

Article

Design and Evaluation of Modified Asphalt with Enhanced Stripping Resistance Based on Surface Free Energy

Tomohiro Fujinaga ^{1,2,*} , Tomohiro Miyasaka ², Yousuke Kanou ¹ and Shouichi Akiba ¹

¹ College of Industrial Technology, Nihon University, Izumi-cho 1-2-1, Narashino 274-0072, Japan; kanou.yousuke@nihon-u.ac.jp (Y.K.); akiba.shouichi@nihon-u.ac.jp (S.A.)

² World Kaihatsu Kogyo Co., Ltd., Wakahowatauchi 7484, Nagano 381-0101, Japan; t-miyasaka@wkk.co.jp

* Correspondence: t-fujinaga@wkk.co.jp; Tel.: +81-(0)26-213-7028

Abstract

Latent stripping has become increasingly apparent in asphalt pavements, particularly in highway rehabilitation and international construction projects supported by Official Development Assistance (ODA) from the Government of Japan. Stripping accelerates structural deterioration, making countermeasures essential. However, in ODA projects, securing high-quality aggregates or evaluating local materials is often difficult due to environmental and budgetary constraints. This study focused on Surface Free Energy (SFE) as a small-sample evaluation method and developed ten types of styrene–butadiene–styrene (SBS) polymers to enhance interfacial adhesion by targeting aggregate surface functional groups. The SFE of each Polymer-Modified Bitumen (PMB) and thirteen aggregates was measured, and the work of adhesion and moisture sensitivity index (MSI) were calculated for all combinations. Twenty-one Hot-Mix Asphalts (HMA) were then prepared and evaluated using the Hamburg Wheel Tracking Test (HWTT) based on load cycles to stripping initiation (LC_{SN}) and to 12.5 mm rut depth (LC_{ST}). The developed PMBs showed a higher work of adhesion, a lower MSI, and substantially increased LC_{SN} and LC_{ST} values. Strong negative correlations were observed between MSI and both HWTT indicators, confirming the utility of SFE-based MSI for material screening. This study demonstrates that interface-targeted PMBs can improve stripping resistance, thereby promoting the use of lower-quality aggregates in durable pavements.



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Keywords: stripping; Surface Free Energy; moisture sensitivity; functional group; hydrogenation; polymer modified bitumen; Hamburg wheel tracking test; asphalt mixture

1. Introduction

In recent years, stripping at the bitumen–aggregate interface has been identified as a key factor in the premature deterioration of asphalt pavements [1–3]. This issue is particularly evident in construction projects funded by the Japanese Official Development Assistance (ODA). Stripping progresses due to the penetration of water and repeated traffic loading, accelerating damage such as cracking. Consequently, improving the stripping resistance of HMA has become a critical challenge for extending pavement service life. This issue is particularly critical in ODA projects, as aggregates constitute approximately 95 wt.% of Hot-Mix Asphalts (HMAs). To minimize transportation costs, these materials are generally procured from locations near the construction site. The challenge of properly evaluating these local materials was exemplified in a road construction project in Cambodia, where premature pavement failure occurred due to stripping (Figure 1). This

selection process is often hindered by limited testing infrastructure and a lack of technical expertise [4,5].

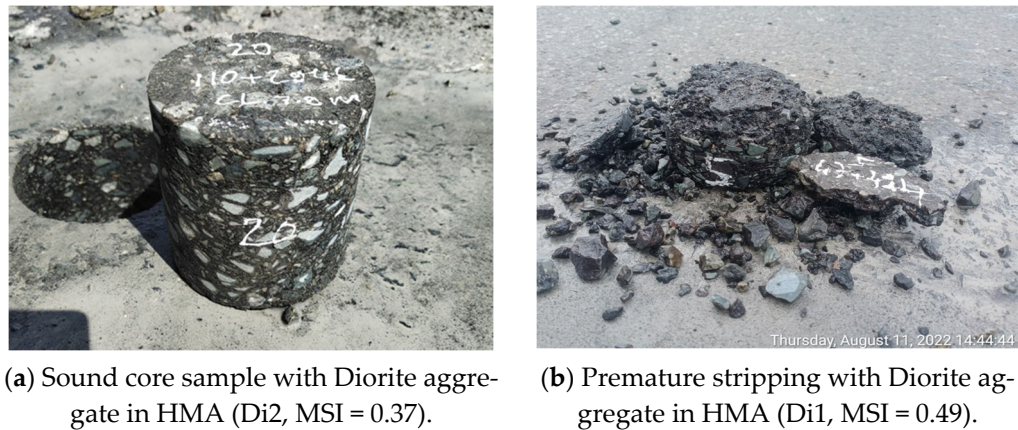


Figure 1. Case studies of premature pavement failures in Cambodia national road #5 projects due to differences in moisture sensitivity index (MSI) at the bitumen–aggregate interface.

The authors focused on the work of adhesion at the bitumen–aggregate interface and conducted a multifaceted evaluation of the relationship between various aggregate characteristics and stripping resistance [6]. Furthermore, the specimen behavior during the Indirect Tensile (IDT) test was observed using Digital Image Correlation (DIC), focusing on the Initial Fracture Point (IFP) and the progression of fracture (Figure 2).

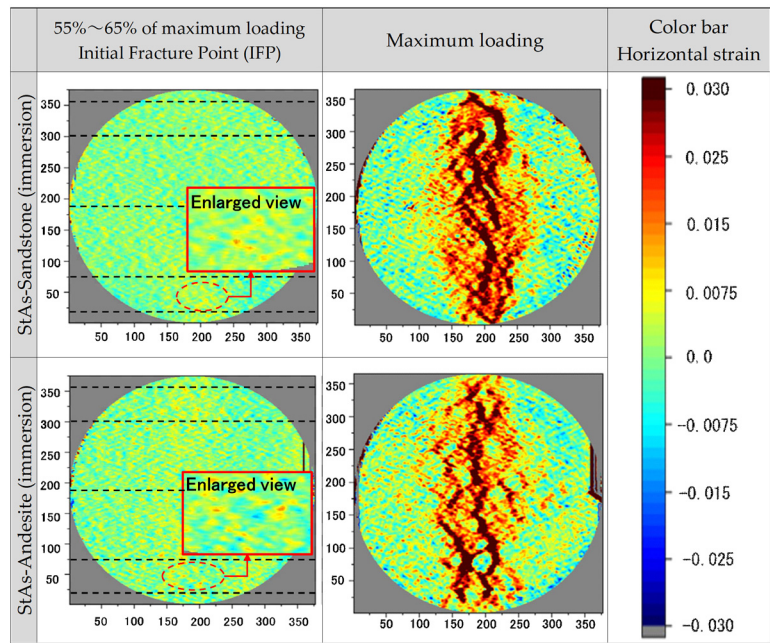
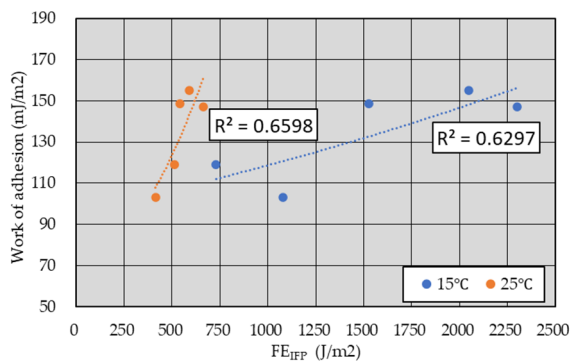
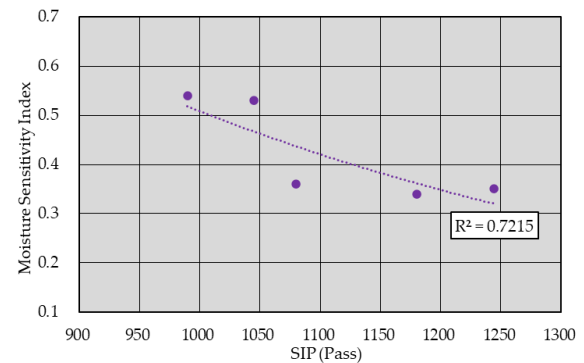


Figure 2. Visualization of horizontal strain distribution during the Indirect Tensile (IDT) test using Digital Image Correlation (DIC).

In addition, as shown in Figure 3, correlations were also found between the adhesive properties, calculated from Equations (1)–(3) based on the work of adhesion and key indicators such as work of adhesion at the IFP due to stripping obtained from the IDT test, as well as the Stripping Inflection Point (SIP) obtained from the Hamburg Wheel Tracking Test (HWTT).



