2017

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Citation/Publisher Attribution

Faramarzi, M., Golestani, B., & Lee, K. W. (2017). Improving moisture sensitivity and mechanical properties of sulfur extended asphalt mixture by nano-antistripping agent. *Construction and Building Materials, 133*, 534-542. doi: 10.1016/j.conbuildmat.2016.12.038
Available at: http://dx.doi.org/10.1016/j.conbuildmat.2016.12.038

Improving moisture sensitivety and mechanical properties of Sulfur Extended Asphalt mixture by Nano- Antistripping Agent

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Abstract

Moisture damage and fatigue cracking are the most common defects of Sulfur Extended Asphalts (SEAs). Moisture damage in asphaltic mixtures occurs due to the weak cohesion and adhesion that cause the creation of different forms of pavement defects. Various methods have been implemented in order to enhance the asphalt mixture's resistance to the moisture damage. One of the main methods is the addition of anti- striping agents (ASAs) which reinforce the bonding between asphalt binder and aggregates. In this study, a series of laboratory testing has been performed to appraise the mechanical properties and moisture sensitivity of the SEA mixtures modified with ASA. In addition, Googas as a new generation of modified-sulfur-mix additive and ASA (nanotechnology Zycotherm) were employed to make warm-mix asphalt (WMA) specimens, through modification of neat asphalt (PG 64-22). Furthermore, four types of mixtures with different additives, containing ASA and sulfur, were prepared, and the moisture susceptibility, resilient modulus, rutting resistance, and fatigue behavior were measured. Obtained results, demonstrated the improvement of mechanical characteristics due to the sulfur modification, exclusively for rutting phenomenon. Moreover, nanotechnology Zycotherm (NZ) as an ASA enhanced the adhesion between aggregates and sulfur-extended asphalt; thus, the resistance of SEAs against moisture damage and fatigue cracking improved.

Keywords: WMA; Sulfur; Antistripping agent; Moisture susceptibility; Mechanical properties

1. Introduction

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Asphalt is a visco-elastic binder that experiences elastic behavior during rapid loading or at low environmental temperatures and viscous behavior during slow loading or at high temperatures. This temperature- dependent behavior causes a desire to improve the properties of asphalt to resist more against the rutting phenomenon, which usually appears at high temperatures, and against cracking phenomenon, which mostly happens at low temperatures [1]. On the other hand, temperature variations between warm and cold months, as well as, increased traffic volume of trucks, create critical pressures in the structure of pavements. Such conditions have caused an increased desire to improve asphalt properties. There are various methods to modify the asphalt properties [2]. One of the most popular and common procedure is using of modifier additives such as sulfur.

Since four decades ago, many studies have demonstrated that sulfur can modify and improve the properties of asphaltic pavements [3]. Application of sulfur as an asphalt binder performance extender is an economical solution to decrease virgin binder usage as well as toxic gas emission. In spite of implementation problems, it was observed that Sulfur Extended Asphalts (SEAs) could improve pavement's mechanical properties such as stiffness compared to conventional asphalt mixtures [4]. The use of sulfur to improve the quality of asphalt began in 1970 and was commercially used during the 1970s and 1980s. Without appropriate technology at the time, handling and safety issues also were of concern, as molten sulfur was difficult to apply and occasionally generated H_2S which had prevented its application during those years. Therefore, there was an interruption period by using sulfur as an asphalt modifier in the 1980s [5], but eventually, the concept of sulfur extended asphalt (SEA) reappeared with the emersion of a new version of solid dust-free sulfur pellets. Solid dust-free sulfur facilitates the displacing of sulfur in a solid pellet shape. This new product was improved by using polymeric compounds in the sulfur pellets. By this change, it became possible to add new product to the asphaltic mixtures while emission of hazardous gasses like

H_2S and annoying odors reduced considerably compared to the conventional-liquid sulfur extended asphaltic mixture [6]. This new product reduced mixing temperature to about 135°C while compaction temperature is reduced to about 90°C. Many of the mentioned safety problems seemed to be disappeared, if the asphalt concrete was constructed at a mixing temperature of 135 ± 5°C. Moreover, the new sulfur pellets could be poured directly into the asphalt-aggregates mixture during the mixing operation [6]. As a result, there was no concern about difficulties of blending it with asphalt before adding the binder to the aggregates. Since mixing operation should be done in the temperature range lower than conventional HMA, it should be considered as a Warm Mix Asphalt. Mixing temperature of WMA is approximately 16-55°C lower than conventional HMA, therefore, using the new sulfur extended asphalt as WMA can reduce required energy to produce and compact asphalt mixture [7].

The bonding between asphalt and aggregates is considerably important as it affects the integrity of asphaltic pavement. Such bonding forms at the beginning of the mixing process when asphalt coats aggregates and this bonding should resist against stresses during its lifetime in the asphaltic pavement, while, insufficient adhesion leads to a low performance of the pavement. Divito et al. [8] showed that pavement strength depends on: (1) the asphalt's cohesive resistance, (2) the resistance of adhesive bond between the asphalt and the surface of aggregate, and (3) the interlock between the aggregates particles. ASAs are substances designed to improve chemically the adhesion between the asphaltic binder and the aggregates. They are available in both liquid and solid forms. One of the most common ASAs which has been extensively used to improve the HMA's resistance against moisture damages is hydrated lime. Other common conventional ASAs are fly-ash and Portland cement. In addition, Liquid ASAs in the form of cationic surface-active agents (principally amines) have become popular in recent years [9]. In this study, a liquid ASA commercially named

Zycotherm was used to make the aggregates hydrophobic while providing improved bonding with the sulfur- extended asphalt binder.

1.1. Literature review

Bencovitz and Boe [10] demonstrated that sulfur could be mixed with asphalt as an extender and make asphalt cement which can modify the asphalt rheological characteristics. For the first time, Sulfur-Extended Asphalt was constructed by Kennepohl et al. [11] and practically applied in asphaltic pavements in the early 1980s as a asphalt extender to decrease asphalt consumption. Some case studies by Beatty et al. [12] showed that SEA has better function in comparison with conventional HMA.

