Moisture damage assessment using surface energy, bitumen stripping and the SATS moisture conditioning procedure

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Abstract

Durability is one of the most important properties of an asphalt mixture. A key factor affecting the durability of asphalt pavements is moisture damage. Moisture damage generally results in the loss of strength of the mixture due to two main mechanisms; the loss of adhesion between bitumen and aggregate and the loss of cohesion within the mixture. Conventional test methods for evaluating moisture damage include tests conducted on loose bitumen-coated aggregates and those conducted on compacted asphalt mixtures. The former test methods are simpler and less expensive to conduct but are qualitative/subjective in nature and do not consider cohesive failure while the latter, though more quantitative, are based on bulky mechanical test set-ups and therefore require expensive equipment. Both test methods are, however, empirical in nature thus requiring extensive experience to interpret/use their results. The rolling bottle test (EN 12697-11) for loose aggregate mixtures and the Saturation Ageing Tensile Stiffness (SATS) test (EN 12697-45) for compacted asphalt mixtures are two such methods, which experience suggests, could clearly discriminate between 'good' and 'poor' performing mixtures in the laboratory. A more fundamental approach based on surface energy (SE) measurements offers promise to better understand moisture damage. This paper looks at results from the rolling bottle and the SATS tests in an attempt to better understand the underlying processes and mechanisms of moisture damage with the help of surface energy measurements on the constituent bitumen and aggregates. For this work, a set of bitumens and typical acidic and basic aggregate types (granite and limestone) were selected. Combinations of these

materials were assessed using both the rolling bottle and SATS tests. The surface energy properties of the binders were measured using a Dynamic Contact Angle (DCA) Analyser and those of the aggregates using a Dynamic Vapour Sorption (DVS) device. From these surface energy measurements it was possible to predict the relative performance of both the simple rolling bottle test and the more complicated SATS test. Mineralogical composition of the aggregates determined using a Mineral Liberation Analyser (MLA) was used to explain the differences in performance of the mixtures considered.

Keywords: Bitumen; Asphalt mixtures; Surface energy; Moisture damage; SATS; Rolling Bottle Test, Adhesion, Mineralogical composition.

1. Introduction

The road network is one of the most important elements of a modern transportation system with the majority of roads throughout the world being constructed from asphalt mixtures. Across the United Kingdom, the total budget spent on road maintenance during 2009/10 was of the order of £3.8 billion with moisture damage considered to be one of the major causes of distress in asphalt pavements (Alarm, 2010; Audit Scotland, 2010). Although not all damage is caused directly by moisture, its presence increases the extent and severity of already existing distresses like cracking, potholes and rutting (Kennedy et al., 1983; Miller and Bellinger, 2003). The presence of moisture results in the degradation of the mechanical properties of the asphalt mixture, i.e. loss of stiffness and mechanical strength, which ultimately leads to the failure of the road structure. Moisture damage thus has a great economic impact as it causes premature pavement failure and hence results in increased rehabilitation activities and maintenance costs.

The physical and chemical properties of the two main constituents of an asphalt mixture (bitumen and aggregate) have a direct influence on the moisture performance of the mixture. A lack of compatibility between bitumen and aggregate is one of the main reasons for distress with moisture damage normally being related to the loss of adhesion between bitumen and aggregate and/or loss of cohesion within the bitumen (or more realistically the bitumen-filler mastic) in the presence of water (Terrel and Al-Swailmi, 1994). Removal of bitumen film from the aggregate surface by water is known as ‘stripping’ with this phenomenon depending largely on the chemical composition of the bitumen and aggregates, and their affinity towards each other (Kandhal, 1994; Emery and Seddik, 1997). Previous studies have indicated that the susceptibility of asphalt mixtures to moisture attack is related to bitumen chemistry, aggregate mineralogy, surface texture of the aggregate and the adhesion between the bitumen and aggregates (Airey et al., 2008; Abo-Qudais and Al-Shweily, 2007; Horgnies et al., 2011; Petersen et al., 1982). In addition, the ambient conditions (including temperature, freeze–thaw cycles and wetting–drying cycles) can also significantly affect the durability of an asphalt pavement material (Huang et al., 2005; Gilmore et al., 1985).

Numerous laboratory test methods have been developed over the years to determine the moisture susceptibility of asphalt mixtures and their response to moisture ingress (Airey and Choi, 2002; Solaimanian et al., 2003). These methods can be divided into two groups: (i) qualitative tests conducted on loose bitumen-coated aggregate, such as the boiling test (Kennedy et al., 1984), and (ii) quantitative tests conducted on compacted asphalt mixtures, such as the wheel tracking test (Aschenbrener, 1995) and the Saturation Ageing Tensile Stiffness (SATS) test procedure (Collop et al., 2004a; Collop et al., 2004a; Airey et al., 2005). The relevant test specimens are typically conditioned in water to simulate in-service conditions and an assessment of any moisture induced damage is made by dividing the conditioned modulus or strength by the corresponding unconditioned property, for example as in the freeze–thaw AASHTO T283-99 procedure (Anon, 2000). In addition to these laboratory test methods, a number of computational approaches have been developed to simulate the in-service conditions experienced by asphalt pavement materials, and hence to attempt to predict the durability and moisture resistance of such materials (Caro et al., 2008a; Caro et al., 2008b; Caro et al., 2010; Masad et al., 2007; Kutay et al., 2007; Shakiba et al., 2013).

Although these various approaches are realistic and logical in terms of simulating in-service asphalt pavement materials, they do not necessarily attempt to understand in detail the adhesion between bitumen and aggregates, and how such interactions are affected by the presence of moisture and other external factors. It is these physico-chemical properties, directly related to the adhesion characteristics of the two materials, that are responsible for adhesion or debonding between the materials (MS-24, 2007; Kennedy et al., 1982). Surface energy (or more correctly surface free energy (SFE)) properties of the materials can be used to assess these adhesion characteristics (Bhasin, 2006). SFE and various thermodynamic calculations can therefore be successfully used to assess the cohesive and adhesive bond strengths of the two materials and the effect of moisture/water on the bond strength of a bitumen-aggregate system (Bhasin et al., 2006; Cheng et al., 2002a; Cheng et al., 2002b). SFE can therefore be considered to truly represent the physico-chemical surface characteristics of bitumen and aggregates and has been successfully used as a tool for selection of moisture resistant materials (Cheng, 2002). The physico-chemical characteristics of bitumen and aggregates, which can be assessed using surface energy

principles, are believed to be a key factor responsible for the adhesion between the two materials.

This paper presents a framework of surface energy testing techniques with bitumen-aggregate stripping and asphalt mixture mechanical moisture sensitivity assessment for identification of compatible bitumen-aggregate combinations. A complete characterisation is possible once results from SFE measurements and intrinsic adhesion calculations are compared with those of standard mechanical moisture damage tests. Tests like the rolling bottle test (RBT) and the saturated ageing tensile stiffness (SATS) test have been used together with intrinsic adhesion and energy ratios to determine if the moisture sensitivity assessment parameters for different bitumen-aggregate combinations can identify 'good' and 'poor' performing asphalt mixtures and to determine how the surface energy-based predictions compare with conventional moisture damage test methods.

2. Intrinsic adhesion

2.1 Surface free energy theory

The surface free energy (SFE) of a material is defined as the energy needed to create a new unit surface area of the material in a vacuum condition. The surface energies of bitumen and aggregate or a bitumen-aggregate system (asphalt mixture) are mainly comprised of an apolar (nonpolar) component and an acid-base component (Fowkes, 1962; Good and van Oss, 1991 and Good, 1992). Equation 1 is used to describe the total surface energy and its components:

$$\gamma = \gamma^{LW} + \gamma^{AB} \quad (1)$$

Where: γ = surface energy of bitumen or aggregate (mJ/m^2);

γ^{LW} = Lifshitz–van der Waals component of the surface energy (mJ/m^2); and

γ^{AB} = acid-base component of the surface energy (mJ/m^2).

The Lifshitz-van der Waals force contains at least three components: London dispersion forces, Debye induction forces, and Keesom orientation forces (Maugis, 1999). The acid-base interaction includes all interactions of electron donor (proton acceptor) - electron acceptor (proton donor) type bonds including hydrogen bonding. To quantitatively predict and treat the acid-base interaction, Good and van Oss (1991) postulated a resolution of the acid-base term, γ^{AB} into a Lewis acidic surface parameter and a Lewis basic surface parameter. The relationship among the γ^{AB} and its components is shown in equation 2:

$$\gamma^{AB} = 2\sqrt{\gamma^{+}\gamma^{-}} \qquad (2)$$

Where: γ^{+} = Lewis acid component of surface interaction, and

γ^{-} = Lewis base component of surface interaction.

2.2 SFE measurements

Five bitumens were included in the study consisting of four conventional bitumens and one modified bitumen. The conventional bitumens ranged from very hard consistency (10/20 penetration grade) to very soft (160/220 pen grade) with intermediate grades of 40/60 pen and 70/100 pen. The modified bitumen was produced by mixing the 40/60 pen bitumen with an amine-based anti-stripping agent at 0.5% additive by weight of binder. Surface energy components of the five bitumens used in this study were determined indirectly using contact angle measurements.

A Cahn Model dynamic contact angle (DCA) analyser was used to measure the contact angles of a set of three carefully selected probe liquids on bitumen coated glass slides under dynamic conditions. The probe liquids used included water, glycerol and diiodomethane. All the tests were conducted at room temperature (23°C ± 2°C) and 50% ± 5% relative humidity.

During the test, a clean 40 mm x 24 mm x 0.45 mm No. 15 microscope glass slide was coated with bitumen and hung from the balance of the DCA equipment with the help of a crocodile clip. A beaker containing a probe liquid was placed on a movable

stage positioned under the glass slide. The bottom edge of the slide was kept parallel with the surface of the probe liquid. The bitumen-coated glass slide was then immersed up to a maximum depth of 5 mm (advancing) and then withdrawn (receding) from the liquid by moving the stage up and down, respectively, at a constant speed of 40 microns/sec while continuously recording the change in mass of the bitumen-coated slide with depth of immersion. The measured mass-depth relationships were used to estimate the force acting on the bitumen-slide while being immersed or removed from probe liquid and used subsequently to determine the contact angle between bitumen and probe liquid.

The contact angle (θ) values are obtained by considering the equilibrium forces acting on the bitumen-coated slide while advancing and receding from the probe liquid using Eq. 3 (Bhasin, 2006):

$$\cos\theta = \frac{\Delta F + V_{im}\left(\rho_L - \rho_{air} g\right)}{P_t \gamma_L} \quad (3)$$

Where: P_t = perimeter of the bitumen coated plate

γ_L = total surface energy of the probe liquid

ΔF = difference between weight of plate in air and partially submerged in probe liquid

V_{im} = volume of solid immersed in the liquid

ρ_L = density of the liquid

ρ_{air} = air density

g = gravitational force

To obtain surface energy values for the bitumen, contact angle values for at least three probe liquids are measured and applied to the Young-Dupré equation (Eq. 4) for the work of adhesion (W_{SL}) between the two materials. Three equations are thus produced using the known surface energy components of the three probe liquids for the determination of the three surface energy components ($\gamma^{LW}, \gamma^{+}, \gamma^{-}$) of the bitumen.

$$W_{SL} = \gamma_L(1+\cos\theta) = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^-\gamma_L^+} + 2\sqrt{\gamma_S^+\gamma_L^-} \quad (4)$$

Where subscripts L and S represents liquid and solid respectively, and θ is the contact angle.

