Enhancing Asphalt Binder Performance with Modified Sulfur

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ABSTRACT

The use of sulfur in pavement was developed since 1980 but it was restricted in the last of 19th century due to its environmental problems and its high reactivity toward oxidation processes which produce sulfuric acid products that capable of destroying the asphalt mixture. The study involve the conversion of elemental sulfur to more stable modified one using the combination of byproducts of olefinic hydrocarbons that were obtained from petroleum fractional distillates and cyclic hydrocarbon bituminous residue at 150°C. The changes in the structural characteristics and morphology of prepared modified sulfur were studied using XRD and SEM respectively. Also DSC curves able to elucidate the changes in sulfur phases from α-orthorombic to β-mono clinic structure. The technique of nanoindentation was able to compare the mechanical properties of modified and pure sulfur including modulus of elasticity and hardness. The prepared modified sulfur was added to asphalt binder with different ratios starting from 1% to 7% with good mixing at temperature below 140 ^{o}C. Not only the classical physical properties of asphalt binder were studied including, penetration, softening point, penetration index, and brookfield dynamic viscosity but also nanoindentation technique were used to compare the hardness of modified asphalt binder. Finally according to Marshall Method, the modified asphalt binders were compacted and the mechanical properties were measured including Marshall Stability, Flow, Air voids, and Marshall Stiffness. From the overall Marshall study, the results recommended that the addition of polymeric sulfur with ratio 3% to Egyptian asphalt binder improves the mechanical performance of asphalt mix.

Key words: Modified sulfur, Modulus of Elasticity, and Nano-indenter.

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INTRODUCTION

Asphalt binder is an organic mixture of thermoplastic material that is widely used in road pavement due to its good visco-elastic properties [1]. Unfortunately, asphalt behaves as an elastic solid at low service temperature or during rapid loading and as a viscous liquid at higher temperature or slow loading, which can result in low-temperature cracking of pavement and high temperature rutting. This temperature susceptibility limits its application. This has lead to an increased demand to modify asphalt binders. Different methods have been used to upgrade the properties of asphalt binders by adding modifiers such as polymer, rubber and clay [2,3, 4, 5, and 6].

Sulfur modified asphalt was originally developed and promoted in Egypt since 1980, which gives an excellent rutting resistance. However, sulfuric acid was detected in the layers of asphalt that is assumed to be formed as a consequence of sulfur oxidation; as the temperature rises at 60 ^{o}C -70 ^{o}C (the temperature of earth in summer) and the presence of quartz and granite serve as a catalyst for transformation of sulfur to sulfuric acid anhydride [7] that able to destruct the asphalt mix layer on the road. Aside from the processing and handling challenges, there were health and safety concerns, which arose from the prolonged exposure of the sulfur to the bitumen at elevated temperatures. The bitumen can function as a hydrogen donor leading to hydrogen sulfide generation. Whilst odor and vapor emissions from the hot paving mixtures during road construction, were incompliance with legislated health standards.

During the last decades in Egypt, the availability of sulfur as by-product has increased considerably. This is mainly due to the implementation of strict environmental restrictions on natural gas refining processes [8]. That's why nowadays it becomes more profitable to use sulfur in building industry and in road construction but with taking into consideration its durability risks and high reactivity to oxidation.

Many improvements in sulfur have been achieved by adding a modifier component to the cement formulations. Diehl **[9]** has shown the improvement of sulfur concrete formulations by the addition of small quantities of dicyclopentadiene as a modifier to the sulfur. Such modified

cement formulations exhibit improved compressive strength characteristics. McBee et al**[10]** have shown a variety of sulfur cement formulations such as sulfur concrete, sand sulfur asphalt paving and the like wherein the sulfur binder component is modified by dicyclopentadiene. Sullivan et al [11,12] (both Bureau of mines reports of investigations) have also described various sulfur cement formulations in which the sulfur binder is modified with dicyclopentadiene. Sullivan et al [13] have also described various sulfur cement formulations in which dicyclopentadiene, dipentene, methylcyclopentadiene, and styrene were investigated as modifiers but dicyclopentadiene produce gases with pungent odor so in this work we tried to find mix of byproducts obtained from fractional distillates and bituminous residue were used to modify sulfur which will be more environmentally friend and economic for pavement requirements. Also the study involved the addition effect of modified sulfur with ratios 1wt% to 7wt% on the physical and mechanical performance of asphalt binder.

Sulfur is readily soluble in bitumen, especially in its aromatic components. The addition of elementary sulfur to paving asphalts initiates chemical reactions whose type depends on the sulfur content and heating temperature and time of a given mixture [14]. For example, some competing reactions can occur, including those with sulfur incorporation into the bitumen molecules or dehydrogenation with liberation of hydrogen sulfide. At heating temperature T < 140°C, elementary sulfur forms polysulfides in which unreacted sulfur dissolves. Along with asphaltenes, the indicated sulfurcontaining compounds play a role of a structure-forming agent, i.e., they initiate formation of a network in which asphaltenes, paraffin, and sulfur stand as a dispersed phase, and molecules of resins and oils (malthenes), as a dispersion medium. Such structures differ considerably in the chemical and thermal stability from similar structures in unmodified oil asphalts.

Above 140°C, dehydrogenation of saturated components of bitumen can occur, whose depth depends on the final temperature of the reaction mixture. Also linear polysulfides can transform into stable cyclic thiophene structures. With increasing temperature, highly reactive asphaltenes and tars and also naphthene aromatic compounds can react with sulfur through formation of the C-S bond. It is known [15] that, at about 240°C, the reaction of sulfur with naphthene-aromatic compounds of bitumens gives asphaltenes, which play the crucial role in formation of a complex structural colloidal unit of bitumen. Therefore, sulfur, as a chemical coreagent and filler, can have a considerable effect on the performance characteristics of paving asphalts. This effect was studied in this work.

MATERIALS AND METHODS

MATERIALS

In the experiment an elementary sulfur were obtained from (E-Chem. Company) as byproduct with 99.9% purity, bitumen 60/70 paving asphalt from the Suez Company, The crushed Limestone aggregate, limestone mineral filler, and crushed sand were originally obtained from Ataka Suez–Egypt and presented in table (1), olefinic hydrocarbons C5 byproducts of Alex petroleum distillates company.

