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Polymeric Aggregate Treatment Using Styrene-Butadiene Rubber (SBR) for Moisture-Induced Damage Potential

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Abstract: The surface free energy (SFE) characteristics of two Oklahoma aggregates with and without styrene-butadiene rubber (SBR) treatment were evaluated for moisture-induced damage potential using a universal sorption device (USD). SBR coating altered the aggregate surface from hydrophilic to hydrophobic, thereby increasing the wettability of asphalt binder over aggregates. Significant reductions in interfacial energy were also observed for both aggregates for increased wetability. SBR markedly reduced the total SFE and polar SFE, increased the non-polar SFE of aggregates, and made the aggregate surface more hydrophobic for increased wettability. The acid SFE of acidic sandstone is significantly reduced, and the base SFE is increased by SBR treatment, thus favoring the adhesion between an acidic asphalt binder and an acidic aggregate. The free energy of adhesion is increased by SBR coating with sandstone performing better than limestone. Aside from this, plugging of air-trapped fine pores with SBR coating reduced surface area that may help in increasing the interlocking and decreasing the asphalt binder content of the mix.

***Key words**: Aggregate; Asphalt binder; Moisture-induced damage; Styrene-butadiene rubber (SBR); Surface free energy (SFE).*

Introduction

Asphalt binders are generally acidic in nature. Carboxylic acid, anhydride, phenol etc. are generally the acidic functional groups in asphalt binder [1]. In an Ion Exchange Chromatography (IEC) analysis on four Strategic Highway Research Program (SHRP) core asphalts, Kim and Branthaver [2] found that the mass fraction of strong acid varies between 3.9 and 9.55%; whereas, the mass fraction of strong base varies between 2.3 and 5.2%. Its acid value is between 0 and 4 mg KOH/g. On the other hand, acidic (also called hydrophilic) aggregates such as quartzite, granite, and sandstone generally exhibit a high silica content. Basic (also called hydrophobic) aggregates exhibit a low silica content. Carbonate rocks, such as limestone and dolomite, produce basic aggregates [3]. Basic aggregates provide good bonding for acidic bitumen although some adhesive bonds such as carboxylic acid salts are easily water replaceable. In case of acidic aggregates, surface chemistry of Lewis acids and bases does not favor adhesion and a good bond between an acidic aggregate, and an acidic asphalt binder is difficult to achieve [4]. On the contrary, water has a much higher affinity for an acidic surface. Therefore, anti-strip additives such as lime and amines are most commonly used to provide a good bond against moisture. Lime reacts with carboxylic acids in asphalt binder and forms insoluble calcium salts while amines react with acidic surface to produce insoluble ammonium salts to resist moisture damage.

A survey (including 50 states) conducted by Aschenbrener [5] indicated that 25 states use a liquid anti-strip additive, 13 states use hydrated lime, and 7 states use either a liquid anti-strip additive or hydrated lime. Lime is corrosive on equipment in bag houses at batch plants and causes problems with dusting and subsequent worker exposure. Odor is the major problem with amines, while reduced viscosity was reported by some others [6].

An attractive alternate method that received limited attention in literature or market place for treating aggregate to reduce or eliminate stripping is to use polymer such as SBR. Emission test data showed that polymer systems are environmentally as safe as anti-strip additives for aggregates. The application of polymer to hot mix asphalt (HMA) is relatively simple and consists of spraying diluted polymer directly on the aggregate as it is conveyed into the drum mixer. The mixing action of the drum is generally adequate to obtain coating [6]. An additional benefit of the polymer treatment is that it shows a significant decrease (0.4-0.85%) in the asphalt binder content as compared to the untreated and lime treated mixtures [7]. The SBR latex is applied directly to the aggregate and forms a rubber coating on the surface of the aggregate. It provides a protective barrier on the aggregate which repels water and water proofs the aggregate while providing an improved bonding with the asphalt binder [8].

Tarrer and Wagh [9] reported that aggregates which are coated with polymer has a decreased tendency to strip. Dunning et al. [6] performed laboratory and field trials and compared the performance of SBR with lime and amines. It was concluded from this study that SBR performed as well as an amine-treated control in the immersion-compression test. In field tests, the polymer increased resistance to stripping and decreased the temperature susceptibility of the resilient modulus. Sebaaly et al. [7] used SBR, commercially available as UP-5000 from Ultrapave, GA, to evaluate its effectiveness compared to lime-treated and untreated aggregates. It was concluded from their study that UP-5000 is as effective as lime in eliminating the moisture sensitivity of a severe stripping aggregate, while significantly improving the performance of a marginal aggregate. Williams and Miknis [10] used an environmental scanning

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electron microscope (ESEM) to study the effectiveness of anti-strip additives. A targeted point on the sample was observed after each freeze-thaw cycle to assess qualitatively the degree of stripping along the binder-aggregate interface of each sample. The reduced binder-aggregate separation in the SBR treated samples indicated that SBR treatments decrease separation at the binder-aggregate interface. The SBR treatment was more effective than the amine treatment, which was more effective than the lime treatment.

