Effects of Asphalt Modification with Nanomaterials on Fresh and Stored Bitumen

Ahmed W. Oda, Ahmed El-Desouky, Hassan Mahdy, Osama M. Moussa

***Abstract*—**Nanomaterials have many applications in the field of asphalt paving. Two locally produced nanomaterials were used in the asphalt binder modification. The nanomaterials used are Nanosilica (NS), and Nanoclay (NC). The virgin asphalt binder was characterized by the conventional tests. The bitumen was modified by 3%, 5% and 7% of NS and NC. The penetration index (PI), and the retaining penetration (RP) was calculated based on the results of the penetration and the softening point tests. The results show that the RP becomes 95.35% at 5% NS modified bitumen and reaches 97.56% when bitumen is modified with 3% NC. The results show significant improvement in the bitumen stiffness when modified by the two types of nanomaterials, either fresh or aged (stored).

***Keywords*—**Bitumen, modified bitumen, aged, stored, nanomaterials.

I. Introduction and Literature Review

Hot mix asphalt (HMA) mainly consists of aggregate (the main material to resist loads), mineral filler (to fill the voids between the aggregate particles), and bitumen (the material that is responsible for binding the particles of aggregates and the particles of the mineral filler together) [1]. The bitumen is responsible for the action of all ingredients together [2]. In some cases, some additives are added to modify the properties of the matrix [3]-[6].

Bitumen is a viscoelastic material that is influenced by the effects of the applying loads, time duration of load application, and temperature [7]-[9]. Bitumen also is responsible for the flexibility of the asphalt pavements besides, the volume of air voids [10]. The behavior of the bitumen inside the asphalt matrix influences the behavior of the HMA [10]. The time consumed due to the mixing, the handling, and the time of storage, and service time cause aging for the bitumen, which means more deterioration and reducing the service life of asphalt pavements [5], [6], [10]-[17].

In the last two decades, nano silica has served as a promising material for designing and preparing new functional materials because of its high surface area, very small particle size, and stability [6], [18], [19].

Zafari et al. [6] showed that asphalt modification by NS improves the storage modulus and elasticity. NS also leads to enhance the rutting resistance of pavements.

Oda et al. [20] showed that asphalt mixtures modification with two nanomaterials (NS and NC) enhances performance of bitumen and asphalt mixtures.

Mahan [21] used two different nanomaterials in bitumen modification. The used nanomaterials were NS and nano hydrated lime (NHL). The results showed that modified bitumen becomes stiffer and less sensitive to temperatures than the original asphalt, the results also an increase in the adhesion and cohesion of asphalt and asphalt mixture.

Abolmagd et al. [22] showed that asphalt modification by NS fume shows an increase in bitumen stiffness and a reduction in temperature susceptibility. They also showed that modified asphalt mixtures have higher resistance to moisture damage, rutting, and cracks due to fatigue.

II. Materials

A. Bitumen

The bitumen used in this research was produced by El-Nasr Petroleum Company, Suez, Egypt. It was taken from one of the constructed roads in the New Administrative Capital. Bitumen was tested to investigate its physical and rheological properties. Bitumen properties are listed in Table I.

TABLE I
Properties of Fresh Bitumen

Property	unit	Value	ASTM
Penetration	dmm	54	D 5 [23]
Softening point	°C	42.5	D 36 [24]
Viscosity at 135 °C	cP	345.5	D4402 [25]
Viscosity at 165 °C	cP	75	D4402 [25]
Flashpoint	°C	250	D 92 [26]
Firepoint	°C	268	D 92 [26]

Bitumen samples were stored for one year in the laboratory conditions of temperature, atmosphere pressure, ventilation, moisture, and light exposure. The stored bitumen is named "self-aged bitumen" or "stored bitumen". The same experimental tests for the stored were the same as the fresh bitumen.

B. Nanomaterials

Two nanomaterials were added to the virgin binder to modify the rheological and physical properties. The two nanomaterials were locally manufactured. The two nanomaterials were Nano Silica (NS) and Nano Clay (NC). NS was shown in Fig. 1, and NC is presented in Fig. 2. Both nanomaterials were provided in the local market. Both were added in percentages of the weights of bitumen samples. The selected percentages of NS, NC were

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3%, 5%, and 7% by the weights of bitumen.

