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Rheological characterization of Nanocomposite modified asphalt binder

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Abstract

Increase in traffic loading on pavement structures has necessitated use of asphalt with high durability, resistant to permanent deformation and most significantly higher service life of pavements. Rutting at high temperature and fatigue cracking under repeated loading are the major structural distresses in asphalt pavements. In some regions the base binder fails to serve the required purpose and their properties need to be modified by adding suitable materials. Nano-materials have unique properties that have led to increased interest of its use as an additive to asphalt binder. Therefore, in this study the effects of Nano titanium dioxide (TiO_2) used as a second modifier to modify polymer (Styrene-Butadiene-Styrene) modified asphalt (PMA) binder have been investigated. Frequency sweep, temperature sweep, Linear Amplitude Sweep (LAS) and Multiple Stress Creep Recovery (MSCR) tests were carried out. The results showed that addition of Nano-TiO_2 in PMA results in overall enhancement of properties of asphalt binder.

Keywords: Asphalt, Nano-TiO_2, PMA, LAS, MSCR, Styrene-Butadiene-Styrene

1. Introduction

Asphalt is a widely used pavement construction material. It is mainly known for its strength and durability. In many cases asphalt pavements experience heavy traffic loads and unfavourable environmental conditions for an acceptable amount of time. Therefore, modification and reinforcement of asphalt binder is necessary to withstand high stresses. Modifiers are added such that it displays the right combination of viscous and elastic properties for good pavement performance in a wider temperature range. The binder should have more elasticity, increased strength and good low temperature flexibility (IDOT Bureau of Materials and Physical Research).

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Pavement with polymer modification exhibits greater resistance to rutting and thermal cracking, and decreased fatigue damage, stripping and temperature susceptibility (Yildrim et al., 2007). Styrene-Butadiene-Styrene (SBS) tri-block copolymer has been widely used to modify asphalt binder. SBS absorbs some of the maltene/resin fraction of asphalt to form homogeneous interconnecting matrix evenly dispersed in the binder (Robinson, 2004). The fatigue life of the SBS polymer modified mix (5.4% by weight of aggregate) at 25 °C and on applied stress of 235 kPa (30% of the failure load) was found to be 4.6 times higher than the unmodified asphalt mix under similar conditions (Kumar et al., 2006). The main disadvantage of using polymer additives is: High temperature storage stability/ Phase Separation (Golestani et. al., 2012). The problem of phase separation in polymer modified binder can be overcome by addition of nanoparticles which then can be referred to as Nanocomposite modified binder. Due to its nature of large surface area and small size, Nano-material shows specific characteristics compared to the common material and exhibits some novel properties and incredible features which make it possible to be applied in the field of asphalt pavement as an additive (Li et al., 2017). Titanium dioxide nanoparticles have large surface area in comparison with normal Titanium dioxide, and are not uniform in size and arrangement (Pinnavaia and Beall, 2000). Nejad et al. (2017) evaluated PAV aged base and Nano-TiO_2 (2% and 4%) modified binder on the basis of its fatigue parameter. Strain controlled test at 0.1 % strain level was performed at 10 rad/sec frequency with temperature varying from 13 ºC to 28 ºC. Phase angle of nano-modified binder was found to be less than the base binder while G* sin (δ) values increased on modification. They concluded that nano-TiO_2 modified binder showed greater stiffness and elastic behaviour compared to base binder. Zhou et al. (2017) investigated on the properties of Nano-TiO_2 modified binder using two different varieties of TiO_2 i.e. TiO_2-50 and TiO_2-100. For TiO_2-50 modified binder had its maximum softening point at 2% nanoparticle content while TiO_2-100 modified binder it was at 1.5% nanoparticle content. Further increase in nanoparticle content showed decrement in softening point values due to agglomeration of nanoparticles in the binder.

