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PAPER

Assessment of moisture resistance and bonding behavior of cup lump rubber modified asphalt mixture containing wax-based surfactant

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Keywords: bitumen, modified asphalt, moisture sensitivity, surface free energy, sessile drop, pneumatic adhesion tensile testing instrument

Abstract

The present study evaluates moisture induced damage potential using a sessile drop method and a pneumatic adhesion tensile testing instrument (PATTI). The bonding behavior of the aggregates (granite and limestone) and cup lump rubber modified asphalt binder (CMB) with wax-based surfactant (WS) was evaluated. The results revealed that the granite aggregate exhibited a higher work of adhesion compared to the limestone. In the dry condition, the addition of more than 0.15% WS to the CMB reduced the work of adhesion and the bonding strength. Using the sessile drop method, the moisture resistance of the limestone aggregate with the CMB and WS was enhanced, but the bonding strength was reduced. The incorporation of WS reduced the surface free energy (SFE) regardless of the aging conditions and made the aggregate surface more hydrophobic for the increased interfacial adhesion. Incorporating WS in the CMB improved the work of adhesion under the wet condition, thus indicating that WS is an effective anti-stripping agent. Considering its comprehensive properties in the CMB, the amount of WS should be limited to 0.15%.

1. Introduction

Continuous effects of temperature and loading impact can cause irreversible deformation of hot mix asphalt (HMA) pavements. Over the past few decades, studies within the asphalt industry have investigated the practicality of employing biopolymers and synthetic polymers to reduce the rutting potential of asphalt pavements. Additives such as natural rubber have been investigated and proven to have a high potential to improve the stiffness, elasticity, and viscosity of asphalt binder. Studies have shown that natural rubber-modified asphalt improved rutting resistance at high temperatures (Wen *et al* 2017, Ansari *et al* 2021). Asphalt modification involving elastomer could enhance the efficiency of asphalt paving. Due to a considerable reduction in their thermal sensitivity, asphalt mixes incorporating biopolymer-modified bitumen exhibit improved rutting resistance at high temperatures, increased fatigue resistance, and greater cracking resistance at low temperatures (Zhu *et al* 2014). A microstructure modifier typically consists of elastomers and plastic-incompatible macromolecules or parts, providing a two-phase mechanism that absorbs light asphalt binder components. This results in, a swollen, cross-linked network structure, facilitating a modified asphalt binder with plasticity, elasticity, and ductility (Kakar *et al* 2016, Yang *et al* 2017). Although asphalt binder resistance to high-temperature deformation can be increased to a certain level, incompatibility may exist due to the varied polarity of molecular structure (Wang *et al* 2015, Pérez *et al* 2019). Consequently, there is a need to enhance water resistance, aging resistance, and durability of the polymer-modified asphalt.

Cup lump rubber (CLR) is a type of natural rubber identified for bitumen modification (Azahar *et al* 2016). This material, which is freshly coagulated rubber collected in cups connected to the trees, has been regarded as a long-term solution for increasing domestic consumption with its function as an asphalt additive. CLR is usually suitable to be mixed with asphalt binder due to its low water content and improved physical, rheological, and mechanical properties (Ansari *et al* 2021). Researchers found that rubberized asphalt binders increased the stiffness of the asphalt mix. The incorporation of 5% CLR significantly increases the resilient modulus, thereby enhancing resistance to permanent deformation (Azahar *et al* 2019). As an elastomeric polymer, CLR exhibits elastic and stretching natures that enhance the stiffness characteristic of asphalt binders as well as the blends to sustain persistent deformation. Compared to other polymeric compounds generated from crude oil, the utilization of natural rubber as an asphalt modifier is considered environmentally friendly and energy efficient (Al-Sabaeei *et al* 2019).

Moreover, studies have determined that applying surfactants with additives, such as the combination of latex and CLR which are stable at high temperatures and pressures, is essential in improving the performances of polymer-modified asphalts (Sani *et al* 2019, Poovaneshvaran *et al* 2020, Abdulrahman *et al* 2021, Ansari *et al* 2022). For example, adding WS was found to increase the homogeneity and stability of the natural rubber-modified asphalt binder (Sani *et al* 2020, Zin *et al* 2023). Tough Fix Hyper, which is a WS manufactured in Japan to enhancing the mixture stripping resistance (Kakar *et al* 2016, Poovaneshvaran *et al* 2023). The presence of moisture at the interface between the binder and aggregate is the primary cause of binder stripping from the aggregate surface. This is due to the reason that water-soluble species are present in the binder causing water to percolate from the film to its interface during exposure. Consequently, this would cause the formation of a thick layer of water at the interface and ultimately resulting in stripping or loss of adhesion in asphalt pavement (Romanowska *et al* 2024). The stripping phenomena can transform into additional undesirable defects beginning with rutting, corrugations, cracking and eventually culminating in total failure of asphalt pavements (Bagampadde and Kiggundu 2007, Canestrari *et al* 2010, Mehrara and Khodaii 2013, Ziari *et al* 2018). Moisture infiltration is commonly regarded as the key factor leading to stripping in asphalt (Liu *et al* 2024). This premature deterioration mechanism necessitates corrective repair, which in turn drives up maintenance costs (Kakar *et al* 2015, Kim *et al* 2024). Continuous and simultaneous effects of moisture and traffic load might result in the gradual dislodging of aggregates (Habal and Singh 2016).

The complex wettability of aggregate surfaces with asphalt involves physical and chemical interactions. As a result of the different sizes and diameters of pores in aggregates, the surfaces are complicated, rough, and uneven, making it challenging to evaluate the wettability with solely the surface-free energy (Kakar *et al* 2015, Kunaev *et al* 2024). The wettability of bitumen on aggregate is influenced by chemical interactions at the interface as well as the non-polar (hydrophobic) and polar (hydrophilic) characteristics of both asphalt binder and aggregates, respectively. Almost all types of asphalt binder are classified as non-polar. The majority of basic and acidic aggregate types have surfaces with high polarity. Therefore, it is challenging to wet a polar aggregate surface with the majority of non-polar bitumen (Saesaei *et al* 2024). Changing the surface of the aggregate from polar to non-polar can enhance the wettability of most non-polar asphalt binder types over polar aggregate. This can be achieved by lowering both the polar and non-polar components of aggregates in the asphalt binders. It is crucial to determine the physico-chemical parameters of the asphalt binder and aggregate during the assessment of moisture damage. These characteristics can be determined via the SFE (Cheng *et al* 2002, Ali *et al* 2013). In addition, various research has demonstrated that while the resistance to moisture damage in asphalt mixtures relies on the cohesive strength of the asphalt, it also depends on the adhesive strength between the binder and aggregate (Bhasin *et al* 2007, Howson *et al* 2011). However, adhesion materials have not been well explained in the literature. Given the complexity, researchers have endeavored to study the adhesion mechanism of adhesion materials. The recent development of incorporating WS in CMB remains underexplored.