Table (1) Physical properties of coarse and fine aggregates

Properties	**Aggregate Gradation C 136/ T 27**		
	Coarse	**Fine**	**Standard**
Bulk specific gravity (kg/m^3)	2.569	2.571	C127/T27
Apparent specific gravity (kg/m^3)	2.607	2.595	C128/T84
Water Absorption (wt %)	9.7	10	C128/T84

METHODS

Preparation of Modified Sulfur

In an oil bath, 10 wt% mix of (7% residual olefinic hydrocarbons petroleum distillate fractions C5 + 3% bituminous residue) and 90 wt% of molten sulfur were mechanically mixed at a controlled temperature of 140°C for a period of about 3 h. The reaction progress was monitored by recording the viscosity variations during the mixing process. Then samples were allowed to cool at a controlled rate of 8–10 ^{o}C/min. The product is polymeric sulfur, which exhibits black color as shown in figure (1b).

(a) Photo of pure sulfur (b) A Photo of modified sulfur

Figure (1) Photograph of pure and modified sulfur

Characterization of Modified Sulfur

The following equipments were used for the characterization:-

- FTIR spectrophotometer (Model 960 Mooog, ATI Mattson Infinity Series, USA for IR spectrum analysis. The IR spectrum of pure and modified sulfur was taken as powder mixed with a small amount of KBr powder to make the IR pellet.

- x-ray powder diffraction Philips PW/1840, with Ni filter, Cu-Kα radiation (λ=1.542 Å) at 40 KV, 30 mA and scanning speed 0.02º / S, for the examination of the interlayer activity in the modified sulfur.

- Scanning electron microscope (SEM; Philips) for characterization of the microstructure.

- Differential scanning calorimeter (Perkin ElmercDSC7), for heat capacity measurements, through phase transitions on heating.

- Nanoindenter supplied by MicroMaterials Ltd. Wrexham, U.K. The indenter is equipped with diamond pyramidal Berkovich tip.

Addition of Modified Sulfur to Asphalt Binder

A modified sulfur was added to asphalt binder with mixing ratios (1%, 2%, 3%, 5%, and 7wt%) and were mechanically mixed with high rate of shear mixing for at least 30 minutes to attain the required compatibility at a temperature above the melting point of the modified sulfur (120°C) and don't exceed 140°C, at that temperature range the sulfur is completely dissolved in asphalt binder and keeping no evolution of any gases like H_2S gases. In this way the sulfur doesn't act as extender but acts only as modifier.

Physical Properties of Modified Asphalt Binder

The physical properties of sulfur modified asphalt were performed, including penetration test at 25°C according to (ASTM D5–97), softening point (Ring and Ball) according to ASTM (D36–95), and dynamic viscosity (poise) at 135°C according to (ASTM D 4402). The temperatures susceptibility of virgin asphalt sample was expressed in term of M can be measured using the penetration (@ 25ºC) and softening point values as shown in equation (1):

$$\mathbf{M= [\log (P_2) - \log (P_1)]/ [t_2- t_1] \quad (1)}$$

Where M is the temperature susceptibility, t_1& t_2 are the temperatures in °C, P_1 and P_2 are the penetration at t_1 and t_2 respectively. Since the penetration value at softening temperature equal 800, the M value can be expressed as follow in equation (2):

$$\mathbf{M= [\log (pen @ 25\ ^{o}C) - \log (800)]/ (25\text{-Soft.point temperature}) \ (2)}$$

From the temperature susceptibility values, the penetration index P.I. values are calculated in equation (3) as follow **[**16**]**:

$$\textbf{P.I.} = (20-500M)/(1+50M) \quad (3)$$

Sample Preparation of Asphalt Binder Films for Nanoindentation

The asphalt binder films were prepared on carbon steel substrate. As a first step, a steel plate surface is polished by a grinding machine rotating at angular speed of 150 rpm with a sequence of SiC papers (emery paper) for making sure a good adhesion. Next, a few droplets of hot sulfur modified asphalt binder is poured on steel surface. The bitumen coated steel substrate is then placed in the oven at 120°C for 5 min in order to have a smooth surface. Next the steel substrate is removed out of the oven, cooled down to room temperature. Then the steel sample is adhered to the holder of nanoindenter test.

Preparation and evaluation of hot mixture asphalt designs

Fourteen hot mix design were prepared from mixing of hot aggregates at 140 ºC with virgin, and sulfur modified asphalt binders then was evaluated using Marshall Method according to (ASTM D-6927). The aggregate mixes were designed according to the standard limits of surface (wearing) course 4c as shown in figure (2). The job mix (%wt) was formulated using coarse and fine aggregates, sand and filler as 23, 33, 40 & 4 wt %, respectively.

