PERFORMANCE EVALUATION OF NANO-CACO$_3$ MODIFIED BITUMEN IN HOT MIX ASPHALT

Hameedullah Raufi, Ali Topal, Derya Kaya and Burak Sengoz
Dokuz Eylul University, 35160 Izmir, Turkey
hameedullah.raufi@ogr.deu.edu.tr; ali.topal@deu.edu.tr;
d.kaya@ogr.deu.edu.tr & burak.sengoz@deu.edu.tr

ABSTRACT

The introduction of nanomaterials as modifiers into bitumen for enhancement of pavements in terms of their overall performance against common distresses have been researched and a considerable number of studies have been devoted to this topic, especially, during the last few decades. To ensure better performing and sustainable pavement design against the distresses caused by common factors such as; moisture susceptibility and high-temperature sensitivity of hot mix asphalt (HMA) components, modification is an inevitable option. In this laboratory study, Nano-CaCO$_3$ is used to modify 50/70 bitumen with various proportions by weight of bitumen. A high-speed shearing mixer is employed to prepare the nano-CaCO$_3$ modified bitumen samples. Fluorescence microscopy (FM) is utilized in order to get a good idea of Nano-CaCO$_3$ particles dispersion in bitumen matrix. The objective of this study is to assess the influence of nano-CaCO$_3$ on physical properties of bitumen by performing conventional and rotational viscosity tests. Additionally, Dynamic Shear Rheometer (DSR) is used to evaluate the rheological behavior. Critical high-temperature performance grading and performance under different loads (frequency) and temperatures are determined through complex modulus (G*) and phase angle (δ) values. Marshall stability and flow test is carried out on both control and nano-CaCO3 modified asphalt mixture. Finally, Modified Lottman test is performed and evaluation of their performances against moisture susceptibility is predicted by obtaining the Tensile Strength Ratio (TSR, %). Based on their performance results, asphalt mixture prepared with 6% Nano-CaCO$_3$ modified bitumen exhibits comparatively good results.

KEYWORDS: Nano-CaCO$_3$; Modification; Dynamic Shear Rheometer; Modified Lottman Test.

1. INTRODUCTION

Asphalt pavements compose the major portion of road infrastructures. Pavements constructed with unmodified base bitumen may not show the expected performances in adverse traffic and environmental conditions. The need for modification of bitumen is an inevitable task to ensure better performing, durable and long-lasting pavements. Moisture-induced damages causing the de-bonding between aggregate and bitumen (stripping) are one of the common distresses witnessed in flexible pavements that end up as the failure of them. This specific distress is considered as one of the most important factors influencing the durability of asphalt mixtures designed for pavement construction [1]. Researchers have suggested numerous options like utilization of different anti-stripping chemicals, hydrated lime, some minerals and amines as modifiers for eliminating this problem. Each of the mentioned potential modifiers has pros and cons but generally, come with drawbacks. In recent past, asphalt modifiers on nanoscale have attracted a significant amount of interest of researchers and engineers. These materials have emerged as the favorite modifiers in asphalt industry that could extensively help out the enhancement of pavement performances. As a consequence of establishing a good ground in the research area of asphalt modifications, in August 2006, a National Science Foundation (NSF) workshop entitled Nanomodification of Cementitious Materials was held in the USA, which focused on using nanotechnology for improvement of asphalt concrete. One of the main conclusions of this workshop was that nanoscience and nanotechnology could lead to improvements in asphalt pavement technology. In this workshop, the field of "asphalt nanomaterial science" was established [2][3].

A nanoparticle is a miniaturized particle that is measured in nanometers (nm) and is often defined as a particle with at least one dimension that is less than 100 nm. The physics and chemistry of nano-sized particles differ from those of conventional materials, primarily because of the increased surface area-to-volume ratio of nanometer-sized grains, cylinders, plates, and because of the quantum effects resulting from spatial confinement [4][5]. In addition, adding nanomaterials leads to the decrease of the acid component of surface Free Energy (SFE) and increases the basic component of SFE of the bitumen that leads to an increase of adhesion between the bitumen and sensitive aggregate against moisture damage [6]. In a study conducted on nano-clay modified asphalt declared that nano-clay could increase the shear complex modulus and reduce the strain failure rate of base asphalt. Furthermore, the addition of nano-clay would decrease the moisture damage of asphalt mixture [2][7]. A research on Nano-$CaCO_3$ proved that it could enhance the quality of base asphalt and asphalt mixture and it showed that the mixture of nano-$CaCO_3$ and asphalt forms a uniform and steady system which improves temperature susceptibility of asphalt at high temperature Another study done on nano-$CaCO_3$ concluded that the mixing of 6% nano-$CaCO_3$ has improved the dynamic stability of asphalt concrete and the residual stability which indicates that both the high temperature performance and water stability of asphalt concrete have been improved [8].

