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Intrinsic adhesive and cohesive assessment of the moisture sensitivity of bio-rejuvenated recycled asphalt binders

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Abstract: Alternative binders not derived from fossil fuels, known as biobinders, are opening new paths for multiple applications in road infrastructure. Biobinders, usually produced from bio-oils obtained from the processing of biomass and industry by-products, are tuneable materials whose properties can be adjusted to meet specific targets. For this reason, an interesting approach is to couple biobinders with Reclaimed Asphalt (RA) by taking advantage of their rejuvenating properties to design bio-asphalt mixtures with high-content RA and no additional virgin bitumen. Recent research has proven the feasibility of this approach through validation at full-scale (BioRePavation project). However certain aspects related to the durability of bio-asphalt mixtures still require further research, one of these being their resistance to moisture damage. This study aims at filling some of these current gaps by conducting an initial investigation of the moisture sensitivity of selected biobinders and bio-rejuvenated asphalt binders. In order to do this, the intrinsic adhesion and cohesion properties of an extracted RA binder, two biobinders, their blends and two types of aggregates were characterised by means of Surface Free Energy (SFE), individually and as a system. The binders/blends-aggregate systems were further tested by means of the Pneumatic Adhesion Tensile Test Instrument (PATTI) to determine their pull-off tensile strength (POTS). The results show that the bio-rejuvenated asphalt binders present equivalent cohesive and adhesive properties to a conventional bitumen and superior performance when compared to the RA binder. Hence, the combination of biobinders and RA has great potential to guarantee resistance to moisture damage of bio-recycled asphalt mixtures with high-content RA and no additional bitumen.

Keywords: biobinder; recycling; asphalt mixture; cohesion; adhesion; moisture damage

1. INTRODUCTION

One of the main environmental concerns associated with the construction and maintenance of flexible pavements is the high demand of non-renewable materials. Most of the pavements around the world are made of asphalt mixtures, whose main components are aggregates and bitumen. On the one hand, aggregates are finite resources whose availability in some countries is already low. On the other hand, bitumen is a petroleum-based binder whose quality, and probably also quantity, is predicted to change in the near future (Lavoie, 2011). Researchers are therefore encouraged to find alternative materials to replace these raw materials (aggregates and bitumen) for the manufacturing of new asphalt mixtures.

To date, the replacement of aggregates with different percentages of Reclaimed Asphalt (RA) has been proven to be a suitable option showing good mechanical performance while saving natural resources (Zaumanis, Mallick & Frank, 2014; Al-Qadi, Elseifi & Carpenter, 2007). In the case of bitumen, the most interesting alternatives from an environmental point of view are renewable materials, by-products or wastes from other industries, commonly known as biobinders. Many different sources are being investigated in this regard such as microalgae, swine manure, waste cooking oil, vegetable oils, etc. (Sun et al., 2017; Chailleux et al., 2012; Fini et al., 2012; Peralta et al., 2012). Biobinders can substitute bitumen in asphalt mixtures in different percentages as modifiers (<20%), extenders (20-75%) or full replacement (100%) (Airey, Mohammed, & Fichter, 2008). Combining the use of RA and biobinders can be seen as an attractive technique for several reasons. Firstly, it helps in reducing the consumption of virgin aggregates and bitumen, pollution from wastes and greenhouse gases emissions. These advantages are optimised if the percentage of RA and bitumen replacement with biobinders in the asphalt mixture are maximised. Secondly, the aged binder in RA may need rejuvenation if the percentage of RA is targeted to be high to avoid early failures, and biobinders have the potential to produce such rejuvenation effect (Zhang et al., 2018; Zhu et al., 2017; Gong et al., 2016; Zaumanis et al., 2014). In this regard, biobinders, in the form of bio-oils, have been extensively used as modifiers (<20% replacement) forconventional bitumen which is added as virgin binder in asphalt mixtures containing RA, but fewer studies have looked at increasing the bitumen replacement rate (Mamat et al., 2015).

Currently, the main concern towards the implementation of asphalt mixtures using high RA and biobinder percentages is the uncertainty in their overall durability (Mamat et al., 2015; Peralta et al., 2012) due to the fact that non-conventional materials are used, i.e. RA and biobinders. Moisture sensitivity is one of the major components in such durability. In fact, the moisture sensitivity of mixtures containing high RA percentages has been studied and generally, as the RA aggregates are already covered with aged binder, their moisture sensitivity is not expected to be worse than conventional mixtures. Different authors (Ghabchi, Singh & Hossain, 2016; Ghabchi, Singh & Zaman, 2014; Al-Qadi et al. 2012; Mogawer et al., 2012; Tran, Taylor & Willis, 2012; Karlsson & Isacsson, 2006) have shown that the moisture damage resistance can increase with increasing RA percentages or that RA does not increase the potential for this type of failure. However, previous stripping problems of the old pavement material or low blending between the fresh binder and old binder in the new mixture can have an important effect and this must be characterised (Zaumanis & Mallick, 2015).

On the other hand, the influence of adding high contents of biobinders on the moisture damage resistance of conventional (not containing RA) mixtures has also been investigated. Wen et al. (2013) showed that mixtures with up to 60% replacement of bitumen with biobinder produced from waste cooking oil passed the requirements for moisture damage resistance, although no general trend was found. Mohammad et al. (2013) used biobinders to replace 20%, 25.5% and 50% of bitumen from pine wood chips processed by fast pyrolosis. They found that the moisture resistance of the asphalt mixtures was not adversely affected by the addition of the biobinder up to 30%, and that at 50% it could be improved by incorporating an anti-stripping agent.

Nevertheless, very few studies exist in the literature regarding the characterisation of this phenomenon for the combination of RA and biobinders in asphalt mixtures, and those found are related to low percentages of biobinders addition in the mixture. Zaumanis et al. (2014) studied the moisture sensitivity of bio-rejuvenators in recycled mixtures with a dosage of 12% over binder mass showing that they decreased the moisture damage resistance of the RA mixture, although most of these mixtures still met the standard moisture damage requirement. In the same way, Gong et al. (2016) used up to 3% over binder mass of bio-oil from the pre-treatment of biodiesel residue from waste cooking oil to modify an aged binder and showed that the aged binder's sensitivity to moisture increased apparently due to the dissolution of hydrophilic groups from the bio-oil.

These results are therefore controversial, since high RA contents do not seem to adversely affect the moisture damage of asphalt mixtures but high contents of biobinders could do. There is therefore a lack of knowledge on the moisture sensitivity of mixtures with high RA and biobinders content, which needs investigation to stimulate the implementation of these environmentally friendly techniques. In this regard, a first step to characterise moisture sensitivity of materials is to study their cohesive and adhesive properties, since moisture damage is associated with water inducing a loss of the adhesive bonding between aggregates and binder and/or a loss of cohesive strength of the binder.

