Experimental Study on the Physical and Rheological Properties of Bitumen Modified with Different Nano Materials (Nano SiO_2 & Nano TiO_2)

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Abstract

This study is carried out to explore the effect of nano materials (SiO2 & TiO2) on the physical and rheological properties of Bitumen. To achieve this goal, Nano materials are blended in bitumen in various percentages (0.3, 0.6, 0.9 and 1.2%). The physical and rheological properties of modified binders are characterized using a penetration, softening point, kinematic viscosity and a dynamic shear rheometer tests and compared with unmodified bitumen. The tensile strength of the bitumens is also tested as a function of nano contents. The results of the study indicate an increase in softening point, kinematics viscosity and decrease in bitumen penetration. The tensile strength of modified bitumen is enhanced by a comparison with the standard 60/70 bitumen. Also, results of DSR test show that modified bitumen significant better rutting resistance than the standard 60-70 bitumen. Tests results show that the best improvements in the modified bitumens were obtained with 1.2% nano SiO2.

Keywords: *Nano technology, Bitumen, Kinematic viscosity, Dynamic shear rheometer.*

1. INRODUCTIO

Bitumen has been widely used as a binder in the construction of highways and runways for a long time due to its good viscoelastic properties [1]. Bitumen is an organic mixture composed of various chemical compounds. The physical properties and chemical structures of bitumen will change when exposed to heat, oxygen, and ultraviolet (UV) light, which is called aging [2]. So the ideal bitumen should possess both: (1) high relative stiffness at high service temperatures (summer) to reduce rutting and shoving and; (2) increased adhesion between the bitumen and aggregate in the presence of moisture to reduce stripping [3].

Nanotechnology has been used in various fields. In pavement engineering research, nanotechnology is used as a form of new material, device, and system at the molecular level. A number of researchers have used nanomaterials in Portland cement materials. However, nanomaterial use in asphalt pavement started relatively late. In recent years, some researchers have started to work on the improvement of asphalt materials with nano materials in asphalt cement and emulsions. There are various nanomaterials which have been or have potential to be used in asphalt modification; such as nanoclay, nanosilica, nano-hydrated lime, nano-sized plastic powders, or polymerized powders, nano fibers, and nano tubes [4].

In recent years, many researches were carried out to improve service life of asphalt pavement against dynamic loads by using of nano materials. Tanzadeh et al. (2006) carried out a laboratory study on the effect of Nano TiO_2 in improving property and rutting resistance in asphalt pavement under dynamic loading. For this purpose, the wheel-tracking test was carried out on ordinary and Nano-TiO_2 modified asphalt mixture samples. The results illustrated that using Nano- TiO_2 in asphalt mixtures caused an improvement in rutting depth in comparison with the ordinary mixtures [5].

Using of nano materials was not limited to nano TiO_2. Chen and Huang (2006) have used nanoclays as a secondary modifier to further enhance the performance properties of styrene–butadiene–styrene (SBS) copolymer modified bitumen by adding the sodium montmorillonite (Na-MMT) and organophilic montmorillonite (OMMT) nanoclays. It was found that the viscosity and stiffness (complex modulus) of the SBS-modified asphalt were increased while the phase angle was decreased [6]. Ghaffarpour et al. (2010) carried out comparative rheological tests on bitumen containing unmodified and nanoclay modified bitumen. Results showed that nanoclay could improve physical properties of bitumen such as penetration, softening point, and ductility [7]. Golestani et al. (2012) evaluated performance of bitumen modified with nano clay. The physical, mechanical and rheological properties of bitumen modified with nano clay have been studied. The results showed that nano clay could improve the physical properties, rheological behaviors bitumen [8]. Khodadadi et al. (2007) investigated the effect of adding nanoclay on long-term performance of asphalt mixtures. Indirect tensile test was conducted on cylindrical specimens made of conventional and modified bitumen at the stress levels of 200, 300, 400 and 500 KPa. The results showed that the addition of 2% nanoclay could increase the fatigue life of the asphalt mixtures [9].

Shafabakhsh et al. (2014) investigated the effect of nano TiO2 on the mechanical properties of asphalt mixtures. The results of this research showed that adding different percentages of nano Tio2 improved ratting and fatigue behavior of asphalt mixtures [10].

