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THERMAL ANALYSIS OF BITUMEN BLENDED WITH GRAPHENE NANOPARTICLES

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ABSTRACT

The reliability of rural transportation infrastructure plays a vital role in agricultural productivity and market access. However, conventional bitumen used in farm roads often fails under extreme temperatures and repeated mechanical loading from agricultural machinery. This study investigates the thermal degradation behavior of graphene nanoparticles (GNP)-modified bitumen to enhance its suitability for farm and rural road applications. Bitumen samples were modified with GNPs at concentrations of 1%, 2%, 3%, 4%, and 5%, and tested using standard penetration, softening point, and flash point methods, along with thermogravimetric analysis (TGA). Results show a significant improvement in thermal resistance, with onset degradation temperatures rising above 650 °C and residual mass at 800 °C exceeding 55% for a 5% GNP blend. These enhancements correlate strongly with conventional thermal indicators, confirming GNPs' effectiveness in improving heat stability and rutting resistance. The findings suggest that GNP-modified bitumen holds considerable promise for constructing durable, low-maintenance rural roads capable of withstanding heavy use and harsh climates. Future work should explore long-term aging, mechanical fatigue, and sustainability impacts to further optimize its application in rural infrastructure development.

1.Introduction

Bitumen is a highly viscous petroleum-based substance found naturally or refined from crude oil. Nigeria ranks sixth in global bitumen reserves, with deposits in Lagos, Ogun, Ondo, and Edo States [1]. Despite Nigeria's crude oil production capacity, its midstream sector limitations necessitate dependence on imported refined petroleum products, including bitumen [2]. The country's annual bitumen consumption exceeds 500,000 metric tonnes, yet domestically processed bitumen does not meet international standards [3].

Pavement durability is highly dependent on bitumen binder properties, which exhibit both elastic and viscous responses under stress [4]. Factors such as increasing axle loads and environmental fluctuations contribute to pavement deterioration, often leading to rutting and

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fatigue cracking [5]. While climatic conditions are commonly blamed for asphalt failures, research suggests that bitumen selection and modification play an equally critical role [6]. Therefore, modifiers and additives are necessary to enhance bitumen performance and reduce fatigue-related distress.

Graphene, a two-dimensional nanostructure composed of carbon atoms, is widely recognized for its exceptional thermal and mechanical properties, making it indispensable in scientific and engineering applications [7]. Its thermal conductivity reaches 5.1×10^3 W/m·K, while electrical conductivity is recorded at 6×10^5 S/m [8]. Graphene is lighter than aluminum yet stronger than steel, with a tensile strength of 130 GPa, far exceeding conventional structural materials [9]. Among graphene derivatives, graphene oxide (GO) and graphene nanoplatelets (GNPs) are the most commonly used across various industries [10].

Bitumen modification enhances its engineering properties, improving stiffness and elasticity at high temperatures while maintaining flexibility at lower temperatures [11]. Due to its superior thermal stability and mechanical reinforcement, graphene is an ideal additive for bitumen modification. In Nigeria, few studies have explored graphene's potential in asphalt enhancement. One notable study by Oladunjoye *et al.* (2021) concluded that graphite-modified bitumen exhibited improved rutting and fatigue resistance [12]. Similarly, Noor et al. (2015) found that GO-modified bitumen demonstrated enhanced elasticity under high temperatures and lower frequencies [13]. Singh and Suman (2018) further reported that graphite powder modification led to increased penetration resistance, a higher softening point, and improved viscosity [14].

Various nanomaterials, including carbon nanotubes, nanoclays, nanosilica, and graphene-based compounds, have been utilized to improve asphalt binder performance [15]. These materials enhance road durability, particularly under extreme environmental conditions, such as high humidity, UV exposure, and salinity [16]. Research has shown that graphene-modified bitumen enhances fatigue resistance, significantly prolonging pavement lifespan [17]. Asphalt pavements typically fail due to fatigue-related distress and permanent deformation, issues that graphene-based modifications help mitigate [18].

