

## Effect of Sulfur on the Storage Stability of Tire Rubber Modified Asphalt

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**Abstract:** The use of tire rubber (TR) as an asphalt modifier to improve the asphalt mixture performance has been succeeded. Because the poor compatibility between TR and asphalt the storage stability of TR modifier is a main concern. The main objective of this study is to enhance the properties of tire rubber modified asphalt binder and improve the storage stability through the addition of Styrene-Butadiene-Styrene (SBS) and elemental sulfur (S). Low quality asphalt paving 60/70 penetration grade was modified with 2, 3, 4, and 5% TR (by asphalt wt.) and equal parts of SBS and TR at 2, 3, 4 and 5% by asphalt wt. were also prepared before and after the addition of sulfur. Physical properties including softening point penetration at 25°C and ductility at 4°C, penetration temperature susceptibility (PTS) and penetration index (PI) of modified binders were examined. The storage stability of modified and unmodified asphalt were tested at 140, 160 and 200°C to detect the optimum and critical vulcanization temperature. The effect of TR modified asphalt binder on the asphalt mixture performance before and after the addition of either SBS or SBS/S were evaluated using Marshall stability and flow test. The effect of the vulcanized blend to resist plastic deformation of asphalt mixture was evaluated through wheel tracking test. Results indicated that PTS of modified asphalt before and after vulcanization was largely decreased. The storage stability of TR/SBS modified asphalt after vulcanization process has been achieved at 160°C while the critical degradation temperature reached to 200°C. Marshall Stability and resistance to plastic deformation of TR/SBS were increased after the addition of sulfur. The best improvements were obtained at 4% TR/SBS/ 1%S.

**Key words:** Tire rubber • Styrene-Butadiene-Styrene • Modified asphalt • Sulfur • Vulcanization • Vulcanized asphalt binder

### INTRODUCTION

The use of tire rubber in asphalt paving industry could contribute to improve some engineering properties of asphalt mixtures and at the same time minimizing the problems related to the disposal of waste tires [1]. The technological development of addition of tire rubber as asphalt paving material through wet process was started in 1960 in Arizona by McDonald. The results of that experience indicated that the addition of about 18 to 22% by weight ground tire rubber (#8 to #20 mesh size) at elevated temperature to the base asphalt lowered temperature susceptibility and increased the ductility, cone penetration, resisted reflective cracking and improved skid resistance over conventional mixtures by about 30% [2,3]. Other techniques using wet process were developed mainly as from the 1980s up till now such as the continuous blending and terminal blending from Florida and Texas, USA. The Florida technology differs from McDonald's process in some important aspects:

lower percentages of rubber, smaller rubber particle size, lower mixing temperature and shorter reaction time [4, 5].

Because the poor compatibility between tire rubber and asphalt, the storage stability of TR-modified asphalt is usually poor at elevated temperature. Once agitation stops, the dispersed tire rubber particles modified asphalt separates quickly from the asphalt and the polymer rich phase migrates to the upper part of the storage tank, while an asphalt rich phase segregates into the lower parts. This results in an inhomogeneous material that is useless for paving and can cause troubles [6]. Thus it is necessary to improve the storage stability of TR-modified asphalt for practical use. The storage stable polymer modified asphalt with sulfur has been reported by a number of patents [7,8,9]. Some researches used virgin polymers to control and improve the storage stability of crumb rubber modified binder [10].

The nature of the mechanism by which the interaction between sulfur and rubber has been reported in the literature as two main mechanisms. Free radicals

vulcanization [11] and ions vulcanization [12]. Based on literature on vulcanization of rubber through sulfur, the optimum sulfur content that required to the best vulcanization of rubber is about 5% of rubber content. But in this study the other expected that the addition of 1% sulfur (by asphalt weight) to the rubberized asphalt binder may be effective in improving the workability of the asphalt aggregate mixture.