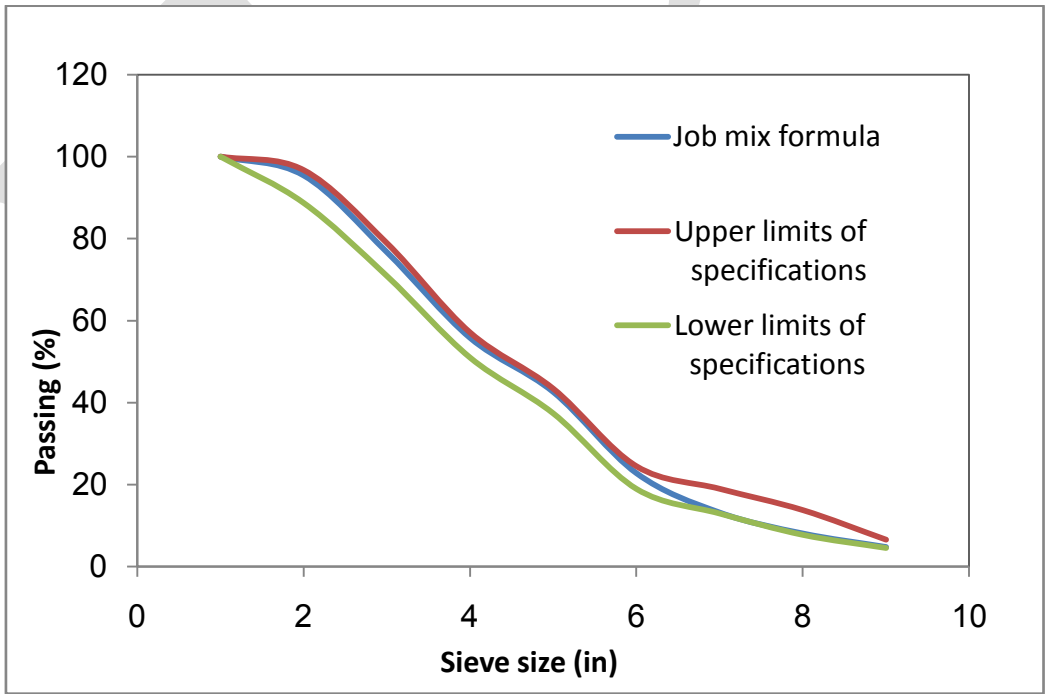


Figure (2) Sieve analysis of Job mix formula

Issue 4 volume 4, July-August 2014
ISSN 2249-9954

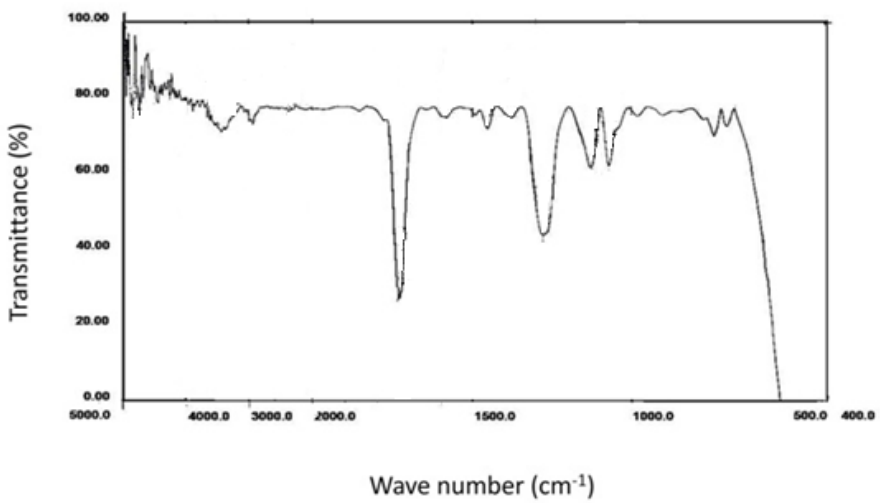
RESULTS AND DISCUSSION

Characterization of Modified Sulfur

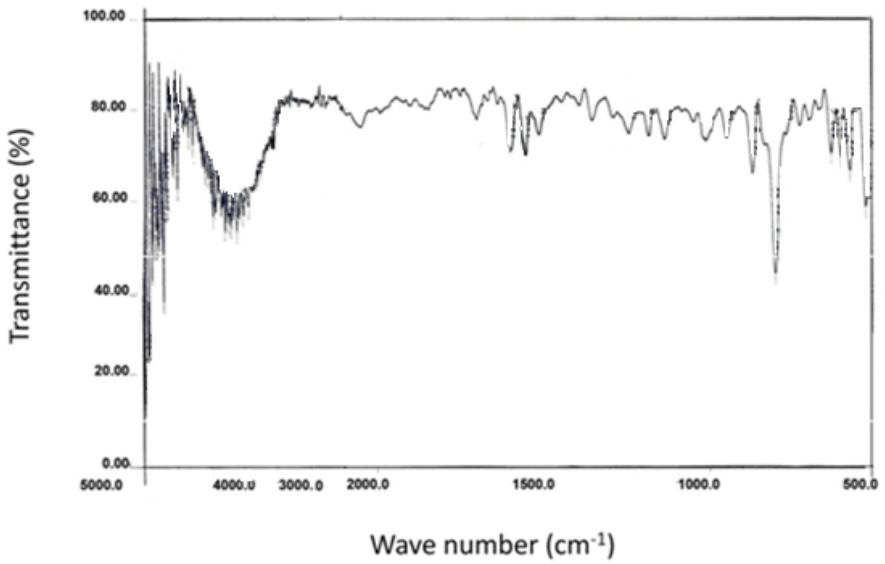
Addition of olefinic hydrocarbon polymeric material to sulfur initiates chemical reactions whose type depends on the polymer content, heating temperature and the time of the reaction. It should be pointed out that, at T < 95 °C sulfur exists as a cyclooctasulfane crown with an S-S bond length of 0.206 nm, and S-S-S bond angle of 108° At T < 119 °C sulfur crystallizes, when elemental sulfur heated to 119 °C, then cooled, with slower cooling rate <1.5 °C /min, resulted in the formation of a dense alpha sulfur crystal (Sα) with orthorhombic sulfur morphology. At 119 °C (melting point of sulfur), the polymer thoroughly dispersed in the liquid sulfur and cyclooctasulfane turns partly into polymeric zigzag chains (bond length of 0.204 nm) [17]. At heating temperature less than 140 °C, elemental sulfur forms polysulfide compounds, which initiates formation of a network. Such structures differ considerably in the chemical and thermal stability from unmodified sulfur [18] as mentioned below.

FTIR Spectra

Modification of sulfur was strongly supported by FTIR spectra shown in figure (3a, b) provided to olefinic additives and modified sulfur respectively. It was observed that the bond of C=C at 1650 cm-1 concerned with olefinic additives has disappeared and the bond formation at 694 cm-1 which is consistent with C-S stretching.



