Engineering Properties of Nanosilica Modified Asphalt Binder

Ahmad Kamil Arshad
Institute for Infrastructure Engineering and Sustainability Management (IIESM) Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia

Mohamad Saifullah Samsudin
Faculty of Civil Engineering, Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia

Khairil Azman Masri
Faculty of Civil Engineering and Earth Resources, Universiti Malaysia Pahang, Pahang, Malaysia

ABSTRACT

The effect of nanosilica (NS) on aging resistance as well as stiffness of asphalt binder was investigated. X-ray diffraction (XRD) was used to evaluate nanosilica dispersion in asphalt binder. Nanosilica modified binder (NSMB) samples were aged using the rolling thin film oven (RTFO) and pressure aging vessel (PAV) to simulate short-term and long-term aging processes of asphalt binder before testing. The fourier transform infrared spectroscopy (FTIR) and dynamic shear rheometer (DSR) were carried out to obtain the chemical and rheological properties of NSMB. From the XRD test, it was found that the addition of NS changed the phase of the base asphalt binder from amorphous to semi-crystalline. FTIR spectroscopy showed that the addition of NS into the asphalt binder can delay and weaken the oxidation reaction binder which could improve the aging resistance. From DSR test, it was found that the addition of NS significantly increased the $G^*/\sin \delta$ value and decreased the strain value of asphalt binder. This showed that the addition of nanosilica in asphalt binder results in higher elasticity and is beneficial in increasing the rutting resistance compared to the base asphalt binder.

Keywords: *modified asphalt binder, nanosilica, x-ray diffraction, fourier transform infrared spectroscopy, dynamic shear rheometer*

ISSN 1823-5514, eISSN2550-164X

Received for review: 2019-06-04
Accepted for publication:2019-10-15
Published:2019-12-31

Introduction

Asphalt or bitumen is a complex hydrocarbon and it can be naturally occurring or residue from the distillation process of crude petroleum. Asphalt binders are composed of organic molecules, it will react with oxygen from the surrounding and change the composition and structure of the asphalt molecules. The term 'age hardening' and 'oxidative hardening' usually refers to the reaction of asphalt and oxygen. The aging of asphalt binder will lead to premature deterioration of the asphalt pavement. At high temperatures, oxidation occurs more quickly compared to low temperature [1]. In the laboratory, the aging of asphalt binder can be accelerated by using rolling thin film oven (RTFO) and pressure aging vessel (PAV). RTFO was used to simulate aging of asphalt binder during storage, mixing, transport and laying down, while PAV was used to simulate the aging during in service life.

The use of nanotechnology in asphalt binder modification promise better results in improving aging resistance. Various materials have been used to modify asphalt binder such as carbon nanotube (CNT) and nanoclay (NC). Santagata et al. [2] found that the addition of CNT reduced the susceptibility of asphalt binder to oxidative aging. Besides that, Onochie reported aging resistance also improved with addition of nanoclay [3].

NS is an inorganic material which has a maximum dimension about 30nm. NS possesses good properties such as large surface area, good dispersal ability, strong adsorption, high chemical clarity and excellent stability [4]. Therefore, in this study, NS was used as a modifier to modify base asphalt binder in order to improve aging resistance and stiffness of asphalt binder.

Material and Properties

Sample Preparation

Asphalt binder was blended with 1% to 5% NS (1% increment) by weight of the virgin asphalt binder. The modification of asphalt binder was conducted by a mechanical mixer. Asphalt binder was heated up to 160°C until it achieves the processing viscosity. A cylindrical container was filled with about 400g of the base asphalt binder and was placed on a hot plate. The temperature of hot plate was set to 160°C to maintain the viscosity of asphalt binder during mixing. NS was gradually added into the asphalt binder while stirring with mechanical steel stirrer. The speed of stirrer was set to 2000 rpm. The mixing process continued for one hour in order to achieve uniform dispersion of NS. The NSMB was placed in the oven to remove the bubbles, before preparing the test sample. To facilitate in referring each sample containing different NS content, they were named by the following abbreviations: NSMB 0%, NSMB 1%, NSMB 2%, NSMB 3%, NSMB 4% and NSMB 5%.

