Preliminary Investigation on Modification of Agbabu Natural Bitumen with Some Polymeric Materials

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Abstract - Bitumen is a very versatile engineering material used in road pavement. Bitumen when used in its natural form in road pavement suffers premature failure as a result of its exposure to some environmental factors such as water, light and heat. Modification of the natural bitumen via addition of some additives such as polymers to its structure prior to its use in road pavement is one of the ways by which the service life of bitumen is improved.

This study attempted a preliminary investigation of the suitability of some selected polymeric materials as modifiers for Agbabu Natural Bitumen (ANB). These materials include: High Density Polyethylene (HDPE) and Polyethylene-co-vinyl Acetate (PEVA) and Polystyrene-co-butadiene (PSCB). The raw ANB sample was purified and subsequently modified in a reactor by heating the ANB to fluid state, after which certain quantity of modifier added. The mixture was then stirred using a high speed mixer at a temperature between 190^{o}C to 195^{o}C for 1hour, after which the heat source was withdrawn and the mixture allowed to cool to room temperature. The rheological parameters such as penetration value, softening point and viscosity were determined on the cooled modified sample.

The results of this study showed that the addition of PEVA and HDPE polymers within 2-6% w/w range to ANB resulted in a decrease in penetration value, increase in softening point, kinematic viscosity and penetration index of the ANB modified samples. However, the reverse was the case for PSCB modified samples. Also, the modified samples have relatively lower flash and fire points compared to neat ANB. The addition of the polymers into ANB improved the rheological properties of the neat ANB and these may bring an increase in service life of the modified samples.

Keywords - *Agbabu Natural Bitumen, Flash and fire points, high speed mixer, Modification, Polymers, rheological properties, Service life*

1 INTRODUCTION

Bitumen has a very wide spectrum of applications in the construction industry [1]. Its applications make it to be in constant exposure to environmental factors with the consequential effect of rapid degradation in the quality [2], [3]. The degradation is predominantly thermal cracking, moisture damage, fatigue and rutting [4]. Various attempts have been made to address this problem and one of the major ways is by incorporating modifiers into the bitumen prior to its application. Polymer modified bitumens (PMBs) are expected to show some desirable characteristics such as a higher penetration index; higher softening point; greater viscosity; lower penetration value and greater ductility, and also show greater resistance to premature failures compared to unmodified ones.

Previous researches had paid attention to physical modification, because most of the physical modifiers are not expensive and the widely used ones amongst others include: Styrene-butadiene-styrene (SBS) and Ethylene-vinyl acetate (EVA) copolymers and Polyethylene (PE) [5]. The durability of pavement with polymer modified bitumen is dependent on the nature of the polymer, amount of polymer incorporated during modification and nature of bitumen, as well as the blending technique [6].

Nigeria has a vast deposit of natural bitumen, which is yet to be tapped for economic purpose. The Nigerian natural bitumen is found in Agbabu, one of the notable towns located within the bitumen belt and it is often called Agbabu natural bitumen, Agbabu being where the natural bitumen in Nigeria was first discovered [7]. Presently, many scientific investigations on the quality and quantity of this material are on-going. As part of our own contribution, it was decided to embark on series of study to improve the service life of ANB when it is applied in road pavement. Our intention in this study was therefore to modify ANB with some selected polymers such as High Density Polyethylene (HDPE), Polyethylene-co-vinyl Acetate (PEVA) and Polystyrene-co-butadiene (PSCB) with a view to evaluating their suitability for improving the service life of ANB. To the best of our knowledge, there is no literature information on modification of ANB using polymers.

2 METHODOLOGY

2.1 Materials

2.1.1 Bitumen

The bitumen used in this study was natural bitumen sample collected from one of the observatory wells sunk by the Nigerian Bitumen Corporation (NBC -7) located opposite Saint Stephen's Primary School, Agbabu, Ondo State, Nigeria. Agbabu is located on the so called bitumen belt of southwestern Nigeria. The belt has a geographical location of Longitude 3°45'E and 5°45'E and Latitude 6°00'N and 7°00'N and spans across Edo, Ondo and Ogun States, Nigeria [7].