Investigation over nanomaterials used in asphalt modification has been the subject of scientific research during past studies and some of them even covered nano-$CaCO_3$ as modifiers, yet the overall evaluation of nano-$CaCO_3$ influence on bitumen and asphalt mixture and the identification of their rheological and mechanical behavior needed further investigation. Thus, this particular laboratory study was dedicated to comprehensively characterize the influence of nano-$CaCO_3$ on bitumen and asphalt mixture, assessing their performance in terms of dispersion in bitumen matrix, thermal stability, oxidation, and moisture susceptibility. The resistance to moisture damage was assessed for control and modified mixtures. Taking the obtained results into considerations, optimal proportion of additive and corresponding bitumen content for the design of asphalt mixtures was suggested.

2. MATERIALS AND EXPERIMENTAL PROCESS

2.1. Materials

The bitumen used in this study was 50/70 penetration grade base bitumen supplied by Aliaga/ Izmir Oil Terminal of the Turkish Petroleum Refinery Corporation (TUPRAŞ Corp). Conventional tests like penetration and softening point tests on both base and RTFOT – aged binders were performed. Viscosity measurements at 135°C and 165°C on unaged bitumen were carried out by means of Brookfield rotational viscometer. All the tests were done in conformance with the relevant standards and the summary for the properties of 50/70 bitumen are tabulated in TABLE 1 The asphalt mixtures were produced with limestone aggregates that were procured from Dere Group Inc./Belkahve Izmir quarry. Dense-graded conforming with Type-1 gradation for wearing such as limestone, basalt, are usually used in the asphalt mixture. In order to ensure the adhesion of the aggregate and bitumen, limestone is widely preferred because of having a good adhesion capability with bitumen. It performs relatively good in terms of resistance to water [9][10]. The physical properties and gradation of aggregate are given in TABLE 2 and TABLE 3, respectively.

TABLE 1 50/70 Bitumen Properties

Test	Results	Spec. Limits	Test Method
Penetration Test (0.1mm))	64	50 - 70	ASTM D5-06/ EN 1426
Softening Point Test (^{o}C)	51.5	46 - 54	ASTM D36-06/ EN 1427
Viscosity (Pa.s) @ 135^{o}C	0.425	3 Pa.s (max.)	ASTM D4402-06
Viscosity (Pa.s) @ 165^{o}C	0.138	-	ASTM D4402-06
Performance after RTFO-Aging			ASTM D2872-12
Change of Mass after RTFOT (%)	0.08	0.5 (max.)	
Retained Penetration (% of original)	60.9	50 (min.)	ASTM D5 EN 1426
Increase in Softening Point	5.7	9 (max.)	TS EN 12607-1
Flash Point	+260	230 (min.)	ASTM D92 EN 22592
Specific Gravity	1.03	-	ASTM D70

TABLE 2 Limestone Physical Properties

Test	Results	Spec. Limits Wear Type-1	Test Method
Specific Gravity (Coarse Aggregate)			ASTM C127-07
• Bulk	2.694	-	
• Saturated surface dry (SSD)	2.701	-	
• Apparent	2.734	-	
Specific Gravity (Fine Aggregate)			ASTM C128-07
• Bulk	2.695	-	
• SSD	2.703	-	
• Apparent	2.737	-	
Specific Gravity (Filler)	2.725	-	
Los Angeles Abrasion (%)	24.4	45 (max.)	ASTM C1252-06
Flat and Elongated particles (%)	7.5	10 (max.)	ASTM D4791-10
Sodium Sulfate Soundness (%)	1.47	10-20 (max.)	ASTM C88-05
Fine Aggregate Angularity (FAA)	47.85	40 (min.)	ASTM C1252-06

TABLE 3 Limestone Type-1 Gradation

Sieve Opening	Passing (%)	Specification limits	
		Min	Max
(3/4) ″	100	0	100
(1/2) ″	92	83	100
(3/8) ″	73	70	90
No.4	44.2	40	55
No.10	31	25	38
No.40	12	10	20
No.80	8	6	15
No.200	5.3	4	10

$CaCO_3$ manufactured on nanoscale has physical appearance as shown in FIGURE 1.It has higher surface area to volume ratio, uniformly dispersible in bitumen continuous phase and relatively added in lower concentrations as compared to additives in microscale. The purpose of using this type of nanomaterial is to enhance the performance of modified asphalt against moisture induced distresses and ensure good stability at high storage temperatures. Nano-$CaCO_3$ used in this study, with mold no. CAN-6607, is manufactured by Guangdong Qiangda New Materials Technology Co., Ltd (China). Properties of nano-$CaCO_3$ are given in TABLE 4.