Aging procedure

All asphalt binders were aged by rolling thin film oven (RTFO) and pressure aging vessel (PAV). RTFO was used to simulate short term aging and measured the effect of heat and air on a moving film of semi-solid asphaltic binder. A temperature of 163°C for a duration of 85 minute were used to produce aging effects comparable to the average asphalt plant condition. PAV was used to simulate long term aging equivalent to 5-10 years of in-service pavement [5].

X-ray diffraction (XRD)

The XRD was used to provide a quantitative analysis of the interlayer gallery spacing and it provided a way to determine the extent of dispersion of the NS in the binder. XRD was performed individually on the base asphalt binder and NSMB. The NSMB was heated and poured into the XRD mould and the sample surface must be ensured that it was flat. XRD (model ULTIMA IV) was used in this study.

Fourier transform infrared spectroscopy (FTIR)

Chemical characterisations of base and NSMB before and after aging were performed using PerkinElmer Spectrum 400 FT-IR, FT-NIR. All spectra were obtained by 32 scans with 5% iris and 4 cm-1 resolutions in wave numbers ranging from 4000 to 500 cm^{-1}. The ratio changes of chemical bonding were calculated using Equation 1 and Equation 2 by neglecting the sample thickness [6].

$$I_{S=O} = \frac{Area\ of\ the\ sulfoxide\ band\ centered\ around\ 1030\ cm{-1}}{\sum Area\ of\ the\ spectral\ bands\ between\ 200\ cm{-1}\ and\ 600\ cm{-1}} \quad (1)$$

$$I_{C=O} = \frac{Area\ of\ the\ carbonyl\ band\ centered\ around\ 1690\ cm{-1}}{\sum Area\ of\ the\ spectral\ bands\ between\ 200\ cm{-1}\ and\ 600\ cm{-1}} \quad (2)$$

Dynamic shear rheometer (DSR)

A stress controlled HAAKE dynamic shear rheometer (DSR) was used in this study to evaluate the rheological properties of NSMB. For this study Dynamic Shear Rheometer (DSR) test were conducted to determine permanent deformation of rutting in terms of complex shear modulus (G*) and phase angle (δ). For permanent deformation or rutting, the test was conducted using unaged and RTFO samples and performed at six different temperatures at 48°C, 52°C, 58°C, 64°C, 70°C, and 76°C. To predict the rutting resistance of asphalt binder, G*/sin δ was used. The repeated shear creep test was conducted under two stress level (100 Pa and 3200 Pa) for 10 cycles with 1s loading time and 9s recovery time at 64°C

Results and Discussions

Xray diffraction (XRD)

The structural characteristics of NSMB were determined by XRD as shown in Figure 1. It can be observed that the base asphalt binder was completely amorphous (non-crystalline) where there is no any clearly defined peaks. The modification of the base asphalt binder with NS changed the phase of the base asphalt binder from amorphous to semi-crystalline where the peak clearly can be seen around the angle 21^0 to 22^0. This peak value was slightly similar with previous research where the peak was around 23^0 [7,8]. XRD also provided the measurement of d-spacing of NS and NS dispersed in the base asphalt binder as shown in Figure 2. The d-spacing of base asphalt binder found to be 0 while for NSMB 1%, NSMB 2%, NSMB 3%, NSMB 4% and NSMB 5% were found to be 4.65, 4.71, 4.79, 4.74 and 4.67, respectively.

