JOURNAL OF Applied Polymer SCIENCE

Utilization of Sulfur and Crumb Rubber in Asphalt Modification

M. Anwar Parvez,[1] Mohammed Al-Mehthel,[3] Hamad I. Al-Abdul Wahhab,[2] Ibnelwaleed A. Hussein[1]
[1]Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
[2]Department of Consulting Service, Saudi Aramco, Saudi Arabia
[3]Department of Civil Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
Correspondence to: I. A. Hussein (E-mail: ihussein@kfupm.edu.sa)

ABSTRACT: In this study, waste crumb rubber and sulfur were utilized to enhance the performance of asphalt binder for pavement applications. About 20–50% of sulfur and 1–6% crumb rubber were used. Melt properties were investigated using thermal analysis, dynamic and steady shear rheology, and artificial aging. Rheological tests were carried out in ARES rheometer. Both steady and dynamic shear rheology showed that crumb rubber improved the viscoelastic properties of the sulfur-extended asphalt binder. Crumb rubber modification reduced temperature susceptibility of sulfur/asphalt, and increased the upper grading (performance) temperature of sulfur asphalt. The combined effect of sulfur and crumb rubber reduced the activation energy compared with that of pure asphalt. Zero-shear viscosity and strategic highway research program rutting parameter ($G^*/\sin\delta$) improved by crumb rubber incorporation into the sulfur asphalt binder. Short-term aging improved $G^*/\sin\delta$ with slight increase in activation energy. The addition of sulfur to asphalt matrix increased the viscoelastic properties (G' and G'') of sulfur asphalt. The addition of crumb rubber to sulfur asphalt enhanced the temperature resistance of the binder. Utilization of waste crumb rubber and sulfur in asphalt modification proved to enhance asphalt pavement life. In addition, utilization of such wastes can help in meeting the extra demand for asphalt, reduce the pavement cost, and help in solving a waste disposal problem. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40046.

KEYWORDS: blends; recycling; rheology; rubber; applications

Received 3 July 2013; accepted 9 October 2013
DOI: 10.1002/app.40046

INTRODUCTION

Asphalt cement is used to construct asphaltic surfaces and produce several products such as waterproofing membranes and emulsified asphalts. It is a strategic commodity that is in huge demand due to massive roads and highways construction plans in many countries. Asphalt binder is a thermoplastic material that behaves as an elastic solid at low service temperatures or during rapid loading; and as a viscous liquid at high temperatures or slow loading. This double behavior creates a need to improve the performance of the asphalt binder to minimize stress cracking, which occurs at low temperatures, and permanent deformation, which occurs at high service temperatures. The daily and seasonal temperature variations plus the growth in truck traffic volume, tire pressure, and axle loading have increased stresses on asphalt pavements. This increases the demand to modify asphalt binders (to reduce cracking and deformation). Different methods have been used to upgrade the properties of asphalt binders.[1–4]

Most of the previous work focused on polymer modification of base asphalt. Also, most of the previous work was performed in cold climates (Canada and Sweden) where improvement of the low-temperature performance of polymer-modified asphalt (PMA) was of great concern. For hot climates, such as Saudi Arabia, the high-temperature performance is important for modified asphalt binders. Limited number of publications used sulfur to modify asphalt with SBS polymer and the amount of sulfur was limited to 5–10%.[5,6] The function of sulfur in asphalt paving mixture depends on the sulfur concentration and the sulfur-asphalt ratio. At low sulfur content, where sulfur/asphalt ratio is less than 0.2, sulfur modifies the chemical and rheological properties of asphalt through chemical reactions. At high sulfur/asphalt ratio (>0.2 L), sulfur acts as filler and "structuring agent," improving the workability of the sulfur–asphalt aggregate mixture at processing temperatures (130–160°C) and the mechanical strength of the mixture at service temperatures.[7]

Meanwhile, the rate of production of elemental sulfur is increasing due to increased oil and gas production. For example, Saudi Aramco produces approximately 6000 tons day^{-1} of elemental sulfur. The rate of production is expected to increase to 10,000 tons day^{-1} in a few years. Although sulfur is a vital raw material to manufacture a myriad of products, its abundance has

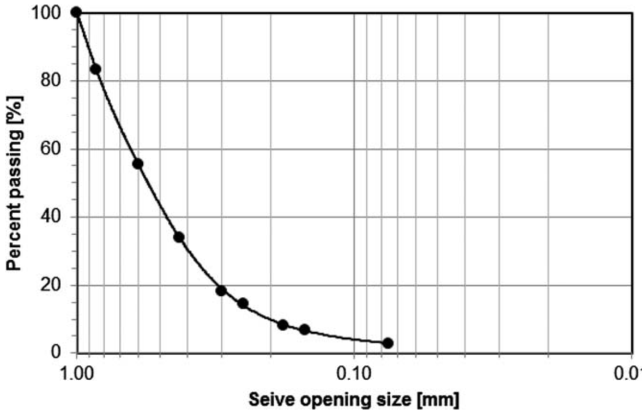

Figure 1. Crumb rubber particles size distribution.

reduced its price worldwide. Meanwhile, the storage of sulfur poses an environmental hazard and usages of this abundant sulfur in a useful, economical, and environmentally friendly way are needed. Sulfur asphalt concrete is one such use.

The early study on the use of sulfur in asphalt mixes showed better properties than the conventional asphalt mixes.[8] But due to high prices of sulfur, the product sulfur asphalt was uneconomical. In view of the increase in asphalt price since the beginning of the 1970s, the product was studied again by the US Bureau of Mines and Federal Highways. However, significant problems with storing hot sulfur at asphalt mix plants as well as preblending the sulfur with the bitumen were encountered. In many oil and gas producing countries, such as the Arabian Gulf countries, there is high production of elemental sulfur from processing plants. Therefore, and for several reasons, there is a renewed interest to seek new and efficient utilization of sulfur. First, sulfur is a valuable natural resource. Second, the income realized from the beneficial use of sulfur can help offset the cost of pollution control and ease a potential disposal problem. Finally, the stockpiling of sulfur in built-up areas without concurrent utilization could create additional pollution problems. Of the several potential uses for sulfur, a sulfur/asphalt combination for highway pavements seems to have the greatest potential for increasing the beneficial consumption of this element. This sulfur asphalt pavement material could utilize much of the elemental sulfur, which will be recovered from fossil fuels.

On the other hand, waste tires discarded every year reach 10 million worldwide.[9] Discarding waste rubber is a huge waste of energy and causes environmental problems because the waste rubber will not degrade. Using waste crumb rubber as dispersant in asphalt is a smart way to solve the waste disposal problem caused by waste tires and to improve the quality of road pavements, such as extending road service life. Waste crumb rubber used in pavement not only can help to solve the waste tire problem, but also can save petroleum resources. The previous use of crumb rubber was limited to modify base asphalt. In some US Patents[10–13] crumb rubber was used to make bituminous pavement, but none of them used sulfur in their embodiments.

The objective of this study is to maximize the utilization of two wastes namely sulfur and crumb rubber in asphalt modification. Here, we used sulfur in the range 20–50% to produce sulfur asphalt binder while rubber was used at 1–6%. Sulfur asphalt with such high amounts of sulfur is brittle. Therefore, it was proposed to add rubber to sulfur asphalt to improve its rheological properties. No previous work was done to examine the effect of crumb rubber on the rheological properties of sulfur asphalt binder. In this article, we will try to explore the use of crumb rubber to improve sulfur asphalt binder performance and possible correlation between crumb rubber content and rheological properties of sulfur asphalt binder at medium and high temperatures of application.