Also nanotechnology is used in concrete mixtures. Keyvani (2007) stimulated the application and development of nanoscientific and nanotechnological concepts of nanofiber materials and their applications in concrete. Results of this paper showed that Nanofibrous cement based materials could monitor regions of partial damages, localized changes in strains, stresses and temperatures of any joints and members [11]. Maghsoudi et al. (2013) investigated the effect of nano-silica as an addition on new concrete generation called as “Self Consolidating Concrete”, SCC, containing type V Portland cement. For designed mixes, the fresh properties (Slump Flow, L-box, V-funnel, J-ring) as well as the hardened concrete properties such as compressive strength, elasticity modulus, swelling and shrinkage values were measured. Results were compared with SCC specimens without nano-silica addition at short and long terms of ages until one year. Results showed that the use of nano-silica with micro-silica could improve the engineering properties of hardened SCC [12].

According the previous researches, different nano materials were used in bitumen and asphalt mixtures, but this field of study require more investigation to evaluate the effect of nano materials on different properties of bitumen such as physical and reologhical. In concolusion, the objective of this study is modification of bitumen with nano SiO_2 & TiO_2. To achieve goals of study, nano SiO_2 & TiO_2 are blended in bitumen in various percentages (0.3, 0.6, 0.9, and 1.2%). These percentages are selected according to previous researches and economic aspects. The blended bitumen are characterized using penetration, softening point, kinematic viscosity and dynamic shear rheometer tests, and the results are compared with results of unmodified bitumen.

2. EXPERIMENTAL DESIGN

2.1. Materials

Pure bitumen 60-70 is used in the preparation of the samples and its properties are shown in Table 1. Also, the properties of nano materials (SiO_2 & TiO_2) used in this study are shown in Table 2. The Nano-bitumen composites are prepared by using a high-shear mixer. Also figures 1 & 2 show nano SiO_2 & TiO_2 used in this study.

In this section we aim to present our main result. Here is an example of a figure, as Figure 1.

The bitumen was first heated to 150 ^{o}C to a fluid state and the nano TiO_2 by different weight contents (0.3, 0.6, 0.9 and 1.2%) were added to the system and mixed at 4000 rpm to disperse the nano materials in bitumen. All the prepared bitumens were left to cool at room temperature.

Table 1. *Properties of bitumen used in this study.*

Test	Standard	Values
Penetration (100 g, 5 s, 25 ºC), 0.1 mm	ASTM D5-73	68
Ductility (25 ºC, 5 cm/min), cm	ASTM D113-79	112
Kinematic Viscosity at 135ºC , C.st	ASTM D-2170	355
Kinematic Viscosity at 150ºC , C.st	ASTM D-2170	205
Solubility in trichloroethylene, %	ASTM D2042-76	99.5
Softening point, ºC	ASTM D36-76	51
Flash point, ºC	ASTM D92-78	250
Loss of heating, %	ASTM D1754-78	0.2

Table 2. *Properties of Nano Materials (SiO2 & TiO2) used in this study.*

Purity %	Surface volume ratio m^2/g	Diameter nm	Density g/cm^3	Type
99.9	160	80	2.40	SiO_2
99.9	60	30	4.23	TiO_2

Figure 1. *Nano SiO2 used in this study.*

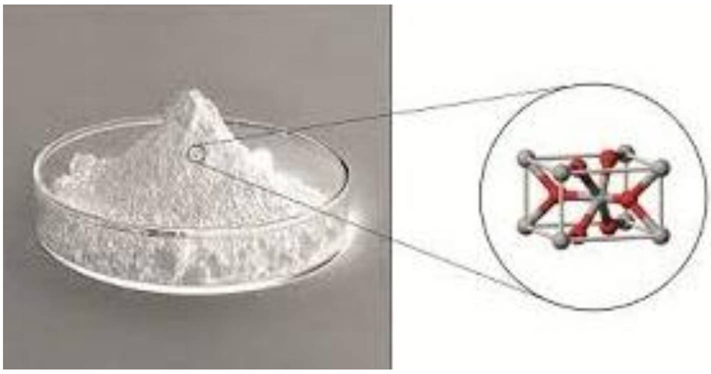

Figure 2. *Nano TiO2 used in this study.*

2.2. Testing Setup and Procedure

The principal test methods on the modified and unmodified bitumen are penetration test at 25°C according to ASTM D5-97, softening point according to ASTM D36-95, and kinematic viscosity at 135 and 150°C according to ASTM D-2170.

