Research Article

Ahmed Mahir Mohammed* and Alaa H. Abed

Effect of nano-TiO_2 on physical and rheological properties of asphalt cement

https://doi.org/10.1515/eng-2022-0520
received June 17, 2023; accepted August 29, 2023

Abstract: In recent years, nano-modified asphalt has gained significant attraction from researchers in the design of asphalt pavement fields. The recently discovered Titanium dioxide nanoparticles (TiO_2) are among the most exciting and promising nanomaterials. This study examines the effect of 1, 3, 5, and 7% of nano-TiO_2 by weight of asphalt on some of its rheological and hardened properties. The experimental study included physical and rheological properties. The asphalt penetration, softening point, ductility, and rotational viscometer tests indicate that 5% nano-TiO_2 is the ideal amount to be added to bitumen as a modifier. The study of the rotating viscosity test showed that the addition of nano-TiO_2 helped to increase viscosity and lessen bituminous sensitivity. Rutting factor in terms of $G^*/\sin\delta$ indicated the addition of 3 to 7% of nano-TiO_2 increased the rutting resistance of asphalt against higher temperatures and promoted performance grade by about one grade at 3% and two grades at a range of 5–7% this suggests that nano-TiO_2 increased the stiffness of the asphalt and leading to enhance the rutting performance of asphalt. While fatigue parameter, $G^*.\sin\delta$ shows that as nanocontent increases, higher stiffness at 5 and 7% of TiO_2 content leads to an increase in complex modulus and a decrease in fatigue parameter. Higher creep stiffness and higher *m*-values were noted at low temperatures as nano increases in asphalt binder, increasing stiffness and decreasing the *m*-value at −6 and 12°C. As a result, using 5% nano-TiO_2 will improve asphalt's physical properties and enhance asphalt anit-rutting and fatigue resistance.

Keywords: nanomaterial, TiO_2, DSR, BBR, asphalt

*** Corresponding author: Ahmed Mahir Mohammed**, Civil Engineering Department, Al-Nahrain University, Baghdad, Iraq,
e-mail: st.ahmed.mahir@ced.nahrainuniv.edu.iq
Alaa H. Abed: Civil Engineering Department, Al-Nahrain University, Baghdad, Iraq, e-mail: Alaa.abed@eng.nahrainuniv.edu.iq

1 Introduction

Asphalt binder is considered one of the unique material components in paving construction and industry. Due to the population's increasing capacity and the demand for cars, the repeated axial loading damage increases on the pavement surface, accompanied by other extrinsic features like hot climate weather and bad construction, which finally lead to the early failure of asphalt pavement. Modifying asphalt binders has been the key solution in recent years to avoid these problems. This is due to the applicability of additives such as polymers, fillers, waste material, and the new generation of nanomaterials. The benefits of nanomaterials include their high-temperature sensitivity, improved extendibility, and higher specific surface area. According to Yao et al. and Li et al. [1,2], adding nanomaterials to asphalt that has already been treated for polymers is more advantageous; as a result, nanomaterials improve the interaction of polymers with the asphalt matrix, decrease polymer segregation, and increase the stability of modified asphalt binder. Numerous studies conducted globally have used nanomaterials to successfully enhance the engineering properties of asphalt binders [3–6]. Hamedi [7] investigated a binder 60–70 with aggregates coated in nano-Al_2O_3 and nano-Fe_2O_3 for an asphalt mixture. Asphalt mixtures with and without nano-additives were tested using a modified Lottman method by the authors. The authors conclude that the nano-additive increased the asphalt mixture's resistance to moisture. Titanium dioxide appears in nature as rutile, anatase, and brookite. Titanium dioxide at the nanoscale comprises 80% anatase and 20% rutile. It has been demonstrated that, compared to regular TiO_2, nano-TiO_2 has a very high surface area, a tiny diameter, and a very low opacity. Because of these unique features, some researchers used nano-TiO_2 to enhance the performance of modified asphalt. The addition of TiO_2 to the asphalt binder increases viscosity [8–10] and the $G^*/\sin\delta$ parameter at high temperatures [11]; TiO_2 causes a slight reduction in the non-recoverable creep compliance and increases the matrix recovery rate [12]; the aging index is decreased [13]; the more nano-TiO_2 is incorporated into the asphalt binder, the greater the mass loss [14]. Other researchers, like Shafabakhsh et al. [15], assessed how nano-TiO_2 affected the rutting and fatigue characteristics of the HMA mixture. According to the results, nano-TiO_2 improved the rutting and fatigue behavior of the combination. Later, the author examined the impact of nano-TiO_2/SiO_2 on the effectiveness of a mixture, showing that nano-TiO_2/SiO_2 improves the binder's rheological behavior and the mixes' rutting behavior [16]. The rutting behavior of hot-mix asphalt modified with nano-TiO_2 was assessed in a study by Tanzadeh et al. [17]. The wheel-tracking test was used to look into how well the specimens rutted. According to the results, nano-TiO_2 improved the rutting performance of the unmodified asphalt mixture. A different combination of nano-TiO_2/$CaCO_3$ was used by Zhang et al. [18]; the author conducted a study to assess the asphalt rheological performance with different dosages with the 5% optimal dosage TiO_2/$CaCO_3$ content, asphalt viscosity improved and enhanced anti-rutting capacity by increasing its rutting parameter (G^*/ sin δ). According to Rocha Segundo et al. [19], a transparent binder modified with 0.5, 3.0, 6.0, and 10.0% nano-TiO_2 is compared to the transparent base binder, conventional binders, and polymer-modified binders in terms of its physicochemical and rheological characteristics. The addition of nano-TiO_2 gradually raised the softening point and reduced penetration by up to 6.0% of modification. Furthermore, TiO_2 would shorten the fatigue life of transparent-binder asphalt pavements. Instead, it would make high contents more resistant to rutting. According to the results, the author recommended that 0.5% of TiO_2 was the best addition rate without degrading the transparent binder's fatigue resistance, and 10.0% was the best for permanent deformation. The rheological parameters G^*/sin δ improve when the amount of nano-TiO_2 and nano-ZnO in the asphalt matrix increases; according to a recent study, the non-recoverable creep compliance caused by stiffness growth at high temperatures increases the resistance to permanent deformations. Filling the porosity of the conventional asphalt binder increases impermeability and decreases the effects of oxidation and volatilization, which lowers the Aging Index values [20]. Both nanoparticles perform better regarding fatigue damage at low deformation amplitudes and worse at large deformation amplitudes. When compared, the binder modified with nano-ZnO exhibits better mechanical and rheological response at high temperatures. In contrast, the binder modified with nano-TiO_2 exhibits a higher number of cycles during the assessment of the fatigue damage tolerance. Low-temperature cracking, which results from the asphalt layer shrinking and the creation of tensile strains greater than the asphalt mixture's fracture strength, is another significant problem with flexible pavements. The likelihood of low-temperature cracks increases due to bitumen's increased creep stiffness and lower viscous behavior. the fatigue parameter (G^*.sin δ) showed that TiO_2/$CaCO_3$ would improve fatigue resistance at intermediate-temperature. Other studies [21,22] indicated that nano-TiO_2 decreases asphalt binder susceptibility against temperature and reduces its sensitivity towards aging since it affects the physical testing and rheological properties of asphalt, causing an increase in asphalt rutting resistance at higher temperatures and enhancement of the elasticity of asphalt, at intermediate temperature performance of bitumen improves so the fatigue lives increase. Also, Cadorin et al. [23] present how the presence of nano-TiO_2 affected the matrix's susceptibility in their study. The author concludes that nano-TiO_2 enhances the matrix's mechanical and rheological properties, increasing its resistance to persistent at specific stress/strain levels, deformation, stiffness, fatigue damage tolerance, and oxidative aging resistance. Different concentrations of nano-TiO_2 were added by Filho et al. to a neat asphalt binder with a penetration grade of 50/70. They discovered that nano-TiO_2 might increase fatigue resistance by conventional testing, linear amplitude sweep, and multiple stress creep recovery [24]. Later, they concluded that including nano-TiO_2 developed a higher performance in high temperatures than the pure binders by promoting a non-recoverable compliant decrease, leading to an increase in the resistance to permanent deformation besides a growing delay in aging, as evidenced by a lower aging index and reduction in mass loss [25]. According to research, nano-TiO_2 in the anatase phase is more effective than the rutile and brookite phase at purifying the environment [26]. The oxidation of a titanium precursor at a high temperature produces nano-TiO_2. Most of the literature on using nano-TiO_2 for asphalt modification focuses on protecting asphalt pavement from photocatalytic oxidation and removing vehicle pollutants like NOx [14,27,28]. According to published studies, nano-TiO_2 has a great potential to reduce atmospheric nitrogen monoxide by maintaining it close to the source of the pollution. Similarly, a few research studies, including nano-TiO_2, have been reported to increase the rheological performance of asphaltic mixtures. Some concerns about human health should be addressed when dealing with any nanoparticles. Regarding nanoparticle safety and related potential health dangers, there are some reservations. Since they are tiny, they can easily pass through biological barriers like cell membranes and human skin and build up in unfavorable places to dangerous levels [29]. According to Grassian et al. [30], breathing in nano-TiO_2 at a concentration of 8.8 mg/m^3 resulted in lung irritation. Although some studies have already been done, there is still much ambiguity about how manufactured nanomaterials may affect the environment and people's health. More articles have recently been published on this subject due to the widespread use of nanotechnology in various sectors, particularly in packaging and food additives [30–34]. There are several stages where exposure can be significant, including creating nanomaterials and modifying the asphalt binder. Inhalation, ocular contact, and dermal adsorption are the most likely exposure modes [34]. The handling and manipulation of such materials should be treated as possible hazards unless the nanomaterials suppliers provide other information, in which case safety handling procedures should be followed. Crucho [35] stated that modified asphalt binder in a laboratory with a fume hood cabinet and personal protections: gloves made of nitrile that are at least 0.5 mm thick, a mask to protect one's eyes, a breathing mask with a particle-filter FFP3, and a protective suit (Tychen C – category III). The related studies show that incorporating TiO_2 nanoparticles into asphalt binders improves asphalt binders' toughness, rutting resistance, stiffness, and resilience to aging while lowering the penetration grade and raising the softening point of binders. Besides, its effect promotes NOx and SO_2 pollutants from the atmosphere through photocatalytic activity. In this context, there is a definite need for new studies to supplement previously published ones targeted the impact of the addition of nano-TiO_2 and how it affects the high-temperature properties of asphalt; changing asphalt binder high-temperature rheology may change the rheology at low and intermediate temperatures. Since more complexity is involved with the fatigue phenomena, less attention has been dedicated to analyzing their impact on the fatigue performance of asphalt. In this article, the effect of adding different content of nano-TiO_2 (1, 3, 5, and 7% by weight of mass) was examined via penetration, softening point, ductility, viscosity, and penetration index were evaluated, and dynamic shear rheometer (DSR) and bending beam rheometer (BBR) assessed the asphalt susceptibility with high, intermediate, and low temperatures.