TABLE 4 Properties of Nano-$CaCO_3$

$CaCO_3$ % ≥	98
Particle size	60-80 nm
pH	8.0-10.0
True Density (g/cm^3)	2.5-2.6
Bulk Density g/ml	0.68
Moisture % ≤	0.3
Whiteness % ≥	96
Active Rate %	95
Appearance	White powder

2.2 Experimental Process

2.2.1 Preparation of Nano-Modified Asphalt

Nano-$CaCO_3$ was introduced in 3%, 6%, and 9% concentrations into base bitumen. The proportions and preparation method was executed as per in the literature. For the production of nano-modified bitumen samples high-speed shearing mixer with a temperature-control chamber illustrated in FIGURE 2 was used to ensure uniform dispersion of nanoparticles in base binder. 50/70 base bitumen was heated up to 160±5°C, subsequently, nano-$CaCO_3$ was added uniformly (2 to 4 gr/min) while the rotation speed was kept at 2500 revolutions per minute (rpm). After adding of nano-$CaCO_3$ was done, the shearing speed was raised to 3000 rpm and continued mixing for half an hour to ensure a homogenous dispersion. The sample was then placed in the oven at 100±5°C for 24±1 hours to ensure maturity. Afterwards, heated the sample back to 160±5°C and mixed it for duration of 20 minutes.

FIGURE 1 Nano-$CaCO_3$

FIGURE 2 High speed shearing mixer with temperature controlled chamber

FIGURE 3 Dynamic shear remoter

2.2.2 Bitumen and Asphalt Mixture Tests

Conventional Bitumen Tests: Bitumen index tests; Penetration (0.1 mm at 25°C, 100 g, 5 s) and Ring and ball softening point tests were performed on both base and nano-modified bitumen samples. RTFOT was conducted in conformance with (ASTM D2872-12) standard to facilitate short-term aging of base and nanomodified binder samples. Bitumen related tests (except Viscosity test) were performed on short-term aged binder in order to get the idea of their performance against aging. Penetration index (PI) was another index considered in this study for estimating the temperature sensitivity of bitumen.

Storage Stability Test (by Conventional Softening Point Test): Modified bitumen may experience long duration of storage in high temperature maintained silos, that may cause the phase separation consequently failing to perform as expected. This test was performed on nanomodified bitumen samples in accordance with European Standard (EN 13399, 2010) to observe the influence of nanomaterials on storage stability of bitumen at high temperatures. Cylindrical molds (32 mm diameter and 160 mm height) were filled with nano-$CaCO_3$ modified samples and kept in the oven straight in position at 163±5°C for 72±1 hours. Then molds were left at room temperature to cool down. Then laid horizontally and cut into three equal parts. The middle portion was discarded and conventional softening point test was conducted separately on top and bottom ends of the mold. If the difference between the top and bottom softening point values is ≥ 2.5°C the sample is considered as storage stable.

Brookfield Viscosity Test: Brookfield Rotational Viscometer was used to determine viscosity values used for selection of mixing and compaction temperature ranges for the preparation of asphalt mixture in conformance with ASTM D4402/D4402M - 12 (2012). The test was performed on both base bitumen and bitumen prepared with 3%, 6% and 9% doses of nano-$CaCO_3$. Samples were subjected to viscosity test at 135°C and 165°C. The mixing and compaction temperatures were selected corresponding to bitumen viscosities of 0.17 ± 0.02 Pa.s and 0.28 ± 0.03 Pa.s, respectively.

Morphology of Nano-modified Bitumen: The Olympus BX43 fluorescence microscope was used to observe the impact of nano-$CaCO_3$ on bitumen. The dispersion of additive in bitumen matrix is imaged at microscale for all the samples. Nano-sized particles dispersed are clearly distinguished in bitumen phase. Studies show that nanomaterials proved to have better dispersion capability in bitumen matrix when produced in a proper manner. In a study on Nano-silica showed that it can have good dispersions and high stability in the composite materials [12][13].

