Effect of polymers on rheological properties of waxy bitumens

Efecto de los polímeros sobre las propiedades reológicas de los betunes céreos

Julide Oner (Main and Corresponding Author)

Department of Civil Engineering, Engineering Faculty, Usak University
Bir Eylul Campus, 64000, Usak (Turkey)
julide.oner@usak.edu.tr

Burak Sengoz

Department of Civil Engineering, Engineering Faculty, Dokuz Eylul University
Tinaztepe Campus, 35600, Izmir (Turkey)
burak.sengoz@usak.edu.tr

Abstract

The definition of bitumen wax has been formulated to facilitate the distinction between harmful wax and less harmful or non-harmful. Since exact behaviour of waxes within bitumens is not completely determined and the absence of cooperative study related to modification of bitumens involving different amounts of waxes, the values found in the study are thought to be useful in determining which content of wax and type of polymer would be better for the needs of petroleum refineries in different countries. The scope of this study is to minimize the negative effects of waxes within bitumens obtained from different sources. For this purpose, modified bitumen samples were prepared by using different types of polymers such as elastomers, plastomers and polyethylene groups. Following the determination of the contents of wax by Differential Scanning Calorimetry and TS EN 12606-1, rheological properties of waxy bitumens and polymer modified bitumens (PMB) were evaluated using dynamic shear rheometer tests. The intermediate temperature performance levels of PMB were also determined by fatigue parameters. Besides, rutting performance of PMB was evaluated using Zero Shear Viscosity and Multiple Stress Creep Recovery tests.

Key words: Wax, dynamic shear rheometer, fatigue parameter, zero shear viscosity, multiple stress creep recovery.

Resumen

La definición de cera bituminosa se ha formulado para facilitar la distinción entre cera nociva y menos nociva o no. Dado que el comportamiento exacto de las ceras en betunes no está completamente determinado y la ausencia de un estudio cooperativo relacionado con la modificación de betunes que involucran diferentes cantidades de ceras, los valores encontrados en el estudio se consideran útiles para determinar qué contenido de cera y tipo de polímero ser mejor para las necesidades de las refinerías de petróleo en diferentes países. El objetivo de este estudio es minimizar los efectos negativos de las ceras en los betunes obtenidos de diferentes fuentes. Para este propósito, se prepararon muestras de betún modificado usando diferentes tipos de polímeros tales como elastómeros, plastómeros y grupos de polietileno. Tras la determinación del contenido de cera por calorimetría de barrido diferencial y TS EN 12606-1, se evaluaron las propiedades reológicas de los betunes céreos y los betunes modificados con polímeros (PMB) utilizando pruebas de reómetro de cizallamiento dinámico. Los niveles intermedios de rendimiento de temperatura de PMB también fueron determinados por los parámetros de fatiga. Además, el rendimiento de celo de PMB se evaluó usando pruebas de Cero Cizalladura de Esfuerzo y Recuperación de Estrés Múltiple.

Palabras clave: Cera, reómetro de corte dinámico, parámetro de fatiga, viscosidad de cizallamiento cero, recuperación de fluencia por estrés multiple.

Introduction

Almost all bitumen is obtained from crude oil by refining process but only certain crude oils contain good quality bitumen for asphalt pavement (Lyne, Wallqvist, & Birgisson, 2013). Naphthenic-base crude oils often give a large amount of bitumen that may be in good quality, while paraffinic crude oils may give bitumen of good quality or yield bitumen that are not suitable for asphalt pavement (Edwards, & Redelius, 2003).

Wax in bitumen has been referred as petroleum wax and is obtained from refining of paraffinic crude oils. The effects of wax on the properties of bitumen depend on the following factors: the source, chemical composition and rheology of the bitumen. There is a lack of literature reviews related to the effect of waxes on rheology and conventional properties of bitumen.

Waxes in bitumen are divided into two general categories such as macro-crystalline and micro-crystalline wax (Edwards, 2009). Macro-crystalline wax also known as paraffin which crystallizes in large flat plates or needles. It refers to the group of n-alkanes with few or no branches (C_{20}–C_{40}) (Soenen et al., 2013). The melting point of macro-

crystalline paraffin waxes are around 50-70°C (Lu, Langton, Olofsson, & Redelius, 2005; Lu & Redelius, 2007). On the other hand, micro-crystalline wax is collected in the bitumen fraction after the distillation process and mainly consists of naphthens and iso-paraffins as well as crystallizes as small microscopic needles. A micro-crystalline petroleum wax is characterized also by a less distinct melting area and its high average molecular weight giving higher viscosity compared to macro crystalline paraffin wax (Das, Kringos, Wallqvist, & Birgisson, 2013; Musser & Kilpatrick, 1998).

Based on literature, the high content of wax affects the properties of bitumen in different ways. The low melting point of wax decreases resistance of asphalt mixtures against rutting at high temperatures (Lu & Redelius, 2006). Physical hardening, poor ductility and poor bitumen adhesion can be listed as the outcomes caused by the high content of wax (Edwards& Redelius, 2003).

The term "polymer" merely refers to very large molecules made by many chemically reacting small molecules to produce long chains (Becker, Mendez, & Rodriguez, 2001). Polymer modified bitumen (PMB) has been developed by asphalt industry to fulfill the needs for making better pavements that exhibit better performance under loads due to high traffic applications. The use of PMB has become a very important part of pavement construction due to its superior performance, including less ageing, enhanced rutting resistance and lower fatigue cracking properties (Dubois, Mehta, & Nolan, 2014). The most commonly used polymer for bitumen modification is the styrene-butadiene-styrene (SBS) followed by other polymers such as ethylene vinyl acetate (EVA) and polyethylene (PE) (Sengoz & Isikyakar, 2008).

SBS block copolymers are classified as elastomers that increase the elasticity of bitumen. Elastomers derive their strength and elasticity from a physical cross-linking of the molecules into a three-dimensional network (Shirini & Imaninasab, 2016). 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 (Whiteoak & Read, 2003).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, high shear mixers are required to adequately disperse thermoplastic elastomers into the bitumen (Whiteoak & Read, 2003).

EVA based polymers are classified as plastomer that modify bitumen by forming a tough, rigid, three-dimensional network to resist deformation. 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 (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 and ability to be used with softer bitumen (Woolley, 1986).

The polyethylene (PE) is a type of product normally not used as additive to bitumen, generally showing a congealing point of 92-100°C; it has been used in plastics and polishes, as thickener for lubricating oils and petrolatum and as paraffin wax improver/upgrader (Edwards, 2009). PE is manufactured from natural gas derived feedstock by two basic polymerization processes. The low pressure polymerization process results in linear polymer chains with short side branches. The high pressure polymerization process results in polymer chains with more highly developed side branches. PE modified bitumen is less expensive as well as shows more resistance to ultraviolet aging and rutting (Zhu, Birgisson, & Kringos, 2014).

Although the many significant researches which have been carried out related to the PMB in road applications, more studies should be undertaken on the compatibility and in the interaction between polymers and the different sources bitumens according to the needs of refineries in different countries. The main purpose behind this study is to minimize the negative effects of waxes within bitumens obtained from different sources. For this purpose; following the determination of wax contents of five types waxy bitumens obtained from two different countries, bitumen samples were modified by recommended content of three different polymers (SBS polymer at concentration of 3.2% by weight of the bitumen, EVA polymer at concentration of 1.4% by weight of the bitumen and PE polymer at concentration of 1.5% by weight of the bitumen). The effects of adding polymers into waxy bitumens have been acquired through rheological test methods. The upper critical temperatures used in performance grading (PG) system have been determined for each bitumen sample using $G^*/\sin\delta$ results from the dynamic shear rheometer (DSR) test (Soudani, Cerezo, & Haddani, 2016). The effects of loading and temperature on the performance of the samples have

been evaluated using G*/sinδ results from low (0.01 Hz) and high frequencies (10 Hz) loadings at five different temperatures (40°C–80°C). The intermediate temperature performance levels of PMB were also determined by fatigue parameters. Rutting performance of PMB samples has been evaluated using the zero shear viscosity (ZSV) and multiple stress creep recovery (MSCR) test performed in the creep mode. The results have been compared with base bitumen and PMB samples.