The aim of this study was to evaluate the SFE in the CMB with or without WS on aggregates, either granite or limestone. The algorithm was further applied to determine the SFE components (non-polar, acid, and base), which were then analyzed using Young's Dupre equations to determine the behavior of bitumen-aggregate interface in terms of adhesion work. The PATTI test was employed to evaluate the bonding strength of the asphalt-aggregate interface.

2. Methodology

2.1. Materials

The conventional asphalt binder with the penetration grade of 60/70 was adopted in this study. The conventional binder and CMB (60/70 + 5% CLR based on the asphalt binder weight) properties are summarized in table 1. Four different percentages of WS, which are 0.1%, 0.15%, 0.2%, and 0.25% were incorporated to balance between the bonding and elastic characteristics of the CMB. This variation aims to assess the effectiveness of the surfactant that can be categorized as an anti-stripping agent in the CMB (Selvadurai

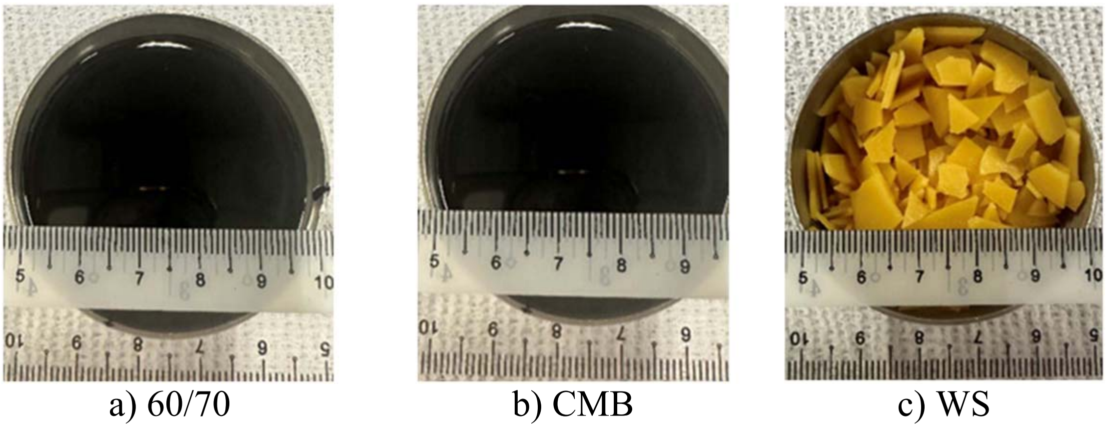


Figure 1. Physical appearance of the materials (a) 60/70; (b) CMB; (c) WS.

Table 1. Properties of the asphalt binder samples.

Properties	Asphalt binder samples	
	60/70	CMB (60/70 + 5% CLR)
Penetration at 25 °C	68	49
Softening point (°C)	48	59
Unaged $G^*/\sin\delta$; 64 °C (kPa)	1.95	—
Unaged $G^*/\sin\delta$; 76 °C (kPa)	—	2.1
RTFO $G^*/\sin\delta$; 64 °C (kPa)	2.47	—
RTFO $G^*/\sin\delta$; 76 °C (kPa)	—	2.24

Table 2. Physical and chemical properties of WS.

Properties	Description
Physical appearance	Solid with flaky shape
Color	Yellow
Solubility in water	Insoluble
Specific gravity	0.870 g cm^{-3}
Flash point	286 °C
Melting point	125 °C
pH value	9.6

et al 2021). The selection of these percentages is based on the manufacturer suggestion and outcomes of the previous study carried out by Poovaneshvaran *et al* (2023), where 0.15% WS was added to 60/70 and natural rubber modified asphalt binders. Figure 1 displays the physical appearance of the materials used in this research. The properties of WS are presented in table 2.

2.2. Sample preparations

The CMB samples were blended with WS at concentrations of 0.1%, 0.15%, 0.2%, and 0.25% by the weight of the asphalt binder, and then heated up to 170 °C. A binder mixer was used for the blending process at 1000 rpm for 30 min. To stimulate the short-term aging condition (RTFOT) during mixing and compaction in the field, the control sample (60/70) and the CMB samples with and without WS, were exposed to 163 °C of temperature for a duration of 85 min following the ASTM D 2872 standards. Subsequently, to simulated the long-term aging on asphalt binder, the RTFOT-aged binder further aged using the pressure aging vessel (PAV) at 100 °C for 20 h in accordance with ASTM D 6521. Figure 2 illustrates the process of sample preparation followed by aging stimulation for both short-term and long-term aging for the binder samples with surfactant (WS). Binder samples without WS can be directly aged based on the similar procedures for the short-term and long-term aged binders. An accelerated laboratory vacuum saturator (ALVS) was used to expose the specimens to the real