Rheological Characterization of Bitumen: Bitumen is a viscoelastic material having both viscous and elastic properties. To characterize its rheological behavior, Dynamic Shear Rheometer (DSR) illustrated in FIGURE 3 is employed by means of which two main parameters (complex shear modulus G* and phase angle δ) are measured. G* is considered as the sample's total resistance to deformation when repeatedly sheared. On the other hand, δ is the time lag between the applied shear stress on the sample and its resultant shear strain. δ values ranges between 0 to 90, the higher the value of δ the more viscous the sample would be. DSR uses 1mm thick and having 25 mm diameter samples being sandwiched in between two parallel plates the lower of which is fixed to base and the upper plate oscillates back and forth at the frequency of 10 rad/s (1.59 Hz) simulating the traffic speed of 90 km/h by inducing the shearing impact on the sample. The obtained values of G* and δ are used to predict the performance of bitumen against rutting ($G^*/\sin\delta$) and fatigue cracking ($G^*.\sin\delta$) as per PG asphalt binder specifications stated in SUPERPAVE binder characterizing system (AASHTO T315). DSR test is generally conducted on unaged, short-term aged (RTFO-aged) and long-term aged (PAV-aged) samples. In this study, only unaged and RTFO-aged samples underwent the DSR test.

Asphalt Mixture Design: Dense-graded limestone, 50/70 grade bitumen, and nano-$CaCO_3$ were components of the asphalt mixture. Marshall method of mix preparation and design (ASTM D1559) was implemented to prepare asphalt mixtures with base and modified bitumen samples. Marshall specimens were cast (3.5%, 4%, 4.5, 5%, 5.5% of bitumen by weight of aggregate, 3 replicates each) by applying 75 blows on both sides of the specimen at given mixing and compaction temperatures obtained as a result of viscosity test. After soaking samples in water at 60°C for 35±5 min, their stability and flow values were measured using Marshall Stabilometer. Bitumen contents were determined for mixtures prepared with 0%, 3%, 6% and 9% nano-$CaCO_3$ (% of bitumen) modified binder corresponding to 4% air voids content as 4.59%, 4.07%, 4.17%, and 4.15% by weight of aggregate, respectively.

Investigation of Moisture Effect on Asphalt Concrete Paving Mixtures (AASHTO T 283-03): Modified Lottman test is a standard test carried out to predict the performance of compacted asphalt mixtures against moisture induced distresses. The influence of nano-$CaCO_3$ modification on asphalt mixture performance against moisture susceptibility and resultant stripping is assessed. Indirect tensile test was performed on specimens prepared at corresponding optimum values of 0%, 3%, 6% and 9% nano-modified asphalt mixtures (4.59%, 4.07%, 4.17%, and 4.15%, respectively). A set of 6 specimens divided into two subsets (3 specimens dry and 3 specimens conditioned) with 7±1% air voids content were prepared by adjusting the number of Marshall hammer blows at each given optimum bitumen values. The conditioned specimens underwent the application of 70 to 80% partial voids saturation with water. Subsequently, a freeze cycle (-18±2°C for 16 h) and then a thaw cycle (in 60±1°C water bath for 24 h) was applied followed by soaking at 25±1°C water bath for 2h±10 min. Dry subset specimens were sealed in plastic bags prior to placing them in 25±1°C water bath for 2h±10min. Both conditioned and dry specimens were subjected to the indirect tensile test (ITS), which apply the splitting (tensile) force on samples. The average of ITS values is calculated for each subset.

$$= \frac{2000}{}$$

Where S_t is ITS of the specimen in KPa, P is measured indirect tensile strength in Newton, t is specimen thickness in mm and D is specimen's diameter in mm. Tensile Strength Ratio (TSR%) was calculated as below:

$$\% = \frac{}{} \quad 100$$

S_1 and S_2 are the average ITS values of dry and conditioned subsets, respectively. The mix is considered as moisture resistant if TSR value is ≥ 80% as per Superpave mix design (AASHTO T 283). Some agencies also accept 70% TSR value as the minimum critical value for a mix design to be moisture resistant.

