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Original Article

Performance characteristics of Agbabu natural bitumen ternary nano composite with polypropylene and multiwall carbon nanotubes

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Abstract

The modification of bitumen using polymers has reached its limits due to rutting and cracking problems under severe temperatures. Yet, there are few studies on bitumen blends using multiple materials. This research investigated the effects of Multiwall Carbon Nanotubes (MWCNT) in a ternary mixture (Agbabu bitumen (ANB) - polypropylene (PP) – MWCNT) and optimized the functional formulation. Certain properties of ANB, such as the loss in ductility, flash, fire, penetration, and softening points were improved by blending MWCNT (0.1 – 1.21 g), PP (0.15 – 4.05 g) and ANB (94.79 – 99.75 g). The improvements were by 43.27, 43.76, 78.41 and 2.80% for flash, fire, penetration, and softening points with the optimal blend of 97.92, 0.1 and 1.98 g of ANB, MWCNT, and PP, respectively. This large improvement in composite properties is superior to the polymeric binary systems, and concordant with ASTM and BS standard requirements.

Keywords: bitumen, modification, multiwall carbon nanotubes, polymeric bitumen, optimization

1. Introduction

Bitumen has found applications in many areas, ranging from an aggregate for roads surfaces to waterproofing membranes in roofing and structural applications (Garcia-Morales *et al*., 2003). Bitumen serves primarily as a binder in compacted asphalt mixtures, which in turn are widely used in many types of roads, streets, runways and parking areas (Shadrach, Jeninifer, Adeyinka, & Victor, 2018). Bitumen can be found naturally at shallow depths or is obtained from vacuum distillation of crude oil. Neat bitumen often possesses adequate performance characteristics, but improved high-temperature performance tends to conflict with ability to resist low-temperature cracking. Consequently, the increasing traffic volumes and loading, coupled with the high demand for longer service life, there is an increasing need for asphalt pavements with improved in-service qualities (D'Angelo, Dongre, Stephens, & Zanzotto, 2007).

Bitumen, being a viscoelastic substance, behaves as an elastic solid at low temperatures or during rapid loading. At high temperatures or slow loading, it behaves as a viscous liquid. This behavioral dichotomy creates a need to improve the performance of bitumen to minimize the stress cracking that occurs at low temperatures and plastic deformation at high temperatures (Wardlaw & Shuler, 1992). Several additives are used to increase the performance of asphalt binders. Polymers are the most widely used additives in asphalt modification (Thodesen, Lerfald, & Hoff, 2012). The modification of bitumen using polymer has a very long history. Before the production of refined bitumen, the practice of modifying natural bitumen has been reported and some patents were granted for natural rubber modification

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(Lewandowski, 1994; Yildirim, 2007). A detailed review of bitumen polymer modification over the last 40 years, including the challenges and various breakthroughs, are well documented in Zhu, Birgisson, and Kringos (2014).

Polymers that are used to modify bitumen can be classified into simple straight chains or variations of linked and cross-linked chains (Rowlett, Martinez, Mofor, Romine, & Thamoressi, 1990). Bitumen modification by polymers improves the mechanical properties, increases the viscosity, allows expanded service temperature range and improves the deformational stability and durability of bitumen (Garcia-Morales *et al*., 2003). The extent of modification and the improvements in the performance characteristics depend on bitumen nature, chemical nature of the polymer additive, its dosage and chemical compatibility, molecular weight, particle size, as well as blending process conditions, such as type of mixing/dispersing device, time and temperature (Perez-Lepe *et al*., 2003). However, high molecular weight polymers have profound effects on the properties of bitumen. As the molecular weight of the polymer increases, its compatibility with bitumen sharply decreases (Yousefi, Ait-Kadi, & Roy, 2000).

Recently the use of nanomaterials to improve construction materials has gathered momentum due to the emergence of new technologies. Nanomaterials are materials with at least one dimension that falls in the length scale 1–100 nm. Due to the small size and high specific surface area, properties of nanomaterials differ strongly from normal sized materials. Thus, research engineers have attempted to apply nanoclay as an additive in bituminous binders (Goh, Akin, You, & Shi, 2011). Yu, Zeng, Wu, Weng, and Liu (2007) used nanosized montmorillonite clay to enhance the mechanical properties of bitumen. The binary mixture of clay and bitumen had slightly improved mechanical properties. Saeed, Galoo-yak, Massoud, Hosein, and Ahmed (2015) investigated rheological and mechanical properties of a binary mixture of Carbon Nanotubes (CNT) and bitumen. The results showed an increased softening point with improved resistance to rutting and changes in the complex modulus. CNT offers good reinforcement due to its high volume ratio, good thermal stability, good tensile strength, low density, and high surface stability and conductivity, when compared with other nanomaterials (Yang & Tighe, 2013).

