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Characterization of Unaged Asphalt Binder Modified with Carbon Nano Particles

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Abstract: In recent years, nanotechnology has been utilized in many engineering applications. In this technology, nano-sized particles are used in improving the properties of various materials. The construction industry, in general, has not embraced this technology; however, these particles could be used to enhance the physical and chemical properties of the materials such as asphalt binders. The objective of this study was to investigate and evaluate the rheological properties of three asphalt binder sources containing various percentages of carbon nano particles. The experimental design for this study included the utilizations of three binder sources (PG 64-22), one type of nano particle, and four nano dosage percentages (0.2%, 0.5%, 1.0%, and 1.5% by weight of the binder). The following rheological properties were tested and evaluated: viscosity, performance grade, creep and creep recovery, and frequency sweep. The results of the experiments indicated that the addition of nano particles was helpful in increasing the viscosity, failure temperature, complex modulus, and elastic modulus values as well as in improving rutting resistance of the binder. On the other hand, the content analysis of nano particles showed that a relatively low percentage (<0.2%) of nano particles did not have a significant effect on improving the binder properties while a relative high percentage (>1.0%) of nano particles is recommended for the modification of an asphalt binder.

***Key words**: Complex modulus; Frequency; Creep recovery; Creep compliance ; Nanotechnology; Performance grade; Viscosity.*

Introduction

Nanotechnology is a relatively new field in science dealing with structures that are on the nano-scale. To illustrate how miniscule the nano-scale is, the following comparison could be made: if a human hair has a diameter of a football field, a nano-sized particle would have the diameter of a pencil. In 1985, Kroto and Smalley first discovered buckminsterfullerene and since then this technology has evolved rapidly [1]. Nano-sized particles have been used in numerous applications to improve various properties. However, due to many reasons including the cost of production and purification, nano-sized particles have seen very little use in the construction field. One of the promising additives in the construction field is the use of carbon nanotubes. In 1991, these materials were first characterized in depth by Iijima [2].

In general, carbon nanotubes are made of sheets of graphite that have rolled up to form a tubular structure. This is accomplished through various methods with a majority of them using electricity and an inert gas in an enclosed chamber [3]. There are two general types of carbon nanontubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Because of the physics involved, MWNTs are easier and cheaper to produce [4]. However, they lack the strength found in SWNTs [4]. Nevertheless, SWNTs are found in bundles whereas MWNTs are found as individual molecules, allowing MWNTs to be dispersed efficiently in a material [4]. MWNTs are also stiffer than SWNTs and have a longer length, sometimes approaching the centimeter range [4]. The type and production of nanotubes will determine the diameter the materials which could range from 0.4nm (the smallest possible value) [5] up to several hundred nm [4]. This combination of long length and small diameter can lead to aspect ratios approaching 1,000,000:1. This gives rise to unique engineering characteristics such as some of these materials having a Young's Modulus of anywhere from 18 GPa to 68 GPa with a failure strain of 0.12 (12%) [6]. In addition, they can possess a tensile strength anywhere from 1.4 GPa to 2.9 GPa [6]. All of these properties make carbon nanotubes ideal candidates for improving the mechanical properties of various construction materials.

Wu *et al*. [7] found that the modification applying nanoclay can not only improve the properties of bitumen but also lower costs to a great extent. In addition, Liu *et al*. [8] indicated that the montmorillonite nanoclay has been used successfully to strongly improve properties of polymer-modified binder. Even though and Xiao *et al*. [9, 10] considered that carbon nano particle is beneficial in improving the rheological properties of modified asphalt binder after short-term and long-term aging procedures, there are still many challenges and difficulties to utilize these carbon nano particles to enhance the properties of construction materials. There is a need for more research in utilizing nanotechnology to improve the rheological and engineering characteristics of unaged asphalt binders and develop some guidelines for their use in construction materials in general. The interaction of unaged modified binders is not well understood from the standpoint of binder properties and field performance. In addition, the research of nano particles in asphalt binders can expand the use of modified binders. Because of the complicated relationships of asphalt binders and carbon nano particles in the modified binders, detailed information will be

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Table 1. Rheological Properties of Virgin Binder.

