Investigation of Laboratory Aging Effects on Nanoclay-modified Asphalt Binders

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Abstract

Asphalt binder aging is recognized as a complex phenomenon that can significantly reduce the serviceability of flexible pavements. To address this issue, the aging behaviour and rheological properties of asphalt binders can be improved through asphalt binder modification. In this regard, the use of nanotechnology and nanomaterials are among the promising approaches for this purpose. The main objective of in this paper is to investigate the use of two types of Organo-Montmorillonite nanoclays with different dosages (2% and 4% by weight of asphalt binder) for enhancing the aging resistance of asphalt binders. Nanoclay-modified asphalt binders are prepared using a high shear mixer at 130±2 °C for 2 h at 3,000 rotations per minute. Initially, for the purpose of evaluating the material properties, various tests are applied to the unmodified and nanoclay-modified binders. The performance grades of the unmodified and modified binders are also investigated. Moreover, by examining the evolution of the fractions (i.e., saturates, asphaltenes, resins, and aromatics) the colloidal index is calculated and the storage-stability of the nanoclay-modified binders is analyzed accordingly. The asphalt binders modified with 4% nanoclays are found to have the best storage-stability among the evaluated binders. After characterizing the unaged properties, rolling thin-film oven (RTFO) aging was carried out for 85 minutes at 163 °C, followed by aging in pressure aging vessel (PAV) for 20 h under 2.1 MPa pressure at 100 °C. Using a dynamic shear rheometer, the complex shear modulus (G*) and phase angles (δ) of the binders were determined at different temperatures and loading frequencies before and after aging. Finally, based on the aging indices, the impact of nanoclay modification on the aging resistance of asphalt binders was investigated. The results of this study showed that nanoclay modification can mitigate the impact of aging on asphalt binders compared to the unmodified binder.

Keywords: Asphalt binder aging; Binder modification; Nanoclay, Rheology; Aging indices.

Introduction

According to the literature, asphalt binder aging is a complex phenomenon that can significantly reduce the serviceability of flexible pavements. In fact, it can lead to different forms of distresses in the pavement, such as loss of flexibility and durability under repeated loading, as well as a higher propensity to crack [1]. The aging behaviour and rheological properties of asphalt binder can be improved through asphalt binder modification. It is worth noting that binder modifiers range from polymer modifiers, such as Styrene-Butadiene-Styrene (SBS) and Amorphous Poly Alpha Olefin (APAO), to nanoclays (NC), asphaltenes, powders, and nano-silica. These modifiers have been previously applied to improve the rutting resistance, aging resistance, low-temperature cracking, and fatigue life of asphalt binders [2–5].

While different mechanical properties can be improved through the addition of the above-mentioned modifiers, there are also drawbacks that need to be taken in to account. For instance, the cost of polymer-modified binders (PMBs) is significantly higher than that of unmodified binders [6]. Moreover, Galooyak et al. have noted thatpoor compatibility between SBS and bitumen can negatively impact the storage stability at high temperatures [7]. However, they compared the physical and rheological properties of SBS polymer-modified bitumen before and after adding nanoclay to the bitumen and showed that the presence of nanoclay improved the storage-stability of polymer-modified binder without adversely affecting on the other properties. Besides, Hao et al., found that aging decreases the molecular weight of SBS polymers and leads to oxidation of the asphalt, thereby damaging the polymer network in the binder, further broadening the relaxation spectrum, and diminishing the efficacy of the polymer in improving asphalt ductility [8]. Another modifier, amorphous poly alpha olefin, which is a kind of non-polar and saturate plastic material that can be easily mixed with asphalt at 165 °C, has been shown to increase the viscosity and elastic properties at high temperatures and increase the high failure temperature, but, on the other hand, negatively affect the low-temperature creep stiffness and creep rate of modified asphalt binders [9]. In another study, a solution of high-impact polystyrene (HIPS) and 2,6-Dimethylphenol (DMP) was found to improve the rutting resistance of the modified binder at higher temperatures, although the low-temperature cracking resistance was not significantly affected [10].

Elsewhere, it has been noted that use of nanoclay can reduce the cost of project by 22%– 33% in comparison to SBS [6]. In addition, nanoclays are naturally abundant, and have favourable intrinsic properties, such as nanoscopic size and high surface area, which may lead to improved aging resistance, as the layered silicates in nanoclay block asphalt oxidation [11].

Generally, nanoclays are defined as clays having at least one nanoscale dimension. These clays can be classified into four groups: Illite, Chlorite, Kaolinite, and Montmorillonite (MMT) [12]. MMT is the most widely used polymer modifier [13]. It is a naturally hydrophilic silicate composed of a 2:1 tetrahedral-to-octahedral layer arrangement [14]. Surface-modified MMT nanoclays disperse into intercalated and exfoliated structures in the asphalt base, whereas unmodified MMTs are not compatible with asphalt [15].

The previous studies on nanoclay modification indicates nanoclay modification helps to improve stiffness, rutting, and aging resistance of binder as well as indirect tensile strength and dynamic creep for the mixture [7,16,17,18]. Moreover, modification with nanoclay has been found to resulted in a higher penetration grade and lower aging index when compared to an unmodified binder [11]. But there is not too much studies to investigate the nanoclay modification particularly on binder aging. Mahdi et al. showed the impact of the short-term binder aging only using rolling thin-film oven (RTFO) [19]. There is no comprehensive study to show impact of nanoclay modification on both short- and long-term aging. In order to bridge the research gap, in this study, the impact of different dosage of nanoclay on both short- and long-term aging was shown using RFTO and pressure aging vessel (PAV).

