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Evaluation of Asphalt Binders Modified with Nanoclay and Nanosilica

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Abstract

During last decade, researchers' interest in nanotechnology applications, particularly in the field of pavement materials, has been increasing. This research work focused on the investigation of the properties of asphalt binder modified with different percentages of two different nanomaterials. These materials are nanoclay, and nanosilica. The nanosilica was manufactured from two different sources: silica fume and rice husk. Nanomaterials and asphalt binder were first characterized. A mechanical mixer was then used at 1500 rpm to mix the nanomaterials with the binder. Required mixing time was determined. Three different nanomaterial percentages were mixed with the binder. The modified binders were tested for rheological properties. Results showed that, nanosilica synthesized from silica fume tends to decrease the penetration value and increase the softening point temperature. The nanoclay on the other hand was found to increase the penetration and decrease the softening point temperature. At temperature of 135°C and up to 150°C, increasing nanosilica percentage was found to increase Brookfield Rotational Viscosity (RV), while nanoclay, at small percentages, increased the RV and then decreased it at higher percentages. At higher temperature, up to 165°C, the RV values did not change significantly using both nanomodifiers. Nanosilica from rice husk showed improvement in the RV results. Finally, the Dynamic Shear Rheometer (DSR) results showed obvious improvement in the performance grade leading to higher resistance to permanent deformation.

Keywords: Nanotechnology; nanocaly; nanosilica; modified asphalt; DSR; RTFO

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1 Introduction

During the last decade, several research studies in the field of highway and airport engineering have been conducted to investigate the use of nanomaterials as an asphalt modifier (Sun et al., 2011). While conventional inorganic fillers are usually added in percentages varying between 20% and 40% by weight, in nanocomposites a typical quantity may be between 2% and 5% (Jahromi & Khodaii, 2009). With the addition of nanoparticles, cohesion and viscosity of asphalt may increase, which are good for high temperature conditions (Ping & Yunlong, 2014).

Nanosilica can enhance the anti-aging performance, fatigue cracking performance, rutting resistance, and anti-stripping property of the asphalt binder (Yang & Tighe, 2013). Literature studies showed that when 1% to 2% silica fume is added to asphalt cement, penetration decreased, ductility reduced, softening point increased, elastic strain recovery increased and temperature susceptibility increased as well (Sarsam, 2015). Sarsam (2013) found that increasing the silica fume from 1% to 4% increased the viscosity and softening point of the asphalt significantly, while it decreased the penetration value. Mojtaba et al., (2012) reported improved mechanical behaviour when a 2% nano-SiO_2 along with 5% Styrene–Butadiene–Styrene (SBS) were added to asphalt mixes.

Incorporation of up to 5% nanoclay in asphalt binder lowered the penetration value and increased the softening point (Zhang et al., 2014). Nanoclay commercial type Cloisite (3% and 6%) was found to increase the stiffness of the bitumen (Van de Ven et al., 2009). Commercial type Nanofill (6%) modification improved the aging resistance of a 70/100 penetration grade binder in both the short and long term (Van de Ven et al., 2009). El-Shafie et al., (2012) mixed a 64 penetration number base asphalt (99.9 cm ductility and 52 °C softening point) with 2%, 4%, 6%, and 8% by weight nanoclay at 2500 rpm and 160 °C for three hours. At 8% nanoclay content, the modified asphalt yielded a higher softening point temperature by 12 °C, decrease in penetration value by 25%, and increase in kinematic viscosity value at 135 °C and 150 °C by 222% and 145%, respectively. Asphalt (PG 70-22M), modified using nanoclay (Cloisite 20A) composite, was prepared at two modification percentages: 2% and 4% by weight. Nanoclay was found to enhance the stiffness and hardness of the asphalt binder at all temperatures (Nazzal et al., 2012). Mahdi et al., (2013) used three percentages of nanoclay (3.0, 5.0, and 9.0% by weight) with base asphalt binder (80 penetration number and 46.5 °C softening point). The blend was prepared mechanically by adding the nanoclay percentage gradually around 1 g/minute to the hot binder at established mixing temperatures of 150 ± 5°C and speed of 500 rpm. The results showed increase in penetration with increasing nanoclay concentration. The authors also reported a significant increase in the binder complex shear modulus (G*) and a decrease in the phase angle (δ) for the nanoclay-modified binders compared to the unmodified one.

