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Performance Evaluation of SBS/sulfur Modified Bitumen and its Effect on Fuel Resistance

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Abstract

The fuel resistance property plays an important role in asphalts, but available standards for determining this characteristic are presently lacking. In the present work, a number of polymer modified bitumen with styrene-butadiene-styrene (SBS) polymer (4, 5, 6% SBS) and SBS/sulfur modified bitumen with various percentages of sulfur (1.65, 3, 3.5% based on polymer content) were prepared. Each sample was immersed in the fuel and after 24 hour its weight loss was measured to determine the effect of fuel on them. Results showed that, increase in SBS content caused improvement in physical and rheological properties of bitumen.

After adding sulfur to SBS, conventional properties (softening point, penetration, ductility and temperature susceptibility) was improved. Rheological properties were determined by Dynamic Shear Rheometer (DSR). Increase in polymer content and sulfur level led to increase in complex shear modulus (G*) and improvement of the rutting factor. Results indicated that more physical bonds with increase in polymer content and more chemically bonding between polymer, sulfur and bitumen by increasing in sulfur content led to more fuel resistance characteristic.

Key words: *Polymer modified bitumen, Fuel resistance asphalt, Rheology, Styrene-butadiene-styrene, Sulfur.*

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Introduction

Conventional bituminous products have tended to perform satisfactorily in the most highway pavement and airfield runway applications. However, in recent years, increased traffic levels, larger and heavier trucks, high tire pressures and higher fuel spillage shave seemed to add to severe demands on the highway system. These problems have led to many requirements for bitumens with high quality. Polymer modification offers one solution to overcome the deficiencies of bitumen and thereby improving the performance of asphalt mixtures [1]. According to some research for better resistance and to protect the pavement surface from gasoline, diesel and fuel spillages, fuel-resistant binders have been applied to the pavements [2, 3, 5].

Unfortunately the currently used fuel resistant materials contain char coal which is harmful due to its carcinogenic character. Coal tar sealers, which are known to be carcinogenic, are often applied to prevent the jet fuel damage [4]. The application of these sealers has two drawbacks: the seal coatings crack, which allows fuel to damage the asphalt pavement and their use places carcinogenic material onto a pavement, may be recycled that eventually leads to skin cancer, lung, liver and bladder [5, 6]. Therefore, the scientists are looking for substances with a lower risk. Another important aspect to be underlined is that actually there are not any methodologies to quantitatively evaluate the fuel resistance of a binder, and there is no standard procedure for this procedure. The most common method is an empirical approach based on the relationship between different asphalt modifiers, such as coal tar bitumen, resins and thermoplastic polymers and the dissolution of asphalt in fuel [7]. The only available technical specifications are those developed in 2005 by the CEN for the determination of the weight loss in asphalt mixtures after 24 hours immersion in the fuel [3, 8]. Previous studies have shown that the addition of some polymers into asphalts has significant effects in improving their fuel resistance, but the polymers should be chosen based on costs, fuel resistance and mechanical and thermal properties. Polymer modification shows great resistance in permanent deformations and cracks. The most important aspect of using polymers for bitumen modification is costs, which this technique shows a high cost effect [9]. There are lots of polymers which have been used for bitumen modifying, but among them, SBS block copolymers are the most common and the most effective polymer for improving the physical and rheological properties of bitumen. The type of mixing process has a significant effect on properties and costs of end product [10-13].

James Shoenberger's study on the fuel resistant pavement sealers in 1992 was one of the initial works on the fuel resistant asphalts [6]. Van

Rooijen and colleagues studied performance evaluation of jet fuel resistant polymer-modified asphalt for airport pavements, and presented the results in 2004 conference in New Jersey. Their results showed that the unmodified bitumens have the least fuel resistance and polymer modified asphalts have good fuel resistance performance [4]. Giuliani et al. (2009) examined the effect of polymer modification on the fuel resistance of asphalt binders. They used a number of polymer modified asphalts for their study. The results indicated that SBS and ethylene-vinyl-acetate (EVA) polymers exhibited the most fuel resistance property [3]. Steernberg and his colleagues used an empirical method to preliminarily establish a relation between different asphalt modifiers, such as coal-tar, resins and thermoplastic polymers, and consideration the dissolution of asphalt in jet fuel [14].