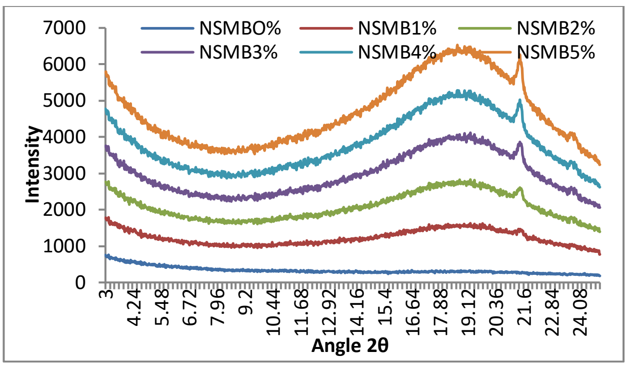

Figure 1: XRD pattern of NSMB

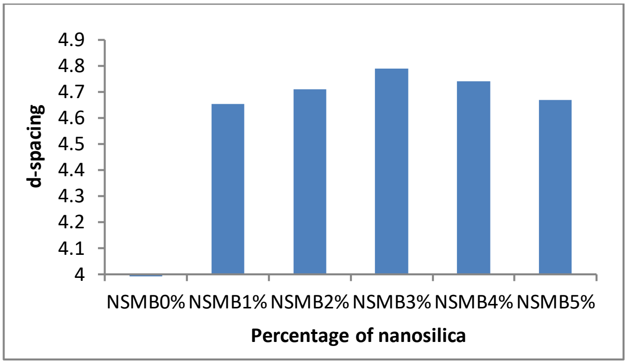

Figure 2: D-spacing of NSMB

Fourier transform infrared spectroscopy (FTIR)

FTIR was used to determine the chemical bonding changes of base and NSMB after RTFO and PAV ageing. Figure 3 (a) to (f) shows the absorbance bands of NSMB samples from 500 cm-1 to 4000 cm-1 of wavenumber collected from FTIR testing. From the figure it can be observed that the trends of base and NSMB are similar for all cases of unaged, RTFO-aged and PAV-aged. Figure 3 (a) to (f) show that the majority of the absorbance bands are between 1375-1530 cm-1 and 2850-3000 cm-1 where these bands attribute to aromatic hydrocarbon and saturated hydrocarbon respectively. These bands are not very usefull to characterize aging present in the NSMB. Since this testing is aimed to analyse the effect of aging on the NSMB, then only the peak areas around spectral bands at 1030 cm-1 and 1700 cm-1 were analysed. These two peaks attribute to sulfoxide (S=O) and carbonyl (C=O).

Figure 4 shows the structural index of NSMB before and after RTFO-aged and PAV-aged. Generally, the carbonyl and sulphoxide index were higher in most NSMB cases (unaged, RTFO and PAV) compared with the base asphalt binder. This phenomenon indicates that the addition of NS increased the carbonyl and sulphoxide index of asphalt binder, these results is similar to the study by You et al. [9]. In addition, during the modification process, the binder undergoes aging process, causing the value of carbonyl and sulphoxide index of NSMB to be higher than that of base asphalt binder. For all binder except NSMB 3%, the sulphoxide index increased after aging by RTFO, indicating that the functional sulphoxide increased during short term aging, however after aging by PAV the value of sulphoxide indexes were inconsistent. Thus, the use of sulphoxide index as an aging index may be inconclusive.

From Figure 4, the carbonyl index of NSMB mostly increased after RTFO and PAV aging. Previous researchers had shown that the higher oxidation rate leads to more carbonyl [10]. Yao et al. found that, the carbonyl index will increase after RTFO and PAV aging. The result form these studies coincided with this study where most of carbonyl index for NSMB increased after RTFO-aged and PAV-aged. The increase of carbonyl index was more pronounced after aging by PAV compared to aging by RTFO. After consideration of carbonyl index, the oxidative index of NSMB was calculated. This is discussed in the next section in this paper.

To evaluate the effect of NS on the resistance of NSMB to oxidative aging for FTIR, the oxidative index was calculated using Equation 3. The main parameters used in this calculation are carbonyl index for unaged sample and PAV aged sample.

$$\text{Oxidation index} = \frac{carbonyl\ index\ after\ PAV\ aged}{carbonyl\ index\ unaged} \quad (3)$$