Objectives and Scope

The main focus of the study was to investigate the impact of nanoclay modification on the both the short-and long-term aging of unmodified and modified binders. The specific objectives of the study can be stated as:

- Investigation of aging impact of asphalt binders with two types of Organo-Montmorillonite nanoclays modification with different dosages (2% and 4% by weight of asphalt binder).
- Comparison of the rheological properties (complex shear modulus (G*) and phase angles (δ)) of the unmodified and nanoclay-modified asphalt binders under short- and long-term aging conditions.
- Comparison of aging resistance of unmodified and nanoclay-modified binders in different concentration of nanoclay by aging indices under short- and long-term aging conditions.

Materials

In this study, nanoclay modifier was used to modify neat PG 64-28 asphalt binder. Five types of asphalt binders were used, including one unmodified and four nanoclay-modified binders. The neat binder was modified using two types of nanoclays, referred to herein as NC 1 and NC 2. The nanoclay-modified asphalt binders were prepared using a high shear mixer at 130±2 °C for 2 h at 3,000 RPM. Two different dosages of each nanoclay were used in this study: 2% NC 1, 4% NC 1, 2% NC 2, and 4% NC 2 by weight of asphalt binder. For the purpose of evaluating the material properties, tests were conducted on both the nanoclay-modified and unmodified binders. The Performance Grade (PG) of the modified and unmodified binders was investigated. The dispersion of nanoclays and the performance grading of nanoclay-modified binders were also evaluated. Moreover, based on an examination of the evolution of the fractions of saturates, asphaltenes, resins, and aromatics (SARA), the Colloidal Index (CI) was determined, and the storage-stability of the nanoclay-modified binders was also analyzed accordingly.

Scanning Electron Microscope

A qualitative analysis of the nanoclay dispersion was conducted using a Zeiss Geminin 500 Field Emission Scanning Electron Microscope (FE-SEM). Nanoclay-modified asphalt binder samples were affixed to FE-SEM pin mounts and observed at magnifications ranging from 500× to 20,000×. The dispersion of the NCs resulting from mixing was visually analyzed in the images observed (see Fig. 1). Fig. 1(a) shows that the 4% NC 1 was well dispersed in the asphalt binder. As indicated by the red circles in the image, there were only a few instances observed of agglomerations (having dimensions smaller than 2 μm) in the case of the 4% NC 1 binder. As shown in in Fig. 1(b), the 4% NC 2 binder was also observed to be well-dispersed, with only a few spaced nanoclay clusters (again having dimensions smaller than 2 μm). Comparing the two images presented in Fig. 1, similar structures were observed for the 4% NC 1 and 4% NC 2 binders, with the main difference being their respective concentrations of surface modifiers. The

4% NC 2 binder had more agglomerations throughout the matrix, and thus exhibited slightly lower interaction with the binder.