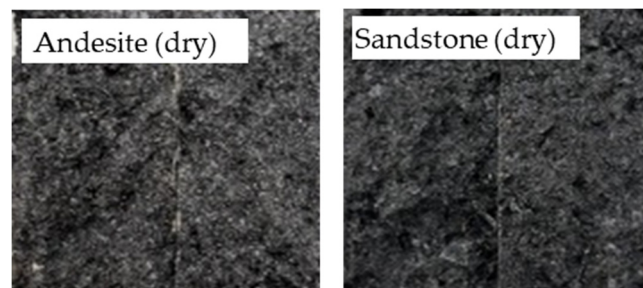
(a) Relationship between fracture energy at initial fracture point (stripping) and work of adhesion.



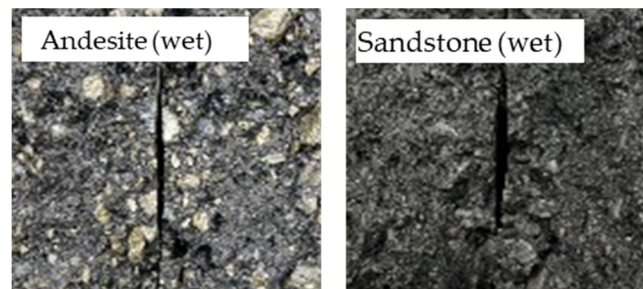
(b) Relationship between stripping inflection point (SIP) and moisture sensitivity index (MSI).

Figure 3. Overview of previous studies on the relationship between stripping resistance tests and moisture sensitivity for Straight-run Asphalt (StAs) with five aggregates (Gr1, Sa1, An1, An3 and Li1).

Moreover, the degree of stripping observed on the fracture surfaces after testing (Figure 4) was consistent with the moisture sensitivity index (MSI) values for different aggregate types.



(a) Fracture surface of specimen after IDT test without conditioning.



(b) Fracture surface of specimen after IDT test with conditioning.

Figure 4. Fracture surface of specimen after IDT test: (a) without conditioning and (b) with conditioning according to AASHTO T283-14.

These results indicate that mixtures with Sandstone aggregate exhibit high stripping resistance, whereas those containing Andesite aggregate are more prone to premature deterioration. In contrast, several studies have reported that Sandstone generally exhibits poor adhesion with asphalt binder and low stripping resistance under moist conditions, with fatigue cracking frequently occurring after water immersion [7]. However, in Japan, Sandstone has long been used empirically as a durable pavement aggregate. This discrepancy is likely due to the fact that Sandstone is a sedimentary rock whose properties vary significantly depending on its parent rock type and mineralogical characteristics, which are closely related to its geological origin.

Based on these findings, this study aims to develop Polymer-Modified Bitumen (PMB) with enhanced adhesion properties by formulating SBS modifiers targeting the bitumen–aggregate interface. The development was guided by the following three criteria:

1. Use of a simplified evaluation method suitable for small quantities of material.
2. By limiting the cost increase to approximately 150% of that for unmodified Straight-run Asphalt (StAs).
3. Setting the minimum performance target to match the stripping resistance between StAs and Sandstone aggregate.

The research methodology first involved evaluating the adhesion performance between bitumen and aggregates using a thermodynamic approach based on the Surface Free Energy (SFE) theory. Specifically, SBS polymers were developed to enhance adhesion by interacting with functional groups on aggregate surfaces. Fourteen types of bitumen, including these PMBs, and thirteen types of aggregates were selected, and their individual SFE values were measured. From these values, the work of adhesion and the MSI were calculated to quantitatively assess the adhesion performance at the bitumen–aggregate interface. Subsequently, the relationships between these indicators and the actual stripping resistance of HMA, evaluated by the HWTT, were analyzed. Furthermore, the effectiveness of the SFE-based approach as a material screening method was validated by identifying clear correlations between material-level properties and mixture-level performance.

These findings confirmed that PMBs incorporating SBS copolymers, intentionally designed to interact with aggregate surface functional groups at the molecular level, can significantly improve interfacial adhesion and effectively reduce moisture sensitivity across a wide variety of aggregate types. Such interfacial-focused polymer design offers new insights into PMB performance enhancement and can contribute to improved pavement durability in developing countries, where rapid infrastructure development depends on the use of locally available aggregates.

2. Materials and Methods

2.1. Materials

2.1.1. Materials Used for Surface Free Energy Evaluation

In this study, ten types of polymer modifiers were developed using two distinct approaches:

1. Functionalization of SBS (SBS_{FG}): This approach involved grafting monomers such as maleic anhydride (MA) or glycidyl methacrylate (GMA) onto the SBS polymer. This process introduced highly reactive functional groups—specifically, carboxyl groups from maleic anhydride and epoxy groups from GMA—into the SBS molecular structure. These functional groups were intentionally selected to enhance interfacial adhesion by forming strong acid-base interactions and chemical bonds with acidic moieties, such as silanol groups (Si-OH), commonly present on aggregate surfaces.
2. Hydrogenation of Functionalized SBS (SBS_{HY}): This second approach involved selectively hydrogenating a portion of the double bonds in the polybutadiene blocks of the functionalized polymers described above. This hydrogenation process served two critical purposes. First, it improved the polymer's weather resistance and thermal-oxidative stability. Second, it increased the hydrophobicity of the polymer. By making the binder itself more hydrophobic, it physically hindered water from penetrating the bitumen-aggregate interface. This reduction in hydrophilicity worked synergistically with the interfacial interaction from the functional groups to improve stripping resistance.

Emtiaz et al. demonstrated that functionalizing SBS improves its compatibility with asphalt binders [8]. Zeng et al. noted that the functional groups on the graphene oxide

surface interact with both SBS and asphalt components, resulting in enhanced interfacial adhesion and a more stable network structure [9]. Zhu et al. found that partial hydrogenation increases compatibility and stability in SBS-modified binders [10]. However, these studies primarily focused on improving compatibility, not specifically on enhancing stripping resistance through interfacial interaction. Thus, the present study aimed to modify SBS during its synthesis to directly improve interfacial adhesion and stripping resistance.

In developing the PMB, cost constraints were considered based on the significant impact of bitumen costs on direct construction expenses, especially in ODA projects. As shown in Table 1, PMB type-II grade in Japan (approximately equivalent to performance grades ranging from PG64-22 to PG70-22) was used as a reference. This material has been used in previous ODA projects and costs approximately 135% of StAs. Accordingly, the target cost of the developed PMB was set to 150% of the StAs cost. Using PMB type-II increases direct construction costs by approximately 2% compared to StAs, and based on experience and implementation records, a cost increase of up to around 3% is generally not expected to cause major practical issues. Therefore, this cost target was considered reasonable. Based on this consideration, the cost target was established. In the future, trial installations will be necessary to verify the appropriateness of the cost setting and to assess the cost-effectiveness.

Table 1. Estimated impact of PMB use on direct construction costs based on past ODA project case studies.

Project	(a) Direct Construction Cost (100 Million JPY)	Quantity of HMA (ton)	Cost of HMA * (100 Million JPY)			Cost Difference (100 Million JPY)	
			(b) StAs	(c) PMB Type-II	(d) StAs * 150%	(c) – (b) ((c) – (b))/(a)	(d) – (b) ((d) – (b))/(a)
A	5788	44,133	485	600	644	115 (2.0%)	159 (2.7%)
B	1600	15,012	165	204	219	39 (2.4%)	54 (3.4%)
C	3507	27,686	305	377	404	72 (2.1%)	99 (2.8%)

* Including the construction cost of the asphalt plant and other related expenses. In Table 1: (a) direct construction cost; (b) cost of HMA using StAs; (c) cost of HMA using PMB type-II; (d) cost of HMA using PMB priced at 150% of StAs.

For testing purposes, the PMBs were produced by blending 5 wt.% SBS into the same batch of StAs using a high-shear mixer. For comparison, three control binders were prepared. CM1 was a PMB type-II binder composed of StAs modified with a commercial SBS. CM2 was produced by adding 0.4% (by binder weight) of a commercially available solid phosphate-ester-based adhesion promoter (SAP) to CM1. CM3 was produced by adding 0.4% (by binder weight) of a commercially available liquid amine-based adhesion promoter (LAP) to CM1. The properties of the base bitumen and PMB are summarized in Table 2.