Binder Type	Source	Aging States					
		Unaged	Unaged	RTFO	PAV		
		Viscosity(135℃) (cP)	$G^*/\sin\delta$(64℃) (kPa)	$G^*/\sin\delta$(64℃) (kPa)	$G^*/\sin\delta$(25℃) (kPa)	Stiffness(-12℃) (MPa)	m-value (-12℃)
PG 64-22	A	645	2.03	4.94	1429	103	0.376
PG 64-22	B	465	1.28	2.87	3229	257	0.312
PG 64-22	C	472	1.46	2.56	3660	175	0.307

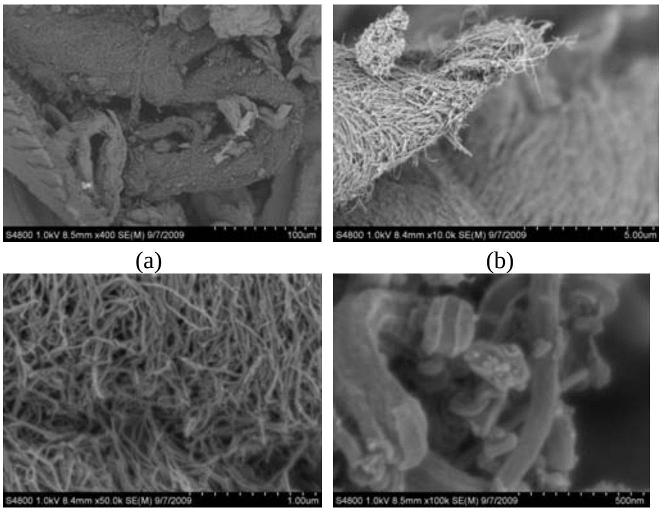

Fig. 1. SEM Images of Carbon Nano Particles, (a) 100 μm; (b) 5 μm; (c) 1 μm; (d) 500 nm.

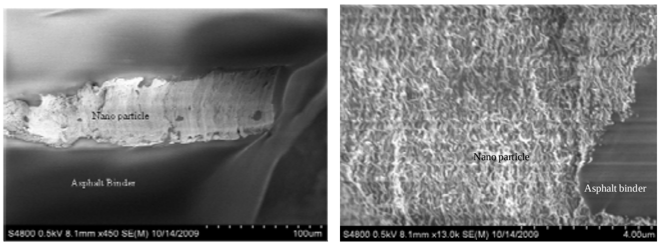

Fig. 2. SEM Images of Carbon Nano Particles with Asphalt binder, (a) 100 μm; (b) 4 μm.

beneficial to help obtain an optimum balance in the use of these materials.

The goal of this study was to determine some of the rheological properties of three asphalt binders containing various dosage percentages of carbon nano particles. Experiments were carried out to evaluate properties of the binder such as, viscosity, complex modulus, phase angle, creep and creep recovery, and frequency sweep utilizing four different dosage percentages of nano particles (i.e., 0.2%, 0.5%, 1.0% and 1.5% by weight of the virgin binder) mixed with three PG 64-22 asphalt binders.

Experimental Process and Materials

Materials and Testing

Three PG 64-22 asphalt binders from various sources (referred to A, B, and C) was used to blend with nano particles (produced from carbon) in this study. The properties of these virgin binders are shown in Table 1. Nano particles, a commercial product, came from a manufacture that has produced carbon nanotubes for various uses in industry (Fig. 1). Four dosage percentages (0.2%, 0.5%, 1.0% and 1.5% by weight of binder) of nano particles (Fig. 2) were employed and these particles were blended with virgin asphalt binder. Approximately 40 grams of asphalt binder were poured into a 140 ml glass beaker, and then nano particles based on various percentages were added into each individual beaker. And then these materials were heated to 163^{o}C (325^{o}F) on a hot plate and were blended using a medium-shear radial flow impeller at a speed of 300 rpm and a temperature of 163^{o}C for 30 minutes in the laboratory. The reaction process used for this research was the same procedure that was developed by Xiao *et al*. [11, 12] for crumb rubber reaction and mixing temperature of virgin binders in previous research projects.

A Brookfield rotational viscometer was used to test the viscosity of the modified binders at four different temperatures (e.g. 120^{o}C, 135^{o}C, 150^{o}C and 165^{o}C) in accordance with AASHTO T316. A number 21 spindle and a specimen size of 8.5 grams were used for this study. Prior to pouring each sample, the container of modified binder was gently stirred for one minute to disperse the nano particles throughout the binder.