The main objective of this research is to evaluate the rheological properties and performance of asphalt binder modified with two different locally manufactured nanomaterials: nanoclay and nanosilica.

2 Materials

Three different locally manufactured nanomaterials; nanoclay (NC), nanosilica synthetized from silica fume (NSF) and nanosilica chemically processed from rice husk ash (NSH) were used in this study. NC and NSF were both manufactured in the laboratories of "Housing and Building National Research Centre". NSH was manufactured as a part of a research study conducted at the Faculty of Science, Damanhur University, Egypt, which focused on producing nanosilica from rice husk ash (Hassan et al., 2014). The asphalt binder utilized in this research was obtained from the Suez Oil Company, Egypt. This is the typical binder that is commonly used in hot mix asphalt (HMA) in Egypt.

3 Experimental Work

The experimental work was divided into three major tasks; i) characterization of nanomaterials and the base asphalt binder, ii) determination of the optimum mixing process of nanomaterials with asphalt binder, and iii) laboratory testing the nanomodified asphalts. Following is a detailed description of these tasks.

3.1 Material Characterization

The investigated nanomaterials were first characterized using the Transmission Electronic Microscopy (TEM) in their dry powder state to evaluate their practical size distribution. The TEM image presented in Figure 1a shows a particle size range of 9 to 25 nm for NSF. Figure 1b shows that most of NSH particles ranged from 15 to 50 nm but some particles exceeded 150 nm. Finally, the nanoclay particles sized down to 6 nm. However, the particles tend to cluster and form batches up to 100 nm in size as shown in Figure 1c. Table 1 summarizes the particle size distribution of the nanomaterials as extracted from the TEM images. This data shows that the investigated NC is much finer compared to the nanosilica. Both NC and NSF can be considered as nanomaterials according to ASTM E2456-06. Some NSH exceeded the 100 nm limit to consider it as nanomaterial.

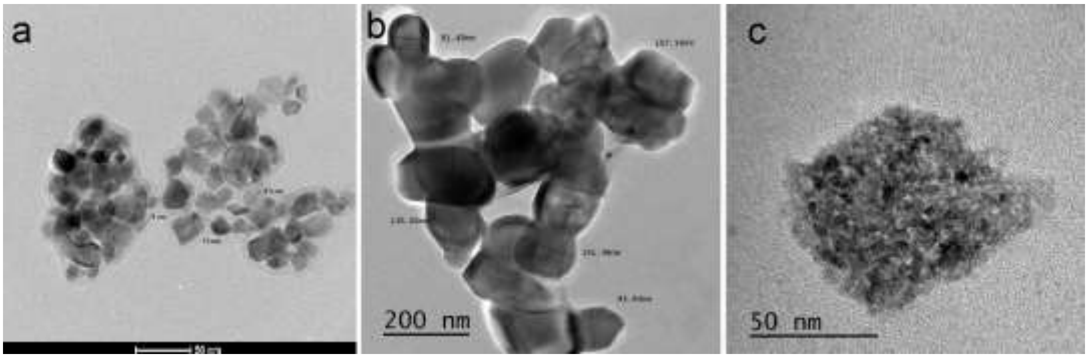

Figure. 1: TEM images for (a) NSF; (b) NSH; (c) NC

Nanomaterial (color)	5 ~15 nm	15 ~40 nm	40 ~100 nm	100 ~150 nm	>150
NC (light cream)	80%	20%	0%	0%	0%
NSF (white)	70%	25%	5%	0%	0%
NSH (white)	10%	20%	40%	20%	10%

Table 1: Nanomaterials rough particle size distribution.

The nanomaterials were also analyzed using the X-ray diffraction (XRD). The results are shown in Figure 2. Both NSF and NSH peak was at $2\theta \cong 22°$. The highest intensity of the peak is much larger for NSH as shown in Figure 2a and Figure 2b. NC peaks its largest at $2\theta \cong 27°$ with intensity at 150 counts as shown in Figure 2c. To calculate the average crystallite size of the nanoparticles, Debye–Scherrer diffraction formula shown by Equation (1) was used (Hall et al., 2000).