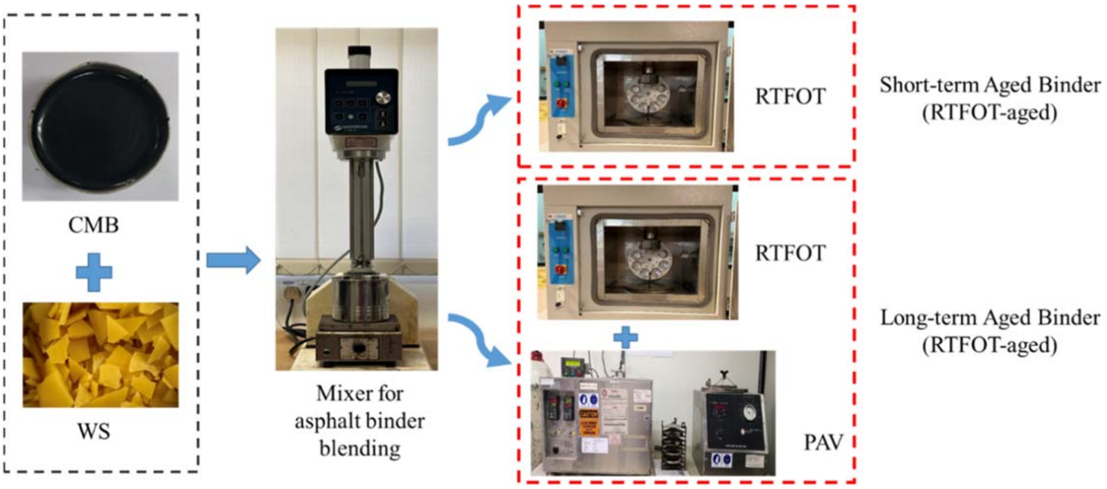


Figure 2. Blending and aging process of the CMB with surfactant (WS) sample.

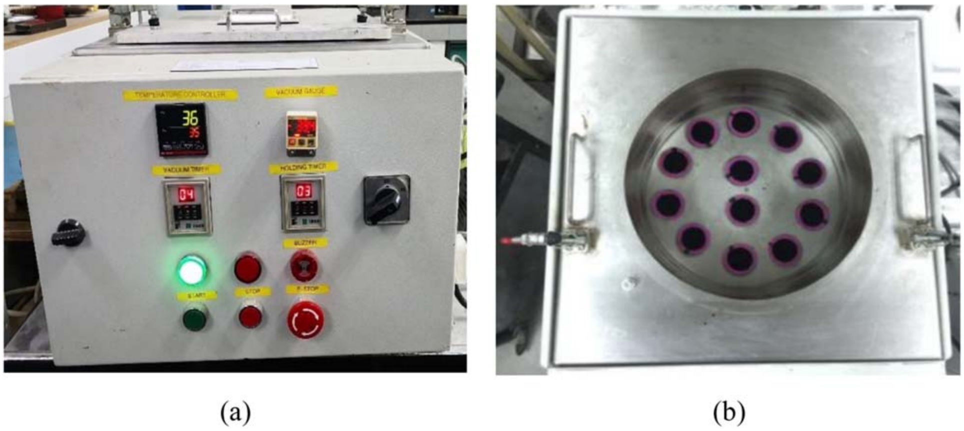


Figure 3. (a) ALVS and (b) The immersed samples in the ALVS chamber.

tropical climate conditions, which commonly lead to moisture-induced damage. Different aggregates and modifiers were analyzed and compared to determine the interfacial moisture damage of the varied materials. During the moisture conditioning process, the specimens were submerged in water within the ALVS-controlled chamber as presented in figure 3. The asphalt-aggregate interface was positioned at a minimum of 25 mm below the water surface. The stripping potential was increased through the addition of sodium carbonate (Na_2CO_3) diluted to a concentration of 6.62 $g\,l^{-1}$ with distilled water. The conditioning duration was set to 30 min at 35 °C. All specimens were prepared in accordance with the ASTM D 4867 standards.

2.3. Sessile drop method

The sessile drop method is a contact angle-based technique for evaluating solid surface energy and wettability. Figure 4 illustrates the contact angle goniometer used in this study to determine the contact angles, which were calculated using the Ossila software. Micro syringe was used to apply 3–5 μl of the selected liquid (deionized water, ethylene glycol, and formamide) onto the surface of the asphalt samples. The droplet was placed perpendicular to the syringe, whereby its formation was solely determined by gravity and interfacial tension. Instantaneous measurement was done on the static contact angles between the liquid probe and any solid surface by taking the photograph of the liquid drop applied onto the surface.

2.4. Bond strength

The PATTI test is used to assess the bond between aggregate and asphalt binder by evaluating fracture or tensile strength. This can involve measuring either the cohesive bond strength or the adhesive strength depending on the type of failure observed (Zaidi *et al* 2021). The PATTI developed by the National Institute of Standards and Technology;

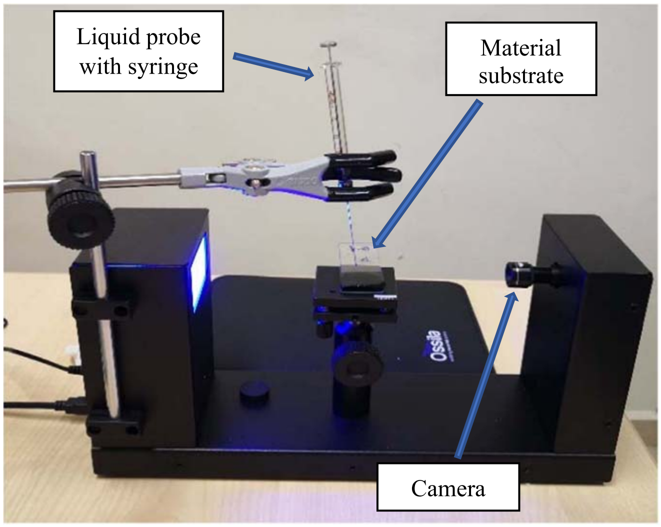


Figure 4. Contact angle device.

Figure 5. PATTI set-up and pull-off stub on substrate.

USA is depicted in figure 5. With the aid of this instrument, the maximum tensile stress applied to separate the binder from the aggregate substrates was recorded. Thin films of the binder samples at the aggregate interface and the pull-off stub were meticulously controlled to precisely identical thickness of 0.8 mm in all cases as shown in figure 5.

3. Analytical approach via SFE using different solvents

The SFE is an analytical method for evaluating and estimating the potential moisture susceptibility of an asphalt mixture, which can potentially be addressed directly as the adhesion and debonding of bitumen and aggregate components (Dalhat 2024). In this study, the SFE method was used to investigate the possibility of moisture-induced deterioration to rubberized asphalt binder materials.