Objectives

The objectives of this study are to evaluate the effect of SBR treatment on the surface free energy (SFE) components (acid, base, and non-polar) and related properties of selected aggregates and, thereby, elucidate the moisture-induced damage mechanisms. The specific objectives are as follows:

- Determine SFE components of SBR treated and untreated aggregates.
- Determine surface area, spreading coefficients, and interfacial energy.
- Evaluate adhesive bond with and without the presence of water.
- Provide a better understanding of the chemical model of binder-aggregate interactions. Discuss moisture-induced damage potential with and without SBR treatment with respect to wettability of asphalt binders over aggregates, adhesion (free energy of adhesion) between asphalt binders and aggregates, and solubility of the adhesive bond.

Surface Free Energy Method

SFE measurements and concomitant bond energy calculations between asphalt binders and aggregates can be used as an effective tool to identify binder-aggregate pairs that are susceptible to premature moisture-induced damage [11]. It also explains causes for poor or good adhesion based on surface characteristics of aggregates and binders. Very recently, Bhasin et al. [12] concluded that the SFE method can supplement the current mechanical tests for measuring moisture susceptibility with fundamental material properties. In a separate study, Wasiuddin et al. [13, 14] used the SFE method to evaluate the acid-base characteristics of asphalt binders with and without anti-strip additives. In another study, Wasiuddin et al. [15] reported the thermal degradation of anti-strip additives due to rolling thin film oven (RTFO) aging and pressure aging vessel (PAV) aging based on the SFE method using the van Oss-Chaudhury-Good (vOCG) analysis [16]. Details of the test methods and related theories were discussed previously by Wasiuddin et al. [13-15].

The SFE of a solid (or liquid) is defined as the work required to increase the surface area of the solid under vacuum by unit length squared. Consequently, the free energy of cohesion is the work done by a unit force acting along the surface of an asphalt binder at a right angle to any line of unit length against a cohesive force to create two interfaces from one under vacuum. Similarly, the free energy of adhesion is the free energy required to create two asymmetric interfaces from a boundary within a heterogeneous material (aggregate and asphalt binder in this case).

The SFE of an aggregate mainly comprises of a non-polar component (also called Lifshitz-van der Waals component) and an acid-base component, as shown in the following equation [16]:

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

where,
Γ = SFE of the aggregate,
Γ^{LW} = Lifshitz-van der Waals component of the SFE, and
Γ^{AB} = Acid-base component of the SFE.

According to Good's postulate [16], the acid-base term can be decomposed to a Lewis acidic surface parameter and a Lewis basic surface parameter as follows:

$$\Gamma^{AB} = 2\sqrt{\Gamma^{+}\Gamma^{-}} \tag{2}$$

where,
Γ^{+} = Lewis acid component of surface interaction, and
Γ^{-} = Lewis base component of surface interaction.

The free energy of adhesion (ΔG^{A}), as defined previously, has two components, Lifshitz- van der Waals or non-polar part of adhesion and acid-base or polar part of adhesion. The following equations are used to determine the non-polar and polar adhesion between an asphalt binder and an aggregate:

$$\Delta G^{A} = \Delta G^{aLW} + \Delta G^{aAB} = -2\sqrt{\Gamma_s^{LW}\Gamma_l^{LW}} - 2\sqrt{\Gamma_s^{+}\Gamma_l^{-}} - 2\sqrt{\Gamma_s^{-}\Gamma_l^{+}} \tag{3}$$

where,
ΔG^{A} = Free energy of adhesion,
ΔG^{aLW} = Non-Polar or Lifshitz-van der Waals part of adhesion, and
ΔG^{aAB} = Acid-base or polar part of adhesion,
Γ_l^{LW}, Γ_l^{+}, and Γ_l^{-} = SFE components of asphalt binder, and
Γ_s^{LW}, Γ_s^{+}, and Γ_s^{-} = SFE components of aggregate.

Also, the following equation was used to calculate the adhesion of asphalt binder with aggregate in the presence of water where subscripts 1, 2, and 3 represent asphalt binder, aggregate, and water, respectively. If the value of free energy of adhesion is negative, it means the two phases of the material tend to bind together and the more it is negative the higher the bonding strength.

$$\begin{aligned} Adhesion = -(&2\Gamma_3^{LW} + 4\sqrt{\Gamma_3^{+}\Gamma_3^{-}} - 2\sqrt{\Gamma_1^{LW}\Gamma_3^{LW}} - 2\sqrt{\Gamma_1^{+}\Gamma_1^{-}} \\ &- 2\sqrt{\Gamma_1^{-}\Gamma_3^{+}} - 2\sqrt{\Gamma_2^{LW}\Gamma_3^{LW}} - 2\sqrt{\Gamma_2^{+}\Gamma_3^{-}} - 2\sqrt{\Gamma_2^{-}\Gamma_3^{+}} \\ &+ 2\sqrt{\Gamma_1^{LW}\Gamma_2^{LW}} + 2\sqrt{\Gamma_1^{+}\Gamma_2^{-}} + 2\sqrt{\Gamma_1^{-}\Gamma_2^{+}}) \end{aligned} \tag{4}$$

where,
Γ_1^{LW}, Γ_1^{+}, and Γ_1^{-} = SFE components of asphalt binder,
Γ_2^{LW}, Γ_2^{+}, and Γ_2^{-} = SFE components of aggregate, and
Γ_3^{LW}, Γ_3^{+}, and Γ_3^{-} = SFE components of water.

