Case Studies in Construction Materials 5 (2016) 39–45

Contents lists available at ScienceDirect

Case Studies in Construction Materials

journal homepage: www.elsevier.com/locate/cscm

Case study

The performance of Agbabu natural bitumen modified with polyphosphoric acid through fundamental and Fourier transform infrared spectroscopic investigations

Ojeyemi M. Olabemiwo, Akintomiwa O. Esan, George O. Adediran, Hassan O. Bakare*

Ladoke Akintola University of Technology (LAUTECH), Ogbomoso, Ilorin Road, Ogbomoso, Nigeria

ARTICLE INFO

Article history:
Received 8 March 2016
Received in revised form 27 April 2016
Accepted 7 June 2016
Available online 23 June 2016

Keywords:
Agbabu natural bitume
Polyphosphoric acid
FTIR analysis
Modification
Fundamental physical and flow properties

ABSTRACT

Nigeria is greatly endowed with large deposit of natural bitumen at Agbabu, Ondo State. The country was reported to have a proven reserve of about 42.47 billion tonnes of bitumen, a quantity which is estimated to be second largest in the world but yet to be explored for economic purposes. However, literature has shown paucity of research work on its modification. This study is therefore carried out to investigate the suitability of polyphosphoric acid (PPA) as a modifier in Agbabu natural bitumen (ANB). The performance of unmodified and PPA modified ANB has been comparatively studied with specific emphasis on Fourier Transform Infrared investigation and fundamental physical tests like penetration, softening point, fire and flash point and specific gravity. Kinematic viscosity (flow) test was also investigated. Penetration indexes of ANB samples were calculated from the penetration values for softening points.

The comparative study of FTIR spectra of both base ANB and PPA modified ANB samples showed appearance of some few new peaks in the infrared spectra of PPA modified ANB samples confirming that the structure of the neat ANB had been modified. On the basis of our experimental results, incorporation of PPA up to 6% into ANB structure greatly enhances the fundamental physical and flow properties of ANB. This showed that PPA has the potential of improving the service life of ANB.

1. Introduction

One of the major applications of bitumen is in road pavement construction [1]. However, experience has shown that application of bitumen in its natural form in pavement did not meet the required service life expectancy. The reason is attributed to increasing traffic volume on the highway and degradation of the binder (bitumen) used for the pavement. In order to meet the rising requirements for durability of the road surfaces, alternative methods of improving bitumen have been developed. One of the methods is the incorporation of modifiers which include organic and inorganic materials such as styrene butadiene (SB), styrene-butadiene-styrene (SBS), ethylene terpolymer, Ethylene-vinyl-acetate (EVA), Poly-ethylene (PE), Styrene-isoprene-styrene (SIS) and polyphosphoric acid [2–5]. The essence of this is to improve its rheological

* Corresponding author.
E-mail address: bakarehassanabuja@yahoo.com (H.O. Bakare).

http://dx.doi.org/10.1016/j.cscm.2016.06.003

properties such as elasticity, viscosity as well as fundamental properties such as penetration value, softening point and flash and fire points prior to its application.

Polyphosphoric acid (PPA) is an acid produced by heating phosphorus pentoxide (P_2O_5) with phosphoric acid (H_3PO_4) [5]. It is a viscous liquid at 25 °C, highly soluble in organics and non-oxidising molecules, [5]. PPA is produced mainly in China and in the USA in various grades containing different amount of phosphoric acid (H_3PO_4) or phosphorus pentoxide (P_2O_5). To produce PPA modified bitumen, concentration of 105, 110 and 114% H_3PO_4 are used (75.9, 79.8 and 82.6% P_2O_5 respectively) [6]. Qunshan and Hongyuan [7] also reported a typical grade of PPA for bitumen containing 115% orthophosphoric acid. The grade contain no water.

