

# RHEOLOGICAL PROPERTIES OF BITUMEN MODIFIED WITH A COMBINATION OF FT PARAFFIN WAX (SASOBIT<sup>®</sup>) AND OTHER ADDITIVES

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Abstract. Fischer–Tropsch paraffin Sasobit<sup>®</sup> is a popular Warm Mix Asphalt (WMA) modifier applied to improve physical and rheological properties of bitumen. Although there are a number of studies investigating the effects of sasobit on bitumen properties, little has been carried out on evaluation of bitumen modified by sasobit along with other additives. In this study, sasobit modified bitumen is used as the base condition and four common modifiers namely anti-stripping agent, Crumb Rubber (CR), Styrene–Butadiene–Styrene (SBS) and Polyphosphoric Acid (PPA) are added separately to the FT – Wax modified bitumen to evaluate the compatibility of these additives with sasobit. Morphological, rheological and physical properties of modified binders are studied using Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Dynamic Mechanical Analysis (DMA), Bending Beam Rheometer (BBR) alongside with conventional tests. Results show that although anti-stripping agent reduce bitumen viscosity and mixing/compaction temperatures of asphalt mixtures, it has significantly increased the stiffness of sasobit modified bitumen at low temperatures.

Keywords: modified bitumen, sasobit, dynamic shear rheometer, morphology, additives.

# Introduction

Loading and weather changes induce stresses and strains to Asphalt Concrete (AC). In the long run, this leads to distresses such as low temperature cracking and high temperature rutting. The formation of distresses is dependent to the performance of asphalt mixture, meaning the better the performance of the asphalt mixture, the longer it takes for the distresses to form and propagate. It is well-known that the performance of the asphalt mixture is highly related to the performance of bitumen (Tasdemir 2009). Softer bitumen with high penetration grade show proper cracking resistance at low temperatures, while very vulnerable to permanent deformation at high temperatures. The adverse is applicable for hard bitumen with low penetration grade; although it exhibit better performance in high temperatures, the behaviour against cracking is weaker than soft bitumen (Tasdemir 2009; Zhang *et al.* 2009). The explanation lies in complex rheological behaviour of bitumen, which can exhibit viscous, elastic or viscoelastic behaviour at various loading times or temperatures (Airey 2004; Isacsson, Lu 1999). The viscoelastic behaviour of AC is dependent to temperature; at high or low temperatures viscous or elastic characteristics may become dominant. At high temperatures,

the viscosity of bitumen drops considerably making AC pavements susceptible to bleeding and permanent deformation. On the contrary, at very low temperatures, bitumen becomes stiff and the elastic behaviour of the AC leads to cracking. So, it is beneficial to expand the operational temperature range of bitumen according to the specific situation of paving region because the softening temperature changes when additives are added. For this, modifying bitumen is one of the most common approaches to improve asphalt mixture performance in various loading and temperature condition. The most common types of modifiers or additives are copolymers (Styrene–butadiene–styrene), mineral polymers (Polyphosphoric acid), crumb rubber and anti-stripping agents.

Styrene-butadiene-styrene (SBS) polymer is a three-block copolymer in which the styrene blocks are responsible for the polymer strength while butadiene blocks give the outstanding viscosity to the polymer. The structure of SBS copolymer molecule is composed of blocks with thermoplastic properties (The end polystyrene blocks) and blocks with elastic properties (The middle blocks of polybutadiene). After mixing with bitumen, three-dimensional network of molecules is formed. The

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elastometric phase of SBS absorbs oily fraction of bitumen, swelling up to nine times. This would help making a continuous phase throughout the bitumen (Isacsson, Lu 1999; Airey 2003).

The styrene–butadiene–styrene polymers used in road industry contains 20 to 30 percent of styrene. Higher amounts of styrene lead to the incompatibility between polymer and bitumen and also lower storage stability (Fu *et al.* 2007; Liu *et al.* 2003). Although many researches confirm the positive effect of SBS on improving bitumen performance (Isacsson, Lu 1999; Airey 2003; Tayfur *et al.* 2007), the mixing/compaction of SBS modified asphalt mixtures should be carried out at very high temperatures, more than 40 °C higher than mixing/compaction of asphalt mixtures with unmodified bitumen. This is one of the most important disadvantages of modifying bitumen with SBS.