The dynamic shear rheometer (DSR) test is carried out according to ASTM D-7175 on bitumen samples to evaluate its viscoelastic behavior. In the DSR test, the value of the complex shear modulus (G*) and the phase angle (δ) of the tested bitumen are measured according to Equations (1) and (2) [13].

By measuring the complex shear modulus of the bitumen material, the total complex shear modulus value as well as its elastic and viscous components are determined. The phase angle is the time lag between the applied shear stress and the resulting shear strain converted into degrees.

$$G^* = \varepsilon_{\max} / \gamma_{\max} \quad (1)$$

$$\delta = 360(t)(f) \quad (2)$$

Where G* is the complex shear modulus and δ is the phase angle (°); ε_{max} is the maximum shear strain; γ_{max} the maximum resulting shear strain; t the time lag (s); and f is the loading frequency.

In this study, The DSR test was conducted at a frequency of 10 rad/s (1.59 Hz) and four test temperatures: 40, 50, 60, and 70 °C at 10 °C increments. The complex shear modulus (G*) value and the phase angle (δ) value are obtained for all the nano contents at the four test temperatures.

3. RESULTS AND DISCUSSION

3.1. Penetration Test Results

Figure 3 shows the penetration test results for different percentages of Nano SiO2 and Nano TiO2. According to the results, with addition of different percentages of Nano SiO2 and Nano TiO2, the penetration is decreased. But the decrease in Nano TiO2 is continued by 0.9% and then the process is increased.

The best results for the bitumen used in this study obtained in the bitumen modified with 1.2% Nano SiO2, which is 15% lower than the normal bitumen. In fact, with addition of 1.2% Nano SiO2, the penetration of bitumen 60-70 can be improved by 15%.

The improved penetration can make the bitumen harder and possibly increase the strength of the asphalt mixtures against rutting. On the other hand, the bitumen becomes harder, more fragile and there is more possibility of the fatigue phenomenon to be overcome in the high number of loadings. But it should be noted that the amount of hardness improvement was not that high to make the bitumen more fragile. Therefore, the increased hardness can be considered as a positive point for the bitumen.

3.2. Softening Point Test Results

Figure 4 shows softening point test results for different percentages of Nano SiO2 and Nano TiO2. According to the results, with addition of different percentages of Nano SiO2 and Nano TiO2, the softening point is increased, but the increase in Nano TiO2 is continued by 0.9% and then the process is decreased. The best results for the bitumen used in this study obtained in the bitumen modified with 1.2% Nano SiO2, which is 16% more than the normal bitumen. In fact, with addition of 1.2% Nano SiO2, the softening point of bitumen 60-70 can be improved by 16%.

In fact, the improved softening point can reduce the thermal sensitivity of bitumen. As a result, 16% increase in the softening point with addition of Nano SiO2 can decrease the bitumen specification changes due to the temperature changes, because the sensitivity of the modified bitumen to the temperature changes is declined. This modified bitumen can be used in areas with high average annual temperature or areas with more and heavier traffic [13].

3.3. Kinematic Viscosity Test Results

Figs. 5 and 6 show the effect of nano content on the Kinematic viscosity of bitumen at 135 and 150 ^{o}C. The viscosity is the strength of object against being fluid, as a result, the more amount of viscosity, the more favourable viscosity quality is. Because the durability and resistance under different loading and temperature conditions will be higher over time. On the other hand, the increased viscosity in bitumen at high temperatures can improve the strength of asphalt mixtures against rutting [14].

According to the results, with addition of different percentages of Nano SiO2 and Nano TiO2, the viscosity of bitumen 60-70 is increased in both temperatures. The increase is in fact due to the improved bond between the bitumen particles caused by the addition of nanoparticles. This increasing trend of Nano SiO2 existed at all the temperatures, but is up to 0.9% for Nano TiO2 and then will be decreased. This phenomenon can be justified so that with addition of more than 0.9% Nano TiO2, the bond between the bitumen particles is broken in the high shear mixer and the bitumen particles are separated and instead, the Nano TiO2 particles have been replaced. These factors change the nature of bitumen, while, Nano SiO2 particles still have to cover and arm the bitumen particles to show higher strength against loading and temperature changes.

