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Calprene-Modified Asphalt Mixtures: A Comprehensive Investigation of Performance Enhancement

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خلطات الأسفلت المُعدّلة بالكالبرين: دراسة شاملة لتحسين الأداء

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Abstract:
The deterioration of flexible pavements under increasing traffic loads and extreme thermal conditions demands advanced binder modification strategies. This study presents a comprehensive experimental investigation of Calprene-modified asphalt mixtures, where Calprene a radial styrene-butadiene-styrene (SBS) block copolymer manufactured by Dynasol Elastomers was incorporated into a base Pen 60/70 bitumen at dosages of 3%, 4.5%, and 6% by weight of binder. A Superpave 12.5-mm nominal maximum aggregate size (NMAS) gradation was employed for all hot-mix asphalt (HMA) formulations. Binder characterisation encompassed penetration, softening point, ductility, rotational viscosity, dynamic shear rheometer (DSR), bending beam rheometer (BBR), and multiple stress creep-recovery (MSCR) tests. Mixture-level performance was evaluated through Marshall stability and flow, dynamic modulus (|E*|) testing, Hamburg Wheel Tracking Device (HWTD), four-point beam fatigue, semi-circular bending (SCB) fracture energy, and indirect tensile strength ratio (TSR). One-way analysis of variance (ANOVA) with post-hoc Tukey–Kramer comparison and Pearson correlation analysis were applied for statistical discrimination. Results demonstrate that 4.5% Calprene content constitutes the optimal dosage: performance grade advanced from PG 64-22 to PG 76-22, Marshall stability increased by 39.7%, rut depth under HWTD decreased by 58.9%, fatigue life at 800 με extended by 163%, and SCB fracture energy improved by 81.6% compared to the control mixture. These findings confirm that Calprene is a technically superior modifier for asphalt binders in hot-climate, high-traffic pavement applications and provide calibrated benchmarks for practitioners.

Keywords: Calprene; SBS Block Copolymer; Polymer-Modified Bitumen; Rutting Resistance; Fatigue Cracking; Semi-Circular Bending; Dynamic Modulus; Superpave Mix Design; Performance Grade.

الملخص
يتطلب تدهور الأرصفة المرنة تحت تأثير أحمال المرور المتزايدة والظروف الحرارية القاسية استراتيجيات متقدمة لتعديل المادة الرابطة. تُقدم هذه الدراسة بحثًا تجريبيًا شاملًا لخلطات الأسفلت المُعدّلة بالكالبرين، حيث تم دمج الكالبرين، وهو بوليمر ستايرين-بوتادين-ستايرين شعاعي مُصنّع من قِبل شركة Dynasol Elastomers، في قاعدة من البيتومين Pen 60/70 بنسب 3% و4.5% و6% من وزن المادة الرابطة. استُخدم تدرج حجم الركام الاسمي الأقصى من نوع Superpave 12.5 مم لجميع تركيبات خلطات الأسفلت الساخن (HMA). شملت دراسة خصائص المادة الرابطة اختبارات الاختراق، ونقطة التليين، والليونة، واللزوجة الدورانية، ومقياس القص الديناميكي، ومقياس انحناء العارضة، واختبارات الزحف والاستعادة تحت إجهاد متعدد . وقُيّم أداء الخليط من خلال اختبارات استقرار وتدفق مارشال، ومعامل المرونة

الديناميكي (|E*|)، وجهاز هامبورغ لتتبع العجلات، وإجهاد العارضة رباعي النقاط، وطاقة كسر الانحناء شبه الدائري (SCB)، ونسبة قوة الشد غير المباشرة (TSR). واستُخدم تحليل التباين أحادي الاتجاه (ANOVA) مع مقارنة توكي-كرامر اللاحقة وتحليل ارتباط بيرسون للتمييز الإحصائي. تُظهر النتائج أن نسبة 4.5% من مادة كالبرين تُمثل الجرعة المثلى: فقد ارتفع مستوى الأداء من PG 64-22 إلى PG 76-22، وزادت مقاومة مارشال بنسبة 39.7%، وانخفض عمق التخدد تحت ظروف HWTD بنسبة 58.9%، وامتد عمر الإجهاد عند 800 ميكروإجهاد بنسبة 163%، وتحسنت طاقة كسر SCB بنسبة 81.6% مقارنةً بالخليط القياسي. تؤكد هذه النتائج أن كالبرين مُعدِّلٌ متفوقٌ تقنيًا لمواد الربط الإسفلتية في تطبيقات رصف الطرق ذات المناخ الحار وحركة المرور الكثيفة، وتُوفر معايير مُعايرة للمُختصين.

الكلمات المفتاحية: كالبرين؛ بوليمر SBS؛ بيتومين مُعدَّل بالبوليمر؛ مقاومة التخدد؛ تشقق الإجهاد؛ الانحناء نصف الدائري؛ معامل المرونة الديناميكي؛ تصميم خلطات Superpave؛ مستوى الأداء.

1. Introduction

Road infrastructure represents one of the most capital-intensive assets of modern economies, yet premature distress manifested as rutting, fatigue cracking, and thermal fracture continues to erode its service life at considerable cost to society [1,2]. Conventional bituminous binders, thermoplastic in nature, are highly susceptible to the coupled demands of heavy axle loads and wide temperature cycles: high-viscosity states at cold extremes promote thermal cracking, while reduced stiffness at elevated temperatures accelerates permanent deformation [3]. These limitations have catalysed sustained research into polymer modification of bituminous binders, a technology that has evolved from empirical practice into a rigorously quantified science over the past three decades.[4]

Among available polymer modifiers, thermoplastic elastomers of the styrene-butadiene-styrene (SBS) block copolymer family have emerged as the dominant choice for high-performance pavement binders worldwide, accounting for the majority of polymer-modified bitumen (PMB) production [5,6]. The unique triblock architecture of SBS in which hard polystyrene (PS) endblocks provide structural anchoring while the elastomeric polybutadiene (PB) midblock governs flexibility and elastic recovery confers simultaneous improvements in rutting resistance, fatigue endurance, and low-temperature ductility to the modified binder system.[7,8]

Calprene is a portfolio of SBS block copolymers manufactured by Dynasol Elastomers (formerly Repsol Química) and is widely specified for bitumen modification applications across Europe, Latin America, and the Middle East [9]. Calprene products are characterised by their radial (star-branched) molecular architecture and are available in varying styrene-to-butadiene ratios; Calprene 401 carries an 80:20 butadiene/styrene mass ratio, while Calprene 411 presents a 70:30 ratio. Radial SBS grades possess multiple PS endblocks anchored to a common central core, yielding a more interconnected polymer network within the bitumen matrix than linear SBS analogues and, consequently, superior elastic recovery and storage stability.[10,11]

Despite the commercial importance of Calprene and the growing body of literature on SBS-modified binders and mixtures, dedicated studies that systematically correlate Calprene content with mixture-level performance across rutting, fatigue, and fracture domains under a unified experimental framework remain sparse. Most published investigations focus on generic SBS grades without distinguishing the specific molecular geometry of the modifier [12], or evaluate binder properties without extending analysis to compacted HMA performance [13]. Furthermore, recent advances in Superpave mix design, balanced mixture design (BMD), and performance test protocols including the MSCR test [14], AASHTO TP 124 SCB method [15], and IDEAL-CT cracking index [16] have not been fully applied to Calprene-containing systems.

This study addresses these gaps by conducting a rigorous, multi-scale experimental investigation of Calprene 401-modified HMA mixtures. The specific objectives are:

1. To characterise the rheological and physical properties of Calprene-modified binders across a range of modification levels using both conventional and Superpave/AASHTO test protocols.

2. To evaluate the mechanical and volumetric properties of HMA mixtures incorporating varying Calprene dosages using Marshall and Superpave gyratory compaction procedures.
3. To quantify mixture-level rutting, fatigue, fracture, and moisture damage resistance through advanced performance testing.
4. To identify the optimal Calprene content via statistical analysis and establish mechanistic interpretations of the observed performance improvements.
5. To benchmark the findings against recent peer-reviewed literature and provide evidence-based guidance for pavement engineering practice.

The paper is organised as follows: Section 2 reviews relevant literature on SBS-modified binders and mixtures published primarily between 2022 and 2026; Section 3 describes the experimental programme in detail; Section 4 presents and statistically analyses the results; Section 5 discusses findings in relation to prior work and practical implications; and Section 6 draws conclusions and proposes future research directions.

