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Rheological properties of modified bitumen: Comparison of waste polymers' performance

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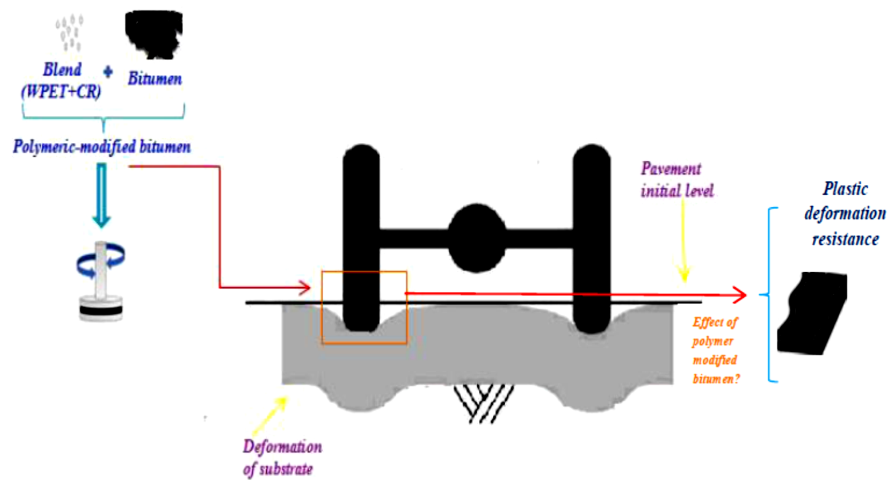
HIGHLIGHTS

- Pure bitumen behaves fully viscously at elevated temperate and it suffers from low elasticity.
- Bitumen to modifier ratio 93/7 is the optimum value for modification process.
- A modifier mixture containing recycled poly (ethylene terephthalate)/ crumb rubber (90/10 weight ratio) gives the best modification results.
- Poly (ethylene terephthalate)/ crumb rubber blend can replace styrene-butadiene-styrene triblock copolymer for bitumen modification purposes

GRAPHICAL ABSTRACT



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ABSTRACT

In this investigation, rheological properties of three different polymer-modified bitumen compounds containing recycled polyethylene terephthalate (R-PET), crumb rubber (CR) and poly (styrene-butadiene-styrene) (SBS) are evaluated and compared. The modified samples were tested by a dynamic shear rheometer (DSR) where complex modulus (G*), phase angle (δ) and rutting resistance (G*/Sinδ) of specimens were measured at different temperatures. The obtained results show that the optimum rheological properties will be gained when 7% wt. of a modifier mixture containing R-PET/CR (90/10 weight ratio) is added to the bitumen. In comparison with un-modified bitumen, the one modified by the latter modifier shows phase angle shift 68.9 °C, complex modulus 2190 (Pa) and rutting resistance 2520 (Pa), at temperature 80 °C. Generally, addition of the polymeric modifier increases complex modulus, rutting resistance and rigidity of the bitumen while a little decrease in phase angle is also observed.

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1. Introduction

Although the amount of bitumen in asphalts does not exceed 6%, addition of bitumen affects strength and wear resistance of asphalt as it acts like an adhesive for stones to adhere to each other [1]. Bitumen shows a very bizarre rheological behavior where it changes from a viscose material into an elastic one after being imposed by load and experiencing temperature change. Thus, bitumen as a viscoelastic material determines the performance of the roads. A bitumen compound, asphalt, should be flexible enough to prevent asphalt overlay from thermal cracking. On the other hand, the compound should be rigid enough at elevated tempera- tures to prevent from rutting. Thus, an asphalt overlay which adapts itself to different environmental and load- ing conditions will be the best coating for a road [2-3]. The aforementioned statements signify the impor- tance of bitumen modification. To do this, various attempts are made and different polymers have been added to bitumen among them SBS copolymer is rec- ognized as the best modifier. This is why SBS increas- es stiffness of the bitumen at elevated temperatures and simultaneously improves elastic modulus, mechanical properties and aging of the bitumen [4-6]. Nowadays, recycled polymers are replacing the pure ones in bitumen modification applications. The driving forces behind this replacement are economic and environmental issues [7]. Industrial, domestic, mineral and agricultural waste materials are widely used in asphalt overlay. Crumb Rubber and poly (ethylene terephthalate) are categorized as industrial and domestic wastes, respec- tively [8]. Comparing with the base bitumen, addition of R-PET results in increase of the bitumen softening point, decrease of bitumen diffusivity as well as im- provement of viscoelastic properties including com- plex modulus, phase angle shift and rutting resistance. However, no improvement in fatigue resistance is re- ported upon R-PET addition. The CR as another bitu- men modifier increases rutting resistance and stiffness of the bitumen [9-11]. In this investigation, blends of R-PET and CR were used for bitumen modification. The rheological properties of the modified bitumen were obtained and compared with a SBS-modified one.