(a) FTIR spectra of olefinic hydrocarbon

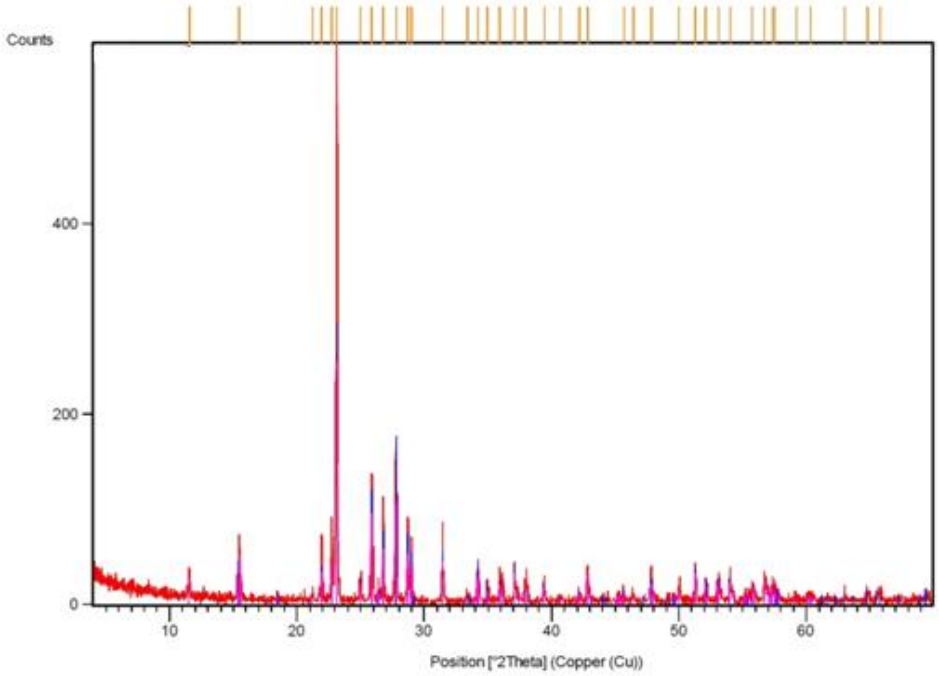


(a) FTIR spectra of modified sulfur

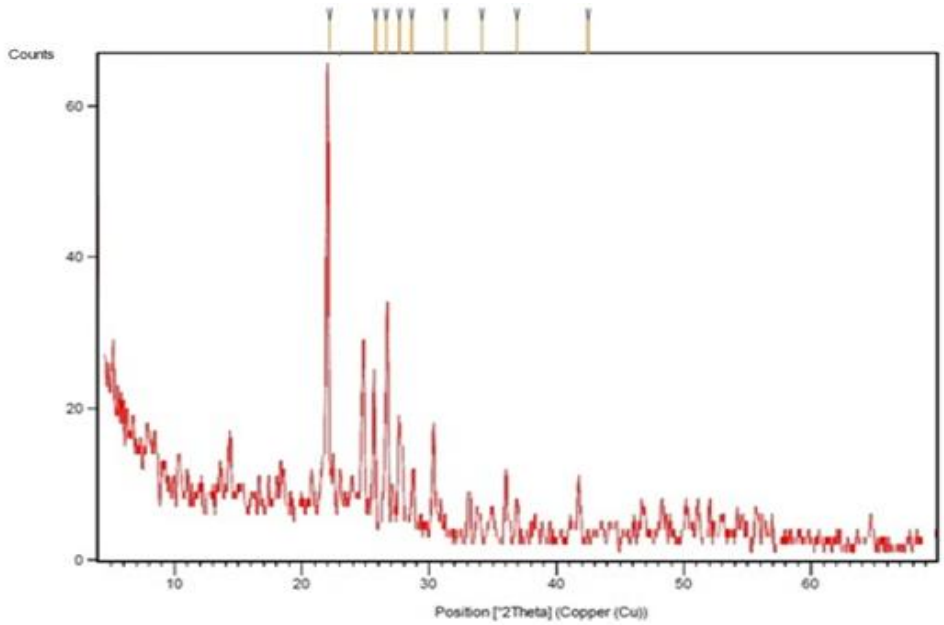
Figure (3) FTIR spectra of (a) Olefinic hydrocarbon and (b) Modified sulfur

Structural Analysis via X- Ray diffraction (XRD)

XRD analysis of modified sulfur (before separation of polysulfide) does not show any significant shift compared with pure sulfur, unreacted sulfur presumably covers modified one. But after separation of unreacted sulfur from polysulfide with CS2, XRD spectra of modified sulfur showed a lower shift in (2-θ) compared with pure sulfur as shown in figure (4 a,b).



(a) XRD of elemental sulfur

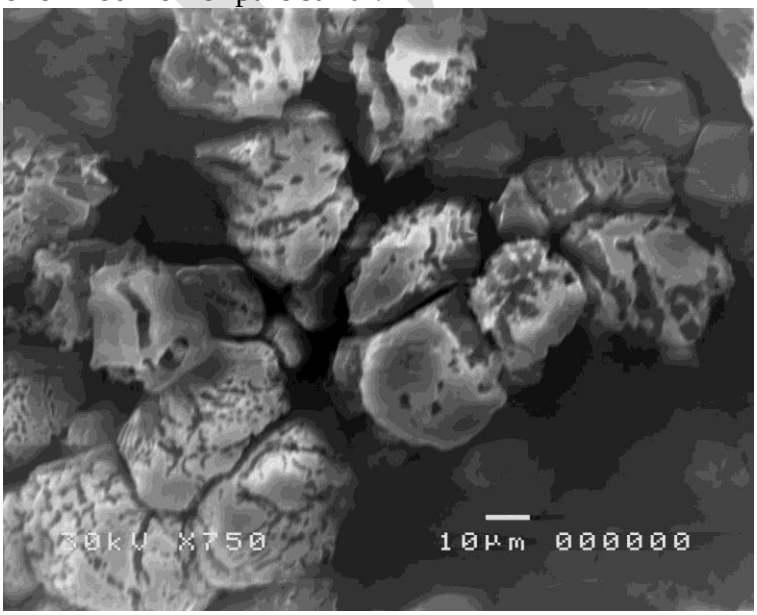


(b) XRD of modified sulfur

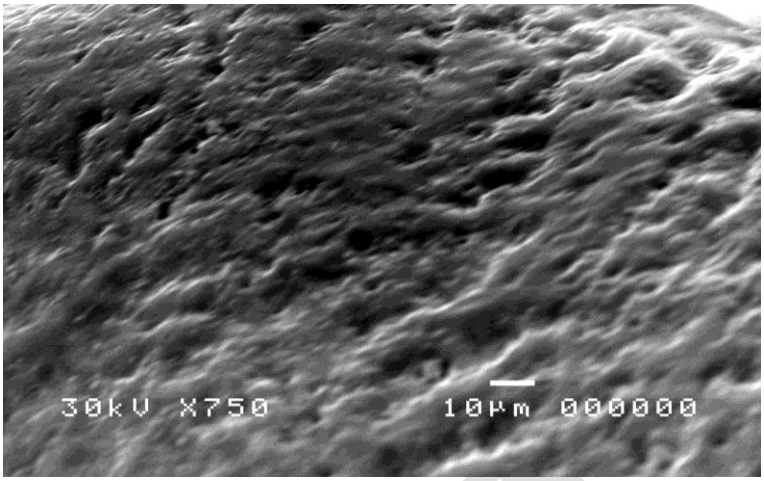
Figure (4) X-ray diffraction of (a) elemental sulfur, and (b) modified sulfur.

Morphological Scan

The effect of the modifier on sulfur morphology was evaluated using SEM. The difference between the structure of pure sulfur and modified one as shown in figure (5 a, b) are quite evident for sulfur modification. In pure sulfur, the presence of high numbers of pores formed due to β to α transitions, the resulting stress, has led to crack propagation in the matrix[19]. On the other hand the plate-like structure of modified sulfur having β- structure can be observed in all parts of the modified sample with no crack. The results make it clear that the modifier is a superior modifier for pure sulfur.



