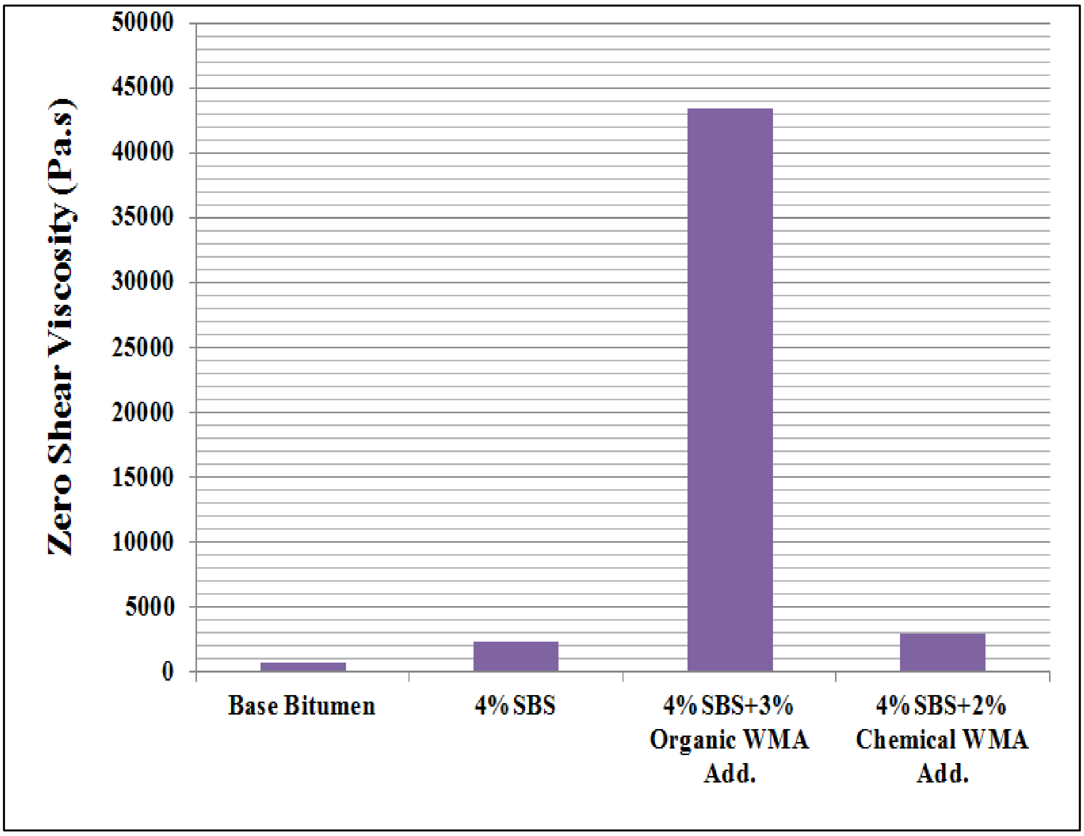


Figure 7.30 ZSV values for 4% SBS modified bitumen and 4% SBS modified bitumen involving organic and chemical WMA additives