In this investigation, the intrinsic cohesion and adhesion properties of bio-rejuvenated recycled asphalt binders were analysed through surface free energy (SFE) tests with the determination of thermodynamic quantities and energy ratios for binders and aggregates. This approach was used as a preliminary assessment since previous investigations have shown strong correlation between these thermodynamic quantities and energy ratios and moisture sensitivity of asphalt mixtures (Ghabchi, Singh & Hossain

2016; Ghabchi, Singh & Zaman 2014; Liu et al. 2014). The bio-recycled binders were manufactured using a long-term aged RA binder source and two biobinders produced from by-products of the paper industry to fully replace the fresh bitumen that would usually be added. Next, the binder bond strength of binder-aggregate systems was determined in the dry condition to mechanically determine the cohesion properties and relate these to SFE. In this way, this paper aims at characterising the intrinsic adhesion and cohesion of bio-rejuvenated recycled asphalt binders as an initial point towards understanding the moisture sensitivity of bio-recycled asphalt mixtures.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1. Binders and blends

RA binder was recovered from a RA source in France according to EN 12697-4:2005 Fractionating Column by distillation. The two bio-materials were considered as binders, namely: BioBinder (BB) and Biophalt® (BP). BB is a binder produced from the blend of a pentaerythritol rosin ester (80% in mass) and linseed oil (20% in mass). The rosin is light-coloured, deodorised and used in various adhesive and road marking Hot Melt formulations. Biophalt® is a vegetal binder manufactured from by-products of the paper industry and distillation of crude tall oil, containing polymers and patented by Eiffage company. A conventional 50/70 penetration grade bitumen (50/70) was included in the investigation for comparison with the binders and blends.

Biobinders were blended in the laboratory with the binder extracted from the selected RA (according to EN 12697-4 2005), which had a binder content of 3.6% (according to EN 12697-1:2012). The composition of the blends were determined by calculating the percentage in which each component would be present in 50% RA mixtures with a 5% total binder content and assuming full blending (all RA binder in the mixture would activate and blend with the fresh binders added). In this regard, the percentage of fresh binder that is replaced by RA binder in the mixture is known as Replaced Virgin Binder (RVB) (Jiménez del Barco Carrión, Lo Presti, & Airey, 2015) and is calculated as shown in Eq. (1).

$$\text{RVB}\ (\%) = 100 \cdot \frac{\text{RA} \cdot \text{DOB} \cdot \text{RABC}}{\text{BC}} = 100 \cdot \frac{0.5 \cdot 1 \cdot 0.036}{0.05} = 36\% \tag{1}$$

Where, RA is the total RA percentage in the mixture by weight, DOB is the assumed degree of blending between RA and virgin binders (100%), RABC is the RA binder content determined in the laboratory and BC is the designed final binder content in the mixture, with all the parameters expressed in decimals. Using Eq. 1, the blends of the different binders and RA binder were compounds of 36% RA binder and 64% of BB and BP respectively by mass. For the manufacturing of the blends between RA and BioBinders, the RA was heated at 160°C (due to its hardness) and BioBinders were heated at 140°C. Then, the materials were then combined in a tin and placed in an oven at 150°C for one hour. After that, the blends were stirred for 15 minutes at 200 r.p.m. over a hot plate to ensure the homogeneity of the final product.

The results of the conventional characterisation of the binders and blends are displayed in Table 1. The low penetration value and high softening point of the RA binder in contrast to the high penetration values of the biobinders and differences in softening point should be noted. Despite the high penetration value, BP presents a high softening point due to its SBS modification. In addition, the effect of the combination of the RA binder and biobinders as blends can be observed where they reach similar penetration values to the 50/70 penetration grade bitumen and softening point in the case of BB, while BP exhibits higher softening point due to its SBS modification.

Table 1. Binders and blends' conventional characterisation.

2.1.2. Aggregates

Two type of aggregates (limestone and granite) were tested with the different binders and blends for comparison. The mineralogical composition of these aggregates was assessed through Mineral Liberation Analyser (MLA) coupled to a Scanning Electron Microscope (SEM). The mineralogical analysis showed compositional differences of the granite and limestone aggregates. The granite predominant compositional minerals were Albite (43.12%), Chlorite (31.37%) and minor proportions of other minerals such as pumpellyte, quartz and orthoclass totalling 24.52%. Limestone aggregates composition was mainly represented by calcite (98.82%) and minor proportions of weathered minerals such as quartz, apatite, rutile, pyrite and kaolinite.

2.2 Methods

The Dynamic Contact Angle (DCA) analyser and Dynamic Vapour Sorption (DVS) device were used to determine the Surface Free Energy (SFE) of binders and aggregates respectively. From the SFE components, the thermodynamics quantities and energy ratios related to the intrinsic cohesion and adhesion properties of the individual materials and binder-aggregate system, namely work of cohesion, work of adhesion, work of debonding and energy ratios, were obtained and analysed. Next, the physical cohesive properties of the aggregate-binder systems were assessed by means of binder bond strength tests in the dry condition and related to the results from the SFE approach.

2.2.1. Determination of Surface Free Energy of binders: Dynamic Contact Angle (DCA) analyser

The determination of the surface free energy of the binders and blends was carried out using contact angle measurements through a ThermoCahn Radian Series 300 equipment (Dynamic Contac Angle Analyser - DCA). DCA was selected over similar equipment, such as Goniometer due to the lower variability, higher accuracy and the automated nature (Ahmad, 2011). Three probe liquids were utilized: (1) deionized water, (2) glycerol, and (3) di-iodomethane; and contact angle measurements taken for, at least, five replicates per probe liquid. Determinations of advancing contact angle were recorded for all the materials (individual binders and blends). Determination of the surface energy were subsequently conducted by using the approach proposed by Wilhemly (Bhasin et al., 2007). Three equations are produced using the surface energy components (Lifshitz-Van der Waals (LW), Lewis acid and Lewis base) of the three probe liquids. The equations are then written in a matrix form in order to obtain the three surface energy components of each investigated material. Ahmad (2011) provides further details and explanations on this mathematical procedure. The equipment used for the contact angle measurements and the visuals of the test specimens are shown in Figure 1. The characteristics of the probe liquids used are shown in Table 2.

Figure 1. Visuals for the contact angle measurement equipment depicting (a) complete test set-up, (b) Dynamic Contact Angle (DCA) analyser, (c) sample results screen, and (d) bitumen coated slides.

Table 2. Characteristics of the probe liquids used for contact angle measurements of bitumen coated slides.

