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Effect of Montmorillonite Nanoclay on the Rheological and Microstructural Performance of AC 20 Asphalt Binder

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Abstract

The study evaluated changes in the physical, rheological, and microstructural properties of montmorillonite nanoclay incorporated into AC-20 asphalt binder at dosages ranging from 1.0% to 3.0% by binder mass. Modified binders were prepared at 165 °C by mechanical mixing at 4000 rpm for 30 min. Penetration, softening point, viscosity, Fourier-transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, dynamic shear rheometry, multiple-stress creep-recovery, and bending-beam rheometry were evaluated. Penetration decreased from 84.3 to 51.3 dmm (39.1%), while softening point increased from 58.7 to 63.9 °C (8.9%). At 3.0% nanoclay, absolute viscosity at 60 °C increased from 1648 to 16,560 P (904.9%) and kinematic viscosity at 135 °C increased from 330 to 958.3 cSt (190.4%). The response was non-monotonic, particularly at 2.0% nanoclay. At 76 °C, none of the unaged binders met the criterion for 1.0-kPa $G^*/\sin \delta$, 3.0% binder however, fell marginally below it at 0.9987 kPa. After RTFO aging, the 1.5% and 2.5% binders met the 2.2-kPa criterion at 76 °C. The BBR results also met the stiffness and m-value criteria at -12 °C. FTIR showed no new peaks, supporting predominantly physical interaction. Considering the combined laboratory results, 2.5% nanoclay provided the most balanced response among the investigated formulations. Mixture-scale and field validation remain necessary.

Keywords: montmorillonite; asphalt binder; rheology; multiple-stress creep recovery; rutting resistance; low-temperature performance

1.0 Introduction

Asphalt binder is a temperature- and loading-rate-dependent viscoelastic material. At high pavement temperatures and under repeated heavy loading, insufficient stiffness and elastic recovery can promote permanent deformation; at intermediate and low temperatures, excessive stiffness can impair stress relaxation and increase cracking susceptibility [1].

Therefore, there is a need to develop sustainable and climate-smart road surfacing solutions that can improve the performance and longevity of asphalt binders [1]. One potential solution is the modification of asphalt materials using nanomaterials. These are particles having at least one dimension smaller than 100 nm [2].

Though several nanomaterials have been used for bitumen modification, like nano-zinc oxide, nano-silica, nano-titanium dioxide, and carbon nanotubes, the potential of nanoclay over a wide range of percentages is yet to be fully explored [3].

Nanoclays are layered aluminosilicates whose large surface area, surface charge, and platelet geometry can alter molecular mobility within asphalt. Adequately dispersed clay platelets generally increase viscosity and high-temperature stiffness, whereas agglomeration can produce non-uniform response and diminish the benefit of additional modifier. Several published studies have reported reduced penetration, increased softening point and viscosity, and improved rutting-related rheological parameters after nanoclay modification, although the magnitude depends on clay mineralogy, surface treatment, binder chemistry, dosage, mixing history, and aging condition [3-6].

Despite growing evidence of high-temperature benefits, some issues remain unresolved which include, a dosage that maximizes stiffness and recovery or low-temperature relaxation. A combined physical, rheological, and microstructural assessment is therefore needed to identify a balanced dosage.

This study evaluated AC-20 binder modified with 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% montmorillonite nanoclay by binder mass. The objectives were to characterize the nanoclay; quantify dosage-dependent changes in empirical and rheological properties; examine chemical and morphological evidence of interaction; and identify the formulation that provided the most balanced laboratory response. The study focused on binder-scale testing and did not evaluate mixture performance, constructability, storage stability, life-cycle impacts, or field durability.

2. Materials and Methods

2.1. Materials

Commercial montmorillonite nanoclay supplied by Intelligent Materials Pvt Ltd was used. The nanoclay material had a nominal platelet thickness of approximately 1 nm, a specific gravity of 2.6, and a purity of 99.9%. AC-20 asphalt binder was used as the base material. Its measured properties are summarized in Table 2. The bitumen used in the study was of AC-20 grade, the physical properties of the bitumen were ascertained according to ASTM standards.

2.2 Modified bitumen preparation

For each formulation, 500 g of AC-20 binder was heated to 165 °C. Nanoclay was added gradually at 1.0%, 1.5%, 2.0%, 2.5%, or 3.0% by binder mass and hand-mixed for 5 min to promote wetting. Mechanical mixing was then conducted at 4000 rpm for 30 min while maintaining the target temperature. The prepared binders were sealed in labelled containers before testing.

2.3 Physical characterisation

Penetration was measured at 25 °C under a 100 g load for 5 s in accordance with ASTM D5/D5M [7]. Softening point was measured using the ring-and-ball method in accordance with ASTM D36/D36M [8]. Absolute viscosity at 60 °C and kinematic viscosity at 135 °C were measured using a Brookfield rotational viscometer following the laboratory procedures cited in the original test programme.

2.3.1 Mineralogical Composition Analysis using the XRD

XRD was conducted using a Bruker D2 Phaser diffractometer with Cu K-alpha radiation ($\lambda = 1.54060$ Å) operated at 30 kV and 10 mA. Specimens were scanned from 5° to 80° 2-theta at 25 °C using a 0.01° step interval. Phase identification was based on the recorded diffraction pattern.

2.3.2 Chemical Composition using the XRF

The nanoclay oxide composition was determined using a Rigaku NEX CG energy-dispersive X-ray fluorescence spectrometer. Four grams of nanoclay were combined with 0.9 g of binder to prepare each pellet. Instrument calibration was performed with a borosilicate reference bead, and major oxides were quantified using the fundamental-parameters method. The reported values are presented in Table 3.

2.3.3 Functional Group Analysis using the FTIR

FTIR spectra of the base and nanoclay-modified binders were collected using an Interspec 200-X spectrometer. Thirty-two scans were acquired for each spectrum. Spectra were compared by band position and relative profile to determine whether modification introduced new diagnostic functional groups.

2.3.4 Morphological Characterisation (SEM)

SEM was used to examine nanoclay morphology and qualitative dispersion features in the binder. Specimens were sputter-coated with gold and imaged using a Zeiss EVO MA 15 microscope at an accelerating voltage of 15 kV and magnifications from 500x to 10,000x. SmartEDX was used for elemental screening. The SEM assessment was treated as qualitative because no image-analysis protocol was applied.