2.Experimental

2-1. Materials

Bitumen, grade number 60/70, was supplied by Isfahan refinery (Jey Oil Com., Iran). The grade specifications are presented in Table 1. R-PET in form of chips was obtained from a local bottle recycling company and CR was purchased from Isatiss Rubber Company, Yazd, Iran. Linear SBS containing 31% styrene was gotten from Murcheh khvort polymeric bitumen incor- poration as well.

Table 1.
Specification of the bitumen (grade number 60/70) supplied by Jey Oil Com.

Specific Weight (25 °C)	1.0145
Penetration grade (dmm)	66
Softening point (°C)	51
Flash point (°C)	334
Loss on heating (wt%)	0.02

2-2 Equipment and Methods

2-2-1. Sample Preparation

At first, the R-PET chips were dried for 4 hours in an oven working at 80 °C. Subsequently, blends of R-PET and CR were prepared by feeding the components to a co-rotating twin screw extruder having screw diameter 2 cm and L/D= 40, Brabender, Germany. The rotation speed of the extruder and the die temperature were set at 65 rpm and 260 °C, respectively. The blend compositions are presented in Table 2.

Table 2.
Composition of the blends prepared in the extruder.

Sample code	Total sample weight (400 g)	Weight ratio of each component in the blend	The polymer kind
A	300	75	CR
	100	25	R-PET
B	200	50	CR
	200	50	R-PET
C	100	25	CR
	300	75	R-PET
D	40	10	CR
	360	90	R-PET
E	360	90	CR
	40	10	R-PET

2-2-2. Mixing Procedure

A high speed homogenizer (Model L4R, Silverson Com., USA) was used to mix the bitumen with the polymer blends. The addition levels of the blends in respect to the bitumen weight are 3, 5, 7%. At the first step of the mixing process, the bitumen temperature was raised to 150 ºC to reduce its viscosity and to improve its flow ability. Subsequently, the polymer blend was added to the hot bitumen and mixed for 15 min at 350 rpm. The obtained mixture was then transferred to the high speed homogenizer to fully homogenize the compound, Table 3. Finally, the obtained material which is named the modified bitumen afterward was discharged to some special pots to do Sharp test. This test which measures physical properties of the materials determines the performance of the asphalt precisely. Moreover, this test is able to simulate real condition in which asphalt overlay experiences environment temperature. The Sharp tests mainly reveal rheological properties of the bitumen and are widely used in asphalt overlay examination [12].

Table 3.
Composition of the blends prepared in the extruder.

The modifier for bitumen	Rotation speed (rpm)	Temperature (ºC)	Time (min)
SBS	3000	170	60
Sample A	3000	160	60
Sample B	3000	155	45
Sample C	3000	150	30
Sample D	3000	150	30
Sample E	3000	160	60

2-2-3. Dynamic Shear Rheometer

The dynamic shear rheometer tests (DSR), with the setting of temperature rate 1ºC/min and shear frequency of 10 rad/s were performed using AR-2000ex with a parallel plate geometry (25 mm diameter, 1 mm gap). The prepared samples were tested in their linear viscoelastic region from 20 to 90 ºC. The elongation value for all tests was 12%.

3. Results and Discussion

Rheological properties of the polymer-modified bitumen in a temperature range of medium to high are measured by a dynamic shear rheometer. This device evaluates elasticity and viscosity of the modified bitumen by measuring complex shear modulus (G*) and phase angle (δ). The former denotes to total resis- tance of the material against deformation and the latter symbolizes irreversible and reversible deformations. In each loading cycle, a fraction of received energy is consumed for the sample irreversible deformations and the rest of the energy is used for elastic deformations. The work dissipation in each loading cycle can be defined by the following equation in which tension and elongation are known values.

$$W_c = \pi\sigma\varepsilon \sin\delta \quad (1)$$

In this equation, Wc, σ, ε and δ are dissipated work per volume unit, tension, elongation and phase angle, respectively.