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where; $k = 0.9$, λ is the X-ray wavelength and β is the full width at half peak height. The obtained values of the crystallite size were around 9 nm for NSF, 26 nm for NSH and 6 nm for NC. Figure 2b. also shows impurities in the NSH indicating that it is not a pure silicon dioxide.

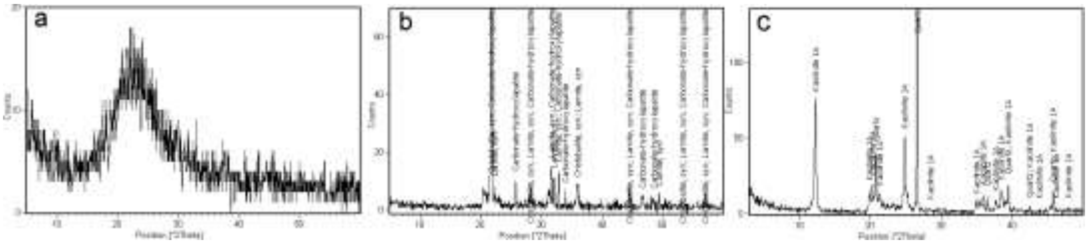

Figure 2: XRD images for (a) NSF; (b) NSH; (c) NC

For the asphalt binder, a control sample was tested first before adding any of the modifiers. This base binder (control) is referred to as (0%) nanomaterial in this research. The basic properties of the base binder are given in Table 2.

Property	Value	Test Method
Penetration at 25°C (*0.1mm*)	56	ASTM D5-06
Ring and ball softening point (*°C*)	41.9	ASTM D36-95
RV viscosity at 135°C/165°C (*cP*)	391.7/111.5	ASTM D4402M-15
DSR performance grade (*PG-xx*)	52	ASTM D7175-08
RTFO performance grade (*PG-xx*)	64	ASTM D2872-12e1

Table 2: Properties of base asphalt.

3.2 Mixing Nanomaterials with Asphalt Binder

Some nanomaterials are known to aggregate or cluster when mixed with the binder. Thus, it is important to select the appropriate mixing process in order to achieve a homogenous mixture of the asphalt and nanomaterial. There are three different types of mixers commonly used to mix the nanomaterials with binders. These mixers are mechanical, high shear, and ultrasonic mixers (Hasan et al., 2012). In this research, a mechanical mixer with a 1500 rpm speed was used. The mixing time was evaluated by mixing 5% of each of the investigated nanomaterials with the asphalt binder for 5, 10, 15, 30, 45, 60 and 75 minutes at a mixing temperature of 145°C ± 5°C. Brookfield rotational viscosity (RV) at 135 °C was selected for the mixing time evaluation. Scanning Electron Microscope (SEM) images were also used to capture the mixing time effect. As Figure 3a shows, NSF modified asphalt reached more than 90% of the viscosity at 75 minute in about 40 minute, while mixing for 5 minutes yielded a viscosity that is less than 20% of the 75- minute viscosity. The NSH modified asphalt reached 10% and 80% of the 75-minute RV viscosity at 5 and 40 minutes, respectively (Figure 3b). Finally, the NC modified asphalt needed an hour to reach 90% of the 75-minute RV viscosity, while it reached only about 65% of the 75-minute RV viscosity at 40 minutes (Figure 3c). In 5 minutes, NC modified asphalt reached 20% of its viscosity at 75 minute. For the three materials, the increase in viscosity between 40 minute and 75 minute was so small compared to the time and effort made.

SEM images confirmed the results when comparing a sample after 5 and 60 minutes of mixing the nanomaterial with the asphalt binder. Mixing for 60 minute provided better dispersion of the nanomaterial in the binder. NSF pockets are seen very clearly when mixing for only 5 minutes (Figure 4a), which are rarely seen after mixing for 60 minute (Figure 4b). The mixing time study concluded that the optimum mixing time is around 45 minute for nanosilica and 60 minute for nanoclay. Thus in this study, a mixing time of 60 minute was selected for all nanomaterials.