2.3.5 Rheological test

Rheological testing was conducted using DSR and BBR in accordance with AASHTO T 315 [9] and AASHTO T 313 [10], respectively. Short-term and long-term aging were simulated using the rolling thin-film oven and pressure aging vessel before the applicable DSR and BBR measurements. The DSR provided complex shear modulus (G^*) and phase angle (δ). High-temperature response was assessed using $G^*/\sin\delta$, while the intermediate-temperature parameter $G^* \sin\delta$ was reported for PAV-aged binders. MSCR testing at 64 °C followed AASHTO T 350 [11] and provided percentage recovery (R) and non-recoverable creep compliance (J_{nr}) at 0.1 and 3.2 kPa. BBR testing at -12 °C provided 60-s creep stiffness (S) and m-value. The criterion or specification limits used for interpretation were $S \leq 300$ MPa and $m\text{-value} \geq 0.300$.

3.0 Results and Discussion

3.1 Characterisation of nanoclay and the base asphalt binder (AC-20)

The supplier data and laboratory characterization identified the modifier as high-purity montmorillonite with a nominal layer thickness of approximately 1 nm, specific gravity of 2.6, and alkaline pH (Table 1). The control AC-20 penetration of 84.3 dmm, softening point of 58.7 °C, absolute viscosity of 1648 P at 60 °C, and kinematic viscosity of 330 cSt at 135 °C.

Table 1. Properties of the nanoclay

Property	Reported value
Mineral	Montmorillonite
Purity	99.9%
Nominal layer thickness	approximately 1 nm
Colour	Light cream/yellowish
Specific gravity	2.6
pH	9

The control values satisfy the applicable ASTM D3381/D3381M AC-20 limits for penetration, absolute viscosity at 60 °C, and minimum kinematic viscosity at 135 °C [12].

Table 2. Physical properties of unmodified bitumen (AC-20)

Property	Test method	Measured value	AC-20 criterion/status
Penetration at 25 °C, 100 g, 5 s (dmm)	ASTM D5/D5M	84.3	≥ 40 dmm; conforms
Softening point (°C)	ASTM D36/D36M	58.7	Reported property; not an ASTM D3381 AC-20 grading criterion
Kinematic viscosity at 135 °C (cSt)	ASTM D2170/D2170M	330	≥210 cSt; conforms
Absolute viscosity at 60 °C (P)	ASTM D2171/D2171M	1648	1600-2400 P; conforms
Specific gravity	ASTM D70/D70M	1.01	Reported property; not an ASTM D3381 AC-20 grading criterion

3.1.1 Viscosity

Nanoclay substantially increased viscosity at both temperatures, but the dosage response was non-monotonic (Figures 5a and 5b). Absolute viscosity at 60 °C increased from 1648 P for AC-20 to 16,560 P at 3.0% nanoclay, a 904.9% increase. Kinematic viscosity at 135 °C increased from 330 to 958.3 cSt, a 190.4% increase. The 2.0% formulation produced lower viscosity than the 1.0% and 1.5% formulations at both temperatures, suggesting sensitivity to dispersion or specimen preparation. The very large viscosity increases at 2.5-3.0% raise important workability, pumping, mixing, and compaction concerns that require mixture-scale evaluation.

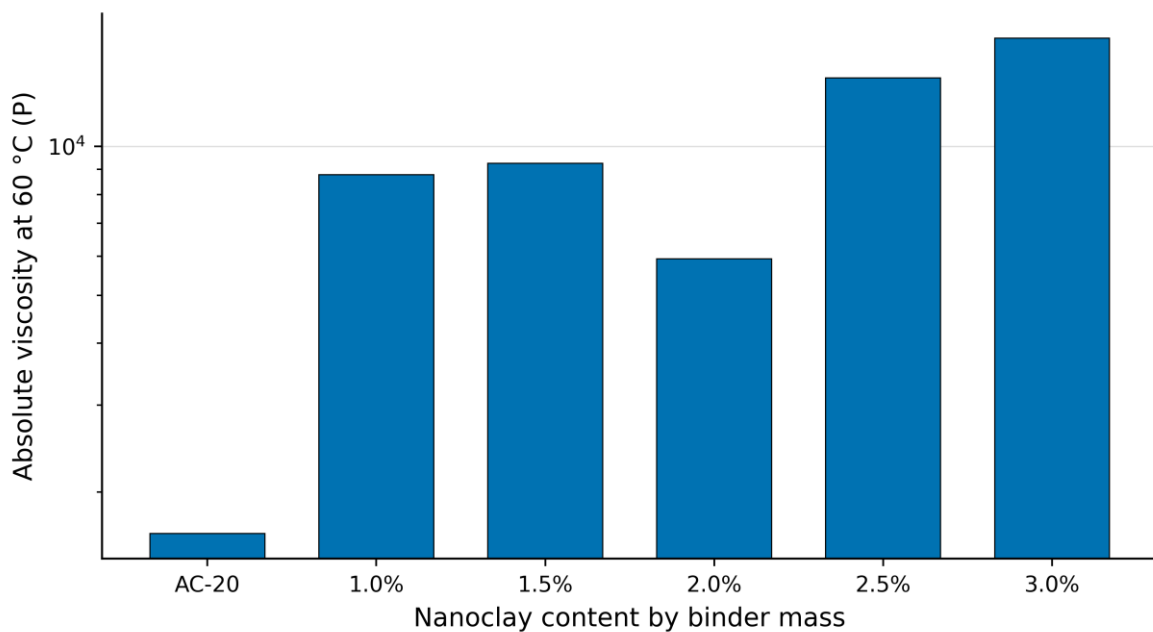


Figure 5a. Absolute viscosity of AC-20 and nanoclay-modified binders at 60 °C.