In this work, modified bitumen was prepared by several polymer percentages (4, 5, 6% SBS) and also different sulfur percentages (1.65, 3, 3.5% based on polymer content). The effects of polymer content on the base bitumen and the effect of sulfur levels on polymer modified bitumen were investigated. Physical and rheological properties were measured and the effect of these properties on fuel resistance of samples was determined.

Experimental

Materials

The base bitumens consist of 60/70 penetration grade and vacuum bottom (VB) bitumen were used. VB contains of 97% maltene, was used to supply the maltene phase in modified bitumen mixture. The physical properties of bitumens have been presented in Table 1. The asphalt was modified with linear SBS (Calprene 501). The properties of polymer are presented in Table 2. The molecular architecture of SBS can be linear or branch. In linear SBS, two polystyrene blocks are positioned at the ends of an elastomeric block. And finally, sulfur is a commercial product from refinery.

Table 1. Properties of 60/70, VB bitumens and base bitumens.

Property	60/70	VB	Base [a]
Penetration(dmm)	65	257.0	78
Softening point(°C)	49.5	40.6	47
Ductility(cm)	>100.0	87.9	79
Elastic recovery(%)	17	14	16

[a] Admixture of 80% of 60/70 + VB

Table 2. Properties of SBS.

Polymer Properties	Content	Test methods
Toluene Solution Viscosity 25 % pa-s	5	MA04-3-064
Toluene Solution Viscosity 25 % 5.23% cst	13	MA 04-3-003
Volatile Matter, %	0.4	ASTM D-5668
Hunterlab Color	2	ASTM D -1925-70
Total styrene (on polymer), %	31	ASTM D -5775
Hardness, shore A	76	ASTM D-2240
Insolubles in Toluene, 325 mesh, %<0.1		MA 04-3-01
Ashes, %<0.35		ASTM D -566

Preparation of samples

The first step was allocated to preparing the polymer modified bitumen. The modified bitumen was prepared by using a high shear mixing homogenizer (IKEA model). Firstly, bitumen was heated up to 180±5 °C in a small container until it flowed fully, then upon reaching 180 °C, VB was added to bitumen in 5 min. A given part of SBS (4%, 5% and 6% of the weight of the base asphalt) was gradually added (5 g/min) to the melted asphalt under a high-speed shear mixer of 5500 to 6000 r/min. Simultaneously, the mixture was stirred by a mechanical stirrer at 180 °C for 2 h while the rotation speed of mechanical stirrer was 300 r/min so that the blends became essentially homogenous. The second step was the curing process which sulfur powder was added to polymer modified bitumen in 10 min. After preparation of specimens, these samples were mixed with aggregates to produce asphaltic samples, then were immersed in fuel for 24 hours, and finally the weight loss of each sample was measured. The prepared specimens are presented in Table 3. The base weight for production of each percent of PMBs or SBS/sulfur modified bitumen was 1 kg.

Table 3. samples prepared in the study.

Compositions	Sample No.
Bitumen + 20%VB + SBS 4%	1
Bitumen + 20%VB – SBS 5%	2
Bitumen + 20%VB – SBS 6%	3
Bitumen + 20%VB –S:1.65% SBS	Cure 1
Bitumen + 20%VB – S:3% SBS	Cure 2
Bitumen + 20%VB – S:3.5% SBS	Cure 3
Asphalt (bitumen 60/70)	4

Measurement of classical properties

The softening point test of different modified bitumens was measured according to ASTM D 36. In this test, two disks of bitumen were cast into shouldered rings, and then the disks were trimmed to remove the excess of asphalt. After that, the disks were heated at a constant rate (5°C/min) in water or each appropriate bath using a special apparatus [15]. The apparatus used in this study, Petro test model PKA5, was made by Germany. The penetration tests were carried out at 25°C according to ASTM D5. The bitumen was thermo-stated in a water bath and the penetration of a standard needle under a standard load (100 g) was measured during 5s and reported in tenth of millimeter. The apparatus used, model PNR12, was made by Germany. Ductility determined according to ASTM D113. The apparatus used in this work, was petro test model DDA3 [16]. In addition, the temperature susceptibility of the modified bitumen samples was calculated in terms of penetration index (PI) using the results obtained from penetration and softening point tests. A classical approach related to PI calculation has been given in the Shell Bitumen Handbooks shown in the following equation:

$$\mathrm{PI} = (1952 - 500 \log(\mathrm{Pen}_{25}) - 20 \times \mathrm{SP}) / (50 \log(\mathrm{Pen}_{25}) - \mathrm{SP} - 120) \qquad (1)$$

Where, Pen_{25} is the penetration at 25 °C and SP (°C) is the softening point temperature of modified bitumens [17, 18].