Due to their complex chemical structures, GMABs require advanced characterization techniques beyond traditional bitumen tests such as penetration and viscosity assessments [19]. Researchers employ methodologies such as Dynamic Shear Rheometer (DSR), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD), and X-ray Photoelectron Spectroscopy (XPS) for more precise material evaluation [20]. Among these, TGA is particularly valuable for assessing thermal stability and oxidation resistance, aiding in optimized graphene-bitumen formulations [18]. Complementing these findings, Wu *et.al.*, (2022) applied grey correlation analysis to link viscosity increases to elevated TGA-derived degradation temperatures, reporting correlation coefficients above 0.90 and affirming the complementary roles of conventional tests and TGA in predicting long-term binder performance [21].

Graphene-modified bitumen offers significant advancements in pavement engineering, improving mechanical strength and thermal resilience. The integration of nanomaterials enhances bitumen's resistance to environmental stressors, ensuring long-term durability and performance. Continued research into graphene-based asphalt binders is crucial for modern infrastructure development and improving road quality worldwide

2. Methodology

2.1 Bitumen blends preparation

The preparation of graphene nanoparticle (GNP)-modified bitumen involves a controlled mixing process to ensure homogeneity and optimal dispersion of nanoparticles within the binder. Initially, the bitumen is heated to 150°C, which facilitates its transition to a fluid state, allowing for effective nanoparticle incorporation.

The shear mixer, operates at 250 RPM (Gear 3) for 15 minutes, ensuring high-speed dispersion and uniform distribution of GNP throughout the bitumen matrix. This continuous agitation prevents agglomeration and promotes consistent integration of the nanoparticles, enhancing the material’s stability and performance characteristics.

The modification process is conducted at varying GNP concentrations (1%, 2%, 3%, 4%, and 5% by weight) to evaluate its impact on thermal and mechanical properties. By progressively increasing the GNP content, the effects on stiffness, thermal stability, and rutting resistance can be systematically assessed. Achieving a perfect blend is crucial, as incomplete mixing may lead to inconsistencies in the material behaviour, affecting its overall performance in high-temperature applications.

After the mixtures are obtained the following tests were conducted according to ASTM standards on the control sample and the blended samples as presented in Table 1.

Table
Laboratory tests on bitumen and bitumen/GNP blends

S/N	Tests	Purpose
1.	Penetration test ASTM D5: (10/20 dmm)	Determines bitumen consistency to ensure suitability for construction applications.
2.	Softening point test ASTM D36 EN 1427 (58-66 ^{0}C)	Evaluates bitumen's temperature susceptibility for application and performance.
4.	Flash point ASTM D92 (250 ^{0}C Minimum)	Determines bitumen's flammability and safety for handling and storage.
5	Ductility (ASTM D70) (100 cm Minimum)	test is done to determine the length to which bitumen can be extended before breaking.
6	TGA (ASTM E1131-20)	evaluating the thermal stability, compositional changes, and volatile content

Thermogravimetric Analysis(TGA) measures the change in a material’s mass as it is heated, cooled, or held at a constant temperature. It helps determine thermal stability, composition, and decomposition behavior.

Differential Thermal Analysis(DTA) measures the temperature difference between a sample and an inert reference under identical thermal conditions. It detects endothermic and exothermic transitions like melting, crystallization, or decomposition. The TGA and DTA curves are powerful tools for understanding the thermal behaviour of materials. Key aspects of interpretation include;

1. The onset temperature of decomposition and the rate of mass loss are indicators of the material's thermal stability. For example, graphene nanoparticle (GNP)-modified bitumen exhibits delayed decomposition and reduced mass loss, reflecting enhanced thermal stability [18].

