Evaluation of rheological effects of waxes on bitumen from different sources

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Digital Object Identifier (DOI): dx.doi.org/10.14311/EE.2016.086

ABSTRACT

Bitumen is adhesive that originates from crude oil and is temperature dependent material including hydrocarbon molecules. Paraffinic crude oils may provide bitumen of good quality or yield bitumen which is not suitable for pavement performance. Wax in bitumen has been referred to as petroleum wax and is obtained from refining of paraffinic crude oils. The effects of wax on bitumen properties depend on the following factors; the source, chemical composition and rheology of the bitumen as well as the content, type, composition and crystallization of the wax. Although high wax contents have been considered as a negative effect on the quality of the bitumen, there is no common agreement among the scientists regarding the effect on bitumen rheology and asphalt performance.

The scope of this study is to evaluate the rheological properties of waxy bitumens obtained from different sources. Following the determination of wax contents by DSC (Differential Scanning Calorimetry) and EN 12606-1, waxy bitumens properties were evaluated using dynamic shear rheometer (DSR) and various conventional methods such as softening point, penetration, viscosity, and ductility. The high temperature performance levels of bitumen were also determined according to Superpave system by dynamic shear rheometer (DSR) test on samples before and after aging processes. Besides, bending beam rheometer (BBR) test has been conducted to investigate the lower critical temperatures of bitumens. Rutting performance of bitumens has also been evaluated using Zero Shear Viscosity (ZSV) and Multiple Stress Creep Recovery (MSCR) tests performed in creep mode.

Keywords: Chemical properties, Low-Temperature, Rheology, Testing, Zero Shear Viscosity

1. INTRODUCTION

Bitumen is adhesive material which is used as an agent at flexible pavements on roads as well as in other areas of application, such as water proofing, flooring and joint materials. Bitumen is very complex material including hydrocarbon molecules with small amounts of heteroatoms consist of sulphur, nitrogen, oxygen and gradually liquefies when heated [1].

Almost all bitumen obtains from crude oil by refining process but only certain crude oils contain good quality bitumen for asphalt pavement [2]. Naphthenic-base crude oils often give a large amount of bitumen that may be good quality, while paraffinic crude oils may give bitumen of good quality or yield bitumen not suitable for asphalt pavement [3].

The term “wax” is generally defined an organic compound that is solid at ambient temperature and melts at higher temperatures, producing a low viscosity liquid [4]. Natural wax is part of practically all bitumens and may affect bitumen rheology in different ways [5].

The definition of bitumen wax has been formulated to facilitate the distinction between harmful wax and less harmful or non-harmful. Waxes in bitumen are divided into two general categories such as paraffin wax (macro-crystalline) and micro-crystalline wax [6]. Paraffin wax also known as macro-crystalline wax crystallizes in large flat plates or needles. It refers to the group of n-alkanes with few or no branches (C_{20}–C_{40}) [4]. The melting point of macro-crystalline paraffin waxes are around 50-70 °C [7, 8]. 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 [9, 10].

Definitions of wax concepts have varied over the years and sometimes been contradictory [1, 6]. Factors that influence the effect of waxes are chemical composition (source of bitumen) and rheological behavior of the bitumen as well as content, and the crystallinity of the wax. Consequently, many bitumen specifications include requirements concerning wax content. It has been reported that wax content in bitumen should not exceed 3% [11]. The wax content is limited to 2.2% in Europe according to European standard EN 12606-1.

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, and the crystallization of wax causes cracking at low temperatures [12]. Physical hardening, poor ductility and poor bitumen adhesion can be listed as the results caused by the high content of wax [3]. The performance grade of bitumen at high temperature may decrease with melting of wax.

Somewhat contradictory, also positive effects of wax in bitumen have been reported, such as improved low-temperature properties and lower handling temperatures (for better compaction) [13]. Strategic Highway Research Programme recommends the performance of some additional rheological and chemical tests on unaged, short-term aged and long-term aged bitumen to evaluate the exact definition of wax concept [14].

This paper evaluates the rheological behavior of waxy bitumens obtained from three different sources. Following the determination of wax contents by DSC (Differential Scanning Calorimetry) and EN 12606-1, the detailed properties of bitumen samples have been evaluated using dynamic shear rheometer (DSR) and various conventional methods. The upper critical temperatures used in Superpave Performance Grading (PG) system have been determined for each bitumen sample using $G^*/\sin\delta$ results gained from Dynamic Shear Rheometer (DSR) test. The effects of loading and temperature on the performance of the waxy bitumen samples have been evaluated by low (0.01Hz) and high frequency (10Hz) loadings at five different temperatures (40°C-80°C). Besides, bending beam rheometer (BBR) test has been conducted to investigate the lower critical temperatures of bitumens. Rutting performance of bitumens has also been evaluated using Zero Shear Viscosity (ZSV) and Multiple Stress Creep Recovery (MSCR) tests performed in creep mode.