In recent studies performed on SEAs by Strickland et al. [13] and Timm et al. [14], sulfur was applied in the form of a solid pellet which could be melted at a temperature round 120°C and added as asphalt extender with the ratio between 30% and 40%. These pellets were pretreated to decrease toxic gas emissions like hydrogen sulfide and also to lower the temperature of mixing and compaction operations. At mixing operation, some of the sulfur homogenizes with the asphalt at 120°C and decreases its viscosity. The remnant crystallized and covered aggregates as the temperature is reduced. They showed that dissolved, and crystallized sulfur makes the mixture stiffer and leads to a more resistant asphalt mixture at high temperatures, and consequently less vulnerable to permanent deformation phenomenon. SEA also advantaged the sulfur as asphalt extender and decreased asphalt consumption about 20-25% of the binder weight [15]. Strickland et al. [16] suggested keeping the volume ratio of the total binder phase (asphalt and sulfur) constant at asphaltic mixture before sulfur extending and after that. This was recommended since the density of sulfur pellets is different from the base asphalt. They established a relationship between asphalt and sulfur content in the SEA based on the following Equation:

$$\text{Sulfur + asphalt\%} = \frac{100AR}{100R - P_S(R - G_{bitumen})} \tag{1}$$

In which:

Sulfur + asphalt % = sulfur- extended binder content by the weight of WMA sample; A = asphalt content by the weight of conventional HMA sample (%); R = specific weight ratio (sulfur to asphalt); Ps = sulfur content in extended binder; and $G_{bitumen}$ = specific weight of the asphalt.

Strickland et al. [16] did an experimental investigation on the functional properties of SEA in the laboratory. Results indicated deteriorated tensile-strength ratio (TSR) but improved dynamic modulus in various ranges of temperature and frequency. According to the results obtained by life cycle costs analysis of SEA pavement structures conducted by Cooper et al. [17] Using SEA amplified the predicted rutting and fatigue resistance and the overall pavement service lives compare to unmodified HMA at various traffic intensities. It was also shown that SEA has the potential to reduce construction and maintenance costs in comparison with a conventional HMA produced with the same binder grade. In a study conducted by Timm et al. [14], dynamic moduli and moisture susceptibility of SEA were evaluated. Results indicated that SEA was more vulnerable against moist condition as had lower TSR in comparison with conventional asphalt mixture: however, the SEA dynamic modulus increased.

1.2. Research Objective

Mechanical properties and moisture sensitivity of anti-stripping agent-modified SEA were evaluated in this paper by the experimental method. Nano-based anti-stripping agent named commercially zycotherm and petroleum base sulfur named commercially Googas were used respectively to replace a portion of asphalt and strengthen the bond between the binder (sulfur and asphalt) and aggregate’s surface. In this study, moisture sensitivity test, rutting performance, resilient modulus and fatigue behavior were evaluated for the proposed samples. Asphalt mixture tests were carried out on four different mixtures including one conventional HMA and three modified WMA (in different combinations of Sulfur and ASA additives).

2. Test materials and mixing

2.1. Materials

2.1.1. Asphalt binder and aggregates

Materials used in this experimental investigation included a PG 64-22 virgin asphalt binder, with the physical properties that are shown in Table 1. Used aggregates have desired mechanical properties such as enough strength, toughness and hardness. Also, crushed aggregates were used to make higher stability. The Superpave mix design [18] was used to prepare the asphalt mixtures and filler material (grinded limestone) were used to meet the aggregate gradation criteria shown in Fig. 1.

Table 1
Physical properties of used asphalt binder

Properties	PG grade	Purity grade	Flash point	Softening point	Penetration Grade at 25ºc	Ductility at 25ºc	Viscosity at 135ºc	Density
Unit	-	(%)	(ºC)	(ºC)	(mm/10)	(cm)	(mPa.s)	-
Value	64-22	99	262	54	67	104	349	1.03