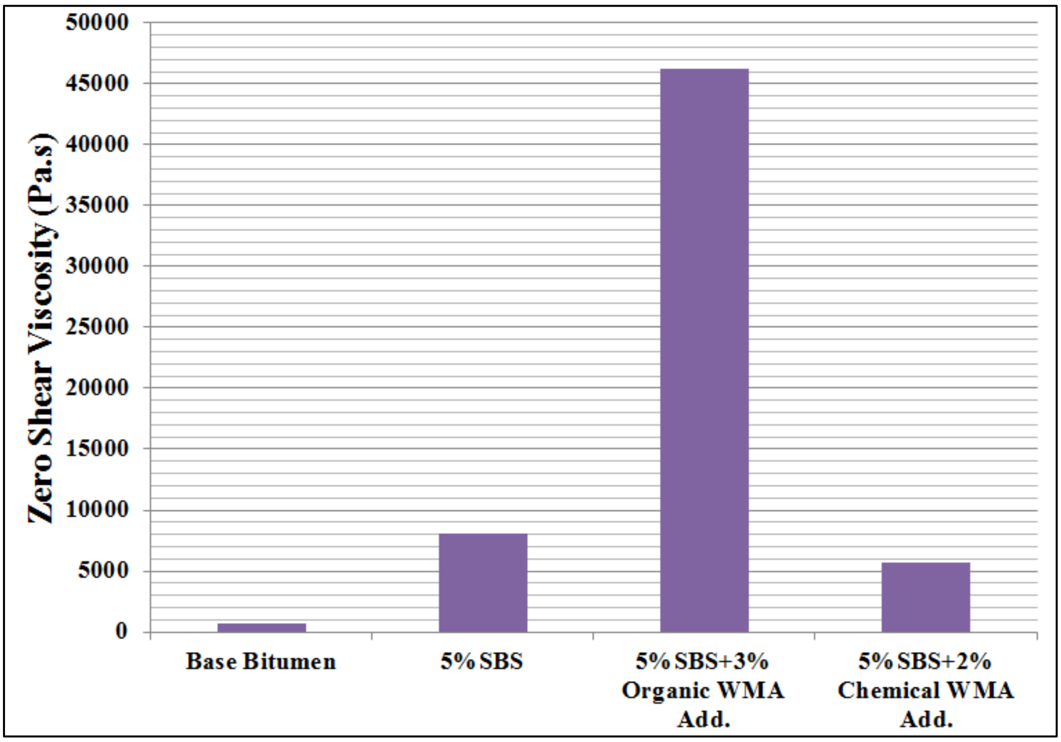


Figure 7.31 ZSV values for 5% SBS modified bitumen and 5% SBS modified bitumen involving organic and chemical WMA additives

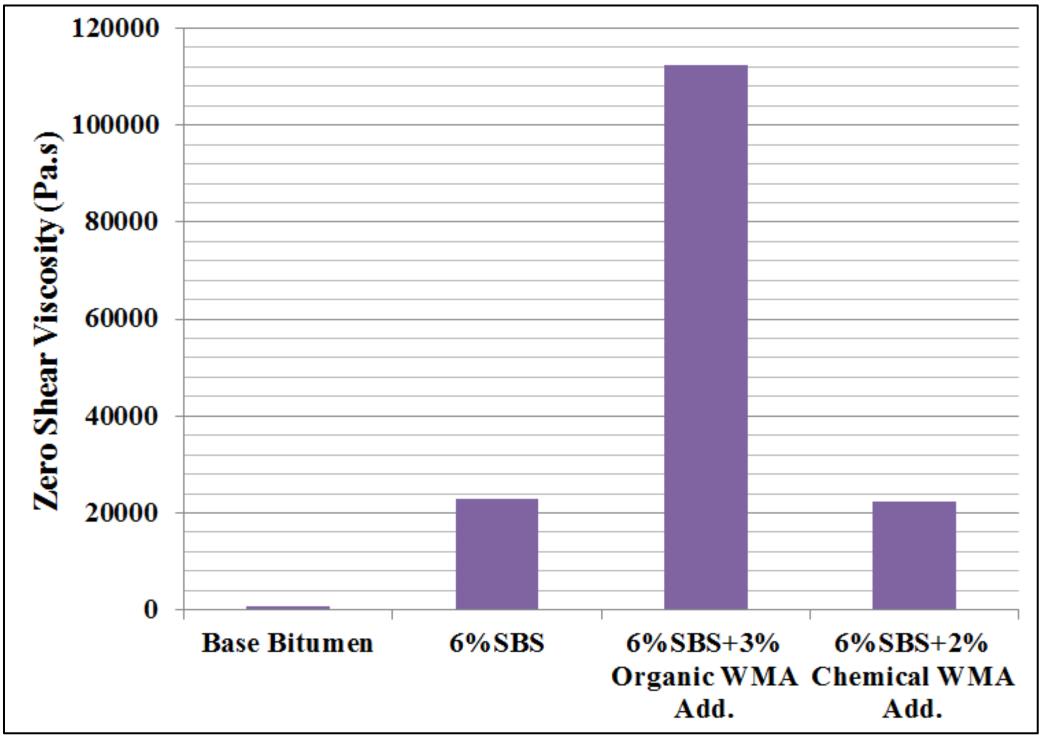


Figure 7.32 ZSV values for 6% SBS modified bitumen and 6% SBS modified bitumen involving organic and chemical WMA additives

