

EVALUATION OF PHYSICAL AND MINERALOGICAL PROPERTIES OF GRAPHITE-MODIFIED BITUMEN

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Abstract — This study aimed to investigate the impact of adding graphite on the physical and mineralogical properties of bitumen in asphalt mixtures, covering a graphite content ranging from 0% to 8%. A variety of tests were conducted to assess these effects, including measurements of softening point, flash and fire values, ductility point, Marshall stability, Marshall flow, and indirect tensile strength. Evaluations also encompassed assessments of particle size distribution through coefficients of uniformity (Cu) and gradation (Cc), aggregate strength via Aggregate Crushing Value (ACV) tests, and impact resistance with Aggregate Impact Value (AIV) tests. The results indicated a desirable well-graded particle size distribution in the soil sample, with Cu and Cc values of 4.5 and 0.5, respectively. The aggregate showed a satisfactory ACV of 28.91%, falling within the recommended range, and an AIV value of 19.84%, meeting road surfacing specifications. Adding graphite to bitumen increased the softening point, reaching a maximum value of 54.1°C at 8% graphite content. This addition also improved flash and fire values, with peak levels at the same graphite content. Furthermore, including graphite led to an enhanced ductility point, indicating improved flexibility. The graphite-modified asphalt concrete exhibited higher Marshall stability and flow, with optimum values of 18.09 kN and 3.80 mm, respectively, at 8% graphite content. The optimum indirect tensile strength of 986.20 kPa also occurred at 6% graphite content. XRD characterization confirmed the presence of various minerals in the unmodified bitumen, such as feldspars, pyroxenes, and quartz, which increased the specific surface area and reduced mechanical strength. In contrast, graphite-modified bitumen exhibited a modified structure with reduced specific surface area, and XRD patterns confirmed the presence of graphite, with a carbon content exceeding 85%. The study strongly recommends incorporating 6% graphite into asphalt mixtures, as this measure significantly enhances their performance and durability.

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Keywords: graphite, bitumen modification, asphalt concrete, mineralogy, strength

1.0 INTRODUCTION

The rapid pace of urbanization and the growing number of vehicles on the roads have resulted in an increased need for new road construction and the renovation of existing ones, thereby driving up construction costs [1, 2]. The depletion of non-renewable resources like bitumen and aggregates has prompted engineers to explore alternative materials for road construction. Bitumen, an engineering material with adhesive and waterproofing properties, has been used for sealing purposes since ancient times. It is an organic chemical derived from the fractional distillation of hydrocarbons [3–5]. Bitumen exhibits liquid characteristics at high temperatures but becomes brittle at low temperatures. In road pavements, bitumen and asphalt are subjected to various chemical and mechanical stresses, including stress, tension, bending, and impact. Therefore, understanding how bitumen withstands these stresses is crucial. Bitumen is a colloidal system composed of two groups of dispersed particles: asphaltenes and aromatic resins, which stabilize the dispersion of asphaltenes, and maltenes, the oil component of bitumen. Bitumen is manufactured through the fractional distillation process of crude oil in refineries and has been widely used in the construction of asphalt pavements worldwide [6, 7]. However, at high temperatures and low frequency of loading, bitumen can become soft with low stiffness, making it susceptible to permanent deformation. Additionally, the complex mixture of aliphatic, aromatic, and naphthenic hydrocarbons in bitumen leads to aging caused by oxygen diffusion and ultraviolet radiation. Repeated loads result in decreased strength due to fatigue, while low temperatures make bitumen brittle, leading to thermal cracking and potential pavement failure [8, 9].

In road construction, flexible pavements are preferred due to their smooth riding quality and lower initial costs compared to rigid pavements. Bitumen, along with aggregates and fillers, is a crucial component of asphalt concrete used in the construction of flexible pavements. Bitumen's high adhesive property, water resistance, and durability make it a valuable material in road construction. It is also used for road maintenance and roofing [10, 11]. To enhance the durability and lifespan of bitumen in asphalt pavements, it is important to identify its structure and modify it accordingly. The use of modified bitumen has been recognized as a solution to reduce maintenance frequency and sustain pavement durability. Modifying bitumen can improve its properties, and different modifiers are available depending on site-specific needs and requirements. Several researchers have conducted research on mitigating the adverse effects of aging by using various additives and also investigate new techniques to evaluate the aging processes [12, 13]. Imanbayev et al. [14] conducted a study on the modification of bitumen using recycled plastics from waste materials. The research aimed to enhance bitumen performance and road durability. The modified bitumen underwent various tests, including penetration and plasticity, softening temperature, brittleness temperature on Fraas, and microscopic analysis. The optimal formulation of the polymer-bitumen binder included the addition of 3 wt.% PET (polyethylene terephthalate) and up to 3% SBS (styrene-butadiene-styrene) to meet the requirements of Kazakhstani standards PBB 40 and PBB 90. The results confirmed that the modified bitumen met the criteria outlined in Kazakhstani standards for polymer-bitumen binders. Wu et al. [8] also investigated the electrical conductivity of asphalt concrete with additives such as carbon black, graphite, and carbon fibers. They found that pure carbon-fiber-modified asphalt concrete exhibited the highest conductivity, followed by graphite and carbon black. The viscoelastic behavior of asphalt binder resulted in significant variations in the mechanical features of asphalt pavement due to daily and seasonal temperature changes. Liu et al. [15] recorded that the softening point of bitumen increased from 45°C to 70°C when graphite was used in the bitumen modification. The rutting parameter increased by 9% at 40°C with the addition of 9% graphite. Similarly, Wu et al. [8] investigated the mechanical characteristics of conductive asphalt concrete using graphite and carbon fiber. The results indicated that conductive asphalt concrete exhibited higher tensile strength under dry conditions but lower wet tensile strength and tensile strength ratio (TSR).

Researchers have also reported the benefits of using recycled materials in asphaltic construction [9–12, 16]. Vasudevan et al. [12] found that recycled polyethylene from shopping bags reduced permanent deformation in the form of rutting and low-temperature cracking. Essawy et al. [1] demonstrated that polypropylene (PP) outperformed polyethylene (PE) as a modifier for hot-mix asphalt (HMA), reducing its temperature susceptibility.

Furthermore, Yao et al. [11] explored the effects of 1-2% graphite nanoplatelets on asphalt binder properties. The study revealed that the amount of graphite-modified binder increased with aging, enhancing its resilience to rutting and moisture damage. Additionally, graphite nanoplatelets were found to increase crack resistance. Pan et al. [17] investigated the addition of graphite to bitumen, confirming its improvement in the anti-aging properties of the binder. Similarly, Oladunjoye et al. [18] evaluated the rheological characteristics of graphite-modified bitumen, finding that a 10% graphite content resulted in a maximum complex shear modulus of 8984 kPa and a rutting parameter of 33387 kPa.