Nano-particles act as driving force to decrease the density difference between polymer and base binder (Galooyak et al., 2010). The research concluded addition of these nanoparticles in the polymer matrix at low concentrations (~0.2 weight %) caused significant improvements in the compressive and flexural mechanical properties of polymeric nanocomposite. Wang et al. (2017) found that Carbon Nanotubes (CNT) functionalised with hydroxyl group showed good bonding with SBS polymer and asphalt binder. Addition of 0.5-1% of CNT in Styrene-Butadiene-Styrene (SBS) modified binder resulted in enhanced fatigue and rutting resistance properties. The morphological studies of modified asphalt showed that nanoparticles create an alignment film between polymer and asphalt which decreases the interfacial tension between them increasing the dispersion of polymer in asphalt (Liang et al., 2016). Merusi et al. (2012) concluded that mixing sequence while preparing the nanocomposite affect the resultant properties of the blend.

Nanoclay is most commonly used by researchers as a second modifier to polymer modified binder. Nanoclay Organic Montmorillonite (OMMT) mixed with polymer modified asphalt (PMA) at a fixed ratio (SBS/OMMT = 100/25) showed enhanced rheological properties (Golestani et al., 2015). At a fixed frequency, with increase in temperature the resistance to permanent deformation increased due to modification. The exfoliation of OMMT in PMA showed increase in its viscoelastic properties. Jasso et al. (2013) studied the influence of SBS polymer, nanoclay and a sulphur based compound on asphalt binder. They found that the amount of SBS polymer and nanoclay were responsible for the increase in viscosity while all the three components were essential for the maximum service temperature of the binder. Mansorian and Gholamzadeh (2016) found 2% of nanocomposite (polypropelene/nanoclay) in asphalt binder increased the non-polar surface free energy (SFE) while decreased the polar SFE. This results in increase in adhesion between binder and aggregate. Liang et al. (2016) obtained the optimum nanoparticle/polymer combination systems using orthogonal experiment design (OED). Three optimal modification systems were found as: 3% nano-ZnO + 0.5% nano-TiO2 + 3.7%SBS, 5% nano-ZnO + 4.2%SBS, 5% nano-$CaCO_3$ + 4%SBR. The softening point of binder modified by 5% nano-ZnO + 4.2% SBS increased by 30 °C as compared to the base binder. Modified binder also gave better anti-ageing, anti-rutting and anti-cracking properties as compared to the base binder.

Very few studies on the use of nanocomposite (using Nano-clay, Carbon Nanotubes and Nano-silica) for modification of asphalt binder were found. Use of Nano-TiO_2 along with SBS polymer for the modification has not yet been researched. SBS and Nano-TiO_2 individually have been proven as good modifier for asphalt binder. But their compatibility together is a great scope of research. The objective of this research was to study the rheological characterization of the binder modified with nanocomposite (made of SBS polymer and Nano-TiO_2).

2. Test Materials

The materials used for the modification of asphalt binder of grade VG-30 were KRATON® D1192 E SBS polymer and Anatase based Nano-TiO_2. The properties of Nano- TiO_2 and SBS polymer used in the study are given in Tables 1-3. Nano- TiO_2 and SBS polymer along with their molecular structures are shown in Figures 1 and 2.

Table 1. Properties of Asphalt binder

Properties	Value
Softening Point	47 ^{O}C
Viscosity @ 60 ^{O}C	3125 poise
Penetration Value	65 dmm
Ductility Value @ 27 °C	86 cm

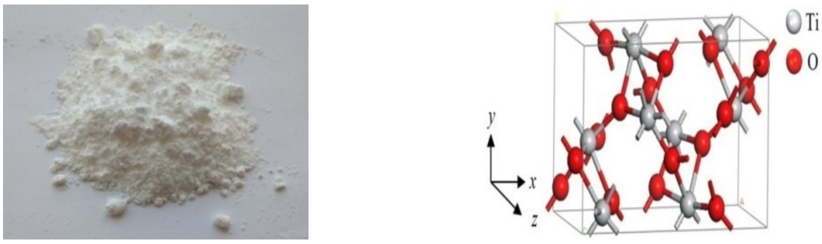


Fig. 1. Nano-TiO_2 and its molecular structure used in the study

Table 2. Properties of Nano-TiO_2.