Dynamic mechanical analysis

The most commonly used method of fundamental rheological testing of bitumen was by means of dynamic mechanical analysis (DMA) using oscillatory-type test. It was generally conducted within the region of linear viscoelastic response. These oscillatory tests were undertaken using dynamic shear rheometer (DSR). It applied oscillating shear stresses and strains to the samples of bitumen sandwiched between parallel plates at different loading frequencies and temperatures. (Figure 1) [17]. The principal viscoelastic parameters obtained from the DSR were the magnitude of the complex shear modulus (G*) and the phase angle (δ). G* was defined as the ratio of maximum (shear) stress to maximum strain [19, 20].

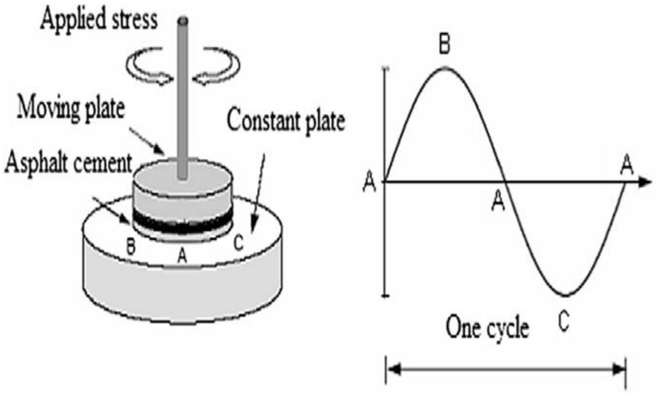

Figure 1. Schematic representation of DSR.

Results and discussion

Physical properties of PMBs in the presence and absence of sulfur

Physical properties of PMBs in the presence and absence of sulfur are shown in Figures 2-5. In all profiles (2-5), Figures A show the effect of raising in SBS contents and Figures B present the influence of increasing in sulfur levels. As shown in Figures 2, 4 and 5, the softening point, PI, and ductility, with increase in polymer contents increased. But penetration grade decreased (Figures A). The same results were approached when the sulfur level was increased in the constant polymer content (Figures B).

The increase in softening point temperature as an indicator of the stiffening effect of PMBs was favorable since bitumen with higher softening point may be less susceptible to permanent deformation (rutting) [21]. Polymer modification reduces temperature susceptibility (as determined by the penetration index—PI) of the bitumen. Lower values of PI indicate higher temperature susceptibility [18].

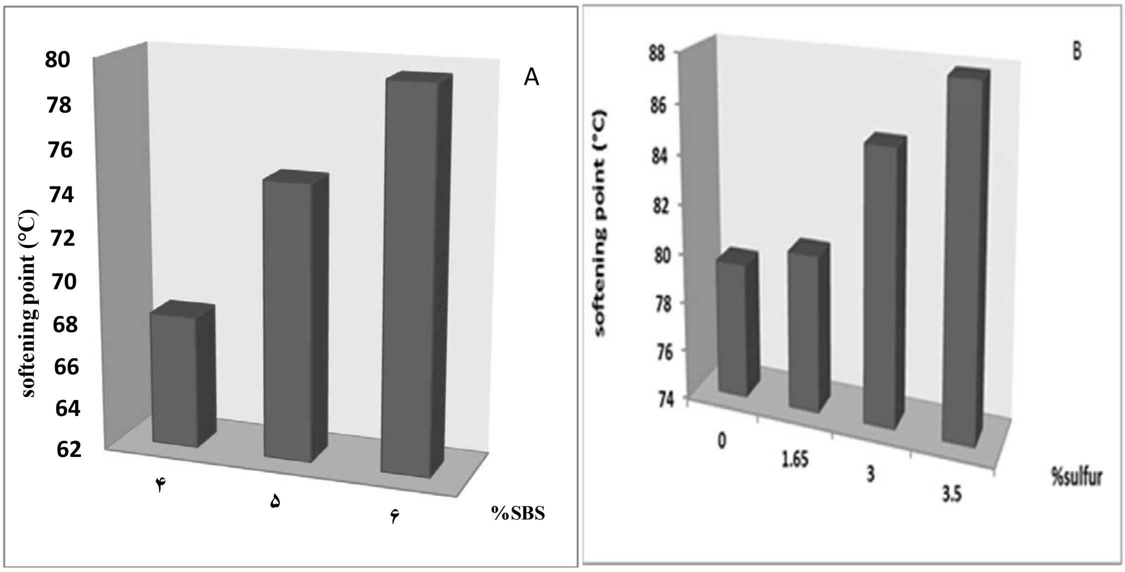

Figure 2. Softening point changes [A: effect of SBS increasing, B: effect of sulfur increasing].

