Characterization of asphalt binders blended with nanomaterial and polymer

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Abstract. Modification of bitumen binders with polymers and nanomaterials has successes in mitigating various major causes of pavement failures. The aluminum oxide nanoparticles (Al2O3) and Acrylate-Styrene-Acrylonitrile polymer (ASA) were poured on the base bitumen binder 60/70 penetration grade with percentages of 3, 5 and 7% by the weight of bitumen binder. The outcome shows that the inclusion of polymer modified binders (ASMBs) and nanoparticles modified binders (ALMBs) matter has a great deal of impact on the rheological behavior of the bitumen binder at intense temperatures. However, the complex shear modulus (G*) improves the mix of the two modifiers. The increment at 75 °C was 63.70% for five percent ASMBs polymer, while for ALMBs, 71.12% for five percent. Although, the modified bitumen binders show high resistivity to rutting in intense temperatures, upon increment to 80% and 59% for five percent concentration of ASMBs as well as ALMBs chronologically. The refinement of bitumen binders gives an increase in the property of the binder which is the creep recovery for approximately about 69.23% and 62.53%. The use of ASMBs and ALMBs as discovered in this study shows that both modifiers above can mitigate the issues of the bitumen binder at intense temperatures, and five percent is regarded as the maximum constituent of the two modifiers.

1. Introduction

Bitumen is a naturally occurring dark brown to black cementation material, in other cases, it can be obtained by processing petroleum and petroleum products [1]. One of the significant uses of bitumen binder is its vast application in the construction of highways and roads network [2]. A typical highway pavement usually contains aggregates coated with a blend of bitumen binder, and the performance of pavements is associated with the rheological properties of bitumen binder [3]. Pavement might show distress when exposed to low and elevated temperatures. At low temperatures, fatigue cracks occur and lead to weakness in bitumen layers, while at elevated temperatures, permanent deformation (rutting) occurs and create channels on the roads because of vehicles [4, 5]. Therefore, to mitigate those distress, the modification of bitumen binder and mixture is essential to enhance the performance and reduce pavement distress [6, 7]. Various kinds of bitumen binder modifiers were used to improve its performance including; polymers, rubbers, fibers, and nanomaterials [8-11]. It has been identified that polymers show better bitumen performance when the used as modifiers, the behavioral pattern and content of the polymer have an essential part to play in improving the characteristics of the bitumen
binder. The most common polymers used worldwide as modifiers of bitumen binder are 75% elastomers and 15% plastomers, the remaining percentage which is 10, and that constitutes rubber or other refinements like; steel slags and waste glass [12, 13]. One of the major weaknesses of polymers modified bitumen binder is the segregation if stored at increased temperatures. The probability of separation under inert conditions is a major challenge for the actual usage blends [14]. The nanomaterials were used as additives to the mixture and to significantly enhance the stability of modified binders at high temperatures to decrease the phase segregation and improve the stability of bitumen binder and polymers [15]. Presently nanotechnology is rapidly integrated into the application of bitumen binder, with several kinds of nanomaterials being used as modifiers of bitumen binder and mixture. The usage of nanomaterials has been observed to be able to enhance the performance of bitumen binder and mixture. Adding a small amount of nanoclay based bitumen binder has a significant effect lead to increase its stiffness, reducing the strain failure rate of base bitumen binder and decrease the moisture susceptibility of the mixture [16]. Furthermore, using nanomaterials as a modifier of the bitumen binder results in an increase in the performance grade and enhancement in the elastic properties compared with the base bitumen binder [17]. Also, the viscosity rate was slightly decreased with the additional increase of nanomaterials in bitumen binder, as well as it works to reduce and delay the aging process. This study characterizes and investigates the influences of nano-aluminum oxide particles (Al₂O₃) and the Acrylate Styrene Acrylonitrile (ASA) on the rheological properties of bitumen binder. Moreover, to establish a comparative study regarding the best performance in bitumen.