The discovery of PPA as a suitable modifier to improve fundamental and high temperature rheological properties of bitumen without adversely affecting its low temperature rheological properties dated back to early 1970s [8]. Since then, there has been avalanche of publications on the use of PPA for investigation on bitumen. Some of these include: low temperature rheology of polyphosphoric acid added to bitumen by Baldino et al. [9]; rheological effect on bitumen of polyphosphoric acid addition by Baldino et al. [10] and performance of VG30 paving grade bitumen modified with PPA at medium and high temperature regimes by Ramayya et al. [11]. Their findings revealed that the stiffness of the bitumen increased as the percentage of PPA increased up to a value that can be considered critical and destabilizing, PPA addition improved mechanical performances of bitumen at high temperature and PPA addition enhanced performance grade (PG) of VG30 binder respectively. Masson and Collins (12) reported that the reaction of PPA with bitumen occurs at the site of heteroatom containing compounds. Sulphur which is predominantly the heteroatom in bitumen had been reported to be inert either in aliphatic or aromatic sulphide group when heated with PPA at 150 °C for 1 h. However, the reactivity of PPA with bitumen is a function of nitrogen and oxygen content [13] and the reaction mechanisms include: acidolysis of alkyl/aromatics and nucleophilic displacement; alkylation of aromatics with sulphides and alcohols; and cyclisation of carboxylic acids amongst others [4].

Nigeria is ranked as one of the first five countries in the world endowed with largest deposit of natural bitumen [14], however, research activities on the vast deposit of Agbabu natural bitumen in Nigeria have largely been concentrated on the physico-chemical and engineering characterization [15]. Our aim in this study was therefore to investigate the potential of PPA in improving the service life of raw ANB.

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 south-western Nigeria. The belt lies within latitude $006^0 38^1$N-$006^0 40^1$N and longitude $004^0 34^1$E-$004^0 37^1$E, falls within the eastern Dahomey Basin and spans across Edo, Ondo and Ogun States [16,17].

2.1.2. Modifier

The modifier used in this study was Polyphosphoric acid (PPA) with concentration of 105% phosphoric acid (75.9% P_2O_5). The specific gravity is 2.05.

2.2. Preparation of PPA modified ANB

The raw natural bitumen sample collected from Agbabu was dehydrated and then purified as described in our previous study [18]. The PPA modified samples were prepared using a high shear mixer. A certain quantity of ANB (400 g) was heated to fluid state in an iron container. When the temperature of ANB was in range of 150–155 °C, the PPA was gradually added. The temperature of the mixture was maintained at 150–155 °C with the speed of the mixer also maintained at 1200 rpm for 1hr to obtain a homogenous mixture. The proportion by weight of PPA added to the base ANB varied from 2 to 6%.

2.3. Rheological properties of modified and unmodified ANB

The following rheological properties of the PPA modified ANB were determined using appropriate standard procedures. They are: Softening point [19], Penetration value [20], Kinematic viscosity [21], Flash and fire point tests of ANB [22].

2.3.1. Penetration index of PPA modified and unmodified ANB

The response of modified bitumen samples to the effect of temperature changes was calculated in terms of penetration index (PI) using the results obtained from penetration and softening point tests.

The PI was calculated using the equation [23] as shown below:

$$PI = \frac{1952 - 500\log(pen25) - 20\,x\,SP}{50\log(Pen25) - SP - 120} \quad (1)$$

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

2.3.2. Determination of specific gravity of ANB

The specific gravity of ANB was determined using specific gravity bottle and trichloroethylene as a solvent for ANB sample, as discussed in our previous study [24].

3. Results and discussion

3.1. Flow and physical properties of unmodified and modified ANB

3.1.1. Flow and physical properties of unmodified ANB

The results of Flow and physical properties of unmodified ANB were discussed in our previous study [24]. The results obtained for the unmodified ANB are as shown in Table 1.

3.1.2. Flow and physical properties of modified ANB

The results of flow and physical properties of PPA modified ANB samples are as shown in Table 2. The penetration values of the PPA modified samples range from 71 dmm in 2%PPA modified sample to 55 dmm in 6%PPA modified sample. Thus, the penetration value of modified samples decreased with increased in content of PPA used in the modification. It was also noted that all the penetration values got for PPA modified samples were less than 82 dmm obtained for base ANB.

The softening point of PPA modified samples were found to increase from 50 °C for 2% PPA modified ANB to 60 °C for 6% PPA modified ANB as against that of base ANB which is 49 °C. This is an indication of an increased resistance of PPA modified samples to temperature susceptibility after modification. The kinematic viscosities of PPA modified samples which ranged from 540 cSt for 2%PPA modified sample to 1005 cSt for 6% PPA modified sample were found to be relatively higher than that of base ANB (350 cSt).