EXPERIMENTAL

Materials

Crumb rubber was collected from a local supplier. The source of the used rubber was waste car tires. Rubber was ground to fine powder to increase the surface area. The crumb rubber gradation was determined using ASTM D5644 procedure. The maximum size of the crumb rubber fines was 1 mm. The sieving results of the crumb rubber fines were given in Figure 1. Waste sulfur (99.9% purity) was collected from Saudi Aramco Gas/Oil Separation Plants. It was a waste product from oil and gas processing plants. Asphalt cement was obtained from a local refinery. The results of the differential scanning calorimetry (DSC) of these samples were presented in Figure 2.

Sample Preparation

Sulfur and pure asphalt were blended in a high shear blender. The elemental sulfur pellets were ground to fine powder before feeding to the blender. The blender acts as a batch stirred tank with a constant temperature bath. Typical mixing procedure was as follows: steel cans of approximately 1000 mL were filled with 250–260 g of asphalt and put in a thermoelectric heater. Crumb rubber was mixed with base asphalt at a temperature of 180°C in the blender for 2 min. The can with the sample was sealed from the top to prevent extra air oxidation. The sealed can was then put in an oven of the same temperature for 2 h for swelling of rubber in asphalt. After 2 h of conditioning, the can with the sample was dipped into oil bath having a temperature controlled at 145 ± 1°C. When the temperature of the rubber mixed asphalt reached 145°C, a locally made high shear

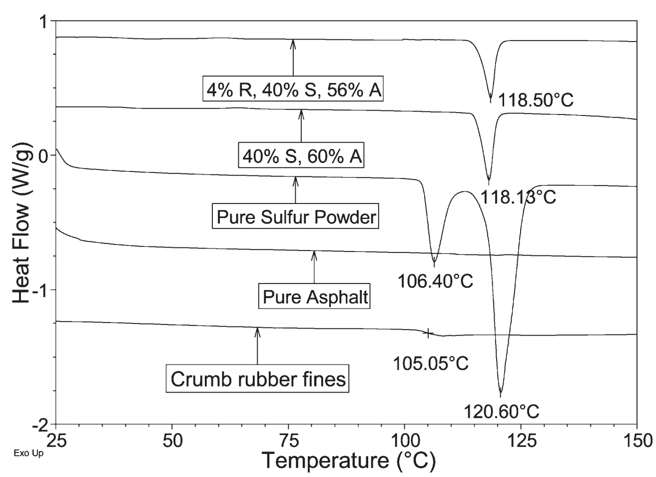

Figure 2. DSC scans of the modified asphalt binder and its compositions.

Table I. Percentage Compositions of Sulfur-Modified Asphalt Binder

	Percentages of different components		
Sample #	Sulfur%	Asphalt%	Crumb rubber%
1	0	100	0
2	20	80	0
3	20	79	1
4	20	78	2
5	20	76	4
6	20	74	6
7	30	70	0
8	30	68	1
9	30	66	2
10	30	64	4
11	30	62	6
12	40	60	0
13	40	58	1
14	40	56	2
15	40	54	4
16	40	52	6
17	50	50	0
18	50	49	1
19	50	48	2
20	50	46	4
21	50	44	6

mixer was dipped into the can and set to about 2500 rpm. Calculated amount of elemental sulfur powder was added gradually with asphalt/rubber. The bath temperature was maintained at 145 ± 1°C. Samples were blended for 20 min at high shear to confirm uniform distribution of sulfur and rubber in the asphalt matrix. Asphalt samples were poured into rubberized molds before being used for rheological testing. The samples specimens were stored in a refrigerator at 5°C. Twenty samples of sulfur-modified asphalt binders and pure asphalt binder were prepared and tested. Detailed samples information is presented in Table I.

DSC Measurements

The thermal behaviors of the pure and modified asphalt binder as well as the compositions of the asphalt binder were determined by means of a TA Q1000 DSC. Samples of 7–10 mg were weighed and sealed in aluminum pans. Melting temperature measurements were performed by heating samples from room temperature to 150°C. A heating rate of 5°C min^{-1} was applied and nitrogen was used as the purge gas at a flow rate of 50 mL min^{-1}.

FTIR Characterization

Fourier transform infrared spectroscopy (FTIR) technique was used to determine the chemical bond changes of pure and modified asphalt binder. FTIR measurement was carried using a Nicolet 6700 spectrometer from Thermo Electron^{TM}. All the FTIR spectra were taken in the absorbance mode and in the range 600–4000 cm^{-1} at room temperature. FTIR spectra were obtained using a spectral resolution of 4 cm^{-1} and 30 co-added scans.

Rolling Thin-Film Oven Test

Rolling thin-film oven test (RTFO) was used to perform aging of asphalt binders according to ASTM D 2872 procedure. This test simulates the aging process that takes place during the production and up to the first year of the service life of the pavement. Base asphalt as well as modified asphalt were poured into cylindrical bottles. About 35 g of asphalt sample were poured in each cylindrical bottle. Then the bottles were placed horizontally in a convection oven, which was rotated at 163°C for 85 min. Air was supplied into the bottle to accelerate aging. This process created a thin film of asphalt on the inside of the bottles. After completing the run, samples were collected for rheological testing in ARES.

Rheological Tests

Dynamic and steady rheological tests were carried out to investigate the effect of rubber on the rheology of sulfur-modified asphalt. The dynamic temperature step measurements for the samples were performed in ARES rheometer. This is a constant strain rheometer equipped with a heavy transducer (range 2–2000 g for normal force; 2–2000 g-cm for torque). All tests were carried out in the range 64–85°C using a parallel plate set of 25 mm diameter. With the sample in position, the oven was closed and the sample heated at 64°C for about 5 min; thereafter, the gap between the plate platen was adjusted to 1.5 mm by lowering the upper platen force transducer assembly at a constant load of 500 g. The melt that extruded beyond the platen rim by this procedure was cleaned off. Strain in the linear viscoelastic range (strain amplitude, $\gamma°$ of 12.5%) and frequency of 10 rad s^{-1} was used in all tests. In all the experiments, nitrogen gas was continuously used for heating the samples during testing to avoid oxidation during testing. A holding period of 5 min was allowed before beginning measurements when the temperature reaches steady state. The Orchestrator software was used to calculate the dynamic shear viscosity, storage modulus, complex modulus, and phase angle for all samples.

Dynamic frequency sweep tests were conducted at 50°C and a frequency of 100–0.1 rad s^{-1} and a constant strain of 12.5%.

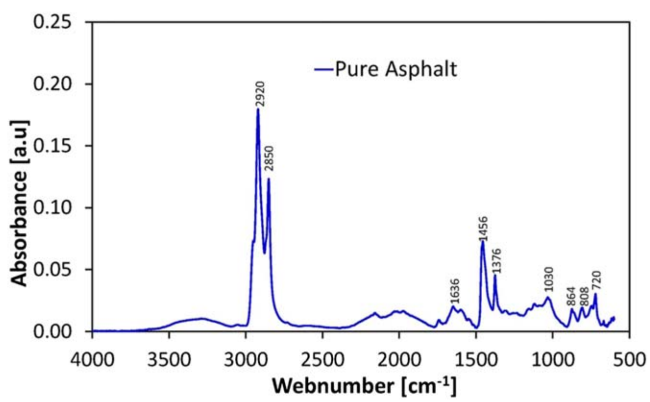

Figure 3. FTIR spectra of pure asphalt binder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Assignations of the Main Bands of the FTIR Spectra

Webnumbers (cm^{-1})	Assigned bands
2920, 2850	υC—H aliphatic
1636	υC=C aromatic
1456	δC—H of —$(CH_2)_n$— (aliphatic index)
1376	δC—H of CH_3 (aliphatic branched)
1030	υS=O sulfoxide
808, 864	υC=C of alkenes
721	δC—H or δC—S

Note: υ = stretching, and δ = bending.

