Chapter 2
Bituminous Binder

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Abstract One of the most important aspects of asphalt pavement deterioration is the ingress of water in pavement which leads to loss of the material characteristics, even material integrity with loss of aggregates. Thus the behaviour of asphalt mixture under moisture conditions is one of the key parameter for specifications. It's a complex phenomenon which is influenced amongst other things by materials properties with wetting, cohesion and adhesion of bituminous binder and by environmental conditions with temperature, moisture, loading and layer type. It has been a research subject for a very long time and still not precisely described. A large

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number of test methods is available to estimate the affinity between aggregates and bituminous binders. These test methods can be subdivided in different ways; a first distinction can be based on the presence or absence of water during the test procedure. If water is present, the evaluation is in fact referred to as water sensitivity or moisture damage testing. Another distinction can be based on the type of sample that is evaluated. The test sample can be loose aggregates coated with a bituminous binder or a compacted asphalt mix sample. Lastly the individual components, bitumen and aggregate, can be tested separately through intrinsic properties. Furthermore, test results can also be based on the quantification of the test results, whether this is based on a qualitative or a quantitative evaluation. In RILEM TC 237 SIB, TG1 the main purpose was to evaluate common test methods, used to assess the affinity of bitumen to aggregate surfaces, to determine, if possible, the repeatability and reproducibility and to give recommendations for improvement. In this study both binders and aggregates have been considered. Three bituminous binders, two unmodified from different sources, one polymer modified binder, and four aggregate types, with different mineralogy, have been selected. The test methods considered in the study include the rolling bottle test, the boiling water stripping test and the bitumen bond strength test; also surface energy was investigated. This chapter presents the results of these tests and their accuracy.

Keywords Bituminous binder · Aggregate affinity · Round Robin test
Water sensitivity · Durability · Surface energy · Adhesion · Rolling bottle test
Boiling water test · Bitumen bond test

2.1 Introduction

One of the most important aspects of asphalt pavement deterioration is the ingress of water in pavement which leads to loss of the material characteristics, even integrity with loss of aggregates. Thus the behaviour of asphalt mixture under moisture conditions is one of the key parameters for specifications. The water

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damage phenomenon is more than complex. The manufacturing of asphalt materials, the type of material with granular composition, void contents, the layer position in the pavement, the climate conditions with temperature and moisture, the loading case either with high shear or high/low speed certainly influence the end behaviour. For the bituminous binder its wetting ability, the cohesion and adhesion properties and to some extent the chemical composition are also parameters affecting the water sensitivity of asphalt materials.

A large number of test methods is available to estimate the affinity between aggregates and bituminous binders. These test methods can be subdivided in different ways; a first distinction can be based on the presence or absence of water during the test procedure. If water is present, the evaluation is in fact referred to as a water sensitivity or moisture damage test. Another distinction can be based on the type of sample that is evaluated and different levels towards moisture damage can be considered. Level 1 is for the individual components, stone and bitumen separately. Level 2 is testing loose mix or a coated stone. Level 3 is on compacted asphalt mixture. And level 4 is on the road itself. Each level adds a different degree of complexity, for example in the compacted asphalt mixture, void content is key; on the pavement, construction, in situ density, and traffic are influencing the end performances. Finally, test methods can also be based on the test results, whether a qualitative or a more quantitative evaluation is obtained.

In RILEM TC 237 SIB TG1, the main purpose was to evaluate common test methods, used to address the affinity of bitumen to aggregate surfaces, to determine, if possible, the repeatability and reproducibility and to give recommendations for improvement. The results obtained from different test methods were compared together.

Three bituminous binders have been selected, two unmodified from different sources and a polymer modified binder. And four aggregate types with different mineralogy have also been selected.

The test methods considered in this study so far included the rolling bottle test with eight laboratories, the boiling water stripping test with three laboratories and the bitumen bond strength test with three laboratories.

Furthermore, the results were compared with a more fundamental assessment of the intrinsic properties of bituminous binder and aggregates through surface energy measurement by two laboratories.

2.2 State of the Art

Adhesion of a bituminous binder onto aggregates is a quality criterion for the mixture performance and durability (Corte et al. 2004; Jakarni 2012). In particular, loss of adhesion can occur when water enters through the bitumen/mineral substrate interface (Bagampadde and Karlsson 2007). As the substrate presents more affinity for water, bitumen is displaced and the mixture's moisture resistance decreases (Hanz et al. 2007). Adhesion is described following several mechanisms (Tan and Guo 2013; Rychen et al. 2010):

- Mechanical adhesion, which causes strong bonding when the binder covers the asperities and fills the voids of the substrate;
- Chemical adhesion, which relates to the high affinity between the acid compounds of bitumen and the basic species from the aggregates;
- Surface free energy theory, which describes the surface energy evolution of the mineral when the binder wets the surface;
- Molecular orientation, which is explained by the orientation adsorption of polar molecules onto bitumen and substrate surfaces;
- Electrostatic adsorption, which indicates the affinity to each other for two materials having opposite charges.

