Performance evaluation of Al₂O₃ nanoparticle-modified asphalt binder

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The rheological and physical properties of asphalt binders modified with aluminium oxide (Al₂O₃) nanoparticles were investigated. Al₂O₃ nanoparticles were added to the base asphalt binder at concentrations of 3, 5, and 7 wt.%. Superpave binder tests were conducted to evaluate the characteristics of the nano-Al₂O₃-modified binders. Rotational viscosity tests and a dynamic shear rheometer were used to analyse the rheological and physical properties of the modified binders, and Fourier transform infrared spectroscopy technique to observe changes in the structure of modified binders compared to the original. The penetration and ductility values decreased with added Al₂O₃ as well as temperature susceptibility. The phase angle δ is reduced with 5 wt.% or less Al₂O₃ added to the binder. The complex shear modulus G* significantly increased with the addition of up to 5 wt.% Al₂O₃. Results recognise 5 wt.% as the optimum level. The performance of nano-Al₂O₃-modified binders was enhanced regarding their resistance to both thermal rutting at high temperatures and fatigue cracking at low temperatures. Furthermore, statistical analysis of penetration, softening point, complex shear modulus, and phase angle results, using both one- and two-way ANOVA tests, show a significant difference level, having remarkable impacts on the dependent variables.

Keywords: Al₂O₃ nanoparticles; rheological and physical properties; dynamic shear rheometer; Fourier transform infrared spectroscopy

1. Introduction

Asphalt is commonly used as a binder in the construction of highways and runways, due to its good viscoelastic properties (El-Shafie, Ibrahim, & Abd El Rahman, 2012; Guo, Li, Cheng, Jiao, & Xu, 2015; Liu, Wu, Liu, & Li, 2015b). Asphalt is an organic composite of several chemical compounds. The chemical structures and physical properties of asphalt are transformed in a process called aging when the material is exposed to heat, oxygen, and UV light (Lamontagne, Dumas, Mouillet, & Kister, 2001; Liu et al., 2015b). With increasing traffic volume and loads, combined with the growing cost of asphalt, the issue of aging in asphalt has led to essential improvement of the safety, efficiency, and durability of the asphalt mixture through binder modification (Modarres & Hamedi, 2014). However, natural asphalt does not have sufficient strength to resist sudden stresses of excessive loading or stress from low temperatures (Maity et al., 2014). Therefore, modification of asphalt is necessary to improve its material temperature.
sensitivity, adhesion, durability, oxidation, and aging resistance. Several categories of asphalt modifiers exist, including polymers, rubbers, sulphur, metals, fibres, and chemical agents (Fang, Yu, Liu, & Li, 2013; Moreno-Navarro, Sol-Sánchez, & Rubio-Gámez, 2015; Munera & Ossa, 2014; Ziari, Babagoli, & Akbari, 2015). Recently nanotechnology has become one of the greatest active research fields in civil engineering and construction materials (Hamedi, Moghadas Nejad, & Oveisi, 2015). Conventionally, it has led to advances in the fields of materials science, microelectronics, and medicine. However, several developments in nanotechnology may be applied to the field of construction engineering (Chong, 2004a; Goddard III, Brenner, Lyshevski, & Iafrate, 2007; Rana, Rana, Kumari, & Kiran, 2009; Rashad, 2013). Nanotechnology has increasingly been used in modified asphalt, with various types of nanomaterials used as binder modifiers. The manufacture of new materials at the molecular level, that is, on the nanoscale, leads phenomena associated with atomic and molecular interactions to strongly affect the materials’ macroscopic properties (Chong, 2004b). Nanoscale modification improves some characteristics of asphalt binders and asphalt mixtures, such as rutting and fatigue problems, but more investigations are required before it can be applied on a large scale (Ghile, 2006; Khattak, Khattab, Rizvi, & Zhang, 2012). Conventional asphalt modifiers are ordinarily added in percentages of 20–30 wt. % (by weight of asphalt), whereas nano composites may achieve similar effects with 1–5 wt. % (Fuentes-Audén et al., 2008; McNally, 2011). The resulting advantage of lighter weight is economically interesting. Other advantages include enhanced mechanical behaviour and improved thermal properties (Paul & Robeson, 2008; Sinha Ray & Okamoto, 2003). One type of nanomaterial that is widely used in the modification of asphalt, known as nanoclay, is able to increase the asphalt’s stiffness and improve its aging resistance. Moreover, small amounts of nanoclay added to asphalt have great impacts on the composite’s physical properties (Jahromi & Khodaii, 2009). In this study, nano-alumina (Al$_2$O$_3$) nanoparticles were used for the first time to modify asphalt binders, allowing the investigation of the physical, chemical, and rheological properties of the Al$_2$O$_3$-modified asphalt binders. The effects of the addition of Al$_2$O$_3$ nanoparticles as a modifier of asphalt binders, using experimental design and statistical analysis, will aid in finding optimum binders for particular properties like penetration, softening points, and rheological parameters.