Different linear viscoelastic variables were calculated using TA Orchestrator software. Steady shear rheological tests were conducted at 50°C and a shear rate in the range 0.01–10 s^{-1}.

RESULTS AND DISCUSSION

Thermal Characterization

DSC results of pure sulfur, crumb rubber, pure asphalt, and two sulfur-modified asphalt binders were shown in Figure 2. There was no peak in the DSC thermogram of pure asphalt. So, asphalt used in this study was virgin asphalt. Crumb rubber had no melting point; rather it had a transition at ~105.5°C. The glass transition of rubber is much below that so this transition is not a glass transition. The DSC scan of pure elemental sulfur showed that sulfur had two melting peaks. The first melting peak is at 106.40°C, which corresponds to rhombic sulfur. The second peak is at 120.6°C and it corresponds to monoclinic form of sulfur. The literature values were also in the same range.[14] The modified asphalt binder had three different constituents namely: crumb rubber, sulfur, and asphalt with different weight percentages. One interesting observation in the DSC scan of sulfur-modified asphalt binder was that it had only one melting point, which was around 118°C. It ensured that rhombic sulfur was converted to monoclinic sulfur in the modification process. DSC scan of 40/60 sulfur/asphalt showed a melting point at 118.13°C, which was very close to the melting point of monoclinic sulfur. The modified asphalt binder with 40% sulfur, 52% asphalt, and 4% rubber had little influence on the melting point of the sulfur (~118.5°C). So, rubber modification had slightly increased the melting point in comparison to the 40/60 sulfur/asphalt binder. The mixing temperature used in the study was 145°C.

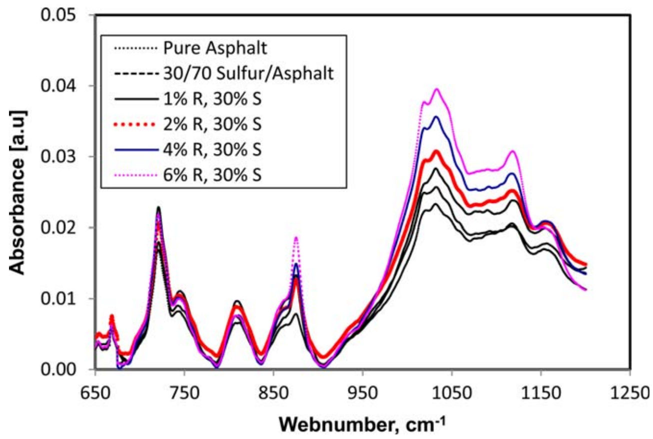

Figure 4. FTIR spectra of pure and modified asphalt binders. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FTIR Results of Asphalt Binders

Figure 3 represents the FTIR spectra of pure asphalt binder and Table II listed the main bonds present in asphalt. Similar results were also mentioned in the literature.[15] We did not elaborate on the method of analysis since we used the same approach. The bonding of sulfur-modified asphalt binders were also similar to the one presented in Figure 3 but with different intensities.

The FTIR spectra for pure and 30% sulfur-modified asphalt binders were shown in Figure 4. The main differences between pure and sulfur-modified asphalt binders were in the range 600–1250 cm^{-1}. The FTIR spectra of other sulfur-modified binders were also similar to that presented in Figure 4. It was noticed that the intensities of the bonds had changed in modified binders. The relative change of bonding was calculated using the following equations:

$$I_{S=O} = \frac{\text{Area of sulfoxide band centered around 1030 cm}^{-1}\text{ for modified asphalt binder}}{\text{Area of sulfoxide band centered around 1030 cm}^{-1}\text{ for pure asphalt binder}} \quad (1)$$

$$I_{C-S} = \frac{\text{Area of C—S band centered around 720 cm}^{-1}\text{ for modified asphalt binder}}{\text{Area of C—S band centered around 720 cm}^{-1}\text{ for pure asphalt binder}} \quad (2)$$

Based on the above eqs. (1 and 2) the ratios of the areas were calculated and the results were given in Figure 5. The relative intensities of the C=S and S=O bonds increased in comparison with pure asphalt binders. This confirmed the chemical crosslinking in modified asphalt binders. It was also mentioned in the literature that part of the sulfur added reacts chemically with asphalt to form carbon–sulfur bond and polysulfide bond.[16] The intensity of C—S in asphalt had increased by ~30% in 30/70 sulfur/asphalt binder as shown in Figure 5. Further increase in crumb rubber concentration had little influence on the intensity of C—S bond. However, the intensity of S=O bond increased significantly with the addition of crumb rubber.

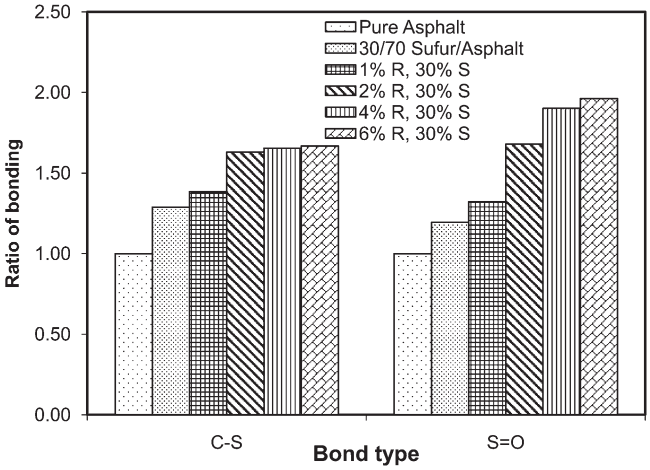

Figure 5. The intensity of bonding in pure and modified asphalt binders.

So, it can be concluded that the increase in C—S bond was due to the addition of sulfur to asphalt whereas the increase in S═O bond resulted from crumb rubber addition. Sulfur was expected to crosslink with unsaturated nonring compounds in asphalt.

Rheological Characterization

Dynamic Frequency Sweep Test. Dynamic frequency sweep test for all binders were conducted at 50°C and 100–0.1 rad s^{-1} in the linear viscoelastic range. Typical linear viscoelastic properties of sulfur-modified asphalt binders with various amounts of crumb rubber and sulfur were displayed in Figure 6. Figure 6(a,b) showed the dynamic storage modulus, G', as function of frequency, ω, for 30 and 50% sulfur-modified asphalt binders. The results were shown for 0, 1, 2, 4, and 6% crumb rubber by weight. The results for 20 and 40% sulfur-modified binders were not shown here as the trends were very similar to the presented figures.