2 Materials and methods

The material in this research is locally available in Iraq and used in paving work, while nano-TiO_2 was imported from SkySpring Nanomaterial, Inc.

2.1 Asphalt

Neat asphalt binder graded 40–50 penetration was obtained from the Al Doura refinery southwest of Baghdad province. The main properties of asphalt are presented in Tables 1 and 2.

Table 1: Physical properties of Al-Doura asphalt

Property	Designation	Units	Result
Penetration at 25°C, 100 g, 5 s	AASHTO T 49	0.1 mm	47
Softening point	AASHTO T 53	°C	49
Specific gravity at 25°C	ASTM-D70	—	1.03
Flash point	AASHTO T 48	°C	288
Ductility	AASHTO T 51	cm	112
Residue from thin-film oven test AASHTO T 179			
Retained penetration, % of original	AASHTO T 49	0.1 mm	61
Ductility at 25°C, 5 cm/min	AASHTO T 51	cm	87

2.2 Nano-TiO_2

Nano-TiO_2 (titanium oxide), shown in Figure 1, is a naturally occurring titanium oxide. Rutile, anatase, and brookite are the most common forms found in nature. Titanium oxide at the nanoscale comprises 80% anatase and 20% rutile. Sky Springs Nanomaterials Inc. sold rutile TiO2 (99.5%, 10–30 nm), employed as a nano-additive in this investigation; SEM image shows the particle shapes in Figure 2, while Table 3 presents physical nanocharacteristics.

2.3 Preparation of nano-modified asphalt

In this study, nano-Tio_2 was added at 1, 3, 5, and 7% by weight of neat asphalt binder. A high-speed mixer with a

Table 2: Rheological properties of Al-Doura asphalt

Property	Designation	Result	Temperature	AASHTO M320 limits
Original test on binder				
Rotational viscosity, Pa s	AASHTO T316	0.63	135°C	Max. 3
		0.16	165°C	—
DSR, 10 rad/s, $G^*/\sin\delta$, kPa	AASHTO T315	2.34	64°C	Min. 1
		0.842	70°C	
Rolling thin film oven (RTFO) Binder Residue				
DSR, 10 rad/s, $G^*/\sin\delta$, kPa	AASHTO T315	3.67	64°C	Min 2.2
		1.68	70°C	
Mass loss, %	AASHTO T240	0.61		Min. 1
Pressure Aging Vessel (PAV) Binder Residue				
DSR, 10 rad/s, $G^*.\sin\delta$, kPa	AASHTO T315	6980	25°C	Max. 5000
		4662	28°C	
Creep stiffness, MPa	AASHTO T313	177	−16°C	Min. 300
Slope *m*-value		0.393	−16°C	Max 0.3

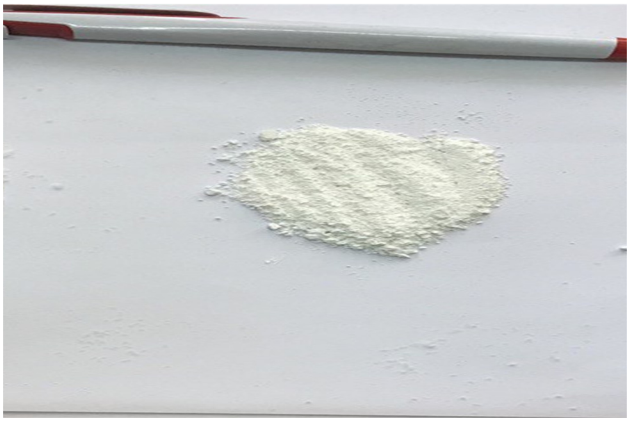

Figure 1: Photo of nano-TiO_2.

jiffy head, as shown in Figure 3, was used to perform the homogenous modified asphalt blend and ensure good nanoparticle dispersion; the basic procedure included heating the asphalt to 160°C for sufficient time and manually stirring. Then, nano-TiO_2 was introduced slowly at a rate of 2 gm per minute. Finally, a shearing rate of 6,000 revolutions was performed for 40 min. Figure 4 summarizes the procedure used for asphalt binder modification.