(a) SEM of pure sulfur



(b) SEM of Modified sulfur

Figure (5) SEM of (a) pure sulfur, and (b) modified sulfur.

Differential Scanning Calorimetry (DSC)

In fact, Sα→Sβ transition has been occurred at 105 °C and the transition of Sβ→Sγ can be seen at 122 °C for pure sulfur[20]. Figure (6, 7) shows the DSC curves of the pure and modified sulfur respectively. It has revealed that the Sα→Sβ transition has disappeared, while the occurrence of Sβ → Sγ is observed at 113 °C, much lower than that for pure sulfur, with a significantly decreased peak height, in comparison with the corresponding peaks in Figure (6). In support of the results concluded from SEM image of modified sulfur in Figure (7), the observed DCS curve clearly revealed that the presence of modifying agent has effectively prevented the α → β transformation in sulfur.

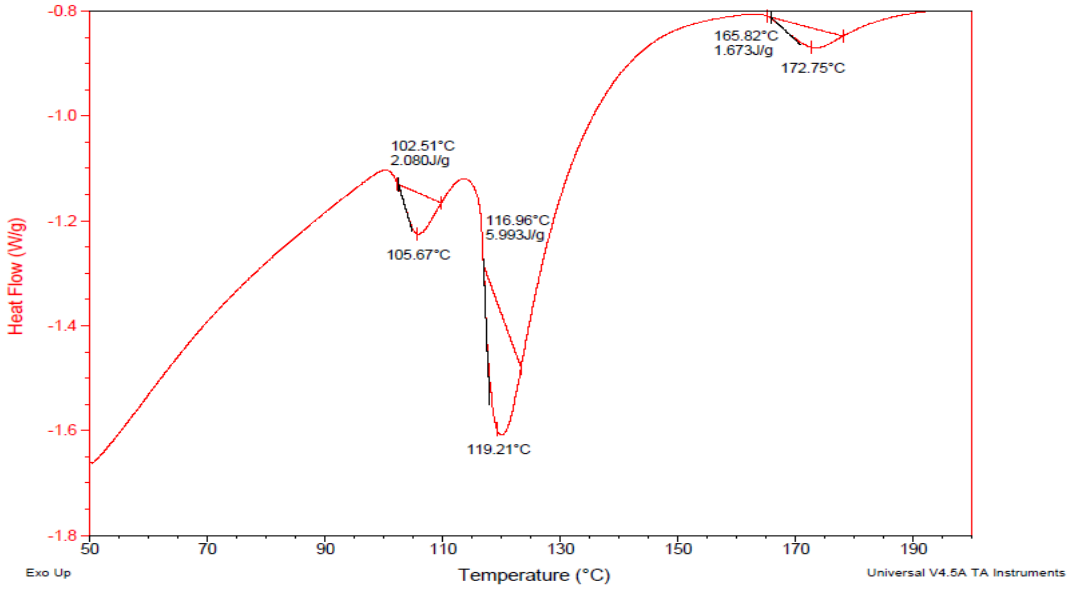


Figure (6) Differential scanning calorimetric (DSC) curve for pure sulfur at a heating rate of 5 deg min-1.

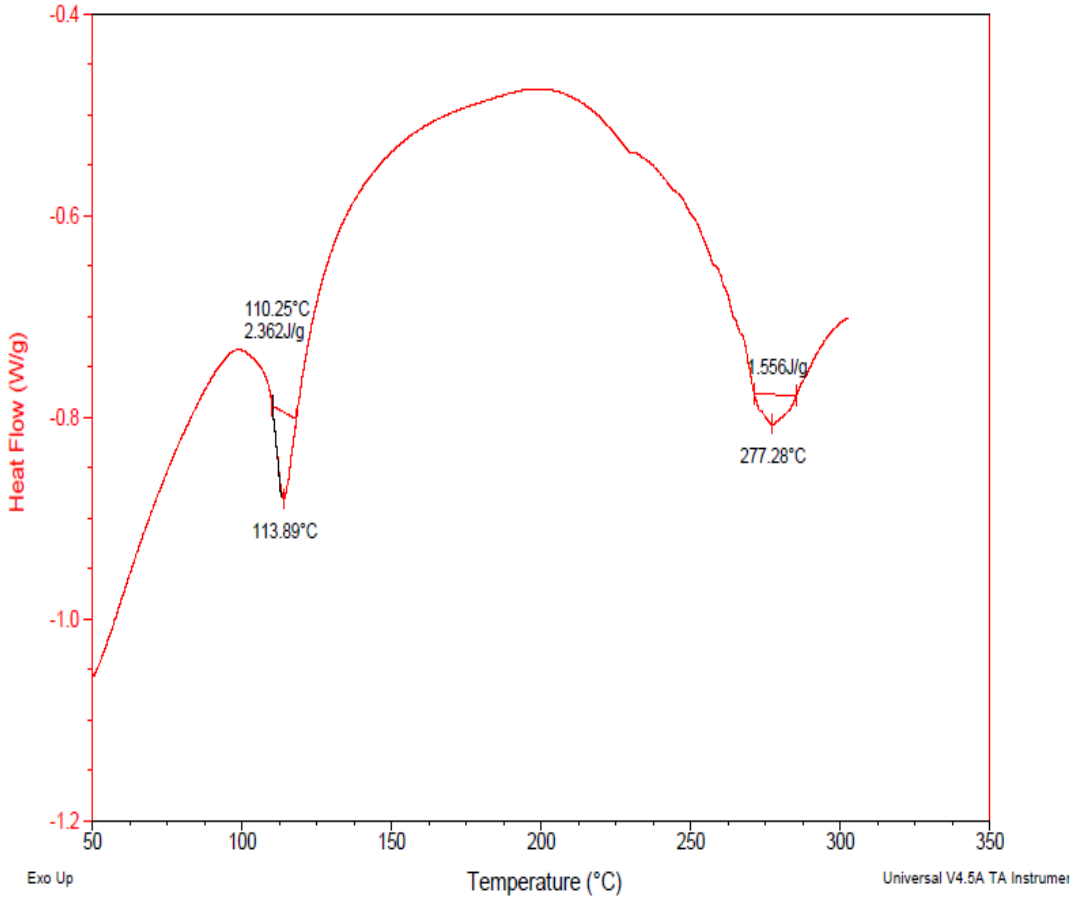


Figure (7) Differential scanning calorimetric (DSC) curves for modified sulfur (DCPD) at heating rate of 5 deg min-1.