Materials

Five bitumens from two different sources (Turkey and Russia) were used in this study. The bitumen samples are identified as Bit TR and Bit R respectively. The general description of samples together with penetration grades are depicted in Table 1.

Table 1. The general description of samples.

Source of Bitumens	Abbreviation	Sample No	Penetration Grades
Turkey	Bit TR	Bit-TR1	50/70
		Bit-TR2	40/60
Russia	Bit R	Bit-R1	60/90
		Bit-R2	60/90
		Bit-R3	70/100

Since the bitumens are originated from different sources, their wax contents are different. Bit-TR1 was manufactured from crude oil deposited in the east part of Turkey. Russia (Bit-R1, Bit-R2 and Bit-R3) bitumens and Bit-TR2 were produced by the blending of crude oil from various sources by a manufacturer in Western Siberia and Middle Eastern countries respectively. Besides, a limited amount of air blowing was used to manufacture Bit-R1 during the refining process.

Among the polymer asphalt modifying agents, SBS styrene–butadiene–styrene) originally developed by LG Chemical Cooperation is widely used in the majority of the asphalt bitumen industry and probably the most appropriate elastomeric type of polymer for asphalt modification. Luprene LG® 501 is a thermoelastoplastic material which consists of linear styrene–butadiene–styrene block copolymer, highly viscous, oil-free. Luprene LG® 501 is used as bitumen modifier for improvement of the quality of PMBs used mainly for road pavements. The concentration of SBS used was 3.2% by weight of the bitumen. Appropriate amount of bitumen (500 g) in 500ml graduated beaker was heated in the stove at 170°C to become fluid enough and then placed under the laboratory type mixer (Sengoz & Isikyakar, 2008). SBS pallets were gradually added to the bitumen. The mixer was set at 800 rpm during 3 hours (mixing period). The mixture's temperature was maintained at 160±5°C during the mixing process (Sengoz & Isikyakar, 2008; Sengoz, Bagayogo, Oner, & Topal, 2017; Topal et al., 2018).

The EVA (ethylene vinyl acetate) polymer used was Elvaloy® 4170 (1.4% by weight of the bitumen) supplied in pellet form by DuPont, USA. Elvaloy® 4170, which contains butylacrylate 20% by weight and glycidyl methacrylate 9%by weight, have proved themselves as good plastomeric type modifiers that reduce permanent deformation and thermal cracking. When bitumen is modified with Elvaloy® 4170, the polymer amount has to be chosen carefully because an excessive quantity can cause the formation of an insoluble bitumen gel. The modifications were done using laboratory type mixer set at 200 rpm during 2 hours (Oner, & Sengoz, 2017; Sengoz, Bagayogo, Oner, & Topal, 2017). During the mixing process, the temperature of the mixture was kept at 180± 5°C.

The used PE (polyethylene)) was Titan® 7686 in white pellet form obtained from Honeywell company, USA. Titan® 7686 is created through the polymerization of ethylene. Titan® 7686 has low molecular weight and semi-crystaline structure. Addition of PE significantly improves the mechanical properties of bitumens. The concentration of PE used was 1.5% by weight of the bitumen. The mixer was set at 800 rpm during 1 hour (mixing period). The mixture's temperature was maintained at 150±5°C during the mixing process.

Test methods

Determination of the paraffin wax content based on European Standard Method EN 12606-1. The European Standard EN 12606-1 is based on DIN 52015, a German method that is performed for determining the paraffin wax

content of bitumen samples (Baldino et al., 2012; European Standard EN 12606-1, 2007). The system includes a distilling system, an electric cooler, a thermo-regulator and compressor refrigeration.

Test procedure is performed on two portions for each of 25 g bitumen samples. The distillate from bitumen is obtained by a specified distillation process. The distillation unit is consisted of a distillation flask, a laboratory burner and erlenmeyer flask used as distillation receiver. The distillation takes place at very high temperatures (up to over 500°C) at which cracking of molecules may occur (Lu & Redelius, 2006). On the second portion of the test procedure; the waxy distillate is dissolved in ether/ethanol (50/50, V/V) solvent and crystallized at -20 °C. The crystallized wax is obtained by filtration (European Standard EN 12606-1, 2007).

Differential Scanning Calorimetry (DSC). The crystallization or melting of waxes in bitumen causes an energy change. Both heating and cooling cycles can be utilized to investigate the presence of wax fraction in bitumen. The exothermic and endothermic effects during the cooling and heating scan generally represent the wax crystallization and wax melting respectively. Differential Scanning Calorimetry (DSC) method has been utilized to register thermal effects of waxes in bitumen through the cooling-heating cycles (ASTM D4419-90, 2015).

In this study, thermal characterization was performed using DSC; Perkin Elmer-Diamond. Approximately 15 mg of bitumen samples is placed in an aluminium pan and sealed under nitrogen atmosphere. The bitumen sample is heated to +120°C and then cooled at 7°C /min to -50°C, followed by heating to +120°C at the same rate. DSC procedure is also used to determine wax content in bitumen. The DSC wax content of bitumen is calculated from an endothermic peak during the heating scan. For the calculation of percentage of wax in the bitumen, a constant melting enthalpy value of 121 J/g is used as a reference (Lu, Kalman, & Redelius, 2008). A typical DSC diagram is presented in Figure 1.

Figure 1. A typical DSC diagram through the cooling-heating cycles. Source: Lu, Langton, Olofsson, & Redelius (2005).
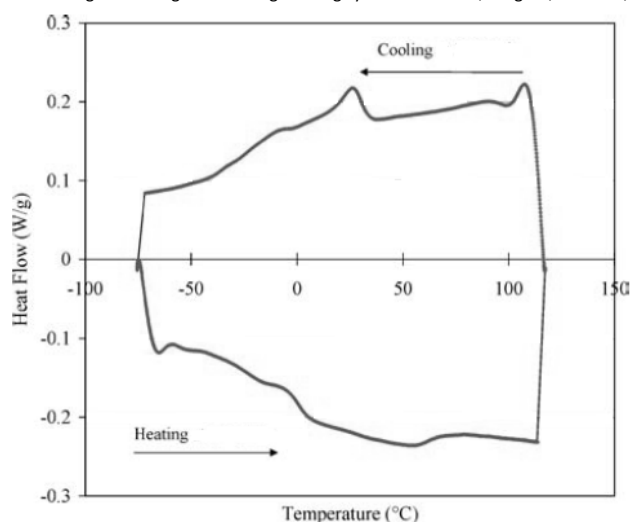
Glass transition temperature, wax crystallization starting temperature and melting out temperature are also determined by DSC results. The glass transition temperature (T_g) which is defined as the half-vitrification temperature is midpoint of the transition region (Edwards, Tasdemir, & Isacsson, 2006). The glass transition temperature obtained from the heating scan is more repeatable and easier to obtain in comparison to the cooling scan. From DSC, bitumen exhibits a kind of phase transition on cooling from high temperature and heating from the low temperature. The first transition has been considered as crystallization starting temperature (T_{ic}) in cooling cycle. Besides, the new phase transition has occurred during the heating cycle. There is an endothermic reaction which is interpreted as the melting of the wax. Wax melting out temperature defined as T_{fm} is the end point of wax melting in bitumen (Oner & Sengoz, 2017).

