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Influence of Nanosilica on Rheological Properties and Oxidative Aging of Polymer Modified Bitumen

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Abstract: In recent years, nanomaterials have led to promising developments in the improvement of pavement performances. In this study, nanosilica was added to LLDPE polymer modified binder at concentration of 1-6% by weight of bitumen binder. Characteristics of nanocomposite modified binders were evaluated using conventional and Superpave binder test techniques. Penetration test, softening point test, Dynamic Shear Rheometer (DSR) and Rolling Thin Film Oven Test (RTFOT) were used to analyze performance and rheological properties of the nanocomposite modified binders. In addition, the aging resistance of nanocomposite modified binders after RTFOT short term aging was evaluated through aging indices. The results show that, nanosilica content has significant effect on polymer modified binder. Nanosilica composite modified binders penetration decreases and softening point increases with increase in nanosilica, this implies enhancement in binders hardness and stiffness. RTFOT aging indices evaluations show that, nanosilica composite modified binders achieved the minimum superpave requirements; this implies that nanosilica reduces oxidative aging. The overall findings show that, nanosilica protects the polyethylene polymer modified binder from binder from oxidative aging.

Key words: Nanosilica, polyethylene, aging, rheology, bitumen, superpave requirements

INTRODUCTION

Bitumen composed of extremely complex mixture of hydrocarbons and its behavior entirely depends temperature and loading time (Yao *et al*., 2012; Olutaiwo and Adedimila, 2008). Bitumen as a colloidal system, it consist of high molecular weight asphaltene micelles which are dispersed in low molecular weight oily medium (Petersen, 2000; Ekott and Akpabio, 2011; Oseghale and Ebhodaghe, 2011). Recent increase in traffic volumes and axle loads with bitumen poor performance on different weather conditions, results in placing much emphasis in its modification to resist defects like moisture damages, deformations and fatigue cracking (Sengoz and Isikyakar, 2008). Polymers such as thermoplastic elastomers and plastomers were found to be among the best materials for bitumen modification after yielding several improvements on the modified binders (Airey, 2003). The major benefits recorded in applying polymers are reduction in temperature sensitivity, increasing resistance to permanent deformation, higher stiffness during high temperature, good resistant to moisture, resistance to cracking at lower temperatures and longer fatigue life (Zhu *et al*., 2014).

Some among the best polymers applied for bitumen modification are polyolefins such as polyethylenes, these includes; Low-Density Polyethylene (LDPE), Linear Low Density Polyethylene (LLDPE), High Density Polyethylene (HDPE) and polypropylenes with their copolymers (Punith and Veeraragavan, 2010; Fang *et al*., 2008). Polyolefins polymers when added to bitumen provide several benefits such as enhancement in properties during service life of pavement, improvement in thermo-mechanical resistance, increase in adhesion and elasticity of binder (Auden *et al*., 2008; Lepe *et al*., 2005; Fawcett *et al*., 1999). Despite the achievements recorded with polymers, several challenges still exist. The major problems related to polymer modified bitumen are lack of morphological stability during hot storage (phase separation), poor resistance to ageing (oxidation), poor compatibility with bitumen and high cost of modification among others (Zhu *et al*., 2014; Ouyang *et al*., 2006).

Recently a lot of researches were carried out to investigate if the application of optimum physical characteristics of nanomaterials can make them suitable for bitumen modification and the results indicate that nanomaterials can enhance bituminous binder properties

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due to their excellent properties like small particle size which makes them easily blend and more compatible with bitumen (Mahdi *et al*., 2013). Nanomaterial is a material having one or more of its external dimensions or an internal structure in an order of 1-100 nm having special characteristics different from the same material without nano scale dimension. Moreover, the specific benefits of using nanomaterials for bitumen modification includes reduction in moisture susceptibility in all conditions, higher storage stability, higher resistance to damage by aging, higher rutting resistance at low and high service temperatures and finally savings in cost, energy and routine maintenance (Yang and Tighe, 2013).