This result is similar with that of previous study by Shulga et al. [25]. They reported that addition of PPA to different grade of bitumen obtained from China, Venezuela, Canada and Russia resulted in reduced values of penetration, increased values of softening point with exception of Canadian bitumen whose softening point remained essentially unchanged, and increased values of dynamic viscosity measured at 60 °C for all tested bitumen samples. Similarly, Huang et al. [26] investigated the effect of 1.5 wt% of PPA on aging characteristics of asphalt binders. Based on their study, PPA modified asphalts was found to increase the initial stiffness and improve the low-temperatures flow properties. D'Angelo [27] studied the effect of 0.5% wt. PPA on high temperature binder grade, Venezuelan and Saudi Light. The findings of this author showed that PPA increased the stiffness of asphalt binders and improved cross-linking, while Styrene butadiene styrene (SBS) increased the elastic response of asphalt binders.

The penetration indexes of PPA modified ANB samples increased as the percentage content of PPA incorporated increased (Table 2). Increase in penetration index indicates increase in hardness of modified bitumen [28].

The values obtained for flash and fire points of PPA modified ANB are as shown in Table 2. The values obtained in this study were found to be lower than the values obtained for base ANB, which are 265 °C and 275 °C for flash and fire points respectively, Table 1.

The specific gravities of PPA modified samples were found to increase as the quantity of PPA in the sample increased. The increase can be ascribed to the fact that the density of PPA (2.04) is relatively higher than that of base ANB (1.047). Rahman et al. [29] had earlier reported that when modifier of higher specific gravity than the neat bitumen is used, the product of modification is a modified sample of higher specific gravity than the neat bitumen. This is in agreement with the present study (Table 2).

Table 1
Flow and Physical Properties of Unmodified ANB.

Property	Value
Penetration at 25 °C (dmm)	82
Softening point (°C)	47
Specific gravity	1.047
Flash point (°C)	265
Fire point (°C)	275
Kinematic Viscosity (cSt)	350
Penetration index	−0.776

Table 2
Flow and Physical Properties of PPA Modified ANB.

Modified Binder type	Penetration at 25 °C (dmm)	Softening point (°C)	Specific gravity	Flash point (°C)	Fire point (°C)	Kinematic Viscosity (cSt)	Penetration index
ANB + 2%PPA	71	50	1.069	185	195	540	−0.34
ANB + 4% PPA	65	54	1.119	170	185	750	0.413
ANB + 6% PPA	55	60	1.165	165	175	1005	1.271

Results are means of triplicate readings.

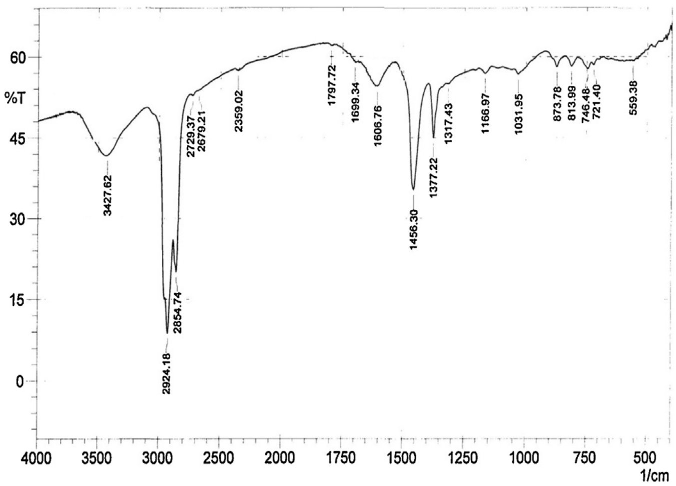

Fig. 1. Infrared Spectrum of Purified ANB.