The methodology established by Cheng et al. [11] was followed in this research, which is based on the van Oss-Choudhury-Good [16] postulation for the analysis of the SFE components of aggregate. The methodology and theory used for measuring the SFE components of an aggregate with the Universal Sorption Device (USD) are as follows.

- Three gas solvents, n-hexane (non-polar), MPK (methyl propyl ketone/2-pentanone, mono-polar), and water (bi-polar) were selected whose SFE components are known.

- The specific amount of solvent adsorbed on the surface of the absorbent (aggregate) was measured and simultaneously the vapor pressure at the surface of the aggregate was measured.
- The specific surface area of the aggregate was calculated using the following BET (after Brunauer, Emmet and Teller) equation:

$$\frac{P}{n(P_0 - P)} = \left(\frac{c-1}{n_m c}\right)\frac{P}{P_0} + \frac{1}{n_m c} \tag{5}$$

where,
P = Vapor pressure,
P_0 = Saturated vapor pressure of solvent,
n = Specific amount adsorbed on the surface of the absorbent,
n_m = Specific amount adsorbed on the monolayer, and
c = Constant.

- The spreading pressure at saturation vapor pressure was calculated for each solvent using the Gibbs adsorption equation, as follows:

$$\pi_e = \frac{RT}{A}\int_0^{P_0} \frac{n}{P}\,dP \tag{6}$$

where,
π_e = Spreading pressure at saturation vapor pressure of solvent,
R = Universal gas constant,
T = Absolute temperature, and
A = Specific surface area of absorbent.

- The work of adhesion of a liquid on a solid, W_A, was expressed in terms of the surface tension (surface energy) of the liquid, Γ_l, and the equilibrium spreading pressure of adsorbed vapor on the solid surface, π_e, as shown in the following equations:

$$W_A = \pi_e + 2\Gamma_l = \Delta G_{sl} \tag{7}$$

$$\Delta G_{sl} = \Delta G_{sl}^{LW} + \Delta G_{sl}^{AB} = 2\sqrt{\Gamma_s^{LW}\Gamma_l^{LW}} + 2\sqrt{\Gamma_s^{+}\Gamma_l^{-}} + 2\sqrt{\Gamma_s^{-}\Gamma_l^{+}} \tag{8}$$

$$\pi_e + 2\Gamma_l = 2\sqrt{\Gamma_s^{LW}\Gamma_l^{LW}} + 2\sqrt{\Gamma_s^{+}\Gamma_l^{-}} + 2\sqrt{\Gamma_s^{-}\Gamma_l^{+}} \tag{9}$$

- The following equation was used to calculate the non-polar component of the SFE from a non-polar solvent:

$$\Gamma_s^{LW} = \frac{(\pi_e + 2\Gamma_l)^2}{4\Gamma_l^{LW}} \tag{10}$$

One monopolar basic liquid vapor (subscript, *m*) and one known bipolar liquid vapor (subscript, *b*) were selected to calculate the acid-base components of the SFE using the following equations:

$$\Gamma_s^{+} = \frac{(\pi_e + 2\Gamma_{lm} - \sqrt{\Gamma_s^{LW}\Gamma_{lm}^{LW}})^2}{4\Gamma_{lm}^{-}} \tag{11}$$

$$\Gamma_s^{-} = \frac{(\pi_e + 2\Gamma_{lb} - 2\sqrt{\Gamma_s^{LW}\Gamma_{lb}^{LW}} - 2\sqrt{\Gamma_s^{+}\Gamma_{lb}^{-}})^2}{4\Gamma_{lb}^{+}} \tag{12}$$

The total SFE of the aggregate was calculated using the following equation:

$$\Gamma_s = \Gamma_s^{LW} + 2\sqrt{\Gamma^{+}\Gamma^{-}} \tag{13}$$

Material Description

Two commonly used aggregates in Oklahoma, namely limestone and sandstone, were selected for SFE measurements. The corresponding sources of the selected aggregates were Sawyer and Vinita. Polymeric anti-strip system SBR, commercially available as UP-5000, was collected from Ultrapave, GA. The UP-5000 (SBR) was received in an emulsion form at 15% solids. The 15% solids emulsion was mixed with the aggregate at 0.67% by dry weight of the aggregate. This corresponds to 0.1% solids (not emulsions) by dry weight of the aggregate. The SBR coated aggregate was then put in the oven at 150°C for 2 h.

Experimental Setup and Procedure

A universal sorption device (USD) from VTI Corporation was used to produce isotherms of different organic liquids and, thereby, the SFE components were determined according to the equations previously described. The major components of the USD are a microbalance, a dew point analyzer, a mass flow controller, and a water bath. Approximately 15 g of an aggregate passing #4 sieve and retaining on #10 sieve (US Standard) was washed thoroughly with deionized water and put into the oven at 110°C for 24 h. The sample was then put in a desiccator and used in the USD test after cooling. A test program was prepared using the VTI software. The aggregate sample was put in the USD for drying at 25°C for 600 min as set in the program. The test started with the increment of the relative humidity from water vapor. A relative humidity step of 10% was set in the program. The relative humidity will change after the sample reaches an equilibrium condition (forms a plateau) at that relative humidity level. Two different equilibrium conditions can be set in the program. One is based on percent change in sample weight and the other on a specified time. An equilibrium condition can be set by combining the two. The USD obtains the percent change in weight data with respect to the change in relative humidity. Equilibrium (plateau) was reached at each relative humidity step.