The thirteen types of coarse aggregates selected for this study were chosen based on two main criteria to ensure the broad applicability of the findings: practical relevance and geological diversity. In terms of practical relevance, the selection includes aggregates with a documented history of use in ODA projects, such as the Diorite from Cambodia which has previously exhibited moisture-related issues. Other aggregates were included based on their extensive practical application in pavement construction in Japan. In terms of geological diversity, the selection covers a wide spectrum of rock types to represent the variety of materials typically encountered in developing countries. This includes acidic igneous rocks like Granite (high SiO₂ content), intermediate rocks such as Andesite and Diorite, basic rocks like Basalt, and sedimentary rocks like Sandstone and Limestone. This

diversity ensures that the developed PMBs were tested against varied surface chemistries and properties, from acidic to basic. The detailed physical and chemical properties of these aggregates are listed in Table 3.

Table 2. The properties of the bitumen for SFE evaluation.

Sample ID	Modifier	PMB Cost * (%)	R&B (°C)	Dynamic Viscosity (Pa·s)			DSR 64 °C (kPa)	
				100 °C	135 °C	160 °C	G*	G* /sinδ
StAs	StAs 60/80	100.0	48.0	3143	476	126	1.5637	1.5650
CM1	SBS	135.4	61.0	14,510	1507	353	5.1854	5.3842
CM2	SBS + SAP	143.2	57.9	11,840	1287	284	4.7749	4.9971
CM3	SBS + LAP	143.8	60.7	12,713	1240	315	3.9059	4.1004
PTM1	SBS _{PG}	138.6	76.6	15,253	1631	416	7.0937	7.5038
PTM2			59.5	31,630	2053	397	5.9051	6.1789
PTM3			60.4	22,750	1468	370	5.5591	5.8741
PTM4			140.1	20,153	1500	384	6.1282	6.4532
PTM5			138.9	31,807	2472	505	4.3636	4.6672
PTM6			149.7	21,690	2622	650	6.1529	6.7294
PTM7	SBS _{HY}	148.4	147.2	29,270	3052	644	9.4822	10.5616
PTM8			65.7	30,167	3163	577	13.0948	14.3576
PTM9			67.8	30,373	3221	578	10.9515	11.5369
PTM10			62.6	16,900	1700	409	8.1894	8.7363

* PMB cost is expressed as a percentage relative to the cost of straight-run asphalt (StAs).

Table 3. The properties of the coarse aggregates for SFE evaluation.

ID	Country of Origin	Type of Rock	X-Ray Fluorescence Analysis		Bulk Sp. Gr. (g/cm ³)	LAA (%)
			SiO ₂ (%)	CaO (%)		
Gr1	Japan	Granite *	71.1	2.0	2.603	14.2
Gr2	Burundi		98.5	0.0	2.592	46.4
Gr3	Sri Lanka		75.0	2.5	2.877	35.0
An1	Japan	Andesite *	57.9	7.3	2.634	14.1
An2			56.4	8.0	2.628	13.4
An3			57.5	8.2	2.651	18.7
Di1	Cambodia	Diorite *	57.2	6.7	2.760	11.8
Di2			57.2	9.2	2.747	12.1
Ba1	Burundi	Basal *	51.5	10.8	2.899	22.6
Ba2	Vietnam		50.2	9.1	2.827	12.9
Sa1	Japan	Sandstone	71.2	1.2	2.641	20.3
Sa2			88.3	0.3	2.630	8.4
Li		Limestone	0.4	98.7	2.692	24.8

* Classification of igneous rocks based on SiO₂ content determined by X-ray fluorescence (XRF) analysis.

2.1.2. Materials Used for the Evaluation of HMA

The HMA mixtures were designed individually for each aggregate type in accordance with the Asphalt Institute MS-2 Superpave method. For each mix design, the bitumen content was kept constant to eliminate binder-related bias in performance results.

Aggregates were selected based on both Surface Free Energy (SFE) characteristics and local availability, with three representative materials—Sandstone, Andesite, and Granite—chosen as coarse aggregates. Sandstone aggregate showed high work of adhesion and low MSI, indicating excellent stripping resistance. Andesite aggregate, by contrast, had high MSI values and demonstrated poor resistance to moisture-induced

damage. Granite aggregate, although commonly used in international projects, generally exhibits poor adhesion due to its high silica (SiO_2) content.

Four types of developed PMB were selected for the HMA, based on their SFE performance and production cost, as shown in Table 4.

Table 4. Selected aggregate and bitumen for HMA.

Material	Material ID	Type
Aggregate	Gr1	Granite
	An1	Andesite
	Sa1	Sandstone
Bitumen	StAs	Straight-run pen.60/80
	CM1	SBS
	CM3	SBS + LAP
	PTM5	SBS _{FG}
	PTM6	
	PTM7	SBS _{HY}
	PTM8	

The PMBs for HMA evaluation were selected through a stepwise process based on their SFE performance and production cost. First, candidate PMBs exceeding the target production cost of 150% relative to StAs were excluded from consideration. From the remaining cost-effective candidates, four representative PMBs were then chosen to comparatively evaluate the effectiveness of different modification strategies at the HMA level based on the following criteria:

- PTM5: Selected from the functionalized (SBS_{FG}) series for its exceptionally high work of adhesion (W_A^{AB}).
- PTM6: Chosen from the SBS_{FG} series for exhibiting the most consistently low MSI values across all aggregate types, indicating superior anticipated stripping resistance.
- PTM7 and PTM8: Selected from the hydrogenated (SBS_{HY}) series as representatives of a balanced performance, demonstrating both high adhesion and low MSI, to evaluate the effect of hydrogenation.

This selection, summarized in Table 4, allowed for a comparative analysis of PMBs with distinct interfacial properties. Mix design results were summarized in Table 5. The bitumen content was held constant across all mixtures.

Table 5. The composition and properties of HMAs.

Agg. ID	Aggregate Type	Composition (%)					Binder (%)	2.36 mm Pass (%)	0.075 mm Passing	Air Void (%)	VMA (%)	VFA (%)
		12.5–5.0 mm	5.0–2.5 mm	Crushed Sand	River Sand	Filler						
Gr1	Granite	37.0	18.0	17.2	24.0	3.8	5.3	45.9	4.8	4.0	14.6	73.3
An1	Andesite	33.0	22.0				5.2	45.2			14.2	72.0
Sa1	Sandstone	33.0	22.0				5.5	45.5			15.6	73.0

2.2. Methods

2.2.1. Measurement and Analysis of Surface Free Energy at the Bitumen–Aggregate Interface

To evaluate the adhesion and stripping resistance of bitumen and aggregate, SFE was adopted as a method suitable for small sample volumes (approximately 1 kg) and multiple material combinations. This limited sample requirement is particularly advantageous when considering the potential need to export locally sourced materials for testing in overseas laboratories.

SFE was calculated based on contact angles measured by automated goniometry (Figure 5), applying acid–base theory with multiple probe liquids (distilled water, formamide, diiodomethane) to model the polar and dispersive SFE components. Contact angles were measured using selected probe liquids (Table 6) to represent different polarities.

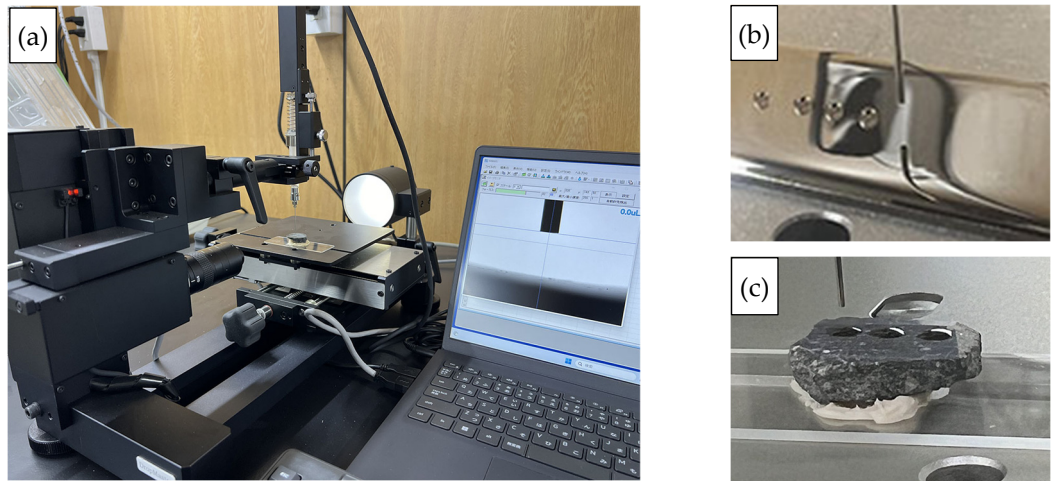


Figure 5. Experimental setup using Kyowa Interface Science DMo-702 automatic contact angle goniometer (25 °C, room temperature). (a) Experimental setup; (b) Application of probe liquid on bitumen surface; (c) Application of probe liquid on aggregate surface.