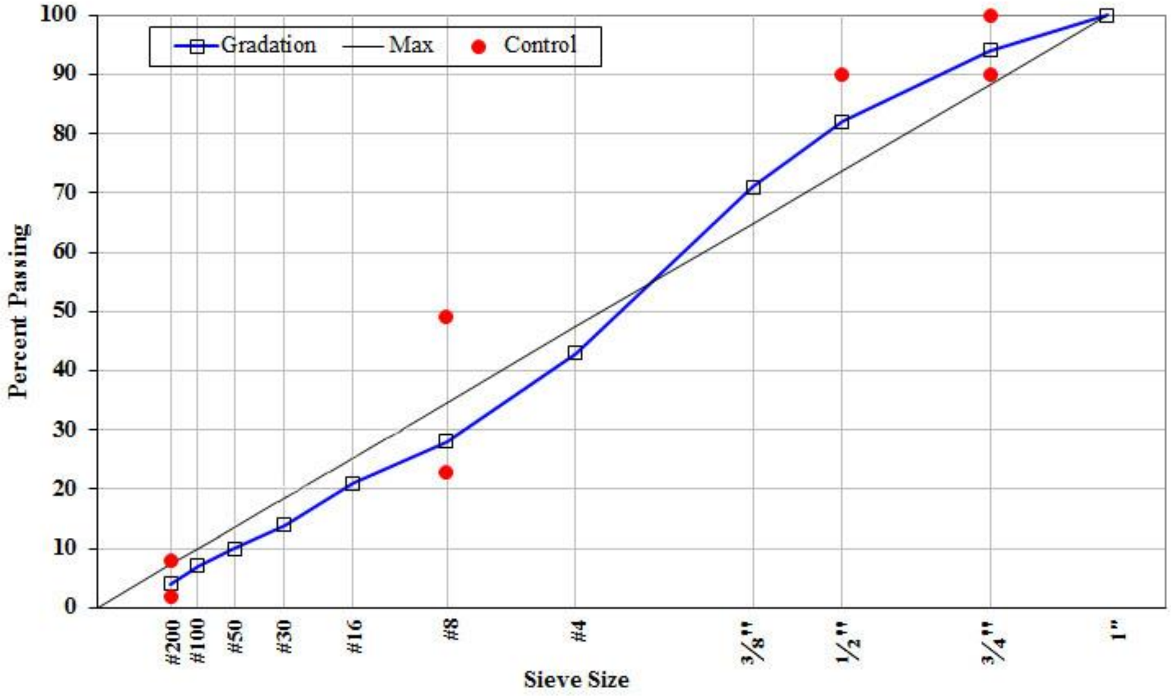

Fig.1. Aggregate Gradation

2.1.2. Sulfur

Googas is produced by compounding neat sulfur, plasticizer and some other additives, which is higher than the range of evaporation, melting and freezing points of sulfur. This polymeric sulfur material has been produced in the ZENIT Company (R&D unit) in granular shape (solid pellet). Produced sulfur pellets can be substituted directly for about half of asphalt in the asphalt concrete and modify the asphalt which was used initially. Using Googas decreases energy consumption via decreasing the temperature needed for mixing and compacting operations. As the asphalt is more expensive than this material, it can decrease the costs of asphalt production and energy consumption [19]. Physical properties of Googas material are shown in Table 2.

Table 2
Physical properties of Googas.

Test title	Result
Physical shape	Granule
Color	Gray
Water solubility	Non-soluble
Relative specific weight to water	1.89 gr/cm3
Average size of pellets	2 mm
Melting point	Minimum 90°C

2.1.3. Nanotechnology zycotherm (NZ)

Nanotechnology Zycotherm (NZ) is a WMA additive produced by Zydex Company, Gujarat, India. This additive provides two significant benefits for WMA mixtures. It lowers production and compaction temperatures, while simultaneously reducing the moisture susceptibility of asphaltic pavements as an anti-strip agent. The first effect is the result of a reduction in viscosity of asphalt and the second is due to reinforced bond between binder and aggregates. NZ is an organosilane compound and can form silanols (Si-OH) groups. As silanols are so reactive, siloxane bonds (Si-O-Si) can be formed between NZ and inorganic surface-like sand and gravel surfaces which constitute from silanol groups. This additive could be used in different asphaltic mixtures consisting of modified or unmodified asphalt binders. This is very compatible with crumb rubber or polymer modified asphalt binder [20]. Since Googas is a polymeric sulfur product, it could be a suitable additive to modify the studied SEA. Using NZ does not affect binder grading or change any other binder properties. Physical properties of zycotherm additive are shown in Table 3.

Table 3
Physical properties of zycotherm.

Properties	Result
Form	Liquid
Color	Pale yellow
Flash point	> 80°C
Explosion hazard	Not known
Density	1.01 g/ml
Freezing point	5°C
Solubility	Miscible with water
PH value	10 % solution in water neutral or slightly acidic
Viscosity	300 cP (25°C)

2.2. Mixing and HMA sample preparation

2.2.1. Mixing NZ in asphalt

The optimum amount of NZ additive was determined 0.15% by weight of asphalt. Viscoelastic characteristics of modified asphalt and ITS parameter of NZ-modified asphalt mixtures were analyzed to achieve this optimum amount, according to the values in Table 4 and Fig. 5, respectively.

The technique which was used to mix NZ in the asphalt binder includes three following steps.

1. The stirrer speed was set high enough (300 rpm) to create a 2-3 cm deep vortex before mixing zycotherm in molten asphalt at 150°C.
2. Zycotherm was added to the center of the vortex at ten drops per minute while maintaining the stirrer speed (According to the dosage of 0.15% by weight of asphalt, adding 1ml or 1g of zycotherm should take approximately 2 minutes for 660g of binder).

3. The mixing operation performed for 10 minutes to make a completely homogeneous blend.

Within the mixing process, the temperature was set at 150°C and kept constant by applying an oil bath heated by a hot plate.

2.2.2. SEA mixtures preparation

The optimum binder content (OBC) was determined following Superpave mix design. The OBC for SEA samples was modified by the equation (1). The OBCs were found to be 5.5% and 4.3% for conventional and SEA mixtures, respectively. The research team used 35% Googas by weight of asphalt for constructing sulfur contained samples, which was the optimum amount obtained by doing Indirect Tensile Fatigue (ITF) and Loaded- Wheel Tracking (LWT) tests. Following steps were taken for making SEA mixtures:

1. Used sulfur (Googas) pellets were heated to 60°C before adding to the aggregate-asphalt mixture.
2. The ASA-modified asphalt was mixed with the hot aggregates at 120°C.
3. Preheated sulfur pellets were poured into the mixture.
4. The obtained blend was mixed completely at 120°C to make all pellets melted and diffused all over the mixture.

Following types of asphaltic samples were constructed and tested:

- Conventional HMA mixtures (CHMA) – mixture made with the neat AC asphalt.
- ASA-modified WMA mixtures (AWMA) – mixture made with ASA-modified asphalt.
- Sulfur- extended WMA mixture (SWMA) – mixture made with sulfur extended asphalt binder.

- ASA- modified and sulfur extended WMA mixture (ASWMA) – mixture made with ASA- modified binder extended by sulfur.

Triplicate specimens were constructed for every type of asphaltic sample.

3. Testing program

3.1. Scanning electron microscopy (SEM)

Taking a photo in nano and micro scales is one of the most precise methods to evaluate the efficiency of used mixing procedure. In this study, the SEM method was applied to observe the morphology of sulfur-modified binder as well as investigate the effectiveness of used mixing method to obtain a homogeneous blend.