3.3 Testing the Modified Asphalt

Samples of the base asphalt binder were mixed with 3%, 5% and 7% of NC, NSF and NSH by weight of the binder for one hour at a temperature of 145 ± 5 °C. Penetration, softening point, RV viscosity and Dynamic Shear Rheometer (DSR) tests were conducted on the original and modified asphalts. A range of testing temperature was selected for the viscosity tests; 135, 145, 155 and 165 °C to evaluate binder behaviour over mixing and compaction temperatures. DSR tests were conducted over a range of temperatures; 46, 52, 58, 64, 70 and 76 °C for both unaged and Rolling Thin Film Oven (RTFO) aged samples.

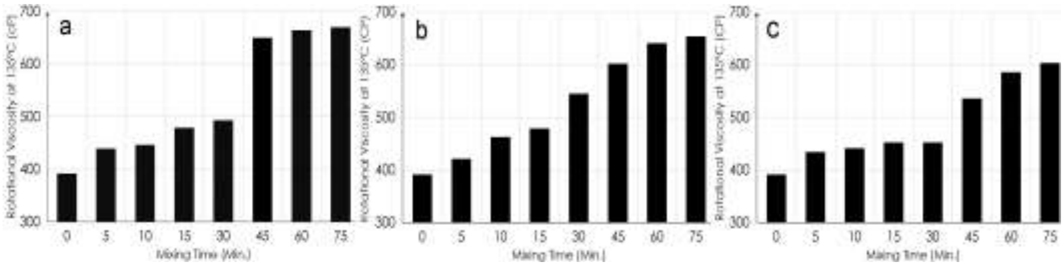

Figure 3: Mixing time effect on rotational viscosity for (a) NSF; (b) NSH; (c) NC

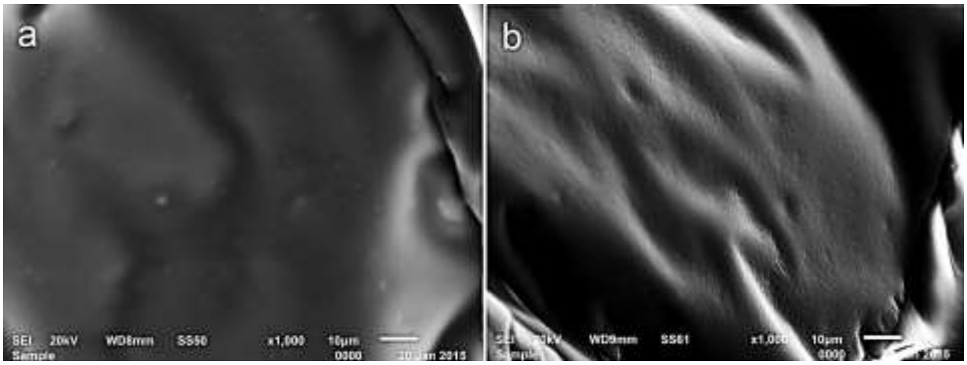

Figure 4: SEM images for 5% nanosilica modified asphalt (a) after 5 minutes; (b) after 60 minute

4 Results and Analysis

4.1 Effect of Heating, Cooling and Reheating the Modified Asphalt

In order to study the effect of asphalt cooling to room temperature after mixing with nanomaterials, batches of the modified binders were prepared and samples were tested for penetration, softening point, and viscosity at times of 1, 5 and 10 days from the mixing time. Nanomaterials with hot liquid asphalt binder were mixed, and then the binder was let to cool in room temperature, down to 18°C in some days. Samples were reheated again to a temperature up to the original mixing temperature of 145°C ± 5°C to pour it for testing. No significant influence was observed on the test results up to 10 days from the first testing day. Table 3 gives a summary of the impact of heating, cooling and reheating on the basic properties of the NSF modified asphalt as well as the mean standard deviation (σ) values for each test.

Property	Day 1	Day 5	Day 10	Mean	σ
Penetration at 25°C (*0.1mm*)	27	25	24	25.33	1.53
Softening point (*°C*)	46.3	47.5	48.0	47.27	0.87
Rotational viscosity at 135°C (*poise*)	6.60	6.75	6.50	661.67	0.13
Rotational viscosity at 165°C (*poise*)	1.60	1.66	1.63	163.00	0.03

Table 3: Test results over time for 5% NSF modified asphalt binder.