Specification	Value
Average Particle Size	30-50 nm
SSA	201-220 m^2/g
True Density	4.23 g/cm^3
Bulk Density	0.15-0.25 g/cm^3
Colour	White
Morphology	Spherical

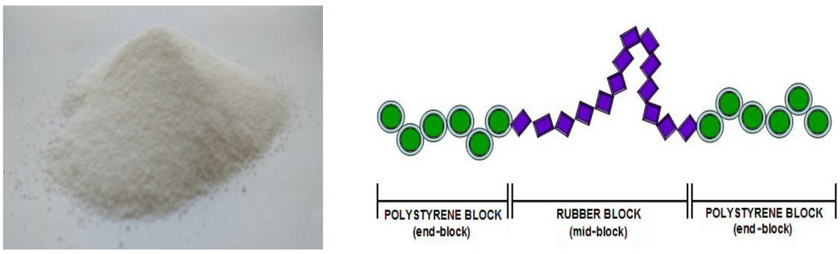


Fig. 2. SBS Polymer and its molecular structure used in the study

Table 3. Properties of SBS Polymer.

Specification	Value
Specific Gravity	0.94
Bulk Density	0.4 kg/dm^3
Colour	White
Morphology	Spherical
Molecular Weight	138-162 kg/mol

3. Methodology

The rheological tests on base and modified asphalt binders were done using Malvern Kinexus Pro+ Dynamic Shear Rheometer (DSR).

3.1 Frequency Sweep

The frequency sweep curve helps in determination how the binder will behave during storage and application. Frequency Sweep test can be performed for different temperatures for a fixed strain rate. For temperatures less than 46 ºC, strain level is usually kept low (2%) while for temperature above 46 ºC, shear strain is between 10-12%. A master curve is constructed with the data of frequency sweep for G* at reference temperature using time temperature super-positioning. Khattak et al. (2013) used sigmoidal function to construct master curve for G*/sin δ generated at 25 ºC from the data obtained from frequency sweep tests. The sigmoidal function can be shown below

$$\log_e |G^*/\sin\delta| = a + \frac{b}{1 + \frac{1}{e^{d+e(\log_e f_R)}}} \tag{1}$$

Where,
G* = complex shear modulus
δ = Phase angle
a, a+b = minimum and maximum value of G*/sin δ respectively
d, e = parameters describing the shape of the function

3.2 Temperature Sweep

The temperature sweep test measures rheological properties under controlled strain condition. The rheological properties are represented in the form of G* variation with respect to temperature at a fixed frequency to form isochronal curves. There exist a strong correlation between rutting resistance of the binder at high temperature and its elastic modulus. Modifiers tend to enhance elasticity of the binder measured in the form of G* and δ values. This test shows the change in complex shear modulus of asphalt binder at different temperature due to addition of modifiers. It is conducted at a fixed frequency of about 10 rad/sec with a temperature ranging from 20 to 90 ºC or 46 to 76 ºC (Golestani et al., 2015). 25 mm diameter plate with 1 mm gap is used for this purpose.

3.3 Linear Amplitude Sweep (LAS)

LAS test essentially measures damage tolerance of asphalt binders. It determines binder's resistance to damage by means of cyclic loading employing linearly increasing load amplitudes. The rate of damage accumulation indicates the fatigue performance of the binder. LAS test is the most preferred method for the calculation of fatigue life of binder as it is a very efficient method and also incorporates the effect of different loading magnitudes and loading rates (Hintz and Bahia, 2011). Different loading magnitudes represent traffic volume while loading rates represents pavement structure. For determination of fatigue life the two parameters A and B (binder properties) of binder fatigue law were measured during this test.

$$\text{Fatigue Life, } N_f = A(\gamma_{max})^{-B} \tag{2}$$

Where,
γ_{max} = Maximum expected binder strain for given pavement structure (%)

This test is done in accordance to AASHTO TP 101-14. The sample is tested in shear using frequency sweep between 0.2 to 30Hz at 0.1% strain. Then the sample is subjected to amplitude sweep with strain increasing linearly from 0 to 30% over the course of 3100 cycles of loading at constant frequency of 10 Hz to cause accelerated fatigue damage. Amplitude sweep is essentially oscillatory shear in strain-controlled mode at fixed frequency. The continuum damage approach is used to calculate fatigue life of binder sample.