Under the condition where the tension is constant, the elongation is defined as ε=σ/G^* . Substituting the latter formula in the equation 1 will lead to equation 2.

$$w_c = \pi\sigma^2 \frac{1}{\frac{G^*}{Sin\delta}} \quad (2)$$

This equation shows that increase of G* and decrease of sinδ reduce work dissipation during a loading cycle. These formulas signify that as the bitumen complex modulus increases, stiffness and rigidity of the material increase while deformation extent decreases. In addition, elastic behavior is intensified when sinδ reduces. Thus, it can be concluded that a bitumen with higher G*/Sinδ ratio will show stronger resistance against permanent deformation [13-14]. Rutting as a problem which occurs at high temperatures can be assessed by both G* and sinδ [7].

In dynamic-mechanical analysis, G* is attributed to the total resistance of materials against deformation while δ is ascribed to viscos-elastic properties. Rheological properties of bitumen are highly dependent on temperature and frequency. In addition, these properties may vary significantly upon addition of polymers. In Figures 1–6, complex modulus, phase angle and Tanδ of each sample in different temperatures and constant frequency, 10 rad/s, are plotted. The Figures show that modulus decreases due to temperature increase; however, it increases upon addition of the polymeric modifier blend.

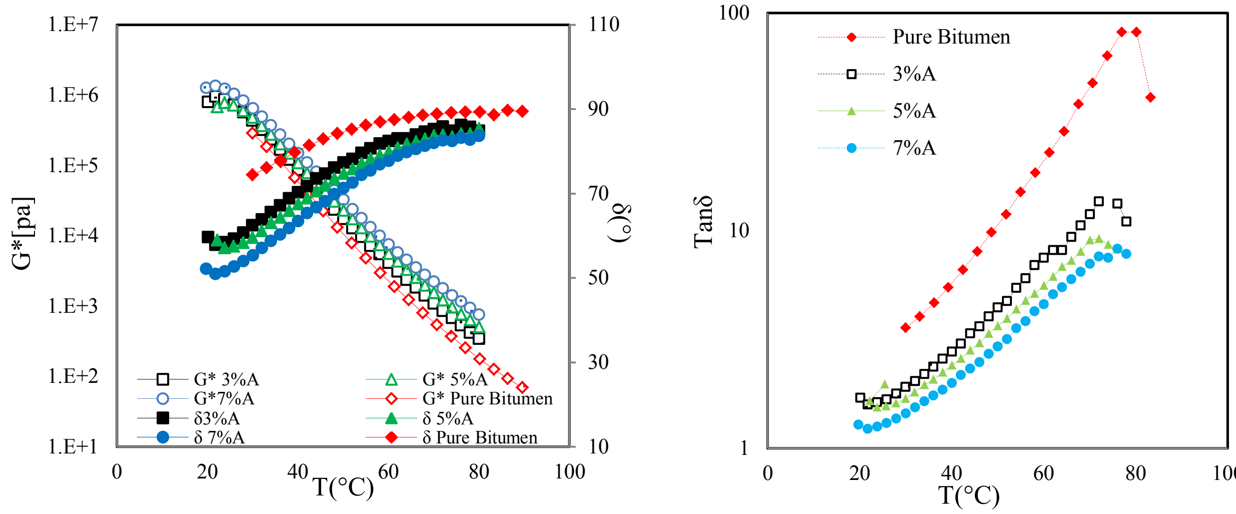

Fig. 1. Complex modulus/phase angle (left) and Tanδ (right) curves for the bitumen modified by blend A.

