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Original Article

Analytical study of silane-based and wax-based additives on the interfacial bonding characteristics between natural rubber modified binder and different aggregate types

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HIGHLIGHTS

- Latex was used in the binder modification with the inclusion of surfactants.
- The wettability of modified binders and the binder-aggregate adhesion performance were determined.
- Fracture and moisture resistance were improved with the addition of the wax-based additive.
- Whereby the silane additive enhanced the binder's spreadability.
- NR-modified binders attained higher adhesion regardless of the aging period.

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ABSTRACT

The modification of asphalt binder with natural rubber latex (NR) significantly improves the rutting and fatigue resistance of asphalt mixtures. However, NR-modified binder is prone to low workability and wettability due to its high viscosity. Therefore, this research focuses on examining the influences of silane and wax-based additives on the wettability of natural rubber-modified binders and the binder-aggregates adhesion performances. In this study, experimental and analytical approaches were used. The contact angles of asphalt binder were measured using a goniometer through the sessile drop method with three solvents: deionised water, formamide, and glycerol. The C++ algorithm was adopted to compute the surface free energy (SFE) elements of the asphalt binder. Analytical methods were employed to analyse the results based on the Young-Dupre equation, followed by linear regression to establish a correlation between the compatibility ratio (CR) and the SFE components. The results inferred that modified asphalt binders with additives possessed improved moisture resistance, wherein dry work adhesion values were less than 210 mJ/m^2 under granite interfaces, whereas the limestone interface exhibited higher dry adhesion values of 340 mJ/m^2 and below. Similar performance results were observed under wet adhesion conditions; with granite wet adhesive values observed below 120 mJ/m^2, while limestone wet adhesion values were ascertained below 180 mJ/m^2 for all tested samples and conditions. According to the spread–ability coefficient results, the limestone interface has greater spread-ability than granite interfaces. Meanwhile, compatibility ratio values indicated better compatibility of 1.9 or higher for tested samples under granite interfaces, whereas compatibility values of 1.7 and below were observed under limestone interfaces.

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Among the SFE components studied for correlation with CR, the acidic SFE component demonstrated excellent correlations (with R^2 values greater than 0.91) under all ageing conditions. An inclusion of micro-level additive enhanced binder adhesion properties, resulting in a more resilient asphalt pavement.

1. Introduction

The significant price decline of natural rubber latex (NR) on the global market over the last decade has prompted researchers to broaden the implementation of NR as an asphalt pavement modifier. As an elastomeric substance, NR possesses elastic and stretching characteristics that strengthen the stiffness of the asphalt binder to withstand the permanent deformation effect. Additionally, unlike other polymeric products derived from crude oil, natural rubber as an asphalt additive is renewable and has less embodied energy (Sani et al., 2020a; Wen et al., 2017). The rutting phenomenon is a plastic deformation that develops in pavement layers as a result of accumulating vertical strains along the wheel path of an asphalt pavement due to repetitive traffic loads. The application of natural rubber in pavement construction dates back to 1823 when a cork manufacturer patented a rubber-modified asphalt binder in England. Research into asphalt modification by using NR gained more interest after World War II but declined towards the late 20th century with increasing innovation in synthetic rubber (Francken, 1998). The utilisation of NR as a modifier in traditional hot mix asphalt (HMA) can increase the asphalt mixture's rutting resistance (Daniel et al., 2019). Natural rubber could display dual properties in an asphalt matrix due to the presence of discrete rubber particles that can easily fuse with asphalt during mixing; at lower pavement temperatures, the NR in a modified binder introduces an elastic band that improves crack resistance, whereas, at higher temperatures, the NR acts as a film that increases viscosity and shear resistance, thus preventing the asphalt binder flow (Al-Sabaeei et al., 2019; Azahar et al., 2016).

In addition, a high-quality biopolymer may provide elasticity and flexibility to an asphalt mixture, thereby improving its mechanical performance. However, the wettability properties of the asphalt binder-aggregate interface are determined by the viscosity of NR-modified asphalt binder, which is defined by the momentum transfer resulting from the thermodynamics of the asphalt binder and the intermolecular interaction between the asphalt binder and aggregate (Tian et al., 2018). Moreover, Wasiuddin et al. (2008) reported that wettability and adhesion are the key parameters that affects the mechanism of the bitumen/aggregate interface. The terms such as adhesive bond solubility, bitumen wettability over aggregate, and free adhesion energy are demonstrative of the interfacial connection between bitumen and aggregate (Kakar et al., 2016). In the wetting mechanism of an aggregate surface with asphalt, three processes are involved: 1) damping, which occurs when asphalt contacts the aggregate surface, 2) continuous damping of the aggregate surface, which results in a complete replacement of the solid-air interface by the asphalt interface (soaking), and 3) a spreading mechanism that describes the substitution of the gas-liquid interface with the solid-liquid interface (Yonemoto and Kunugi, 2014).

The complexity of aggregate surface wettability when combined with asphalt binder stems from the fact that it includes both physical and chemical interactions. Aggregates with complex, rough, and uneven surfaces have varied pore sizes and diameters, making it difficult to measure their wettability using surface free energy alone (Schirmer, 1999). The wettability of bitumen over aggregate is determined by the molecular reactions that emerge at the interface, as well as the non-polar and polar properties of aggregate and bitumen. Generally, bitumen is often regarded as non-polar. As stated by Wasiuddin et al. (2010), the majority of basic and acid aggregates have highly polarised surfaces. Consequently, it is difficult to increase the wettability of a surface composed of a polar aggregate with a non-polar asphalt binder. Consequently, the wettability of non-polar asphalt binder on polar aggregate may be enhanced by altering the surface composition of the aggregate from polar to non-polar. This is best accomplished by lowering the non-polarity of the asphalt binder and the polar components of the aggregates and the addition of an additive (Bionghi et al., 2021; Hu et al., 2020; Sani et al., 2020b; Sarsam, 2021). Furthermore, numerous research has shown that the resistance of asphalt mixtures to degradation depends on either the cohesive force of the asphalt binder or the adhesive force of the asphalt binder-aggregate interface under dry and wet conditions (Howson, 2011; Jo et al., 1997; Mirzababaei, 2016; Shafabakhsh et al., 2015; Zhang et al., 2020).

On the other hand, the increasing usage of natural rubber-modified asphalt has currently attracted growing interest, especially in countries like Malaysia with a large natural rubber production. Nevertheless, rubber modification necessitates the addition of chemical additives to optimise its performance (Sani et al., 2020a, 2020b, 2021; Tai et al., 2021). This research used the conventional moisture damage test to assess the effects of additives on the bonding interactions between natural rubber-modified asphalt binder and aggregate.

Surface free energy (SFE) measurement was employed to evaluate the effects of different additives incorporation on the aggregate-rubberised binder bond. The C++ algorithm was also adopted to derive the SFE components (non-polar, and acid and base polar components), which were further tested using the Young-Dupre equation to examine the asphalt binder-aggregate interface behaviour with regard to the work of adhesion, coefficient of spreadability, and compatibility ratio (Kakar et al., 2016). Linear regression was utilised to associate the CR with the surface free energy components and the acidic and basic ratio (A/B) of asphalt binders.

2. Materials and methods

2.1. Materials

The PEN 60/70 asphalt binder and the NR utilised in this study were supplied by Kuad Kuari Sdn. Bhd., Malaysia and a local vendor in Penang, Malaysia, respectively. Table 1 displays the rheological properties of the conventional asphalt binder used in this study. Meanwhile, the silane additive and the wax-based surfactant were used as surface agents to improve the bonding and wettability of bitumen-aggregate combinations. The silane-based chemical additive served as an anti-stripping agent, and added at a concentration of 0.1% by mass of the asphalt binder (Ameri et al., 2018; Hasan et al., 2017; Taiyu Vietnam Co., LTD., 2018). Likewise, the manufacturer of the substance recommends adding 0.3% by mass of a wax-based additive (consisting of an amphoteric high molecular compound) to the asphalt binder. The physical appearances of the wax and the silane additive used are illustrated in Fig. 1. Tables 2 and 3, provide the basic physical and chemical properties of the NR and silane and wax additives, respectively (van Oss et al., 1988).

2.2. Sample preparation

The blending compositions of NR with different additives and dosages are presented in Table 4. Prior to the blending process, the asphalt binder

Table 1
Basic and rheological properties of PEN 60/70 (Sani et al., 2020a).

Property	PEN 60/70	Test specification
Penetration at 25 °C (mm)	61	ASTM D5-1997
Softening point (°C)	50.5	ASTM D36-1995
Viscosity at 135 °C (Pa·s)	0.66	ASTM D4402-2012
Rutting, $G^*/\sin\delta$ at 64 °C (kPa)	2.5	ASTM D7175-2011

(a) (b)

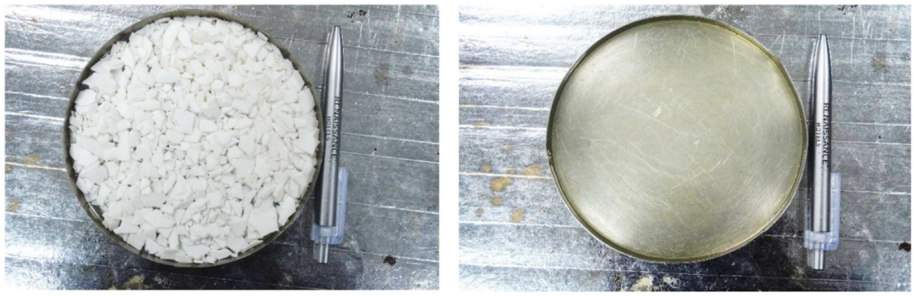

Fig. 1. Physical appearances of additives of study. (a) Wax. (b) Silane.

Table 2
Physical and chemical properties of NR.