3.4 Multiple Stress Recovery (MSCR)

This test determines percent recovery and non-recoverable compliance of asphalt binder. This test is essential for the characterization of polymer modified asphalt binder. This test is done in accordance to ASTM: D7405 – 15. This method is appropriate for both unaged and aged binder. The presence of elastic response is determined under shear creep and recovery at two stress levels at specified temperature. 25 mm parallel plate geometry with a 1 mm gap setting is used. This test is conducted at highest working temperature for the binder. For this study the test is conducted at 64 °C. For each cycle a haversine shear load is applied to the sample at constant stress for 1 sec and then allowed to recover for 9 sec. 20 creep and recovery cycles are run at 0.1 kPa creep stress followed by 10 creep and recovery cycles at 3.2 kPa creep stress. Using this data % recovery and non-recoverable creep compliance is determined.

4. Preparation of Nanocomposite modified binder

The base asphalt was heated in a small container until it was completely flowable. A certain amount of Nano TiO_2 was added slowly and mixed into asphalt binder and stirred continuously till it blends homogeneously. Similarly for nanocomposite modified binder, firstly SBS polymer was added to the binder and mixed for about 30 minutes and then Nano TiO_2 was added to it.

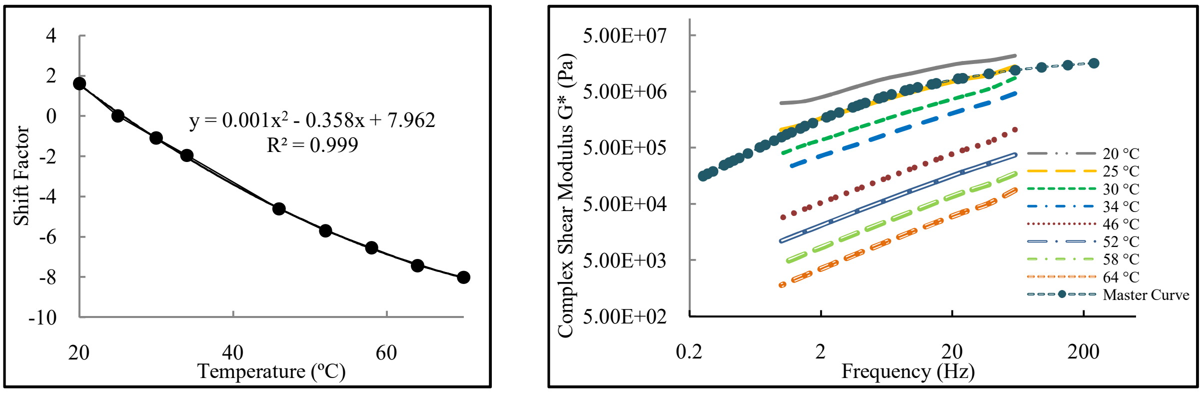
5. Results and Discussion

5.1 Selection of optimal Nano-TiO_2 content for modification

The optimal amount of nano-TiO_2 required for modification of the base binder was found out using the frequency sweep and Linear Amplitude Sweep (LAS) tests. Frequency sweep was conducted at 2% strain for temperatures 20, 25, 30 and 34 °C and at 10% strain for temperatures 46, 52, 58 and 64 °C. A master curve was created by shifting the frequency sweep data of different temperature to a reference temperature i.e. 25 °C using the sigmoidal equation. The different frequencies corresponding to a given temperature were shifted to the reference frequency to obtain a shifting factor curve. Shifting factor was logarithm of ratio of reference frequency to frequency at a given temperature. The shifting factor curve and master curve for base binder can be seen in figure 3(a) and (b). The equation for master curve obtained for base binder is given below

$$log_e|G^*| = 7.5 + \frac{9.4}{\frac{1}{e^{0.6+0.5(log_e f_R)}}+1} \tag{2}$$

Where,
F_R = frequency (Hz) and G* = Complex shear modulus (Pa)



(a) (b)

Fig. 3. (a) Shift Factor for base binder (b) Master curve at 25 °C for base binder