3 Asphalt test

3.1 Physical and rheological tests

Routine physical testing was established to assess the impact of various nano-modified asphalt concentrations, including a penetration test to measure the consistency of asphalt

Table 3: Physical properties of nano-Tio_2

Properties	Nano-TiO2
Appearance	White powder
Average particle size (nm)	10–30
Specific surface area: m^2/g	50–100
Bulk density (g/cm^3)	0.08
Purity	99.5%
Solubility	Insoluble

based on ASTM D5. At the same time, the softening point is conducted based on ASTM D36. Furthermore, ASTM-D113 provides an accurate measure of tensile property for asphalt by a ductility test. The penetration and the softening point result were later used to compute the penetration Index (PI) presented in equation (1) to quantify asphalt temperature sensitivity [36].

$$\mathrm{PI} = \frac{1952 - 500\log_{10}P25 - 20\mathrm{SP}}{50\log_{10}P25 - \mathrm{SP} - 120}. \quad (1)$$

3.2 DSR

The DSR test describes the viscous and elastically behavior of asphalt at medium to high temperatures. DSR measures the phase angle (δ) and the shear modulus (G^*). Unaged, RTFO aged, and PAV aged bitumen is all done per AASHTO T 315.

3.3 BBR

The BBR test measures bitumen's stiffness and relaxation characteristics at low temperatures. These variables

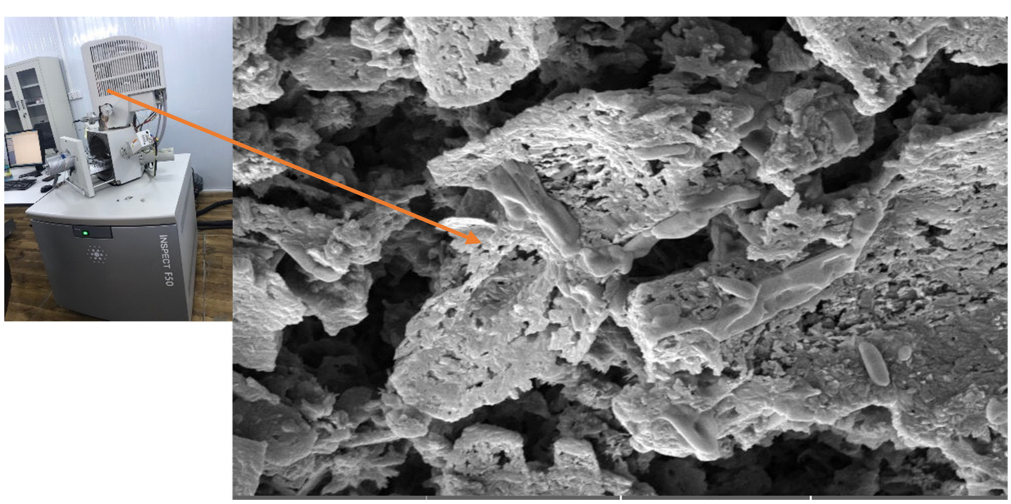

Figure 2: SEM image of nano-TiO_2.

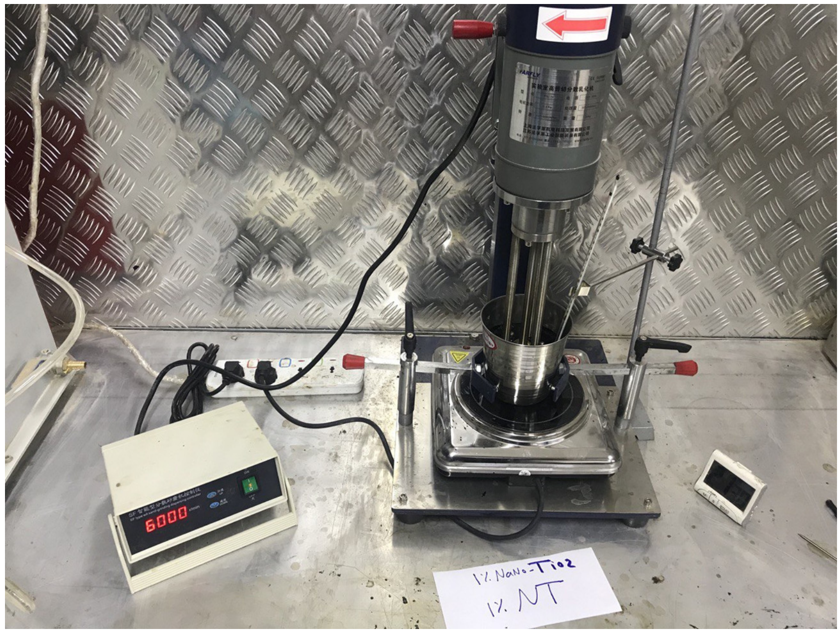

Figure 3: Mixing of nanomaterial with asphalt.

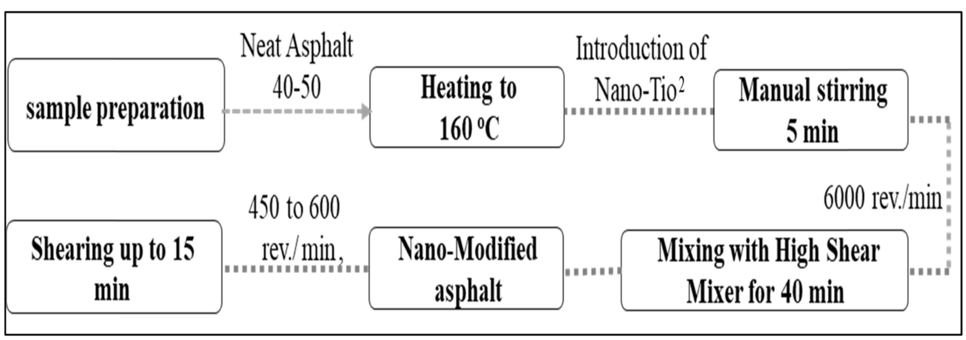

Figure 4: The procedure of asphalt modification.

indicate an asphalt resistance to low-temperature cracking. On PAV-aged bitumen, a BBR test is conducted per AASHTO T 313.

3.4 Rotational viscometer (RV)

The RV test can assess asphalt workability during the mixing and compacting processes. According to the AASHTO TP48 standard, the asphalt RV readings are calculated. The RV Brookfield (DV-III) measures bitumen viscosity at 135°C, and a 165°C test is run. Figure 5 presents the testing setup for identifying neat and nano-modified asphalt's physical and rheological properties.