**Objective:** The main objective of this study is to enhancement the properties of tire rubber modified asphalt binder and improves its storage stability through the addition of SBS and sulfur. The best and critical storage stability temperatures were determined. The effect of vulcanization process of rubberized asphalt binder in the aggregate mix was also examined.

**Materials and Experimental Program**

**Materials:** Low quality paraffinic waxy asphalt penetration grad 60/70 (low quality paving asphalt grade) produced by Alexandria Petroleum Company was applied, Table 1. Crushed dolomite as fine and coarse aggregates comply with ASTM C 136 and lime stone as mineral filler comply with AASHTO T37 were used for hot mix asphalt, Table 2 and 3. Fine tire rubber (100% pass #30, 66.46% pass #50, 13.66% pass # 100 and 2.48 % pass # 200) Produced by MARSO Factory Egypt, Styrene Butadiene-Styrene (SBS) produced by Shell Chemical Co. [Kraton D-1101 is a linear SBS polymer (powdered) containing 31% styrene] produced by Shell Chemical Co. and commercial elemental sulfur were applied as modifiers.

**Experimental Program:** The experimental program is divided to two main parts. The first part was designed to

Table 1: Physical properties and chemical constituents of asphalt cement 60/70

Properties	Values	Standard methods
Physical properties:		
- Penetration at 25°C 100 g, 5 seconds, 0.1 mm	66.00	ASTM D 5
- kinematic viscosity at 135°C, m pa.s	254.00	ASTM D 2170
- Absolute viscosity at 60°C, poise.	961.00	ASTM D 2171
- Flash point, °C (Cleveland open cup).	250.00	ASTM D92
- Ductility at 25°C, 5 cm/min, cm.	+150.00	ASTM D 113
- Softening point °C (Ring and Ball).	49.00	ASTM D 36
- Solubility in trichloroethylene, %.	99.90	ASTM D 2042
- Specific gravity at 25°C	1.018	ASTM D 70
Chemical constituents, wt %:		
- (Oils + Wax) %	29.57	ASTM D 412
- Wax %	7.13	
- Resins %.	55.63	
- Asphaltens %.	14.79	

Table 2: Characteristics of the used aggregates

Type	Crushed dolomite		Artificial sand	Dust Limestone	Standard specification limits
	Size2	Size1			
Pass (wt) %	Pass%	Pass%	Pass%	Pass%	
Sieve size					
1"	100				
¾"	99.8	100			
½"	59.6	99.9			
3/8"	8.7	97.5			
No.4	1.9	47.1	100		
No.8	1.7	13.1	97		
No.30	1.6	8.2	68	99	100*
No.50	1.5	5.6	43	98	-
No.100	0.5	1.6	19.7	87.2	More than 85*
No.200	0.1	0.5	1.7	74	More than 65*
Abrasion Resistance (loss %wt)					
-After100 revolutions	8.3	7.9			Max .10
-After500 revolutions	31.2	30.3			Max 40
- bulk specific gravity	2.541	2.34			
- bulk specific gravity (SSD basis)***	2.567	2.577			
Apparent specific gravity	2.642	2.636			
Absorption (wt%)	1.02	1.10			Max.5
% in blend	20	34	42	4	

\* Standard specification limits of limestone mineral filler.

\*\* Standard specification limits of Mineral aggregate.

\*\*\* Saturated surface dry basis.

Table 3: Gradation of the applied mixture

Sieve size	Design Gradation	Specification Limits (4-C)
1"	100.0	100
3/4"	96.1	80-100
1/2"	80.0	68-88
3/8"	70.0	60-80
No. 4	50.1	48-65
No. 8	45.7	35-50
No. 16	28.2	19-30
No. 30	18.0	13-23
No. 50	94.0	7-15
No.100	5.9	3-8

study the effect of SBS and its content on improving the properties of tire rubber modified asphalt and also improve its storage stability through vulcanization process and achieve the best and critical storage stability temperatures. The effect of the best content of each modifier type on asphalt mixture was investigated in part two through Marshall and Wheel Tracking tests. The storage stability test for each blend was examined at 140, 160 and 200°C.