Similar master curves were created for modified binders at different nanoparticle contents. At different modification with nano-TiO_2, G* values were similar but higher than the base binder for high frequencies. At low frequencies, G* values for asphalt + Nano-TiO_2 1.5% was maximum compared to others. G* values of nanoparticle content 2% and 3% respectively were found to be similar to that of the base binder as can be seen in figure 4. This justifies that excess of nanoparticle content deteriorates the properties of the base binder. Increased G* values (increased stiffness) are favourable for rutting resistance but unfavourable for fatigue cracking. Hence, asphalt + Nano-TiO_2 1% shows optimum increase in G* values both at low and high frequencies. Figure 5 shows the phase angle master curves which have decreased values as compared to the base binder favourable for fatigue resistance. The increase in δ values with decrease in frequency signifies decrease in elasticity.

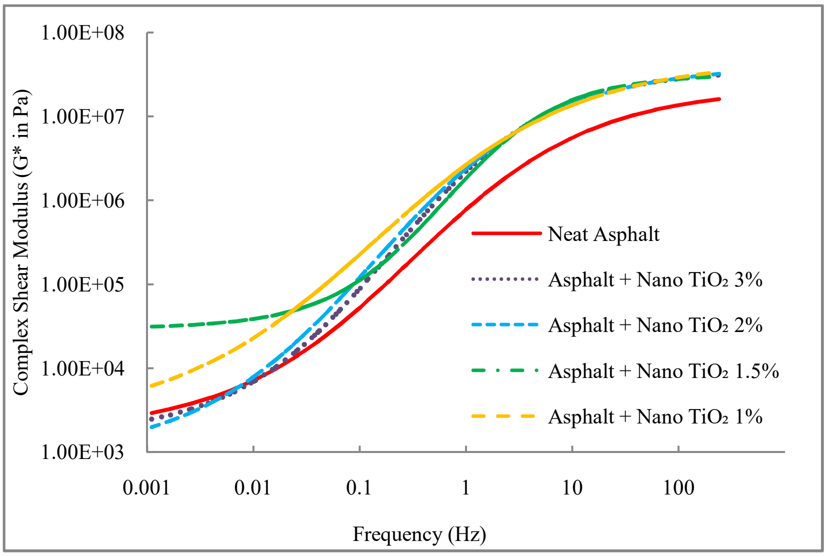


Fig. 4. G* Master Curves for different levels of Nano-TiO_2 modification

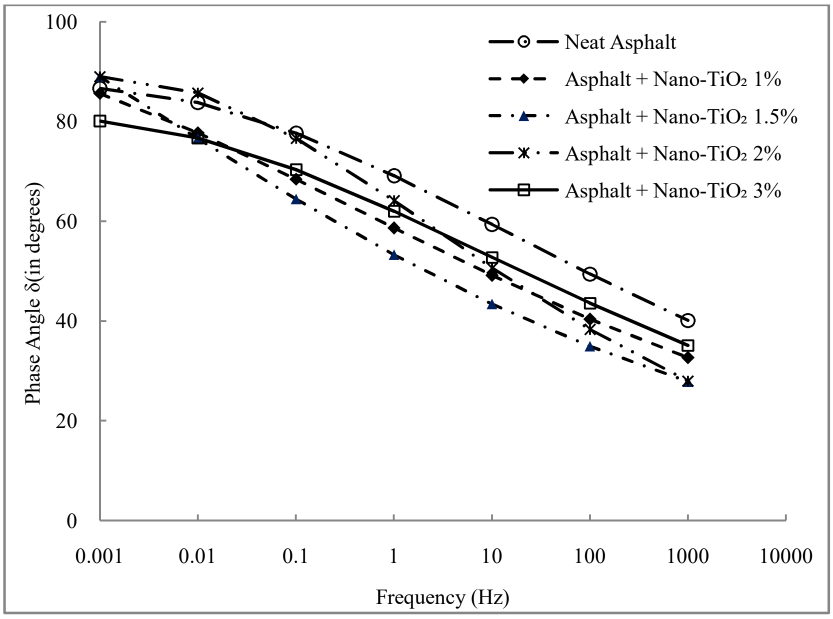


Fig. 5. Phase Angle Master Curves for different levels of Nano-TiO_2 modification