4 The test result of asphalt

4.1 Physical tests

Figures 6–9 show how different TiO_2 concentrations affect the properties of asphalt in terms of penetration, softening point, ductility, and PI values. Nano-modified asphalts show a noticeable decrease in penetration, with the highest difference at 5% TiO_2, up to 22% from the neat asphalt. Conversely, the softening point values increased positively at 6,13,16, and 14% for 1, 3, 5, and 7% for adding nano-TiO_2, respectively. According to the results, 5% nano-TiO_2 causes a decrease in the penetration grade and increases the softening point of binders. This behavior will promote asphalt

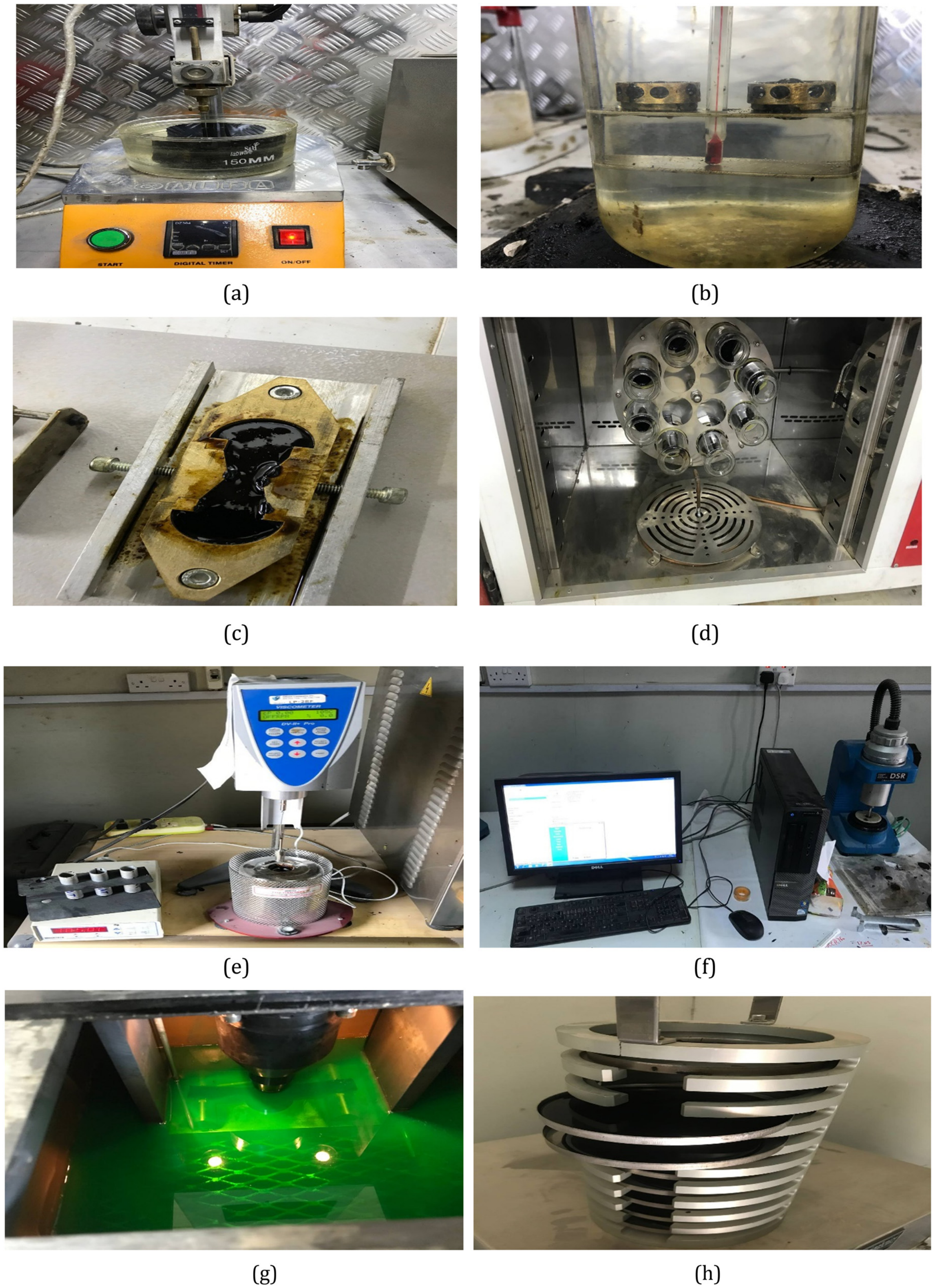

Figure 5: The testing device used in this study: (a) penetration test, (b) softening point, (c) ductility, (d) RTFO, (e) rotianle viscometer, (f) DSR, (g) BBR, and (h) PAV.

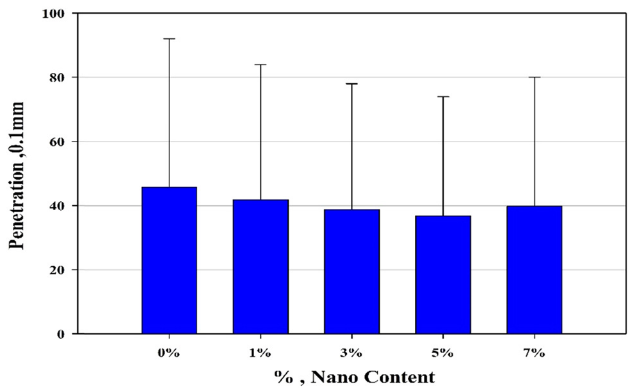

Figure 6: Asphalt penetration modified asphalt with TiO_2.

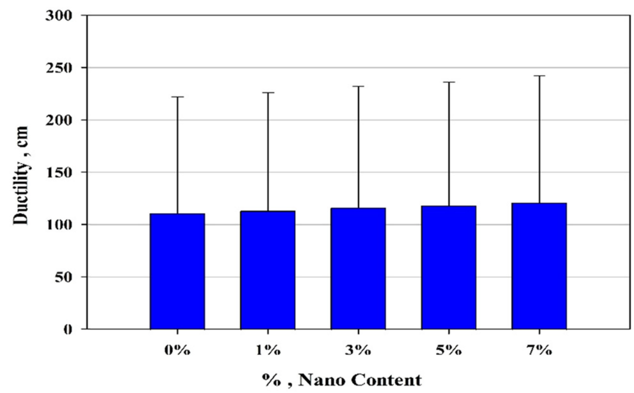

Figure 8: Asphalt ductility modified asphalt with TiO_2.

stiffness and improve the resistance towards higher temperatures. PI value, shown in Figure 9, guaranteed the blend's stiffness. Increasing the PI value indicated increasing hardness, which improved the TiO_2 blend's temperature susceptibility and *vice versa*. It has been noted that among asphalt blends, asphalt with 5% TiO_2 has the highest hardness and is most closely related to neat asphalt. Furthermore, ductility value increased with increasing Nanocontent in a wide range between 112 and 123 cm for neat and 7% nano-TiO_2. Based on penetration, softening point, and ductility tests, it was determined that asphalt's hardness had increased, improving its susceptibility to temperature changes.

4.2 Rheological test results

4.2.1 Viscosity

Figure 10 indicates that with the increase of nano-TiO_2 from 1 to 7%, the viscosity of neat asphalt binder would enhance at both 135 and 165°C temperatures. Viscometer testing result exhibited in Figure 9 shows an increasing rate in the value of viscosity by nearly 29, 42, 56, and 53% at 135°C at increasing content of nano-TiO_2 from 1 to 7%, respectively, compared to neat asphalt binder. Meanwhile, the same trend was noted at 165°C with less effective than up to 7% with 0.288 Pa s showing an increase by about 44% as associated with neat asphalt.

It can be concluded that after 5% of nano-modified asphalt, the values of viscosity take the lead of the same increase or less; this could be attributed to the broken bond among asphalt particles as a result of utilizing high Shear mixer making asphalt particles separated leading to be replaced by nano-TiO_2 particles [37]. It can be inferred that adding nano-TiO_2 helped to increase viscosity and lessen bituminous sensitivity. Viscosity variation, meanwhile, revealed a marked upward tendency.

