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INVESTIGATION OF SILVER NANO-PARTICLES (AgNPs) AS MODIFIER TO ENHANCE THE PHYSICAL AND FLOW PROPERTIES OF AGBABU NATURAL BITUMEN

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Abstract

Bituminous road performances depend on the flow properties of bitumen which in turn is controlled by the composition of bitumen. Environmental factors such as sunlight, heat and moisture impact negatively on the composition of bitumen, leading to rapid deterioration of bituminous road. To militate against this, conventional bitumen is often modified to improve its performance and increase its service life. This study investigated the suitability of biosynthesized silver nanoparticles (AgNPs) using the pod extract of *Cola nitida* (Kolanut) as modifier of bitumen to enhancing the flow and physical properties of Agbabu natural bitumen (ANB). The neat ANB was mixed with the AgNPs at three different modification levels (3, 9 and 15 v/w) of bitumen using melt blend technique, after which the cooled modified ANB samples were characterized for their physical and flow properties; softening point, penetration, and kinematic viscosity. The Fourier Transform Infrared Spectroscopic spectra (FTIR) showed C-H, C=O and Sulphoxide absorption peaks at 2854, 1701 and 1031 cm^{-1} respectively for the unmodified ANB, while presence of new peaks at 1218 and 1317 cm^{-1} for C-N amines and C-O amides were seen in the modified ANB. The results showed 22% reduction in penetration value, increment of 29% in softening point and 24% increment in kinematic viscosity of AgNPs modified ANB samples compared with neat ANB. These results confirm that AgNPs modification can significantly improve the rutting resistance and fatigue cracking in raw bitumen.

Keywords: Bitumen, Nanoparticles, Rutting resistance, Fatigue cracking, Flow and physical properties, FTIR

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Abbreviation

AgNPs	Silver Nano Particles	cSt	centistoke
ANB	Agbabu Natural Bitumen	FTIR	Fourier Transform Infra-Red
ASTM	America Society for Testing and Measurements	IR	Infra-Red
		OMMT	Organic Montmorillonite

Introduction

Bitumen is the residue or one of the products of fractional distillation of crude oil (Tapase and Kadam, 2014). Road pavement construction is one of the major applications of bitumen. The composition of bitumen is affected by environmental factors such as sunlight, heat and moisture. The exposure of bitumen to the environmental conditions makes the flexible pavement to become vulnerable to structural degradations, such as; rutting, pothole, and fatigue cracking.

The high susceptibility of bitumen to deterioration due to environmental factors limits its usage in the raw form in construction of road pavement (Olabemiwo *et al.*, 2015). In order to overcome this problems posed by harsh environmental conditions and the growing challenges of heavy traffic load, engineers and scientists have come up with the idea of modification of bitumen with some selected modifiers to enhance the durability of road pavement (Pareek *et al.*, 2012; Kumar and Tanveer-Khan, 2013; Teppala *et al.*, 2014; Alhamali, *et al.*, 2015; Olabemiwo *et al.*, 2015).

Lu and Isacson (2001) defined bitumen modification as the dissolution and /or dispersion of modifier(s) into molten medium of bitumen either by chemical reaction or mechanical mixing to improve rheological and mechanical properties of the mixture. Bitumen modification is aimed at producing new bitumen mixes with improved rheological and mechanical properties (Praveen *et al.*, 2013), reduced thermal susceptibility, permanent

deformation under load and increased resistance to low temperature cracking.

Therefore, modification of bitumen is required to build a pavement that will be able to withstand the stresses of vehicles and environmental factors (Teppala *et al.*, 2014). Very many literature have shown that bitumen properties had been modified by certain binders which are economical and eco-friendly products such as polymer (Pareek *et al.*, 2012), crumb rubber (Teppala *et al.*, 2014), nano-particles (Alhamali *et al.*, 2015), gilsonite (Ameri *et al.*, 2011), jute geotextile (Pareek *et al.*, 2012), and jute (Shridha, 2015).