3.2. Effect of PPA on the infrared spectrum of ANB

3.2.1. Infrared analysis of unmodified ANB

The Infrared (IR) spectrum of neat ANB was recorded in the range of 4000–400 cm^{-1} as shown in Fig. 1. Unmodified ANB has absorption peaks at 2924 cm^{-1}, 2854 cm^{-1},1699 cm^{-1}, 1606 cm^{-1}, 1456 cm^{-1}, 1377 cm^{-1} and 1031 cm^{-1} and peaks in the region 873 cm^{-1}, 813 cm^{-1}, 746 cm^{-1}, and 721 cm^{-1} appear as shoulder. The infrared absorption peaks are similar to the submission of Lamontagne et al. [30] who identified absorption bands related to asphalt binder of grade of PG 64–22 to include 2922 cm^{-1}(υasCH2 CH3), 2882 cm^{-1}(υsCH2 CH3), 1601 cm-1(υ C=C), 1455 cm^{-1}, 1376 cm^{-1}, 1031 cm^{-1}(υ SO2), 868 cm^{-1},813 cm^{-1}(C=C), 747 cm^{-1}, and 722 cm^{-1}). Assignment of functional groups in the neat ANB is based on some previous studies [18,31] and is as shown in Table 3.

Table 3
Infrared Absorption Peaks of Purified ANB and PPA ANB modified Samples.

Peak, cm^{-1}				Bond/Functional Group
Purified ANB	2% PPA modified ANB	4% PPA modified ANB	6% PPA modified ANB	
3427	3450	3433	3431	NH, OH stretch (H-bonded)
2924	2924	2924	2924	C—H asymmetric stretch in CH_3
2854	2854	2854	2854	C—H out of phase stretch in CH_2
1699	1699	1707	1697	C=O (str) in carbonyl/carboxylic
1606	1614	1612	1624	C=C (str), aromatic compound
1456	1456	1458	1458	C—CH_3 and methylenic asymmetric
1377	1377	1377	1377	C—CH_3 asymmetric
Absent	976	1004	1001	P—O—P stretching
1031	Absent	absent	absent	Sulphoxides
873	873	873	875	One H on ring
813	813	813	815	Two adjacent H on ring
746	746	746	746	Four adjacent Hydrogen on ring
721	723	721	721	Aromatic bending H—C modes
Absent	511	497	497	P—O—P bending vibration
Absent	418	410	420	P—O—P bending vibration

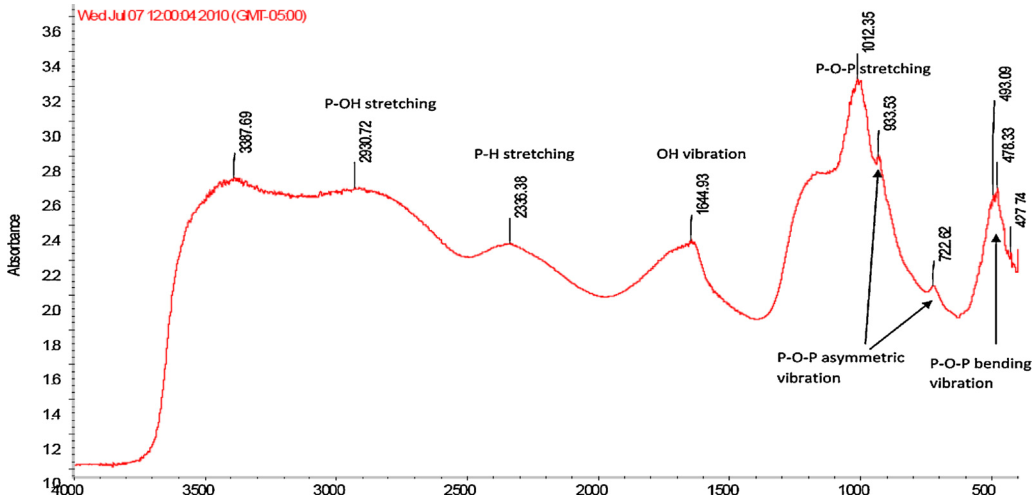

Fig. 2. Major Infrared absorption Peaks of PPA [32].