Generally, road failure, which can be functional or structural, is caused by factors such as axle load repetition, heavy traffic, and temperature variations. Traffic loading leads to rutting and fatigue cracks, while temperature variations result in thermal cracks. These factors impose various stresses and strains on different pavement points, leading to pavement damage over time. Fatigue cracks originate in the bitumen phase of the asphalt mixture and expand with the continuity of loading. To address these issues, this research focuses on investigating the use of graphite to modify bitumen and evaluate its physical and mineralogical properties. This research therefore aims to contribute to the understanding and advancement of Graphite modified bitumen (GMB), facilitating its practical application in the construction and maintenance of high-quality asphalt pavements. Natural waste materials such as sludge, rice husk ash (RHA), groundnut husk ash (GHA), coconut shell, and oil palm shell are mainly used as cement or fine and coarse aggregates replacer. These alternative materials are used to reduce waste and to provide alternative and greener materials in making concrete. Cement replacements are carried out using sludge, rice husk ash (RHA), and groundnut husk ash (GHA) [1–3]. Waste or agricultural by-products or solids such as coconut and palm oil shells, sawdust, recycled aggregates, mining tiling waste, and tyre are used as alternatives for natural aggregate [4].

This research therefore aimed to evaluate the physical and mineralogical properties of graphite-modified bitumen (GMB) to enhance its performance in asphalt mixtures. By exploring the potential of graphite as a modifier for

bitumen, this study contributes to the advancement of sustainable road construction practices and the development of high-quality asphalt pavements.

2.0 MATERIALS AND METHODS

2.1. Materials

The experimental materials consisted of several components. Natural graphite from Sama-Borkono in Warji Local Government Area, Bauchi State, Nigeria, was utilized. Additionally, 60/70 penetration grade bitumen for road construction was purchased from KK Hassan Nigeria Limited in Akure, Ondo State. Stone dust served as the fine aggregate, and granite as the coarse aggregate, both sourced from Francisca Muinat Mining Limited in Ijare road, Akure, Ondo State. A filler product meeting specification was also procured from the same mining company.

2.2. Sample Preparation

The graphite was processed into powder using a pulverizing ball mill machine and then sieved [19]. The bitumen was heated until liquid, and graphite was gradually added, blending for 60 minutes for homogeneity. Different graphite concentrations (2%, 4%, 6%, and 8%) created binders labelled GMB-2, GMB-4, GMB-6, and GMB-8. These graphite-modified bitumen (GMB) samples were stored for testing.

2.3. Tests on Bitumen

Various laboratory tests were conducted on pure bitumen and graphite-modified bitumen, including the penetration test [20], flash and fire point test [21], ductility test [22], and softening point test [23]. X-ray diffraction analysis identified minerals in the samples by comparing diffraction data to standard mineral data.

2.4. Strength and Durability Tests

Durability tests on asphalt concrete included the Marshall stability test [24] (Table 1) and indirect tensile test [25], assessing stability, flow, and strength of asphalt mixtures produced with conventional and modified bitumen. The Marshall stability test measured resistance to plastic flow, while the indirect tensile test evaluated tensile strength.

Table 1 Mix Design for Marshall Stability Test

Sample Type	Bitumen (g)	Powder Graphite (%)	Granite (g)	Stone Dust (g)	Filler (g)
GMB-2	66	2	660	480	60
GMB-4	66	4	660	480	60
GMB-6	66	6	660	480	60
GMB-8	66	8	660	480	60

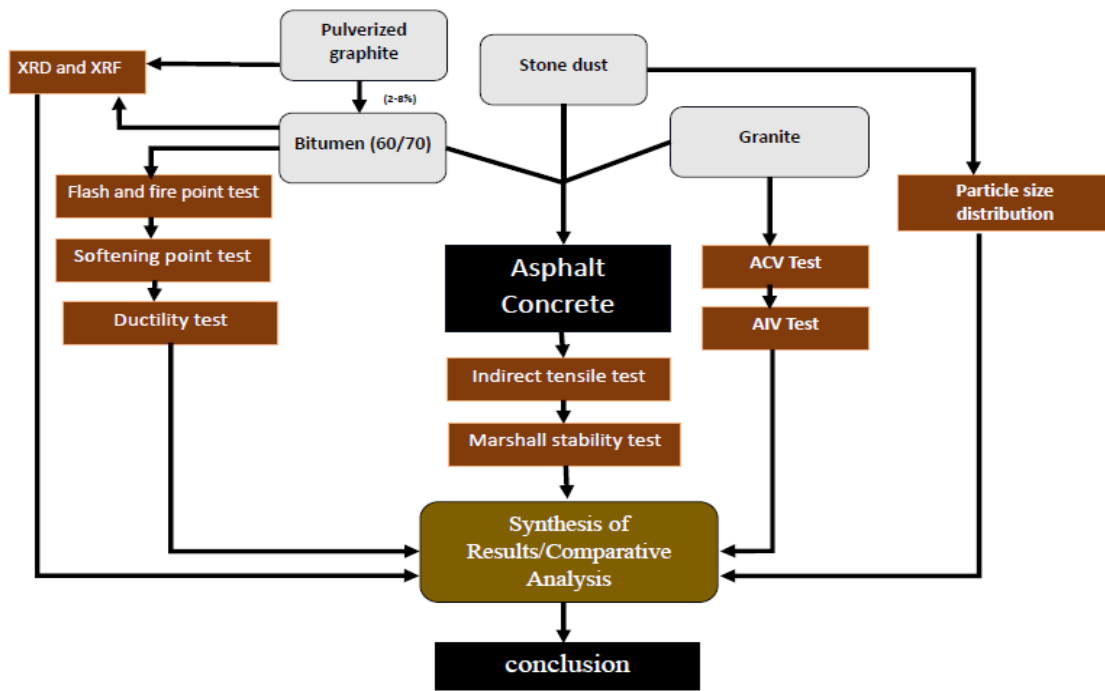


Figure 1 Flow chart / experimental design

3.0 RESULTS AND DISCUSSION

3.1. Particle Size and Distribution

The coefficient of uniformity (C_u) and coefficient of gradation (C_c) are essential parameters used to evaluate the particle size distribution of soil samples. C_u is calculated by dividing the diameter of soil particles for which 60% are finer (D_{60}) by the diameter of particles for which 10% are finer (D_{10}). On the other hand, C_c is determined by squaring the diameter for which 30% are finer (D_{30}) and dividing it by the product of D_{60} and D_{10} . In this particular case, the values obtained from Figure 1 for particle sizes are as follows; $D_{60} = 0.20$, $D_{30} = 0.30$, and $D_{10} = 0.90$. Using these values, the coefficients of uniformity and gradation can be calculated.