### 2. Experimental design

#### 2.1. Materials

Two materials, a commercially available asphalt binder and Al$_2$O$_3$ nanoparticles, were used to produce a base and modified binders in the laboratory. The base binder was 60/70 penetration-grade (PG 69-19) asphalt obtained from the Port Klang Factory in Malaysia, while the nanomaterial (nanoscale aluminium oxide Al$_2$O$_3$ white powder) was supplied by the Shijiazhuang Chanchiang Corporation company in China. The physical properties of the base asphalt and Al$_2$O$_3$ nanoparticles are shown in Table 1.

| Material       | Properties          | UNIT | LIMITS          | Value |
|----------------|---------------------|------|-----------------|-------|
| Asphalt 60/70  | Specific gravity    | –    | 1.00–1.05       | 1.03  |
| Penetration    | mm                  | 60–70| 70              |
| Penetration    | @ 25°C              |       |                 |
| Softening point| °C                  | 47 Minimum | 47.0  |
| Viscosity      | Pa.s                | 3 Max | 0.5             |
| Viscosity      | @ 135°C             |       |                 |
| Ductility      | cm                  | 100 Minimum | ≥ 100  |
| Ductility      | (cm) @ 25°C         |       |                 |
| Nano Al$_2$O$_3$| Size                | nm   | 13              |
| Nano Al$_2$O$_3$| Specific gravity    | –    |                 |
2.2. Sample preparation

The samples were prepared by melting $\text{Al}_2\text{O}_3$ nanoparticles to produce three modified asphalt binders with 3, 5, and 7 wt.% $\text{Al}_2\text{O}_3$ nanoparticles, in addition to one base asphalt sample as a control sample. The asphalt was oven-heated until it became fluid as desired (150–160°C); a Silverson high shear mixer was used to mix the materials at a constant temperature of $170 \pm 1^\circ\text{C}$ at 5000 rpm for 90 min to ensure the production of homogenous mixtures. The homogeneity of mixtures was evaluated using the softening point test. The samples from the softening point test were taken every 30 min during mixing duration of 2 h until the value of softening point become stable, and the sample can then be considered as a homogeneous mixture.

3. Experimental procedures

3.1. The physical properties

The physical properties of each fabricated binder were evaluated based on the American Society for Testing and Materials (ASTM) specifications using conventional tests such as penetration ASTM D5, softening point ASTM D36, and ductility ASTM D113 to evaluate the differences between the base and $\text{Al}_2\text{O}_3$-modified asphalt binders.

3.2. Temperature susceptibility

Asphalt is a thermoplastic material and, therefore, its properties change with temperature. Temperature susceptibility, a very important property of asphalt, is defined as the temperature at which the consistency of asphalt changes with a change in temperature. Two different properties for determining the temperature susceptibility of asphalt have been in regular use: the penetration index (PI) and pen-vis number (PVN). The PI and PVN are measured as in Equations (1) and (2) (Brown et al., 2009; Ohinola, Felode, & Jonathan, 2012) as follows:

\[
\text{PI} = \frac{1952 - 500 \log(\text{pen}) - 20 \text{ Softening point}}{50 \log(\text{pen}) - \text{Softening point} - 12}, \tag{1}
\]

where PI is the penetration index, and \(\text{pen}\) is the value of the penetration test in tenths of a millimetre at 25°C.

\[
\text{PVN} = \frac{\log(L) - \log(X)}{\log(L) - \log(M)}(-1.5), \tag{2}
\]

where \(X\) is the viscosity in centistokes of the asphalt as measured at 135°C, \(L\) is the viscosity at 135°C for a PVN of 0.0, \(M\) is the viscosity at 135°C for PVN of \(-1.5\). However, the approximations in Equations (3) and (4), based on the least squares regression line can be used to calculate more accurate values of \(L\) and \(M\).