2. Residual Mass: The remaining mass at the end of the experiment represents the non-volatile or inorganic components of the material. This is useful for determining the composition of complex mixtures.
3. Endothermic Peaks (Heat Absorption): Shown as downward dips, indicating melting, phase transitions, or softening points.
4. Exothermic Peaks (Heat Release): Shown as upward peaks, representing oxidation, crystallization, or material restructuring

3. Results

3.1 Conventional Properties of bitumen and bitumen/GNP blends

This section discusses the results obtained from the penetration, softening point, flash point and ductility of the bitumen and GNP modified bitumen blends. The physical properties of both the unmodified bitumen and the graphene nanoparticle (GNP)-modified binder are presented in Table 1, where all experimental tests were conducted in triplicate. The average values and standard deviations of these tests are reported to ensure statistical reliability.

Analysis of the physical characteristics of the GNP-modified bitumen as presented in Table 2 indicates that increasing the GNP content induces notable changes in the material behaviour. Specifically, penetration test results demonstrate a progressive reduction in penetration values, decreasing from 22 at 0% GNP to 13 at 5% GNP. This decline suggests an increase in stiffness with the incorporation of GNP, thereby improving the binder's resistance to deformation under applied loads. Such enhancements in rigidity are particularly advantageous for applications requiring superior structural stability, notably in high-temperature environments where deformation resistance is critical.

Table 2
The conventional properties of bitumen and bitumen/GNP blends

Test/GNP	0%	1%	2%	3%	4%	5%
Penetration (dmm)	22.0	15.6	15.0	14.2	13.5	12.5
Softening Point (^{0}C)	49.0	56.0	59.0	62.0	66.0	71.0
Flash point (^{0}C)	231.9	282.8	288.3	292.3	306.0	314.1
Ductility (mm)	43.0	41.0	29.0	31.0	27.6	21.3

3.1.1 The effect of GNP portions on thermal properties

Thermogravimetric analysis (TGA) of graphene-nanoparticles (GNP)–modified bitumen reveals a clear enhancement of thermal stability as GNP content increases as depicted in Figure 1. The onset temperature—defined as the point at which significant mass loss begins—rises from 205.8 °C in the neat binder (0 % GNP) to 207.9 °C at 1 % loading, indicating only a marginal improvement at very low GNP content. However, from 1 % to 2 % GNP there is a dramatic jump in onset temperature to 303.4 °C, after which it remains relatively stable (304.7 °C at 3 % GNP) before climbing further to 397.4 °C at 4 % and reaching 659.2 °C at 5 %. This nonlinear increase suggests a percolation-like behaviour, where a critical GNP threshold (around 2 %) must be exceeded before a continuous network forms that substantially impedes thermal degradation.

Residual mass at 800 °C follows a similar trend, rising from only 3.8 % in the unmodified binder to 16.5 % with 1 % GNP, then plateauing around 16.9 % at 2 % before dipping to 13.3 % at 3 %. Above 3 %, residue sharply increases—18.3 % at 4 % and 55.8 % at 5 %—reflecting much more charred, thermally resistant material. The dip at 3 % likely reflects suboptimal dispersion or agglomeration effects that temporarily reduce GNP efficacy. Overall, the marked increases in both onset temperature and residual mass at higher GNP loadings confirm that graphene nanoparticles significantly enhance bitumen's resistance to thermal decomposition, with the greatest benefits observed beyond about 2 % by weight.

The Figure 2 presents the differential thermal analysis. The evolution of the endothermic peak with increasing GNP content reveals how graphene nanoparticles alter the binder's thermal transitions. In the neat bitumen (0 % GNP), the modest endothermic feature at approximately 44 °C likely corresponds to the glass-to-rubbery transition and initial volatilization of light components. With just 1 % GNP, this transition shifts upward to about 55 °C, reflecting the nanoparticles' restriction of polymer chain mobility. Beyond 1 %, the endothermic peak climbs dramatically—reaching nearly 196 °C at 2 % and 240 °C at 3 % suggesting the formation of a percolated graphene network that requires substantially more heat to induce the same thermal softening. Interestingly, at 4 % the peak retreats slightly to 208 °C, perhaps due to nanoparticles agglomeration disrupting network uniformity, before surging to an exceptional 456 °C at 5 %, where the high graphene loading dominates the thermal response and may be capturing heat in micro-cavities or triggering secondary, higher-temperature transitions in the bitumen matrix.