In LAS the fatigue life was calculated from the data obtained from the frequency sweep (parameter B) and amplitude sweep (parameter A) tests using Viscoelastic Continuum Damage (VECD) theory. The equations for fatigue life for different modified binders were calculated. The A and B parameters for different modification levels are shown in table 4. Higher A value increases fatigue life whereas higher B value decreases fatigue life (at a constant A). From the results shown in figure 6 it can be seen that the fatigue life of binder modified with nano-TiO_2 decreased compared to base binder. This suggests modification with nano-TiO_2 stiffens the binder at lower temperature. Hence, nanoparticle modified binders are more suitable to be used in the regions where rutting is a primary concern. The fatigue life of binder modified with 1.5% Nano-TiO_2 content was found least as compared to base asphalt (which is due to its brittle nature). But as the amount of modification was increased (i.e. at 2% and 3%) the rate of decrease in fatigue life was less than the base binder. The rate of decrease in fatigue life was least for asphalt + nano-TiO_2 1%.

Table 4**.** LAS results of different nanocomposite modified binders

Binder	A	B
Neat Asphalt	186589.16	3.823
Asphalt + Nano- TiO_2 1%	20385.33	2.467
Asphalt + Nano- TiO_2 1.5%	34387.69	4.618
Asphalt + Nano- TiO_2 2%	85138.12	2.8
Asphalt + Nano- TiO_2 3%	126487.76	2.74

From the frequency sweep and LAS tests asphalt + nano-TiO_2 1% was found to be optimum modification. According to Indian weather condition rutting is primary concern and asphalt + nano-TiO_2 1% shows adequate rutting resistance (increased G* values). The difference between its Fatigue life compared to that of base binder is not that large.

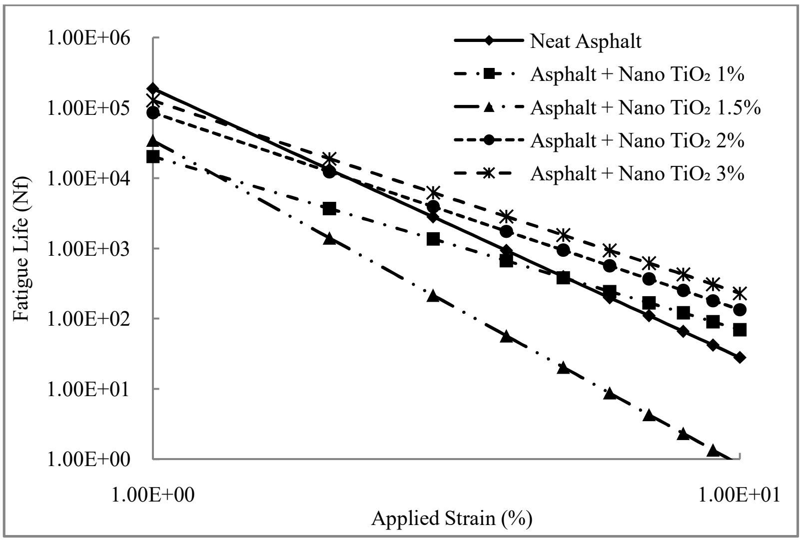


Fig. 6. Fatigue Life (N_f) vs Strain Level (%) for different levels of Nano-TiO_2 modification

5.2 Nanocomposite modified Asphalt Binder

Nanocomposite modified asphalt binder was formed by adding SBS polymer 3% and 4% by weight respectively along with 1% nano-TiO_2. Temperature sweep, LAS and MSCR tests were conducted on the nanocomposite modified binder. The results of LAS test reflect increase in fatigue life on addition of SBS polymer to the base binder. On increasing the amount of Nano-TiO_2 to SBS polymer modified binder the rate of decrease in fatigue life of the binder increased as can be seen in figure 7. This increment may be due to increase in stiffness as both polymer and nanoparticle modification increase the stiffness of the binder. Asphalt + SBS polymer 4% + Nano-TiO_2 1% showed higher fatigue life at low strain levels while reduced fatigue life at higher strain levels. Asphalt + SBS polymer 4% + Nano-TiO_2 1.5% were much lower compared to the base binder.