#### Preparation of Modified Asphalt Binders Using Wet Process:

The calculated amount of the base asphalt was heated to 160°C in an oil bath and the required amount of tire rubber (2%, 3%, 4%, and 5% by asphalt weight) was reacted with the asphalt at 160°C using mechanical mixer (200rpm) for 3 minutes, after which the speed was lowered to 80 rpm. mixing was continued for 3 h.

In case of tier rubber styrene-butadiene-styrene modified asphalt (TR/SBS) The base asphalt was first heated to 180°C and mixed with 1, 1.5, 2 and 2.5% by asphalt wt. of SBS using high speed mechanical mixer for two hrs. Then the temperature was reduced to 160°C and four doses of tire rubber (1, 1.5, 2 and 2.5% by asphalt wt.) were added. After which the speed was lowered to 80 rpm. and mixing was continued for 3 h.

In case of vulcanized rubber after TR/SBS blended was completed 1% of sulfur by asphalt wt. was added. Mixing was continued to one hr. using low speed mechanical mixer (80rpm).

When blended was completed, the individual modified blends were divided for testing to penetration at 25°C, softening point, ductility at 5°C according to ASTM D5, ASTM D 36 and ASTM D 113, respectively. Penetration temperature susceptibility (PTS) and penetration index (PI)[13] were also investigated.

**Preparation of Vulcanized Blends, Tr and R/sbs Modified Asphalt:** Preparation of TR/SBS/S modified asphalt binder was carried out at two steps as follows:

Step 1: The calculated amount of asphalt was heated to 180 in an oil bath. Four doses of dry SBS (1, 1.5, 2 and 2.5%) by asphalt wt. were mixed with the base asphalt at 180 using high speed mechanical mixer for two hrs.

Step 2: After preparation of SBS modified asphalt the temperature was reduced to below 130°C then 1, 1.5, 2 and 2.5 of TR by asphalt wt. were added to SBS modified asphalt stirring was continued for 3 hrs. to obtain 2, 3, 4 and 5% of equal parts TR/SBS modified asphalt at low speed (80rpm). The temperature was reduced to below 120°C then 1% of elemental sulfur by asphalt wt. was added to each blend and stirring was continued for 20 minutes at low speed (80rpm) so as to ensure unreacted homogenous blends were obtained. Below 120°C neither the reaction between asphalt and sulfur nor the vulcanization of TR/SBS/ sulfur blend would take place according to Al-dobouni et al [14] and Jin et al [15]. Each blend was divided to two main parts and every part was divided to three equal parts. The temperature of each blend type was rapidly increased to 140, 160, and 200°C while stirring for 1 h (one part for each temperature for the same blend).

In the case of TR modified asphalt binder, 2, 3, 4 and 5% of TR was mixed with the base asphalt according to step two without the addition of sulfur.

The storage stability for modified and unmodified asphalts was measured as follows:

Each sample was sealed in an aluminum fail tube (32 mm in diameter and 160 mm in height) without an air enclosure. The tube stored in an vertical position in an oven at 140, 160 and 200°C for 48 h, then the tube was cooled to room temperature and divided horizontally to three equal parts.

The upper and lower parts were melted and tested to softening point, if the difference between top and bottom softening temperature is less than 2.5°C the blend is considered as good storage stability modified asphalt binder and stirring is not required up to 48h storage[15].

### Mixture Tests

**Preparation and Evaluation of Asphalt Mixture:** To determine the asphalt mixture properties at the optimum asphalt content for modified and unmodified asphalts, Marshall method was applied on 4% of each modifier type only according to ASTM D1559. Five asphalt mixtures were prepared for each modified and unmodified asphalt binder using 4.5, 5, 5.5, 6, 6.5% by aggregate wt of each asphalt binder. The specimens were compacted using, 75 blow/side to simulate heavy traffic load. Test specimens were tested at 60°C.