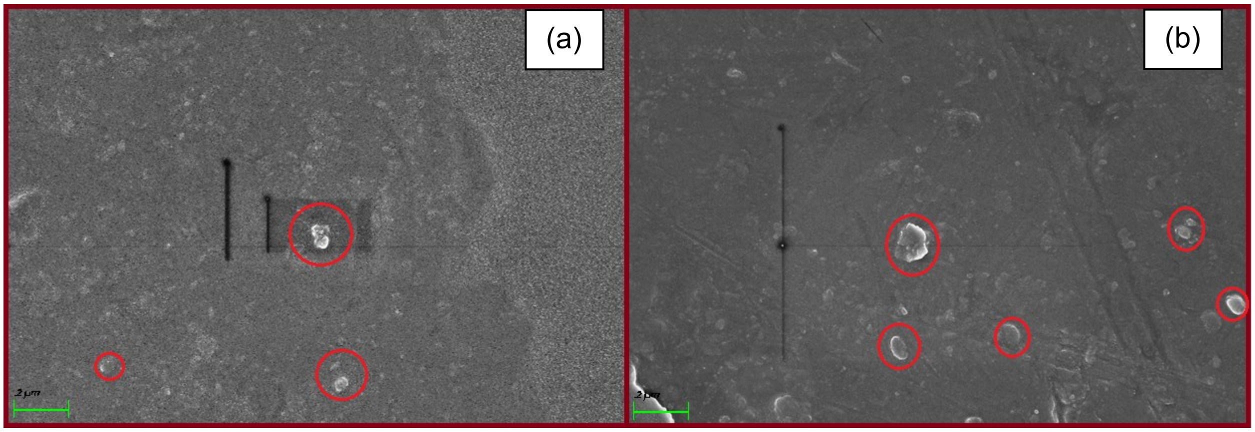

Fig. 1. SEM magnifications of binder modified with: (a) 4% NC 1, (b) 4% NC 2

SARA Fractions and CI Analysis

Asphalt binder comprises of four fractions—saturates, aromatics, resins, and asphaltenes (SARA)—that largely govern its properties [20]. The SARA analysis method used in this study involves the gravity-driven chromatographic separation of saturates, resins, and aromatic fractions. The asphaltenes were first separated by mixing the sample with heptane and heating it under reflux in accordance with ASTM D6560-18 [21]. The saturate, aromatic, and resin fractions were then determined through a clay–gel adsorption chromatography method in accordance with ASTM D2007-19 [22]. The SARA analysis for the modified and unmodified binders were then compared as shown in Fig. 2. The asphaltenes fraction, which is an essential indicator of a binder's stiffness, was found to be lower in the modified asphalt binders. Higher concentrations of nanoclays decreased the fractions of asphaltenes to 15.49% and 16.31%, for 4% NC 1 and 4% NC 2, respectively, from 21.09% in the unmodified asphalt binder. The opposite behavior was observed with regard to the saturates and resins, as they increased with the addition of the nanoclays. Hence, SARA test results indicate that nanoclay absorbs asphaltenes in the modified binder and as a result, the asphaltenes content decreases and saturates content increases in the modified binders after nanoclay modification. This is noteworthy to mention that Saturates fraction is the prominent indicator of rheological properties in asphalt binders, and that an increase in this fraction is indicative of a lower G* and higher δ. It indicates nanoclay modification can help to improve the rheological properties.

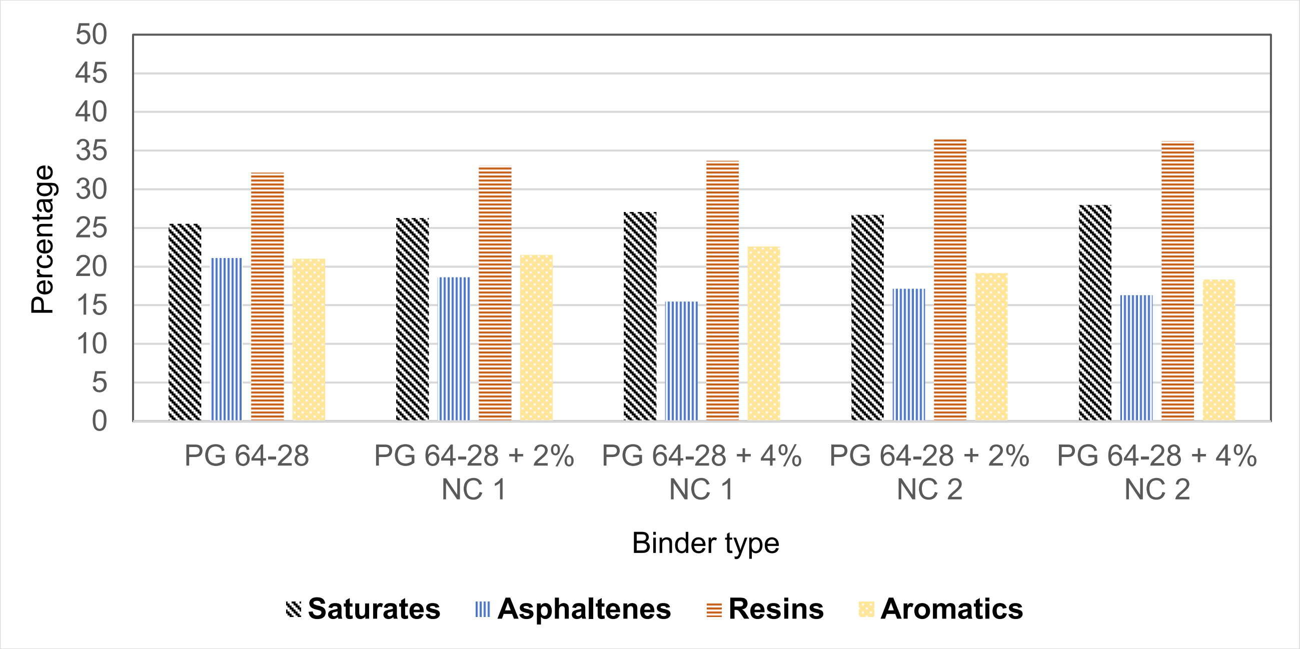

Fig. 2. Comparison of SARA analysis for unmodified and modified binders

Due to the colloidal nature of asphalt, the SARA fractions can be used to calculate its storage-stability [23]. Thus, the SARA analysis results were used to calculate Colloidal Indices (CI) as shown in Equation (1) [24]. The calculated CI values are listed in Table 1.

$$CI = \frac{\text{Saturates}+\text{Asphaltenes}}{\text{Resins}+\text{Aromatics}} \tag{1}$$

Table 1. CI of Unmodified and Modified Binders

Sample	**CI**
PG 64-28	0.88
PG 64-28 + 2% NC 1	0.82
PG 64-28 + 4% NC 1	0.76
PG 64-28 + 2% NC 2	0.79
PG 64-28 + 4% NC 2	0.81

According to the literature, a CI value higher than 0.9 indicates a stiff and unstable binder, while a value below 0.7 indicates a very stable and soft material [23,24]. Therefore, an asphalt binder with a CI value in the range of 0.7–0.9 can be considered to be storage-stable while also resistant to rutting. According to Table 1, the CI values of the samples with the 4% NC 1 and 4% NC 2 binders were found to be 0.76 and 0.81, respectively, while the CI of the unmodified binder was 0.88. As per the explanation above, they were found to be storage-stable, but also stiff enough to resist rutting. The samples with the 2% NC 1 and 2% NC 2 binders, meanwhile, were also found to be stable, with CI values of 0.82 and 0.79, respectively. Moreover, given that the 4% NC 1 and 4% NC 2 binders were found to be more stable than the 2% NC 1 and 2% NC 2, it can be concluded that the addition of the nanoclays increased the storage-stability.