Sulfur-modified asphalt binders improved, G' as compared to base asphalt for the whole ω range. The increase in G' values was higher for higher concentration of crumb rubber. The storage modulus, G', was highly sensitive to the morphological state of a heterogeneous system. The value of G' is an indication of elasticity boosting due to asphalt modification. The relative increment in G' was well understood by the modification index as defined by the following equation:

$$I_{G'} = \frac{G' \text{ of crumb rubber modified sulfur asphalt binder}}{G' \text{ of sulfur asphalt binder}} \quad (3)$$

Here, the definition of $I_{G'}$ was used for the binders that contain sulfur as well as crumb rubber. For example, $I_{G'}$ for 30% sulfur-modified binders is the ratio of G' of rubber-modified binders to the G' of 30/70 sulfur/asphalt binder. So, the significance of this index was to calculate the relative influence of replacing the portion of asphalt by the same amount of crumb rubber. $I_{G'}$ values were calculated for $\omega = 1$ rad s^{-1} at 50°C and showed in Table III for different binders.

Table III showed that $I_{G'}$ increased with respect to both sulfur and crumb rubber concentration. According to time–temperature superposition principle low-frequency data corresponds to high-temperature properties. So, High values of G' at lower frequency provide more flexibility of asphalt binder at higher temperature. Further analysis of the frequency sweep data were carried out to correlate G' with crumb rubber and sulfur concentrations. The influence of crumb rubber concentration on G' was shown in Figure 7. The data were well fitted to the equation given below:

$$G' = aC_R + bC_s \quad (4)$$

where C_R and C_S are the percentage of crumb rubber and sulfur in asphalt matrix. Table IV listed two parameters (a, b) and fit quality R^2. It showed that storage modulus, G' increased linearly with crumb rubber for all sulfur/asphalt binders. Adjusted constant a increased with sulfur content whereas b decreased with sulfur content. The slope of the straight line increased with the increase in sulfur content suggesting that the amount of sulfur also contributes to the increase in G'. Another observation from the linear viscoelastic results was that the increment in G' at high ω is lower than that at low ω. The high ω corresponds to low-temperature behavior of asphalt binders. So, comparatively

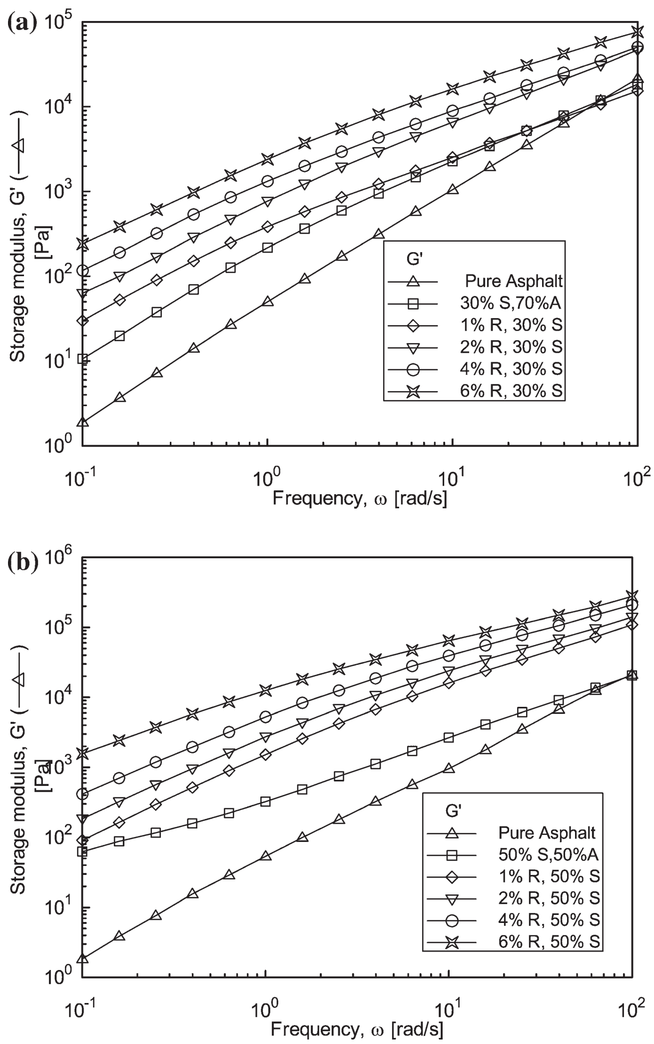

Figure 6. $G'(\omega)$ for (a) 30% sulfur-modified asphalt binders at 50°C and (b) 50% sulfur-modified asphalt binders at 50°C.

Table III. Modification Indexes for Crumb Rubber-Modified Sulfur Asphalt Binders

Crumb rubber content (%)	$I_{G'}$ for 20% sulfur	$I_{G'}$ for 30% sulfur	$I_{G'}$ for 40% sulfur	$I_{G'}$ for 50% sulfur
1	2.17	1.67	2.04	2.92
2	2.53	2.05	3.30	5.14
4	3.09	3.07	6.31	10.31
6	4.57	5.34	8.93	23.61

lower values of G' at high frequency were favorable for asphalt pavement.

Figure 8(a,b) displayed the well-known Black diagram (phase angle vs. G^*) representation for 30 and 50% sulfur binders at 50°C. The reduction of phase angle is related to the presence of elastic networks or entanglements in the modified binder.[17] It was noticed that incorporation of crumb rubber in sulfur/asphalt binder decreased the phase angle which indicated improvement in elastic behavior. This improvement can be due to the degree of crosslinking and entanglement produced by crumb rubber and sulfur with asphalt matrix. The combined effect of shear and heat in the blender could result in several phenomena in the modified asphalt matrix. Some of them can be as: (1) polymerization of sulfur to form longer chain, (2) increase in crumb rubber particle size due to swelling effect in the asphalt matrix, and (3) change in compositions of asphalt by thermal and mechanical degradation.[18] The combination of these phenomena could lead to crosslinking/entanglement and enhance the viscoelastic properties of modified asphalt binders. The reaction and crosslinking of sulfur asphalt were discussed earlier in the FTIR section.

Temperature Sweep Measurements

Temperature sweep test was conducted for all binders to extract the values of complex moduli, G^*, and phase angle, δ, as function of temperature. According to the strategic highway research program (SHRP), the stiffness parameter $G^*/\sin\delta$ is a factor used to estimate the rutting resistance of asphalt binder.[19] It should be larger than 1 kPa at the maximum pavement design

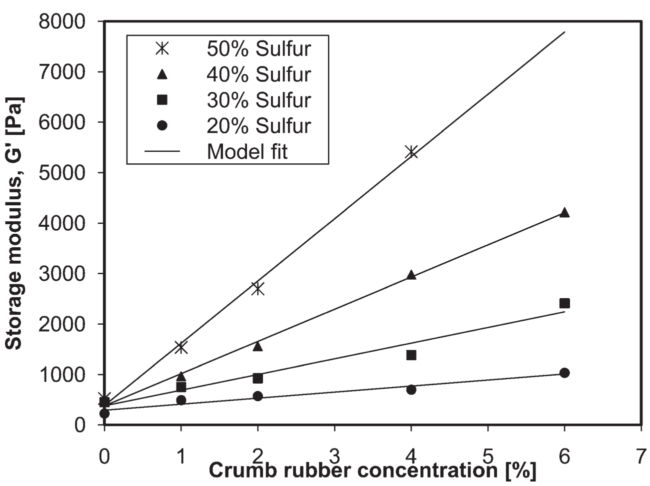

Figure 7. Storage modulus as function of sulfur and crumb rubber concentration (ω=1 rad s^{-1} at 50°C).