2. EXPERIMENTAL

2.1. Materials

Three bitumens from three different sources (Turkey, Iraq and Russia) were used in this study. The bitumen samples are identified as Bit T; Bit I and Bit R respectively. Turkey (Bit-T) bitumen was 50/70 penetration grade bitumen, while the others, from Iraq (Bit-I) and Russia (Bit-R) bitumens were 70/100 penetration grade bitumens. Since the bitumens are originated from different sources, their wax contents are different. Bit-T and Bit-I were manufactured from crude oil deposited in the east part of Turkey and the north part of Iraq respectively. Bit-R was produced by the blending of crude oil from various sources in Western Siberia by a manufacturer.

2.2. Test methods

2.2.1. 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 the determining the paraffin wax content of bitumen samples [15, 16]. 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 [12]. 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 ºC. The crystallized wax is obtained by filtration [16].

2.2.2. Differential Scanning Calorimetry (DSC)

The crystallization or melting of waxes in bitumen causes an energy change. Both heating and cooling cycle can be used to investigate the presence of wax fraction in bitumen. The exothermic and endothermic effect during the cooling and heating scan generally represents 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 [17].

In this study, thermal characterization was performed using DSC; Perkin Elmer-Diamond. Approximately 15 mg of bitumen samples is placed in an aluminum 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 [18]. A typical DSC diagram is shown in Figure 1.

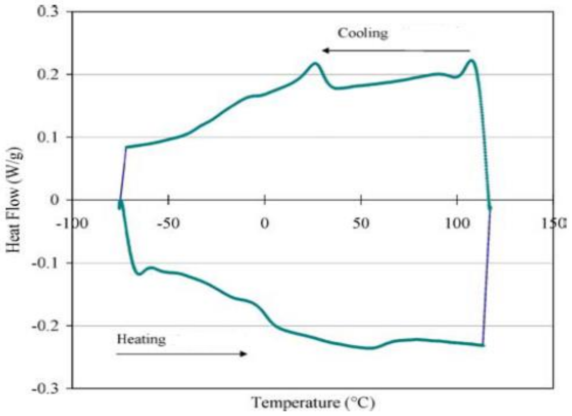

Figure 1: A typical DSC diagram through the cooling-heating cycles [7].

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 [19]. 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 melting of the wax. Wax melting out temperature that is defined as T_{fm} is the end point of wax melting in bitumen.

2.2.3. Conventional bitumen tests

In order to characterize the properties of the different sources bitumens, conventional bitumen tests such as: penetration test (ASTM D5-06), softening point test (ASTM D36-06), ductility test (ASTM D113-86), fraass breaking point test (EN 12593), viscosity at 60 ºC (ASTM D4402-06) and rolling thin film oven test (RTFOT) (ASTM D2872-12) as well as penetration, softening point, viscosity at 60ºC and ductility after RTFOT were performed [20-25].

In addition, the temperature susceptibility of the bitumen samples has been calculated in terms of penetration index (PI) using the results obtained from penetration and softening point tests [26].

The effect of viscosity on workability of bitumen is very important in selecting proper mixing and compacting temperatures. Brookfield Viscometer was employed to inspect the mixing and compaction temperatures in according to ASTM D4402-06 [24]. The test was performed at 135°C and 165°C. The temperatures corresponding to bitumen viscosities 170±20 mPa.s and 280±30 mPa.s were chosen as mixing and compaction temperatures respectively.

The minimization of bituminous hardening during storing, transportation and mixing depends on careful control of bitumen temperature. The hardening factor is a measure of how sensitive viscosity of bitumen is to aging. Obviously, bitumens having low hardening rates are desired. The ratio of the dynamic viscosity after RTFOT to dynamic viscosity before aging at 60 °C has been calculated as hardening factor.

2.2.4. Bending beam rheometer test (BBR)

Creep test with BBR was carried out according to ASTM D6648-01 standard test method [27]. BBR performs flexural tests, providing a measure of the stiffness related to bitumen at low temperatures. Before the test is performed, bitumen samples are subjected to short term and long term aging procedure. Two parameters of bitumen samples are calculated by engineering beam theory under a constant creep load. The first parameter is creep stiffness (s) that is a measure of resistance to constant loading. The second parameter is the creep rate (m) that is a value of how bitumen stiffness changes as load is applied.