Based on the calculated coefficient of gradation (C_c), the fine aggregate in this soil sample was classified as well graded. This classification holds true because a soil sample with a C_c value falling within the range of 0.5 to 3 is considered well graded [19].

The grainsize distribution diagram in Figure 2 corroborates these findings. These coefficients provide valuable information about the particle size distribution of the soil, aiding in the classification and characterization of the material for various engineering applications.

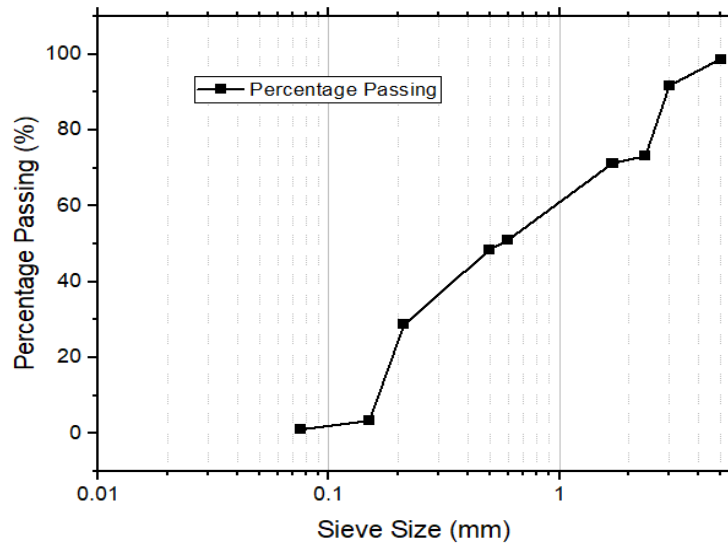


Figure 2 Particle size distribution of the aggregates

3.2. AIV and ACV Test Results

The Aggregate Crushing Value (ACV) is a measure of the strength of an aggregate and its resistance to crushing under a gradually applied compressive load. It provides a relative indication of the aggregate's robustness. In this study, the ACV tests were carried out in triplicates, resulting in average ACV values of 28.91% for sample A, 29.05% for sample B, and 28.73% for sample C. These values fell within the recommended range of 27% to 31% specified by BS 812: part 110:1990. Therefore, the aggregate used demonstrates satisfactory crushing values, indicating its suitability for use in construction. Another important parameter is the Aggregate Impact Value (AIV), which quantifies the percentage of fines produced from an aggregate sample after subjecting it to a standard amount of impact. For the surface course of a road, the desired range value typically falls between 17% and 21%. The average AIV values obtained in this study were 19.84% for sample A, 19.92% for sample B, and 19.75% for sample C (Figure 3). These values were within the specified limit for road surfacing. Hence, the aggregate met the requirements for road construction in terms of impact resistance. By assessing both the ACV and AIV, it can be concluded that the aggregate used in this study exhibited satisfactory strength and resistance to crushing and impact. These results affirm the suitability of the aggregate to be used in road construction.

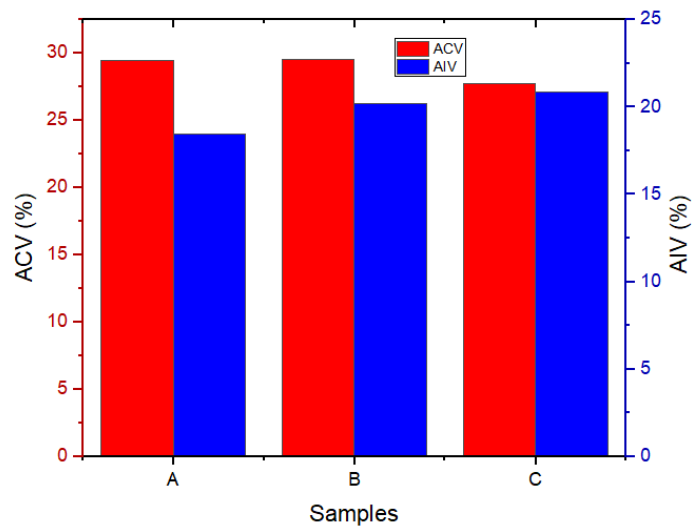


Figure 3 ACV and AIV values for aggregates

3.3. Index Properties

The moisture content test was conducted on the fine aggregate to determine the amount of water present in the soil. The average moisture content was calculated by adding the values 2.43%, 5.02%, and 2.83% and dividing the sum by 3, resulting in an average of 3.43% (Table 2). The maximum permissible moisture content for fine aggregate is 5%, and the obtained average value of 3.43% confirms that the moisture content of the fine aggregate used in this work is within the specified limit. Next, the specific gravity test was performed on the coarse aggregate to determine the relative density of particles finer than 2mm. The specific gravity obtained for the coarse aggregate was 2.77. This value is above the minimum requirement of 2.67 for coarse aggregate. The specific gravity falls within the acceptable limit, indicating the suitability of the coarse aggregate for use in the project.

Furthermore, the bulk density test was carried out on the fine aggregate to determine its unit weight and void content. The recommended range for bulk density is between 1800 kg/m³ and 3200 kg/m³. The bulk density obtained in this test was 2157 kg/m³, which falls within the acceptable limit. The measured bulk density value aligns with the requirements specified by BS 1377-2:1995, confirming the suitability of the fine aggregate for use. Overall, the moisture content, specific gravity, and bulk density tests have indicated that both the fine and coarse aggregates meet the necessary criteria and are suitable for use in the project. These results contribute to ensuring the quality and performance of the aggregates in their respective applications.