4.2.2 DSR test results

4.2.2.1 Rutting parameter $G^*/\sin\delta$

The rheological testing used in the current study is to assess the Performance Grade (PG) classification for the upper-critical temperature over a range of temperatures

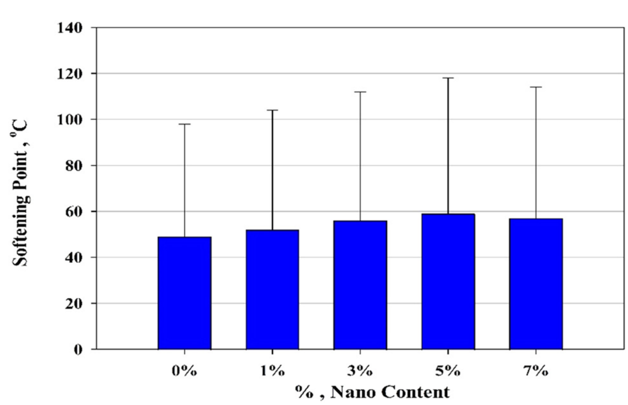

Figure 7: Asphalt softening point modified asphalt with TiO_2.

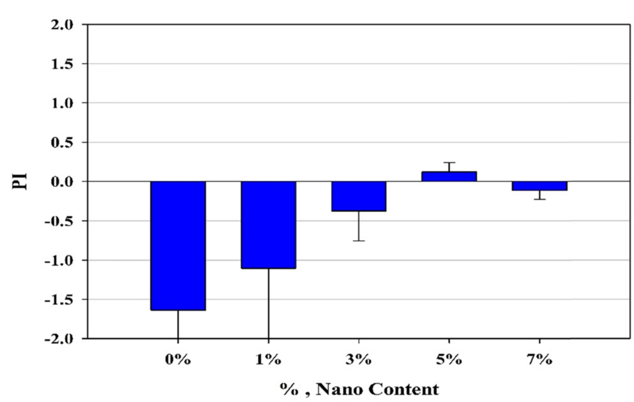

Figure 9: Asphalt PI-modified asphalt with TiO_2.

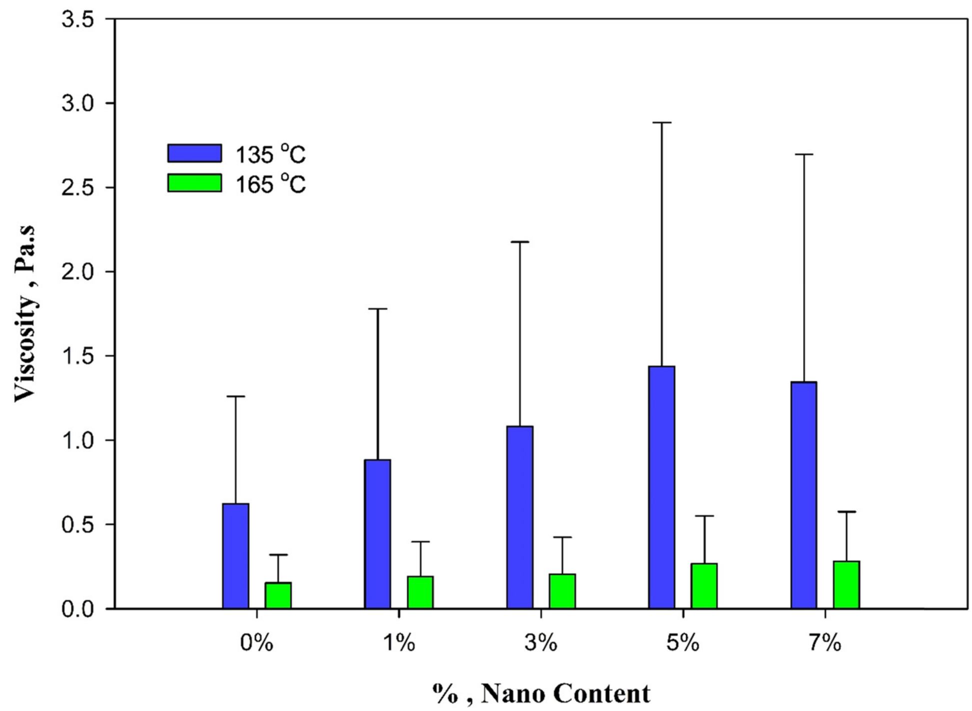

Figure 10: The viscosity of nano-modified asphalt.

and different nanocontent. The study examined neat asphalt and nano-modified asphalt binder samples regarding original, RTFO, and PAV. Specimen subjected to DSR oscillatory shear at 10 rad/s (1.59 Hz) corresponds to traffic traveling around 90 km/h. With a run-up in 6°C increments, the preliminary temperature values were adjusted to 64°C for unaged and RTFOT-aged samples. The presented result is in Table 4, and Figures 11–15 indicate an enhancement in asphalt binder properties as nano-TiO_2 content increased from 1 to 7%. In the case of the original and RTFO binder,

Table 4: Performance-graded asphalt test results

Temperature, °C	Property	0%	1%	3%	5%	7%
Test on original binder						
64	$G^*/\sin\delta$	2.34	2.71	4.85	6.57	6.66
	δ	84	82	80	77	75
70	$G^*/\sin\delta$	—	—	1.22	2.41	2.53
	δ	—	—	82	79	77
76	$G^*/\sin\delta$	—	—	—	1.77	1.82
	δ	—	—	—	81	80
Test on RTFO binder						
64	$G^*/\sin\delta$	3.67	4.64	6.28	9.21	9.45
	δ	68	66	63	60	59
70	$G^*/\sin\delta$	—	—	4.22	5.58	5.80
	δ	—	—	66	64	62
76	$G^*/\sin\delta$	—	—	—	2.05	2.21
	δ	—	—	—	65	64
Test on PAV binder						
25	$G^*.\sin\delta$	*6980	*6433	*5741	4850	4552
	δ	52	51	48	44	43
28	$G^*.\sin\delta$	4662	4421	3951	3420	3105
	δ	58	57	56	52	50
Actual PG		64–16	64–16	70–16	76–16	76–16

*failed to specify the limit.

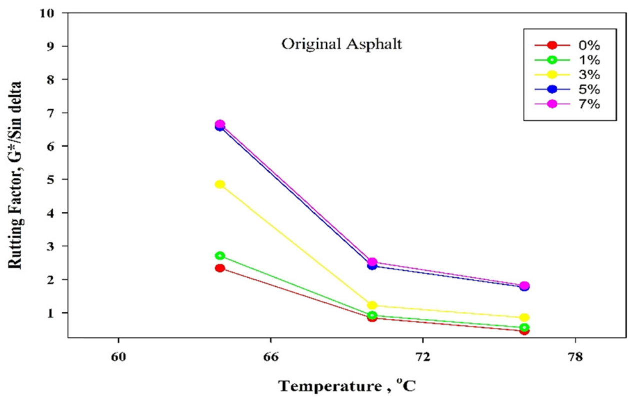

Figure 11: Rutting parameter of original nano-modified asphalt, $G^*/\sin\delta$.