The high temperature rheological properties of each binder were measured using a dynamic shear rheometer (DSR) according to AASHTO T315. In this research project, a one millimeter gap and 25 mm diameter plate were used to obtain DSR values at the high temperatures. Each binder was measured in terms of the complex shear modulus (G^*) and phase angle (δ) values starting from 64ºC until failed in accordance with Superpave mix design specifications.

In addition, some tests such as creep/creep recovery, viscous flow measurements, and frequency sweep also were performed at 60ºC for each blended binder. Creep/creep recovery tests were run at three different stresses in this study, 3 Pa, 10 Pa, and 50 Pa (loading for 50 sec. and 200 sec. recovery). These stresses represent the low, medium and high stress levels on a pavement. In addition, viscous flows of the binders were measured at varying shear stresses. Moreover, for the frequency sweep tests, frequency ranges from 0.01 to 20 Hz were run at the lowest possible strain. Typically, a frequency of 1.59 Hz simulates the shearing action corresponding to traffic speed of about 55 mph.

Results and Discussions

Viscosity

The viscosity of an asphalt binder is used to determine the flow

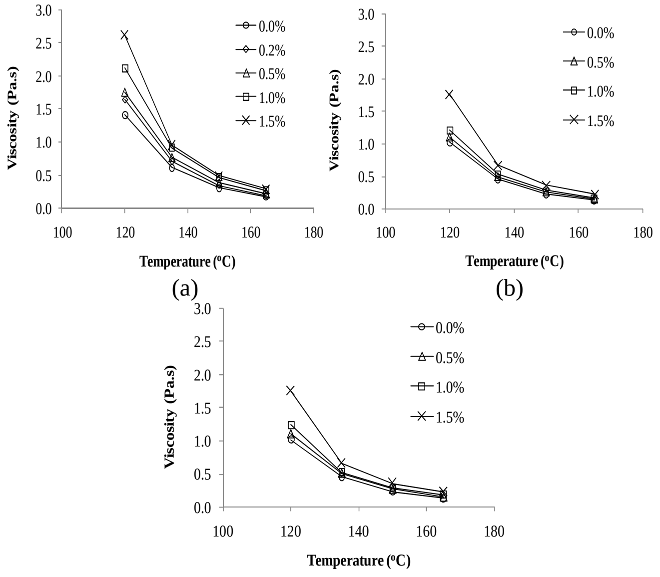

Fig. 3. Effects of Nano Dosage Percentage on Viscosity at Various Testing Temperatures, (a) Binder A; (b) Binder B; and (c) Binder C.

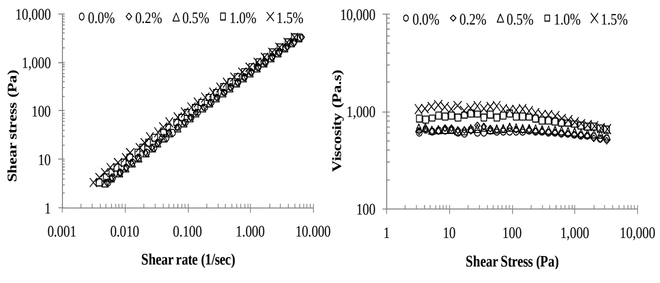

Fig. 4. Typical Effects of Nano Dosage Percentage at 60^{o}C, (a) Flow Curves; (b) Viscosity Curves.

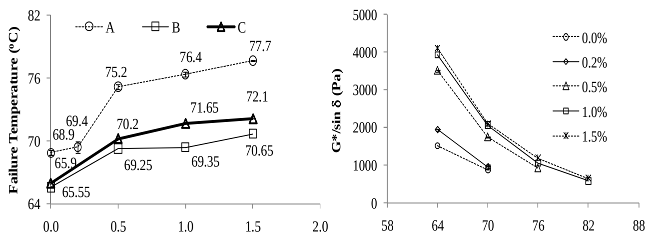

Fig. 5. Effects of Nano Dosage Percentage on Binders, (a) Failure Temperature; (b) G*/sin δ of Binder A.