The resulting surface energy components for the five binders are presented in Table 1. The results for the 70/100 pen bitumen exhibited comparatively lower total surface energy (19.1 mJ/m^2) compared to the results for the 40/60 pen and 10/20 pen bitumens. However, in general all the results, including the anti-stripping modified binder (AAS1), are very similar.

Table 1. Surface energy characteristics of bitumen.

Bitumen	Surface energy components (mJ/m^2)			
	γ^{LW}	γ^+	γ^-	γ
10/20 pen	31.1	0.01	3.37	31.5
40/60 pen	30.6	0.00	2.40	30.6
70/100 pen	19.1	0.00	0.78	19.1
160/220 pen	28.2	0.00	0.30	28.8
AAS1	30.9	0.00	1.00	30.9

It is difficult to use the contact angle technique on high surface energy materials like aggregates (SFE values generally > 60 mJ/m^2) as probe liquids readily spread on high energy surfaces and it is difficult to obtain accurate contact angles. Therefore, for this part of the study a dynamic vapour sorption system (DVS Advantage 2, Surface Measurement Systems, Middlesex, UK) was used to determine sorption isotherms for the various aggregates and probe vapour combinations and the results used to determine the SFE components of the aggregate. The desired partial vapour pressures were varied from 0 to 95% with 5-10% increments (14 steps).

Five aggregates commonly used in UK asphalt mixtures were chosen for the study. The aggregates (two 'limestones' and three 'granites') were selected based on their difference in mineralogy and the fact that they exhibit different moisture damage performance (Airey et al., 2007). The mineralogy of the different aggregates was studied using a Mineral Liberation Analyser (MLA) in order to understand their morphology and to help with the overall analysis of results.

MLA comprises a procedure used to identify the mineral phases present in aggregates by combining a large specimen chamber automated Scanning Electron Microscope (SEM) and multiple Energy Dispersive X-ray detectors with automated quantitative mineralogy software. The software controls the SEM hardware to quantitatively analyse mineral and material samples. Automated stage control and image acquisition allows for rapid and systematic Back Scattered Electron (BSE) imaging and subsequent X-ray analysis of thousands of mineral grains and particles. Automatic recalibration ensures consistent results.

An FEI Quanta 600 SEM with MLA capability was used for the mineral phase determination. Aggregate samples were prepared by casting aggregates in resin, followed by polishing of the surface. The samples were then carbon coated to make them electron conductive and scanned in BSE mode with Electron Dispersive X-ray analysis (EDX) being carried out in an array of spots across the particles. The resultant spectra were then used to determine mineral phases at specific points in the microstructure which allowed mineralogical maps to be generated for each of the aggregate types (Grenfell et al., 2014).

Table 2. Mineral composition of aggregates obtained using MLA.

Mineral name	Composition (%)		
	Granite A	Granite B	Granite C
Quartz	19.11	15.86	33.17
Albite	27.13	32.73	28.30
K-feldspar	4.82	9.64	16.93
Chlorite	31.53	13.52	11.90
Muscovite	2.39	3.43	4.58
Other	0.74	1.91	1.19
Epidote	11.11	1.37	1.06
Biotite	0.99	0.34	1.00
Anorthite	0.10	18.54	0.82
Calcite	0.20	0.08	0.78
Hornblende	1.88	2.57	0.27
	Limestone A	Limestone B	
Calcite	96.98	98.94	
Dolomite	1.30	0.00	
Clay	0.93	0.37	
Quartz	0.49	0.55	
Other	0.30	0.13	

K-feldspar = potassium-dominant feldspar

The MLA results (in terms of mineral composition) for the five aggregates are presented in Table 2 and examples of the MLA scans for two of the aggregates

(Limestone A and Granite A) are presented in Figures 1 and 2. The results show that the aggregates have significantly different mineralogical make-up with Limestone A (Figure 1) being made up of predominantly (about 97%) calcite. Granite C, on the other hand, is made up of a number of different mineral phases with the predominant phase being quartz, but with significant quantities of albite and K_feldspar (see Figure 2). It is believed that the large proportion of the quartz phase has the potential to lead to deleterious moisture properties, due to the poor adhesion between quartz and bitumen. However, there is also evidence that high feldspar content can be responsible for interfacial failure between bitumen and aggregate surfaces (Horgnies et al., 2011).

In general, the limestone aggregates, being basic, are believed to perform better in practice as well as in moisture sensitivity tests, while the granite aggregates have been found to perform poorly in previous moisture sensitivity work (Grenfell et al., 2012).

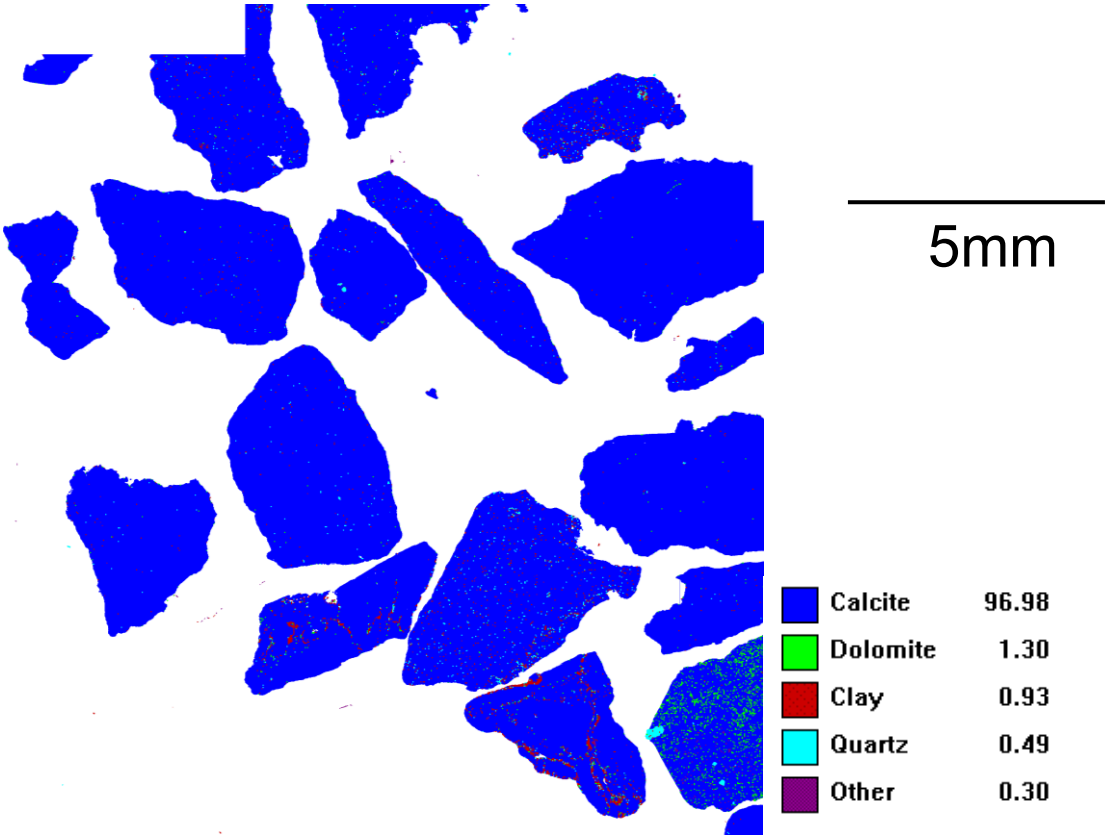

Figure 1. MLA analysis of Limestone A.

Prior to surface energy testing, the aggregates were first washed with deionised water and then dried in an oven to constant mass (up to 16 hours). An aggregate fraction passing 5mm and retained on 2.36mm was used. The upper limit on aggregate size is dictated by the material holding capacity of the DVS sample chamber. The cleaned oven-dried aggregate samples (less than 10 g) were again pre-heated in the DVS sample chamber at a temperature of 110°C for up to five hours to completely dry the samples before the sorption test.

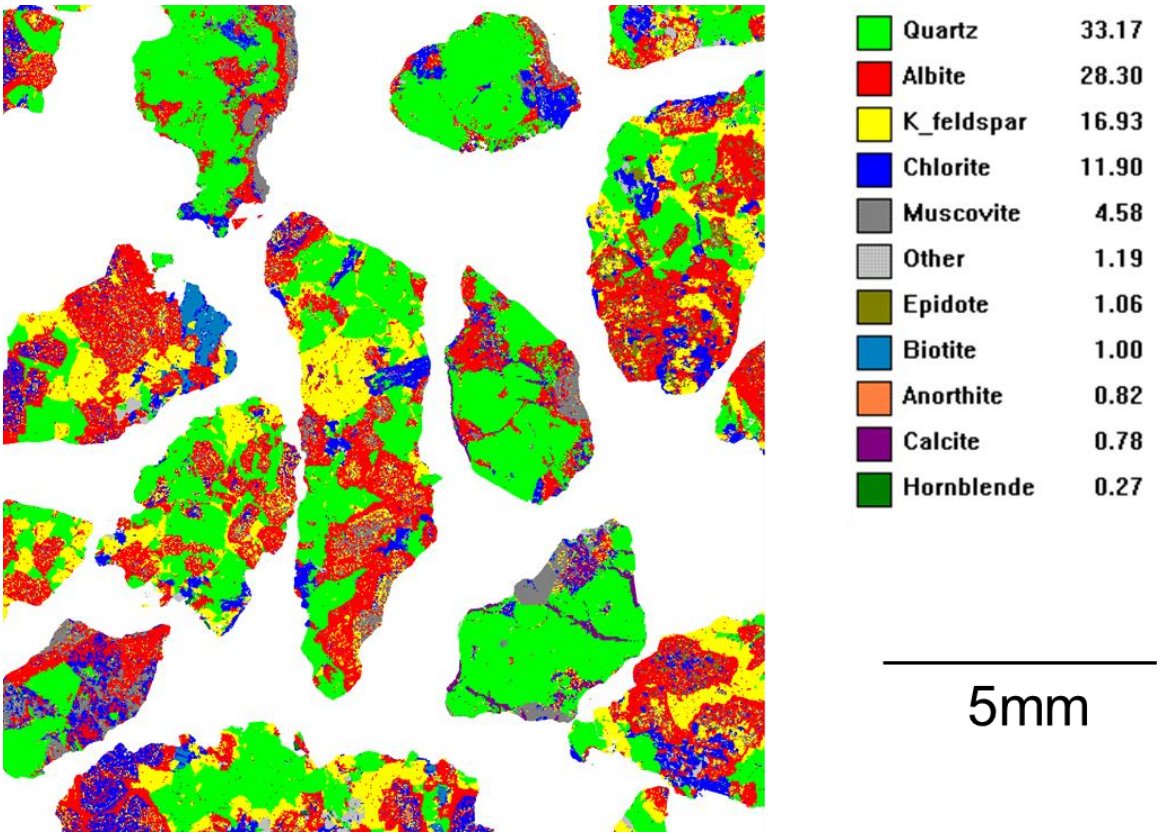

Figure 2. MLA analysis of Granite C.