Nigeria is endowed with a vast deposit of natural bitumen, which is yet to be processed for commercialization. Because bitumen is found in Agbabu town located within the bitumen belt, it is often called Agbabu Natural Bitumen (ANB). Previous studies on ANB have mainly concentrated on its effects on the environment, while the report on its application pave roads is limited and rarely available (Olabemiwo, Akintomiwa, George, & Hassan, 2016). Olabemiwo, Akintomiwa, and Hassan (2015) performed a preliminary investigation on the suitability of some selected polymers such as polyethylene, polyethylene-co-vinyl acetate and polystyrene-co-butadiene for the enhancement of rheology and mechanical properties of ANB. Only polyethylene co-vinyl acetate (PEVA) and polyethylene were found to improve the rheological properties of ANB. Olugbenga, Olugbenga, and Jonathan (2012) designed and fabricated a cost-effective and efficient softening point tester to determine the softening point and penetration index of ANB for road pavement. They reported that the ANB is temperature susceptible, therefore needs to be modified for industrial uses.

This present study, therefore, investigated the effects of MWCNT in a ternary mixture of PP, MWCNT, and ANB on the physical and mechanical properties of ANB.

2. Materials and Methods

2.1 Materials

The bitumen was obtained from Agbabu (longitude 3°45E and 5° 45E and latitude 6°00'N and 7°00'N) in Ondo State, Nigeria. The polypropylene used was manufactured by Polypropylene Malaysia Bhd SDN while MWCNT was manufactured by Zyvex, Germany and supplied by Cahaya Bhd SDN, Malaysia. Table 1 shows the properties of MWCNT and PP used in this study.

Table 1. Properties of materials used.

Property	MWCNT	PP
Purity %	>95	High degree
Melting point °C	>1366	140-160
Specific gravity	>1	0.905

2.2 Preparation of bitumen

The ANB was purified using the American Association of State Highway and Transportation method (American Association of State Highway and Transportation Officials [AASHTO], 2014). Bitumen (100 g) was weighed and then dried in a thermostatically controlled oven operated at 110 ± 5 °C until a constant weight was achieved. This was done to remove unwanted moisture for easy modification. The de-moisturized sample was then filtered from all the adherent sand and particles using a sieve while the temperature was maintained at 110 °C. The sample was cooled and stored at room temperature.

2.3 Design of experiments

To develop the ternary composite, the ANB, MWCNT, and PP contents were randomized in a D –Optimal Mixture Design. A total of 13 samples were generated for the range of actual values of MWCNT (0.1 – 1.21 g), PP (0.15 – 4.05 g) and ANB (94.79 – 99.75 g). For each sample, the total of the components is preserved according to equation 1, while the mixing of the composites was done by melt mixing (American Association of State Highway and Transportation Officials [AASHTO], 2010). Here, a predetermined mass of bitumen was weighed in a beaker and heated on a thermostatically controlled hot plate operating at 160 ºC for 30 minutes to make it flow. A specific amount of PP was added according to the experimental design and the binary mixture was stirred using a mechanical stirrer at 1,200 rpm, at a constant temperature of 160 °C for 60 minutes. This was followed by adding a known amount of MWCNT to make the ternary mixture. The resulting thirteen (13) composites produced were kept in well-labeled containers and allowed to cool before further analysis was carried out. The polymeric binary composite (ANB - PP) on the other hand was prepared accordingly. The resulting composites were analyzed for loss of ductility, flash, fire, penetration and softening points.

$$ANANB(AA) + MWCNTMWCNT\ (BB) + PPPP\ (CC) = 100 \tag{1}$$

2.4 Test for physical and mechanical properties

The physical and mechanical testing of the composites produced was carried out using ASTM standard procedures: D92-05; D5; D6154 and D113 for Flash/Fire point, Penetration point, Softening point and Ductility test, respectively.

2.5 Morphology characterization with scanning electron microscope (SEM)

SEM ASPEX 3020 was used to examine and compare for microstructural changes in the ANB with the addition of PP and MWCNT. The characterization was carried out at magnification 527X. The samples were gold coated due to the low electric conductance of ANB.