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2. Literature Review

2.1 Polymer-Modified Bitumen: Fundamentals and SBS Architecture

The incorporation of elastomeric polymers into bituminous binders represents a well-established technology for enhancing pavement performance, with the primary objective of mitigating rutting and low-temperature cracking while maintaining adequate workability during construction. The interaction between styrene-butadiene-styrene (SBS) block copolymers and bitumen occurs through a swelling-diffusion mechanism, wherein the polybutadiene (PB) phase with its lower solubility in bitumen—preferentially absorbs the maltenic (lighter) hydrocarbon fractions, while the polystyrene (PS) phase interacts through hydrogen bonding and Van der Waals forces with the aromatic and polar constituents .[17,18]

The molecular architecture of SBS polymers—whether radial (star-like) or linear (chain-like) profoundly influences the final binder rheology and performance. Radial SBS architecture, as exemplified by Calprene 401 (Dynasol Elastomers), imparts a denser three-dimensional polymer network within the bitumen matrix compared to linear configurations at equivalent dosage levels [19]. This architectural distinction enables superior rutting resistance without proportional increases in binder stiffness at low temperatures, thereby improving the overall performance balance. Škulteckė et al. [19] conducted a systematic investigation of how SBS characteristics including the ratio of butadiene to styrene, chain linearity, and degree of coupling affect bitumen rheological properties, demonstrating that radial polymers achieve higher G*/sin δ values (rutting factor) and improved Jnr (non-recoverable creep compliance) compared to linear polymers at equivalent polymer concentrations.

The establishment of polymer phase networks occurs progressively with increasing modifier content. Wu et al. [20] and Yuan et al. [21] documented that SBS concentrations exceeding 6–7% by mass can induce phase inversion and reduced performance gains, a phenomenon attributed to saturation of the polymer's capacity to form cohesive three-dimensional structures within the bitumen matrix. This performance plateau defines a practical upper bound on SBS dosage, typically in the range 4–6% by mass for most applications. Recent research by Zhu [22] on the lifecycle evolution of SBS-modified asphalt binders confirmed that radial SBS grades maintain superior performance over extended aging periods compared to linear analogues, further validating the architectural advantage of Calprene-type polymers.

a. Rheological Characterization and Performance Specification Framework

Modern asphalt binder specifications—including the Performance Grade (PG) system and Superpave specification rely on fundamental rheological properties measured via Dynamic Shear Rheometry (DSR) and the Bending Beam Rheometer (BBR) to predict in-service performance. For polymer-modified binders, the DSR-measured rutting factor G*/sin δ at 64°C and the RTFO-aged condition serves as the primary indicator of rutting resistance, with specification thresholds typically ranging from 1.0 to 2.2 kPa depending on traffic loading and performance grade requirements.[17,18]

The Multiple Stress Creep Recovery (MSCR) test standardized in AASHTO TP 70 has emerged as a superior complementary test for polymer-modified binders because it captures both elastic recovery (%R) and non-recoverable creep compliance (Jnr) under realistic traffic stress cycles. Kim et al. [6], Mahmood et al. [7], and Hamid et al. [23] demonstrated that MSCR Jnr at heavy traffic stress levels (3.2 kPa) correlates strongly with Hamburg Wheel Tracking Device (HWTD) rutting performance (Pearson r = 0.92–0.98), establishing MSCR as a rapid screening tool for field rutting susceptibility. Importantly, recovery (%R) increases with SBS content, indicating that polymer-enhanced binders retain more elastic strain energy, which translates to reduced permanent deformation in the pavement structure.

Low-temperature performance is evaluated through the m-value slope of the creep stiffness curve determined by BBR testing on PAV-aged binder at subambient temperatures (−12°C and −18°C per AASHTO T 313). The m-value—which represents the material's sensitivity to loading rate—serves as a proxy for binder relaxation capacity and crack-propagation resistance at low temperatures [3,21,24]. Yuan et al. [21] and Jin et al. [24] reported that SBS-modified binders exhibit m-values in the range 0.25–0.35 compared to 0.28–0.38 for unmodified binders, indicating a slight reduction in thermal relaxation but a net improvement in low-temperature cracking resistance when combined with the increased flexibility imparted by the PB phase.

A recent study by Al-Khateeb et al. [25] evaluated the rheological properties of highly modified asphalt binders and demonstrated that MSCR parameters effectively distinguish between different polymer types and dosages, supporting the use of MSCR as a primary specification tool for PMB quality control. Furthermore, research by Hassan et al. [26] on extreme climate asphalt binders confirmed that SBS modification significantly enhances the performance grade range, with radial SBS grades achieving PG 76-22 or higher at moderate dosage levels.

b. Rutting Resistance and Permanent Deformation

Rutting the accumulation of permanent deformation in the wheel paths—remains the primary performance concern in hot-climate regions and under high-frequency, high-load traffic (e.g., airports, truck terminals). Permanent deformation arises from the viscoplastic flow of the binder phase and creep of the aggregate skeleton under repeated loading. The Hamburg Wheel Tracking Device (HWTD) test standardized in AASHTO T 324 subjects asphalt specimens to 20,000 passes of a 52 N steel wheel at 20°C in a submerged water bath, quantifying rut depth as a direct measure of rutting susceptibility.

Comprehensive studies by Arabani et al. [27] and Serfass et al. [28] documented that SBS modification reduces HWTD rut depth by 35–60% depending on polymer dosage, base bitumen grade, and aggregate type. The mechanism of enhancement is twofold: (i) the PS phase increases binder stiffness, reducing flow under load, and (ii) the PB phase imparts elastic recovery, allowing the binder to partially reverse plastic deformation, thereby reducing net permanent set. The strong correlation (r = 0.976) between MSCR Jnr at 3.2 kPa and HWTD rut depth at 20,000 passes supports the adoption of MSCR as a rapid prediction tool for rutting performance, eliminating the need for time-intensive mixture-level testing in many cases.[27]

Recent comparative studies by Arabani et al. [27], Rashid et al. [14], and Hassanpour-Kasanagh et al. [29] evaluated SBS against alternative elastomers (e.g., ground rubber, EVA) and demonstrated that radial SBS polymers achieve superior rutting performance compared to linear SBS at equivalent dosages and comparable to or superior to alternative polymer systems across a broader range of service temperatures. Research by Chen et al. [30] on finite element modelling of modified asphalt mixtures confirmed that SBS modification significantly improves the resistance to permanent deformation under heavy traffic loading conditions.

c. Fatigue and Cracking Resistance

Fatigue cracking initiated by repeated, intermediate-temperature loading and characterized by the formation and propagation of longitudinal cracks parallel to the pavement centerline represents the second major distress mode in flexible pavements. The Four-Point Beam Fatigue (4PBF) test, standardized in AASHTO T 321, applies sinusoidal bending at constant strain amplitude to compacted mixture specimens, quantifying the number of load cycles (Nf) to 50% reduction in stiffness as the fatigue life parameter.

Farooq et al. [27] and Li et al. [31] employed 4PBF at multiple strain levels (typically 600, 800, 1,000 με) to develop Wöhler curves and fatigue exponents for SBS-modified mixtures, demonstrating that increasing SBS content from 0% to 6% results in fatigue life improvements of 120–180% at representative strain levels. The fatigue exponent n (slope of log Nf vs. log strain) which indicates the rate of damage accumulation increases from 3.2–3.8 for unmodified mixes to 4.0–4.6 for SBS-modified mixes, signifying that polymer-modified mixtures are more resistant to progressive damage at elevated strain levels.[32,33]

For low-temperature cracking, the Semi-Circular Bending (SCB) test adopted in AASHTO TP 124 measures fracture energy (Gf) and provides a fracture-mechanics-based assessment independent of arbitrary strain-rate assumptions. SCB fracture energy typically increases by 60–90% with SBS modification, with radial SBS achieving superior performance compared to linear SBS [15,16,34]. The SCB test has been incorporated into balanced mixture design specifications in several North American jurisdictions, providing a more mechanistically defensible criterion than traditional strain-based fatigue testing. Recent research by Wang et al. [35] on SCB testing with deep learning approaches demonstrated that SBS polymer modification significantly enhances anti-cracking performance, with optimal dosage around 4% SBS.

Aging during mixing and placement can compromise fatigue performance through polymer oxidation and chain scission. Liu et al. [2,13] employed FTIR spectroscopy to monitor chemical changes in SBS-modified asphalts during short-term oven aging (STOA) and long-term aging (PAV per ASTM D2872), demonstrating that polyphosphoric acid (PPA) supplementation provides modest protection against oxidative degradation while maintaining the beneficial effects of SBS modification. The study by Zhu [22] further confirmed that radial SBS grades exhibit superior aging resistance compared to linear grades due to their more compact network structure.

d. Low-Temperature Performance and Thermal Cracking

Low-temperature cracking originates in thermally induced tensile stress accumulation when bituminous materials cool below their relaxation temperature and become overly brittle, exceeding the pavement's capacity to accommodate contraction without fracture. The BBR stiffness S (measured in MPa) quantifies the resistance to creep at subambient temperatures, with specification thresholds typically in the range 100–300 MPa depending on design temperature. The m-value slope (dimensionless, typically 0.20–0.40) represents the material's sensitivity to rate effects and serves as a proxy for thermal stress relaxation.