Rheological test methods. The dynamic shear rheometer (DSR) is used to describe the viscous and elastic behaviour of asphalt bitumen at medium to high temperatures (Santagata, Baglieri, Tsantilis, & Dalmazzo, 2012). This characterization is used in the Superpave PG asphalt bitumen specification. The basic DSR test uses a thin bitumen 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. DSR tests are conducted on unaged, RTFOT aged and PAV (pressure aging vessel) aged bitumen samples (ASTM D 2872-12, 2012; ASTM D6521-05, 2005; Santagata, Baglieri, Tsantilis, & Dalmazzo, 2012; Soudani, Cerezo, & Haddani, 2016).

The determination of complex rheological properties of bitumen is currently possible with the utilization of DS). Parameters most commonly tested in DSR include the bitumen complex shear modulus (G*) and phase angle (δ), tested in various temperature and frequency ranges. 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. G* and δ are used as predictors of rutting and fatigue behaviours. Fatigue properties of bitumen can be evaluated by the fatigue factor at intermediate temperatures. The fatigue behaviour was investigated by applying continuous oscillatory shear loadings with using DSR. Early in pavement life rutting is the main concern, while later in pavement life fatigue cracking becomes the major concern. G*/sinδ is described as rutting indicating parameter and G*.sinδ as fatigue cracking indicating factor (Asphalt Institute, 2001).

The Superpave® specification parameter, G*/sin δ, was identified as the term to be used for high temperature performance grading of paving asphalts in rating the bitumens for their rutting resistance (Xiao, Hou, Amirkhanian, & Kim, 2016). Although used for many years as a rutting parameter, it has been demonstrated that the relationship between G*/sin δ and rutting is poor. This term was found to be inadequate in describing the rutting performance of bitumens (Subhy, 2017).

Zero Shear Viscosity (ZSV) is the viscosity measured in shear deformation at a shear rate approaching to zero. This parameter is an indicator for rutting related bitumen characteristics. It has been observed by researchers in the recent years, that the rutting parameter G*/sin δ is not very effective or failed to predict the rutting performance of bitumen (De Visscher, Soenen, Vanelstraete, & Redelius, 2004). The determination of ZSV in this study is performed by the application of creep test using DSR. 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 (Xiao, Hou, Amirkhanian, & Kim, 2016; Gungor, & Saglik, 2012). All of the samples were short-term aged using a RTFOT procedure. The ZSV of the samples have been predicted by application of creep test at 60°C (CEN/TS 15325, 2008). The test geometry for the creep tests consisted of 25 mm parallel plates and the gap between the plates was 1mm. The stress level was 10 Pa for bitumen samples and each creep test was continued for 30 minutes.

Developments led to the existence of Multiple Stress Creep and Recovery (MSCR) test (Dubois, Mehta, & Nolan, 2014). MSCR test was run on RTFOT aged samples in accordance to ASTM D7405-08 using the dynamic shear rheometer (ASTM D7405-08, 2008; Shenoy, 2008). The ASTM standard procedure establishes the use of two stress levels (0.1 and 3.2 kPa), 1 s creep time, 9 s recovery time, and 10 creep-recovery cycles at each stress level. Anton Paar DSR with its parallel-plate geometry loading device and a control and data acquisition system were utilized for conducting the MSCR test in the present study. Specimens were tested using a 25 mm parallel plates and with 1 mm gap setting at temperature of 60°C and at a stress of 100 and 3200 Pa. The tests were performed at the selected temperature using a constant stress creep of 1 second duration and a relaxation period of 9 seconds, for ten cycles at each stress level. Percent recoverable and non-recoverable components of creep compliance were determined at the end of 10 cycles (Shenoy, 2008).

Results and discussions

Determination of wax content in bitumens through EN 12606-1 and DSC

Calculation of the wax content is based on the following formula based on European Standard Method EN 12606-1. Wax content is calculated as:

$$P = \frac{m_1 * m_w}{m_b * m_2} * 100$$

(1)

where P (m%) is wax content, m_b (g) is the mass of specimen, m_1 (g) is the total mass of distilled oil, m_2 (g) is the mass of distilled oil for wax extraction and m_w (g) is the mass of wax extracted (European Standard EN 12606-1, 2007).

The crystallization or melting of waxes in bitumens involves energy change that can be easily determined by DSC. The results of the EN 12606-1 and DSC measurements are summarized in Table 2 in terms of wax content, crystallization starting temperature, wax melted out temperature and glass transition temperature (Oner, & Sengoz, 2017).

Bitumen	Bit-TR1	Bit-TR2	Bit-R1	Bit-R2	Bit-R3
Sources	Turkey	Turkey	Russia	Russia	Russia
Wax content by EN 12606-1 (%)	0.8	2.70	2.0	2.1	2.3
Wax content by DSC (%)	2.61	3.52	4.81	3.93	4.04
Parameters obtained from DSC Crystallization starting temperature - T_{ic} by DSC (°C)	39.11	45.93	50.22	47.95	55.40
Melting out temperature - T_{fm} by DSC (°C)	65.97	84	80	65	83
Glass transition temperature - T_g by DSC (°C)	-7.05	-15.16	-16.08	-21.65	-20.56

Table 2. DSC and EN 12606-1 analysis of bitumens.

As indicated in Table 2, bitumen samples from different sources exhibit different wax content based on DSC and EN 12606-1 methods. It is clearly seen that, EN 12606-1 method gives much lower values in wax contents as compared with DSC. It is believed that the high temperature (up to over 500 °C) distillation step in EN 12606-1 method may destroy the molecular structure of waxes (thermal cracking) (Edwards, 2009). The resulting smaller paraffin molecules could be soluble in ether/ethanol and do not crystallize in the solvent at the specified low temperature (-20 °C), leading to lower apparent wax content. These might be reasons for the low wax contents as determined by the EN 12606-1 method. The difference in wax content between the two tests may also be due to the solubility of wax in the bitumen providing unlike crystallisation/melting response in DSC. In fact, all the available methods used for determining wax content in bitumen only demonstrate relative results. Bitumen sample from Turkey (Bit-TR1) contains the lowest amount of wax compared to other bitumen samples according to EN 12606-1 and DSC methods (Oner & Sengoz, 2017).

DSC has been widely applied to characterize the thermodynamics properties of bituminous materials. In cooling cycle, crystallization occurs at different temperatures which is interpreted as wax crystallization starting temperature (T_{ic}). The transition continues down to the glass transition temperatures. In heating cycle, there is an endothermic reaction which is interpreted as melting of the wax. Wax melting out temperatures of bitumens is defined as T_{fm}. The temperature at which all wax is completely melted is considerably higher than the start of crystallization. This is due to the super cooling effect at cooling cycle. Effects of low temperature on bitumen properties are typically evidenced by the glass transition temperature (T_g). When temperature is lower than T_g, bitumens are glassy, hard and brittle, whereas for the temperature higher than T_g visco-elastic properties are exhibited. The transition continues down to the glass transition which can be seen at the lowest temperature (-21.65 °C) for Bit-R2. Consequently; Bit-R2, which includes average value of wax percentage, with the lowest value of T_g may have more resistance to low temperature cracking compared to other sources bitumens at a specific low temperature (Oner, & Sengoz, 2017).

Rheological test results

This section includes the results of rheological tests applied on all of the bitumen samples obtained by the different sources. The results have been presented into three groups of Dynamic Shear Rheometer (DSR) test results, Zero Shear Viscosity (ZSV) test results, Multiple Stress Creep Recovery (MSCR) test results. The coefficient of variation (which is calculated as the ratio of standard deviation to mean value) related to rheological bitumen tests such as G*/sinδ, G*.sinδ, ZSV and MSCR varies between 0.59% and 1.85% indicating a reasonable consistency. The calculated variances indicate that the determined results of rheological tests vary in acceptable ranges.