Workability of Unmodified and Modified Asphalt Binders

Viscosity is a good indicator of the fluidity and workability of the binder. The impacts of nanoclay modification on workability of unmodified and modified binders were investigated by the viscosity test. A rotational viscometer was used to conduct this test according to AASHTO T316 [25].

Workability of the binder can be predicted from the viscosity test results of the unmodified and modified binders. The viscosity test result is presented at Fig. 3. According to the Superpave binder specification, if the rotational viscosity of a binder is less than 3.0 Pa.s at 135°C, then the binder can be regarded as workable [26]. Fig. 3 shows at the temperature of 135°C, all the unmodified and modified binders have viscosity lower than the requirement. It is interesting to note that the nanoclay modified binders have slightly higher viscosity in comparison to the unmodified one. With the higher concentration of nanoclay, the viscosity of the binder gets higher, but the viscosity range of modified binder remains within the acceptable Superpave binder requirement.

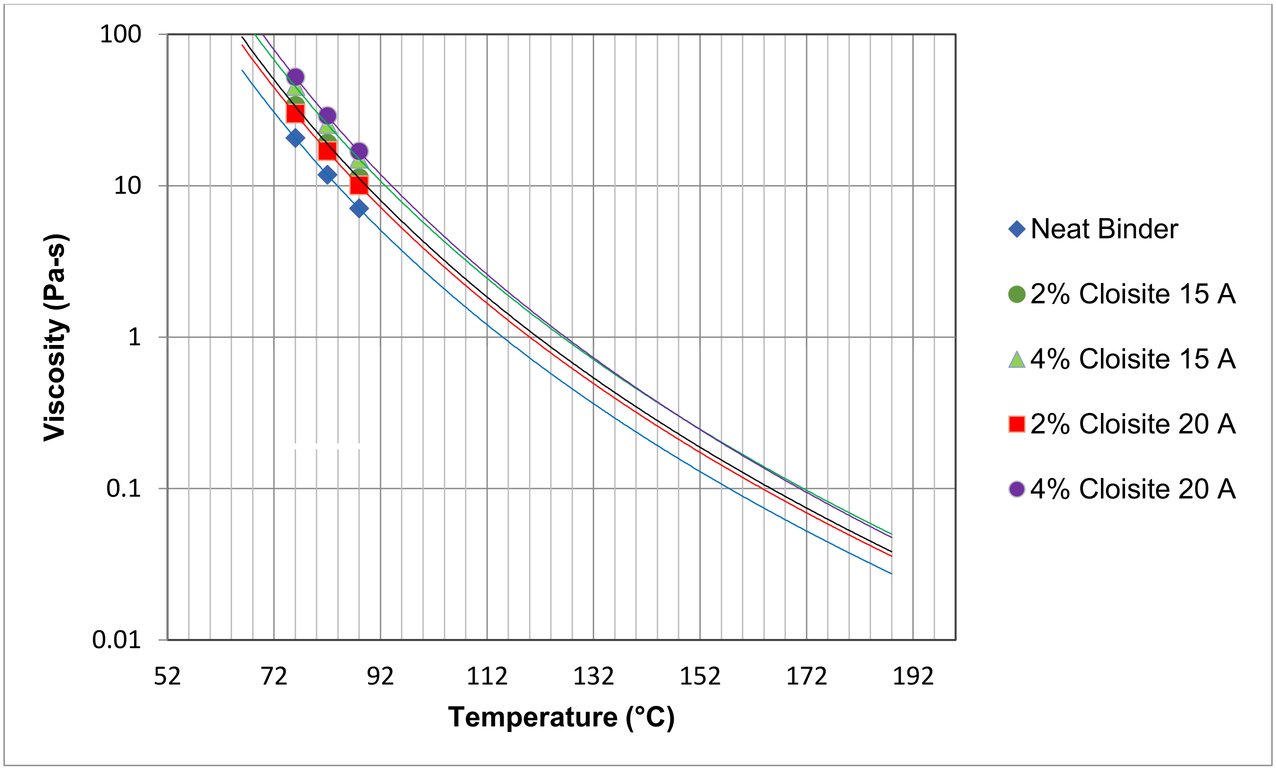

Fig 3. Viscosity test result of unmodified and modified binders

Methodology

Analyzing nanoclay modification on asphalt binder aging, the binders were aged using RFTO and PAV. The underlying aim of this work was to compare the properties of unmodified and nanoclay-modified asphalt binders under short- and long-term aging through frequency sweep tests and aging indices.

Laboratory Aging Procedures

Aging due to the effects of heat and air at the mixing and compaction stage is typically simulated using the RTFO test. Hence, the five types of binders used in this study were aged for 85 minutes at 163 °C in an RTFO oven in accordance with AASHTO T 240-21 [27]. On the other hand, simulation of the aging occurring later in the pavement's service life (e.g., 5 to 10 years of service life) is typically carried out using the PAV test. The RTFO-aged binders were thus subsequently subjected to PAV aging for 20 h, under 2.1 MPa air pressure at 100 °C, in accordance with AASHTO R 28-21 [28].