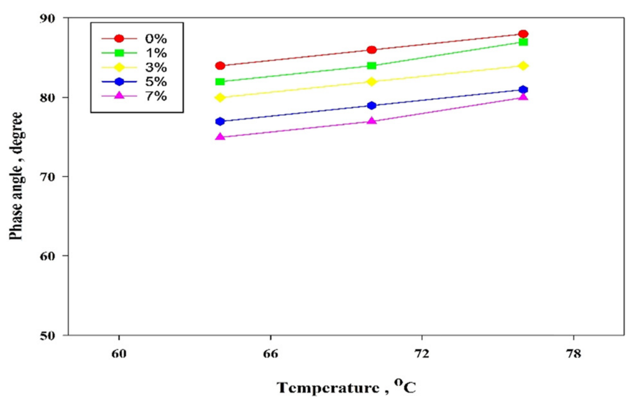

Figure 12: Rutting parameter of original nano-modified asphalt, phase angle δ.

the Superpave specifies a minimum amount of 1 and 2.2 kPa, respectively. Generally, a slight increase in rutting parameter $G^*/\sin$ is shown with 1%, while these values exhibit an increase by about 51% for 3% TiO_2 and nearly 64%. When nanocontent is from 5 to 7% at 64°C in the case of the original binder, the same trend at this temperature has been

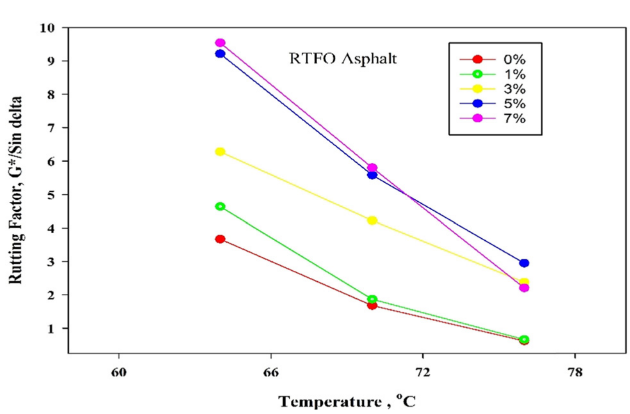

Figure 13: Rutting parameter of RTFO nano-modified asphalt, $G^*/\sin\delta$.

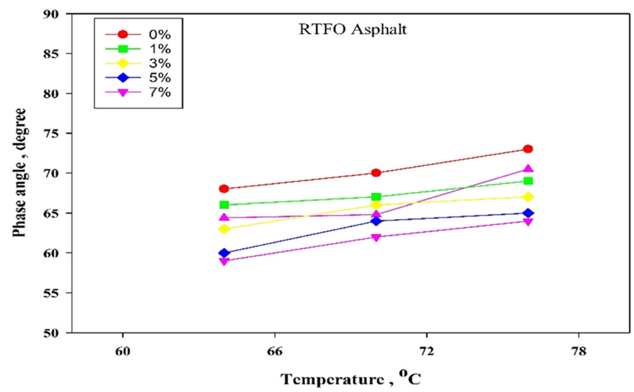

Figure 14: Rutting parameter of RTFO nano-modified asphalt, phase angle δ.

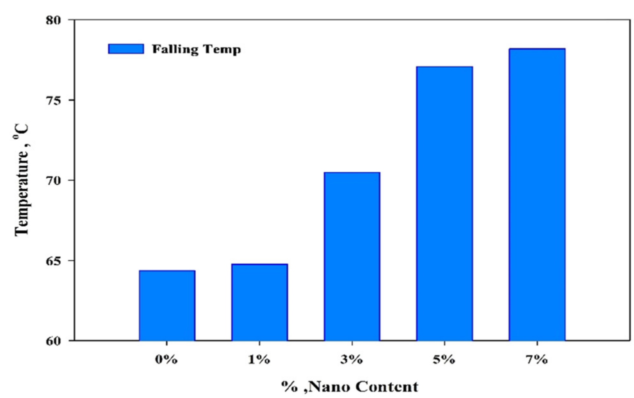

Figure 15: Falling temperature of neat and nano-modified asphalt.

noted, with a slight change for the RTFO binder at the same temperature. It was noted that adding 5% to 7 of nano-TiO_2 by weight of neat asphalt increased the value of $G^*/\sin\delta$ beyond the specification limit and survived against high temperatures, reaching a temperature of 76°C with a negligible increase behind 5% of nanocontent. TiO_2 can increase

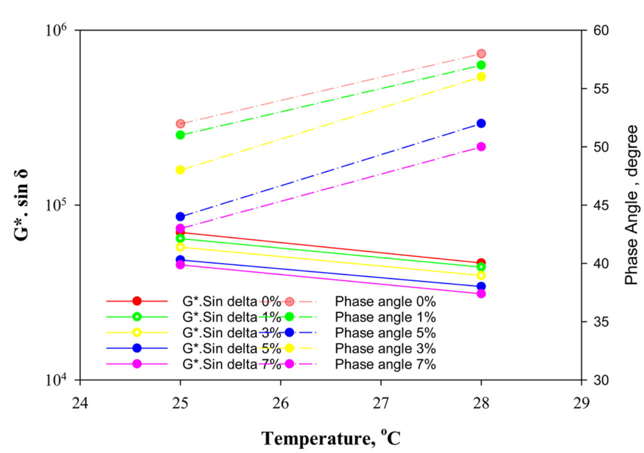

Figure 16: $G^*.\sin\delta$ and δ values of neat and nano-TiO_2-modified asphalt.

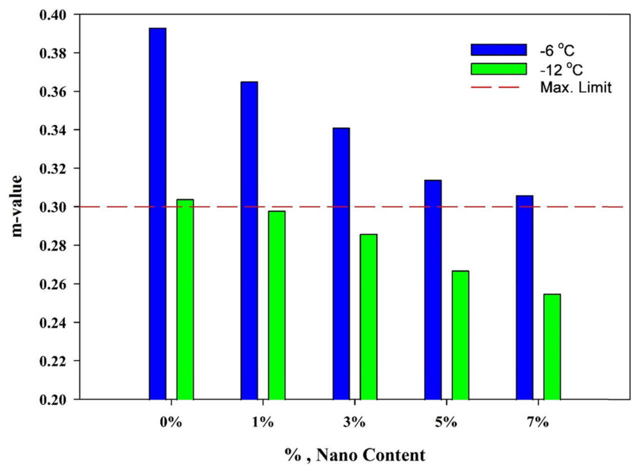

Figure 17: *m*-Value of neat and nano-modified asphalt.

PG grading by two grades to 76-16, which could be attributed to the vaporization of light elements and the consequences of change in asphalt nature aromatics and resins to asphaltness [11]. The outcomes of these results indicated that the addition of 3–7% of nano-TiO_2 increased the rutting resistance of asphalt against higher temperatures and promoted PG by about one grade at 3% and two grades at a range of 5–7% this suggests that nano-TiO_2 increased the stiffness of the asphalt and leading to enhance the rutting performance of asphalt. In conclusion, it can be stated that adding nano-TiO_2 by an amount of 5% enabled the asphalt to maintain higher stiffness at a higher temperature than its PG specification. Additionally, the binder was changed into a more advanced "high-temperature PG graded" binder.

4.2.2.2 Fatigue parameter $G^*.\sin\delta$

Testing values for Superpave fatigue parameter $G^*.\sin\delta$ and phase angle δ for neat and nano-modified asphalt are listed in Table 4 and compared in Figure 16. It can be noted that δ values decrease with the continuous increase of nano-TiO_2 at temperatures 25 and 28°C. A slight difference is seen at 1% nano-TiO_2. However, this decrease gradually increases, showing an improvement in the elastic nature of asphalt by about 8, 16, 18% at 25°C and 4, 11, and 14% at 28°C, when nano-TiO_2 content increased from 3 to 7%, respectively. Additionally, it can be seen that the δ values difference between changed samples and neat asphalt is lessened at lower temperatures due to the asphalt matrix behaving more elastically as the temperature drops. On the other hand, the behavior of decreasing rate in $G^*.\sin\delta$ values was obtained as nanocontent increased, highlighted with higher stiffness at 5 and 7% of TiO_2 content, leading to an increasingly complex modulus and decreasing fatigue parameter by about 30 and 34% from neat asphalt concerning this content of nano at both temperatures 25 and 28°C. These results agree with another researcher [38].