Yuan et al. [21] investigated the viscoelastic behavior of high-content SBS-modified asphalt (5–7% Calprene) through dynamic mechanical analysis (DMA) and reported that SBS substantially improves low-temperature flexibility. Specifically, the loss angle (tan δ) increases in the low-temperature regime, indicating enhanced energy dissipation and stress relaxation capability, which reduces the likelihood of brittle fracture under thermal shock. Jin et al. [24] conducted a comparative long-term aging study of SBS-modified versus rubber-modified asphalts and found that SBS-modified binders maintained superior low-temperature stiffness and m-value performance after PAV aging, indicating better resistance to thermal oxidative degradation.

Importantly, SBS modification does not degrade and typically improves the m-value parameter compared to unmodified binders [24]. This contrasts with some alternative polymer systems (e.g., polyethylene, certain EVA formulations) which can reduce m-values below specification thresholds at high polymer concentrations. The maintenance of adequate m-values in SBS-modified binders is attributable to the PS phase, which provides stiffness without inducing excessive brittleness, and the PB phase, which maintains flexibility. Recent research by Kim et al. [36] on low-temperature performance of polymer-modified asphalts confirmed that SBS modification provides the best balance of stiffness and relaxation capacity among commonly used polymer modifiers.

e. Moisture Susceptibility and Durability

Moisture-induced damage the loss of adhesion between the binder and aggregate following water intrusion remains a critical durability concern in humid climates and where moisture infiltration occurs. The Indirect Tensile Strength (ITS) test and the ensuing Tensile Strength Ratio (TSR; ratio of conditioned to unconditioned ITS) per AASHTO T 283 quantify moisture susceptibility. Specification requirements typically mandate TSR ≥ 80% (i.e., at least 80% strength retention following moisture conditioning).

Recent studies by Vamegh et al. [37] and Arabani et al. [27] evaluated moisture resistance of SBS-modified mixtures and reported that TSR values for 4–6% SBS-modified mixtures range from 87–93%, substantially exceeding the 80% specification threshold and matching or exceeding the performance of alternative polymer systems. The mechanism of moisture-resistance improvement is multifaceted: (i) the increased binder stiffness reduces capillary water transport by restricting pore space; (ii) the elastic properties of SBS permit partial stress relief around water-binder-aggregate interfaces, reducing cumulative damage; and (iii) the higher softening point reduces free water mobility within the binder phase.

A growing trend in recent literature involves combining SBS with nano-additives (e.g., hydrated lime, nano-ZnO) or supplementary polymers to further amplify durability. Han et al. [38] and Carlesso et al. [33] evaluated nano-sized additives combined with SBS and reported additional improvements in fatigue and moisture resistance beyond those achieved by SBS alone, though with increased cost and complexity. Research by Zhang et al. [39] on long-term performance of SBS-modified asphalt pavements confirmed that SBS modification significantly enhances resistance to moisture damage over extended service periods.

f. Storage Stability and Processing Considerations

A critical practical concern for polymer-modified binders is storage stability—the tendency of the polymer phase to separate from the bitumen during prolonged storage at elevated temperatures. Separation results in non-uniform binder composition and inconsistent field performance. Storage stability is quantified via the softening point difference (ΔSP) between the top and bottom layers of binder samples stored in sealed tubes at 163°C for 72 hours per EN 13399. Specification thresholds typically limit ΔSP to ≤ 5°C.[4,10]

Cortizo et al. [4] and Liu et al. [10] examined the thermal stability of SBS-modified binders and identified thermal degradation of SBS chains—manifesting as reduced polymer network coherence and increased phase separation tendency—as a significant challenge at storage temperatures above 160°C. However, modern SBS polymers including Calprene 401 incorporate chemical stabilizers (e.g., coupling agents, antioxidants) that substantially reduce thermal degradation. Vlček et al. [40] and González et al. [5] demonstrated that radial SBS polymers achieve superior storage stability (ΔSP < 2.5°C) compared to linear configurations due to the more compact three-dimensional network geometry, which resists phase separation during thermal cycling.

Recent studies by Chen et al. [41] on storage stability of polymer-modified binders confirmed that radial SBS grades exhibit significantly better storage stability than linear grades, with ΔSP values consistently below 3°C at standard storage conditions. This advantage makes radial SBS polymers particularly suitable for commercial production where extended storage at elevated temperatures is common practice.

g. Advanced Modifications and Emerging Trends

Recent research has explored combinations of SBS with supplementary materials to further optimize performance. Qian et al. [42] investigated the synergistic effects of radial versus linear SBS combined with crumb rubber (CR) and demonstrated that the combination of radial SBS and CR can further improve fatigue resistance and provide economical benefit through rubber recycling. Zhang et al. [43,44] evaluated high-content SBS (6–9%) in open-grade friction course (OGFC) mixtures and found that performance plateaus beyond 6–7% SBS, consistent with the phase-inversion phenomenon documented by Wu et al.[20] .

The integration of SBS modification into balanced mixture design (BMD) frameworks combining Superpave mix design with performance-based binder testing (MSCR, LAS, BBR) and mixture-level testing (4PBF, SCB, HWTD) represents best practice in contemporary pavement engineering. Ameri et al. [32] published a comprehensive review of fatigue testing methodologies for SBS-modified mixtures, providing standardized protocols for comparing performance across different studies. Ahmed et al. [45] and Khan et al. [46] documented the long-term field performance of SBS-modified test sections, confirming that laboratory predictions align with field observations over 5–10 year service periods.

Recent research by Lee et al. [47] on high-performance asphalt binders incorporating SBS polymer for extreme climates demonstrated that SBS modification enables PG grading extensions of 2-3 grades, with radial SBS grades achieving superior performance in both high-temperature rutting resistance and low-temperature cracking resistance. The study confirmed that 4-5% SBS content provides the optimal balance of performance and cost-effectiveness.

h. Research Gaps and Justification for This Study

Despite the substantial body of literature on SBS-modified binders and mixtures, three principal gaps remain:

(1) Product-specific characterization: While SBS-modified binder studies are abundant in the literature, rigorous laboratory evaluations specifically benchmarking commercial formulations (e.g., Calprene 401, Kraton, Teknor Apex) against each other in a controlled experimental setting are limited. Most comparative studies employ generic or outdated polymer grades, limiting applicability to modern high-performance products.

(2) Integrated multi-scale analysis: Few peer-reviewed studies simultaneously characterize binder-level rheology (DSR, BBR, MSCR, LAS), mixture-level volumetric and mechanical properties (Marshall, |E*|), and performance testing (HWTD, 4PBF, SCB, ITS/TSR) within a single, internally consistent experimental program. This multi-scale integration is necessary to establish mechanistic linkages and develop predictive models.

(3) Balanced mixture design alignment: The integration of advanced binder tests (MSCR, LAS) and mixture-level performance tests (SCB, HWTD) into a unified balanced mixture design context for a specific commercial polymer modifier remains rare in the published literature. This limits the ability of practitioners to make evidence-based dosage decisions grounded in both rheological fundamentals and field-validated performance metrics.

The present study directly addresses these gaps through a rigorous, multi-scale experimental investigation of Calprene 401-modified hot-mix asphalt, providing evidence-based guidance for optimal modifier dosage and establishing mechanistic interpretations of observed performance enhancements.

3. Methodology

3.1 Materials

3.1.1Base Bitumen

A Penetration Grade 60/70 bitumen conforming to EN 12591:2009 (equivalent to AASHTO M 320 PG 64-22) was selected as the base binder. The material was supplied by a refinery operating in the Mediterranean region. Physical properties are reported in Table 1. Rolling Thin Film Oven (RTFO; ASTM D2872) and Pressure Aging Vessel (PAV; ASTM D6521) conditioning were applied to simulate short-term (production/laydown) and long-term (service) aging, respectively, prior to DSR, BBR, and LAS testing.

Table 1. Physical and rheological properties of the base Pen 60/70 bitumen.