Performance Grading of Unmodified and Modified Asphalt Binders in Unaged and Aged Conditions

The impacts of nanoclay modification on workability, permanent deformation, fatigue cracking, and low-temperature cracking of the asphalt binder were investigated by subjecting them to Superpave Performance Grading (PG). The PG of the asphalt binders in unaged and aged conditions were investigated in accordance with AASHTO M 320-21 [29]. The high-temperature grades of the binders were determined by employing an Anton Paar SmartPave 102 DSR. Additionally, the low-temperature grades of the PAV-aged samples were obtained using a bending beam rheometer (BBR) in accordance with AASHTO T 313-19 [30].

Asphalt Binder Frequency Sweep Test

The frequency sweep (FS) test is useful for evaluating the viscoelastic properties of asphalt binders. By analyzing the G* and δ values, one can characterize the rheological properties of the binder at a wider range of frequencies [1,31]. In this study, the FS test was conducted at the frequency range of 0.1 to 300 rad/s and at five different temperatures (10 °C, 20 °C, 25 °C, 30 °C, and 40 °C) on both the aged and unaged binders. The DSR was configured to an 8 mm diameter, 2 mm gap, and 1% shear strain under the linear viscoelastic range for the purpose of testing the samples.

Two aging indices—the complex modulus aging index (CAI), expressed in Equation (2), and the phase angle aging index (PAI), defined by Equation (3)—were determined in this analysis, where a high CAI value indicates a high degree of aging, while a high PAI value indicates a low degree of aging [5].

$$CAI = \frac{\text{Complex Modulus of Aged Binder}}{\text{Complex Modulus of Unaged Binder}} \tag{2}$$

$$PAI = \frac{\text{Phase Angle of Aged Binder}}{\text{Phase Angle of Unaged Binder}} \tag{3}$$

Results and Discussion

Impact of Aging on Performance Grading of the Binders

To investigate the impact of aging on the PG of the unmodified and modified binders, the high and low PGs before and after aging were compared as presented in Fig. 4. Comparing the true unaged PGs of the five binders, the high-temperature PG indicated improvement after nanoclay modification in all cases. The true high-temperature PG was 64.2 for the unmodified binder, increasing to 70.6 and 70.0 after modification with 4% NC 1 and 4% NC 2, respectively. At a lower dosage (2%), the true high-temperature PG increased to 66.6 and 67.9 for the NC 1 and NC 2, respectively. Overall, the PGs were found to be 64-28 and 70-28, at 2% and 4% modifier concentrations, respectively.

In order to compare the aging behavior of the binders in both high- and low-temperatures, both the high- and low-PG was calculated. As per the results, it was found that, after RTFO aging, the true high PG of 65.3 for the unmodified sample increased to 67.3, 67.0, 70.0, and 70.2 for 2% NC 1, 2% NC 2, 4% NC 1, and 4% NC 2, respectively. On the other hand, BBR testing on the PAV-aged samples indicated that the low-temperature PG decreased slightly after aging for all the binders. The true low PG of −30.6 for the unmodified sample decreased to −32.9, −32.8, −32.6, and −31.7 for 2% NC 1, 4% NC 1, 2% NC 2, and 4% NC 2, respectively. Overall, the aged PGs were found to be 70-28 and 64-28 for NC 1 and NC 2, both at 4% and 2% concentrations, respectively.