A bitumen sample beam (125 mm. in length, 12.5 mm. in width and 6.25 mm. in thickness) was submerged into the constant temperature bath for 1 h. A constant load of 100 g was applied to the midpoint of bitumen beam which was supported at ends. The deflection was then measured continuously. Creep stiffness and creep rate of bitumens were evaluated at a loading time of 60 s. Creep stiffness must not exceed 300 MPa and m value must be at least 0.3 for a qualified low temperature cracking resistance.

2.2.5. 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. 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 non-aged and RTFOT aged bitumen samples. 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. G* and δ are used as predictors of rutting behaviour. G*⁄sinδ is described as rutting indicating parameter [28].

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 very effective in predicting the rutting performance of bitumen. ZSV has been evaluated to be a more appropriate indicator in predicting the rutting behaviour of bitumen [29]. The determination of ZSV in this study is made 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. If the stress is applied for a sufficiently long duration of time, the deformation in the bitumen reaches a constant value, which corresponds to the steady state flow of the bitumen. The viscosity of the bitumen at this stage is known as the steady state viscosity or the ZSV [30]. 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 in accordance to prCEN/TS 15325 [31]. 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 bitumen samples and each creep test was continued for 30 minutes.

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. 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. Developments led to the existence of Multiple Stress Creep and Recovery (MSCR) test [32]. MSCR test was run on RTFOT aged samples in accordance to ASTM D7405-08 using the dynamic shear rheometer [33]. 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.

3. RESULTS AND DISCUSSIONS

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

Calculation of the wax content was based on the following Equation (1) according to European Standard Method EN 12606-1. Wax content is calculated as;

$$P = \frac{m_1 * m_w}{m_b * m_2} * 100 \tag{1}$$

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 [16].

The crystallization or melting of waxes in bitumens involves energy change. This can be easily determined by DSC. In Table 1, results of the EN 12606-1 and DSC measurements are summarized in terms of wax content, crystallization starting temperature, wax melted out temperature and glass transition temperature. It should be noted that the wax content as calculated by using a constant enthalpy in this study is not an absolute value. The DSC measures transformation enthalpy and in fact different waxes can have different enthalpies, meaning the wax content in bitumen may vary with a constant melting enthalpy value.

Table 1: DSC and EN 12606-1 analysis of bitumens

	Bitumen	Bit-T	Bit-I	Bit-R
	Penetration Grade	*50/70*	*70/100*	*70/100*
	Sources	*Turkey*	*Iraq*	*Russia*
	Wax content by EN 12606-1 (%)	*0.80*	*1.12*	*2.30*
	Wax content by DSC (%)	2.61	3.27	4.04
Parameters obtained from DSC	• **Crystallization starting temperature - T_{ic} by DSC (°C)**	39.11	37.85	35.40
	• **Melting out temperature - T_{fm} by DSC (°C)**	65.97	86.42	83.00
	• **Glass transition temperature - T_g by DSC (°C)**	-7.05	-15.78	-20.56

As indicated in Table 1, bitumen samples from different sources differ widely in the wax content according to DSC and EN 12606-1 methods. It is clearly seen that, EN 12606-1 method gives much lower values in wax content 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). 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. Although both DSC method and EN 12606-1 methods are basically very different, they exhibit a reasonably good correlation. Bitumen sample from Russia (Bit-R) contains large amount of wax compared to other bitumen samples according to EN 12606-1 and DSC methods. However, Bit-T from Turkey has the lowest amount of wax.

DSC has been widely applied to characterize the thermodynamics properties of bituminous materials. In cooling cycle, crystallization occurs at 39.11 °C, 37.85 °C and 35.40 °C for Bit-T, Bit-I and Bit-R respectively 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 (T_{fm}) of Bit-T, Bit-I and Bit-R are 65.97 °C, 86.42 °C and 83 °C respectively. The temperature at which all wax is completely melted is considerable higher than the start of crystallization. This is due to 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 -7.05 °C, -15.78 °C and -20.56 °C for Bit-T, Bit-I and Bit-R respectively. Consequently, Bit-R with the lowest value of T_g has more resistance to low temperature cracking compared to other sources bitumens at a specific low temperature.

3.2. Conventional test results

The conventional properties of different sources bitumens are presented in Table 2. The effects of wax on different sources bitumen can be explored using Table 2. Results indicated that Bit-T with the lowest wax content sample depicted a significant decrease in penetration value and increase in softening point temperature as compared to bitumens including relatively high wax content (Bit-I and Bit-R).