As indicated in the literature, the non-polar and acid–base parts of asphalt binder and aggregates are primarily the components of SFE according to the Good-van Oss-Chaudhury (GVOC) theory (Van Oss *et al* 1988, Cheng *et al* 2002). The SFE of both liquid and solid can be calculated utilizing the equations below equation (1) and equation (2):

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

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

Where;

γ_a = the SFE of liquid,
γ_s = the SFE of solid,
$\gamma_a{}^{LW}$ = the Lifshitz–van der Waals component of liquid,
$\gamma_s{}^{LW}$ = the Lifshitz–van der Waals component of solid,
$\gamma_a{}^{AB}$ = the polar component of liquid, and
$\gamma_s{}^{AB}$ = the polar component of solid.
The SFE of the liquid–solid interface is expressed as equation (3):

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

The relationship between the SFE and the contact angle is explained by the following Young-Dupre equation:

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

3.1. Algorithm for arithmetic calculus of the SFE components

An algorithm was formulated to obtain the calculated SFE components of the 60/70 and CMB samples (with and without WS). The parameters used as inputs for this algorithm were the contact angle probe liquid and the SFE components which contained the asphalt binder blends. The following equation (5) was applied to evaluate the required SFE components of the binder samples:

$$\gamma_a(1 + \cos\theta)2(\sqrt{\gamma_b^{LW}\gamma_a^{LW}} + \gamma_b^{-}\gamma_a^{+} + \sqrt{\gamma_b^{+} + \gamma_a^{-}}) \tag{5}$$

where γ_a represents the probe liquid total surface energy, θ represents the contact angle, γ_a^{LW}, $\gamma_a{}^{+}$, and $\gamma_a{}^{-}$ represent the lifshitz-van der waals, acid, and base SFE components of the probe liquid, while γ_b^{LW}, γ_b^{+}, and γ_b^{-} refers to the lifshitz-van der waals, acid, and base SFE components of the probe binder.

Rearranging equation (5), equation (6) was obtained:

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

Equation (6) was further broken into two components, the known and unknown components, as shown in the following equation (7) and equation (8):

$$(1 + \cos\theta_i) = Y_i,\ 2\sqrt{\gamma_b^{LW}} = X_1,\ 2\sqrt{\gamma_b^{-}} = X_2,\ 2\sqrt{\gamma_b^{+}} = X_3 \tag{7}$$

$$\frac{\sqrt{\gamma_a^{LW}}}{\gamma_a} = M_{1i},\ \frac{\sqrt{\gamma_a^{-}}}{\gamma_a} = M_{2i},\ \frac{\sqrt{\gamma_a^{+}}}{\gamma_a} = M_{3i} \tag{8}$$

where 'i' represents the obtained values of the probe liquid, and '1', '2', and '3' represent water, ethylene glycol, and formamide.

The segmented components were then written as three independent equation (9), equation (10) and equation (11):

$$(M_{11} + M_{21} + M_{31})X_1 = Y_1 \tag{9}$$

$$(M_{12} + M_{22} + M_{32})X_2 = Y_2 \tag{10}$$

$$(M_{13} + M_{23} + M_{33})X_3 = Y_3 \tag{11}$$

where X_1, X_2, and X_3 represent the three unknowns. The calculated SFE components of the probe liquids in this study are listed in table 3.

Table 4 presents the SFE calculation results of the granite and limestone aggregates used. As can be seen, limestone exhibited a higher polarity component compared to granite. This is due to the mineralogical composition of the aggregates (Bhasin *et al* 2006).

3.2. Work of adhesion

Based on the surface physical chemistry theory, SFE refers to the energy required to separate liquid or solid to establish a new interface in a vacuum. The work of adhesion (*W*) is described as the work when a separated material forms two different surfaces that are not homogenous. Accordingly, for a homogenous separated material, the energy is referred to as cohesion (Tan and Guo 2013). The adhesion property of bitumen with aggregates can be calculated and interpreted based on the W values in the SFE analysis. For the materials in both the dry and wet interface conditions, W results were obtained using equation (12) until equation (18), respectively.

Table 3. SFE components of the probe liquids (ergs/cm^2) (Habal and Singh 2016).

Solvents	Non-polar (γ^{LW})	Acidic (γ^{+})	Base (γ^{-})	Total (γ^{T})
Water	21.78	25.5	25.5	72.8
Ethylene Glycol	29.0	47.0	1.9	48.0
Formamide	39	39.6	2.28	58

Table 4. SFE components of the aggregates (ergs/cm^2).

Aggregates	Non-polar (γ^{LW})	Polar (γ^{AB})	Total (γ^{T})
Granite	21.35	22.21	43.56
Limestone	18.21	22.51	40.72

Table 5. Contact angles of probe liquids for each asphalt binder sample.

Binder type	Solvent	Contact angle with probe (in degree)					
		Unaged		RTFOT		PAV	
		Average	SD	Average	SD	Average	SD
60/70	Deionized Water	93.55	1.28	98.08	0.45	102.61	0.76
	Ethylene Glycol	69.80	0.00	69.90	0.00	74.10	0.00
	Formamide	72.49	0.79	83.02	0.94	80.52	0.98
CMB	Deionized Water	87.97	0.05	88.61	0.33	80.26	1.96
	Ethylene Glycol	72.12	0.04	72.25	0.15	77.53	0.06
	Formamide	68.29	2.39	81.45	1.94	86.43	0.34
CMB-0.1WS	Deionized Water	82.44	0.81	89.31	1.54	95.41	1.18
	Ethylene Glycol	72.96	1.27	73.66	1.57	78.60	1.27
	Formamide	73.26	0.45	76.01	0.48	88.45	1.18
CMB-0.15WS	Deionized Water	85.21	0.78	93.35	2.60	96.47	0.23
	Ethylene Glycol	77.81	0.11	78.18	2.70	79.75	0.17
	Formamide	74.27	0.22	77.35	1.31	89.89	1.65
CMB-0.2WS	Deionized Water	89.70	0.25	91.87	0.58	98.07	0.62
	Ethylene Glycol	82.28	0.60	82.61	0.26	83.28	1.80
	Formamide	76.54	1.35	84.56	0.97	94.45	1.41
CMB-0.25WS	Deionized Water	91.37	1.30	88.95	1.35	102.93	1.21
	Ethylene Glycol	83.88	0.11	83.92	0.42	84.27	0.02
	Formamide	79.97	0.34	89.42	1.53	94.80	1.77

