UPGRADE OF POLYMER MODIFIED BITUMEN FOR DURABLE ASPHALT PAVEMENT: A NEW APPROACH

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Abstract: *Asphalt pavements face higher axle loads and rising temperatures, requiring improved binders. A first study in 2024 compared AC22 BASE mixtures using PmB 45/80-65 and B50/70 modified with 3% of an isocyanate reactive additive (ISO P101). Both met moisture resistance; the isocyanate-based mix had slightly lower rut depth and substantially higher high-temperature stiffness while maintaining comparable low-temperature stiffness. Fatigue tests favored PmB in lab indirect-tension, though isocyanate's higher stiffness may reduce structural strains in pavements. Building on this, hybrid mix designs combining SBS and isocyanate chemistry were developed. Rheological tests (BTSV, MSCR, elastic recovery) and mix trials showed that adding ISO P101 to commercial PmB increases high-temperature stiffness and rutting resistance while preserving low-temperature behavior, with field trials demonstrating workability, storage stability and compatibility with up to 50% of Reclaimed Asphalt. These results support reactive isocyanate modifiers as a practical route to more durable and perpetual pavements***.**

Keywords: reactive modifier, polymeric isocyanate, polymer modified bitumen, rutting resistance, perpetual pavement.

MODIFIKACIJA POLIMEROM MODIFIKOVANOG BITUMENA ZA IZDRŽLJIV KOLOVOZ: NOVI PRISTUP

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Rezime: *Asfaltne saobraćajnice podležu većim opterećenjima osa i rastućim temperaturama, pa su potrebni poboljšani veziva. Istraživanje iz 2024. godine upoređivalo je smeše AC22 BASE koristeći PmB 45/80-65 i B50/70 modifikovan sa 3% reaktivnog izocijanatnog aditiva (ISO P101). Obe su ispunile otpornost na vlagu; smeša sa izocijanatom imala je nešto manju dubinu kolektivnog oštećenja (rut depth) i znatno veću krutost na visokim temperaturama, pri čemu je zadržala uporedivu krutost na niskim temperaturama. Testovi zamora favorizovali su PmB u laboratorijskom indirektnom zatezanju, iako veća krutost izocijanatne smeše može smanjiti strukturne deformacije u kolovozima. Na ovom iskustvu zasnovani su hibridni dizajni smeša koji kombinuju SBS i izocijanatnu hemiju. Reološki testovi (BTSV, MSCR, elastic recovery) i probni uzorci smeše pokazali su da dodatak ISO P101 komercijalnom PmB-u povećava krutost na visokim temperaturama i otpornost na kolektivno oštećenje, uz očuvanje ponašanja na niskim temperaturama, a terenska ispitivanja su demonstrirala obradivost, stabilnost pri skladištenju i kompatibilnost sa do 50% recikliranog asfalta (Reclaimed Asphalt). Ovi rezultati podržavaju reaktivne izocijanatne modifikatore kao praktičan put ka izdržljivijim i dugotrajnijim saobraćajnicama.*

Ključne reči: *Réactif modificateur, izocijanat polimer, polimerom modifikovan bitumen, otpornost na kolektivno oštećenje (rutting), večni kolovoz..*

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1. INTRODUCTION

Asphalt pavements are facing increasing axle loads and rising temperatures, which heighten the need for improved binders able to resist common distresses such as rutting, thermal cracking and fatigue. The binder is the key performance component: a complex colloidal system with a polar (asphaltene) fraction and a less polar maltene fraction. Polymer modification (for example SBS, recycled tire rubber or EVA) is the most common strategy to extend the binder's useful temperature range by increasing high-temperature stiffness (to resist rutting) while preserving the ability to relax stresses at low temperatures. Each modifier class has trade-offs, including phase separation, emissions, storage stability or the risk of low-temperature brittleness. Reactive polymers can form chemical networks with asphaltenes, improving high-temperature stability but carrying their own risks such as low-temperature cracking or gelation if overdosed.