The softening point temperature can be used along with the penetration to determine the temperature susceptibility of bitumen. The Penetration Index (PI) is an indicator of temperature susceptibility of bitumen. A high PI indicates low temperature susceptibility [26]. The results show that Bit-T with the lowest wax content has a higher PI and thus depicts lesser temperature susceptibility as compared to Bit-I and Bit-R. It can be also concluded from the results that bitumen containing low amount of wax significantly lowers temperature susceptibility of samples.

With regard to the physical properties, the ductility is sometimes helpful for the evaluation of the low-temperature failure properties of bitumen [34]. The ductility is increased by 45 cm and 61 cm for Bit-R in comparison with Bit-T and Bit-I respectively, indicating an improved low temperature failure resistance of Bit-R with high content of wax.

The low temperature properties of the bitumen may be affected in a negative way with higher breaking point according to fraass. As presented in Table 2, fraass breaking point is decreasing with increasing of wax content of bitumens. Ductility and fraass breaking point tests may indicate that utilization of Bit-R containing high content of wax provides an advantage for fatigue cracking due to its high elasticity and low temperature cracking.

As can be seen in viscosity results at 60°C, 135°C and 165°C, bitumen containing low wax content may also give high viscosity. Bit-I shows positive effects in decreasing the viscosity values at 60°C, 135°C and 165°C compared to Bit-T. The lowest viscosity value was achieved at Bit-R samples containing the highest content of wax. The reduced viscosity may results the decreasing of mixing and compaction temperature of the mixture which would lead to reduce emission and energy consumption [35].

The results of viscosity test related to all samples at 135°C and 165°C were drawn at semi logarithmic figures presented in Figure 2. The determined mixing and compaction range temperatures for Bit-T, Bit-I and Bit-R samples including different content of wax are listed in Table 3.

Table 2: Conventional test results of bitumens

	Bitumen		Bit-T	Bit-I	Bit-R
	Sources		*Turkey*	*Iraq*	*Russia*
	Penetration Grade		*50/70*	*70/100*	*70/100*
	Penetration at 25 °C (0.1 mm)		50	75	76
	Softening Point (°C)		54	48	48
	Penetration Index (PI)		-0.25	-0.62	-0.59
Rolling Thin Film Oven Test (RTFOT) (163°C; 85 min.)	**Retained Penetration after RTFOT (%)**		62	59	55
	Softening Point Diff. after RTFOT (°C)		9	17	5
	Ductility at 25 °C after RTFOT (cm)		14	14	58
	Viscosity at 60 °C after RTFOT (Pa.s)		1292	1193	636
	Hardening factor (the ratio of the dynamic viscosity after RTFOT to dynamic viscosity before aging at 60 °C)		2.2	4.2	3.4
	Ductility at 25 °C (cm)		64	48	109
	Fraass breaking (°C)		-12	-13	-18
	Viscosity (Pa.s)	**at 60 °C**	577	285	189
		at 135 °C	0.613	0.400	0.388
		at 165 °C	0.150	0.138	0.137

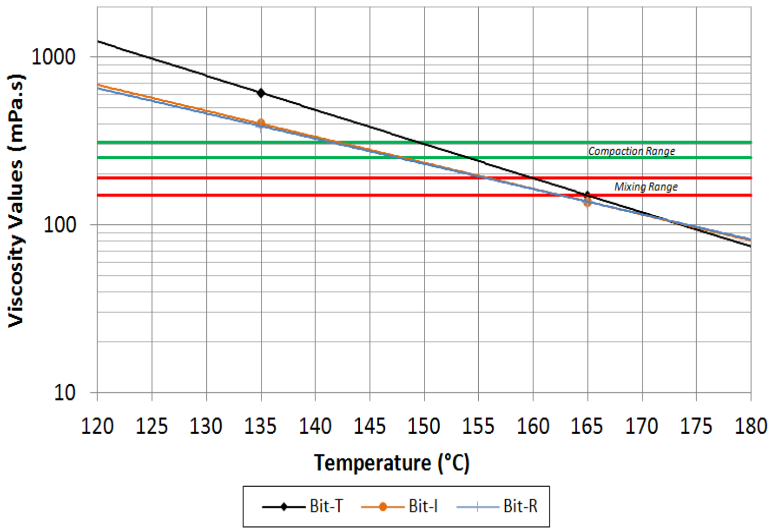

Figure 2: Determination of mixing and compaction temperatures for different sources bitumen.