Table 6. Selected probes of contact angle for SFE analysis.

Probe Liquid	Chemical Formula	Polarity	γ^{LW}	γ^+	γ^-
Distilled water	H ₂ O	High	21.80	25.50	25.50
Formamide	HCONH ₂	Moderate	39.00	2.28	39.60
Diiodomethane	CH ₂ I ₂	Non-polar	50.80	0.00	0.00

To ensure the accuracy and repeatability of the contact angle measurements, which are critical for SFE calculations, a strict measurement protocol was implemented. For the aggregate samples, flat surfaces suitable for measurement were obtained by cutting and sequentially polishing the coarse aggregate particles with #100, #800, and finally #1500 grit diamond wheels to achieve a smooth finish. Following polishing, the aggregate samples were thoroughly cleaned using an ultrasonic bath in a sequence of acetone, ethanol, and distilled water to completely remove any organic and inorganic surface contaminants. Bitumen samples were prepared by pouring the heated binder onto clean glass slides to create a smooth, representative surface. The contact angles were measured using an automated goniometer (model: DMo-702; Kyowa Interface Science Co., Ltd., Saitama, Japan), as shown in Figure 5, which minimized operator-induced variability by automating the droplet deposition and image capture process. Furthermore, to account for the inherent heterogeneity of the material surfaces, at least twenty measurements were taken at different locations on each sample (thirteen for the Diorite aggregates due to limited sample quantity). The average of these measurements was then used to calculate the SFE components, ensuring that the final value was representative of the overall surface.

Previous studies have demonstrated the effectiveness of SFE-based approaches in evaluating bitumen–aggregate adhesion and predicting moisture damage resistance. Wei et al. applied the sessile drop method to determine the SFE components of both asphalt and aggregate [11], while Grenfell et al. correlated adhesion energy derived from SFE models with moisture sensitivity and Rolling Bottle Test results [12]. Furthermore, Zarroodi et al.

reported that carbon black-modified bitumen showed improved moisture resistance, as evaluated by SFE and validated through tensile strength ratio (TSR) testing [13].

SFE was computed using Equation (1):

$$W_A^{SL} = \gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^+\gamma_L^-} + 2\sqrt{\gamma_S^-\gamma_L^+} \quad (1)$$

where W_A^{SL} is the work of adhesion between solid and liquid (mJ/m^2), γ^L is the surface tension of the liquid, θ is the contact angle, γ^{LW} is the Lifshitz–van der Waals component of Surface Free Energy, γ^+ is the Lewis acid component of Surface Free Energy, γ^- is the Lewis base component of Surface Free Energy, subscripts S is solid and L is liquid.

Work of adhesion using Equation (2):

$$W_A^{AB} = 2\sqrt{\gamma_A^{LW}\gamma_B^{LW}} + 2\sqrt{\gamma_A^+\gamma_B^-} + 2\sqrt{\gamma_A^-\gamma_B^+} \quad (2)$$

where W_A^{AB} is the work of adhesion between aggregate and bitumen (mJ/m^2), subscripts A is aggregate, B is bitumen.

And the moisture sensitivity index (MSI) using Equation (3):

$$\text{MSI}^{ABW} = \frac{W_A^{AW} - W_A^{AB}}{W_A^{AB}} \quad (3)$$

where MSI is the moisture sensitivity index, subscripts A is aggregate, B is bitumen, W is water.

The work of adhesion at the bitumen–aggregate interface (W_A^{AB}) and the moisture sensitivity index (MSI) were computed, with MSI indicating the reduction in interfacial adhesion in the presence of water—a higher MSI thus implying higher susceptibility to moisture-induced stripping.

2.2.2. Evaluation Method for Stripping Resistance of HMA Using the HWTT

The stripping resistance of the HMA was evaluated using the HWTT. A test temperature of 60 °C was selected, which is higher than the commonly used 50 °C, to accelerate the evaluation of moisture-induced damage, particularly for high-performance polymer-modified bitumen mixtures, and to simulate severe conditions in tropical and humid regions. Instead of the conventional assessment based on the inflection point of the rutting curve, known as the SIP, this study employed an alternative approach in which three mathematical models were used to separately evaluate the stripping initiation point (SN), the stripping resistance after initiation (ϵ^{ST}), and the rutting resistance (ϵ^{VP}) [14].

The stripping number (SN) can be determined numerically as the point at which the second derivative of the curve model described by Equation (4) becomes zero. As shown in Figure 6, the general relationship between rut depth and load cycles in the HWTT can be modeled using Equation (4):

$$\text{RD}_{LC} = \rho \left[\ln \left(\frac{\text{LC}_{\text{ult}}}{\text{LC}} \right) \right]^{-\frac{1}{\beta}} \quad (4)$$

where RD_{LC} is the rut depth (mm), LC is the number of load cycle (pass), LC_{ult} , ρ and β are model parameters (fitting coefficients). In simple terms, these parameters define the shape of the initial rutting curve, such as its ultimate depth and how quickly it develops before stripping becomes dominant.

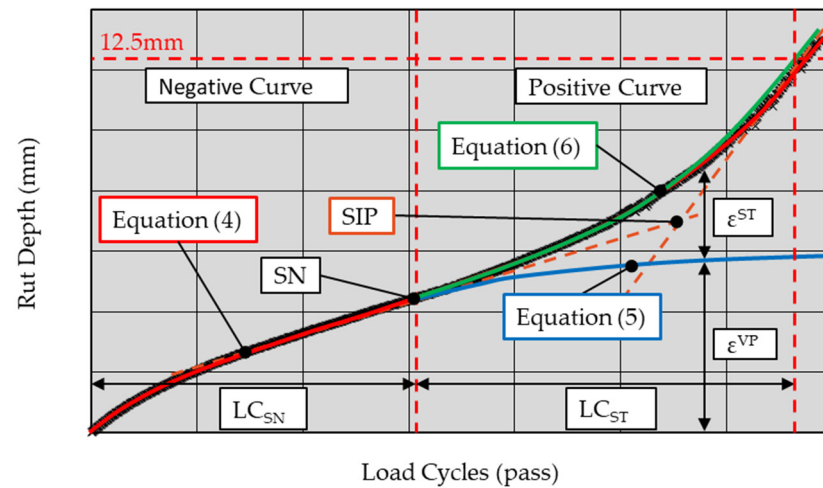


Figure 6. Conceptual diagram of the analytical method using fitting of HWTT results.

The viscoplastic strain is approximated using the Tseng–Lytton model, as shown in Equation (5):

$$\varepsilon^{VP} = \varepsilon_{\infty}^{VP} \exp \left[- \left(\frac{\alpha}{LC} \right)^{\lambda} \right] \quad (5)$$

where ε^{VP} is the viscoplastic strain, $\varepsilon_{\infty}^{VP}$ is the saturated viscoplastic strain, LC is the number of load cycle (pass), LC_{ult} . α and λ are model parameters (fitting coefficients). In this model, $\varepsilon_{\infty}^{VP}$ represents the maximum potential permanent strain if no stripping was to occur, while α and λ are shape parameters that describe the rate at which this strain accumulates.

In the Positive curve section of the figure, the deformation attributed to viscoplastic strain—estimated using Equation (5)—is subtracted, and the remaining curve is modeled using Equation (6) to determine the number of load cycles required to reach a rut depth of 12.5 mm:

$$\varepsilon^{ST} = \begin{cases} \varepsilon_0^{ST} \{ \exp[\theta(LC - LC_{SN})] - 1 \} & LC - LC_{SN} \geq 0 \\ 0 & LC - LC_{SN} \leq 0 \end{cases} \quad (6)$$

where ε^{ST} is the stripping strain, LC is the number of load cycle (pass), LC_{SN} is the number of load cycle at stripping number (pass). In this model, ε_0^{ST} represents the initial rate of rutting right at the onset of stripping, and θ is a coefficient that controls how rapidly the rutting accelerates after stripping has initiated.

