Improved Adhesion Bond between Asphalt Binder-Aggregate as Indicator to Reduced Moisture Damage

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Abstract. Improving the adhesion bonding strength between asphalt-aggregate combinations has a significant influence on the field performance and durability of asphalt pavement and minimizing the moisture damage that can appear in form of losing adhesion in asphalt-aggregate system by using modifiers will increase the service life of pavements.

The work of adhesion, de-bonding work, wettability and energy ratios were estimated based on surface free energy theory to evaluate the potential moisture-induced damage of combinations of pure and modified asphalt binders by (Styrene–Butadiene Styrene (SBS), Butyl Rubber (BR), and anti-stripping agent BG plus) with different types of aggregate. The sessile drop method is used to determine the components of the surface energy of different aggregate and asphalt binder types by performing direct contact angle measurements.

The experimental results showed that in general, the addition of SBS and BR modifiers will increase adhesion work and decrease de-bonding work and decrease ER₂ and wettability for both types of asphalt binders and aggregates while the addition of an anti-stripping agent (BG plus) caused a reduction in adhesion work and de-bonding work and increase ER₂ and wettability between the asphalt binder and aggregate surface and that will provide a better possible aggregate-asphalt binder bond strength and asphalt mixture’s resistance to moisture-induced damage.

1. Introduction

Understanding the mechanism of moisture-induced damage in flexible pavements and evaluate the suitable asphalt binder-aggregate combination to resist this damage is essential. Moisture or water presence is considered as the most essential environmental factor that affects the performance, quality, and serviceability of the asphalt pavements. The existence of moisture in flexible pavements structure and its harmful effects on asphalt mixtures properties can participate in various kinds of pavement deformations like fatigue cracking, raveling, stripping and rutting.

Moisture damage is a quite complex mode of failure that can appear in different forms like a cohesive failure within asphalt binder, adhesive failure occurs between asphalt binder and aggregates, cohesive
failure within aggregates and freezing of trapped water within pavement structure. Moisture-induced damage can be defined as losing asphalt mixtures its strength and durability due to the existence of water in pavement structure [1]. The most familiar forms of moisture-induced damage caused by losing the adhesion bond between asphalt binder and aggregates (adhesive failure) which is the most prevailing form of failure and loss of cohesion within asphalt cement (cohesive failure) [2].

Based on the study conducted by Fromm (1974), moisture damage is mainly characterized by the adhesive failure between asphalt binders and aggregates. Adhesive failure is primarily a result of when asphalt binder coatings the aggregates are displaced by water or moisture, and a phenomenon referred to as stripping becomes visible in the asphalt mixtures. Water penetrates between the asphalt binder films and aggregates surface, strips the asphalt binder from the surface of aggregates and breaks the bond between them because of the higher affinity of aggregates to water than to asphalt binder. Many factors affected stripping such as the chemical composition of asphalt cement and the properties of the asphalt cement mixtures like (quantity of filler aggregates mineralogy and surface characteristics) [3].

Many test methods developed to evaluate the loss of adhesion and cohesion in asphalt binders, recent studies show that surface free energy (SFE) characteristics of binders and aggregates can be used in a mechanics-based approach to quantify moisture damage potential of asphalt mixes [4].

Surface free energy can be used to determine the best asphalt binder-aggregate combination in terms of adhesive and cohesive bonding and hence on moisture damage. The bonding strength at asphalt binder- the aggregate interface is predictable by comparing t adhesive bond strength in the presence of water (i.e., surface energy in wet condition) with adhesive bond strength without moisture (i.e., surface energy in dry condition) between asphalt binders – aggregate combination [4].

Several techniques have been performed to determine the surface free energy of asphalt binder, which are the pendant drop method, nuclear magnetic resonance (NMR), atomic force microscopy (AFM), inverse gas chromatography (IGC), Wilhelmy plate method and sessile drop method [5].

The adhesion strength is affected by wetting and interlocking. Wetting is controlled by the attraction forces between the two surfaces - solid and liquid and it shows how the substrate interacts with liquid [6].

The properties of aggregate show a stronger impact compared to the adhesive layer [7]. A convenient way for measuring the wettability of a solid surface is by determining the contact angle of a liquid, which is formed when a drop of liquid is placed on a rigid and completely smooth solid [6,8]. Amin and co-workers in 2010, studies the wettability of several different surfaces of the substrate and determined the contact angles on each substrate by observing the dispersal area of the water droplets indicating the surface tension of the droplets towards the surface of the substrate [8].

The adhesion work reflects the required energy for the asphalt binder to stripping from the aggregate interface, which could typify the bond strength of the asphalt binder -aggregate system [7,9].