2.2.2. Determination of Surface Free Energy of aggregates: Dynamic Vapour Sorption device

The fact that high surface energy materials cannot be tested using the DCA requires the use of other advanced thermo-dynamical techniques such as Dynamic Vapour Sorption (DVS) (Figure 2). The conventional aggregate fractions used for the DVS analysis include those passing 5mm and retained on 2.36 mm sieve, passing 150 µm and retained on 75 µm sieve, and passing 75 µm sieve. For this research, the fraction passing 5mm and retained on 2.36 mm sieve was used, based on recommendations from literature (Bhasin, 2007). Octane (non-polar), Chloroform (acid), and Ethyl Acetate (basic) are the probe liquids used for determining the surface energy components for the two aggregate types considered in this research study (i.e., granite and limestone). The concentrations and vapour pressures of the probe liquids is progressively increased by the high-precision automated system embedded in the DVS, typically conducted at 25°C. The changes in vapour pressure and concentration induce an increase in the mass of the aggregates, which depends upon the individual absorption capacity, and are recorded as a plot of change in mass (y-axis) versus the increase of the partial pressure of the probe liquid (x-axis), known as an adsorption isotherm. The isotherm is later analysed with specialized mathematical techniques for determining the specific surface area of the aggregates to be subsequently used for surface free energy of the aggregates. One of those techniques is the Brunauer-Emmett-Teller (BET) that was used in this research study. A more detailed theoretical explanation to the equations, their derivation and the details for sample preparation is available elsewhere (Bhasin, 2007; Ahmad, 2011).

Figure 2. Dynamic Vapour Sorption Device (DVS) for surface energy measurements on aggregates. (a) General view, and (b) detailed view of the main system components (adapted from Grenfell et al. (2014))

2.2.3. Assessing cohesion and adhesion properties of binders – aggregate system: Work of cohesion, work of adhesion, work of debonding and energy ratios

The surface energy of a material is defined as the amount of work required to create a unit area of new surface of that specific material (Bhasin et al., 2007). The origin of the surface free energy is the acid-base theory as detailed by van Oss (1994) and van Oss et al. (1988). According to this theory, the total surface free energy of a material has three components based on the type of molecular forces on the surface, namely: Lifshitz-Van der Waals (LW), Lewis acid component and Lewis base component. Therefore, the total surface free energy of a material is a combination of these three components as shown in Eq. (2).

$$\gamma = \gamma^{LW} + \gamma^{+-} = \gamma^{LW} + 2\sqrt{\gamma^{+}\gamma^{-}} \quad (2)$$

where γ is the total surface free energy, γ^{LW} is the LW component, γ^{+-} is the acid-base component, γ^{+} is the Lewis acid component and γ^{-} is the Lewis base component. If the surface free energy components of binders and aggregates are known, a better insight into the moisture sensitivity can be obtained through the calculation of the work of cohesion of the binder and the work of adhesion between binder and aggregate. The work of cohesion is an inner property of a binder and is considered as the energy to separate a column (binder) of unit area into two new surfaces. The work of adhesion is the necessary energy to separate the binder-aggregate system at the interface, which can also be understood as the compatibility or affinity of the two materials (Liu, Yu, & Dong, 2017). These thermodynamic quantities are determined using Eq. (3) and Eq. (4) respectively.

$$W_{BB} = 2\gamma_{B} \quad (3)$$

$$W_{BA} = 2\sqrt{\gamma_{B}^{LW}\gamma_{A}^{LW}} + 2\sqrt{\gamma_{B}^{+}\gamma_{A}^{-}} + 2\sqrt{\gamma_{B}^{-}\gamma_{A}^{+}} \quad (4)$$

where the subscripts B and A refer to the binder and aggregate respectively. Furthermore, the work of debonding between the binder and the aggregate is the reduction in free energy when water displaces the binder at their interface and can be determined as in Eq. (5).

$$W_{BAW}^{wet} = \gamma_{BW} + \gamma_{AW} - \gamma_{BA} \tag{5}$$

where the subscripts BW, AW and BA refer to the interfacial energy in the binder-water, aggregate-water and binder-aggregate systems respectively. The interfacial energy in a two materials system i-j can be calculated from the surface free energy components of both materials as in Eq. (6).

$$\gamma_{ij} = \gamma_i + \gamma_j - 2\sqrt{\gamma_i^{LW}\gamma_j^{LW}} - 2\sqrt{\gamma_i^{+}\gamma_j^{-}} - 2\sqrt{\gamma_i^{-}\gamma_j^{+}} \tag{6}$$

Finally, the thermodynamic quantities defined in equations (3) to (5) can be used to determine the energy parameters related to the moisture sensitivity of asphalt mixtures (Bhasin et al., 2007). In Eq. (7), the work of adhesion and work of debonding are combined to obtain the Energy Ratio 1 (ER_1). Bhasin et al. (2007) modified ER_1 to include another important quantity to study the moisture damage of mixtures: wettability. Wettability is defined as the ability of a material to wet the surface of another material and mathematically is the difference between the work of adhesion of a binder-aggregate system and the work of cohesion of the binder. Other authors have defined this quantity as a spreading coefficient, relating it to the ability of a binder to adequately coat the aggregate (Ghabchi et al. 2014; Liu et al. 2017). The Energy Ratio 2 (ER_2) is therefore calculated as in Eq. (8).

$$ER_1 = \left|\frac{W_{BA}}{W_{BAW}^{wet}}\right| \tag{7}$$

$$ER_2 = \left|\frac{W_{BA} - W_{BB}}{W_{BAW}^{wet}}\right| \tag{8}$$

2.2.4. Mechanical characterisation of binder-aggregate system: binder bond strength

The binder-aggregate systems were further evaluated by determining the pull-off strength and type of failure by means of binder bond strength tests using the Pneumatic Adhesion Tensile Testing Instrument (PATTI), originally developed in the United States (Copeland, Youtcheff & Shenoy, 2007) (Figure 3). The standard method followed was ASTM D4541-17. The sample preparation procedures included the following steps: (1) slabs manufacturing (coring and cutting) from rock boulders (i.e., granite and limestone), (2) polishing and washing of the circular slabs and immersion in distilled water for a period of 24h, (3) drying of the circular slabs at 110°C for 24 h, (4) conditioning of slabs and metal stubs at 70°C for 3 hours, (5) bitumen heating at 160°C until soft and pouring on the slab central portion to place metal stub on top, (6) temperature conditioning of the samples at 5°C for 5 hours, (7) pull-off test procedure (PATTI test), and (8) recording of the tensile strength data (tensile pressure), failure type, and retrieving of microscopic images through the use of the hand microscope shown in Figure 3e. It must be mentioned that in step (6), the samples were conditioned at 5°C instead of the usual 25°C because of the soft and sticky nature of the biobinders, which did not allow the pull-off test at that temperature to be performed since the binder would not fail.