Dynamic Shear Rheometer (DSR) test results. In order to determine upper critical temperature used in performance grading (PG) system, un-aged and RTFOT aged specimens of bitumens containing different content of wax 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 un-aged and 64°C for RTFOT aged samples an run up in 6°C increments. The upper critical temperatures (Tcrit) used in PG system were determined for each sample using the obtained G*/sinδ results and DSR specifications for PG bitumen. In PG system, the upper critical temperature is the temperature at which G*/sinδ = 1.0 kPa for un-aged bitumen, and G*/sinδ = 2.2 kPa for RTFOT aged bitumen (Asphalt Institute, 2001). The upper critical temperatures (Tcrit) for each sample modified with SBS, EVA and PE are presented in Table 3, Table 4 and Table 5 respectively.

Table 3. Determination of PG upper critical temperatures for SBS modification.

Bitumen	Temperature (°C)	DSR, **G*/sinδ (Pa)** Non-aged	Aged	Upper Performance Grades
Bit-TR1	52	1.25E+04		70
	58	5918		
	64	2820	5816	
	70	1384	2868	
	76	702	1462	
Bit-TR1	52	6.33E+04		82
+	58	3.38E+04		
SBS	64	1.71E+04	3.23E+04	
	70	8963	1.81E+04	
	76	4609	9980	
	82	1471	3345	
	88	943	1850	
Bit-R1	52	7006		64
	58	3392		
	64	1628	4009	
	70	797.5	1903	
Bit-R1	52	2.92E+04		82
+	58	1.60E+04		
SBS	64	8498	1.72E+04	
	70	4523	9643	
	76	2408	5164	
	82	1334	2801	
	88	739.5	1550	
Bit-R2	52	6785		64
	58	3241		
	64	1551	3650	
	70	769.7	1775	
Bit-R2	52	2.42E+04		82
+	58	1.29E+04		
SBS	64	6418	1.59E+04	
	70	3209	8635	
	76	1615	4651	
	82	1058.6	2390	
	88	725.1	1321	
Bit-R3	52	5165		64
	58	2431		
	64	1147	3346	
	70	556.7	1648	
Bit-R3	52	1.66E+04		76
+	58	9079		
SBS	64	4784	1.28E+04	
	70	2508	6834	
	76	1344	3487	
	82	710.3	1853	
Bit-TR2	52	8047		64
	58	3493		
	64	1592	3356	
	70	779	1493	
Bit-TR2	52	2.03E+04		70
+	58	9202		
SBS	64	4159	8064	
	70	1915	3888	
	76	943.6	1931	

Table 4. Determination of PG upper critical temperatures for EVA modification.

Bitumen	Temperature (°C)	DSR, G*/sinδ (Pa) Non-aged	Aged	Upper Performance Grades
Bit-TR1	52	1.25E+04		70
	58	5918		
	64	2820	5816	
	70	1384	2868	
	76	702	1462	
Bit-TR1	52	2.90E+04		88
+	58	1.55E+04		
EVA	64	7550	2.55E+04	
	70	4478	1.41E+04	
	76	3087	7832	
	82	2491	4358	
	88	1369	2412	
Bit-R1	52	7006		64
	58	3392		
	64	1628	4009	
	70	797.5	1903	
Bit-R1	52	2.00E+04		88
+	58	1.19E+04		
EVA	64	7156	1.40E+04	
	70	4445	8606	
	76	3200	5393	
	82	2038	3484	
	88	1388	2308	
Bit-R2	52	6785		64
	58	3241		
	64	1551	3650	
	70	769.7	1775	
Bit-R2	52	1.69E+04		82
+	58	9708		
EVA	64	5402	1.11E+04	
	70	2910	6548	
	76	2014	3959	
	82	1245	2418	
	88	803.5	1535	
Bit-R3	52	5165		64
	58	2431		
	64	1147	3346	
	70	556.7	1648	
Bit-R3	52	9344		76
+	58	5125		
EVA	64	3027	6773	
	70	2024	4009	
	76	1275	2473	
	82	836.5	1548	
Bit-TR2	52	8047		64
	58	3493		
	64	1592	3356	
	70	779	1493	
Bit-TR2	52	1.16E+04		70
+	58	5441		
EVA	64	2644	4280	
	70	1342	2186	
	76	713.2	1056	

Table 5. Determination of PG upper critical temperatures for PE modification.

Bitumen	Temperature (°C)	DSR, G*/sinδ (Pa) Non-aged	Aged	Upper Performance Grades
Bit-TR1	52	1.25E+04		70
	58	5918		
	64	2820	5816	
	70	1384	2868	
	76	702	1462	
Bit-TR1	52	2.29E+04		76
+	58	1.12E+04		
PE	64	6362	2.15E+04	
	70	3458	1.08E+04	
	76	1764	6534	
	82	932	3500	
	88		1964	
Bit-R1	52	7006		64
	58	3392		
	64	1628	4009	
	70	797.5	1903	
Bit-R1	52	1.37E+04		76
+	58	7088		
PE	64	3697	1.28E+04	
	70	1962	6664	
	76	1054	3525	
	82	570.2	1882	
Bit-R2	52	6785		64
	58	3241		
	64	1551	3650	
	70	769.7	1775	
Bit-R2	52	1.59E+04		76
+	58	8028		
PE	64	3938	9232	
	70	2085	4736	
	76	1103	2472	
	82	601.6	1296	
Bit-R3	52	5165		64
	58	2431		
	64	1147	3346	
	70	556.7	1648	
Bit-R3	52	8379		70
+	58	4255		
PE	64	2234	5606	
	70	1195	2930	
	76	660.5	1537	
Bit-TR2	52	8047		64
	58	3493		
	64	1592	3356	
	70	779	1493	
Bit-TR2	52	1.33E+04		70
+	58	6137		
PE	64	2853	5201	
	70	1426	2408	
	76	750.1	1167	

As presented in Table 3-5, modifications of base bitumens containing different wax contents with SBS, EVA and PE increases the PG upper critical temperature (T_{crit}). Higher T_{crit} value is an indicator of higher resistance to permanent deformation. On the other hand, EVA polymer modified samples depicted the highest critical temperatures. Bit-TR2 containing the highest wax content has the lowest PG upper critical temperature for all modifications. There is no significant variation for T_{crit} values of Bit-TR2 with modification process. However, the addition of polymers into bitumens containing low wax content changes T_{crit} value of the modified bitumen appreciably.

All of the modified RTFOT aged samples including different contents of wax were subjected to oscillating shear in the DSR at low (0.01Hz) and high (10Hz) frequency levels at five different temperature cycles ranging from 40°C to 80°C with 10°C increment. The variation of G*/sinδ (rutting parameter) values of the modified samples with SBS, EVA and PE at low and high frequencies are presented in Figure 2-7.

