Case Studies in Construction Materials 19 (2023) e02492

Contents lists available at ScienceDirect

Case Studies in Construction Materials

journal homepage: www.elsevier.com/locate/cscm

Enhancing asphalt binder performance through nano-SiO2 and nano-CaCO3 additives: Rheological and physical insights

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ARTICLE INFO

Keywords:
Nanomaterial
SiO_2
$CaCO_3$
DSR
BBR
Asphalt

ABSTRACT

During the last two decades, nanomaterial application has gained a significant attraction into asphalt technology due to their effect in enhancing asphalt binder improving the asphaltic mixture. This study will modify the asphalt binder with two different nano types, nano SiO2 and CaCO3, at levels ranging from 1% to 7%. The resulting optimum nano-modified Asphalt will be subject to a series of rheological tests, including dynamic shear rheometer (DSR), Viscosity, and bending beam rheometer (BBR) to determine asphalt binder sensitivity towards low-medium-high temperature range. Results indicate that both nano types improved the physical characteristics of Asphalt, and 5% by weight of Asphalt was suggested as a reasonable dosage of nano-SiO_2 and nano-$CaCO_3$ based on the overall desirability analysis of physical tests. The viscosity and temperature sensitivity of bitumen were improved by adding nano SiO2 and CaCO3. On the other hand, the asphalt rutting resistance's capabilities were improved at higher temperatures. In contrast, it decreases resistance against fatigue at intermediate temperatures due to the lowest phase angles and higher loss moduli. The BBR test, however, reveals a modest decrease in bituminous anti-cracking.

1. Introduction

Due to a sharp increase in traffic loads in recent years, the world's highway pavement construction sector has been growing. The practical requirements for building highway pavement today and in the future are challenging for traditional paving materials. Therefore, pavement materials of higher quality, safety, excellent dependability, and incredible environmental friendliness are critically needed. Silicon dioxide (SiO_2) nanoparticles are referred to as nano-silica. Silicon dioxide, an inorganic substance mostly made from silica precursors, such as silica fume or rice husk ash, has undergone chemical processing [1–4]. Researchers worldwide try to investigate the beneficial effect of binder modification using Nano-SiO2, resulting in higher Viscosity, higher softening point, decreased Ductility, and increased elastic modulus [5-7]. Asphalt mixtures with binder modified with Nano-SiO2 had some of their qualities improved, including their dynamic and psychological modulus [8], Marshall resistance, susceptibility to temperature variations [9], and hardness [10]. According to research done in the lab over the years, asphalt mixtures modified with Nano-SiO_2 have longer fatigue lives [5,11], greater rutting resistance and minimum rutting depth [12], increased resistance to permanent deformation [13], increased anti-aging properties through delayed oxidation [14] increased resistance to moisture damage [15], increased anti-stripping property, and decreased creep strain deformation [14] Additionally, the self-healing capabilities of asphalt mixtures are enhanced by the simultaneous addition of Nano-SiO2 and SBS [15]. Furthermore, [16], correlated nano-modified with nano silica (NS)

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https://doi.org/10.1016/j.cscm.2023.e02492
Received 4 July 2023; Received in revised form 7 September 2023; Accepted 19 September 2023
Available online 20 September 2023

with asphalt mixture characteristics via Multiple stress creep recovery (MSCR) and linear amplitude sweep (LAS) to study how NS affects modified asphalt rutting and fatigue behavior. Marshall stability, dynamic creep, and four-point bending beam fatigue tests assessed mixture performance. The author indicated that high-temperature modified asphalt binders improve elastic characteristics. NS decreases stress sensitivity and improves rutting resistance in modified Asphalt. However, changed asphalt binders have a shorter fatigue life at high strain levels than unmodified ones. The LAS and four-point bending beam tests show that adding NC up to 8% binder content can significantly increase fatigue resistance. In another study, [17] employed NS as a binder modifier to SBS-modified Asphalt. The results of the experiments revealed that the viscosity value at high temperatures somewhat decreased; in reality, at low temperatures, the modified binder with NS behaved similarly to control binder samples; additionally, NS increased binder antioxidation properties. The performance of the asphalt binder modified by NS in terms of rutting and fatigue cracking was enhanced. Recently, nano-$CaCO_3$ has been used as a stable and inexpensive material to prepare modified Asphalt. Although previous studies looked into nanomaterials used in asphalt modification, some even included nano-CaCO3 as a modifier; overall evaluation of nano-CaCO3 influence on bitumen and asphalt mixtures and the identification of their rheological and mechanical behavior required more research. Nano-$CaCO_3$ is a solid white powder with an average of 10–100 nm particle size and calcium Carbonate of about 98.5%; it increases the quality of base asphalt and asphalt mixtures, and the combination of nano-CaCO3 with Asphalt generates a consistent and stable system that enhances asphalt temperature susceptibility at high temperatures. A study conducted by [18] found that adding 6% nano-CaCO3 to asphalt concrete enhanced the dynamic and residual stability, indicating that both the high-temperature and water stability of asphalt concrete has improved. Other researchers conducted a study to assess the rheological, physical, and performance of hot mix asphalt modified with nano-CaCO3. It shows that as nano content increases, it becomes slightly softer penetration, increases softening and Viscosity, improves sensitivity towards permanent deformation, and good anti-aging performance as indicated by a higher penetration index value this was confirmed by [19] when they concluded that increasing nano-TiO2/CaCO3 by up to 5% would significantly improve the mechanical properties of bituminous materials in terms of reducing penetration and ductility and showing an increasing trend for softening Point and Viscosity which reduce bituminous sensitivity. As well as increase the capacity of bituminous anti-rutting resistance and medium-temperature fatigue resistance. $TiO_2/CaCO_3$ increased bitumen stiffness modulus while increasing bitumen viscosity. The unique property of using nano-$CaCO_3$ lies in their ability to improve the stability at higher temperatures of modified asphalt binder through a reinforcement mechanism to stand for a long time via dispersion ability; this was confirmed through the study of Xing et al., 2019 presenting that The least particle size indicates the lesser average distance between the particles which better the yield stress of the modified Asphalt by Orowan mechanism. On the other hand, the atomic arrangement is irregular, and the phase contact prevents the modified Asphalt from deforming plastically according to the Hall–Petch reinforcement mechanism.The literature above shows that Nano-CaCO3 can increase the temperature of asphalt performance, moisture susceptibility, good anti-cracking fatigue resistance, aging, adhesion, dispersion in asphalt binder, and aging. In their study, Nejad et al., 2020 suggested that nano-CaCO3 promoted the rutting of asphalt mixtures, acquiring less sensitivity to higher temperatures. On the other hand, increasing the Viscosity of the asphalt binder allows for increasing tensile and compressive strengths of the HMA, causing fatigue life to increase by 55.8% with the addition of 4% CaCO3. This study investigates the effect of nano SiO_2 and $CaCO_3$ at different content ranging from 1% to 7% via physical and rheological properties. The resulting optimum nano-modified Asphalt will be subject to a series of rheological tests, including dynamic shear rheometer (DSR), Viscosity, and bending beam rheometer (BBR) to determine asphalt binder sensitivity towards low-medium-high temperature range.