3.2.2. Infrared spectral analysis of PPA modified bitumen

The major absorption peaks of infrared spectra of PPA and PPA modified ANB samples are as shown in Figs. 2 and 3 (a–c), respectively. In addition, the wave number of the absorption peaks of PPA modified ANB samples are as shown in Table 3 with the assignment of functional groups based on some previous studies [18,31,32]. Some similarities in the PPA modified ANB

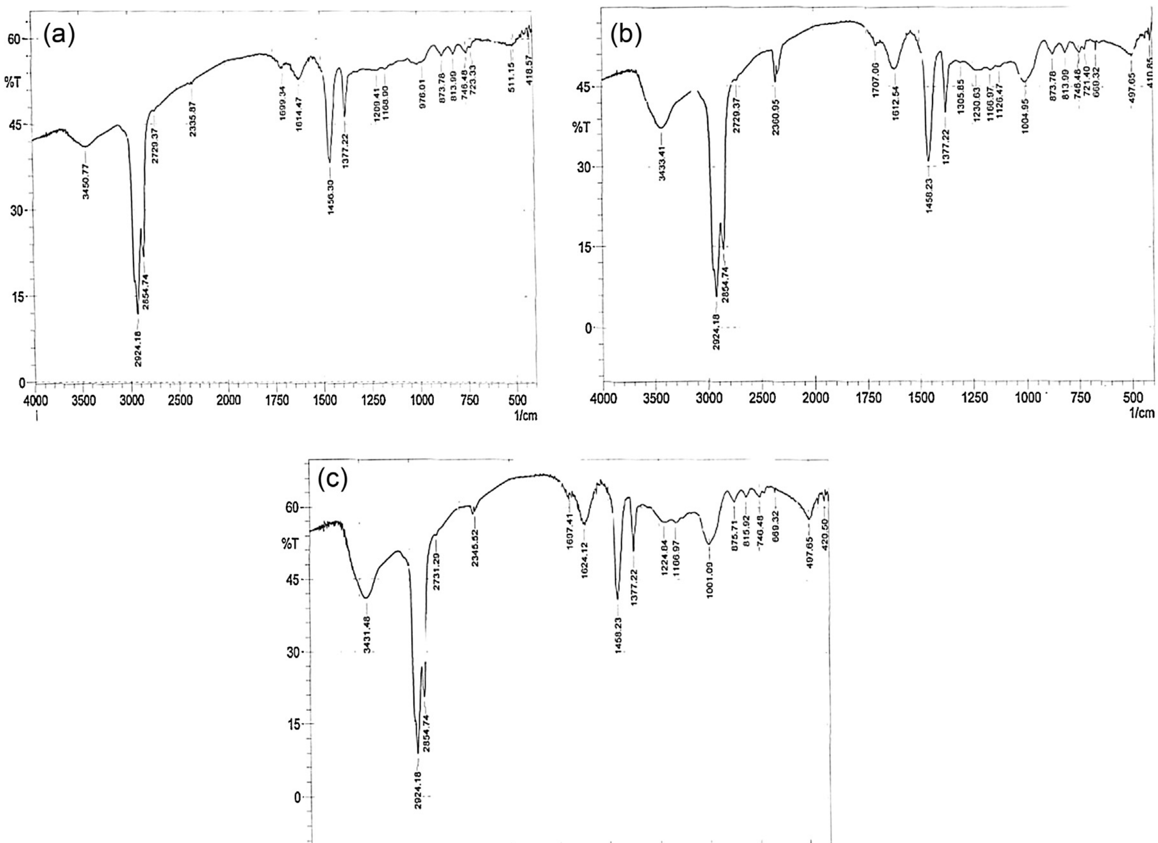

Fig. 3. (a) FTIR of Agbabu natural bitumen modified with 2% PPA. (b) FTIR of Agbabu natural bitumen modified with 4% PPA. (c) FTIR of Agbabu natural bitumen modified with 6% PPPA.

spectral are noted with the submission of Zhang and Yu [32] on major spectrum of PPA who reported infrared absorption peaks to include 1012 cm^{-1}, 933 cm^{-1}, 772 cm^{-1}, and 478 cm^{-1} as shown in Fig. 2. However, P-O-P asymmetric vibrations at 933 cm^{-1} and 772 cm^{-1} were absent in the PPA modified ANB spectral.

The comparison of peak position and intensities of various peaks appearing in the infrared spectra of base bitumen and PPA modified ANB (containing 2, 4, and 6% PPA compositions) reveal that there is appearance of additional new peaks with wave numbers in the ranges of 976–1004 cm^{-1} for P-O-P stretching and 497–511 cm^{-1} for P-O-P bending vibration in the spectra of PPA modified ANB samples. This indicates that the PPA has undergone some type of interactions with bitumen resulting in structural changes in the modified bitumen. There is no noticeable disappearance of peaks, in contrast to findings of Gupta et al. [33] who reported disappearance of some infrared peaks in modified bitumen. However, peak shifting occurred in the infrared spectra of PPA modified ANB samples prepared in this study.