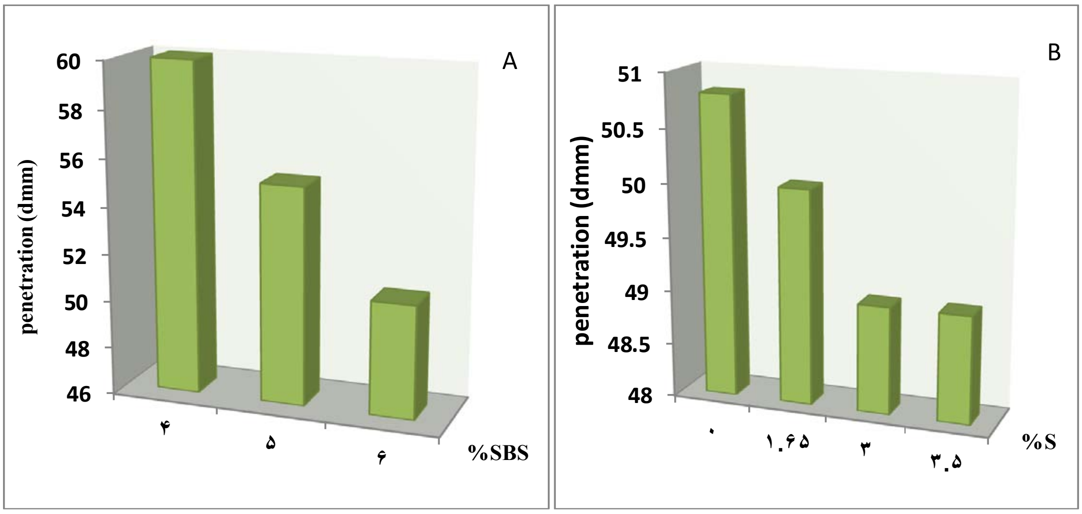

Figure 3. Penetration changes [A: effect of SBS increasing, B: effect of sulfur increasing].

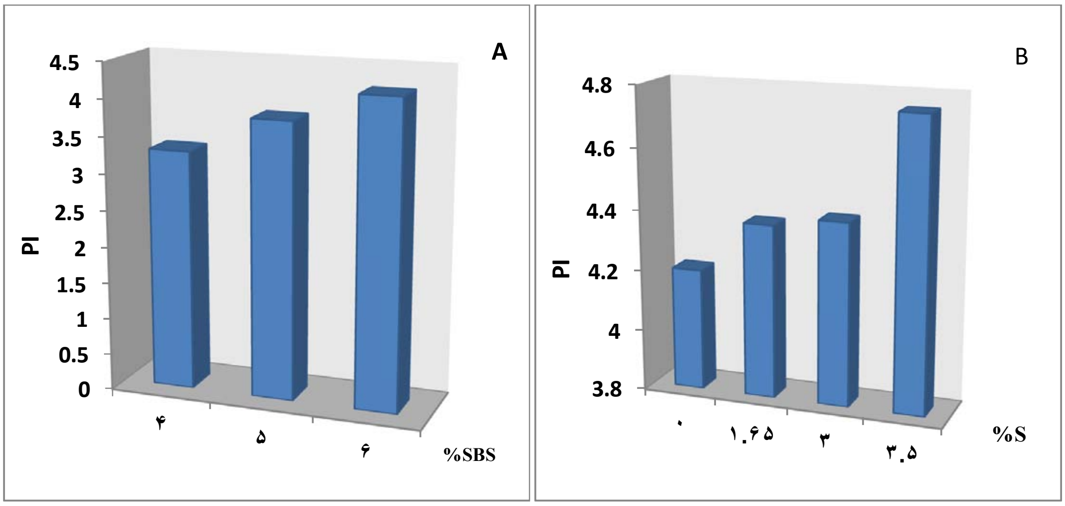

Figure 4. PI changes [A: effect of SBS increasing, B: effect of sulfur increasing].