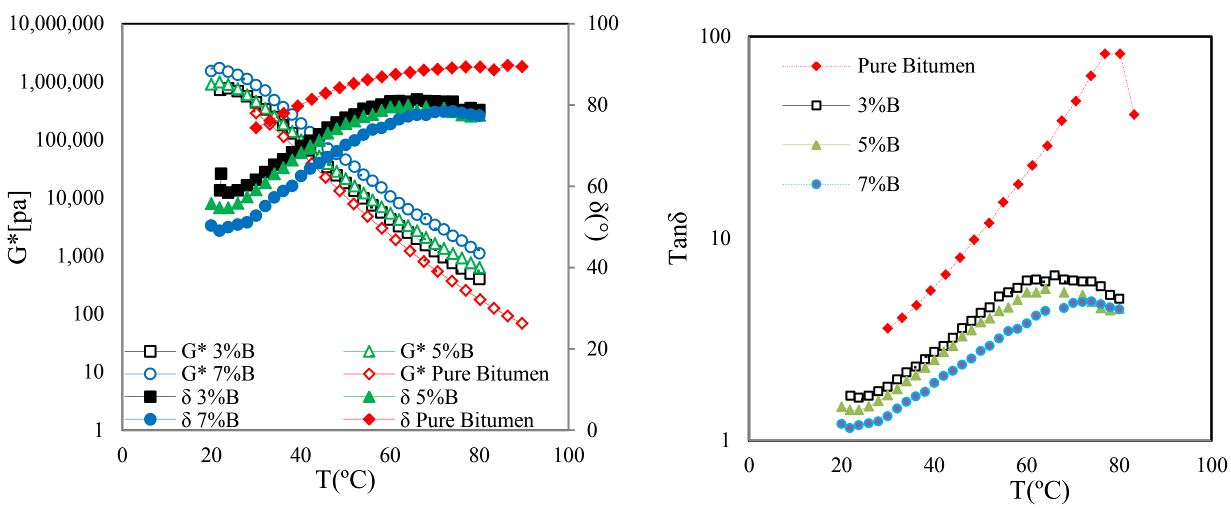

Fig. 2. Complex modulus/phase angle (left) and Tanδ (right) curves for the bitumen modified by blend B.

Bitumen with higher complex modulus shows higher rigidity and stiffness and consequently shows greater resistance against deformation. The Figures 1–5 show that increase of the polymeric modifier content from 3% to 7% does not affect the complex modulus of the system significantly. The Figure 4 represents the sample containing 7% of the modifier D (G* 7%) which has higher modulus comparing with all other modified and unmodified bitumen in entire scanned temperature range. Here, it should be emphasized that for this sample the effect of the polymeric modifier on modulus of the pure bitumen is significant

Moreover, phase angle which shows viscos/elastic trade-off of the material changes subtly for this sample. Bitumen usually behaves like a viscous substance at elevated temperatures and one of the aims of the modifier addition is improving bitumen elasticity in such temperatures to prevent from its deformation upon repetitive loading cycles. The Figure 2 corroborates that addition of the polymeric modifier to the bitumen leads to an improved elastic response in higher temperatures. This observation vindicates that polymeric modifiers positively affect mechanical properties of the bitumen in elevated temperatures.

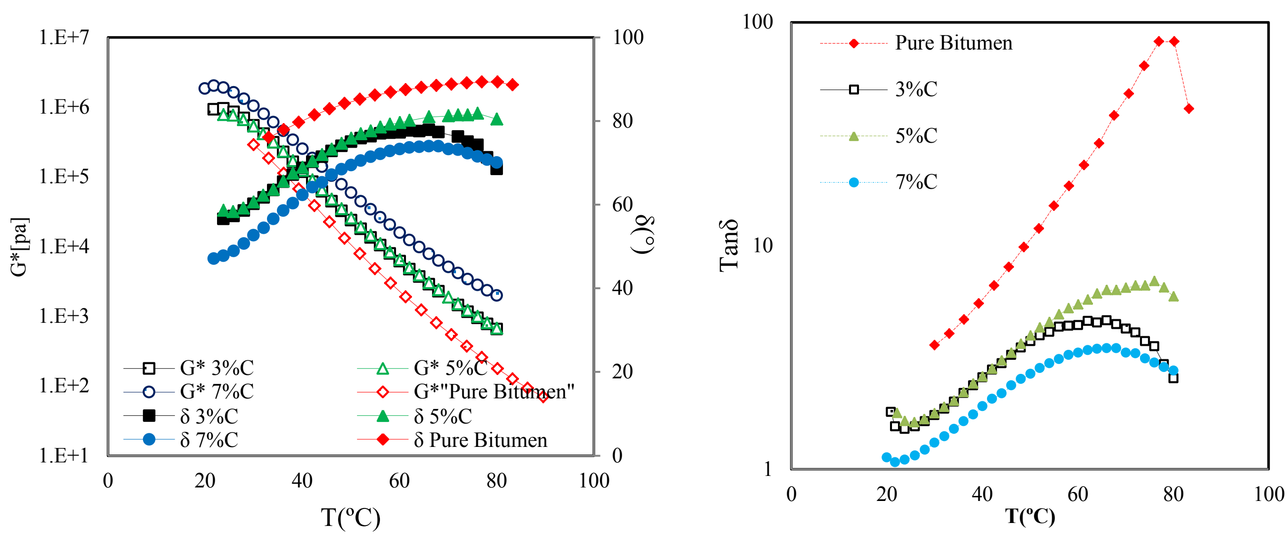

Fig. 3. Complex modulus/phase angle (left) and Tanδ (right) curves for the bitumen modified by blend C.