To perform the sorption test, carefully selected probe vapours (octane, ethyl acetate, and chloroform) with known SFE components were passed through the aggregate sample, under controlled temperature and partial vapour pressure conditions, with the aid of an inert carrier gas (nitrogen). The probes that were chosen for the aggregate testing had relatively low surface tension values as compared to the ones that are used for testing the bitumen to aid the ability to achieve a uniform adsorption/monolayer of the probe on the aggregate surface. Due to the surface characteristics of the aggregate,

vapour probes get adsorbed on their surfaces which results in an increase in the mass of the aggregate sample that is then measured using a sensitive balance.

During the test, the aggregate material was exposed to different concentrations/vapour pressures of the probe liquids and the increase in mass of the aggregates, because of adsorption of the probe vapours on the aggregate surface, was measured. All the tests were performed at a temperature of 25°C. The change in mass of an aggregate sample was plotted against the increasing partial vapour pressure values to generate sorption isotherms which were used to estimate specific surface area and spreading equilibrium pressures of the aggregates.

A typical obtained adsorption isotherm is shown in Figure 3 for Limestone A aggregate with octane probe vapour for partial vapour pressures (concentrations) ranging from 0 to 95%. Similar isotherms were obtained for the other aggregates.

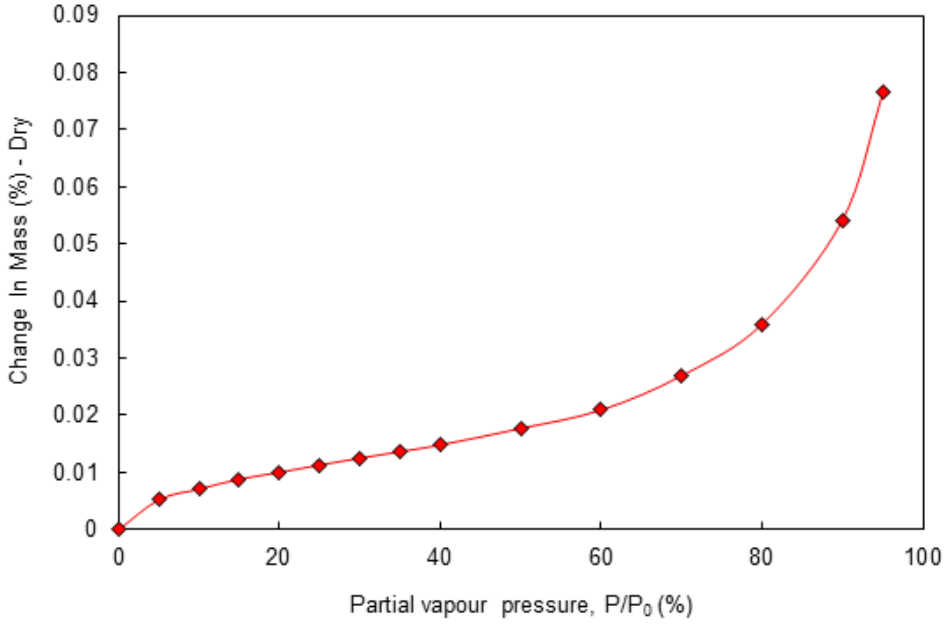

Figure 3. Typical sorption isotherm obtained for Limestone A aggregate using octane vapour as probe for partial vapour pressures (concentration) ranging from 0 to 95% with 5-10% increments (14 steps).

From Figure 3, it can be seen that the plot of adsorbed mass versus partial vapour pressures for Limestone A shows characteristics typical of Type II isotherms (Erbil,

2006). This suggests that the BET model can be used to fit the sorption isotherms (up to 35% partial vapour pressure) using the Langmuir approach (Eq. 5) where a plot of $P/(P_0-P)n$ against P/P_0 gives a straight line from which the BET constant (c) and the specific amount of vapour adsorbed on the surface of aggregate (n_m), can be obtained. The results were used to estimate the specific surface area of the aggregates using Eq. 6 (Shaw, 1991; Sing, 1969).

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

Where: P = partial vapour pressure, Pa

P_0 = saturated vapour pressure of solvent, Pa

n = specific amount adsorbed on the surface of the absorbent, mg; and

c = BET constant (parameter theoretically related to the net molar enthalpy of the adsorption)

$$SSA = \left(\frac{n_m N_o}{M}\right)\alpha \quad (6)$$

Where: SSA = specific surface area of solid, m^2

n_m = monolayer specific amount of vapour adsorbed on the aggregate surface, mg

N_0 = Avogadro's number, 6.022×10^{23} mol^{-1}

M = molecular weight of the vapour, g/mol

α = projected or cross-sectional area of the vapour single molecule, m^2

In addition to estimating the specific surface as previously described, the sorption isotherms were also used to calculate the spreading pressure which is required to determine surface energy components of the aggregates. Adsorption of vapour molecules on the aggregate surface reduces its SFE, so spreading pressure, as a result of adsorption of the vapour molecules, can be expressed as:

$$\pi_e = \gamma_S - \gamma_{SV} \quad (7)$$

Where: π_e = spreading pressure at maximum saturated vapour pressure or equilibrium spreading pressure, mJ/m^2

γ_S = aggregate surface energy in vacuum

γ_{SV} = aggregate surface energy after exposure to vapour

Spreading pressure at maximum saturation vapour pressure, π_e, for each solvent is calculated by using the following Gibbs free energy model (Eq. 8):

$$\pi_e = \frac{RT}{A}\int_0^{Po}\frac{n}{P}dP \qquad (8)$$

Where: R = universal gas constant, 83.14 cm^3 bar/mol.K

T = absolute temperature, K

By introducing spreading pressure, π_e, in the Young-Dupré relation (Eq. 4), the following relationship is obtained:

$$W_{SL} = \pi_e + \gamma_{LV}(1+\cos\theta) \qquad (9)$$

The contact angle value for high energy solids such as aggregates is zero, therefore, Eq. 9 can be re-written as:

$$W_{SL} = \pi_e + 2\gamma_{LV} \qquad (10)$$

By substituting the above relation in Eq. 4, the following equation is obtained:

$$2\gamma_L + \pi_e = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^+\gamma_L^-} + 2\sqrt{\gamma_S^-\gamma_L^+} \qquad (11)$$

From Eq. 11, if the spreading pressures from three different probe vapours are measured, then the three surface energy components of the aggregates ($\gamma_S^{LW}, \gamma_S^+, \gamma_S^-$) can be determined by solving three simultaneous equations.

For the five aggregates, only fractions passing the 5 mm sieve and retained on the 2.36 mm sieve were tested and reported in this paper. The results were used to estimate specific surface area (SSA) and equilibrium pressure from which the surface energy parameters were calculated.

Specific surface area obtained for the five aggregates are presented in Table 3 using octane as the probe vapour. Specific surface area for the various aggregates showed large differences depending on aggregate type. The differences can be attributed to the different microstructure of the aggregates. The specific surface area obtained for each aggregate was used in two different ways: 1) to determine the equilibrium spreading pressure and 2) to calculate the moisture compatibility ratios.

Table 3. Surface energy characteristics of aggregates.

Aggregate	Surface energy components (mJ/m^2)				SSA (m^2/g)
	γ^{LW}	γ^+	γ^-	γ	
Limestone A	75.3	108.9	49.7	222.4	0.1708
Limestone B	66.3	2.9	4.9	73.8	0.7863
Granite A	69.1	17.3	568.3	267.4	0.3819
Granite B	68.3	16.4	40.8	120.0	0.3807
Granite C	68.0	163.9	122.7	351.6	0.4420

The SSA values were used to calculate the equilibrium spreading pressures on the aggregate surfaces for all three probes. Octane, being non-polar in nature, is supposed to give more accurate values of surface area (because non-polar substances do not have affinity for polar substances). The obtained spreading pressures were then used to compute the surface energy components ($\gamma_S^{LW}, \gamma_S^+, \gamma_S^-$) as well as the total surface energy (γ_S) for the aggregates as listed in Table 3.

The results show that surface energy properties vary considerably, in terms of surface energy components as well as total surface energy, amongst the different aggregates. The differences can be attributed to different elemental and mineralogical compositions of the aggregates. The test results indicate that there is not a significant difference between the van der Waals components of the aggregates (all approximately 70 mJ/m^2) but there are significant differences between the acid-base components of the limestone and granite aggregates. On the basis of total surface energy alone, and for the same bitumen, Granite C (γ = 351.6 mJ/m^2) should

theoretically form stronger adhesive bond than Limestone B (γ = 73.8 mJ/m^2). Note that this assertion assumes a completely dry aggregate.

2.3 Adhesion calculations

The surface energy properties of the bitumen and the aggregates on their own have very little significance. However, when combined thermodynamically, they are helpful for estimating the interfacial work of adhesion between the two materials, with or without the presence of moisture.

The main objective for measuring surface energy of bitumen and aggregates is to be able to estimate the moisture sensitivity of asphalt mixtures using the principles of thermodynamics and physical adhesion. This objective was accomplished by using the surface energy properties of the aggregate and bitumen to calculate their interfacial work of adhesion (dry bond strength) and the reduction in free energy of the system (work of debonding) when water displaces bitumen from the aggregate-bitumen interface (Eqs 12 and 13). For an asphalt mixture to be durable and less sensitive to moisture, it is desirable that the work of adhesion between the bitumen and the aggregate be as high as possible.

In addition to the two parameters: dry bond strength and work of debonding, a third parameter, the cohesion of bitumen, can be calculated from the surface energy properties of bitumen. These three bond energy parameters (bitumen cohesion, dry bond strength, and work of debonding) can then be used to assess the moisture sensitivity of an asphalt mixture. Bitumen cohesion is the cohesive bond strength of the material and is estimated as twice the total surface energy of the material. Dry bond strength (W_{BA}^{a}) is defined as given in Eq. 12 as the interfacial work of adhesion between the bitumen (B) and aggregate (A). A higher value of dry bond strength suggests greater adhesion between the two materials and hence more resistance against debonding.

$$W_{BA}^{a} = 2\sqrt{\gamma_B^{LW}\gamma_A^{LW}} + 2\sqrt{\gamma_B^{+}\gamma_A^{-}} + 2\sqrt{\gamma_B^{-}\gamma_A^{+}} \qquad (12)$$

Eq. 13 gives the work of debonding (W^a_{BWA}) which is considered as the reduction in bond strength of a bitumen-aggregate system when water (W) is introduced into the system or when water displaces the bitumen from the aggregate surface. This quantity might also be interpreted as the energy required for water to separate or break the bond of bitumen-aggregate systems.