Reactive polymeric modifiers (epoxy- or isocyanate-functional systems) offer a complementary strategy to SBS modification. By chemically bonding with polar bitumen fractions (e.g. asphaltenes), they change the colloidal balance and form dispersed in-situ networks that improve high-temperature rigidity, storage stability and ageing resistance without relying on elastomeric domains (Figure 1). Isocyanate-based modification thus enhances resistance to permanent deformation but does not produce the large elastic recoveries characteristic of SBS. Consequently, elastic-recovery alone is an inadequate universal metric. Given increasing thermal loads and higher RAP contents, specification frameworks should move to multi-metric, performance-based evaluation (i.e. rheology, Multiple Stress Creep Recovery, fatigue master curves and field validation), so reactive chemistries can be assessed and deployed on equal footing.

Despite its widespread use, SBS has practical and performance limitations that merit consideration. Key issues include:

- Environmental ageing: SBS is vulnerable to UV-induced photo-oxidation and thermal oxidation, which cause chain scission, embrittlement and loss of flexibility over time.
- Thermal cycling sensitivity: Repeated expansion/contraction promotes micro-fatigue and can accelerate cracking, particularly under large diurnal or seasonal temperature swings.
- Storage and processing constraints: High polymer dosages increase binder viscosity, complicating mixing, pumping and plant operations and raising storage-stability concerns.
- Compatibility with high RA: Achieving target performance with high recycled content can require higher SBS loads or additional compatibilizers, increasing cost and viscosity challenges.
- Specification bias and procurement effects: Normative emphasis on elastic recovery favors SBS and can exclude alternative modifiers that improve durability by different mechanisms.
- Cost and lifecycle: Higher polymer contents and additional mitigation measures (antioxidants, vulcanisation, fillers) raise material and processing costs and may shift environmental trade-offs unless balanced by demonstrable lifespan gains.

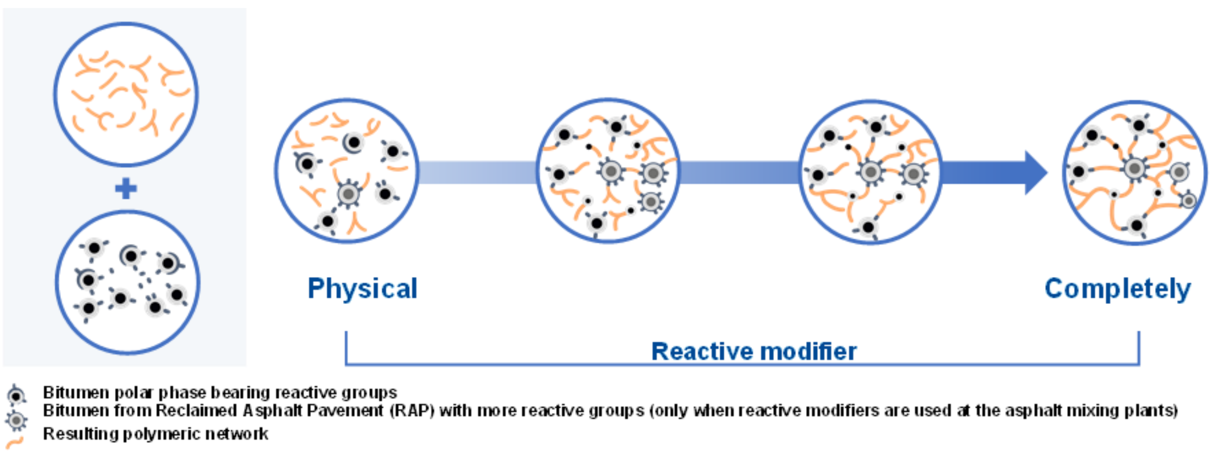

Figure 1. *Schematic representation of reactive modification of bitumen by multifunctional isocyanate polymer and polymeric network formation (conceptual). Source: BASF.*

Reactive modifiers reported in the literature include epoxy-functional ethylene-based polymers and isocyanate-terminated polymers [1–13]. Their classification as modifier of bitumen and/or asphalt mixes depends on dosage and points of application (pre-manufacture into ready-made bitumen or direct addition at the asphalt plant). In practice, polymeric isocyanate-based additives act simultaneously as polymer modifiers, chemical additives, adhesion promoters/anti-stripping agents, compatibilizers for high RAP contents, odor suppressants (e.g., H_2S scavengers) and viscosity/workability aids that enable warm-mix production.