Polyphosphoric acid (PPA) is a liquid mineral polymer, which is used to modify and enhance paving grade bitumen. This additive reacts with many of the functional groups in bitumen. It breaks the asphaltene agglomerates and creates the possibility for better distribution of asphaltene in the malten phase. As PPA breaks asphaltene and turns them to Individual particles, it is more effective in contributing to elastic behaviour (Yadollahi, Sabbagh Mollahosseini 2011; Haung *et al.* 2008; Distin 2008). Previous studies show that adding PPA to bitumen enhances the bitumen performance at both low and high temperatures (Edwards *et al.* 2006, 2007).

Application of Crumb Rubber (CR) in asphalt mixtures is very common. Apart from technical issues, low cost of raw material (recycled rubber from scrap tires) and positive environmental aspects in using recycled materials contribute to this high popularity. Various researches show that CR improves bitumen performance at a wide range of temperatures (Navarro *et al.* 2002, 2004; González *et al.* 2010). The main disadvantage of adding CR to bitumen is the increase of modified bitumen viscosity and therefore higher mixing/compaction temperatures (Xiang *et al.* 2009)

Application of anti-stripping agents is a common practice to improve durability of asphalt mixtures. These additives enhance bitumen-aggregate bonding. The effect is more for siliceous aggregates because of their relatively higher hydrophilicity. Lime, Portland cement and liquid agents are among the most common additives used to prevent stripping of asphalt mixtures. However, applying lime and Portland cement to the mix result in harder and more brittle asphalt mixtures. Liquid anti-stripping agents are more favourable alternatives. In addition to be adhesion boosters, liquid agent reduce viscosity as well which means improved mixing and compaction procedures.

Manufacturing bituminous mixes with appropriate amount of filler is crucial in achieving an optimum void content in the mix and hence reducing the plastic deformations caused by traffic loading. There are also fillers that make a good mix with the aggregates and improve the adhesiveness of the mixture (Movilla-Quesada 2012, 2013).

Although modifiers such as styrene-butadiene-styrene (SBS), Crumb Rubber (CR) and Polyphosphoric Acid (PPA) can have desirable effects on the performance of asphalt mixture; these additives must be mixed with bitumen at high temperatures and the compaction temperature of asphalt mixture must also be higher to compensate for high bitumen viscosity. There are some other types of additives that can be used to reduce viscosity and facilitate construction operations by decreasing mixing/compaction temperature. Sasobit (Fischer-Tropsch Paraffin wax) can reduce energy costs and environmental pollution by decreasing the viscosity and therefore mixing and compaction temperatures of AC. This leads to the introduction of Warm Mix Asphalt (WMA), a mixture with lower mixing/compaction temperature in comparison with Hot Mix Asphalt (HMA).

Sasobit® is a long chain aliphatic hydrocarbon (chain lengths of 40-115 carbon atoms), obtained from coal gasification using Fischer–Tropsch process. At temperatures below the melting point, it forms a crystalline network structure in the binder which is reported to provide added stability for the bitumen (Lee *et al.* 2008).

Sasobit® forms a homogeneous solution with the base bitumen during the stirring process and cause a noticeable reduction of bitumen's viscosity. After crystallization, Sasobit® forms a lattice structure in the bitumen, which is the basis of the structural stability of the bitumen containing Sasobit®. The recommended addition rate is 0.8% to 3% by weight of the bitumen (Hurley *et al.* 2005, 2006).

Addition of sasobit to bitumen can help reducing the bitumen viscosity which in turn leads to lower mixing/compaction temperature. Decreasing the void content through proper compaction is a solution to increase resistance against permanent deformation (Sanchez-Alonso 2011a). The void content has a considerable effect on the performance of the asphalt mix in terms of permanent deformation and moisture susceptibility (Movilla-Quesada 2012, 2013). Selecting a proper filler percentage and reducing the viscosity are two important approaches to reach an appropriate void content. Researches show that decreasing compaction temperature has an impact on asphalt mix characteristics such as permanent deformation, resilient modulus, and moisture susceptibility. Regarding this, samples made with warm mix additives and lower compaction temperature demonstrate better performance compared with additive-free asphalt mixes (Sanchez-Alonso et al. 2011b; DelRio-Prat et al. 2011).