In general, (W^a_{BWA}) is found to be a negative value for most aggregate-bitumen systems. This means that the process of water breaking or separating the existing adhesive aggregate-bitumen bond is a thermodynamically favourable process. In other words, no external work is required for this separation process to occur once water reaches the aggregate-bitumen interface. A smaller absolute value of this parameter for a given bitumen-aggregate system is indicative of a better moisture damage performance of that system.

$$W^a_{BWA} = \left\{\left(\left(\sqrt{\gamma^{LW}_A} - 4.67\right)^2\right) + \left(2\times\left(\sqrt{\gamma^{+}_A} - 5.05\right)\times\left(\sqrt{\gamma^{-}_A} - 5.05\right)\right)\right\}$$
$$+\left\{\left(\left(\sqrt{\gamma^{LW}_B} - 4.67\right)^2\right) + \left(2\times\left(\sqrt{\gamma^{+}_B} - 5.05\right)\times\left(\sqrt{\gamma^{-}_B} - 5.05\right)\right)\right\}$$
$$-\left\{\left(\left(\sqrt{\gamma^{LW}_B} - \sqrt{\gamma^{LW}_A}\right)^2\right) + \left(2\times\left(\sqrt{\gamma^{+}_B} - \sqrt{\gamma^{+}_A}\right)\times\left(\sqrt{\gamma^{-}_B} - \sqrt{\gamma^{-}_A}\right)\right)\right\} \quad (13)$$

Work of adhesion results for the various aggregate-bitumen combinations are presented in Table 4. The results show both the influence of the different aggregates and bitumen on work of adhesion.

Table 4. Work of adhesion between bitumen and aggregates.

Bitumen	Work of adhesion (mJ/m^2)				
	Limestone A	Limestone B	Granite A	Granite B	Granite C
10/20 pen	136	98	113	108	141
40/60 pen	128	95	105	104	131
70/100 pen	94	74	80	79	95
160/220 pen	104	88	93	92	102
AAS1	117	94	101	100	117

Work of debonding values for the aggregate-bitumen combinations are presented in Table 5.

490 Table 5. Work of debonding in the presence of water.

Bitumen	Work of debonding (mJ/m^2)				
	Limestone A	Limestone B	Granite A	Granite B	Granite C
10/20 pen	-47	56	-174	-32	-103
40/60 pen	-51	58	-177	-35	-109
70/100 pen	-67	55	-185	-52	-128
160/220 pen	-64	63	-177	-16	-126
AAS1	-57	62	-176	-13	-117

491

492 In addition to the work of adhesion, the greater the magnitude of work of debonding
493 when water displaces bitumen from the aggregate-bitumen interface (in terms of
494 absolute values of this quantity), the greater will be the thermodynamic potential that
495 drives moisture damage. Granite A and Granite C therefore have a far greater
496 potential for moisture damage compared to the limestone aggregates and Granite B. In
497 addition, the positive values for Limestone B indicate that external work or energy
498 would be required for water to be able to separate the existing adhesive bond between
499 the different binders and this aggregate. In other words, of all the aggregate-bitumen
500 combinations, those with Limestone B have the greatest potential resistance to
501 debonding caused by water.

502

503 The results also show that for a given aggregate, work of debonding (absolute values)
504 generally increases slightly (in magnitude) for softer bitumen compared to harder
505 (stiffer) binders. This is true for Limestone A and B as well as Granite C although the
506 results for Granite A are fairly consistent for all four penetration grade bitumens and
507 there is a considerable decrease in absolute value for the soft 160/220 pen bitumen for
508 Granite B.

509

510 ***2.4 Adhesion bond energy parameters***

511

512 The ratio (ER_1) between the adhesive bond energy values in the dry condition (W_{BA}^{a})
513 and in the presence of water (W_{BWA}^{a}) can be used to predict the moisture sensitivity of
514 asphalt mixtures. A higher value of energy ratio indicates better resistance to moisture
515 damage for that bitumen-aggregate combination. Bhasin et al. (2006) used energy
516 ratio ER_1 to study different types of asphalt mixtures and concluded that mixtures with
517 a ratio higher than 1.5 were more moisture resistant than the ones with ratios lower
518 than 0.8.

519 $$ER_1 = \left| \frac{W_{BA}^a}{W_{BWA}^a} \right| \quad (14)$$

520

521 Aggregates with higher surface roughness and greater surface area are supposed to
522 bond better with bitumen by providing more bond area and better interlocking. In
523 order to accommodate this effect, a second bond energy parameter (ER_1*SSA or ER_3)
524 obtained by multiplying the bond energy ratio (ER_1) with specific surface area (SSA)
525 has been proposed in addition to ER_1 to predict moisture sensitivity of asphalt
526 mixtures (Bhasin et al., 2006).

527

528 Wetting/coating of an aggregate with bitumen is not only affected by the surface
529 properties of the two materials; the viscosity or cohesion of the bitumen itself also
530 plays a very important role. Bitumen with lesser cohesion and greater affinity for the
531 aggregates will have a higher wettability and will coat the aggregate surface more
532 than bitumen having lesser wettability characteristics. However, softer bitumen
533 having lesser cohesion may be more prone to emulsification (decrease in cohesion) in
534 the presence of water. The effects of cohesion and wettability on moisture resistance
535 can be accounted for by modifying the ER_1 parameter by replacing the bond strength
536 in the dry condition (W_{BA}^a) with a wettability relationship ($W_{BA}^a - W_{BB}$). This new
537 moisture sensitivity assessment parameter (ER_2) is given in Eq. 15 (Bhasin, 2006). In
538 order to accommodate the effects of aggregate micro-texture on the bitumen-
539 aggregate bond strength in the presence of moisture, the bond parameter ER_2 can be
540 multiplied by specific surface area of the aggregates to obtain a fourth bond energy
541 parameter (ER_2*SSA or ER_4) (Bhasin, 2006).

542

543 $$ER_2 = \left| \frac{W_{BA}^a - W_{BB}}{W_{BWA}^a} \right| \quad (15)$$

544

545 Where (W_{BA}^a) and (W_{BB}) represent bitumen-aggregate dry bond strength and bitumen
546 cohesion respectively.

547

548 These four bitumen-aggregate bond energy parameters (ER_1, ER_2, ER_3 and ER_4) were
549 used to assess the moisture susceptibility of the asphalt mixtures. In all cases, higher

energy ratios are associated with mixtures with better moisture resistance. It is important to note that the energy ratios have been developed for aggregate-binder systems that demonstrate a negative value for the work of adhesion under 'wet' conditions (W^a_{BWA}) and are therefore are not applicable for the systems containing Limestone B which produced positive values of W^a_{BWA} as shown in Table 5.

Table 6 shows the aggregate-bitumen bond energy parameters (ER_1, ER_2, ER_3 and ER_4) for the asphalt mixtures (bitumen-aggregate combinations). Values have been included for the aggregate-bitumen combinations containing Limestone B although, as explained above, they do not represent the actual resistance of the mixture to moisture damage.

Table 6. Bond energy parameters for aggregate-bitumen combinations.

Bitumen	Limestone A	Limestone B	Granite A	Granite B	Granite C	Threshold criteria[a]
ER_1						
10/20 pen	2.90	1.74[b]	0.65	3.41	1.37	≥ 0.75
40/60 pen	2.52	1.64[b]	0.59	2.93	1.20	
70/100 pen	1.40	1.36[b]	0.43	1.54	0.74	
160/220 pen	1.63	1.40[b]	0.52	5.81	0.81	
AAS1	2.07	1.52[b]	0.57	7.86	1.00	
ER_2						
10/20 pen	1.56	0.62[b]	0.29	1.86	0.76	≥ 0.50
40/60 pen	1.32	0.59[b]	0.25	1.56	0.64	
70/100 pen	0.83	0.66[b]	0.23	0.94	0.44	
160/220 pen	0.74	0.51[b]	0.21	2.26	0.36	
AAS1	0.98	0.52[b]	0.22	3.00	0.47	
ER_3						
10/20 pen	0.49	1.37[b]	0.25	1.30	0.61	≥ 0.50
40/60 pen	0.43	1.29[b]	0.23	1.12	0.53	
70/100 pen	0.24	1.07[b]	0.17	0.59	0.33	
160/220 pen	0.28	1.10[b]	0.20	2.21	0.36	
AAS1	0.35	1.19[b]	0.22	2.99	0.44	
ER_4						
10/20 pen	0.27	0.49[b]	0.11	0.71	0.34	≥ 0.35
40/60 pen	0.22	0.46[b]	0.09	0.59	0.28	
70/100 pen	0.14	0.52[b]	0.09	0.36	0.20	
160/220 pen	0.13	0.40[b]	0.08	0.86	0.16	
AAS1	0.17	0.41[b]	0.08	1.14	0.21	

[a]after Little and Bhasin (2006)
[b]Computed but not applicable for moisture damage assessment

It is worth reiterating that the energy ratios used in this paper and presented in Table 6 are based on absolute values. These ratios therefore do not take into account differences in the thermodynamic processes associated with debonding caused by water which means that all four bond energy ratios treat all five aggregates the same. Clearly this is not the case with Limestone B showing a positive value for the work of debonding (W^a_{BWA}) compared to the negative values obtained for the other four aggregates. This implies that all combinations with this aggregate should have higher energy ratios than those reported in Table 6 in order to reflect the greater resistance to debonding in the presence of water. As this has not been done in the paper, it is important to consider the energy ratio results for Limestone B as conservative values.

The four bond energy parameters can be used to predict the moisture sensitivity of asphalt mixtures using threshold values defined to separate 'good' from 'poor' moisture damage performing aggregate-bitumen combinations. The threshold limits are 0.75 for ER_1, 0.50 for ER_2, 0.50 for ER_3 and 0.35 for ER_4 (Bhasin, 2006; Bhasin et al., 2006; Little and Bhasin, 2006). Once again, the criteria given by Bhasin to differentiate between 'good' and 'poor' performing mixtures were obtained using data in which all aggregate-binder combinations had negative values of work of adhesion in the presence of water and are therefore are not applicable for any of the combinations with Limestone B.

In general the limestone aggregate-bitumen combinations tend to have higher values compared to the granite aggregate-bitumen combinations although the values for Granite B, especially ER_1 and ER_2, are very high. The results show that the ranking of the 'good' versus 'poor' moisture damage performing aggregate-bitumen combinations for ER_1 and ER_2 are quite similar; both parameters placing the same number of combinations in 'good' versus 'poor' categories. The results for the other two parameters, ER_3 and ER_4, are also similar but the later placed more mixtures in the 'poor' category. The results suggest, for the materials considered, that ER_1 and ER_2 are sensitive to binder cohesion as the softer 70/100 pen bitumen showed lower ratios irrespective of the aggregate type. In addition, the use of an anti-stripping additive (binder AAS1) has not appeared to affect the bond energy ratios compared to

those found for the 40/60 pen base bitumen with the only exception being the values for Granite B which showed a significant increase.

Compared to the ER_1 and ER_2 parameters, the results for ER_3 and ER_4 show the significant influence of SSA on the selection of 'good' versus 'poor' moisture damage performing aggregate-bitumen combinations. Because of the apparent large influence of SSA on moisture sensitivity of asphalt mixtures shown in Table 6, the bond parameters ER_3 and ER_4 appear to be more suitable indices for determining the performance of the different aggregate-bitumen combinations with a clear distinction in terms of 'good' and 'poor' aggregates.