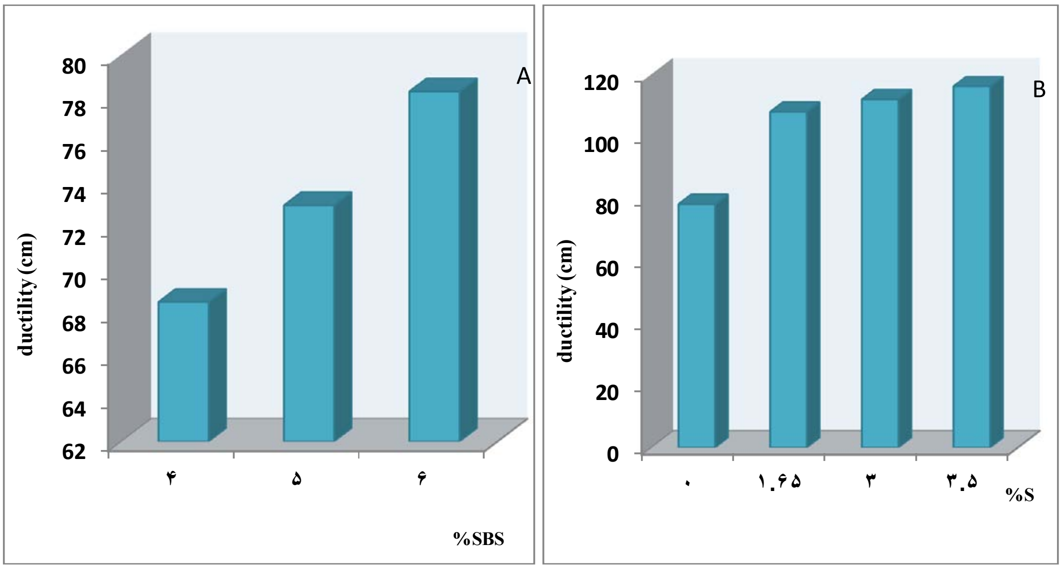

Figure 5. Ductility changes [A: effect of SBS increasing, B: effect of sulfur increasing].

Rheological properties

Rheological properties were measured by DSR. The apparatus DSR used in this paper was in model Antonpaar, Smart pave. Complex modulus was managed at 10 rad/s frequency in temperature range between 40°C to 82°C.

Effect of polymer content

In dynamic-mechanical Analysis, G* Parameter is an indicator of material strength against permanent deformation. Moreover, **δ** parameter shows the viscoelastic behavior of bitumens [12]. Rheological parameters of bitumen have a function of temperature and frequency which may be significantly modified by adding the polymer. As it can be seen in Figure 6, the G* parameter is reduced by increasing the test temperature and explanatory the fact that compositions with 4, 5 and 6% SBS and 20% VB than 60/70 bitumen are more resistant to deformation. Also, Phase angle shift (Elastic or viscous behavior) will be peaked if temperature rises. But the trend for compounds containing 4, 5 and 6% SBS are less than the base bitumen and the samples are more elastic. This behavior can be seen due to optimized polymer network in the compounds.

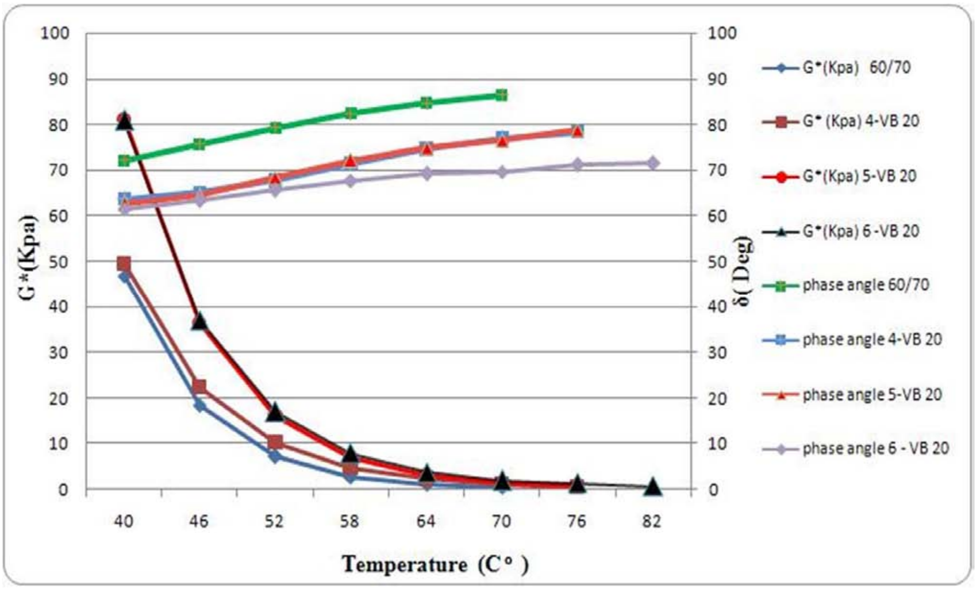

Figure 6. Rheological graph in 10 rad/ s frequency.