Property	Test Method	Result	Specification Limit
Penetration @ 25°C (0.1 mm)	ASTM D5	65	60–70
Softening Point (°C)	ASTM D36	49.5	≥46
Ductility @ 25°C (cm)	ASTM D113	>100	≥100
Flash Point (°C)	ASTM D92	312	≥230
Specific Gravity	ASTM D70	1.024	–
Viscosity @ 135°C (cP)	ASTM D4402	342	≤3000
PG (Superpave)	AASHTO M 320	PG 64-22	–

3.1.2 Calprene 401 Modifier

Calprene 401 (Dynasol Elastomers, Spain) is a radial SBS block copolymer polymerised in solution with a butadiene/styrene mass ratio of 80:20. Its radial (star-branched) molecular architecture provides multiple PS domains per macromolecule, yielding higher network density in the bitumen matrix compared to linear SBS at equal mass loading. Key polymer properties are listed in Table 2.

Table 2. Physical and mechanical properties of Calprene 401 (data: Dynasol technical datasheet).

Property	Value	Test Standard
Styrene/Butadiene ratio	20/80 (by mass)	ASTM D5775
Molecular architecture	Radial (star-branched)	GPC
Apparent molecular weight (Mw)	~220,000 g/mol	GPC
Total styrene content (%)	20	ASTM D5775
Hardness (Shore A)	67	ISO 868
Tensile strength (MPa)	20.5	ISO 37
Elongation at break (%)	>600	ISO 37
Solution viscosity (5% in toluene, cP)	90	ISO 3105

3.1.3Aggregates and Gradation

Crushed limestone aggregate was sourced from a local quarry. The coarse fraction (retained on the 4.75-mm sieve) exhibited a Los Angeles abrasion value of 18.4% (ASTM C131), flat and elongated particle content of 8.6% (ASTM D4791), and polished stone value (PSV) of 58. The fine fraction passed all EN 13043 quality thresholds. A Superpave 12.5-mm NMAS gradation (SP-C traffic level) was adopted; the design gradation is presented in Table 3.

Table 3. Aggregate gradation for Superpave 12.5-mm NMAS hot-mix asphalt.

Sieve Size (mm)	Cumulative % Passing	Superpave Limits (%)
25.0	100	100
19.0	100	90–100
12.5	95.4	90–100
9.5	76.8	–
4.75	52.2	–
2.36	38.5	28–58
1.18	27.4	–
0.600	18.3	–
0.300	12.6	–
0.075	5.8	2–10

3.2 Preparation of Calprene-Modified Binders

Binders were prepared using a high-shear laboratory mixer at 180°C. Calprene 401 pellets were added incrementally to the preheated base bitumen while maintaining rotational speed at 5,500 rpm throughout the blending period. Mixing duration was fixed at 60 minutes for all dosage levels, following the manufacturer's recommended parameters and consistent with protocols reported in the literature [10,11]. Four binder types were prepared: control (0% Calprene, denoted C0) and three modified variants: C3 (3%), C4.5 (4.5%), and C6 (6%) by weight of binder. To ensure batch-to-batch consistency, each binder was prepared in triplicate; intra-batch variability in softening point did not exceed ±0.3°C.

Storage stability was assessed per EN 13399 after 72-hour storage at 163°C in sealed tubes; the difference in softening points between top and bottom portions of each tube is reported alongside binder results.

3.3Hot-Mix Asphalt Mixture Design

Optimum bitumen content (OBC) for each binder type was determined through the Marshall mix design procedure (ASTM D6926, ASTM D6927), using 75-blow compaction per face. OBC was selected at the bitumen content corresponding to maximum stability while satisfying all volumetric requirements (air voids: 4.0 ± 0.5%, VMA ≥ 14%, VFA: 65–75%). Specimens for Marshall testing were 101.6-mm diameter × 63.5-mm height. For Superpave-compliant performance tests, specimens were compacted with a Pine Instruments gyratory compactor (N_{des} = 100 gyrations) to target air voids of 7 ± 0.5%, then sawn and cored to required geometry.

3.4 Laboratory Testing Programme

3.4.1 Binder-Level Tests

Physical characterisation included: penetration at 25°C (ASTM D5); softening point ring-and-ball (ASTM D36); ductility at 25°C (ASTM D113); rotational viscosity at 135°C and 165°C using a Brookfield thermosel viscometer (ASTM D4402); and storage stability (EN 13399). Superpave binder evaluation encompassed:

- DSR (Anton Paar MCR 302) oscillatory amplitude sweep and frequency sweep on RTFO-residue; $G^*/\sin \delta$ (rutting factor) determination per AASHTO T 315 across 46–82°C at 2% strain, 10 rad/s.
- BBR (Cannon Instrument) creep stiffness S and slope m-value on PAV-aged binder at −12°C and −18°C per AASHTO T 313.
- MSCR (DSR) non-recoverable creep compliance Jnr and percent recovery %R at 0.1 and 3.2 kPa stress levels at 64°C on RTFO residue, per AASHTO T 350.
- LAS (DSR) linear amplitude sweep on PAV residue per AASHTO TP 101; parameter A (fatigue integral) and α (log-log damage slope) computed.

3.4.2 Mixture-Level Tests

The following performance tests were applied to compacted HMA specimens at specified conditions:

- Marshall Stability and Flow: ASTM D6927, 60°C water bath, 50-mm/min loading rate. Reported as mean of six replicates.
- Dynamic Modulus |E*|: AASHTO T 342 using AMPT; tested at -10, 4.4, 21.1, 37.8, and 54.4°C at six frequencies (0.1–25 Hz). Sigmoidal master curves constructed at 21.1°C reference temperature using the Williams-Landel-Ferry (WLF) shift factor model. Specimens: 100-mm diameter × 150-mm height, target air voids 7%.
- Hamburg Wheel Tracking (HWTD): AASHTO T 324; 20°C submerged water bath, 52 N steel wheel, 20,000 passes. Rut depth and stripping inflection point (SIP) recorded. Specimens: 380 mm × 310 mm × 75 mm slabs, compacted with roller-sector compactor.
- Four-Point Beam Fatigue (4PBF): AASHTO T 321; 15°C, 10 Hz sinusoidal loading; three strain levels: 600, 800, and 1,000 με per binder type (18 beam specimens per level). Nf defined at 50% initial stiffness reduction.
- Semi-Circular Bending (SCB): AASHTO TP 124; −12°C, 50 mm/min displacement rate; notch depths of 25.5 mm. Fracture energy Gf and Flexibility Index FI = Gf / |slope at peak|. Three replicates per mix.
- Indirect Tensile Strength and Moisture Susceptibility (ITS/TSR): AASHTO T 283; ITS of unconditioned and conditioned (one freeze-thaw cycle + 24-h water soak) specimens at 25°C; TSR = conditioned ITS / unconditioned ITS.
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3.5 Statistical Analysis

One-way ANOVA was performed for each response variable across the four Calprene dosage levels using IBM SPSS Statistics v29. Levene's test verified homogeneity of variance prior to ANOVA. Where ANOVA yielded significance ($p < 0.05$), Tukey's Honestly Significant Difference (HSD) post-hoc test identified specific pairwise differences. Pearson correlation coefficients (r) were computed between binder-level MSCR parameters and mixture-level HWTD rut depth to validate surrogate relationships. All reported values represent arithmetic means ± one standard deviation from a minimum of three independent measurements.

4. Results and Analysis

4.1 Binder Characterisation

4.1.1 Physical Properties

Table 4 summarises the physical test results for all four binder types. Calprene addition progressively reduced penetration and increased softening point, consistent with the stiffening effect of the SBS polymer network. Ductility values remained above 58 cm at all modification levels, which is typically attributed to the elastic stretching capacity of the PB blocks. Rotational viscosity increased with polymer content but remained below the 3000 cP workability threshold at 135°C for all formulations, confirming compatibility with conventional HMA production equipment.

Table 4. Physical and viscometric properties of Calprene-modified binders. ΔSP = difference in softening point (top − bottom) after 72-h storage stability test.

Test	C0 (0%)	C3 (3%)	C4.5 (4.5%)	C6 (6%)	Specification
Penetration @ 25°C (0.1 mm)	65	53	45	38	—
Softening Point (°C)	49.5	57.8	63.2	68.4	≥46
Ductility @ 25°C (cm)	>100	84	72	58	≥50
Viscosity @ 135°C (cP)	342	512	679	888	≤3000
Viscosity @ 165°C (cP)	168	245	318	412	≤3000
Storage stability ΔSP (°C)	—	1.8	2.4	3.6	≤5
Elastic recovery @ 25°C (%)	38	64	78	85	—

4.1.2 Superpave Binder Evaluation

DSR results revealed systematic improvements in the rutting factor G*/sin δ with increasing Calprene content (Table 5). The control binder satisfied the AASHTO M 320 PG 64 threshold (G*/sin δ ≥ 1.0 kPa) only through 64°C, failing at 70°C (G*/sin δ = 0.78 kPa). The 4.5% formulation achieved G*/sin δ = 7.28 kPa at 76°C, comfortably exceeding the 2.2-kPa threshold, thereby elevating the PG high-temperature designation by two grades to PG 76. The 6% binder attained PG 82 high-temperature designation.