Figure 3. (a) Schematics for the PATTI test, standard piston assembly, (b) Piston and device schematics detail (from PATTI Quantum Series operation manual); (c) PATTI specimens in dry condition; (d) result summary screen for the pull-off tests; and (e) hand-microscope used for visual inspection of failure patterns.

After the tests, the Pull Off Tensile Strength (POTS) is calculated following Eq. (9).

$$POTS = \frac{(AP \cdot A_g) - C}{A_{ps}} \tag{9}$$

where, POTS is the pull-off tensile strength (kPa), AP is air pressure (kPa), Ag is the contact area of gasket with relation plate (mm^2), C is the piston constant and Aps is the area of pull-stub (mm^2).

3. RESULTS AND DISCUSSION

3.1 Contact angle of binders and blends

The raw data of the contact angle measurements obtained for the three probe liquids are shown in Figure 4 for all the binders and blends. The higher a contact angle measurement is, the less prone to wetting the surface of the material, and usually a threshold of 90° is used to define wetting or not. Due to the polar nature of water and glycerol, and according to the results the primarily non-polar nature of the binders and blends, the contact angles for all the materials are high, meaning that both probe liquids do not wet the surface of the binders and exhibiting a hydrophobic behaviour. On the contrary, due to the non-polar nature of diiodomethane, the contact angle measurements decrease showing more hydrophilic behaviour.

Figure 4. Contact angle measurements for binders and blends with different probe liquids

3.2 Surface free energy of binders, blends and aggregates

The surface energy components and total surface free energy of the binders, blends and aggregates were obtained from the DCA and DVC tests and are displayed in Table 3 and Figure 5. The SFE is calculated using Eq. (2) and is graphically represent in Figure 5. As can be observed in Table 3, the Lifshitz-Van der Waals component (γ^{LW}) is the highest for all the materials, which means that γ_{LW} is the most significant factor contributing to the total SFE, followed by the Lewis base component for all the binders, including biobinders, and granite aggregate, and the Lewis acid component in the case of limestone aggregate. As seen in Figure 5, the SFE of the RA binder is the lowest, while biobinders (BB and BP) exhibit significantly higher values. This fact leads to an increase of the SFE of the blends of RA binder and biobinders in comparison to the RA binder itself, which reach comparable values to the 50/70 penetration grade bitumen.

Table 3. Surface energy components of binders, blends and aggregates

Figure 5. Surface free energy of binders, blends and aggregates

3.3 Work of cohesion, adhesion and debonding

The work of cohesion is an inner property of a binder and is considered as the energy to separate a column (binder) of unit area into two new surfaces, calculated using Eq. (3) based on the SFE components. In general, a higher work of cohesion would provide higher resistance to moisture damage (Liu et al., 2017). The work of cohesion of the binders and blends is shown in Figure 6. As seen, the work of cohesion has a similar trend to the SFE, with both biobinders exhibiting greater cohesion than the rest of materials and therefore are able to improve the work of cohesion of the RA binder when they are blended for bio-recycling in 37% for BB and 62% for BP.

The work of adhesion is the necessary energy to separate the binder-aggregate system at the interface, which can also be understood as the compatibility or affinity of the two materials (Liu et al., 2017). For an asphalt mixture to have the highest resistance to moisture damage, the work of adhesion is required to be as high as possible. The work of adhesion of the binders and blends combined with granite and limestone aggregates respectively was calculated using Eq. (4) and is displayed in Figure 6. As the first observation, the RA binder exhibits lower work of adhesion than the 50/70 penetration grade binder, which indicates that the ageing state of the RA binder is detrimental to the aggregate-binder bond strength. On the other hand, the biobinders present improved work of adhesion in comparison to the conventional bitumen. In this way, the blend of the RA binder and the biobinders are able to reach a balance in which their work of adhesion is better or comparable to that of the conventional bitumen, increasing the work of adhesion of the RA binder by 18% for BB and 27% for BP. In addition, Figure 6 shows that limestone aggregate has a better work of adhesion with all the binders and blends than granite aggregate, meaning that it would provide higher resistance to moisture damage.

Figure 6. Work of cohesion of binders and blends, and adhesion with the different aggregates

The previous thermodynamic quantities do not include the influence of water in the system. Therefore in order to introduce the effect of water, the work of debonding is calculated as in Eq. (5), defined as the reduction in free energy of the system when water displaces the binder from its interface with the aggregate (Bhasin et al., 2007), and is shown in Figure 7. For an asphalt mixture to have high resistance to moisture damage, the work of debonding is desirable to be as low as possible (Ghabchi et al., 2016). Analysing Figure 7, it can be observed that when water is introduced in the system, the RA binder is the material showing the lowest work of debonding, consequently the lowest energy released in the system and potentially the best resistance to moisture damage. In this regard, the blend of the RA binder with biobinders result in higher values of the work of debonding, up to 13% increase, than that of the RA binder itself, implying lower resistance to moisture damage, but still better than the 50/70 penetration grade binder. In addition, Figure 7 reveals that the work of debonding is higher with limestone aggregates than with granite aggregates. This fact should be related to the mineralogy of the aggregates described in section 2.1.2 of this article, which showed the high calcite content in limestone aggregates and is in accordance to previous studies which revealed the positive influence of this mineral in the moisture sensitivity of limestone aggregates (Zhang et al., 2015).

Figure 7. Work of debonding of binders and blends with the different aggregates

3.4 Assessing moisture sensitivity: energy ratios

In order to better understand the response of the system to moisture, Bhasin et al. (2007) proposed the calculate of energy ratios by combining the thermodynamic quantities calculated earlier. In order to have a durable and resistant asphalt mixture to moisture damage, the work of adhesion is required to be as high as possible, while the work of debonding is required to be as low as possible. Therefore, the higher the ER1, defined in Eq. (7), the less sensitive to moisture damage the asphalt mixture should be. Little and Bhasin (2006) defined a set of threshold values to distinguish among 'good' and 'poor' binder-aggregate combinations, giving a value of $ER1 \geq 0.75$ to have a good moisture resistance. Figure 8 shows the values of ER1 for the different binder-aggregate systems and reveals that all the binders and blends passed that threshold. However, it must be noted that these threshold values are not absolute and in general the combinations with higher ratios are preferred to those with lower ratios. Therefore, in terms of ranking, the biobinders present the highest resistance to moisture damage followed by the RA binder and 50/70 penetration grade binder. Consequently, the blends of the RA binder and biobinders result in an reduced moisture sensitivity increasing from up to 19% when compared to the RA binder, and an even higher increase when compared to conventional bitumen. Furthermore, Figure 8 reveals that the moisture sensitivity is lower with limestone aggregates.