In the dry state, adhesion strength of bituminous mixtures is mainly a function of the cohesive strength of the bitumen. In the presence of moisture, adhesion strength depends on substrate mineralogy (Zhang et al. 2015; Apeagyei et al. 2014, 2015). In road engineering, the bitumen/limestone combination exhibits strong adhesion even when exposed to moisture. However, siliceous aggregates are subject to stripping (Bourrel and Verzaro 1998) when exposed to moisture. Surface texture of the aggregate also plays an important role in adhesion (Yazgan 2003). Binder properties and operating conditions may also affect the wettability and the adhesion (Rychen et al. 2010; Some et al. 2013, 2014; Ziyani et al. 2016).

As adhesion is the bonding between two different materials, in any case of testing one needs two materials to investigate the adhesion phenomena. However each component, separately, have their intrinsic characteristics that can provide an estimation of combined adhesion. For example for the aggregates this could be based on the mineralogy or also the refractive index (Laurell Lyne et al. 2013a, b).

Finding an adhesion test for road applications has been a long search starting in the early 1900s. The Riedel and Weber test (1933) is a visual test that was published in 1933 and uses boiling water doped with increasing sodium carbonate concentration. Several other visual similar tests were introduced (Curtis 1990). Andersland and Goetz showed in (1955) that a sonic test can give information on the deterioration of asphalt mixes. An overview of different tests with pros and cons are published by Mathews et al. in (1965). In 1973 the interaction between bitumen and aggregate was investigated with the micro calorimetric method (Ensley 1973).

In the 80s and 90s during the Strategic Highway Research Program (SHRP) a huge amount of data was gathered, reviewed and published and made available on internet. Some reports combine molecular structures of bitumen components with aggregate components to identify possible adhesion and absorption (Jeon and Curtis 1992; Curtis et al. 1993; Lee et al. 1990; Tarrer and Wagh 1991). Other reports showed proof of test methods with road experience (Hicks and Finn 1994). Several literature sources concluded that binder or aggregate alone was not valid to rank but pairs are needed for ranking (Scholz et al. 1994; Terrel and Al-Swailmi 1994). The amount of papers concerning the adhesion over time was reviewed by Renken et al. (2003). He showed two different periods in time, around 1940 and around 1960. The concern on adhesion was high resulting in more published work on this topic.

Then it was end of 80s that new interest resulted in a state of the art report (NCAT 1988).

Recent studies followed different paths to identify adhesion. For example Chaudhury et al. (1992), Chaudhury (1996) and Chung and Chaudhury (2005) published, among other publications on adhesion and a Science review on the contact angle measurements in 1992. Several theses (Shah 2003; Hefer 2004; Bhasin 2006) and publications (Howson et al. 2011; Hirsch et al. 2009) relate the same topic to asphalt mix performance.

The adhesion between aggregate and binder was identified as one of the most important parameters influencing moisture sensitivity. The importance of anti-stripping material was one of the solutions for the problem (LTRC 1995). Congresses and workshops addressing only moisture sensitivity (Committee 2003) were organised to discuss the experience and way forward. The outcomes revealed that 78% of the US agencies tested asphalt mix for water sensitivity. Over 80% used the indirect tensile test to indicate resistance against loss of adhesion. Gubler et al. (2005) showed that actually the ITS-test is not the best method to be used and recommended the Coaxial Shear Test (CAST) instead. Wong et al. showed that the Asphalt Pavement Analyser (APA) can identify the influence of water on permanent deformation (Wong et al. 2004) while Castaneda introduced the use of the mechanical characteristics in a Cole-Cole plot (Castenada Et al. 2004). A new state of art was published by The Royal Institute of Technology of Stockholm (RIO Technology 2003) showing that the modified Lottman was the best test method available but careful selection of materials and good construction practice are essential.

The combined effort of the European Asphalt Pavement Association, EAPA, the Federal Highway Agencies, FEHRL, and the European Bitumen Association, Eurobitume, identified several bitumen properties related to asphalt properties. These were, except for adhesion where the conclusion was "In contrast to other tests, interfacial properties. Therefore, adhesion is possibly the most difficult one to conceive. It has to describe the suitability of binders to adhere to various pavement components such as aggregates, sand and fillers. Although a lot of interesting ideas are included in the tests already described in this chapter, the subject of adhesion still needs future research in order to establish well validated and performance-based specification" (BitVal 2006). In the European committee on standardisation, CEN, the technical committees on TC227 "Road materials" and TC336 "Bituminous binders" combined their effort to identify the current test methods used (Besamusca et al. 2012). They showed that most test methods are related to other aspects than adhesion resulting in ranking of products not related to adhesion and the influence of aggregate is bigger than the bitumen source. Bagampadde et al. also concluded (2006) that the influence of aggregate is more pronounced on adhesion properties than the influence of bitumen.

The adhesive-cohesive behaviour is simulated by the work of Kringos (Kringos et al. 2008) showing that surface energy alone is not enough to predict bitumen-aggregate interaction.

Jorgensen published in (2002) round robin results of the boiling water test based on a slightly modified protocol of the Texas boiling test, where the quantitative test result is obtained by visual evaluation of the residual percentage of coating, and the rolling bottle test. It was shown that the boiling water test, as used in this study, was valid to identify bad combinations of binder and aggregate but the rolling bottle test could rank combinations. Several publications (Grönniger et al. 2010; Källén et al. 2013; Morgenstern et al. 2010; Renken et al. 2010; Grönniger 2008) showed that the visual inspection is very subjective and is the main disadvantage of the method used. Introducing digital analysing techniques could improve the test (Lamperti et al. 2015).