3. Aggregate-bitumen stripping

The same five aggregates (two limestones and three granites) and two of the binders (40/60 pen and 160/220 pen) were tested using the four aggregate-bitumen stripping tests. In addition, the anti-stripping modified binder AAS1 was also used with the five aggregates but only for two of the aggregate-bitumen stripping tests due to shortages in the supply of the amine-based anti-stripping agent. Based on field experience, the limestone aggregates tend to be more resistant to moisture damage than the granite aggregates. Therefore, it was expected that a discriminating laboratory test should be able to distinguish between the mixtures based on the selected aggregates.

In most of the existing test standards for evaluating moisture resistance of loose asphalt mixtures, the most commonly used aggregate sizes range from 6.3 mm to 9.5 mm. Therefore, for each of the five aggregate types selected for testing, only material passing the 9.6 mm sieve size but retained on the 6.3 mm sieve was used.

3.1 Static immersion test

The static immersion test was conducted in accordance with ASTM D1664 (AASHTO T182). During the test, a 100 g sample of aggregate with sizes ranging from 6.3 to 9.5 mm coated with 5.5 g of bitumen was immersed in distilled water at 25°C for 16 to 18 hours in a 500 ml glass bottle. The sample was then observed through the glass to estimate the percentage of total visible area of aggregate that remains coated as above or

below 95%. Three replicate 100 g aggregate samples coated with bitumen were tested and the average percentage coated estimated. Some of the disadvantages of the test are 1) the test is subjective and therefore has high variability and, 2) the test does not involve any strength tests that directly relate to mixture performance.

The results in terms of percentage of total visible area of aggregate that remains coated after 16 to 18 hours of soaking are presented in Figure 4. The results indicated that 100% of the aggregate remained coated at the end of the test for all the limestone aggregate mixtures. For the granite mixtures, the percentage coated area observed for each aggregate was above 95% with the exception of Granite C that showed about 90% coated area.

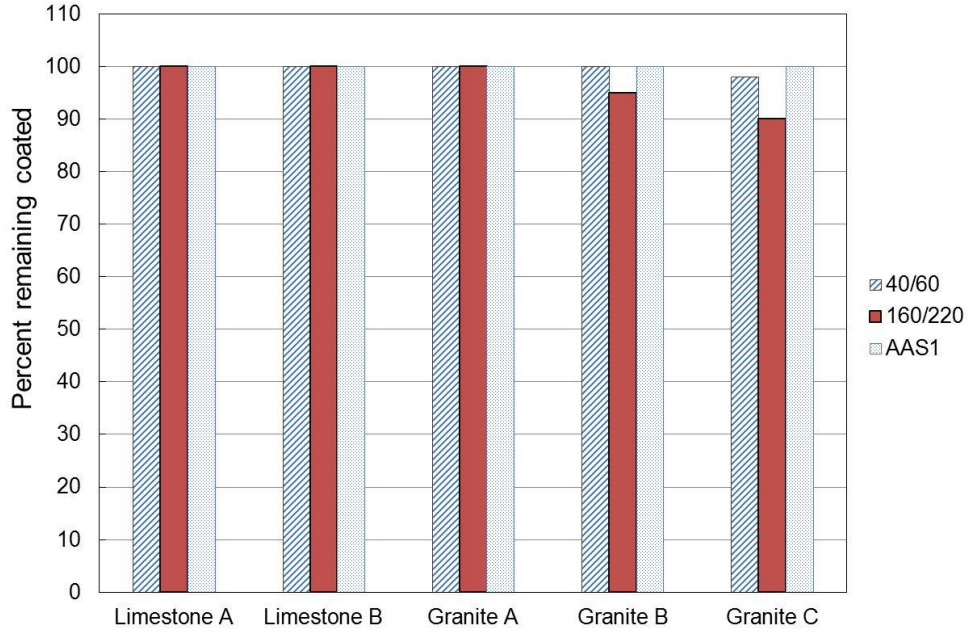

Figure 4. Percent aggregate coating after static immersion test

The results suggest that most of the aggregate/binder combinations showed similar bonding (greater than 95% of coated aggregates) properties after undergoing the static immersion test. The exception was the combinations of Granite C which showed a 10% striped aggregate result with the 160/220 pen bitumen. Granite B showed a 5% stripping value with the 160/220 pen bitumen. These results are in agreement with previous studies (Vuorinen and Hartikainen, 2001; Liu et al., 2014) that used similar aggregates. Results for the mixtures containing amine-based anti-stripping agents with retained binder greater

than 95% appear to be in agreement with previous research (Ahmad 2011). Even though the static immersion test ranked the Granite C - 60/200 pen combination as worst in terms of moisture sensitivity, the test appears not to be sensitive to the different aggregate types as it ranked the remaining aggregates with all the binders, except 160/220 pen, equally.

3.2 Rolling bottle test

The rolling bottle test (RBT) was conducted in accordance with BS EN 12697-11 (Bituminous mixtures - Test methods for hot mix asphalt part 11 - Determination of the affinity between aggregate and bitumen). The RBT is a subjective test in that affinity is expressed by visual estimation of the degree of bitumen coverage on uncompacted bitumen-coated mineral aggregate particles after the influence of mechanical stirring action in the presence of water. To perform the test, dust-free aggregate samples weighing 170 g were dried in an oven at 105±5°C overnight to constant mass and then coated with 5.7 g of molten binder. Mixing of the aggregates with binder was conducted at 120±5°C. The aggregate-binder mixture was then cooled loose at room temperature. The loose mixture was stored at ambient temperature for 12 to 64 hours before testing. Each of the test bottles were filled to about half their volume with deionized water and about 150 g of the loose aggregate-mixture was placed in each bottle. The whole assembly was put in the bottle roller rotating at a speed of 60 rotations per minute for six hours. At the end of the six-hour period, the aggregate particles were emptied from the test bottle into a test bowl which was then filled with fresh, de-ionized water to a level just above the top of the surface of the particles. Subsequently, the test bowl was placed on a white surface. The purpose of adding fresh water was to allow for optimal visual determination of binder coverage on the aggregate particles. At least three replicates of each sample were tested.

At the end of the test, the degree of bitumen coverage of the aggregate particles was estimated by visual observation and recorded to the nearest 5%. The degree of bitumen coverage was defined as the average proportion of the surface area of the aggregate particles covered with bitumen, expressed as a percentage (equal to 100 minus the percentage of stripping). The procedure (i.e. rotation in the bottle roller and measuring of bitumen coverage) was repeated for three more cycles (24 hours, 48 hours, and 72 hours) with fresh water replacing the fouled water in the test bottle at the end of each cycle and

the degree of bitumen coverage being measured. For each rolling time (6, 24, 48, and 72 hours), the mean value for each repeat was calculated to the nearest 5% and the results averaged to obtain the average degree of bitumen coverage for a given mixture.

Mixtures containing the unmodified binders showed higher binder loss than the modified binder containing anti-stripping agent. Binder losses in the mixtures containing the 160/220 pen binder were highest for each aggregate type tested (Figure 5). Binder losses in the 40/60 pen mixtures were just slightly less than 160/220 pen binder although both were higher than the mixtures containing anti-striping agent for all of the aggregates considered.

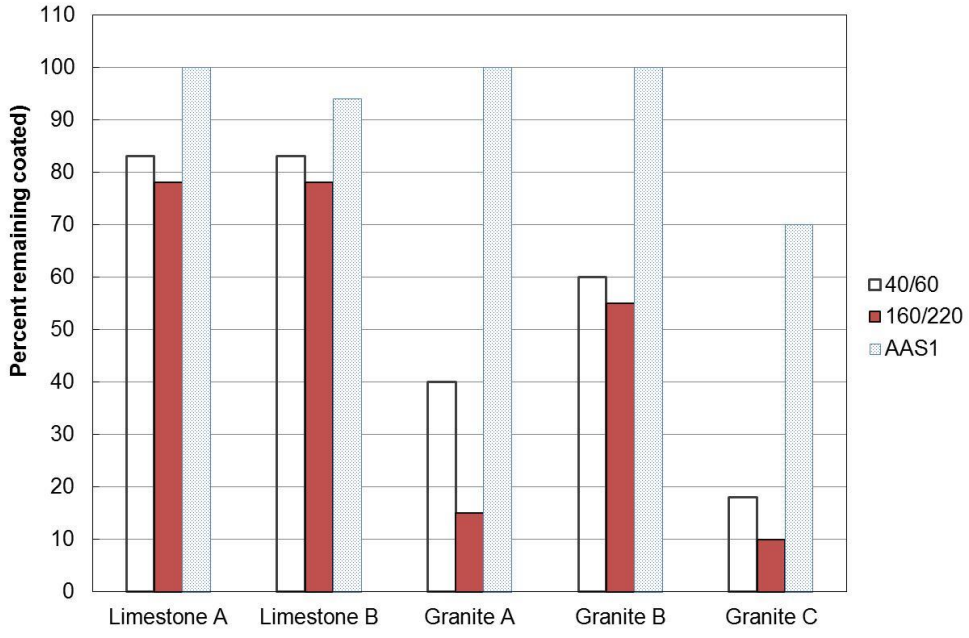

Figure 5. Percent aggregate coating after 72 hours of RBT

The results show that the rolling bottle test is sensitive to changes in aggregate and binder property including binder modification. Compared to the static immersion test, the rolling bottle appears more discriminatory as it was able to show small differences in moisture susceptibility in the good performing limestone aggregates. For example, ranking in this case was (in increasing order of resistance) 160/220 pen, 40/60 pen and amine-based anti-stripping agent, which was to be expected.

Compared to the static immersion test, the sensitivity of the rolling bottle test was higher. Figure 6 shows the binder loss versus conditioning time obtained for mixtures containing 40/60 pen binder that illustrates the sensitivity of the rolling bottle test to different aggregate types. The limestone aggregates (Limestone A and B) perform better than the granite aggregates (Granite A, B and C). The results showing Granite C as the worst performing aggregate again are as expected based on field performance.

From the curves in Figure 6, it could be seen that the percentages of bitumen coverage decreased slowly with testing time for limestone, while on the contrary, percentages for granite reduce sharply during the test period. For instance, during the first six hours, Limestone B showed only a 2% binder loss while Granite C showed about 20% loss. In addition, the percentage of binder loss for Granite C at 6 hours is equal to that for the limestone aggregates at 72 hours. Among the granite aggregates, Granite B showed the best bonding properties as illustrated by the 10%, 15%, 30%, 40% of binder loss for 6, 24, 48 and 72 hours, respectively. Although the total loss of binder for Granite A was more than Granite B, these two aggregate had almost the same percentage of binder loss after the first 24 hours. Similar results were obtained for the softer 160/220 pen binder.