During the progression of HMA failure, PMB is considered to contribute to suppressing the initiation of stripping at the bitumen–aggregate interface, the progression of stripping, and cohesive failure. Therefore, in this study, stripping resistance of HMAs was evaluated by the HWTT. Two main performance indicators were defined:

- Load cycles to stripping initiation (LC_{SN}).
- Additional load cycles after stripping initiation until a rut depth of 12.5 mm was reached (LC_{ST}).

Curve fitting and data modeling were performed using the `scipy.optimize` module (version 1.15.2) in the Python (version 3.13.2) to analyze rutting and stripping behavior as functions of loading cycles.

3. Results

3.1. Adhesion and Moisture Sensitivity Based on Surface Free Energy

3.1.1. Contact Angle Between Aggregate Surface and Probe Liquid

The stripping resistance of bitumen–aggregate interface is strongly influenced by its wettability on aggregate surfaces and its competitive adsorption behavior with water. In

this study, the surface characteristics of the aggregates were evaluated based on their contact angles with water, formamide, and diiodomethane. The results are shown in Figure 7.

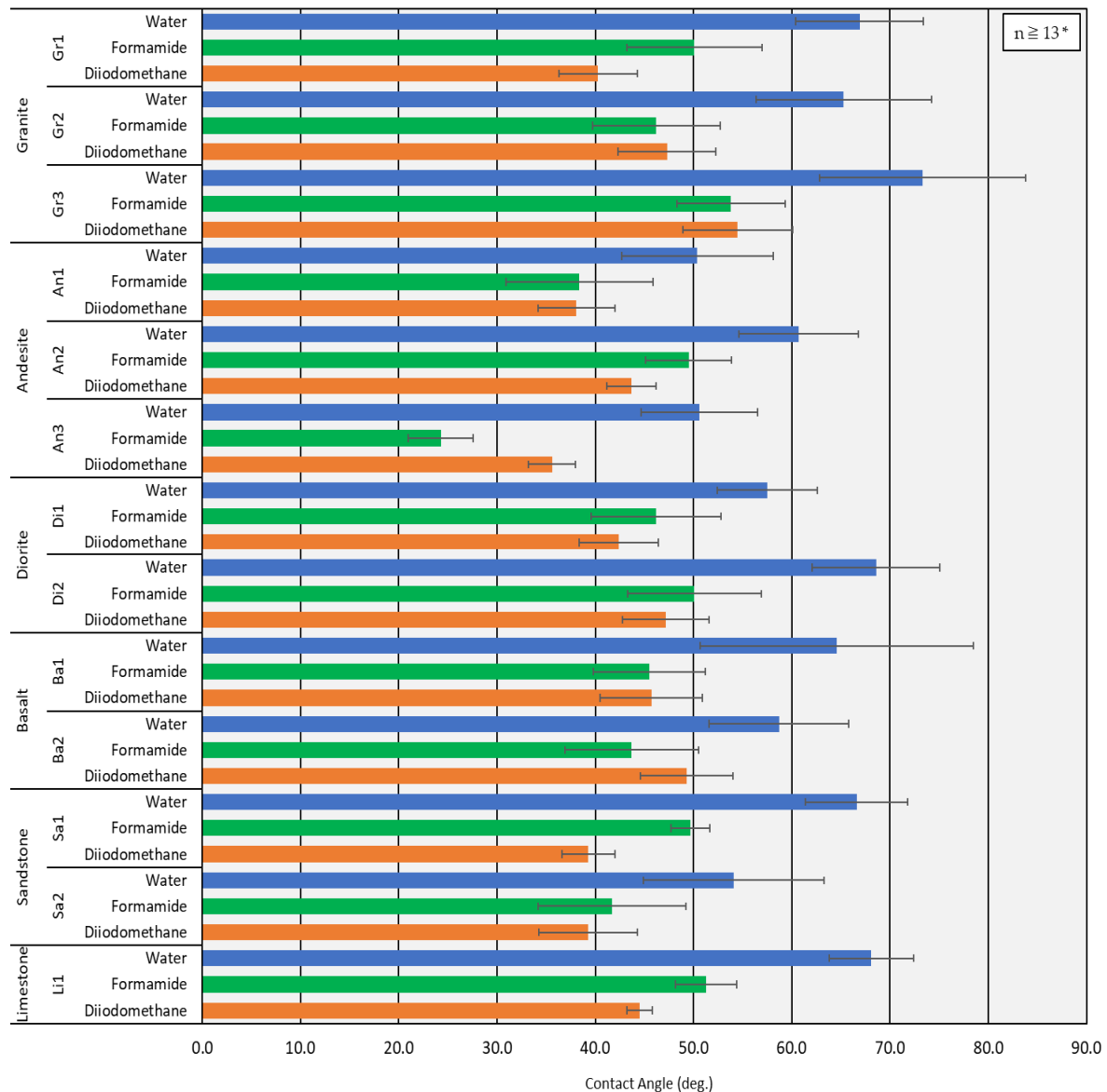


Figure 7. Contact angle measurement of aggregates with water, formamide, and diiodomethane. * Number of tests: Di1 and Di2 ($n = 13$) due to limited sample quantity; others ($n = 20$).

Granite aggregates (Gr1–Gr3) displayed high water contact angles (maximum 73.3°), indicating strong hydrophobicity and low overall wettability. Gr3, in particular, demonstrated high contact angles for all probe liquids, which corresponds to a reduced tendency for both water and bitumen interaction.

Sandstone (Sa1) demonstrated moderate contact angles with all probe liquids (e.g., 66.6° with water), indicating well-balanced wettability. Its relatively low contact angle with diiodomethane (39.3°) suggests high affinity for non-polar components, favorable for adhesion with bitumen.

Andesite aggregates, on the other hand, showed low contact angles with both polar and non-polar liquids, reflecting greater wettability as well as higher susceptibility to water-induced stripping.

These results indicate that the surface properties vary significantly among aggregates, highlighting the necessity of adjusting the Surface Free Energy of the bitumen accordingly.

This supports the importance of appropriate polymer design tailored to the characteristics of the aggregates used.

3.1.2. Contact Angle Between Bitumen and Probe Liquid

Contact angle measurements for bitumen (Figure 8) were used to characterize their surface properties.