Although nano-modification also enhanced the elastic behavior of asphalt binder, as evidenced by decreased phase angles, the high complex moduli led to more significant values of $G^*.\sin\delta$. According to the Superpave fatigue parameter data, the change of asphalt binder with nanoparticles causes a decrease in resistance against fatigue cracking. Keeping in mind that the Superpave fatigue parameter is based on the results of a single loading cycle, it should be noted that there may be some differences between the parameter and the field findings.

4.2.3 BBR stiffness and *m*-value

The BBR testing result exhibited in Figures 17 and 18 shows that nano-TiO_2 particles decreased the elasticity of asphalt at low temperatures. Nano-modified asphalt failed to meet

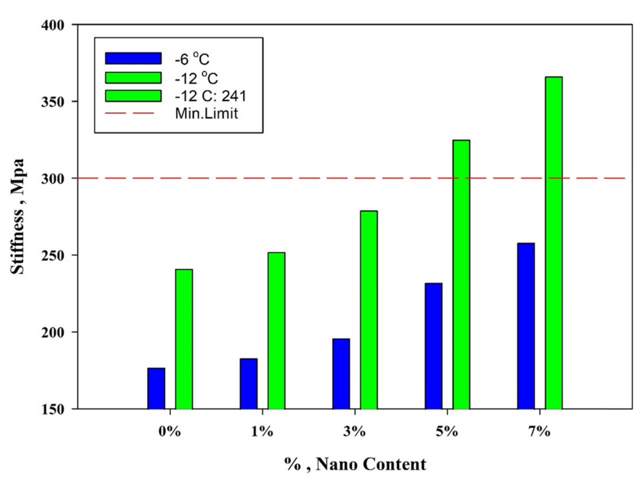

Figure 18: Stiffness value of neat and nano-modified asphalt.

the Superpave criteria for creep stiffness or creep slope at −12°C; instead, at −6°C, the binders achieved the specifications. Incorporating nano-TiO_2 into asphalt binder at different contents increased its stiffness and decreased the *m*-value at both temperatures, showing a higher chance of low-temperature cracking.

Dealing with samples at −12°C, the phase angle in Figure 16 presented a lower *m*-value than neat asphalt; 1% nano-TiO_2 decreased *m*-value to 0.363, showing a slight decrease of nearly 7% ad with increasing nanocontent from 3, 5, to 7%, *m*-value lowered by 14,21 and 23% to neat asphalt that is related to an enhancement in the elastic characteristics of asphalt. Additionally, it can be seen that the phase angle difference between neat and nano-modified asphalt is lessened at lower temperatures. This might be because the asphalt matrix will behave more elastically as the Temperature is lowered. At temperatures as low as −12°C, asphalt nano-modified with 1–7% nano-TiO_2 would demonstrate the necessary fatigue resistance. Therefore, it can be concluded that nano-TiO_2 addition to PG 64-16 is negligible and has no impact on the base binder's low-temperature PG. The creep stiffness modulus of neat and nano-TiO2-modified asphalt was presented in Figure 18 at two temperatures, −6 and −12°C. At −6°C, all samples meet the Superpave speciation below 300 MPa When the Temperature dropped to −12°C, a significant increase was noted up to 3% for nano-TiO_2 modified asphalt as compared to neat sample, hence beyond threshold limits of 3% higher stiffness observed causes the asphalt to be stiff and less elastic. In addition, nano-modified asphalt with a 3% concentration shows a greater modulus with a lower *m*-value when compared to neat asphalt, showing that fracture resistance for nano-modified asphalt has been slightly lowered but can still meet specification criteria.

4.3 Evaluation of the cost

Considering the financial effects of utilizing nanomaterials as AC modifiers is essential. Nanotechnology produces nanoparticles in tiny quantities, but asphalt pavement building uses enormous quantities of materials – measured in tons. Due to the intricate processing steps necessary to produce such high purity levels, restricted size range, and high specific surface area, nanomaterials are expensive. Currently, 1 kg of nano-TiO_2 costs $188 from Skyspring (the source of imported nano in this study). However, as demand rises, more alternative energy sources are used, and manufacturing technology advances, the cost has been falling over time, and this trend is anticipated to continue. For the addition of modifiers to be cost-effective at current costs, a significant increase in durability must be obtained. Additionally, from an economic perspective, modifiers requiring smaller optimum amounts are more competitive. Adding 5% TiO_2 is more cost-effective and improves asphalt rheology at various temperatures.

5 Conclusion

This study examines the effect of 1, 3, 5, and 7% of nano-TiO_2 by weight of asphalt on some of its rheological and hardened properties. The physical and rheological properties of nano-modified asphalt were assessed the asphalt susceptibility with high, intermediate, and low temperatures. The following conclusion can be drawn: based on tests for penetration, softening point, viscosity, and ductility, it was determined that asphalt's hardness had increased, improving its susceptibility to temperature changes. The rutting factor, which measures the binder's resistance to rutting at high temperatures, showed that whether RTFO was aged or original, increasing the content of nano-TiO_2 from 3 to 7% increases the rutting resistance of asphalt against higher temperatures and promoted PG by about one grade at 3% nanolevel and two grades at a range of 5–7%, which suggests that nano-TiO_2 increased the stiffness of the asphalt. While at medium Temperature, fatigue factor value for PAV aged asphalt, $G^*.\sin\,\delta$ shows that higher stiffness at 5 and 7% of TiO_2 content increases complex modulus and decreases fatigue parameters as nanocontent increases. Higher creep stiffness and higher *m*-values were noted at low temperatures as nano increases in asphalt binder, increasing stiffness and decreasing the *m*-value at both −6 and 12°C, leading to a higher chance of low-temperature cracking. Finally, 5% of nano-TiO_2 will improve asphalt's physical properties and enhance asphalt anit-rutting and fatigue resistance.

Conflict of interest: Authors state no conflict of interest.

Data availability statement: Most datasets generated and analyzed in this study are comprised in this submitted manuscript. The other datasets are available on reasonable request from the corresponding author with the attached information.

References

[1] Yao H, Dai, Q, You, Z, Ye, M, Yap, YK. Rheological properties, low-temperature cracking resistance, and optical performance of exfoliated graphite nanoplatelets modified asphalt binder. Constr Build Mater. 2016 Jun 15;113:988–96.