Nanoindentation

Nanoindentation tests were conducted using a nanoindenter supplied by MicroMaterials Ltd. The indenter is equipped with diamond pyramidal Berkovich tip and the direction of indentation is horizontal. The load and displacement resolution of the indenter are 1 mN and 0.01 nm (nanometer) respectively. The load controlled tests (maximum load 50 mN) are conducted on pure and modified sulfur. Indentations are performed on randomly selected areas. The indents are located at least 60 µm (micrometer) apart to avoid the influence of residual stresses from adjacent impressions. All testing is conducted at room temperature (25°C) controlled by the temperature chamber attached with the nanoindenter. As shown in figure (8) the load-displacement curve for modified sulfur are more shifted to left side (low in depth) indicating to higher hardness than pure molten sulfur. By comparing the elastic modulus and reduced modulus plotted in figure (9) the results indicate that modified sulfur had higher mechanical strength than pure sulfur.

Issue 4 volume 4, July-August 2014
ISSN 2249-9954

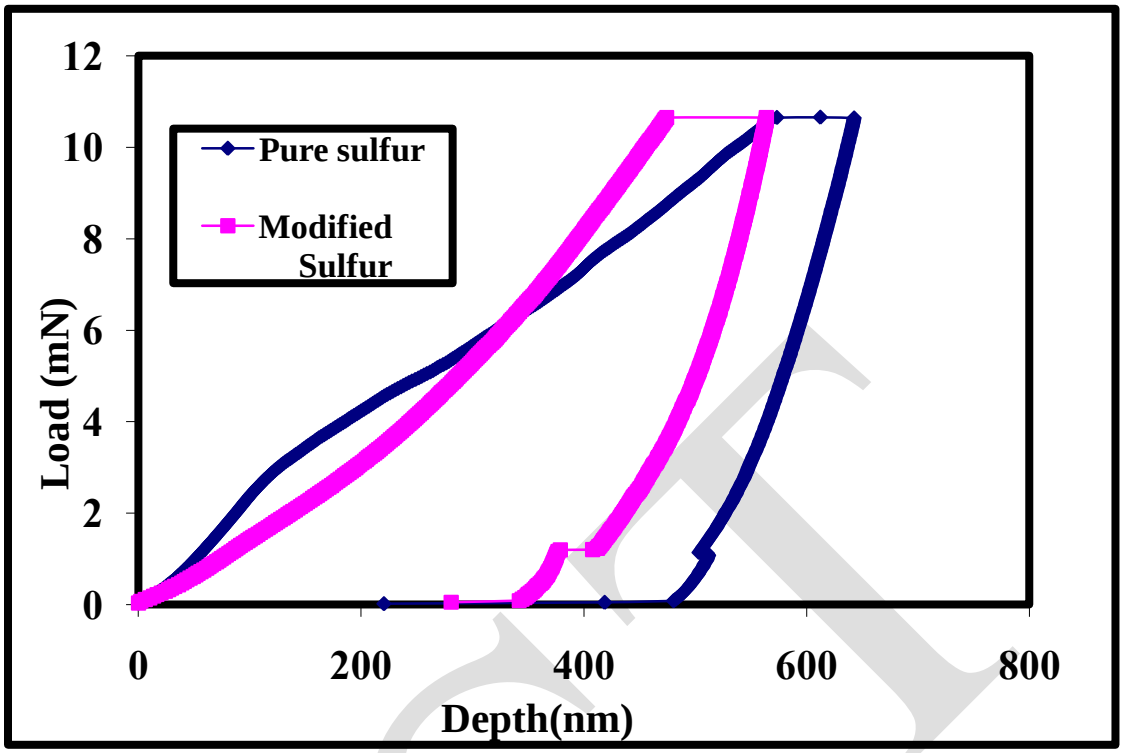


Figure (8) Load - depth curve of pure and modified sulfur

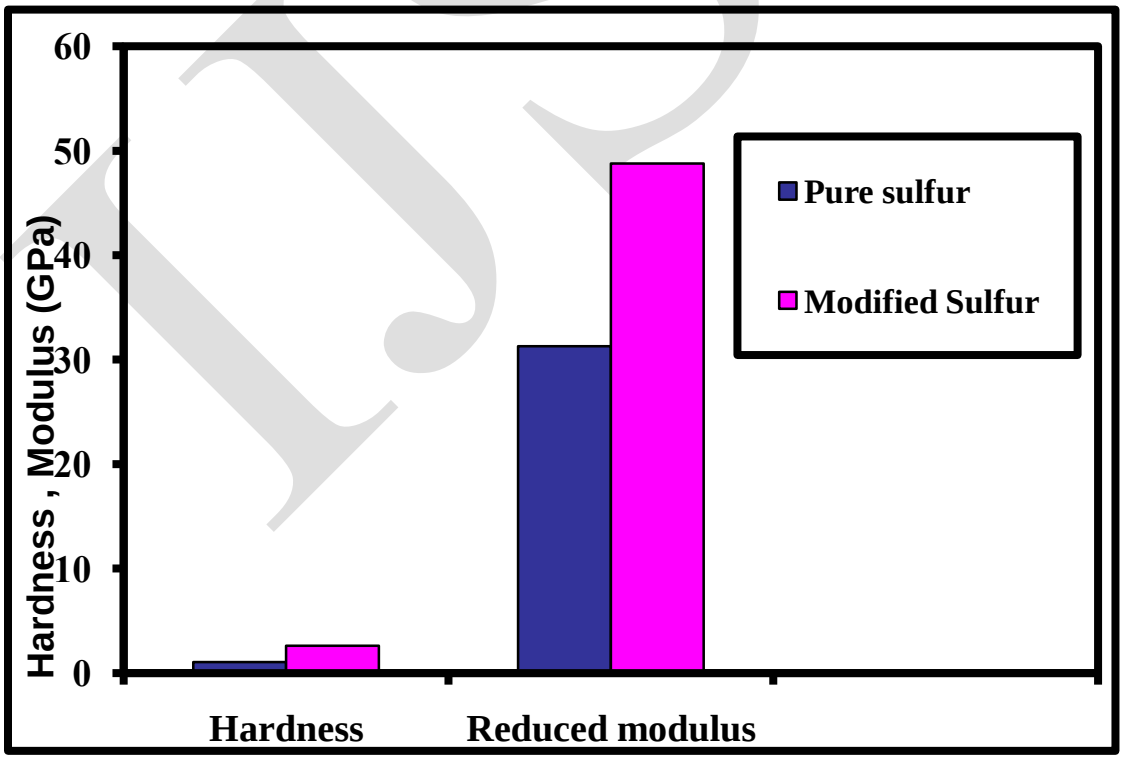


Figure (9) Hardness and reduced modulus of pure and modified sulfur

Engineering Properties of Asphalt Blend

Physical Properties of The Blends.