3. RESULTS AND DISCUSSIONS

3.1. Conventional Bitumen Test Results

The influence of nano-$CaCO_3$ modification on basic properties of 50/70 bitumen is summarized in TABLE 5. Results of penetration test which is the indicator of bitumen's consistency show that the modified bitumen gets slightly softer as compared to base bitumen. The softening point values also increase with the increment of modifier content. The results for penetration test agrees with a study done by Hao et al [8]. The increase in softening point is a good sign since bitumen with a higher softening point can be less susceptible to permanent deformation [11].

TABLE 5 Conventional Bitumen Test Results for Base and Modified Bitumen

Test	Nano-$CaCO_3$ Content			
	0%	3%	6%	9%
Penetration	64	66.3	70.7	69.7
Softening Point (°C)	51.5	52.8	53.2	54.7
Penetration Index	-0.23	0.18	0.45	0.77
Viscosity (Pa.s) @ 135°C	0.425	0.425	0.463	0.575
Viscosity (Pa.s) @ 165°C	0.138	0.125	0.125	0.175
Performance after RTFOT- Aging				
Change of Mass after RTFOT (%)	0.08	-0.01	0.03	0.04
Retained Penetration (% of original)	60.9	68.1	64.5	64.8
Increase in Softening Point	5.7	4	4.7	4.4
Storage Stability Test				
Softening Point (°C) Upper Segment	-	54.5	57.2	56.2
Softening Point (°C) Lower Segment	-	53.7	55.9	55
Difference (°C)	-	0.8	1.3	1.2

PI values get higher with the increment of modifier content, which indicates the enhancement of modified bitumen against high-temperature susceptibility. Asphalt mixtures prepared with bitumen having high PI values are more resistant to low temperature cracking as well as permanent deformation [11]. The after short-term aged modified bitumen performance was satisfactory. Higher retained penetration and lower increment in softening point values were obtained that depict good anti-aging performance of the modified bitumen. Storage stability test also exhibited promising results for nano-modified bitumen. Since bitumen becomes storage stable when modified with nanomaterials, in most of the studies they were used and recommended for producing nano-PMB nanocomposites to impart storage stability and avoid phase separation between bitumen and polymer.

3.2. Mixing and Compaction Temperatures

The mixing and compaction temperature ranges for bitumen with and without nano-$CaCO_3$ are presented in TABLE 6. As per the results, nano-$CaCO_3$ did not bother the temperatures at 3% and 6% additive content, while for 9%, bitumen gets more viscous. Thus, the temperature needed to mix and compact is higher for 9% additive content as compared to base bitumen.

TABLE 6 Mixing and Compaction Temperature Ranges for Neat and Modified Bitumen

Mixture Type	Additive (%) by Binder Weight	Mixing Temp. (°C)	Compaction Temp. (°C)
Control Mixture	0	156-163	143-149
Nano-$CaCO_3$ Modified Mixture	3	154-161	143-149
	6	155-161	144-150
	9	163-169	150-157

3.3. Rheological Analysis of Bitumen

Dynamic Shear Rheometer (DSR) was employed to determine the upper critical temperature (T_{crit}) used in Superpave Performance grading system. The unaged and RTFOT-aged samples of the base and nano-modified bitumen were subjected to DSR oscillating shear maintaining a frequency of 10 rad/s (1.59 Hz) which represents the field traffic moving at approximately 90 km/h. The initial temperature values were set to 52°C for unaged and 64°C for RTFOT-aged samples a run-up in 6°C increments. The upper critical temperatures used in PG system were determined for each sample by obtaining the G*/sinδ values. TABLE 7 shows the criteria in DSR specifications for rutting and fatigue distresses. The upper critical temperatures for each bitumen sample are presented in TABLE 8.

TABLE 7 Performance Graded Asphalt Binder DSR Specifications [14]

Material	Value	Specification	HMA Distress of Concern
Unaged binder	G*/sinδ	≥ 1.0 kPa (0.145 psi)	Rutting
RTFO residue	G*/sinδ	≥ 2.2 kPa (0.319 psi)	Rutting
PAV residue	G*sinδ	≤ 5000 kPa (725 psi)	Fatigue cracking

Upper critical temperature (T_{cric}) is an indication for appraising the rutting performance of a particular bitumen sample. The higher the G*/sinδ value for a sample means the more resistant to permanent deformation. The results obtained for samples explain that 3% and 6% of nano-$CaCO_3$ addition did not bother the PG grade. While for 9%, the PG was one grade elevated to 70°C. One thing here is noticeable that the G*/sinδ values for un-aged and RTFOT aged samples remained fixed at the same temperature. Which implies that nano-$CaCO_3$ modified RTFOT aged samples do not harden or oxidize fast generally caused by the aging process.