3.2. Asphalt binder tests

To obtain the optimum percentage of NZ as an antistripping agent additive and evaluate the properties of used binders, empirical rheological tests were performed on neat and NZ-modified asphalt binders in different NZ percentages. The research team applied the asphalt tests in accordance with the relevant standards. The penetration degree test is a classic test which determines the hardness of asphalt binder according to the ASTM-D5 standard [21] [22]. Also for determination of softening point degree, the ASTM-D36 was applied [23]. Ductility test was performed to evaluate the cohesion of used asphalt; in this test specimens were stretched at 25°C with a constant speed of 5 cm/min in accordance with the ASTM-D113 [24]. A Brookfield rotational viscometer apparatus was applied to measure the Viscosity of different asphalt binders. During this test, the temperature was set at 135°C according to the ASTM-D4402 standard [25]. A number 21 spindle and a specimen size of 8.5 grams were used for this study.

3.3. Asphalt tests

Different asphaltic samples including CHMA, AWMA, SWMA and ASWMA were constructed according to the aforementioned procedures, afterward; Resilient Modulus (RM), ITF, LWT and Indirect Tensile Strength (ITS) tests were conducted on them as follow:

3.3.1. Resilient modulus test

In this study, the resilient modulus of asphaltic mixtures was evaluated by the indirect tensile method according to ASTM standard [26] [27]. This test can be used to achieve a good understanding of the elastic properties of studied asphaltic mixture. A Nottingham Asphalt Testing apparatus was applied to determine the resilient modulus of different samples. Dimensions of used cylindrical specimens were 101.6 mm and 65mm in diameter and thickness respectively. The time of an entire loading cycle is 1.0 s long, which consists of 0.1 s loading and unloading time and 0.9 s resting time. When the indirect tensile method is applied for evaluation of elastic properties, the following equation could be utilized to calculate the resilient modulus parameter:

$$\mathrm{RM} = \frac{P\ (\nu+0.27)}{t*\Delta H} \tag{2}$$

Where RM = resilient modulus (MPa); t= sample height (mm); ν = Poisson ratio; P = maximum dynamic load; and ΔH = recoverable horizontal deformation (mm).

3.3.2. Modified Lottman test

Moisture susceptibility of the specimens was determined by modified lottman test according to AASHTO T283 [28]. Specimens used for Modified Lottman test should be compacted to reach the air voids of 7% ±1.0. Dimensions of prepared specimens for this test are 150 mm and 95 mm respectively for height and diameter. Six specimens were prepared for every sample including three for unconditioned and three for conditioned mode. Unconditioned specimens were not under moisture conditioning before the test, but conditioned specimens were treated by the following stages:

- Immersing in water (up to 55–80% saturation level).
- Freezing at -18°C for 16 h.
- Placing in a 60°C water bath for 24h.

When this process completed, the ITS for both conditioned and unconditioned specimens was measured at 25°C. The average ITS was considered as the final values for both conditioned and unconditioned specimens. The TSR parameter is defined as the fraction of conditioned on unconditioned ITS.

3.3.3. Indirect tensile fatigue (ITF) test

Research team utilized a Nottingham Asphaltic Mixture Tester to perform the fatigue test. Nottingham tester measures the fatigue life and strains by applying repetitive Indirect Tensile stress to the prepared samples in accordance with relevant ASTM standard for indirect tensile method [26]. The tested specimens were in cylindrical shape and standard dimensions (40 mm height and 100 mm diameter). Asphalt mixtures were mixed and compacted in accordance with the superpave mix design standard for construction of specimens [18]. The frequency of loading was 1 Hz and it continued until the specimen experienced the failure point. The failure point was also defined as 12.7 mm final vertical deformation or occurring rupture in the loaded specimen. Controlled stress mode was chosen as the condition of loading for the fatigue test in this study. In the controlled stress mode, the applied stress should be kept constant to increase the strain of loaded specimen.

In this study 5, 15 and 25°C were chosen as the temperature of test to simulate the fatigue phenomenon at the low-temperature condition. Two stresses of 100 kPa and 300 kPa were selected as the constant values of applied load. A common equation (Wohler's fatigue equation) is usually used to show the relationship between the number of cycles to failure and tensile strain. Such an equation could be obtained if the linear diagram of the relationship between the "loading number to the failure point" (fatigue life) and the "applied strain" be drawn on a logarithmic scale using a regression analysis [29]. Developed fatigue equations would be in the form of Wohler's fatigue equation (Eq. (3)):

$$N= a \left[\frac{1}{\varepsilon_t}\right]^b \tag{3}$$

Where "N" = loading number to the failure point; ε_t = measured strain; "a" and "b" = coefficients effected by asphalt mixture properties.

3.3.4. Loaded- Wheel tracking (LWT) test

The LWT test has been applied for asphaltic mixtures accelerated performance testing in terms of its rutting resistance according to AASHTO T324 [30]. A Hamburg wheel rut tester was used to measure rut depth of different sample influenced by repetitive loading condition in which specimens with a 30 - 30 - 6 cm dimensions were used to simulate rutting phenomenon of real loaded pavement. In this study, the wheel track testing was carried out by applying 703-N steel wheel on the submerged specimen at temperature 50 °C. The wheel-tracker apparatus was programmed to finish rolling after 20,000 cycles or when the maximum displacement recorded by LVDT was 20 mm. The maximum allowable permanent deformation was determined to be 6 mm after 20,000 passes at 50°C. This value is required to consider a sample resistant against rutting phenomenon.