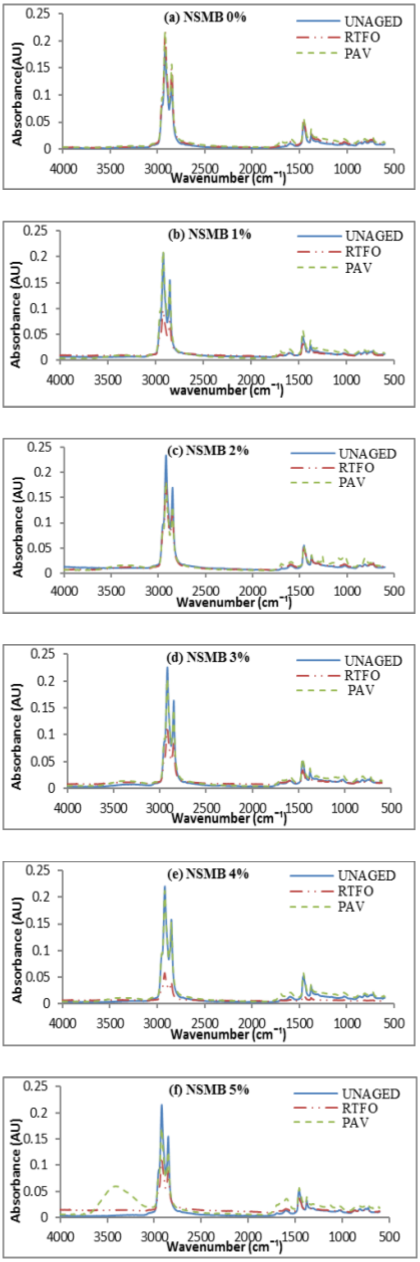

Figure 3: FTIR spectra of NSMB

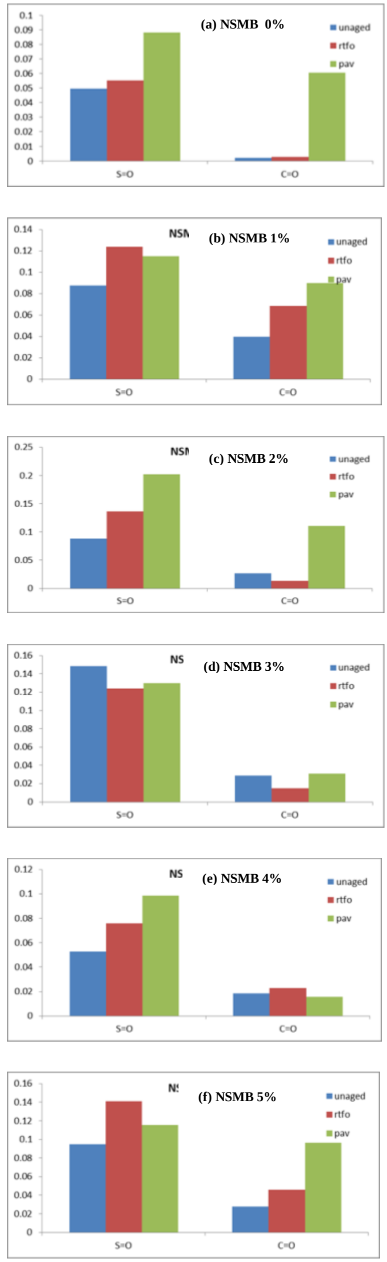

Figure 4: Structural index of NSMB

Figure 5 shows the oxidative index of NSMB. It can be seen that the oxidative index values of NSMB were lower than that of base asphalt binder. It was found that the oxidative values of NSMB-0%, NSMB-1%, NSMB-2%, NSMB-3%, NSMB-4% and NSMB-5%, were 27.3, 2.3, 4.1, 1.1, 0.8, and 3.5, respectively. NSMB-4% shows that the lowest oxidation among all NSMB. These values indicated that NSMB are more resistance to oxidative aging. Thus, it can be concluded that by addition of NS into asphalt binder, it can delay the oxidation process of asphalt binder.

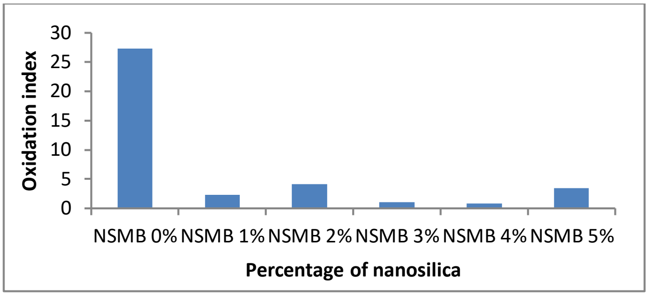

Figure 5: Oxidation index of NSMB

Dynamic shear rheometer (DSR)

Temperature sweep

Figure 6(a) shows the value of complex modulus is decreasing as the temperature increased. The difference of complex modulus between base asphalt binder and NSMB is higher at intermediate temperature but become lower at higher temperature after 64°C. Besides that, the complex modulus of NSMB is higher than the base asphalt binder. The higher value of complex modulus indicates that the binder has high potential to resist rutting. Therefore, NSMB has better performance as compared to the base asphalt binder. Lower and higher value of phase angle represents elastic and viscous property of asphalt binder respectively [11]. The typical asphalt binder has a phase angle between 0 and 90°C at a high performance temperature.