A nanoparticle is an aggregation of atoms bonded together with radius between 1-100 nanometre (Hamad, 2016). Recently, the biological synthesis of nanoparticles and their applications have witnessed rapid development. Biosynthesized AgNPs have also been produced using countless numbers of biological resources such as, arthropods and plant materials for different applications such as antioxidant, antimicrobial, catalytic, anticoagulant and thrombolytic applications (Adelere and Lateef, 2016; Lateef *et al.*, 2016a).

The use of nanotechnology in various fields is also receiving global attention. Nanoparticles had been reported to have broad and diverse applications in biomedical field (Rajeshkumar *et al.*, 2016). According to Rajeshkumar and Malarkodi, (2017) AgNPs have properties like shape, size and biocompatibility which make them useful in

biomedical applications. Recently, nanoparticles, a non-polymeric material has started attracting the interest of scientists in the modification of bitumen.

Ratnasamy *et al.* (2013) applied organic montmorillonite nano-clay (OMMT) in modification of asphalt binder, and reported a positive improvement in both the physical properties of the asphalt binder and its rheological properties. They reported an increase in softening point and viscosity as a result of OMMT added, but a reduction in asphalt binder penetration compared with unmodified bitumen. Application of nanoparticles in producing long-lasting and high performance asphalt mixtures has been attributed to their outstanding advantageous properties; large surface area, excellent dispersion ability, stability, strong absorption and chemical purity (Bala *et al.*, 2018).

Other nanoparticles which have been applied for bitumen modification include Nanosilica, $\text{Ca}(\text{OH})_2$ nanoparticles, nanoclay, nano zinc oxide, nano TiO_2 , Al_2O_3 , Fe_2O_3 (Khodary *et al.*, 2014; Bala *et al.*, 2018). Nanosilica modified bitumen had also been reported to show better performance in respect of dynamic modulus, flow number and rutting resistance (Yao *et al.*, 2012). The higher the portion of nanoparticles used as modifiers, the better the mechanical and physical properties of the bitumen. Consequent upon the above, it was decided to investigate the suitability of silver nanoparticles to modifying ANB for better performance and improved durability.

Materials and Methods

Bitumen

The natural bitumen used in this research was obtained from Agbabu, a town near Ore town in Ondo State, South-Western Nigeria situated within Longitude $4^\circ 40'E$ and $5^\circ 00'E$ and Latitude $6^\circ 20'N$ and $6^\circ 40'N$ (Adedosu *et al.*, 2016).

Silver nanoparticles (AgNPs)

Freshly biosynthesized AgNPs using the pod extract of *Cola nitida* was used as modifier in this study. It was used as supplied, by the Laboratory of Industrial Microbiology and Nanobiotechnology, Department of Pure and Applied Biology, Faculty of Pure and Applied Sciences, Ladoke Akintola University of Technology (LAUTECH), Ogbomoso, Nigeria.

Production of AgNPs Modified Bitumen

The AgNPs modified ANB samples were prepared in a stainless reactor using melt blend technique as reported by Kumar and Tanveer-Khan, (2013). Exactly 100g of ANB was heated to melt at a temperature range of $100-120^\circ\text{C}$ in a stainless reactor. An appropriate measured quantity of freshly biosynthesized AgNPs in v/w of ANB was slowly added to the agitated ANB in the reactor. The temperature was minimized to a range of $100-110^\circ\text{C}$ while the speed of the mechanical stirrer was maintained at a frequency of 1200 rpm. The agitation was done for 1 h to allow for homogeneity of the

blend. The AgNPs was mixed with the ANB at three different modification levels (3, 9 and 15 v/w) of bitumen.

Flow and Physical Properties Tests

The following physical and flow properties were conducted on the modified and raw ANB samples using appropriate standard procedures; Penetration value (ASTM D5-97), Softening point (ASTM D36-09), Kinematic viscosity (ASTM D2170-95).