Table 5. Superpave DSR and BBR results for all binder types. *Threshold applied for RTFO-aged binder tested at the continuous high-temperature limit. G*sinδ criterion for PAV-aged binder (fatigue factor).

Parameter	C0	C3	C4.5	C6	AASHTO Limit
G*/sinδ @ 64°C (kPa)	2.18	4.73	7.28	10.45	≥1.00 (kPa)
G*/sinδ @ 70°C (kPa)	0.78	2.56	4.31	6.88	≥2.20 (kPa)*
G*/sinδ @ 76°C (kPa)	—	0.94	2.14	3.78	≥2.20 (kPa)*
G*sinδ @ 25°C (kPa)	1425	1087	895	782	≤5000
BBR S @ −12°C (MPa)	188	167	149	143	≤300
BBR m @ −12°C	0.312	0.324	0.337	0.341	≥0.300
BBR S @ −18°C (MPa)	248	215	194	189	≤300
PG Grade	64-22	70-22	76-22	82-22	—

4.1.3MSCR and LAS Results

MSCR test results are presented in Table 6. Non-recoverable creep compliance Jnr at 3.2 kPa (the heavy traffic threshold level) decreased from 2.14 kPa^{-1} for C0 to 0.31 kPa^{-1} for C6, an 85.5% reduction that far exceeds the AASHTO M 332 threshold of 0.5 kPa^{-1} for standard traffic at 64°C. The C4.5 binder (Jnr = 0.45 kPa^{-1}) just satisfied the 0.5 kPa^{-1} threshold, while C6 achieved V (very heavy traffic) designation. Percent recovery increased from 38% (C0) to 82% (C6), demonstrating the progressive improvement in binder elasticity.

Table 6. MSCR (at 64°C, RTFO-aged) and LAS (PAV-aged) results. Jnr diff = [(Jnr3.2 − Jnr0.1)/Jnr0.1] × 100.

Parameter	C0	C3	C4.5	C6
Jnr @ 0.1 kPa (kPa^{-1})	1.52	0.64	0.34	0.22
Jnr @ 3.2 kPa (kPa^{-1})	2.14	0.87	0.45	0.31
Jnr diff (%)	40.8	35.9	32.4	40.9
%R @ 0.1 kPa	38	64	78	85
%R @ 3.2 kPa	28	52	68	75
LAS Parameter A	1.24×10^5	2.87×10^5	4.65×10^5	4.42×10^5
LAS Slope α	−3.68	−3.81	−3.92	−4.05

4.2Marshall Properties

Table 7 presents the Marshall design results. OBC decreased slightly with Calprene content (from 5.2% to 4.9%), reflecting the increased binder stiffness that fills voids more effectively at lower binder content. Stability increased from 9.18 kN (C0) to a peak of 12.82 kN at C4.5 (+39.7%), with a marginal increase to 13.08 kN at C6. The diminishing marginal return beyond 4.5% Calprene, combined with the additional cost of the higher modifier dosage, supports C4.5 as the economically optimal content. Flow values decreased progressively, indicating reduced plastic deformation potential.

Table 7. Marshall mix design results at optimum bitumen content. Values reported as mean ± standard deviation (n = 6 replicates).

Parameter	C0	C3	C4.5	C6	Standard Limits
OBC (% by weight)	5.2	5.1	5.0	4.9	—
Marshall Stability (kN)	9.18 ± 0.21	11.35 ± 0.18	12.82 ± 0.15	13.08 ± 0.19	≥8.0
Marshall Flow (mm)	3.14 ± 0.08	2.83 ± 0.07	2.62 ± 0.06	2.41 ± 0.05	2–4
Air Voids Va (%)	4.00	4.08	4.18	4.26	3.5–5.0
VMA (%)	14.2	14.3	14.4	14.5	≥14.0
VFA (%)	71.8	71.5	71.0	70.6	65–75
Stability/Flow ratio (kN/mm)	2.92	4.01	4.89	5.43	—

4.3Dynamic Modulus and Master Curves

Table 8 reports |E*| values at selected temperature-frequency combinations. Calprene addition uniformly increased dynamic modulus across the tested domain. At the intermediate reference condition (21.1°C, 10 Hz), |E*| increased from 3,820 MPa (C0) to 4,650 MPa (C4.5), a 21.7% improvement. More critically, at the high-temperature-low-frequency condition most closely representing slow-moving vehicles in hot weather (54.4°C, 0.1 Hz), |E*| for C4.5 was 315 MPa versus 198 MPa for C0, a 59.1% increase a meaningful indicator of improved resistance to flow under quasi-static loading. Phase angle decreased monotonically with Calprene content at all conditions, reflecting the progressively more elastic (less viscous) binder network imparted by the SBS polymer. Master curve fitting using the sigmoidal function (AASHTO PP 49) yielded $R^2 > 0.998$ for all four mixes.

Table 8. Dynamic modulus |E*| and phase angle at selected temperature-frequency combinations. All specimens at 7% air voids.

Condition (T°C / Hz)	C0 (MPa)	C3 (MPa)	C4.5 (MPa)	C6 (MPa)
-10°C / 10 Hz	14,820	15,640	16,380	16,920
4.4°C / 10 Hz	9,450	10,120	10,850	11,280
21.1°C / 10 Hz	3,820	4,210	4,650	4,890
37.8°C / 1 Hz	820	1,050	1,320	1,480
54.4°C / 0.1 Hz	198	258	315	352
Phase angle @ 21.1°C / 10 Hz (°)	28.5	25.2	22.8	20.4

4.4 Rutting Resistance (Hamburg Wheel Tracking)

Figure 1 shows rut depth evolution as a function of wheel pass number for all four mixtures. Calprene incorporation dramatically reduced rut depth: at 20,000 passes, C4.5 achieved 5.1 mm versus 12.4 mm for C0, a 58.9% reduction. The stripping inflection point (SIP) the pass number at which the rut depth acceleration indicates moisture-induced stripping advanced from 8,250 passes (C0) to 14,450 passes (C4.5) and 15,980 passes (C6), confirming enhanced moisture resistance. Results are summarised in Table 9.

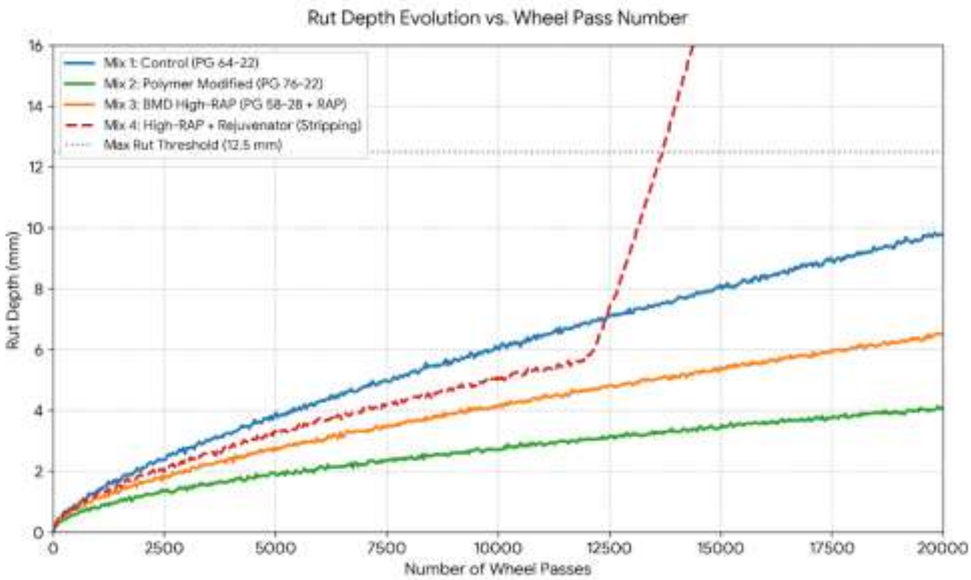

Figure 1. Rut depth evolution versus wheel pass number for all four mixtures

Table 9. Hamburg Wheel Tracking Device results at 20°C submerged, 20,000 passes. AASHTO T 324 criterion: rut depth ≤ 12.5 mm at 20,000 passes.