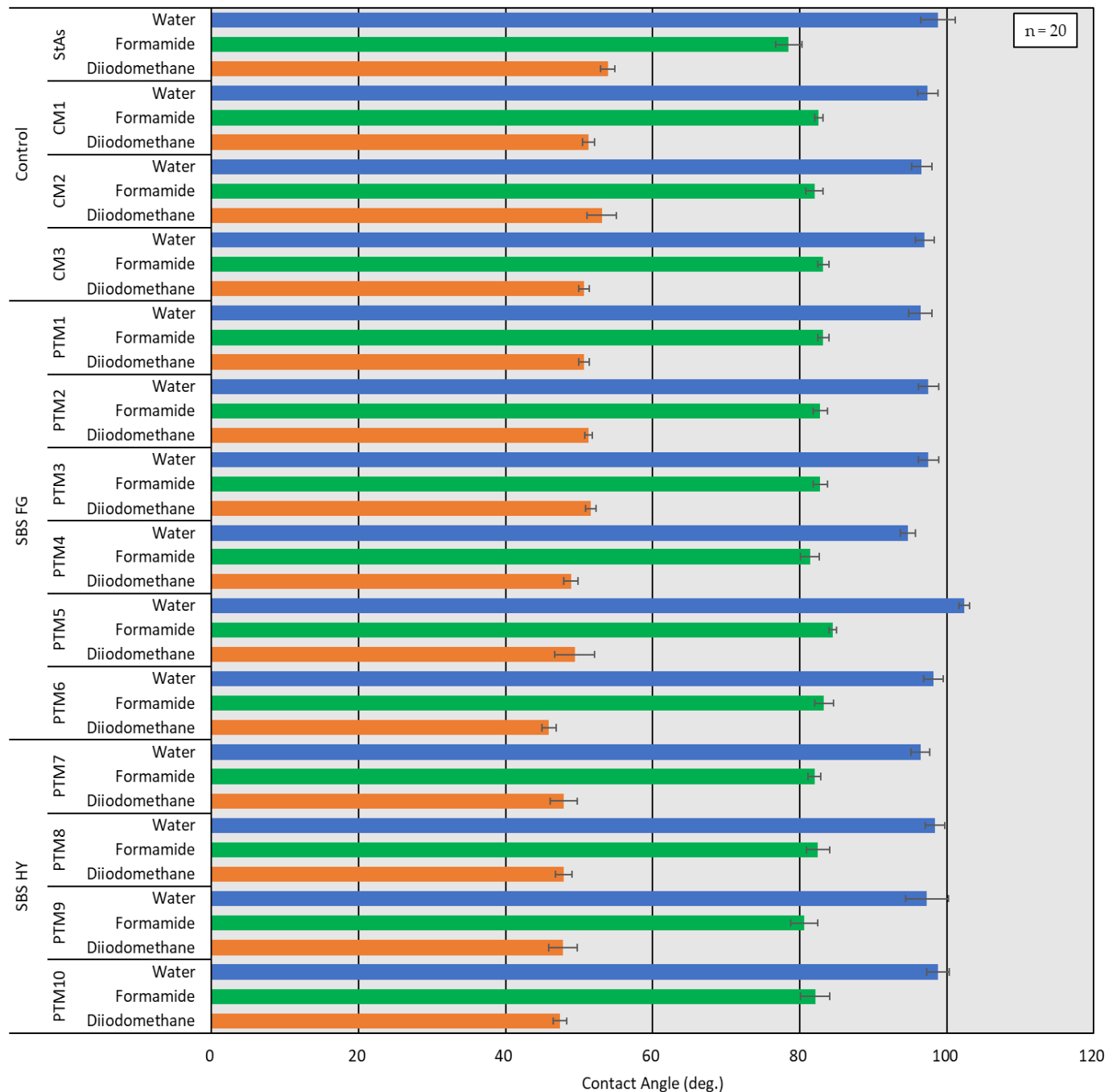


Figure 8. Contact angle measurement of bitumen with water, formamide, and diiodomethane.

StAs exhibited a high contact angle with water (98.8°), indicating significant hydrophobicity. It also showed high contact angles with the polar liquids— 78.5° for formamide and 53.9° for diiodomethane—suggesting limited wettability on aggregate surfaces.

In contrast, the commercial modified binders (CM1 to CM3), which included anti-stripping agents, had similar water contact angles (96 – 97°) to StAs, but significantly lower

contact angles for the diiodomethane ($<60^\circ$). This suggested that the addition of anti-stripping agents can modify the SFE of the bitumen, thereby improving its wettability on aggregate surfaces.

In PTM1 to PTM6, which were formulated using SBS_{FG} , the contact angle with water was relatively high, ranging from 94.7° to 102.4° , while the contact angle with diiodomethane was generally low, around 50° . In particular, PTM5 (49.4°) and PTM6 (45.9°) exhibited high affinity for dispersive components and also showed moderate contact angles with formamide (84.5° and 83.3° , respectively), indicating a well-balanced response to both polar and non-polar components.

On the other hand, PTM7 to PTM10, formulated with SBS_{HY} , exhibited high contact angles with water (96.4° to 98.8°), and relatively low contact angles with formamide (around 80°) and diiodomethane (47° to 48°). These binders demonstrated good wettability with all probe liquids, suggesting excellent surface properties that maintain good adhesion to aggregates while suppressing moisture intrusion.

Therefore, by designing SBS to interact with functional groups on aggregate surfaces, it is possible to adjust and optimize the SFE characteristics of bitumen, thereby enhancing its wettability and interfacial adhesion with aggregates. In particular, modifiers such as PTM6 and PTM7, which exhibit well-balanced contact angles with both polar and non-polar components, demonstrate stable wettability and interactions with a wide range of functional groups on aggregate surfaces. This interfacial design approach suggests a significant contribution to improving stripping resistance.

3.1.3. Work of Adhesion at the Bitumen–Aggregate Interface

As shown in Figure 9, the work of adhesion at the bitumen–aggregate interface (W_{A}^{AB}) was calculated using SFE theory to quantitatively assess stripping resistance. In W_{A}^{AB} assessments, HMAs with StAs exhibited relatively low work of adhesion ($100\text{--}130\text{ mJ/m}^2$), especially with Granite, correlating with poor moisture stability. CM-series PMBs increased W_{A}^{AB} by $10\text{--}15\text{ mJ/m}^2$ over StAs.

For PMBs using SBS_{FG} (PTM1–PTM6), W_{A}^{AB} values reached $150\text{--}180\text{ mJ/m}^2$, particularly with Granite and Sandstone, indicating enhanced interfacial interaction. SBS_{HY} -based PMBs (PTM7–PTM10) showed consistently high adhesion energy with all aggregates, reaching up to 188.7 mJ/m^2 , confirming that hydrogenation optimized interfacial bonding.

These findings confirmed that the developed PTM series improved the work of adhesion and exhibited excellent interfacial performance with reduced dependence on aggregate surface polarity. This result indicates that the introduction of functional groups into SBS enhances interactions with aggregate surfaces, quantitatively demonstrating the effectiveness of interfacial design.

3.1.4. Moisture Sensitivity Index at the Bitumen–Aggregate Interface

The moisture sensitivity index (MSI), shown in Figure 10, was used to assess the bitumen–aggregate interface's susceptibility to moisture.

MSI values for StAs mixtures ranged from 0.34 to 0.53, with notably high values for certain Andesite and basalt combinations, demonstrating high moisture susceptibility. In contrast, PMBs reduced MSI values ($0.23\text{--}0.36$), confirming the positive effect of interface-oriented modification.

Although PTM1–PTM5 (SBS_{FG} series) achieved high W_{A}^{AB} values, their MSI values remained moderate ($0.20\text{--}0.39$). However, PTM6 (SBS_{FG}) showed a consistently low MSI ($0.16\text{--}0.28$) across all aggregates, demonstrating excellent stripping resistance. This was considered to reflect the modification effect designed to form double bonds with the functional groups at the bitumen–aggregate interface.

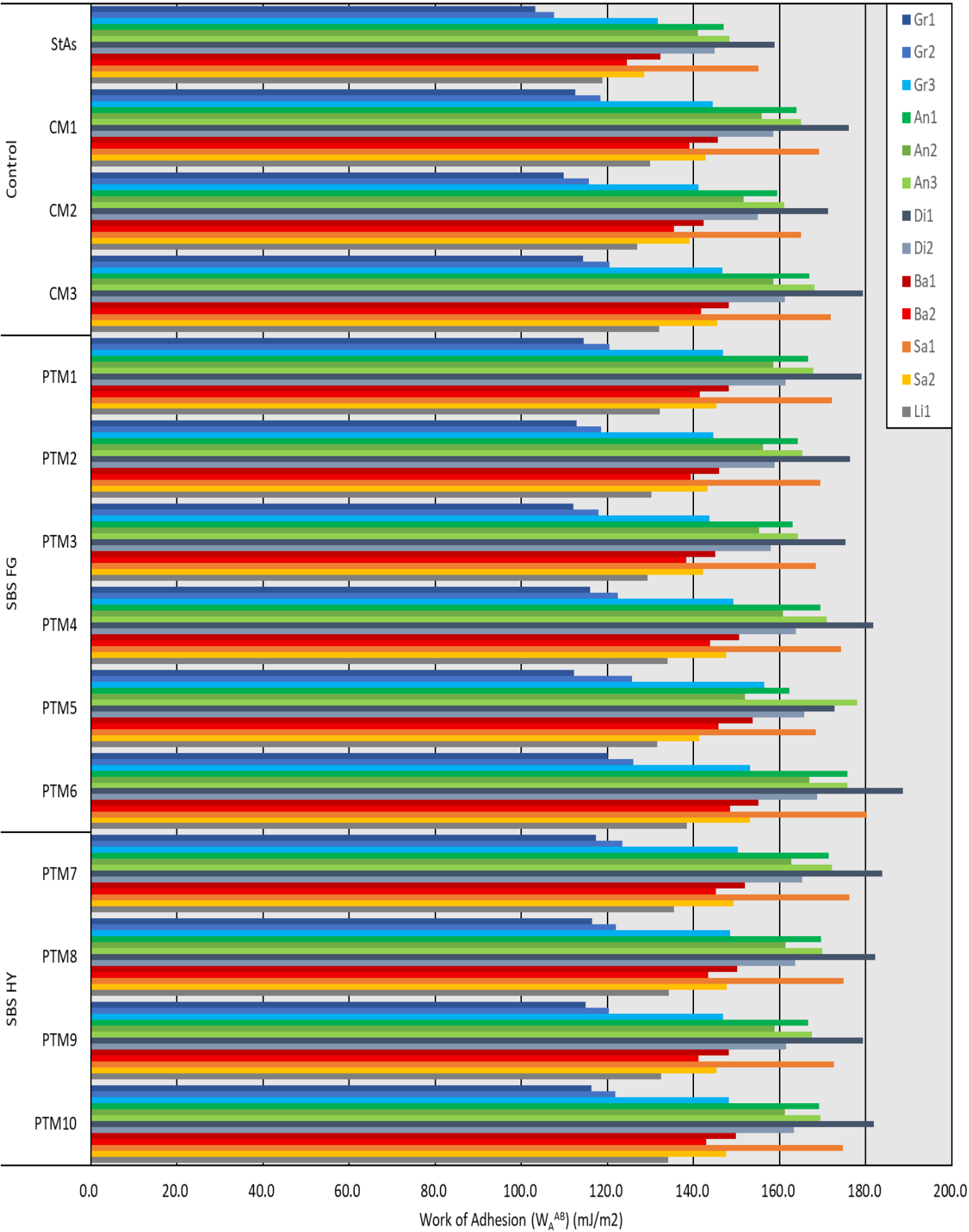


Figure 9. Calculated work of adhesion at the bitumen–aggregate interface.