Furthermore, the infrared spectra of PPA modified samples showed that sulphoxide bands were absent, which agree with the findings of Masson and Collins [12] who carried out FTIR study of the reaction of polyphosphoric acid and model asphalt sulphur compounds. Their finding showed that sulphide groups (aliphatic or aromatic), was inert when heated with PPA at 150 °C for 1 h i.e. the aliphatic or aromatic sulphur compounds did not react with PPA during blending.

4. Conclusion

PPA was successfully incorporated into the structure of ANB. The appearance of some few peaks and shifting of peaks after modification of ANB using PPA confirm this. In addition, the incorporation of PPA into ANB has resulted in an increase in softening point, kinematic viscosity, specific gravity, penetration index and a decrease in penetration value as well as flash and fire points of ANB. All changes in flow and physical properties recorded for the PPA modified ANB in this study are strong indexes for the suitability of PPA in improving the service life of ANB. However, it is noted that ANB required relatively higher concentration of PPA compared with some previous studies on other bitumens.

Acknowledgement

The authors are very grateful to Tertiary Education Trust Fund (TETFUND), Abuja, Nigeria for the project intervention grant for this study.

References

[1] M.E. Khalid, Polymeric additives effect on mechanical properties for bitumen based composites, Eng. Technol. J. 29 (12) (2011) 2501–2519.
[2] A.A. Yousefi, Preparation and rheological behaviour of polymer-modified asphalt, Ph.D. Dissertation, Department of Chemical Engineering, Laval University, Canada, 1999.
[3] Y. Yildirim, Polymer modified asphalt binders, Constr. Build. Mater. 21 (2007) 66–72.
[4] G.L. Baumgardner, J.F. Masson, J.R. Hardee, A.M. Menapace, A.G. Williams, Polyphosphoric acid modified asphalt: proposed mechanisms, J. Assoc. Asphalt Paving Technol. 74 (2005) 283–305.
[5] J.F. Masson, A brief review of the chemistry of polyphosphoric acid (PPA) and bitumen, Energy Fuels 22 (2008) 2637–2640.
[6] Hanna Jaroszek, Polyphosphoric acid (PPA) in road asphalts modification, CHEMIK 66 (12) (2012) 1340–1345.
[7] Y. Qunshan, F. Hongyuan, Rheological properties of polyphosphoric acid modified asphalt binder, Indian J. Eng. Mater. Sci. 21 (2014) 214–218.
[8] P. De Filippis, C. Giavarini, M. Scarsella, Improving the ageing resistance of straight-run bitumens by addition of phosphorus compounds, Fuel 74 (6) (1995) 836–841.
[9] N. Baldino, D. Gabriele, C.O. Rossi, L. Seta, F.R. Lupi, P. Caputo, Low temperature rheology of polyphosphoric acid added to bitumen, Constr. Build. Mater. 36 (2012) 592–596.
[10] N. Baldino, D. Gabriele, F.R. Lupi, R.C. Oliviero, P. Caputo, T. Falvo, Rheological effect on bitumen of polyphosphoric acid (PPA) addition, Constr. Build. Mater. 40 (2013) 397–404.
[11] V.V. Ramayya, V.V. Ram, S. Krishnaiah, K.A. Sandra, Performance of VG30 paving grade bitumen modified with PPA at medium and high temperature regimes, Constr. Build. Mater. 105 (2016) 157–164.
[12] J.F. Masson, P. Collins, FTIR study of the reaction of polyphosphoric acid and model bitumen sulphur compounds, Energy Fuels 23 (2009) 440–442.
[13] J.F. Masson, P. Collins, J.R. Woods, S. Bundalo-Perc, J.C. Margeson, Chemistry and effects of polyphosphoric acid on the microstructure, molecular mass, glass transition temperatures and performance grades of asphalts, J. Assoc. Asphalt Paving Technol. 78 (2009) 403–430.
[14] O.S. Adegoke, Geological guide to some Nigerian cretaceous-recent localities, Special Publication No. 2, Nigerian Mining and Geosciences Society, 16 Annual Conference (1980) 27–36.
[15] O.M. Olabemiwo, G.O. Adediran, F.A. Adekola, A.A. Olajire, Aliphatic and polycyclic aromatic hydrocarbons profiles of photomodified natural bitumen of Agbabu, southwestern Nigeria, Bull. Chem. Soc. Ethiop. 24 (3) (2010) 461–466.
[16] O.S. Adegoke, B.D. Ako, E. Enu, Geotechnical Investigations of the Ondo State Bituminous Sands, vol. 257, Report of Geological Consultancy Unit, Geology Department, Obafemi Awolowo University, Ile Ife, Nigeria, 1980, pp. 27–36.
[17] A. Akinmosin, O.O. Osinowo, M.A. Oladunjoye, Radiogenic components of the Nigerian tar sand deposits, Earth Sci. Res J. 13 (1) (2009) 64–73.
[18] H.O. Bakare, A.O. Esan, O.M. Olabemiwo, Characterisation of Agbabu natural bitumen and its fractions using Fourier transform infrared spectrometry, J. Chem. Mater. Res. 7 (8) (2015) 1–16.
[19] ASTM D36/D36M-09. Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus.
[20] ASTM D5-97. Standard Test Method for Penetration of Bituminous Materials (1998). Annual Book of ASTM Standards, Volume 04.03, American Society for Testing and Materials, Philadelphia 19103–1187.
[21] ASTM D2170-92. Standard Test Method for kinematic Viscosity of Asphalts, Experiment No. 12.
[22] ASTM D92-01, Standard Test Method for Flash and Fire Points by Cleveland Open Cup, ASTM, International, West Conshohocken, PA, 2001.
[23] R. Roque, B. Birgisson, M. Tia, B. Kim, Z. Cui, Guidelines for the Use of Modifiers in Superpave Mixture: Evaluation of SBS Modifier, State Job 99052793, Florida Department of Transport, Tallaassee, FL, 2004.
[24] O.M. Olabemiwo, O.E. Akintomiwa, H.O. Bakare, Preliminary investigation on modification of Agbabu natural bitumen with some polymeric materials, Int. J. Sci. Eng. Res. 6 (9) (2015) 1342–1349.