**Resistance of Asphalt Mixture to Rutting:** The effect of untreated asphalt, 4% TR modified asphalt, 4%TR/SBS modified asphalt and 4% TR/SBS/S modified asphalt on rutting resistance of asphalt mixture was evaluated in the laboratory using the Transport and Road Research Laboratory (TRRL) method [16]. The compaction of the mix was conducted applying a hydrostatic load at a stress level of 8.7 Kg/cm<sup>2</sup> and curing period of three days. The test was carried out at 60°C

## RESULTS AND DISCUSSION

**Storage Stability:** Figure 1, shows the storage stability of TR modified asphalt, TR/SBS and TR/SBS/S modified asphalts at 140, 160 and 200°C with and without sulfur. It can be seen that:

- The softening point of the upper section of TR, and TR/SBS and TR/SBS/S at 140°C is higher than those of the bottom section at all rubber contents and increase with increasing rubber content. This is due to the difference in density between the rubber and asphalt which leads to separate and float the rubber particles on the top of the asphalt [15]. We noticed also that the highest softening point for both the upper and lower sections was obtained with blends that were modified with TR/SBS/S. This means that the vulcanization process started to form at this temperature between TR and TR/SBS. It can be seen also that the softening point of blends modified with TR/SBS is higher than those modified with TR alone. This means also that a net work structures are formed between TR and TR/SBS rubber particles. These results can be realized because the different in softening point of the lower section for the two rubbers modified asphalt is not significant.
- When the mixing and storage temperatures increased to 160°C there is no difference in the softening point between upper and lower sections of the blends modified with TR/SBS/S (have the same values). This means that a complete and stable vulcanization have been occurred between the asphalt particles and the rubber particles due to the dehydrogenation of the asphalt and formation carbon sulfur bond between the asphalt and sulfur [15]. At the same time chemical cross linking had been formed between rubber particles and sulfur. This chemical bond that formed between the asphalt particles and sulfur and cross linking between rubber particles and sulfur prevent the formation of the separation phase to form between rubber and asphalt. So this temperature can be conceder the best vulcanization and storage temperature. It can be seen also that TR and TR/SBS modified asphalt without sulfur showed higher softening point for the upper section than the lower once. This proved that the separation face still form between the rubber phase and the asphalt phase. So sulfur could improve the storage stability of TR modified asphalt and TR/SBS modified asphalt binders.
- We can notice also that the softening point of the upper section for the same rubber type depends on the storage temperature. The highest softening point of the upper section was achieved at 160°C storage stability followed by 140°C then dramatic decrease in softening point has been observed for both the upper and bottom sections at 200°C storage stability. We can seen also that the softening point of the bottom section at 160°C for the same rubber is higher those at 140°C. This is because at 140°C the swelling of rubber particles by absorbing the asphalts oil is very poor. When the temperature raised to 160°C the rate of swelling of rubber particles increases by time up to 3 h then stopped. At this temperature the asphalt liquid phase became stiffer due to the loss of most liter fractions by rubber particles which lead to increase the softening point of the base asphalt that migrate to the lower section. On the other hand a net work structure was formed between the accumulated upper rubber phases which increased the softening point of the upper section.

- When the mixing and storage temperatures increased to 200°C dramatic decrease in softening was obtained for all modified blends and also between lower and upper sections. We can notice also that the softening point of the lower section for some samples is higher than those of the upper sections. This proved that the cross linking and chemical bonds that formed by sulfur are destroyed at this high temperature. On other hand when the blends were stored at 200°C for 48 h the swelling rubber particles start to de-polymerize and release more components back to the liquid phase of the binder which leads to decrease the softening point of the bottom section. At the same time the sulfur-sulfur or carbon sulfur bonds that were formed by the vulcanization process during tire rubber preparation start break also by time leading to decrease the softening point of both upper section comparing to thus stored at 160°C [17,18].