Special attention should be given to the work of Ulmgren (2004). This publication investigated the bonding between mastic and aggregate while almost all other publications focus on binder and aggregates. The mastic-aggregate interaction is of special interest in case of porous asphalt pavement, and is most probably related to ravelling (Mo 2010).

In recent work from KTH and Nynas (Laurell Lyne et al. 2010, 2013) the adhesion between minerals and bituminous binders was estimated from the dispersive, non-polar van der Waal's interaction component of adhesion. In literature (van Oss et al. 1988), the dispersive component can be estimated using the refractive index. This approach was used and allowed ranking minerals and corresponding aggregates according to their degree of stripping; the stripping ranking was derived from literature (Cordon 1979). The study also indicated that aggregates with a refractive index higher than approximately 1.6 are expected to be less susceptible to stripping. And, it was also shown that the elemental composition of a mineral affects its refractive index and hence it's dispersive adhesion to bitumen. Especially the presence of alkali metals was seen as critical for obtaining a good resistance to moisture damage.

The recovery of oil and bitumen from sandstone reservoirs are similar with the research performed on asphalt mix adhesion, but contrary. The recovery from sandstone reservoirs are focussed on the release of oil and bitumen while asphalt mix research wants to increase the adhesion. Both researches aim for the understanding of the process and therefore it is worthwhile to look at the approach of several researchers (Dudásová et al. 2008; Chukwudeme and Hamouda 2009; Tu et al. 2005).

Still new test methods are introduced to gain understanding of the adhesion phenomenon. For example the proposal of the blister tests (Fini et al. 2008) to address the interfacial fracture energy. The fracture energy was also investigated by combining energy from a peeling test and X-ray measurements (Horgnies et al. 2011).

Recent publications combined visual tests with mechanical tests and surface energy (Grenfell et al. 2014; Liu et al. 2014) to find the best fit for roads and even more fundamental properties like van der Waal forces (Laurell Lyne et al. 2013) are investigated. Moisture ingress by diffusion was previously studied by Kassem et al. (2006) and recently by Apeagyei et al. (2014).

Considering the affinity between aggregates and bituminous binder, there are different test methods available. One of the most widely used tests in Europe is the rolling bottle test as described in the standard EN 12697-11. The boiling water stripping test is also part of the EN 12697-11 standard. And in recent years the Bitumen Bond Strength, BBS, test was introduced in the US with AASHTO TP91.

2.3 Organisation of the Round Robin Test

2.3.1 Participating Laboratories

In RILEM TC 237 SIB TG1, the initial intention is to further understand the fundamental mechanism of water interaction in asphalt mixtures, and to review the various test methods available, to identify which test is the most suitable. In these conditions, one main purpose is to evaluate the repeatability and reproducibility of common test methods used to evaluate the affinity of bituminous binder to aggregate surfaces, and to provide recommendations for improvement.

Within the round robin test from TG1, a total of 13 laboratories participated, running different test methods addressing the affinity between aggregates and bituminous binder as listed in Table 2.1. Results from all of these participants were received and further analysed.

2.3.2 Bituminous Binder

A total of three bituminous binders from two different suppliers were used for coating the aggregates. Two unmodified 50/70 paving grade bituminous binders according to EN 12591 and one polymer modified bitumen graded as 45/80-60 PmB according to EN 14023. The basic properties of the three binders are reported in Table 2.2 and were defined in terms of:

- Penetration value at 25 °C in accordance with EN 1426, which reflects the consistency of the bitumen at ambient temperature. The higher it is, the softer the bitumen is.
- Ring and ball temperature (softening point) in accordance with EN 1427, which reflects the consistency of the bitumen at high temperature. The higher it is, the more heat the bitumen needs in order to soften (or to flow).

The three bituminous binders had similar values in term of penetration values at 25 °C meaning that their consistency/viscosity at ambient temperature were in the same range of magnitude. Thus test run at ambient temperature should eventually not to be affected by the binder consistency. On the other hand, the softening point temperature for the polymer modified binder was higher around 60 °C, than those for the neat binders. Thus, the tests run at high temperature may be expected to have different results if viscosity is affecting the cohesion/adhesion of the bitumen with aggregates.

Table 2.1 List of the laboratories participating in the RRT and their tests

Institution	Country	Test method	Standard
IBDiM	Poland	Rolling bottle	EN 12697-11 clause 5
Nynas	Belgium	Rolling bottle	EN 12697-11 clause 5
University of Nottingham	UK	Rolling bottle	EN 12697-11 clauses 5
		Bitumen bond strength	ASTM D 4541
		Surface energy	In house method
Repsol	Spain	Rolling bottle	EN 12697-11 clause 5
IFSTTAR	France	Boiling water stripping	XP T66-043
		Angle contact between rock and binder	Specific device drop method
Arizona Chemical	The Netherlands	Rolling bottle	EN 12697-11 clause 5
BRRC	Belgium	Boiling water stripping	EN 12697-11 clause 7
University of Parma	Italy	Bitumen bond strength	ASTM D 4541
University of Ancona	Italy	Bitumen bond strength	ASTM D 4541
Wisconsin University	US	Bitumen bond strength	ASTM D 4541
VTI	Sweden	Rolling bottle	EN 12697-11 clause 5
		Boiling water stripping	EN 12697-11 clauses 7
TU Braunschweig	Germany	Rolling bottle	EN 12697-11 (A)
University Roma La Sapienza	Italy	Rolling bottle	EN 12697-11 clause 5

