Rheological and rutting evaluation of composite nanosilica/polyethylene modified bitumen

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Abstract. In this research, composite nanosilica/polyethylene modified binder samples were prepared at varying concentration of nanosilica. The modified binder samples are prepared by adding 1%, 2% and 3% nanosilica by weight of bitumen in to 6% linear low density polyethylene (LLDPE) polymer modified binder. Effects of nanosilica on physical and rheological properties of composites were investigated through penetration, softening point, temperature susceptibility, dynamic mechanical analysis and rutting resistance evaluations. Results shows that, nanosilica affects the rheological properties of LLDPE modified binder due to decrease in penetration and increase in softening point observed with increase in nanosilica content, this enhances composite binders hardness and resistance to temperature. Temperature susceptibility shows that, composite modified binders are less susceptible to temperature compared to LLDPE modified binder. DSR rheological analysis shows that, nanosilica enhances the composite modified binders properties at intermediate to high temperatures. Also rutting parameter evaluation indicates that composite modified binders have high resistance to rutting deformations due to increase in elastic behavior and stiffness of the composites.

1. Introduction

Bitumen consists of complex chemical composition, it often exhibits both elastic and viscous behaviors which largely depends on loading time and temperature[1, 2]. Bitumen is generally known as aggregates binder applied for flexible pavements constructions due to its unique viscoelastic properties [3, 4]. However, current increase in axle loads globally together with varying climatic conditions leads to rapid deterioration of pavements, to overcome such effects, pavement demands binder with higher performance than normal grade bitumens applied [5]. Consequently, now a day more and more modified bitumens are applied for pavement constructions. Recently, over the past ten years, composite polymer/inorganic nanomaterials modification becomes more interested for construction of pavements as it improves both physical and rheological properties of binders [6, 7].
Nanomaterial are material having one of its external dimensions or internal structure in order of 100 nm or less, and this material can exhibit novel properties that the same material without nanoscale structure cannot [8]. However, there is limited research conducted on composite polymer/nanomaterial modified binder performance properties characterization. Therefore, in this study the performance characteristics of composite LLDPE/Nanosilica modified binder were evaluated.

2. Materials and modification process

2.1 Materials
The binder modified is penetration grade 80/100 bitumen supplied by PETRONAS refinery Melacca, Malaysia. Polymer used in pellet form is linear low density polyethylene (LLDPE) produced by Etilinas polyethylene Sdn Bhd in Kerteh, Malaysia. Nanosilica supplied by Benua Sains chemical Sdn Bhd Malaysia is used in this research.

2.2 Modification process
The composite LLDPE/nanosilica modified binder samples were preferred by first melting the binder at temperature of 150 °C. Upon reaching temperature of 150 °C it becomes sufficiently fluid, a weighted 1%, 2% and 3% amounts of nanosilica by weight of bitumen binder were gradually added to 6% LLDPE polymer modified binder. The composites were mixed using a desktop propeller blade multimix high shear mixer at high blending rate of 4000 rpm for 2 hours to obtain a homogenous composite mixture.

3. Experimentation methods

3.1 Penetration Test
An empirical needle Penetration test (ASTM D5-13) is used to establish binders consistency at a temperature of 25°C under a load of 100g and time period of 5 seconds which produces penetration depth in units of 1/10 mm on the tested sample. The depth of penetration in units of 0.1 mm is recorded as the penetration value of the binders.

3.2 Softening Point Temperature Test
Ring and ball test (ASTM D36-12) is used to characterize and establishes the temperature at which bitumen binder softens. Softening point is taken as the temperature under which bitumen binder sample cannot support steel ball of 3.5g weight, when heated at uniform rate of temperature of 5°C/ min.

3.3 Temperature susceptibility
Temperature susceptibility for composite nanosilica modified binders was evaluated based on penetration index (PI) parameter. Estimation of PI is described by Shell Bitumen Hand book [9] as shown by Eq. 1.

$$PI = \frac{1952 - 500\log P_{25} - 20T_{R&B}}{50\log P_{25} - T_{R&B} - 120}$$

where PI is the penetration index, $P_{25}$ is the binder penetration at temperature of 25 °C, and $T_{R&B}$ is the softening point temperature.
3.4 Dynamic shear rheometer test
A Malvern Kinexus rheometer was used to determine the rheological characteristics of composite LLDPE/nanosilica modified binders. Temperature sweep test was conducted under controlled strain loading mode over a temperature range of 20-60 °C and constant frequency of 10 rad/s. A heated sample of modified binder about 1.0 g weight was placed on top of the DSR lower plate. The upper parallel plate was then lowered to a height of 50 μm plus the required testing gap geometry of 1mm or 2mm and excess binder around the plates were trimmed out and the final gap was adjusted to a required 1mm or 2mm testing gap geometry.