4.2 Rheological Properties of Modified Asphalt Binders

Figure 5 shows the influence of the nanomaterial type and content on penetration and softening point properties of the asphalt. Figure 5a. shows a relatively linear indirect relationship between the NSF content and penetration. The Figure shows that a significant improvement in the penetration occurs with the increase in the modifier concentration. For the NSH modified binder, as the percentage of the modifier increases, a linear decrease in the penetration occurs till 5% NSH. Adding more than 5% NSH did not show a significant improvement in the penetration (Figure 5b). The Nanoclay (NC) on the other hand decreased the base asphalt penetration from 55.5 down to 33.33 at NC content of 3% by weight. However, it increased the penetration afterwards up to 67 at 7% NC by weight of the asphalt binder. For the softening point, both nanosilica types increased it from 41.1°C to more than 48.0°C (Figure 5a, and b). Nanoclay increased the softening point up to 49.6°C at 3% then the values slightly decreased afterwards (Figure 5c). NC results indicated that higher percentages of NC material tended to cluster and form batches as presented earlier in (Figure 1c), therefore the optimum percentage of 3% NC was recommended.

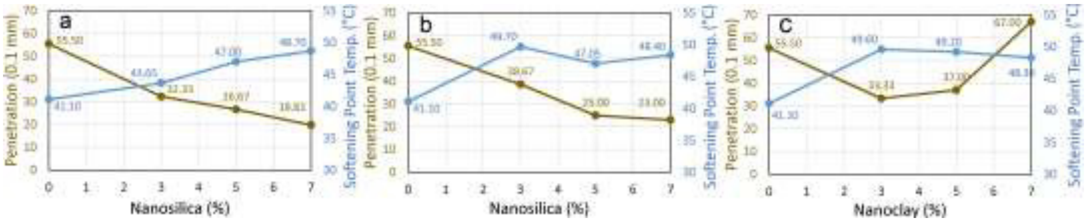

Figure 5: Effect of nanomodifier type and amount on penetration and softening point (a) NSF; (b) NSH; (c) NC

At temperature of 135°C, increasing the NSF to 7%, increased the RV viscosity by 210% as shown in Figure 6a. As the temperature increased, the influence of NSF presence on RV was minimized to become as small as 16.6% at temperature of 165°C. NC increased the viscosity at 135°C by more than 230% at 3% as shown in Figure 6c. However, increasing NC content to 7% decreased the viscosity to 153% compared to the base asphalt. At temperature as high as 165°C, the impact of increasing the NC content on the viscosity could be neglected. NSH changed the viscosity of the modified binders but it is almost the same for all the three percentages as shown in Figure 6b. This may be attributed to its large particles size. Therefore, NSH was not considered for further testing.

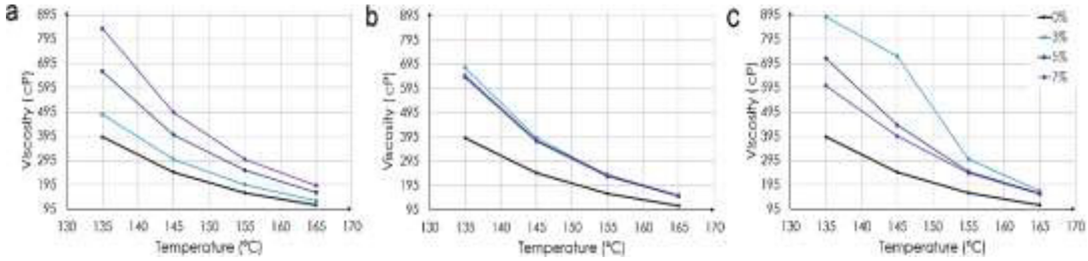

Figure 6: Rotational viscometer readings for asphalt binder modified with (a) NSF; (b) NSH; (c) NC

4.3 Performance Properties of Modified Asphalt Binders

It is clear from Figure 7 and Figure 8 that modified asphalt binders generally exhibited higher G* and lower δ values compared to the base asphalt, indicating better resistance to pavement rutting. In Figure 7, NSF increased the high temperature performance grade of the base asphalt (PG52-xx) to a higher performance grade of (PG70-xx) for both unaged (Figure 7a) and RTFO aged (Figure 7b) binders. This was achieved at the 7% NSF by weight of the base asphalt. Only 3% NC was found enough to pump the binder performance grade to (PG64-xx). Figure 8 shows that increasing the NC percentage above the optimum value of 3% results in a reduction in the performance grade. The low temperature performance of the binder was not studied in this research as the weather in Egypt is mostly hot to mild.