2.1.2 Polymers

Three selected polymers were used for modifications in this study. The three polymers were supplied by Sigma Aldrich and they are: High Density Polyethylene (HDPE), Styrene-co-butadiene (PSCB) and Polyethylene-co-vinyl acetate (PEVA). The polymers were in pellet form and used as supplied.

TABLE 1
SOME PROPERTIES OF THE POLYMERS USED IN THIS STUDY

Properties	Polymer		
	HDPE	PEVA	PSCB
Melt Index	12g/10min	8g/10min	6g/10min
Melting Point	125-140°C	95°C	-
Specific gravity (25°C)	0.952	0.933	1.04
Composition	-	Vinyl acetate 12wt. %	Butadiene 4wt. %

Source:[8]

2.2 Extraction of Moisture from Bitumen Sample

A modified method of Vernon and Katy [9] as described below was employed for extracting moisture from ANB. 100g of raw natural bitumen sample were spread on a tray to a thickness of 1cm. 1g of calcium chloride granular salt was then spread over the sample at room temperature and the mixture stirred manually with stirring rod for three minutes. The mixture of the salt and the sample was transferred into an oven and heated to 65^0C to get rid of moisture. Meanwhile, the moisture content was monitored using an infrared moisture analyser (Sartorius AG, Germany), MA 35M-00023012 until it was approximately zero. This took about three weeks for complete extraction of moisture. The added salt was drained alongside the moisture as salt solution. The essence of calcium chloride in the sample is to ease moisture separation at lower temperature (65^0C).

2.3 Purification of Bitumen Sample

The Bitumen sample was purified using the modified method of Rubinstein and Strausz [10]. 1000 cm^3 chloroform was added to 100g of natural bitumen sample in a beaker. The mixture was stirred with a glass rod to ensure outright dissolution of the sample followed by filtration. The bitumen in the filtrate was recovered by vacuum evaporation of the solvent using rotary evaporator.

2.4 Preparation of polymer modified ANB

All the modified ANB samples were prepared using melt blending technique at 190-195^oC for HDPE, PSCB and PEVA with a shearing speed of 1200rpm for 1 hour. Summarily, a quantity (400gm) of ANB was heated in an iron container. After reaching the desirable temperature, the modifier was added to the ANB samples. Various blend compositions were prepared according to the following content rates: 2%, 4%, and 6% by weight of ANB.

$$Weight\ of\ the\ incorporated\ polymer = \frac{Wa}{100}\ X\, Wb \ldots\ldots\ldots\ldots Eqn. 1$$

$$Where: Wa = percentage\ quantity\ of\ polymer\ incorporated\ into\ ANB$$

$$Wa\ may\ be\ 2,4,or\ 6\ in\ the\ study$$

$$Wb = weight\ of\ the\ ANB\ intended\ to\ be\ modified$$

2.5 Rheological properties of Modified and Unmodified ANB

The rheological properties determined on modified sample of ANB are as described below. Each of the determination was made in triplicate and mean value recorded.

2.5.1 Softening Point of Polymer Modified and Unmodified ANB

The softening point is a measure of the temperature at which bitumen begins to show fluidity. It was determined for modified and unmodified ANB samples using the ring and ball test, [11].

2.5.2 Penetration of Polymer Modified ANB and Unmodified ANB

Penetration is a measure of the consistency or hardness of bitumen and is the most common control test for penetration grade. The penetration tests on modified and unmodified ANB were carried out at 25°C, [12].

2.5.3 Penetration index of Polymer Modified and Unmodified ANB

Penetration index (PI) is referred to as temperature susceptibility of the modified bitumen samples. PI was calculated using the equation [13] as shown below:

$$PI = \frac{1952 - 500\log(pen25) - 20\ x\ SP}{50\log(Pen25) - SP - 120} \ldots\ldots\ Eqn.2$$

Where P25 is the penetration at 25°C and SP is the softening point temperature of the modified bitumen samples.