Property	Description
Form	Liquid
Color	Milky white
pH	10
Water content (%)	35–40
Total solid content (TSC) (%)	58
Dry rubber content (DRC) (%)	60.1
Mechanical stability time (MST) (s)	720
Viscosity at 100 rpm (cP)	163.2
Alkalinity with cationic stabilizer	0.35
Alkalinity with anionic stabilizer	0.40
Potassium hydroxide (KOH) number	0.97
Volatile fatty acid (VFA) number	0.18

Table 3
Basic physical and chemical properties of additives.

Property	Wax	Silane
Colour	White	Pale yellow
Form	Flaky	Liquid
Density (g/mL)	0.955	–
Solubility in water	Insoluble	10% soluble
pH	2.3	–
Flash point (°C)	199	80
Melting point (°C)	70	–
Viscosity (Pa·s)	0.1	0.1–0.5

Table 4
Blending parameters of asphalt binders.

Binder designation	NR dosage (wt%)	Additive dosage (wt%)	Time (min)	Blending temperature (°C)
PEN 60/70	–	–	–	–
L	6	–	20	160
L+Z	6	0.1 (silane)	30	160
L+G	6	0.3 (wax)	30	160

Note: L = PEN 60/70 binder + NR, L+Z = PEN 60/70 binder + NR + silane, L+G = PEN 60/70 binder + NR + wax.

Table 5
SFE components of probe liquids (mJ/m^2).

Solvent	γ^{LW}	γ^{+}	γ^{-}	γ^{T}
Water	21.7	25.50	25.5	72.7
Glycerol	35.0	3.93	57.4	63.9
Formamide	39.0	2.28	39.6	58.0

was first heated at 160 °C into a flowable state. The asphalt binder and NR were blended using a propeller mixer with the incorporation of additives at their respective dosages. Each asphalt binder mixture was blended at a speed of 1000 rpm for 30 min at 160 °C. Initially, the respective additive was thoroughly blended with the asphalt binder for approximately 10 min. NR was then gradually poured into the mixture of the asphalt binder to prevent unnecessary foaming. The modified asphalt binder was further blended for an additional 20 min. Subsequently, asphalt binder mixtures were subjected to three different ageing environments: unaged, short-term ageing (STA), and long-term ageing (LTA). A rolling thin film oven (RTFO) test was performed at 163 °C to mimic an STA phase of an asphalt binder throughout the manufacturing and placement phases of an asphaltic concrete mixture. The asphalt binder samples were placed in cylindrical glass bottles attached to the rotating carriage within the oven, which was operated at 15 rpm for 85 min of temperature ageing with continuous exposure to heat and air. Likewise, the pressurized ageing vessel (PAV) conditioning process was conducted to simulate the LTA of an asphalt binder during its in-service performance. RTFO-aged asphalt binders were subsequently aged for 20 h in a PAV chamber to produce long-term aged asphalt binder. The PAV was heated to 100 °C and compressed to 2.10 MPa. Prior to sample removal from the PAV, the pressure was gradually released at the end of the ageing phase. The PAV-aged asphalt binder samples were then located in a container and transferred to a vacuum oven, where they were heated to 170 °C for 30 min to eliminate any trapped air.

Table 6
SFE components of aggregates (mJ/m^2).

Aggregate	γ^{LW}	γ^{+}	γ^{-}	γ^{AB}	γ^{T}
Granite*	58.01	401.07	1.76	53.14	111.15
Limestone*	44.30	46.37	678.98	354.88	399.18

Note: * adopted from the works by Howson et al. (2011) and Hesami et al. (2013).

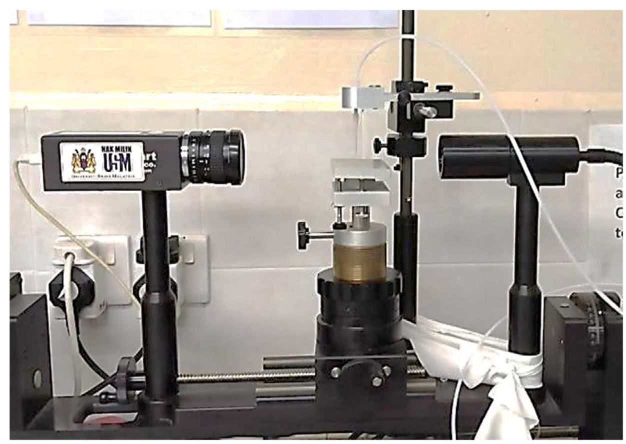

Fig. 2. Contact angle test: goniometer assembly.

Table 7
Contact angles of PEN 60/70 and modified asphalt binders.

Sample	Solvent	Contact angle (°)					
		Unaged		STA		LTA	
		Average	CV (%)	Average	CV (%)	Average	CV (%)
PEN 60/70	Deionised water	93.53	2.19	101.06	0.16	106.70	1.83
	Glycerol	93.51	0.22	102.14	2.71	91.75	2.00
	Formamide	92.22	1.74	83.61	0.38	86.56	0.51
L	Deionised water	74.57	0.41	82.02	3.63	86.03	0.36
	Glycerol	89.03	0.52	101.37	2.48	106.04	3.01
	Formamide	84.16	1.44	87.87	1.86	97.63	2.41
L+Z	Deionised water	83.85	1.03	85.46	3.08	88.46	2.26
	Glycerol	81.85	1.40	99.28	0.03	94.94	1.06
	Formamide	80.45	1.80	85.66	3.49	100.80	1.02
L+G	Deionised water	71.12	2.42	87.70	0.18	89.31	1.56
	Glycerol	75.92	1.62	97.14	1.07	97.39	0.28
	Formamide	71.73	1.39	82.19	2.48	91.07	3.17

Table 8
Surface free energy components of PEN 60/70 and modified binders in various ageing conditions.

Sample	Ageing condition	γ^{LW} (mJ/m^2)	γ^+ (mJ/m^2)	γ^- (mJ/m^2)	γ^{AB} (mJ/m^2)	γ^T (mJ/m^2)	*A/B*
PEN 60/70	Unaged	6.30	11.00	1.30	12.30	18.60	8.45
	RTFO-aged	73.54	3.04	14.52	17.57	91.11	0.21
	PAV-aged	14.63	0.48	0.86	1.33	15.97	0.55
L	Unaged	17.69	32.69	0.22	32.92	50.60	145.95
	RTFO-aged	51.90	26.54	12.88	39.43	91.33	2.06
	PAV-aged	25.76	28.36	5.29	33.65	59.41	5.36
L+Z	Unaged	9.80	13.78	1.95	15.73	25.52	7.08
	RTFO-aged	48.93	19.24	9.36	28.60	77.53	2.06
	PAV-aged	0.00	23.44	6.57	30.00	30.00	3.57
L+G	Unaged	19.97	24.83	0.19	25.02	44.99	133.49
	RTFO-aged	61.56	13.43	11.63	25.06	86.63	1.15
	PAV-aged	19.43	16.26	0.68	16.93	36.36	24.08

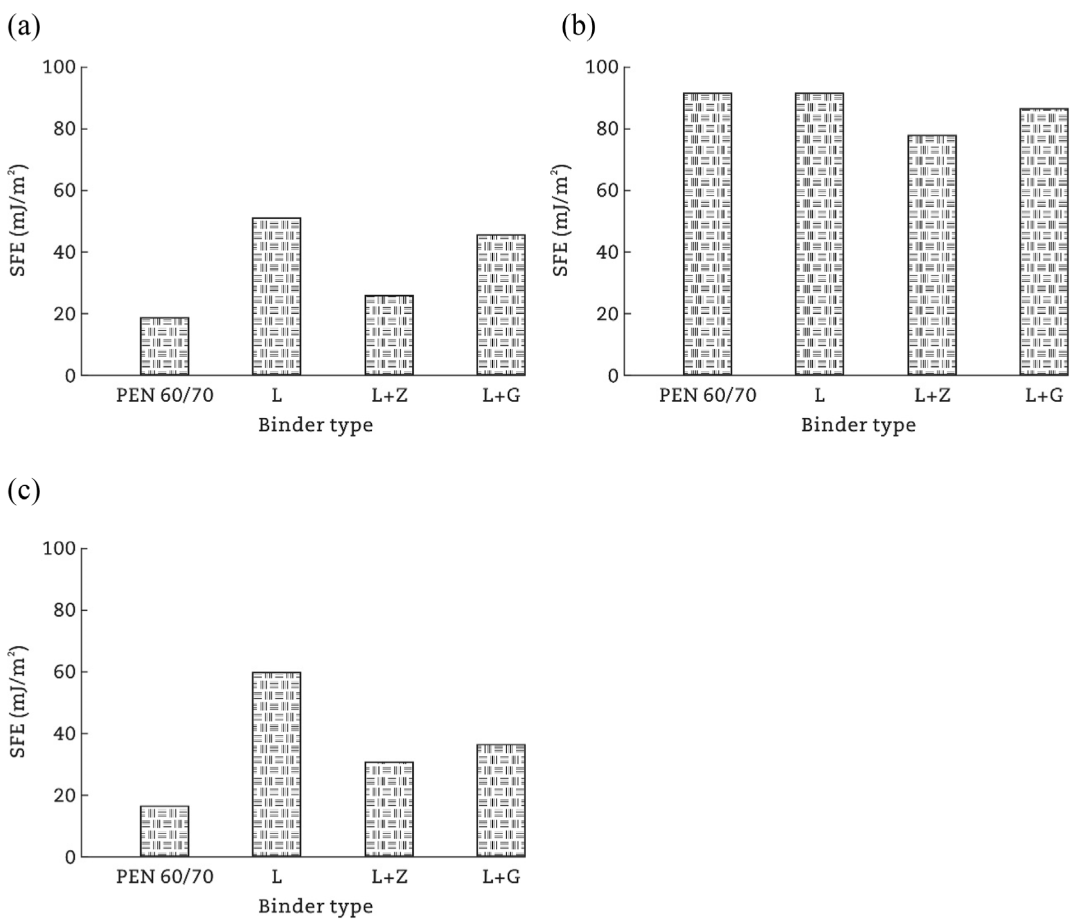

Fig. 3. Total surface free energies of PEN 60/70 and modified binders under different ageing conditions. (a) Unaged. (b) STA. (c) LTA.