A large number of laboratory and field studies have been performed to evaluate the effects of moisture damage on the performance of hot asphalt mixtures. Most of the studies were performed to assess the sensitivity of hot mix asphalt to moisture by measuring the deterioration in the properties of the mixture as a result of conditioning that simulates the moisture action in the field. Research is needed to identify the moisture-sensitive mixes which show the material loss in the wheel-path under a combined influence of traffic and moisture [9]. Arepalli et al. in (2019) evaluate moisture susceptibility by simulating and analyzing the material loss due to moisture and also identifying a mixture with the potential material loss due to the effect of water that has demonstrated damage in the field but not under regular testing in the laboratory. The Moisture Induced Stress Tester, Ultrasonic Pulse Velocity, Dynamic Modulus in Indirect tensile mode, Indirect Tensile Strength and Model Mobile Load Simulator tests were used to evaluate moisture susceptibility of mixtures. The results of the mix mechanical properties showed that the use of MIST in combination with UPV or ITS can identify moisture susceptible mixes, in particular for mixes with the potential of aggregate breakage [10].
In recent decades using additives such as recycled crumb and reclaimed rubber and polymers has gained popularity successfully adopted by transportation agencies in hot mix asphalt (HMA) pavements due to the environmental benefits and the ability to improve asphalt mixtures performance that related to rutting and moisture-induced damage [11]. The asphalt binder modification with polymers and anti-stripping agents are some methods to reduce the destructive impacts of moist on hot asphalt mixtures. In the last few years, it has been a growing interest in the utilization of nanoclay as an additive to enhance the resistance of asphalt mixture to the water. In 2020, Wang et al. investigated the effect of adding three types of nanoclay with different percentages to modified asphalt binder with SBS and assessed asphalt mixture resistance to moisture damages by using different tests such as atomic force microscopy (AFM), freeze-thaw splitting test and surface free energy (SFE) tests with different conditions. The results showed a significant improvement in the resistance of asphalt binder aggregate combination to water damages and the degree of improvement differed depending on the types and amount of nanoclay, as well as the type of aggregate (acid or base)[12].

There are many various methods used to improve the strength of asphalt moisture against moisture damage. Using anti-stripping materials is the most common way. Also, there are different ways to evaluate the effect of utilizing anti-stripping modifiers. The existing laboratory tests to determine the sensitivity of asphalt mix to moisture have some deficiencies. Hamedi et al. in (2019) studied the effect of adding the anti-stripping materials to the asphalt binder. Also, to study the impact of these modifiers by using methods based on thermodynamic concepts and performed mechanical tests. Two different types of polymer with two different percentages are added to asphalt binder and different tests on samples under different sensitivities of moisture have been done. The results of this study showed that using anti-stripping materials has been reducing asphalt mixtures strength to reduce moisture damage. The main causes for this trend are the decrease in the amount of separation in the modified asphalt mixtures [13].

Huang and Sun (2020) investigated the impact using two different modifiers (styrene-butadiene-styrene and crumb rubber) on the permanent deformation (rutting), moisture damage, and workability characteristics of hot mix asphalt (HMA) mixtures. In this research, three kinds of mixtures were used, control, modified with crumb rubber, and modified with styrene-butadiene-styrene mixtures to be assessed. The Multiple Stress Creep Recovery (MSCR) test and the wheel tracking device and were used to evaluate rutting properties while using the Indirect Tensile Strength (modified Lottman) and bitumen bond strength (BBS) tests were used to assess the moisture or water damaged properties. The workability properties were evaluated using densification indices (Bahia and locking point method) and a viscosity test. The experimental results showed that the mixtures modified with crumb rubber were less workable and exhibited better resistance to rutting than the mixtures modified with styrene-butadiene-styrene and control mixtures. Further, the mixtures modified with styrene-butadiene-styrene had increased resistance to moisture-damage, while the impact of the mixtures modified with crumb rubber was negligible compared to the control mixtures [14].

Flexible pavements are susceptible to the damaging effects of moisture, causing different types of problems for asphalt such as stripping. That reduces the durability and serviceability life of pavements and consequently increases the construction and maintenance cost. High-density polyethylene was used as an asphalt binder modifier to evaluate the moisture sensitivity of the hot asphalt mixture. Conventional and HDPE-modified asphalt mixtures' moisture susceptibilities were evaluated through indirect tensile strength (IDT) and loss of stability tests. Results of scanning electron microscopy (SEM) showed that HDPE was homogeneously dispersed through the binder with no polymer cluster formations. Testing results revealed that adding high-density polyethylene at a concentration of 4% gives superior performance in most tests. Adding HDPE significantly improved the properties of asphalt binder, increased the hardness of the asphalt mixture, and reduced the effect of moisture damage [15].
2. Research objective
The main object of this study is evaluating the susceptibility of asphalt cement-aggregate system to moisture-induced damage based on the adhesion and de-bonding work and energy parameters (ER1 and ER2) of base and modified asphalt binders over different types of the aggregates that determined from the surface energy components.

3. Experimental work

3.1. Materials
Two types of aggregate and twenty different base and modified asphalt cement were collected to measure surface free energy components of asphalt binder and aggregate by using the sessile drop test method and determined adhesion work and de-bonding work between asphalt binder and aggregate combination. Two types of limestone aggregates brought from the Dukan and Samawa regions were used to test in a combination with different types of asphalt cement. The samples were utilized in the experimental work included two AC 40-50 base asphalt binder sampled provided from two refineries (Al-Basrah and Al-Durah refineries) their properties shown in Table 1. One is radial Styrene–Butadiene Styrene (SBS)-modified asphalt cement containing (3,5and 7% by weight of asphalt cement) mixing at temperature 180 Cº for 2 hours, and asphalt cement modified with Butyl Rubber (BR) containing (6,9 and 12% by weight of asphalt cement ) mixing for one hour at 165 Cº and modified asphalt cement with an anti-stripping agent with a commercial name (BG plus) from Sika IRAQ L.L.C company with (0.05, 0.075 and 0.1% by weight of asphalt cement) with mixing time 30 minutes at 150 Cº. The properties of BG plus and SBS are presented in Tables 2 and 3 respectively and the types of modifiers are shown in Figure 1.