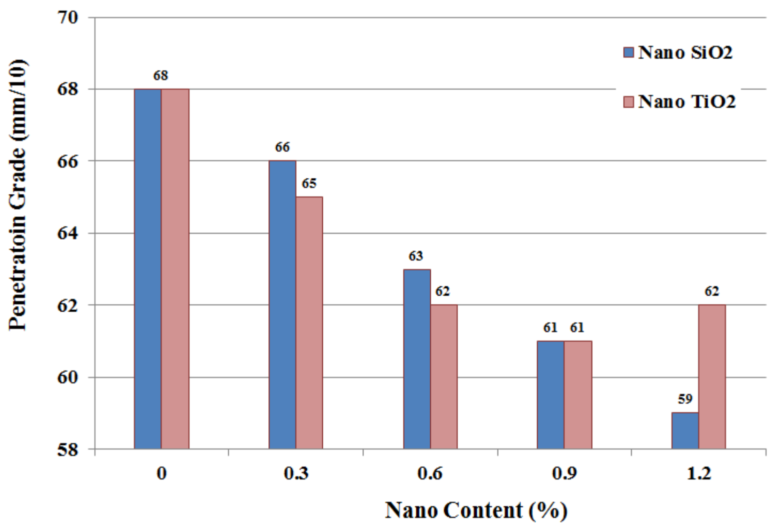

Figure 3. *Variation of penetration value versus nano TiO2 content.*

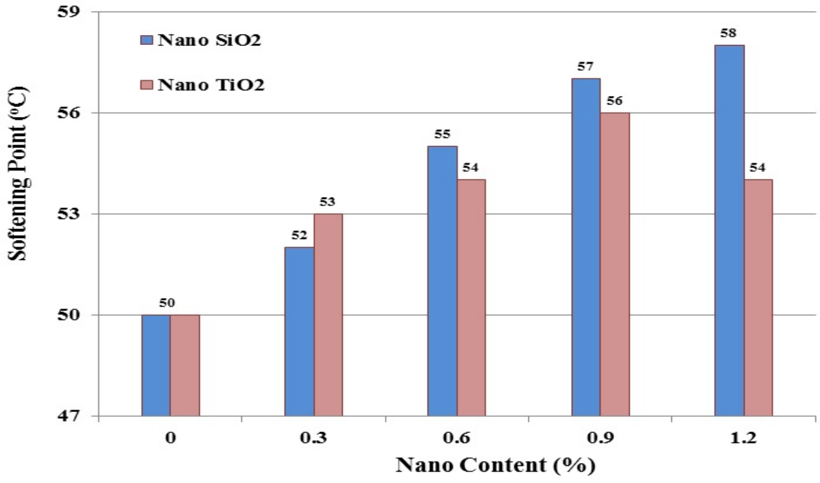

Figure 4. *Variation of softening point versus nano TiO2 content.*

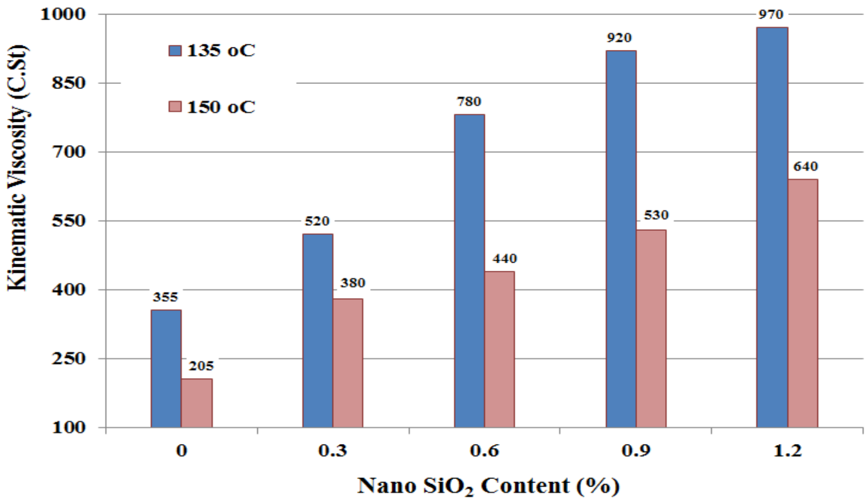

Figure 5. *Variation of kinematic viscosity versus nano SiO2 content.*

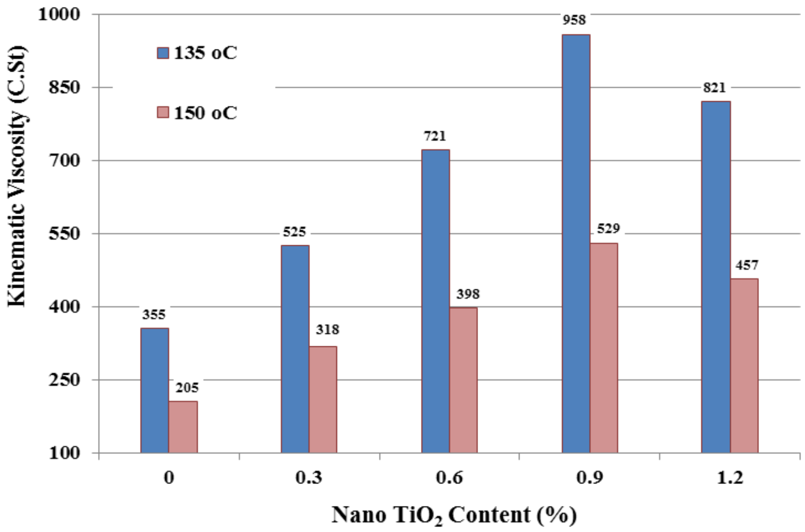

Figure 6. *Variation of kinematic viscosity versus nano TiO2 content.*

3.4. DSR Test Results

The G* values obtained for the unmodified and modified bitumens at the different temperatures were plotted with the nano contents as shown in Fig. 7 and 8. According to the results, with addition of different percentages of Nano SiO2 and Nano TiO2, the amount of G* is increased.

This can be due to the improved bitumen elastic and viscoelastic behavior at different temperatures with addition of nanomaterial different percentages.

When, Nano SiO2 and Nano TiO2 particles at nano-scale added to the bitumen particles with high surface to volume ratio, it strengthen the bond between bitumen particles and create an appropriate cover. The cover can prevent the viscous nature of bitumen at high temperatures and delay the withdrawal from the elastic behavior to the viscous area. What has been said can be summarized in the increased amount of G*.

According to the results, the increasing amount of G* in all the Nano SiO_2 percentages used in this study is maintained and show that the compatibility between Nano SiO_2 particles and bitumen with the increased percentages has been still maintained and its addition would improve the bitumen rheology.

This is not true about Nano TiO2 and with addition of 1.2% Nano TiO2, the amount of G* is decreased.

This can be justified so that the compatibility between Nano TiO2 particles and bitumen with the excessive increased nano, is removed and nano particles by being among the constituent particles of bitumen causes an excessive increase in them and change the nature of bitumen and its rheological behavior. As a result, it is predicted that among the percentages used in this study, 1.2% for Nano SiO2 and 0.9% for Nano TiO2 create the best performance.

Another conclusion according to Figures 7 and 8 is the high impact of temperature on the normal and modified bitumen performance. The temperature has great impact on the physical and rheological properties of bitumen and many asphalt pavements damages will happen more intensely with the increased temperature. The increased temperature breaks the bond between particles and leads to the separation between the constituent particles.