A substantial work demonstrates that isocyanate-based reactive polymers can raise binder viscosity, improve storage stability and enhance rutting resistance at elevated temperatures [5–13]; Carrera *et al.* first described in-situ crosslinking of bitumen constituents using polymeric isocyanates [13]. Through appropriate processing, these modifiers can be used to produce binders and mixes at reduced production and laydown temperatures, supporting lower-energy practices.

A first study evaluated a liquid polymeric isocyanate additive (ISO P101, BASF) that reacts with nucleophilic functionalities in bitumen (alcohol, amine, thiol groups) to form a flexible chemical network, thereby increasing high-temperature stiffness and resistance to permanent deformation. Two AC22 BASE limestone mixtures were compared: one made with polymer-modified bitumen PmB 45/80-65 (a reference for heavily loaded Serbian roads) and one made with conventional bitumen B50/70 modified with 3% ISO P101 [14].

Both mixtures met moisture-sensitivity requirements. The B50/70 modified with 3% ISO P101 mixture showed slightly better resistance to permanent deformation and lower rut depths in wheel-tracking tests. Master curves for stiffness modulus indicated substantially higher stiffness for B50/70 and the reactive isocyanate at elevated temperatures and across a broad temperature/frequency range, consistent with the improved rutting results and implying reduced structural strains in service. At low temperatures, the stiffness of the isocyanate-modified mixture approaches that of the PmB, though additional low-temperature cracking tests are recommended to complete the assessment.

In laboratory indirect-tension fatigue tests, the PmB 45/80-65 mixture exhibited superior fatigue resistance and higher strain values. However, the higher stiffness of a base layer containing B50/70 and ISO P101 could reduce pavement strains (including tensile strain at the bottom of the asphalt layer), so fatigue implications should be evaluated in the context of full pavement designs.

Practically, the reactive isocyanate additive can be dosed directly at asphalt plants, enabling on-demand modification and operational flexibility. Potential benefits not covered in this former study, such as anti-stripping effects on acidic aggregates, improved mix workability, and the possibility to reduce production and laydown temperatures, warrant further investigation. Overall, both AC22 BASE mixtures display comparable performance: the reactive isocyanate additive notably boosts high-temperature stiffness and rutting resistance of conventional bitumen while preserving low-temperature behavior, whereas the PmB retains an advantage in laboratory fatigue resistance. Further studies were needed to evaluate design-level implications, optimal dosing, long-term field performance and additional operational benefits of isocyanate modification.

In order to combine both effect, from SBS elastomers and reactive isocyanate additive, further paving trial were performed in Germany related to highly modified asphalt mixes for heavy loaded traffic.

Combining SBS with reactive modifiers or using hybrid formulations can exploit complementary strengths. Recoverable elasticity from SBS and stiffness/ageing resistance from reactive chemistries, while mitigating the individual limitations of each approach, might be complimentary taking advantages of both type of modifications: elastomeric and plastomeric.

To address rising thermal loads and the growing use of reclaimed asphalt, a pragmatic strategy is hybrid modification: combining SBS elastomers (for recoverable elasticity) with reactive polymeric modifiers (for stiffness, compatibility and ageing resistance) to exploit complementary mechanisms. This paper presents one paving trial that apply this approach: a high-demand logistics/manufacturing site in Dingolfing (Germany), illustrating practical implementation and performance.

2. MATERIALS AND METHODS

2.1. Materials

PmBs 10/40-65 and 25/55-55, commercially available, were purchased from different bitumen suppliers or collected directly at the asphalt mixing plant. Those PMBs were modified with a reactive modifying additive, based on a specific polymeric isocyanate (ISO P101) obtained from BASF SE, or the modified bitumen binder was extracted from the asphalt mix produced on site. The main properties of the additive (ISO P101) are listed in Table 1.