Figure 6(b) shows the phase angle lies between 60°C to 90°C. The phase angle of asphalt binder increased as the test temperature increases. Moreover, it is noted that the NSMB has a lower phase angle than base asphalt binder and exhibit more elastic and greater rutting resistance. By comparing unaged and RTFO aged samples, the complex modulus increased significantly while, the phase angle decreases slightly and this indicates that the stiffness of the binder increased after aging by RTFO. Both results of complex modulus and phase angle of unaged and RTFO aged, the NSMB 2% sample shows the most pronounced increase in complex modulus and decrease in phase angle, thus leading to the most strongly improved temperature susceptibility among all NSMB samples.

For further evaluation of rutting resistance of the asphalt binder at high temperature, the ratio G*/sinδ is commonly used. The G*/sinδ is defined as the stiffness indicator for evaluating the rutting resistance of asphalt binder (al-mansob 2014)[12]. The Superpave technique requires G*/sinδ = 1 kPa for unaged sample and G*/sinδ = 2.2 kPa for the RTFO sample as the minimum rutting parameter [13]. Figure 7(a) shows the G*/sinδ values of NSMB reduced as the temperature increased from 46°C to 76°C. Figure 7(a), all the NSMB passed the minimum value of G*/sinδ (1.0 kPa) for all testing temperature, while the value of G*/sinδ for based asphalt binder achieved 1 kPa after the test temperature reached 72.2°C. Similar trends for NSMB after RTFO aging can be observed in Figure 7(b). Again, all the NSMB passed the minimum value of G*/sinδ (2.2 kPa) for all testing temperature for RTFO sample. The value of G*/sinδ for base asphalt binder achieved 2.2 kPa after 69.6°C. Comparing the values of G*/sinδ between for both unaged and RTFO aged samples, NSMB 2% has the highest value compared to other sample for all testing temperature.

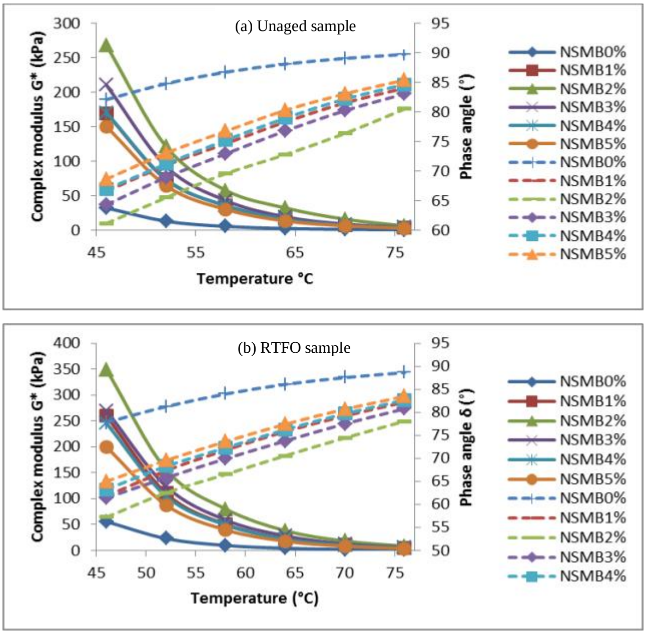

Figure 6: Isochronal plot of the complex modulus and phase angle at 10 Hz (a) unaged sample (b) RTFO sample.