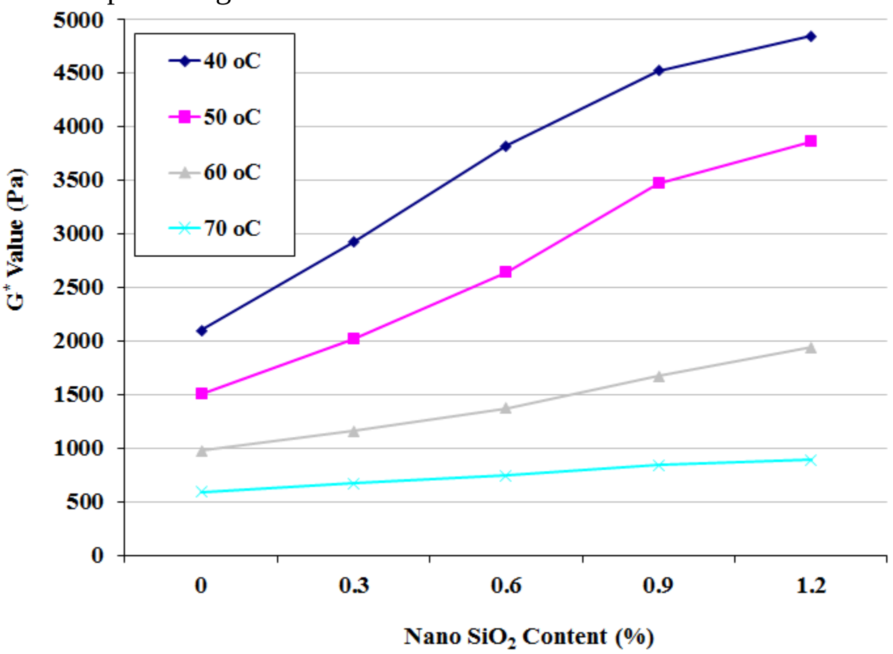

Figure 7. *G* value versus nano SiO2 content at different temperatures.*

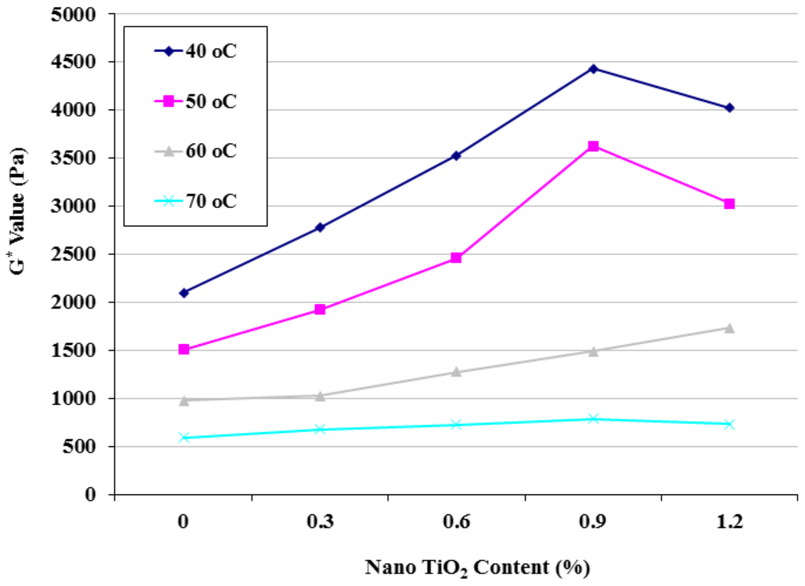

Figure 8. *G* value versus nano TiO2 content at different temperatures.*

According to the bitumen duties as an adhesive factor in the asphalt mixture, breaking the bond between particles causes failure to perform duties in the asphalt mixtures and resulted in numerous damages such as rutting and fatigue. As shown in the results, the addition of Nano SiO2 and Nano TiO2 particles to bitumen decreases the thermal sensitivity of bitumen and improves the rheological behavior even in the high temperatures.

3.4.1. Evaluate the Effect of Nanomaterial on Bitumen Rutting Behavior

The rutting is the main result of deformation on the surface of pavement layer caused by the cycle loading. During each cycle loading of the passing traffic, a constant amount of work done for the pavement deformation. A part of the work is amortized caused by the elastic movement of the pavement layer surface, while the remaining part of work (W_c) causes deformation and heat at the pavement surface. Accordingly, the amount of W_c mentioned in Equations 3 and 4 should be reduced to decrease the rutting.

According to the constant stress and

$$Wc = \pi \sigma \varepsilon . \sin \delta \quad 3$$

$$\delta = \delta_0 , \varepsilon = \frac{\delta_0}{G^*} \quad 4$$

relationship between ε, σ and G* obtained in Equation 4, the Equation 5 is achieved:

$$Wc = \pi \sigma_0{}^2 \left(\frac{1}{G^* / \sin \delta} \right) \quad 5$$

According to Equation 5, any increase in G* or decrease in sinδ, will reduce W_c. The equation represents that with greater amount of G*, the bitumen is stiffer and the strength against deformation of pavement surface is higher. Also, with the lower amount of sinδ, the elastic properties of bitumen is higher and damping is increased on the pavement surface. Therefore, the greater $\frac{G^*}{\sin\delta}$, the strength against rutting will be more.

In the Superpave system, the parameter that is believed to correlate highly with rutting (permanent deformation) of asphalt pavements is the $G^*/\sin\delta$ value. The Superpave specifications specify a minimum value of 1.0 kPa for the $G^*/\sin\delta$ of original bitumen at the high performance grade temperature.