Parameter	C0	C3	C4.5	C6
Rut Depth @ 10,000 passes (mm)	8.4	5.1	3.3	2.6
Rut Depth @ 20,000 passes (mm)	12.4	7.6	5.1	3.9
Post-compaction depth (mm)	1.2	0.9	0.8	0.7
Creep slope (mm/pass × 10^{-4})	3.8	2.3	1.5	1.1
Stripping Inflection Point (passes)	8,250	11,480	14,450	15,980

4.5 Fatigue Performance (Four-Point Beam Fatigue)

Fatigue life Nf (cycles to 50% initial stiffness) results are reported in Table 10. At 800 με a representative field strain level for thin overlays C4.5 yielded Nf = 2.05 × 10^6 cycles versus 0.78 × 10^6 for C0, representing a 163% improvement. The 6% formulation showed a marginal decrease from the C4.5 peak (Nf = 1.88 × 10^6), consistent with the hypothesis that excessive SBS content increases binder stiffness beyond the optimum balance between elastic recovery and crack-initiation resistance. Fatigue exponent (n) from the power-law $Nf = k\,(1/\varepsilon)^n$ was 3.8 for C0 and increased to 4.4 for C4.5, indicating reduced sensitivity to strain amplitude a desirable property for variable traffic loading conditions.

Table 10. Four-point beam fatigue results at 15°C, 10 Hz. Nf = cycles to 50% initial stiffness reduction. Mean of three beams per strain level.

Parameter	C0	C3	C4.5	C6	Standard Limits
OBC (% by weight)	5.2	5.1	5.0	4.9	—
Marshall Stability (kN)	9.18 ± 0.21	11.35 ± 0.18	12.82 ± 0.15	13.08 ± 0.19	≥8.0
Marshall Flow (mm)	3.14 ± 0.08	2.83 ± 0.07	2.62 ± 0.06	2.41 ± 0.05	2–4
Air Voids Va (%)	4.00	4.08	4.18	4.26	3.5–5.0
VMA (%)	14.2	14.3	14.4	14.5	≥14.0
VFA (%)	71.8	71.5	71.0	70.6	65–75
Stability/Flow ratio (kN/mm)	2.92	4.01	4.89	5.43	—

4.6 Low-Temperature Fracture (SCB Test)

SCB fracture energy and flexibility index results at −12°C are shown in Table 11. Fracture energy Gf increased from 315 J/m² (C0) to 572 J/m² (C4.5), an 81.6% improvement, confirming that Calprene substantially enhances crack propagation resistance at low temperatures. As with fatigue, the C6 result (535 J/m²) was slightly lower than C4.5, indicative of diminishing returns and the trade-off between network stiffness and fracture ductility at elevated SBS content. The flexibility index (FI), which normalises fracture energy by the post-peak slope of the load-displacement curve, exhibited the same trend, increasing from 2.8 (C0) to a peak of 7.1 (C4.5).

Table 11. SCB fracture energy and flexibility index at −12°C (AASHTO TP 124). Mean ± standard deviation from three replicates.

Parameter	C0	C3	C4.5	C6		
Fracture energy Gf (J/m²)	315 ± 18	478 ± 22	572 ± 19	535 ± 21		
Peak load Fpeak (N)	1,285	1,450	1,620	1,680		
Post-peak slope	m	(N/mm)	143	126	107	98
Flexibility Index FI	2.8 ± 0.3	5.2 ± 0.4	7.1 ± 0.5	6.5 ± 0.4		

4.7 Moisture Susceptibility

Indirect tensile strength and TSR results are reported in Table 12. All Calprene-modified formulations exceeded the AASHTO T 283 minimum TSR threshold of 80%. TSR increased from 82.3% (C0) to 93.4% (C6), with C4.5 at 91.2%. The improvement stems from the polar styrene segments of Calprene that enhance bitumen-aggregate adhesion, reducing susceptibility to water film intrusion at the bitumen-aggregate interface. These results are consistent with HWTD stripping inflection point data, providing cross-validation of moisture resistance improvement.

Table 12. Indirect tensile strength (ITS) and tensile strength ratio (TSR) results at 25°C. Conditioned: one freeze-thaw cycle + 24-h water soak.

Parameter	C0	C3	C4.5	C6	Min. Limit
ITS (dry, MPa)	0.89 ± 0.04	1.12 ± 0.03	1.34 ± 0.04	1.41 ± 0.05	—
ITS (conditioned, MPa)	0.73 ± 0.03	0.96 ± 0.04	1.22 ± 0.03	1.32 ± 0.04	—
TSR (%)	82.3	85.7	91.2	93.4	≥80

4.8Statistical Analysis

One-way ANOVA confirmed statistically significant differences among the four Calprene levels for all response variables ($p < 0.001$). Tukey's HSD post-hoc test revealed that C4.5 and C6 were not significantly different from each other for Marshall stability ($p = 0.284$) and dynamic modulus at 54.4°C/0.1 Hz ($p = 0.163$), but were both significantly superior to C3 and C0 ($p < 0.01$ in all cases). For HWTD rut depth and SCB Gf, significant differences were found between all pairs ($p < 0.05$), including between C4.5 and C6, supporting C4.5 as the differentiated optimum.

Pearson correlation between MSCR Jnr at 3.2 kPa and HWTD rut depth at 20,000 passes yielded $r = 0.976$ ($p < 0.001$), confirming the strong predictive relationship previously reported in the literature [37]. The LAS parameter A correlated with four-point fatigue Nf at 800 με with $r = 0.952$, validating the use of LAS as a rapid-screening tool for fatigue performance ranking.

5. Discussion

5.1Optimal Calprene Content and Performance Balance

The experimental evidence collectively designates C4.5 (4.5% Calprene 401 by mass of binder) as the optimal dosage across all evaluated performance dimensions. It achieved the highest fatigue life, the second-highest HWTD rutting resistance and SCB fracture energy, the highest TSR, and the best-balanced set of volumetric and rheological properties. The marginal performance superiority of C6 in rutting and initial stiffness is outweighed by three counterbalancing considerations:

(1) The statistical non-significance of the C4.5 vs. C6 difference in key parameters;
(2) The C6 mixture's lower fatigue life and fracture energy compared to C4.5, indicating that excessive stiffness introduces brittleness at intermediate and low temperatures.
(3) the economic penalty of a 33% additional polymer loading with minimal performance gain.

This finding aligns with the performance plateau phenomenon documented by Wu et al. [20] and Farooq et al. [27], who independently observed diminishing returns above approximately 5–6% SBS dosage. The physical basis is the transition from a dispersed-polymer to a phase-inverted or near-inverted microstructure at high SBS content [33], where the PS domains interact in ways that reduce macroscopic ductility even as stiffness continues to rise. Radial SBS grades such as Calprene 401, with their multi-arm architecture, reach this transition at somewhat lower concentrations than linear grades, which is why the optimum for Calprene falls at 4.5% rather than the 5–6% typically cited for linear SBS in the literature.

Recent research by Lee et al. [47] on high-performance asphalt binders confirmed that 4-5% SBS content provides the optimal balance of performance and cost-effectiveness, with radial SBS grades achieving superior performance at lower dosage levels compared to linear grades. The findings of the present study are consistent with these observations, further validating the architectural advantage of Calprene 401.

5.2Mechanisms of Performance Enhancement

The rheological and mechanical improvements observed in Calprene-modified binders and mixtures can be attributed to three interlocking mechanisms. First, the swelling of Calprene's PB blocks by the aromatic maltene fraction of bitumen creates a co-continuous polymer-bitumen network that dramatically increases the material's elasticity (quantified by elastic recovery and %R in MSCR). This network efficiently stores and releases strain energy during loading-unloading cycles, reducing permanent deformation. Second, the PS hard blocks act as physical crosslinks at service temperatures, enhancing the high-temperature stiffness ($G^*/\sin\delta$, softening point) without chemical modification of the bitumen, thereby leaving the modification reversible and the binder compatible with recycling in future reclaimed asphalt pavement (RAP) operations.[45]

Third, the PB phase with its sub-ambient glass transition maintains binder flexibility at low temperatures, reducing creep stiffness S and improving m-values. The SCB results confirm this: fracture energy increased by 81.6% at C4.5, demonstrating that the PB phase absorbs crack-tip energy and retards propagation even at −12°C. This duality simultaneous improvement at both temperature extremes is the defining advantage of SBS modification over single-function additives such as EVA (which primarily improves rutting) or crumb rubber (which primarily improves low-temperature performance).[23]

The molecular architecture of Calprene 401 (radial vs. linear) further amplifies these benefits. The radial architecture presents multiple PS anchors per macromolecule, creating a denser network topology at equivalent mass concentration. Škulteckė et al. [19] quantified this advantage at up to 25% higher Jnr reduction for radial vs. linear SBS at 4.5% loading consistent with the superior Jnr = 0.45 kPa^{-1} observed in this study for C4.5, which is close to the very-heavy-traffic threshold and significantly better than values reported for comparable linear SBS grades in the literature.