| Table 1. Physical properties of base asphalt cement. |
|---------------------------------|-----------------|
| Property                        | Asphalt cement type |
| Penetration (100g, 5sec, 25°C) ASTM-D5. | Basrah | Durah |
| Viscosity (c.p) at 135 °C, ASTM D4402 | 527.5 | 479.2 |
| Ductility (5 cm/min, 25°C), ASTM-D 113. | >100 | >100 |
| Softening point ('C) ASTM –D36 | 52 | 51.3 |
| Penetration index (PI) | -1.156 | -1.215 |

| Table 2. The properties of anti-stripping agent (BG plus). |
|---------------------------------|-----------------|
| Properties                      | Requirement     |
| Chemical Base                   | Nanotechnology, Silane based |
| Form                            | Liquid          |
| Appearance                      | Pale yellow     |
| Density                         | 1.0 Approximately @ 27° C |
| pH Value                        | Approximately 9.00 |
| Dosage                          | 0.02% to 0.1%. By weight of asphalt binder |

| Table 3. The properties of the SBS modifier. |
|---------------------------------|-----------------|
| Properties                      | Unit            |
| Density                         | Kg\m³            |
| Specific gravity                | Kg/dm³          |
| Tensile Strength (σt)           | MPa             |
| Melting point                   | C°              |
| Elongation                      | %               |
| Molecular structure             | Radial          |
| Minimum                        | min.32          |
| Requirements                    | 1240            |
|                                | 0.95            |
|                                | 170-190         |
|                                | 880             |
|                                | Radial          |
3.2. Methodology

3.2.1. Two Surface Free Energy (SFE) Components of Asphalt Binder and Aggregate.

The components of surface free energies of asphalt binder-aggregate combinations were obtained by utilizing the sessile drop method to evaluate moisture susceptibility. The sessile drop technique considers an easy and simple maneuverable way that was used to measure the contact angles between three different probe liquids and different kinds of asphalt cement and aggregates by using an image processing software (Surftens 4.6) to analyze the captured image as shown in Figure 2. The components of surface free energies of 20 tested asphalt cement and two types of aggregate were measured based on Owen-Wendt’s theory in 1969 [16] and Fowkes in 1964[17] are used to calculate work of adhesion, work of de-bonding and energy parameter.

3.2.2. Adhesion of Asphalt-Aggregate Interfacial based on Surface Free Energy.

The quality of the physical adhesion between asphalt binder and aggregate affects the durability of HMA mixtures. From the standpoint of thermodynamics, the change in the surface free energy of adhesion is related to the break of the interface between the asphalt binder and the aggregate surfaces [18]. Adhesion work is a function of the SFE of both the asphalt binder and aggregate.

By using the surface free energy and its components of both asphalt binders and aggregates data in the surface free energy sections, the work of adhesion between different types of asphalt binders and aggregates is calculated.
different types of aggregate under dry and wet conditions, the work of adhesion can be characterized by using Eq.(1 to 4). Both dispersion and polar interactions play major roles in the adhesion between the asphalt binder and aggregate.

The following equations present the work of adhesion of asphalt-aggregate under dry conditions. The following equations present the adhesion work of asphalt-aggregate under dry conditions.

\[
W_{\text{Adhesion}} = \gamma_{\text{asphalt-aggregate}} - \gamma_{\text{asphalt-aggregate}}
\]

\[
W_{\text{Adhesion}} = 2 \sqrt{\gamma_{\text{asphalt}} \gamma_{\text{aggregate}}} + 2 \sqrt{\gamma_{\text{asphalt}} \gamma_{\text{aggregate}}}
\]

In this case, the energy that water needed it to separate the asphalt binder from the surface of aggregate is almost always less than zero which is called hydrophobic interaction (i.e., removing the asphalt binder from the surface of aggregate by water considering a thermodynamically favorable process).

Eq. (3, 4) present the work of adhesion of asphalt-aggregate under wet condition.

\[
W_{\text{Adhesion}} = \gamma_{\text{asphalt-water}} + \gamma_{\text{aggregate-water}} - \gamma_{\text{asphalt-aggregate}}
\]

\[
W_{\text{Adhesion}} = 2 \left( \gamma_{\text{water}} + \sqrt{\gamma_{\text{asphalt}} \gamma_{\text{aggregate}}} + \sqrt{\gamma_{\text{asphalt}} \gamma_{\text{aggregate}}} - \sqrt{\gamma_{\text{asphalt}} \gamma_{\text{water}}} \right)
\]

Where:

\( \gamma_{\text{asphalt}} \): Total surface energy of asphalt binder in (ergs/cm²).

\( \gamma_{\text{aggregate}} \): Total surface energy of aggregate in (ergs/cm²).

\( \gamma_{\text{water}} \): Total Surface free energy of water in (ergs/cm²).

\( \gamma_{\text{asphalt-aggregate}} \): Interfacial free energy between asphalt and aggregate in (ergs/cm²).

\( \gamma_{\text{asphalt}}^d \): Dispersion part of surface free energy of asphalt, in (ergs/cm²).

\( \gamma_{\text{aggregate}}^d \): Dispersion part of surface free energy of aggregate in (ergs/cm²).