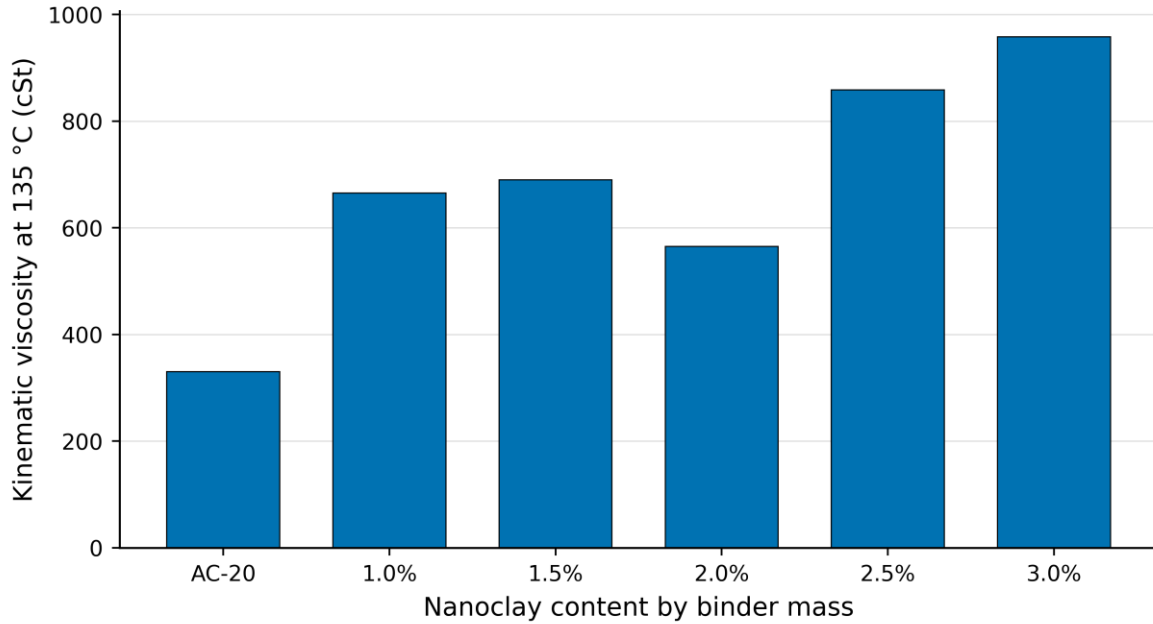


Figure 5b. Kinematic viscosity of AC-20 and nanoclay-modified binders at 135 °C.

3.2 Chemical and Microstructural Characterization

3.2.1 X-ray fluorescence (XRF)

XRF showed that SiO_2 (69.9%) and Al_2O_3 (19.4%) were the dominant oxides, consistent with an aluminosilicate clay (Table 3). The high SiO_2 content confirms the predominance of silicate which essential for layered platelet structure, this enhances stiffness and barrier properties in asphalt binders. Al_2O_3 contributes to clay polarity, improving interfacial bonding with polar binder molecules. This supports enhanced adhesion. CaO and MgO act as exchangeable cations in the clay's interlayers, potentially influencing cation exchange capacity and facilitating intercalation of asphalt molecules.

Table 3: Major Oxides of Nanoclay

Component	Average mass (%) Nanoclay
SiO ₂	69.9
Al ₂ O ₃	19.4
CaO	0.8
Ironoxide (reported as Fe ₂ O)	5.2
MgO	2.4
P ₂ O ₅	0.5
SO ₃	0.3
TiO ₂	0.4
K ₂ O	0.4
Na ₂ O	0.3
ZrO ₂	0.3

3.2.2 X-ray powder diffraction (XRD)

The X-ray powder diffraction (XRD) pattern of the nanoclay shows a broad peak around (d_{001}) is $2\theta = 20^\circ$. The XRD results confirms crystalline phases in the nanoclay within the binder. This also indicates that the nanoclay lamellas are not exfoliated but intercalated and would enable dispersion in bitumen, as shown in figure 6b.