The exothermic (oxidation-onset) peaks tell a complementary story about aging resistance. The neat binder begins to oxidize near 460 °C; adding 1 % GNP slightly lowers this onset to 454 °C, implying that small graphene additions can catalyze early oxidation, perhaps by introducing defect sites. This oxidation onset drops further to ~446 °C at 2 % and bottoms out around 423 °C at 3 %, indicating that until a critical GNP concentration is reached, graphene may accelerate oxidative reactions. However, once the GNP content crosses the ~3–4 % threshold, the oxidation onset leaps to ~595 °C at 4 % and remains high at ~566 °C for 5 % GNP. This dramatic increase reflects the formation of a protective graphene barrier that effectively shields the bitumen from oxygen ingress and thermal attack. Taken together, these thermal analyses pinpoint a tipping point around 3–4 % GNP: below it, graphene's high surface area can paradoxically promote early degradation, but beyond it, a continuous nanoparticles network both elevates the energy required for thermal softening and massively delays oxidative breakdown. For high-performance, heat-resistant asphalt binders, targeting a GNP loading in the 4–5 % range appears optimal. Future work should explore dispersion methods that suppress low-loading oxidation catalysis and refine the nanoparticles architecture to maximize both endothermic heat capacity and exothermic stability.

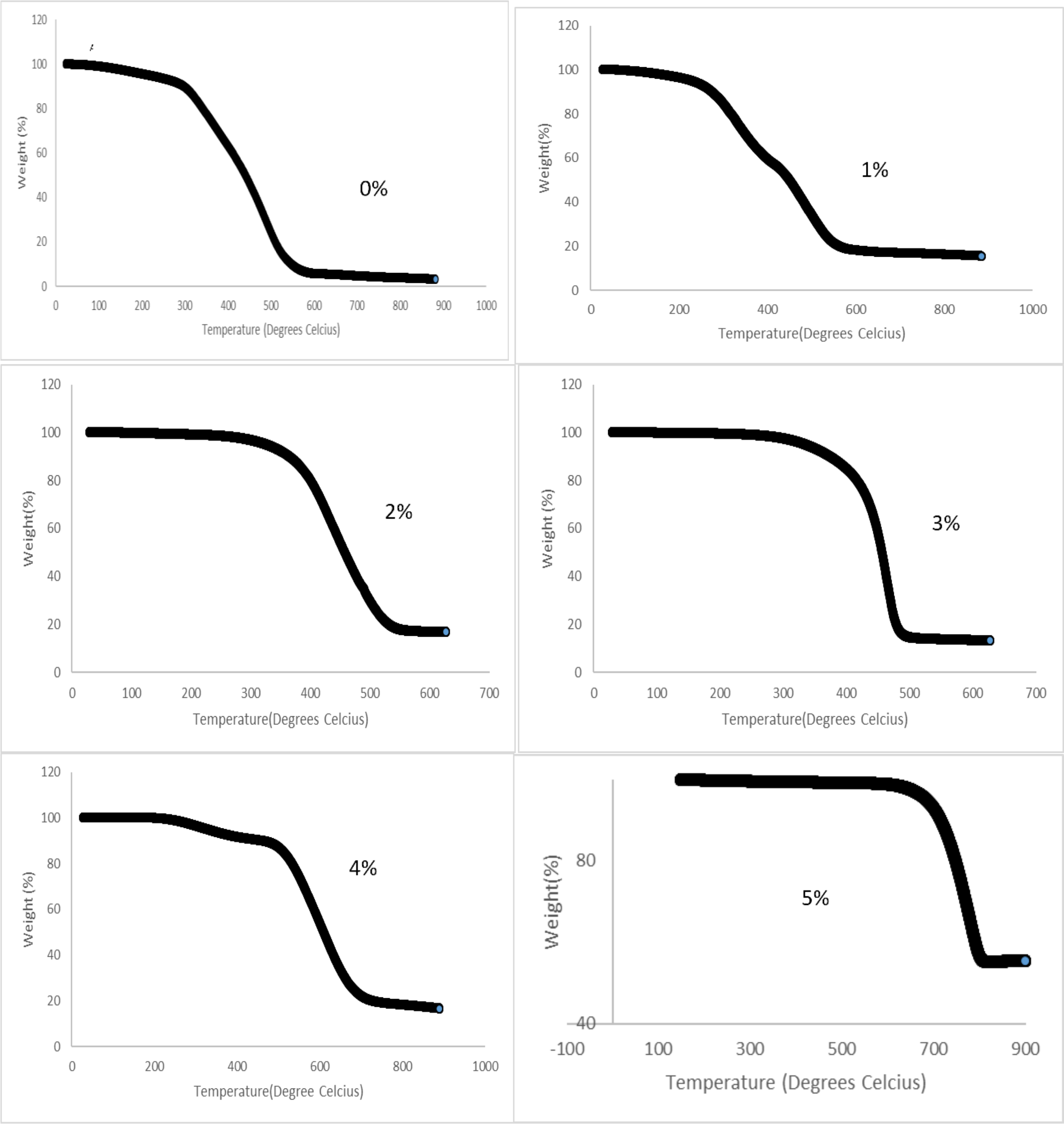

Fig. 1. Thermogravimetric Analysis of GNP blended bitumen results at 1,2,3,4, 5%

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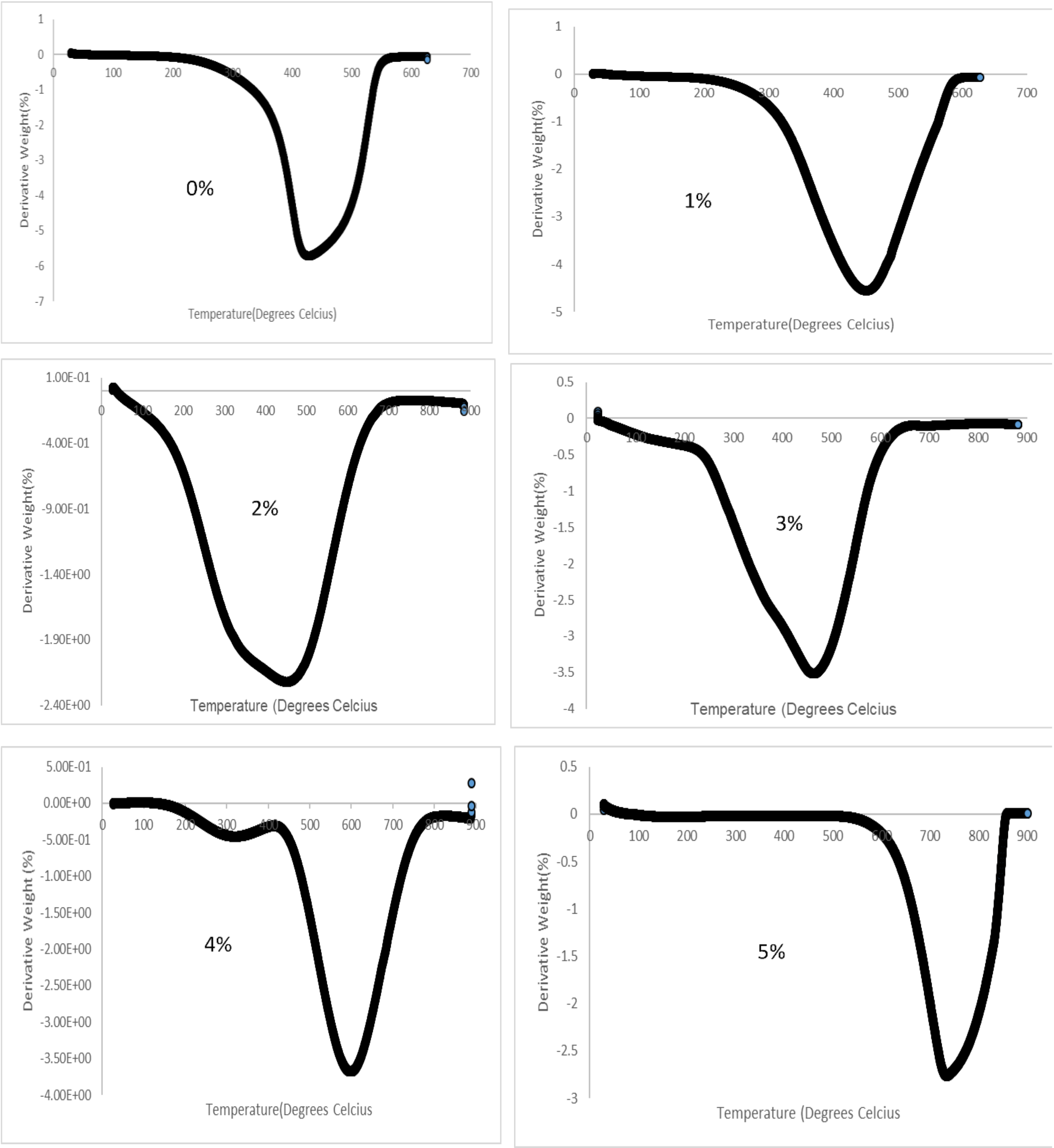