The equation for the line representing a PVN of 0.0 is

\[
\log(V) = 4.25800 - 0.79670 \log P. \tag{3}
\]

The equation for the line representing a PVN of \(-1.5\) is

\[
\log V = 3.46289 - 0.61094 \log P, \tag{4}
\]

where \(V\) is the viscosity in centistokes at 135°C and \(P\) is the penetration at 25°C.
3.3. **Rotational viscosity**

A Brookfield rotational viscometer was used to measure the rotational viscosity of the binders according to ASTM D4402 (Liu, Wu, Liu, & Li, 2015a). Each test used 10.5 ± 0.5 g of binder to obtain the viscosity value at a constant speed of 20 rpm. The viscosity at different temperatures was measured to observe the variation of the base binder and Al₂O₃ nanoparticle-modified asphalt binders.

3.4. **Storage stability**

The storage stability test was conducted by pouring the samples into an aluminium foil tube with dimensions of 16 cm length and 3 cm diameter. The foil tubes were closed and stored vertically at a temperature of 163 ± 5°C in an oven for 48 h, then cooled at room temperature and divided into three equal parts horizontally. The top and bottom of the samples were taken to evaluate the storage stability by measuring the softening points of the samples. If the variation of the results between the top and the bottom parts was 2.5°C or less, then the asphalt binder could be considered to have good storage stability. On the other hand, if the difference is higher than 2.5°C, the asphalt binder can be considered to be unstable (Zhang, Yu, & Han, 2011).

3.5. **Field emission scanning electron microscopy**

The addition of a modifier will change the composition and internal structure of the asphalt binder. The morphology of the base and Al₂O₃-modified asphalt binders was captured by Field Emission Scanning Electron Microscopy (FE-SEM). The FE-SEM images of Al₂O₃ nanoparticle-modified asphalt cement are very helpful to understand the microstructure change of modified asphalt, as well as the physical dispersion of nanoparticles inside asphalt blends. A vacuum coating method (coated with gold/palladium alloy) was used on the surface of the base and modified asphalt samples. The FE-SEM micrographs were obtained under a merlin compact brand Zeiss FE-SEM LEO SUPRA 55VP field emission scanning electron microscope at magnification levels of 1000 x.

3.6. **Fourier transform infrared spectroscopy**

Fourier Transform Infrared Spectroscopy (FTIR) analysis has been used to investigate macromolecular materials especially for nanomaterial-modified asphalt and polymer-modified asphalt binders [4, 28]. The results of this investigation were indicated by the functional groups such as single, double, and triple bonds between the carbon and other groups mixed with asphalt for modification. FTIR analysis was carried out by the PerkinElmer spectrometer Model 400, for unmodified and modified binders under wavenumbers from 4000 to 650 cm⁻¹ at room temperature.

3.7. **X-ray diffraction**

X-Ray Diffraction (XRD) used in this study is a D8 Advance; brand Bruker Germany with a power of 40 kv, step size of 0.025 and time of 0.1/0.025. The angle (2θ) from 5° up to 80° and the wavelength around 0.15406 nm with detector lynx eye type was used for all binders to compare the crystallite parameters of the base and modified asphalt binders with different concentrations of Al₂O₃ nanoparticles. The test was conducted at room temperature (25°C) and the thickness of samples was controlled using DSR sample moulds at the thickness of 2 mm.
3.8. Dynamic shear rheometer