Table 3: Mixing and compaction temperatures.

Bitumen	Mixing Temperature (°C)	Compaction Temperature (°C)
Bit-T	160-165	149-154
Bit-I	156-163	143-147
Bit-R	155-163	142-146

As can be seen in Figure 2 and Table 3, low content of wax in the bitumen significantly increases mixing and compaction ranges of the bitumen. As the wax content increases, mixing and compaction temperatures decrease. As seen from the results, there is a decrease of average 8°C in the mixing ranges of Bit-I and Bit-R samples compared to Bit-T samples. The effects of both Bit-I and Bit-R in reducing compaction ranges decreases 4°C compared to Bit-T. Both of the tested Bit-I and Bit-R were similar in results from the application temperature point of view.

The most intense bitumen ageing processes take place when bitumen is mixed with hot aggregate in the batching plant's mixer. Under these circumstances the evaporation of light fractions and bitumen oxidation is the fastest and most intense, and bitumen rapidly hardens. The process is referred to as short-term ageing. The hardening of the bitumen is gauged by the ductility, viscosity at 60°C and retained penetration and softening point temperature difference after RTFOT. Bit-T containing the lowest wax content exhibited a better performance in terms of retained penetration as compared to Bit-I and Bit-R. However, Bit-I exhibits almost identical values in terms of increase in softening points after RTFOT compared to other bitumen samples. A appreciable increase (44 cm) in terms of ductility after RTFOT could be seen in Bit-R containing the highest wax content sample as compared to Bit-T and Bit-I. Thus, low temperature failure resistance can be improved by Bit-R including high wax content before and after aging process. In this study, hardening factor was calculated as the ratio of the dynamic viscosity after RTFOT to dynamic viscosity before aging at 60 °C for each different sources bitumens. A desirable bitumen would have a comparatively low value of hardening factor which indicates that viscosity of bitumens increases slowly with oxidation. As presented in Table 2; the value of hardening factor depends on the source of bitumens. Bit-R containing high amount of wax have lower hardening factor than Bit-I, and Bit-T has the lowest hardening factor. Bit-I hardens and oxidizes much faster than Bit-T and Bit-R. On the other hand, the utilization of Bit-T containing the lowest wax content is expected to provide a positive effect on pavement performance over time.

3.3. Bending beam rheometer test (BBR) results

The BBR test was conducted to identify the impact of different content of wax into the bitumens under low temperatures. A BBR test was performed at temperatures of -10 °C, -16 °C and -22°C for aged (RTFOT and PAV) bitumen samples. The creep stiffness (S) and slope of the stiffness curve (m-value) are determined from BBR tests and presented in Table 4. Regarding all of bitumen samples, creep stiffness values increase with decrease in temperature. Besides, m-values decrease with decrease in temperature for all of the bitumen samples. Increase in stiffness indicates that thermal stresses develop in the pavement due to low temperature also increase and consequently thermal cracking become more likely. On the other hand, decreasing m-value indicates declining the rate of stress relaxation which also increases the probability of thermal cracking.

Table 4: Creep stiffness and m-value of bitumen samples at a loading time 60 s and after different temperatures.

Bitumens	Sources	Creep stiffness (MPa)			m-Value		
		-10 °C	-16 °C	-22 °C	-10 °C	-16 °C	-22 °C
Bit-T	**Turkey**	88.57	170.08	246.00	0.338	0.309	0.295
Bit-I	**Iraq**	65.12	95.93	135.53	0.334	0.261	0.241
Bit-R	**Russia**	74.03	136.85	219.69	0.370	0.289	0.260

As can be seen in Table 4, for all low temperatures, the highest increase in creep stiffness values were observed in Bit-T which contains the lowest amount of wax. This implies that the bitumen becomes harder when contains low amount of wax. The results obtained from the BBR test support the results obtained from conventional tests and rotational viscosity tests.

As presented in Table 4, at all test temperatures, creep stiffness parameters of all of the bitumen samples depicted values lower than 300 MPa, which is the maximum value specified in Superpave specifications. Since the creep stiffness values were lower than 300 MPa, the low temperature PG value has been determined on the basis of m-value higher than 0.3.

As can be seen, with the decreasing of temperature, the m-values exhibited values higher than specification limit. It can be concluded from the Table 4 that PG lower critical temperature of Bit-T containing the lowest wax content (-16 °C) is lower than Bit-I and Bit-R (-10 °C). There is no significant variation for lower critical temperature values of Bit-I and Bit-R. This means that due to high wax content, there is a possible negative effect on low temperature performance of bitumen.