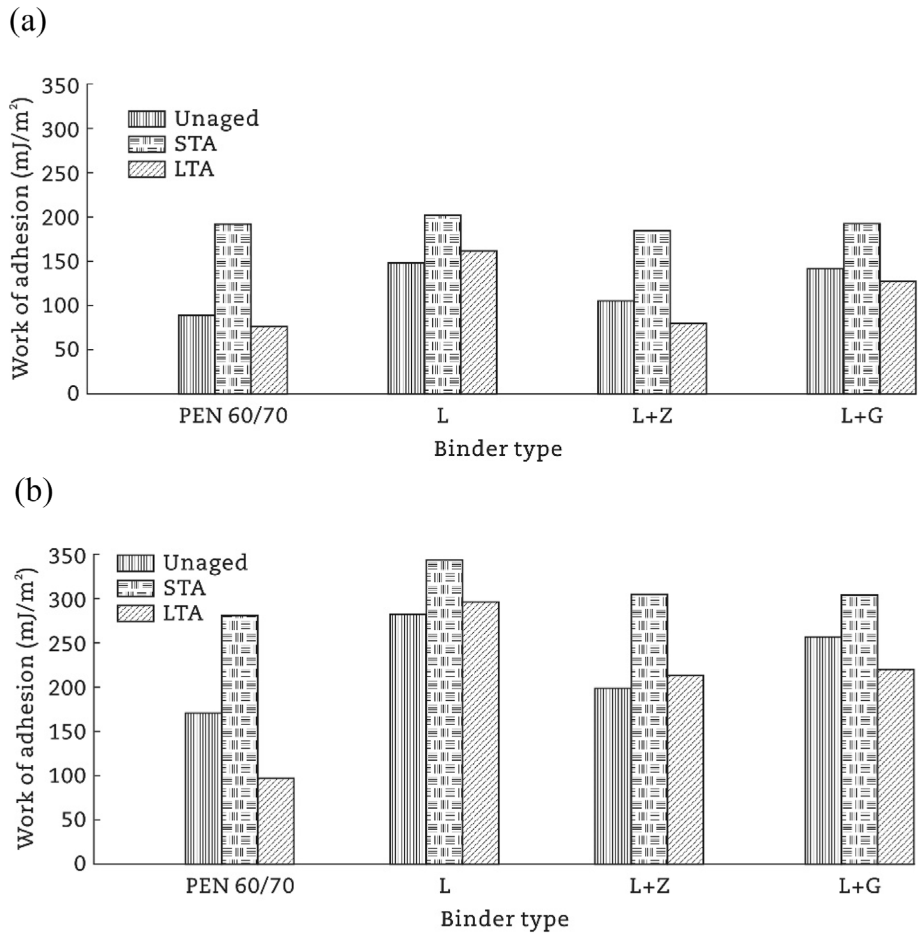

Fig. 4. Adhesion in dry condition of the PEN 60/70 and modified binders with different aggregate types. (a) Granite. (b) Limestone.

2.3. Contact angle test

Generally, wettability entails the quantification of contact angles as the main data, which connotes the degree of wetting as a solid and liquid come into contact. There are two common methods for measuring contact angle, namely the direct optical and the indirect force methods. In this study, the direct optical method based on the sessile drop method was adopted. This technique was applied to quantify the contact angles between asphalt binders and three distinct solvents, specifically deionised water, formamide, and glycerol, whose relative polar and non-polar characteristics are described in Table 5. Likewise, Table 6 shows the SFE components of the aggregates used in this study. The contact angles and the surface free energies (SFE) of the asphalt binders were assessed using a goniometer coupled with DROPimage Advanced software, as displayed in Fig. 2.

Prior to testing, the base and modified asphalt binders were preheated in an oven into a flowable state at the temperatures of 150 °C and 165 °C, respectively. Subsequently, the surfaces of the 25 mm × 50 mm microscopic glass slides were flame-dried to remove moisture and dust. The clean glass slides were then dipped vertically in hot asphalt binders and rapidly removed while maintaining the same vertical position to provide a uniform, smooth coating on the glass slide substrate. Lastly, the coated glass slides were allowed to cool down to room temperature before conducting the test. Each kind of probe liquid was poured at a rate of 5 μL per sample over the surface of the asphalt binder samples to ensure consistency and eliminate gravitational impact. The built-in DROPimage Advanced software was used immediately to measure the contact angles and surface free energies of the respective samples.

2.4. Analytical approach using surface free energy

Surface free energy (SFE) acts as an analytical tool for determining and measuring the potential moisture susceptibility of an asphalt mixture, which may be broken down into adhesion and debonding work components of asphalt binder and aggregate. The SFE approach was implemented to study the potential moisture degradation of the rubberised asphalt binders. The C++ algorithm was adopted to compute the SFE elements of the asphalt binders (Kakar et al., 2016).

As reported in the literature, the essential components of SFE are the non-polar and acid-base constituents of asphalt binder and aggregates. According to the Good-van Oss-Chaudhury (GvOC) concept (van Oss et al., 1988), Cheng (2002) established the SFE components of liquid and solid which can be expressed and computed using the listed equations.

$$\gamma_a = \gamma_a^{LW} + \gamma_a^{AB} \tag{1}$$

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB} \tag{2}$$

where γ_a is the SFE of liquid, γ_s is the SFE of solid, γ_a^{LW} is the SFE of Lifshitz-van der Waals component of liquid, γ_s^{LW} is the SFE of Lifshitz-van der Waals component of solid, γ_a^{AB} is the SFE of polar component of liquid, γ_s^{AB} is the SFE of polar component of solid.

The surface free energy of liquid-solid interface is therefore stated as follows.

$$\gamma_{as} = \gamma_s + \gamma_a - 2\sqrt{\gamma_s^{LW} + \gamma_a^{LW}} - 2\sqrt{\gamma_s^{AB} + \gamma_a^{AB}} \tag{3}$$

The relationship between surface free energy and contact angle can be represented by the Young-Dupre equation as follows.

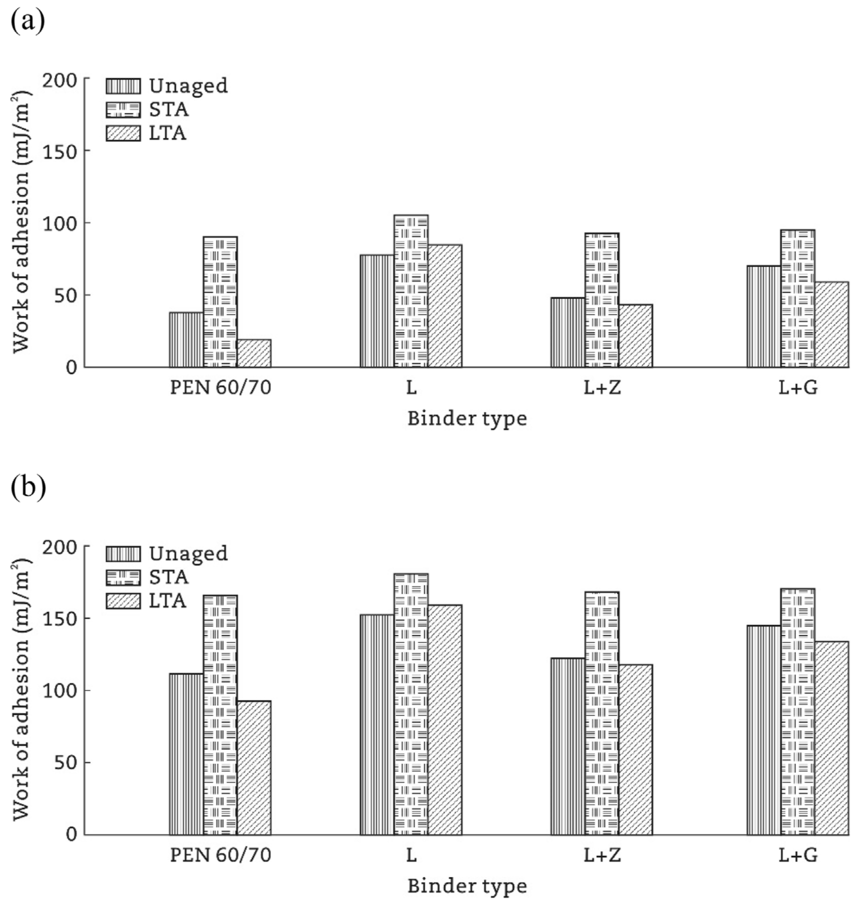

Fig. 5. Adhesion in wet condition of the PEN 60/70 and modified binders with different aggregate types. (a) Granite. (b) Limestone.

$$\gamma_a \cos(\theta) = \gamma_s - \gamma_{as} \tag{4}$$

2.5. Arithmetic calculus algorithm of surface free energy components

The algorithm developed by Kakar et al. (2016) was applied to compute the SFE components of the PEN 60/70 and NR-modified binders. The algorithm was analysed based on the determinants method (Crammer's rule), which operates on the concept of an explicit equation to solve a linear equation system with variables “$n \leq 3$”. This rule stipulates that each entity of the solution to a linear system with $Mx = n$ form is specified in Eq. (5) (Habgood and Arel, 2012).

$$X_i = \det(M_i(n))/\det(M) \tag{5}$$

where M_i (n) denotes a matrix of M with a column of ith column substituted by the n entity.