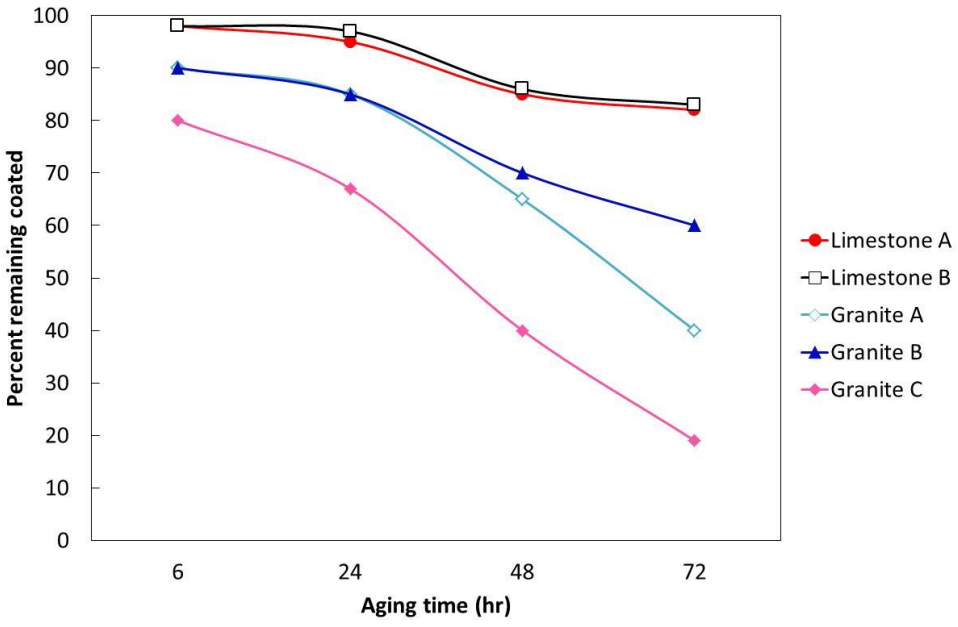

Figure 6. Kinetics of bitumen coverage of aggregates during RBT

3.3 Boiling Water Test

The boiling water test was performed in accordance with ASTM D3625 - 96(2005) (Standard Practice for Effect of Water on Bituminous-Coated Aggregate Using Boiling Water). Compared with the static immersion and rolling bottle tests, the boiling water test is a quicker approach to evaluate the moisture sensitivity of the bitumen and aggregate combination since it only takes about 60 minutes to condition the sample compared with more than 72 hours for the rolling bottle test or 16 to 18 hours in the case of the static immersion test. Like the static immersion test, the boiling water test cannot be used as a measure of field performance because such correlations have not been established. At least three replicates of each sample were tested.

To perform the test, 600 g of clean oven-dried aggregates were fully coated with 30 g of molten binder. About 300 g each of the aggregate-bitumen mixture was submerged under boiling water in a glass beaker and the mixture boiled for 10 minutes. The percentage of the total visible area of the aggregate that retained its original coating of bitumen was used as an estimate of moisture damage. Only two binders (40/60 pen and 160/220 pen) were evaluated using the boiling water test.

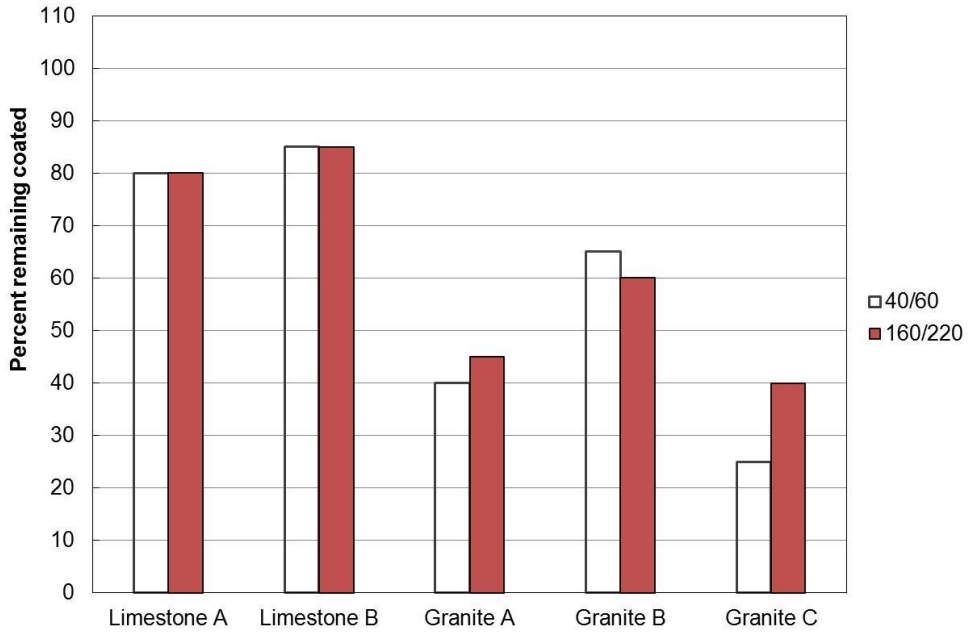

Figure 7. BWT results for different aggregate-bitumen systems

The results are shown in Figure 7 where Granite C again exhibited the worst bonding properties. Considering the limestone aggregates, the performance of Limestone A and B was similar for both 40/60 pen and 160/220 pen binder. In terms of the granite aggregates, the 160/220 pen binder showed better bond performance than the 40/60 pen binder except for Granite A.

3.4 Total Water Immersion Test

The total water immersion test (TWIT) was performed in the laboratory to compare the performance of bitumen doped with an adhesion agent against the non-doped bitumen. This is necessary to check each aggregate with non-doped and doped bitumen to assess the effectiveness of the additive or whether the aggregate needs additive in the binder to provide proper adhesion. Three replicates of each sample were tested.

The test assesses the average percentage of binder coverage after immersion in 40℃ water after 3 hours of soaking. The test is an improvement on the static immersion test. It uses water at 40℃ rather than room temperature (25℃) used in the static immersion test to provide a better result. Again only two binders (40/60 pen and 160/220 pen) were evaluated using the total water immersion test.

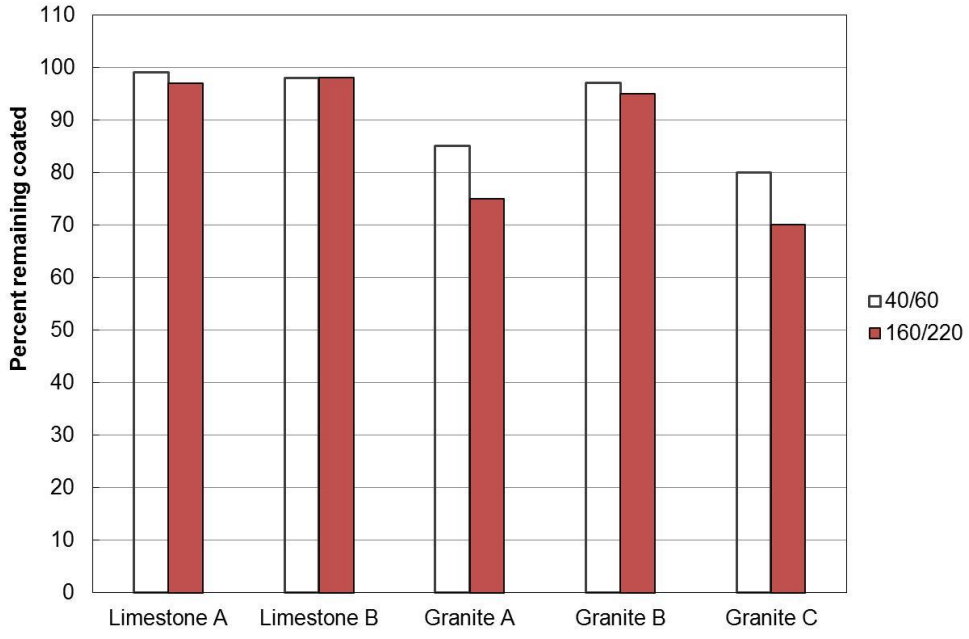

Figure 8. TWIT results for different aggregate-bitumen systems

Figure 8 shows the average percentage of binder coverage after immersion in 40℃ water for 3 hours obtained during the total water immersion test. From Figure 8, it can be seen that the limestone aggregates had very little binder loss compared with the granite aggregates. The percentages of binder loss for limestone were all less than 5% for the two binder types. The results for the granite aggregates showed higher percentages of binder loss. As in the previous stripping tests, Granite C showed the worst performance with 20% and 30% binder loss, for 40/60 pen and 160/220 pen, respectively.

4. Asphalt mixture moisture conditioning using the SATS procedure

SATS is the first procedure of its kind that combines both ageing and water damage mechanisms (subjected to asphalt pavements in service) within a single laboratory test protocol. The procedure has been found to successfully reproduce the moisture damage observed in asphalt materials in the field (Collop et al. 2004a) as well as distinguish between poor performing material and alternative asphalt mixtures incorporating aggregate with good durability track records (Choi et al, 2002, Airey et al. 2003, Collop et al. 2004b and Choi, 2005). The results obtained from the SATS moisture conditioning procedure tend to rank asphalt mixtures in terms of moisture sensitivity in the same order as the AASHTO T283 procedure (Anon, 2000), although the relative performance of a mixture containing a moisture sensitive aggregate is usually significantly lower in the SATS test (Airey et al., 2005).

The standard SATS procedure involves conditioning five pre-saturated specimens simultaneously in a pressure vessel under 0.5 MPa air pressure at a temperature of 85ºC for a period of 24 hours. This conditioning is followed by a cooling period of 24 hours before the air pressure is released and the vessel opened to remove the specimens for stiffness testing (Grenfell et al., 2012). The pressure vessel used can hold five nominally identical specimens (100 mm in diameter and 60 mm in thickness) in a custom-made specimen tray. The dimensions and specifications of the SATS testing equipment, including the size and spacing of the holes in the perforated trays are detailed in Clause 953 of Volume 1 of the UK Manual of Contract Documents for Highway Works, 2004 (MCHW, 2004). The conditions used with the SATS procedure were selected in order to reproduce in the laboratory, the field observed moisture damage as demonstrated by a decrease in stiffness modulus for

particular asphalt mixtures as detailed by Airey *et al*. (2005). The key features of the conditioning procedure can be summarised as follows:

- A well-insulated, heated pressure vessel capable of holding five compacted asphalt specimens (100 mm diameter × 60 mm height).
- Conditioning set-up allowing simultaneous pressure and temperature control.
- Asphalt specimens, which have been pre-saturated with water (under vacuum), located on a purpose-built tray.
- A pre-determined quantity of water placed in the vessel so that the bottom specimen is fully immersed during the conditioning procedure.
- Simultaneous conditioning of five specimens under 0.5 MPa air pressure at a temperature of 85°C for 24 hours, followed by a cooling-down period of 24 hours before the pressure is released and the vessel opened to remove the specimens for stiffness testing.