3. Results and Discussion

3.1 Flash and fire point

The flash and fire points are those temperatures at which the bitumen ignites in the presence of an open fire. Table 2 shows the loss of ductility, penetration, softening, flash and fire points obtained for the virgin ANB and its corresponding binary and ternary composites. The ANB has the flash and fire points of 156.34 and 159.39 °C, respectively. However, the flash and fire points recorded for its binary composite with PP are 181 and 224 °C, respectively, increased by 15.77 and 40.54% from those of the virgin ANB. In the experimental layout, run 7 with the composition of 97.8 g ANB, 0.1 g MWCNT and 2.1 g PP gave the maximal results for the ternary system, with the flash and fire points recorded at 224 and 229 °C respectively, for increases by 43.28 and 43.67% over the virgin ANB. This performance also supersedes over the binary composites. The property enhancement was therefore attributed to the presence of MWCNT in the ternary composites. Comparing the experimental results with the standards American Society for Testing and Materials (ASTM, 2010) and British Standard Institution (BS, 2000), it is observed that the 224 °C flashpoint obtained for the ternary system is close to the 230 °C recommended by ASTM and BS.

Table 2. Physical and mechanical properties of virgin ANB and its composites.

Property	ANB	ANB+PP	ANB+PP+ MWCNT
Flash point (°C)	156.34	181	224
Fire point (°C)	159.29	224	229
Penetration point (mm)	47.25	10.5	10.2
Softening point (°C)	79	90	97
Ductility (cm)	24.58	6.25	4.58

*Percentage enhancement (ANB+PP+MWCNT): Flash point 43.27%, Fire point 43.76%

*Percentage enhancement (ANB+PP+MWCNT): Pen point 78.41, Soft. Point 22.80

3.2 Loss of ductility, penetration and softening points

The penetration test distinguishes different grades of bitumen and is often used for measuring the consistency or hardness of bitumen (Olugbenga *et al*., 2012). The results in Table 2 indicate a sharp reduction in the penetration from 47.25 mm (ANB) to 10.50 mm (ANB - PP) and 10.20 mm (ANB - PP - MWCNT). This implies that ANB alone has poor load-bearing capacity, and therefore, when applied in its pure natural form, may not have the capacity to accommodate heavy traffic loads. However, the penetration was significantly reduced in the ternary system, due to the high specific surface and good tensile properties of MWCNTs. When comparing the experimental results with the standards (ASTM, 2010; BS, 2000), the measured penetration values of 10.5 and 10.2 mm for binary and ternary systems, respectively, were close to the recommended penetration grade ranges 8.5 - 10.0 mm and 7.0 – 10 mm in ASTM and BS, respectively.

The visco-elastic nature of bitumen makes its tendency to crack emerge at low temperatures. Consequently, the cohesion of bitumen is characterized by its ductility at low temperatures. It is a property that depends on the grade of the bitumen. As shown in Table 2, the virgin ANB has a ductility point of 24.58 cm. The binary mix with PP impacted negatively on elongation, with ductility point reduction by about 74.6% (6.25 cm) when compared with ANB. Further addition of MWCNT to the binary mixture reduced the ductility by 81.37% (4.58 cm) when compared with ANB. This implies that ANB is sensitive to modification using PP and MWCNT as additives that impacted negatively the ductility point of virgin ANB. However, the measured values are within the acceptable range according to ASTM D113.

The softening point is where the bitumen becomes fluid and therefore a high softening point is desired (Olugbenga *et al*., 2012). The results shown in Table 2 reveal that ANB is softer with the least temperature resistance (79 °C) than its composites. The ternary composite, however, showed a more resistant mix with a softening point at 97 °C, while the binary composite softened at 90 °C. This could be related to the high Young's modulus and tensile strength of MWCNT, and these gave the bitumen composite a good resistance to flow. According to ASTM and BS standards, the minimum allowable bitumen softening point ranges are 42 – 51 °C and 55 - 63 °C. Higher softening points recorded for ANB - PP and ANB – PP - MWCNT indicate higher grade for the composites, which suggest that ANB with PP and a low MWCNT fraction can be a good candidate for paving roads.

4. Optimization Study

4.1 Model development

For determining the optimal mixing ratio of ANB, PP, and MWCNT for effective road pavement, Response Surface Methodology (RSM) was adopted to maximize the flash, fire and softening points while minimizing the penetration and loss of ductility. The D- optimal design matrix, as well as the responses, are presented in Table 3. The estimated coefficients of the terms in the fit and keeping significant contributions at the confidence limit of 95% ($p < 0.05$) from among all possible terms resulted in equation (2) for loss of ductility, flash, fire, penetration and softening points. The analysis of variance of the models is presented in Table 4. The constants for different properties are presented in Table 5.

$$\beta = a(A) + b(B) + c(C) + d(AB) + e(BC) + f(AC) + g(ABC) + h(AB)(A - B) + j(AC)(A - C) + k(BC)(B - C) \quad (2)$$

The R^2 values for all the estimated properties β ranged from 0.993 to 0.9999. These R^2 values agreed with the parity plots of actual and predicted responses (Figure 1). If the model would perfectly fit the experimental data, then all of the points would lie on the $x = y$ line. On these plots, the vast majority of the points are along the $x = y$ line. A ratio of adequate precision greater than 4 is desirable (Arinkoola & Ogbe, 2015) and this ranged between 46.47 and 1282.261 in this study. The models' F values (2136.3, 174.7, 63006.5, 4465.5 and 239 632.8) were all significant, which indicates adequate signal-to-noise ratio with $p < 0.05$ for all the models. This suggests that all the fitted models are predictive and are therefore amenable for numerical optimization.