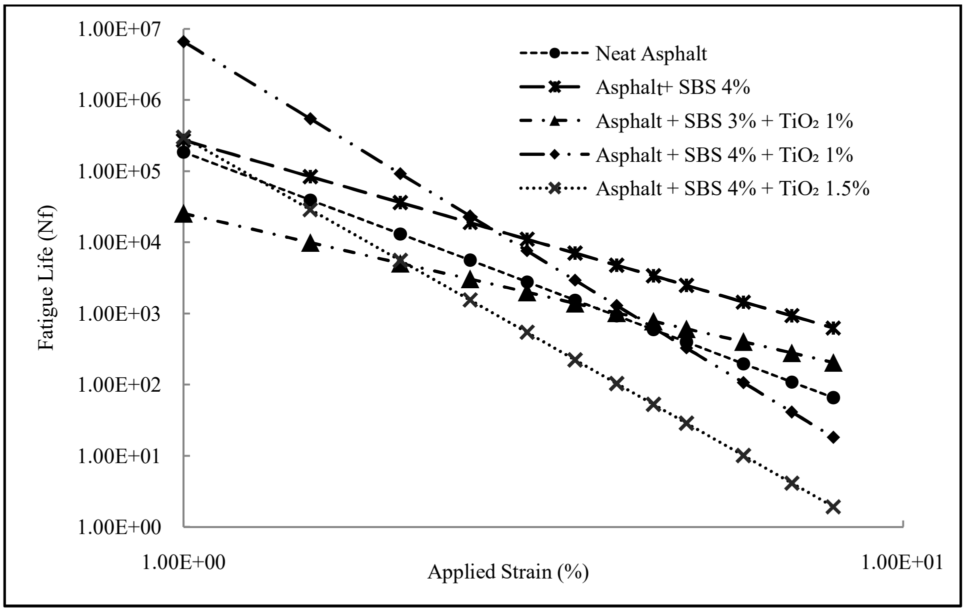


Fig. 7. Fatigue Life for different levels of SBS polymer/nano-TiO_2 modification

Figure 8 shows results from temperature sweep test in which SBS 4% + Nano-TiO_2 1% showed substantially higher value of shear complex modulus (G*) than the base binder. The test was conducted in same conditions as for Nano-TiO_2 modified asphalt binder samples. At higher temperature δ values approached 90° for all the binders while at lower temperature the phase angle reduced.. Nanocomposite modified binder showed reduced δ values indicating improvement in its elastic behaviour. A very small improvement was observed on increasing the amount of SBS in the binder.