\( \gamma_{\text{water}}^d \): Dispersion part of surface free energy of water in (ergs/cm²).

\( \gamma_{\text{asphalt}}^p \): Polar part of surface free energy of asphalt in (ergs/cm²).

\( \gamma_{\text{aggregate}}^p \): Polar part of surface free energy of aggregate in (ergs/cm²).

\( \gamma_{\text{water}}^p \): Polar part of surface free energy of water in (ergs/cm²).

\( \gamma_{\text{asphalt-water}} \): Interfacial free energy between asphalt and water in (ergs/cm²).

\( \gamma_{\text{aggregate-water}} \): Interfacial free energy between aggregate and water in (ergs/cm²).

### 3.2.3. Bond Energy Ratio Parameters (ER)

There are two bond energy ratio parameters (ER1) and (ER2) introduced by Bhasin and Little (2006) [19] which suggest based on the surface energies of the asphalt-aggregate interface in wet and dry conditions used in asphalt mixture and they used to evaluate the adhesion of the asphalt-aggregate interface affected by water or moisture sensitivity of asphalt mixtures [19] and is expressed as shown in Eq.(5) below:

\[
\text{ER1} = \frac{W_{\text{adh.}}}{W_{\text{asphalt-aggregate-water}}}
\]

The ER1 is based on the assumption that adhesion work between the asphalt binder and the surface of aggregate is directly proportional to the moisture resistance and inversely proportional to the work of de-bonding [20].

By taking into account the comprehensive wettability and de-bonding work, the bond energy ratio parameter (ER2) was put ahead under NCHRP 9-37 research project as a parameter to evaluate asphalt-aggregate system’s compatibility, considering water shared in. By considering the cohesive bond energy of the asphalt binder, another parameter, (ER2) was introduced [19, 20] and expressed by Eq. (6) below:

\[
\text{ER2} = \frac{W_{\text{adh.}} - W_{\text{coh.}}}{W_{\text{asphalt-aggregate-water}}}
\]
In general, a higher value of ER2, better resistance to moisture damage in asphalt mixture. In Eq. (6, 7) above, the terms $W_{\text{adh}}$, $W_{\text{coh}}$, and $W_{\text{asphalt-agg-water}}^{\text{adh}}$ represent the adhesive bond energy between the asphalt cement and the surface of aggregate as represented in Eq. (2), cohesive bond energy of the asphalt cement represents $(W_{\text{Cohesion}} = 2 \cdot \gamma_{\text{Total}})$ and the work of de-bonding when water removes asphalt binder from the interface between it and aggregate is represented in Eq. (4), respectively. The term $(W_{\text{adh}} - W_{\text{coh}})$ represents the wettability (the ability of the asphalt cement to cover the aggregate’s surface). The lower value of de-bonding work represents the lower energy potential for water to remove the asphalt binder from the interface between it and aggregate and hence higher resistance to moisture damage [20].

4. Results and Discussion
Using the concept of surface free energy to assess the susceptibility of asphalt binder-aggregate combination to moisture-induced damage based on asphalt binder-aggregate interface Energies (adhesion energy, de-bonding energy, and wettability) and energy parameters (ER1 and ER2).

4.1. Adhesion Work Results
The adhesion works of asphalt binder-aggregate interfaces for twenty types of asphalt binder (base and modified) and two kinds of aggregates are computed, and the results are presented in Table 4 and Figures 3 to 5. According to the results in Table 6, the different asphalt binder-aggregate combinations give different work of adhesion and hence, the ability to choose the best asphalt-aggregate combination based on the actual situation.

Table 4. Adhesion work between different types of asphalt binder and aggregate.

| Modifiers | The average value of adhesion work (ergs/cm²) for 3 specimens |
|-----------|-------------------------------------------------------------|
|           | Dukhan asphalt binder | Basrah asphalt binder |
|           | Dukan aggregate | Samawa aggregate | Dukan aggregate | Samawa aggregate |
| Type      | Percent |                   |                  |                   |                   |
| Base      | 0%      | 66.108             | 64.396           | 65.255            | 63.707            |
|           | 3%      | 68.563             | 66.679           | 67.774            | 66.724            |
|           | 5%      | 69.187             | 67.087           | 68.318            | 67.341            |
|           | 7%      | 72.426             | 70.563           | 70.060            | 68.989            |
|           | 9%      | 72.063             | 71.035           | 68.912            | 68.089            |
| SBS       | 9%      | 69.702             | 68.064           | 68.027            | 67.168            |
|           | 12%     | 68.15               | 67.429           | 65.449            | 64.543            |
| BR        | 9%      | 72.603             | 71.035           | 68.912            | 68.089            |
|           | 12%     | 68.15               | 67.429           | 65.449            | 64.543            |
|           | 0.05    | 62.236             | 60.955           | 62.029            | 61.725            |
|           | 0.075   | 64.228             | 63.252           | 64.286            | 63.099            |
|           | 0.1     | 61.179             | 60.258           | 62.516            | 60.643            |

Figures 3 to 5 show the addition of any percent of SBS modifier to both types of asphalt cement resulted in a significant improvement in adhesion work with both kinds of aggregates. For example, adding 7% of the SBS modifier caused maximum improvement in adhesion bonds for both types of asphalt cement (Durah and Basrah). This improvement is more pronounced with a higher increment rate of 9.6% in the Durah asphalt binder and 7.4% in Basrah asphalt binder with Dukan aggregate case, while the adhesion work of modified asphalt binder by BR modifier will increase to a maximum at 9% of BR modifier and then decrease as BR content increase comparing with the base asphalt binder. The addition of thermoplastic typically increases the total surface free energy by increasing both non-polar ($\gamma{LW}$) and base components and consequently the adhesion energy. Having an asphalt
mixture with a higher value of adhesion energy as possible is desirable to be more durable and less sensitive to moisture [8].