A dynamic shear rheometer (DSR) was used to describe the viscoelastic behaviour of asphalt at low, intermediate, and high temperatures, by measuring the complex shear modulus ($G^*$) and phase angle ($\delta$), from a single test run. For viscoelastic materials like asphalt, the shear modulus is composed of the loss modulus (viscous component, $G''$) and storage modulus (elastic component, $G'$). The values of $G^*$ and $\delta$ for asphalt are reliant on both the frequency (time of loading) and temperature. DSR testing provides fundamental data on the properties of asphalt; such data can be used as a guideline for the performance of asphalt under test conditions (Liu et al., 2015a; Read & Whiteoak, 2003). Frequency sweep testing was conducted for all binders, using a plate of 8 mm diameter with a 2000 microns gap for low and intermediate temperatures of 10°C, 15°C, 25°C, and 35°C, and a plate of 25 mm diameter with a 1000-micron gap for intermediate and high temperatures of 25–75°C (Valtorta, Poulilakos, Partl, & Mazza, 2007). The tests were performed at nine frequencies from 1–100 rad/s or approximately 0.159–15 Hz. The failure temperature for all binders was noted, as declared in the Superior Performing Asphalt Pavements (Superpave) specifications, by the point at which $G^*/\sin(\delta)$ value increases above 1.0 kPa for an unaged asphalt. The correlation between $G^*/\sin(\delta)$ and the reduced frequency at any reference temperature ($T_{ref}$) is defined as the master curve of an asphalt composite (Marateanu & Anderson, 1996; Soleymani, Bahia, & Bergan, 1999; Walubita, Alvarez, & Simate, 2011; Zhao, Tang, & Liu, 2012). Experiments of repeated creep and recovery were conducted at 64°C with a diameter plate of 25 and 1.0 mm gap using a DSR machine. Ten cycles of repeated creep and recovery were adjusted with a loading time of 1 s and off-loading time of 9 s. Two stress levels were used in this study for these measurements, 100 and 3200 Pa (Khadivar & Kavussi, 2013).

4. Results and discussion

4.1. Physical properties testing

The effect of various concentrations of Al₂O₃ nanoparticles on the performance of asphalt, as measured by penetration, softening point, and ductility values, is shown in Table 2. A decrease in penetration occurred with the addition of up to 5 wt.% of Al₂O₃ nanoparticles.

The softening points of the binders increased with Al₂O₃ nanoparticles up to 5 wt.%, then decreased for 7 wt.% Al₂O₃ nanoparticles; the decrease for the 7 wt.% Al₂O₃ nanoparticles was due to the irregular dispersion of the nanoparticles in asphalt when agglomeration occurs. The decrease in penetration and the increase in softening point correspond to the increasing stiffness of the Al₂O₃-modified asphalt binders. The increased stiffness led to increased PI, which led to the enhancement of temperature susceptibility of Al₂O₃-modified asphalt binders (Airey, 2002a). Lower PVN values of asphalt correspond to higher temperature susceptibility; the same trend holds for PI values. Meanwhile, the ductility was observed to decrease with the addition of Al₂O₃ nanoparticles up to 5 wt.%, which is in accord with the increasing stiffness of the modified binders.

Table 2. Physical properties of unmodified and modified binders.

| Asphalt cement | Penetration @ 25°C (dmm) | Softening point (°C) | PI | Penetration viscosity number (PVN) | Ductility@ 25 (cm) |
|----------------|--------------------------|---------------------|----|-----------------------------------|-------------------|
| Base binder    | 70.0                     | 46                  | −1.48 | −0.295                           | > 100             |
| 3% Al₂O₃      | 27.64                    | 51                  | −2.14 | −0.863                           | 95                |
| 5% Al₂O₃      | 25.45                    | 53                  | −1.84 | −0.558                           | 62                |
| 7% Al₂O₃      | 38.18                    | 51                  | −1.54 | 0.053                            | 91                |
Table 3. ANOVA analysis of penetration and softening points for all binders.

| Variables       | Sum of squares | df   | Mean square | F     | Sig. |
|-----------------|----------------|------|-------------|-------|------|
| Penetration     |                |      |             |       |      |
| Between groups  | 3802.144       | 1267.381 | .000       |       |      |
| Within groups   | 8.000          | 1.000 |             |       |      |
| Total           | 3810.144       |      |             |       |      |
| Softening point |                |      |             |       |      |
| Between groups  | 77.583         | 25.861 | 19.097     | .001  |      |
| Within groups   | 10.833         | 1.354 |             |       |      |
| Total           | 88.417         |      |             |       |      |

These results were evaluated using one-way Analysis of Variance (ANOVA) to compare the effective differences, or significance level, of all base and modified binders. The mean difference is assumed to be significant at 0.05. Table 3 shows the one-way ANOVA analysis of penetration and softening point data for all binders. From Table 3, it was observed that changes in the percentage of the Al$_2$O$_3$ nanoparticle modifier have great effects on the binder’s physical properties, as the level of significance for penetration and softening point were 0.000 and 0.001, respectively, which are less than the assumed level of 0.05.