Researches show that sasobit has considerable effect on rheological properties of bitumen at high temperatures. Moreover, adding sasobit can help reducing the viscosity of bitumen. However, it must be mentioned that asphalt mixtures with sasobit modified bitumen show higher fatigue cracking and low temperature cracking susceptibility at intermediate and low temperatures (Fazaeli *et al.* 2012)

Application of sasobit along with each of the mentioned additives may reduce the problem of high mixing/ compaction temperature for SBS, PPA and CR modified mixtures. Furthermore, this combination does not exhibit poor behaviour of sasobit modified bitumen at low temperatures.

In this research, the effect of PPA, CR, Antistripping agent and SBS on physical and rheological behaviour of sasobit modified bitumen at low, intermediate and high temperature has been studied. Characteristics and mixing procedure of these additives will be explained in following sections.

# 1. Materials and sample preparation

#### 1.1. Bitumen (Base bitumen)

In this study, bituminous cement with penetration grade of 60/70 obtained from Bandar–Abbas Refinery is selected as the base bitumen because it is the most common bitumen type used in Iran. The performance grade of the bitumen is determined to be 58–22. Physical properties of this bitumen can be seen in Table 1.

Table	1.	Physical	properties	of the	base	bitumen
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Test	Standard test	Unit	Test results
Specific Gravity (25 °C)	ASTM D70-09e1 (2009)	gr/cm <sup>3</sup>	1.03
Flash Point (Cleveland)	ASTM D92-12b (2013)	°C	308
Penetration (25 °C)	ASTM D5/D5M-13 (2013)	°C	62
Ductility (25 °C)	ASTM D113-07 (2007)	cm	100
Softening point	ASTM D36M-12 (2012)	°C	49
Kinematic viscosity: 120 °C	ASTM D2170M-10 (2010)	mm <sup>2</sup> /s	810
Kinematic viscosity: 135 °C	ASTM D2170M-10 (2010)	mm <sup>2</sup> /s	420
Kinematic viscosity: 150 °C	ASTM D2170M-10 (2010)	mm <sup>2</sup> /s	232
Penetration index (PI) <sup>a</sup>	-	_	-1.12
Penetration Viscosity Number ( PVN) <sup>b</sup>	_	_	-0.56

<sup>a</sup> 
$$PI = \frac{\left[1952 - 500\log(\text{Pen}_{25}) - 20SP\right]}{\left[50\log(\text{Pen}_{25}) - SP - 120\right]}$$
  
<sup>b</sup>  $PVN = \frac{\left[-6.387 + 1.195\log(\text{Pen}_{25}) + 1.5\log(\text{Vis}_{135})\right]}{\left[0.79511 - 0.1858\log(\text{Pen}_{25})\right]}$ 

#### 1.2. Sasobit

In this research sasobit is added to base bitumen in amount of 2.5 weight percent of base bitumen at 130 °C. At this same temperature, mixing is carried out for 10 minutes with low shear mixer at a frequency of 300 rpm. Regarding the relatively low melting point of sasobit (around 105 °C), 130 °C is adequate for mixing and compaction time period considered for this purpose. Other studies show the same temperature (Fazaeli *et al.* 2012). Table 2 shows the properties of sasobit used in this research.

#### 1.3. Polyphosphoric acid

Polyphosphoric acid used in this study is "STARPHOS 04" from STAR ASPHALT co., Italy. To ensure that PPA is mixing appropriately with sasobit modified bitumen, PPA is mixed in amount of 1 weight percent of bitumen at 160 °C for 60 minutes. The properties of STARPHOS 04 used in this study can be seen in Table 3.

#### 1.4. Anti-stripping agent

Anti-stripping agent used in this study is "STARDOP 130 p" provided from STAR ASPHALT co., Italy. STAR-DOP 130 P is a liquid cationic adhesion promoter for pure bitumen and polymer modified bitumen base on inorganic esters and vegetable oils. The properties of STARDOP 130 P can be seen in Table 4. In this research, anti-stripping agent is added to base bitumen in amount of 0.4 weight percent of base bitumen at 145 °C. At this same temperature, mixing is carried out for 30 minutes with low shear mixer at a frequency of 1000 rpm.