Fourier Transform Infra-Red (FTIR) Analysis

Fourier Transform Infra-Red (FTIR) spectroscopy measurements were also carried out on both the raw and AgNPs-modified ANB samples so as to know the main functional groups in the bitumen and their interaction with the modifiers used after modification.

Results and Discussion

Physical and Flow Properties of Neat ANB Samples

The physical and flow properties of neat bitumen sample were determined and the results obtained are as follows: Penetration value at 25 °C, 110.80dmm; Softening point, 48.2 °C; and Kinematic Viscosity, 249 cSt.

Effect of AgNPs on Penetration Value of ANB Sample

The penetration values of unmodified and AgNPs-modified ANB are as represented in

Figure 1. It is clearly seen from Figure 1 that incorporation of AgNPs caused a decrease in the penetration value of the neat ANB. Also as the quantity of AgNPs used for modification increased, penetration values decreased. This substantial reduction in penetration of the AgNPs-modified samples will translates to a reduction in the degree of occurrence of rutting process as reported by Khodary *et al.* (2014) since penetration is a function of hardness of bitumen (Nassar *et al.*, 2012).

Effect of AgNPs on Softening Point of Neat ANB

The effect of AgNPs on softening points of neat ANB is as shown in Figure 2. The softening points of AgNPs-modified ANB samples were greater than that of unmodified ANB (48.2 °C). The increment in the softening point of the modified ANB samples is as a result of the added AgNPs. This is an inkling of a high resistance of AgNPs-modified samples to temperature susceptibility after modification (Dixit and Deepak, 2013). A rise in softening point implies an increased rigidity of bitumen, which support penetration point results (Figure 1). The reduction in penetration values as well as increment in softening points as modifier levels increase, confirms increased solidity and rigidity of the AgNPs-modified bitumen (Alhamali *et al.*, 2015). The result obtained in this study conforms to the earlier findings of Olabemiwo *et al.* (2016).

Effect of AgNPs on Kinematic Viscosity of ANB

The results of the kinematic test on the modified and neat ANB samples are as presented in Figure 3. The result showed that addition of AgNPs to neat ANB increased the kinematic viscosity of the neat

bitumen. Besides, the kinematic viscosity increases with the increase in the quantity of AgNPs added. The appreciable higher kinematic viscosities recorded by AgNPs modified samples might be due to increase in compaction of ANB molecules as a result of the modification and relatively higher adhesive forces between the molecules of ANB and AgNPs in the modified samples.

Figure 1: Effect of AgNPs on penetration value of ANB sample

Figure 2: Effect of AgNPs on softening point of ANB sample

This inference is based on the fact that AgNPs are known to have excellent dispersion ability, strong absorption and

biocompatibility properties (Bala *et al.*, 2017). Hence, more energy would be needed to break the bonds between the molecules.

The result corroborated the earlier findings of Khodary *et al.* (2015) and Alhamali *et al.* (2015).

FTIR Analysis of Unmodified and AgNPs-Modified ANB Samples

The FT-IR spectra of AgNPs, unmodified and AgNPs-modified ANB samples were recorded in the range of 4000-400 cm^{-1} as shown in Figures 4, 5 and 6(a-c) respectively. Assignment of IR absorption peaks of unmodified ANB sample was based on the previous results of Dragan *et al.* (2012).

FTIR Analysis of AgNPs

The FTIR spectrum of AgNPs is as shown in Figure 4. The spectrum shows strong absorption peaks at 3425, 1631, 1384, 1049 and 1076 cm^{-1} which is in line with results of study of Jyoti *et al.* (2016). The result also corroborated the findings of Bakare and Olabemiwo (2016) and Lateef *et al.* (2016). However, peaks at 1384, 1049 and 1076 cm^{-1} were not observed in the work of Lateef *et al.* (2016). Rather, they reported strong peaks at 3336 cm^{-1} due to the presence of N-H bond of amines and 1639 cm^{-1} to be an indication of C=C stretch of alkenes and C=O stretch of the carbonyl in amides.