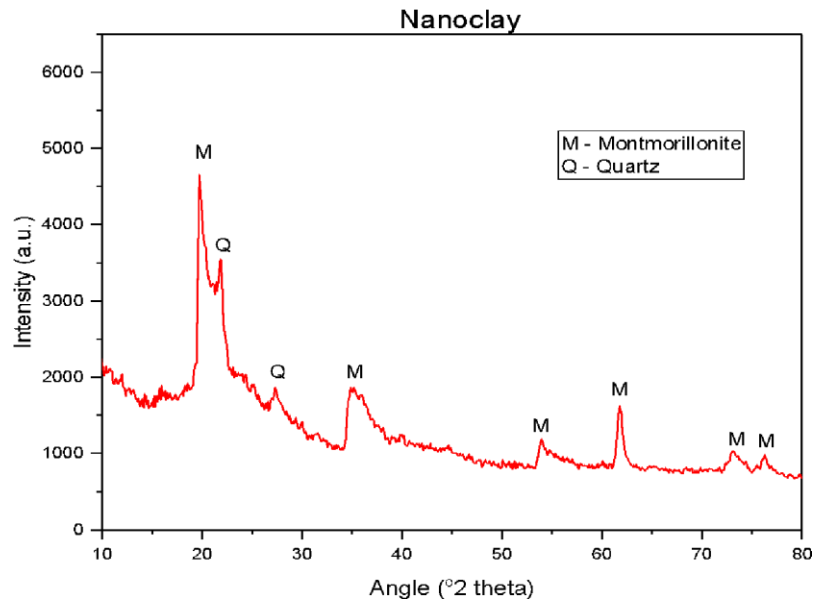
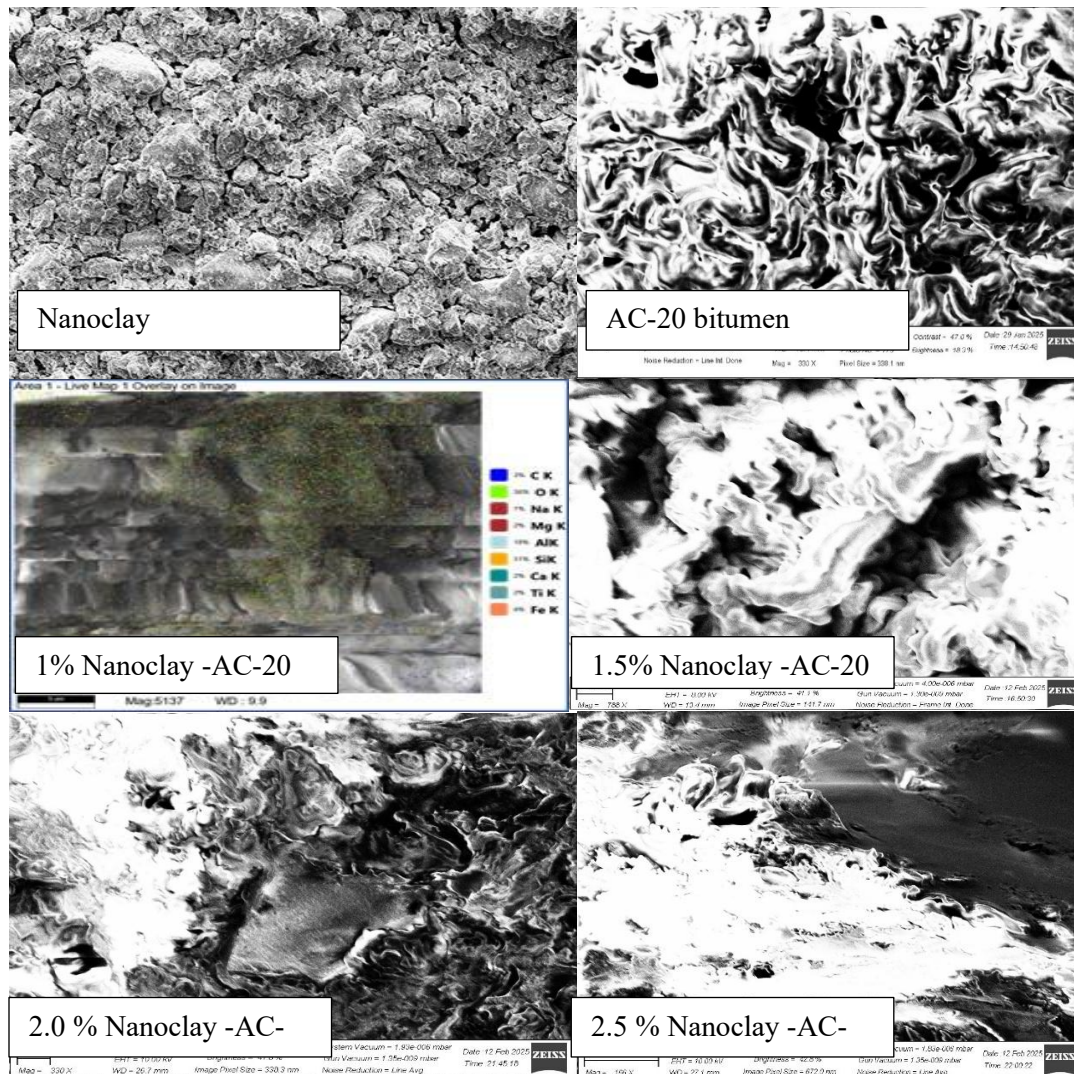


Figure 6. XRD pattern of nanoclay

3.2.3 Scanning electron microscopy (SEM)

SEM images showed an aggregated platelet morphology for the nanoclay and visually heterogeneous clay-rich domains in the modified binders (Figure 7). Some modified specimens appeared more compact than the control, while larger agglomerated regions were evident at higher dosages. The results observed are consistent with dosage-dependent dispersion.



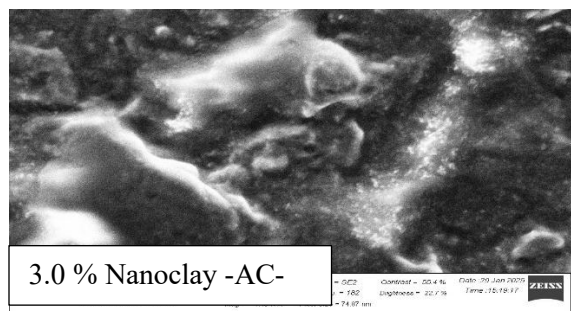


Figure 7. SEM Images of Nanoclay, AC-20, and modified binders

3.2.4 Fourier Transform Infrared (FTIR)

The base and modified binders exhibited major bands near 2916 and 2851 cm^{-1} , assigned to aliphatic C-H stretching, and bands near 1601 , 1454 , and 1375 cm^{-1} associated with aromatic and aliphatic structures (Figure 8). Differences in the 1079 - 1031 cm^{-1} region were consistent with clay-related Si-O/Al-O vibrations and possible overlap with the binder sulfoxide region. No new diagnostic absorption band appeared after modification. The FTIR result exhibited predominantly physical interaction after the binder modification.