$$W_{adhesion(dry)} = W_s + W_b - W_{bs} \tag{12}$$

$$W_s = \gamma_s = \gamma_s^{LW} + \gamma_s^{\mathrm{AB}} \tag{13}$$

$$W_b = \gamma_b = \gamma_b^{LW} + \gamma_b^{\mathrm{AB}} \tag{14}$$

$$W_{bs} = \gamma_b + \gamma_s - 2\sqrt{\gamma_b^{LW}\gamma_s^{LW}} - 2\sqrt{\gamma_b^{AB}\gamma_s^{AB}} \tag{15}$$

$$W_{stripping(wet)} = W_{wb} + W_{ws} - W_{\mathrm{adhesion}(dry)} \tag{16}$$

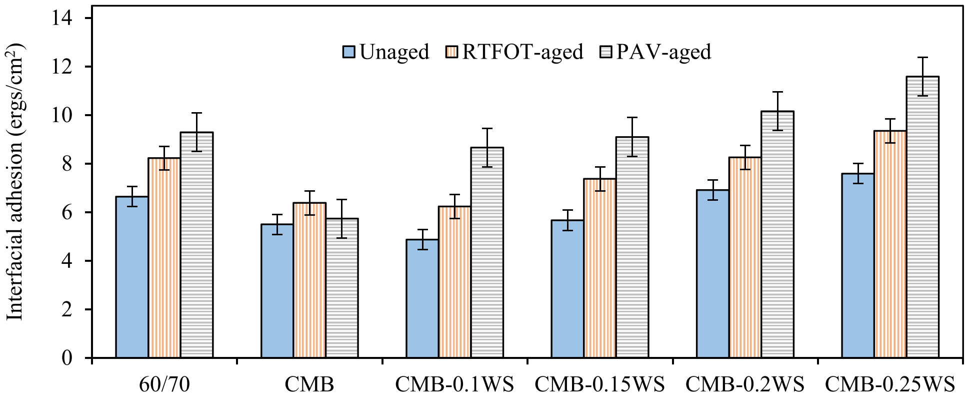
$$W_{wb} = 2\sqrt{\gamma_w^{LW}\gamma_b^{LW}} + 2\sqrt{\gamma_w^{AB}\gamma_b^{AB}} \tag{17}$$

$$W_{ws} = 2\sqrt{\gamma_w^{LW}\gamma_s^{LW}} + 2\sqrt{\gamma_w^{AB}\gamma_s^{AB}} \tag{18}$$

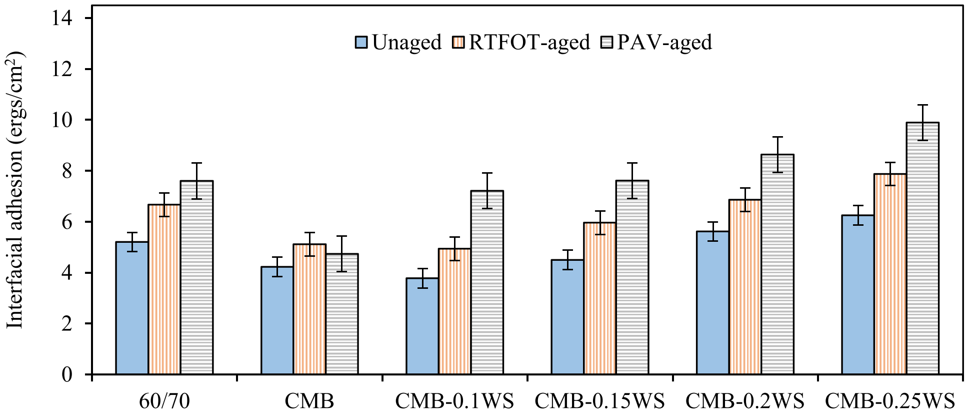
where $W_{adhesion\ (dry)}$ and $W_{stripping\ (wet)}$ denote the work of adhesion in dry and wet conditions, respectively, while the *b*, *s*, and *w* in subscripts represent binder, aggregate, and liquid surface energy, respectively.

3.3. Wettability and bond energy parameters

The ratio of work of adhesion in dry conditions to the free energy release in wet conditions is represented as the compatibility ratio (CR). Specifically, a higher CR value is the targeted outcome as this value marks the existence of a higher bond energy in the dry condition as well as a lower release of free energy when moisture is present.



a) Granite



b) Limestone

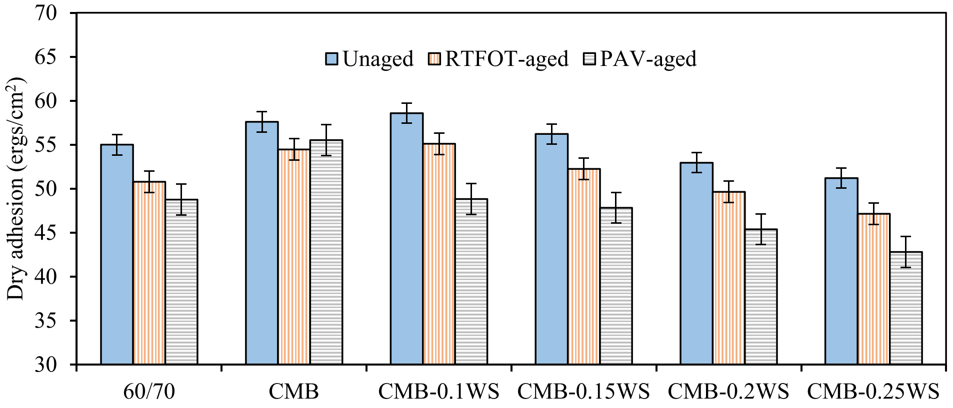
Figure 6. Interfacial adhesion of binders and aggregates.

Table 6. SFE components of the 60/70 and modified binder samples in various aging conditions.