Finally, the modified energy ratio, ER2 calculated as in Eq. (8), takes into account the wettability of the aggregate by the binder or blend. The higher the wettability, the stronger the affinity between the binder and the aggregate, due to a stronger mechanical bond and better coating. Thereby, the greater ER2 the higher resistance to moisture damage of the binder-aggregate system. In the same way then for ER1, Little and Bhasin (2006) identified an indicative threshold for ER2≥0.5 to have a good performance against moisture damage. The results of ER2 are displayed in Figure 9 showing that considering this property, the RA binder – aggregate system is the best and the biobinders show poorer results than the rest, not even passing the threshold value for the combination with the granite aggregate. The reason for this is the high work of cohesion of the biobinders (Figure 6), which is subtracted in the numerator of E2. However, when the RA binder and biobinders are blended, the moisture damage resistance of the system still shows less sensitivity to moisture damage than the 50/70 penetration grade bitumen and passes the threshold value of 0.5. Moreover, Figure 9 reveals that the moisture sensitivity is lower with limestone aggregates.

Thereby, considering ER1 and ER2 results, it is not straightforward to establish definitive conclusions about the moisture sensitivity of the binders individually, since different ranking are observed regarding the RA binder and biobinders based on ER1 and ER2. Nevertheless, the blends of RA binder and biobinders do seem to have better potential to resist moisture damage than the conventional bitumen for both energy ratios ER1 and ER2. In the same way, limestone aggregate exhibits lower moisture sensitivity than granite aggregate for both ratios.

Figure 8. Energy Ratio 1 of binders and blends with the different aggregates and treshold value (dashed line)

Figure 9. Energy Ratio 2 of binders and blends with the different aggregates and treshold value (dashed line)

3.5 Mechanical characterisation of binders through bond strength tests

Once the fundamental properties of the materials related to moisture damage were analysed, the actual binder/blends-aggregate systems were tested to determine the bond strength by means of the Pull-Off Tensile Strength (POTS). Figure 10 displays these results for binders, blends and aggregates combinations tested at 5°C. At least four replicates were performed on each combination and the POTS was calculated using Eq. (9). The type of failure was analysed after each test and was found to be always cohesive, which means that the adhesive bond between the aggregate and the binder or blend is larger than the cohesive strength of the binder for all the different combinations. This result is in accordance with the results of the thermodynamic quantities in which the work of cohesion of the binders and blends was always lower than the work of adhesion with the aggregates (Figure 6).

Firstly, the results in Figure 10 show that the pull-off strength of the RA binder is less than that of the 50/70 penetration grade binder. Previous studies have shown that the stiffness of the binder plays a significant role in the value of POTS (Bahia, Moraes, & Velasquez, 2012) showing that stiffer binders have a higher POTS. However, the comparison here between the RA binder and the 50/70 penetration grade bitumen shows the opposite trend. This might be due to the extremely aged state of the RA binder in this study, whose penetration is lower than 10mm-1 (Table 1), and since the type of failure was cohesive in both cases, it means that the inner cohesion of the RA is lower than that of the 50/70 penetration grade binder, having lower resistance to the pull-off loading.

On the other hand, the biobinders show different performances. BB presents lower POTS than the 50/70 penetration grade bitumen which could be related to its high penetration value, while BP shows an improved POTS despite its high penetration value.

This improvement can be attributed to its SBS content, given that previous studies (Moraes, Velasquez, & Bahia, 2011) have shown that polymer modification enhances the POTS of binders.

The blend of the RA binder and biobinders has a beneficial effect, increasing the pull-off strength of the RA binder, except in the case of RA+BB with limestone. This increase is particularly noticeable in the case of the biobinder BP, which reaches higher POTS than the conventional bitumen, and could be again related to the polymer modification of BP.

Figure 10. POTS of binders and blends with the different aggregates

3.6 A relation between POTS and work of cohesion

As mentioned, the type of failure in the bond strength test in dry condition was cohesive for all the combinations of binder, blend and aggregate. Therefore, the POTS and work of cohesion can be compared to find a correlation between both properties. Figure 11 shows the comparison between both magnitudes for all the binders and blends and the different aggregates and no correlation was found. However, previous studies have shown that this relationship exists for bitumen-based binders (Mohammed et al., 2018; Moraes, Velasquez, & Bahia, 2017). One important observation from this paper is the high work of cohesion of the biobinders which do not contain any bitumen. In Figure 11, the points related to the biobinders (Group 2) appear to be those breaking the possible relationship between POTS and work of cohesion, allowing the division in two clusters: Group 1 (binders including bitumen) and Group 2 (bio-based binders). In this regard, Figure 12 displays the comparison between both magnitudes excluding the biobinders and revealing a correlation, higher for granite aggregate than limestone aggregate. These results suggest that due to their different nature of the biobinders, their cohesive properties may exhibit a different link to the cohesive properties of bitumen-based binders. This fact does not imply that biobinders do not show such link, but it needs to be further investigated.

Figure 11. Comparison between POTS and work of cohesion of binders and blends

Figure 12. Comparison between POTS and work of cohesion of binders and blends excluding biobinders

4. CONCLUSIONS

The intrinsic cohesive and adhesive properties of bio-rejuvenated asphalt binders have been investigated by means of Surface Free Energy (SFE) measurements enriched by a physical characterisation through pull-off tests. The experimental plan included an extracted RA binder, two biobinders and two types of aggregate (limestone and granite). The RA binder and biobinders were blended according to the proportions of a mixture design to have 50% RA content, biobinders as the only virgin binder to be added in the mixture and assuming full blending between the biobinders and RA binder. The binders, blends aggregates were tested firstly individually to obtain their SFE and subsequently the moisture sensitivity of the tested combinations by calculating energy ratios suggested by Bhasin et al. (2007). Next, the cohesive strength of the binders/blends-aggregate systems was determined by means of PATTI tests. Based on the results and discussion, the following conclusions can be drawn:

(1) The biobinders present the highest surface free energy in comparison to the conventional bitumen and RA binder. This leads to an increase in the surface free energy of the blends of RA binder and biobinders in comparison to the RA binder of 37% in the case of BB and 62% for BP. As the work of cohesion is an internal

property of the binders and blends directly related to the surface free energy, the same conclusions and trends were obtained.

(2) The work of adhesion of the RA binder was the lowest among the investigated binders, while the biobinders presented superior values. Therefore, the blends of the RA binder with BB and BP increased work of cohesion by 18% and 27% respectively, presenting equivalent or improved values in comparison to the conventional bitumen.