2. Materials and procedures for experiments

2.1. Asphalt

Al-Doura refinery supplied the 40/50 penetration grade AC utilized as this study's primary material; their main properties are listed in Tables 1 and 2, which correspond to PG 64–16.

2.2. Nanomaterial

Nano-CaCO3 and Nano-SiO_2 nanoparticles came from a local supplier in Baghdad and were obtained from the Sky Spring Company in North America. The characteristics of these nanomaterials are detailed in Table 3 and illustrated in Figs. 1 and 2.

Table 1
Physical Properties of Al-Doura Asphalt.

Property	Designation	Units	Result
Penetration at 25 °C, 100 gm,5 s	AASHTO T 49	0.1 mm	47
Softening Point	AASHTO T 53	°C	49
Specific gravity at 25 oC	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

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,	AASHTO T315	2.34	64 °C	Min.1
G* /Sin δ, kPa		0.842	70 °C	
RTFO Binder Residue				
DSR, 10 rad/s,	AASHTO T315	3.67	64 °C	Min 2.2
G* /Sin δ, kPa		1.68	70 °C	
Mass Loss, %	AASHTO T240	0.61		Min.1
PAV Binder Residue				
DSR, 10 rad/s, G* . Sin δ, 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

2.3. Preparation of nano-modified asphalt

A dry blending technique was proposed in this study, which consists of using high-speed stirring to disperse the nanomaterials in the asphalt binder matrix. Two different Nano material types were added to a single asphalt PG (64−16) at varying concentrations, i.e., 1, 3,5%, and 7% by weight of neat Asphalt. The dry mixing technique uses a high-speed shear mixer system (HSMs) to distribute the nanomaterials throughout the asphalt binder matrix. Then, the Nanomaterial is added, and the HSMs differ from conventional mixers under the distinctive tip design; Fig. 3 shows the applied shear mixing effect for a particular time.

The original base bituminous 500 ± 2 g material was heated to 140 °C before being manually stirred for 20 min; the required amount of nano additive was slowly added at a rate of 2–4 gm per minute at 2500 rpm with HSM until complete and then selected the condition in Table 4 to ensure all the nanoparticles were well dispersed inside the binder. The mixing homogeneity, at the same time, is also enough to avoid bitumen aging; after completion, the Asphalt was poured into metal cans to rest for cooling at room temperature for further Testing. Fig. 4. Summarize the nano-modified asphalt modification.

2.4. Asphalt laboratory test

2.4.1. Testing for penetration and softening points

The penetration test, the most popular technique for determining an asphalt material's consistency, was carried out following ASTM D5 at a predetermined temperature of 25 °C. According to ASTM D36, the softening point test is frequently used to assess Asphalt's high-temperature susceptibility. This temperature is the threshold at which the asphalt sample can no longer sustain the weight of a 3.5-g steel ball. A numerical indicator of Asphalt's sensitivity to temperature change is the penetration index (PI). The following Eq. (1) uses the ASTM softening point and penetration at 25 °C to define PI [20]:

$$PI = \frac{1952 - 500\log_{10}P25 - 20SP}{50\log_{10}P25 - SP - 120} \tag{1}$$

P25 is penetration at 25 °C, and SP is Asphalt's softening point.

2.4.2. Ductility

A standard-sized briquette of Asphalt is stretched to the Point of failure as part of the ductility test to gauge the material's ductility. Then, ductility is provided as the stretched distance in centimeters at breaking. Like the penetration test, this test has restricted use because it is empirical and carried out at a certain temperature.

According to ASTM D113, the ductility test in this article was carried out using a ductility test device at 25 °C and a speed of 5 cm/min.

Table 3
Physical properties of Nanomaterial.

Properties	Nano-SiO_2	Nano-CaCO3
Appearance	white powder	white powder
Average Particle Size (nm)	15–20	15–40
True Density, g/cm^3	2.648	2.552
Specific Surface area: m^2/g	640	40
Purity	99.5%	97.5%
Solubility	Insoluble	Insoluble

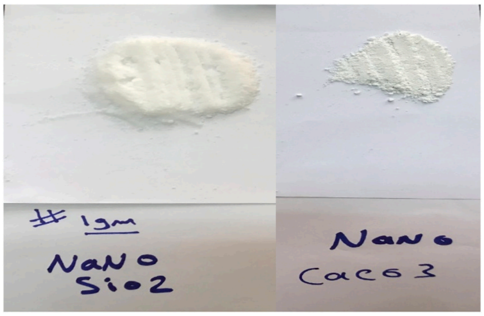
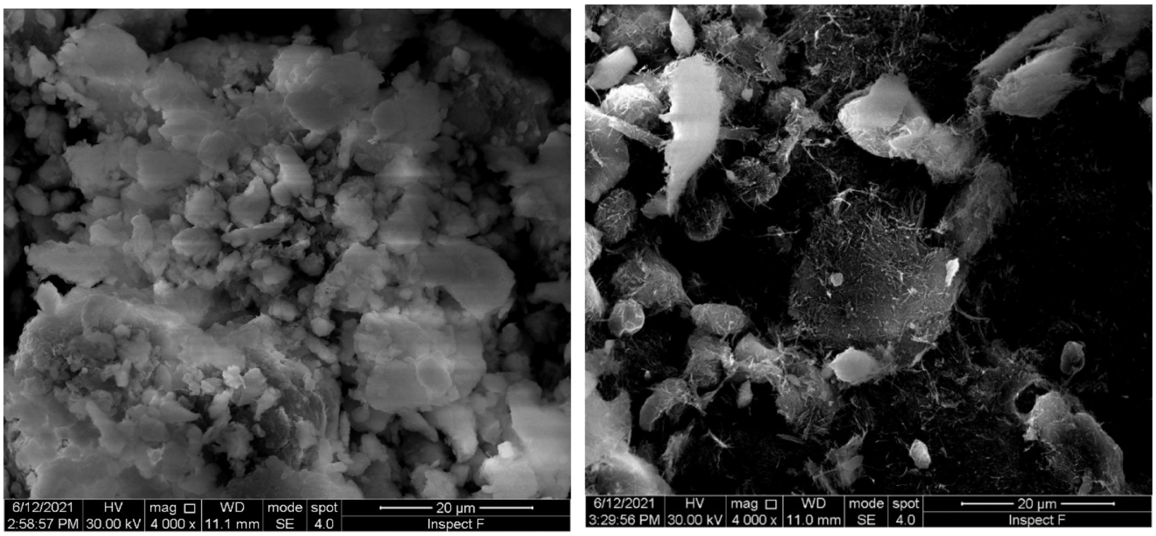


Fig. 1. Image of used Nanomaterial.



a b

Fig. 2. SEM image of Nanomaterial a.Sio2 b. $CaCO_3$.