4. Results and discussions

4.1. SEM analysis results

One of the most reliable methods to evaluate mixing operation-effectiveness is to take photos in micro and nano scales by SEM microscopes [31]. Morphology of neat asphalt and Googas-modified asphalt is illustrated in Fig. 2. Photos were taken at a voltage of 5 KV with 300-60000 magnification scale. As illustrated in Table 2, the average size of unmixed Googas pellets was about 2mm. To use the full potential of Googas as asphalt extender, it is necessary to dissolve it in asphalt and make a homogeneous blend as much as possible. As shown in Fig. 2-D, a major part of Googas pellets almost dissolved into the asphalt bulk and made it more viscous, but other part was not fully dissolved at high mixing temperature and, therefore, became crystallized at lower temperatures which can be seen in Fig. 2-C. In these two figures white parts are sulfur and black parts are asphalt. In Fig. 2-D dissolved sulfur can be distinguished because of high focus of picture as could be understood from the scales. In SEA mixtures, sulfur gets cooled and crystallized around the coarse aggregates and makes the mixture stiffer than before. Extra stiffness caused by dissolved and crystallized sulfur improves rutting performance of SEA [7].

Increased viscosity normally raises the necessary temperature for mixing and compaction operations, while Googas which is a polymeric sulfur product, reduces these temperatures beside increment of viscosity that could be so favorable. This mechanism occurs due to the improved properties of Googas product compared to the neat sulfur as a result of applied treatments.

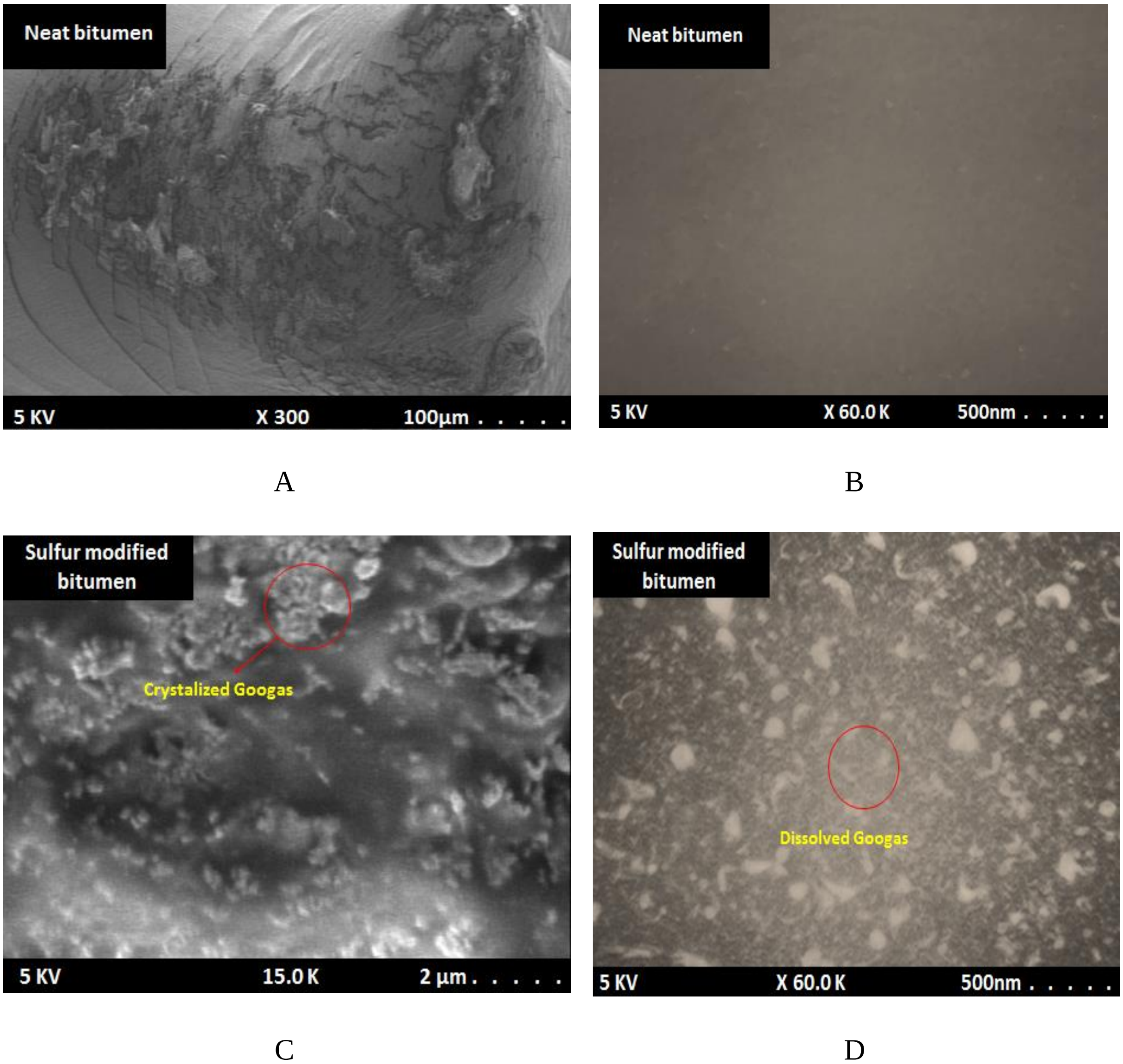

Fig. 2. SEM images of sulfur - modified/unmodified asphalt, (A) Neat asphalt - 100µm; (B) Neat asphalt – 500nm; (C) sulfur-modified asphalt binder - 2µm; (D) sulfur-modified asphalt binder – 500nm.

4.2. Asphalt binder test results

To obtain the optimum percentage of NZ as an antistripping agent additive and evaluate the properties of the used binders, empirical and rheological tests were performed on the neat asphalt, the NZ modified asphalt in different NZ percentages as well as sulfur and/or NZ modified asphalts in optimum percentages. As shown in Table 4, the more the NZ content, the more penetration degree, and consequently, the less softening point observed. These changes were due to the lower viscosity of NZ- modified asphalt compared to the neat asphalt. As shown in Table 4, NZ- modified asphalt has better ductility than the neat one. This improvement could be attributed to the formation of bonds between chemical compositions of AC with NZ particles. The viscosity data of different samples including neat and modified asphalt at a temperature of 135 °C was collected by standard Rotational Viscosity (RV) test. As it is shown in Table 4, all samples had a viscosity value less than the SHRP limit of 3000MPa.s at 135 °C. Addition of NZ to asphalt should not affect the binder grading negatively, so 0.15% NZ was chosen as the optimum percentage of ASA additive. According to the rheological and empirical tests' results, adding sulfur made asphalt more brittle by increasing RV and softening point as well as decreasing ductility and penetration degree, while using ASA restores these properties to the neat asphalt condition to a high extent.