4.2. Viscosity

Viscosity is defined as the flow characteristics of the asphalt to show that it can be pumped and handled at the hot mix facility. It is also used to estimate the mixing and compaction temperature for asphalt mixture design. In general, higher-viscosity asphalt requires higher mixing and compaction temperatures (Asphalt Institute, 2007). Figure 1 shows that the viscosity values decline directly with increasing test temperature, regardless of the asphalt’s state of modification. Furthermore, the base binder has the lowest viscosity, while the binders modified with Al$_2$O$_3$ nanoparticles have successively higher viscosities with increasing concentration (Xiao, Amirkhanian, Wang, & Hao, 2014). The viscosity results for the Al$_2$O$_3$-modified asphalt binders remain within the Superpave specification at a temperature of 135°C, which was less than the maximum limit of 3 Pa.s, as the values of concentrations of 3, 5, and 7 wt.% Al$_2$O$_3$ nanoparticles

Figure 1. Rotational viscosities of base and Al$_2$O$_3$-modified asphalt binders.
Figure 2. Storage stability illustrated by the change in softening points of the base and Al$_2$O$_3$-modified asphalt binders stored at high temperature for 48 h.

were 0.64, 0.87, and 1.04 Pa·s, respectively. The results are comparable with a previous study which showed that viscosity values of binders modified with nano-silica decreased slightly with increasing test temperature (Yao et al., 2012).

4.3. Storage stability

Due to the small particle volume of the modifier, good workability and compatibility between Al$_2$O$_3$ nanoparticles and asphalt during storage at higher temperatures is expected (Wen, Zhang, Zhang, Sun, & Fan, 2002; Zhang, Yu, & Wu, 2010). The differences in softening points between the upper and lower sections of the tested binders are shown in Figure 2. The results confirmed that the Al$_2$O$_3$-modified asphalt binder has good compatibility and workability, as the differences in softening point between the upper and lower sections were less than 2.5°C for all binders, which means that the Al$_2$O$_3$-modified asphalt binders was quite stable during high-temperature storage.

4.4. Field emission scanning electron microscopy

The micrographs of the base and Al$_2$O$_3$-modified asphalt binders were obtained, even when the surface temperature of the samples was too high, due to the electron beam. From the FE-SEM micrographs (see supplementary Figure), it can be observed that the Al$_2$O$_3$ nanoparticles were dispersed uniformly and spread regularly in a continuous asphalt phase. The agglomeration process among Al$_2$O$_3$ nanoparticles occurs at 3 and 5 wt.%, but it is still within the nano dimension of nanoparticles as per the size measured by the FE-SEM machine. Meanwhile the 7% displays a clear agglomeration between the Al$_2$O$_3$ nanoparticles which effects their dispersion in asphalt binder.

4.5. Fourier transform infrared spectroscopy

Figure 3 shows the FTIR spectrum of the base and Al$_2$O$_3$-modified asphalt binder samples which included all functional groups that show modification of asphalt after being mixed with Al$_2$O$_3$. There is no peak of the O–H groups at wavenumbers more than 3500 nm, which confirms no water retention in the samples (Ba-Abbad, Chai, Takriff, Benamor, & Mohammad, 2015). For the
base sample, two broad peaks were observed in the 2851.40–2920.63 cm$^{-1}$ range which can be assigned for the group of C–H stretching vibrations form aliphatic chains. However, the weaker absorption at wave number of 1599.37 cm$^{-1}$ can be ascribed to stretching vibrations of C–C groups which indicate aromatic compounds. Moreover, a smaller peak was obtained between 1455.62 and 1376 cm$^{-1}$ due to stretching vibrations of the C–H from CH3, and S–O stretching vibrations were detected at 1032.81 cm$^{-1}$. Finally, the peak at range between 740–910 cm$^{-1}$ was attributed to the benzene which due to the stretching vibration of C–H bond. The sulphoxide bonds as S–O stretching vibrations were detected at 1032.81 cm$^{-1}$. The FTIR spectra of Al2O3-modified asphalt binders were close for all peak positions, which confirmed that no change in the structure of the modified binders compared with the base binder was obtained. The intensities of all Al2O3-modified asphalt samples (3–7%) declined compared to the pure sample of base asphalt, which indicates that functionalised with asphalt molecules was successfully occurred and enhanced other properties (Ba-Abbad, Kadhum, Mohamad, Takriff, & Sopian, 2010).