characteristics of the binder to provide some assurance that it can be pumped and handled at the hot mixing facility; also to determine the mixing and compacting temperatures of asphalt mixtures. Fig. 3 illustrates that, as expected, the viscosity values of all asphalt binders decrease as the test temperature increases. These values decrease at a higher rate from 120^{o}C to 135^{o}C than 150^{o}C to 165^{o}C. In addition, it can be noted that the viscosity value increases as nano particles content of binder increases. The binder with 1.5% nano particles shows the greatest viscosity value compared to other binders. This result illustrates that the highest mixing and compaction temperatures are needed for this binder. However, statistical analysis results indicate that the viscosity values between 0.2% and 0.5% are not significant at all test temperatures (Fig. 3(a)). Additionally, at 120^{o}C, the differences amongst five binders are noticeable, but at 160^{o}C, the viscosity values of all binders are close. Obviously, at a relatively high temperature, the effect of nano particles on the viscosity is weakened.

On the other hand, the absolute viscosity values of the binders with or without nano particles were also measured at varying shear rates at 60^{o}C and their relationships are shown in Fig. 4. It can be seen that the binders exhibited an increasing shear stress as the shear rate is increased. Also, it can be noted that binders exhibits a non Newtonian, shear thinning flow, as the viscosity decreases with an increase in shear rate. It can be seen that the addition of the nano particles increased the viscosity of the binders at 60^{o}C, but the binder with a low nano dosage percentage (e.g., 0.2% and 0.5%) only exhibits a slight increase in viscosity value. However, the statistical results indicate that the binder containing 1.0% or 1.5% nano particles has a significantly high viscosity in comparison with the virgin binder. This means that the nano particles makes the binders stiffer at the maximum pavement service temperature and is beneficial in improving resistance of permanent deformation.

Performance Grade

The grade determination feature of the DSR was used to determine the failure temperature for each binder with or without nano particles in the original unaged state. This procedure tests the sample at a starting temperature (i.e., 64^{o}C for PG 64-22 base binder) and increases the temperature to the next PG grade (e.g., 70^{o}C) if the G*/sin δ value is greater than the value required by AASHTO M320 (1.000 kPa for original binder). After recording all of the data, the failure temperature is determined through interpolation as the temperature at which the G*/sin δ value is less than the required value. Two replicates were tested for each aging condition of each binder. Fig. 5(a) illustrates that addition of nano particles results in an increase in failure temperature, especially, as the dosage percentage of nano particles increases from 0.2% to 0.5%, the failure temperature rises remarkably. In general, a PG grade (6^{o}C) is achieved as the addition of nano particles is greater than 0.5%. In addition, based on the values of complex modulus (G*) and phase angle (δ), Fig. 5 (b) also indicates that, regardless of at a starting temperature of 64^{o}C or higher test temperatures, Binder A containing 1.5% nano particles has the highest G*/sin δ value while virgin binder shows the lowest value. Moreover, both virgin binder and the binder with 0.2% nano particles have the G*/sin δ value less than 1.000 kPa at 70^{o}C. However, the G*/sin δ values of binders with 1.0% and 1.5% nano particles is greater than 1.000 kPa at 76^{o}C. Binders B and C have similar trends with Binder A. As a result, one can conclude that the addition of nano particles has a significant effect on PG grade of this binder and contributes to an improvement of rutting resistance at a high performance temperature [13].

Creep and Creep Recovery

Creep is defined as the slow deformation of a material measured under a constant stress. In a creep test, a fixed shear stress is applied to the sample and the resultant strain is monitored for a predetermined amount of time. This gives an idea of the permanent deformation that the binder will undergo. After a predetermined period of time, the stress is removed, and the strain is further monitored. This allows the material to recover for a longer duration of time [14, 15]. Since the actual change of strain depends on the applied stress, compliance is used as a measure of creep rather than strain. The compliance is expressed as the ratio of strain to the applied stress. Thus, a lower value of compliance at any given stress level implies higher deformation resistance. As mentioned earlier, this test was repeated at three different applied loadings 3 Pa, 10 Pa, and 50 Pa. These stresses simulate the low, medium and high intensity of traffic on the pavement. Fig. 6 shows the creep and creep recovery curves for all binders at various stresses. It can be seen that, as expected, the virgin binder has the highest compliance value while the binder containing 1.5% nano particles exhibits the lowest one regardless of the loading stress level. This result indicates that the nano particles can effectively improve the deformation resistance of the asphalt binder due to the reduction of compliance value. In addition, the test results illustrate that the compliance value has a very slight reduction due to the removal of stress after a 50-second loading and each of binders exhibits an obvious viscous property at this test temperature (60^{o}C). Furthermore, Fig. 6 also presents that, in general, the binder does not show a noticeable different compliance values after three loadings. The only difference is that the binder with 1.5% nano particles has an obvious lower compliance value as using a loading stress of 50 Pa. The reason for this may be that a relative high dosage percentages of nano particles yield higher deformation resistance under a higher loading stress.