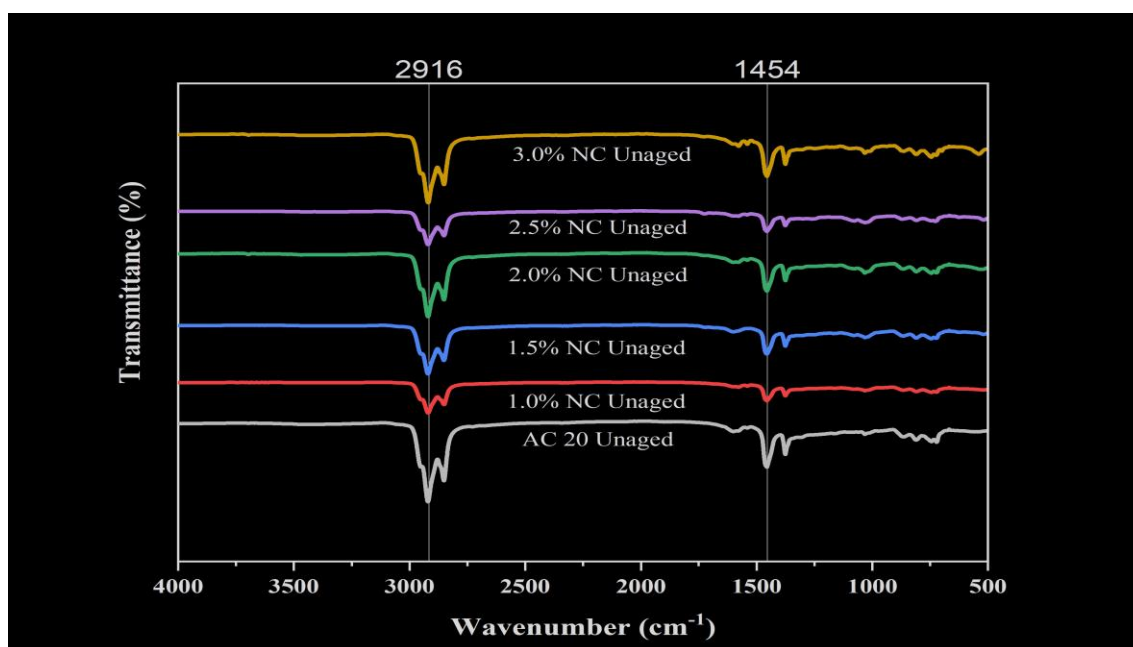


Figure 8. FTIR of unaged, unmodified, and modified asphalt binder

The absorption peaks in the unmodified asphalt occurred at 2916 cm^{-1} and 2851 cm^{-1} and these are characteristic peaks for alkane C-H asymmetric and symmetric vibrations, respectively. The absorption peak at 1601 cm^{-1} characterises the conjugated alkene double bond C=C stretching vibration. Fingerprint regions of 1375 cm^{-1} represents the C-O stretching vibration. The absorption intensities of the asphalt binder showed slight modification at the fingerprint region of $1030\text{-}1031\text{ cm}^{-1}$. The addition of nanoclay to the asphalt binder resulted in a slight change in the characteristic peak at the fingerprint region of $1079\text{-}1031\text{ cm}^{-1}$ due to the bending and stretching vibrations of the Al-OH-Al and S=O sulfoxide within the MMT molecule. Therefore, after modification, the binder did not show much significant difference between the modified asphalt and the unmodified asphalt, suggesting a predominantly physical interaction rather than chemical reaction between nanoclay and binder.

3.3 Rheological Property

3.3.1 Dynamic Shear Rheometry (DSR)

The unaged $G^*/\sin \delta$ results showed a strong temperature effect and non-monotonic dosage response (Figure 9). At 64 °C, all reported binders exceeded 1.0 kPa. At 70 °C, the control failed and the 2.0% binder was marginally below the criterion at 0.9995 kPa, whereas the other modified binders passed. At 76 °C, none of the reported binders met 1.0 kPa; the 3.0% binder was closest at 0.9987 kPa, followed by 2.5% at 0.9648 kPa. These results indicate that an unaged grade above the 70 °C interval may not be supported .

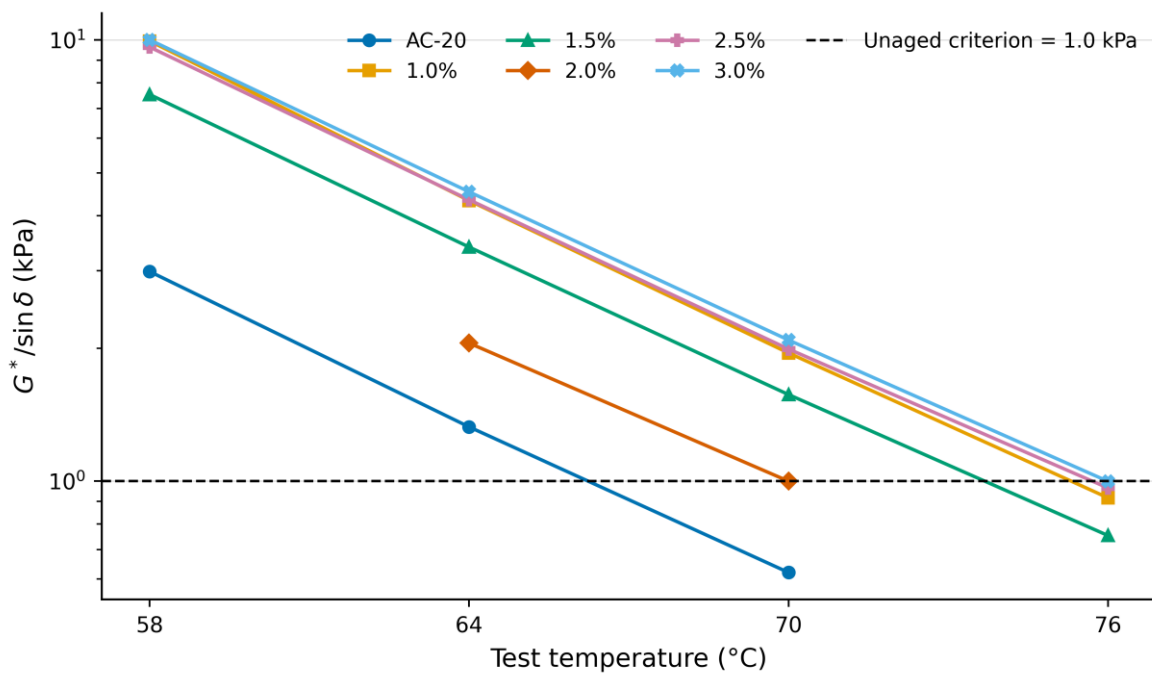


Figure 9. Unaged $G^*/\sin \delta$ of AC-20 and nanoclay-modified binders.

After RTFO aging, all binders exceeded the 2.2-kPa criterion at 64 and 70 °C. At 76 °C, only the 1.5% (2.2889 kPa) and 2.5% (2.4580 kPa) binders met the criterion. The 3.0% binder decreased to 1.1902 kPa, confirming that the highest dosage did not provide the best aged high-temperature response. The PAV-aged binders, the reported $G^* \sin \delta$ values remained below 5000 kPa except for the 3.0% formulation at 22 °C (Figure 11). Thus, the highest dosage did not maintain the same balance.