The addition of (BG plus) to asphalt binder caused a reduction in adhesion work with increase modifier content comparing with the base asphalt cement. The reduction rate in adhesion work due to the addition of 0.1% of BG plus to Durah and Barah asphalt binder-Samawa aggregate interfaces case was 6.4% and 4.8%, respectively. The addition of anti-stripping agent like (BG plus) to asphalt binder reduces total surface energy by reducing \((\gamma_{lv})\) and acid components with increasing modifier content because its surface-active agents, when mixed with asphalt cement, reduces surface tension providing a better coating of the aggregate by the asphalt, and increases the ability of asphalt binder to react with aggregate, therefore, promote increased interfacial adhesion to the aggregate. These results are supported by Howson [21].

In addition, the results in Figures 3 and 4 showed that the adhesion of asphalt binder- Samawa aggregate is lower than that of asphalt binder- Dukan aggregate. This can also be attributed to the higher surface free energy of Dukan aggregate and its chemical composition.

While Figure 5 showed that the Durah asphalt binder exhibited higher adhesion energy than the Basrah asphalt binder. Maybe it's related to the higher surface energy of the Durah asphalt binder. This made the Durah asphalt binder exhibited more resistance to moisture damage than the Basrah asphalt binder.

**Figure 3.** Work of adhesion between Durah asphalt binder and different types of aggregate.

**Figure 4.** Work of adhesion between Basrah asphalt binder and different types of aggregate.

**Figure 5.** Work of adhesion between Dukan aggregate and different types of asphalt binder.
4.2. *De-bonding Work Results*

The results mentioned in Table 5 and Figures 6 and 7 showed that in the presence of water, that the work of adhesion or adhesion energy for the base and modified asphalt binder decreased significantly. The main reason for that is the surface energy of water is high enough to prevent the effective bonding in the asphalt binder-aggregate system.

Table 5, illustrated that in general, the addition of modifiers decreased the de-bonding work for both types of asphalt binders and aggregates. The maximum reduction in the de-bonding work was 18.4% for the Dukan aggregates-Basrah asphalt binder system modified by 9% of BR. Similarly, a reduction of 18.5% was observed in de-bonding work for Samawa aggregate-Basrah asphalt binder modified in the same percent of BR.

According to Figures 6 and 7, the asphalt binder-Samawa aggregate system has de-bonding work less than the Dukan aggregate-asphalt binder system. Also, a given type of aggregate-Basrah asphalt binder system has de-bonding work less than Durah asphalt binder-aggregate system.

**Table 5. Work of de-bonding different types of asphalt binder and aggregate.**

| Modifiers | Work of de-bonding (ergs/cm²) | Durah asphalt binder | Basrah asphalt binder |
|-----------|-------------------------------|---------------------|----------------------|
| Type      | Percent | Dukan aggregate | Samawa aggregate | Dukan aggregate | Samawa aggregate |
| Base      | 0%      | 60.653        | 56.523          | 58.792        | 54.827          |
| SBS       | 3%      | 62.030        | 57.729          | 51.339        | 47.873          |
| SBS       | 5%      | 64.650        | 60.133          | 50.185        | 46.791          |
| SBS       | 7%      | 60.373        | 56.092          | 50.806        | 47.317          |
| SBS       | 9%      | 58.383        | 54.328          | 48.747        | 45.470          |
| SBS       | 12%     | 56.432        | 52.446          | 47.943        | 44.703          |
| BR        | 0.05%   | 56.661        | 52.758          | 50.282        | 46.959          |
| BG Plus   | 0.075%  | 56.365        | 52.666          | 56.747        | 53.025          |
| BG Plus   | 0.1%    | 52.0150       | 48.676          | 50.906        | 47.615          |

**Figure 6.** De-bonding work between Basrah asphalt binder and different types of aggregate.

**Figure 7.** De-bonding work between Durah asphalt binder and different types of aggregate.
4.3. Wettability of Asphalt cement to Aggregate Surface

Wettability is the ability of the asphalt binder to wet and saturated the micro textural features of the aggregate surface. Increasing the wettability of asphalt binder, increasing its affinity to coat aggregate surface and the opposite is true. A better coating to the aggregate surface will reduce the number of initiation locations of water in asphalt binder-aggregate mixture and reduce its sensitivity to moisture damage [19]. Therefore, the ability of asphalt binder–aggregate mixture to resist moisture damage is directly compatible with the wettability of the asphalt binder to aggregate surface and inversely proportional to the reduction in adhesion energy when moisture causes de-bonding.

When the modifiers are added to asphalt binder increased its viscosity and reduces its ability to wet the aggregate surface, so it is necessary to assess the wettability of asphalt binder with different amount of modifiers to different types of aggregate.