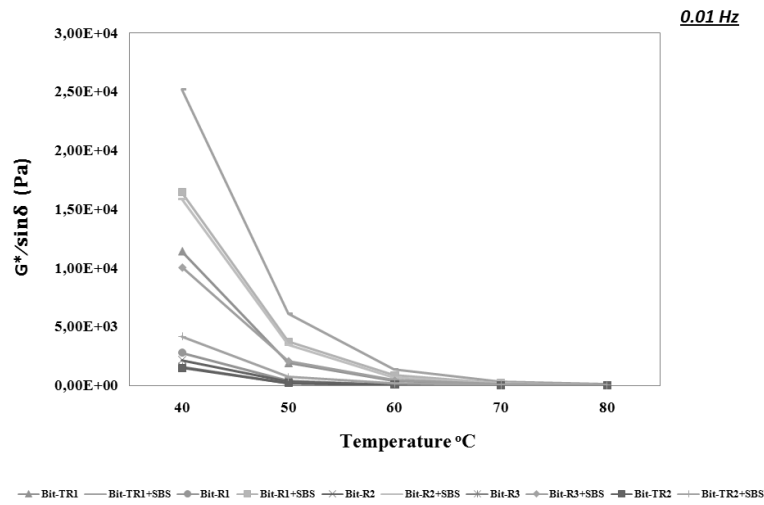**Figure 2.** G*∕sinδ values for SBS modified bitumens at 0.01Hz.
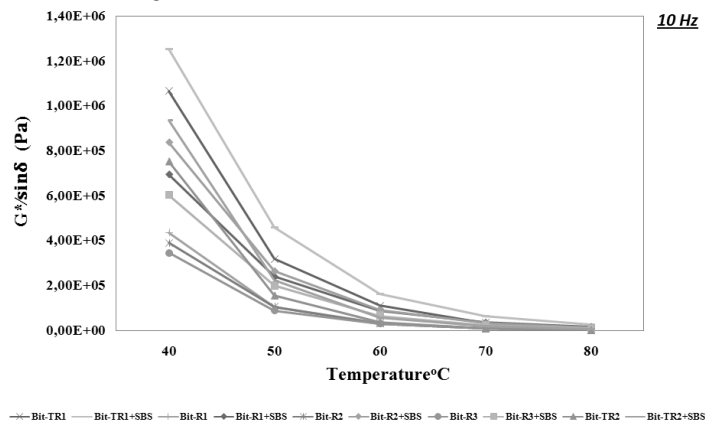
Figure 3. G*∕sinδ values for SBS modified bitumens at 10Hz.

Figure 4. G*∕sinδ values for EVA modified bitumens at 0.01Hz.

Figure 5. G*⁄sinδ values for EVA modified bitumens at 10Hz.
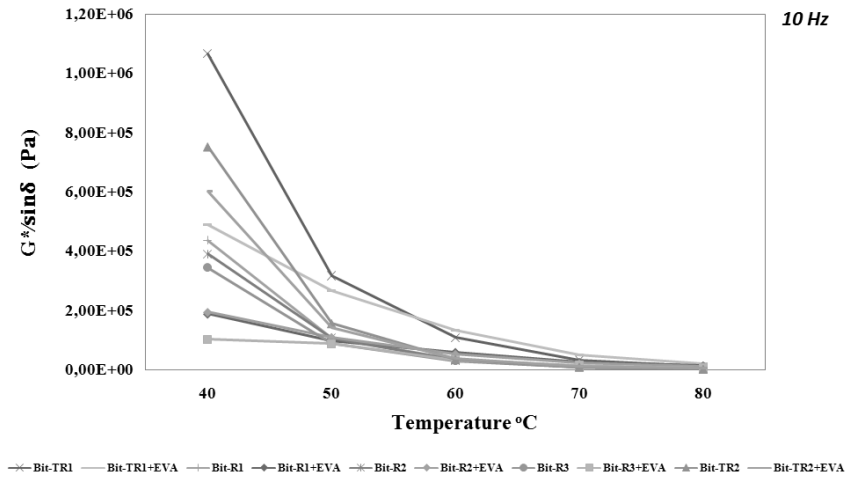
10 Hz

Legend: —✕— Bit-TR1 —+— Bit-TR1+EVA —+— Bit-R1 —◆— Bit-R1+EVA —✳— Bit-R2 —— Bit-R2+EVA —●— Bit-R3 —■— Bit-R3+EVA —▲— Bit-TR2 —— Bit-TR2+EVA

Figure 6. G*⁄sinδ values for PE modified bitumens at 0.01Hz.

0.01 Hz

Legend: —▲— Bit-TR1 —— Bit-TR1+PE —●— Bit-R1 —■— Bit-R1+PE —✳— Bit-R2 —— Bit-R2+PE —— Bit-R3 —◆— Bit-R3+PE —■— Bit-TR2 —+— Bit-TR2+PE

Figure 7. G*⁄sinδ values for PE modified bitumens at 10Hz.

10 Hz

Legend: —✕— Bit-TR1 —— Bit-TR1+PE —+— Bit-R1 —◆— Bit-R1+PE —✳— Bit-R2 —— Bit-R2+PE —●— Bit-R3 —■— Bit-R3+PE —■— Bit-TR2 —— Bit-TR2+PE
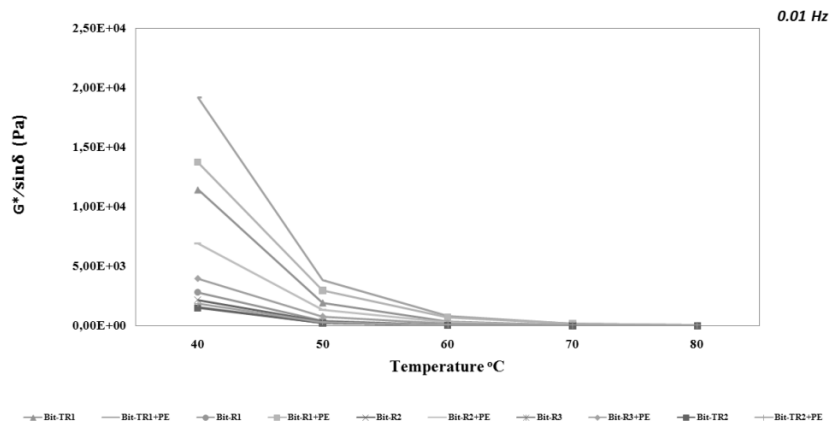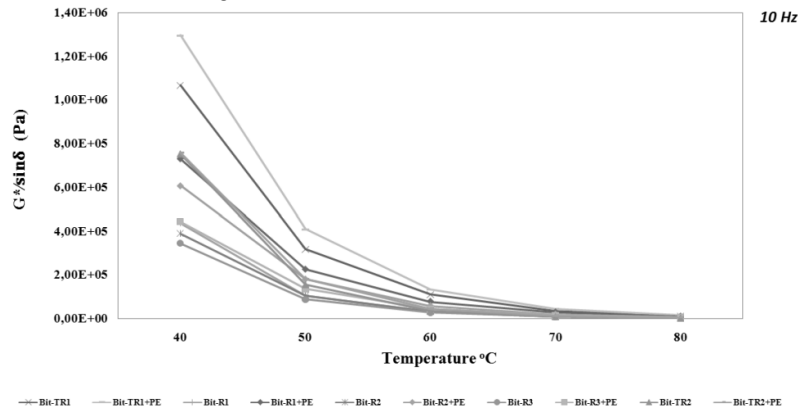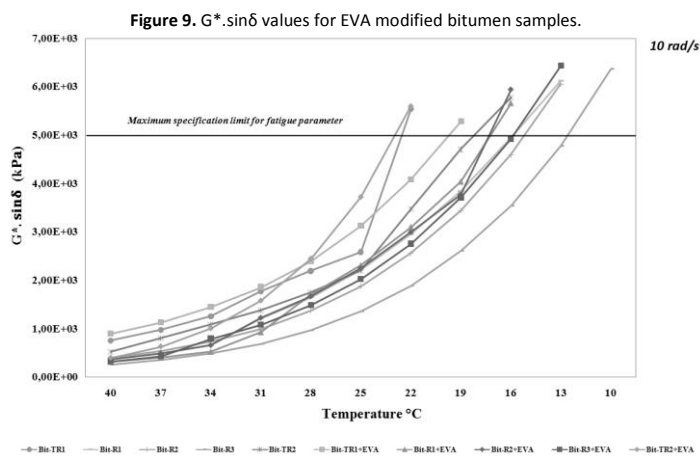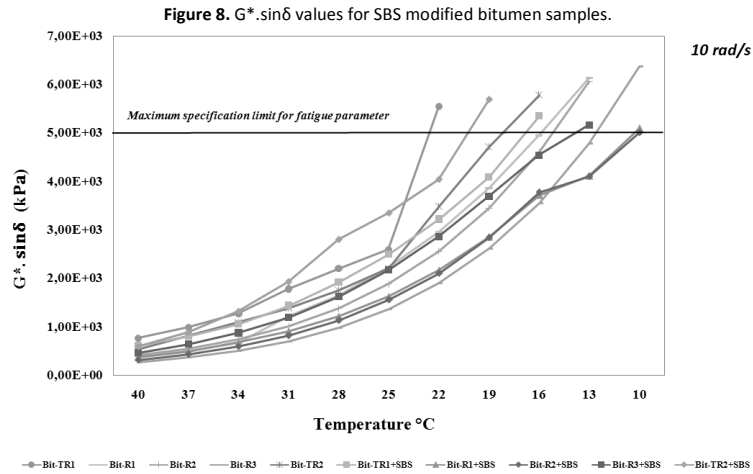
As presented Figure 2-7; regarding all of bitumen samples, G*⁄sinδ values increase with decrease in temperature at both frequencies. An increment in G*⁄sinδ value indicates higher performance against rutting. Besides, as expected G*⁄sinδ values increase with an increase in frequency for all of the bitumen samples. This is due to the rheological behaviour of the bitumen since bitumen under shorter loading times (high frequency level) exhibit elastic behaviour (Whiteoak, & Read, 2003).