Test Results

Adsorption isotherms of n-hexane, MPK, and water vapors for both limestone and sandstone were collected at different humidity levels using the USD. It was observed that limestone has higher adsorption than sandstone with all the three vapors. This was expected because in general limestone has a much greater surface area than sandstone.

Fig. 1 shows the adsorption of n-hexane, MPK, and water at different relative pressures of different vapors on sandstone with and without SBR treatment. It can be observed that the adsorption of n-hexane increased with SBR treatment. It was expected because SBR provides a relatively non-polar coating which increases the adsorption of non-polar n-hexane. The adsorption of MPK is significantly reduced with the SBR treatment (Fig. 1). It could be due to the fact that MPK (having a very high base SFE) repels SBR-treated aggregates (having increased base SFE) due to SBR

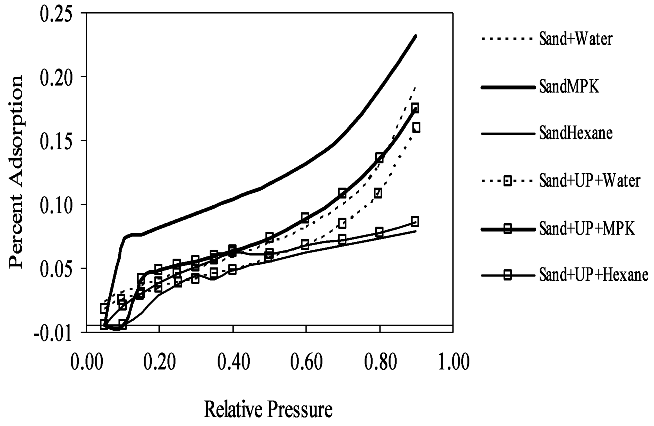

Fig. 1. Adsorption of N-hexane, MPK, and Water at Different Relative Pressures on Sandstone With and Without SBR Treatment.

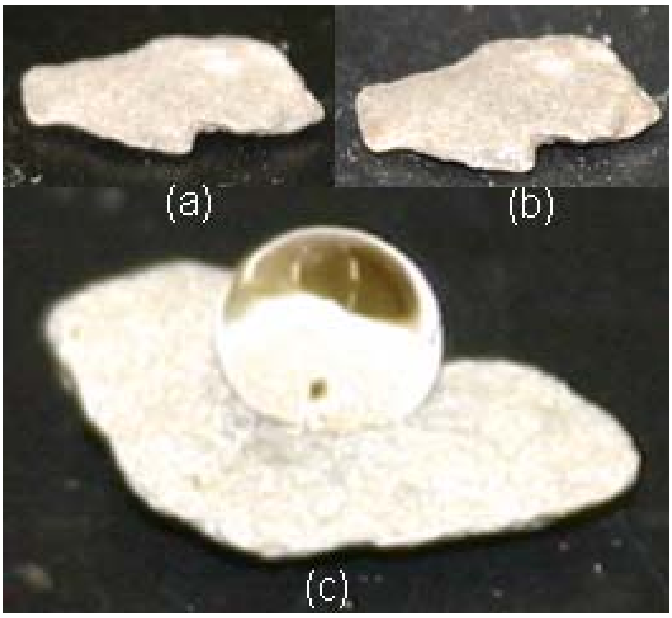

Fig. 2. (a) A Dry Limestone (between #4 and #10), (b) Drop of Water Spreads on a Limestone, and (c) Water Drop Retains on a SBR Coated Limestone.

treatment as will be seen in a subsequent section. In the case of water vapor, SBR treatment reduced adsorption to sandstone, which should be helpful in resisting moisture damage. Finally, spreading pressure, specific surface area, spreading coefficient, interfacial energy, and SFE components were calculated from the adsorption data, as will be discussed in the following sections. Also, all these parameters were discussed with respect to their effect on wettability of asphalt binders over aggregates, adhesion (free energy of adhesion), and solubility of adhesive bonds.

Effect on Hydrophobic/Hydrophilic Characteristics

Zettlemoyer [17] defined a surface hydrophobic (water-repelling) if water does not spread on it. Instead, the water stands up in the form of drops, and a contact angle can be measured from the plane of the surface, tangent to the water surface at the three phase boundary line. It is believed that hydrophobic aggregates (considered to be basic) provide better resistance to stripping of asphalt binder films than hydrophilic aggregates (water-loving, considered to be acidic). Carbonate rocks, such as limestone, usually produce hydrophobic aggregates [3], while sandstone exhibits hydrophilic characteristics due to high silica content.

In this study, a syringe drop of water was placed on a limestone aggregate and a sandstone aggregate (both passing #4 sieve and retaining on #10 sieve) and was observed that the drop of water immediately spreads over both the dry aggregates (Fig. 2(b)). Spreading of the drop of water was expected for the sandstone as it exhibits hydrophilic surface. The drop of water spreads over the hydrophobic limestone aggregate perhaps due to the adsorbed layers of water molecules from the air. Both the limestone and the sandstone aggregates were then treated with SBR, and it was observed that the water from the syringe formed a stable drop on both the aggregate surfaces (Fig. 2(c)). It was evident from this simple test that UP-5000 (SBR) polymeric aggregate treatment turns a hydrophilic aggregate (likes water) into a hydrophobic aggregate (dislikes water and likes oil), increasing the water resistance potential of the HMA. This is consistent with the immiscible nature of aliphatic and aromatic hydrocarbon with water.