The input parameters involved in the developed algorithm included contact angle and probe liquid SFE components. The computation demonstration of the aforementioned parameters is presented in pseudocode given in studies carried out by Kakar et al. (2016, 2019). The algorithm was developed using the Microsoft Visual C++ 2010 version platform. Eq. (6) below is utilised to evaluate the desired SFE components of asphalt binder.

$$\gamma_a(1+\cos(\theta)) = 2\left(\sqrt{\gamma_b^{LW}\gamma_a^{LW}} + \sqrt{\gamma_b^{-}\gamma_a^{+}} + \sqrt{\gamma_b^{+}\gamma_a^{-}}\right) \tag{6}$$

where γ_a is the probe liquid total surface free energy, θ is the contact angle, γ_a^{LW}, γ_a^{+}, and γ_a^{-} are the non-polar and polar (acid and base) SFE components of probe liquid, γ_b^{LW}, γ_b^{+}, and γ_b^{-} are the non-polar and polar (acid and base) SFE components of the probe binder.

The γ_a^{LW}, γ_a^{+} and γ_a^{-} of each probe liquid used for the contact angle measurement were accounted for using previously established data on the SFE components of such liquids as shown in Table 4. The γ_a represents the γ^T values, i.e., the total surface free energy of each probe liquid used. Meanwhile, the γ_b^{LW}, γ_b^{+}, and γ_b^{-} components are unknown variables to be determined.

Hence, re-arranging Eq. (6) into Eq. (7) by diving both sides with γ_a.

$$1+\cos(\theta) = 2\sqrt{\gamma_b^{LW}}\,\frac{\sqrt{\gamma_a^{LW}}}{\sqrt{\gamma_a}} + 2\sqrt{\gamma_b^{-}}\,\frac{\sqrt{\gamma_a^{+}}}{\sqrt{\gamma_a}} + 2\sqrt{\gamma_b^{+}}\,\frac{\sqrt{\gamma_a^{-}}}{\sqrt{\gamma_a}} \tag{7}$$

Eq. (7) is further segmented into known and unknown components, as presented in the equations as $1+\cos(\theta) = Y_i$, $2\sqrt{\gamma_b^{LW}} = X_1$, $2\sqrt{\gamma_b^{-}} = X_2$, $2\sqrt{\gamma_b^{+}} = X_3$, $\frac{\sqrt{\gamma_a^{LW}}}{\sqrt{\gamma_a}} = A_{1i}$, $\frac{\sqrt{\gamma_a^{+}}}{\sqrt{a}} = A_{2i}$, $\frac{\sqrt{\gamma_a^{-}}}{\sqrt{\gamma_a}} = A_{3i}$, where i signifies the attained values for probe liquids one, two, and three, which are denoted by the terms water, glycerol, and formamide, respectively.

The segmented components are then rewritten into three independent Eqs. (8)–(10).

$$(M_{11}+M_{21}+M_{31})X_1 = Y_1 \tag{8}$$

$$(M_{12}+M_{22}+M_{32})X_2 = Y_2 \tag{9}$$

$$(M_{13}+M_{23}+M_{33})X_3 = Y_3 \tag{10}$$

where X_1, X_2, and X_3 are the three unknowns of asphalt binder SFE components.

2.6. Work of adhesion

According to the theory of physical surface chemistry, SFE refers to the energy required to detach a solid or liquid in a vacuum to create a

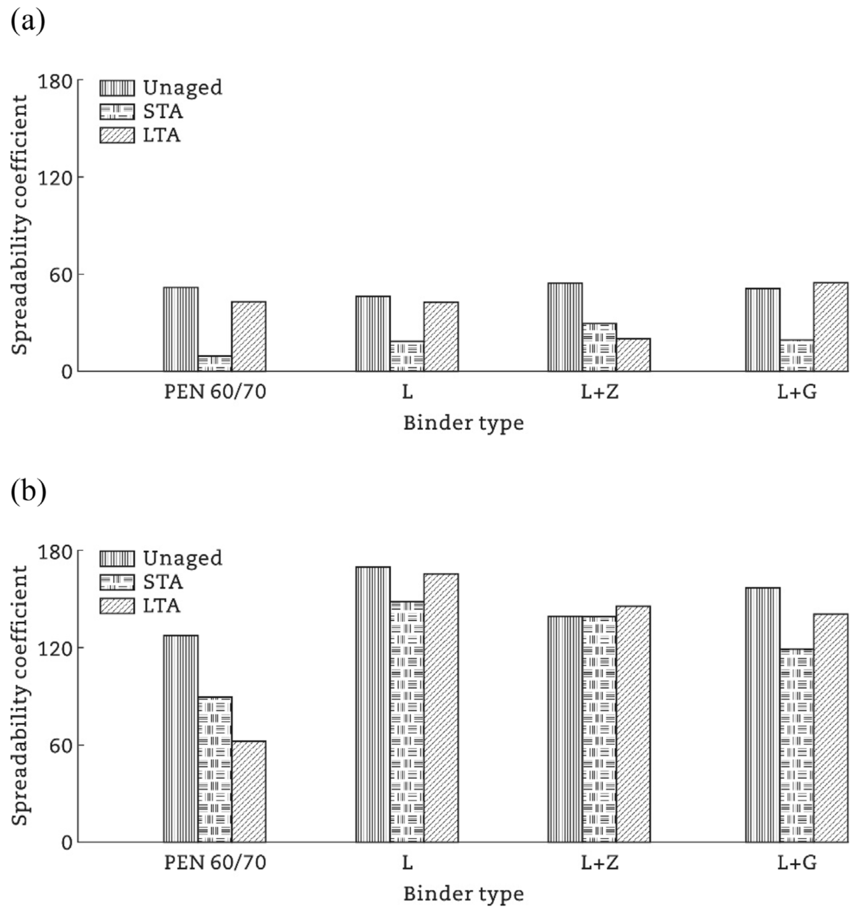

Fig. 6. Spreadability coefficients of the PEN 60/70 and modified binders with different aggregate types. (a) Granite. (b) Limestone.

new interface. Work of adhesion (*W*) is defined when a separate material is heterogeneous and creates two dissimilar surfaces. Likewise, energy is defined as cohesion when a separate material is homogenous (Tan and Guo, 2013). The adhesion property of asphalt with aggregate may be analytically calculated by comparing the effects of the SFE regarding *W*. The *W* of asphalt binder and aggregate can be estimated in dry and wet interface circumstances, utilizing Eqs. (15)–(20), respectively. Table 5 details the surface-energy components of the aggregates used.

$$W_{\text{adhesion}} = W_{\text{s}} + W_{\text{b}} - W_{\text{bs}} \tag{11}$$

The work of adhesion between the aggregate and binder are the resultant difference between their work of adhesion before interaction and adhesion as a result of their interaction.

Thus, the work of adhesion of the aggregate (s) and the binder (b) is given as.

$$W_{\text{s}} = \gamma_{\text{s}} = \gamma_{\text{s}}^{\text{LW}} + \gamma_{\text{s}}^{\text{AB}} \tag{12}$$

$$W_{\text{b}} = \gamma_{\text{b}} = \gamma_{\text{b}}^{\text{LW}} + \gamma_{\text{b}}^{\text{AB}} \tag{13}$$

The work of adhesion before the interaction of each aggregate and binder component W_{s} and W_{b} is the same as the individual surface free energy component of the aggregate and binder γ_{s} and γ_{b}, respectively.

Meanwhile, the adhesion between the two due to their interaction W_{bs} would be like the following.

$$W_{\text{bs}} = \gamma_{\text{b}} + \gamma_{\text{s}} - 2\sqrt{\gamma_{\text{b}}{}^{\text{LW}}\gamma_{\text{s}}{}^{\text{LW}}} - 2\sqrt{\gamma_{\text{b}}{}^{\text{AB}}\gamma_{\text{s}}{}^{\text{AB}}} \tag{14}$$

Placing Eqs. (12)–(14) in Eq. (11).

$$W_{\text{adhesion(dry)}} = 2\sqrt{\gamma_{\text{b}}{}^{\text{LW}}\gamma_{\text{s}}{}^{\text{LW}}} + 2\sqrt{\gamma_{\text{b}}{}^{\text{AB}}\gamma_{\text{s}}{}^{\text{AB}}} \tag{15}$$

Similarly, for the effect of wet moisture conditions.

$$W_{\text{stripping(wet)}} = W_{\text{wb}} + W_{\text{ws}} - W_{\text{bs}} \tag{16}$$

$$W_{\text{wb}} = \gamma_{\text{w}} + \gamma_{\text{b}} - 2\sqrt{\gamma_{\text{w}}{}^{\text{LW}}\gamma_{\text{b}}{}^{\text{LW}}} - 2\sqrt{\gamma_{\text{w}}{}^{\text{AB}}\gamma_{\text{b}}{}^{\text{AB}}} \tag{17}$$

$$W_{\text{ws}} = \gamma_{\text{w}} + \gamma_{\text{s}} - 2\sqrt{\gamma_{\text{w}}{}^{\text{LW}}\gamma_{\text{s}}{}^{\text{LW}}} - 2\sqrt{\gamma_{\text{w}}{}^{\text{AB}}\gamma_{\text{s}}{}^{\text{AB}}} \tag{18}$$

$$W_{\text{bs}} = \gamma_{\text{b}} + \gamma_{\text{s}} - 2\sqrt{\gamma_{\text{b}}{}^{\text{LW}}\gamma_{\text{s}}{}^{\text{LW}}} - 2\sqrt{\gamma_{\text{b}}{}^{\text{AB}}\gamma_{\text{s}}{}^{\text{AB}}} \tag{19}$$

Hence, Eq. (16) becomes as follow.

$$W_{\text{stripping (wet)}} = 2\gamma_{\text{w}} - 2\left(\sqrt{\gamma_{\text{w}}{}^{\text{LW}}\gamma_{\text{b}}{}^{\text{LW}}} - \sqrt{\gamma_{\text{w}}{}^{\text{AB}}\gamma_{\text{b}}{}^{\text{AB}}}\right) + 2\left(\sqrt{\gamma_{\text{b}}{}^{\text{LW}}} - \sqrt{\gamma_{\text{w}}{}^{\text{LW}}}\right)\sqrt{\gamma_{\text{s}}{}^{\text{LW}}} + 2\left(\sqrt{\gamma_{\text{b}}{}^{\text{AB}}} - \sqrt{\gamma_{\text{w}}{}^{\text{AB}}}\right)\sqrt{\gamma_{\text{s}}{}^{\text{AB}}} \tag{20}$$

where $W_{\text{adhesion(dry)}}$ and $W_{\text{stripping(wet)}}$ are the work of adhesion in dry and wet conditions, respectively. The subscripts b, s, and w are the asphalt binder, aggregate, and water surface energies, respectively.