Fig. 1 Nanosilica (NS)

Fig. 2 Nanoclay (NC)

The physical properties of NS and NC were presented in Tables II and III.

TABLE II
PHYSICAL PROPERTIES OF NS

Property	Value
Physical state	Powder
Color	White
Shape of particles	Spherical
Purity	99.8%

TABLE III
PHYSICAL PROPERTIES OF NC

Property	Value
Physical state	Powder
Color	Grey
Shape of particles	Spherical
Purity	92%

NS was composed of 99.8% of SiO_2. The remaining compositions were impurities. On the other hand, the chemical analysis of the sample reflected its composition from SiO_2 (46.3%), MgO (40.2%), and Al_2O_3 (5.5%) in addition to other traces for other elements that related to the impurities of the using natural raw materials.

III. Mixing Nanomaterials with Bitumen, and Blend Characterization

From the previous studies [27]-[29], mechanical mixing was a proper method to mix and distribute nanomaterials inside the bitumen. The mixing process was performed under specified conditions of temperature, mechanical mixer speed, and period of mixing duration. Nanomaterials were added and blended into the bitumen gradually for 30 minutes of mixing. After that the bitumen and the modifier added were mixed for another 30 minutes, to become the total mixing times 60 minutes. The time duration of mixing is 60 minutes at a speed of 2200 rpm at temperature 145 ± 5 °C [30]. The second 30 minutes was only for mixing the nanomaterials to achieve the full distribution within the bitumen. If the blend is mixed for a longer period than 60 minutes, it would have higher cost due to time, effort wasting and more consumption in energy, and less efficiency of mixing. It could lead to a harmful effect on the ductility of the bitumen because of the agglomeration of the nanoparticles [29]. After mixing the nanomaterials with bitumen SEM images were taken to ensure that the modifiers were homogeneously distributed inside the bitumen. Fig. 3 showed the homogeneity of the particle distribution of both nanomaterials after mixing with bitumen.

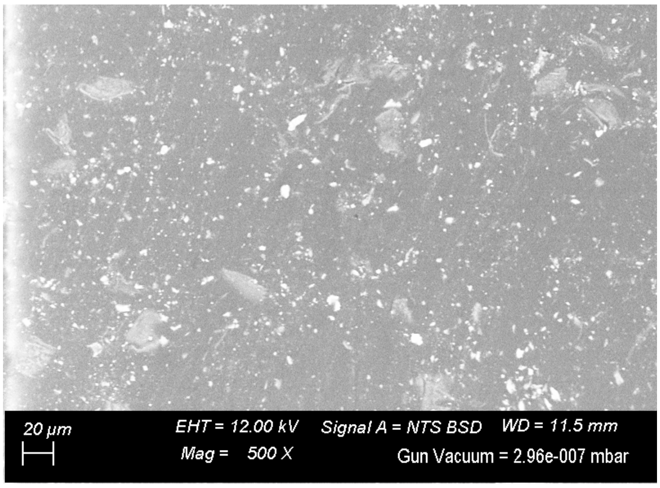

Fig. 3 Homogenous distribution inside the asphalt binder

IV. Methodology, Results, and Discussion

NS and NC were added to bitumen as modifiers to enhance the properties of bitumen. The contents of both nanomaterials were 3%, 5%, and 7% by the weight of bitumen. Virgin bitumen (with no content of nanomaterials) was used as a reference to evaluate the effects of bitumen modification with both nanomaterials. The aged (stored bitumen) samples were similar bitumen samples, from the same source, have the same properties. The stored bitumen samples are modified by NS and NC under the same conditions of mixing and the contents of NS and NC. The only difference is that the fresh samples were tested just after manufacturing and modification, but the aged bitumen samples were stored in the laboratory conditions under the ordinary atmosphere.

In this study, penetration (Pen) and penetration index (PI) values were used to characterize the bitumen and evaluate the effects of nanomaterials on the service temperature as Pen, and PI are adequate tools to evaluate the rheology of the bitumen at service temperatures [31].