Table 2.2 Basic properties of the used bituminous binders

	Unit	Standard	Bit 1	Bit 2	Bit 3
Binder type			50/70	50/70	PmB 45/80-60
Penetration value at 25 °C	×0.1 mm	EN 1426	51	57	50
Softening point temperature	°C	EN 1427	51.2	50.8	65.4

2.3.3 Aggregates

The four aggregates (granite, basalt, greywacke and limestone) were all supplied by Aggregate Industries from different quarries located in the UK. These aggregate types were selected expecting a difference in moisture susceptibility based on the differences in mineralogy or composition.

Granite is an intrusive igneous rock composed of interlocking crystals. It is coarse grained, with similar sized individual crystals randomly arranged. Petrographic examination of the granite used in this study showed that the rock comprised mainly of quartz, feldspars (orthoclase), amphibole and biotite. Feldspars and amphibole grains are angular and coarse grains. Biotite grains, on the other hand, are elongated and smaller than the feldspars. X-ray Fluorescence, XRF, analysis of the granite indicated relatively high silica content of 64%. Silicates in this granite comprise of quartz, feldspars, amphibole and biotite. Quartz is composed of pure silica. Orthoclase feldspars are alumino-silicates containing potassium and are the main component in the granite (46%). Amphibole is an inosilicate or chain silicate containing iron and magnesium in its structure. It might also contain sodium and calcium. Biotite is a phyllosilicate (sheet silicate) mineral rich in iron and magnesium.

Basalt is a fine-grained igneous rock comprised primarily of plagioclase feldspars, pyroxene and quartz. Plagioclase feldspars are alumina-silicates with different percentages of sodium and calcium. Pyroxene, on the other hand, is an inosilicate mineral containing calcium, sodium, iron and magnesium. XRF analysis of the basalt indicated a silica content of 50% approximately.

Greywacke is a sedimentary rock belonging to the sandstone group. Petrographic examination showed that greywacke aggregate comprised of several mineral grains namely quartz, feldspars, chlorite and biotite. Quartz and feldspars grains are angular and relatively coarse grains. Chlorite and biotite mineral grains, on the other hand, are elongated and smaller in size. Moreover, in the greywacke coarse angular quartz and feldspar grains are cemented by the much finer matrix of chlorite and biotite minerals. XRF analysis of the greywacke indicates relatively high silica content (66%). The silica combines with the main oxides (iron, magnesium, calcium, sodium and potassium oxide) to form the silicates. In the greywacke theses silicates comprise of quartz, feldspars, chlorite and biotite. Quartz is composed of pure silica. Feldspars are alumina-silicates containing potassium, sodium and calcium. Chlorite and biotite are phyllosilicate minerals, i.e. with a tendency to split along defined crystallographic structural planes, rich in iron and magnesium.

Limestone is a sedimentary rock formed in a marine environment from the precipitation of calcium carbonate and compressed to form a solid rock. It is composed primarily of calcium carbonate ($CaCO_3$) in the form of calcite. Petrographic examination of the limestone used in the study showed an almost single mineral phase nature of the aggregate.

The aggregates can be ranked according to their degree of stripping as slight (greywacke), slight to moderate (limestone and basalt) and severe (granite)

(Hicks and Finn 1994). However, limestone, in particular if it consists almost exclusively of calcite, has been classified as having a good resistance to stripping (Laurell Lyne et al. 2013a). Therefore, it was expected that a reliable laboratory test should be able to distinguish between the mixtures based on the selected aggregates. The aggregates were supplied as crushed with nominal aggregate size expected of 8/11 mm. Bulk stones were also supplied for the bitumen bond strength test.

2.3.4 Experimental Procedure

2.3.4.1 Rolling Bottle

The Rolling Bottle Test (RBT) was conducted in accordance with EN 12697-11 clause 5 (EN 12697) with minor modifications based on each laboratory practice. It should be noted that the RBT is a subjective test in that affinity is expressed by visual estimation of the degree of bitumen coverage on un-compacted bitumen-coated mineral aggregate particles after the influence of mechanical stirring action in the presence of water (Fig. 2.1).

For the aggregates, only material retained between the 8 and 11 mm sieve was used for conducting the rolling bottle tests. To prepare samples for testing, dust-free aggregate samples weighing 510 g are dried in an oven at 110 ± 5 °C overnight to constant mass and then coated with about 17 g of hot bitumen (150 °C for the 50/70 pen and 180 °C for the 45/80 PmB) binder in a mixing bowl. The aggregate-binder mixture is then cooled loose at room temperature. The mixed material is stored at ambient temperature between 12 and 64 h before testing. Each of the test bottles is filled to about half their volume with cold (5 °C) deionised water, and about 150 g of the loose aggregate-mixture is placed in each bottle before topping the bottle with deionised water to the shoulder (about 2/3 full). The whole assembly

Fig. 2.1 Rolling bottle test equipment

is put in the bottle roller rotating at a speed of 60 rotations per minute for 6 h. The room temperature throughout the test has to be maintained between 15 and 25 °C. At the end of the 6 h period, the aggregate particles are emptied from the test bottle into a test bowl which is then filled with fresh, cold deionised water to a level just above the top of the surface of the particles. Subsequently, the test bowl is placed on a white surface. The purpose of adding fresh water is to allow for optimal visual determination of binder coverage on the aggregate particles. At least three replicates of each sample are tested.