temperature for unaged original asphalt, when measured at 10 rad s^{-1} to simulate traffic loading. Higher values of $G^*/\sin\delta$ were expected to give a high resistance to permanent deformation. Figure 9 showed $G^*/\sin\delta$ versus temperature for all the sulfur-modified asphalt binders as function of crumb content at 76°C. This temperature was chosen on the basis that the maximum local pavement temperature for Saudi Arabia is 76°C for hot summer season.[20] It showed that sulfur-modified asphalt binders without crumb rubber modification cannot fulfill SHRP criteria as the value of $G^*/\sin\delta$ was less than 1 kPa for all samples. So, there is a necessity of modification of these binders to increase $G^*/\sin\delta$ to improve rutting resistance. $G^*/\sin\delta$ for the 20% sulfur-modified asphalt was less than 1 kPa when even 6% crumb rubber was used. In the case of 30% sulfur-modified binders, 4% crumb rubber was required to reach $G^*/\sin\delta \geq 1$ kPa, whereas for 40 and 50% sulfur-modified binders, 1% crumb rubber was enough to reach $G^*/\sin\delta \geq 1$ kPa.

The maximum temperature attained by sulfur-modified asphalt binders at $G^*/\sin\delta$ equal to 1 kPa was given in Table V. Addition of crumb rubber to sulfur/asphalt binders increased the maximum attainable temperature for all the binders. The value of $G^*/\sin\delta$ for pure asphalt was 1 kPa at 68°C which indicated the need of pure asphalt for modification to achieve the performance grading. The maximum temperature of all the sulfur-modified asphalt binders without crumb (zero crumb content) was less than 76°C. However, additions of crumb rubber to those binders improved it significantly. So, crumb rubber improved rutting resistance of sulfur-modified asphalt. Also, for the same percentage of rubber, the increase in sulfur content increased $G^*/\sin\delta$ (see Fig. 9). Addition of crumb rubber was expected to add toughness and flexibility to the binders.

The effect of temperature on pure and modified asphalt binders was shown in Figure 10. With increasing temperature $\tan\delta$ increased and complex modulus decreased for pure asphalt binder. The variations in $\tan\delta$ and G^* slowed down for the sulfur-modified asphalt binders. A similar phenomenon was

Table IV. Model Parameters for Eq. (4)

Sulfur content (%)	Model parameters		
	a	b	R^2
20	119.60	14.65	0.948
30	310.47	12.62	0.958
40	637.80	9.49	0.998
50	1233.40	7.72	0.996

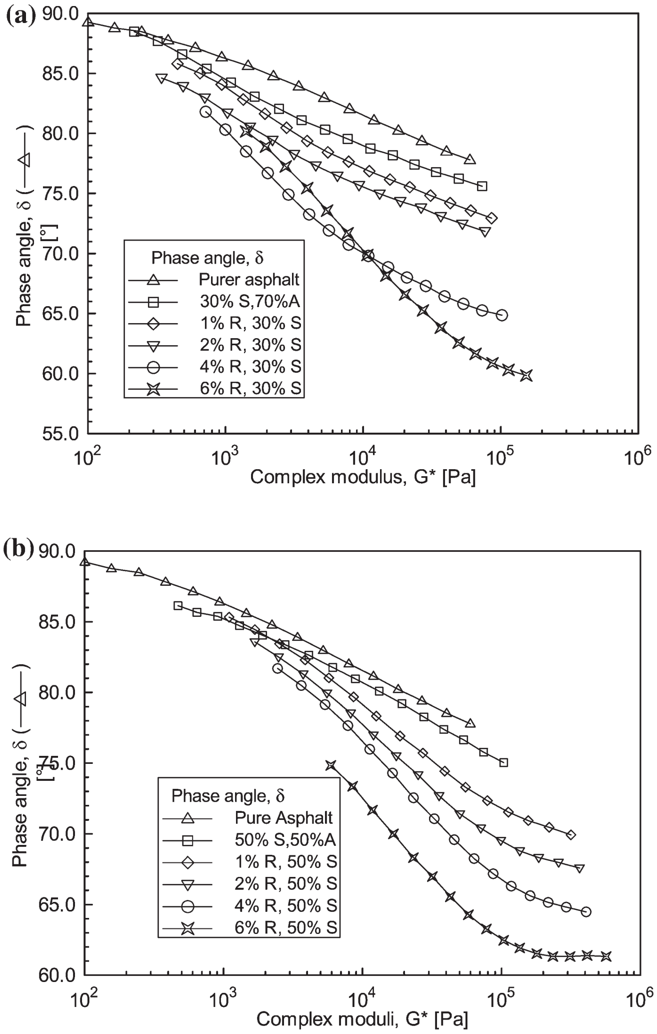

Figure 8. Black diagram representation of (a) 30% sulfur binders at 50°C and (b) 50% sulfur binders at 50°C.

reported in an early publication[21] for polymer-modified asphalt binder. The addition of sulfur led to the increase in G^* more significantly at elevated temperatures, and tanδ curve became flatter over a wide range of tested temperatures. It indicated that the elasticity of the modified binder had improved effectively with the addition of sulfur due to the formation of a chemically crosslinked network in the modified binders as described in the FTIR results. However, the variation of tanδ with sulfur content was inconsistent with sulfur content, which suggests a complex morphology sensitive to sulfur content.

Temperature sweep data were further analyzed to check the effect of temperature on asphalt viscosity. Viscosity-temperature relationships of asphalt binder were expressed by the well-known Arrhenius equation as follow:

$$\frac{G^*}{\omega} = {}^* = \mathrm{Ae}^{\left(E_a/_{\mathrm{RT}}\right)} \tag{5}$$

where E_a is the flow activation energy, A is the pre-exponential term, and R is the universal gas constant. E_a is an important factor that strongly influences the viscosity. Figure 11 showed complex viscosity versus $1/T$ for the 30% sulfur-modified

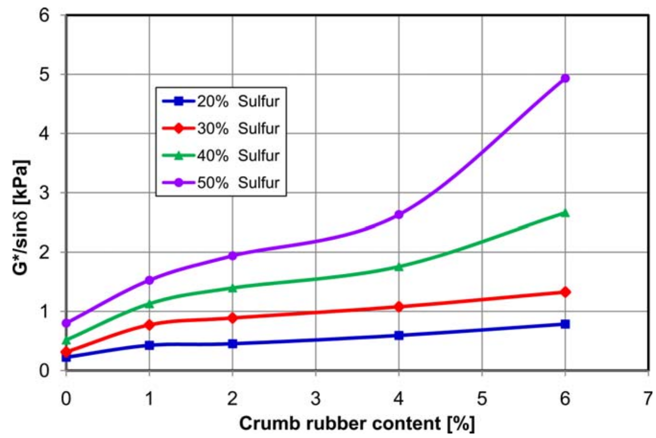

Figure 9. $G^*/\sin\delta$ versus crumb rubber content for unaged modified binders at 76°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

asphalt binders at 10 rad s^{-1}. As the trend is very similar for other binders, only one figure was shown here. The data given in Figure 11 showed good fit to Arrhenius model. E_a was calculated using equation 5 and the values for different binders were given in Table VI. Activation energy for pure asphalt was calculated to be 113.07 kJ mol^{-1}.