Table 3. D - optimal design matrix for ANB – MWCNT - PP system.

Run	A:Bitumen (g)	B:MWCNT (g)	C:PP (g)	Pen. point (ºC)	Soft. point (ºC)	Flash point (ºC)	Fire point (ºC)	Ductility (cm)
1	94.79	1.16	4.05	10.5	86	142.57	146.5	4.58
2	95.78	0.98	3.24	24.5	89	138.15	141.1	13.33
3	96.31	0.43	3.26	12.6	87	143.2	183.3	10.8
4	98.64	1.21	0.15	22.7	86.5	158.5	162.4	21
5	95.85	0.1	4.05	21	88	183	187	9.58
6	97.98	0.71	1.31	10.5	95	182	187	5
7	97.8	0.1	2.1	10.2	97	224	229	4.58
8	96.72	1.21	2.07	12.5	88	142.6	182.5	10.5
9	98.64	1.21	0.15	22.5	86	158.3	162.24	20.83
10	99.75	0.1	0.15	10.7	85.5	156.42	160.25	4.6
11	95.85	0.1	4.05	22	82	161	165	21.25
12	99.75	0.1	0.15	10.5	85	156.34	159.29	4.58
13	99.2	0.66	0.15	9.625	86	150.44	153.39	3.96

Table 4. Analysis of variances for loss of ductility, flash, fire, penetration and softening points.

Response	Source	Sum of square	DF	F- ratio	p - value
Pen point	Model	384.5364063	9	2136.313368	0.0005
	Pure error	0.04	2		
	Cor.total	384.5764063	11		
R-Squared = 0.9998; Adj R-Squared = 0.9994; Adeq Precision = 115.2213					
Soft. Point	Model	196.5	9	174.6666667	0.0057
	Pure error	0.25	2		
	Cor. total	196.75	11		
R-Squared = 0.9987; Adj R-Squared = 0.9930; Adeq Precision = 46.47					
Flash point	Model	6577.877267	9	63006.48723	< 0.0001
	Pure error	0.0232	2		
	Cor. total	6577.900467	11		
R-Squared = 0.9999; Adj R-Squared = 0.999981; Adeq Precision = 873.1763					
Fire Point	Model	5243.926939	7	4465.509816	< 0.0001
	Residual	0.503278988	3		
	Cor. otal	5244.430218	10		
R-Squared = 0.9999; Adj R-Squared = 0.9997; Adeq Precision = 236.0858					
Ductility	Model	431.3390727	9	239632.8182	0.0016
	Pure error	0.0002	1		
	Cor. total	431.3392727	10		
R-Squared = 1.000; Adj R-Squared = 0.9999; Adeq Precision = 1282.261					

Table 5. Coefficients of terms in the RSM fits.

β	a	b	c	d	e	f	g	h	j	k
Pen. Point	0.2497	-1332195.021	-8813.0762	20126.6749	135.7918	19560.2399	-129.906	-68.0627	-0.478	61.4731
Soft. Point	0.8482	-369305	7733.23223	5575.82528	-120.249	5478.42954	-37.1066	-18.8311	0.4315	16.9824
Flash Point	1.5826	-2219150	54585.5555	33516.5134	-843.476	34020.2394	-234.941	-113.274	2.9896	116.199
Fire Point	1.5116	-19590.427	-1763.1432	307.72244	18.44788	1099.8372	-10.5097	-1.12053	0	0
Loss of Ductility	0.1247	-561366.509	-2966.3988	8491.00189	46.61673	7818.73861	-50.5532	-28.7815	-0.17	23.1181