So this temperature may be consider the damage temperature for mixing and storage rubberized asphalt.

Effect of rubber content and vulcanization process on Physical properties of modified blends:

The physical properties of the modified asphalts prepared at the best vulcanized temperature (160°C) as detected by storage stability test is plotted in Table 4. It can be seen that:

- The penetration decreases and the softening point increases with increasing rubber content. The more reduction in penetration (54.5%) combined with more increase in softening point (57.2%) were obtained when the base asphalt was modified with 7% TR/SBS/S comparing to TR and or/TR/SBS modification at the same polymer content. The less decrease in penetration (13.6%) combined with less increase in softening point (8.1%) were shown as the base asphalt was modified with 2%TR alone while it was 39.4% and 22.4% at TR7% respectively. When SBS is introduced to asphalt binder modified with TR alone the softening point increased to 40.8% and the penetration decreased to 50% at 7% TR/SBS modification comparing to the control. It is clear also that the difference between 4% and 5% modification is not significant. The decreases in penetration and increase in softening point indicate an increased hardness and stiffness of modified binder.
- Significant decrease in penetration temperature susceptibility (PTS) and significant increase in

penetration index (PI) were achieved with all modified blends [low PTS value combined with high PI indicates improvement in sensitivity to temperature changes]. This result will enhance rheological performance for pavement during summer months and cold winter temperatures<sup>17</sup>. the more decrease in PTS combined with more increase in PI was obtained with vulcanized blends followed by TR/SBS modified asphalt comparing to those modified with TR alone at the same rubber content.

- The effect of modification and vulcanization processes on low temperature ductility (4°C) is shown in Fig. 1. It can be seen that low temperature ductility of pure TR modified asphalt is smaller than those modified with TR/SBS. High increase in low temperature ductility was achieved when 1% of sulfur was introduced to TR/SBS modified asphalt. The increase in low temperature ductility indicates an increased low temperature flexibility of the modified binders. The increase percent in low temperature ductility of modified binders relative to the base asphalt ranged between (133.3% and 216%), (333.3% and 410%) and (600% and 633.3%) for (2%TR and 5%TR), (2%TR/SBS and 5%TR/SBS) and (2%TR/SBS/S and 5%TR/SBS/S).

The data presented on the modified asphalt binders show that the development in binder properties reflective changes in internal structure developing during the interaction process. Particle swelling stiffens the asphalt liquid phase as lighter fraction are absorbed leading to increase in softening point and decrease penetration of the rubberized asphalt. While the improvement, in the asphalt ductility is due to the formation of gel-like rubberized structure that formed in the base asphalt. The more improve in the asphalt properties when equal parts of TR and SBS are combined is due to the compatibility between SBS and TR and the cross linking that formed between TR and SBS during mimicking process at 160°C for 3 h [17]. When sulfur is introduced to TR/SBS modified asphalt binder at 160°C more improvement was obtained due to the formation of sulfur carbon bond between the asphalt phase and sulfur. At the same time cross linking formed between the rubber particles and sulfur<sup>17</sup>. More over the unreacted elemental sulfur solidifies in the modified asphalt blend and improved its physical (softening point, penetration, PTS, PI and ductility at low temperature) and mechanical properties as will be seen later in Marshall properties and resistance to rutting.