Table 6 and Figures 8 to 10. display the results of different types of asphalt binder wettability to different kinds of aggregate surfaces showed that:

1- The wettability of all modified asphalt binders with SBS and BR is lower than the base asphalt binder that means the addition of any amount of SBS or BR will have a negative impact on the coating of asphalt binder to aggregate surfaces for both types of asphalt cement and aggregate because SBS and BR modifiers increased the viscosity of asphalt binder and thus reduce the wettability of them to aggregate surfaces.

2-While the addition of anti-stripping agent BG plus to asphalt binder increases its wettability comparing with pure asphalt binder for both types of aggregates.

3-The wettability of Basrah asphalt cement (base and modified with different types of modifiers) is higher than the Durah asphalt binder because it is more polar (more acid) than the Durah asphalt binder. Abed (2020), through her laboratory work on Durah and Basrah asphalt binder, reached the conclusion that the Basrah asphalt binder is more polar than the Durah asphalt binder [22].

4-The wettability between a given type of asphalt and Dukan aggregate combination is greater than the wettability of asphalt binder to Samawa aggregate.

5-The wettability of SBS-modified asphalt binder decrease with increase SBS content because of increasing the viscosity of asphalt binder with increasing modifier content.

6-The wettability of modified asphalt binder with BR and BG plus decreased to a minimum then increase as modifier content increase.

### Table 6. Wettability of different types of asphalt binder to different kinds of aggregate surface.

| Modifiers | Wettability (ergs/cm²) |
|-----------|------------------------|
|           | Durah asphalt binder | Basrah asphalt binder |
|           | Dukan aggregate | Samawa aggregate | Dukan aggregate | Samawa aggregate |
| Base      | 10.345 | 9.742   | 12.066 | 10.518 |
| %3        | 6.938  | 7.758   | 9.478  | 8.429  |
| SBS       | 4.133  | 6.656   | 8.791  | 7.814  |
| %5        | 2.458  | 4.975   | 7.178  | 6.646  |
| %7        | 5.911  | 7.378   | 8.536  | 7.677  |
| %6        | 4.392  | 5.124   | 7.637  | 6.815  |
| BR        | 7.239  | 8.042   | 10.705 | 9.798  |
| %9        | 12.939 | 12.463  | 13.888 | 12.584 |
| %12       | 11.468 | 10.838  | 12.328 | 11.141 |
| BG Plus   | 11.314 | 12.675  | 12.598 | 11.724 |
**Figure 8.** The wettability of SBS-modified asphalt binder with different types of aggregate (A) Basrah (B) Durah.

**Figure 9.** The wettability of BR-modified asphalt binder with different types of aggregate (A) Basrah (B) Durah.

**Figure 10.** The wettability of BG plus-modified asphalt with different types of aggregate (A) Basrah (B) Durah.
4.4. Analysis of Bond Energy Parameters (ER1 and ER2)

Tables 6 and 7 display the values of the two bond energy ratio parameters ER1 and ER2 of different types of asphalt binders with the two types of aggregates. The asphalt binder-aggregates mixture with the highest values of bond energy parameters (ER1 and ER2) will be relatively more resistant to moisture damage and less sensitive to water than other mixtures. The adhesion works of asphalt binder-aggregate interfaces for twenty types of asphalt binder (base and modified) and two kinds of aggregates are computed, and the results are presented in Table 4 and Figures 1 to 3.

4.4.1. ER1 Parameter

Based on the results in Table 7, at a given aggregate type, changing the asphalt binder’s type can result in a range of different ER1, and consequently a range of different predicted asphalt mixture sensitivities to moisture. At the same time, keeping the type of asphalt binder constant and changing the type of aggregate can produce a significant difference in the value of the bond strength between aggregates and asphalt binder and in the moisture sensitivity of asphalt mixture.

The values of ER1 of modified asphalt binder-aggregates (Dukan and Samawa) combinations are higher than base asphalt binder-aggregate combination. Also, ER1 increases with an increase in modifier content.

The results presented in Table 7 showed that using Samawa aggregate with different types of asphalt binder provides a higher value of ER1 more than Dukan aggregate. And Durah asphalt-Samawa aggregate has the highest value among ER1 among the other combination of asphalt-aggregate.

Table 7. Energy Ratio Parameter (ER1) of different types of asphalt binders and aggregates.

| Modifiers | Energy Ratio Parameter (ER1) |
|-----------|-----------------------------|
|           | Durah asphalt binder | Basrah asphalt binder |
| Type | Percent | Dukan Rock | Samawa Rock | Dukan Rock | Samawa Rock |
| Base | %0    | 1.089 | 1.139 | 1.109 | 1.162 |
|      | %3    | 1.105 | 1.155 | 1.320 | 1.394 |
| SBS   | %5    | 1.070 | 1.116 | 1.361 | 1.439 |
|      | %7    | 1.199 | 1.258 | 1.379 | 1.458 |
|      | %6    | 1.194 | 1.253 | 1.396 | 1.477 |
| BR    | %9    | 1.287 | 1.354 | 1.437 | 1.523 |
|      | %12   | 1.216 | 1.278 | 1.302 | 1.374 |
|      | 0.05  | 1.104 | 1.157 | 1.093 | 1.145 |
| BG Plus | 0.075 | 1.244 | 1.311 | 1.182 | 1.243 |
|      | 0.1   | 1.176 | 1.238 | 1.228 | 1.295 |

4.4.2. ER2 Parameter

By taking into account the comprehensive wettability and de-bonding work, the bond energy ratio parameter (ER2) was put ahead under NCHRP 9-37 research project as a parameter to evaluate the asphalt-aggregate system’s compatibility, considering water shared in. After that, both Howson et. al (2007)[21] and Little and Bhasin (2006) [19] gathered the adhesive and cohesive energies into a single term which is ER2.