As can be seen in Figure 2-7, unmodified sample containing the highest wax content depicted the lowest G*⁄sinδ value at both high and low frequencies and at all temperatures. Besides; all of the polymer modified bitumen samples depicted higher G*⁄sinδ value than the base bitumens at both high and low frequencies and at all temperatures. However, SBS and PE modified samples exhibited greater G*⁄sinδ value as compared to EVA modified samples especially at high frequency level and at intermediate temperatures (40°C and 50°C).

Hence based on G*∕sinδ values, it is found that modification of waxy bitumen and with SBS or PE resulted in improved rutting resistance performance at both low and high frequencies. Besides it is also found that modification of waxy bitumen with SBS has more pronounced effect against rutting compared to the modification with EVA polymer.

Temperature sweep test is performed under the strain controlled mode at a frequency of 10 rad/s (1.59 Hz.). The temperature cycles were set to start at 40°C within the PAV aged samples a run up in 3°C decrements. During the test procedure, an 8 mm diameter plate with a 2 mm gap between parallel plates was used for each PAV aged bitumen sample. There is a limiting maximum stiffness at the intermediate temperature to mitigate fatigue cracking. G*.sinδ values of PAV aged bitumen samples does not exceed 5000 kPa and low values of these parameters are considered good indicators of fatigue cracking resistance (Asphalt Institute, 2003). Variation of the fatigue parameters (G*.sinδ) for PAV aged SBS, EVA and PE modified bitumens containing different contents of wax at different intermediate temperatures are illustrated in Figure 8, Figure 9 and Figure 10 respectively.


Figure 8. G*.sinδ values for SBS modified bitumen samples.

Figure 9. G*.sinδ values for EVA modified bitumen samples.

Figure 10. G*.sinδ values for PE modified bitumen samples.
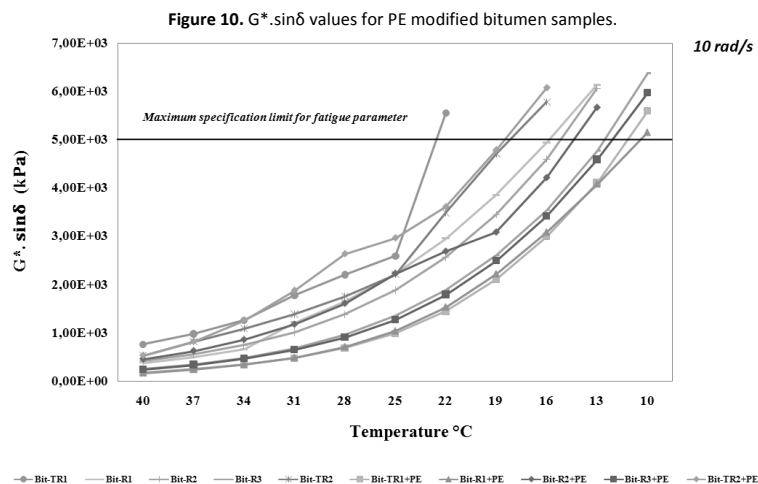
As depicted Figure 8-10, regarding all of bitumen samples, G*.sinδ values increase with decrease in temperature at 10 rad/s. Owing to the aging, the lower G*.sinδ value indicates less shearing energy loss and better ability of the fatigue resistance (Ali, Mashaan, & Karim, 2013). Bit-TR1 samples containing the lowest wax contents exhibit the highest G*.sinδ value at all intermediate temperatures. Higher G*.sinδ values is not preferable since the samples with higher G*.sinδ values exhibit fatigue cracking.

The addition of SBS and EVA polymers into the base bitumens containing different contents of wax did not make any significant effect on the fatigue cracking properties on the samples. However, the limitation of 5000 kPa value is reached at Bit-TR1+PE, Bit-R1+PE, Bit-R2+PE and Bit-R3+PE which occur at the test temperature 13 °C as well as Bit-TR2+PE meets with specification limit at the temperature 19 °C.

Hence, modification process with PE depicted slightly improved fatigue cracking properties of waxy bitumens compared to SBS and EVA modifications that expresses the ability of the material to resist cracking at intermediate temperatures.

Zero Shear Viscosity (ZSV) test results. The zero shear viscosity (ZSV) results of all of the modified bitumen samples including different content of wax, determined by the utilization of DSR machine applied in creep mode are illustrated in Figure 11.

Figure 11. ZSV values for PMB containing different content of wax.
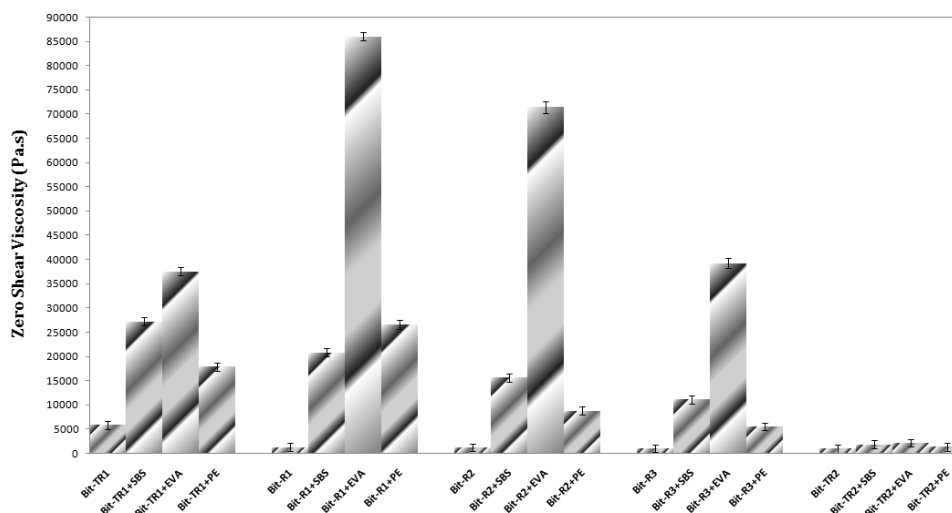
As illustrated in Figure 11, samples containing low amount of wax yield higher ZSV value than other base bitumen samples. A higher ZSV value indicates higher resistance to permanent deformation under long-term loading. The ZSV values decrease with increasing in the content of wax in the unmodified (base) bitumen samples. Besides all of the modified bitumen samples exhibit higher ZSV values than the base bitumen samples. The increment is more obvious at 1.4% concentration of EVA into bitumens containing different wax content compared to SBS and PE modification processes. Modification with EVA yields the peak ZSV value in Bit-R1 samples.