Fig. 3. Procedure for mixing Nanomaterial within HSMs.

Table 4
Dry blending configurations with HSMs.

Nano Type	Coding	% Content	Temperature (°C)	Rotation Speed (rpm)	Duration (min.)
Nano $CaCO_3$	NCC	1,3,5% and 7%	150–160	6000	45
Nano SiO_2	NS	By wight of neat binder		4000	

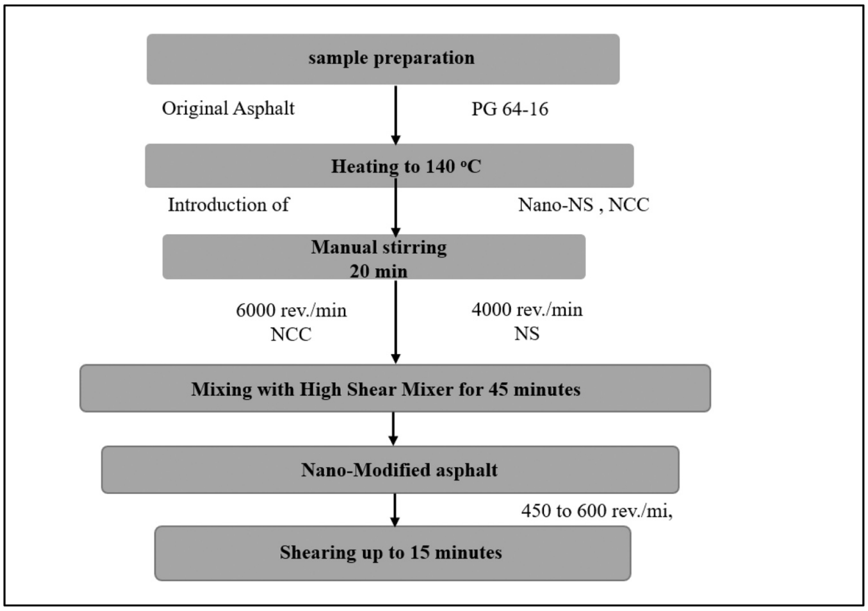


Fig. 4. Mixing procedure of nano-modified Asphalt.

2.4.3. Dynamic shear rheometer (DSR)

DSR was used to examine the viscoelastic behavior of original and nano-modified Asphalt. Calculating (G*) and (δ) along with the rut factor (G*/sin δ) and aged Asphalt using (RTFO) for short-term aging and (PAV) for long-term aging were used to measure these behaviors.The high-temperature grade of Asphalt and its resistance to high and moderate-temperature situations. Limiting the G* /sin δ to more than 1 kPa for the original bitumen and 2.2 kPa for aged Asphalt resulting from the RTFO prevents deformation as a long-term sign. In order to prevent fatigue cracking as a long-term symptom, PAV limits the G* .sin δ of aged bitumen to less than 5 kPa at test temperatures.

2.4.4. Rotational viscometer (RV)

The RV test can assess asphalt binder workability during mixing and compacting. According to the AASHTO TP48 standard, the bitumen's rotational viscometer readings are calculated. The rotational viscometer Brookfield DV-III is used to measure bitumen viscosity. The test is conducted at temperatures of 135 and 165 °C.

2.4.5. Bending beam rheometer (BBR)

The BBR test measures bitumen's stiffness and relaxation characteristics at low temperatures. These variables show how well bitumen can withstand low-temperature cracking. On PAV-aged bitumen, a BBR test is conducted. BBR is carried out per AASHTO T 313.

2.4.6. Storage stability

The storage stability test was carried out to ensure proper dispersion of the nano NS and NCC and homogeneity of the blends. Generally, a material mixture's strong storage stability indicates homogenous additive/modifier dispersion. Nano-modified Asphalt may be kept for an extended period in silos with strict temperature control, which could prevent phase separation from working as it should. In order to investigate the impact of nanoparticles on bitumen's storage stability at high temperatures, this test was carried out on samples of bitumen following European Standards (EN 13399, 2010). samples were placed in cylindrical molds measuring 32 mm in diameter and 160 mm in height, and they were left in the oven set at 163 °C for 72 h. Molds were then allowed to cool at ambient temperature and cut into three equal pieces; the top and bottom ends underwent separate conventional softening point tests. The sample is considered storage stable if the difference between the top and bottom softening point values is 2.5 °C.

3. Discussion of testing result

3.1. Physical test

It is observed that both Nano NCC and NS have impacted the physical characteristics of Asphalt, especially with the addition of 5–7% nano content; the overall trend shows a decrease in penetration value, an increase in softening Point, and lower ductility. According to Fig. 5.a, both modifiers reduced penetration value compared to the original Asphalt. When more NS was applied, lower penetration values were noted. Penetration values decrease from 40 at 1% NS content to 33 for 5% NS up to 30 for 7% NS content. The same pattern of behavior was observed with NCC, where penetration values dropped as nano content increased. The values for penetration dropped from 43 for 1% NCC content to 37 for 5% NCC content and then tended to stabilize at 7% with a value of 36. NS presents a significant decrease in penetration value compared to NCC, taking 5% as a reference due to a minor effect with NCC beyond this value; the penetration value decreases by about 28% and 19% for both NS and NCC concerning the original Asphalt, this may be attributed to higher dispersion across the Asphalt, making it stiffer and harder to penetrate, which showed a sign of increasing stiffness. The failure temperature of the nano-modified increased compared to that of the original Asphalt; Fig. 5. b demonstrates that adding NS or NCC to the Asphalt positively impacted the softening Point. The trend of NS and NCC can be attributed to the fact that these materials made Asphalt less sensitive to extreme temperature changes and more resistant to plastic deformation. Both Nano types (from 49 °C) indicate a relatively higher increment in softening Point as compared to neat Asphalt and NCC-modified Asphalt, that has relatively smaller than NS by showing an average increase by 4, 6,8 and 9 °C when its content ranged from 1% to 7% by weight of Asphalt. The decrease in penetration and increase in softening point may be attributed to an increase in the nanoparticle's surface area, which might lead to the Asphalt [21].