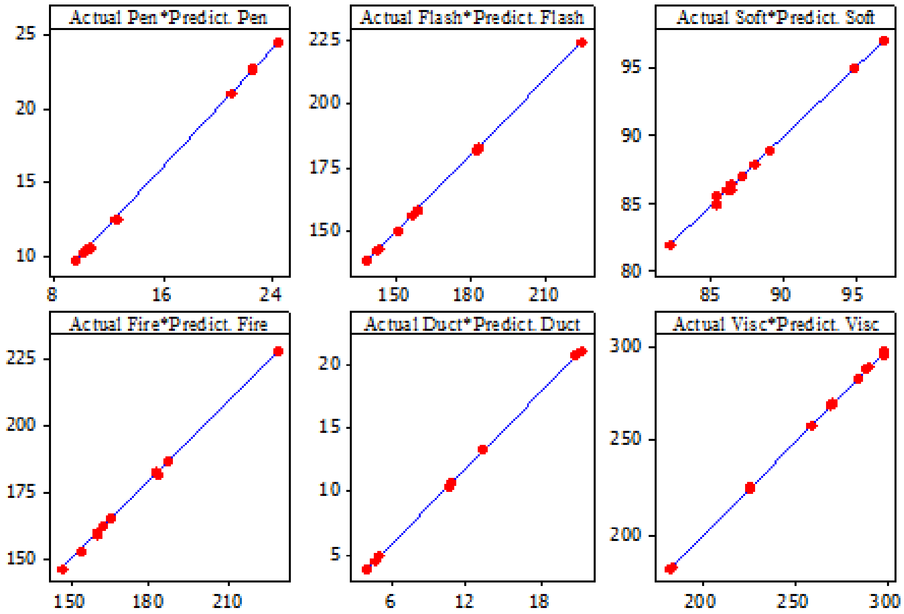


Figure 1. Scatter plots showing good agreement of model fits with experimental data for (a) penetration point ($R^2 = 0.9998$), (b) flash point ($R^2 = 0.9999$), (c) softening point ($R^2 = 0.9987$), (d) fire point ($R^2 = 0.9999$), (e) ductility ($R^2 = 0.9999$) and (f) viscosity index ($R^2 = 0.9999$).

The optimal mixing ratio for ANB, MWCNT, and PP that minimized the loss of ductility; maximized flash, fire and softening points; and minimized the penetration, were solved for by multi-objective numerical optimization, with each factor constrained to the experimental range. Figure 2 shows the most likely result with a 99 percent probability. A maximum flash point (225.654 °C), fire point (228.585 °C), and softening point (97.4313 °C), with minimum penetration (9.4854 mm) and ductility (3.959 cm) were obtained at ANB (97.92 g), MWCNT (0.1 g) and PP (1.98 g) at desirability value of 0.999.

4.2 Solution validation

To establish the validity of the simulated results, the optimal condition was run in the laboratory and the properties of the composite were measured in triplicate. The average measured properties were: penetration point (10.01±0.25 mm), softening point (96.46±0.31 °C), loss of ductility point (4.02±0.51 cm), flash point (223.53±1.02 °C) and fire point (230.5±0.08 °C). These results remain within the experimental range, and the match with the model-predicted properties validates the fitted models.

4.3 Effect of components

The coefficient estimates in the models represent expected effect size in response to a unit change in the factor, when all the other remaining factors are held constant. The intercept in an orthogonal design like the one in this study is the overall average response of all the 13 runs. The coefficients are adjustments around that average based on the factor effects. Table 6 shows the estimated coefficients for main factors and their interactions. The degree of significance is signified by the magnitude and statistically validated by the respective p-value. A p-value less than or equal to 0.05 indicates significance with a 95% confidence level. The smaller the p-value below the threshold value 0.05, the more significant that factor or interaction is.