Composite nanosilica/polymer modification draws attention as the best alternative to polymers for bitumen modification (Yusoff *et al*., 2014). Composite nanomaterial/polymer modification is generally more cost effective as it reduces the quantities of polymer and nanomaterial used at the same time increasing compatibility of polymers with bitumen (Yu *et al*., 2015). The most common nanomaterials used for bitumen modification includes Carbon Nanotubes (CNT), Titanium dioxide (TiO_2), Nanoclay (OMMT), nano $CaCO_3$, nano Silicon Oxide (SiO_2) and nano Zinc Oxide (ZnO) (Fang *et al*., 2013). However, composite modification with nanomaterials requires the use of high shear energy for mixing rather than ordinary mixing techniques, this was due to possibility of forming time dependent segregation as a result of poor mixing among the composite materials (Santagata *et al*., 2012).

Silica is one of the abundant compounds deposited worldwide which is largely used by industries to produce colloidal silica, silica gels and fumed silica. After invention of nano sized silica, it is mainly used by industries producing medicines, cement and concrete mixtures and also in industries to reinforce elastomers as rheological solutes. Nanosilica is a new inorganic that popularly used as a strength agent for rubbers, catalyst carrier and a plastic filler due to its high beneficial properties such as a large surface area, excellent dispersion ability, high absorption, excellent stability and high chemical purity (Yao *et al*., 2012). Nanosilica composites recently attracted scientific research interest due to its greatest benefit of reduction in cost of production and excellent performance features (Yusoff *et al*., 2014). Now a days, because of the high surface area and stability of nanosilica, it is widely used as inorganic filler in polymers and bitumen binder to improve properties of polymers and bituminous materials (Yang and Tighe, 2013; Fini *et al*., 2015).

Nanosilica becomes very attractive for use in bitumen modification, this is because its interaction surface area which is much larger compared to that of conventional fillers (Fini *et al*., 2015). Generally, the surface of nanosilica is more chemically active with high polarity unlike other nanomaterials (Yao *et al*., 2012). Nanosilica has strong surface free energy and its interface atoms are arranged in a disordered manner which allows for these atoms to be bonded strongly to other outside atoms by external forces (Fang *et al*., 2013).

Currently, there are limited experimental studies on evaluation of rheological and oxidative aging effects of nanosilica on composite polymer modified binders. The main objectives of this research was to characterized the properties of composite nanosilica/LLDPE modified binders through conventional properties as well as evaluation of the aging effects through assessment of aging indices of the modified binders.

MATERIALS AND METHODS

Materials and modification process: The base bitumen modified in this research is 80/100 penetration grade which was obtained from Petronas industry Melacca, Malaysia. The physical properties of the base bitumen binder used are listed in Table 1. Polymer Linear Low Density Polyethylene (LLDPE) in pellet form was supplied by Etilinas Polyethylene Malaysia Sdn. Bhd, Kerteh, Malaysia. The nanosilica used was supplied by Benua Sains chemical Sdn Bhd Malaysia with properties presented in Table 2.

Preparation of composite modified binders: The composite nanosilica/polymer modified binders was prepared by modifying the optimum concentration of 6% LLDPE with the addition of 1-6% nanosilica by weight of bitumen binder, respectively. Bitumen binder was first heated in an oven at temperature of 150°C until it became sufficiently fluid. For the composites mixing a propeller blade desk top multimix high shear mixer was used at high shear rate of 4000 rpm for 2 h. During the mixing process, the temperature was maintained at a rate of 150±5°C throughout.

Experimentation methods

Conventional properties test: Conventional test penetration and softening point for classifying binders consistency were carried out on aged and unaged modified and control bitumen binders in this research. A needle penetration test was use to establish the consistency of binder at a temperature of 25°C under an applied load of 100 g within time period of 5 sec according to ASTM D5 13 specification.

Table 1: Physical properties of base binder

Physical property	Values	Units
Penetration (25°C, 0.1 mm)	84	dmm
Softening point	42	°C
Ductility at 25°C	>150	cm
Viscosity at 135°C	0.64	Pa.s
Specific gravity	1.03	g/cm^3

Table 2: Physical properties of nanosilica

Physical property	Values
Appearances	High dispersive white powder
Hydrophobicity	Strong hydrophobicity
SiO_2 content (%) (950°C, 2 h)	99.8
Purity (%)	>99.9
Loss of ignition (%)	≤6
Surface density (g/mL)	0.15
Average particle size (nm)	10-25
PH value	6.5-7.5
Specific surface area (m^2/g)	100±25

Ring and ball softening point test was used to characterize and establishes the temperature under which binder easily softens. Ring and ball softening point was taken as the temperature at which binder will not support a steel ball of weight 3.5 g heated at a uniform temperature rise of not more than 5°C/min in accordance to ASTM D36 12.