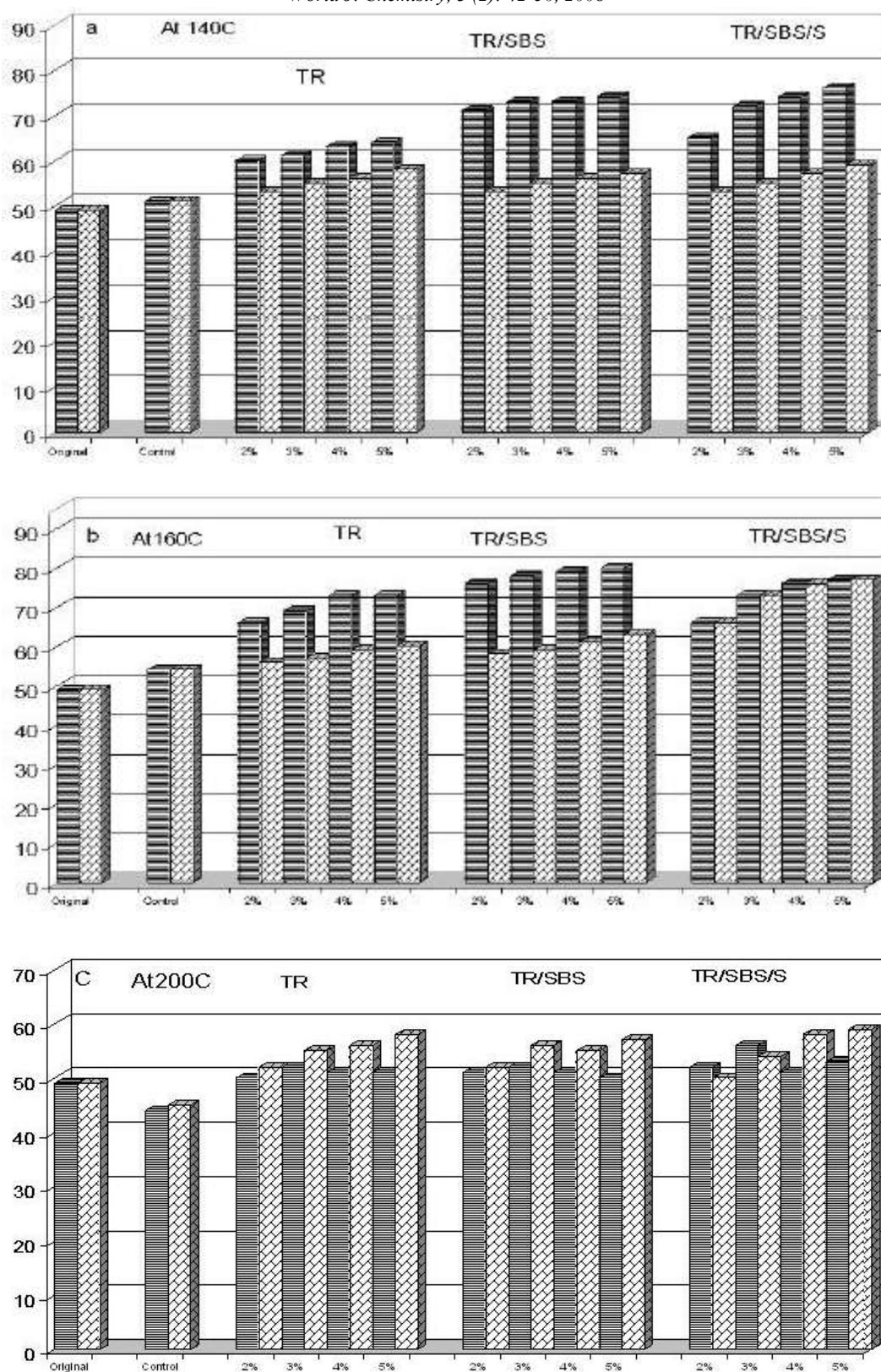


Fig. 1: Effect of different storage temperatures on modified binders

Table 4: Effete of modifier type and its content on the base asphalt

Blend type	Penetration 0.1mm	Softening point (°C)	PTS	PI
Control	66	49	0.04514	-0.79017
TR 2%	57	53	0.04097	-0.15909
TR 3%	51	56	0.03857	0.2442
TR 4%	46	59	0.03648	0.3232
TR 5%	40	60	0.03717	0.4946
TR/SBS 2%	55	61	0.03229	1.4727
TR/SBS3%	45	64	0.03205	1.5274
TR/SBS 4%	38	68	0.03077	1.8180
TR/SBS 5%	33	69	0.03147	1.6579
TR/SBS 2% +1% S	52	66	0.0645	2.2566
TR/SBS3% +1% S	43	73	0.02645	2.917003
TR/SBS 4% +1% S	43	76	0.02689	2.7947
TR/SBS 5% +1% S	30	77	0.02722	2.6522