[25] O. Shulga, R. Maldonado, L. Lewandowski, H. Romagosa, Application of polyphosphoric acid for HMA modification, US and European Experience, 5th Eurobitume Congress, Istanbul, Turkey, 2012, pp. 13.
[26] S.C. Huang, T.F. Turner, F.P. Miknis, K.P. Thomas, Long-term Aging Characteristics of Polyphosphoric Acid Modified Asphalts, Transportation Research Record: Journal of the Transportation Research Board, Washington, D.C, 2008, pp. v2051.
[27] J. D'Angelo, PPA and Binder Modification, Office of Pavement Technology. https://engineering.purdue.edu/NCSC/PPA%20Workshop/2009/index.html, 2010.
[28] G.D. Airey, Rheological properties of styrene butadiene styrene polymer modified road bitumens, Fuel 82 (14) (2003) 1709–1719.
[29] N. Rahman Md, A. Mohammad, M.A. Sobhan, T. Ahmed, Performance evaluation of waste polyethylene and PVC on hot asphalt mixtures, Am. J. Civil Eng. Archit. 1 (5) (2013) 97–102.
[30] J. Lamontagne, P. Dumas, V. Mouillet, J. Kister, Comparison by Fourier transform infrared (FTIR) spectroscopy of different ageing techniques: application to road bitumens, Fuel 80 (2001) 483–488.
[31] F.M. Adebiyi, A.A. Omode, Organic, chemical and elemental characterization of components of Nigerian bituminous sands bitumen, Energy Sour. Part A: Recov. Util. Environ. Eff. 29 (8) (2007) 669–676.
[32] F. Zhang, J. Yu, The research for high-performance SBR compound modified asphalt, Constr. Build. Mater. 24 (3) (2010) 410–418.
[33] R. Gupta, V. Sangita Kaur, Characterization of bitumen and modified bitumen (e-PMB) using FT-IR thermal and SEM techniques, international science congress association, Res. J. Chem. Sci. 2 (8) (2012) 31–36.