[2] Li R, Xiao F, Amirkhanian S, You Z, Huang J. Developments of nano materials and technologies on asphalt materials–A review. Constr Build Mater. 2017 Jul 15;143:633–48.
[3] Golestani B, Nam BH, Nejad FM, Fallah S. Nanoclay application to asphalt concrete: Characterization of polymer and linear nano-composite-modified asphalt binder and mixture. Constr Build Mater. 2015 Aug 30;91:32–8.
[4] Cheraghian G, Wistuba MP, Kiani S, Behnood A, Afrand M, Barron AR. Engineered nanocomposites in asphalt binders. Nanotechnol Rev. 2022 Mar 2;11(1):1047–67.
[5] Zhang D, Zhang H, Zhu C, Shi C. Synergetic effect of multi-dimensional nanomaterials for anti-aging properties of SBS modified bitumen. Constr Build Mater. 2017 Jul 30;144:423–31.
[6] Aljbouri HJ, Albayati AH. Effect of nanomaterials on the durability of hot mix asphalt. Transp Eng. 2023 Mar 1;11:100165.
[7] Hamedi GH. Investigating the use of nano coating over the aggregate surface on moisture damage of asphalt mixtures. Int J Civ Eng. 2018 Jun;16:659–69.
[8] Buhari R, Abdullah ME, Ahmad MK, Chong AL, Haini R, Bakar SK. Physical and rheological properties of Titanium Dioxide modified asphalt. In E3S Web of Conferences; 2018. Vol. 34, EDP Sciences. p. 01035.
[9] Günay T, Ahmedzade P. Physical and rheological properties of nano-TiO2 and nanocomposite modified bitumens. Constr Build Mater. 2020 May 20;243:118208.
[10] Chen M, Liu Y. NOx removal from vehicle emissions by functionality surface of asphalt road. J Hazard Mater. 2010 Feb 15;174(1-3):375–9.
[11] Qian G, Yu H, Gong X, Zhao L. Impact of Nano-TiO2 on the NO2 degradation and rheological performance of asphalt pavement. Constr Build Mater. 2019 Sep 10;218:53–63.
[12] Mahali I, Sahoo UC. Rheological characterization of Nanocomposite modified asphalt binder. Int J Pavement Res Technol. 2019 Nov;12:589–94.
[13] Zhang H, Zhu C, Yu J, Shi C, Zhang D. Influence of surface modification on physical and ultraviolet aging resistance of bitumen containing inorganic nanoparticles. Constr Build Mater. 2015 Nov 15;98:735–40.
[14] Hassan MM, Dylla H, Asadi S, Mohammad LN, Cooper S. Laboratory evaluation of environmental performance of photocatalytic titanium dioxide warm-mix asphalt pavements. J Mater Civ Eng. 2012 May 1;24(5):599–605.
[15] Shafabakhsh GH, Mirabdolazimi SM, Sadeghnejad M. Evaluation the effect of nano-TiO2 on the rutting and fatigue behavior of asphalt mixtures. Constr Build Mater. 2014 Mar 15;54:566–71.
[16] Shafabakhsh GH, Ani OJ. Experimental investigation of effect of Nano TiO2/SiO2 modified bitumen on the rutting and fatigue performance of asphalt mixtures containing steel slag aggregates. Constr Build Mater. 2015 Nov 15;98:692–702.
[17] Tanzadeh J, Vahedi F, Kheiry PT, Tanzadeh R. Laboratory study on the effect of nano TiO2 on rutting performance of asphalt pavements. Adv Mater Res. 2013 Feb 6;622:990–4.
[18] Zhang L, Gao X, Wang W, Wang H, Zheng K. Laboratory evaluation of rheological properties of asphalt binder modified by nano-tio2/caco3. Adv Mater Sci Eng. 2021 Feb 12;2021:1–3.
[19] Rocha Segundo I, Landi Jr S, Margaritis A, Pipintakos G, Freitas E, Vuye C, et al. Physicochemical and rheological properties of a transparent asphalt binder modified with nano-TiO2. Nanomaterials. 2020 Oct 28;10(11):2152.
[20] Staub de Melo JV, Manfro AL, Barra BS, Dell'Antonio Cadorin N, Borba Broering W. Evaluation of the rheological behavior and the development of performance equations of asphalt composites produced with titanium dioxide and zinc oxide nanoparticles. Nanomaterials. 2023 Jan 10;13(2):288.
[21] Ameli A, Pakshir AH, Babagoli R, Norouzi N, Nasr D, Davoudinezhad S. Experimental investigation of the influence of Nano TiO2 on rheological properties of binders and performance of stone matrix asphalt mixtures containing steel slag aggregate. Constr Build Mater. 2020 Dec 30;265:120750.
[22] Kleizienė R, Paliukaitė M, Vaitkus A. Effect of nano SiO 2, TiO 2 and ZnO modification to rheological properties of neat and polymer modified bitumen. In Proceedings of the 5th International Symposium on Asphalt Pavements & Environment (APE) 5 2020. Springer International Publishing; p. 325–36.
[23] Cadorin ND, de Melo JV, Broering WB, Manfro AL, Barra BS. Asphalt nanocomposite with titanium dioxide: Mechanical, rheological and photoactivity performance. Constr Build Mater. 2021 Jun 28;289:123178.
[24] Filho PG, Rodrigues dos Santos AT, Lucena LC, de Sousa Neto VF. Rheological evaluation of asphalt binder 50/70 incorporated with titanium dioxide nanoparticles. J Mater Civ Eng. 2019 Oct 1;31(10):04019235.
[25] Filho PG, dos Santos AT, Lucena LC, Tenório EA. Rheological evaluation of asphalt binder modified with nanoparticles of titanium dioxide. Int J Civ Eng. 2020 Oct;18:1195–207.
[26] Beeldens A. An environmental friendly solution for air purification and self-cleaning effect: the application of TiO2 as photocatalyst in concrete. Proceedings of transport research arena Europe–TRA. Göteborg, Sweden: 2006 Jun 1. p. 1–9.
[27] Hassan M, Mohammad LN, Asadi S, Dylla H, Cooper III S. Sustainable photocatalytic asphalt pavements for mitigation of nitrogen oxide and sulfur dioxide vehicle emissions. J Mater Civ Eng. 2013 Mar 1;25(3):365–71.
[28] Venturini L, Bacchi M. Research, design, and development of a photocatalytic asphalt pavement. In Proceedings of 2nd International Conference on Environmentally Friendly Roads: ENVIROAD; 2009 Oct 15.
[29] Ramesh KT. Nanomaterials. Berlin, Germany: Springer; 2009.
[30] Grassian VH, O'Shaughnessy PT, Adamcakova-Dodd A, Pettibone JM, Thorne PS. Inhalation exposure study of titanium dioxide nanoparticles with a primary particle size of 2 to 5 nm. Environ Health Perspect. 2007 Mar;115(3):397–402.
[31] Forbes TZ. Occurrence of nanomaterials in the environment. In Nanomaterials in the environment 2015 179–218.
[32] National Research Council. A research strategy for environmental, health, and safety aspects of engineered nanomaterials, 2012.
[33] Haase A, Luch A. Genotoxicity of nanomaterials in vitro: Treasure or trash? Arch Toxicol. 2016 Nov;90:2827–30.
[34] Ramachandran G, Ostraat M, Evans DE, Methner MM, O'Shaughnessy P, D'Arcy J, et al. A strategy for assessing workplace exposures to nanomaterials. J Occup Environ Hyg. 2011 Nov 1;8(11):673–85.
[35] Crucho JML. Development of an accelerated asphalt concrete aging method and utilization of nano-modifiers to improve durability of asphalt concrete. Ph.D. thesis. Lisboa, Portugal: Instituto Superior Técnico, Universidade de Lisboa; 2018.
[36] Wang W, Cheng Y, Tan G, Liu Z, Shi C. Laboratory investigation on high-and low-temperature performances of asphalt mastics modified by waste oil shale ash. J Mater Cycles Waste Manag. 2018 Jul;20:1710–23.

[37] Sadeghnejad M, Shafabakhsh G. Experimental study on the physical and rheological properties of bitumen modified with different nano materials(Nano SiO2 & Nano TiO2). Int J Nanosci Nanotechnol. 2017 Aug 1;13(3):253–63.

[38] Nejad FM, Nazari H, Naderi K, Karimiyan Khosroshahi F, Hatefi Oskuei M. Thermal and rheological properties of nanoparticle modified asphalt binder at low and intermediate temperature range. Pet Sci Technol. 2017 Apr 3;35(7):641–6.