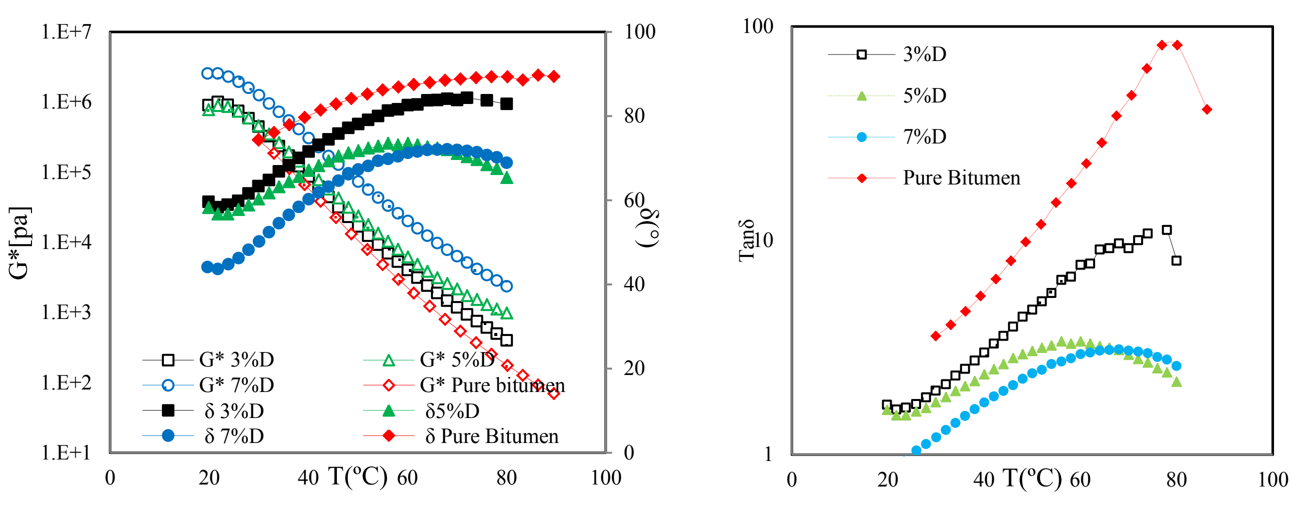

Fig. 4. Complex modulus/phase angle (left) and Tanδ (right) curves for the bitumen modified by blend D.

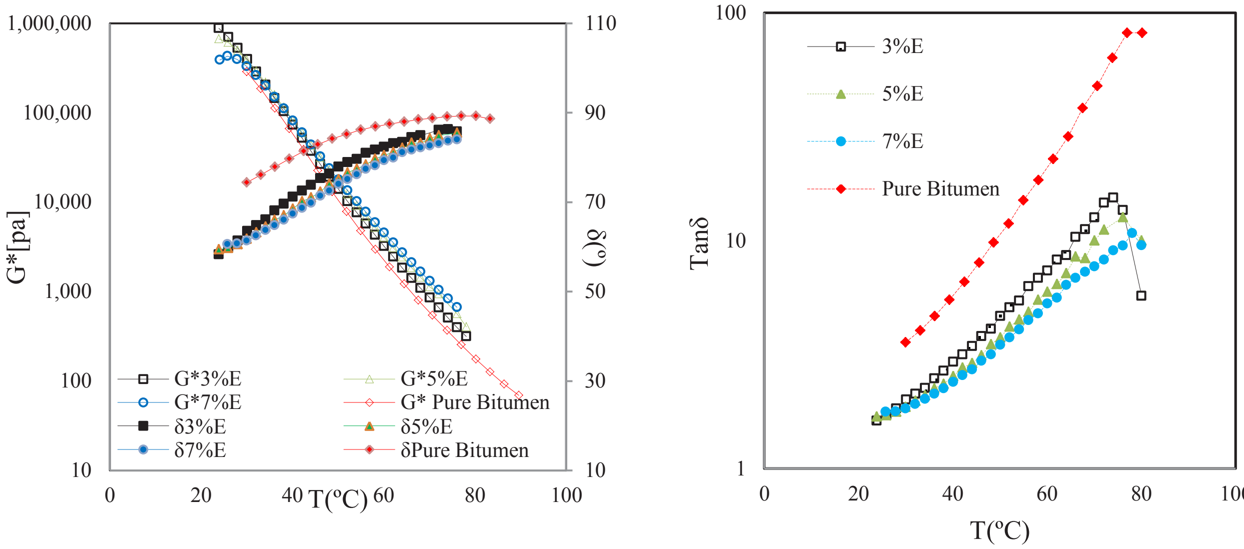

Fig. 5. Complex modulus/phase angle (left) and Tanδ (right) curves for the bitumen modified by blend E.