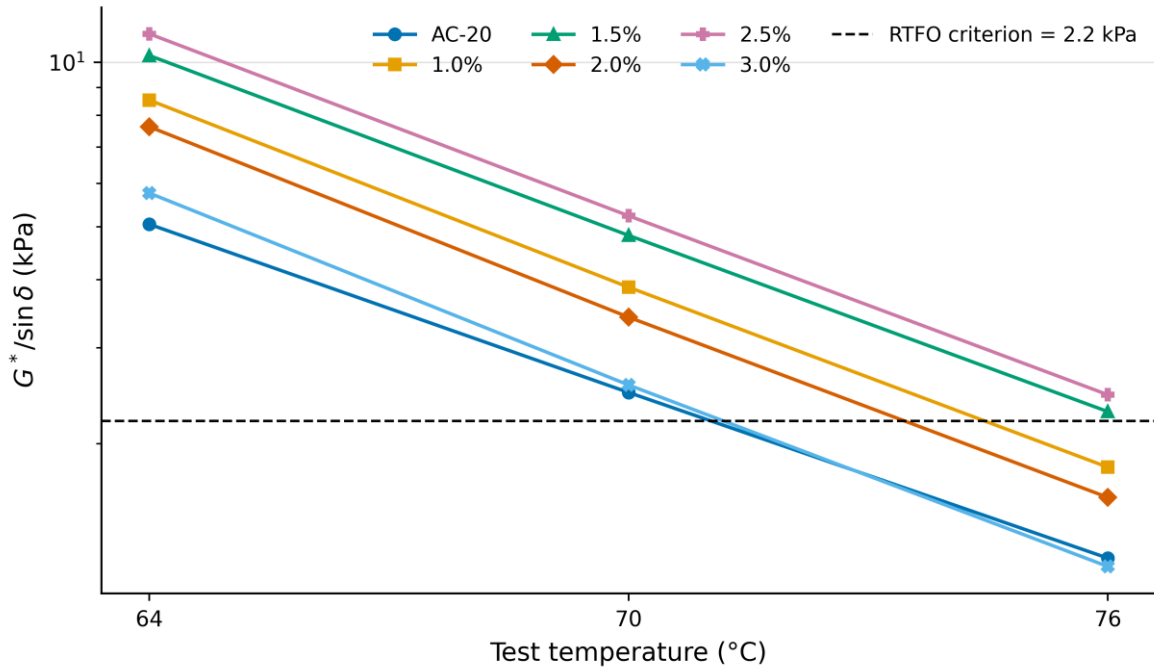


Figure 10. RTFO-aged $G^*/\sin \delta$ of AC-20 and nanoclay-modified binders.

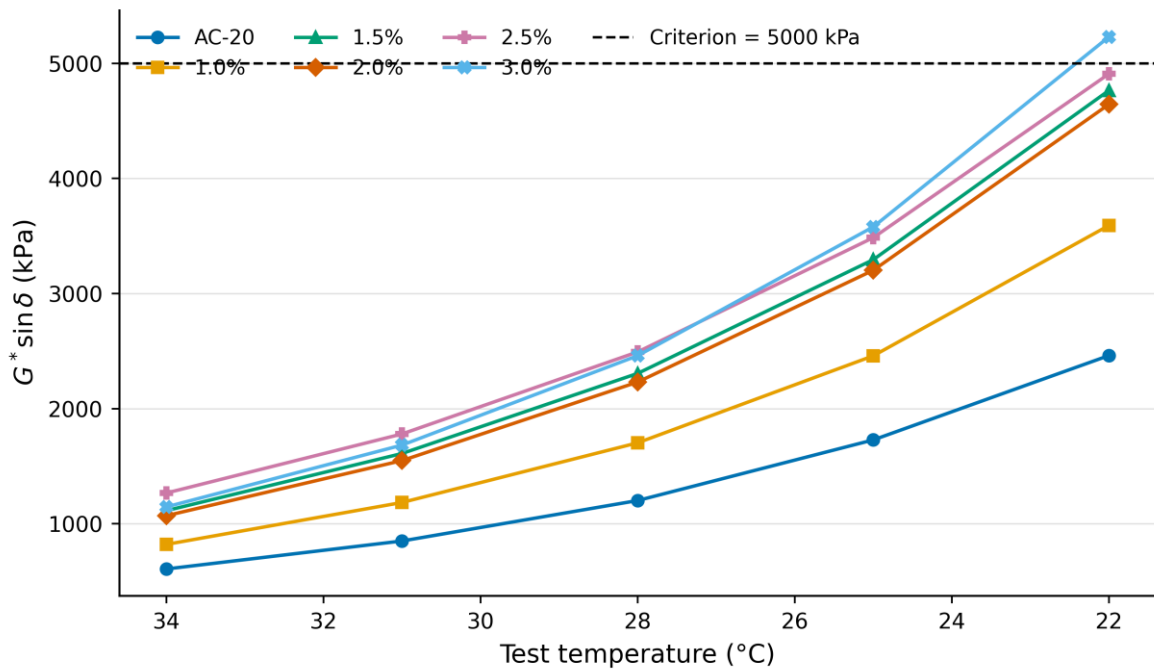


Figure 11. $G^* \times \sin \delta$ of PAV-aged binder

3.3.2 Multiple stress creep recovery

At the MSCR test temperature of 64 °C, recovery depended on both nanoclay dosage and stress level (Figure 12). At 0.1 kPa, R was 23.90% for AC-20 and ranged from 10.68% to 23.60% for the modified binders. At 3.2 kPa, R increased from 7.40% for AC-20 to a maximum of 12.25% at 2.5% nanoclay, before decreasing to 3.30% at 3.0%. Thus, 2.5% nanoclay provided the most favourable recovery at the higher stress level, whereas the 3.0% dosage impaired elastic recovery.