#### 1.5. Crumb rubber

The mixing process of CR and sasobit modified bitumen is implemented at 175 °C for 120 minutes with 6000 rpm high shear mixer following by 60 minutes at 1000 rpm

Table 2. Sasobit characteristics

Characteristics	Standard	Description
Congealing point	ASTM D938-12 (2012)	106 °C
Penetration @ 25 °C	ASTM D1321-10 (2010)	<1 dmm
Penetration @ 65 °C	ASTM D1321-10 (2010)	6 dmm
Appearance	_	Prills ( $D = 1 \text{ mm}$ )

Table 3. Characteristics of polyphosphoric acid of the study

Characteristics	Description		
Appearance @ 25 °C	viscous liquid		
Melting point	20–30 °C		
Colour	Clear		
Viscosity @ 25 °C in cP	840		
Density @ 25 °C	2.02		
Boiling point	<275 °C		

Table 4. Characteristics of anti-stripping agent of the study

Characteristics	Description
Appearance @ 25 °C	Dark liquid
Colour	Brown
Flammability	>140 °C
РН	N.A.
Viscosity @ 50 °C	6.4°E
Density @ 15 °C	0.975 Kg/Lt
Boiling point	<275 °C

Table 5. Characteristics of Crumb Rubber used in this study

Characteristics	Description		
Moisture content	0.1%		
Maximum grain size	0.4 mm		
Unit weight	0.31 gr/cm <sup>3</sup>		
Ash content	10%		

at 150 °C. Crumb rubber is applied in amount of 10% of the weight of the base bitumen. The properties of crumb rubber are shown in Table 5.

The type of CR and its particles' size are amongst the major factors which affect the behaviour of CR modified bitumen (Putman 2005; Bahia *et al.* 1994). Figure 1 illustrates the grading of CR used in this study.

#### 1.6. Styrene-butadiene-styrene

SBS from Dynasol co. (Spain) is used for this study. The properties of this polymer are summarized in Table 6. The mixing of SBS with sasobit modified bitumen is similar to the process used for crumb rubber. SBS content of the mix is 3 weight percent of the bitumen.



Fig. 1. Grain size distribution of CR

Table 6. Characteristics of SBS used in this study

Test method	Quantity	Test
MA 04-3-064	5	Toluene soluble viscosity (Pa.s)
MA 04-3-018	<0.1	Toluene insoluble materials (%)
ASTM D-5669	< 0.35	Ash content (%)

#### 1.7. Nomenclature

The modified bitumen was named as BS–X. In this abbreviating system, letter B stand for base bitumen (PG 58–22), S for Sasobit® and X for other additives. The amount of Sasobit®, PPA, CR, Anti-stripping agent and SBS are selected to be 2.5, 1, 10, 0.4 and 3 weight percent of bitumen, respectively. These proportions are based on previous studies and experiences. Based on this labelling system, samples are named as BS–P (base bitumen, sasobit and PPA), BS–C (base bitumen, sasobit and CR), BS–A (base bitumen, sasobit and SBS).

#### 2. Test method

# 2.1. Conventional bitumen tests

Conventional bitumen tests such as softening point (ASTM D36M-12 2012) and penetration grade (ASTM D5 / D5M-13 2013) are performed to characterize modified bitumen. Furthermore, to evaluate the effect of additive on the thermal sensitivity of modified bitumen, the Penetration Index (PI) of bitumen is determined. The Rotational Viscometer (RV) test is used to determine the variation of bitumen viscosity in the high temperature range of manufacturing and construction according to ASTM D4402M-12 (2012).

#### 2.2. Aging procedure

Short and long term laboratory ageing of the base bitumen and modified bitumen is carried out using the Rolling Thin-Film Oven (RTFO) test (ASTM D2872-12e1 2012) and the pressure ageing vessel (ASTM D6521-13 2013), respectively.

# 2.3. Dynamic mechanical analysis

#### 2.3.1. High temperatures

Dynamic mechanical analysis (DMA) is performed on base and modified bitumen before and after RTFO aging process in compliance with ASTM D7175-08 (2008) using a Bohlin DSR50 rheometer. DMA is done at high temperature (HT) sweeps from 46 to 82 °C at constant frequency of 10 rad/s. The in-phase (G'') and out-of-phase (G'') components of G\* are determined in these temperature range. These two components are related to each other through the phase angle ( $\delta$ ), which is the phase shift between the applied shear stress and shear strain responses during the test. The phase angle is a measure of the viscoelastic balance of the material behaviour (tan  $\delta = G'' / G'$ ).