At the end of the test, the degree of bitumen coverage of the aggregate particles is estimated by visual observation and recorded to the nearest 5% using the scale set in the standard EN 12697-11 as per Fig. 2.2. As during the test itself there is a polishing effect of the stone edges more or less important depending on the stone types, which makes difficult to use the variation of mass before and after the test to assess the degree of coating.

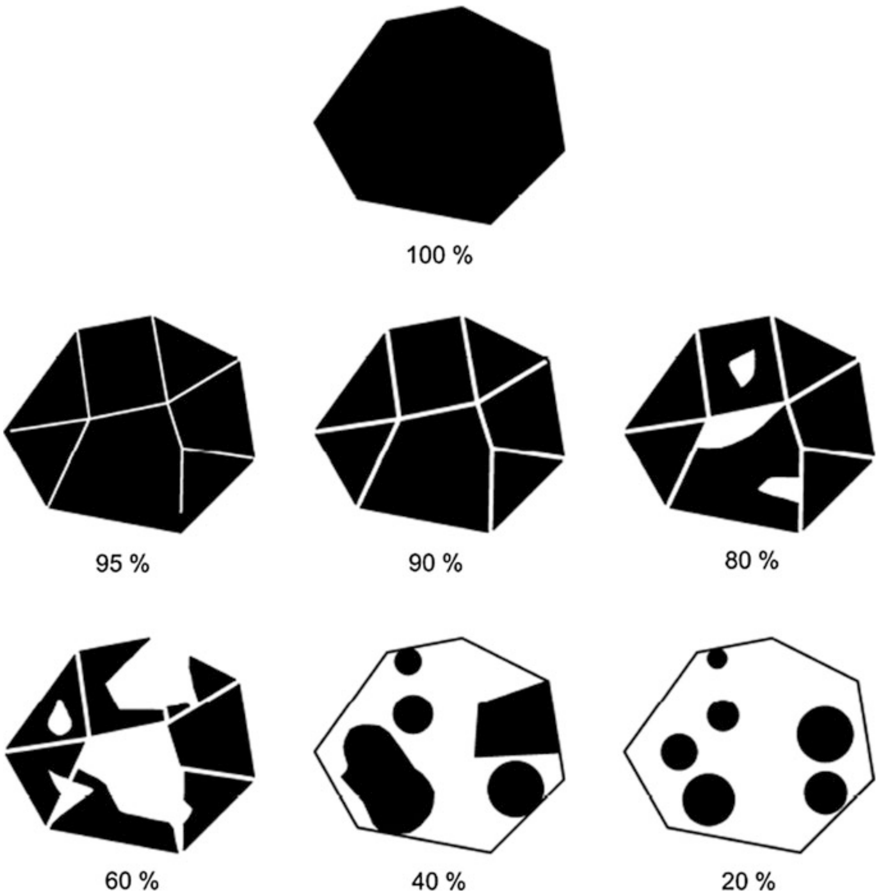

Fig. 2.2 Rolling bottle test scale for bitumen coating (from EN 12697-11)

The degree of binder coverage is defined as the average proportion of the surface area of the aggregate particles that are covered with the binder, expressed as a percentage, 100% being fully coated and 0% being totally uncoated. The degree of binder coverage on the aggregate particles is visually estimated by two experienced technicians independently. The procedure (i.e. rotation in the bottle roller and measuring of binder coverage) is repeated for another cycle up to 24 h and eventually two more cycles (up to 48 and 72 h) with the original fouled water. The degree of binder coverage is estimated as described previously. For each rolling duration (6, 24, 48 and 72 h), the mean value of each technician's recordings of the average degree of binder coverage obtained on the three samples (three bottles) is calculated to the nearest 5%, and the results are averaged to obtain the degree of binder coverage for a given mixture.

In the EN 12697-11 standard, there is not yet an officially established level of precision. It is estimated from normal practice with a coefficient of repeatability and reproducibility of respectively 20 and 30%.

2.3.4.2 Boiling Water Stripping Test

The Boiling Water Stripping (BWS) method, was carried out according to EN 12697-11 clause 7 (EN 12697) and for one laboratory also according to the French standard XP T 066-043 (066-043). The test determines, in a quantitative way, the affinity between any mineral aggregate and bituminous binder combinations in which the mineral is calcareous, silico-calcareous or siliceous by nature. As the percentage of stripping is measured by an acid/base titration while making use of a calibration curve, it is anticipated to be a more objective assessment of the affinity between a binder and aggregate as compared to the rolling bottle method.