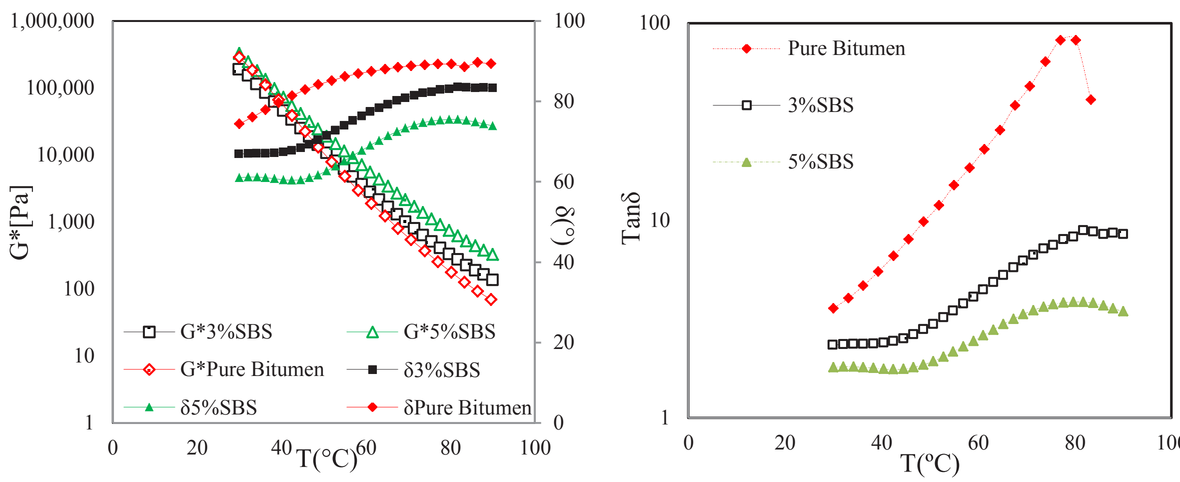

Fig. 6. Complex modulus/phase angle (left) and Tanδ (right) curves for the bitumen modified by SBS.

Inspecting Figures 3 and 4 also reveal that damping capacity decreases upon addition of the polymeric modifiers. This confirms that there is an interaction between bitumen as the continuous phase and the polymeric modifier as the dispersed phase. In the entire temperature range, the sample containing 7 wt. % of the modifier D, 7%D, shows the highest elastic behavior and the greatest properties improvement. The Figure 5 displays the bitumen modified by the polymeric modifier E. As the graph shows, the presence of the modifier E does not affect complex modulus and phase angle at higher temperatures. The Figure 6 shows the SBS-modified bitumen. This block copolymer increases complex modulus and this effect is easily observable for the bitumen containing 5 wt.% SBS. It is believed that this improvement originates from the polymer network formation [14]. Figure 6 also represents phase angle versus temperature at a constant frequency. In comparison with the bitumen containing 3% SBS, the decrease of phase angle shift in high temperatures is more significant for the compound containing 5% SBS. This improvement in elastic response originates from low viscosity of the bitumen and accordingly formation and subsequently diffusion of the SBS network in the bitumen matrix.

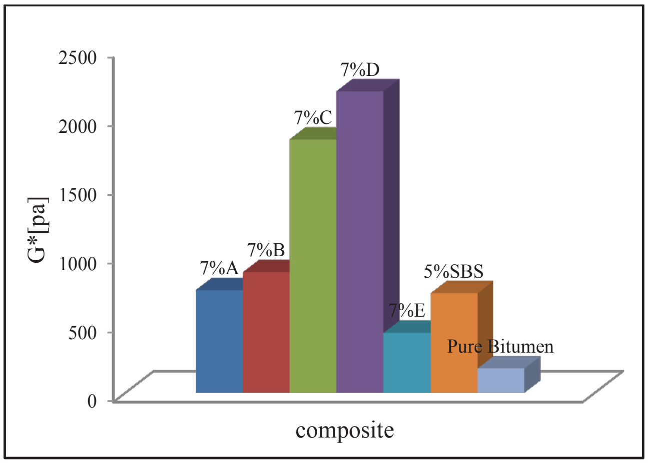

Fig. 7. complex modulus of the pure bitumen and the modified ones at 80.1 ºC.