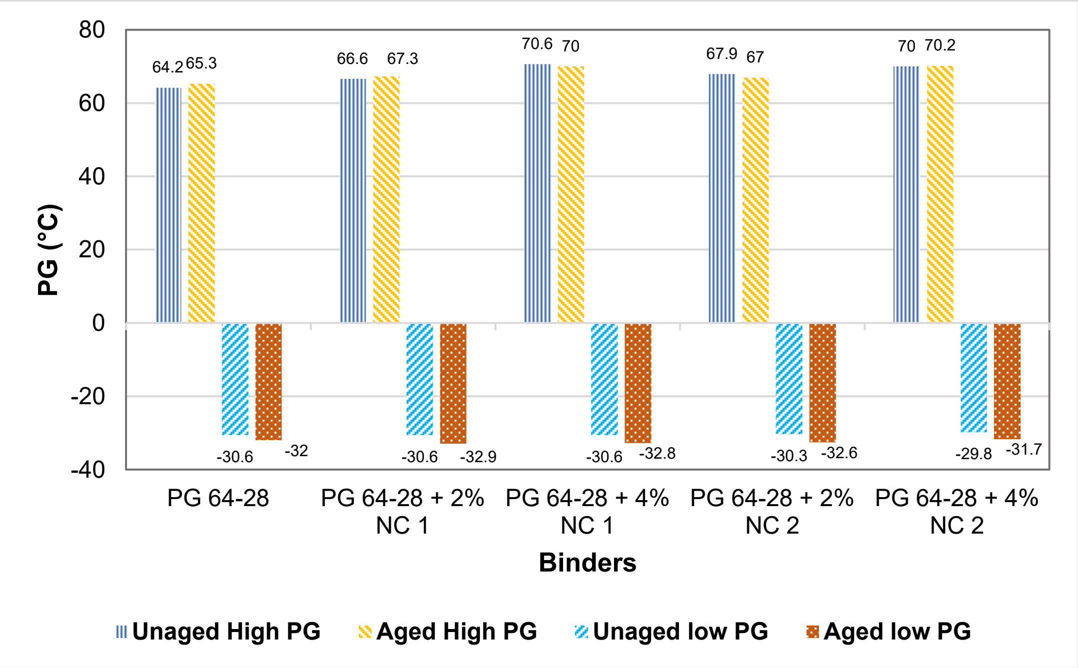

Fig. 4. Comparison of PG of Aged and Unaged binders

Frequency Sweep Test Results

To study the aging behaviour of nanoclay-modified binders, series of FS tests were applied to both the unmodified and modified asphalt binders under unaged, RTFO-aged, and PAV-aged conditions. The complex shear modulus (G*) values were compared in order to gain understanding of the effect of aging on both modified and unmodified binders. As suggested in the literature, the complex shear modulus (G*) values should be superpositioned at reference temperature (e.g., 25 °C) [19, 25]. The trends of G* values at 25 °C for the five binders at unaged, RTFO-aged, and PAV-aged conditions are presented in Fig. 5. As can be seen, it was found that the PAV-aged samples showed the highest G* values for all the binders. Among the modified binders, the 4% NC 2 and 4% NC 1 binders were found to have the highest G*, followed by the 2% NC 1 and 2% NC 2, and then the unmodified binder across all frequencies. Our results are in line with the findings by Xu et al. who indicated in study that, an increase in saturates corresponds with a lower G* [24]. The binders having higher saturates (from SARA analysis) found to have lower G*.

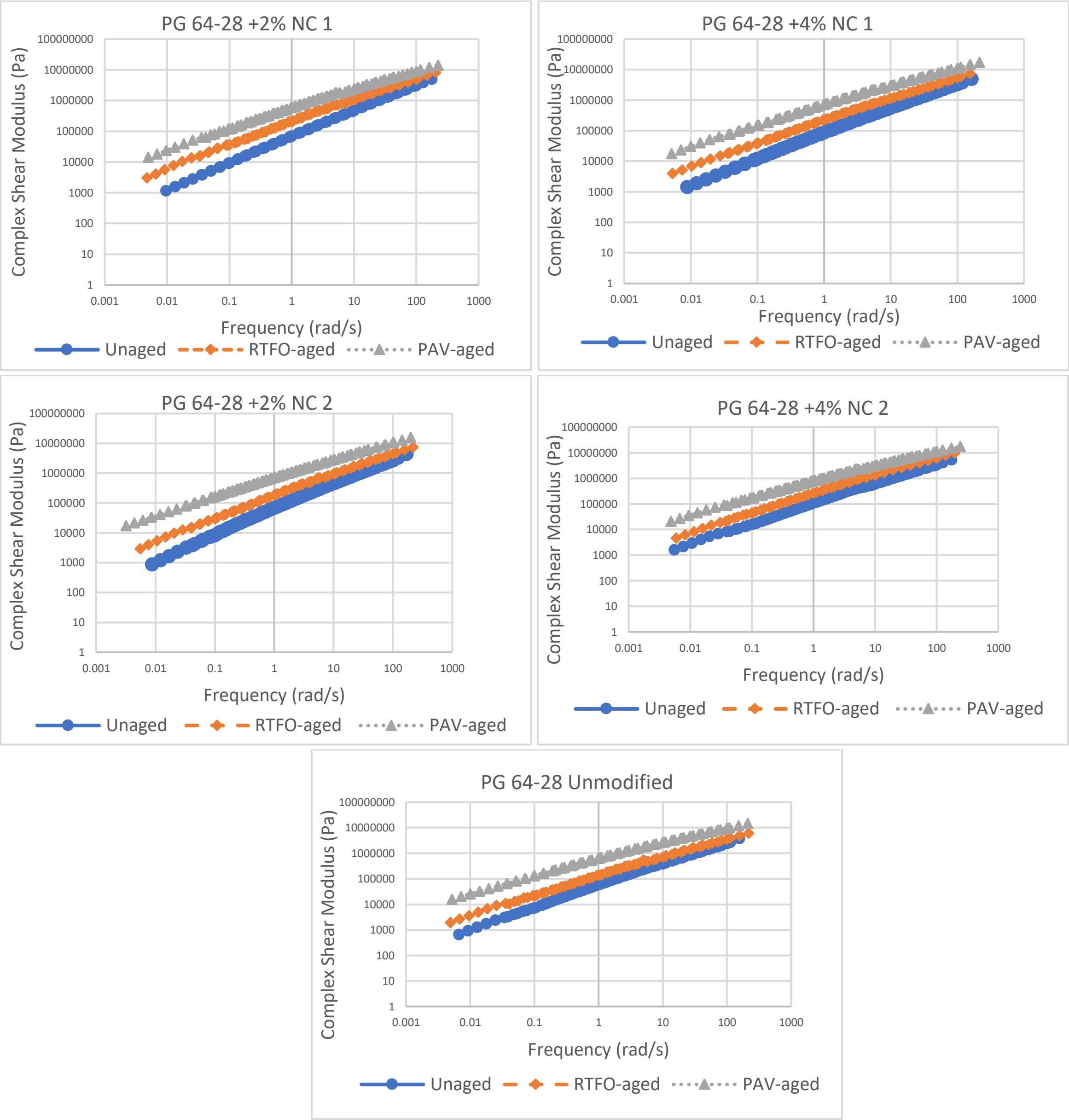

Fig. 5. Comparison of complex shear modulus for unmodified and modified binders under unaged, RTFO-aged, and PAV-aged conditions at 25 °C