It was observed that addition of sulfur to asphalt reduced the activation energy of sulfur/asphalt binder as compared to pure asphalt. The crumb rubber-modified asphalt binders showed lower activation energy than pure asphalt except for the 50% sulfur-modified binders. The exception of the 50% sulfur-modified binders is likely due to a difference in the morphology as suggested by the high complex modulus for this blend at all temperatures as shown in Figure 10. Activation energy, E_a was related to the binder thermal susceptibility.[22] The lower activation energy of asphalt binders means lower temperature susceptibility. So, from Table VI it could be concluded that the 20, 30, and 40% sulfur-modified asphalt binders would be less temperature susceptible than pure asphalt. However, the 50% sulfur-modified asphalt binder showed higher E_a, consequently the binders would be more temperature susceptible.

Rheological data of sulfur-modified asphalt binders were analyzed by introducing a modification index I_M.[23] A simple

Table V. Maximum Temperature at Which $G^*/\sin\boldsymbol{\delta}$ is Equal to 1 for Sulfur-Modified Binders

	Maximum temperature attained (°C) at $G^*/\sin\delta$ =1 kPa			
Crumb rubber content (%)	20% Sulfur	30% Sulfur	40% Sulfur	50% Sulfur
0	64	65	67	73
1	67	73	77	79
2	68	75	79	82
4	71	77	81.5	85
6	73.5	80	85	89

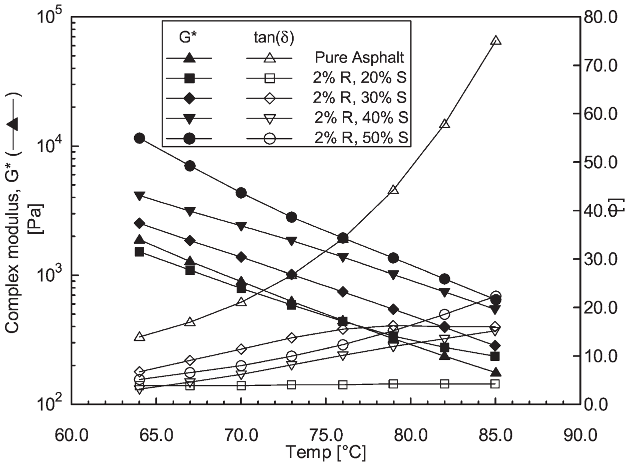

Figure 10. Complex modulus and tanδ versus temperature for selected binders.

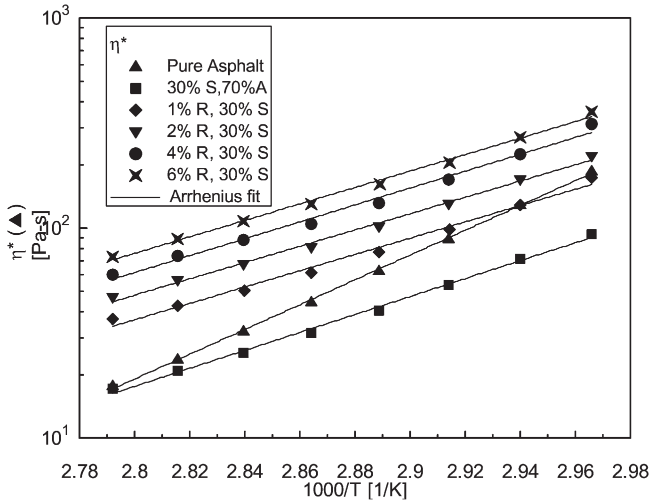

Figure 11. Effect of temperature on complex viscosity (30% sulfur-modified binders).

modification index was obtained from temperature sweep data using the following equation:

$$I_M = \frac{G'_R}{G'_S} \quad (6)$$

where G'_S was the storage modulus of sulfur-modified asphalt binder with zero rubber content and G'_R was the storage modulus of the corresponding sulfur/asphalt binders with rubber content 1–6% for $\omega = 1$ rad s^{-1}. Equation 6 showed the effect of rubber modification on sulfur/asphalt binders. The modification index was calculated from temperature sweep test and presented in Figure 12. Figure 12(a,b) depicted that the viscoelastic properties of rubber-modified sulfur asphalt binder increased with respect temperature as the crumb rubber content increased. The effect is minimum for the case of 20% sulfur binders and significant for other binders (30–50% sulfur). Figure 12(a) showed the effect of crumb rubber content whereas Figure 12(b) showed the effect of sulfur content. Both additives had positive effect on the modification index. The slope of the straight line increased as the amount of additives was increased. It was also interesting to observe that the variation of the modification index within a certain temperature interval is controlled by the material sensitivity to temperature variation. In this way, the variation of I_M with temperature was an indirect indicator of the thermal sensitivity and could be used to describe the influence of temperature on the rheological properties. However, higher I_M values could also indicate that the corresponding sample would be stiff at lower temperature, which might lead to formation of cracks. So, there should be an optimum amount of the additives (sulfur and crumb rubber) to be used for both high- and low-temperature range application. The improvements of the elastic properties with temperature were likely due to the crosslinking of sulfur with asphalt. The reason for the increase in the elastic properties with temperature was due to the swelling of crumb rubber and filling of the free volume in asphalt created by thermal expansion. The addition of sulfur to asphalt matrix increased the viscoelastic properties (G' and G'') of the modified binder. The addition of crumb rubber to sulfur asphalt enhanced the temperature resistance of the binder.

Steady Shear Rheology

Steady rate sweep tests were conducted for all binders at 50°C and a shear rate in the range 0.01–10 s^{-1}. Steady shear viscosity as function of shear rate was plotted in Figure 13 for 40% sulfur-modified binders. As the behaviors of the other binders were also very similar, only one figure was provided to show the general trend. Pure asphalt samples displayed long Newtonian plateau up to a shear rate of ~2 s^{-1}. The crumb rubber-modified binders showed very small width of Newtonian plateau followed by shear thinning behavior at high shear rate. Similar behavior was also reported for polymer-modified asphalt binders.[24] These types of shear viscosity data can be well

Table VI. Activation Energy of Crumb Rubber-Modified Sulfur Asphalt Binders

Crumb rubber content (%)	E_a for 20% sulfur-modified binders (kJ mol^{-1})	E_a for 30% sulfur-modified binders (kJ mol^{-1})	E_a for 40% sulfur-modified binders (kJ mol^{-1})	E_a for 50% sulfur-modified binders (kJ mol^{-1})	E_a for pure asphalt (kJ mol^{-1})
0	99.98	81.90	72.89	93.79	113.07
1	86.21	74.31	85.84	133.71	
2	91.10	76.09	95.90	135.95	
4	97.64	77.03	99.64	133.94	
6	99.34	77.91	103.22	130.85	