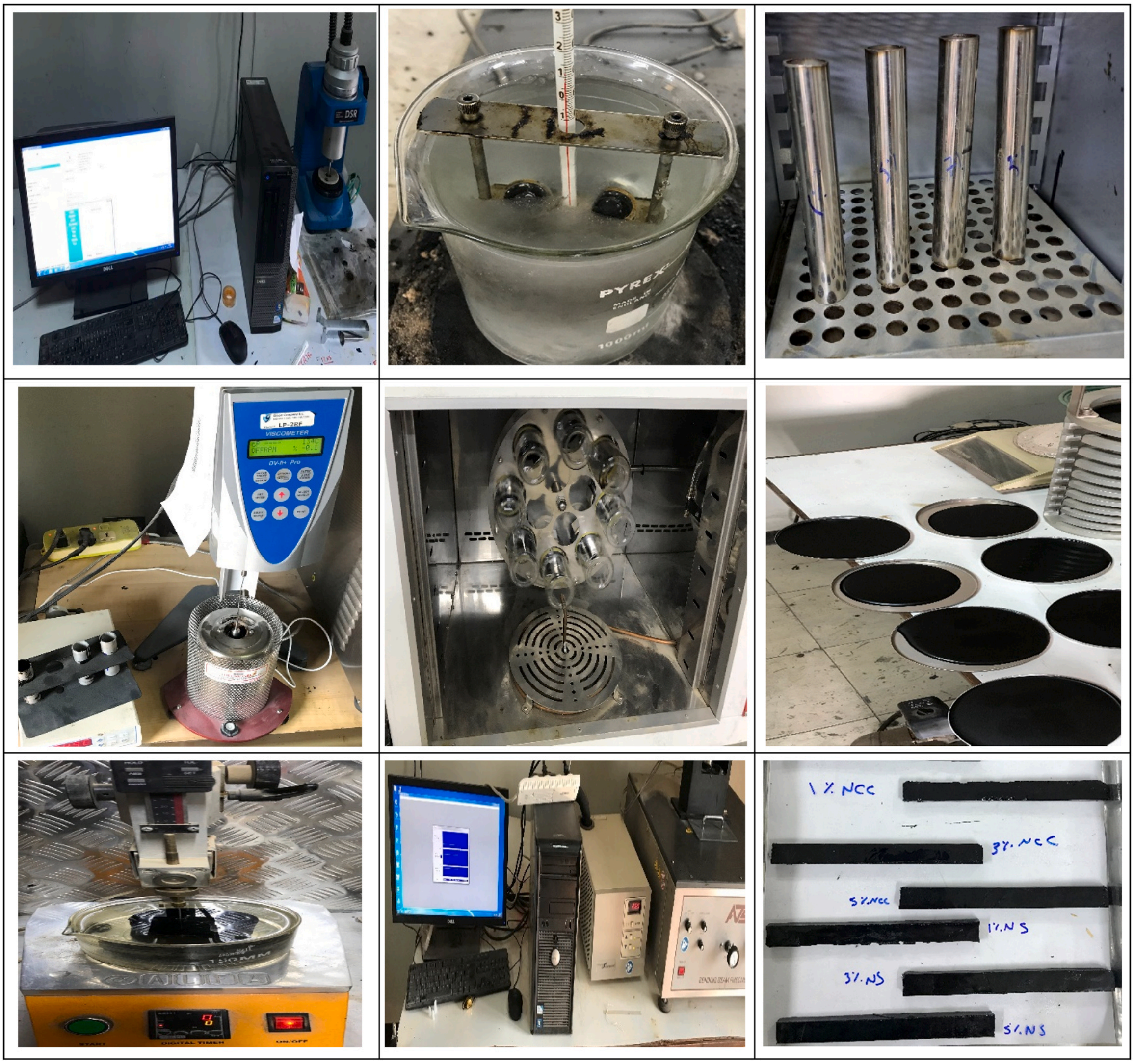
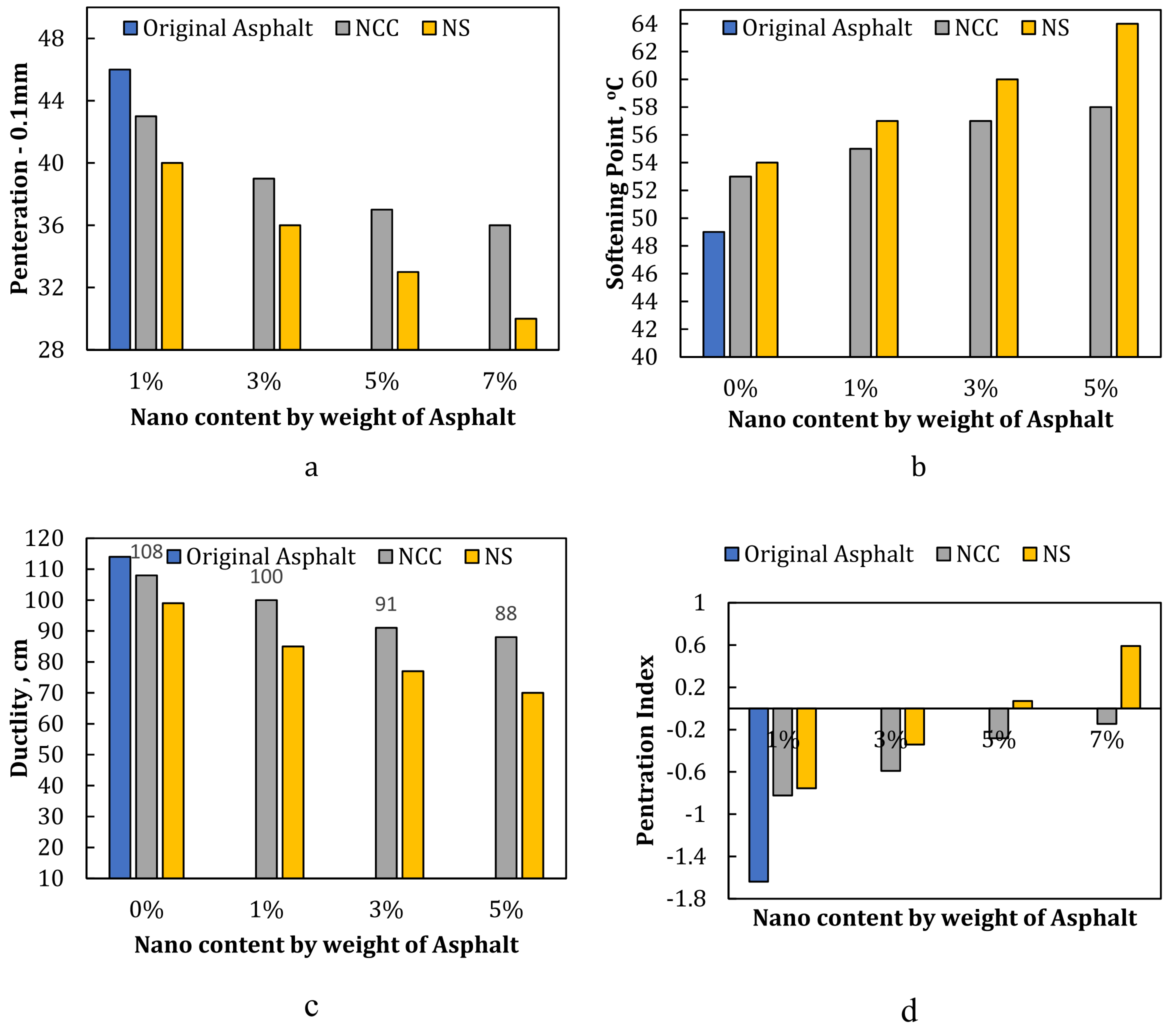