Table 2 Index Properties

Test Type	Test Results
Moisture Content	Average: 3.43% Maximum Permissible: 5%
Specific Gravity	Coarse Aggregate: 2.77 Minimum Requirement: 2.67
Bulk Density	Fine Aggregate: 2157 kg/m ³ Recommended Range: 1800 kg/m ³ - 3200 kg/m ³

3.4. Tests on Bitumen

3.4.1. Penetration test (ASTM D5-95)

The penetration test values obtained from both pure and modified binders are presented in Figure 4. The results represent the average of five measurements conducted on each test sample. As observed in Figure 3, an increase in the graphite content resulted in a gradual reduction in the penetration value. Comparing the penetration values of the graphite modified bitumen with different percentages (2%, 4%, 6%, and 8%) to the pure binder, it can be seen that all modified binders exhibited lower penetration values. Specifically, the penetration values decreased by 4.4%, 7.4%, 8.8%, and 10.3% for the respective graphite contents mentioned. This indicates that the addition of graphite renders the modified bitumen harder and more consistent in nature. The increased hardness achieved through the inclusion of graphite is beneficial in terms of enhancing the resistance of the asphalt mixture to rutting. However, it is important to consider the potential impact on the flexibility of the bitumen. The increased stiffness resulting from the addition of graphite may adversely affect the resistance to fatigue cracking in the asphalt [2, 26]. Therefore, while the modified bitumen with higher graphite content exhibited improved rutting resistance, it is crucial to carefully assess the trade-off between stiffness and flexibility to ensure optimal performance and durability of the asphalt mixture. Balancing these factors becomes essential to achieve an ideal combination of hardness and flexibility in the modified bitumen.

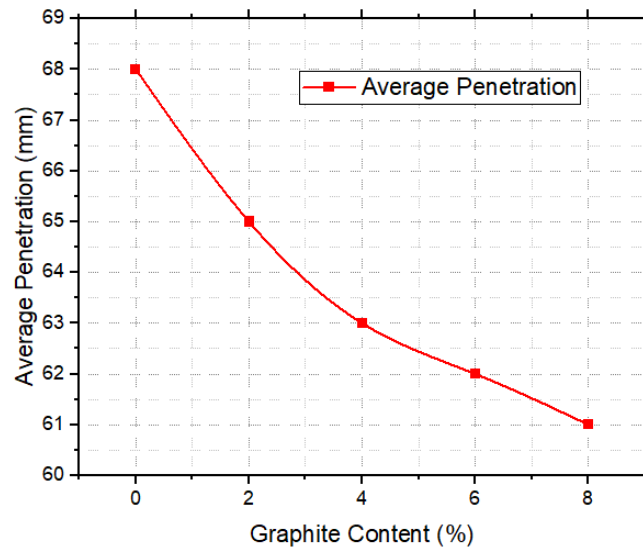


Figure 4 Graphite modified bitumen penetration test

3.4.2. Softening point test (ASTM D36-2002)

The relationship between graphite content and softening point is evident from Figure 5. The findings clearly demonstrate that the addition of graphite to bitumen led to an increase in the softening point value. As the graphite content increased, there was a corresponding increase in the softening point. The increase in softening point ranged from 4% to 10% when incorporating graphite contents of 2% to 8%. The highest softening point value of 54.1°C was obtained with the 8% graphite modified binder. This observation highlights that the inclusion of graphite enhanced the binder's resistance to the effects of heat, reducing its propensity to soften under hot weather conditions. Consequently, the modified binder with graphite exhibited improved thermal stability. It became less susceptible to temperature changes, ensuring that it maintained its structural integrity even in high-temperature environments. The increased softening point is indicative of the modified binder's heightened resistance to temperature-induced softening, contributing to its overall durability and performance. By incorporating graphite into the binder, the modified binder's ability to withstand the detrimental effects of heat was significantly enhanced. This advantageous characteristic holds considerable promise in areas characterized by high ambient temperatures, reducing concerns related to the potential softening and deformation of the binder under such conditions [1, 27].

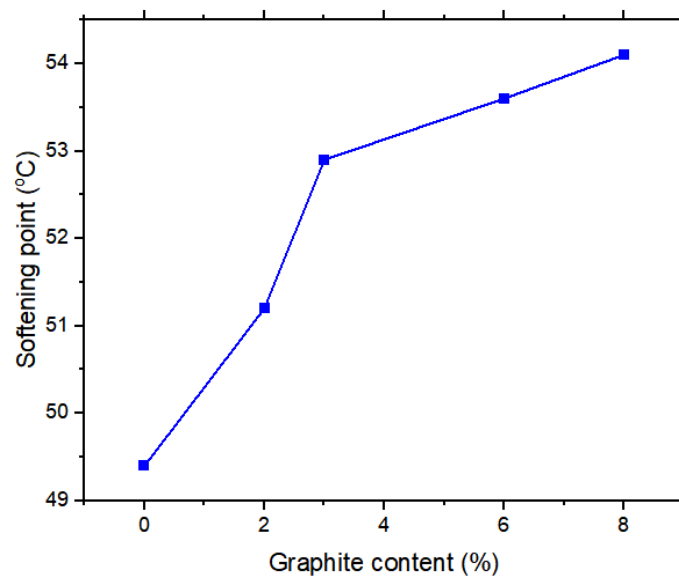


Figure 5 Softening point of graphite-modified bitumen

3.4.3. Flash and fire point test (ASTM D92-18)

The results obtained from the flash and fire point tests conducted on both pure and graphite modified bitumen reveal a clear relationship between graphite content and the flash and fire values. As the graphite content increased, there was a corresponding increase in the flash and fire values of the modified bitumen. The addition of graphite to the binder had a substantial impact on enhancing the flash and fire values. Among the various graphite contents tested, the modified bitumen with 8% graphite content exhibited the highest flash value of 295°C, while the lowest flash value of 282°C was recorded for the unmodified bitumen (0% graphite content). Similarly, the highest fire value of 318°C was obtained for the modified bitumen with 8% graphite content, while the lowest fire value of 300°C was recorded for the unmodified bitumen (0% graphite content). These findings indicate that graphite modified bitumen demonstrated an increased capacity to withstand higher temperatures compared to unmodified bitumen (*see figure 6*). The inclusion of graphite imparted thermal stability to the modified bitumen, resulting in improved resistance to heat-related effects [18, 28]. The higher flash and fire values of the graphite modified bitumen signify its ability to withstand more heat before igniting or undergoing combustion. This characteristic holds significant importance as it implies that the graphite modified bitumen can effectively endure higher temperatures, making it suitable for applications where exposure to heat is a concern. The improved thermal resistance of the modified bitumen contributes to its enhanced performance and durability, particularly in environments characterized by high temperatures or potential heat sources.