Multiple Stress Creep and Recovery (MSCR) test results. The percent recoveries (R), the non recoverable compliance (J_{nr}) at two different stress level of 100 Pa and 3200 Pa and stress sensitivity as well as the percent differences in non recoverable compliances ($J_{nr-diff}$) of the bitumens are presented in Table 6.

As presented in Table 6; Bit-TR2 samples containing the highest content of wax have the lowest recovery at any of the stress levels which indicates that Bit-TR2 perform less rutting resistance than other unmodified samples. This can be due to the low stiffness and the low elastic behaviour of Bit-TR2 samples. The addition of polymer into bitumen samples containing different wax content depicted higher recovery at any of the stress levels. Higher percent recoveries indicate that the bitumen can recover a higher portion of its total strain at the end of each loading–unloading cycle, which is favourable to the resistance of the material to rutting. On the other hand; EVA modified bitumen samples exhibited the highest recovery values in comparison with SBS and PE modified bitumen samples. Similar conclusion may also be evaluated for the non-recoverable creep compliance (J_{nr}) values. Lower J_{nr} values indicates lower susceptibility of bituminous material to rutting.

Table 6. Average values of the MSCR test parameters calculated from the test data.

Bitumen	R @100 Pa (%)	R @3200 Pa (%)	Jnr @100 Pa (1/kPa)	Jnr @3200 Pa (1/kPa)	Jnr diff. (%)	Stress Sensitivity
Bit-TR1	35.029	29.862	0.211	0.231	9.522	0.095
Bit-TR1+SBS	58.398	58.297	0.051	0.051	1.306	0.031
Bit-TR1+EVA	69.355	68.951	0.047	0.047	0.942	0.009
Bit-TR1+PE	56.081	51.368	0.075	0.084	12.386	0.124
Bit-R1	24.774	10.080	0.826	1.069	29.401	0.294
Bit-R1+SBS	70.225	62.027	0.066	0.086	28.203	0.282
Bit-R1+EVA	90.850	92.598	0.018	0.016	7.094	0.071
Bit-R1+PE	70.452	57.544	0.079	0.118	48.897	0.489
Bit-R2	23.339	9.509	0.849	1.094	28.649	0.286
Bit-R2+SBS	60.630	56.366	0.084	0.096	13.274	0.132
Bit-R2+EVA	88.485	86.906	0.032	0.036	12.628	0.127
Bit-R2+PE	55.853	33.710	0.183	0.309	68.999	0.689
Bit-R3	17.455	5.991	1.164	1.474	26.615	0.266
Bit-R3+SBS	58.314	52.723	0.129	0.149	16.362	0.163
Bit-R3+EVA	86.232	85.821	0.073	0.072	0.578	0.005
Bit-R3+PE	48.533	20.028	0.357	0.660	65.161	0.651
Bit-TR2	5.148	2.688	1.305	1.404	7.596	0.076
Bit-TR2+SBS	24.443	17.589	0.557	0.669	20.192	0.202
Bit-TR2+EVA	42.517	32.925	0.516	0.592	14.537	0.145
Bit-TR2+PE	12.154	4.992	0.865	0.990	14.758	0.148

The percent differences in non-recoverable compliances ($_{Jnr-diff}$) and the stress sensibility of the samples are also presented in Table 6. This percent difference is a measure of the sensitivity of the bitumen to the increase in the stress level; therefore lower values are associated with a less stress sensitive material. The $_{Jnr-diff}$ and the stress sensitivity are low for EVA modified bitumen samples which indicates that the sample can be considered to be less stress sensitive with a 3200 Pa within the all bitumen samples.

The scope of the research is to reduce the negative effects of waxes within bitumens containing various wax contents. For this purpose, modified bitumen samples were prepared by using different types of polymer additives. The values found in the study can be considered as useful parameters in determining which content of wax and type of polymer would be better for the needs of refineries in different countries. The following conclusions can be withdrawn from the extensive laboratory research.

EN 12606-1 method gives much lower values in the wax content as compared to DSC. DSC method may be recommended for determining wax content since the high temperature distillation step in EN 12606-1 method destroys the molecular structure of waxes.

According to high temperature performance test results; it can be evaluated that modifications of base bitumens containing different wax contents increases PG upper critical temperature with SBS, EVA and PE. Modification with EVA increases more the PG upper critical temperature of both Bit-TR1 and Bit-R1 than modification with SBS and PE.

The frequency sweep test results indicated that modification of bitumens containing different wax contents had an influence on the bitumen rheology. The DSR test results indicated that rutting parameter increases as the temperature decreases at both low and high frequency. Furthermore, when the frequency increases, the rutting parameter also increases. This derives from the rheological behavior of bitumen since bitumens exhibit an elastic behavior under sorter loading periods. Besides, it is found that modification of waxy bitumen and with SBS or PE resulted in improved rutting resistance performance at both low and high frequencies. Nevertheless it is also found that modification of waxy bitumen with SBS improves more the performance of the materials against rutting than modification with EVA.

The fatigue parameter test results obtained by DSR showed that the fatigue increases when the temperature decreases. Under the PAV aging condition, the temperature of bitumens of high wax content is lower than that for bitumen with low wax content at the time the stiffness value of $G^*.\sin \delta$ reaches 5000 kPa. Modification process with PE depicted slightly improved fatigue cracking properties of waxy bitumens compared to SBS and EVA modifications that expresses the ability of the material to resist cracking at intermediate temperatures.

In the light of findings from ZSV values, it is indicated that samples containing low amount of wax yield higher ZSV value than other base bitumen samples. This can be due to high viscosity and low wax content that give the mixture stability at service temperature. Besides all of the modified bitumen samples show a higher ZSV value than the base bitumen samples. Modification process improves the rutting resistance and the improvement is more pronounced with EVA polymer. A higher ZSV value indicates higher resistance to permanent deformation under long-term loading.

In light of findings from MSCR test results, the addition of polymer into bitumens containing different wax content depicted higher recovery and lower J_{nr} values at any of the stress levels. EVA modified bitumen samples exhibited the highest recovery and the lowest J_{nr} values in comparison within the polymer modified bitumen samples. In terms of the asphalt mixture, bitumens with lower J_{nr} values and/or higher recovery values will less contribute to the accumulation of unrecovered strain in the asphalt layer. Based on the rheological test results, $G^*/\sin\delta$ and ZSV values have a good correlation with the MSCR parameters.

Hence, modification process with EVA and PE can be recommended to improve rutting and fatigue cracking properties of waxy bitumens respectively.

In this study, the rheological bitumen tests have been performed on different sources bitumen samples involving different types of polymers in order to reduce negative effects of waxes. It is recommended to conduct Bending Beam Rheometer (BBR) test on polymer modified bitumen samples to evaluate their performance at lower temperatures.

Ali, A.H., Mashaan, N.S., & Karim, M.R. (2013). Investigations of physical and rheological properties of aged rubberised bitumen. *Advances in Materials Science and Engineering*, *2013*, 1-8. DOI: 10.1155/2013/239036

Asphalt Institute (2001). SUPERPAVE mix design series no: 2. Asphalt Institute Research Center, Lexington, USA.

ASTM D2872-12 (2012). Standard test method for effect of heat and air on a moving film of asphalt (Rolling Thin-Film Oven Test). West Conshohocken PA, USA.

ASTM D4419-90 (2015). Standard test method for measurement of transition temperatures of petroleum waxes by differential scanning calorimetry (DSC). West Conshohocken PA, USA.