The principal viscoelastic parameters determined in these temperatures were the complex shear modulus (G\*), phase angle ( $\delta$ ), storage modulus (G') and the loss modulus (G'').

#### 2.3.2. Intermediate temperatures

The stiffness of bitumen at intermediate service temperature is a crucial parameter in prevention of fatigue cracking. Using the results of dynamic mechanical analysis, it would be possible to investigate the fatigue behaviour of modified bitumen. The fatigue parameter was chosen to reflect the energy dissipated per load cycle, which can be calculated as G\*. Sin  $\delta$  (Anderson, Kennedy 1993). The specification prescribed a relationship whereby a reduction in G\*. Sin  $\delta$  at 1.59 Hz corresponds to improved fatigue resistance. In order to evaluate the effect of additive type on the performance of bitumen samples at intermediate service temperatures, DSR test (ASTM D7175-08 2008) is implemented on the Pressure Aging Vessel (PAV) aged bitumen in a temperature range of 19–34 °C and with constant frequency of 1.59 Hz.

#### 2.3.3. Low temperatures

Creep stiffness test (ASTM D6648-08 2008) is executed by the Cannon Thermoelectric Bending-Beam Rheometer (TE-BBR) on base and the modified bitumen after the PAV ageing process. This will help figuring out the effect of various additives on the performance of modified bitumen at low temperatures. The beam of bitumen (127 mm long, 12.7 mm wide and 6.35 mm thick) is submerged in a constant temperature bath at each test temperature (starting from -24 °C) for 60 min. Then, a 980±50 mN seating load is applied for  $1\pm0.1$  second to the rectangular beam of the binder, which was supported at both ends by stainless steel half-rounds (102 mm apart), and the deflection of centre point is measured continuously. By implementation of this test, creep rate (m-value) and creep stiffness (St) were determined for all the specimens from -24 °C to -6 °C with intervals of -6 °C following ASTM D6373-13 (2013) procedure. The creep rate (m-value) and creep stiffness (St) are also investigated at aforementioned temperatures and various loading times (from 8 seconds to 240 seconds).

#### 3. Result and discussion

#### 3.1. Chemical structure evaluation

Fourier Transform Infrared Spectroscopy (FT–IR) test is used to evaluate components and the consistency of bitumen modification compounds. The FT–IR spectra were



Fig. 2. FT-IR test result for BS

recorded on a Shimadzu FT–IR–460 spectrometer as a KBr disc with gasoline as the solvent. Results of FT-IR test for BS sample is shown in Figure 2.

According to Figure 2, all the samples exhibit C–H asymmetrical stretching bond in wavenumber range of 2850–2920 cm–1 and symmetrical stretching bond in wavenumber range of 1375–1460 cm–1 which can be related to hydrocarbon structure of sasobit. Thus, it can be concluded that sasobit is very well distributed in the samples.

Results of FT-IR test for BS-S, BS-C, BS-P and BS-A samples are shown in Figure 3(a) to 3(d). For BS-S sample (Fig. 3(a)), C = C bond in butadiene and benzene rings in styrene lead to the expectation of a peak in 1580-1670 cm-1 range which is also the case in Figure 3(a). As a result of double bonds of C = C in polyethylene compounds of BS-C (Fig. 3(b)), A peak in wavenumber range of 1590-1650 cm-1 is anticipated. The peak on 1630 cm-1 confirm with the expectations. For samples BS-A and BS-P (Fig. 3(c) and (d)), P-O and P = O bonding peaks in molecular structure of polyphosphoric acid and polyphosphoric ester (antistripping agent) can be detected in 1010-1040 cm-1 and 1590-1610 cm-1, respectively. Reduction in P-O and P = O bonding peaks intensity can be attributed to high concentration of hydrocarbon compounds of bitumen. It must be noted that higher intensity of C-H peaks compared to other bonding peaks is due to the higher concentration of these compounds and usage of gasoline as the solvent. Overall, with the occurrence of expected peaks in FT-IR results, it can be concluded that the compounds are well distributed in all modified bitumen mixes.

Scanning Electron Microscopy (SEM) imagery technique is used to study the morphology and to assess the quality of modifier distribution in modified bitumen samples. Figure 4 shows SEM image for each sample. According to this figure, it can be concluded that modifier particles/agents are distributed relatively homogenous in the bitumen.