The Figure 7 shows that the highest complex modulus is obtained by addition of 7 wt.% of the modifier D. As a result, comparing with the other modified bitumen compounds, the one containing 7 wt.% of the modifier D possesses the highest stiffness and the best performance. Moreover, the latter sample shows the lowest phase angle which confirms formation of interaction between the bitumen and the modifier chains.

To accurately compare the effect of the modifier on the rheological properties, phase angle shifts for all samples are illustrated in Figure 8. It can be found that the bitumen containing 7 wt.% of the modifier D shows the lowest phase angle which signifies more interaction of the modifier chains with the bitumen and consequently more elastic behavior.

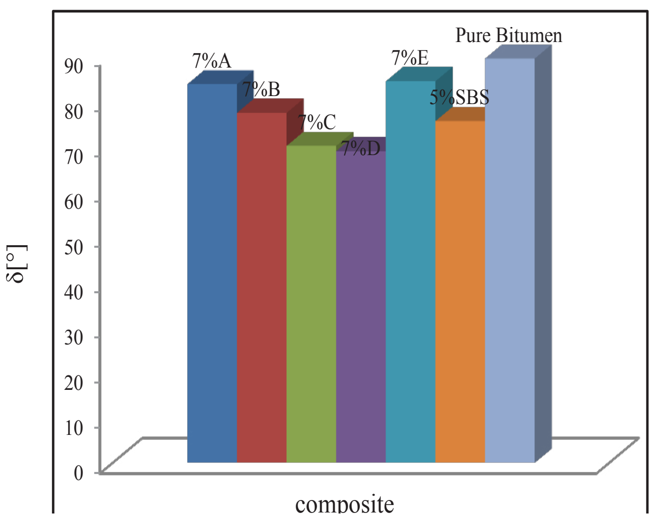

Fig. 8. Phase angle shift of the pure bitumen and the modified ones at 80.1 ºC.

Rutting resistance shows stiffness of the bitumen at elevated temperatures or its resistance against deformation. A bitumen with higher G*/Sin δ value shows a greater resistance against permanent deformation. As Figure 9 displays, this value for the entire modifier loading levels (3%, 5% and 7%) decreases upon temperature raise. Comparing these graphs also reveals that the samples containing 7 wt.% of the modifier C and D have the highest rutting resistance at the elevated temperatures.

As it is shown in Figure 9, increasing loading level of the modifier E does not affect rutting resistance significantly even at higher temperatures. Comparing the modified bitumen with their pure counterpart shows that the effect of the polymeric modifier addition on rheological properties of the bitumen is significant at elevated temperatures. It means that bitumen rheological properties do not have a great dependence on the added modifier in lower temperatures. Due to substantial fraction of the rubbery component (CR) in the modifier E, the viscosity of this modifier increases and thereby its mixing with the bitumen matrix will be limited. It means diffusion of this modifier into the bitumen matrix to establish physical interactions is hindered. This is why this modifier does not improve the bitumen rheological properties significantly.

Assessing Figure 10 reveals that the highest (G*/sinδ) value is obtained for the bitumen modified by 7 wt.% of modifier D. It should be emphasized that rutting resistance of this sample is more improved even in comparing with SBS-modified one.