ASTM D6521-05 (2005). Standard practice for accelerated aging of asphalt binder using a pressurized aging vessel (PAV). West Conshohocken PA, USA.

ASTM D7405-08 (2008). Standard test method for multiple stress creep and recovery (MSCR) of asphalt binder using a dynamic shear rheometer. West Conshohocken PA, USA.

Baldino, N., Gabriele, D., Rossi, C.O., Seta, L., Lupi, F.R., & Caputo, P. (2012). Low temperature rheology of polyphosphoric acid (PPA) added bitumen. *Construction and Building Materials, 36*, 592-596. DOI: 10.1016/j.conbuildmat.2012.06.011

Becker, Y., Mendez, M.P., & Rodriguez, Y. (2001). Polymer modified asphalt. *Vision Tecnologica, 9*(1), 39-50.

CEN TS 15325 (2008). Bitumen and bituminous binders: Determination of zero shear viscosity (ZSV) using a shear stress rheometer in creep mode. European Committee for Standardization, EU.

Das, P.K., Kringos, N., Wallqvist, V., & Birgisson, B. (2013). Micromechanical investigation of phase separation in bitumen by combining AFM with DSC results. *Road Materials and Pavement Design, 14*, 25-37. DOI: 10.1080/14680629.2013.774744

De Visscher, J., Soenen, H., Vanelstraete, A., & Redelius, P.A. (2004). Comparison of the zero shear viscosity from oscillation tests and the repeated creep test. *Proceedings of Euroasphalt & Eurobitume Congress*, Vienna, AUSTRIA.

Dubois, E., Mehta,D., & Nolan, A. (2014). Correlation between multiple stress creep recovery (MSCR) results and polymer modification of binder. *Construction and Building Materials, 65*, 184-190. DOI: 10.1016/j.conbuildmat.2014.04.111

Edwards, Y. (2009). Influence of waxes on bitumen and asphalt concrete mixture performance. *Road Materials and Pavement Design, 10*(2), 313-335. DOI: 10.1080/14680629.2009.9690197

Edwards, Y., Tasdemir, Y., & Isacsson, U. (2006). Effects of commercial waxes on asphalt concrete mixtures performance at low and medium temperatures. *Cold Regions Science and Technology, 45*(1), 31-41. DOI: 10.1016/j.coldregions.2006.01.002

Edwards, Y., & Redelius, P. (2003). Rheological effects of waxes in bitumen. *Energy and Fuels, 17*(3), 511-520. DOI: 10.1021/ef020202b

European Standard EN 12606-1 (2007). Bitumen and bituminous binders – determination of the paraffin wax content – part 1: method by distillation. European Committee for Standardization, EU.

Gorkem, I.C. (2014). Orta sıcaklıktaki asfalt karışımlarının performanslarının değerlendirilmesi. *PhD. Thesis*, Dokuz Eylul University, Izmir, TURKEY.

Gungor, A.G., & Saglik, A. (2012). Evaluation of rutting performance of neat and modified binders using zero shear viscosity. *5th Eurasphalt & Eurobitume Congress*, Istanbul, TURKEY.

Lu, X., Kalman, B., & Redelius, P. (2008). A new test method for determination of wax content in crude oils, residues and bitumens. *Fuel, 87*(8), 1543-1551. DOI:10.1016/j.fuel.2007.08.019

Lu, X., Langton, M., Olofsson, P., & Redelius, P. (2005) .Wax morphology in bitumen. *Journal of Materials Science, 40*(8), 1893-1900. DOI: 10.1007/s10853-005-1208-4

Lu, X., & Redelius, P. (2006). Compositional and structural characterization of waxes isolated\n from bitumens. *American Chemical Society: Energy & Fuels, 20*(2), 653-660. DOI: 10.1021/ef0503414

Lu, X., & Redelius, P. (2007). Effect of bitumen wax on asphalt mixture performance. *Construction and Building Materials, 21*(11), 1961-1970. DOI: 10.1016/j.conbuildmat.2006.05.048

Lyne, A., Wallqvist, V., & Birgisson, B. (2013). Adhesive surface characteristics of bitumen binders investigated by Atomic Force Microscopy. *Fuel, 113*, 248-256. DOI: 10.1016/j.fuel.2013.05.042

Musser, B.J., & Kilpatrick, P.K. (1998). Molecular characterization of wax isolated from a variety of crude oils. *Energy Fuels, 12*(4), 715-725.

Oner, J., & Sengoz, B. (2017). Investigation of rheological effects of waxes on different bitumen sources. *Road Materials and Pavement Design, 18*(6), 1269-1287. DOI: 10.1080/14680629.2016.1209123

Santagata, E., Baglieri, O., Tsantilis, L., & Dalmazzo D. (2012). Rheological characterization of bituminous binders modified with carbon nanotubes. *Procedia Social and Behavioral Sciences, 53*, 546-555. DOI: 10.1016/j.sbspro.2012.09.905

Sengoz, B, Bagayogo, L., Oner, J., & Topal, A. (2017). Investigation of rheological properties of transparent bitumen. *Construction and Building Materials, 154*, 1105-1111. DOI: 10.1016/j.conbuildmat.2017.07.239

Sengoz, B., & Isikyakar, G. (2008). Evaluation of the properties and microstructure of SBS and EVA polymer modified bitumen.*Construction and Building Materials, 22*(9), 1897-1905. DOI: 10.1016/j.conbuildmat.2007.07.013

Shenoy, A. (2008). Nonrecovered compliance from dynamic oscillatory test vis-à-vis nonrecovered compliance from multiple stress creep recovery test in the dynamic shear rheometer. *International Journal of Pavement Engineering, 9*(5), 329-341. DOI: 10.1080/102984307016350953

Shirini, B., & Imaninasab, R. (2016). Performance evaluation of rubberized and SBS modified porous asphalt mixtures. *Construction and Building Materials, 107*, 165-171. DOI: 10.1016/j.conbuildmat.2016.01.006

Soenen, H., Besamusca, J., Fischer, H. R., Poulikakos, L. D., Planche, J., Das, P.K., Kringos, N., Grenfell, J.R. , Lu, X., & Chailleux, E. (2013). Laboratory investigation of bitumen based on round robin DSC and AFM tests. *Materials and Structures, 47*(7), 1205-1220. DOI: 10.1617/s11527-013-0123-4

Soudani, K., Cerezo, V., & Haddani, S. (2016). Rheological characterization of bitumen modified with waste nitrile rubber (NBR). *Construction and Building Materials, 104*, 126-133. DOI: 10.1016/j.conbuildmat.2015.12.029

Subhy, A. (2017). Advanced analytical techniques in fatigue and rutting related characterisations of modified bitumen: Literature review. *Construction and Building Materials, 156*, 28-45. DOI: 10.1016/j.conbuildmat.2017.08.147

Topal, A., Kok, B.V., Kaya, D., Sengoz, B., Dokandari, P., & Yilmaz, M. (2018). Investigation of the properties of warm mix asphalt involving organic additive. *Turkish Journal of Science & Technology, 13*(1), 45-53.

Whiteoak, D., & Read, J. M. (2003). *The Shell bitumen handbook*. Thomas Telford Services Ltd: London, UK.

Woolley, G. (1986). Polymer modified bitumen for extra value asphalt. *Asphalt Technology, 38*, 45-51.

Xiao, F., Hou, X., Amirkhanian, S., & Kim, K.W. (2016). Superpave evaluation of higher RAP contents using WMA Technologies. *Construction and Building Materials, 112*, 1080-1087. DOI: 10.1016/j.conbuildmat.2016.03.024

Zhu, J., Birgisson, B., & Kringos, N. (2014). Polymer modification of bitumen: Advances and challenges. *European Polymer Journal, 54*, 18-38. DOI: 10.1016/j.eurpolymj.2014.02.005