More specifically, the procedure involves the coating of 1.5 kg of aggregate of an 8–11.2 mm fraction (basic set plus set 1) with 2.0% by mass of binder. The mixing temperature is equal to the reference temperature for mixtures as defined in EN 12697-35. For the 50/70 pen graded bitumen it is 150 °C. In a next step, a series of mixtures of uncoated (= bare) aggregates and coated aggregates are produced in well-defined proportions (corresponding to 0, 10, 20, 30, 50 and 100% of uncoated aggregate) and subjected to chemical attack of an acid for a predefined time to produce a calibration curve of acid consumption against the proportion of uncoated aggregates. The acid attacks any bare surface of the aggregates and therefore its consumption is proportional to the stripped surface area. The acid to be used is either hydrochloric acid (0.1 N) in case of calcareous aggregates (e.g. limestone) or, in case of aggregates of siliceous nature (e.g. igneous rock), the more reactive and concentrated hydrofluoric acid (1 N) is applied.

In a subsequent step, 200 g of the coated aggregate to be tested is boiled in 600 ml of de-mineralised water for 10 min, allowed to dry and subjected to an acid attack in order to calculate, while using the calibration curve, the degree of bitumen coverage and therefore the extent of stripping (the test result is the average of two individual values of stripping obtained).

In the EN 12697-11 standard a repeatability coefficient of variation of 15% of the determined value is stated (absolute precision threshold on the determination of the stripping of 2%). No reproducibility data have been established yet.

For the French XP T 66-043 standard (66-043), the test is carried out with the granular fraction 6–10 mm. Aggregates are firstly washed and dried in a ventilated oven for 12 h at 110 °C. Then, 100 g of aggregates are mixed with bitumen at the temperature defined in EN (12594), according to penetration grade. The bitumen content is 5% and the mixing time is 60 s. The mix is immersed in hot deionised water at 60 °C for 16 h. The percentage of uncoated aggregates is estimated by visual observation. Results are expressed as follows:

100: when no aggregate surfaces are uncoated
90: for 90% of the aggregate surfaces are coated with bitumen
75: between 75 and 90% of the aggregate surfaces are coated with bitumen
50: between 50 and 75% of the aggregate surfaces are coated with bitumen
<50: less than 50% of the aggregate surfaces are coated with bitumen
0: the binder does not coat the aggregates anymore.

Some examples of visual evaluation are given in Fig. 2.3.

The Table 2.3 compares both test methods.

Fig. 2.3 Example of coating class according to XP T 66-043

Table 2.3 Comparison of boiling water stripping methods

Method	EN 12697-11 clause 7	XP T 066-043
Aggregate	8/11.2 mm	6/10 mm
Weight	200 g	100 g
Binder content	2%	5%
Test temperature	Boiled water	60 °C
Test duration	10 min	16 h
Interpretation	Acid titration after calibration	Visual interpretation

2.3.4.3 Bitumen Bond Strength

Two different types of pull-off adhesion tests were used to characterise the aggregate-bitumen bond strength. They included the standard Bitumen Bond Strength (BBS) test also known as the PATTI test and the new pull-off test. The main advantage of the new pull-off test is the ability to control bitumen film thickness, control loading rate, and test asphalt mastics bonding capability on stone.

The Bitumen Bond Strength test, BBS, (AASHTO TP-91) test uses a Pneumatic Adhesion Tensile Testing Instrument, PATTI®, adapted from the paint and coatings industry (ASTM D4541) (Fig. 2.4).

The test device and procedure have been modified and developed in recent research (Youtcheff and Aurilio 1997 1997) to measure the moisture susceptibility of bituminous binders (Meng 2010; Moraes et al. 2011; Miller et al. 2010). The BBS test protocol requires a bond of an aggregate substrate with a binder under controlled conditions of temperature and humidity. The main components of the BBS equipment are the pressure hose, a portable pneumatic adhesion tester, a piston, the reaction plate and a metal pull-off stub (Fig. 2.5).

Before running a test, the piston is placed over the pull-off stub and the reaction plate screwed on it. Then, compressed air is introduced through the pressure hose to the piston. An upward pulling force on the specimen is applied by the pull-off stub. During the test, failure occurs when the applied pressure exceeds the cohesive strength of the asphalt binder or the adhesive strength of the binder-aggregate interface. The pressure at failure is recorded and the pull-off tensile strength (POTS) is calculated according to the following equation:

Fig. 2.4 PATTI® test equipment

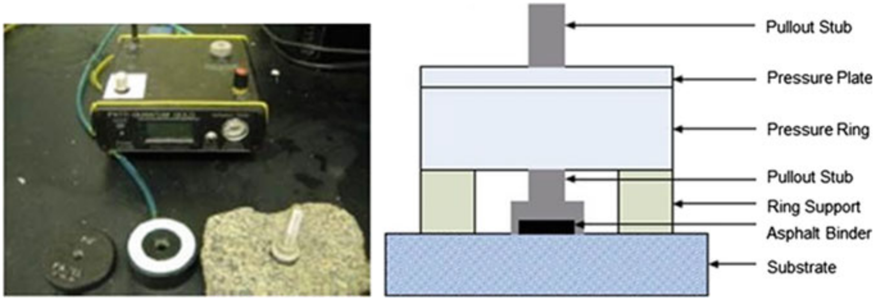

Fig. 2.5 Bitumen bond strength test

$$\text{POTS} = [(\text{BP} * \text{Ag}) - \text{C}]/\text{Aps}$$

where,

Ag contact area of gasket with reaction plate (mm^2)
BP burst pressure (kPa)
Aps area of pull stub (mm^2)
C piston constant

The pull-off stub has a rough surface that can prevent asphalt debonding from the stub surface by providing mechanical interlock and larger contact area between the asphalt binder and stub. The pull-off stub in the new pull-off BBS test has a diameter of 20 mm with a surrounding edge, used to control film thickness. The stub edge has a thickness of 800 μm, as shown in Fig. 2.6. This geometry and surface treatment was described in two extensive recent studies (Meng 2010; Canestrari et al. 2010) in an effort to improve repeatability of the testing system.