Fig. 5. Testing of nano-modified Asphalt.



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Regarding the ductility test results in Figure 5.2.c, it was found that lower ductile response was induced by the increase in the NS content up to 7% with 70 cm as contrasted to the original Asphalt with 114 cm. This behavior was probably due to an increase in the hardness (stiffness) of the Nano-modified Asphalt caused by the Nano SiO2 absorption of the volatiles and the increase in stiffness, which supports the finding of earlier research (Gholampour et al., 2020, Fini et al., 2016, Taherkhani and Afroozi, 2016, Zghair, 2020, Enieb and Diab, 2017). on the other hand, Nano CaCO3 exhibited the least ductility compared to NS by showing a step reduction of 108, 100,91, and 88 cm for each Nano increment from 1% to 7%, suggesting that a low-temperature crack resistance of Asphalt was increased.

The original and nano-modified Asphalt with NS and NCC are evaluated for their temperature susceptibility using the penetration index (PI), which is determined using Eq. (1) and shown in Fig. 5.d. A higher value of PI indicates a lower temperature susceptibility. Higher PI values were seen at 7% NS, followed by NCC, which decreased to 0.589 and − 0.146 for both nano as compared to the original Asphalt. They indicated that Asphalt is less sensitive at moderate temperatures, resulting in less rutting throughout the hot summer months and less low-temperature cracking. Based on the testing result presented in Fig. 5, the utilization of 5% Nano content showed the highest effect on the properties of the Asphalt with NS, followed by NCC by stiffening Asphalt within penetration grade. While softening point and penetration index increase both nano content, decreasing its temperature sensitivity and improving resistance toward permanent deformation and low-temperature cracking due to decreasing its temperature sensitivity also reduces asphalt ductility.

3.2. Storage Stability

Fig. 6. displays the results for storage stability. The difference between the softening point values (Δs) between the top and bottom of the aluminum tube should be less than 2.2 °C, which has been established as the allowable limit for confirming homogenous

dispersion, according to earlier research [22]. The Δs were below one °C for the two types at all concentrations, which is within this limit and guarantees appropriate storage stability. These outcomes confirm the effectiveness of blending with HSMs to produce uniformly blended suspensions. Except for 7% NS, it was found that the increase in NS content resulted in increased Δs values beyond 1.

3.3. Overall desirability analysis (OD)

Transforming the original sequence to a comparable sequence is known as data normalization. Sequences typically have a "the-larger-the-better" or "the-smaller the-better" feature; the relevant normalizing formulae are provided by:

the-larger-the-better :

$$x_i^*(k) = \frac{x_i^{(0)}(k) - minx_i^{(0)}}{maxx_i^{(0)} - minx_i^{(0)}} \tag{2}$$

the-smaller the-better:

$$x_i^*(k) = \frac{maxx_i^{(0)} - x_i^{(0)}(k)}{maxx_i^{(0)} - minx_i^{(0)}} \tag{3}$$

Where i = 1, 2,., m (m is the index number); k = 1, 2,., n (n is the data number); and $x_i^{(0)}(k)$ is the kth value of the ith original sequence; $x_i^*(k)$ Is the kth value of the ith normalized sequence; $maxx_i^{(0)}$ i is the maximum value of the ith original sequence, and $minx_i^{(0)}$ i is the minimum value of the ith original sequence. Each index is standardized as a value between 0 and 1 when the data is normalized. The overall desirability (OD) [23], which has the following definition, could therefore be calculated:

$$\gamma(k) = \left[x_1^* \quad (k)x_1^*(k).....x_m^* \quad (k)\right]^{1/m} \tag{4}$$

To assess the main desirable characteristics of nano-modified Asphalt using an overall desirability analysis, the usual properties of nano-modified Asphalt with NS and NCC at varying content: penetration, softening Point, Ductility, and penetration index are used as the analysis index in this paper. The experimental original and normalized sequences are provided in Tables 5 and 6, where the original sequences are in the third, fourth, fifth, and sixth columns, and the corresponding normalized sequences are in the seventh, eighth, ninth, and tenth columns.

The OD analysis is shown in Tables 5 and 6. Different physical characteristics are more desirable than others. The OD value increases first in the findings of the OD analysis of Asphalt modified with nano-Ns and NCC, but it decreases when the nano content exceeds 5%. It can be considered that 5% is the optimum dosage of asphalt mass should be NS and NCC, which is a suitable percentage.

3.4. Rheological properties

3.4.1. Rotational viscosity

The Viscosity, a measure of asphalt resistance to flows, is crucial in determining the compaction and mixing temperatures. Fig. 7 shows the viscosity plots for original and Nano-modified Asphalt at 135 and 165 °C. Both nano types appear to significantly enhance the values of asphalt viscosity at both temperatures, causing the asphalt film thickness to grow and coat the aggregates in the heated mixture.