2.7. Wettability and compatibility ratio

The quantitative indices of wettability and resistance to moisture have been established for further study of adhesion despite the presence of moisture using asphalt binder and aggregate SFE components (Alvarez et al., 2012). The compatibility ratio (CR) is the ratio of adhesion work in dry conditions to free energy release in moist condition. As reported by Bhasin (2004), the CR parameter is used to rate mixtures of bitumen/aggregate with respect to their susceptibility to moisture. A greater CR value is preferable as it implies a higher bond energy under dry

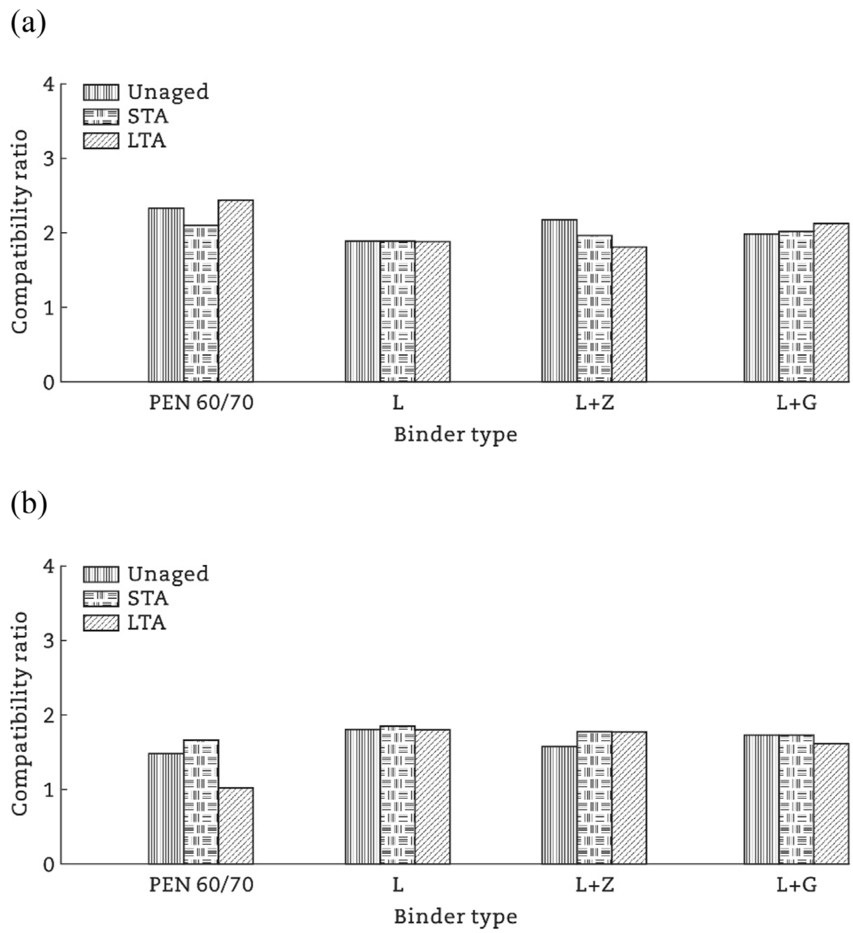

Fig. 7. Compatibility ratio of the PEN 60/70 and modified binders with different aggregate types. (a) Granite. (b) Limestone.

Table 9
Moisture damage mixture test results for the CR verification.

Sample	Coatability test (percent of binder remain coated) (%)		Modified Lottman test		
	Static water immersion	Water boiling	Indirect tensile strength (kN/m^2)		Tensile strength ratio (TSR) (%)
			Dry	Wet	
PEN 60/70	95.0	75.0	506.3	446.4	83
L	97.0	95.0	518.9	462.6	93
L+G	99.9	99.5	665.9	611.6	92

conditions and a lower free energy release in the presence of moisture. Stronger bond energy corresponds to greater bond and aggregate adhesion. The optimal CR is between 0.5 and 1.5. Spreading coefficient (SC) and CR can be computed using Eqs. (21)–(23), respectively (Alvarez et al., 2012).

$$SC = W_{adhesion(dry)} - W_{ca} \tag{21}$$

$$W_{ca} = 2\gamma^{T} \tag{22}$$

$$CR = \frac{W_{adhesion(dry)}}{\left|W_{stripping\ (wet)}\right|} \tag{23}$$

where W_{ca} and γ^{T} are the work of cohesion of binder and the total surface free energy of binder, respectively.

3. Results and discussion

3.1. Total surface free energy

Results on the analysis of the surface free energy (SFE) components of PEN 60/70 grade of asphalt binder and NR modified asphalt binders (with and without the addition of additives) are presented. A goniometer was used to estimate contact angles and further characterisation was made for the interfacial characteristics study of the aggregate-binders. The findings are illustrated in terms of work of adhesion in dry and wet situations, spreadability coefficient, and compatibility ratio. Table 7 presents the asphalt binder contact angles with deionised water, glycerol, and formamide under different ageing conditions. The SFE components of the asphalt binders are summarised in Table 8. Fig. 3(a)–(c) demonstrate the ageing effects on the total SFE of PEN 60/70 and modified

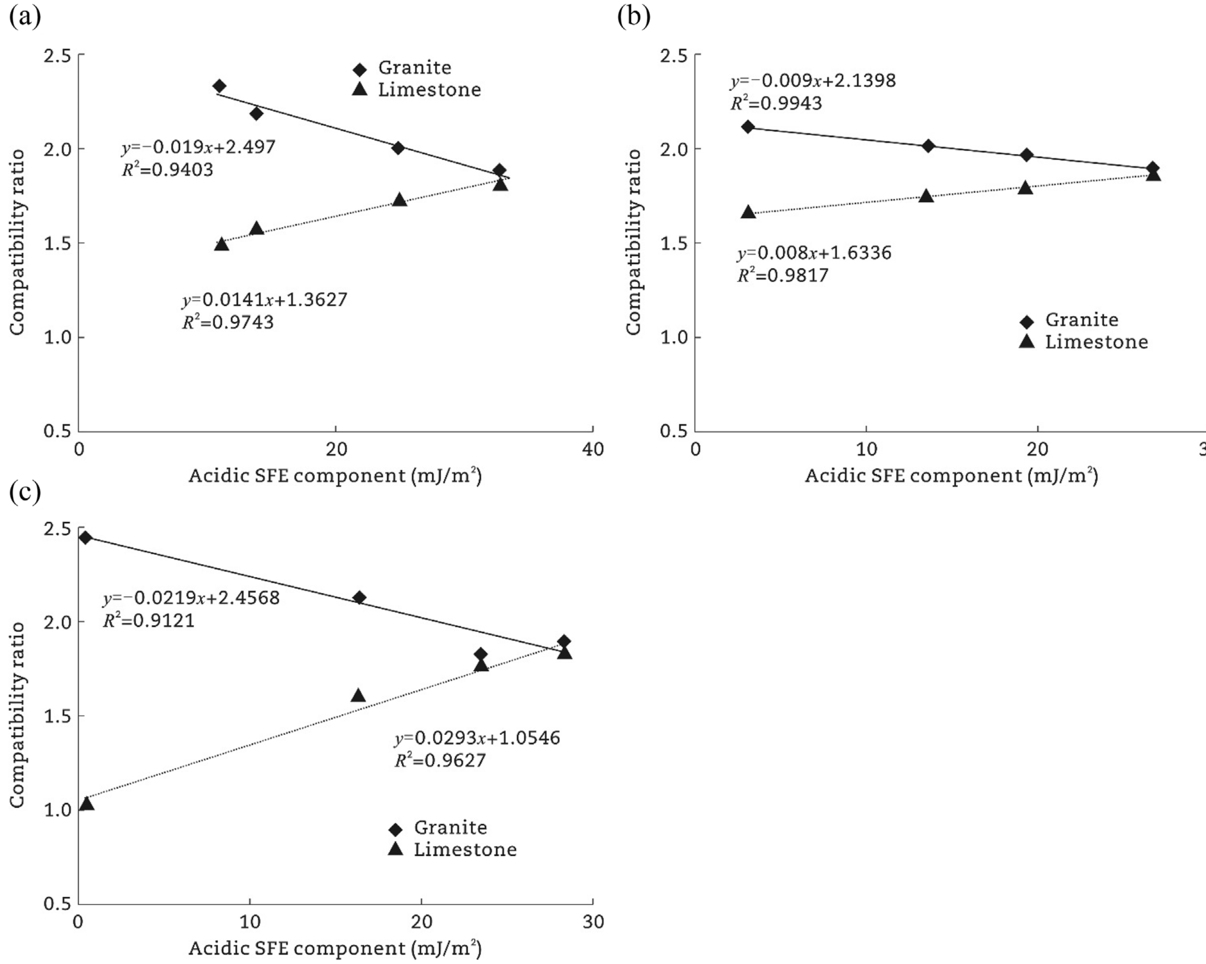

Fig. 8. Correlation between CR and acidic SFE component of asphalt binders. (a) Unaged. (b) STA. (c) LTA.