Dynamic shear rheometer test: The most common technique currently used for the determination of fundamental rheological characteristics of modified binders is through dynamic mechanical analysis using oscillatory type testing under region of linear viscoelastic response. A Kinexus Malvern Instruments DSR was used for rheological evaluation. Amplitude sweep tests were conducted first for determining LVE region for the bituminous binders to ensure that the specimen was tested in the linear region. The gap between the upper and lower plates of DSR were set at a height of 50 μm plus the required testing gap of 1 or 2 mm at the specified testing temperature or at the mid-point of an expected testing temperature range. After gap setting, a sufficient amount of hot modified bitumen was poured onto the surface of DSR lower plate. Upper DSR plate was then released down until it reaches the required nominal testing gap plus 50 μm. The excess binder outside the DSR plates was then trimmed out from the DSR plates edges using a sharp hot DSR blade and immediately after sample trimming, the gap was further closed by 50 μm to reach the specified testing gap and to have a slight bulge within the circumference of the testing geometry. Temperature sweep test were conducted based on Table 3.

Aging methods: RTFOT was conducted based on ASTM D2872 specification for the simulation of short term aging occurrence causes by oxidation which usually happens during mixing of binders. Binder samples of 35 g weight were poured in to RTFOT glass containers. The containers with binder samples was then placed in the RTFOT carriage with the top opening of the containers directly facing a jet of air inside and then closed. Ageing process continues for 85 min with the carriage rotating at speed of 15 rpm at an uninterrupted temperature of 163°C.

Table 3: Rheological test conditions

Parameters	Conditions
Mode of loading	Controlled strain
Test temperatures	20-60°C (with the interval of 5°C)
Frequency	10 rad/sec
Temperature rise rate	2°C/min
Spindle geometries	8 mm diameter with 2 mm testing gap (20-35°C) 25mm diameter with 1mm testing gap (25-60°C)
Strain	(0.2%) within the LVE response

RESULTS AND DISCUSSION

Penetration: The influence of nanosilica concentration on the properties of LLDPE polymer modified binder before and after aging is shown in Fig. 1. It is observed that, there is reduction in penetration values of the nanosilica modified binders with increase in nanosilica content. The pronounced decrease in penetration values within the composite LLDPE/nanosilica modified binders indicates that nanosilica has strong effect on the binders physical properties due to increase in stiffness. This can provide an enhancement on the modified binders resistance against rutting and temperature defects. However, after aging of the modified binders, a large difference in penetration values were observed between the aged and unaged composites, this may be attributed due to nanosilica presence which prevents oxygen penetration within the binder as such, increases binders hardness and resistance to aging effects.

Softening point: Ring and ball softening point test is used to describe the temperature at which the bitumen binder becomes soft and flow. It is evident that, bitumen binders exhibiting high softening point temperature forms asphalt mixture with high deformation resistance (Fontes *et al*., 2010). Figure 2 presents the ring and ball softening point temperature of LLDPE and composite nanosilica modified binders. It can be seen that, for unaged composite modified binders, the softening point temperature increases remarkably up to 4% nanosilica content after which start to decline. The increase in softening point temperature up to 4% for composite modified binders can be attributed due to presence of nanosilica additive. The increment in stiffness indicates that nanosilica composite modified binders will be more resistant to plastic deformation. Softening point test conducted on aged samples also shows an increase in softening point