Fig. 2. Differential Thermal Analysis results of GNP blended bitumen at 1,2,3,4, 5%

The Table 2 presents the correlation matrix, illustrating the relationships between various physical and thermal properties of unmodified bitumen and graphene nanoparticle (GNP)-modified bitumen. Each row and column represents a specific property, with numerical values denoting the correlation coefficients between them. These coefficients quantify the strength and direction of relationships, ranging from 1.0 (perfect positive correlation) to -1.0 (strong negative correlation), while values near zero indicate weak or negligible associations.

A strong negative correlation (-0.9) exists between penetration and softening point, indicating that as penetration values decrease (suggesting increased stiffness), the softening point rises. This suggests that higher GNP content enhances thermal stability by making the bitumen less susceptible to deformation at elevated temperatures. Similarly, a perfect positive correlation (1.0) between softening point and flash point signifies that an increase in softening point directly corresponds to a higher flash point, reinforcing the improved heat resistance of the modified binder.

The ductility of bitumen exhibits a notable negative correlation (-0.9) with penetration, suggesting that as the material becomes stiffer, its ability to stretch reduces. This trade-off indicates that while GNP modification enhances structural stability, it also affects flexibility, which may influence crack resistance in certain applications. Additionally, a positive correlation (0.7) between residual mass at 800°C and onset decomposition temperature suggests that higher thermal resistance results in greater material retention, further validating the improved durability of GNP-modified bitumen.

The oxidation onset (exothermic peak) shows moderate correlations with other thermal properties, such as decomposition temperature and residual mass. These relationships highlight the potential of GNP in delaying thermal degradation processes, thereby extending the material's functional lifespan. Overall, this correlation analysis supports the conclusion that GNP integration significantly enhances bitumen's thermal and mechanical performance, making it more suitable for high-temperature applications, particularly in road construction.