Frequency Sweep Tests

The frequency sweep tests were performed in two types of loadings which were under control stress and stress proportional to frequency. The former used frequencies between 0.1 to 10 Hz while the latter employed a range of frequency from 0.01 to 20 Hz. The overall frequency sweep tests were run with the 25 mm diameter and 1 mm testing gap geometry at 60°C. Previous research papers indicated that the frequency sweep tests at various frequencies and temperatures could identify the linear viscoelastic response of binders [15-20].

Control Stress Tests (0 Loading)

The frequency dependency of the modified binder in terms of complex modulus and phase angle was assessed by employing rheological master curves. The master curves for binders with and without nano particles (under control stress = 0) are presented in Fig. 7. It can be seen that the complex modulus values of all binders increase as a higher frequency is used. In addition, as shown in Fig. 7, the results show that the complex modulus values of binders are the same regardless of their materials while their phase angle values were zero.

Stress Proportional to Frequency Tests

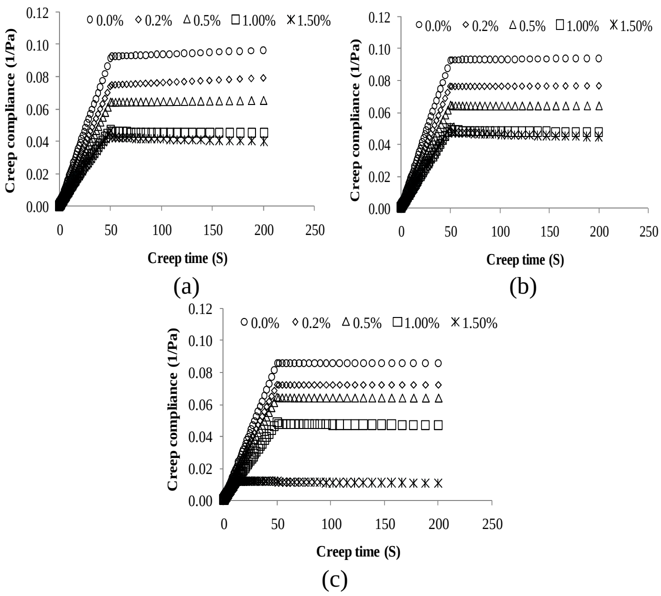

Fig. 6. Typical Effects of Nano Dosage Percentage on Creep Compliance, (a) 3 Pa; (b) 10 Pa; (c) 50 Pa.

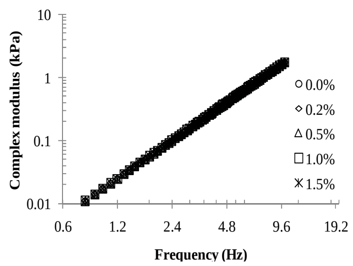

Fig. 7. Typical Master Curves of the Binders (Control Stress).