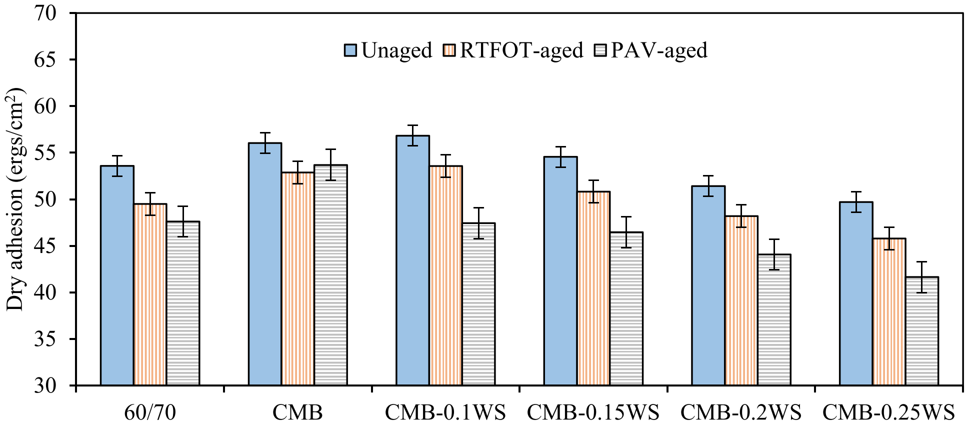
Binder type	Aging condition	Non-polar component γ^{LW} (ergs/cm^2)	Basic component γ^- (ergs/cm^2)	Acidic component γ^+ (ergs/cm^2)	Polar component γ^{ab} (ergs/cm^2)	Total SFE γ^T (ergs/cm^2)
60/70	Unaged	5.35	5.62	7.21	12.73	18.08
	RTFOT	4.49	5.61	5.36	10.97	15.45
	PAV	3.71	5.04	5.78	10.80	14.51
CMB	Unaged	6.51	5.30	8.00	13.03	19.54
	RTFOT	6.37	5.29	5.62	10.91	17.28
	PAV	8.30	4.59	4.81	9.40	17.70
CMB-0.1WS	Unaged	7.78	5.19	7.07	12.12	19.90
	RTFOT	6.22	5.10	6.57	11.58	17.80
	PAV	4.98	4.45	4.50	8.95	13.93
CMB-0.15WS	Unaged	7.13	4.56	6.89	11.20	18.33
	RTFOT	5.39	4.51	6.33	10.69	16.07
	PAV	4.78	4.31	4.28	8.59	13.37
CMB-0.2WS	Unaged	6.14	4.00	6.48	10.17	16.31
	RTFOT	5.68	3.96	5.11	8.99	14.68
	PAV	4.49	3.88	3.63	7.50	11.99
CMB-0.25WS	Unaged	5.79	3.80	5.88	9.46	15.24
	RTFOT	6.30	3.80	4.35	8.13	14.43
	PAV	3.66	3.76	3.58	7.33	10.99

The CR can be calculated using equation (19):

$$CR = \frac{Wadhesion(dry)}{Wstripping(wet)} \tag{19}$$



a) Granite



b) Limestone

Figure 7. Work of adhesion of 60/70 and modified binders in the dry condition.

4. Results and discussion

Contact angles were measured using a goniometer and further characterization was performed to study the interfacial aggregate-binder characteristics. The pull-off test approach was employed to ascertain the adhesive and cohesive properties of the rubberized asphalt binders. The findings are presented in terms of the work of adhesion under both dry and wet conditions, as well as the bond strength determined by the PATTI test. Table 5 presents the measured contact angles of 60/70, CMB, and CMB samples with WS with deionized water, ethylene glycol and formamide in varying aging conditions. The summarized SFE components of asphalt binders are presented in table 6. As can be seen from the results, total SFE of the CMB samples with the incorporation of WS reduced at different aging conditions, in comparison to the control sample (60/70). The addition of WS at higher than 0.2% reduced the surface tension of the CMB. This indicates that increasing WS could lead to decreased cohesion in the modified asphalt binder samples, CMB-0.2WS and CMB-0.25WS. Both the short-term and long-term aging conditions exhibited reduced total SFE for all the asphalt binder samples (Hamedi *et al* 2024).

4.1. Fracture resistance using work of adhesion in the dry condition

As illustrated in figure 6, the granite aggregate exhibited better interfacial adhesion bonding compared to limestone, attributed to its surface roughness and texture. Silica (SiO_2) which is present in the aggregate is another factor influencing the adhesion properties (Hossain *et al* 2015, Habal and Singh 2018). Furthermore, limestone has a significantly smoother surface texture in conjunction with granite. Therefore, it has a lower resistance to adhesive failure at the asphalt-aggregate interface under similar wheel loads and environmental stresses. The interfacial adhesion between the limestone aggregate and the asphalt binder decreased, could be due to the presence of clay minerals (Cheng *et al* 2003, Sun *et al* 2024). Thus, increasing WS content in the CMB improved the interfacial adhesion on aggregates under the PAV aging.

The work of adhesion for the control sample (60/70) and the CMB samples (with and without WS) is shown in figure 7. As can be seen, the CMB sample with 0.15% WS exhibited an improved work of adhesion compared