4. Results and discussions

4.1 Penetration Test
Fig. 1 shows the effect of nanosilica on penetration of LLDPE and composite LLDPE/nanosilica modified binders. It can be seen that, nanosilica causes reduction in penetration values of the LLDPE modified binders, and the reduction is observed to increase with increase in nanosilica content. This may result in an enhancement of the modified binders resistance against temperature defects there by increasing its durability and performance during service life stages. Also, large decrease in penetration observed within nanocomposite modified binders indicates that nanosilica addition makes the binder to be more consistent and harder, this might increase the binders resistance against rutting

4.2 Softening point test
Fig. 2 shows the softening point temperatures for LLDPE and composite LLDPE/nanosilica modified binders. It can be seen that nanosilica addition causes an increase in softening point temperatures of the modified binders. The increment in softening point temperature is observed to be increase with increase in nanosilica, binder containing 3% nanosilica shows the highest softening point increment of 64 °C. The increase in softening point temperature for the composites indicates a reduction in their ability to soften easily under influence of temperature, and this will results in binders higher resistance against rutting.

![Figure 1](image1.png)  ![Figure 2](image2.png)

**Figure. 1** Effects of penetration on modified binders

**Figure. 2** Softening point temperature of modified binders
4.3 Temperature susceptibility

Fig. 3 shows penetration index values as an indication of temperature susceptibility for LLDPE and composite modified binders. It can be observed that, the initial PI value for LLDPE modified binder is 1.2, but with addition of nanosilica up to 3%, the PI value increases to 1.8, this shows that, composite modified binders exhibit high temperature resistance compared LLDPE modified binder, and the resistance increase with increase in nanosilica content. Increase in PI values observed in composites modified binders with increase in nanosilica can be attributed to exfoliated structure formed due to nanosilica addition which increases service temperature range and resistance to low temperature cracking and permanent deformation [10].

4.4 Rheological evaluation

Fig. 4, 5 and 6 are isochronal plots of complex modulus, complex viscosity and phase angle of LLDPE and composite modified binders against temperature. It can be seen that, composite modified binders complex modulus (Fig. 4) and complex viscosity (Fig. 5) increases with increase in nanosilica, however, phase angle (Fig. 6) a different phenomenon were observed where by phase angle decreases with an increase in nanosilica content. From isochronal plot of complex modulus in Fig. 4, it can be seen that, for composite modified binders, there is slight increase in G* at lower concentrations of nanosilica, but at high temperatures, higher increment was observed, this indicates that, addition of nanosilica enhances complex modulus which increases binders resistance to permanent deformation.

From isochronal plot of phase angle in Fig. 5 it can be observed that, nanosilica addition to form composites reduces phase angle values of LLDPE modified binders at intermediate to high temperatures. However, the decrease in phase angle values as nanosilica was added especially at intermediate temperatures confirms the formation of exfoliated nanostructure which enhances the binders performance [10].

From isochronal plot of complex viscosity in Fig. 5, it is observed that, there was increase in viscosity of the composites; this implies that, composite modified binders will results in formation of strong bond between aggregates and binder due to thicker film of binder that will surround the aggregates.
4.5 Rutting resistance

For evaluation of bituminous binder resistance to rutting, a $G*/\sin \delta$ ratio is used as specified by Superpave specifications. Superpave specification sets a limit of $G*/\sin \delta \geq 1$ kPa [11] as the minimum requirement for rutting resistance of unaged binders. The $G*/\sin \delta$ ratios for modified binders at varying temperature ranges are presented in Fig. 7. It can be observed that, LLDPE polymer modified binder have the minimum $G*/\sin \delta$ ratio, and composite modified binders have the highest $G*/\sin \delta$ ratio.

However, it can also observed that, at intermediate temperatures of 20°C to 40°C all modified samples have the minimum required value of 1.0 kPa for rutting resistance, while for high temperatures above 50°C only 2% and 3% NS composite modified binders achieved the required minimum value of 1.0 kPa. This shows that, composite modified binders can be used to achieve higher enhancement in resistance to permanent deformation at high temperatures.

5. Conclusions

Based on observations in this research for composite modification, the results shows that, the composite penetration decreases and softening point temperature increases which enhances the binders hardness and better resistance to temperature effects. Temperature susceptibility evaluation indicates that, composite nanosilica modified binders have less susceptibility to temperature, due to higher PI.
values observed in composites compared to LLDPE modified binder. A rheological evaluation shows that, nanosilica enhances the rheological performance of the composite modified binders at intermediate to high service temperatures. Rutting estimations, shows that, composite modified binders are more resistant to deformations, this makes them more suitable for paving applications compared to LLDPE modified binder. From analysis of the outcome, 3% NS can be recommended as the optimum content for composite modification.

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