In general, a higher value of ER2, better resistance to moisture damage in asphalt mixture. In the results presented in Table 8, the values of ER2 were determined for different combinations of modified asphalt binders and different types of aggregates. At a given type of asphalt binder, the addition of SBS and BR modifier decreased the value of ER2 for both types of tested aggregates comparing with pure asphalt binder because it increases the wettability of BG plus-modified asphalt binders.
binder to different types of aggregate surfaces and the reduction rate increased with increase SBS and BR modifiers. Furthermore, the pure asphalt binder has a higher ER than the modified asphalt binders with different contents of SBS.

In addition, it can be concluded that the addition of SBS and BR additives has a negative effect on the asphalt mixture’s resistance to potential moisture damage. The addition of a 7% SBS modifier caused the lowest value of ER2 for all tested aggregates due to the reduction in the wettability of the modified asphalt binder with SBS to the surface of aggregate.

From results illustrated in Figure 11, at a given type of asphalt binder and aggregate all the values of ER2 improved with the addition of any amount of BG plus anti-strip agent comparing with pure asphalt because it increases the wettability of BG plus- modified asphalt binder to different types of aggregate surfaces. This means that the addition of any amount of BG plus anti-strip agent will improve the resistance of asphalt mixture to moisture damage.

Table 8. Energy Ratio Parameter (ER2) of different types of asphalt binders and aggregates.

| Modifiers | Energy Ratio Parameter (ER2) |
|-----------|-----------------------------|
|           | Durah asphalt binder | Basrah asphalt binder |
|           | Dukan Rock | Samawa Rock | Dukan Rock | Samawa Rock |
| Base      | %0         | 0.189     | 0.172     | 0.205     | 0.192     |
|           | %3         | 0.155     | 0.134     | 0.185     | 0.176     |
| SBS       | %5         | 0.135     | 0.111     | 0.175     | 0.167     |
|           | %7         | 0.113     | 0.089     | 0.152     | 0.140     |
| BR        | %7         | 0.154     | 0.136     | 0.175     | 0.169     |
|           | %9         | 0.119     | 0.098     | 0.159     | 0.152     |
|           | %12        | 0.168     | 0.152     | 0.213     | 0.209     |
| BG Plus   | %0.05      | 0.244     | 0.237     | 0.245     | 0.237     |
|           | %0.075     | 0.229     | 0.225     | 0.227     | 0.219     |
|           | %0.1       | 0.261     | 0.260     | 0.247     | 0.246     |

Figure 11. ER2 of BG plus-modified asphalt binder prepared from two sources (A) Basrah (B) Durah to different types of aggregate.
5. Conclusions

Analysis of experimental results of the two types of asphalt cement and aggregates with three kinds of modifiers as a modifier showed:

1- Adhesion work of asphalt binders modified with different modifiers is higher than the pure asphalt binder.
2- The polarity of asphalt binder plays an important role in the bonding between different types of asphalt binder and aggregates.
3- The type and amount of modifiers affect the adhesion bond and wettability of asphalt binder with a different can of aggregates.
4- Maximum improvement in adhesion work due to the addition of 7% of SBS modifier with an increment rate of 9.577% in the Durah asphalt binder and 7.363% in Basrah asphalt binder with Dukan aggregate case.
5- Wettability and ER2 values of all modified asphalt binders with SBS and BR are lower than the pure asphalt binder that means the addition of any amount of SBS or BR will have a negative impact on the coating of asphalt binder to aggregate surfaces for both kinds of asphalt binder and aggregate and the resistance to moisture damage.
6- The addition of any amount of BG plus to asphalt binder increases its wettability and improves ER2 comparing with pure asphalt binder for both types of aggregates surfaces and hence improved the resistance of asphalt mixture to moisture-induced damage.
7- Basrah asphalt binder-aggregate combination is considered as the better mixture to resist moisture-induced damage resistance comparing with other combinations.