asphalt binders. The results display that the total surface free energies of the NR-modified binders under different ageing conditions were higher compared to PEN 60/70. Wen et al. (2017) and Sani et al. (2020a) stated that NR as a modifier increases the viscosity of an asphalt binder. This causes an upsurge in the production temperature of asphalt. However, the incorporation of additive (silane or wax) in the NR-modified binder reduces the surface tension. This indicates that additives serve as surfactants in asphalt binders to reduce their surface free energy. The short-term ageing condition displays a higher total surface free energy in comparison to the long-term ageing, respective of all types of asphalt binder. The non-polar component significantly contributes to the total surface free energy of asphalt binders, whereas the effects of magnitudes of polar components are minor (Little and Bhasin, 2006). The SFE of asphaltenes and resins may vary depending on the specific chemical composition of the crude oil and the conditions under which tests are conducted. Basically, asphaltene is a vital element with no specific melting temperature and often froths and expands when heated, leaving a carbonaceous residue. Asphaltene components are the crude oil molecules with the highest molecular weight, heaviest, greatest surface activity, and greatest polarity. Technically, it is extracted from petroleum by adding a hydrocarbon, which is a non-polar solvent with surface tension of less than 25 dyn/cm at 25 °C. The constituents of resin are soluble in n-pentane or n-heptane; however, they cannot be extracted from the earth using these solvents. The oil fraction is another constituent. It consists of saturates and aromatic fractions that can be extracted from the earth using n-pentane or n-heptane (Speight, 2006). Bitumen with high resin/asphaltene ratios produced stable bituminous work with adhesion values greater than 55 mJ/m^2. The measurement of the acidity and basicity of a surface by measuring the contact angles at a water-bitumen interface appears to be a more helpful approach than the non-aqueous potentiometric titration. The study revealed a high correlation between the surface charge of the bitumen droplet, as assessed by zeta potential, and the work of adhesion at the water-bitumen interface (Jada and Salou, 2002). The findings of this study in relation to SFE components and the ageing process conform with those of existing studies (Kakar et al., 2016, 2019).

3.2. Fracture resistance via work of adhesion in dry condition

The work of adhesion for the PEN 60/70 and the NR-modified binders (with and without additive incorporation) is illustrated in Fig. 4. The findings demonstrate that the NR-modified binders (with and without additive incorporation) have improved work of adhesion than the PEN 60/70 binder alone. The simulations of short-term and long-term ageing had minimal to no effect on the adhesion of modified asphalt binders. A higher adhesion was observed in the RTFO-aged binder compared to the PAV-aged binder. Likewise, the NR-modified asphalt binder with additive incorporation exhibited a smaller adhesion reduction than the NR-modified binder alone. Both additives demonstrated comparable performances; however, the NR-modified binder with the wax additive performed slightly better under all ageing circumstances than that with the silane additive. This occurs as a result of the different compositions and origins of the additives. The asphalt binders (with and without additive incorporation) with limestone aggregate recorded higher fracture resistance than those with granite aggregate at all ageing conditions. This infers that the bonding capability of limestone aggregate is superior to

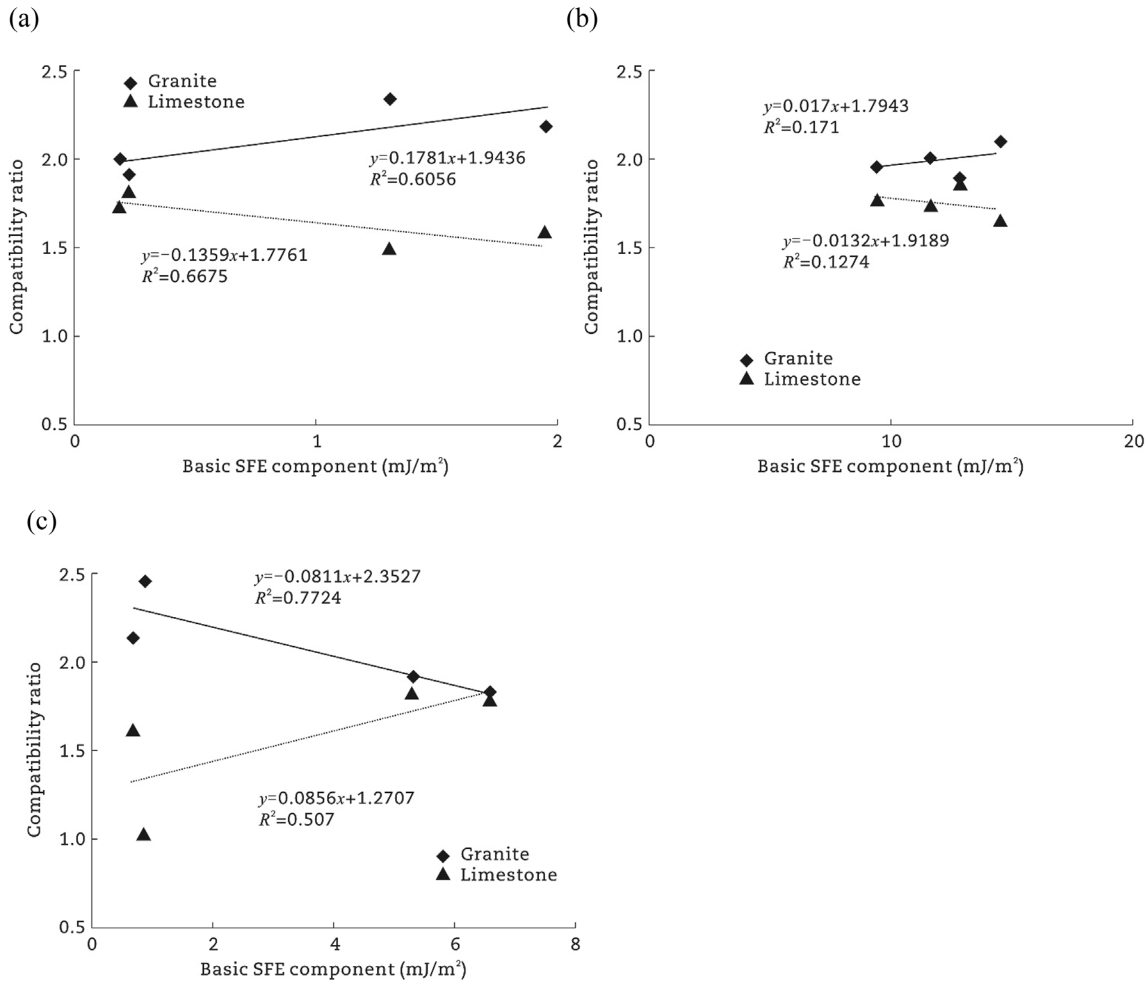

Fig. 9. Correlation between CR and basic SFE component of asphalt binders. (a) Unaged. (b) STA. (c) LTA.

that of granite aggregate (Kakar et al., 2016). According to Cheng et al. (2001), the surface area of limestone is three times than that of granite. Therefore, under uniform conditions of wheel force and environmental impact, it is considerably simpler to initiate an adhesive fracture at the asphalt-granite interface. Conclusively, as reported by previous studies (Kakar et al., 2016, 2019; Oliveira et al., 2013; Sani et al., 2021), the establishment of a good bond between asphalt and aggregate is basically dependent on the ability of the asphalt to wet the aggregate. The aggregate wettability increases when the surface tension or surface free energy (SFE) of adhesion decreases. Therefore, depending on the nature of the aggregate, the incorporation of additives successfully improved the NR-modified binder's wettability potential.

3.3. Moisture resistance via work of adhesion in wet condition

The adhesion energy in wet conditions, i.e., asphalt binder-aggregates interface energy bonding in the presence of water, was determined using Eq. (15). Wet adhesion energy with a lower absolute value is more favourable for an exemplary behaviour of an asphalt mixture against moisture degradation, indicating a stronger bonding between asphalt binder and aggregates and vice versa (Hamzah et al., 2013). The wet adhesion energy results for PEN 60/70 are shown in Fig. 5. Meanwhile, the addition of NR to the binder resulted in a small improvement. Similar to the case of dry adhesion conditions, limestone aggregates showcased a better improvement in adhesion over granites. Despite that, both aggregate types in conjunction with the introduction of the additive improved the adhesion energy of the NR-modified binders at all ageing conditions. Furthermore, the results of both granite and limestone aggregates portrayed a similar consistent trend with respect to the ageing conditions. The adhesion energies of granite aggregate asphalt binder combinations are lower than those with limestone. However, the NR-modified binders with additive slightly improve higher than those without additives at all ageing conditions. The NR-modified binder containing 0.1% silane-based additives performed slightly better than the binder blends of 0.1% wax additive. Overall, this indicates that the presence of additives in binder samples can improve the asphalt-aggregate bonding better than without.