A. Penetration

The penetration test was performed according to ASTM D5 [26], and AASHTO T 49 [27]. The penetration test was performed for both fresh and stored bitumen. Table IV presents the results of bitumen (fresh and aged).

TABLE IV
PENETRATION TEST

Samples		Fresh	Aged
Virgin	0%	54	50
NS	3%	52	44
	5%	43	41
	7%	55	50
NC	3%	41	40
	5%	57	53
	7%	56	52

TABLE V
VALUES OF RP (%)

Samples		RP%
Virgin	0%	92.59
NS	3%	84.62
	5%	95.35
	7%	90.91
NC	3%	97.56
	5%	92.98
	7%	92.86

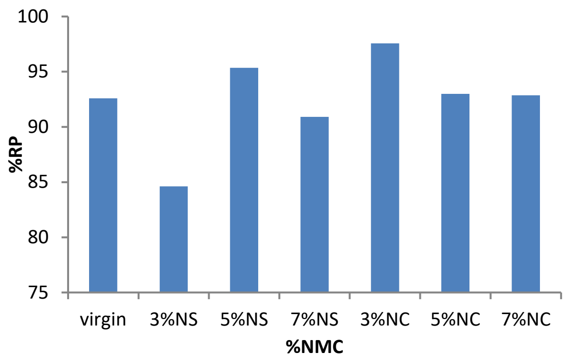

Fig. 4 RP (%)

As mentioned in Table IV, in the case of fresh bitumen penetration decreased from 54 to reach 52 at 3% NS content. Pen continued to decrease with increasing NS content. At 5% NS (Pen) became 43, after that value (Pen) increased. On the other hand, the modified bitumen with NC showed sharp decrease in the penetration values at 3% NC content. After that penetration returned to increase.

In the case of stored bitumen (aged), penetration decreased from 50 at zero NS content to become 44 at 3% NS content. As the same manner of fresh bitumen, penetration continued to decrease at 5% NS, then the penetration value increased with the increase of NS content. Furthermore, the stored bitumen had the lower value of penetration at 3% NC content.

B. Retained Penetration

Retained penetration (RP) is an indication of the hardness of bitumen. The increase of RP value indicates that the stored bitumen became harder and stiffer. RP is calculated from (1):

$$RP(\%) = \frac{\text{Aged penetration (Stored bitumen)}}{\text{Fresh penetration (unaged bitumen)}} * 100 \quad (1)$$

Table V and Fig. 4 present the values of RP%.

The results showed that the highest values of RP were at 5% NS, and 3% NC modified bitumen. That means that they are the harder samples between the modified and virgin samples.

C. Softening Point

The softening point (SP) is an indication of the ability of the material to flow at high temperatures during the pavement service. The procedures of determining the SP of bitumen are described in AASHTO T 53 [28] and ASTM D36 [29]. Values of SPs for fresh and stored bitumen samples were listed in Table VI. ISP (increase in softening point value) was presented in (2) [32]:

$$ISP = \text{Aged softening point} - \text{Fresh softening point} \quad (2)$$

TABLE VI
VALUES OF SOFTENING POINT

Samples		Fresh	Aged	ISP
Virgin	0%	42.5	45	2.5
NS	3%	44.25	48	3.75
	5%	46	50	4.0
	7%	45.75	48	2.25
NC	3%	47.5	50.5	3.0
	5%	45	48.1	3.1
	7%	40	42.5	2.5

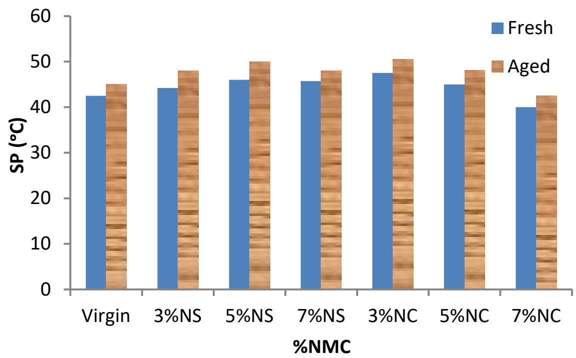

Fig. 5 ISP for fresh and stored bitumen

The increase in softening point is an indication of the improvement in the bitumen behavior under weathering conditions. The 5% NS content gave the higher value of ISP for fresh and aged bitumen in the case of asphalt modification with NS.