2.5.4 Kinematic viscosity of Polymer Modified and Unmodified ANB

The kinematic viscosity tests on modified and unmodified ANB were carried out at 135 ± 5.5 °C, [14]. The time required for the leading edge of the meniscus of test sample to pass from the first timing mark to the second was measured.

$$Kinematic\ viscosity - \text{cSt} = \text{C.t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..Eqn.3$$

Where $C = caliberation\ constant, and$

$t = time\ taken\ the\ sample\ to\ flow$

$from\ the\ first\ \ to\ the\ second\ timing\ marks, s$

2.5.5 Determination of Specific Gravity of ANB

Agbabu natural bitumen sample was heated in the oven to melt. 100g of the heated sample was weighed into a gravity bottle of a known weight and volume. The weights of the bottle plus the sample was taken and recorded. The sample was allowed to cool for about 30 minutes and the solvent (trichloroethylene) was added to the sample in the bottle to the standard mark. It was ensured that the bottle was shaken while adding the solvent to allow for outright dissolution of the sample. The bottle was then put in the water bath at 25°C for about one hour and refilled to the mark due to a little decrease in the level of the solvent in the bottle and weighed.

The specific gravity of ANB was calculated as shown below:

$Weight\ of\ the\ flask\ (already\ known) = Ag$

$Weight\ of\ the\ sample = 100g = Bg$

$Weight\ of\ the\ flask + sample = Cg$

$Weight\ of\ the\ flask + sample + trichloroetylene = Dg$

$Weight\ of\ the\ trichloroethylene\ (D - C) = Eg$

$Specific\ gravity\ of\ trichloroethylene\ using\ hydrometer = \frac{1.455g}{Ml} = Fg$

$Standard\ volume\ of\ the\ flask\ = GMl$

$Volume\ of\ the\ solution = \frac{E}{F} = Hg$

$Volume\ of\ the\ sample (G - H) = Ig$

$$Density = \frac{D}{I} = \frac{Jg}{Ml} = \frac{weight\ of\ the\ sample}{volume\ of\ the\ sample}$$

$$Specific\ gravity = \frac{density\ of\ ANB}{density\ of\ water\ at\ 4o_C}$$

2.5.6 Flash and fire point tests of ANB [15]

The flash and fire point tests of Agbabu Natural Bitumen sample were conducted using Pensky-Martens apparatus, Flash Point Tester (HFP 386 Cleveland) Open Cup and Thermometer- High range: 90 – 370°C, Graduation 2°C. The test cup was filled with bitumen sample to the standard mark and thermometer was inserted into the cup and heated at the rate of 5°C/min. A lighted flame was passed across the sample at interval of 15 secs. The flash point was considered as the lowest liquid temperature at which application of the test flame caused the vapours of the sample to flash, while the fire point was considered as the temperature at which the test flame causes the sample to ignite and remain burning for at least 5 seconds.

3 RESULTS AND DISCUSSION

3.1 Rheological and Physical Properties of Modified and Unmodified ANB

The results of Rheological and Physical Properties of Modified and Unmodified ANB are as shown in Tables (2-4).

TABLE 2

RHEOLOGICAL AND PHYSICAL PROPERTIES OF MODIFIED ANB WITH PEVA

Binder type	Penetration at 25 °C (dmm)	Softening point (°C)	Specific gravity	Flash point (°C)	Fire point (°C)	Kinematic Viscosity (cSt)	Penetration index
ANB	82	47	1.047	265	275	350	-0.776
ANB+ 2%PEVA	68	54	1.034	255	260	610	0.537
ANB + 4%PEVA	60	59	1.036	245	255	960	1.299
ANB + 6%PEVA	51	66	1.039	235	250	1460	2.204

Results are means of triplicate readings

TABLE 3

RHEOLOGICAL AND PHYSICAL PROPERTIES OF MODIFIED ANB WITH HDPE

Binder type	Penetration at 25 °C (dmm)	Softening point (°C)	Specific gravity	Flash point (°C)	Fire point (°C)	Kinematic Viscosity (cSt)	Penetration index
ANB	82	47	1.047	265	275	350	-0.776
ANB + 2%HDPE	70	52	1.033	260	265	560	0.132
ANB +4% HDPE	62	56	1.035	255	260	810	0.743
ANB + 6%HDPE	52	65	1.037	245	250	1390	2.076