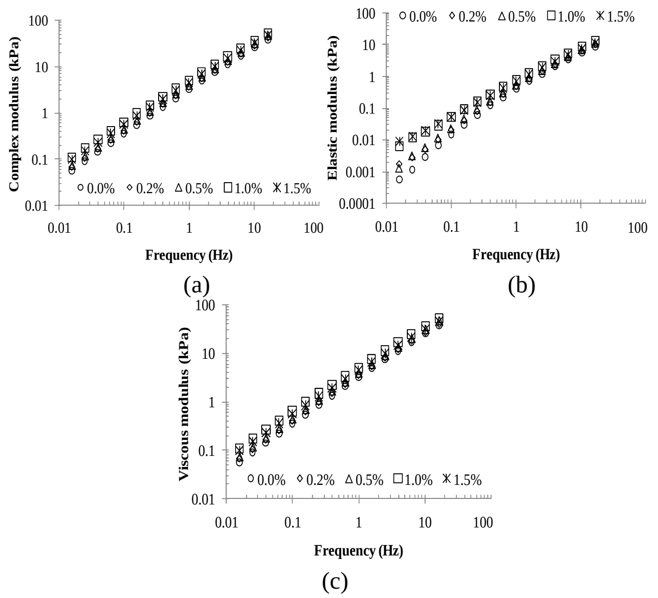

Fig. 8. Effects of Nano Dosage Percentage on the Binder at Various Frequencies (Auto-stress), (a) Complex Modulus; (b) Elastic Modulus; (c) Viscous Modulus.

In the stress proportional to frequency tests, not only complex modulus and phase angle but also elastic modulus and viscous modulus were evaluated in accordance with various frequencies and

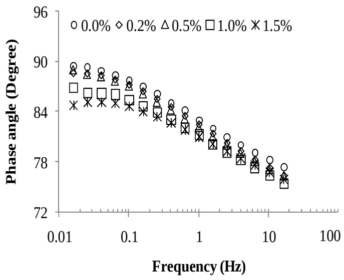

Fig. 9. Phase Angle Changes in Terms of Frequency (Stress Proportion).

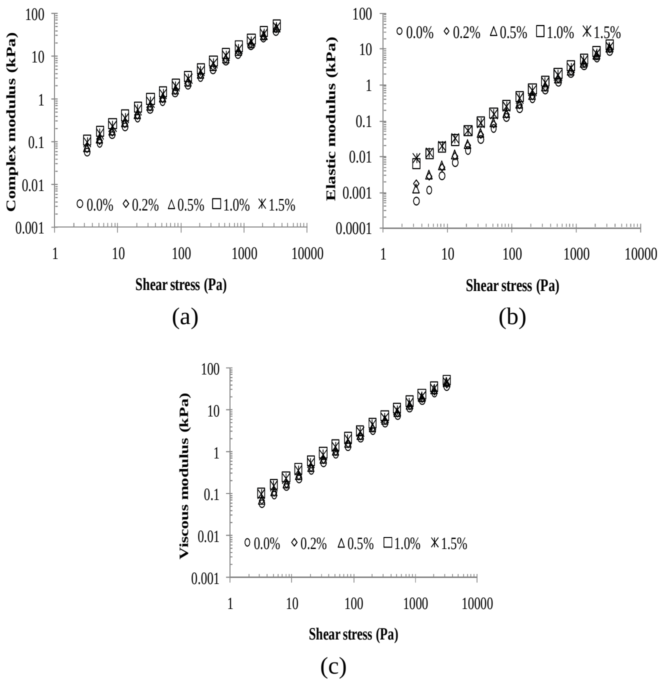

Fig. 10. Effects of Nano Dosage Percentage on Asphalt Binder at Various Shear Stresses, (a) Complex Modulus; (b) Elastic Modulus; (c) Viscous Modulus.

stresses. Fig. 8 displays the influence of frequency sweeps on the complex, elastic, and viscous modulus values of all binders at 60^{o}C. It can be found that an increase in frequency yields an increase in these modulus values for all binders regardless of nano particles' amount. However, the binder with 1.5% nano particles shows a slightly higher complex, elastic, and viscous modulus values in comparison with other binders while virgin binder has the lowest values at varying test frequencies. Moreover, as the binder was tested at a lower frequency (less than 1 Hz), the addition of nano particles is remarkably beneficial in increasing these modulus values, but the influence of nano particles is weakened after the frequency increases to 10 Hz (significantly viscous).

The phase angle with testing frequencies are shown in Fig. 9. Generally, an increase in frequency results in a decrease of phase angle for all binders. At a low frequency, the binder containing 1.5% nano particles presents the lowest phase angle while virgin binder has the highest value. This means that the addition of nano particles to these binders increases the elastic characteristics of the binder. Similar to the modulus analysis, at a higher frequency, the difference of phase angle amongst five binders is not significant.