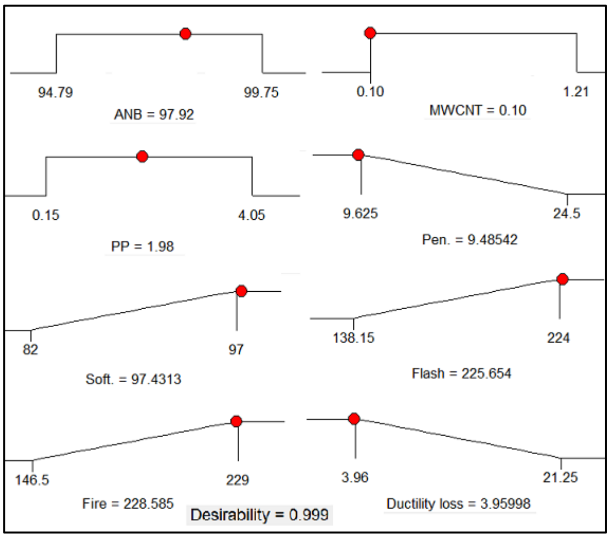


Figure 2. Optimized bitumen (ANB), MWCNT and PP with corresponding properties

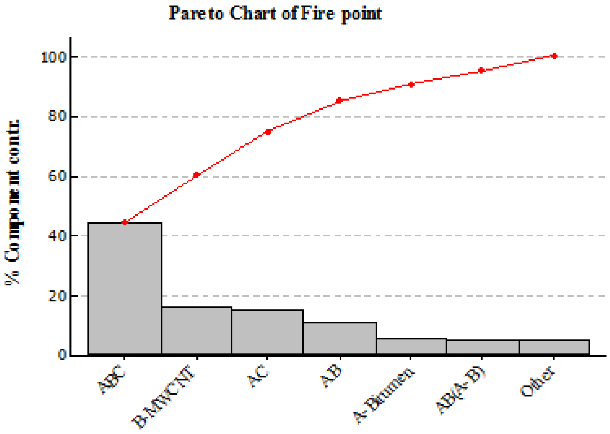


Figure 3. Pareto chart showing the contributions of the mixture components and their interactions on fire point of the modified ANB.

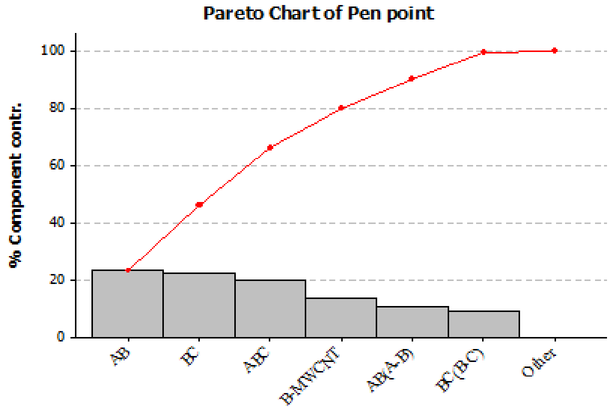


Figure 4. Pareto chart showing the contributions of the mixture components and their interactions on the penetration point of the modified ANB.

The contributions of different components and their interactions in the mix are presented as Pareto charts. It was observed that the binary interaction of ANB and MWCNT was dominant in all other properties except for the fire point. This is also evident from the p-values in Table 6. Figure 3 is the Pareto chart showing the percentage contributions of the mixture components to the fire point of modified ANB. It is observed that about 44% of the measured fire point is attributed to the ternary mixture of ANB – MWCNT - PP followed by MWCNT with about 19.2%. The cumulative contribution of the ternary system and MWCNT to fire point increase is approximately 60%. Thus, a larger improvement in the fire point may be achieved by focusing efforts on the amount of MWCNT in the ternary composite. However, increasing carbon nanotube content in the mix, according to Saeed *et al.* (2015) can significantly affect some other properties, such as ductility, as corroborated by our results.

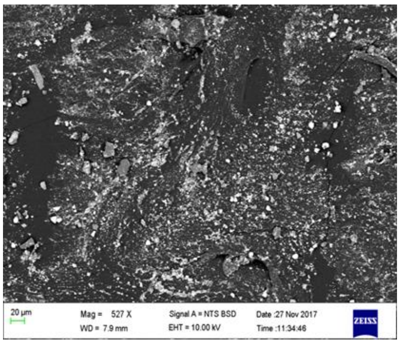
Figure 4, on the other hand, shows the Pareto chart for the contributions of the mixture components to the penetration point of modified ANB. About 23% of the measured penetration point reduction is attributed to the binary interaction ANB – MWCNT followed by MWCNT-PP interaction with about 21.1%. The cumulative contribution of the binary system to penetration point reduction was about 44%. Thus to ensure greater effects on properties other than the fire point, efforts could be focused on the binary mixture of ANB and MWCNT. The addition of PP to the ANB-MWCNT impacted negatively the desired properties.

Table 6. Coefficients in terms of coded factors indicating the significances of factors and their interactions.

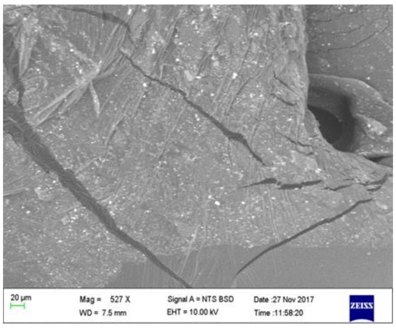
Factors	A	B	C	AB	AC	BC	ABC	AB(A-B)	AC(A-C)	BC(B-C)
Pen. point	10.6	-10953.9	16.4413	18782.8	1.16254	18211.8	-15851.6	-8305.27	-58.3247	7501.19
p-values	0.0006	0.0006	0.0006	0.0002	0.6569	0.0002	0.0002	0.0002	0.0022	0.0002
Soft. point	85.25	-3093.84	76.2821	5370.78	52.7733	5276.11	-4527.89	-2297.84	52.6586	2072.26
p-values	0.5879	0.5879	0.5879	0.0147	0.0112	0.015	0.0151	0.015	0.0164	0.0175
Flash point	156.38	-18460.4	209.765	31631.4	117.494	31463.4	-28668.4	-13822.1	364.799	14179
p-values	< 0.0001	< 0.0001	< 0.0001	< 0.0001	0.0002	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
Fire point	159.777	462.076	74.4029	-299.245	430.748	-63.8808	-1282.44	-136.732		
p-values	< 0.0001	< 0.0001	< 0.0001	0.0603	< 0.0001	0.4492	0.0002	0.0786		
Ductility	4.59	-4222.46	31.9138	7479.36	-40.6214	6863.26	-6168.7	-3512.03	-20.8026	2820.97
p-values	0.002	0.002	0.002	0.0022	0.0035	0.0024	0.0023	0.0021	0.0084	0.0025