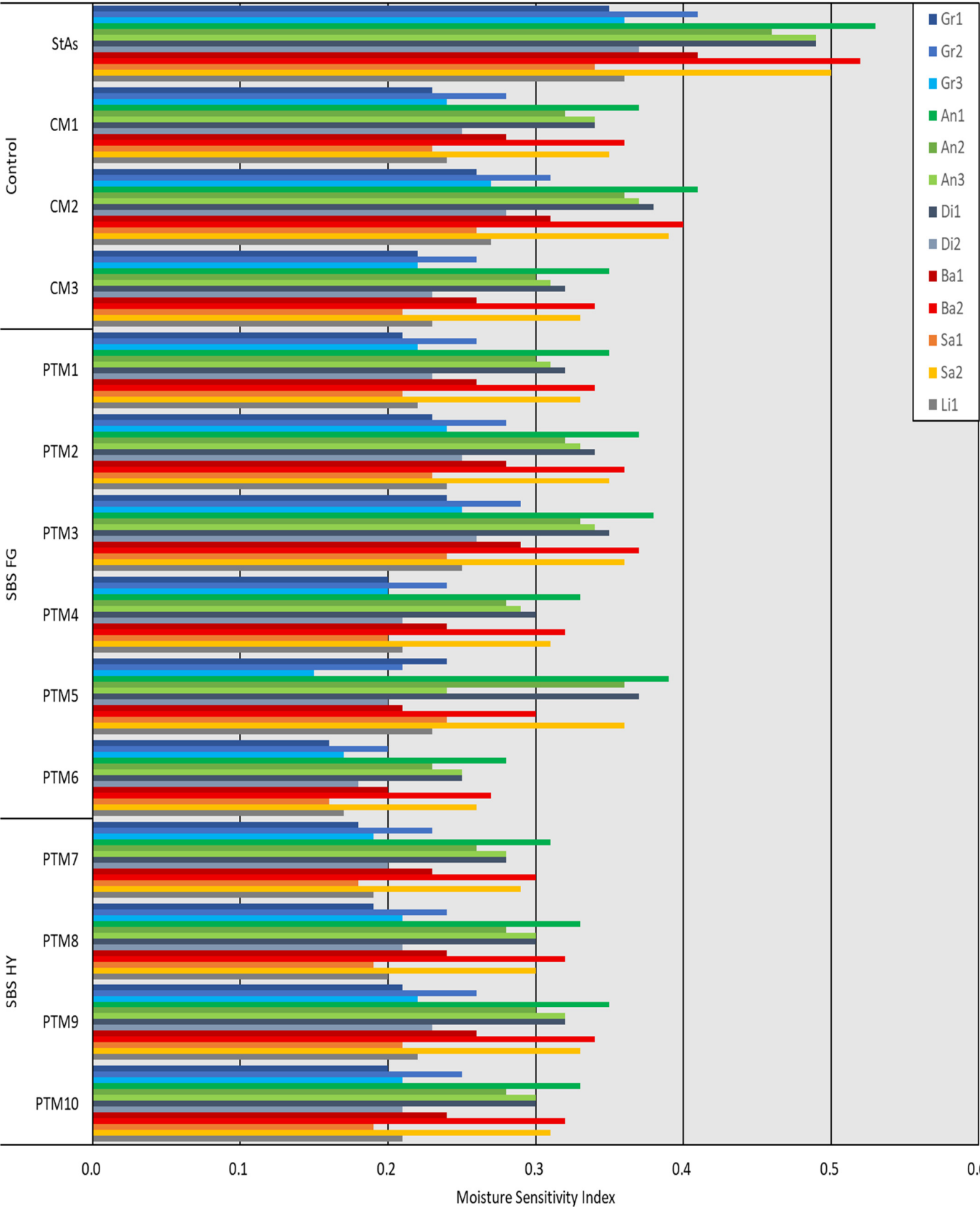


Figure 10. Moisture sensitivity index (MSI) at the bitumen–aggregate interface.

PMBs using PTM7–PTM10 (SBS_{HY} series) exhibited stable and low MSI values (0.15–0.33), even with hydrophobic aggregates such as Gr3 and Sa1, indicating their high potential to resist moisture damage.

These results demonstrated that by controlling the SFE characteristics of SBS and enhancing its interactions based on the polarity and functional group structures of aggregate surfaces, it is possible to reduce moisture sensitivity and improve stripping resistance. In particular, PTM6, which was designed with reactivity toward functional groups in mind, and PTM7–PTM10, which were tailored for balanced wettability with both polar and non-polar components, consistently exhibited low MSI values across various aggregates, indicating excellent and practical interfacial stability. Therefore, the SFE-based evaluation method proves to be effective for PMB design and material screening, suggesting its superiority as a tool for rationalizing material development, selection, and performance prediction.

3.2. Influence of Stripping Resistance on HWTT of HMA

In the preceding sections, the fundamental stripping resistance of the developed PMBs were evaluated based on the contact angles of individual aggregates and bitumen, the work of adhesion (W_A^{AB}), and the MSI. The materials used for the asphalt mixtures were selected based on stripping resistance and production cost. Specifically, PMBs PTM5 to PTM8 were chosen for their balanced performance, and aggregates Gr1, Sa1, and An1 were selected from Granite, Andesite, and Sandstone, respectively, due to their notable stripping resistance characteristics and availability.

Figure 11 shows the relationship between the MSI and the number of load cycles to stripping initiation (LC_{SN}) for each mixture.

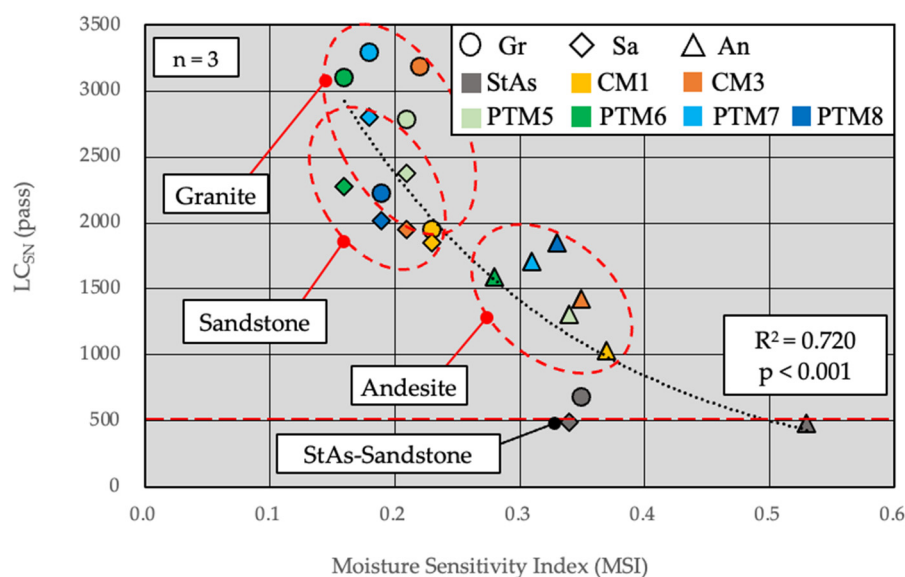


Figure 11. Correlation between MSI and LC_{SN} derived from HWTT.

The results indicated a clear trend: as MSI decreases, LC_{SN} increases, suggesting that the moisture susceptibility at the bitumen–aggregate interface strongly governs the water resistance and durability of HMAs.