Table 1. *Main properties of additive ISO P101 (composition, density, physical form).*

Properties ISO P101	
Chemical composition Density (25 °C) Physical form	isocyanate-based 1,2 g/cm3 Black liquid

2.2. Methods

European bitumen specification still relies on penetration-grade criteria (EN 13924, EN 12591), typically expressed by needle penetration and Ring & Ball softening point. New rheological methods (for example BTSV: "Bitumen Test Schnell Verfahren" – Binder-Fast-Characterization-test) are being introduced to better characterize modern binders; however, BTSV correlations validated for unmodified bitumen do not always translate directly to polymer-modified binders such as SBS-PmB.

All rheological tests were performed on Anton Paar DSR instruments (MCR 702 Multidrive and SmartPave 101) using 25 mm plate–plate geometry and within the linear visco-elastic range unless stated otherwise.

- BTSV (Binder-Fast-Characterization-Test) [15]: The complex shear modulus and phase angle were recorded while temperature was ramped from 20 °C to 90 °C at 1.2 K·min-1, at 10 rad·s-1 and a stress of 500 Pa (stress-controlled mode). The temperature at which |G*| = 15 kPa (T(G* = 15 kPa)) and the corresponding phase angle δ(G* = 15 kPa) were taken as rheological softening indicators. δBTSV serves as a qualitative indicator of modification level ; literature thresholds classify binders as unmodified (δBTSV > 75°), moderately modified (65° < δBTSV < 75°) or highly modified (δBTSV < 65°).
- MSCR (Multiple Stress Creep and Recovery, DIN EN 16659) [16-17]. Tests were run at 60 °C with 25 mm plates and a 1 mm gap. Each cycle comprises 1 s creep under 3.2 kPa shear stress and 9 s recovery, for ten cycles. The reported metrics are mean % recovery (R) and mean non-recoverable creep compliance (Jnr). These parameters characterize binder susceptibility to permanent deformation and correlate well with mixture rutting.

Conventional indicators like Ring & Ball softening point was measured by standard procedure and reported alongside rheological metrics. Elastic recovery (DIN EN 13398) was used to classify PmB binders: specimens cast in molds were conditioned 90 min at 25 °C, stretched to 200 mm at 50 mm·min-1 and cut. The distance between the two threads after 30 minutes yields elastic recovery as a percentage of extension. If failure occurs before 200 mm, the actual extension is used. Elastic recovery remains a common specification metric for SBS-type modification.

Mixture production and performance testing Laboratory mixes and field cores (AC 8 DS, AC 16 BS / AC 16 DS) were produced with the specified PmB variants and co-modified binders. RA was incorporated up to 50 % and binder dosages adjusted accordingly. Rutting (track formation) tests were performed at an elevated test temperature (up to 70 °C) to assess deformation resistance; workability and compactability were recorded during production and storage trials.

2.3 Paving project

Dingolfing logistics site (2024) was a project involving a repaving of bus and truck lanes using 1500 tons of AC 16 DS with 50 % RAP based on PmB 10/40-65 modified with 2.5 % ISO P101. The mix travelled ~120 km from plant to site and was stored for 4–5 hours before laydown; laydown temperature was at about 160 °C.

3. RESULTS

3.1 Laboratory results

The initial laboratory work focused on multi-modifying an asphalt mix to increase deformation resistance under high temperatures and heavy loads typical of bus stations and logistic areas. Adding a reactive modifier to a ready-to-use PmB 25/55-55 A produced a clear rheological shift in the base binder toward properties associated with deformation-resistant pavements. Several key indicators exceed those of a typical PmB (Table 2). For comparison, a PmB 10/40-65, presumed to contain a higher SBS content, was also evaluated as a reference binder.