Additionally, the slightly changing in spectra of all base and Al2O3-modified asphalt binders was focused only for carbonyl bonds, (C–O) butadiene double bonds, (HC=CH) and sulphoxide bonds, (S–O) which standard centred at 1599.37, 966.1, and 1032.81 cm$^{-1}$, respectively. The ratio of their changing functional groups is summarised in Table 4. The ratio showed an increase

![Figure 3. FTIR spectra of the base and Al2O3-modified asphalt binders.](image-url)
in the modified samples' values for HC=CH and S–O compared with C–O from the base sample. The results show that asphalt has no obvious changes before and after modification, which indicates that modification of asphalt with Al₂O₃ nanoparticles is merely a physical process.

4.6. XRD analysis

Results obtained from an XRD test, displayed in Figure 4, show that the base asphalt binder lacks peaks, indicating its amorphous (non-crystalline) structure. The Al₂O₃ nanoparticles are non-crystalline as well. Modified asphalt binders with 3, 5, and 7 wt.% Al₂O₃ nanoparticles are shown not to present new crystalline phases. Even if there were new phases compared with the base asphalt, they were not observed. This might mean that the Al₂O₃ nanoparticles were distributed randomly inside the blends.

4.7. Rheological properties of modified binders

4.7.1. Isochronal plot

A plot of any viscoelastic function, such as $G^*$, versus temperature at a constant frequency or loading time is known as an isochronal plot. Viscoelastic data can be presented over a range of temperatures at a given frequency using this type of plot. The most easily apparent benefit of isochronal plots is the ability to compare $G^*$ and δ at different temperatures. Furthermore, many properties of asphalt, such as temperature susceptibility, can be interpreted from this type of visualisation. The isochronal plot of $G^*$ versus temperature at a frequency of 10 rad or 1.59 Hz is shown in Figure 5. The $G^*$ increases with additional increase of modifier concentration up to
5%, which indicates that Al₂O₃ nanoparticles’ dispersion in asphalt cement provides strength to the asphalt cement, where the increase of $G^*$ with temperature was consistent for all binders, and the binder containing 5 wt.% Al₂O₃ nanoparticles has a greater increase in $G^*$, which may correspond to improved temperature susceptibility than the other binders (Airey, 2002a).

4.7.2. Master curves

In order to represent the measurements of rheological values such as $G^*$ and $\delta$ at varying temperatures and frequencies, it is necessary to construct a master curve. This is used to visualise data over a wide range of frequencies. Therefore, the master curve reflects the time dependency of asphalt’s viscoelastic properties over a wide range of loading times. To construct the curve, a reference temperature $T_{\text{ref}}$ is selected, and the data at all other temperatures are shifted horizontally to produce a single smooth curve. The shifting uses the shift factor, which varies for each test temperature (Anderson et al., 1994). In this study, the master curve of $G^*$ and $\delta$ was created with $T_{\text{ref}} = 25^\circ$C, and the shifting factors were calculated using a numerical method. The $G^*$ master curves for all tested binders is presented in Figure 6. A smooth rise in $G^*$ occurs through the increase of modifier content to 5 wt.% Al₂O₃ nanoparticles, whereas in the binder containing 7 wt.% Al₂O₃ nanoparticles $G^*$ decreases. Similar behaviour was observed with a binder containing Organically Modified Montmorillonite nanoclay, with increasing $G^*$ and decreasing $\delta$ compared to the base binder (Muniandy, Bt, Hasham, & Aburkaba, 2013). In addition, DSR results obtained using nanoclay as modifier of asphalt also showed increasing $G^*$ with increasing frequency or decreasing temperature, while $\delta$ increased as frequency decreased or temperature increased (Galooyak, Dabir, Nazarbeygi, Moeini, & Berahman, 2011; Jahromi & Khodaii, 2009).

The phase angle $\delta$ is defined as the ratio of the loss modulus to storage modulus, and it reflects the viscous response of asphalt (Valtorta et al., 2007). The $\delta$ master curves for all binders are shown in Figure 7. The smooth decrease of $\delta$ is observed with increasing the amount of Al₂O₃ nanoparticles. It is also shown that a binder modified with 5 wt.% Al₂O₃ nanoparticles has a smaller phase angle compared with the other binders, meaning it has better elastic recovery.
Figure 6. Complex modulus master curves for all tested binders at a reference temperature of 25°C.