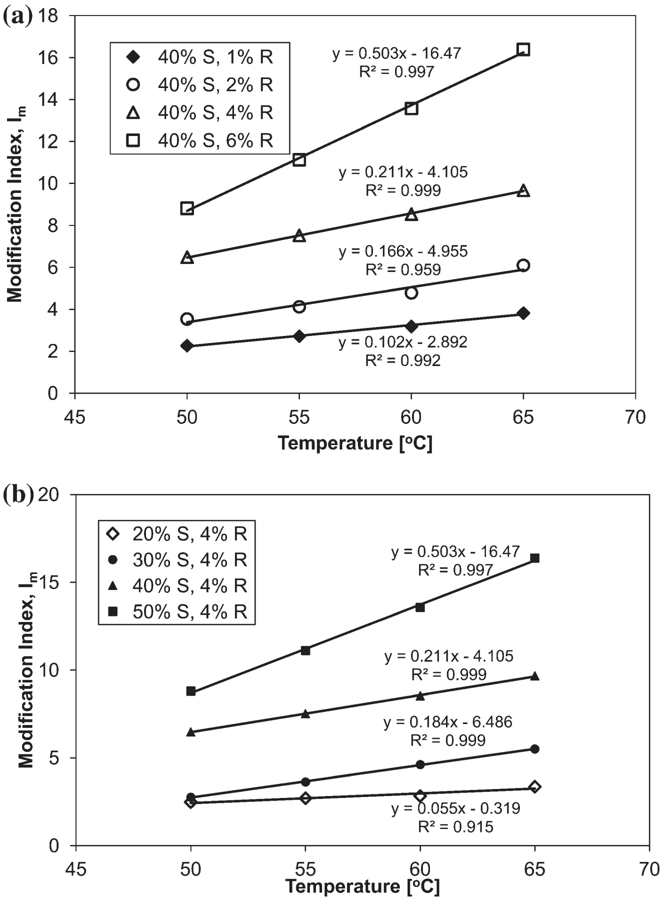

Figure 12. Modification index for (a) 40% sulfur-modified binders for 1–6% rubber content and (b) 4% crumb rubber content for 20–50% sulfur binders.

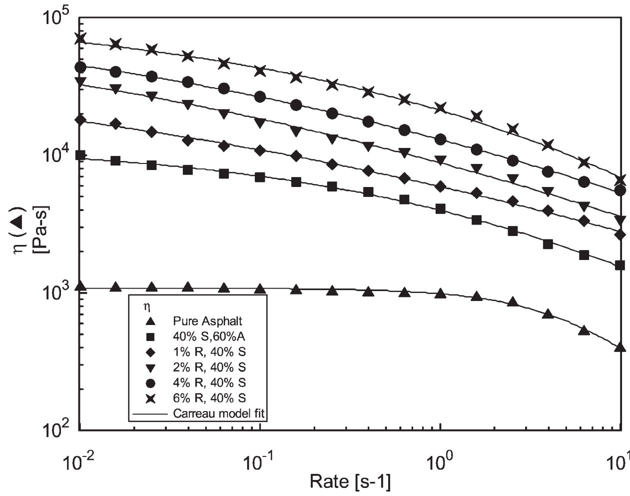

Figure 13. Steady shear viscosity of 40% sulfur/asphalt binders at 50°C.

modeled by Carreau model which is given by the following equation:

$$\eta = \frac{\eta_o}{\left[1+(\dot{\gamma}/\dot{\gamma}_c)^2\right]^a} \tag{7}$$

where, η_0 is the zero-shear viscosity, $\dot{\gamma}_c$ is the critical shear rate at the onset of shear thinning region and a is a parameter related to the slope of shear thinning region. The shear rate viscosity data were well fitted by the model as can be seen from Figure 13. Addition of crumb rubbers decreased the Newtonian plateau and broadened the shear-thinning region. This shear thinning behavior was attributed to the crosslinking of sulfur and asphalt molecules as well as the heterogeneity in molecular weight caused by the addition of rubber. As shear rate was increased, it would likely destroy the network and thereby reduces viscosity sharply.

In the last decade, researchers have observed that the SHRP rutting parameter $G^*/\sin\delta$ is not very effective in predicting the rutting performance of binders, especially in the case of modified binders.[25,26] For such case a new parameter zero-shear viscosity, η_o was suggested by many researchers as a possible measure for the rutting resistance of modified asphalt binders.[27,28] η_o and $\dot{\gamma}_c$ were calculated for all binders using the eq. 7 and the values were shown in Table VII. η_o increased with the increase in sulfur and crumb rubber content which supports the previous results from dynamic shear rheology. The increment in η_o was more pronounced in binders with high sulfur content (40 and 50%). The onset of shear thinning ($\dot{\gamma}_c$) decreased with the increase in sulfur and crumb in the binder. The steady shear data analysis showed that both sulfur and crumb rubber modification added non-Newtonian behavior to the modified asphalt binder. Also, the increase in η_o for rubber-modified sulfur asphalts suggested improved rutting resistance. So, the steady shear data analysis supports our previous findings through dynamic shear measurements.

Rolling Thin-Film Oven Test

Figure 14(a,b) showed the effect of short-term aging on selective crumb rubber-modified sulfur/asphalt binders. Aging increased

Table VII. Carreau Model Parameters for Crumb Rubber-Modified Sulfur/Asphalt Binders at 50°C

Crumb rubber content (%)	η_o (Pa-s)				$\dot{\gamma}_c$ [s^{-1}]			
	20% S	30% S	40% S	50% S	20% S	30% S	40% S	50% S
0	2672	7324	12,053	22,054	2.512	2.100	1.527	1.262
1	3548	7679	18,526	33,489	0.441	0.020	0.015	0.012
2	4455	8551	25,640	45,685	0.067	0.010	0.007	0.006
4	5354	14,236	52,497	78,452	0.033	0.007	0.005	0.004
6	6129	36,600	95,175	202,411	0.022	0.006	0.004	0.003

SHRP rutting parameter $G^*/\sin\delta$ as well as complex viscosity, η^* for the whole temperature range covered in this study. Table VIII listed the values of $G^*/\sin\delta$ at 76°C and activation energy E_a extracted from Figure 14(a,b). According to SHRP the values of $G^*/\sin\delta$ should be $\geq$1 kPa before RTFO and $\geq$2.2 kPa after RTFO. So, all binders met short-term aging criteria for Superpave binder's requirement (see Table VIII). In addition, aging increased the activation energy of the selected binders. The increase in activation energies for the selected RTFO samples was in the range 6–25% over unaged samples.

The improvement in rheological properties after aging was attributed to three major factors. First, aging has changed the chemical compositions of asphalt. A modification of both the quantity and quality of asphaltenes and resins is likely to occur. The increase in asphaltenes and resins contents was a consequence of the effect that aging has on the elastic properties of asphalt. Second, polymerization of sulfur and its crosslinking with asphalt composition, which was accelerated by high temperature (163°C) and air oxidation. Also, crosslinking and entanglement of crumb rubber with asphalt and sulfur could happen through aging.

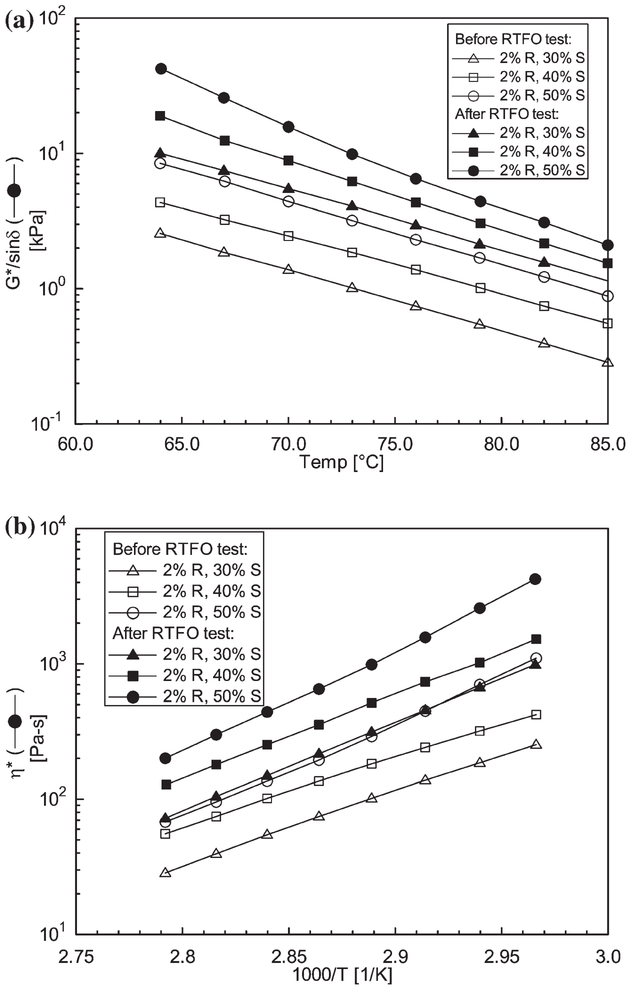

Figure 14. Effect of aging on (a) $G^*/\sin\delta$ for selective modified binders and (b) complex viscosity, η^* for selective modified binders.