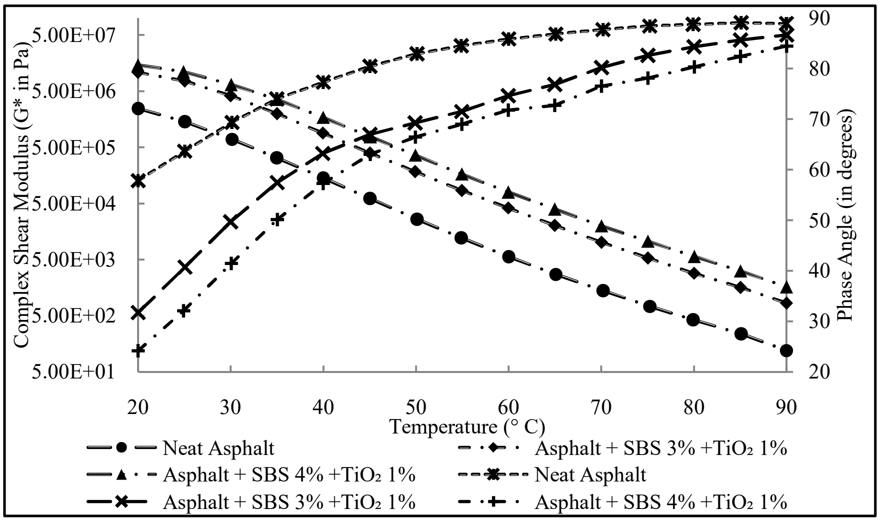


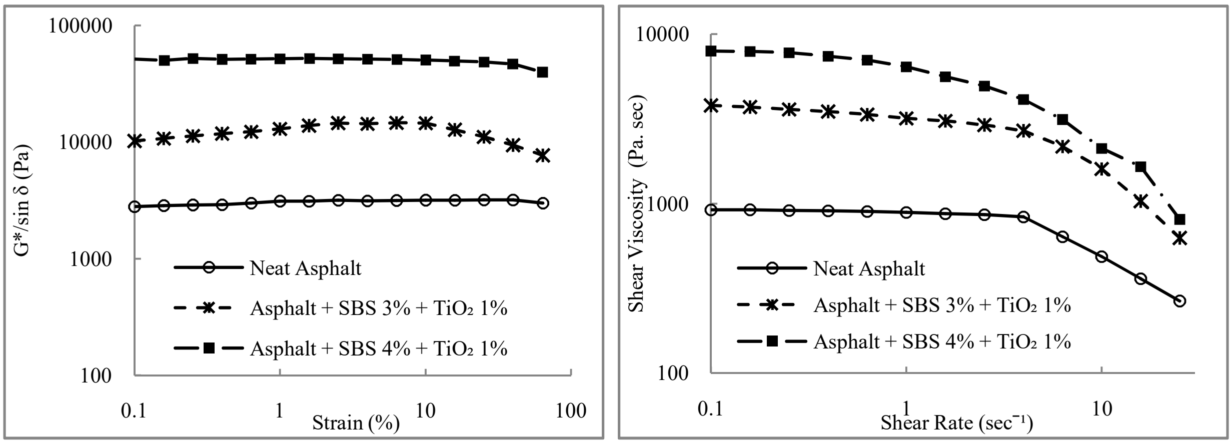
Fig. 8. Temperature Sweep for different levels of SBS polymer/nano-TiO_2 modification

The results of MSCR test as shown in table 5 concluded that the percent recovery of SBS 4% + Nano-TiO_2 1% was higher (mainly due to the presence of SBS) than base binder. This signifies that modified binder has greater resistance to permanent deformation than the base binder. Generally addition of polymer (SBS) decreases the phase angle increasing its elastic properties. This test was carried for unaged binders at 64 °C.

Table 5. MSCR Test results of different nanocomposite modified binders

Binder	Jnr (kPa^{-1})	% Recovery
Base Binder	2.06	0.019
Binder +SBS 3% + Nano TiO_2 1%	0.4968	8.809
Binder + SBS 4% + Nano TiO_2 1.5%	0.097	26.24
Binder + SBS 4% + Nano TiO_2 1%	0.0256	29.41

The rutting parameter of 4 % SBS polymer and 1% Nano TiO_2 modified binder was higher suggesting that the modified asphalt binder has more rutting resistance compared to the base binder as can be seen in Figure 9(a). The modified binder also conforms performance graded superpave specification i.e. G*/sinδ > 1kPa for unaged binder. The viscosity at 60 ^{O}C as shown in figure 9(b) is similarly higher for SBS 4% + Nano-TiO_2 1% modified binder. We can conclude that modified binder showed increased visco-elastic behaviour than the base binder.



(a) (b)

Fig. 9. Comparison of different nanocomposite modification levels (a) Rutting at 60°C (b) Viscosity at 60°C

6. Summary and Conclusions

This study was done to investigate the effect of nano--TiO_2 and SBS polymer on the asphalt binder. Tests were done on both nano- and nanocomposite (SBS polymer + nano--TiO_2) modified binders. Results from the tests lead us to the following conclusions:

a) Binder modified with nano-TiO_2 showed enhanced binder strength and other properties. The modified binder was found to be more elastic (lower δ values) and stiff (higher G* values).

b) The high temperature properties of modified binder increased as compared to the base binder, while the low temperature properties like fatigue life at 25 ºC decreased.

c) The nanocomposite (4% SBS polymer + 1% nano-TiO_2) modified binder also showed improved high temperature properties but less than the nano-TiO_2 modified binder, however the low temperature properties of nanocomposite modified binder were found better than the nano-TiO_2 modified binder.

d) The excessive addition of modifiers led to deterioration of the properties of asphalt binder which may be due to the agglomeration of particles in the binder.

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