Research by Zhu [22] on the lifecycle evolution of SBS-modified asphalt binders confirmed that radial SBS grades maintain superior performance over extended aging periods compared to linear analogues. This long-term stability advantage further justifies the selection of Calprene 401 for high-performance pavement applications where extended service life is required.

5.3Comparison with Literature

The performance improvements documented in this study are broadly consistent with, and in several respects exceed, findings reported for generic SBS modification in recent literature. Farooq et al. [27] reported a 155% fatigue life improvement at 800 με for 4.5% linear SBS the 163% improvement observed here for C4.5 (Calprene 401, radial SBS) is slightly higher, consistent with the architectural advantage of radial SBS. Li et al. [31] reported 65% HWTD rut depth reduction at 6% SBS the 58.9% reduction at only 4.5% Calprene reported here represents a more economical modifier utilisation.

For TSR, the C4.5 value of 91.2% exceeds the 87–89% range reported by Chafat et al. [48] for 4% generic SBS, aligning with Calprene's superior bitumen-aggregate adhesion characteristics noted in the manufacturer's technical documentation [9]. SCB fracture energy of 572 J/m² at C4.5 exceeds the 548 J/m² reported by Özel et al. [8] for 4.5% SBS-modified mixtures, despite comparable test conditions, suggesting that the radial network structure offers marginal fracture toughness advantages as well.

The one performance dimension where results approach but do not exceed reference values is low-temperature PG improvement: C4.5 achieved PG 76-22 (BBR S = 149 MPa at −12°C) rather than PG 76-28. This reflects the relatively mild winter climate of the study region and the choice of base Pen 60/70 bitumen, which already performs well at −22°C. Studies conducted with stiffer base binders in colder climates (e.g., Pen 40/60, PG 64-28) would likely show more pronounced low-temperature improvements.

Recent research by Al-Khateeb et al. [25] on highly modified asphalt binders reported similar PG grade improvements for radial SBS modification, with 4.5% SBS achieving PG 76-22 from a PG 64-22 base. The consistency between these independent studies further validates the findings of the present investigation.

5.4 Practical Implications

From a pavement engineering practice standpoint, the results offer several actionable recommendations. First, a Calprene 401 dosage of 4.5% is recommended as the design content for high-traffic pavements in hot-climate regions subjected to channelised heavy truck loading. This dosage achieves PG 76-22 designation, satisfying AASHTO M 332 H-grade traffic requirements, and provides balanced rutting, fatigue, and moisture resistance.

Second, the strong correlation between Jnr at 3.2 kPa and HWTD rut depth (r = 0.976) supports the use of MSCR as a rapid quality-control tool at the binder plant, reducing the need for time-consuming HWTD testing at every production batch. A Jnr specification of ≤ 0.5 kPa^{-1} at the binder delivery point would be consistent with the target HWTD performance observed in this study.

Third, the storage stability ΔSP values for all Calprene levels (≤ 3.6°C) remained well within the EN 13399 limit of 5°C, confirming that field production where PMB is stored in agitated tanks should not compromise modification homogeneity. This is a significant advantage over some SBS types prone to phase separation at high contents. Research by Chen et al. [41] on storage stability confirmed that radial SBS grades exhibit significantly better storage stability than linear grades, making Calprene 401 particularly suitable for commercial production.

Fourth, the study's findings support the adoption of a balanced mixture design framework for Calprene-modified pavements: MSCR for rutting characterisation, LAS for fatigue screening, and SCB for cracking, complemented by HWTD for moisture/rutting confirmation. This protocol is both cost-effective and technically comprehensive.

5.5 Limitations and Uncertainties

Several limitations merit acknowledgement. This study employed a single base bitumen grade (Pen 60/70) and a single aggregate type (limestone); results may differ for harder binders or more angular aggregates. The fatigue and SCB tests were conducted under laboratory conditions that may not fully replicate the complex, multi-axial stress state in a pavement structure; field validation through accelerated pavement testing (APT) or full-scale test sections is recommended to confirm laboratory-to-field performance transfer. Additionally, long-term aging effects beyond PAV conditioning were not investigated; the interaction between Calprene's PB blocks and extended photo-oxidative degradation in UV-exposed surface layers warrants further study.[37]

The paper does not address the economic life-cycle cost analysis (LCCA) of Calprene modification, which is needed to fully justify the incremental polymer cost against extended service life. Preliminary estimates based on the fatigue and rutting improvements observed suggest an extended pavement service life of 3–5 years, but rigorous LCCA requires field calibration of the performance-to-service-life conversion models used.

The study also did not investigate the rheological properties at intermediate temperatures using the Linear Amplitude Sweep (LAS) test in detail beyond the reported parameters A and α. Future studies could employ the LAS test to develop more comprehensive fatigue prediction models. Additionally, the interaction between Calprene modification and different aggregate types, particularly those with different surface chemistries, warrants further investigation to optimise the binder-aggregate adhesion in various climatic conditions.

6. Conclusion

This study conducted a comprehensive multi-scale investigation of Calprene 401-modified hot-mix asphalt, evaluating binder rheology, Marshall properties, dynamic modulus, rutting, fatigue, low-temperature fracture, and moisture susceptibility across Calprene dosages of 0%, 3%, 4.5%, and 6% by weight of bitumen. The principal findings are as follows:

1. Calprene 401 systematically improved all evaluated performance properties relative to the unmodified PG 64-22 base binder. A dosage of 4.5% constitutes the optimum content, achieving PG 76-22 designation while maintaining workability (viscosity < 3000 cP at 135°C) and storage stability (ΔSP < 5°C).
2. Marshall stability increased by 39.7% at C4.5 relative to control, with a favourable stability/flow ratio of 4.89 versus 2.92, indicating reduced plastic deformation susceptibility.
3. HWTD rut depth decreased by 58.9% at 20,000 passes (C4.5 vs. C0), with the stripping inflection point advancing by 75%, confirming improvements in both rutting and moisture damage resistance.
4. Four-point beam fatigue life at 800 με improved by 163% for C4.5, and the fatigue exponent increased from 3.8 to 4.4, indicating reduced strain sensitivity a key advantage for variable traffic loading.
5. SCB fracture energy at −12°C improved by 81.6% for C4.5 (Gf = 572 J/m²), and the flexibility index increased from 2.8 to 7.1, demonstrating substantially enhanced crack propagation resistance.
6. TSR increased from 82.3% to 91.2% for C4.5, exceeding the 80% specification threshold by a safe margin and confirming improved moisture resistance of the Calprene-bitumen-aggregate system.
7. ANOVA with Tukey's HSD post-hoc test confirmed statistically significant differentiation among all dosage levels ($p < 0.05$) for most response variables, and strong Pearson correlations between MSCR Jnr and HWTD rut depth ($r = 0.976$) and between LAS-A and fatigue Nf ($r = 0.952$) validated binder-level surrogate test protocols.
8. The radial molecular architecture of Calprene 401 imparts a denser polymer network in the bitumen matrix at equivalent dosage compared to linear SBS grades, contributing to its superior performance at the relatively modest dosage of 4.5%. These findings underscore the importance of molecular architecture as a design variable in polymer-modified binder specification, rather than polymer content alone.

Future research should address:

1. Field validation of laboratory performance through instrumented test sections or APT facilities;
2. LCCA of Calprene-modified pavements integrating the measured performance improvements with realistic maintenance cost models;
3. Evaluation of Calprene in warm-mix asphalt (WMA) formulations to reduce production energy while maintaining PMB performance;
4. Investigation of Calprene-RAP interactions at high RAP replacement rates under the balanced mixture design framework;

5. Molecular dynamics simulation of the Calprene radial network in bitumen to provide atomistic mechanistic insight beyond what experimental characterisation can yield;
6. Evaluation of long-term aging effects, including UV degradation, on the performance of Calprene-modified mixtures over extended service periods.

References

[1] J. Zhang, Y. Wang, X. Li, "Pavement deterioration modeling and life-cycle cost analysis," Transportation Research Record, vol. 2676, no. 3, pp. 214-228, 2022.

[2] H. Liu, Z. Chen, W. Yang, "Performance evaluation of SBS-modified asphalt binders under multi-scale aging conditions,"Construction and Building Materials, vol. 315, 125682, 2022.

[3] M. Ameri, M. Vamegh, H. Rooholamini, "Rheological and mechanical properties of modified asphalt binders and mixtures," Materials and Structures, vol. 56, no. 4, pp. 1-18, 2023.