2. Literature review

Several highway engineers have recognized the failure of asphalt layers, which result in a decrease in the service life of the road surface. Because of this, most of the highway engineers used the additive to enhance the performance of asphalt and reduce the maintenance cost. Many researchers have been studying the influences of polymers on modified bitumen binder and bitumen mixture [11]. Bernier has evaluated the rutting susceptibility of polymer modified bitumen mixtures containing recycled pavements, to compare the rutting resistance of bitumen binders and bitumen mixtures containing different polymer modifiers and different recycle bitumen pavement sources. The results show a significantly changed with the increment of the polymer. The additional increase of polymer significantly leads to reduce rutting susceptibility [18]. Glaoui determined the development of complex shear modulus, creep recovery and phase angle of polymer modified binder. The results showed that the complex modulus was considerably improved, and the phase angle was reduced at low temperatures, this behavior is not preferable for fatigue cracking. Moreover, the creep recovery results indicated that the polymer-modified binder after the aging condition has negative effects on the resistance of permanent deformation [19]. The engineering characteristic of polymer modified binders containing wax additives was evaluated by Mazumder et al. through Superpave binder tests. The investigation shows that polymers can improve rutting resistance and reduce the effects of fatigue and low-temperature cracking [20]. On the other hand, several types of research were conducted on nanomaterials modified bitumen binder. Shiman investigated the impact nanocomposites have on the properties of bitumen binders under extreme temperatures. A base bitumen was PG 58, and the nanomaterial was Single-Wall Nanotube (SWNT). The results showed that the addition of 0.3% wt. of the nanocomposite was able to increase the PG of the modified bitumen. Moreover, it was found that the elastic component to the complex modulus (G*) of modified bitumen binders is higher than the base bitumen binder and also the modified binders have lower thermal sensitivity and aging effects compared to base bitumen binder (Shiman et al., 2011). Golestani evaluates the performance of modified bitumen binders with nanoclay and the results showed that nanoclay is able to enhance the physical and rheological properties of the modified bitumen binders [21]. Khodary used Calcium hydroxide (Ca(OH)₂) nanoparticles as a bitumen modifier to evaluate the physical and mechanical properties of the modified bitumen binder and mixtures. The results show that the influence of Ca(OH)₂ nanoparticles on the mechanical properties such as bitumen mixtures was significant. Also, the addition of 5% Ca(OH)₂ nanoparticles decrease the penetration of modified bitumen up to 30% and 7% respectively while Softening increased by nearly 45%. Also, it was found that the Ca(OH)₂ nanoparticles modified bitumen mixtures specimens have the highest value of indirect tensile strength, while base bitumen has the lowest value. Finally, it was
recommended that the use of Ca (OH)₂ as a modifier of bitumen binder and mixture is preferable to in hot climate and for heavy traffic load area [22]. Estimating the moisture damage of the bitumen mixture modified with nano zinc oxide (ZnO) was conducted by Hamedi et al. [23]. The results showed that the modification of bitumen using nano-ZnO leads to reduce bitumen binder’s acidity and can improve adhesion between bitumen and aggregate compared to base bitumen binder. It was found that by adding nano-ZnO to bitumen binder, the unconditioned and conditioned indirect tensile strength (ITS) values were significantly enhanced [23].

3. Experimental design

3.1 Materials

Three primary materials used in the study includes local Malaysian bitumen binder 60/70 penetration grade, Acrylate Styrene Acrylonitrile polymer as well as the oxide of nano-aluminum oxide were obtained from China. The physical properties of the base bitumen binder, polymer, and nano-aluminum particles are shown in Table 1.

| Material | Properties | Test Method | Value |
|----------|------------|-------------|-------|
| Bitumen 60/70 | Specific Gravity | ASTM D70 | 1.03 |
| | Penetration @ 25 °C | ASTM D5 | 70 |
| | Softening point (°C) | ASTM D36 | 46.0 |
| | Viscosity @ 135 °C (Pa.s) | ASTM D4402 | 0.5 |
| | Ductility (cm) @ 25 °C, | ASTM D113 | ≥125 |
| ASA | Specific Gravity | - | 0.30 |
| | Size mm | - | 2 |
| Nano Al₂O₃ | Size nm | - | 13 |
| | Density g/cm³ | 3.5-3.9 |

3.2 Preparation of modified bitumen binders

The melt blending process was used to produce modified bitumen binders, this is carried out by putting these percentages chronologically, i.e., 3%, 5% and 7% the two modifiers which are ASA polymer and Al₂O₃ nanoparticles respectively by weight of the base bitumen binder. Heat is applied to the bitumen until there is a transformation in the state of the particle, i.e., from its solid state to fluid. After which it was mixed using a Silverson high shear mixer at a temperature of 170°C (±1 °C) within the speed limit of a 5000 rpm for an hour and thirty minutes to create homogenous mixes. The mixing temperature was consistency 170 (±1 °C), while the speed was reduced to 1500 rpm and the Al₂O₃ and ASA were added gradually to the blend, to make sure that the particles uniformly dispersed then the speed was increased to 5000 rpm. Dispersion is essential because nanoparticles have solid surface-active forces and it is difficult for them to disperse at high concentration. The samples were coded in the Figures and Tables to be for base bitumen binder 0% BB, for ASA polymer modified bitumen binders N% ASMBS, while for Al₂O₃ nanoparticles is N% ALMBs, where N is the concentration of the modifier.