Aggregate plates were cut with a constant thickness and parallel top and bottom surfaces. The aggregate plates were then lapped on both sides using 280 grit

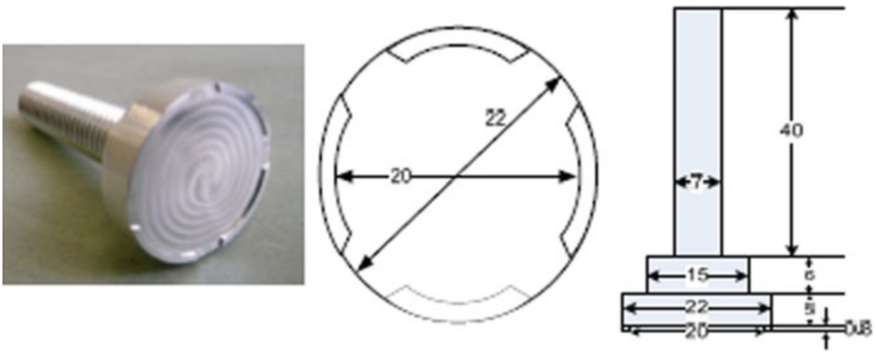

Fig. 2.6 Pull-off stub for the Bitumen bond strength test (BBS)

silicon carbide material after cutting. Lapping is to control the roughness of the surface. After cutting and lapping, aggregate plates are immersed in distilled water in an ultrasonic cleaner for 60 min at 60 °C to remove any residue from the cutting process and neutralise the surface of aggregate to its original condition.

Then the aggregate surface and pull-off stubs are cleaned with acetone to remove moisture and dust, which could affect adhesion. They are heated in an oven at 65 °C for a minimum of 30 min to remove absorbed water on the aggregate surface and provide a better bond between the bituminous binder and the aggregate. The bituminous binders are heated in an oven at 150 °C. The stubs are removed from the oven, and the bituminous binder sample is placed immediately on the surface of the stub for approximately 10 s. Then the aggregate plate is removed from the oven, and the stub with the binder is pressed firmly into the aggregate surface until the stub attaches the surface and no bituminous binder is observed to be flowing out from the bond. The stubs must be pushed down as straight as possible with uniform force, and twisting should be avoided to reduce the formation of trapped air bubbles inside the sample and to minimise stresses. Before testing, dry samples are cured at three temperatures (15, 22, 30 °C) in an environmental chamber for 24 h. For wet conditioning, samples are first cured at room temperature for 1 h to allow for the aggregate-binder-stub system to reach a stable temperature. Then, samples are immersed in a water tank at a specific temperature of 40 °C for the specified conditioning time of 20 h. When the conditioning time is completed, the samples are maintained at room temperature for 1 h before testing.

After testing, the maximum pull-off tension the failure type is recorded. If more than 50% of the aggregate surface is exposed, then failure is considered to be adhesive; otherwise, it is a cohesive failure.

A modified protocol for the new pull-off test was also used to determine bond strength between the aggregates and asphalt mastics as shown in Fig. 2.7

Asphalt mastics were fabricated for testing using a 40/60 pen bitumen, granite fine aggregate and mineral filler. The same mastic has been shown to produce

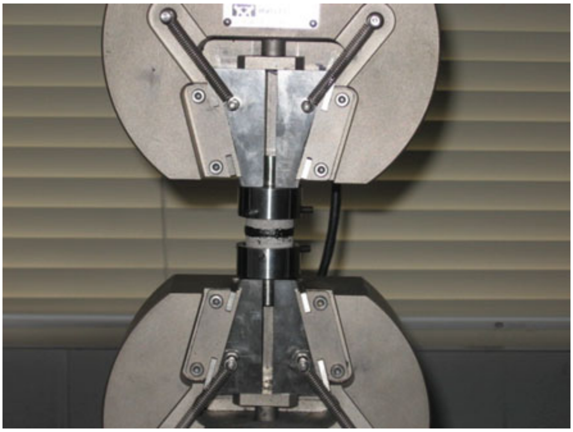

Fig. 2.7 New pull-off test

moisture susceptible bonds with certain aggregate types. Note that the granite used for producing the mastics came from a different source than the one used as substrates in the study. The proportion of the constituent components (fine aggregate, mineral filler, bitumen) of the mastics was 50:25:25 by weight of mixture and was chosen to mimic mastic mix design commonly used in open-graded friction courses. The mastics were produced by combining the dried aggregates and molten bitumen using a Hobart mechanical mixer at a mixing temperature of 185 °C.