In the case of using NC as modifier, 3% and 5% NC content were nearly equal while, 7% NC content had the lower value of ISP.

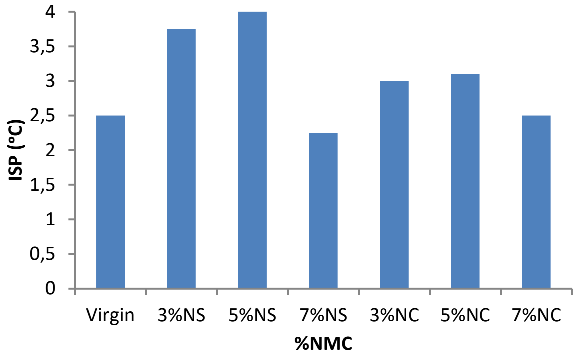

Fig. 6 ISP and %NMC relationship

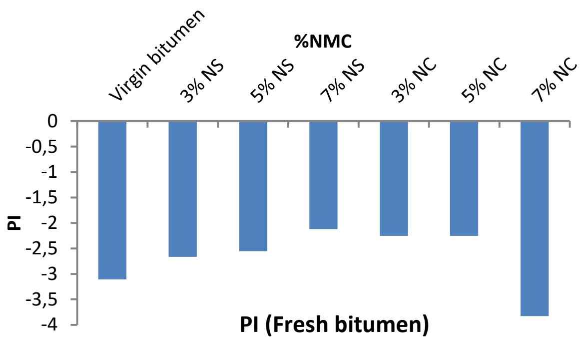

Fig. 7 PI for fresh bitumen

D. Penetration Index

The response of bitumen to variation in temperatures is expressed by the value of the penetration index (PI). So, it could be the indication of the behavior of pavements under the variation in temperatures during the years seasons [2], [29], [33], [34]. PI is calculated from (3); the increase in the values of PI expresses the decrease in the susceptibility to temperatures (thermal susceptibility) [10], [35]. Also, the increase in PI is caused by the increase in stiffness due to the bitumen modification. Tables VII and VIII, and Figs. 7-15 presented a comparison between the results of fresh and stored bitumen samples.

$$PI = \frac{1952 - 500\log(Pen.) - 20\,SP}{50\log(Pen.) - SP - 120} \quad (3)$$

where, (Pen.) is the penetration value of bitumen at 25 °C.

TABLE VII
PI

Samples		Fresh		Aged	
		PI	Change in PI (%)	PI	Change in PI (%)
Virgin	0%	-3.11	0	-2.53	0
NS	3%	-2.66	14.5	-1.98	21.74
	5%	-2.55	18	-1.63	35.57
	7%	-2.12	31.83	-1.72	32.02
NC	3%	-2.25	27.65	-1.56	38.34
	5%	-2.23	28.3	-1.56	38.34
	7%	-3.83	-23.2	-3.18	-25.7

TABLE VIII
CHANGES IN PI DUE TO STORAGE

		Change in SP (%)	Change in PI	Change in PI (%)
Virgin	0%	2.5	-0.58	0
NS	3%	3.75	-0.68	17.36
	5%	4.0	-0.92	58.65
	7%	2.25	-0.4	-32
NC	3%	3.0	-0.69	18.72
	5%	3.1	-0.69	19.16
	7%	2.5	-0.65	11.18

PI values increase gradually while the percentage of NS increases. PI increases from -3.11 for the virgin bitumen -2.12 for 7% modified bitumen.

Fig. 8 presents the estimated model that describes the relationship between the percentage of NS, and the PI values for fresh bitumen. Fig. 9 also describes the relationship between NC content and PI for fresh bitumen. The estimated models are presented in (4) and (5).