Effect on Surface Area

On the basis of purely mechanical considerations, large areas of aggregate interfacial contact with an asphalt binder provide good adhesion and reduced moisture susceptibility. Limestone is porous and, thereby, has greater surface areas than some other aggregates [18]. It appears to exhibit stronger bonds with asphalt binder than do aggregates having fewer or smaller surface pores such as quartz [19]. Table 1 shows the surface areas of limestone and sandstone used in this study. It was observed that limestone has about two times greater surface area than sandstone as measured by each of the three solvent vapors namely, n-hexane, MPK, and water.

In addition to greater surface areas, a porous aggregate such as limestone provides greater interlock. Conversely, when an asphalt binder coats a rough surface that has fine pores instead of large pores, the beneficial effect of porosity is reduced, air is trapped, and the asphalt binder can hardly penetrate the fine pores. Yoon and Tarrer [18] observed that dolomite with fine pores performed worse than limestone with large pores, probably because only a fraction of the aggregate's apparent surface area was actually in contact with the asphalt binder. In general, the depth of penetration of the asphalt binder depends on the size of the pore as well as the viscosity and SFE of the asphalt binder at the temperature of mixing [18].

The mechanism by which UP-5000 (SBR) works is that SBR coats the surface of the aggregate and penetrates the fine pores of the aggregate surface providing a strong mechanical bond. Thereby, it works as a bridging material between the aggregate surface inside the fine pores to the depth to which asphalt binder can penetrate. Thus, SBR reduces the aggregate surface area by filling up the fine pores which otherwise trap air. Table 1 shows that for each of the three solvent vapors, SBR reduces surface area for both limestone and sandstone. The reductions in surface areas for limestone and sandstone are 6.3 and 12% in case of water vapor, 23.3 and 33.4% for MPK, and 11.6 and 18.6% for n-hexane, respectively. The reductions are higher for limestone. It was expected because limestone has

Table 1. Specific Surface Area, Spreading Coefficient, Interfacial Energy, SFE Components, and Free Energy of Adhesion.

		Limestone	Limestone +SBR	Sandstone	Sandstone +SBR	PG 64-22*
Specific Surface Area (*m^2/gm*)	n-Hexane	2.24	2.10	1.30	1.15	
	MPK	3.23	2.47	1.51	1.01	
	Water	2.31	2.04	1.23	1.00	
Spreading Coefficient (*$ergs/cm^2$*)	Binder on Aggregate	103.7	116.3	103.8	111.2	
	Water on Aggregate	193.1	219.0	207.7	203.6	
Interfacial Energy (*$ergs/cm^2$*)	Binder-Aggregate Interface	106.8	70.6	180.6	66.7	
	Water-Aggregate Interface	-45.8	-95.4	13.4	-89.0	
SFE Components (*$ergs/cm^2$*)	Total SFE (Γ)	219.9	196.2	293.7	187.2	9.28
	Non-Polar SFE(Γ^{LW})	51.9	62.8	43.5	63.1	7.025
	Acid SFE (Γ^{A})	13.0	6.5	28.2	6.3	2.91
	Base SFE (Γ^{B})	540.7	687.7	555.2	610.5	0.44
	Acid-Base (Polar) SFE (Γ^{AB})	168.0	133.4	250.3	124.0	2.256
Free Energy of Adhesion (*$ergs/cm^2$*)	Binder-Aggregate	-122.3	-134.8	-122.4	-129.8	
	Water-Aggregate	-338.3	-364.2	-352.9	-348.8	
	Binder-Aggregate in Water	119.3	132.7	133.9	122.3	

*Wasiuddin et al. [*13-14]*

higher amount of fine pores than sandstone. Aside from this, a significant decrease in asphalt binder content of HMA with SBR treated aggregate compared to the untreated and lime treated aggregates, as found by other researchers [6, 7], could be due to the reduced surface area of the SBR treated aggregates. Thus, reduced surface area explains two important mechanisms of SBR treatment, better mechanical interlocking, and reduction in asphalt binder content.

Effect on Spreading Coefficient

Asphalt binder is generally hydrophobic in nature and aggregates are more or less hydrophilic [9]. Therefore, it is difficult to wet hydrophilic aggregates with a hydrophobic asphalt binder. Spreading coefficient is a quantitative measure of wetting. In this study, the spreading coefficient for asphalt binder over aggregate with and without SBR treatment was calculated. The SFE components of a PG 64-22 binder was obtained from a previous study (Table 1) by the authors [13, 14]. Spreading coefficient of a liquid over a solid ($S_{L/S}$) is simply the reduction in SFE on losing the bare solid surface and forming the new solid/liquid and liquid/vapor interface [17]. It can be calculated according to the following equation:

$$S_{L/S} = \Gamma_S - \Gamma_{SL} - \Gamma_{LV} \tag{14}$$

where,

$S_{S/L}$ = Spreading coefficient of liquid L on solid S,

Γ_S = SFE of solid S, *$ergs/cm^2$*,

Γ_{SL} = Solid-liquid interfacial energy, *$ergs/cm^2$*, and

Γ_{LV} = SFE of liquid L, *$ergs/cm^2$*.