(3) The work of debonding of the RA binder was the lowest, and therefore potentially the best in terms of moisture sensitivity. In this regard, the blend with the biobinders has a negative effect, increasing up to 13% for both biobinders. Nevertheless, the work of debonding of the bio-rejuvenated blends is lower than that of the conventional bitumen.

(4) Having the results from the work of adhesion and work of debonding, the energy ratios were needed in order to better understand the response of the binder/blend-aggregate systems to moisture. In this regard, for ER_1, the biobinders presented the highest resistance to moisture damage followed by the RA binder and conventional bitumen. Consequently, the blend of the RA binder and biobinders resulted in a reduced moisture sensitivity in comparison to that of the RA binder, increasing ER_1 from 5% to 19% depending on the system, and better than the conventional bitumen.

(5) In the case of ER_2, the RA binder – aggregate system was the best and the biobinders show poorer results than the rest. However, when the RA binder and biobinders are blended, the moisture damage resistance of the system showed less sensitivity to moisture damage than the conventional bitumen. Limestone

aggregates exhibited better resistance to moisture damage than granite aggregate for both energy ratios.

(6) In most of the cases, the blend of the RA binder with the biobinders has a positive effect, increasing the pull-off strength of the binder-aggregate system. Only the combination of the RA binder with BB and limestone showed a poorer strength.

(7) A correlation between the pull-off strength and work of cohesion was found for bitumen-based binders when the biobinders were excluded. This result indicates that due to the different nature of the biobinders, their cohesive properties (pull-off strength and work of cohesion) may exhibit a different link to the cohesive properties of bitumen-based binders and should be further investigated.

In summary, for the materials studied in this paper, the blend of the RA binder and biobinder generally improves the cohesion and adhesion of the RA binder or keep it up to an equivalent level to a conventional bitumen, showing therefore promising results to resist moisture damage. Further work is being carried out to extend the results to bio-recycled asphalt mixtures.

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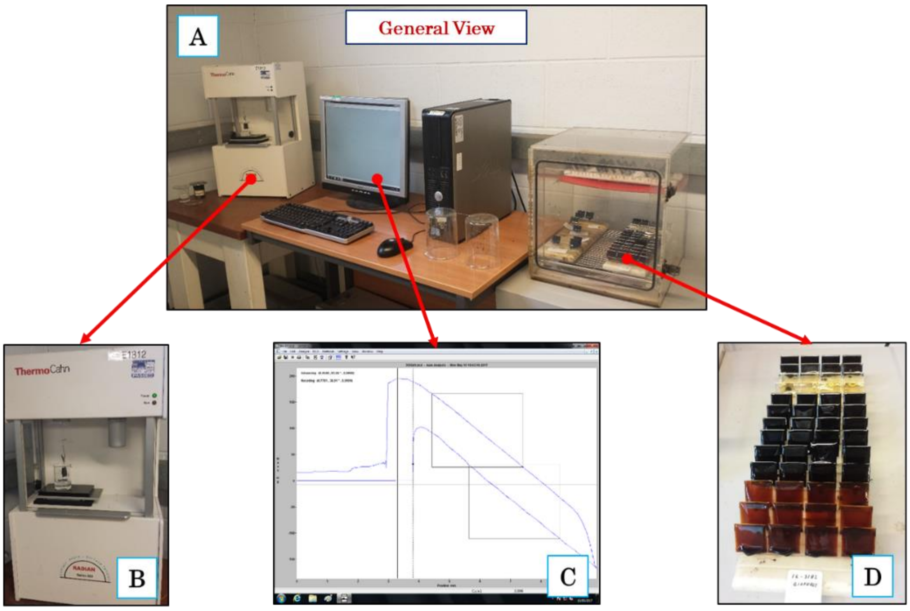

Figure 1. Visuals for the contact angle measurement equipment depicting (a) complete test set-up, (b) Dynamic Contact Angle (DCA) analyser, (c) sample results screen, and (d) bitumen coated slides.

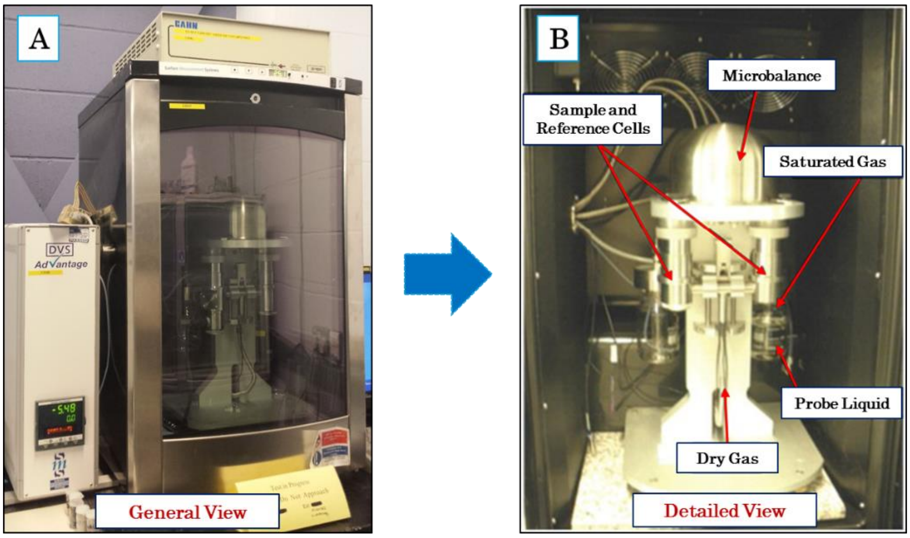

Figure 2. Dynamic Vapour Sorption Device (DVS) for surface energy measurements on aggregates. (a) General view, and (b) detailed view of the main system components (adapted from Grenfell et al. (2014))