Table 2. *Bitumen binder test results (lab trials)*

	Softening point R&B [°C]	T(G* = 15 kPa) BTSV [°C]	Phase angle δ (G* = 15 kPa) - BTSV [°]	Elastic Recovery [%]
10/40-65	72,2	66,6	66,4	69
25/55-55	61,0	61,2	69,2	75
25/55-55 + 2,5 M.-% (ISO P101)	81,4	71,5	55,7	77

3.2. Logistic site of a large auto maker (Dingolfing, Germany, June 2024)

A major automotive manufacturing site in Germany sought to upgrade its on-site pavement and agreed to trial the reactive modifier to improve the PmB typically used there. The project included repaving large bus-station areas and renewing a truck delivery lane at the Dingolfing site. For this work, 1,500 tonnes of AC 16 DS containing 50 % reclaimed asphalt (RA) and based on a PmB 10/40-65 were modified with 2.0 % ISO P101. The plant-to-site distance was about 120 km and the mix was held in storage for 4–5 hours before placement; despite this, laydown at approximately 160 °C delivered excellent workability and compaction. Extracted binder results show a marked increase in softening point, corroborated by higher T(G* = 15 kPa) and a reduced phase angle δ(G* = 15 kPa), indicating an elevated degree of modification (Table 3). MSCR tests further confirm that the modified binder meets the demands of very heavy traffic and higher load conditions.

Parameters of extracted bitumen		PmB 10/40-65 + 50% RA	PmB 10/40-65 + 50% RA + 2,5% AS P101
Softening point	T [°C]	64,4	86,0
BTSV (G* = 15kPa)	T [°C]	59,72	72,4
	δ [°]	71,71	60,9
MSCR Test (at 60°C and 3,2 kPa)	Recovery [%]	33,2	81,6
	J_{nr} [1/kPa]	0,821	0,018
Elastic Recovery	[%]	50	68

Table 3. *Bitumen binder test results (extracted bitumen from production trials)*

Further testing at the mixture level confirmed that multi-modification markedly increased the asphalt's resistance to deformation at elevated temperatures. Notably, the track-formation tests conducted at an adjusted temperature of 70 °C showed pronounced reductions in permanent deformation (see Figure 2).

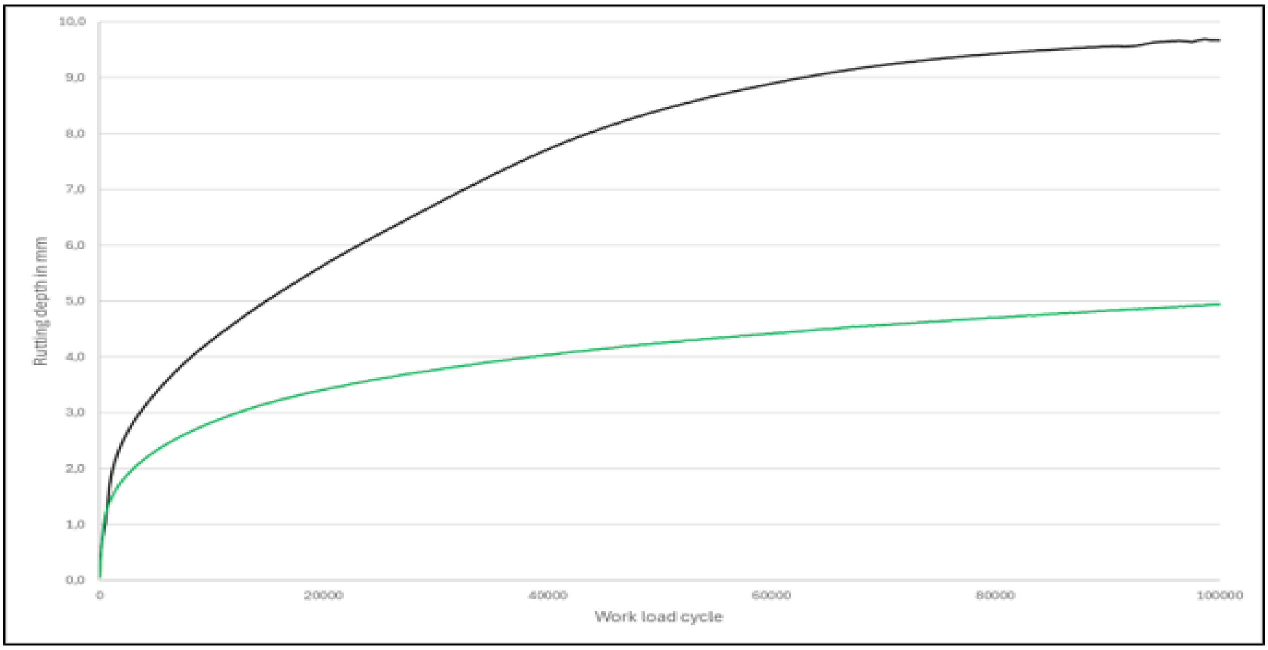

Figure 2. *Rutting comparison for AC 16 BS: reference with PmB 10/40-65 versus the same mix co-modified with ISO P101, showing reduced permanent deformation for the co-modified material.*