From the above equation, the free energy change of spreading coefficient will be positive for spontaneous spreading. Table 1 shows the spreading coefficient of a PG 64-22 binder over both the limestone and the sandstone with and without SBR (UP-5000) treatment. It was observed that SBR treatment increased the wetting of asphalt binder over both the aggregates. It improved the sandstone surface better than the limestone. These findings are consistent with the observed hydrophobic character of the SBR treated aggregate in the water droplet test and with the known relative wetting properties of sandstone and limestone.

Table 1 also shows that water wets the aggregate surface better than the asphalt binder as all the spreading coefficients of water over aggregates are higher than the ones for asphalt binder over aggregates. SBR treatment performed better for the sandstone reducing the wettability of water on its surface. The spreading coefficient of asphalt binder over sandstone increased from 103.8 to 111.2 *$ergs/cm^2$*; whereas, the spreading coefficient of water over sandstone decreased from 207.7 to 203.6*$ergs/cm^2$* due to SBR treatment.

Effect on Interfacial Surface Energy

Aggregates have a highly polar surface while asphalt binders have a continuous phase of non-polar materials with organized and structured polar molecules [20]. Therefore, it becomes difficult to wet polar aggregate surface with mostly non-polar asphalt binder.

The factor that affects wetting of the aggregate surface by asphalt binder is the interfacial surface energy between the asphalt binder and the aggregate [19]. Some of the additives can be extremely beneficial by reducing the surface energy, promoting wetting, and facilitating close contact between the asphalt binder and the aggregate surface. However, the effectiveness of an additive, particularly an anti-strip additive, varies with the type of the additive as well as with the asphalt binder and aggregate [19]. Aside from this, interfacial energy plays an important role in emulsification. When two immiscible liquids need to be mixed, a surface active agent (surfactant) is added whose molecules tend to be oriented between the two faces with the polar ends in the polar phase and the non-polar end in the non-polar phase, which lower interfacial tension. This results in miscibility of the two liquids. Therefore, changes in binder-aggregate interfacial energy due to SBR treatment were calculated in this study using the following equations [16]:

$$\Gamma_{SL} = \Delta G^{a}_{SL} + \Gamma_{S} + \Gamma_{L} \quad (15)$$

$$\Gamma^{LW}_{SL} = \Delta G^{aLW}_{SL} + \Gamma^{LW}_{S} \Gamma^{LW}_{L} \quad (16)$$

$$\Gamma^{AB}_{SL} = \Delta G^{aAB}_{SL} + \Gamma^{AB}_{S} \Gamma^{AB}_{L} \quad (17)$$

where,
Γ_S, ${\Gamma^{LW}}_S$ ${\Gamma^{AB}}_S$= Total, non-polar and polar SFE of aggregate,
Γ_L, ${\Gamma^{LW}}_L$ ${\Gamma^{AB}}_L$= Total, non-polar and polar SFE of asphalt binder,
Γ_{SL}, ${\Gamma^{LW}}_{SL}$ ${\Gamma^{AB}}_{SL}$= Total, non-polar and polar SFE of interfacial energy, and
$\Delta {G^a}_{SL}$, $\Delta {G^{aLW}}_{SL}$, $\Delta {G^{aAB}}_{SL}$= Total, non-polar and polar free energy of Adhesion.

Table 1 shows that limestone used in this study has much lower interfacial energy with PG 64-22 than does the sandstone. It was expected because limestone in general is a better performer than sandstone in resisting moisture-induced damage. SBR coating significantly decreased the interfacial energy of both limestone and sandstone for increased wettability by asphalt binder. It was observed that with SBR treatment, the limestone-PG 64-22 interfacial energy reduced from 106.8 to 70.6*ergs/cm*^{2}, while the sandstone- PG 64-22 interfacial energy reduced from 180.6*ergs/cm*^{2} to only 66.7*ergs/cm*^{2}. Therefore, it can be concluded that SBR coating markedly decreases the binder-aggregate interfacial energy for increased wettability, hence better adhesion.

Effect on Total SFE (Γ) of Aggregates

In order to have a good bond between hydrophobic asphalt binders and hydrophilic aggregates, the nature of the aggregate surface must be changed. The surface tension should be decreased so that the aggregate becomes more hydrophobic [9]. Table 1 shows the effect of SBR treatment on the total SFE of limestone and sandstone. It was observed that the total SFE of sandstone is higher than limestone and SBR treatment reduced the total SFE of both the aggregates. The total SFE of sandstone decreased significantly from 293.7 to 187.2 *ergs/cm*^{2} for improved wettability and adhesion. One important finding is that SBR treatment reduced the total SFE of limestone (219.9*ergs/cm*^{2}) and sandstone (293.7*ergs/cm*^{2}) to nearly the same level (196.2 and 187.2*ergs/cm*^{2}, respectively). This implies the SBR encapsulates the aggregate particles so that the effectiveness of SBR on reducing the total SFE does not depend on the aggregate mineralogy. The reduction in total SFE by styrene-butadiene rubber (SBR) coating can be explained by the fact that, in general, polymer, especially one with no heteroatoms, has a much lower total SFE than aggregates.