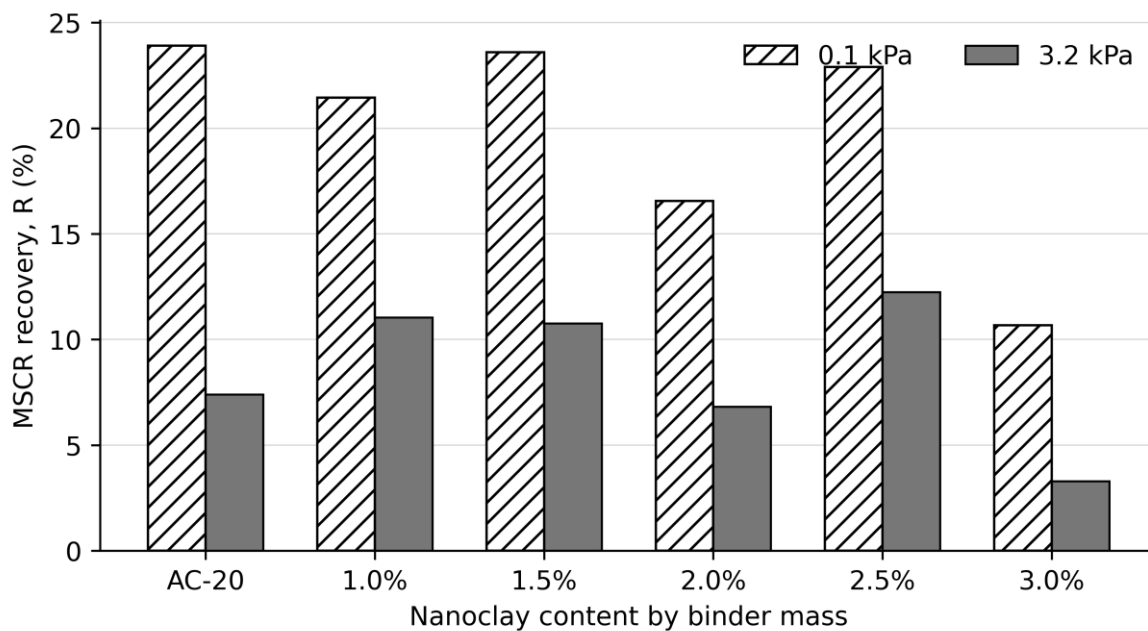


Figure 12. MSCR percentage recovery of AC-20 and nanoclay-modified binders at 64 °C under creep stresses of 0.1 and 3.2 kPa.

At the confirmed MSCR test temperature of 64 °C, Jnr increased with stress level for every percentage replacement (Figure 13). At 3.2 kPa, Jnr decreased from 1.4952 kPa⁻¹ for AC-20 to 0.7240 kPa⁻¹ at 2.5% nanoclay, a 51.6% reduction, before increasing to 1.9150 kPa⁻¹ at 3.0%. The Jnr,diff values from 21.29% to 38.82%. These results demonstrate that the strongest resistance to non-recoverable deformation was at 2.5% nanoclay under the reported MSCR conditions.

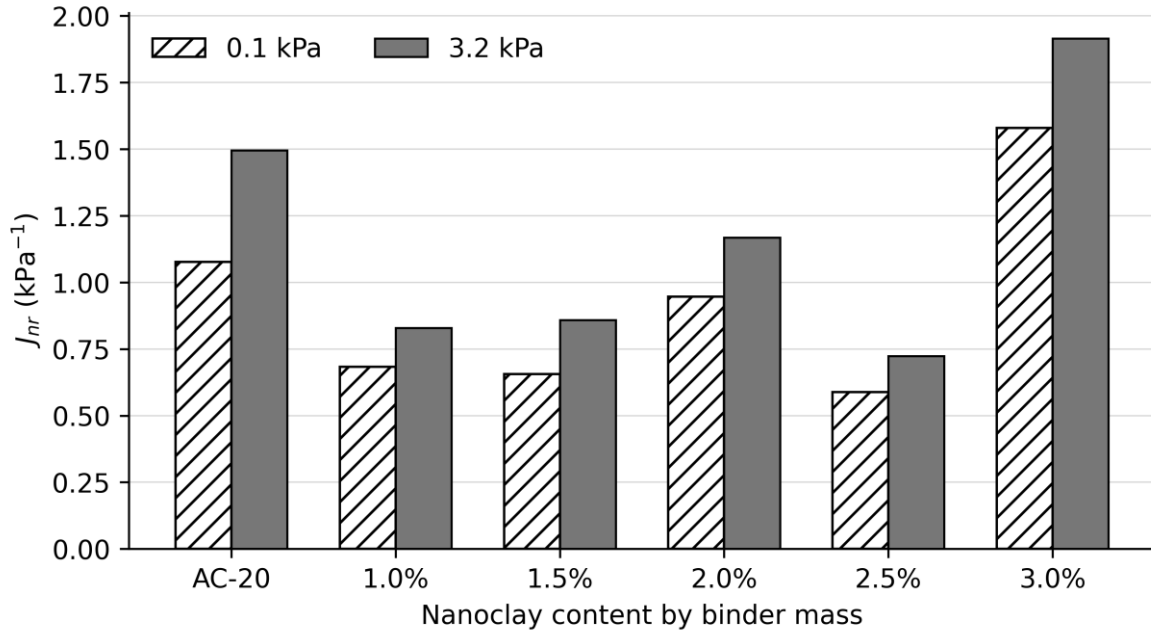


Figure 13. MSCR non-recoverable creep compliance of AC-20 and nanoclay-modified binders at 64 °C under creep stresses of 0.1 and 3.2 kPa.

3.3.3 Bending Beam Rheometer

All reported binders satisfied $S \leq 300$ MPa and $m\text{-value} \leq 0.3$ at -12 °C (Figures 14 and 15). Nanoclay increased creep stiffness modestly, while the intermediate dosages retained adequate relaxation. The result demonstrates compliance at the single test temperature.