TABLE 8 Determination of PG Temp. for Base and Nano-$CaCO_3$ Modified Bitumen

Binder Type	Additive (%) by weight of Binder	Temperature (°C)	DSR, G*/Sinδ (Pa)		Upper Critical Temp. (T_{crit}) (°C)
			Unaged	RTFOT Aged	
Neat Binder	0	52	7652		64
		58	3074		
		64	1385	2857	
		70	644.5	1328	
Nano-CaCO3	3	52	9895		64
		58	4300		
		64	1830	4285	
		70	843.7	2020	
	6	52	8245		64
		58	3567		
		64	1578	4011	
		70	787.4	1837	
	9	52	12950		70
		58	5509		
		64	2459	5753	
		70	1132	2710	
		76	574	1304	

RTFO-aged base and modified bitumen samples were subjected to oscillating shear conducted at 0.01 and 10 Hz frequencies and 4 different temperatures ranging from 50 to 80°C with 10°C increment. This is done in order to have a good idea of how the mixture prepared with modified bitumen will behave after it is being placed and subjected to traffic loads and field temperatures. The correlation between G*/sinδ and selected temperatures is illustrated in FIGURE 4 and FIGURE **5** FIGURE 5 for low and high frequencies, respectively. All of the bitumen samples showed almost the same trend for G*/sinδ. The G*/sinδ values increase with the decrease in temperature at both frequencies. An increment in G*/sinδ value indicates higher performance against rutting. At lower temperatures, all the samples showed higher rutting resistance. Besides, as expected G*/sinδ values increase at higher a frequency (10 Hz) for all of the bitumen samples. This is due to the rheological behavior of the bitumen since bitumen under shorter loading times (high-frequency level) exhibit elastic behavior **[9]**. Another trend observed here is that as the modifier content increases the rutting performance gets substantially improved for both frequencies applied especially at lower temperatures.

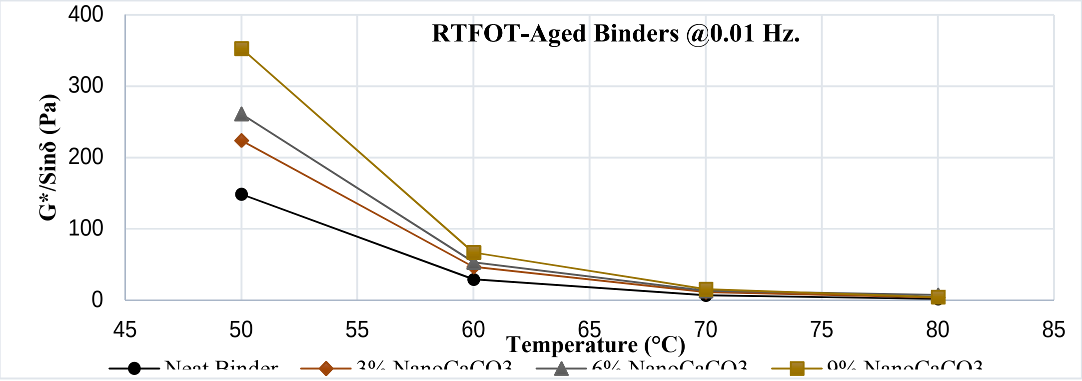

FIGURE 4 G*/sinδ values of base and modified samples at 0.01 Hz.

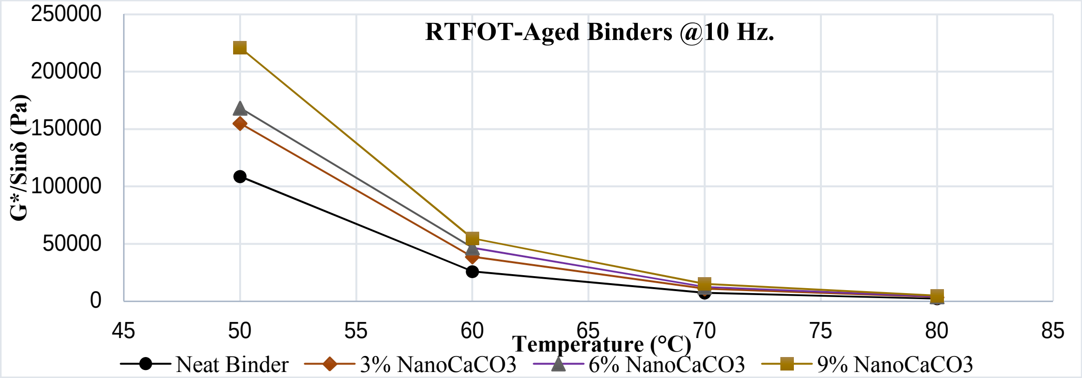

FIGURE 5 G*/sinδ values of base and modified samples at 10 Hz.