In the super pave methodology, measure of stiffness or resistance to high temperature of bitumen samples is shown by rutting factor. In Figure 7, G* /Sin(δ) curve versus temperature changes is shown for the base and modified bitumens (6% SBS and 20% VB). It Can be seen that the G* /Sin (δ) decreased with increasing in the temperature for all specimens. The results show that the addition of polymers to the bitumen were significantly improved

G* /Sin (δ) parameter of modified bitumens in comparison with 60/70 penetration grade bitumen. Also the temperature range wherein the polymer modified bitumens can be used will rise. The works by Zora et al. showed that polymer modified asphalts could be improved viscous elastic properties of asphalt mixtures at high temperatures and were significantly reduced rutting under repeated loads [22]. In Figures 6 and 7, the G* and G*/sin (δ) parameters increased by increasing the SBS content. Thereupon, overall samples strength under the pressures and traffic loads leading to increasing resistance against the damage caused by the loss of fuel.

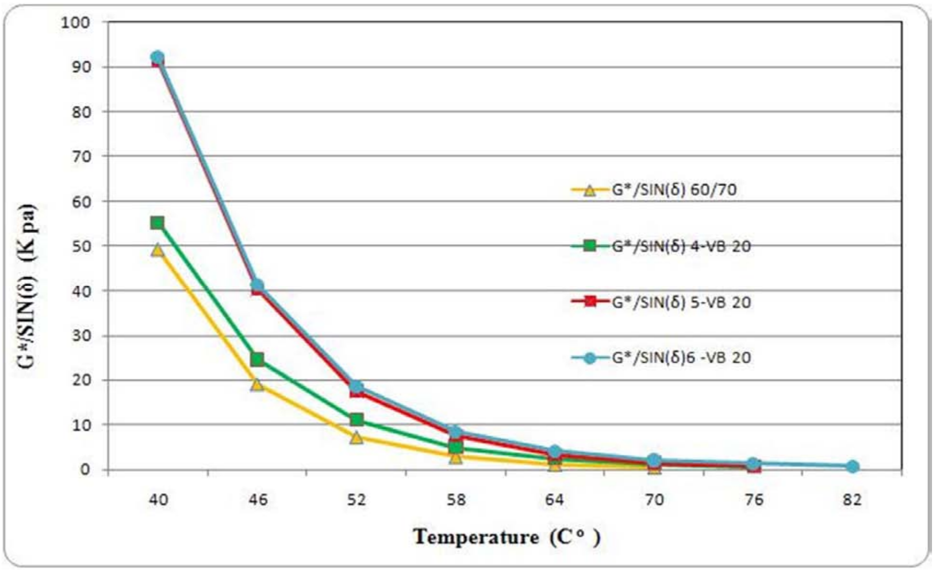

Figure 7. Rutting factor vs. temperature in 10 rad/ s frequency.

Effect of sulfur content in constant polymer content

As shown in Figure 8, after adding sulfur, complex modulus shows higher values. The complex modulus of pure bitumen was lower than SBS-modified bitumen. And the complex modulus of SBS modified bitumen (as shown in Figure 8) is lower than the SBS/sulfur modified bitumens. However, with the help of sulfur acting as a vulcanization agent, higher deformation resistance was obtained. As seen in figure 8, addition of sulfur in low levels, led to higher complex modulus and lower phase angle. Higher complex modulus show higher resistance against permanent deformation. Figure 8 also shows better behavior in high temperatures for specimens which had sulfur in compare with the specimens without sulfur.