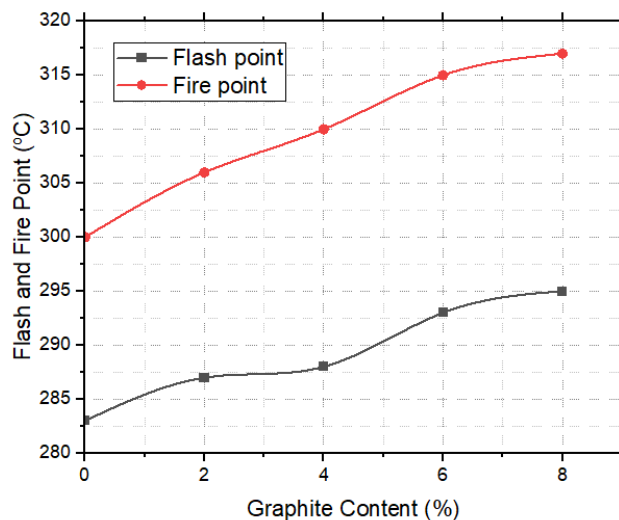


Figure 6 Flash and fire point test

3.4.4. Ductility test (ASTM D113-17)

From Figure 7, it is evident that the addition of graphite to the binder led to an increase in the ductility point. This phenomenon may be attributed to the uneven dispersion of graphite particles within the binder. The maximum ductility value was observed in the 8% graphite modified binder. However, it should be noted that this binder also had a 12°C higher softening point compared to the pure binder. These results suggest that the addition of graphite had minimal effect on the ductility point of the bitumen. The increase in elasticity was primarily influenced by the arrangement of molecules and their interactions with one another. The incorporation of graphite brought about changes in the values of the ductility point, resulting in a physical stiffening effect. Although the addition of graphite influenced the ductility point, the impact was relatively small compared to other factors, such as the softening point. The main contribution of graphite appears to lie in its role in modifying the physical properties of the binder, rather than directly affecting the ductility point. These findings highlight the complex nature of the interactions between graphite and the binder, suggesting that the primary effect of graphite is the physical stiffening of the modified binder [9, 11]. Overall, while the addition of graphite induced some changes in the ductility point values, its influence was secondary to the effects observed in parameters such as the softening point and overall physical stiffening of the binder. The presence of graphite introduced unique properties to the modified binder, offering potential benefits in terms of enhanced stiffness and performance in specific applications.

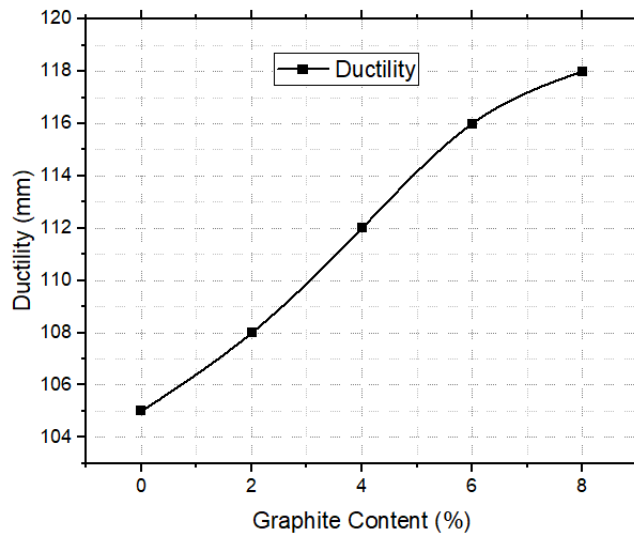


Figure 7 Ductility test

3.5 Test of Asphalt Concrete

3.5.1. Marshal stability test (ASTM D6927-15)

The Marshall stability test results depicted in Figure 8 demonstrate a consistent increase in the strength of the asphalt concrete from 0% to 6% graphite content. However, a decline in strength was observed at 8% graphite content. Based on these findings, it can be concluded that the addition of graphite can enhance the strength of the asphalt concrete up to a maximum of 6%. Considering the typical Marshall Design criteria outlined by the Asphalt Institute (1997) (Table3), which recommend stability values of 2.224 kN for light traffic, 3.336 kN for medium traffic, and 6.672 kN for heavy traffic, the percentage compositions of graphite in the binder have met the requirements for light, medium, and heavy traffic applications. Similarly, the results of the Marshall flow test, as shown in Figure 7, reveal an increase in flow values up to 6% graphite content, followed by a sharp decline at 8% graphite content. From these observations, it can be stated that graphite can only enhance the flow characteristics of the asphalt concrete up to a maximum of 6. The flow values obtained conform to the specifications outlined in the Nigeria General Specification for road and bridge [29], which specifies a range of 2-4mm for flow values. This indicates that the asphalt concrete with different percentages of graphite content met the specified requirements for flow within Nigeria's road and bridge construction standards as shown in Table 1. Overall, the addition of graphite to the asphalt concrete demonstrated positive effects on both strength and flow characteristics. However, the optimum improvement was observed up to 6% graphite content, beyond which there was a diminishing return. These findings provide valuable insights for optimizing the composition of asphalt concrete in relation to strength and flow properties, ensuring compliance with industry standards and improving the performance of the asphalt mixture.

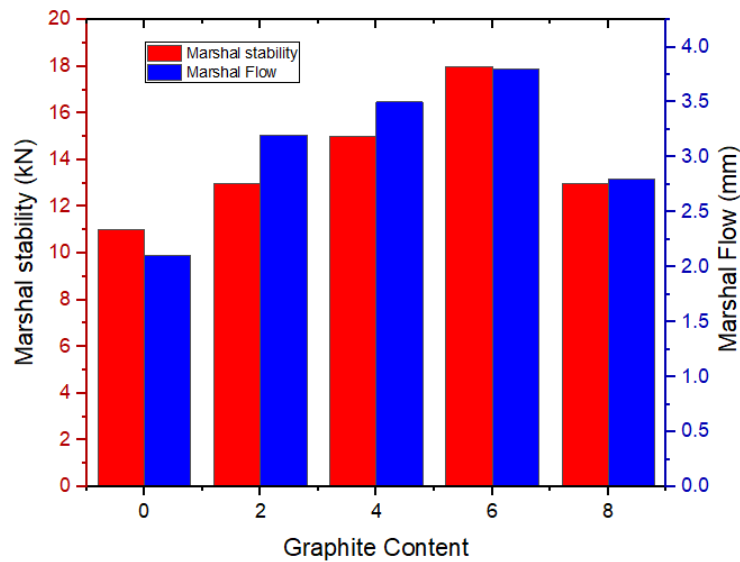


Figure 8 Marshall stability and Marshall flow test

Table 3 Typical Marshall Design Criteria

Marshall Mix Criteria	Light Traffic (<10 ⁴ ESALs)		Medium Traffic (<10 ⁴ ESALs)		Heavy Traffic (<10 ⁴ ESALs)	
	Min	Max	Min	Max	Min	Max
Compaction (number of blows on each end of the sample)	35		50		75	
Stability	2224N (500Ibs)		3336 (750Ibs)		6672 (1500Ibs)	
Flow (0.25mm (0.01 inch))	8	20	8	18	8	16
Percent Air Voids %	3	5	3	5	3	5