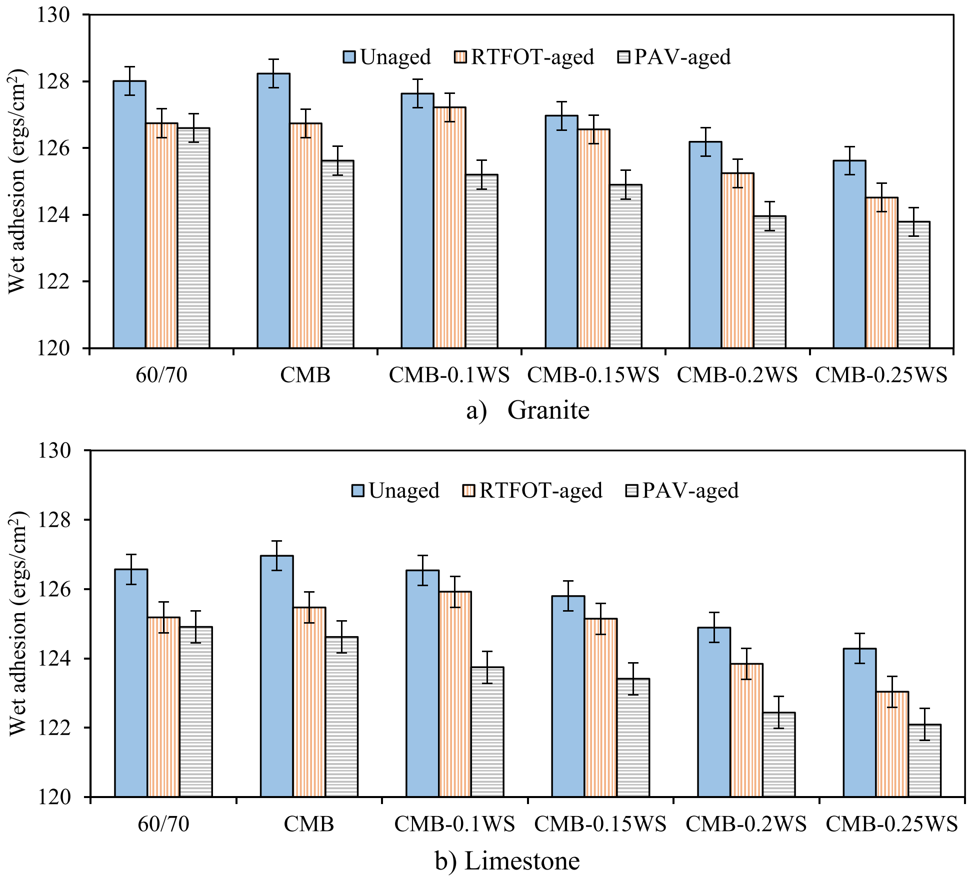


Figure 8. Work of adhesion of 60/70 and modified binders in the wet condition.

to the 60/70 sample at all aging conditions. The CMB sample with more than 0.2% WS showed a reduction in the dry adhesion. This indicates that CLR improved the wettability of the asphalt binder and fracture resistance, attributed to its alkene aromatics bonds. Hence, structure formation provides greater reaction elasticity properties and increased work of adhesion (Azahar *et al* 2021). The CMB samples with granite and limestone aggregates indicated the highest dry adhesion result under PAV aging conditions, due to the wettability of CLR of the asphalt binder and the increased work of adhesion (Jamal and Giustozzi 2022).

4.2. Moisture resistance using work of adhesion in the wet condition

The decreased polar component in the SFE indicates improved resistance to moisture damage (Habal and Singh 2016). A lower absolute value of work adhesion energy in the wet condition signifies that the asphalt mix performs better in terms of its resistance against moisture damage, thus suggesting that there is a stronger bond exists between the asphalt binder and the aggregates. Figure 8 shows that the limestone aggregate exhibited better moisture resistance. This aggregate has a larger value of basic component compared to granite, while the asphalt binder has high acid component. During the mixing process, the aggregates absorbed some components of the binder. The type and amount of absorption influence the degree of aggregate-binder adhesion (Bhasin and Little 2007, Duan *et al* 2024). Increasing pH in the modified asphalt mixtures decreased the degree of stripping.

The CMB with the inclusion of WS showed improved adhesion energy in the wet condition. This is consistent with the observation showing the ability of the WS agents to reduce the SFE and improve interfacial adhesion and moisture resistance (Cheng *et al* 2002, Sani *et al* 2023). These findings demonstrate that increasing WS significantly enhances the anti-stripping properties of the CMB. Increasing the proportion of WS as an anti-stripping agent decreased the acid-to-base ratio in the binders, making them more compatible with the acidic aggregates (Shafabakhsh *et al* 2015).

4.3. Moisture susceptibility using compatibility ratio

The compatibility ratio (CR) of the aggregate-asphalt binder mixtures was calculated by considering both dry and wet conditions. Figure 9 presents the CR values for all modified binders and aggregates.

The results of all the sample mixtures are comparably consistent at all aging conditions, except the CMB mixture. This is due to elasticity and high formation of unsaturation in the alkene and aromatic bonds. Hence,

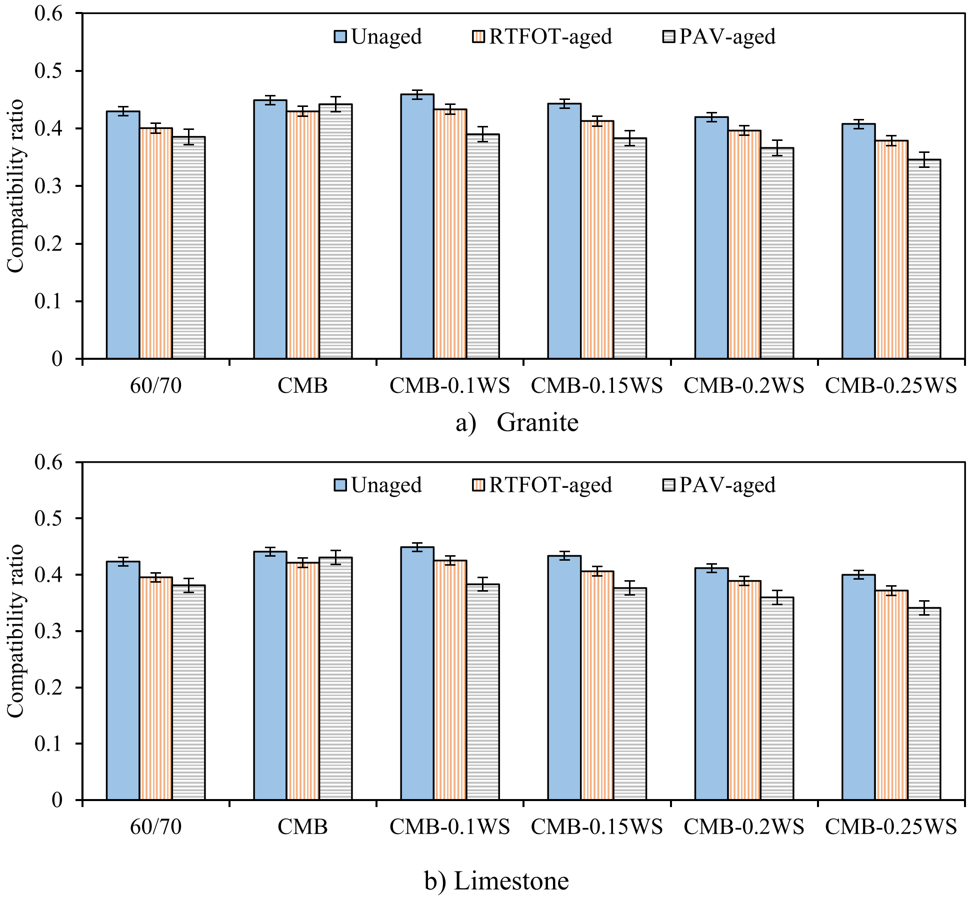


Figure 9. Compatibility ratio of the 60/70 and modified binders.