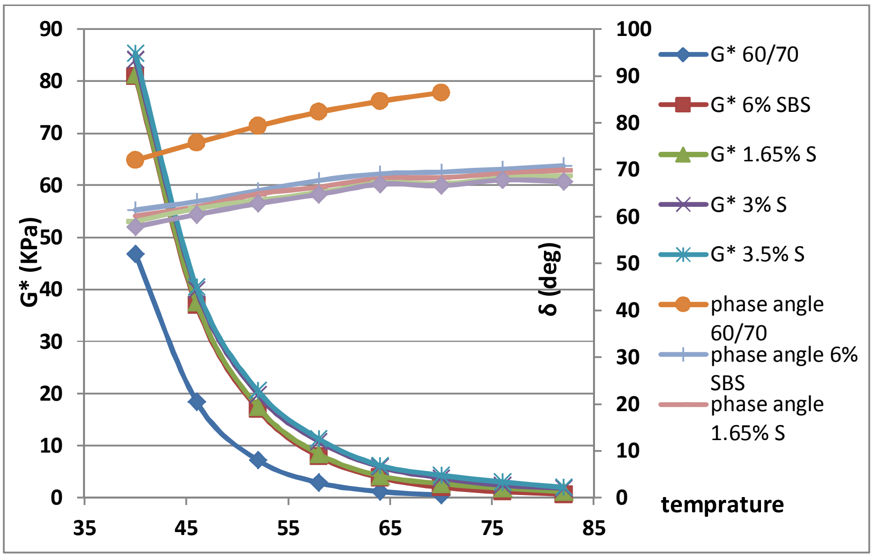

Figure 8. Rheological curves for 6% SBS modified bitumen and different percentages of sulfur/polymer modified bitumen and comparison between them.

Sample weight loss after 24h immersion in the fuel

Effect of SBS content on the fuel resistant

The penetration and softening point of the PMAs, before and after immersion in the fuel, are reported in Table 4. Figure 9 shows weight loss curve against time after 24h immersion in the fuel. Fuel can decrease the softening point of asphalt samples as shown in Table 4. As the content of polymer increases, fuel resistance of binders increases too which implies the formation of three-dimensional network in asphalt. As it is shown in Figure 9, increase in polymer content, can improve the fuel resistance of asphalt samples. Polymer constitutes the nodes of a physical elastomeric network which preserved configuration after mixing with asphalt. This configuration led to different physico-mechanical properties of PMAs. As mentioned above and in Table 4 and Figure 9, SBS were found to improve the softening point of base asphalt and its fuel resistance. About 90% of weight loss took place in initial 4 hours of immersion in fuel.

Table 4. Penetration and softening point of PMAs before and after immersion.

SBS-modified asphalt	Penetration (dmm)	Softening point (°C)
4%SBS		
Before immersion	60	70.4
After immersion	78	60.9
5%SBS		
Before immersion	55.2	74.8
After immersion	70.2	66.7
6%SBS		
Before immersion	50.8	79.5
After immersion	62.8	71

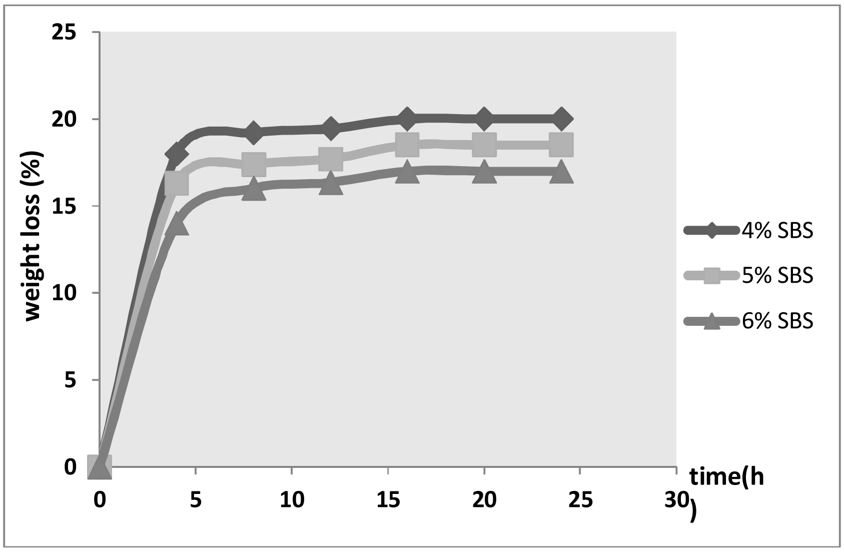

Figure 9. Weight loss of PMBs after immerion in the fuel.