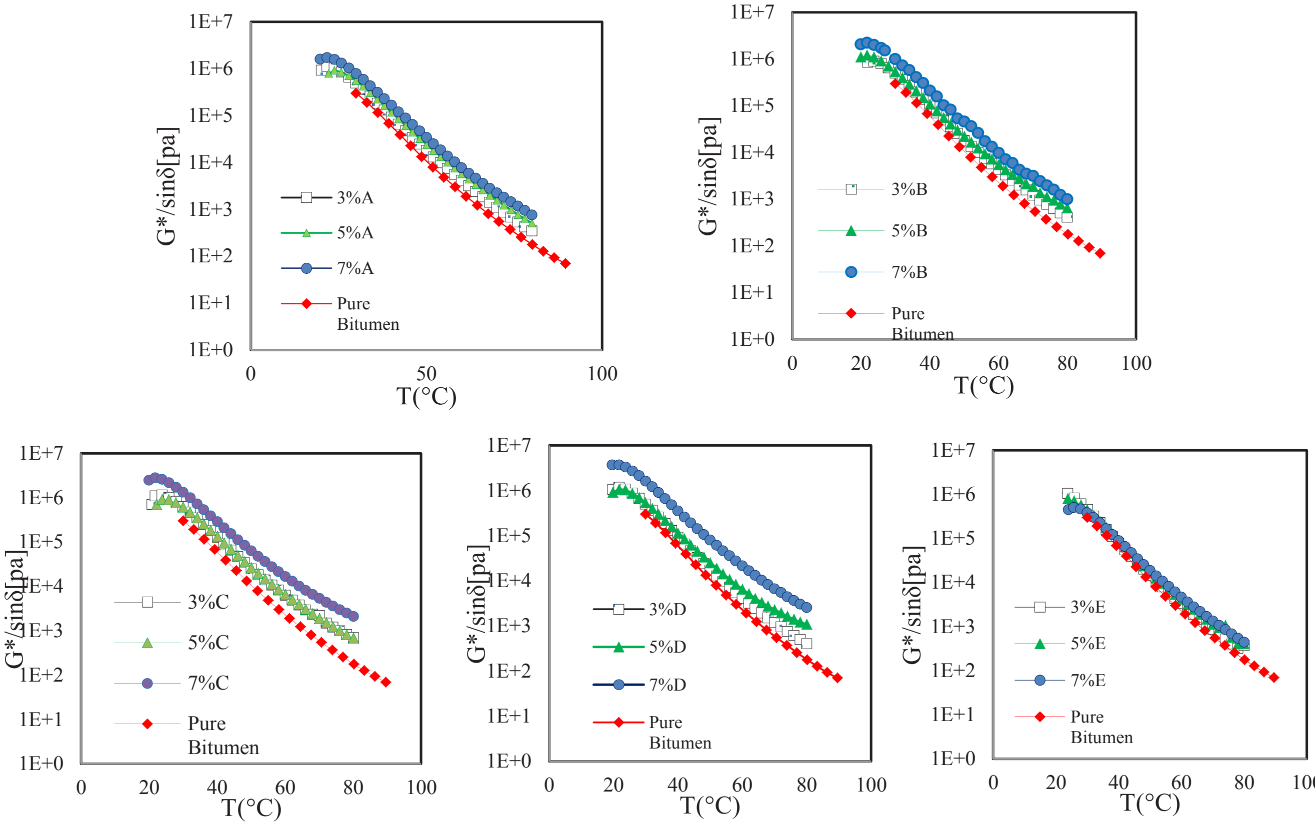

Fig. 9. Rutting resistance for the pure bitumen and the ones modified by blend A (top row, left), blend B (top row, right), blend C (down row, left), blend D (down row, middle) and blend E (down row, right) at different temperatures.

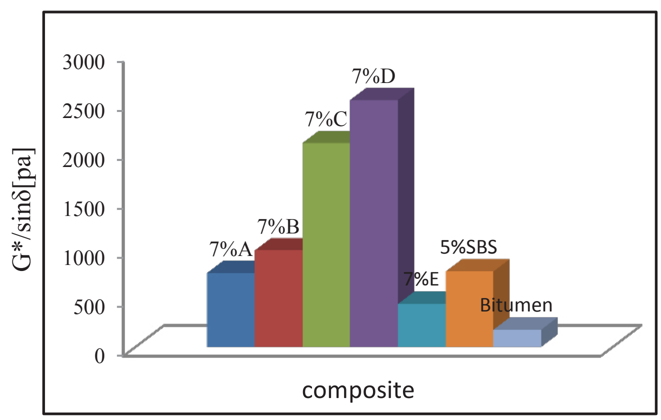

Fig. 10. rutting resistance of pure bitumen and the modified ones.

4.Conclusions

Evaluating rheological properties of the polymer-modified bitumen compounds show that pure bitumen behaves fully viscously at elevated temperate and it suffers from low elasticity. However, the bitumen containing appropriate amount of the modifier has elastic behavior even in higher temperatures. Thus, the latter one can be used in areas with higher temperatures. According to the rheological test results, bitumen to modifier ratio 93/7 is the optimum value for modification process. The composition of the best modifier is also 10% CR and 90% R-PET. Complex modulus, rutting resistance and phase angle shift values at 80.1 oC for un-modified bitumen are 176 (Pa), 250 (Pa) and 89.3o ,respectively, which are changed into 2190 (Pa), 2520 (Pa) and 68.9o upon addition of 7 wt.% of the modifier D. This modifier endows the highest complex modulus, the lowest phase angle and the strongest resistance against rutting. This investigation verifies that the blend CR/R-PET can replace SBS for bitumen modification purposes. This replacement is associated with economic and environmental benefits.

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