3.4. 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 and Multiple Stress Creep Recovery (MSCR) test results.

3.4.1. 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, non-aged and RTFOT aged specimens of bitumens containing different content of wax (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*/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 non-aged bitumen, and G*/sinδ = 2.2 kPa for RTFOT aged bitumen [28]. The upper critical temperatures (T_{crit}) for each sample are presented in Table 5.

Table 5: Determination of PG upper critical temperatures for different sources of bitumens

			DSR, G*/sinδ (Pa)		
Bitumen	***Sources***	**Temperature (°C)**	**Non-aged**	**Aged**	**Performance Grades**
Bit-T	**Turkey**	**52**	1,25E+04		**B 70 -**16
		58	5918		
		64	2820	5816	
		70	1384	2868	
		76	702	1462	
Bit-I	**Iraq**	**52**	5160		**B 64 -**10
		58	2253		
		64	1012	1,17E+04	
		70	460,9	5837	
		76		2791	
		82		1307	
Bit-R	**Russia**	**52**	5165		**B 64 -**10
		58	2431		
		64	1147	3346	
		70	556,7	1648	

It can be concluded from the Table 5 that PG upper critical temperature of Bit-T (T_{crit}) containing the lowest wax content is higher than Bit-I and Bit-R. There is no significant variation for T_{crit} values of Bit-I and Bit-R. Higher T_{crit} value is an indicator of higher resistance to permanent deformation. G*/sinδ values for non-aged Bit-I sample and RTFOT aged Bit-I sample does not fix at the same temperature. Lower temperature (64°C) was selected to be on the safe range as PG upper critical temperature. Difference of G*/sinδ values for non-aged and RTFOT aged sample implies that Bit-I hardens and oxidizes much faster than other bitumen samples because of aging process.

All of the 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 samples at low and high frequencies are presented in Figure 3 and Figure 4 respectively.

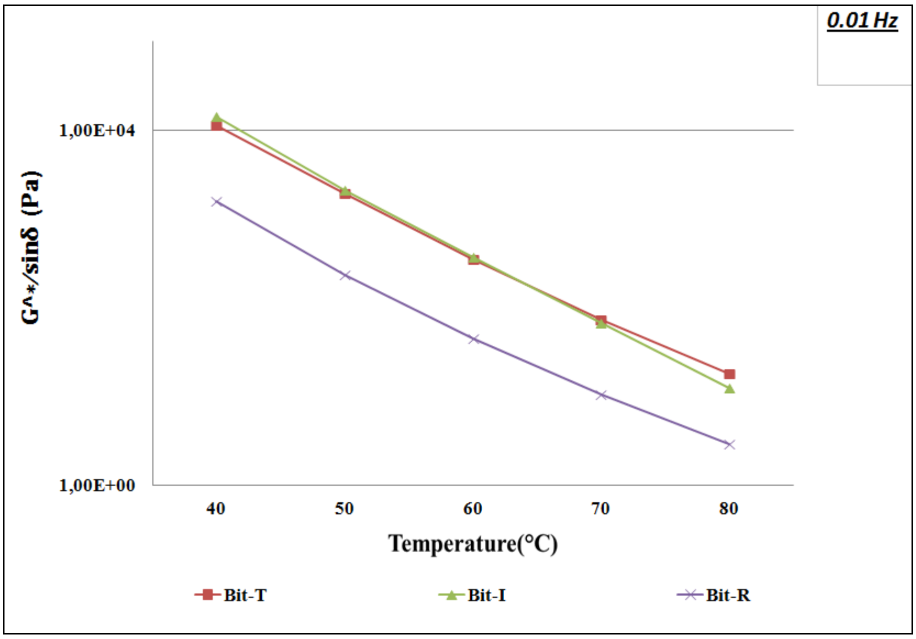

Figure 3: G*⁄sinδ values for different sources bitumens at 0.01Hz.