In order to gain understanding of the aging effect see, the binders were also compared in terms of phase angle (δ) under unaged, RTFO-aged, and PAV-aged conditions at 25 °C as shown in Fig. 6. The highest phase angle was observed for the unaged binder, followed by the RTFO-aged binder, while the PAV-aged binder had the lowest δ. It was also observed that the 2% NC1- and 4% NC1-modified asphalt binders had similar phase angles after short-term (i.e., RTFO) aging. A similar phenomenon was observed for the 2% NC2- and 4% NC2-modified asphalt binders after RTFO aging.

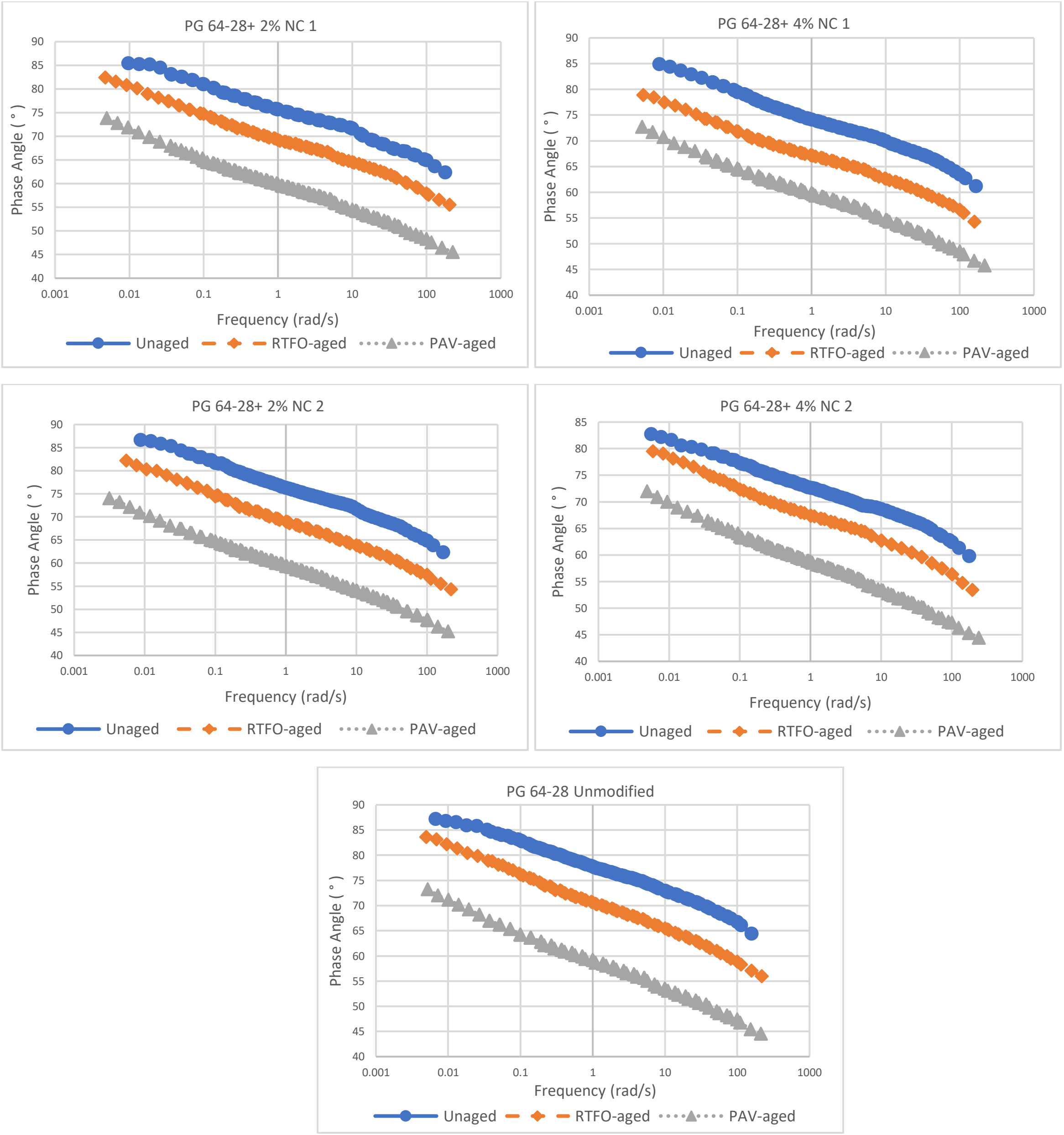

Fig. 6. Comparison of phase angles for unmodified and modified binders under unaged, RTFO-aged, and PAV-aged conditions at 25 °C

Analysis of Aging Indices

The CAI and PAI values of modified and unmodified binders were calculated using Equations (2) and (3), respectively. Table 2 shows the CAI and PAI values of all binders under both RTFO and PAV aging conditions.