FTIR of Unmodified ANB

The FT-IR spectrum of unmodified ANB is presented in Figure 5. It shows strong peaks at 1924.18 and 2854.74 cm^{-1} which indicate C-H stretch in CH_3 and CH_2 . Similarly, peaks observed at 1458.23 and 1377.57 cm^{-1}

signify C-H stretch in alkyl group and C-H bending in CH_3 respectively. Peak at 1610.61 cm^{-1} confirmed C-C stretch (in-ring) aromatics, while 1701.27 cm^{-1} , a weak peak showed the presence of carbonyl stretch, C=O (stretch) in ketones, amides, aldehydes and carboxylic acid (Sahoo *et al.*, 2007). Furthermore, the weak absorption peak, 1031.95 cm^{-1} , also indicated sulphoxide while the shoulders observed at 888.00, 813.99 and 746.48 cm^{-1} could be as a result of aromatic bending C-H modes which is equivalent to aromatics C-H bending. The peaks obtained in the FTIR spectrum of neat ANB are similar to peaks identified earlier on similar works on Agbabu bitumen (Bakare *et al.*, 2015; Olabemiwo *et al.*, 2016; 2017).

FTIR Analysis of AgNPs-modified ANB Samples

The spectra of AgNPs-modified ANB samples are as shown in Figures 6 (a-c). The peak positions when compared with the various peaks intensities in the IR spectra signified that there were appearances of additional new peaks indicating the existence of interaction between the AgNPs and the ANB. The new peaks, 1218 and 1317 cm^{-1} correspond to C-N and C-C stretching in amines, respectively (Bakare and Olabemiwo, 2016; Jyoti *et al.*, 2016). However, the absorption peak, 1031 cm^{-1} present in the base ANB remained unaltered in this study. But, there was an appearance of new absorption peak, 1091 cm^{-1} corresponding to C-O stretch in amide (He *et al.*, 2013; Bakare and Olabemiwo, 2016).

Figure 3: Effect of AgNPs on kinematic viscosity of ANB sample

Figure 4: FTIR spectrum of AgNPs

The appearances of these new peaks might be due to the physical interaction of the AgNPs with bitumen molecules and also the anti-oxidation ability of the nanoparticles (Bakare and Olabemiwo, 2016; Lateef *et al.*, 2016).

Conclusion

A biosynthesized silver nanoparticle was used to modify neat ANB in order to evaluate its suitability as an asphalt modifier in road pavement construction. AgNPs was successfully incorporated into the ANB

structure as confirmed by appearances of new peaks and shifting of peaks after modification. Characterization of the modified samples showed that AgNPs improved the physical and flow properties of the neat ANB. The level of improvement in these properties was a function of the content of the AgNPs added to the ANB. The increasing order of improved physical properties achieved with different concentration of silver nanoparticles is $3 < 9 < 15$ v/w. Penetration values of AgNPs-modified ANB decreased as the quantity of AgNPs added increased. This decrease in penetration value confers high temperature resistance to the modified bitumen when

used in hot climate area. In the same manner, softening points and kinematic viscosity increased with increase in concentration of the AgNPs in the bitumen; which is also an affirmation that the AgNPs modified bitumen can resist high temperature. The all the changes in physical and flow properties of ANB observed in this study as a result of incorporating AgNPs into its structure, are strong indications of the ability of AgNPs to enhancing the shelf life of ANB.

Figure 5: FTIR spectrum of purified ANB

Figure 6 (a): FTIR spectrum of 3 v/w AgNPs modified ANB sample

Figure 6 (b): FTIR spectrum of 9 v/w AgNPs modified ANB sample

Figure 6 (c): FTIR spectrum of 15 v/w AgNPs modified ANB sample

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Conflict of Interest

The authors did not report any potential conflict of interest.

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