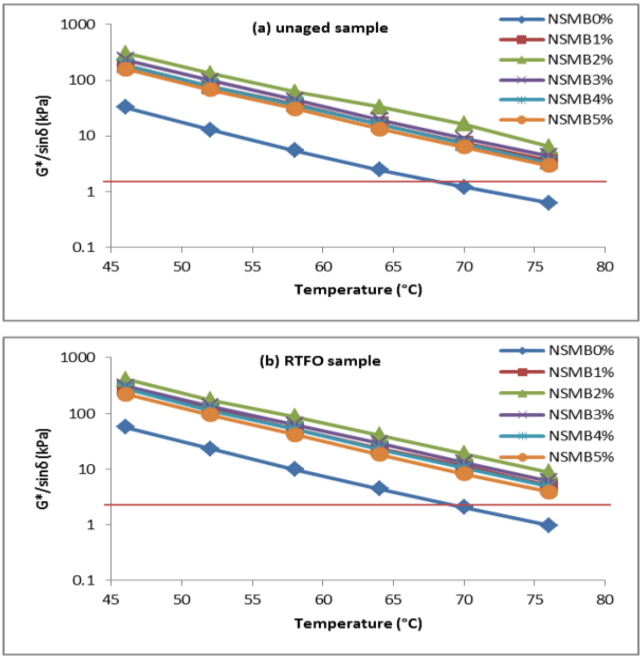

Figure 7: Rutting parameter (G*/sinδ) vs temperature of NSMB (a) unaged sample and (b) RTFO sample

Shear creep

Figure 8(a) shows the typical strain outputs from MSCR testing of NSMB for unaged and RTFO aged at 64°C for the whole cycles. The first 100 s represents low stress level and next 100 s represent a high stress level as shown in Figure 8. The MSCR test result included two phases which are creep phase and recovery phase to complete one cycle. At one-second creep phase, the strain was increasing under loading. At nine-second recovery phase, the strain recovered when the loading was removed. In the recovery phase, the strain recovered immediately at the beginning but the recovery rates decreased with time. Also, the strain and recovery rate was very high at the beginning of the cycle, but the rate decreased with time [14].

Figure 8(b) shows the accumulated strain at low stress level is lower than accumulated strain at high stress level. This indicates that, with the increasing stress level, the accumulated strain also increased. With the addition of NS into base asphalt binder, the accumulated strain was significantly reduced. This indicates that NS improved the stiffness of the asphalt binder at high service temperature. Besides that, it can be observed that the accumulated strain increased when the temperature increased. The percentage of increase can be seen clearly, especially for NSMB-0%. Additionally, the rapid increase in strain of NSMB-0% could indicate that it has higher temperature susceptibility compared to other NSMB. By comparing the effect of NS percentage, it could be seen that NSMB-2% has the lowest accumulated strain than other percentages of NSMB for both unaged and RTFO aged condition. In addition, the accumulated strain of RTFO aged sample was observed to be lower than unaged sample.

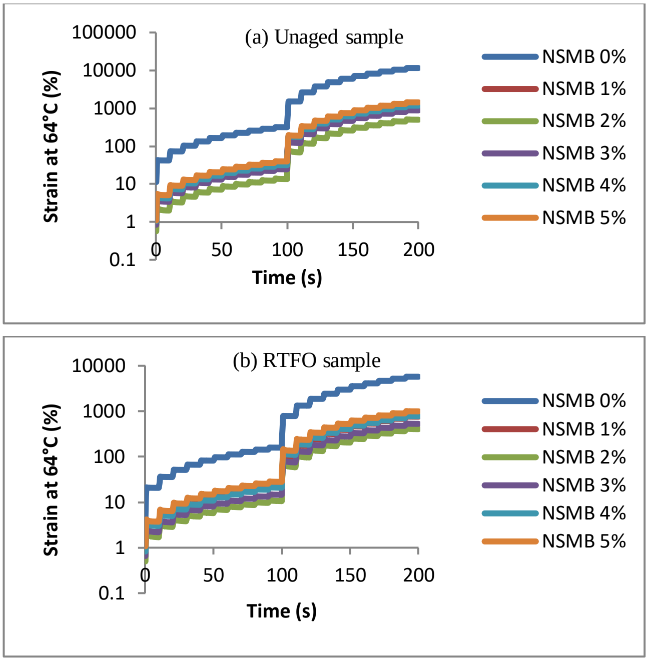

Figure 8: MSCR result at temperature of 64°C, (a) unaged sample (b) RTFO sample

Conclusion

From the XRD test result, the modification of the base asphalt binder with NS changed the phase of the base asphalt binder from amorphous to semi-crystalline. It also indicates that NS dispersed well in the asphalt binder.