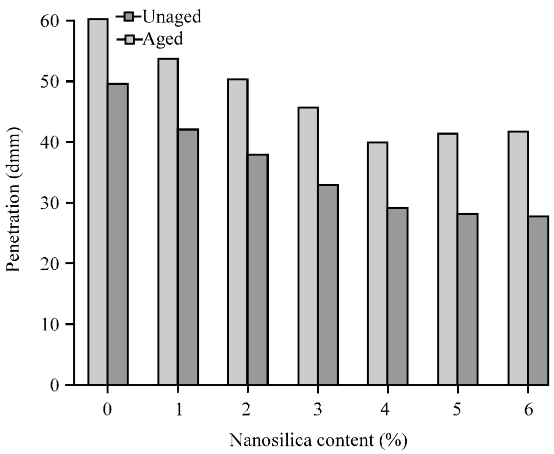

Fig. 1: Penetration of modified binders before aging and after RTFOT aging

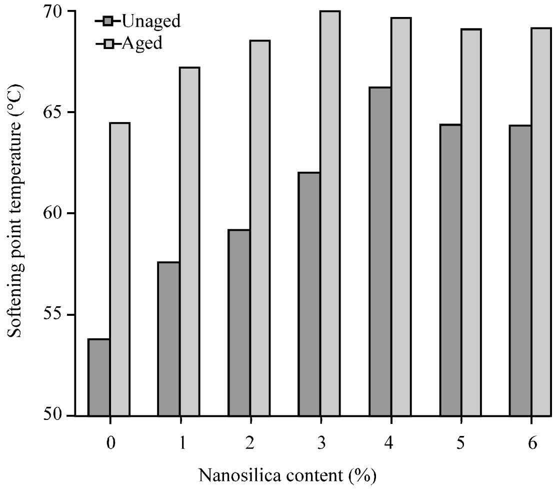

Fig. 2: Softening point temperature for modified binders before aging and after aging

temperature up to 3% nanosilica content after which stars to decrease with increase in nanosilica content. This shows that, presence of nanosilica as an additive prevents the PMB from oxidative aging and allows formation of strong chemical bond between bitumen and LLDPE polymer which makes aromatic compounds to remain, instead of decreasing at the time of aging.

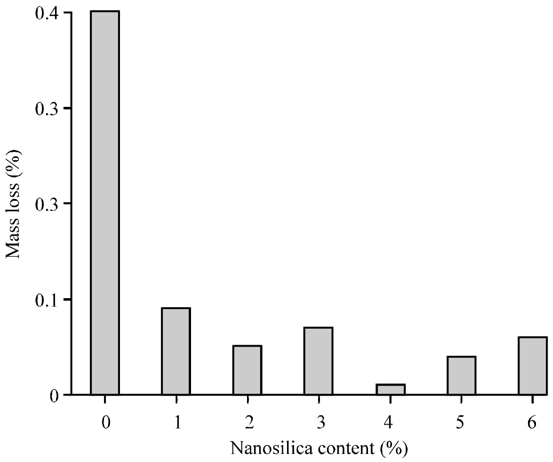

Fig. 3: Mass loss of modified binders at various percentages of nanosilica

Mass loss: Mass loss in bitumen binders is used to check effects of aging on binders during mixing or construction process. Superpave specifications requirements, described that, the percentage of mass loss shall not be more than 1% for all binder grades. Figure 3 describes the mass loss of composite modified binders obtained in this study. From the results, it can be seen that, the least values of mass loss 0.01-0.06% are found within composite modified binders. This shows that all composite modified binder samples have mass loss less than the required value of 1%. This indicates that aging may not have influence on the composite modified binders during mixing or constructions.

Rheological aging indices

Complex modulus aging index: Complex modulus aging index is used for evaluation of binder resistance against aging defects. Low value of complex modulus aging index are generally desirable for binder to have high aging resistance, complex modulus aging index is computes as Eq. 1:

$$\text{CAI} = \frac{G^*_{(\text{RTFOT}_{\text{aged}})}}{G^*_{(\text{Unaged})}} \tag{1}$$

Where:

CAI = The complex modulus aging index

$G^*_{(\text{RTFOTaged})}$ and $G^*_{(\text{unaged})}$ = The aged and unaged complex modulus, respectively

Figure 4 shows the effects of nanosilica content on complex modulus aging index both before and after binders aging. As observed, the nanocomposite modified binders have lower complex modulus aging index compared to LLDPE polymer modified binder. Comparing the nanocomposite modified binders, the CAI decreases progressively with increase in nanosilica content as such nanosilica can be used as an antiaging material for plastomeric polymer modified binders. The continuos decrease in CAI value with increase in nanosilica content fully indicates that nanosilica modified binder samples are more resistant to oxidative aging effects. The higher