4.4 Surface morphology

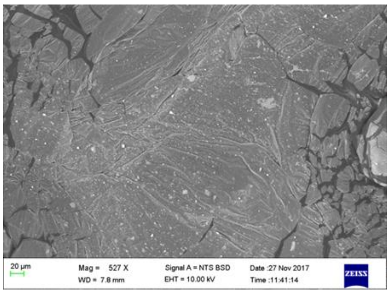
Figure 5 shows the SEM images of ANB, ANB-PP, and ANB-PP-MWCNT taken at 527X magnification. On visual observation, subjectively PP was dispersed in the ANB to form polymeric phase bitumen and created a connecting matrix through the bitumen. The SEM images of the ternary composite of ANB, PP and MWCNT showed an array of tube-like carbon dispersed in the bitumen matrix. Due to some agglomeration of MWCNT, the surface of MWCNT mixed with the polymeric modified bitumen and the new structure of nanotubes modified bitumen binder was formed, which also displayed a continuous interconnecting matrix. This means that there was a structural modification in the ternary composite, which was responsible for the changes in properties. The white patches are aggregates of MWCNTs in the polymer matrix, which increased the hardness of bitumen and decreased the penetration.



ANB:527X



PP/ANB: 527X



PP/ ANB/MWCNT: 527X

Figure 5. SEM images of ANB, PP/ANB and PP/ANB/MWCNT.

5. Conclusions

Ternary composites of ANB, PP, and MWCNT have been produced and analyzed. Based on the results obtained, the following conclusions were drawn: Agbabu natural bitumen in its virgin state is of a low grade. However, it is a candidate for paving roads when modified as demonstrated in this study, by using PP and MWCNTs. The properties such as penetration, softening, and flash and fire points were enhanced appreciably and compared favorably with both British and American standards after modification.

References

American Association of State Highway and Transportation Officials. (2014). *Moisture content of hot mix asphalt (HMA) by oven method: AASHO T329-05*. Washington, DC: Author.

American Association State Highway and Transportation Officials Standard. (2005a). *Standard test method for flash and fire point by Cleveland open cup tester of Bituminous materials: AASHO No. T48, DIN 51 376. Book of American national standard, American Association State Highway, and Transportation Officials Standard*. Washington, DC: Author.

American Association State Highway and Transportation Officials Standard. (2005b). *Standard test method for softening point by ring and ball apparatus of Bituminous materials. Book of American Association State Highway and Transportation Offi-cials Standard*. Washington, DC: Author.

American Association State Highway and Transportation Officials Standard. (2010). *Standard test method for ductility of bituminous materials: D113-07. Book of ASTM standards.* Washington, DC: Author.

American Society for Testing and Materials. (2010). *Standard test method for penetration - graded Bitumen for use in pavement construction: D946 / D946M. Annual book of American Standard Testing Methods (Revised Edition)*. West Conshohocken, PA: Author.

Arinkoola, A. O., & Ogbe, D. O. (2015). Examination of experimental designs and response surface methods for uncertainty analysis of production forecast: A Niger delta case study. *Journal of Petroleum Engineering.* doi:10.1155/2015/714541

British Standard Institution. (2000). *Bitumen for building and civil engineering, specification for road purposes: B.S. 12591*. London, England: Author.