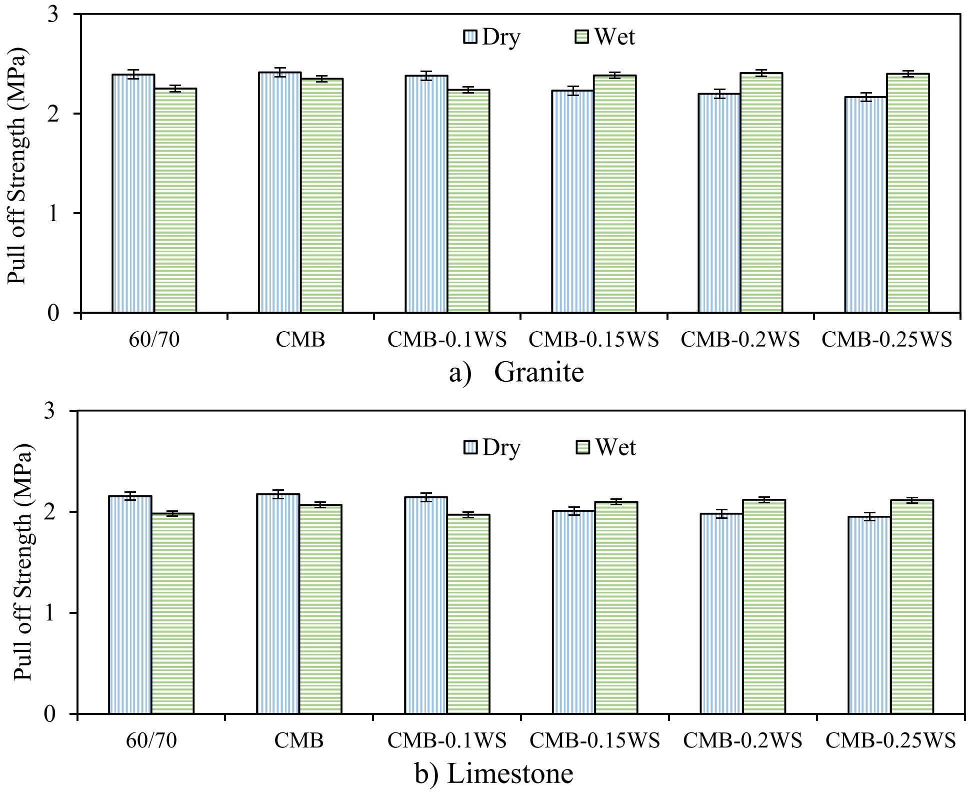


Figure 10. Bitumen bond strength test results of the aggregate substrates.

the work of adhesion in the dry condition was high in PAV aging. The CR of granite slightly increased than that of limestone, due to the improved work of adhesive on granite aggregate surface.

4.4. Effects of moisture conditioning and aging on the bond strength

Figure 10 illustrates the results of pull-off strength for the 60/70 asphalt binder and the CMB (with and without WS) under short-term aging conditions. As observed, the value of bonding strength in granite is higher than in limestone. The PATTI test represents the failure surface from adhesive interactions between granite and limestone aggregates. This finding correlates well with the findings of the sessile drop method. There was a strong interfacial adhesion between the granite aggregate surface and the CMB with WS. Studies by Kunaev *et al* (2023) and Zhang *et al* (2015), revealed that limestone contained the clay mineral. The mineral composition diminishes interfacial adhesion, which results in declined tensile strength. As a result, limestone aggregates have lower pull-off strengths in both dry and wet conditions than granite aggregates.

The addition of WS in the CMB significantly increased bonding strength due to the wet condition, which is also in line with the sessile drop method. The presence of WS tends to modify either the molecular polarity or the surface chemistry of the aggregate surface, leading to improved adhesion at the binder-aggregate interface (Yang *et al* 2015). Therefore, the mixture containing WS had improved moisture resistance (Bahmani *et al* 2021).

5. Conclusions

The effects of WS at different concentration percentages on the CMB were evaluated based on the sessile drop method and PATTI test. The test was done to determine the effects of modified asphalt binders on the mineralogical composition aggregates. Based on the results, the following conclusions can be drawn:

- The presence of CLR as a modifier contributed towards the increased SFE of the asphalt binder and enhanced the binder wetting efficiency on the aggregates. There was a positive impact on the work of adhesion in the dry condition of the granite aggregates after PAV aging. However, the CMB with 0.2% and 0.25% WS exhibited decrease work of adhesion in the dry condition.
- According to the moisture sensitivity test result, WS was utilized to improve the work of adhesion and anti-stripping agent properties of the CMB binder-aggregate combinations.
- WS affected the RTFOT-aged and PAV-aged binders in wet conditions by improving the work of adhesion properties of the modified asphalt binders. In this condition, the result of adhesion exhibited superior characteristics for the LTA binders compared to the STA binders.
- The CMB with WS combined with the limestone aggregates showed better work of adhesion in the wet conditions compared to the granite aggregates. The result was in line with the binder-aggregate substrate test, showing that increasing the amount of WS in the CMB contributed to increased bond strength in the wet condition.
- The work of adhesion energy for the asphalt mixture with the granite aggregate in the dry condition was higher than that of the limestone aggregate which exhibited lower bonding strength compared to the granite aggregate.
- Optimizing the addition of 0.15% WS to CMB improves performance in both the work of adhesion in the dry conditions and the work of adhesion in the wet conditions.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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