Figure 7. Phase angle master curves for all tested binders at a reference temperature of 25°C.

$G^*$ and $\delta$ were evaluated in terms of significance levels using a two-way ANOVA method. In this analysis the dependent variables were $G^*$ and $\delta$, while the explanatory variables were the binder, temperature, and frequency. Analysis using the two-way ANOVA method reveals three results, as shown in Table 5 for $G^*$ and Table 6 for $\delta$. Notably, all variables had significant differences, as the levels of significance were less than 0.05. This means the binder, temperature, and frequency all have a great influence on $G^*$. However, $\delta$ was only significantly affected by temperature and binder type. In general, the three explanatory variables have significant influences on the dependent variables, as the level of significance for all explanatory variables combined on $G^*$ and $\delta$ was 0.000 and 0.012, respectively.
Table 5. ANOVA results for dependent variable $G^*$ (complex modulus).

| Source                        | $F$            | Sig. |
|-------------------------------|---------------|------|
| Binders                      | 58804226.662  | .000 |
| Temperature                  | 2418621516.611| .000 |
| Frequency                    | 416177621.644 | .000 |
| Binders * Temp. * Freq.      | 1596104.093   | .000 |

Table 6. ANOVA results for dependent variable $\delta$ (phase angle).

| Source                        | $F$   | Sig. |
|-------------------------------|-------|------|
| Binders                      | 7.447 | .000 |
| Temperature                  | 9.876 | .000 |
| Frequency                    | 1.094 | .366 |
| Binders * Temp. * Freq.      | 1.319 | .012 |

Figure 8. Black diagram comparing complex modulus to phase angle for all binders.

4.7.3. Black diagram

A plot of $G^*$ versus $\delta$ obtained by dynamic testing is known as a Black diagram (Airey, 2002b). Viscoelastic data were plotted over a wide range of temperatures and frequencies using this format. Measurement errors, changes in composition, or variations in asphalt structure can cause deviations within the Black diagram. The values of $G^*$ and $\delta$, measured with the different sample compositions, are plotted in the Black diagram in Figure 8, which shows that the binder containing 5 wt.% Al$_2$O$_3$ nanoparticles has a greater $G^*$ at low $\delta$ compared with the other binders. This signifies that the 5 wt.% Al$_2$O$_3$-modified asphalt binder had the best rutting resistance of all modified binders.

4.7.4. Failure temperature

The failure temperature of asphalt is defined as the point at which the factor of $G^*/\sin(\delta)$ falls below 1.0 kPa, according to Superpave binder grade specifications. The property is frequently
used to identify the performance grade of asphalt binders (Xiao et al., 2014). The results obtained from DSR testing are shown in Figure 9. The base binder and Al₂O₃-modified asphalt binders have failure temperatures falling between 69°C and 78°C. Moreover, the base binder has the lowest failure temperature of approximately 69°C, whereas the modified binders with 3, 5, and 7 wt.% Al₂O₃ nanoparticles have failure temperatures around 74°C, 76°C, and 78°C, respectively.

4.7.5. Rutting parameter

The $G*/\sin(\delta)$ formula was used to describe the resistance to rutting, or permanent deformation, of asphalt at high temperatures. Superpave standards require that $G*/\sin(\delta) = 1$ kPa as a minimum for the rutting parameter for an unaged sample (Khadivar & Kavussi, 2013; McGennis, Shuler, & Bahia, 1994). The resistance of asphalt to rutting was measured by the DSR test. The measurement of the rutting parameter was conducted on unaged base and Al₂O₃-modified asphalt binders at different temperatures of 45°C, 55°C, 65°C, and 75°C. Figure 10 shows that the lowest value of $G*/\sin(\delta)$ was obtained from the base asphalt, while the highest value of $G*/\sin(\delta)$ was shown by the binder containing 5 wt.% Al₂O₃ nanoparticles. Higher values of $G*/\sin(\delta)$ indicate greater resistance to permanent deformation. The binder containing 7 wt.% Al₂O₃ nanoparticles displayed a relative decrease in $G*/\sin(\delta)$ compared to the other modified binders. Generally, it is evident that all modified binder values of $G*/\sin(\delta)$ exceeded 1.0 kPa at 70°C. The results from this study are in accordance with a previous study, which showed that nanoscale calcium carbonate (CaCO₃)-modified asphalt binder improved the rutting resistance and low-temperature toughness of asphalt (Zhen, 2007). Moreover, the addition of nanoscale silica (SiO₂) also significantly enhanced the rutting resistance of asphalt binders (Chen & Zhang, 2012; Yao et al., 2012).