Results are means of triplicate readings

TABLE 4

RHEOLOGICAL AND PHYSICAL PROPERTIES OF MODIFIED ANB WITH PSCB

Binder type	Penetration at 25 °C (dmm)	Softening point (°C)	Specific gravity	Flash point (°C)	Fire point (°C)	Kinematic Viscosity (cSt)	Penetration index
ANB	82	47	1.047	265	275	350	-0.776
ANB + 2%PSCB	66	54	1.044	260	270	590	0.455
ANB + 4% PSCB	69	53	1.039	255	265	450	0.338
ANB + 6% PSCB	71	50	1.032	250	260	400	-0.351

Results are means of triplicate readings

dmm= decimillimeter, cSt=centistoke, °C=degree centigrade

The penetration and softening point values of the base ANB were found to be 82dmm and 49°C respectively. The result contradicted the findings of Guma *et al.* [16]. In their own study, they reported 120mm and 116mm for penetration values for two bitumen samples (Ondo S-A and Ondo S-B, respectively) obtained from Agbabu. Similarly, softening points of the two samples were reported to be 36.5°C and 37°C respectively by the same authors. The difference might be due to the fact that Guma *et al.* [16] used ANB samples which were neither purified nor dehydrated.

3.1.1 Effect of polymers on penetration value of ANB

Penetration is a measure of the consistency or hardness of bitumen. An increase in penetration value of bitumen makes it harder [17]. An increase in penetration value of bitumen signifies hardening of the material. Hardening of bitumen has a negative effect on the quality of bitumen. Hardening has been implicated to be responsible for distresses such as breakdown and rupture in the pavement which led to premature failure [17]. The penetration values of HDPE and PEVA modified samples in Tables 2 and 3 were found to decrease with an increase in the quantity of polymer incorporated into the ANB except the PSCB modified sample which behaved contrary to what was obtained for other modified samples. This might be due to the issue of compatibility (Table 4). It was inferred that when the polymer was added to the bitumen during modification process, the polymer absorbed some oils and released fractions of its low molecular weight into the bitumen samples, leading to increase in the viscosity of the polymer modified bitumens (PMBs) [18]. By the time the PMBs cooled, it turned into a hard mixture having an increased stiffness. This accounts for the lower penetration value of PMBs.

3.1.2 Effect of polymers on softening point of ANB

The effects of polymers used in this study on the softening point of ANB are as shown in Tables (2-4). It is clearly seen that as the content of modifiers added to ANB increased, the softening point of the modified samples increased except for PSCB which may be due to poor compatibility at the levels of 4 and 6% polymer contents. Decrease in softening point means a reduction in hardness of bitumen, which corroborates the results obtained from penetration tests (Table 4).

This result is in agreement with the results obtained by Zhang *et al.* [6] as shown in Table 5. In their studies, they reported that the addition of the polymers to bitumen led to increase in the softening point which was found to increase with quantity of polymer incorporated into the bitumen.

TABLE 5
INFLUENCE OF SBR CONTENTS ON THE CONVENTIONAL PROPERTIES OF UNAGED A-H 90 PAVING PETROLEUM BITUMEN SAMPLE

SBR content (%)	Softening Point (^oC)	Penetration (25^oC, mm)	Penetration index (PI)
Base bitumen	47.0	74	-0.946
SBR 1%	49.7	62	0.032
SBR2%	51.3	56	0.074
SBR 3%	53.0	41	0.083

Source:[6]

3.1.3 Effect of polymers on penetration index of ANB

Penetration index (PI) is referred to as temperature susceptibility of a material. The PI for each of the modified ANB is as shown in Tables (2-4). The PI of PEVA and HDPE modified samples of ANB were found to increase as the quantity of polymer incorporated increased. However, for PSCB modified samples, the reverse was the case due to poor compatibility in samples modified with 4 and 6% PSCB, (Table 4). The high value of PI implies high temperature susceptibility of bitumen and vice versa. Thus, the use of bitumen with low penetration index value (low temperature susceptible) in tropical region will result in rutting. While, the use of bitumen with high penetration index value in cold weather areas will result in cracking. It was reported that asphalt binders with high penetration number (called 'soft') are used for cold weather while asphalt binders with low penetration number (called 'hard') are used in warm climates [19].