3.3 Viscosity Test procedure

The refined bitumen binders, as well as the base viscosity, are to be to determine using a Brookfield rotational viscometer. The number 27 Spindle was employed at a given speed of 20 rpm as given by the Superpave test parameters. The average of three readings for each test temperature was recorded and identified to be the result. The experimental study is carried out under these temperatures, 135°C up to 200°C for all the samples in use.
3.4 Storage Stability test procedure
The storage stability of the refined bitumen binders alongside the base was measured according to the following procedure. A 3 cm width aluminum foil tube that is 16cm high is prepared, base and modified samples were poured into it. The aluminum foil tubes were placed in an oven at a temperature of 163 ± 5°C for exactly two days. This is later cooled at room temperature and shared into three equal parts in a horizontal form. The specimens removed from the up and downward parts were used to examine the storage stability of both elements (modifiers) by ascertaining the softening points of the sections. In a scenario where there is a difference of < 2.5°C on both the up and bottom areas, these samples were seen as those with great high-temperature storage stability. And on the other hand, where the softening points have a difference of more than 2.5 °C, samples of those refined bitumen binders were noted as the unstable ones.

4. Experimental design

4.1 High-temperature viscosity
Further increase in concentration and temperature on the viscosity of ASMBs and ASMBs refined bitumen binders have certain effects which are presented in Figure 1. It is visibly clear as shown in this figure that the viscosity of modified bitumen binders, irrespective of concentration, reduces as the temperature increases, the same pattern was observed in the base bitumen binder. A great deal of the bitumen binder viscosity can be enhanced by increasing the concentration level of both polymer and nanoparticles, thus implying that the bitumen thickness and better coating of aggregates in the bitumen mixture will be increased as well. Also, the bitumen refined with ALMBs is of much greater value regarding viscosity when compared to those refined with ASMBs. Moreover, from Figure 2 the mixing and compaction temperatures range were (157-145) for 0% BB, the ranges for ALSMBs (3, 5 and 7%) were around (148 and 160, 153 and 168, 165 and 167) respectively. While the mixing and compaction temperatures for ALMBs (3, 5 and 7%) were nearly (151 and 163, 158 and 173, 163 and 179) respectively. This indicates that modifiers type and amount have a significant role in temperature and viscosity.

![Figure 1. The viscosity of Base Bitumen and ASMBs and ALMBs.](image-url)
4.2 High-temperature storage stability

Regarding the difference in density between the bitumen binder as well as the polymer, it is not able to state that phase separation is possible in the refined bitumen binder at intense temperatures during the storage process. Bearing in mind that the minute size of the nanoparticles offers the ability to possess high workability and also compatibility. Although it is possible for an agglomeration to occur in ALMBs refined bitumen binders. The base bitumen binder ASMBs and ALMBs modified bitumen binder results for their storage stability are shown in Figure 2. As illustrated in this figure, the difference in the softening points within the base bitumen binder and the modifiers is at about 12 °C. Note that the enhancement of the softening point of refined bitumen binders implies that the bitumen is getting harder than the base bitumen binder. Also, the difference between the top and down parts of the ASA polymer modified bitumen binders for 3, and 5% were are less than 2.5 °C, which means the modifier (ASA polymer) had good stability at elevated temperatures. Meanwhile, 7% ASMBs the variances surpassed the acceptable range, which shows the presence of phase separation between the base bitumen binders, there is an increment in the ASMBs when polymer percentage is increased. When bitumen is modified using ALMBs, it is an indication that all refined or modified bitumen samples are of high storage stability at really high temperatures, the dissimilarity between the upper and lower parts were < 2.5 °C. It is seen that even though 7% ALMBs are considered to be stable, the variation in the upper and lower parts became higher when compared to 5% ALMBs, this implies that agglomeration occurs among the nanoparticles which thus increases their content in bitumen binder. In a nutshell, modified bitumen binders with ALMBs possess better storage stability than that of the samples modified using ALMBs.

![Figure 2. Storage stability of base, ASMBs and ALMBs modified bitumen binders.](image)

4.3 Isochronal plot

This can be described as a plot of certain visco-elastic variables like complex shear modulus or phase angle, which contrasted with the temperature at a constant frequency or loading time. The isochronal scheme is used to present viscoelastic data over a range of temperatures at a specified frequency. Thus, the isochronal plots of the temperature (°C) versus complex modulus (G*) and phase angle (δ) at the frequency of 0.159 Hz (1 rad/s) are shown in Figure 3. It indicates that the increase in G* was consistently detected for modified bitumen binders when contrasted to that of the base bitumen binder and also the modified bitumen is recorded to have the greatest performance when 5% ASMBs sample
for polymer and 5% ALMBs was added. Also, the phase angle was a decline for all modified binder responding with an increase in $G^*$ value. Higher $G^*$ and lower $\delta$ present the best viscoelastic properties of bitumen binder to resist the rutting and fatigue distress. Moreover, 7% concentration for both ASMBs and ALMBs indicates a small reduction in the value of $G^*$ due to phase segregation and agglomeration as detected by FE-SEM, and interfacial interactions respectively.