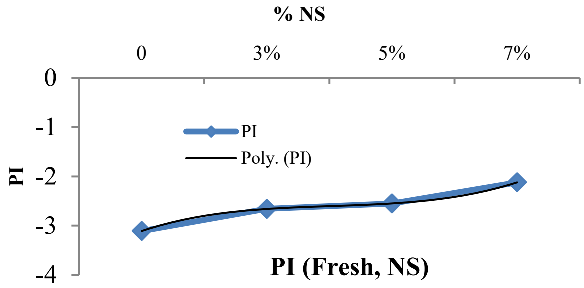

Fig. 8 The relationship between NS content and PI

$$PI = 0.11(\%NS)^3 - 0.83(\%NS)^2 + 2.17(\%NS) - 4.56, \quad R^2 = 1 \quad (4)$$

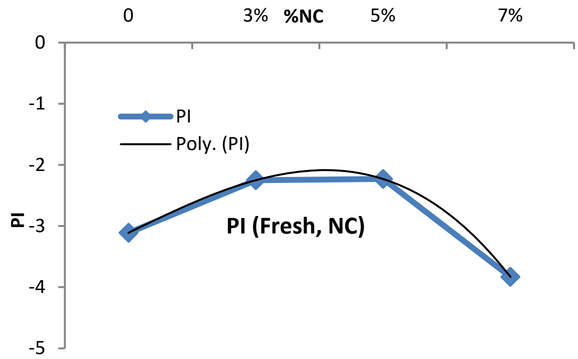

Fig. 9 The relationship between NC content and PI for fresh bitumen

$$PI = -0.13(\%NC)^3 + 0.36(\%NC)^2 + 0.69(\%NS) - 4.03, \quad R^2 = 1 \quad (5)$$

For the stored bitumen, Fig. 10 presented the values of PI with respect to the nanomaterial content. Relationship between PI values of NS and NC were presented in Figs. 11 and 12, respectively. The estimated models that described the behavior of the stored bitumen samples were simulated in (6) and (7).

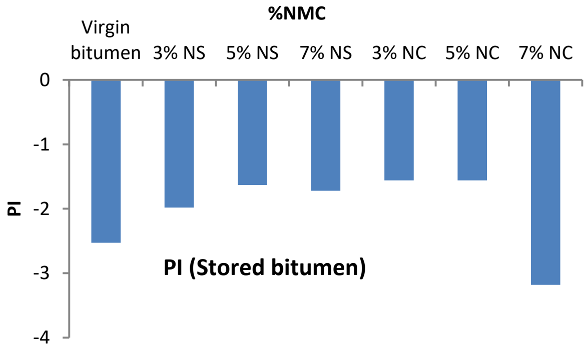

Fig. 10 PI values for the stored bitumen

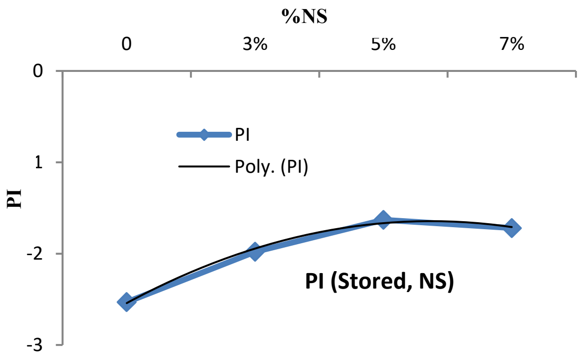

Fig. 11 The relationship between NS content and PI for aged bitumen

$$PI = -0.16(\%NS)^2 + 1.078(\%NS) - 3.46,\ R^2 = 0.9941 \quad (6)$$

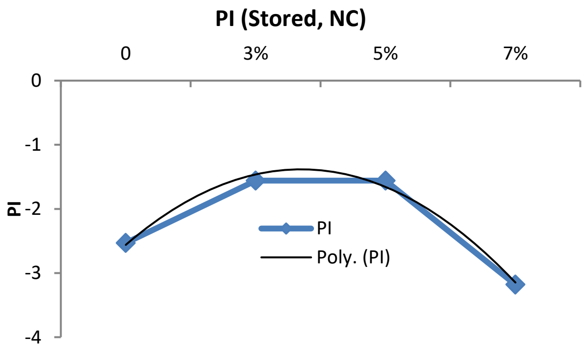

Fig. 12 The relationship between NC content and PI for aged bitumen

$$PI = -0.6475(\%NC)^2 + 3.4025(\%NC) - 4.9575,\ R^2 = 0.9888 \quad (7)$$

Fig. 13 shows the percentage of changing PI between the fresh and the aged bitumen. The higher changes occur at 5%NS, and 5% NC. The difference between 3% NC and 5% NC is very tight. PI decreased by 58.65% at 5%NS, 18.72% at 3% NC, and 19.16% at 5%NC. Fig. 14 presents the percentages of increasing PI due to the bitumen modification.