Table 5: Effect of modifier type on Marshall properties

Mix No.	Bitumen content (%)	Density (Kg/cm <sup>3</sup> )	Stability (N)	Flow (mm)	Air voids (%)	VMA* (%)
Control	5	2.374	1420	3.2	3.2	15.1
4%TR	5.5	2.357	1510	3.4	3.4	15.0
4%TR/SBS	5.6	2.347	1800	3.5	3.5	15.0
4%TRSBS/s	5.6	2.338	1920	3.6	3.6	15.0

\*Air voids % in mineral aggregate

**Asphalt Mixture Results:** The effect of 4%TR, 4%TR/SBS and 4%TR/SBS/S on properties of asphalt mixture are plotted in Table 5. It can be seen that we can see that

- The addition of 4%TR, 4%TR/SBS and 4%TR/SBS/S to the asphalt binder increased the asphalt content in the asphalt mixtures. This may be due to the disparaged of rubber particles in the asphalt binder increased its volume in the mix. We can notice also that the asphalt content in mixes modified with TR alone is lower than those modified with TR/SBS or TR/SBS/S. This may be due to the cross linking that formed between the TR particles and SBS during the interaction process at 160°C for 2hrs. AS mentioned above.
- The Marshall stability and flow values of all modified asphalt mixture increased. This may be due to the absorption of the asphalts oil by rubber particles as mentioned above. Only the marshal stability of mixes modified with 4%TR/SBS and 4% SBS/S were within the Egyptian Standard Specification limits for the dense graded asphalt mixtures (min. 1800lbs.). TR modified asphalt mixture was excluded from further evaluation.
- The Marshall stability and flow values of asphalt mixtures modified with 4%TR/SBS and 4% TR/SBS/S were higher than that of the control asphalt mixture by (26.8% and 9.4) and (35.2%and12.5%) respectively. This may be as previously mentioned due to the absorption of the asphalts oil and the stiffness effect of styrene in SBS and the chemical bonds that formed between the two types of rubber

and the sulfur carbon bond that formed between the asphalt and sulfur.

- The air voids content in the modified mixes were higher than the control mix by 9.4% and 12.5% and for TR/SBS and TR/SBS/S, respectively. While the voids in mineral aggregates were slightly decreased. This is because the above reasons which stiffen the asphalt binder leading to compaction difficult.
- The Effect of modified asphalt binder on asphalt mixture to resist rutting is shown in Fig. 3 and Table 6. As can be seen the addition of 4%TR to asphalt binder reduced the rutting depth of asphalt mixture after 45 minutes to 23.5% as compared to the control mixture and 38.5 when TR is combined with equal parts of SBS (4%TR/SBS). When 4% TR/SBS was vulcanized by the addition of 1% sulfur the rutting depth decreased by 56.4%. This may be, as mentioned above attributed to the absorption of asphalt liquid phase by TR and SBS particles. That leads to stiffen the base asphalt and increased its softening point which consequently reduced the rutting depth. More decrease in rutting depth was obtained by the addition of SBS to TR modified asphalt binder. This may be due to the stiffness effect of styrene in SBS beside the cross linking that was formed between TR and SBS during mixing process at 160°C leading to more stiffen of the asphalt binder. When sulfur is added to TR/SBS it forms chemical bonds and cross linking as mentioned above that leads to more stiffness in the asphalt binder and reduced rutting depth. More over the unreacted sulfur melts during mixing the hot