Across all mixtures, a strong correlation was observed: lower MSI values consistently resulted in higher numbers of load cycles to stripping initiation (LC_{SN}). For the Granite–StAs combination, LC_{SN} averaged 679 cycles, whereas Granite–PTM6 and Granite–PTM7 achieved 3098 and 3290 cycles, respectively. Similar improvements were confirmed for Sandstone and Andesite aggregates. These results were consistent with the evaluations

based on W_A^{AB} and contact angles, indicating that the interfacial properties between bitumen and aggregate play an essential role in determining stripping resistance.

Next, to examine the progression of stripping after its initiation, the relationship between the number of load cycles required to reach a rut depth of 12.5 mm (LC_{ST}) and the MSI is shown in Figure 12.

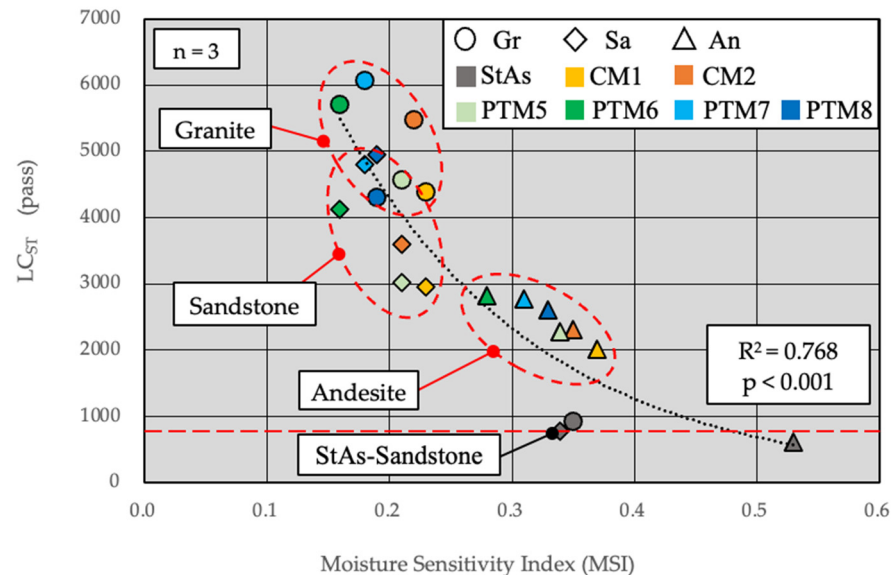


Figure 12. Correlation between MSI and LC_{ST} derived from HWTT.

LC_{ST} represents the mixture's resistance to stripping deterioration that becomes evident as rutting on the surface, serving as an indicator of long-term moisture durability. A clear negative correlation was observed between MSI and LC_{ST} , indicating that mixtures with lower MSI values tend to have higher LC_{ST} . This suggested that materials with more stable bitumen–aggregate interfaces against moisture are more effective in suppressing rutting even after stripping has progressed, thereby demonstrating higher durability.

In particular, HMA with MSI values below 0.25 exhibited LC_{ST} values exceeding 3000 cycles, confirming sustained resistance to rutting after the onset of stripping. In particular, PTM6 and PTM7 demonstrated over 4000 cycles with Granite and Sandstone, and around 3000 cycles with Andesite, indicating significantly enhanced stripping resistance.

These findings confirmed that modifying SBS to interact effectively with aggregate surface functional groups increases the work of adhesion and improves the MSI, thereby delaying the onset of stripping and slowing its progression even after it begins, across a wide range of aggregate surface characteristics.

Moreover, the coefficient of determination (R^2) between MSI and LC_{SN} and LC_{ST} was 0.720 and 0.768, respectively ($p < 0.001$ for both correlations), indicating that MSI—a measure of moisture susceptibility at the bitumen–aggregate interface—is strongly correlated with both stripping initiation and rutting progression.

Therefore, SBS interface design based on SFE theory is supported as a meaningful and practical approach for improving the performance of HMA.

4. Discussion

The results of this study demonstrated that a strategic, SFE-based interface design can yield PMBs with superior adhesion across a wide range of aggregates. This effectiveness stems from two mechanisms: interactions between the introduced functional groups and the aggregate surface, and a reduction in the polymer's hydrophilicity. The strong and statistically significant correlation observed between MSI and HWTT performance indicators

($R^2 > 0.7$, $p < 0.001$) provides robust support for this approach, with no significant outliers deviating substantially from the SFE predictions. Minor variations arise because SFE quantifies thermodynamic affinity at the interface, whereas HWTT measures the mechanical response of the bulk mixture.

The practical implications of these findings are particularly relevant for developing regions. Because the underlying SFE-based design framework is grounded in universal physicochemical principles, the approach is highly transferable to aggregate sources and climatic conditions not directly examined in this work. For practical implementation in resource-limited settings, a collaborative model is proposed in which central laboratories establish SFE databases for local aggregates, providing simplified selection guidelines for practitioners. This facilitates the selection of design solutions tailored to local conditions, such as pairing an interface-engineered PMB with lower-quality aggregates in moisture-dominant environments. While such combinations may not universally replace high-quality aggregates in mechanically demanding scenarios, they substantially broaden the portfolio of viable material options. From an economic standpoint, the modest 2–3% increase in total project cost associated with the initial PMB investment is expected to be offset by considerable life-cycle savings due to extended pavement service life, making it a cost-effective solution. The marked improvement in stripping initiation cycles observed in the HWTT strongly suggests significant potential for mitigating premature structural distress and extending the service life of real pavements.

Nevertheless, this study has certain limitations. The selection of a 60 °C test temperature for the HWTT, while effective for accelerating damage, clarifying PMB performance, and simulating severe tropical conditions, represents a demanding evaluation scenario. The observed performance therefore provides a conservative estimate for pavements in more temperate climates, which should be acknowledged when interpreting the results.

5. Conclusions

This study developed polymer-modified bitumen (PMB) using SBS copolymers designed according to Surface Free Energy (SFE) to optimize the bitumen–aggregate interface. Stripping resistance was quantitatively evaluated using thermodynamic (W_A^{AB} , MSI) and performance-based (HWTT) indicators. The main conclusions are as follows:

- SBS modification, when tailored at the molecular level to complement aggregate surface chemistry, can significantly enhance interfacial adhesion and reduce moisture sensitivity.
- SFE-based evaluation and the rational selection of modifiers facilitate predictive control over HMA durability and stripping resistance.
- This interface-focused approach is particularly promising for enabling the effective use of locally available aggregates in infrastructure projects across developing regions, while simultaneously improving long-term pavement performance.

Future research will involve field-scale trials and further refinement of MSI-based material screening criteria. A key priority will be to expand the current SFE-based framework, which focuses on moisture-induced stripping, to include other critical long-term degradation mechanisms. This will involve characterizing the developed PMBs' resistance to oxidative aging (e.g., using pressure aging vessel tests) and fatigue cracking (e.g., using beam fatigue tests). The ultimate goal is to integrate these performance indicators to build a more comprehensive model for predicting pavement service life under combined environmental and traffic loading.

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Abbreviations

The following abbreviations are used in this manuscript.

ODA	Official Development Assistance from the Government of Japan
SFE	Surface Free Energy
W_A^{AB}	Work of Adhesion at the Aggregate–Bitumen interface
MSI	Moisture Sensitivity Index
IDT	Indirect Tensile (test)
HWTT	Hamburg Wheel Tracking Test
SIP	Stripping Inflection Point
LC_{SN}	Number of Load Cycle maximum number of load cycles that the asphalt mixture can resist in the HWTT before the adhesive fracture
LC_{ST}	Number of additional load cycles after LC_{SN} needed for the rut depth accumulated by the predicted stripping strain to reach 12.5 mm
StAs	Straight-run asphalt (binder)
PMB	Polymer Modified Bitumen
SBS	Styrene-Butadiene-Styrene copolymer
SBS_{FG}	SBS modified by functional group interaction
SBS_{HY}	SBS with partial hydrogenation treatment
SAP	Solid phosphate-ester-based Adhesion Promoter
LAP	Liquid amine-based Adhesion Promoter
CM	Control Material (PMB)
PTM	Prototype Material (PMB)
HMA	Hot-Mix Asphalt
Gr	Granite aggregate
An	Andesite aggregate
Di	Diorite aggregate
Ba	Basalt aggregate
Sa	Sandstone aggregate
Li	Limestone aggregate

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