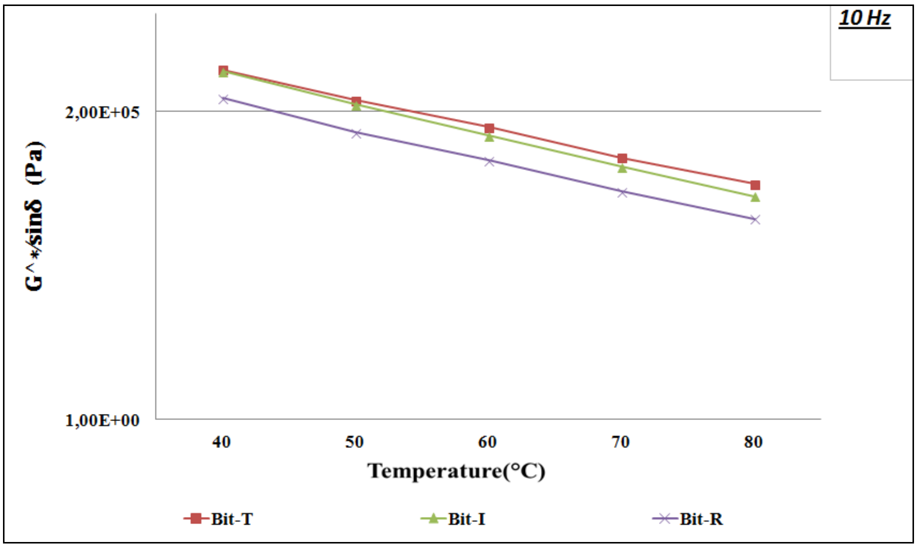

Figure 4: G*⁄sinδ values for different sources bitumens at 10Hz.

As presented Figure 3 and Figure 4; 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 [26].

As can be seen in Figure 3 and Figure 4, Bit-R sample containing the highest wax content depicted lower G*⁄sinδ value than Bit-T and Bit- I at both high and low frequencies and at all temperatures. Among the bitumen samples which contains low wax content, the highest value in the G*⁄sinδ values can be seen regarding Bit-T sample at 10 Hz. frequency and all temperatures. However this case is only valid for Bit-T at low frequency level (0.01 Hz) and at 40 ºC, 50 ºC and 60 ºC. Under longer loading times (at low frequency level), a significant increase in G*⁄sinδ values can be seen at Bit-I sample at intermediate temperature levels (40 ºC, 50 ºC and 60 ºC).

3.4.2. Zero Shear Viscosity (ZSV) test results

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 in accordance to prCEN/TS 15325 [31]. ZSV results of all of the bitumen samples including different content of wax are illustrated in Figure 5.

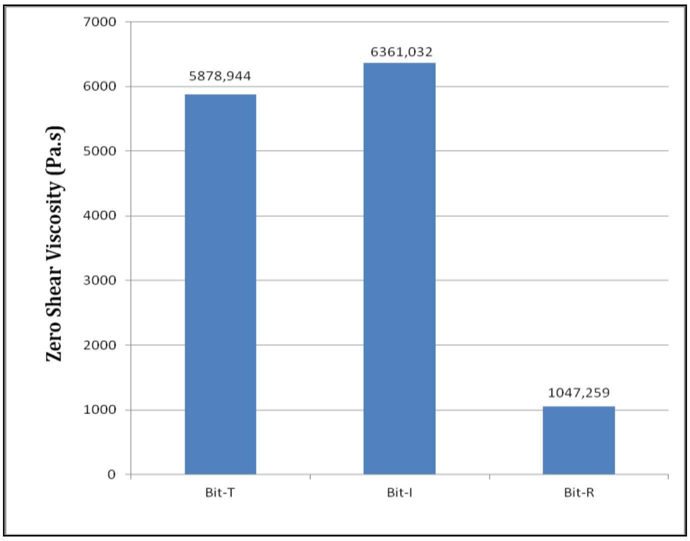

Figure 5: ZSV values for bitumens containing different content of wax.

As depicted in Figure 5, Bit-I and Bit-T samples show higher ZSV value than Bit-R which contains the highest content of wax. Bit-I sample yields the peak ZSV value at 60ºC compared to Bit-T and Bit-R. A higher ZSV value indicates higher resistance to permanent deformation under long term loading. As can be seen in the figure, the presence of high wax content significantly decreases the ZSV values of Bit-R. In spite of the fact that Bit-I contains relatively higher wax content than Bit-T, there is a slightly augmentation in terms of ZSV value of Bit-I compared to Bit-T. The short term aging process is expected to have a positive effect on the ZSV value of Bit-I.

3.4.3. Multiple Stress Creep and Recovery (MSCR) test results

The percent recoveries (R), the compliance (Jnr) at two different stress level of 100 Pa and 3200 Pa and stress sensitivity as well as the percent differences in non recoverable compliances (Jnr-diff) of the bitumens are presented in Table 6.