Table 2. CAI and PAI values of unmodified and modified binders

Aging Method	Frequency (rad/s)	PG 64-28		PG 64-28 + 2% NC1		PG 64-28 + 2% NC2		PG 64-28 + 4% NC1		PG 64-28 + 4% NC2	
RTFO		CAI (Pa/Pa)	PAI (°/°)	CAI (Pa/Pa)	PAI (°/°)	CAI (Pa/Pa)	PAI (°/°)	CAI (Pa/Pa)	PAI (°/°)	CAI (Pa/Pa)	PAI (°/°)
	0.1	3.05	0.92	3.91	0.92	3.62	0.91	3.13	0.90	2.81	0.94
	1	2.42	0.91	3.06	0.91	2.71	0.90	2.60	0.91	2.49	0.93
	10	1.85	0.90	2.26	0.90	2.05	0.89	2.04	0.90	2.28	0.91
	100	1.48	0.88	1.59	0.89	1.65	0.89	1.61	0.89	1.87	0.90
PAV	Frequency (rad/s)	PG 64-28		PG 64-28 + 2% NC1		PG 64-28 + 2% NC2		PG 64-28 + 4% NC1		PG 64-28 + 4% NC2	
		CAI (Pa/Pa)	PAI (°/°)	CAI (Pa/Pa)	PAI (°/°)	CAI (Pa/Pa)	PAI (°/°)	CAI (Pa/Pa)	PAI (°/°)	CAI (Pa/Pa)	PAI (°/°)
	0.1	18.44	0.77	12.93	0.80	20.07	0.79	12.27	0.81	10.89	0.82
	1	11.03	0.76	8.71	0.79	10.45	0.78	8.25	0.81	7.50	0.81
	10	6.95	0.73	5.04	0.76	6.27	0.75	5.29	0.78	5.32	0.78
	100	4.04	0.71	2.89	0.74	3.96	0.74	3.32	0.76	3.44	0.76

Firstly, the effects of short-term aging were compared for all binders. Given that a higher value of CAI represents a more significant effect of aging on the specimen, it was interesting to notice that unmodified binder had lower CAI values for almost all the frequencies under RTFO-aged condition implying that the unmodified binder was less affected by RTFO-aging in comparison to modified binders. The RTFO-aged NC 1 binders had higher CAIs than NC 2 binders, indicating that greater aging impact for the NC1 binder than for the NC2 binder.

Secondly, the effects of long-term aging were compared for all binders. At higher loading frequencies, the modified binders had lower CAI values compared to the unmodified binder regardless of NC concentration. However, at mid-frequencies, the binders with 4% NC had the lowest CAI values, followed by the binders with 2% NC concentration, and then the unmodified binder. It was thus concluded that the addition of nanoclay reduces the impact of long-term aging, with the 4% NC binders exhibiting the highest resistance to long-term aging.

On the other hand, a high PAI value usually represents high resistance of the asphalt binder to aging. The 4% NC2-modified binder had the highest PAI value after RTFO aging among all, indicating that this binder is more resistant than the others to short-term aging. The PAI value was found to increase in the following order: unmodified binder, 2% NC 2, 2% NC 1, 4% NC 1, and 4% NC 2. This finding indicates that nanoclay-modified asphalt binders are more resistant than unmodified binders to long-term aging, and that this resistance improves with increasing concentration of nanoclays.

In order to understand if there is statistically significant difference in the values after nanoclay modification, Analysis of Variance (ANOVA) was also conducted on the CAI and PAI values obtained for the modified binders with 2% and 4% NC 1 and 2. The ANOVA (P-values and F-values) outputs for CAI and PAI values for both dosage of nanoclay binders at different frequencies were calculated for the significance level (α) of 0.05. The results showed that in all cases, the F-values are larger than F-critical, and all the P-values are smaller than 0.05 except the RFTO-aged NC 1 modified binder for 2% and 4% dosage. which shows the nanoclay modification and testing frequencies have significant impacts on the aging indices.

Conclusions

The main purpose of this research was to investigate the aging behaviour of nanoclay-modified and unmodified binders. In specific, the impact of nanoclay modification on the chemical (SARA fractions) and rheological (G^* and δ) properties of unmodified and modified asphalt binders was investigated, while the aging behaviour of the nanoclay-modified binders was evaluated by comparing the PGs of the binders along with their rheological properties under different aging conditions. According to the results obtained; it was found that the high-temperature PG of the binders increased for the binders modified with nanoclays compared to the unmodified binders. Moreover, among the RTFO-aged and PAV-aged samples, the unmodified binder had the lowest complex shear modulus (G^*), followed by the binders modified with 2% and 4% nanoclays. According to the CAI and PAI analysis, moreover, the 4% NC 2 modified binder behaved the best in terms of rheological properties compared with the other samples under short- and long-term aging conditions, indicating that this binder is more resistant to aging than the other binders under study. It can thus be concluded that nanoclay modification can reduce the impact of aging on asphalt pavement. This main focus of this study is to investigate the nanoclay modification impact on aging properties of modified binders. For future studies, nanoclay impact on other different properties (such as moisture induced damage, fatigue, healing) of modified binders can be investigated.

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