Source: Asphalt Institute (1997)

3.5.2. Indirect tensile strength test (ASTM D6931-17)

The indirect tensile strength test was conducted on asphalt concrete produced using conventional bitumen and graphite modified bitumen in order to assess its cracking index. The results of the indirect tensile strength test are illustrated in Figure 8. As depicted in Figure 9, it is evident that the strength of the asphalt concrete increased with an increase in the graphite content. Among the various percentages of graphite tested, the highest strength was obtained by the asphalt concrete with 6% graphite modified binder. Notably, this binder exhibited a significant 59% increase in strength compared to the pure binder (from 402-993kN/m²). These findings suggest that the addition of graphite to the bitumen composition enhanced the strength of the resulting asphalt concrete. The increased strength is attributed to the modified binder's improved properties, which contributed to the asphalt concrete's ability to resist cracking and withstand applied loads. The higher strength obtained with the 6% graphite modified binder indicates its potential for delivering enhanced performance in terms of durability and structural integrity [13, 28]. By incorporating graphite into the binder, the modified bitumen offered valuable improvements in the strength characteristics of the resulting asphalt concrete. These results highlight the potential benefits of utilizing graphite modified bitumen in asphalt mixtures, particularly in applications where higher strength and crack resistance are desired.

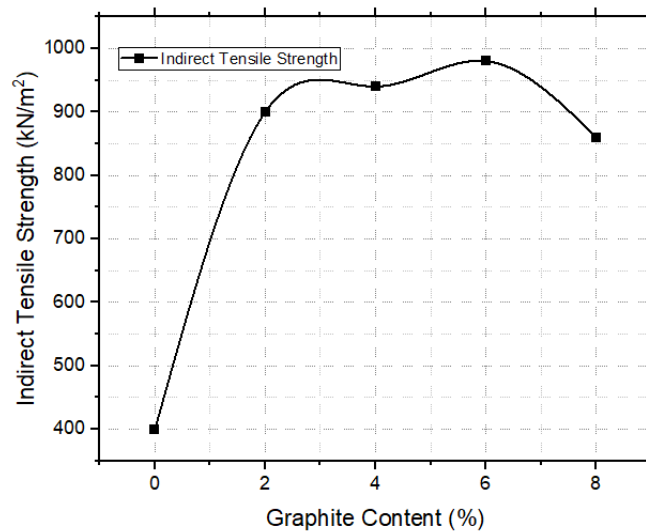


Figure 9 Indirect tensile strength test

3.6. Microstructural Analysis

3.6.1. Elemental composition of graphite

X-ray fluorescence (XRF) analysis was employed to determine the elemental composition of the graphite. The results are presented in Table 4, indicating the predominant presence of Silicon Oxide (39.195%), Aluminum Oxide (12.07%), and Ferric Oxide (14.49%) in the graphite. Additionally, there were minor proportions of other elements, including Loss of Ignition (12.31%), Calcium Oxide (13.29%), Magnesium Oxide (8.28%), Potassium Oxide (3.01%), Sulphide (5.81%), Sodium Oxide (1.68%), Titanium Oxide (0.28%), Zinc Oxide (0.04%), and Manganese Oxide (0.18%). These findings provide insight into the elemental composition of the graphite material. The presence of Silicon Oxide, Aluminum Oxide, and Ferric Oxide in significant proportions suggests their influence on the properties and behavior of the graphite. The additional presence of various other elements indicates the complex nature of the graphite composition and its potential interactions with the surrounding environment.

Table 4 XRF Analysis of Oxide Composition of Graphite

S/N	Basic Oxide	Formulae	% Composition
1	Silicon Oxide	SiO ₂	39.41
2	Aluminum Oxide	Al ₂ O ₃	10.07
3	Ferric Oxide	Fe ₂ O ₃	14.49
4	Calcium Oxide	CaO	13.29
5	Magnesium Oxide	MgO	8.28
6	Sodium Oxide	Na ₂ O	1.68
7	Potassium Oxide	K ₂ O	3.01
8	Sulphide	SO ₃	5.81
9	Manganese Oxide	MnO	0.18
10	Zinc Oxide	ZnO	0.04
11	Titanium Oxide	TiO ₂	0.28
12	Loss of Ignition	LOI	12.31

3.6.2. X-RAY diffraction analysis of unmodified and modified bitumen

The morphology of the samples was examined using XRD characterization techniques. X-ray diffraction patterns were obtained using a Rigaku D-Max/IIIIC powder diffractometer with CuK α radiation. The diffraction patterns were recorded at room temperature with a step size of 0.02° in the 2 θ range of 2-80°. The crystallographic structure of graphite, its presence in the bitumen blend, and its dispersion level were evaluated based on these patterns. The mineralogical composition of the unmodified bitumen is presented in Table 5. Based on the results,

it can be concluded that the compositions of the unmodified bitumen varied, primarily consisting of feldspars (anorthite), pyroxenes, and quartz in different proportions. The presence of feldspar increased the specific surface area and decreased the mechanical strength of the pavement. This will require higher bitumen usage and reduce the lifespan of the pavement due to the low mechanical strength of clay minerals [11, 18, 28]. Specifically, the presence of 25% feldspar (anorthite) increased the specific surface area, leading to increased bitumen consumption, reduced mechanical strength, and a shorter lifespan for the asphalt pavement. In summary, pure bitumen exhibited a macro-molecular structure with two separate amorphous phases. The amorphous phase around $2\theta = 40^\circ$ was located within the main macro-molecular structure. The chemical composition of the graphite modified bitumen are presented in Table 6. The carbon content (CC) analysis was conducted on a single graphite mineral. The carbon content of the graphite mineral was found to be 85.30% with an ash content of 2.20%.