3.4. Wettability of asphalt binders (spreadability coefficient)

Fig. 6 depicts the spreadability results of the PEN 60/70 blends with aggregates. The results show that the spreadability of the unaged PEN 60/70 decreased with the incorporation of NR using granite aggregate. However, the asphalt binder blends with limestone aggregate exhibited a better improvement in spreadability than with granite at unaged, short-term ageing, and long-term ageing conditions. These findings are in agreement with the existing literature (Alvarez et al., 2012; Kakar et al., 2016, 2019). Obviously, the introduction of NR to an asphalt binder increases its viscosity, stiffening the mixture (Sani et al., 2020a, b) and may affect the wettability of the binder. Besides, surface-active agents are added to the asphalt mix as additives (Wasiuddin, 2007). As Howson (2011) reported, wax and liquid-based surfactants usually decrease the surface free energy of asphalt binders, hence increasing their wettability. Improved wettability of an asphalt binder will also improve the interfacial adhesion, fracture resistance, and moisture resistance. Both wax and silane additives act as surface-active agents, increasing wettability and

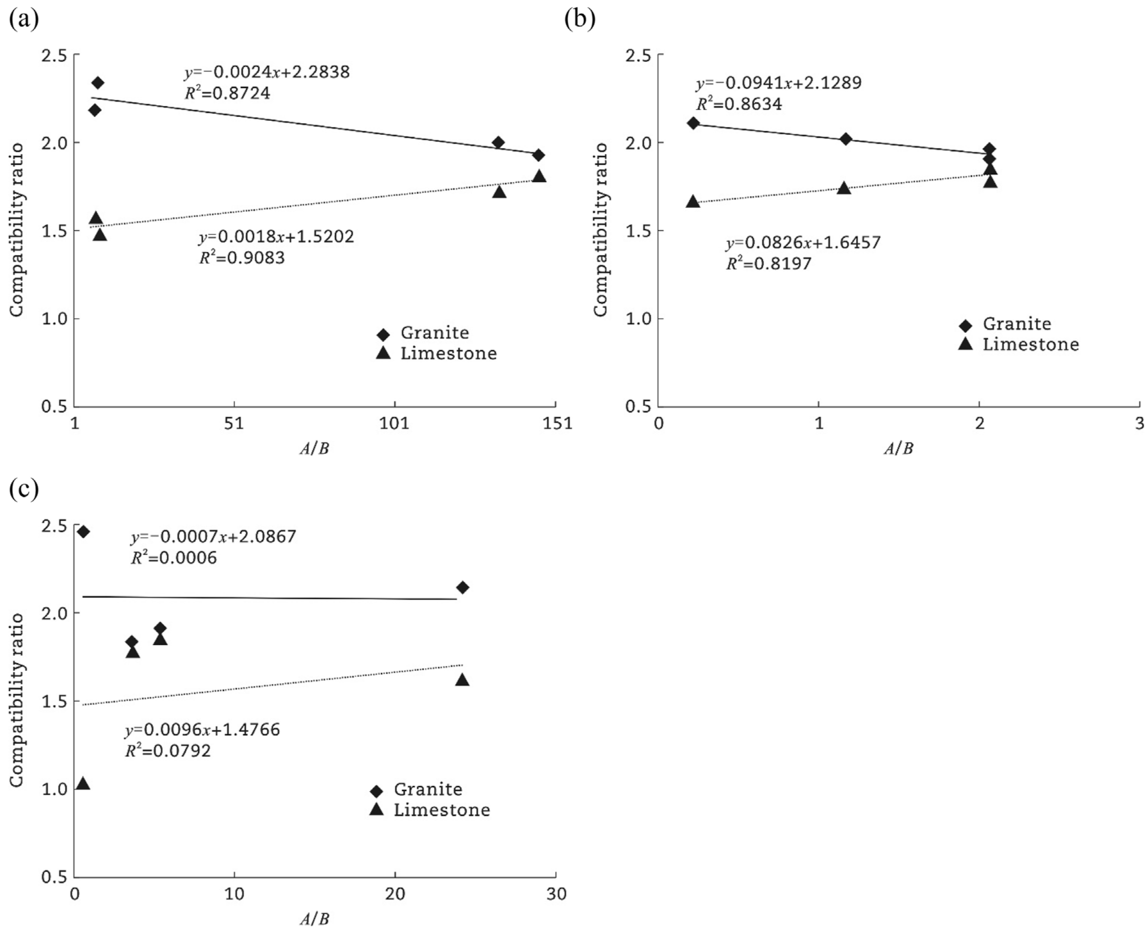

Fig. 10. Correlation between CR and *A/B* ratio of asphalt binders. (a) Unaged. (b) STA. (c) LTA.

wetting surface area while promoting adhesion between binders and aggregates. The spreadability coefficients of the binders with granite aggregate were lower than those with limestone possibly due to its rough interfacial structure and low surface tension. The effect of ageing on all tested samples also slightly lowered the spreadabililty performance of the binders due to oxidation leading to higher stiffness and viscosity. However, the incorporation of additives reduced its stiffness leading to an improved spreadability rate. This suggests that the chemistry determines the interface between aggregate and binder adhesive strength and bonding interaction (Wasiuddin, 2007). For this reason, the impact of ageing can be inferred to be dependent upon the initial chemistry of different asphalt binders and aggregate types. In the PAV-ageing condition, the adhesion of the limestone aggregate binders strengthened more than in the short-term ageing, except for the PEN 60/70 binder. This finding was evident in all types of additives used. Conclusively, the spreadability of asphalt binders over limestone aggregate was higher than that of granite, regardless of the additive types.

3.5. Moisture susceptibility via compatibility ratio (CR)

The compatibility ratio (CR) of the aggregate-asphalt binder blends was calculated using Eq. (23) in view of both dry and wet conditionings. The CR of all the control and modified asphalt binders used in this study is shown in Fig. 7. The results of all samples are comparably more or less consistent across all ageing conditions as compared to the control sample. Theoretically, aggregate-asphalt binder mixtures with a higher CR value are more resistant to moisture damage than those with a lower CR value. In Fig. 7(b) of samples involving limestone aggregate, the NR-modified binders, regardless of the additive incorporation, demonstrated comparable moisture damage resistance under all ageing conditions, with the exception of the PEN 60/70, which exhibited a remarkably lower CR value than other samples initially conditioned at LTA. Despite minor variations in the moisture resistance of the respective asphalt-aggregate interfaces under different ageing conditions, all the results exceeded the minimum requirement of 0.5. The presence of silica (SiO_2) in aggregate is an influential factor in affecting the adhesive properties. Cheng (2002) and Kakar et al. (2016) reported that limestone is less prone to stripping than granite. The inconsistency may arise from the various asphalt binder compositions, which may influence the interface chemistry for the binder-aggregate bonding resistance.

Furthermore, the compatibility ratio results were validated using available mixture test results (Table 9) from the research project, comprising samples prepared using granite and wax additive. Unfortunately, no mixture test was conducted with limestone aggregate, silane additive, and STA/LTA ageing conditions. The presented results involved loose and compacted asphalt mixtures tested using the coatability test and the modified Lottman test, respectively. The coatability test that mimicked the stripping potential was assessed using boiling water and static water immersion tests. An image analysis approach was employed to assess the level of stripping for both coatability tests based on the digital images taken. Overall, the incorporation of the NR modifier and additive has enhanced the moisture resistance of the mixtures prepared using modified binders (L and L+G). Based on the static immersion and boiling water tests, the modified asphalt mixtures with additive incorporation efficiently enhance the stripping resistance. This indicated that the additives served as surfactant agents, reducing the surface free energy and enhancing the bonding at the binder-aggregate interface in asphalt mixtures, as presented by the modified Lottman test results. Similar

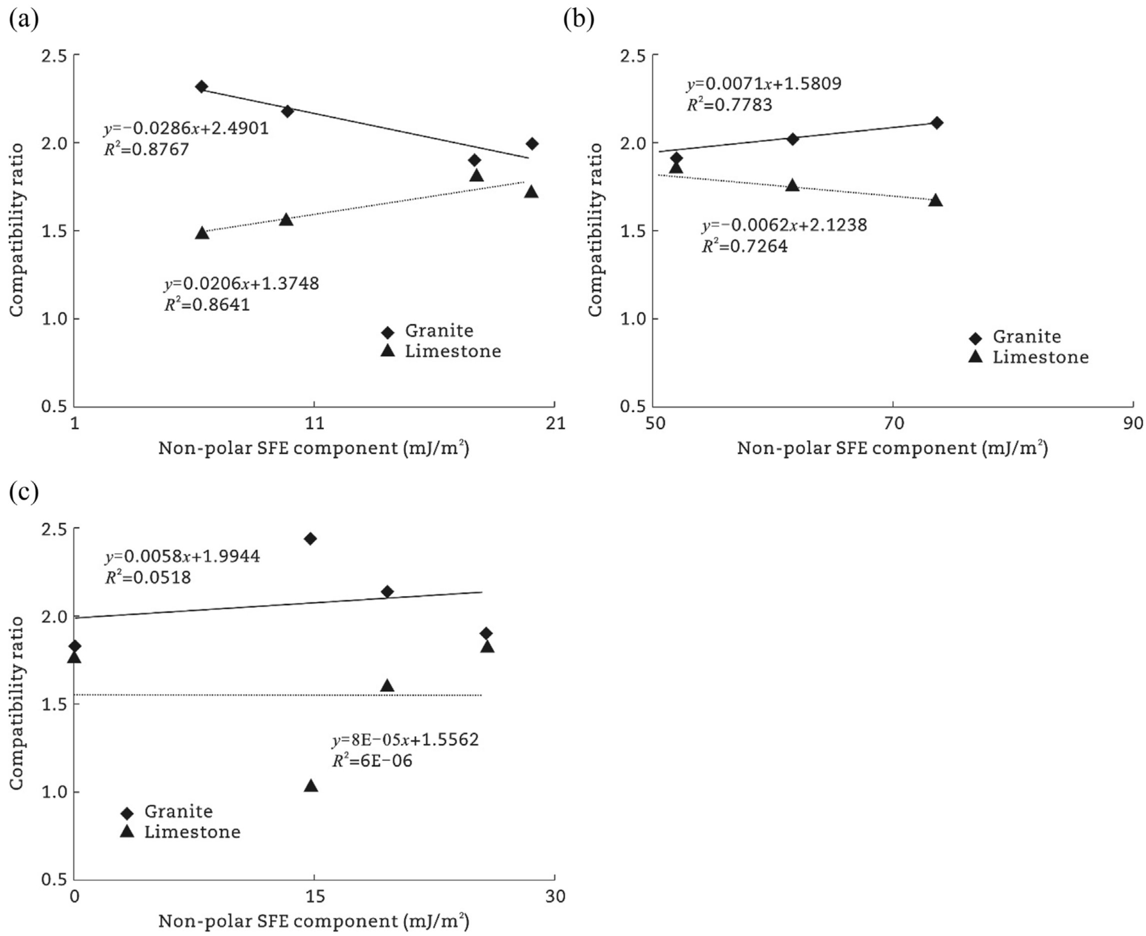

Fig. 11. Correlation between CR and non-polar SFE component of asphalt binders. (a) Unaged. (b) STA. (c) LTA.

findings were also reported by Oliveira et al. (2013), who used a modified Lottman approach to examine the effect of surfactant-based additives on the efficiency of rubberized warm asphalt mixtures.