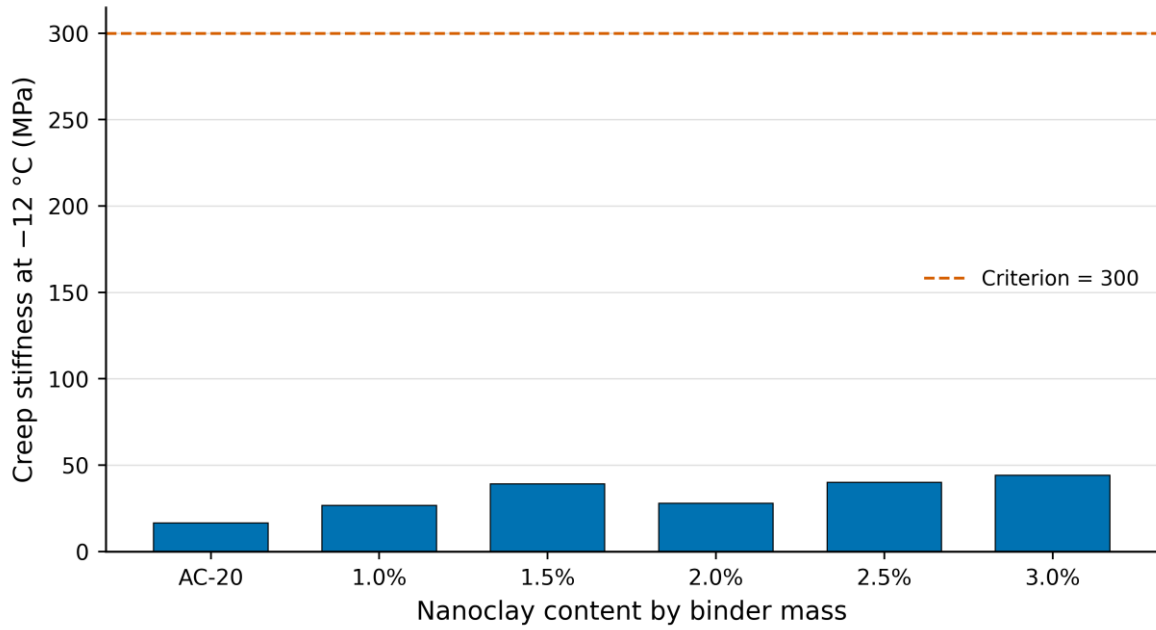


Figure 14. BBR creep stiffness of AC-20 and nanoclay-modified binders at -12 °C.

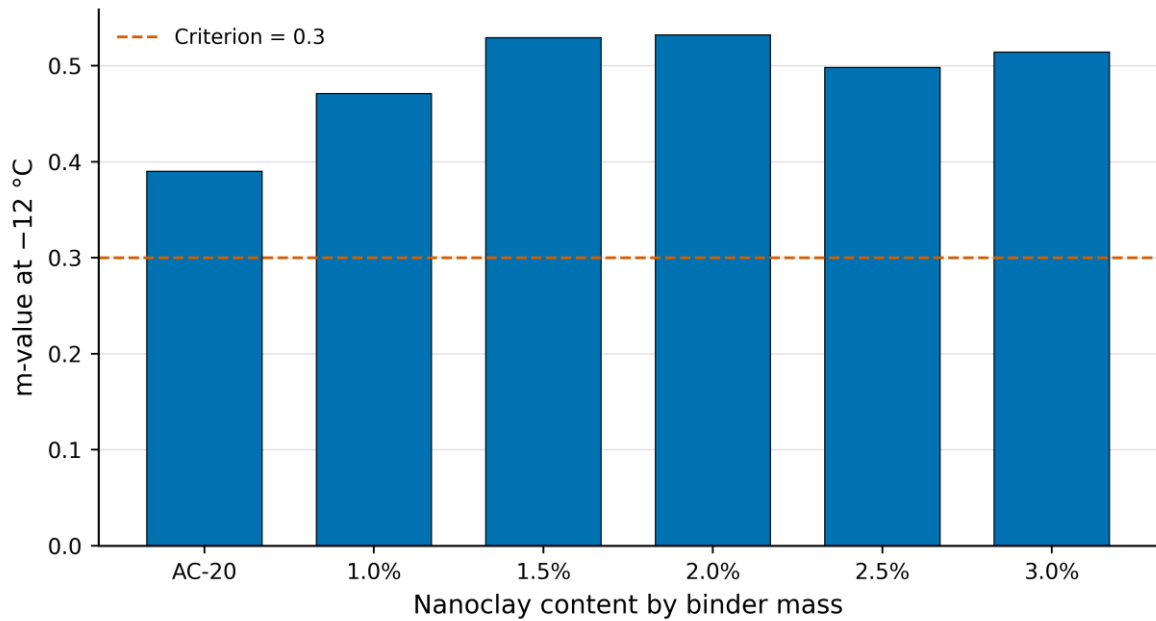


Figure 15. *m*-value of the nanoclay-modified asphalt binders

3.4 Integrated dosage assessment

Dosage selection was based on converging binder-scale evidence rather than any single empirical index. The 2.5% formulation produced the lowest Jnr at both MSCR stress levels, the highest recovery at 3.2 kPa, and met the RTFO $G^*/\sin \delta$ criterion at 76 °C. Its high viscosity nevertheless represents a constructability penalty. Accordingly, 2.5% is identified as the most balanced laboratory sample, not as a universally applicable field optimum.

Dosage	RTFO at 76 °C	MSCR Jnr at 3.2 kPa	BBR at -12 °C	Integrated interpretation
AC-20	Fail	1.4952	Pass	Control
1.0%	Fail	0.8289	Pass	Improved Jnr
1.5%	Pass	0.8591	Pass	Strong aged DSR
2.0%	Fail	1.1686	Pass	Inconsistent response
2.5%	Pass	0.7240	Pass	Best rheological balance
3.0%	Fail	1.9150	Pass	Performance decline; highest viscosity

4.0 Conclusions

Montmorillonite nanoclay altered the physical and rheological response of AC-20 binder in a strongly dosage-dependent manner.

The principal conclusions are as follows:

- (1) The unaged high-temperature response improved at selected dosages, but none of the reported binders met $G^*/\sin \delta \geq 1.0$ kPa at 76 °C.
- (2) After RTFO aging, the 1.5% and 2.5% binders met the 2.2-kPa criterion at 76 °C, whereas the 3.0% binder did not.
- (3) The 2.5% formulation produced the most favourable combined RTFO and MSCR response; recovery declined and Jnr increased at 3.0%.
- (4) All reported binders met the BBR stiffness and m-value criteria at -12 °C, although one temperature is insufficient for a complete low-temperature grade.
- (5) FTIR supported predominantly physical interaction, while the available XRD data were insufficient to prove intercalation or exfoliation
- (6) 2.5% nanoclay was the most balanced option, but its high viscosity requires mixture workability, storage-stability, and field validation before implementation.

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Author contributions

Conceptualization and investigation: Delali H. Adjei. Supervision and technical guidance: Anthony Andrews, Kenneth A. Tutu, and Yaw A. Tuffour. Writing - original draft: Delali H. Adjei. Writing - review and editing: all authors. All authors read and approved the final manuscript.

Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request

Competing interests

The authors declare that they have no competing interests.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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