The x-ray diffraction (XRD) pattern of the graphite single mineral, depicted in Table 7 and Figure 10, along with the carbon analysis result, indicates that the sample contains graphite with a weight percentage of over 85%. In the modified sample, the presence of feldspar (anorthite) in relatively low amounts reduces the specific surface area. As observed in Figure 9, the gaps between components in the macro-molecular structure have been closed under the influence of temperature and high pressure. In the region where 2θ ranged from 7.5° to 32.5° , the semi-crystalline region transformed into a fully amorphous structure, while the amorphous structure around $2\theta = 40^\circ$ expanded and spread in accordance with the graphite modified bitumen. However, when the ratio of graphite modified bitumen reached 8%, the structure transformed into a fully amorphous form due to the macro-molecular arrangement influenced by pressure and temperature.

Table 5 Mineralogical Composition of Unmodified Bitumen

	Anorthite %	Quartz %	Dikite %	Chabasite %	Vermiculite %	Augite %	Andesine %
Pure Bitumen	25	1.0	1.0	4.5	7.5	6.0	55

Table 6 Mineralogical Composition of Graphite Modified Bitumen

	Carbon Content %	Ash Content %	Anorthite %	Quartz %	Dikite %	Chabasite %	Augite %	Andesine %
GMB	85.30	2.20	3.0	2.0	1.0	2.0	1.5	5.0

Table 7 XRD Pattern of Graphite

Peak	$2\theta/\text{degree}$	Plane	Intensity I/I_0	d-Value (\AA°)	Mineral present
1	13.54	1 1 1	16.31	6.5386	Graphite
2	26.00	0 2 2	16.45	3.4270	Corondum
3	29.00	0 0 2	90.26	3.0787	Graphite
4	40.00	1 0 0	10.64	2.2541	Graphene Oxide
5	57.00	1 0 1	18.52	1.6156	Graphite
6	62.01	0 0 4	39.42	1.4966	Graphite
7	68.00	1 1 0	27.64	1.3786	Graphite
8	81.47	1 1 2	10.44	1.1814	Chlorofluorocarbon

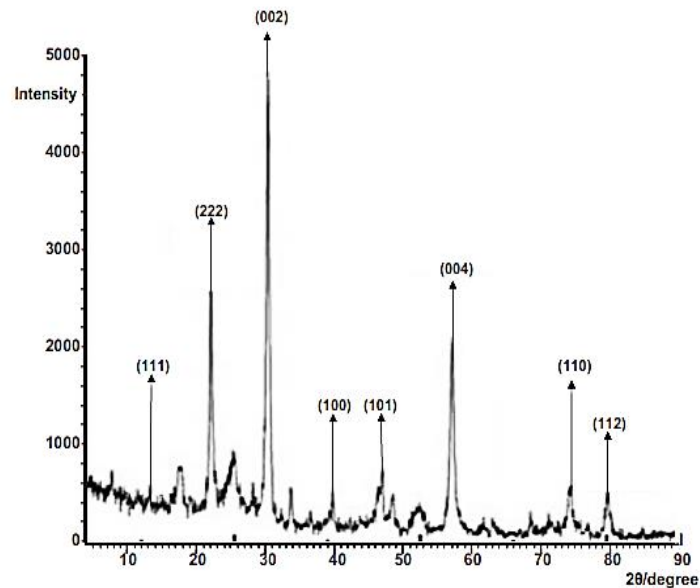


Figure 10 XRD pattern of graphite

4.0 CONCLUSION

The research aimed to explore the impact of incorporating graphite into bitumen on the properties of asphalt mixtures. The findings can be summarized as follows:

1. The soil sample exhibited well-graded characteristics, indicated by coefficients of uniformity (Cu) and gradation (Cc) values of 4.5 and 0.5, respectively, suggesting a desirable particle size distribution for engineering applications.
2. The aggregate used in the study demonstrated a satisfactory Aggregate Crushing Value (ACV) of 28.91%, falling within the recommended range of 27% to 31% specified by BS 812: part 110:1990.
3. The Aggregate Impact Value (AIV) obtained was 19.84%, which falls within the desired range of 17% to 21% for road surfacing according to B.S 812.1990.
4. Incorporating graphite into bitumen increased the softening point, reaching a maximum value of 54.1°C at an 8% graphite content.
5. The addition of graphite enhanced the flash and fire values, with the modified bitumen containing 8% graphite exhibiting the highest flash value of 295°C, while the unmodified bitumen had a flash value of 282°C.
6. The inclusion of graphite in the binder increased the ductility point, particularly in the 8% graphite-modified binder, which had a 12°C higher softening point compared to the pure binder.
7. Graphite-modified asphalt concrete demonstrated improved strength, with stability values ranging from 10.90 kN to 18.09 kN across different graphite contents. The highest stability of 18.09 kN was observed at a 6% graphite content.
8. The flow values of the asphalt concrete ranged from 2.10 mm to 3.80 mm, with a maximum flow of 3.80 mm observed at 6% graphite content.
9. The asphalt concrete with 6% graphite-modified binder exhibited the highest indirect tensile strength, showing a significant 59% increase in strength compared to the pure binder.

10. XRD characterization confirmed the presence of various minerals in the unmodified bitumen, including feldspars, pyroxenes, and quartz. The presence of feldspar increased the specific surface area and reduced the mechanical strength of the pavement. Conversely, graphite-modified bitumen exhibited a modified structure with reduced specific surface area, and XRD patterns confirmed the presence of graphite, with carbon content exceeding 85%.

These findings provide valuable insights into the positive effects of incorporating graphite into bitumen, contributing to improved performance and durability of asphalt mixtures.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