Table 3
Correlation analysis of TGA/DTA parameters of bitumen and bitumen /GNP blends

	GNP Content (%)	*Penetration (dmm)*	*Softening Point, °C*	*Ductility (mm)*	*Flash Point, °C*	*Onset Decomp. Temp. (°C)*	*Residual Mass at 800°C (%)*	*Endo-thermic Peak (°C)*	*Exo-thermic Peak, °C)*
GNP Content (%)	1.0								
Penetration (dmm)	-0.9	1.0							
Softening Point, °C	1.0	-0.9	1.0						
Ductility(mm)	-0.9	0.8	-0.9	1.0					
Flash Point, °C	0.9	-1.0	0.9	-0.9	1.0				
Onset Decomp. Temp. (°C)	0.9	-0.7	0.9	-0.9	0.7	1.0			
Residual Mass at 800°C (%)	0.8	-0.7	0.8	-0.8	0.7	0.9	1.0		
Endothermic Peak°C	0.9	-0.7	0.9	-0.9	0.8	1.0	0.9	1.0	
Exothermic Peak, °C	0.7	-0.4	0.7	-0.6	0.5	0.7	0.6	0.5	1.0

4. Conclusions

The incorporation of graphene nanoparticles (GNP) in bitumen results in substantial improvements in both thermal and mechanical properties. As the GNP content increases, notable changes in material behaviour are observed. The penetration values decrease from 22 dmm at 0% GNP to 13 dmm at 5% GNP, indicating increased stiffness and enhanced resistance to deformation under load. This structural reinforcement is further supported by the softening point, which rises from 48°C to 60°C, confirming the improved ability of GNP-modified bitumen to withstand elevated temperatures without losing cohesion.

Another crucial enhancement is seen in the flash point, which increases from 267°C to 294°C, demonstrating the material’s increased stability against ignition at high temperatures. Additionally, thermogravimetric analysis (TGA) further validates these improvements. The onset decomposition temperature shows a remarkable increase of over 320%, while the residual mass at 800°C 55%, indicating a significant enhancement in thermal durability and material retention. These findings confirm that incorporating GNP delays thermal degradation, ultimately extending the lifespan of the modified bitumen.

The correlation analysis provides further insights into the relationships between these enhanced properties. A strong negative correlation (-0.9) between penetration and softening point suggests that increased stiffness directly contributes to improved thermal stability. Similarly, a perfect correlation (1.0) between softening point and flash point reinforces the idea that a higher softening point leads to superior heat resistance. The moderate correlations between oxidation onset, decomposition temperature, and residual mass suggest that GNP integration strengthens bitumen's resistance to thermal breakdown, further improving long-term performance.

Overall, these findings highlight the significant advantages of GNP-modified bitumen in high-temperature applications. The improved stiffness, thermal stability, and oxidation resistance suggest that this material is well-suited for infrastructure projects requiring enhanced durability. Future studies should explore optimizing flexibility to balance stiffness with crack resistance, investigate the effects of long-term aging, and assess the environmental implications of GNP-enhanced bitumen for sustainable infrastructure development.

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References

[1] Christina, Milos. 2010. Bitumen in Nigeria: Weighing the True Costs of Extraction. Heinrich Böll Foundation Nigeria. Available here.

[2] Olutoye, M. A. 2006. "Improvement of Nigeria Crude Residue." Leonardo Journal of Science, 7: 33-42. Available here.

[3] Honarmand, M., Marasteanu, M., Bahia, H., and Christensen, D. 2019. "Transfer Learning for Pavement Performance Prediction." International Journal of Pavement Research and Technology, 13: 154–167. DOI: 10.1007/s42947-019-0096-z.

[4] Vasudevan, R., Reddy, K., Pavithra, P., and Sekar, A. 2012. "Using Waste Plastics in Road Construction." Indian Road Congress. Available here.

[5] Rhee, Seung-Wook. 2020. "Graphene Applications in Engineering." Materials Science Journal, 45(3): 112-125.

[6] Rahman, Mustafizur, Hossain, M. S., Islam, T., and Choudhury, A. 2019. "Graphene Thermal Conductivity." Multiscale Science and Engineering, 1: 267–279. DOI: 10.1007/s42493-019-00024-2.

[7] Tarun, M., Shenoy, V., and Kolpak, A. M. 2015. "Properties of Graphene." European Centre for Research Training and Development UK. DOI: 10.1038/SREP00613.