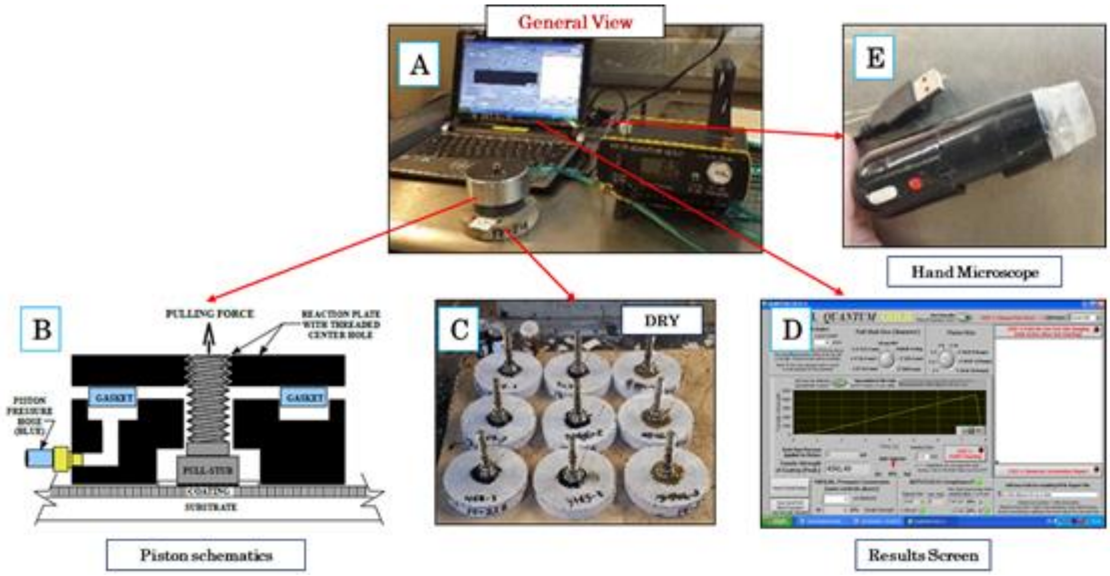

Figure 3. (a) Schematics for the PATTI test, standard piston assembly, (b) Piston and device schematics detail (from PATTI Quantum Series operation manual); (c) PATTI specimens in dry condition; (d) result summary screen for the pull-off tests; and (e) hand-microscope used for visual inspection of failure patterns.

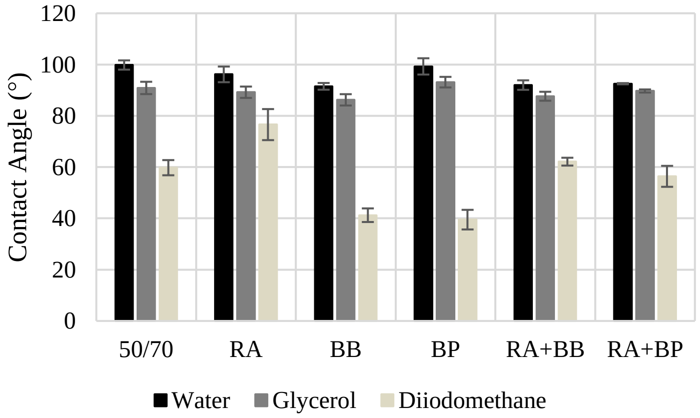

Figure 4. Contact angle measurements for binders and blends with different probe liquids

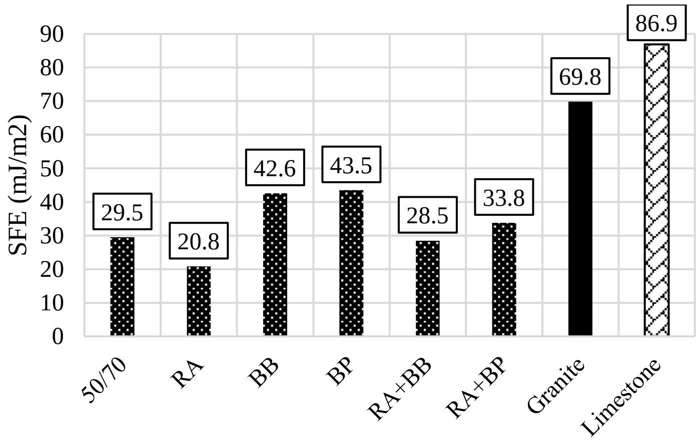

Figure 5. Surface free energy of binders, blends and aggregates

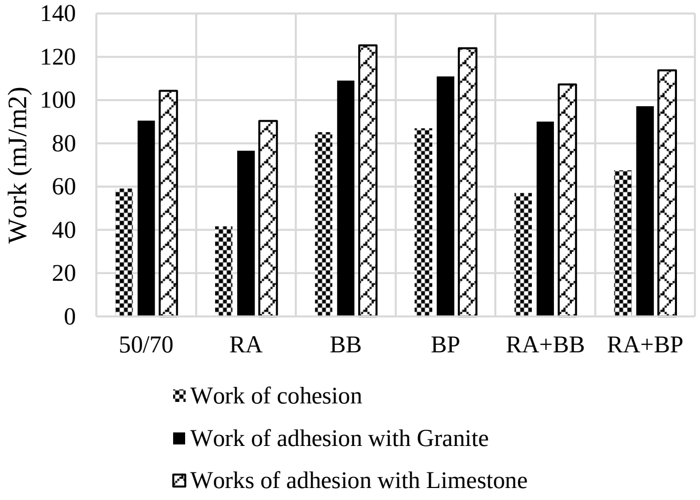

Figure 6. Work of cohesion of binders and blends, and adhesion with the different aggregates

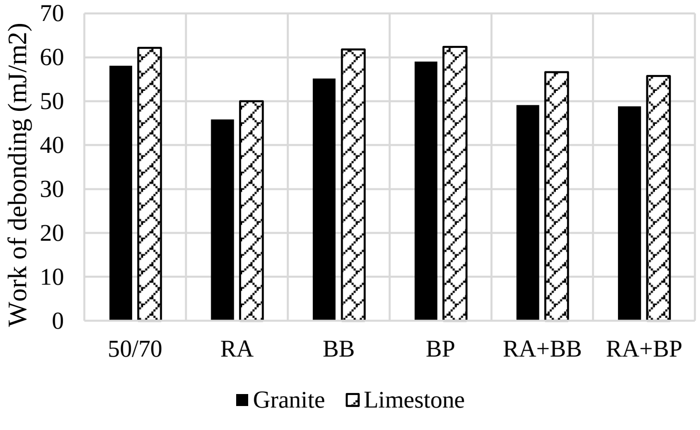

Figure 7. Work of debonding of binders and blends with the different aggregates

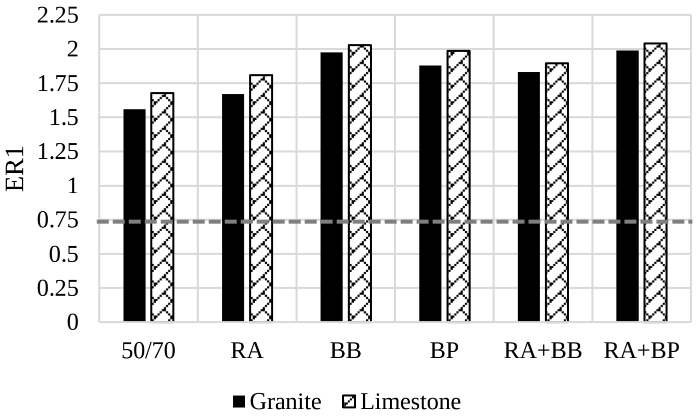

Figure 8. Energy Ratio 1 of binders and blends with the different aggregates and treshold value (dashed line)