The ten steps of the SATS conditioning and test procedure as specified in Clause 953 are as follows:

1. The unconditioned (initial) indirect tensile stiffness modulus of each asphalt mixture specimen is determined at 20°C using the Nottingham Asphalt Tester (NAT) (Cooper and Brown, 1989) in accordance with BS EN 12697-26 Annex C (124msec rise time, 5µm peak transient horizontal diametral deformation) (BSI 2004a).
2. The dry mass of each specimen is determined by weighing.
3. The specimens are subsequently immersed in distilled water at 20°C and saturated using a residual pressure of 35 kPa (i.e. 65 kPa below atmospheric pressure) for 30 minutes.
4. The wet mass of each specimen is determined by weighing, and the percentage saturation of each specimen calculated, referred to as ‘initial saturation’.
5. The SATS pressure vessel is partly filled with a pre-determined amount of distilled water (final water level between the bottom, submerged specimen and the above ‘dry’ (pre-saturated specimen)). The pressure vessel and water are

maintained at the target temperature of 85°C for at least 2 hours prior to introducing the specimens.

6. The saturated asphalt specimens are then placed into the pressure vessel, the vessel is sealed and the air pressure is gradually raised to 0.5 MPa.
7. The specimens are maintained at the testing conditions, i.e. 0.5 MPa and 85°C for 24 hours.
8. After 24 hours, the target vessel temperature is reduced to 30°C and the vessel is left for 24 hours to cool. When the pressure vessel display temperature has reduced to 30°C (after the 24 hour cooling period) the air pressure is gradually released. When the vessel has achieved atmospheric pressure, it is opened and the specimens removed. Each specimen is then surface dried and weighed in air. The percentage saturation calculated at this stage is referred to as the 'retained saturation' (BSI 2003a, BSI 2004b, BSI 2009).
9. The specimens are finally brought back to 20°C and the conditioned (final) stiffness modulus determined using a NAT.
10. The ratio of the final stiffness modulus / initial stiffness modulus can thus be calculated, and is referred to as the 'retained stiffness modulus'.

During the test there is a continuous cycling of moisture within the pressure vessel, which causes condensation on the underside of the top lid and 'dripping' onto the top specimen. There is then a cascading effect where progressively smaller amounts of water 'drip' onto the specimens below, resulting in a decrease in retained saturation level for specimens that are located lower down inside the pressure vessel.

Ten combinations of the five aggregates (two limestones and three granites) and two bitumens (10/20 and 40/60 penetration grades) were included in the study. A standard continuously graded 0/32 mm (28 mm) dense bitumen macadam (DBM) base material was used with the five aggregate types. A target binder content of 4% by total mixture mass was selected for all the asphalt mixtures and roller compacted slabs (305 mm x 305 mm x 100 mm) were manufactured and finally cored and trimmed to produce 100 mm diameter by 60 mm high specimens with a target air voids content of between 8 and 10% (typical of field cores). Only cores that achieved this target were selected for the SATS test.

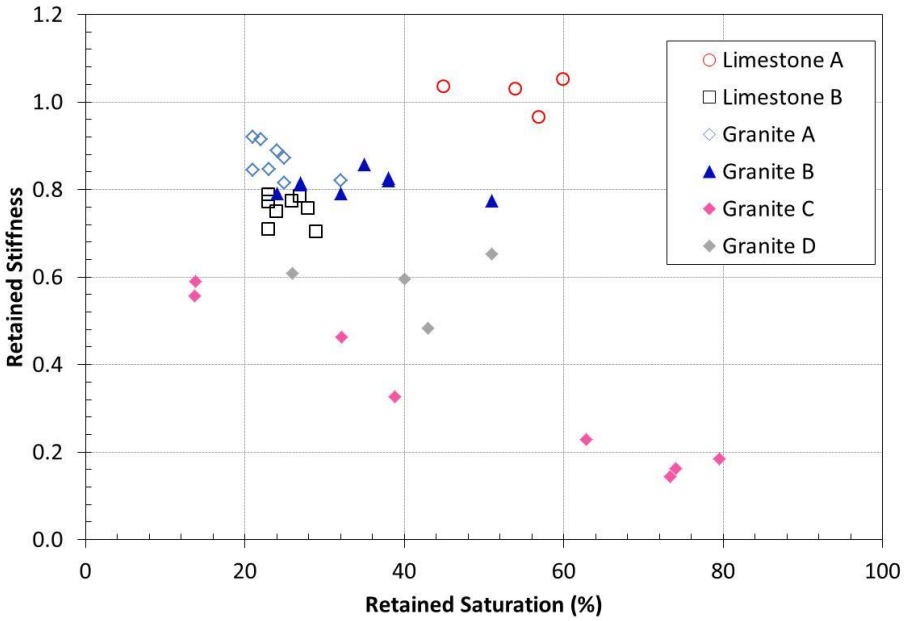

Figure 9. SATS results for asphalt mixtures with 10/20 pen bitumen

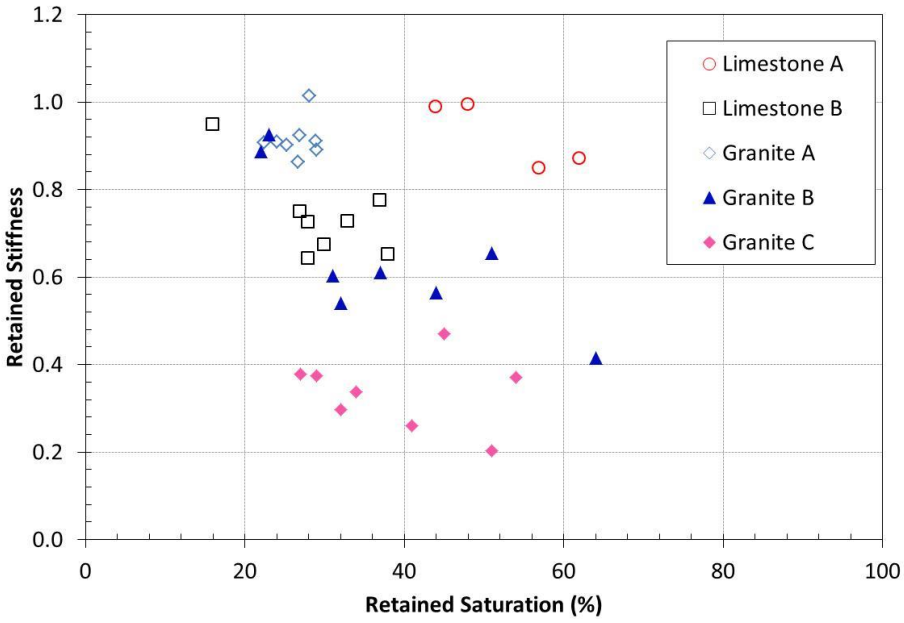

Figure 10. SATS results for asphalt mixtures with 40/60 pen bitumen

Results from the SATS tests using the 10/20 and 40/60 pen bitumen can be seen in Figures 9 and 10. Both sets of results demonstrate the high moisture resistance of the mixtures made with limestone aggregate. It can be seen that the retained stiffness for the limestone mixtures is in excess of 0.6, whereas the results for Granite C mixtures are generally in the range between 0.2 and 0.5. The results for Granite A and B mixtures for asphalt mixtures using both the 10/20 and 40/60 pen bitumen tend to be

superior to those seen for Granite C. The results for the 10/20 pen bitumen (Figure 9) even show the performance for Granite A and B to be comparable to those of the two limestone mixtures although the saturation levels for the Granite A mixtures are relatively low. Granite A also has a similar performance to the two limestone aggregates for the softer 40/60 pen bitumen asphalt mixtures in Figure 10, although once again the saturation levels are considerably lower than those experienced for the other four mixtures.

5. Relation between intrinsic adhesion, stripping and moisture damage

As previously indicated, the key objective of this study was to determine if the moisture sensitivity assessment parameters for different bitumen-aggregate combinations obtained by using surface energy parameters of the individual materials can identify 'good' and 'poor' performing asphalt mixtures and to determine how the surface energy-based prediction compare with two standard types of test, for example the RBT (stripping) and SATS (asphalt mixture) procedures. Previous studies have shown that both the BWT and TWIT empirical tests have poor correlation with surface energy parameters and SATS results due to the insufficient sensitivity of these two aggregate-bitumen stripping tests (Liu et al., 2014).

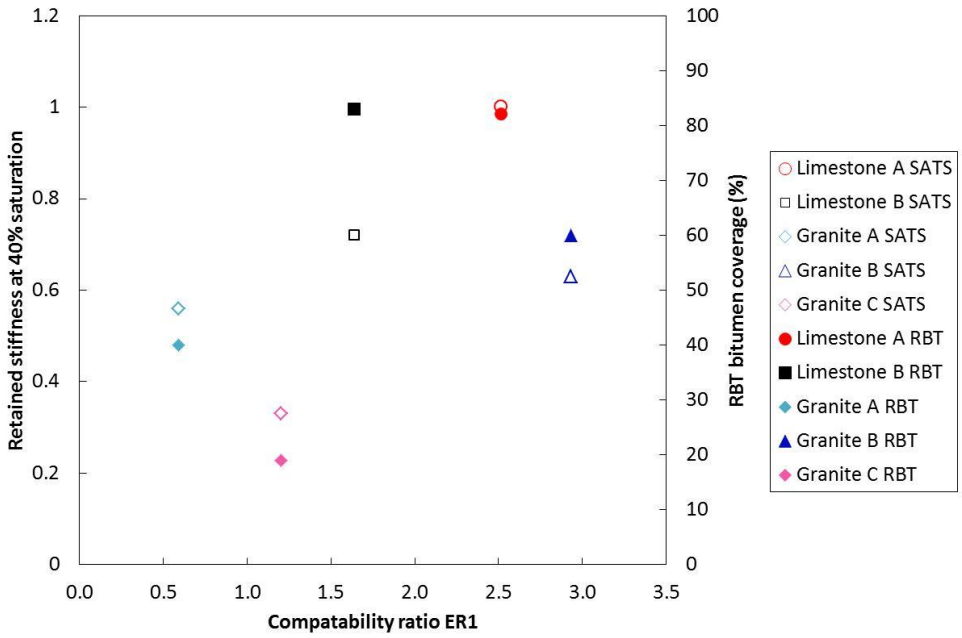

Figure 11. Relationship between SATS, RBT and ER_1

Figures 11 to 14 show plots depicting the relationships between SATS retained stiffness (at 40% moisture saturation), the RBT percent bitumen coverage (after 72 hours) and the four bond energy parameters (ER_1, ER_2, ER_3 and ER_4) for all mixtures produced with the 40/60 pen bitumen. It is worth reiterating that the energy ratios used in Figures 11 to 14 for Limestone B (black squares) are conservative values and are expected to be higher (located further to the right in the graphs) as discussed in Section 2.4. The SATS results at 40% moisture saturation have been determined by fitting a linear regression line to the data in Figure 10 and calculating the resulting retained stiffness at 40% moisture saturation (Grenfell et al., 2012).

In all cases a higher value of the parameter suggests better resistance to moisture damage. On this basis, aggregate-bitumen combinations plotting near the upper right hand side of the plot (equivalent to higher values of energy ratio, RBT coverage and/or SATS retained stiffness) are expected to be more moisture resistant than mixtures plotting in the lower left hand side. The results show in general that for all four plots the limestone mixtures tend to perform better than the granite mixtures with results in the upper right hand quadrant. The order of the two limestones does however change once the SSA of the two aggregates is included in the energy ratio (ER_3 and ER_4 in Figures 13 and 14) compared to ER_1 and ER_2 in Figures 11 and 12.