Effect of curing agent (sulfur) content on fuel resistant characterization

The penetration and softening point of the PMAs with sulfur before and after immersion in the fuel are reported in Table 5. Figure 10 shows weight loss curve against time of the PMAs with sulfur after 24h immersions in the fuel. As it is shown in Figure 10, increasing in sulfur level leads to significant improvement in fuel resistance of samples in compare to PMBs without sulfur. The addition of sulfur to SBS modified asphalt resulted in the formation of a chemically vulcanized SBS network structure in the modified binders, and the high temperature performance of the binders was improved. Increasing sulfur levels led to increasing cross linking density in the modified binders which led to higher fuel resistance. In fact, sulfur chemically crosslinks the polymer molecules and chemically couples polymer and asphalt through sulfide and/or polysulfide bonds. In all cases, more than 90% erosion was occurred in initial 4 hours after immersion. Due to commercial aspect of these products, and competition between different companies for producing of such compounds, there is no enough scientific information on these products.

Table 5. Penetration and softening point of PMAs with sulfur before and after immersion.

Sulfur levels	Penetration (dmm)	Softening point (°C)
S: 1.65% SBS		
Before immersion	50	80.36
After immersion	61.5	72.16
S: 3% SBS		
Before immersion	49	85
After immersion	59.1	76.7
S: 3.5% SBS		
Before immersion	49	87.8
After immersion	58.5	80.3

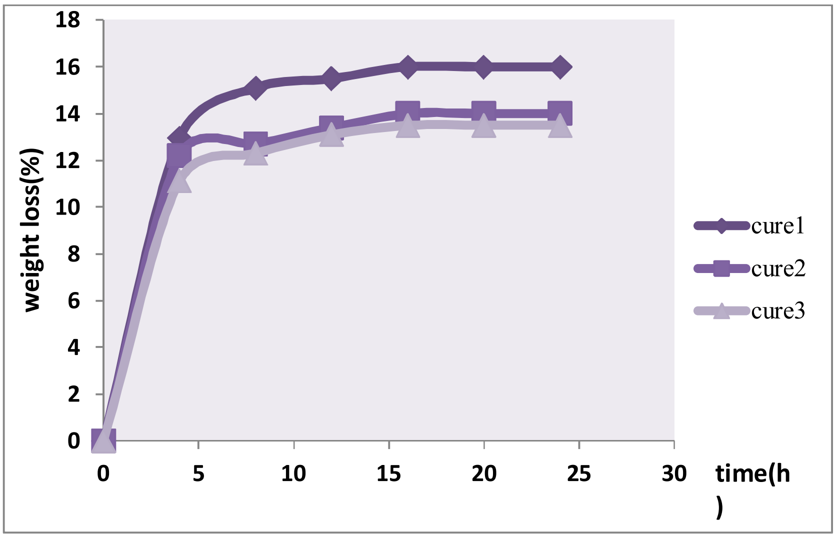

Figure 10. Weight loss of PMBs in the presence of sulfur after immerion in the fuel.

Conclusions

Due to asphalt damages as spillage of fuels and oils occurs, the fuel resistant binders have been developed. These binders were used specially in filling stations, parking lots and passenger terminals. In this work, different content of SBS and sulfur were used to modify the basic asphalt. Conventional properties such as penetration index, softening point and ductility were increased by addition of SBS and sulfur. Adding SBS from 4% to 6%, decrease penetration and temperature susceptibility. Increasing in sulfur level from 1.65% to 3.5% also show the same results. Values of these parameters in PMBs with sulfur were higher than PMBs without sulfur. Rheological properties were improved by modifiers. Increasing in SBS content led to increasing in complex shear modulus and as a result reducing in rutting factor. These values for SBS/sulfur modified asphalts were higher than SBS modified samples. In other word, improvement of the rheological properties like G* and G*/sin δ were reduced the asphalt damages and leading to higher fuel resistance. Also, the standard test method for determining the fuel resistant (immersion in fuel for 24h), were shown that in one hand with increase in SBS content, fuel resistant were improved and weight loss reduced, and in the other hand with increasing in sulfur level in constant SBS content, these values were optimized and weight loss was lower than the SBS modified samples. The addition of sulfur has a significant effect on the compatibility of SBS-modified asphalt. This compatibility led to higher fuel resistance property. Results indicated that more physical bonds with increase in polymer content and more chemically bonding between polymer, sulfur and bitumen by increasing in sulfur content led to more fuel resistance characteristic.

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