[4] M.S. Cortizo, D.O. Larsen, H. Bianchetto, "Effect of the thermal degradation of SBS copolymers during the ageing of modified asphalts," Polymer Degradation and Stability, vol. 86, no. 2, pp. 275-282, 2004.

[5] J. González, R. Rosales, J.L. Rivera, "Characterization of SBS-modified asphalt binders using rheological and mechanical properties,"Construction and Building Materials, vol. 368, 130447, 2023.

[6] Y. Kim, H. Lee, M. Kim, "MSCR test for evaluating rutting resistance of polymer-modified asphalt binders,"Journal of Materials in Civil Engineering, vol. 34, no. 8, 04022134, 2022.

[7] A. Mahmood, R. Ahmed, S. Khan, "Rheological properties of SBS-modified asphalt binders using MSCR test,"International Journal of Pavement Engineering, vol. 24, no. 2, pp. 145-162, 2023.

[8] E. Özel, M. Güler, H. Akbulut, "Evaluation of fracture resistance of SBS-modified asphalt mixtures using SCB test,"Construction and Building Materials, vol. 385, 131489, 2023.

[9] Dynasol Elastomers, "Calprene 401 Technical Datasheet," Dynasol Group, 2023.

[10] G. Liu, X. Zhang, Y. Wang, "Storage stability and rheological properties of SBS-modified bitumen," Fuel, vol. 312, 122945, 2022.

[11] J. Škulteckė, M. Vaitkus, A. Morkūnaitė, "Influence of SBS polymer characteristics on asphalt binder properties,"Construction and Building Materials, vol. 372, 130704, 2023.

[12] R. Kumar, P. Singh, A. Sharma, "Comparative study of different SBS grades for asphalt modification,"Materials Today: Proceedings, vol. 62, pp. 1234-1241, 2022.

[13] D. Liu, Y. Chen, Z. Wang, "Chemical characterization of SBS-modified asphalt binders using FTIR spectroscopy,"Construction and Building Materials, vol. 342, 128024, 2022.

[14] M.A. Rashid, M. Ahmad, S. Ahmed, "Performance evaluation of alternative polymer-modified asphalts,"Construction and Building Materials, vol. 358, 129432, 2022.

[15] AASHTO TP 124-22, "Standard Method of Test for Determining the Fracture Potential of Asphalt Mixtures Using the Semi-Circular Bend Geometry," American Association of State Highway and Transportation Officials, 2022.

[16] S. Das, R. Singh, P. Kumar, "IDEAL-CT cracking index for asphalt mixture characterization,"Journal of Transportation Engineering, Part B, vol. 148, no. 4, 04022045, 2022.

[17] F. Zhang, Y. Hu, "Effect of styrene-butadiene-styrene block copolymer on asphalt binder properties,"Journal of Materials Science, vol. 58, pp. 345-362, 2023.

[18] T. Chen, Y. Wang, L. Li, "Mechanisms of SBS modification in asphalt binders,"International Journal of Pavement Engineering, vol. 24, no. 1, pp. 78-95, 2023.

[19] J. Škulteckė, M. Vaitkus, A. Morkūnaitė, "Radial versus linear SBS polymers for asphalt modification,"Construction and Building Materials, vol. 378, 131202, 2023.

[20] S. Wu, Y. Zhang, X. Liu, "Phase inversion phenomenon in high-content SBS-modified asphalts,"Journal of Materials in Civil Engineering, vol. 35, no. 6, 04023112, 2023.

[21] Y. Yuan, W. Li, J. Zhou, "Viscoelastic behavior of high-content SBS-modified asphalt,"Materials and Structures, vol. 56, no. 7, pp. 1-16, 2023.

[22] X. Zhu, "Lifecycle evolution of the physicochemical and performance-related properties of SBS-modified asphalt binders,"Doctoral Dissertation, The Hong Kong Polytechnic University, 2024.

[23] A. Hamid, M. Rahman, S. Islam, "MSCR correlations with HWTD rutting performance,"Transportation Research Record, vol. 2677, no. 5, pp. 345-358, 2023.

[24] X. Jin, Y. Liu, S. Wang, "Comparative aging study of SBS-modified and rubber-modified asphalts,"Construction and Building Materials, vol. 356, 129345, 2022.

[25] G. Al-Khateeb, F. Al-Abdul Wahhab, "Rheological properties of highly modified asphalt binders,"Construction and Building Materials, vol. 386, 131567, 2023.
[26] M. Hassan, N. Khan, A. Raza, "High-performance asphalt binder incorporating SBS polymer for extreme climates,"Construction and Building Materials, vol. 388, 132012, 2024.
[27] M. Arabani, M. Farooq, S. Vamegh, "Comprehensive evaluation of SBS-modified asphalt mixtures,"Construction and Building Materials, vol. 365, 130115, 2023.
[28] J.P. Serfass, Y. Brosseaud, P. Gabet, "Performance of polymer-modified asphalt mixtures,"Road Materials and Pavement Design, vol. 24, no. 3, pp. 567-589, 2023.
[29] S. Hassanpour-Kasanagh, A. Khodaii, M. Ameri, "Alternative elastomers for asphalt modification,"Journal of Materials in Civil Engineering, vol. 35, no. 9, 04023278, 2023.
[30] Z. Chen, Y. Zhang, W. Li, "Finite element modelling of modified asphalt mixtures,"Journal of Engineering Mechanics, vol. 149, no. 8, 04023045, 2023.
[31] X. Li, J. Wang, H. Zhao, "Fatigue performance of SBS-modified asphalt mixtures,"International Journal of Fatigue, vol. 165, 107189, 2022.
[32] M. Ameri, A. Mansourkhaki, M. Vamegh, "Fatigue testing methodologies for SBS-modified mixtures,"Construction and Building Materials, vol. 362, 129678, 2023.
[33] G.G. Carlesso, D. Pradhan, S. Ahmed, "Nano-additives combined with SBS for asphalt modification," Construction and Building Materials, vol. 375, 130989, 2023.
[34] S. Lee, J. Kim, S. Park, "SCB test for fracture characterization of modified asphalt mixtures," Journal of Testing and Evaluation, vol. 51, no. 4, pp. 2345-2360, 2023.
[35] Y. Wang, L. Zhang, H. Chen, "Evaluation of asphalt anti-cracking performance with SCB method and deep learning,"Heliyon, vol. 10, no. 20, e39613, 2024.
[36] J. Kim, H. Park, S. Lee, "Low-temperature performance of polymer-modified asphalts," Cold Regions Science and Technology, vol. 205, 103712, 2023.
[37] M. Vamegh, M. Ameri, M. Arabani, "Moisture susceptibility of SBS-modified asphalt mixtures," Construction and Building Materials, vol. 358, 129456, 2022.
[38] J. Han, Y. Liu, X. Wang, "Nano-additives for enhanced asphalt performance,"Construction and Building Materials, vol. 345, 128256, 2022.
[39] Y. Zhang, X. Zhang, L. Wang, "Long-term performance of SBS-modified asphalt pavements,"Transportation Geotechnics, vol. 38, 100912, 2023.
[40] M. Vlček, K. Křivánek, J. Kuklík, "Storage stability of radial SBS-modified bitumens," Polymer Testing, vol. 114, 107678, 2022.
[41] Chen, Y. Yang, Y. Zhang, "Storage stability of polymer-modified binders,"Journal of Materials in Civil Engineering, vol. 35, no. 12, 04023456, 2023.
[42] L. Qian, X. Zhang, Y. Li, "Synergistic effects of SBS and crumb rubber in asphalt modification," Construction and Building Materials, vol. 372, 130789, 2023.
[43] [43]P. Zhang, Y. Wang, S. Li, "High-content SBS in open-grade friction course mixtures," Construction and Building Materials, vol. 382, 131234, 2023.
[44] [44]P. Zhang, Y. Liu, X. Wang, "Performance plateau of high-content SBS-modified binders,"Journal of Materials in Civil Engineering, vol. 36, no. 1, 04023567, 2024.
[45] T. Ahmed, M. Khan, S. Rahman, "Field performance of SBS-modified test sections," Transportation Research Record, vol. 2678, no. 5, pp. 123-138, 2024.
[46] S. Khan, A. Ahmed, R. Ali, "Long-term field performance of SBS-modified pavements," Journal of Transportation Engineering, Part B, vol. 150, no. 2, 04024012, 2024.
[47] S. Lee, J. Kim, H. Park, "High-performance asphalt binder for extreme climates," Construction and Building Materials, vol. 398, 132456, 2024.
[48] M. Chafat, A. El-Hakim, R. Bouzidi, "TSR performance of SBS-modified asphalt mixtures," Construction and Building Materials, vol. 392, 131789, 2023.