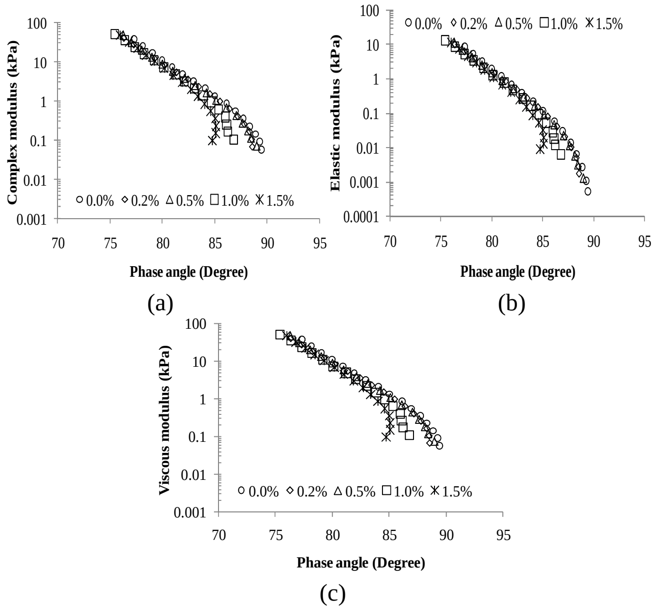

Fig. 11. Effects of Nano Dosage Percentage on Asphalt Binder at Various Phase Angles, (a) Complex Modulus; (b) Elastic Modulus; (c) Viscous Modulus.

The reason is that all binders exhibit the relative high viscous property due to the high testing frequency and thus the influence of nano particles on phase angle can be ignored.

The effects of shear stress on complex, elastic, and viscous modulus values are presented in Fig. 10. The test results illustrate that the increase in shear stress results in an increase in complex and elastic modulus, as well as viscous modulus values. Under various loadings, the binder with 1.5% shows a slightly higher modulus value compared to other binders. At a low shear stress, the binder with nano particles shows a higher modulus value since the addition of nano particles makes the binder's elastic more predominate. A high shear stress creates a viscous binder and thus the modulus values of all binders are close to each other.

Fig. 11 indicates that the increase of phase angle reduces the complex, elastic, and viscous modulus values for all binders. The test results illustrate that the influence of nano particles is not noticeable on the modulus values as the phase angle is less than 80 degrees. As shown in Fig. 11, the binder with a higher percentage of nano particles has a lower phase angle value while the binders containing the lower percentage particle and virgin binder have the curves with a shift towards more viscous response (higher phase angles).

Findings and Conclusions

In this limited study, the viscosity results indicate that, as expected, the addition of nano particles increased the viscosity values of asphalt binders, tested in this research work, at the same test temperature; this may result in a higher mixing and compaction temperatures. However, this increase is not significant if a low percentage of nano particles (0.2%) or being tested in a relatively high temperature (more than 135^{o}C) were employed. In addition, at a test temperature of 60^{o}C, the viscosity value resulted in a reduction as the shear stress value increases. The binders with 1.0%

and 1.5% nano particles exhibit obviously greater viscosity values at various shear stress conditions.

The addition of nano particles has a significant effect on PG grade of the binder and contributes to an improvement of rutting resistance at a high performance temperature. Though a higher percentage of nano particles produces a higher failure temperature, however, a binder containing 1.0% nano particles caused an increase of one level of PG grade (6^{o}C). In addition, complex modulus and phase angle results indicate that the binder containing a higher percentage of nano particles has a greater $G^*/\sin\delta$ value. Thus, for the binders tested, a nano content greater than 1.0% is recommended to use in the modification of these asphalt binders.

Creep and creep recovery results illustrate that the nano particles can effectively improve the deformation resistance of an asphalt binder due to the reduction of compliance value. In addition, the test results illustrate that the compliance value of each binder with or without nano particles has a very slight reduction and exhibits an obvious viscous property after removing a 50-second loading.

Frequency sweep results show that the addition of a higher percentage of nano particles results in a greater phase angle, complex modulus, elastic modulus, and viscous modulus values. Moreover, under a relatively low frequency and shear stress loading, the binder containing 1.5% nano particles exhibits the lowest phase angle and the highest elastic modulus.

In summary, the research findings show that the addition of nano particles in asphalt binders tested in this research program improves some of the rheological properties such as performance grade and rutting deformation. This technology may be used for further research in asphalt pavement area.

Acknowledgments

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