Effect on Non-Polar SFE (Γ^{LW}) of Aggregates

Aggregates have highly polar surface making it very difficult for mostly non-polar asphalt binder to wet. SBR treatment alters the aggregate surface increasing its non-polarity for increased wettability. It was observed (Table 1) that limestone (51.9*ergs/cm*^{2}) has higher non-polar SFE than sandstone (43.5*ergs/cm*^{2}), which was expected because limestone performs better against moisture-induced damage. As in the case of the total SFE, SBR treatment increased the non-polar SFE of both the limestone and the sandstone to the same level (62.8 and 63.1*ergs/cm*^{2}, respectively).

Good [16] reported comparatively higher non-polar SFE and lower polar SFE of some polymers. On the other hand, aggregates are known to have high polarity. Therefore, styrene-butadiene rubber coating increases the non-polar SFE of aggregates and, thereby, increases the wettability of asphalt binder.

Effect on Acid SFE (Γ^A) and Base SFE (Γ^B) of Aggregates

Asphalt binders generally are acidic in nature [13, 21]. As mentioned earlier, surface chemistry of Lewis acids and bases does not favor the bond between an acidic asphalt binder and an acidic aggregate. Also, zeta potential measurements by Hagen et al. [21] indicated that both the asphalt binder and aggregate have an overall negative charge in the presence of water.

Table 1 shows that SBR treatment reduced the acid SFE and increased the base SFE of both the aggregates and, thereby, favors the adhesion. The acid SFE of sandstone reduced significantly from 28.2 to 6.3*ergs/cm*^{2}, while the base SFE increased from 555.2 to 610.5 *ergs/cm*^{2}. Once again, SBR is more effective in sandstone, and it reduced the acid SFE of both the limestone and sandstone to the same level (6.5 and 6.3*ergs/cm*^{2}). This further proves that the performance of SBR does not depend on aggregate mineralogy.

One important point to note (Table 1) is that the base SFE of the selected aggregates are much higher than the acid SFE irrespective of the mineralogy of the aggregates. The same observation was noted by Bhasin et al. [12]. As found by previous researchers [12], a high base SFE (relative to acid SFE of the same aggregate) is a manifestation of the selected scale proposed by this method. The base SFE of an aggregate obtained from this method cannot be compared with the acid SFE of that particular aggregate and can only be compared with the base SFE of any other aggregate. So, comparing the acid SFE of different aggregates with and without SBR treatment is acceptable. The same is true for comparison of base SFE. Therefore, though the base SFE of the aggregate is higher than the acid SFE of the corresponding aggregate; aggregates like sandstone are considered to be acidic.

Effect on Acid-Base (Γ^{AB}) or Polar SFE of Aggregates

Zeta potential measurements of aggregates by Yoon and Tarrer [18] showed that aggregates having a relatively high surface electrical potential exhibit a high susceptibility to stripping. Peltonen [22] conducted SFE measurements of aggregates and found that the increase in the silica dioxide content causes an increase in the polarity of the aggregate surface and the adhesion is decreased. Table 1 shows that the acid-base (polar) SFE of the limestone (168.0*ergs/cm*^{2}) is much lower than that of the sandstone (250.3*ergs/cm*^{2}). It was expected that limestone performs better than sandstone in general. A significant decrease in the polar SFE of sandstone was observed with SBR treatment (from 250.3 to 124.0*ergs/cm*^{2}). The SBR treated limestone and sandstone exhibited similar polar SFE values.

Effect on Free Energy of Adhesion

Besides the wettability of asphalt binder over aggregate, adhesion (free energy of adhesion) is a very important factor for moisture-induced damage in HMA. According to Good [16], the free energy of adhesion is negative and the more negative the free energy of adhesion, the better the bond. It was observed (Table 1) that SBR treatment improved the adhesion between the asphalt binder (PG 64-22 in this case) and the selected aggregates. It is important to note that binder-aggregate bonds (-122.3 and -122.4*ergs/cm*^{2} for limestone and sandstone, respectively) are much weaker than water-aggregate bonds (-338.3 and -352.9*ergs/cm*^{2} for limestone and sandstone, respectively). It was expected because water is a highly polar liquid and has a high affinity for the aggregate surface.

As was expected, it was found that breaking the binder-aggregate bond and forming the water-aggregate bond is a spontaneous process. It is due to the positive free energy of adhesion for all the binder-aggregate bonds in the presence of water. Table 1 shows that limestone performs comparatively better as its free energy of adhesion is lower in the presence of water. SBR treatment performed well with sandstone reducing its free energy of adhesion in the presence of water (from 133.9 to 122.3*ergs/cm*^{2}).

Effect on Water Solubility of the Adhesive Bond

Wettability of asphalt binders over aggregates, adhesion (free energy of adhesion) between asphalt binders and aggregates, and water solubility of adhesive bonds are the three major factors for moisture-induced damage. Performance enhancement after SBR treatment can be attributed to increased wettability and adhesion. However, improved mechanical interlocking due to plugging of fine pores by SBR was also discussed.

Yoon and Tarrer [18] reported that the water solubility of the binder-aggregate bond is the main factor affecting stripping of asphalt binder from the aggregate surface. Curtis et al. [19] found that acidic groups, carboxylic acids, and sulfoxides have the highest adsorptions, while ketone and nonbasic nitrogen groups had the least. Conversely, the sulfoxide and carboxylic acids were most susceptible to desorption in the presence of water. Such adhesive bonds are water soluble and, thereby, moisture susceptible. SBR is not soluble, rather it repels water. Thereby, improvement against moisture susceptibility by SBR treatment as found by previous studies can be justified.