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

Bitumen	Sources	R @100 Pa (%)	R @3200 Pa (%)	Jnr @100 Pa (1/kPa)	Jnr @3200 Pa (1/kPa)	Jnr diff. (%)	Stress Sensitivity
Bit-T	Turkey	35.029	29.862	0.211	0.231	9.522	0.095
Bit-I	Iraq	43.155	28.095	0.229	0.289	26.555	0.265
Bit-R	Russia	17.455	5.991	1.164	1.474	26.615	0.266

Bit-R sample containing the highest content of wax has the lowest recovery at any of the stress levels which indicates that Bit-R performs less rut resistance than other samples. This can be due to the low stiffness and the low elastic behaviour of Bit-R sample. While Bit-I exhibits more recovery at 100 Pa stress levels, Bit-T has the highest recovery value at 3200 Pa. Higher percent recoveries mean 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.

In stress levels of both 100 and 3200 Pa, Bit-T with the lowest content of wax has the lowest Jnr value. Lower non recoverable compliances indicate a minor contribution of the bitumen to the appearance of rutting in the asphalt mixture or, in other words, a lower susceptibility of the bituminous material to rutting. As the results show, Bit-R has the highest the compliance (Jnr) value at 100 Pa and 3200 Pa. It can be concluded that Bit-R is the most susceptible sample to rutting.

The stress sensitivity of the bitumens was evaluated by means of the percent differences in non- recoverable compliances (Jnr-diff). This parameter indicates the percentage of increase in the Jnr value of the bitumen when the stress level is increased from 0.1 to 3.2 kPa. It evaluates the susceptibility of the bitumens to rutting when unexpected heavy traffic loadings are applied on the pavement structure or unusually high temperatures are observed in the field. The percent differences in non-recoverable compliances (Jnr-diff) and stress sensitivity results at the creep and recovery test is also shown 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 value of the Jnr-diff parameter and stress sensitivity are particularly high for Bit-I and Bit-R. Therefore these bitumens can be considered to be highly stress sensitive as the creep stress of 3200 Pa.

4. CONCLUSIONS AND RECOMMENDATIONS

Based on the results presented in this paper, the following conclusions can be drawn. EN 12606-1 method gives much lower values in the wax content as compared with DSC. Although both the DSC method and EN 12606-1 method are basically very different methods, they show a reasonably good correlation based on the selected bitumen samples. Crystallization starting temperatures (T_{ic}), wax melted out temperatures (T_{fm}) and glass transition temperatures (T_g) for waxes are different for different sources of bitumens. It is obvious that the crystallization takes place during a range of temperatures, indicating the presence of molecules with different crystallization points. At lower temperatures, mobility of molecules can vary with wax molecular characteristics and bitumen composition.

Conventional bitumen tests indicated that bitumen containing low amount of wax significantly lowers temperature susceptibility of samples. Based on the findings from Brookfield viscosity test, it can be concluded that the presence of wax decreases viscosity values at 60°C, 135°C and 165°C. The most hazardous feature of wax in bitumen is the sudden decrease in viscosity due to the melting of crystallized wax. Should this occur within a temperature range, the resistance to permanent deformation will decrease.

The low temperature properties of bitumens are evaluated through different parameters, including Fraass breaking point, glass transition temperature (T_g), and PG lower critical temperature obtained using the bending beam rheometer (BBR). It is found that Fraass breaking point and T_g results are related to bitumen wax content. However, PG lower critical temperature obtained by BBR test does not correlate with the increment in wax content. While Fraass breaking point and DSC tests are performed on unaged bitumen samples, bitumen samples are subjected to short term and long term aging procedure in BBR test. In terms of low temperature properties of bitumens, the differences between the test results can be varied with aging procedures.

Detailed investigation performed by DSR test indicates that bitumen containing the highest wax content depicts lower $G^*/\sin\delta$ value than other bitumen samples, thereby possibly decreasing the rutting resistance. In the light of findings from ZSV values indicate that the utilization of bitumen containing low amount of wax improves rutting performance of mixtures. This can be due to high viscosity and low wax content that give the mixture stability at service temperature. According to MSCR test results, bitumen containing the lowest content of wax has the highest recovery and the lowest Jnr values in any of the stress levels. Higher percent recovery, lower non-recoverable compliances may suggest that bitumens are less prone to rutting after the application of loading–unloading cycles at a common high temperature. In terms of the asphalt mixture, bitumens with lower Jnr 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.

In terms of this study, the conventional and rheological bitumen tests have been conducted to evaluate the rheological properties of waxy bitumens obtained from different sources. It is recommended to perform rheological tests on different sources bitumen involving different types of polymers in order to reduce negative effects of waxes.

ACKNOWLEDGEMENTS

The authors are thankful to ABZ-1 Group for their support for performing laboratory tests.

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