References

- [1] Essawy, A. I., Saleh, A. M. M., Zaky, M. T., Farag, R. K., & Ragab, A. A. (2013). Environmentally friendly road construction. *Egyptian Journal of Petroleum*, 22(1), 189–198. <https://doi.org/10.1016/j.ejpe.2012.09.010>
- [2] Chen, A., Liu, G., Zhao, Y., Li, J., Pan, Y., & Zhou, J. (2018). Research on the aging and rejuvenation mechanisms of asphalt using atomic force microscopy. *Construction and Building Materials*, 167(1), 177–184. <https://doi.org/10.1016/j.conbuildmat.2018.02.008>
- [3] Liu, Y., Han, S., Zhang, Z., & Xu, O. (2012). Design and evaluation of gap-graded asphalt rubber mixtures. *Materials and Design*, 35(1), 873–877. <https://doi.org/10.1016/j.matdes.2011.08.047>
- [4] Baghaee Moghaddam, T., Soltani, M., & Karim, M. R. (2014). Experimental characterization of rutting performance of Polyethylene Terephthalate modified asphalt mixtures under static and dynamic loads. *Construction and Building Materials*, 65(1), 487–494. <https://doi.org/10.1016/j.conbuildmat.2014.05.006>
- [5] Nuñez, J. Y. M., Domingos, M. D. I., & Faxina, A. L. (2014). Susceptibility of low-density polyethylene and polyphosphoric acid-modified asphalt binders to rutting and fatigue cracking. *Construction and Building Materials*, 73(1), 509–514. <https://doi.org/10.1016/j.conbuildmat.2014.10.002>
- [6] Oyedepo, O., & Oluwajana, S. (2014). Evaluation of properties of bitumen modified with waste tyre. *Nigerian Journal of Technology*, 33(1), 119. <https://doi.org/10.4314/njt.v33i1.16>
- [7] Habib, N. Z., Kamaruddin, I., Napiah, M., & Mohd Tan, I. (2010). Rheological properties of polyethylene and polypropylene modified bitumen. *World Academy of Science, Engineering and Technology*, 72, 293–297.
- [8] Wu, S., Zhang, Y., & Chen, M. (2009). Research on mechanical characteristics of conductive asphalt concrete by indirect tensile test. *Fourth International Conference on Experimental Mechanics*, 7522(1), 752265. <https://doi.org/10.1117/12.851473>
- [9] Yusoff, N. I. M., Breem, A. A. S., Alattug, H. N. M., Hamim, A., & Ahmad, J. (2014). The effects of moisture susceptibility and ageing conditions on nano-silica/polymer-modified asphalt mixtures. *Construction and Building Materials*, 72(1), 139–147. <https://doi.org/10.1016/j.conbuildmat.2014.09.014>
- [10] Yuhong Wang, P. E., Zhao, K., Glover, C., Chen, L., Wen, Y., Chong, D., & Hu, C. (2015). Effects of aging on the properties of asphalt at the nanoscale. *Construction and Building Materials*, 80(1), 244–254. <https://doi.org/10.1016/j.conbuildmat.2015.01.059>
- [11] Yao, H., Dai, Q., You, Z., Ye, M., & Yap, Y. K. (2016). Rheological properties, low-temperature cracking resistance, and optical performance of exfoliated graphite nanoplatelets modified asphalt binder. *Construction and Building Materials*, 113(1), 988–996. <https://doi.org/10.1016/j.conbuildmat.2016.03.152>
- [12] Vasudevan, R., Ramalinga Chandra Sekar, A., Sundarakannan, B., & Velkennedy, R. (2012). A technique to dispose waste plastics in an ecofriendly way - Application in construction of flexible pavements. *Construction and Building Materials*, 28(1), 311–320. <https://doi.org/10.1016/j.conbuildmat.2011.08.031>
- [13] Singh, H., Chopra, T., Jain, S., Kaur, A., & Kamotra, S. (2019). Effect of aggregate type and polymer modification on the performance of bituminous concrete mixes. *International Journal of Applied Science and Engineering*, 16(1), 1–13. [https://doi.org/10.6703/IJASE.201906_16\(1\).001](https://doi.org/10.6703/IJASE.201906_16(1).001)
- [14] Imanbayev, Y., Bussurmanova, A., Ongarbayev, Y., Serikbayeva, A., Sydykov, S., Tabylganov, M., Akkenzheyeva, A., Iztelev, N., Mussabekova, Z., Amangeldin, D., & Tileuberdi, Y. (2022). Modification of Bitumen with Recycled PET Plastics from Waste Materials. *Polymers*, 14(21), 1–11. <https://doi.org/10.3390/polym14214719>
- [15] Liu, X., Wu, S., Ye, Q., Qiu, J., & Li, B. (2008). Properties evaluation of asphalt-based composites with graphite and mine powders. *Construction and Building Materials*, 22(3), 121–126. <https://doi.org/10.1016/j.conbuildmat.2006.10.004>
- [16] Tongyan, P., Yang, L., & Zhaoyang, W. (2012). Development of an atomistic-based chemophysical environment for modelling asphalt oxidation. *Polym. Degrad. Stab.*, 97(1), 2331–2339.
- [17] Pan, P., Wu, S., Xiao, Y., Wang, P., & Liu, X. (2014). Influence of graphite on the thermal characteristics and anti-ageing properties of asphalt binder. *Construction and Building Materials*, 68(1), 220–226. <https://doi.org/10.1016/j.conbuildmat.2014.06.069>

- [18] Oladunjoye, O. O., Oyedepo, O. J., Olukanni, E. O., & Akande, S. P. (2021). Evaluation of Rheological Characteristics of Graphite Modified Bitumen. *Journal of Civil Engineering and Urbanism*, 11(5), 51–57. <https://doi.org/10.54203/jceu.2021.7>
- [19] BS 812-112: 1990. (1990). *Testing aggregates- part 112: Methods for determination of aggregate impact value (AIV)*. (bsi, Ed.)British Standard. 2 PARK STREET LONDON, United Kingdom W1A 2BS.
- [20] Astm, D. 5-05. (2005). *Standard Test Method for Penetration of Bituminous Materials*.
- [21] Astmd92-18. (2018). *Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester*.
- [22] Astmd113-99. (1999). *Standard Test Method for Ductility of Bituminous Materials*.
- [23] Astmd36-06. (2006). *Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus)*.
- [24] Astmd6927-15. (2015). *Standard Test Method for Marshall Stability and Flow of Asphalt Mixtures*.
- [25] Astmd6931-17. (2017). *Standard Test Method for Indirect Tensile (IDT) Strength of Bituminous Mixtures*.
- [26] Kim, Y., Lim, J., Lee, M., Kwon, S., Hwang, S., & Lee, J. (2015). Comprehensive evaluation of warm SMA using wax-based WMA additive in Korea. *Journal of Testing and Evaluation*, 43(5), 1230–1238. <https://doi.org/10.1520/JTE20130144>
- [27] Deori, S., Choudhary, R., Devesh, T., & K, S. (2012). Deterioration Modelling of Flexible Pavements with Modified Bitumen. In *Third International Conference on Construction In Developing Countries (ICCIDC–III)* (pp. 450–455).
- [28] Ashish, P. K., & Singh, D. (2021). Use of nanomaterial for asphalt binder and mixtures: a comprehensive review on development, prospect, and challenges. *Road Materials and Pavement Design*, 22(3), 492–538. <https://doi.org/10.1080/14680629.2019.1634634>
- [29] Federal Ministry of Works and Housings. (1997). *“Nigerian general specification for roads and bridges”* (2nd ed.). New York: Oxford University Press. Retrieved from <http://www.scribd.com/doc/40333915/General-Specifications>, 1997.