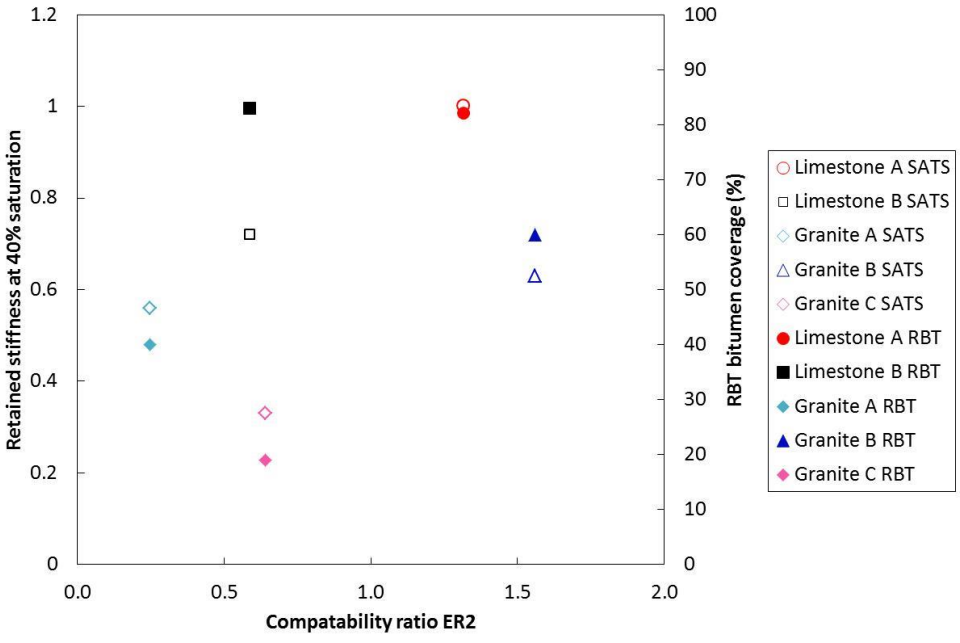

Figure 12. Relationship between SATS, RBT and ER_2

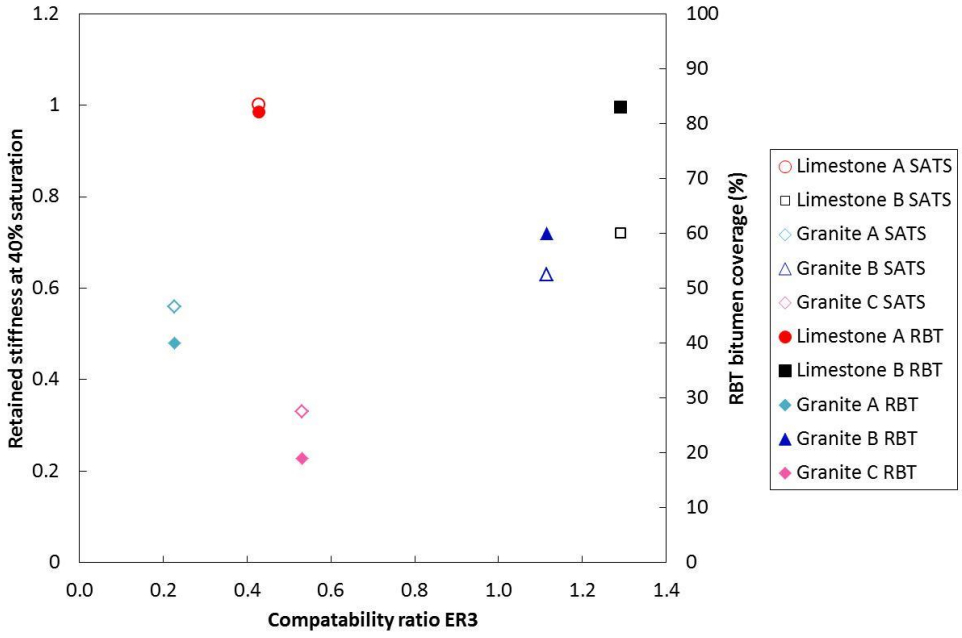

Figure 13. Relationship between SATS, RBT and ER_3

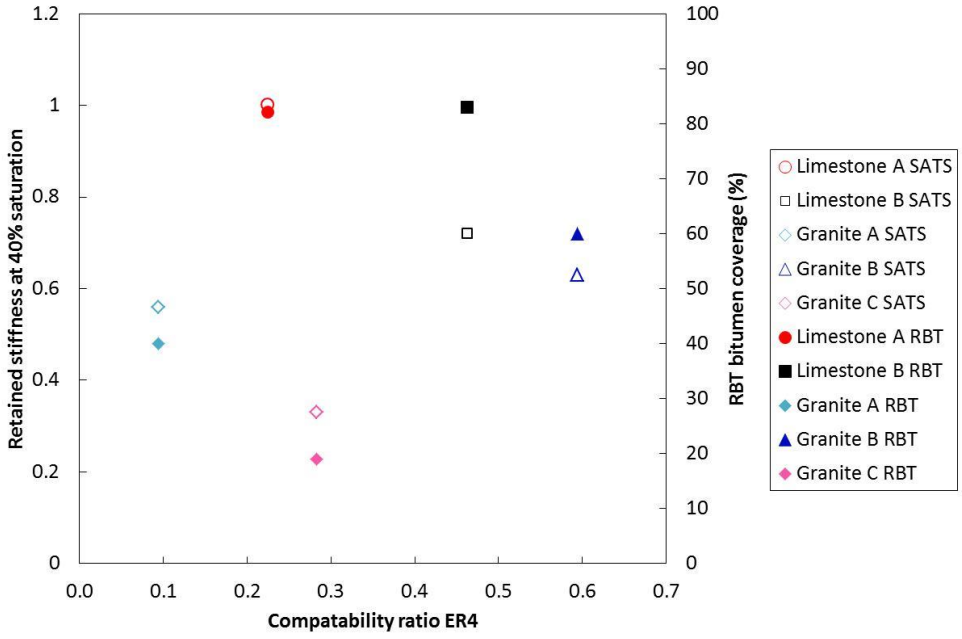

Figure 14. Relationship between SATS, RBT and ER_4

In terms of the three granite aggregates, there is a far degree of scatter with Granite A tending to have the lowest values (low predicted moisture performance) based on intrinsic adhesion and energy ratios but intermediate actual performance in terms of RBT and SATS). The results for Granite B tend to sit in the upper right hand quadrant

and demonstrate comparable moisture damage performance to that seen for the two limestone aggregate mixtures. However, the results for Granite C tend to consistently fall in the lower left hand quadrant.

The 'good' performance of most of the limestone mixtures observed in this study can be attributed to their physico-chemical and mineralogical characteristics, while the range of performance found for the granite aggregates reflects the mineralogical complexity of these aggregate types.

6. Conclusions

This paper presents results from stripping tests, such as the RBT, and asphalt mixture moisture conditioning procedures, such as SATS, in an attempt to better understand the underlying processes and mechanisms of moisture damage with the help of surface energy measurements on the constituent materials (bitumen and aggregates) and aggregate mineralogy from MLA measurements. The following conclusions were reached based on the results presented in the paper.

- Surface energy parameters obtained from the DCA testing suggests cohesive strength varies with bitumen grade. Surface energy of the soft bitumen (70/100 pen) was approximately 60% that of the stiffer bitumens (10/20 and 40/60 pen).
- The adhesive bond strengths for both the dry and the wet conditions were used to compute four compatibility ratios using the surface energy parameters obtained for the bitumen and aggregates. Higher magnitudes of the ratios suggest better resistance to moisture damage. The results show that for a given aggregate, moisture resistance of stiffer binders is higher than softer binders. The results also show that for a given bitumen grade, and for the aggregates considered in this study, the limestone aggregate mixtures should exhibit higher resistance (higher ratios) to moisture damage.
- The four aggregate-bitumen bond energy parameters (ER_1, ER_2, ER_3 and ER_4) can be used to predict moisture sensitivity of asphalt mixtures using threshold values (0.75 for ER_1, 0.50 for ER_2, 0.50 for ER_3 and 0.35 for ER_4) defined to separate 'good' from 'poor' moisture damage performing aggregate-bitumen

combinations. Most of the aggregates that were identified as 'poor' aggregates in this study have also been found to perform poorly in previous studies. In general Limestone A and B can be defined as 'good' while Granite C can be defined as 'poor'. The remaining two granite aggregates (Granite A and B) can be considered to have intermediate moisture damage performance.

- The bond energy parameters (ER_1, ER_2, ER_3 and ER_4) have been developed for aggregate-binder systems that demonstrate a negative value for the work of adhesion under 'wet' conditions (W^a_{BWA}) and are therefore are not applicable for the systems containing Limestone B which produced positive values of W^a_{BWA}. It is therefore important to consider the energy ratio results for Limestone B as conservative values.
- Compared to the ER_1 and ER_2 parameters, the results for ER_3 and ER_4 showed the significant influence of SSA on the selection of 'good' versus 'poor' moisture damage performing aggregate-bitumen combinations. Because of the apparent large influence of SSA on moisture sensitivity of asphalt mixtures shown in this study, the bond parameters ER_3 and ER_4 appear to be more suitable indices for determining the performance of the different aggregate-bitumen combinations with a clear distinction in terms of 'good' and 'poor' aggregates.
- Results from the RBT showed that the percentage of bitumen coverage (a measure of adhesiveness) varies depending on aggregate type. About 90% of the limestone aggregates remained coated with bitumen at the end of the rolling bottle test compared with only 20% for one of the granite aggregate. This suggests that in the presence of moisture, limestone aggregates will generally tend to maintain a better adhesive bond with bitumen than granite aggregates although this will depend on the specific mineralogy of the granite.
- Moisture damage factors (moisture factors) obtained from the SATS tests for limestone aggregate asphalt mixtures were comparatively higher than that for certain granite mixtures. Higher moisture factors indicate better moisture resistance.
- Mineralogical testing of the aggregates, using MLA, showed considerable differences not only between limestone and granite but also between different granites. Differences in moisture sensitivity of the mixtures observed in this

study for the different aggregates can be attributed in part to aggregate mineralogy.

- It is concluded that moisture resistance of asphalt mixtures are influenced by the mineralogical composition of the aggregates as well as the adhesive bond between the aggregate and bitumen in the presence of moisture. Both the RBT and SATS are useful in evaluating moisture damage in asphalt mixtures as the ranking obtained in these empirical tests are similar to surface energy and mineralogical characteristics of the asphalt mixtures.
- The surface energy testing protocols and adhesive bond strength calculations can be used to compliment available asphalt mixture design methods by identifying compatible bitumen-aggregate combinations. Surface energy properties of the materials combined with the parameters obtained by conventional moisture sensitivity assessment techniques can also contribute towards the development of a material screening protocol. This protocol can then be used for determining the best combinations of bitumen and aggregates for the local road material providing better bitumen-aggregate adhesion and less susceptibility to moisture damage/stripping.

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