The $G^*/\sin\delta$ values were plotted against the temperature at the different nano SiO_2 &TiO_2 content as shown in Figs. 9 & 10. A similar relationship to the G* value - nano content relationship was obtained in this case.

The Superpave criterion of $G^*/\sin\delta$ value of 1.0 kPa minimum was displayed by the dashed horizontal line in Figs. 9 & 10. results show that at the temperature of 70°C, despite the addition of different percentages of Nano SiO2 and Nano TiO2, the amount of $G^*/\sin\delta$ is lower than the minimum amount of regulation (1Kpa), representing that at this temperature both normal and modified bitumen with different percentage of nanomaterial are prone to rutting. But the main effect on the addition of nanomaterial is determined at the temperature of 60 °C, where the normal bitumen did not meet the minimum required amount, but with addition of different percentages of Nano SiO2 and

Nano TiO2, the amount of G*/sinδ is increased and more than 1. The conclusion is so important, because with addition of nanomaterial, the temperature range for using bitumen can be increased to 60°C, so that it is not prone to rutting. The results at temperatures of 40 and 50°C is so that with addition of different percentages of Nano SiO2 and Nano TiO2, the bitumen performance is improved against the rutting. But the increase for Nano TiO2 is not continued and the best performance happened at 0.9%.

In general, the addition of the nano SiO_2 & TiO_2 to the bitumen improves the $G^*/\sin\delta$ value at all temperatures. It conclusion, the visco elastic behavior of bitumen will be improved at higher temperatures.

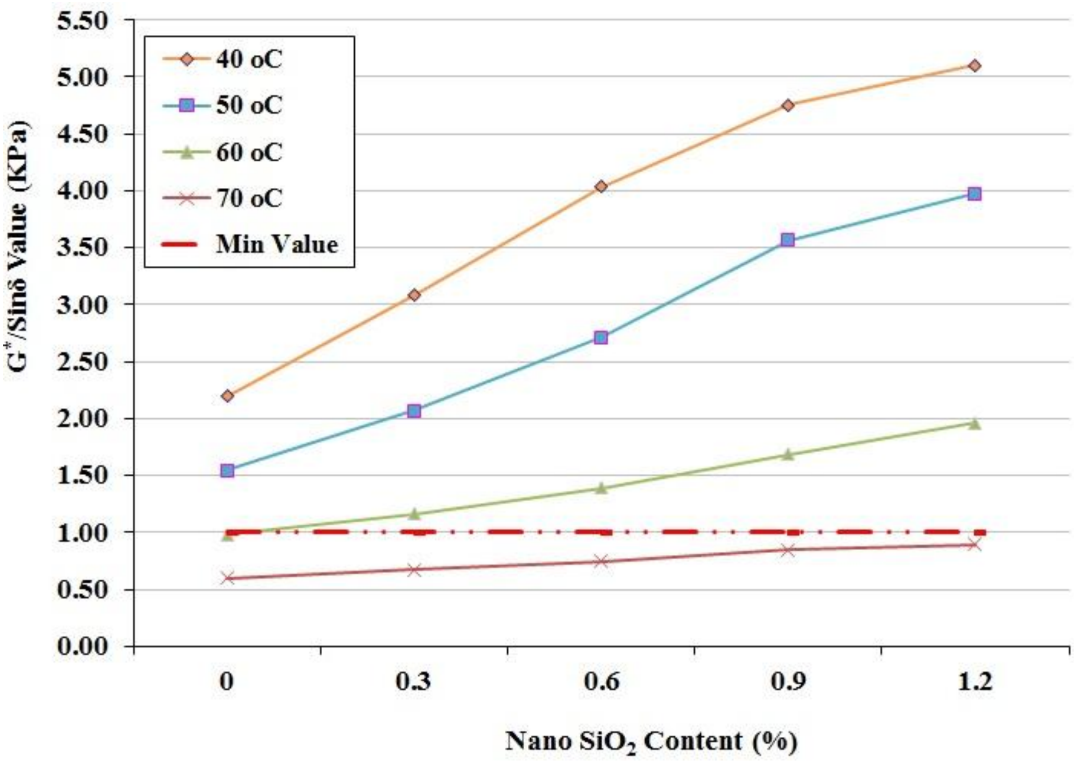

Figure 9. *$G^*/\sin\delta$ versus temperatures at different nano SiO_2 content.*

4. CONCOLUSION

1. Results show that adding 1.2% nano SiO2 & 0.9% nano TiO2 to bitumen give higher softening point than the base bitumen. Also, in these nano contents, penetration value is decreased compared with the control bitumen.