It was also found that the NSMB can delay and weaken the oxidation reaction binder which could improve the aging process based on the FTIR spectroscopy results. In other words, the oxidation reaction of modified binders can be weakened when exposed to the weathering process especially from the effects of heat and daylight.

The addition of NS significantly increased the G*/sinδ value and decreased the strain of asphalt binder which exhibits higher elasticity and beneficial in increasing the rutting resistance compared to the base asphalt. Therefore, the use of NS as a modifier in asphalt binder modification improved aging resistance and stiffness of asphalt binder.

Acknowledgments

The authors expressed utmost gratitude to FRGS Research Grant: FRGS/1/2015/TK08/UITM/02/3 from Ministry of Higher Education, Malaysia for financial support which enables this paper to be written.

References

[1] McGennis, R.B., Anderson R.M., Kennedy, T.W., and Solaimanian. M. "Background Of Superpave Asphalt Mixture Design And Analysis" Federal Highway Administration (FHWA), *Report No. FHWA-SA-5-003*, pp 1-3, Julai 1995

[2] Santagata. E., Baglieri, O., Tsantilis, L. and Dalmazzo, D. "Rheological Characterization Of Bituminous Binder Modified With Carbon Nanotubes" *Social And Behavior Sciences*, 53 2012 546-555, 2012.

[3] Onochie, A., Fini, Elham., Yang, X., Beale, J. M., and You, Z. "Rheological Characterization Of Nano-Particle Based Bio-Modified Binder" 2012.

[4] Hsieh, T.H., Kinloch, A.J., Taylor, A.C., and Sprenger, S. " The Effect of Silica Nanoparticles and Carbon Nanotubes on the Toughness of a Thermosetting Epoxy Polymer ". *Journal of applied polymer science*, Vol. 119,2135-2142(2011)©2010 wiley periodicals, 2010.

[5] Bahia, H.U., and Anderson, D.A. " The Pressure Aging Vessel (PAV): A Test to Simulate Rheological Changes Due to Field Aging" *ASTM Special Technical Publication* 1241, 1994.

[6] Ouyang C., Wang S., Zhang Y., and Zhang Y. " Improving The Aging Resistance of Asphalt By Addition of Zinc Dialkyldithiophosphate". Fuel, 2006.

[7] Ali S. I. A., Ismail A., Md. Yusof N. I., Karim M. R., Al-Mansob R. A., and Alhamali D. I." Physical And Rheological Properties Of Acrylate-Styrene-Acrylonitrile Modified Asphalt Cement " *Construction and Building Materials* 93, 326-334, 2015.

[8] Ali A. H., Mashaan N. S., and Karim M. R. " Investigations of Physical and Rheological Properties of Aged Rubberised Bitumen" *Advances in Materials Science and Engineering*, Volume 2013, Article ID 239036, 2013.

[9] You, Z., Beale, J. M., Foley, J. M., Roy, S. and Odegard, G. M. "Nanoclay-Modified Asphalt Materials: Preparation And Characterization" *Construction And Building Materials* 25 1072-1078, 2011.

[10] Cortizo M.S., Larsen D.O., Bianchetto H., and Alessandrini J.L. "Effect of the thermal degradation of SBS copolymers during the ageing of modified asphalts" *Polymer Degradation and Stability* 86, 275-282, 2004.

[11] Yao. H., You. Z., Li. L., Lee. And Goh. S. W. " Evaluation of the Master Curves for Complex Shear Modulus for Nano-modified Asphalt Binder" , 2012.

[12] Al-Mansob R. A., Ismail A., Md Yusoff N. I., Azhari C. H., Karim M. R., Alduri A., Baghini M. S., "Rheological characteristics of epoxidized natural rubber modified bitumen" *Applied Mechanics and Materials* 505-506, 2014.

[13] Khadivar A. and Kavussi A," Rheological Characteristic of SBS and NR Polymer Modified Bitumen Emulsions at Average Pavement Temperatures" *Construction and Building Materials*, 47, 1099-1105, 2013.

[14] Yang X and You Z. " High Temperature Evaluation of Bio-Oil Modified Asphalt Binder Using the DSR and MSCR Tests" *Construction and building Materials*, 76, 380-387, 2015.