As expected, higher viscosity values at 135 °C were obtained with asphalt samples modified with NS, and the viscosity values were raised to 1.587 Pa.s from the original Asphalt (0.63 Pa.s) with the inclusion of 5% NS by weight of Asphalt; this happened due to a higher surface area and reactivity of NS. The same trend holds for NCC, which demonstrated a moderate increase in viscosity values compared to NS. It was found that a viscosity value of 1.121 Pa.s was noticed with 5% NCC. As a result, both Nano materials exhibited

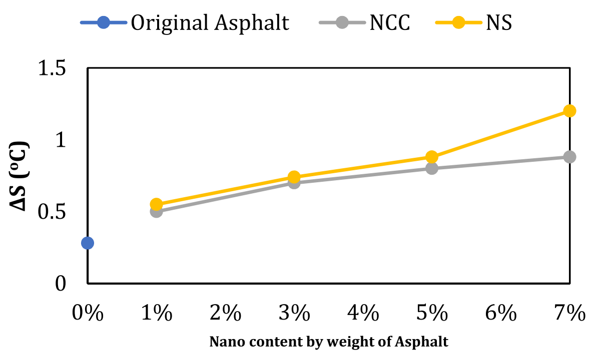

Fig. 6. Impact of Nano NS and NCC content on storage stability (S).

Table 5
The original and normalized nano-modified Asphalt with NS sequences.

Type	Nano Content,%	P $x_1^{(0)}$	SP $x_2^{(0)}$	D $x_3^{(0)}$	PI $x_4^{(0)}$	P x_1^*	SP x_2^*	D x_3^*	PI x_4^*	OD γ
NS	0%	46	49	114	-1.637	0.375	0	0	1	0
	1%	40	54	99	-0.755	0.625	0.375	0.333	0.659	0.424
	3%	36	57	85	-0.341	0.375	0.625	0.533	0.340	0.507
	5%	33	60	77	0.069	0.187	0.812	0.733	0.159	0.519
	7%	30	64	70	0.589	1	1	1	0	0

P: Penetration, SP; Softening Point, D: Ductility, PI: Penetration Index

Table 6
The original and normalized nano-modified Asphalt with NCC sequences.

Type	Nano Content,%	P $x_1^{(0)}$	SP $x_2^{(0)}$	D $x_3^{(0)}$	PI $x_4^{(0)}$	P x_1^*	SP x_2^*	D x_3^*	PI x_4^*	OD γ
NCC	0%	46	49	114	-1.637	0.375	0	0	1	0
	1%	43	53	108	-0.824	0.3	0.444	0.769	0.545	0.486
	3%	39	55	100	-0.591	0.7	0.666	0.461	0.701	0.623
	5%	37	57	91	-0.282	0.9	0.888	0.115	0.908	0.538
	7%	36	58	88	-0.146	1	1	0	1	0

P: Penetration, SP; Softening Point, D: Ductility, PI: Penetration Index

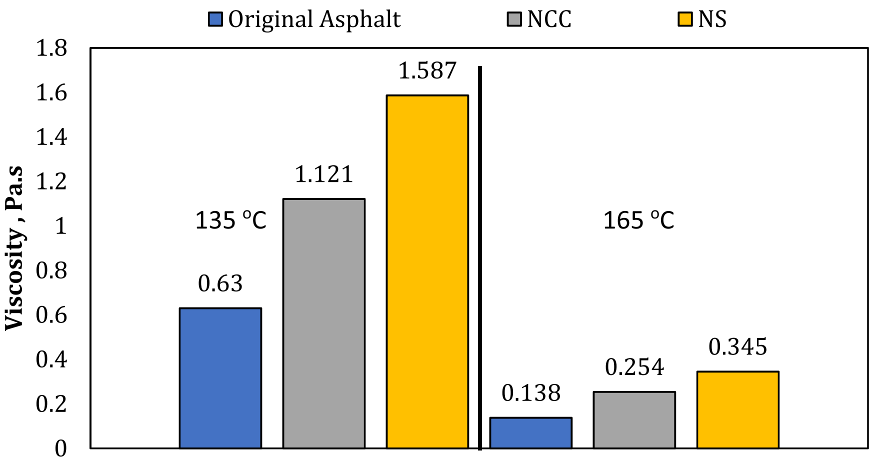

Fig. 7. Impact of Nano NS and NCC on modified asphalt viscosity.

an increase in Viscosity at 135 °C; it can be said that 5% NS shows an enhancement of nearly 60% as compared to the original Asphalt, which, in other words, asphalt sample will maintain their stability in the mixture, then followed by 5% NCC that increase asphalt viscosity by 43%. This behavior was also noted when nano-modified Asphalt with 5% NS and NCC tested at 165 °C; hence, viscosity values reached 0.254 and 0.345 Pa.s for both NCC and NS, respectively.

Table 7
Performance-Graded Asphalt Test Results.

Temperature,°C	Property	Original Asphalt	Nano content 5% NCC	Nano content 5% NS
Test on original Asphalt				
64	G* /Sin δ	2.34	5.42	8.68
70		0.84	3.37	4.64
76		–	1.06	1.87
Test on RTFO asphalt				
70	G* /Sin δ	1.68	3.49	7.84
76		–	1.89	4.52
82		–	–	2.31

3.4.2. DSR

3.4.2.1. Rutting resistance (G/sin δ).* The Superpave specification defines the rutting factor as G/sin δ, which measures the rutting resistance of the Asphalt. The effectiveness of the modified Asphalt in high temperatures to prevent rutting increases with increasing G/sin δ. In this study, DSR was utilized to assess the impact of different types and content of Nanomaterials on asphalt stiffness factor or rutting factor termed as G* /Sinδ to show better rut resistance on two conditions: un-aged Asphalt (original) and short-term aging (RTFO) at initial testing temperatures 64 and 70 °C. it appears from Table 7., that at 5% NS and NCC, Nano modified Asphalt show a higher G* /Sinδ as compared to original Asphalt, which indicated a better performance against permanent deformation.

The outcomes of the original Asphalt revealed that using both nano types increases the rutting parameter beyond the SHRP limit of 1 kPa. In contrast, original Asphalt will lose yield at a higher temperature than 64 °C since it functionally corresponds to 64–16 PG. On the other hand, Nano modified Asphalt appeared to influence the stiffness with Nano NS and at higher temperatures, indicating a higher ability to sustain external loading and improvement in the rutting resistance. Simultaneously, nano-modified Asphalt with 5% NCC has the same trend but less effect.