D'Angelo, J., Dongre, R., Stephens, K., & Zanzotto, L. (2007). Revision of the superpave high-temperature binder specification: The multiple stress recovery test. *Proceedings of the Technical Sessions 76*, 123-162. Retrieved from https://asphalttechnology.org/about-aapt/

Garcia-Morales, M., Partal, P., Navarro, F. J., Martý´nez-Boza, F., Gallegos, C., Gonzalez, N., . . . Mun˜oz, M. E. (2003). Viscous properties and microstructure of recycled EVA modified bitumen. *Fuel, 83,* 31-38. doi:10.1016/S0016-2361(03)00217-5

Goh, S. W., Akin, M., Yu, Z., & Shi, X. (2011). Effect of deicing solutions on the tensile strength of micro- or nano-modified asphalt mixture. *Construction and Building Materials*, *25*(1), 195–200. doi:10.1016/j.conbuildmat.2010.06.038

Lewandowski, L. H. (1994). Polymer modification of paving asphalt binders. *Rubber Chemical Technology, 67* (3), 447–480. doi:10.5254/1.3538685

Olabemiwo, O. M., Akintomiwa, O. E, George, O. A., & Hassan, O. B. (2016). The performance of Agbabu natural bitumen modified with polyphosphorus acid through fundamental and fourier transform infrared spectro-scopic investigations. *Case Studies in Construction Materials*, *5,* 29-45. doi:10.1016/j.cscm.2016.06.003

Olabemiwo, O. M., Akintomiwa, O. E., & Hassan, O. B. (2015). Preliminary investigation on modification of Agbabu natural bitumen with some polymeric materials. *International Journal of Scientific and Research, 6*(9), 1342-1448. Retrieved from https://ecotert.com/pdf

Olugbenga, A. E., Olugbenga, A. F., & Jonathan, G. (2012). Softening point and penetration index of Bitumen from parts of southwestern Nigeria. *NAFTA*, *63*(9-10), 319-323. Retrieved from https://hrcak.srce.hr/file/136086

Perez-Lepe, A., Martinez-Boza, F. J., Gallegosa, C., Gonzalez, O., Munoz, M. E., & Santamaria, A. (2003). Influence of the processing conditions on the rheological behaviour of polymer-modified bitumen. *Fuel, 82,* 1339-1348. doi:10.1016/S0016-2361(03) 00065-6

Rowlett, R. D., Martinez, D. F., Mofor, D. A., Romine, R. A., & Thamoressi, M. (1990). Performance of asphalt modifiers: Classification of modifiers and literature review. Houston, Texas: Centre for Construction Materials Technology.

Saeed, S., Galooyak, M. P., Hosein, Z. F., & Ahmed, G. (2015). Effect of carbon nanotubes on the rheological properties of bitumen. *Journal of Petroleum and Coal*, *57*(5), 556-564. Retrieved from http://search.ebscohost.com/login.aspx?

Shadrach, O. O., Jeninifer, O. A., Adeyinka, S. Y., & Victor, A. (2018). Physical properties of Agbabu and Yegbata bitumen in Nigeria. *Journal of Applied Science and Process Engineering*, *5*(1), 227-241. Retrieved from https://www.researchgate.net/publication/324200829_Physical_Properties_of_Agbabu_and_Yegbata_Bitumen_in_Nigeria

Thodesen, C. C., Lerfald, B. O., & Hoff, I. (2012). Review of asphalt pavement evaluation methods and current applications in Norway. *Baltic Journal of Road and Bridge Engineering, 7*(4), 246-252. Retrieved from https://www.ntnu.edu/employees/carl.thodesen

Wardlaw, K. R., & Shuler, S. (1992). *Polymer modified asphalt binders. ASTM STP1108*. West Conshohocken, PA: ASTM International.

Xiaohu, L., Hilde, S., & Redelius, P. (2011). Rheological characterization of polymer modified bitumen. *Annual Transactions of the Nordic Rheology Society*, *19,* 1-8. Retrieved from https://pdfs.semanticscholar.org/c37f/be322d17988884c4f73fb09b17b06e17d3e2.pd

Yang, J., & Tighe, S. (2013). A review of advances of nanotechnology in asphalt mixtures. *Proceedings of Social and Behavioural Science 96,* 1269-1276. doi:10.1016/j.sbspro.2013.08.144

Yildirim, Y. (2007). Polymer modified asphalt binders. *Construction and Building Materials*, *21*(1), 66–72. doi:10.1016/j.conbuildmat.2005.07.007

Yousefi, A. A., Ait-Kadi, A., & Roy, C. (2000). Composite asphalt binders: Effect of modified rpeon asphalt. *Journal of Materials in Civil Engineering*, *12*, 113-123. doi:10.1061/(ASCE)0899-1561(2000)12:2(113)

Yu, J., Zeng, X., Wu, S., Weng, L., & Liu, G. (2007). Preparation and properties of montmorillonite modified asphalts. *Journal of Material Science and Engineering*, *447,* 233-238. doi:10.1016/j.msea.2006.10.037

Zhu, J., Birgisson, B., & Kringos, N. (2014). Polymer modification of bitumen, advances, and challenges. *European Polymer Journal*, *54,* 18-38. doi:10.1016/j.eurpolymj.2014.02.005