3.1.4 Effect of polymers on kinematic viscosity of ANB

The effect of polymer on the kinematic viscosity (Tables 2-3) showed that as the quantity of the polymer in the bitumen increased, so also the kinematic viscosity increased except for PSCB modified sample (Table 4) which showed a decreased in kinematic viscosity. Thus, an increase in quantity of polymer incorporated into bitumen resulted in an increase in hardness or stiffness of modified bitumen which translates into an increase in kinematic viscosity [20].

3.1.5 Effect of polymers on Specific gravity of Polymer Modified ANB

The specific gravities of the modified and unmodified ANB are as contained in Tables (2-4). The specific gravity of the unmodified ANB (1.047) obtained in this study compared favorably with that reported earlier for the ANB in the previous study which is 1.03 [21].

The specific gravities of HDPE (0.952), PEVA (0.933) and PSCB (1.04) are much closer to that of unmodified ANB (1.047). Incorporation of these polymers into ANB as modifiers resulted in modified samples with lower specific gravities than that of the ANB (control). For the PSCB modified samples the specific gravities though lower than that of control, they decreased with increasing quantity of polymer incorporated in ANB due to the poor compatibility. The effect of Polyethylene (PE) and Polyvinyl acetate (PVC) on properties of 80/100 penetration grade petroleum bitumen had earlier been investigated by Nobinur *et al.* [22]. It was reported that the specific gravity of the binder (1.023) decreased with increasing PE content due to low specific gravity of PE (0.94) but increased with increasing PVC content due to higher specific gravity of PVC (1.25) [22].

31.6 Effect of polymers on Flash and Fire Points of Polymer Modified ANB

The flash point and fire point of all the modified ANB samples produced in this study were lower than that of the unmodified ANB (Tables 2-4). It can be inferred that the modifiers used had a decreasing effect on the flash and fire points of modified ANB due to their lower melting points.

4 CONCLUSION

The Addition of the modifiers (PEVA, HDPE, PSCB) enhanced the rheological properties of the ANB. However, the extent of the effect of the modifiers is dependent on the content of the modifier incorporated. The decrease in penetration value, increase in softening point and penetration index exhibited by the modified ANB samples are indications of improved rheological properties of the modified samples. Improvement in rheological properties may translate to an improved service life. Investigations are in progress to assess the impacts of some aging factors on the PEVA-, HDPE- and PSCB - modified samples.

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REFERENCES

[1]. A. A. Yousefi, ''Rubber-polyethylene Modified Bitumens,'' *Iran Polymer Journal,* 13(2), pp.101-112, 2004.

[2]. A. Montepara, E. Santagata, and G. Tosi, ''Photochemical Degradation of Pure Bitumen by UV Radiation,'' *Proc. 1st Eurasphalt & Eurobitume Congress E&E,* 5, pp.133, 1996.

[3]. H. C. A. Brandt and P. C. De Groot, ''Aqueous Leaching of Polycyclic Aromatic Hydrocarbons from Bitumen and Asphalt,'' *Water Research,* 35 (17), pp. 4200–4207, 2001.

[4]. J. S. Muller and W. Y. Bellinger, ''Distress Identification Manual for the Long- Term Pavement Performance Program,'' US *Department of Transportation, Federal Highway Administration,* pp. 1-169, 2003.

[5]. A. A. Yousefi, ''Preparation and Rheological Behaviour of Polymer-Modified Asphalt, Ph.D dissertation, Department of Chemical Engineering,'' Laval University, Canada, 1999.