As depicted in Figures 7.30 to 7.32, all of the SBS modified bitumen samples show a higher value in terms of ZSV than the base bitumen samples. The values of ZSV increase with an augmentation in the content of SBS in the base bitumen. Modification of base bitumen with SBS yields the peak ZSV value at 6% concentration of SBS in the base bitumen. As can be seen in all of the figures, incorporation of organic WMA additive into all three concentrations of SBS significantly increases the ZSV values of SBS modified bitumen. This rate of increment is more obvious at 4% concentration of SBS into base bitumen as illustrated in Figure 7.30. A higher ZSV value indicates higher stiffness and thus higher resistance to permanent deformation under long term loading. As presented in Figure 7.30, incorporation of chemical WMA additive into 4% SBS modified bitumen slightly increases the ZSV value of SBS modified bitumen. However in Figures 7.31 and 7.32 at 5% and 6% concentrations of SBS into base bitumen, incorporation of chemical WMA additive in SBS modified bitumen decreases the ZSV values of SBS modified bitumen.

Consequently, based on the values of ZSV from Creep Test it was seen that modification of base bitumen with SBS improves the resistance of base bitumen against permanent deformation. The performance of SBS modified bitumen against rutting improves with an increment in the concentration of SBS into base bitumen. Incorporation of organic WMA additive into SBS modified bitumen improves the rutting performance of the SBS modified bitumen especially in the 4% concentration of SBS in the base bitumen. This is because with a melting range between 85°C and 115°C, the organic WMA additive shows high viscosity at lower temperatures, and low viscosity at higher temperatures (Hurley & Prowell, 2005) and forms a lattice structure in the asphalt binder that gives the mixture stability at service temperatures (Zaumanis, 2010). However the effects of incorporating chemical WMA additive into SBS modified samples is less significant or negative in terms of ZSV and resistance to permanent deformation.

CHAPTER EIGHT
CONCLUSIONS AND RECOMMENDATIONS

Warm mix asphalt (WMA) technologies yield substantial reduction in mixing and compaction temperatures of bitumen and mixes by varieties of methods and additives. Reduction in fuel consumption and emissions in plants, there are many other favorable benefits of using warm mix asphalt technologies including, but not limited to, longer paving seasons, longer hauling distances, earlier traffic opening, reduced binder aging, and reduced cracking.

Polymer modified bitumen (PMB) has turned into a very significant portion of pavement industry due to its superior performances including less aging, better rutting resistance, and lower fatigue cracking properties.

In terms of this study, the conventional and rheological bitumen tests have been utilized to quantify the difference in the properties and performance of SBS polymer modified bitumen involving organic and chemical WMA additives.

Conventional bitumen tests conducted on three different concentrations of SBS modified bitumen samples (4%SBS, 5%SBS and 6%SBS) and each concentration involving 3% organic WMA additive and 2% chemical WMA additive indicate a significant decrease in penetration and increase in softening point temperatures of SBS modified bitumen samples for all concentrations of SBS, compared to base bitumen. The penetration test is an empirical test which measures the hardness of bitumen at a specified test condition. The increase in softening point is favorable since bitumen with higher softening point may be less susceptible to permanent deformation. Addition of both organic and chemical additives into SBS modified bitumen decrease the penetration value of the SBS modified bitumen at similar levels. The effects of organic WMA additive in increasing the softening point values are more evident than that of the chemical WMA additives in all concentrations of SBS. Incorporation of chemical WMA additive into 5% SBS modified bitumen slightly decreased the softening point of SBS modified bitumen.

The results show that all of the modified samples including three different concentrations of SBS and SBS modified bitumen involving organic and chemical WMA additives have a higher PI and thus exhibit lesser temperature susceptibility as compared to base bitumen. It can be also concluded from the results that addition of organic WMA additive significantly lowers SBS modified bitumen samples' temperature susceptibility.