The blends of bitumen were prepared using 1-7wt% of modified sulfur as illustrated in Table 2 and the physical properties of the resulting blends were summarized in the same table. According to Table 2, addition of the modified sulfur would cause increments in softening point and decrease in penetration. A significant increase in the softening point temperature of the sulfur modified bitumen was observed at 3% polymer content. Since with low modified sulfur content 1-3wt%, polymeric sulfur dissolves with asphaltenes, and they initiate the formation of a network in which asphaltenes, and modified sulfur stand as a dispersed phase, and molecules of resins and oils (maltenes), as a dispersion medium, but with further addition of higher modified sulfur contents than 3%, they acted as extender in maltene phase which slightly compensate the positive effect of addition of low modified sulfur content. Since, the decreased penetration and the increased softening point temperature indicated an increased hardness of the modified bitumen; the results demonstrated that the sulfur modified bitumen might be less sensitive to permanent deformations. This is expected due to the polymeric structure of modified sulfur.

Table (2) Physical properties of virgin and sulfur modified asphalt binder

Characteristics	**ASTM Standard**	**Sulfur modified asphalt binder**					
Sulfur content in asphalt samples		**(0%) Virgin**	**1%**	**2%**	**3%**	**5%**	**7%**
Penetration at 25ºC	D5	52	50	45.5	40.1	45	50
Softening point (ring and ball) ºC	D36	50	56	59	62	58	52
Specific gravity (at 25 ºC)	D2041	1.02	1.025	1.0537	1.071	1.1025	1.150
Brookfield viscosity (at 135 ºC)* c.p	D4402	1623	1650	1669	1895	1471	1465
Penetration Index		-1.108	0.1968	0.597	0.883	0.380	-0.69

(*) Shear rate 20 s^{-1}, Spindle: SC4-25 using Brookfield viscometer (model LV- Rheocal V3.3 build 49 1)

The penetration index (PI) is used to classify bitumen. PI values can be used to determine the stiffness (modulus) of bitumen at any temperature and loading time. It may also be used to

identify a particular type of bituminous materials in a limited extent. Typical values of PI are shown in Table 3 [21].

Table (3) Typical value of penetration index.

Bitumen type	Penetration index
Blown bitumen	>1
Conventional paving bitumen	-1 to 1
Temperature susceptible bitumen (tars)	<-1

Polymer modification reduces the temperature susceptibility of the bitumen. Lower values of PI indicate higher temperature susceptibility. Asphalt mixtures containing bitumen with higher PI are more resistant to low temperature cracking as well as permanent deformation [22].

Penetration index results of the prepared modified bitumens are presented in Table 2. It is clearly seen that with increased sulfur content to 3% in bitumen formulations, the PI is increased (from -1.10 to 0.8). The PI of the bitumens modified with 1-7 wt% modified sulfur is within the range of conventional paving bitumen. However, a less negative PI value upon the addition of modified sulfur is an indication of improved PI. As it is observed in Table 2, the PI value of 3 wt% modified bitumen attains 0.8 which is ten times larger than that of the base bitumen. This represents ten times slower in bitumen consistency loss. This behavior stems from the very low temperature susceptibility of the added modifier which has a polymeric nature. This will result in turn in a higher resistance against thermal cracking of the pavement at low temperatures, whereas at high temperatures less permanent (plastic) deformation will appear on the road surface under traffic loadings.

Load-Displacement Characteristics of Bitumen Blend

Load-controlled tests were performed on both of virgin and blended binder, where the maximum load is set to 1.5 mN. A spherical indenter has been used as recommended by Rafiqul A. Tarefder et al. [23] based on the fact that the spherical indenter tip is a "blunt" tip that more suitable for working on soft materials such as asphalts while it is important to keep the stress in the contact region low, to do meaningful experiments without considerable deformation of the asphalt film or mastic surface. The indentations that were drawn are the average of 250 indents for each sample.

Figure (10) showed that at the same load 1.5 mN, virgin asphalt gives higher depth than modified asphalt which means that virgin asphalt is more plastically deformed by creep than modified asphalt. It was noticed that in case of virgin binder the slope of unloading curve is nearly dP/dH= 0 and there is no area under the unloading curve which represents the release in elastic strain energy (i.e. energy recovered Ue=0) due to the delayed (viscous) flow of virgin asphalt binder. However, this is not the case for modified asphalt samples which clearly show an unloading path that represent the elastic recovery arise from the elasticity of polymeric sulfur.

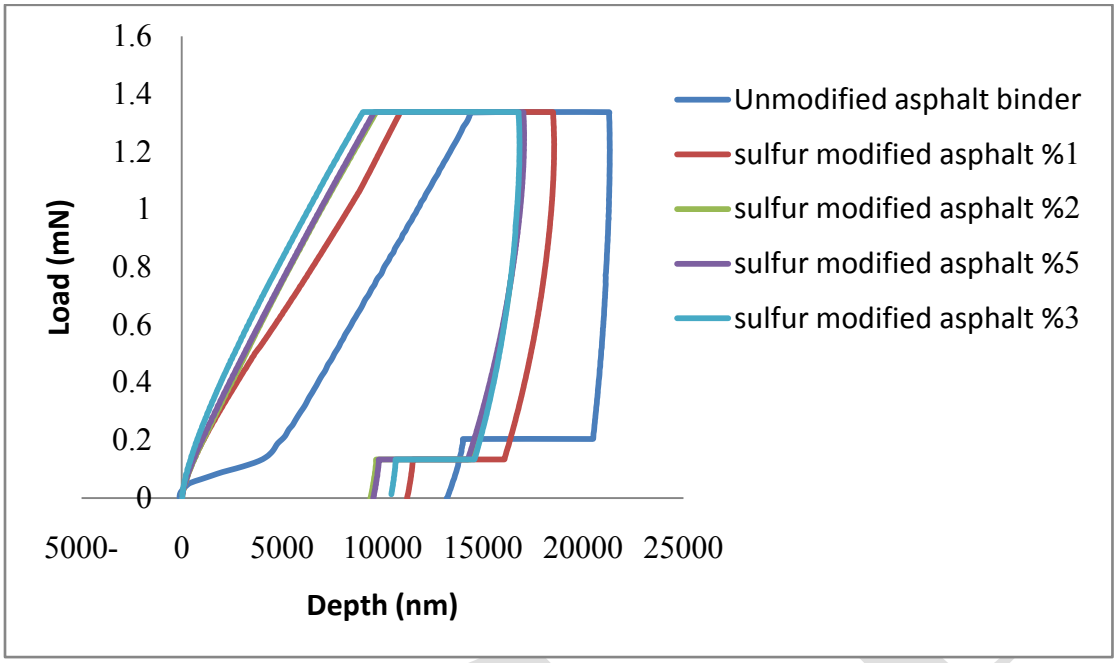


Figure (10) Load versus depth of virgin and modified asphalt binder samples using spherical indenter.