[6]. J. Zhang, J. Wang, Y. Wu, W. Sun and Y. Wang, ''Thermal Behaviour and Improved Properties of SBR and SBR/Natural Bitumen Modified Bitumens,'' *Iranian Polymer Journal,* 18(6), pp. 465-478, 2009.

[7]. O. S. Adegoke, B. D. Ako and E. 1. Enu, ''Geotechnical investigations of the Ondo State bituminous sands,'' *Report of Geological Consultancy Unit, Geology Depar tment, Obafemi Awolowo University, Ile Ife, Nigeria,* 257, pp. 27-36, 1980.

[8]. www.sigmaaldrich.com/427977/polyethylene, 15-8-2015.

[9]. H. S. Vernon and T. Katy, ''Processing for Removing Water from Heavy Crude Oil,'' United State Patent. Patent no: 6,007,702, 1999.

[10]. I. Rubinstein and O. P. Strausz, ''Thermal Treatment of the Athabasca Oil Sand Bitumen and its Component Parts,'' *Geo-chim. Cosmochim. Acta* 43, pp. 1887-1893, 1979.

[11]. ASTM D36/D36M-09 ''Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus''.

[12]. ASTM D5-97. ''Standard Test Method for Penetration of Bituminous Materials,'' *Annual Book of ASTM Standards, Volume 04.03, American Society for Testing and Materials, Philadelphia* 19103-1187.

[13]. R. Roque, B. Birgisson, M. Tia, B. Kim and Z. Cui, ''Guidelines for the Use of Modifiers in Superpave Mixture: Evaluation of SBS Modifier,'' state Job 99052793, f*lorida department of Transport, Tallaassee,* FL, 1, 2004.

[14]. ASTM D2170 – 92 ''Standard Test Method for kinematic Viscosity of Asphalts,'' *Experiment No. 12.*

[15]. ASTM D92-01 ''Standard Test Method for Flash and Fire Points by Cleveland Open Cup, '' *ASTM International, West Conshohocken, PA,* www.astm.org.

[16]. T. N. Guma, P. B Madakson, D. S. Yawas and S. Y. Aku, ''Assessment of Physicochemical Properties of some Bitumens from Nigerian Resources,'' *Nigerian Journal of Basic and Applied Science,* 20(2), 177-181, 2012.

[17]. I. M. Nassar, K. I. Kabel and I. M. Ibrahim, ''Evaluation of the Effect of Waste Polystyrene on Performance of Asphalt Binder,'' *ARPN Journal of Science and Technology,* 2(10), pp. 927-935, 2012.

[18]. M. Garcia-Morales, P. Partal, F. J. Navarro, F. Martý´nez-Boza, C. Gallegos, N. Gonza´lez, O. Gonza´lez and M. E. Mun˜oz ''Viscous Properties and Microstructure of Recycled EVA Modified Bitumen,'' *Fuel*, 83, pp. 31-38, 2003.

[19]. A. E. Olugbenga, A. F. Olugbenga and G. Jonathan, ''Softening Point and Penetration Index of Bitumen from Parts of Southern Nigeria,'' *NAFTA,* 63(9-10), pp. 319-323, 2012.

[20]. M. Singh and P. Kumar, ''Laboratory Study on Bitumen Modification for Improved Physical, Rheological Properties and the Effect of Short Term Ageing,'' *25th ARRB Conference-Shaping the Future: Linking Policy, Research and Outcomes, Perth, Australia, @ ARRB Group Ltd,* pp. 1-12, 2012.

[21]. E. A. Adebayo, ''Extraction and Characterization of Bitumen from Ondo State Tar sand,'' P*roceedings of the 8th National Engineering conference of Kaduna Polytechnic, Nigeria,''* pp. 82-88, 2014.

[22]. R. M. Nobinur, M. Ahmeduzzaman, M. A. Sobhan and T. Ahmed, ''Performance Evaluation of Waste Polyethylene and PVC on Hot Asphalt Mixtures,'' *American Journal of Civil Engineering and Architecture,* 1(5), pp. 97-102, 2013.

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