4. DISCUSSION & CONCLUSION

Current European binder specifications have been shaped around dominant technologies, most notably styrene-butadiene-styrene (SBS), and often elevate elastic recovery to a primary pass/fail metric. While elastic recovery is an appropriate control for elastomeric SBS behavior, its use as a prescriptive acceptance criterion can unintentionally exclude alternative chemistries that achieve equal or superior in-service performance by different mechanisms.

Reactive isocyanate-based modifiers such as ISO P101 typically do not produce the very high elastic-recovery values characteristic of SBS, yet they increase high-temperature stiffness, rutting resistance and long-term durability through in-situ chemical interactions with polar binder fractions. These mechanisms, network formation, improved compatibility with aged binders, and enhanced rigidity, are not fully captured by single-number elastic-recovery tests. To foster meaningful innovation, specification practice should therefore move from narrow, single-metric pass/fail tests toward performance-based frameworks that combine complementary rheological and mechanistic indicators (for example G*/sinδ and phase angle trends, MSCR, fatigue master curves, BTSV/T(G*), and mechanistic-empirical pavement predictions) along with clearly defined field validation pathways for novel additives.

SBS modification remains a powerful approach to provide recoverable elasticity, but it is susceptible to environmental ageing (UV photodegradation, oxidation, thermal cycling) that causes chain scission, increased polarity, embrittlement and loss of fatigue resistance. Practical mitigation measures, like antioxidants and UV stabilisers, controlled sulphur cross-linking, compatibilizers, hydrophobic or nano-treated fillers, surface protective overlays, and pavement design measures that reduce peak temperatures, can slow degradation. However, hybrid strategies that combine elastomeric polymers (for recoverable elasticity) with reactive modifiers (for stiffness, RA compatibility and enhanced ageing resistance) can exploit complementary mechanisms and achieve a more balanced performance envelope across service temperatures.

This study shows that multi-modification, exemplified by ISO P101 added to commercially available PmB (Table 2), produces a pronounced rheological shift toward deformation-resistant behavior and results in significant reductions in track formation in demanding field trials. In mixtures with high reclaimed asphalt (RA) contents, reactive modification mitigates the common dilution of polymer networks: Table 3 illustrates that an extracted binder from a PmB 10/40-65 mix with 50% RA has an elastic recovery near 50%, whereas the addition of a reactive isocyanate during production raises the recovered binder's elastic recovery to about 68%, restoring the original specification threshold (see table 2, elastic recovery of PmB 10/40-65 at 69% and falling at 50% after production of the asphalt mix in Table 3, while maintained at 68% when reactive isocyanates are added). Beyond elasticity, reactive modification improves high-temperature rigidity, rutting resistance and, in some aggregate systems, anti-stripping performance, and it can reduce certain VOC emissions during hot-mix production.

For practical adoption, several conditions must be satisfied. Specifications should permit alternative compliance routes based on a suite of laboratory performance indicators corroborated by field performance. Continued, structured field monitoring across climates and traffic regimes is essential to validate laboratory predictions and quantify service-life benefits. Procurement confidence will be strengthened by transparent life-cycle assessments and supply-chain disclosures for additives, and by factoring occupational-health co-benefits arising from lower production temperatures and reduced emissions into tender evaluations.

In conclusion, a performance-focused multi-modification strategy that integrates reactive isocyanate-based additives with established elastomeric approaches offers a viable path to more durable, circular and practically producible pavements under rising thermal loads and increased recycled-content demands. Realizing these benefits at scale will require specification reform, rigorous field validation programs and clear lifecycle transparency to ensure reliable long-term performance.

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