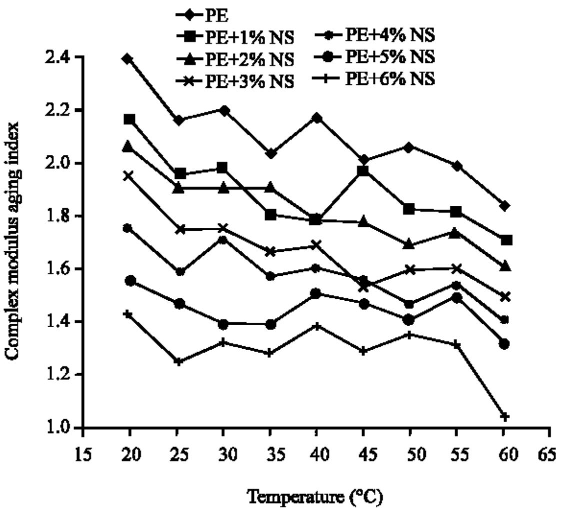

Fig. 4: Effect of aging on complex modulus of LLDPE and nanosilica modified binders

resistance in oxidative aging could be attributed to the large surface area of nanosilica material which increases its interaction with bitumen molecules which leads to a decrease in oxidative reaction (Fini *et al*., 2015).

Also, it can be seen that, nanosilica modified binder containing 6% NS shows the least complex modulus aging index, this implies that, the binder will be more resistant to oxidative aging compared to other nanosilica modified binders. The large improvement achieved in oxidative aging resistance of nanocomposite modified binders can be related to the barrier formed by nanosilica particles which protect oxygen molecules from penetration in to the binder.

Phase angle aging index: Phase angle aging index is used for further evaluation of bitumen binder susceptibility to aging effects. Generally, for a binder to have good aging resistance, a high value of phase angle aging index is desirable. Phase angle aging index is computed as in Eq. 2:

$$\text{PAI} = \frac{\text{Aged}_{(\text{phaseangle})}}{\text{Unaged}_{(\text{phaseangle})}} \tag{2}$$

Where:

PAI = The phase angle aging index

$\text{Aged}_{(\text{phaseangle})}$ and $\text{Unaged}_{(\text{phaseangle})}$ = The phase angles before and after aging

Figure 5 presents the effects of nanosilica on the phase angle aging index of LLDPE polymer modified binder before and after aging. It can be observed that, nanocomposite modified binders shows higher complex modulus aging index compared to LLDPE polymer modified binders. It can also see that as the nanosilica content increases, the PAI continuously increases with 6% nanosilica showing the highest PAI value of 1.06 at 60°C among all modified samples. This indicates that nanosilica modified samples at all concentrations of nanosilica are more resistant to oxidative aging compared to PMB.

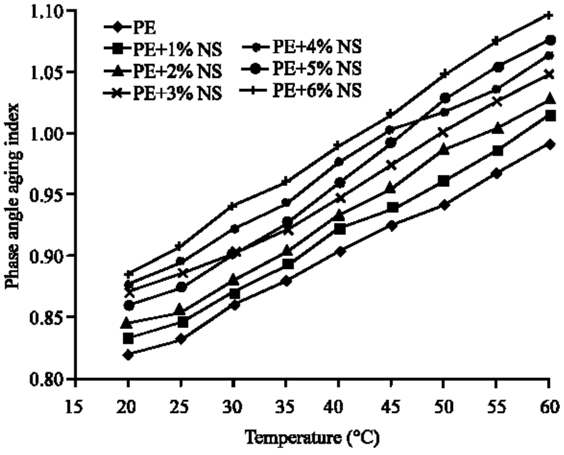

Fig. 5: Effect of aging on phase angle of LLDPE and nanosilica modified binders

The large enhancement observed in PAI within nanosilica modified binder samples can be attributed due to effects of nanosilica which enhances compatibility between polymer and bitumen binder. This in turn, can make the binder to be more stable and resistant during aging process. At low to intermediate temperature range of 20-45°C, it is observed that, 5% NS modified binder shows poor aging resistance compared to 3 and 4% NS, this shows that 5% NS can only perform excellent at high service temperatures.

Penetration aging ratio: Penetration Aging Ratio (PAR) is an alternative parameter that fully describes changes in binder physical properties at the time of aging process. PAR used to reflect bitumen binder behavior and aging susceptibility, PAR is computed as in Eq. 3:

$$\text{PAR} = \frac{\text{Penetration}_{(\text{Aged})}}{\text{Penetration}_{(\text{Unaged})}} \times 100 \tag{3}$$

Where:

PAR = The penetration aging ratio

$\text{Penetration}_{(\text{aged})}$ and $\text{Penetration}_{(\text{unaged})}$ = The aged and unaged penetrations