Proposed Chemical Model of the Binder-Aggregate Interactions

The binder-aggregate interactions can be explained with respect to wettability of asphalt binders over aggregates, adhesion (free energy of adhesion), and solubility of the adhesive bond. Wettability of the asphalt binder over the aggregate is controlled by the polar (hydrophilic) and non-polar (hydrophobic) nature of the aggregate and the binder. It can be calculated from the changes in polar and non-polar SFE, spreading coefficient, interfacial tension, etc. Alteration of polar aggregate surfaces (hydrophilic) to non-polar aggregate surfaces (hydrophobic) is an important mechanism for increased wettability with mostly non-polar asphalt binders. Reduction in total SFE and polar SFE will increase wettability but may decrease the free energy of adhesion between aggregate and the asphalt binder. Therefore, wettability and adhesion need to be balanced carefully.

Both the carbonaceous and siliceous aggregate surfaces have high polarity. In case of siliceous aggregates, polarity increases with an increase in the amount of silica dioxide [22]. On the other hand, asphalt binders have a continuous phase of non-polar materials with organized and structured polar molecules [20]. Therefore, it becomes difficult to wet the polar aggregate surface with mostly non-polar asphalt binder. SBR treatment increases the non-polar SFE and reduces the polar SFE of aggregates significantly,thereby increasing wettability.

Asphalt binder surfaces are not absolutely non-polar. Wasiuddin et al. [13, 14] reported that polar or acid-base SFE of a PG 64-22 binder (2.26*ergs/cm*^{2}) is much lower than non-polar SFE (7.03*ergs/cm*^{2}) making the asphalt binder mostly non-polar. Conversely, aggregates (i.e., sandstone) have much higher polar or acid-base SFE (250.3 *ergs/cm*^{2}) than non-polar SFE (43.5*ergs/cm*^{2}) although aggregate polarities are one order of magnitude higher than the asphalt binder polarities. Hagen et al. [21] reported that both the asphalt binders and the siliceous aggregates have an overall negative charge as observed from zeta potential measurements and can be considered acidic [13, 14]. In this study, it was found that SBR treatment reduces the acid SFE and decreases the base SFE significantly to almost the same level for limestone and sandstone and, therefore, favors the adhesion between an acidic aggregates and an acidic binder. It should be mentioned here that with SBR treatment reduction in total SFE and polar SFE did not cause a reduction in free energy of adhesion rather it increased the free energy of adhesion.

Adhesive bonds with carboxylic acids and sulfoxides are water soluble and, thereby, moisture susceptible [19]. Acid-base adhesion between asphalt binder and aggregate could be strong but may be water soluble [18]. SBR is water insoluble and creates a hydrophobic barrier against water.

Among the three factors, wettability, adhesion. and solubility, increased wettability can be obtained by other anti-strip additives such as lime, amines, and organosilanes. Increased wettability in all these cases is obtained by altering the hydrophilic aggregate surface to the hydrophobic surface as in the case of SBR in this study. In the case of lime, Ca^{2+} migrates to the aggregate surface to replace H^+, Na^+, K^+, and other cations that are comparatively more water susceptible. Mg^{2+} and Ca^{2+} ions are relatively hydrophobic and increase the wettability of hydrophobic asphalt binder over aggregates [22-24]. The amines consist of a long chain hydrocarbon and amine group. The amine group reacts with the aggregate surface, and the hydrocarbon portion, which is hydrophobic, is directed into the binder. The net effect is that the long hydrocarbon chain acts as a bridge between the hydrophilic aggregate and hydrophobic bitumen surfaces, thus encouraging a strong bond between them. Sometimes a newly crushed aggregate when used in an asphalt paving mixture exhibits a poor stripping resistance as compared to the same aggregate after it has been stockpiled (or aged) for some period of time [9]. Upon aging, the outermost adsorbed water molecules may become partially replaced or covered by organic contaminants present in air, such as fatty acids and oils, and this increases the wettability, thereby reducing the stripping potential of the aggregate.

Conclusions

The following conclusions can be drawn from this study:

- SBR coating alters hydrophilic aggregate surface to hydrophobic, thereby repelling water as seen from a drop of water. It plugs the fine pores of aggregates and work as a bridging material between aggregate surface inside the fine pores and asphalt binder to increase interlocking. This also reduces the surface area of aggregates as has been found in this study. Reduced surface area may help in reducing asphalt binder content.
- SBR increases spreading coefficient and interfacial tension, thereby increasing the wettability of asphalt binders over aggregates.
- SBR significantly reduces the total SFE and polar SFE, increases the non-polar SFE of aggregates, and makes the aggregate surface more hydrophobic. This helps increase the wettability of aggregates.
- The acid SFE of acidic sandstone is significantly reduced and base SFE is markedly increased by SBR treatment. The Lewis acid-base chemistry does favor the adhesion between acidic asphalt binder and acidic aggregate with SBR treatment.
- The free energy of adhesion is increased by SBR coating with sandstone performing better than limestone.
- Finally, SBR increases the wettability of asphalt binders over aggregates, adhesion (free energy of adhesion) between asphalt binder and aggregate, and decreases solubility of the binder-aggregate bond. It improves both the limestone and the sandstone to the same level and, thereby, is independent of the aggregate mineralogy.

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