#### 3.2. Temperature susceptibility

Table 7 shows the penetration grade, softening point and Penetration Index (PI) of modified bitumen samples. Results indicate the modification of bitumen with additives can have a considerable effect on penetration grade and softening point. BS–C sample has the highest softening point and lowest penetration grade among all modified bitumen that leads to higher PI and consequently lower thermal sensitivity of this type of bitumen. It can be said that Sasobit® – additive type X combination increases stiffness and reduces thermal sensitivity of bitumen, although these changes are trivial for BS–A and BS–P.

#### 3.3. Effect of additive type on viscosity

The viscosity of bitumen at high temperature is considered an important property because it represents the



Fig. 3. FT-IR test results for (a) BS–S, (b) BS–C, (c) BS–P and (d) BS–A

bitumen's ability to be pumped through an asphalt plant, thoroughly coat aggregate in asphalt concrete mix, and be placed and compacted to form a new pavement surface (Burger *et al.* 2001). Consequently, the viscosity of modified bitumen are determined by Brookfield Viscometer (ASTM D7175-08 2008) at 120, 135 and 150 °C and the viscosity versus temperature change is depicted for modified bitumen in Figure 5.

As anticipated, Sasobit<sup>®</sup> decreases the viscosity of bitumen. The lowest viscosity belongs to BS–A. The results reveal that Sasobit<sup>®</sup>– PPA, Sasobit<sup>®</sup> – SBS and particularly Sasobit<sup>®</sup> – CR combinations escalate the viscosity of base bitumen.

To evaluate the effect of sasobit on CR, SBS and PPA modified bitumen, their respective viscosity are measured in separate tests. Table 8 illustrates the results. From this table, it can be stated that sasobit can reduce



Fig. 4. SEM images of various additive types of the study:
a) Sasobit; b) Crumb rubber; c) Polyphosphoric acid;
d) SBS; e) Anti-stripping agent; f) Sasobit – CR distribution;
g) Sasobit – PPA distribution; h) Sasobit – Anti-stripping agent distribution; i) Sasobit – SBS distribution



Fig. 5. Dynamic viscosity curves of modified bitumen

the viscosity of base and modified bitumen. The amount of viscosity reduction effect depends on the percentage of modifiers, but in this study, viscosity reduction of 10–30 percent is observed.

The mixing and compaction temperature of the asphalt mixtures have been determined according to the viscosity-temperature diagram and this is a temperature at which the bitumen viscosity will be accordingly 170±20, 280±30 centistokes (ASTM D6926-10 2010). Table 9 shows temperature ranges for mixing and compaction of modified bitumen types of the study.

Based on Table 8, among all the samples, asphalt mixtures with Sasobit® and Anti-stripping agent can be mixed and compacted at lowest temperature which results in energy and operation time savings. BS–C modified asphalt mixtures have the highest compaction and mixing temperature. As said earlier, application of sasobit reduces the viscosity of AC and mixing/compaction temperature.

Table 7. Results of conventional bitumen tests

Binder	В	BS	BS–P	BS–C	BS–S	BS–A
P <sup>a</sup> (dmm)	65	46	46	40	42	43
SP <sup>b</sup> °C	48	59	61	73	68	61
PIc	-1.1	0.62	1.01	2.73	2.05	0.85

a: Penetration; b: Softening point; c: Penetration index.

Table 8. The effect of sasobit on the viscosity of base and modified bitumen

	Viscosity @ 135 °C						
Binder	Without sasobit (B–X)	With sasobit (BS–X)	Change in viscosity (%)				
Base bitumen	420	300	-29				
SBS modified bitumen	937	675	-28				
PPA modified bitumen	626	552	-12				
CR modified bitumen	1633	1384	-15				

Table 9. Mixing temperature ranges of modified bitumen

Binder Type	Mixing temperature range (°C)	Compaction temperature range (°C)
В	154–161	142–148
BS	145–152	134–139
BS–S	164–170	153–159
BS–P	157–163	147–152
BS–C	175–179	165-170
BS–A	143–149	133–138

#### 3.4. Performance at high temperature

Elastic and viscous behaviour of modified bitumen are investigated by measuring the complex modulus (G\*) and the phase angel ( $\delta$ ). G\* and  $\delta$  are highly dependent upon temperature and loading cycles. At high temperatures, the bitumen behaviour is more viscous. When  $\delta$ reaches to 90°, G\* would have no elastic component. On the other hand, at low temperatures, the bitumen tends to be more elastic than viscous. This time when  $\delta = 0$ , the viscous component G\* would be eliminated. Figure 6 shows the G\* versus temperature for unaged base and modified bitumen. According to this figure, modified samples have higher complex modulus compared to the base bitumen at all temperatures. This shows that the viscous behaviour of modified binders is lower than the base bitumen.