In the light of findings from short term aging tests, there is a slight increase in terms of mass loss after RTFOT in all of the modified bitumen samples compared to base bitumen. Compared to organic WMA additive, the addition of chemical WMA additive increases susceptibility of bitumen to aging. Addition of organic WMA additive into SBS modified bitumen samples almost does not show noticeable variation in percentage of mass loss on SBS modified samples especially at higher concentrations of SBS. All of the samples exhibit a better performance in terms of retained penetration compared to base bitumen. Both of the organic and chemical additives exhibit almost identical values in terms of increase in softening points after RTFOT. The results also indicate that addition of WMA additives do not exhibit any noticeable adverse effect on storage stability of SBS modified bitumen.

The entire SBS polymer modified bitumen samples and SBS modified samples involving WMA additives exhibit higher values in terms of viscosity compared to base bitumen. Higher viscosity values indicate higher mixing and compaction temperatures of bituminous mixtures. Compared to SBS PMB samples, the addition of both organic and chemical WMA additive decreases the viscosity values at 135°C and 165°C. Besides as expected the increase in SBS concentration from 4% to 6% raises the viscosity values. Based on the detailed investigation regarding viscosity tests, the results show a decrease of average 5°C in the mixing ranges of the polymer modified bitumen samples containing both organic and chemical WMA additives compared to SBS modified samples.

Rheological tests indicate that the utilization of SBS into base bitumen improves rutting performance of the base bitumen in terms of PG upper critical temperature

(T_{crit}). T_{crit} results have been determined for each sample using the obtained G*/sinδ results from DSR test and specifications for PG bitumen which indicate that in most cases, the use of organic WMA additive into SBS modified bitumen improves the rutting performance of the SBS modified bitumen. However, based on T_{crit} values, the use of chemical WMA additive decreases (in most cases) or does not improve the rutting performance of SBS modified bitumen.

The results of oscillating shear in the DSR machine at low (0.01Hz) and high (10Hz) frequency levels at four different temperature cycles ranging from 50°C to 80°C with 10°C increment indicate an increase in G*⁄sinδ values with decrease in temperature values at both low and high frequencies. Besides, G*⁄sinδ values increase with an increase in frequency regarding all of the bitumen samples. This is due to the rheological behavior of the bitumen samples since bitumen under shorter loading times (high frequency level) exhibit elastic behavior.

Based on the G*⁄sinδ values from the oscillating shear in the DSR machine both at low and high frequencies, it has been found that modification of base bitumen with SBS improves the performance of the base bitumen against rutting. In addition, the use of organic WMA additives into SBS modified bitumen also significantly increases the performance of the bitumen against rutting. This is because the organic WMA additive is an aliphatic hydrocarbon, which crystallizes in the bitumen at temperatures below 85°C, thereby increases the stiffness of the bitumen. However the effects of using chemical WMA additive into SBS modified samples is less significant in terms of rutting performance. This may be because the chemical WMA additive is referred to as product package formed by surfactants (Surface Active Agent) and adhesion agents, among other components that chemically enhance active adhesion and improve the wetting of aggregates by bitumen without changing considerably the bitumen performance.

Zero shear viscosity (ZSV) from Creep Test indicates improvement in the resistance of base bitumen against permanent deformation in the case modified with SBS. The performance of SBS modified bitumen against rutting improves with an increment in the concentration of SBS into base bitumen. The use of organic WMA additive into SBS modified bitumen improves rutting performance of the SBS modified bitumen especially in the 4% concentration of SBS into base bitumen. This is because with a melting range between 85°C and 115°C, the organic WMA additive shows high viscosity at lower temperatures and low viscosity at higher temperatures and forms a lattice structure in the asphalt binder that gives the mixture stability at service temperatures. However the effects of incorporating chemical WMA additive into SBS modified samples is less significant or negative in terms of ZSV and resistance to permanent deformation.

It is recommended to conduct Pressure Ageing Vessel (PAV) and Bending Beam Rheometer (BBR) tests on the SBS polymer modified bitumen samples involving WMA additives in order to further investigate their long term-aging properties and performance at intermediate and low temperatures.

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