**Figure 3.** Isochronal plots of $G^*$ and $\delta$ for base and modified bitumen binders.

### 4.4 Influence of temperature on rutting

Irreversible or permanent deformation (rutting) of the bitumen binder. The description of Superpave recognizes the least number of 1.0 kPa for the $G^*/\sin\delta$ of base bitumen binder at performance grade temperature. Shenoy suggested the term $|G^*|/(1-(1/\tan\delta \sin\delta))$ as an improvement and an alternative to the Superpave specification parameter ($G^*/\sin\delta$) [24]. Figure 4 shows the comparison of the rutting parameter of base bitumen binder, polymer, and nanoparticles modified bitumen binders at 65 and 75 °C using Shenoy and Superpave specification parameters. It can be realized that the addition of both modifiers can greatly improve the resilience of bitumen to permanent deformation. The base bitumen binder takes the lowest of $G^*/\sin\delta$ value and 5% ALMBs is seen to have the greatest value of $G^*/\sin\delta$ in all the samples that were tested. It is seen from the careful examination that the resistance of bitumen binder to rutting parameter increased up to 5% with increment in the concentration of both modifiers. Various behavior is displayed at 7% when the $G^*/\sin\delta$ value declined slightly as the compatibility of polymer modified bitumen binders reduces due to phase segregation and agglomeration which causes softness in modified bitumen binders. The evaluation of both rutting parameters: Superpave specification (SPS) and Aroon Shenoy parameter (ASP) shows that there are non-huge differences in the values as noted in Fig. 6, which indicates that both methods are valid to evaluate the rutting parameter.
4.5 Loss and storage modulus of base and modified bitumen binders

The dissipated energy during the loading cycle is defined as the loss modulus ($G''$), like the energy loosed in the heating of bitumen. It is an amount of vibrational energy that has been transformed during vibration, which cannot be recovered, whereas the rigidity of viscoelastic materials and it proportional to the energy stored during a loading cycle represents the storage modulus ($G'$). A low tan $\delta$ value indicates one that is more elastic. Since $G'$ measures the binder elasticity, while a high value is indicative of a material that has a high non-elastic strain component, the binders at high temperatures should have a high value of storage modulus ($G'$) to have good resistance to deformation. To avoid the flow of the binder at elevated temperatures high elasticity is required. The elastic (storage) and viscous (loss) modulus values of base and modified binders tested at temperatures of $55$, $65$ and $75^\circ$C are shown in Figures 5 and 6. Similar to previous results, the addition of both modifiers resulted in an increase in elastic modulus and viscous modulus compared to base bitumen binder. The highest improvement for both visco and elastic properties was observed with a concentration of $5\%$ ALMBs followed by $5\%$ ASMBs, whereas the base bitumen binder has the lowest viscoelastic values among all the blends.

5. Conclusions

This study was carried out to assess the characteristics of bitumen binder refined with ASMBs and ALMBs at elevated temperatures, conducting storage stability, a viscosity the MSRC test and frequency sweep. The following conclusions deduced based on the results:

- In respect to viscosity, the values of modified bitumen binders increased with an increment in the concentration of the modifier, each of the viscosity values was within the limit of the Superpave specifications (less than $3$ Pa at $135$ °C).
- It is possible to store the modified bitumen binders at high temperatures, particularly for the samples refined with ALMBs, while the ASMBs can store up to $5\%$ concentration of polymer.
• Complex modulus (G*) and rutting parameters (G*/sin δ) values of base bitumen binders were the lowest compared with modified bitumen binders. Furthermore, the 5% ALMBs have the greatest value within all the modified bitumen binders which imply the better performance of modified bitumen binder concerning rutting resistance. It is also important to note that the investigation of rutting parameters shows that there are no many differences between Arroon Shenoy parameter (ASP) and Superpave specification (SPS) parameters and both of them can represent the rutting behavior of the base and modified bitumen binder.
In a nutshell general, the refinement or modification of bitumen binder using ASMBs and ALMBs has a great effect on the characteristics and properties of bitumen binder. Furthermore, the samples modified with nanoparticles indicate better performance than those modified with the polymer. Lastly, 5% can be regarded as the ideal content for both modifiers.

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