Table VIII. Effect of Short-Term Aging on the Selective Binders

Sample	$G^*/\sin\delta$ (kPa) at $T = 76°C$ Before RTFO	$G^*/\sin\delta$ (kPa) at $T = 76°C$ After RTFO	E_a (kJ mol^{-1}) Before RTFO	E_a (kJ mol^{-1}) After RTFO
30% S, 2% R	0.75	2.96	76.09	97.25
40% S, 2% R	1.38	4.32	95.90	118.23
50% S, 2% R	2.30	6.53	135.95	144.55

CONCLUSIONS

Utilization of waste sulfur and rubber in asphalt modification was investigated. The influence of crumb rubber on the rheology of sulfur-modified asphalt binders were investigated by FTIR, rheological and thermal characterization techniques. The following conclusions were drawn on the basis of this investigation:

1. FTIR results showed increase in C—S bond due to sulfur incorporation and S=O bond increased due to crumb rubber addition to sulfur asphalt binder.
2. The addition of crumb rubber had increased the elastic properties of the sulfur-modified asphalt binders as manifested by the increase in G' and the modification indexes. A linear relationship was obtained for the low-frequency ($\omega = 1$ rad s^{-1}) dynamic shear data. It was shown that crumb rubber increases both viscous and elastic properties linearly. This improvement was higher for higher concentration of sulfur and crumb rubber.
3. SHRP rutting parameter ($G^*/\sin\delta$) as well as zero shear viscosity increased with the increase in crumb rubber percentages for all sulfur extended asphalt binders, which suggested that crumb rubber modification would likely increase rutting resistance at high temperature.
4. A modification index (I_M) was defined to quantify the improvement of viscoelastic properties of crumb rubber-modified sulfur extended asphalt binders. It was shown that crumb rubber improved the high-temperature viscoelastic properties.
5. Steady shear rheology indicated that crumb rubber modification of sulfur extended asphalt binders increased the steady shear viscosity. Addition of crumb rubber to sulfur extended asphalt decreased the Newtonian plateau and increased the shear thinning behavior.
6. Short-term aging through RTFO improved the rheological properties of the modified binders by crosslinking and entanglement of sulfur and crumb rubber asphalt compositions.

The crumb rubber-modified sulfur asphalt showed better properties compared to the conventional asphalt binder. Utilization of these two industrial wastes in asphalt modification can meet the extra demand for asphalt, reduce the price, and improve asphalt pavement life. Application of this process will help in solving the waste disposal problem and keep environment clean.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of Saudi Aramco through research project # CHE 02336. They are also thankful to KFUPM for supporting this research and Saleh Al-Idi for his suggestions.

REFERENCES

1. Iqbal, M. H.; Hussein, I. A.; Al-Abdul Wahhab, H. I.; Amin, B. *J. Appl. Polym. Sci.* **2006**, *102*, 3446.
2. Hussein, I. A.; Iqbal, M. H.; Al-Abdul Wahhab, H. I. *Rheol. Acta* **2005**, *45*, 92.
3. Hussein, I. A.; Al-Abdul Wahhab, Iqbal, M. H. *Can. J. Chem. Eng.***2006**, *84*, 480.
4. Polacco, G.; Stastna, J.; Biondi, D.; Antonelli, F.; Vlachovicova, Z.; Zanzotto, L. *J. Colloid Interface Sci.* **2004**, *280*, 366.
5. Zhang, F.; Yu, J.; Han, J. *Constr. Build. Mater.* **2011**, *25*, 129.
6. Zhang, F.; Yu, J.; Wu, S. *J. Hazard. Mater.* **2010**, *182*, 507.
7. Lee D. Y. *Ind. Eng. Chem. Prod. Res. Dev.* **1975**, *14*, 171.
8. Benzowitz, J.; Boe, E. S. *Proc. ASTM* **1938**, *38*, 539.
9. Qingxi, Y. *World Rubber Ind.* **2010**, *37*, 50.
10. Liang, Canada, U.S. Pat. 5,719,215, **1998**.
11. Syvester, USA, U.S. Pat. 7,074,846B2, **2006**.
12. Benko USA, U.S. Pat. 6,387,965B1, **2002**.
13. Bernard, USA, U.S. Pat. 5,936,015, **1999**.
14. Zupancic, A. *Zumer, M. Can. J. Chem. Eng.* **2002**, *82*, 253.
15. Larsen, D.; Alessandrini, J.; Bosch, A.; Cortizo, M. *Constr. Build. Mater.* **2009**, *23*, 2769.
16. Airey, G. *Fuel* **2003**, *82*, 1709.
17. Miguel Rodrıguez, V.; Christopher Mark, L.; Norman Sidney, A.; Michele, E.; Eusebio, F. *Polym. Degrad. Stab.* **2006**, *91*, 154.
18. The Asphalt Institute. Performance Graded Asphalt Binder Specification and Testing, SP.
19. Al-Abdul Wahhab, H. I.; Asi, I. M.; Dubabe, I. A.; Ali, M. F. *Constr. Build. Mater.* **1997**, *11*, 15.
20. Lu, X.; Isacsson, U. Rheological characterization of styrene–butadiene-styrine copolymer modified bitumines. *Constr. Build. Mater.* **1997**, *11*, 23.
21. García-Morales, M.; Partal, P.; Navarro, F. J.; Martinez-Boza; F.; Gallegos, C.; González, N. *Fuel* **2004**, *83*, 31.
22. Airey, G. Airy, In Polymer Modified Bitumen—Properties and Characterization; McNally, T., Ed.; Woodhead Publishing in Materials, 80 High Street, Sawston, Cambridge, CB22 3HJ, UK, **2011**; p 390–405.
23. Polacco, G.; Stastna, J.; Biondi, D.; Zanzotto, L. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 230.
24. Shenoy, A.; *ASTM J. Test. Eval.* **2002**, *30*, 95.
25. Bahia, H.; Zeng, M.; Khatr, H. Z.15th Quarterly Progress Report for NCHRP Project 9–10, National Cooperative Highway Research Program, Washington: DC, **1999**.
26. Binard, C.; Anderson, D.; Anderson, Lapalu, L.; Planche, J. Proceedings of the 3rd Eurasphalt & Eurobitume Congress, Vienna, **2004**.
27. Phillips, M.; Robertus, C. Eurasphalt & Eurobitume Congress, *Strasbourg*, **2006**.