Table 4
Basic properties of NZ and/or Sulfur modified asphalt.

property	PG	Rotational viscosity at 135°C (mPa.s)	Ductility at 25°C at	Penetration at 25°C	Softening Point (°C)
Standard Unit	ASTM D 6373 -	ASTM-D4402 (mpa)	ASTM D113 (cm)	ASTM-D5 (mm*0.1)	ASTM-D36 (°C)
Neat asphalt	64-22	349	104	67	54
Modified asphalt with 0.1% NZ	64-22	336	110	69	51
Modified asphalt with 0.15% NZ	64-28	329	114	70	49
Modified asphalt with 0.20% NZ	58-28	325	120	71.3	48
ASA- modified asphalt (15%NZ)	64-28	329	114	70	49
Sulfur- modified asphalt (35% Googas)	70-10	412	92	58	52
ASA and sulfur- modified asphalt (15%NZ and 35% Googas)	70-22	371	101	60	46

4.3. Asphalt test results

4.3.1. Resilient Modulus Test

In general, a pavement which has high resilient modulus is expected to resist appropriately against permanent deformation [32]. Results of resilient modulus test at different temperatures for CHMA, AWMA, SWMA and ASWMA mixtures have been illustrated in Fig. 3. As seen, the stiffness of studied mixes reduced by increasing the temperature. According to the Fig 3, the resilient modulus of asphaltic samples amplified by about 30% and 100 % respectively for SEAs (SWMA and ASWMA) and sulfur- unmodified samples (CHMA and AWMA) by lowering the temperature from 25 °C to 5°C. At any constant temperature, the highest stiffness quantity was achieved for SWMA follow by ASWMA, CHMA, and AWMA mixtures. As depicted in Fig 3, in comparison of CHMA with AWMA, the rate of resilient modulus reduction due to the addition of ASA is more considerable at lower temperatures. On the other hand, in comparison of CHMA with SWMA, the rate of resilient modulus improvement due to the addition of Googas was more considerable at higher temperatures. The reduction of the binder viscosity around the aggregate particles at high temperatures was the main reason for this difference. Dissolved sulfur in the asphalt made it stiffer, and more viscose in different temperatures; also, crystallized sulfur around the aggregates made a more powerful bond between sulfur- modified binder and aggregates. Therefore, the binder film around the aggregates was more stable for SEAs samples compared to the other samples especially at higher temperatures [33]. According to the viscosity test data, increasing NZ content had decreased binder viscosity that led reduction of binder film around aggregates; therefore, as illustrated in Fig.3, AWMA has lower stiffness modulus in comparison with CHMA at different temperatures. As obviously portrayed in Fig. 3, the highest resilient modulus improvement rate of SWMA and ASWMA occurred at higher temperatures. Using ASA reduced SEA mixture's resilient modulus slightly, but this deterioration was negligible especially at higher temperatures.

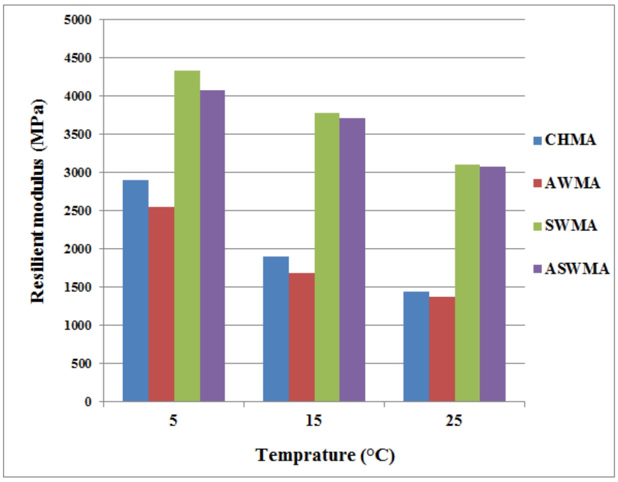

Fig. 3. Comparison of resilient modulus values at 5, 15and 25°C.

4.3.2. Moisture resistance performance

The results of the ITS test are summarized graphically in Fig.4 and Fig. 5. Diagrams in Fig. 4 show a reduction (approximately 19%) in the splitting tensile strength of the ASWMA versus the AWMA in a conditioned situation as a consequence of adding Googas. The same parameter increased 41% for AWMA in comparison with CHMA due to applying ASA-modified asphalt. By considering 80% as the minimum acceptable TSR value, CHMA and SWMA samples showed inadequate moisture resistance (respectively77% and 68%).Fig. 5 shows that both AWMA and ASWMA had an acceptable resistance to moisture damage, with TSR value above 0.8 for each mixture (0.90 for AWMA and 0.85 for ASWMA). Therefore, AWMA and ASWMA samples which were modified by NZ as an anti- stripping agent showed improved moisture susceptibility compared to CHMA and SWMA samples. Comprehensively, these comparisons demonstrated that Googas lowers indirect tensile strength (ITS) and tensile strength ratio (TSR), but ASA improves them significantly.