[8] Li, Xianwei, Sun, Zhi, Yin, Xueying, Zhou, Bo, and Wang, Peng. 2018. "Detection and Quantification of Graphene-Family Nanomaterials." Environmental Science & Technology, 52(8): 4491-4513. DOI: 10.1021/acs.est.7b04938.

[9] He, Xinjian, Zhang, Min, Liu, Lei, and Wang, Jun. 2021. "Effects of Graphene-Family Nanomaterials on Plant Growth." Nanomaterials, 12(6): 936. DOI: 10.3390/nano12060936.

[10] Oladunjoye, O. O., Adekunle, F. T., Akindele, T. B., and Adebayo, S. 2021. "Evaluation of Rheological Characteristics of Graphite Modified Bitumen." Journal of Civil Engineering and Urbanism, 11: 51–57. DOI: 10.54203/jceu.2021.7.

[11] Li, Zhipeng, Liu, Jian, Cao, Wenbin, and Zhang, Hong. 2021. "Carbon Nanomaterials for Asphalt Binders." Materials, 14: 2585. DOI: 10.3390/ma14102585.

[12] Noor, Zainab H., Hassan, M., Ghazi, R., and Iqbal, M. 2015. "Use of Graphene Oxide as a Bitumen Modifier." Advanced Materials Research, 1105: 365-369. DOI: 10.4028/www.scientific.net/AMR.1105.365.

[13] Singh, Prashant K., and Suman, Sandeep K. 2018. "Influence of Graphite on Bituminous Binder Properties." Construction and Building Materials, 192: 866-873. DOI: 10.1016/j.conbuildmat.2018.10.122.

[14] Eisa, Mohamed S., El-Badawy, Sherif, Salah, Mohamed, and Abdel-Rahman, Ali. 2021. "Laboratory Evaluation of Graphene Platelets in Asphalt." Materials, 14(19): 5599. DOI: 10.3390/ma14195599.

[15] Chen, Wei, Zhang, Zhicheng, Liu, Xiaoming, and Yang, Haoran. 2020. "Graphene-Modified Bitumen Performance." Construction and Building Materials, 254: 119261.

[16] Adnan, Ahmad M., Syed, H., Karim, N., and Farooq, N. 2021. "Fatigue Performance of Graphene Oxide Modified Asphalt." Materials, 14(11): 3073. DOI: 10.3390/ma14113073.

[17] He, Xinjian, Chen, Lian, Zhou, Yuan, and Wu, Ying. 2022. "Characterization of Modified Asphalt Binders." Frontiers in Built Environment, 8: 937199. DOI: 10.3389/fbuil.2022.937199.

[18] Şahan, Ahmet, Demir, Faruk, Kaya, Mustafa, and Tekin, Ozan. 2024. "Thermal Degradation of GNP-Modified Bitumen." Materials and Structures, 57(2): 318–330. DOI: 10.1007/s00289-024-01722-1.

[19] Behera, S., Mohanty, B., Nayak, S., and Das, P. 2025. "Thermal Stability and Decomposition Behavior of Graphene-Modified Bitumen." Journal of Materials Science and Engineering, 58(3): 1127–1142. DOI: 10.1007/s10853-025-01722-1.

[20] Adnan, A. M., Lü, C., Luo, X., Wang, J., and Liu, G. 2023. "Fatigue Performance of Graphene Oxide Modified Asphalt Mixture: Experimental Investigation and Response Surface Methodology." Petroleum Science and Technology, 1-18. DOI: 10.1080/10916466.2023.2175854.

[21] Wu, Fan, Wenyuan Xu, Fengfa Zhang, and He Wu. “Grey Correlation Analysis of Physical Properties and Evaluation Index of Graphene-Oxide-Modified Asphalt.” Coatings 12, no. 6 (2022): 770. https://doi.org/10.3390/coatings12060770.

[22] ASTM International. 2020. “ASTM E1131-20, Standard Test Method for Compositional Analysis by Thermogravimetry.” West Conshohocken, PA: ASTM International.