Table 6: Effect of the best modifier type and its content on rutting depth

Time (min)	No. of Wheel Passes	Rut Depth (mm)			
		Traditional 60-70 HMA	TR	TR/SBS	TR/SBS/S
0	0	0.00	0.00	0.00	0.00
5	210	1.56	0.83	0.82	0.349
10	420	3.01	1.86	1.60	0.91
15	630	4.36	2.78	2.40	1.60
20	840	5.75	3.69	3.18	2.23
25	1050	7.06	4.64	3.95	3.00
30	1260	8.18	5.63	4.89	3.69
35	1470	9.24	6.72	5.66	4.13
40	1680	10.23	7.74	6.36	4.68
45	1890	11.47	8.77	7.05	4.99
50	2100	12.43	9.46	7.63	5.60
55	2310	13.36	10.00	8.07	5.70
60	2520	14.06	10.45	8.22	5.60
Rut depth (mm)		11.47	8.77	7.05	4.99

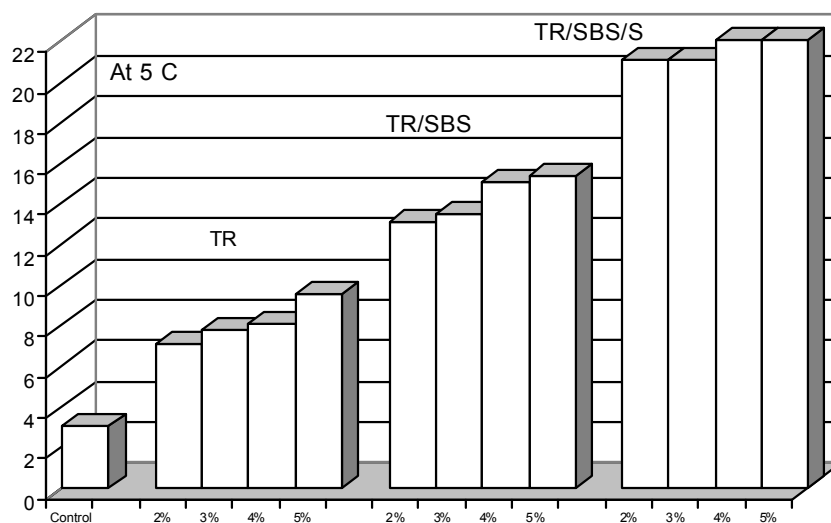


Fig. 2: Effect of modifier type and its content on ductility at 5°C

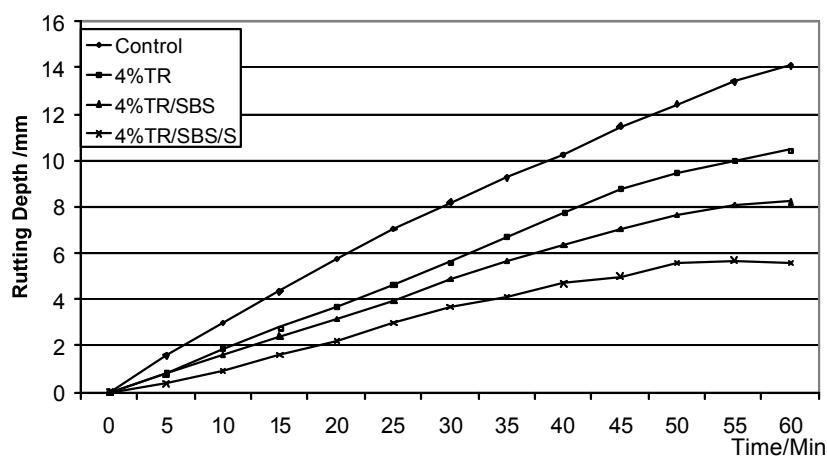


Fig. 3: Rutting depth of modified and unmodified asphalt mixes at 60°C



aggregate (150°C) with the hot asphalt (160°C) and reduced the viscosity of the asphalt binder in the mix leading to improve the workability. Which produced completely homogenous hot mix asphalt with good compaction properties [18] as proved above.

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