4.7.6. Fatigue parameter

$G*\cdot\sin(\delta)$ is regularly used to describe the fatigue resistance of an asphalt cement at intermediate temperature. The Superpave method requires a maximum fatigue parameter of 5000 kPa (McGennis et al., 1994). A fatigue test was conducted at the four test temperatures of 10°C, 15°C, 25°C, and 35°C. The fatigue test utilised a constant loading frequency of 1.59 Hz or 10 rad/s, as
identified by the Superpave method. Figure 11 shows that all binders, including the base binder, have values less than the required Superpave minimum at 20°C test temperature. The $G^* \cdot \sin(\delta)$ value is observed to decrease with the addition of up to 5 wt.% of Al$_2$O$_3$. This observation is in accordance with another study on binders modified with 1% of nano-powdered VP401 rubber; the modified binder showed better intermediate temperature fatigue resistance compared to other nanomaterial-modified asphalt binders (Chen & Zhang, 2012).

### 4.8. Repeated creep and recovery

A repeated creep and recovery test is used to investigate the quantity of permanent deformation after the applied stress is removed on asphalt samples. Besides, the creep and recovery test can simulate the continuous traffic movements on the road (Kim, Lee, & Amirkhanian, 2011). The test was conducted according to ASTM D7405 at two stress levels indicating the low and high stress levels of traffic on the asphalt concrete. Figures 12 and 13 display schemas of creep and
recovery test for the base and Al₂O₃-modified binders at both stress levels (100 and 3200 Pa). The results show that the binder with concentration of 5 wt.% Al₂O₃ nanoparticles has the lowest compliance values for both levels of stress (1.266, 43.811 Pa) indicating high resistance to permanent deformation. This is due to the hardness of 5 wt.% Al₂O₃ nanoparticles, which is harder than other Al₂O₃-modified asphalt binders. Meanwhile, it was found that the base asphalt binder has the highest compliance values (4.035, 168.377 Pa), which means the lowest resistance to permanent deformation compared to other binders.

5. Conclusion

In this study, the physical and rheological characteristics of asphalt modified by Al₂O₃ nanoparticles were investigated using conventional and DSR testing methods. Different amounts of Al₂O₃ nanoparticles were added to asphalt at levels of 3, 5, and 7 wt.%. Based on the investigations in
In this study, conventional testing showed that the stiffness of asphalt binder increased with increasing Al$_2$O$_3$ nanoparticles, which led to improved temperature susceptibility of a modified asphalt binder. Moreover, the storage stability test results clarify that the Al$_2$O$_3$-modified asphalt binders were stable after storage at high temperatures. Meanwhile, the rheological properties presented by isochronal plots showed that 5 wt.% Al$_2$O$_3$ nanoparticles provided an additional pronounced increase in the stiffness of asphalt binder, as shown by the complex modulus, and as a result improved the temperature susceptibility of the asphalt binder. Master curves show that all Al$_2$O$_3$-modified asphalt binders displayed a reduction in elastic behaviour, as characterised by the phase angle, compared to the base binder. In addition, the binder with 5 wt.% Al$_2$O$_3$ nanoparticles was found to have greater elasticity than the other binders. The complex modulus was enhanced for all Al$_2$O$_3$-modified asphalt binders except that with 7 wt.% Al$_2$O$_3$ nanoparticles, which displayed a decrease in complex modulus. All Al$_2$O$_3$-modified asphalt binders had larger failure temperatures than the base binder.

ANOVA one- and two-way analyses were used to evaluate the significance of the test results. It was found that the binder, temperature, and loading frequency have a great effect on the complex modulus and phase angle. Likewise, SHRP Rutting Parameter and SHRP Fatigue Parameter testings support that use of Al$_2$O$_3$ nanoparticles as a modifier of asphalt binder effectively increases the resistance to rutting at high temperatures and resistance to fatigue at intermediate temperatures. Finally, the modified asphalt binder that displayed the best properties in this investigation was 5 wt.% Al$_2$O$_3$ nanoparticles and is considered as an optimum value.

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