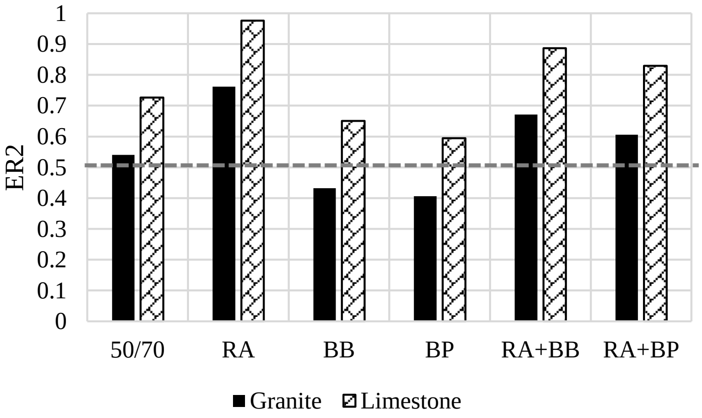

Figure 9. Energy Ratio 2 of binders and blends with the different aggregates and treshold value (dashed line)

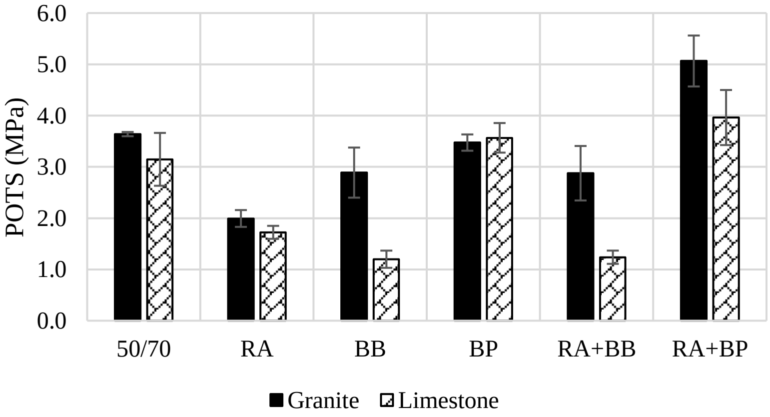

Figure 10. POTS of binders and blends with the different aggregates

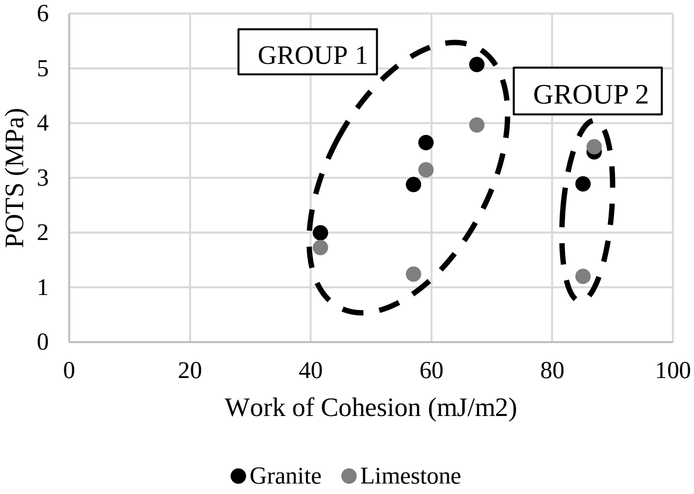

Figure 11. Comparison between POTS and work of cohesion of binders and blends

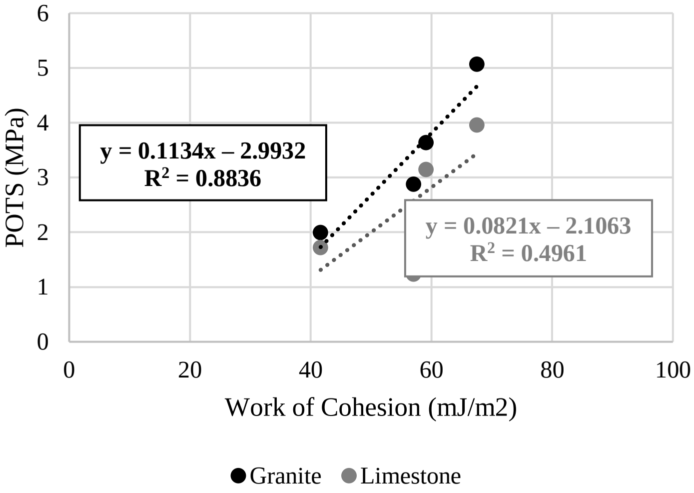

Figure 12. Comparison between POTS and work of cohesion of binders and blends excluding biobinders

Table 1. Binders and blends' conventional characterisation.

BINDER and BLENDS`	**NAME**	**PENETRATION @ 25° (dmm)** (EN 1426, 2007)	**SOFTENING POINT (°C)** (EN 1427, 2007)
50/70 penetration grade bitumen	50/70	68	48
Reclaimed asphalt binder	RA	8.7	75.8
BioBinder (80% pine resin + 20% linseed oil)	BB	235	40
Biophalt®	BP	147	73.5
Reclaimed asphalt binder plus BioBinder	RA+BB	69	45
Reclaimed asphalt binder plus Biophalt®	RA+BP	63	62

Table 2. Characteristics of the probe liquids used for contact angle measurements of bitumen coated slides.

Probe liquid	**Formula**	**Polar type**	**Molecular weight (g/mol)**	**Density (g/mL)**	**Total γ**	**Lifshitz-Van der Waals γ^{LW}**	**Lewis acid γ^{+}**	**Lewis base γ^{-}**
Water	H_2O	Polar	18	1.0000	72.80	21.80	25.50	25.50
Glycerol	$C_3H_8O_3$	Polar	92	1.2613	63.40	34.00	3.92	57.4
Diiodomethane	CH_2I_2	Non-Polar	268	3.3212	50.80	50.80	0.00	0.00

Table 3. Surface energy components of binders, blends and aggregates

Materials	**Surface Free Energy Components**			**Total**
	γ^{LW}	γ^{-}	γ^{+}	γ
50/70	28.7	1.8	0.1	29.5
RA	19.3	4.0	0.2	20.8
BB	34.0	4.4	0.7	42.6
BP	39.9	2.1	1.6	43.5
RA + BB	27.4	5.6	0.1	28.5
RA +BP	30.7	5.8	0.4	33.8