Original Asphalt modified with NS presented the highest G* /sin δ values compared to NCC at 76 °C, which satisfies the "high temperature" specification requirement with 1.87 Kpa. At the same temperature, similar behavior was also noted with NCC but with less G* /sin δ values, presenting a value of 1.06 Kpa; this suggests that Nano-modified Asphalt with NCC has little impact on the cracking resistance of Asphalt. The RTFO-aged asphalt test result indicated that at 5%, NS would pass the SHRP minimum requirement of 2.2 Kpa for G* /sin δ at 76 °C except for one modified with CaCO3 that fail at 70 °C, which implies RTFO samples with nano-CaCO3 do not typically harden or oxidize quickly as a result of aging (**Raufi et al., 2017**). Furthermore, the Nanomaterial shows a positive sign of enhancement towards rutting resistance and deformation phenomena, which significantly slow down the decrease in G* /sin δ values with the temperature increase. It is revealed that the addition of 5% NS can significantly increase G* /sin δ values as compared to original Asphalt at 76 °C to 4.52 Kpa, which provides a superior value by extending asphalt critical temperature up to 82 °C presenting rutting factor with 2.31 Kpa.Regarding high temperatures, 5% NCC may lead to lower stiffness, slightly improving the rutting factor G* /sin δ after the RTFO process. The result at 76 °C clarifies that 5% NCC did not seem satisfactory to the minimum requirement of 2.2Kpa of Asphalt. While at a lower temperature, 70 °C Nano-modified asphalt exhibits better rutting resistance by improving G* / sin δ reaching 3.49 Kpa, compared to neat Asphalt at the same temperature with 1.68 Kpa; Fig. 8. shows the improvement gained in G* /sin δ values of nano-modified Asphalt in both testing conditions: original and RTFO. Indicating that a higher stiffness value was obtained with NS, followed by a slight improvement in rutting seen with NCC under different temperature ranges.

It can also be noted that the fail temperature has been increased with the inclusion of Nanomaterial. However, both NS and NCC-modified asphalt were stiff enough to transform the Asphalt into a more advanced "high-temperature PG graded." Hence, 5% Nano content asphalt will satisfy the requirement specification and resist rutting at 82 °C for NS. Similarly, NCC moves asphalt specification when tested at PG + 6 °C, i.e., 64 °C, indicating less susceptibility to fatigue damage. The improvement in the characteristic of the rutting factor suggests that nano-modified with 5% NS is more resistant to permanent deformation, and rutting at high temperatures will perform better in hot regions where the pavement permanently deforms better than NCC. An increase in this characteristic also suggests that Asphalt will perform better when manufactured and used (short-term aging stage).

3.4.2.2. Fatigue resistance (G.sin δ).* An additional factor termed fatigue factor (G*.sin δ) was investigated at intermediate temperatures (i.e., 25 and 28 °C) to evaluate the resistance to fatigue cracking. G* .sin δ value must be less than 5000 kPa according to the criteria for long-term aging (PAV). Therefore, lower G* .sin δ is regarded as a desirable characteristic regarding resistance to fatigue cracking. Fig. 9. demonstrates the fatigue factor values after PAV.

Both nano-modified Asphalt with 5% exhibited lower phase angle value than the original Asphalt; also, it appears slight for asphalt blends containing NS. Phase angle, linked to an increased elastic response of the asphalt binder, is more prominent. Additionally, it can be seen that at lower temperatures, there is a decrease in the phase angle difference between modified samples and original Asphalt; this is due to the effect that the asphalt matrix will behave more elastically as a result of the lower temperature. A Superpave fatigue factor of nano-modified Asphalt with NS may have a negative effect since Asphalt gained a significant increase in stiffness of complex modulus regardless of aging, which may be prone to fatigue cracks and has a higher loss in moduli. A reduction noted was seen in G* . Sinδ value by nearly 50%, including 5% NS at 25 and 28 °C. While at the same temperature, it reduces to 45% and 33% with NCC at the same temperature sequence. On the other hand, It can be inferred that such nanoparticles possess more viscous behaviors than the original and modified Asphalt with nano NCC, indicating the anti-oxidant effect of NS; these facts show a good agreement with other studies ([24,25]). Finally, nano-modified Asphalt with NS and NCC decreases resistance against fatigue cracking, according to the results of the Superpave fatigue parameter. It must be understood that the Superpave fatigue parameter is based on the outcomes of a single loading cycle and may not be entirely comparable with the field results. Asphalt with the lowest phase angles and higher loss moduli was NS-modified in comparison to NCC; it was found that NS had a more significant impact on the physical characteristics of the asphalt binder, and this is intriguing because, in comparison to NCC, NS is the hardest particle. However, the high amount of dispersion of nano-silica particles in the bitumen matrix and their larger specific surface area led to a more pronounced effect on physical attributes, which is damaging in this case.

3.4.3. Creep stiffness and M-value

In order to prevent low-temperature cracking at lower pavement temperatures, the Asphalt should maintain a low stiffness value. In addition, it can induce stress relaxation since stiffer Asphalt will also tolerate HMA mixtures with thermal stress. This study utilized

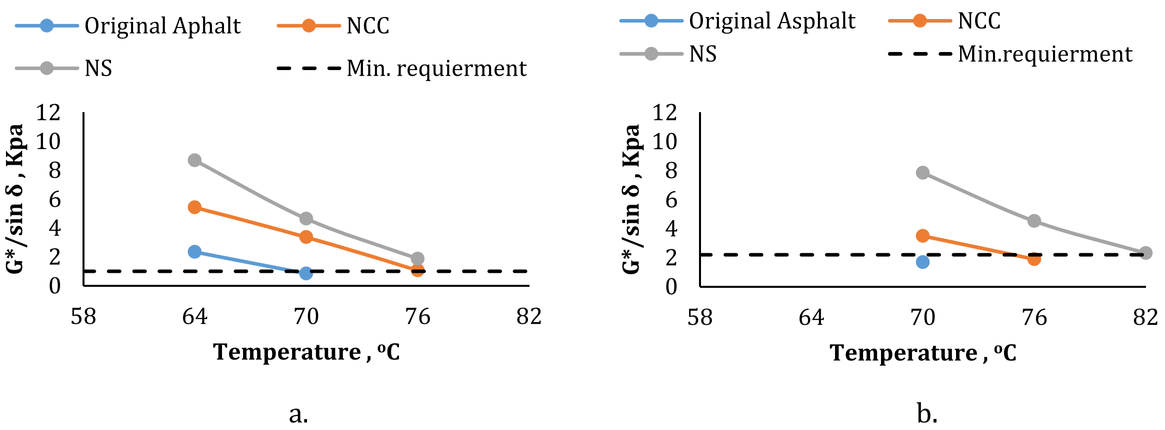

Fig. 8. Effect of 5% Nano content on rutting factor G* /sin δ a. original b. RTFO.