3.4. Morphological Study of Bitumen on Microscale

Though it is not very common to examine the distinctions of the contents of $CaCO_3$ in bitumen on the nanoscale with a fluorescence microscope, the reason for performing morphological study is to exhibit the homogenous distribution of the nano-$CaCO_3$ with the bitumen matrix. The microscopic images are illustrated in FIGURE 6 The homogenous dispersion for 6% modifier content in bitumen imparts the qualities that make it perform comparatively better than for other proportions. As depicted in FIGURE 6 due to the higher concentration percentage of modifier the nanoparticles start agglomerating and making micro-sized bulk structures which imply that bitumen prepared with this proportion may not perform as better as prepared with 6% of nano-$CaCO_3$. In addition, the mechanical strength and bonding enhancement is ensured in the mixture.

Nano-$CaCO_3$ is primarily a nano-sized filler which can potentially increase the viscosity and thus resistance to permanent deformation gets improved.

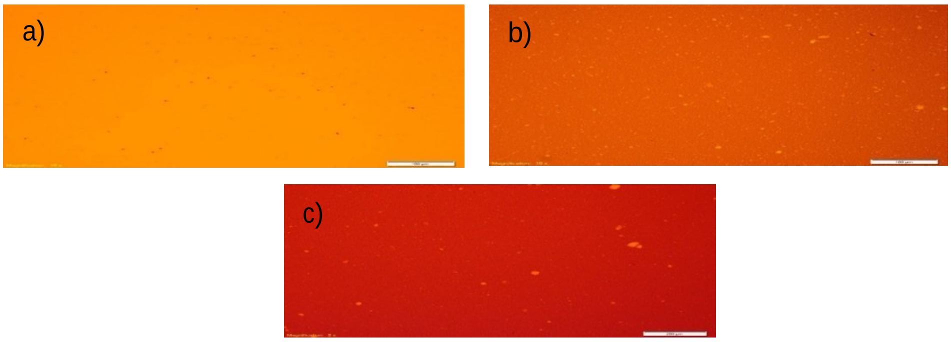

FIGURE 6 Fluorescent micrographs a) 3% Nano-$CaCO_3$ modified bitumen b) 6% Nano-$CaCO_3$ modified bitumen c) 9% Nano-$CaCO_3$ modified bitumen

Modified Lottman Test (AASHTO T 283 – 03 or ASTM D 4867-D5867-09)

TABLE 9 presents the summary of optimum bitumen contents for control and nano-$CaCO_3$ modified bitumen mixtures at all three concentrations obtained by performing Marshall test. In order to evaluate the influence of nano-$CaCO_3$ modification on the performance against moisture susceptibility, the prepared mixtures with and without modifiers were plotted against their ITS results achieved for both dry and conditioned specimens as illustrated in FIGURE 7. The resultant TSR % values were also shown on the plot. It was observed that the ITS values for the conditioned specimens are lower than those for dry specimens. This is the behavior expected, because in conditioning process the presence of water causes weakening of the bond between aggregate and bitumen, subsequently getting lower ITS values for them. After conditioning, mixtures with nano-$CaCO_3$ generally exhibited less decrease than control mixtures.

As seen in FIGURE 7, TSR values remain between 70% and 80% and are very close to the lower limit of 80% for modified specimens, while specimens prepared with base bitumen do not meet the minimum criteria and are considered as moisture susceptible. This infers that the performance against moisture improves significantly when modified with nano-$CaCO_3$. Higher values of TSR give better resistance to moisture damage in mixtures. The ITS values for dry specimens did not increase in comparison with control mixture. In contrast, for wet conditions, the increase in the ITS values of modified samples is higher. It can be concluded that adding nano-$CaCO_3$ to mixtures improves the adhesion and cohesion of the binder and does not allow the displacement of asphalt components from the aggregate surface easily by water. Thus, nano-$CaCO_3$ provides more reasonable mixtures than unmodified mixtures [6]. Although for 9% content it decreases marginally, the ITS values and resultant TSR values were maximum for 6% nano-$CaCO_3$ modified bitumen prepared specimens. This infers that it can perform relatively better in terms of resistance to moisture damages. Therefore 6% concentration of nano-$CaCO_3$ was suggested as the optimal proportion for bitumen modification.