3.6. Correlation evaluation between CR and SFE components

The correlation between CR and the corresponding SFE components (acidic, basic, *A/B* ratio, non-polar, and total SFE components) of asphalt binder was established to ascertain the relationship among them. Without the need for further research, such a connection may help provide a clearer picture of their resistance to moisture damage based on the relevant elements of SFE components (Wasiuddin, 2007). Table 8 presents the variation of acidic, basic, and non-polar components in terms of the *A/B* ratio of rubberised asphalt binders with and without additives incorporation at different ageing conditions. Figs. 8–12 display the correlations of CR with the acidic, basic, *A/B* ratio, non-polar, and total SFE components. Prevalent poor correlations ($R^2 < 0.5$) were observed for the PAV-aged samples. Fig. 8 clearly shows that the acidic SFE components of the asphalt binders demonstrated significant correlations with CR for both aggregate types at unaged, RTFO-ageing, and PAV-ageing conditions. This infers that the acidity and basicity of asphalt binder influence its aggregate component compatibility, with a more acidic binder being more compatible with basic aggregates than acidic ones and vice versa. Nonetheless, a strong rate of correlation was observed with respect to granite aggregate at RTFO-ageing condition ($R^2 = 0.99$) compared to the limestone aggregate ($R^2 = 0.98$). Likewise, Fig. 9 illustrates that the degree of correlation of basic SFE components with aggregates was lower than that of acidic components ($R^2 < 0.9$) at unaged and PAV-ageing conditions. However, in the RTFO-ageing condition, both aggregates exhibited poor correlations ($R^2 < 0.5$), although the acidic components of the asphalt binders versus CR displayed a moderate correlation. Hence, deteriorating pavement conditions seemingly reduce the compatibility of binder acidity/basicity to aggregate interfaces. Fig. 10 shows the relationship between the acid-base component ratio and CR in view of all asphalt binder combinations with both aggregate types. At the unaged condition, granite aggregate displayed a good correlation ($R^2 = 0.91$), while limestone aggregate exhibited a relatively unsatisfactory correlation ($R^2 = 0.87$). Moreover, from the ageing conditioning perspective, it can be deduced that granite aggregates are highly responsive to the *A/B* ratio in comparison to limestone at all conditions except the PAV-ageing. On the other hand, limestone aggregate shows fairly good correlations between CR and the non-polar and total SFE components compared to granite aggregate, as illustrated in Figs. 11 and 12, respectively. The correlations between limestone and granite aggregates and their corresponding non-polar and total SFE components showcased similarities in CR values at all ageing conditions. Conclusively, all the results indicated that CR values possessed better correlations with the acidic SFE component and *A/B* ratio of the blends of asphalt binders with granite aggregate. Limestone as aggregate in asphalt binders has better CR correlations with non-polar and total SFE components. The SFE components and *A/B* ratio were excellently correlated with CR at the unaged condition, while the acidic SFE component displayed better correlations at unaged, RTFO-ageing, and PAV-ageing conditions. The analysis may aid in forecasting the CR value of a specific combination of aggregate-asphalt binder according to the surface free energy components and the asphalt binder *A/B* ratio. Moreover, more validations between the CR and *A/B*

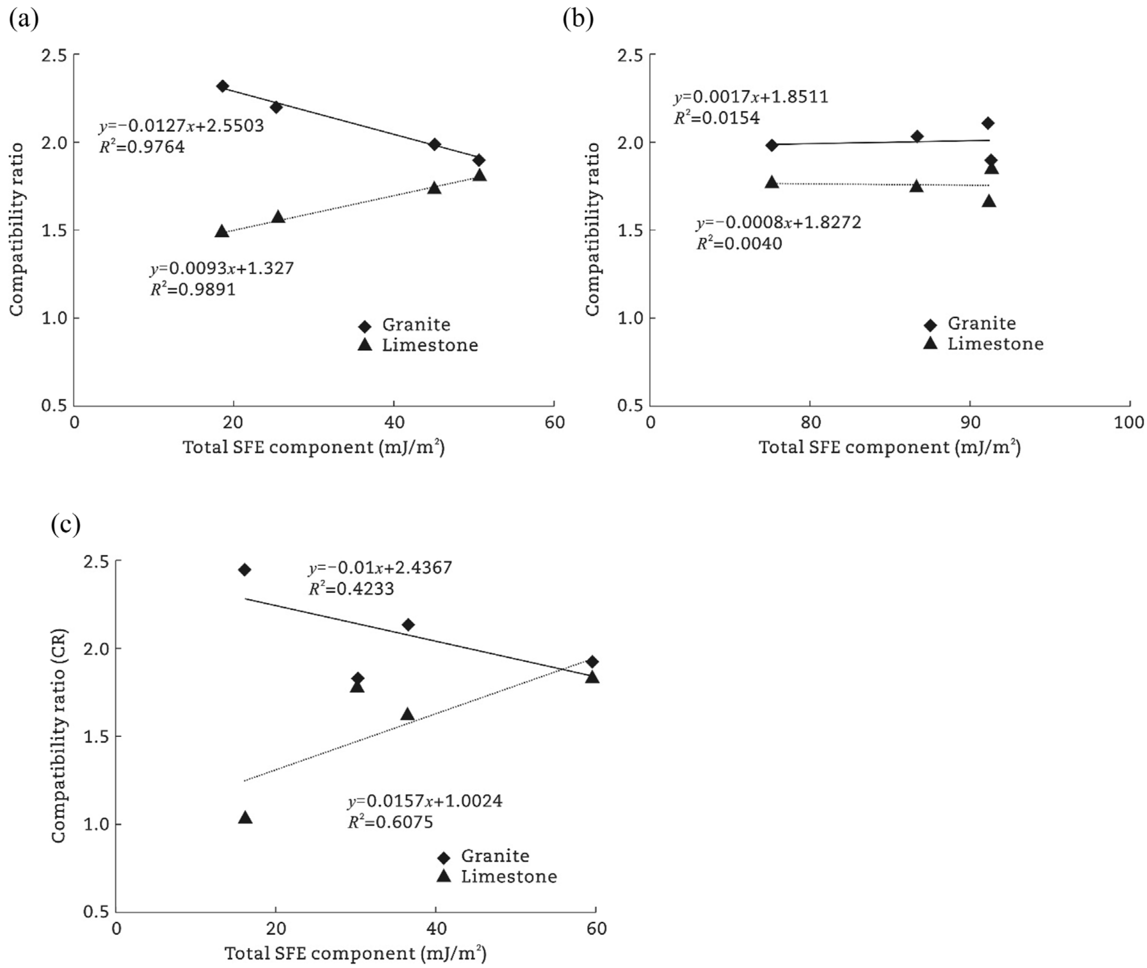

Fig. 12. Correlation between CR and total SFE component of asphalt binders. (a) Unaged. (b) STA. (c) LTA.

ratios are needed in order to generalize these relationships, as stated by Singh et al. (2018).

4. Conclusions

In this study, wax and silane additives were used as the surface agents to improve the bonding and wettability of NR-modified asphalt binder-aggregate combinations. The SFE components were employed to analytically evaluate the fracture resistance, spreadability coefficient, and moisture susceptibility of the binder-aggregate combinations. Two different aggregates (limestone and granite) were considered to be interrelated with the aggregate properties. The following conclusions can be attained from the current research.

(1) The presence of NR as a modifier increased the surface free energy of the PEN 60/70 binder. However, the subsequent incorporation of an additive (silane or wax) slightly reduced the surface free energy but improved the wetting ability of the binder on aggregate.
(2) The short-term aged samples exhibited the highest total surface free energy compared to the long-term aged samples of all asphalt binder combinations. The long-term aged binder, on the other hand, showed a decrease in surface free energy.
(3) The modified asphalt binders demonstrated improved adhesion under all conditions compared to the PEN 60/70 binder. The mimicked short- and long-term ageing conditions had minimal to no influence on the adhesive properties of the modified asphalt binder. The adhesion work was more pronounced in RTFO-aged binders than in PAV-aged.
(4) The adhesion energies between binders and granite aggregate in both dry and wet situations were slightly lower than those for limestone aggregate.
(5) Limestone aggregate promoted a higher coefficient of spreadability than granite under all asphalt binder combinations at different ageing conditions.
(6) Wax and silane additives performed identically in modified asphalt binders, with minimal differences. However, binders containing a wax-based additive showcased better fracture and moisture resistance, whereas binders containing silane demonstrated better spreadability.
(7) All surface free energy components and the A/B ratio showed excellent correlations with CR in the unaged condition, while the acidic SFE component displayed better correlations under the unaged, RTFO-ageing, and PAV-ageing conditions. The interrelationships shown by this research could be beneficial in predicting CR based on the SFE components of an asphalt binder.

Declaration of competing interest

The authors do not have any conflict of interest with other entities or researchers.

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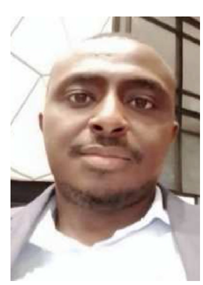

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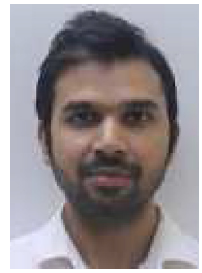

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