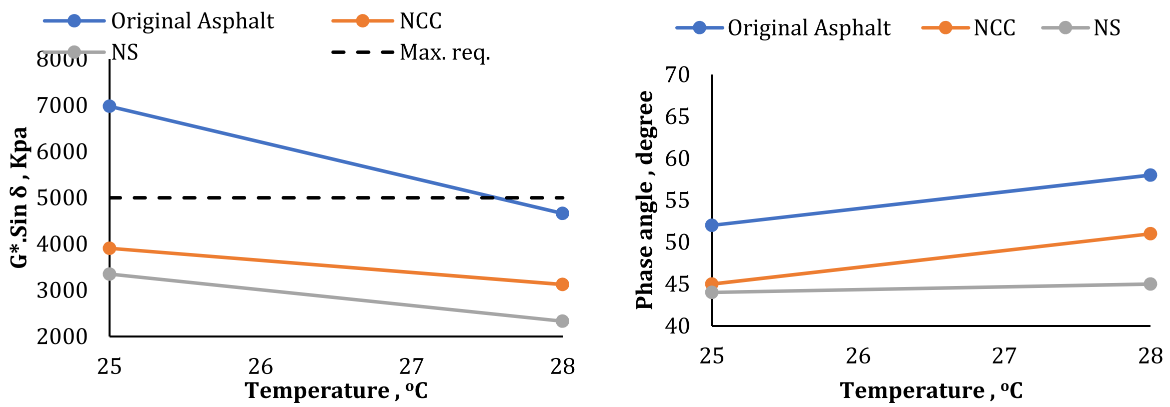

Fig. 9. Fatigue factor parameters of Original and nano-modified Asphalt with NS and NCC.

BBR to investigate the stiffness of original and nano-modified Asphalt with NS and NCC temperatures − 6 and − 12°C. Table 8 shows that adding Nano particles will reduce the m-value at both temperatures. Modified Asphalt with NS shows lower m-values than NS and original Asphalt. This trend held at − 12 °C since it did not meet the minimum Superpave specification of 0.3, which increased the risk of low-temperature cracking. While at − 6°C for NS, this value would reduce the m-value to 0.288 below the specification limit. Furthermore, a higher m-value was noted for modified Asphalt with NCC than NS.

On the other hand, Asphalt with a lower stiffness is less prone to low-temperature cracks, according to AASHTO T 313 standards. 5% NS increased creep stiffness. For instance, at − 6 °C, %5 NS produced the highest increase by 20.2%, reaching 222 Mpa; the same trend was noted as the temperature dropped to − 12 °C which exhibited an increment in stiffness value by 26%, noting that it passed the maximum Superpave criteria of 300 Mpa, yielding a value of 322 Mpa for 5% NS. Otherwise, the stiffness value of NCC-modified Asphalt has changed slightly at − 6 and − 12 °C concerning neat Asphalt by increasing creep stiffness by nearly 10% at both temperatures. In other words, the Asphalt modified with NCC has not substantially improved the Asphalt at low temperatures. The overall result from BBR indicated that the addition of Nanomaterial did not significantly improve low-temperature cracking as the nano content increased, stiffness increased, and the m-value decreased significantly for 5% NS and had no impact on the asphalt grade at low-temperature performance. While Asphalt modified with NCC at the same temperatures had a minor effect on low-temperature cracking, other researchers reported these results [24,15,18].

Table 8
BBR testing result of Original and nano-modified Asphalt with NS and NCC.

Asphalt Type	Creep Stiffness Modulus, S (Mpa)		Creep curve slope,m	
	-6°C	-12°C	-6°C	-12°C
Original Asphalt	177	241	0.38	0.322
NCC	194	274	0.321	* 0.294
NS	222	325	0.288	* 0.261

*below the specified limit of 0.3

4. Conclusion

This study examined the addition of NS and NCC nanoparticle effects on the physical and rheological properties of asphalt binder performance. The following findings are reached:

1-The 5% Nano content utilization showed the highest effect on the properties of the Asphalt with NS, followed by NCC by stiffening Asphalt within penetration grade. While softening point and penetration index increase both nano content, decreasing its temperature sensitivity and improving resistance toward permanent deformation and low-temperature cracking due to decreasing its temperature sensitivity also reduces asphalt ductility.

2- Based on the OD analysis, It can be considered that 5% is the optimum dosage of asphalt mass should be NS and NCC, which is a suitable percentage.

3- Both nanomaterials exhibited an increase in Viscosity at 135 °C since 5% NS showed an enhancement of 60% as compared to the original Asphalt; this Asphalt will maintain its stability in the mixture, followed by 5% NCC, increasing asphalt viscosity by 43%.

4- The improvement in the characteristic of the rutting factor suggests that nano-modified with 5% NS is more resistant to permanent deformation and rutting at high temperatures and will perform better in hot regions where the pavement permanently deforms better than NCC.

5- Nano-modified Asphalt with NS and NCC decreases resistance against fatigue cracking, according to the results of the Superpave fatigue parameter. Asphalt with the lowest phase angles and higher loss moduli was NS-modified compared to NCC.

6- Overall, the result from BBR indicated that the addition of Nanomaterial did not significantly improve low-temperature cracking. The stiffness increased, and the m-value decreased significantly for 5% NS and had no impact on the asphalt grade at low-temperature performance. While Asphalt modified with NCC at the same temperatures had a minor effect on low-temperature cracking.

7- NS has more influence characteristics on asphalt binder than NCC, especially at higher temperature levels.

Recommendation

Considering the economic implications of using nanomaterials as AC modifiers is crucial. Nanotechnology creates nanoparticles in minimal quantities, while constructing an asphalt road requires tons of materials. Nanomaterials are expensive because of the complex processing methods required to generate materials with such high purity levels, a narrow size range, and a large specific surface area. Skyspring (the supplier of imported nano in this study) charges $1267 and 89 $ for 1 kg of nano NS and NCC, respectively. However, the cost has decreased over time as demand has increased, alternative energy sources are more utilized, manufacturing technology has advanced, and this trend is expected to continue. A significant increase in durability must be attained for the addition of modifiers to be economical at the going rate. In addition, from an economic standpoint, lower optimum quantity modifiers are more competitive. At different temperatures, improving asphalt rheology by 5% NS and NCC is more cost-effective, considering the fact concluded in this research that at higher temperatures, NS has more influence features on asphalt binder than NCC.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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