Based on the hardness results of nanoindentation test, the addition of modified sulfur with 3wt% on asphalt binder increase the mechanical strength (Hardness) from 1.5 (MPa) to 8.9 (MPa) as observed in figure (11).

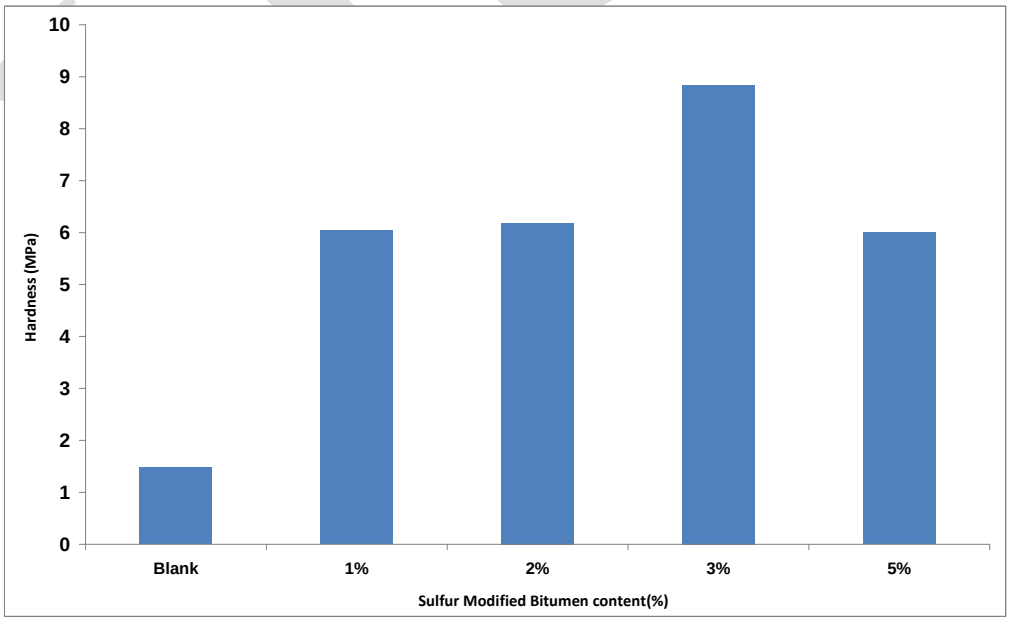


Figure (11): Hardness of virgin and modified asphalt binder.

Marshall Mixtures Design

All the prepared mixes are complying with the standard specification of HMA for surface course in roads of high traffic volume. The first Marshall Design was carried out on virgin asphalt at which the optimum asphalt binder content was found to be 5.7 wt% of total solid content as illustrated in table (4).

Table (4): Marshall mix properties of virgin asphalt

Characteristics	Hot mix numbers			
	1	2	3	4
Optimum asphalt content (%)	5	5.7	6	6.7
Stability of the mix (Ibs)	1750	2117.3	1830	1740
Flow of the mix (1/100in)	11.8	12.8	13.8	15.7
Air Voids in the mix (%)	4.4	3.37	2.8	2
Air Voids in solid agg. (%)	15.89	14.5	15.43	16.25
Marshall stiffness	148.3	165.4	132.6	110.8

Based on the physical properties and nanoindentation results, Blended bitumen with 3wt% modified sulfur content was chosen for making marshall mixtures design. As illustrated in table (5), the mix no (6) gives the highest marshall stiffness compared with all prepared hot mixed asphalt samples and particularly with HMA no (2) (virgin binder) with the percentages of 123.34%

Table (5): Marshall Mix Properties of 3% Sulfur Modified Asphalt Samples.

Characteristics	Hot mix numbers			
	5	6	7	8
Optimum asphalt content (%)	4	5	6	7
Stability of the mix (Ibs)	3175	4109	3730	2190
Flow of the mix (1\100in)	10.5	11.3	13.5	15.7
Air Voids in the mix (%)	4.4	4	2.8	2
Air Voids in solid agg. (%)	17.89	16.76	17.43	18.25
Marshall stiffness	302.3	363.6	276.3	139.4

Also from table (5) it was noticed that the optimum asphalt content of mix no (6) is 5wt% which is lower than that of virgin asphalt 5.7wt% by percentage 12.28 that may be attributed to the increase of viscosity of modified asphalt that contributed to decrease the quantity absorbed by the aggregate.

CONCLUSION

- After characterization and elucidation of prepared modified sulfur using FTIR, XRD, SEM, DSC studies, the selected mix of residues obtained from petroleum distillate (C5 fractions and bitumen) was acted as good modifier for producing stable polymeric sulfur.

- A Nanoindentaion for pure and modified sulfur approved that modified sulfur had higher mechanical strength than pure molten sulfur.

- The addition of modified sulfur on asphalt binder with 3wt% improves their physical properties by decreasing the penetration value and increasing both of viscosity, softening temperature, and penetration index (increasing low temperature crack resistance).

- Based on the results of nanoindentation tests on virgin and blended asphalt binders, it was observed that for the virgin binder are more plastically deformed under creep than blended one. Also modified asphalt samples clearly show an unloading path that represent the elastic recovery arise from the elasticity of polymeric sulfur.

- Not only the Marshall stiffness of the asphalt mix is significantly enhanced by using the modified bitumen but the optimum binder content (wt %) is decreased as well from 5.7wt% to 5wt% which helping us to reduce the cost of paving.

RECOMMENDATION

The mixing temperature of sulfur modified bitumen doesn't exceed 145 ^{o}C to avoid the evolution of H_2S gases.

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