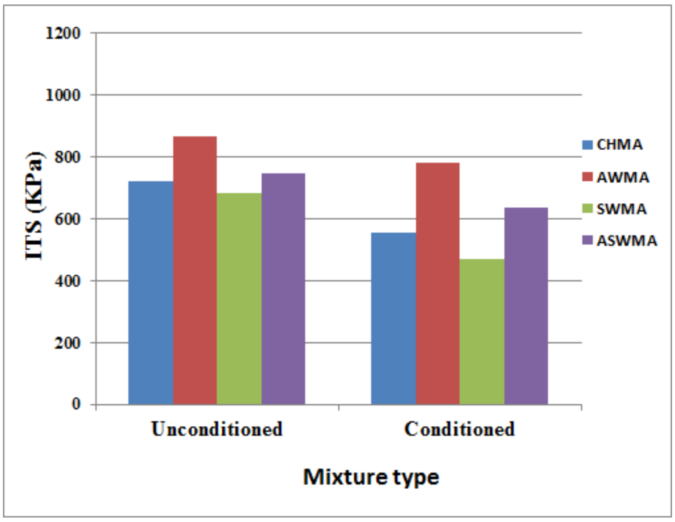

Fig. 4. The indirect tensile strength of unconditioned and conditioned specimens.

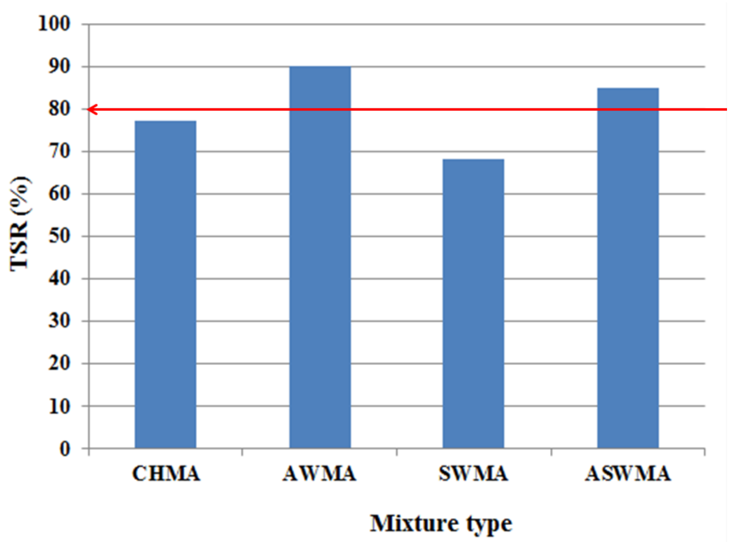

Fig. 5.TSR values vs. mixture type.

4.3.3. Fatigue performance

As results of performed fatigue tests, the correlations between the number of cycles and the strain level applied to the specimens at 5, 25 and 40 °C under 100 and 300 KPa stresses are illustrated in Fig. 6. Results indicated the beneficial effects of NZ and deteriorative effect of Googas on the fatigue life of studied mixtures. Also, reduction in the mixtures' temperature led to the increment of the fatigue life at aforementioned stress levels. Fig. 6 compares the fatigue curves of four specimens including CHMA, AWMA, SWMA and ASWMA. Between these specimens, AWMA showed the finest performance following CHMA, ASWMA and SWMA. As mentioned earlier, the crystallized part of sulfur particles and dissolved part in the asphalt during the mixing process, decreases the binder's ductility and flexibility; thus, a lower fatigue resistance and flexibility were observed in the SEA mixtures. However, considering stiffness properties exhibited in the previous section, the improved resilient modulus of SEA mixtures will decrease strain magnitude applied to the pavement structure. This phenomenon could have a beneficial effect on the SEAs fatigue behavior in real condition, in which the pavement structure bears stress-controlled vehicular loading instead of strain-controlled loading, as was chosen as loading condition in the laboratory [7].

AWMA had the longest fatigue life which could be justified by the lower stiffness and viscosity of this sample as well as a developed bond between asphalt and aggregates as a result of ASA- modification. On the other hand, as demonstrated by ITS test in the previous section, using NZ can lead to high tensile strength in NZ- modified asphalt mixtures. Improved tensile strength leads to the postponing of micro-cracks generation and propagation which subsequently postpones fatigue failure. As illustrated in Fig.6, the ASWMA had slightly flatter slope compared to the SWMA, which demonstrates that NZ-modified SEA possesses higher fatigue life at a greater strain. Coefficients of fatigue equations are shown in the table. 5.

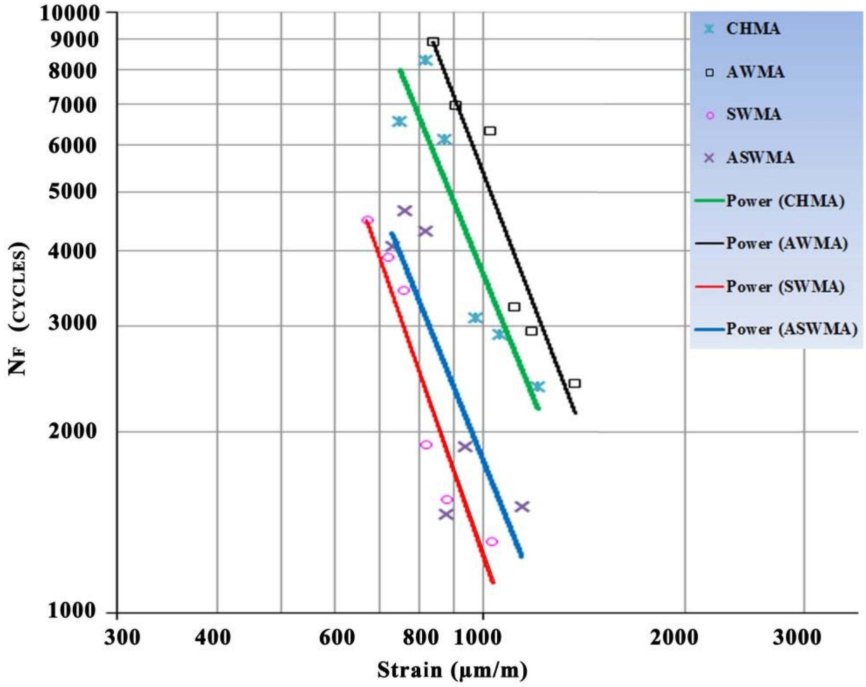

Fig. 6.ITF test results.