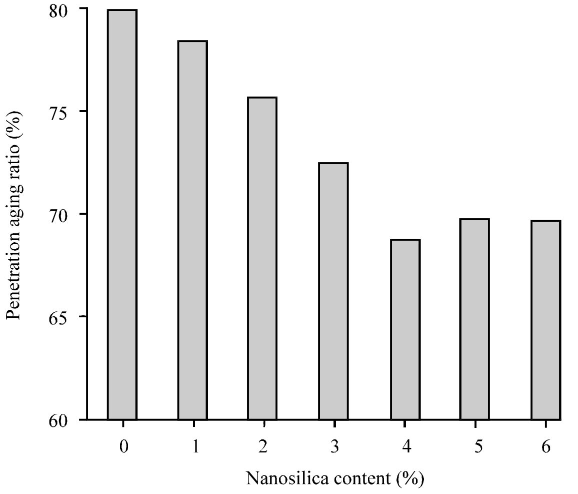

Fig. 6: Penetration aging ratio of LLDPE and nanosilica modified binders

Figure 6 presents aging effects on the penetration for LLDPE and nanosilica/LLDPE composite modified binders. It can be seen that, nanocomposite modified binders shows lower values of PAR compared to LLDPE modified binder. And the PAR is observed to decrease with increase in nanosilica content. This shows that nanosilica has effect in reducing PAR which is an enhancement in thermo oxidative aging characteristics of the binder. The reduction in PAR values confirms that, the binders susceptibility to thermo oxidative aging reduces after introduction of nanosilica. Binder sample containing 6% LLDPE+2.5% NS was found to have the least PAR value as such it will have better resistance to thermo oxidative aging compared to all other nanosilica modified samples.

Ductility retention rate: A Ductility Retention Rate (DRR) is a parameter that describes changes on bituminous binders ductility after aging process and it is computed as in Eq. 4:

$$DRR = \frac{D_{Aged}}{D_{Unaged}} \times 100 \quad (4)$$

Where:

DRR = The ductility retention rate

D_{Aged} and D_{unaged} = The aged and unaged ductilities of the binder

Figure 7 presents the effect of aging on the ductility of LLDPE and nanocomposite modified binders. It can be observed that, there is large increase in DRR between LLDPE and nanocomposite modified binders but it was also observed that, DRR of the asphalt binder increased with increase in the content of nanosilica. The DRR of LLDPE polymer modified binder before adding nanosilica was 62% after RTFOT aging, however, immediately after adding nanosilica at concentration of 6%, it increase to 88%, indicating almost 40% increment. This implies that, nanosilica greatly reduces the deterioration in ductility of nanocomposite modified binders during aging process.

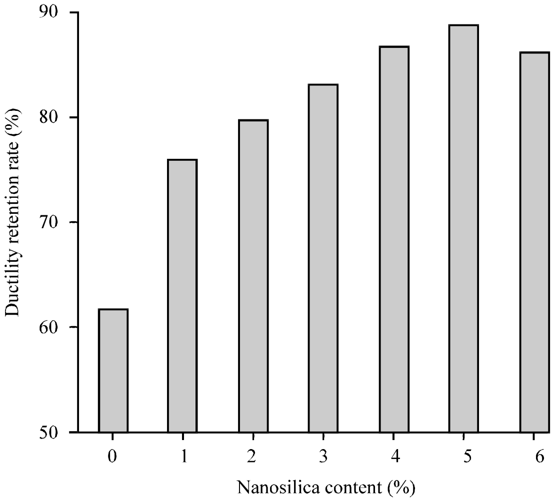

Fig. 7: Aging effects on ductility on LLDPE and nanosilica modified binders

CONCLUSION

Based on results of this research on nanosilica/LLDPE nanocomposite modified binders, the following conclusions can be drawn and summarized as follows: conventional properties tests shows an increase in penetration values and decrease in softening point temperatures, thus implies an enhancement in modified binders hardness which leads to higher temperature susceptibility. Addition of nanosilica into the LLDPE polymer modified binder, minimizes oxygen penetration and reduces oxidant reactions within the binder as such, reduces oxidative aging of nanocomposite modified binders.

The rutting and fatique analysis shows that all the nanocomposite modified binders have the minimum required values by superpave compared to LLDPE modified binders. This implies that, the rutting and fatique resistance properties of nanocomposite modified binders enhances greatly. Rheological aging indices show that, addition of nanosilica can delay rapid aging within the binders modified due to decrease in the rheological aging indices observed in nanocomposite modified binders.

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