2. According to the results, with addition of different percentages of Nano SiO2 and Nano TiO2,

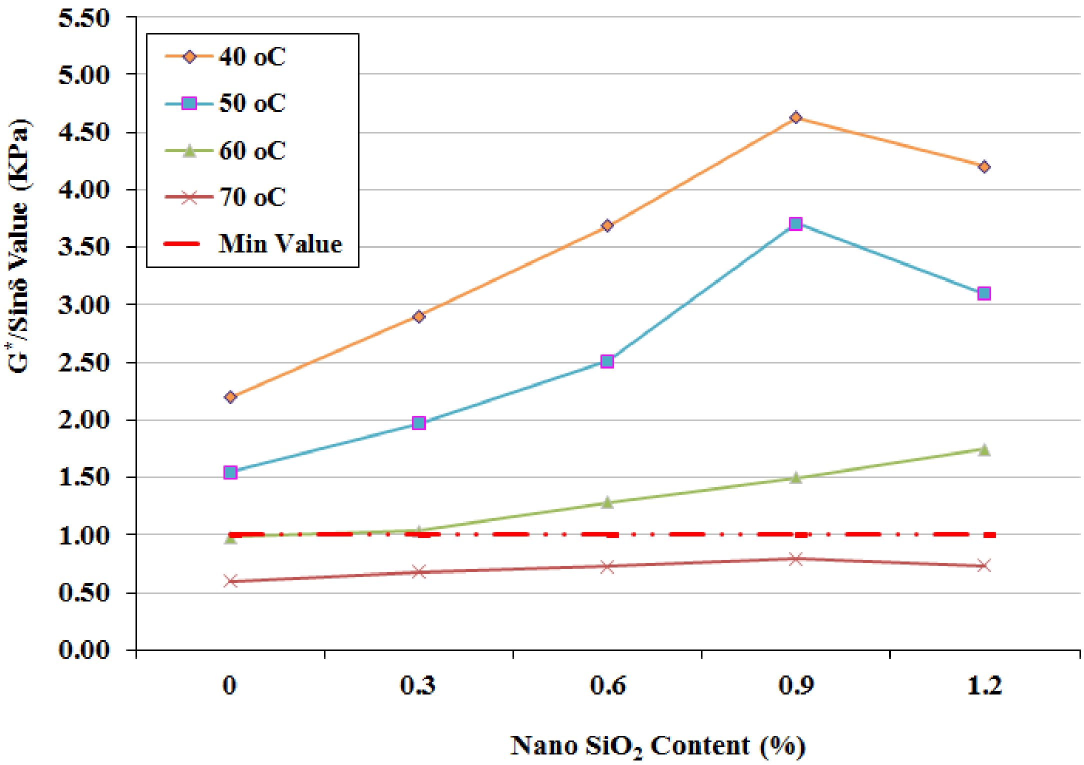

Figure 10. *G^*/sinδ versus temperatures at different nano TiO_2 content.*

the amount of viscosity in the bitumen 60-70 increased at both temperatures. The increase is due to the improved bond between the bitumen particles caused by the addition of nano particles. The increasing trend in Nano SiO2 is at all the temperatures but for the Nano TiO2 is up to 0.9% and then it will be decreased.

3. It is shown that among the percentages used in this study, the use of 1.2% Nano SiO2 and 0.9% Nano TiO2 is the best result for shear modulus in bitumen 60-70, while the shear modulus in the bitumen modified with 1.2% Nano SiO2 compared to the bitumen modified with 0.9% Nano TiO2, is almost 10% higher.

4. The results clearly showed that due to the improved performance of bitumen with addition of nanomaterial in penetration, viscosity and shear modulus tests, the strength against the rutting phenomenon increased significantly. On the other hand, the improved performance of bitumen in the softening point test increases its sensitivity to the temperature changes.

5. In results, although adding nano materials to bitumen increase initial cost of production, damage will reduced after using modified bitumen in asphalt mixtures, and reconstruction cost will saved.

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