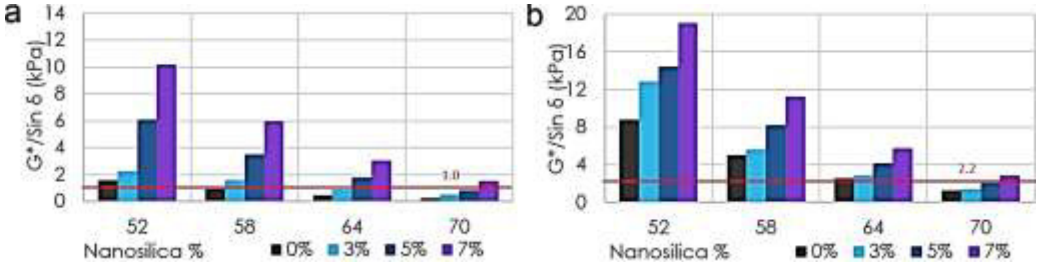

Figure 7: DSR results for NSF for (a) Unaged binder; (b) RTFO aged binder

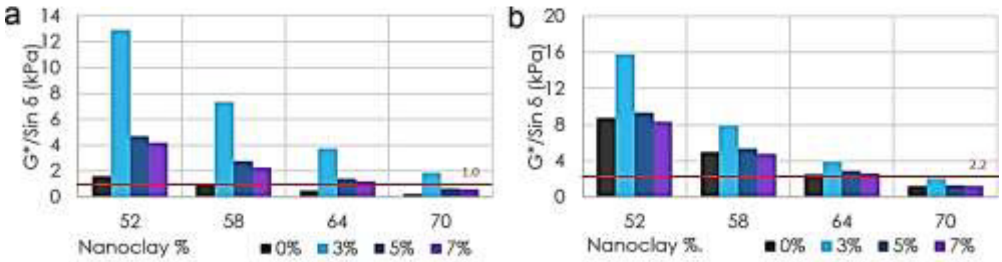

Figure 8: DSR results for NC for (a) Unaged binder; (b) RTFO aged binder

5 Conclusions

This study focused on the impact of using nanoclay and nanosilica to modify a base asphalt binder and the following can be concluded:

- When using a high-speed mechanical mixer at 1500 rpm, 30 to 40 minutes of mixing time was found enough to obtain good dispersion of the nanomaterial in the hot liquid asphalt binder. Longer mixing time may achieve slightly better dispersion but with higher energy consumption and cost.
- Storing the nanomodified asphalt binder for future usage up to ten days had no significant effect on its properties gained by modification in the first place.
- A 3% nanoclay by weight of asphalt improved the performance of the asphalt binder. The binder became more suitable for hot climatic conditions. The results showed lower penetration value, increased softening point temperature, and increased viscosity. An enhancement was also achieved in the high temperature performance grade.
- Increasing the nanoclay percentage to higher than 3% had an adverse effect on the binder properties and this appeared more clearly at the 7% nanoclay content.
- Nanosilica synthesized from silica fume is recommended for use in hot climates since it decreased the penetration and increased both the softening point temperature and the viscosity of the asphalt.
- Increasing the content of nanosilica synthesized from silica fume (NSF) increased the high performance grade of the binder and the Superpave rutting parameter (G*/sin δ).
- Asphalt resistance to permanent deformation could be enhanced using the right content of nano-modifier. Maximum performance grades of PG64-xx and PG70-xx for unaged and RTFO aged asphalts were achieved at 3% nanoclay and 7% nanosilica by weight of asphalt, respectively.

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