High rate of Complex module drop versus increasing temperature for BS–A must be mentioned here. Although the complex modulus of BS–A is approximately eight times higher than BS–P at 46 °C, it falls to about one third of the complex modulus of BS–P at 82 °C. This may affect negatively on the performance of BS–A at high temperatures.

In the Superpave binder specification, rutting is taken into account using rutting resistance factor of  $G^*/Sin \delta$ , which is merely dependent on the rheological properties of the asphalt binder. The higher the rut factor for the binder, the stiffer and more rutting resistant the asphalt concrete would be. To minimize permanent deformation, the value of  $G^*/Sin \delta$  for unaged bitumen must



Fig. 6. The parameter  $G^*$  versus temperature for unaged base and modified bitumen



Fig. 7. G\*/Sin  $\delta$  for unaged bitumen binder at 1.59 Hz

be limited to 1 kPa. For bitumen that went through RTFO aging process, this value must be higher than 2.2 kPa. Figure 7 and Figure 8 show the G\*/Sin  $\delta$  trend for base and modified bitumen before and after the RTFO ageing process in the temperature range of 46 °C to 86 °C with a constant frequency equal to 1.59 Hz.

In Figure 7, a significant difference can be observed between shear resistance of modified and unmodified bitumen. The drop of G\*/Sin & against increasing temperature for BS-A is more rapid than that of other modified bitumen. BS-P and BS-C have higher shear resistance, which demonstrates the improved elastic behaviour of bitumen with containing these additives. Furthermore, from Figures 7 and 8 derive this conclusion that aging increases the amount of  $G^*/Sin \delta$  and consequently it improves the strength of bitumen and mixture against permanent deformation. The reason lies in bitumen oxidation and change in chemical properties of bitumen and additives. The increase of  $G^*/Sin \delta$  for BS-A is less than other binder types and PPA, SBS and CR demonstrate the worst results with sasobit regarding the improvement of bitumen shear resistance after aging

Tan  $\delta$  is a parameter that indicates the viscoelastic behaviour of bitumen. Tan  $\delta$  is the ratio of the viscous component to the elastic component of the binder. Figure 9 shows the variation of tan  $\delta$  in a temperature sweep test for unaged binders. The increased amount of tan  $\delta$  demonstrates the viscous behaviour of bitumen which in turn



Fig. 8. G\*/Sin  $\delta$  for bitumen binder aged with RTFO at 1.59 Hz



Fig. 9. Plot of tan  $\delta$  against temperature for study binders at constant frequency of 1.59 Hz

can be related to reduction of shear resistance. According to Figure 9, BS–A demonstrates higher viscous behaviour at high temperatures. Tan  $\delta$  for the binders with CR and SBS has a milder gradient which states a lower thermal sensitivity of these types of binders.

#### 3.5. Performance at intermediate temperatures

The intermediate service temperature is the minimum temperature at which the G<sup>\*</sup>.Sin  $\delta$  for PAV aged bitumen (ASTM D2872-12e1 2012) remains below 5000 kPa. Intermediate temperature can be calculated from Eqn (1), where IT, LT and HT are intermediate service temperature, high service temperature and low service temperature, respectively:

$$IT - [(HT + LT)/2] + 4.$$
 (1)

Figure 10 shows the effect of additive type on  $G^*$ .Sin  $\delta$  for PAV aged binders. All the FT Wax modified bitumen types exhibit lower fatigue resistance compared to the base bitumen particularly in cases of BS–P and BS–S. This shows that the additives of the study cause the bitumen to show more brittle behaviour at intermediate temperature. Utilization of CR in comparison with other modifiers can improve fatigue resistance of FT Wax modified bitumen. A possible explanation is that CR modified bitumen demonstrates more flexible behaviour at intermediate intermediate temperature.