TABLE 9 Summary of ITS and TSR Values of Base and Modified Bitumen with OBC%

Mixture Type	**Modifier Content by OBC %**	**OBC %**	**ITS values (KPa)**		**TSR %**
			Dry	**Conditioned**	
Control Mixture	Base Bitumen	4.59	727	497	68
Nano-$CaCO_3$	3	4.07	721	524	73

Mixture Type	Modifier Content by OBC %	OBC %	ITS values (KPa)		TSR %
			Dry	Conditioned	
Modified Mixture	6	4.17	740	562	76
	9	4.15	719	535	74

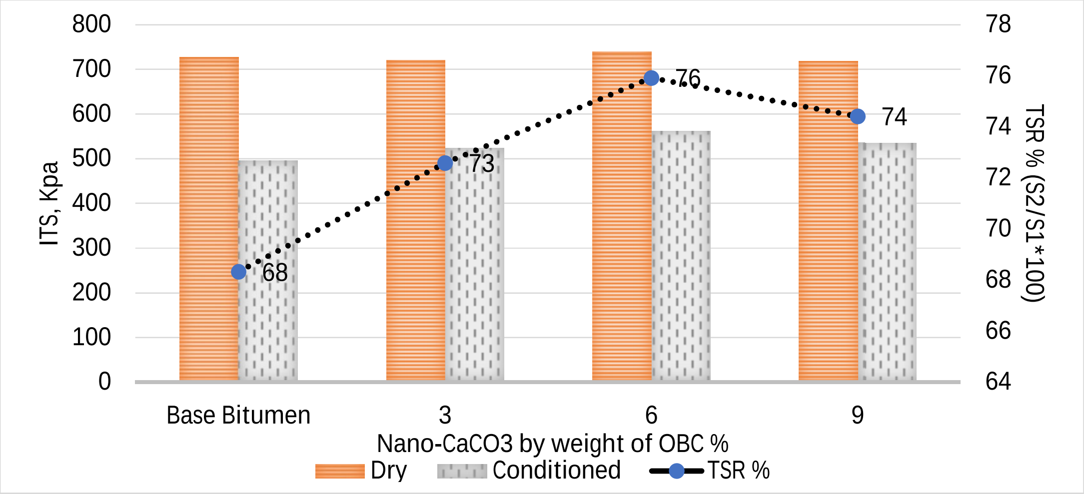

FIGURE 7 ITS and TSR results for mixtures prepared with base and nano-modified bitumen

4. CONCLUSIONS AND RECOMMENDATIONS

The utilization of nano-$CaCO_3$ as a modifier in asphalt is most commonly intended to enhance the performance of bitumen in terms of thermal stability, oxidation, increase the inter-compatibility between polymer and bitumen when used in nanocomposites. Asphalt mixture prepared with nano-$CaCO_3$ modified bitumen gains good resistance ability against moisture induced damages.

The conclusions drawn from this study are as follows:

- Softening point test values increased with the increment in modifier content indicating their good resistance to temperature.
- Showed satisfying results for the bitumen's after short-term aging performance due to nano-CaCO3 modification.
- The modified bitumen became significantly storage stable and their viscosity values were not increased significantly expect for 9% content of bitumen modifier.
- Fluorescence micrographs exhibited a homogenous dispersion of modifier in bitumen matrix, especially for 6% modifier content.
- Nano-CaCO3 improves the adhesive bonding of bitumen to aggregate. Limestone is more favorable than other types of aggregates in bonding with bitumen binder.
- ITS results proved the positive impact of nano-CaCO3 on moisture resistance of mixtures prepared with modified bitumen.
- The highest ITS and resultant TSR values were achieved with 6% nano-CaCO3 modified bitumen prepared asphalt mixture.

- 6% nano-CaCO3 by weight of OBC% of 4.17% was suggested as optimum additive content for achieving an asphalt mixture with the best performance.

Further performance tests need to be performed to get a thorough understanding of nano-$CaCO_3$ influence on asphalt mixtures. And look for other positive impacts that it can potentially have by its usage as modifier beside the ones stated in this study.

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