Empirical equations (4)-(7) were conducted to describe the relationship between PI and the nanomaterial content (%NMC). The figures and equations described the behavior of fresh and stored bitumen (virgin, modified with NS, and modified with NC).

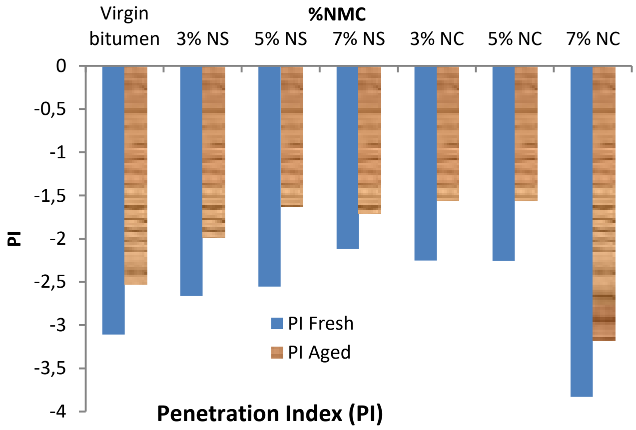

Fig. 13 PI for fresh and aged bitumen

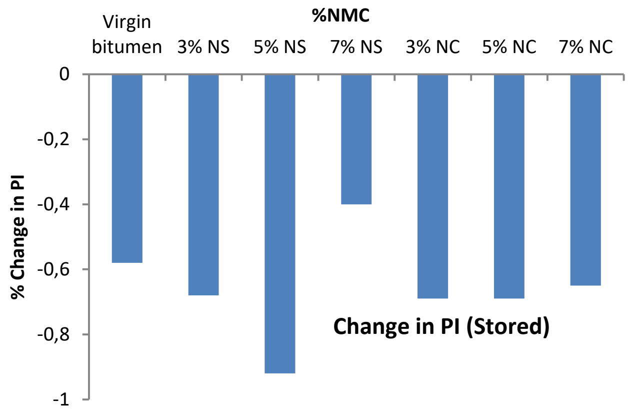

Fig. 14 % Change in PI for storage bitumen

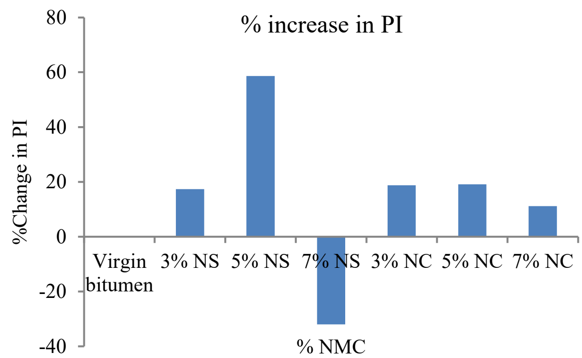

Fig. 15 % Change in PI for storage bitumen

With increasing the NS content, modified bitumen possessed higher thermal stability. Thermal stability indicates better performance at higher temperature. This occurred based on the decrease in the temperature susceptibility.

In the case of NC, 3% and 5% contents gave the same results and the same values of PI. The 7% NC content showed lower PI that means higher sensitivity to temperature. This behavior may occur because of the agglomeration of NC particles together inside bitumen with increasing NC content over 5%.

V.Conclusion

The increase in PI due to the bitumen storage indicates improvements in the temperature sensitivity and weathering resistance. It also expresses higher storage stability. The improvement in temperature sensitivity indicates better performance in the varying temperature, and higher resistance to cracking. NS shows better improvements than NC, although NC gives significant enhancement in the bitumen properties. The higher values of PI for the stored samples modified by NS compared to others modified by NC expresses better storage stability and lower temperature susceptibility.

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