#### 3.6. Performance at low temperatures

A noticeable disadvantage of sasobit when applied as the only bitumen additive is the undesirable behaviour of the mix at low temperature and the increase in low temperature cracking probability (Fazaeli *et al.* 2012). In this study, performance of bitumen modified with sasobit in conjunction with other additives at low temperature is studied using Bending Beam Rheometer (BBR) test. Low temperature for pavement design is defined as 10 °C lower than the temperature at which the creep stiffness of PAV aged bitumen beam remains below 300 MPa, 60 seconds after bending beam rheometer apparatus loading. The m-value of the bitumen beam must be more than 0.3. at the time of loading. Table 10 and Figure 11 show the creep stiffness and m-value of binders against temperature, respectively.



Fig. 10. Plot of G\*.Sin  $\delta$  for binders aged with PAV

Table 10. Creep stiffness change at low temperature range

Stiffness	Temperature (°C)				Stiffness change
(Mpa)	-6	-12	-18	-24	vs. base bitumen at -18 °C, %
В	66	201	337	715	_
BS	105	234	381	759	+13
BS–S	90	227	324	679	-4
BS-P	79	209	322	698	-4
BS–C	48	126	216	518	-36
BS–A	94	234	402	794	+19

Table 11. Performance grade of base and modified bitumen

Binder	В	BS	BS–A	BS–S	BS-P	BS–C
(PG)	58–22	70–22	70–22	76–22	76–22	82–28



Fig. 11. M-value of binders at low temperature range

It can be claimed that FT Wax increases bitumen stiffness. This increase is more evident for BS–A which result in higher low temperature cracking probability of asphalt mixtures containing this type of bitumen. Among all tested binders, the lowest stiffness belongs to BS–C. It can be concluded again that CR demonstrate highest compatibility with FT Wax. Together, they reduce bitumen stiffness by 36 percent compared to the no-additive case at –18 °C. Applying sasobit and CR cause the m-value to increase and low temperature cracking to decrease. SBS and PPA slightly enhance low temperature performance of Sasobit<sup>®</sup> modified bitumen.

# **3.7. Effect of additive type on SHRP performance grade**

Table 11 shows the effect of various study additives on performance grade of binders according to Superpave performance classification system (ASTM D6373-13 2013). In this figure the effect of bitumen modification on high-end of performance grade can be observed clearly. However, no performance grade expansion can be observed on low-end, except for BS–C.

This can be stated that FT Wax contributes to improvement of high performance grade of the base bitumen only. Results of DSR and BBR tests lead to the same deduction. Although application of SBS and PPA, along with FT Wax does not have significant effect on improvement of low performance grade of bitumen, but pushed the high performance grade higher, meaning better performance against permanent deformations. Antistripping agent causes no changes on performance grade of FT wax modified bitumen.

Among all tested additives, crumb rubber and Sasobit<sup>®</sup> can be called as the best partners. They display the most compatibility with each other for the purpose of improving the performance grade of modified bitumen. This fact can help removing the problems caused by using these additives alone. Sasobit reduces the problem of high mixing/compaction temperature of CR modified binder.

# Conclusions

FT paraffin sasobit reduces the penetration grade and increase softening point of bituminous cement. Combination of FT wax with other additives results in still better results. CR is the most influential additive but anti-stripping agent showed marginal effect. A similar trend is also observed regarding PI changes.

Addition of anti-stripping agent to FT Wax modified bitumen is to some extent effective for reducing bitumen viscosity and mixing/compaction temperatures. Bitumen modified with the sasobit – CR combination exhibited highest viscosity and mixing/compaction temperature. However, it may be expected that due to the presence of FT Wax and its flow enhancing property, this type of modified bitumen would have lower compaction and mixing temperature, compared to bitumen modified with CR alone. This may facilitate field compaction procedure of this asphalt mixture.

Effect of anti-stripping agent on permanent deformation is not so drastic and less important. BS–C with lowest G\*.Sin  $\delta$  value indicates the best fatigue resistance among all asphalt mixture compared in the study.

Adding anti-stripping agent to sasobit modified bitumen, in contrast with CR, SBS and PPA, increases the stiffness of bitumen at low temperature. This may increase the probability of low temperature cracking. On the other hand, CR modified bitumen has the lowest stiffness and highest resistance against thermal cracking at low temperatures.

Crumb rubber has expanded the performance grade of FT Wax modified bitumen at high and low temperatures while PPA and SBS have merely improved high temperatures. Anti-stripping agent has no considerable effect on the performance grade of FT wax modified bitumen.

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