Table 5

Coefficients of the fatigue equations.

Asphalt mixture	Coefficient of the fatigue equations		R^2
	a	b	
CHMA	6E+11	-2.74	0.841
AWMA	3E+12	-2.91	0.918
SWMA	6E+12	-3.22	0.903
ASWMA	4E+11	-2.78	0.764

4.3.4. Rutting performance

The rutting resistance of the four evaluated samples is illustrated in Fig. 7. As it was mentioned previously, maximum permissible rut depth of 6 mm after 20,000 cycles at 50°C is acceptable. As seen in Fig. 7, the results of the Hamburg testing showed that both the ASWMA and SWMA had met the desirable deformation resistance considering the stated criterion. These two samples almost showed a similar rate of increase and ultimate resistance which demonstrate that adding NZ as the anti-stripping agent does not have a considerable effect on the rutting resistance of asphaltic mixtures. On the other hand, sample AWMA showed the weakest resistance against rutting at 20,000 cycles, followed by CHMA, as shown in Fig. 7. Both of these samples were not modified with sulfur, therefore had less stiffness than SEA samples and consequentlywere weaker against rutting phenomenon.

As shown in Fig. 7, specimens ASWMA and SWMA showed a rutting value at 20,000 cycles that were less than 6.0 mm; therefore, SEA samples had sufficient rutting resistance, unlike two other samples.

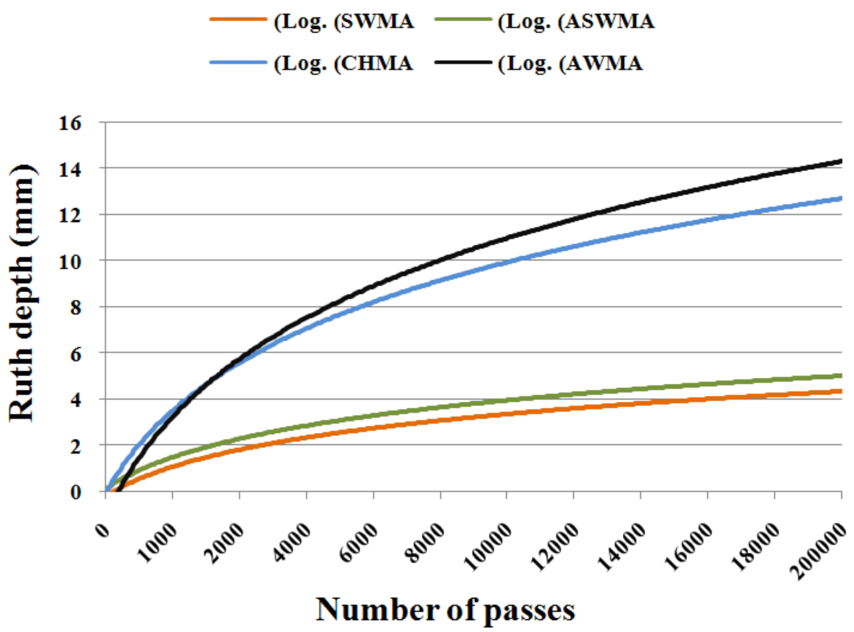

Fig. 7. Wheel track test results at 50 °C.

5. Conclusion

This study evaluated the effectiveness of using a new generation of modified- sulfur and ASA additives in the production of warm-mix asphalt. In this study, the moisture susceptibility and some of the mechanical properties of conventional HMA and ASA and/or sulfur- modified mixtures were evaluated and compared. The modification of asphalt mixture with Googas (treated sulfur) and the use of nanotechnology Zycotherm as the anti-stripping agent resulted in an efficient additives combination which leads benefiting improved properties of SEAs while omitting or attenuating its defects. In addition:

- As it was shown in SEM pictures, mixing procedure was a successful technique to mix Googas in asphalt mixtures and make an almost homogeneous Googas-asphalt matrix. Some parts were dissolved to an acceptable degree and some crystallized at micro and nano scales.
- Extending a portion of asphalt by Googas led to a mixture with a higher resilient modulus which was more resistant to permanent deformation. This increase was about 50 % and 100 % at low and high temperatures respectively. Using ASA reduced SEA mixture's resilient modulus slightly, but this deterioration was negligible especially at higher temperatures (lower than 4%).
- Obtained results by Lottman test demonstrated that Googas reduced indirect tensile strength (ITS) about 8 % and tensile strength ratio (TSR) about 12 %, but on the other hand, ASA improved them significantly by about 42 % and 28 % respectively. Therefore, moisture susceptibility of ASA-modified SEA (ASWMA) was significantly improved compared with unmodified SEA. As a result, modification of SEA by the use of ASA (Zycotherm) was a successful method to reduce moisture susceptibility of SEA mixture.
- SEA mixtures showed the least fatigue life. However, the greater modulus of SEA mixtures reduced the magnitude of strain induced in the sample (about 20 %). Furthermore, antistripping agent increased fatigue life (about 25 %) by developing adhesion between asphalt and aggregates.
- As a result of higher stiffness, the rut depth of SEA mixtures decreased by about 300% at the last cycle of the loading process in comparison with conventional asphalt

mixture. Using ASA attenuated this improvement slightly, but the reduction was negligible (about 25%).

Overall, conclusions of this research indicate that mechanical characteristics of asphaltic mixture improve by sulfur modification, essentially about rutting phenomenon. On the other hand, nanotechnology Zycotherm as an anti-stripping agent could improve adhesion between aggregates and sulfur- extended asphalt, therefore, improve the deteriorated parameters caused by sulfur modification, such as moisture susceptibility and fatigue resistance.

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