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References
[1] Kim S and Coree BJ 2005 Evaluation of Hot Mix Asphalt moisture sensitivity using the Nottingham Asphalt Test equipment: IHRB Project TR-483 Centre for Transportation Research and Education: Iowa State University. doi=10.1.1.443.4456&rep=rep1&type.
[2] Kanitpong K and Bahia H U 2003 Role of Adhesion and Thin Film Tackiness of Asphalt Binders in Moisture Damage of HMA Asphalt Paving Technology 72 pp502–528. http://worldcat.org/issn/02702932.
[3] Fromm H J 1974 The mechanisms of asphalt stripping from aggregate surfaces Proceedings of the Association of Asphalt Paving Technologists 43 pp191-223.
[4] Robert L Lytton, Eyad A Masad, Corey Zollinger, Rifat Bulut and Dallas Little 2005 Measurements of Surface Energy and its Relationship to Moisture Damage Report 0-4524-2 Submitted to Texas Department of Transportation and Federal Highway Administration Texas A&M University. https://static.tti.tamu.edu/tti.tamu.edu/documents/0-4524-2.pdf.
[5] Jianming Wei and Yuzhen Zhang 2012 Application of Sessile Drop Method to Determine Surface Free Energy of Asphalt and Aggregate Journal of Testing and Evaluation 40(5). https://doi.org/10.1520/JTE20120060.
[6] Fini E and Abu-Lebdeh T 2011 Bonding property of bituminous crack sealants in the presence of water Am. J. Eng. Applied Sci. http://thescipub.com/abstract/10.3844/ajeassp. DOI: 10.3844/ajeassp.2011.124.129
[7] Guangyang, Li, Wang Hong, Yuan Yang, Yao Jinyuan, Yang Zhuoqing, and Ding Guifu. 2010 Research in the improvement of wettability of micro-structure in patterned electrodeposition. American Journal of Nanotechnology 1(1) pp.23-31. DOI:10.3844/ajnsp.2010.23.31
[8] Amin, N., A. Y. Cheah, and Ibrahim Ahmad. 2010 Effect of plasma cleaning process in the
wettability of flip chip PBGA substrate of integrated circuit packages. *Journal of Applied Sciences* **10** *(9)* pp. 772-776. DOI:10.3923/jas.2010.772.776.

[9] Bhasin, Amit, Dallas N. Little, Kamilla L. Vasconcelos, and Eyad Masad. 2007 Surface free energy to identify moisture sensitivity of materials for asphalt mixes. *Transportation Research Record* **2001** *(1)* pp. 37-45. DOI:10.3141/2001-05.

[10] Arepalli, Uma Maheswar, Nivedya Madankara Kottayi, and Rajib B. Mallick 2019 Moisture susceptibility evaluation of Hot Mix Asphalt: combined effect of traffic and moisture. *International Journal of Pavement Research and Technology* **12**(2) pp. 206-214.

[11] Zhang, Weiguang, Shihui Shen, Shenghua Wu, and Louay N. Mohammad. 2017 Prediction model for field rut depth of asphalt pavement based on Hamburg wheel tracking test properties. *Journal of Materials in Civil Engineering* **29**(9) pp.899-1561. DOI:10.1061/(ASCE)MT.1943-5533.0001946.

[12] Wang, Han, Yinchuan Guo, Aiqin Shen, Xiaolong Yang, and Peng Li. 2020 Effect of Nanoclays on Moisture Susceptibility of SBS-Modified Asphalt Binder. *Advances in Materials Science and Engineering* 2020. https://doi.org/10.1155/2020/2074232.

[13] Hamed, Gholam Hossein, Mohyedin Asadi, Fereidoon Moghadas Nejad, and Mohamad Reza Esmaeeli. 2019 Applying asphalt binder modifier in reducing moisture-induced damage of asphalt mixtures. *European Journal of Environmental and Civil Engineering*. DOI:10.1080/19648189.2019.1615554.

[14] Huang, Jiandong, and Yuantian Sun. 2020 Effect of modifiers on the rutting, moisture-induced damage, and workability properties of hot mix asphalt mixtures. *Journal of Applied Sciences* **10**(20) pp. 7145. doi:10.3390/app10207145.

[15] Moussa, Ghada, Ashraf Abdel-Raheem, and Talaat Abdel-Wahed. 2020 INVESTIGATING THE MOISTURE SUSCEPTIBILITY OF ASPHALT MIXTURES MODIFIED WITH HIGH-DENSITY POLYETHYLENE. *Journal of Engineering Sciences* **48**(5) pp. 765-782. DOI: 10.21608/jesaun.2020.39052.1001

[16] Owens, Daniel K., and R. C. Wendt. 1969 Estimation of the surface free energy of polymers." *Journal of applied polymer science* **13**(8) pp.1741-1747. https://doi.org/10.1002/app.1969.070130815.

[17] Fowkes, Frederick M. 1964 Attractive forces at interfaces. *Industrial & Engineering Chemistry* **56**(12) pp. 40-52. https://doi.org/10.1021/ie50660a008.

[18] Chen, Jian-Shiuh, Min-Chih Liao, and Ming-Shen Shiah.2002 Asphalt modified by styrene-butadiene-styrene triblock copolymer: Morphology and model. *Journal of materials in civil engineering* **14**(3) pp. 224-229. DOI: 10.1061/(ASCE)0899-1561(2002)14:3(224)

[19] Little, Dallas N., and Amit Bhasin 2006 Using surface energy measurements to select materials for asphalt pavement. No. NCHRP Project 9-37. DOI: 10.17226/23182

[20] Bhasin, Amit. 2007 Development of methods to quantify bitumen-aggregate adhesion and loss of adhesion due to water. Ph.D. diss., Texas A&M University. DOI: 10.1617/s11527-012-0012-2.

[21] Howson, Jonathan, Eyad A. Masad, Amit Bhasin, Veronica Castelo Branco, Edith Arambula, Robert Lytton, and Dallas Little.2007 System for the evaluation of moisture damage using fundamental material properties. Texas Transportation Institute, Texas A&M University. http://tti.tamu.edu/documents/0-4524-1.pdf

[22] Yasameen Hadi Abed. 2020 The Deformation Strength Characterization of A Thin Film Bitumen Material. Ph.D. thesis, Mustansiriyah University.