The aggregate substrates measuring 20 mm diameter by 20 mm thick cores were obtained using carbide-tipped, electrically operated water-cooled core-drills. The top and bottom surfaces of the substrates were ground using No. 5 sandpaper, to remove all blemishes left by the sawing process, in order to get parallel surfaces to ensure complete adhesion of mastic to aggregate surfaces during the adhesion testing. The fabrication of the substrates was completed by washing the substrates in deionised water (25 °C) and then drying them in an oven at 70 °C for 48 h. For each testing condition (aggregate type, mastic type and moisture conditioning time), six substrates measuring 20 mm diameter by 20 mm thick were cored in order to fabricate three replicate aggregate-mastic butt joints.

The substrates and mastic were heated to a temperature of 140 °C. Small amounts of mastic were then poured into silicone moulds to form mastic films of dimensions approximately 3 mm thick and about 26 mm diameter. The mastic films were annealed to the 20 mm diameter hot (130 °C) aggregate substrates. A second aggregate substrate, also at 130 °C was annealed to the exposed face of the mastic to form a butt joint comprising the 3 mm thick mastic sandwiched between two aggregate substrates. Moisture conditioning was performed at 20 °C by partially submerging the substrate in water such that only about 1–2 mm of the bottom aggregate substrate was exposed to the open air. This arrangement ensured that the aggregate-mastic interface was completely dry at the beginning of a test and, therefore, moisture reached the aggregate/mastic bond only through the aggregate.

2.4 Results of the RRT for Aggregate, Bitumen Affinity

2.4.1 Rolling Bottle Test

A total of 8 laboratories conducted the rolling bottle test following EN 12697-11 clause 5. The test was performed for 6 and 24 h, three laboratories have run the test to 48 and 72 h as well. For these conditions for the three different bituminous binders, four different aggregates and two time periods for eight laboratories and additional two time periods for three laboratories a total of 264 pieces of data were generated and further analysed (Porot et al. 2015).

After each period of the test, the aggregate coating was reported as the percentage of residual binder covering the aggregates, 100% being fully coated and 0% being not coated anymore. Table 2.4 displays the whole results for all laboratories with, after the 6 and 24 h period, the individual values, the average and standard deviation values. After 48 and 72 h, only the individual values and mean values are displayed.

The standard deviation after 6 h was between 4 and 19%, being lowest for limestone and highest for granite. After 24 h, the standard deviation was between 6 and 21%; still limestone was displaying the lowest value while the granite value was improved as the average value was very low or null. For an intermediate coating value, the standard deviation was high. The determination of

Table 2.4 Rolling bottle test results

	Granite			Basalt			Greywacke			Limestone		
	Bit 1 (%)	Bit 2 (%)	Bit 3 (%)	Bit 1 (%)	Bit 2 (%)	Bit 3 (%)	Bit 1 (%)	Bit 2 (%)	Bit 3 (%)	Bit 1 (%)	Bit 2 (%)	Bit 3 (%)
Rolling bottle results after 6 h												
Lab 1	25	25	35	50	60	75	85	80	80	95	90	95
Lab 2	65	60	70	65	65	65	80	75	85	80	80	85
Lab 3	70	70	75	70	80	90	85	85	95	85	85	90
Lab 4	50	30	70	60	60	75	85	85	85	90	90	95
Lab 5	55	70	70	70	75	80	80	80	80	85	85	85
Lab 6	30	30	70	90	90	100	80	80	95	95	90	95
Lab 10	35	40	50	80	90	95	50	60	70	90	90	90
Lab 13	65	65	70	85	75	90	65	65	85	85	85	85
Average	49	49	64	71	74	84	76	76	84	88	87	90
Std. dev.	17	19	14	13	12	12	12	9	8	5	4	5
Max	*70*	*70*	*75*	*90*	*90*	*100*	*85*	*85*	*95*	*95*	*90*	*95*
Min	*25*	*25*	*35*	*50*	*60*	*65*	*50*	*60*	*70*	*80*	*80*	*85*
Rolling bottle results after 24 h												
Lab 1	0	0	5	10	20	40	30	50	50	85	85	90
Lab 2	20	5	30	20	30	30	75	45	60	75	70	75
Lab 3	30	25	40	30	40	60	60	65	75	65	75	80
Lab 4	5	5	20	15	10	30	40	60	60	60	85	85
Lab 5	20	20	30	60	60	70	50	45	55	65	70	75
Lab 6	5	5	5	35	25	75	20	15	40	80	80	90
Lab 10	5	5	15	20	35	40	25	15	25	70	75	85
Lab 13	15	5	35	60	50	70	30	15	50	75	70	75
Average	13	9	23	31	34	52	41	39	52	72	76	82
Std. dev.	10	9	13	19	16	19	19	21	15	8	6	7
Max	*30*	*25*	*40*	*60*	*60*	*75*	*75*	*65*	*75*	*85*	*85*	*90*
Min	*0*	*0*	*5*	*10*	*10*	*30*	*20*	*15*	*25*	*60*	*70*	*75*

(continued)

Table 2.4 (continued)

	Granite			Basalt			Greywacke			Limestone		
	Bit 1 (%)	Bit 2 (%)	Bit 3 (%)	Bit 1 (%)	Bit 2 (%)	Bit 3 (%)	Bit 1 (%)	Bit 2 (%)	Bit 3 (%)	Bit 1 (%)	Bit 2 (%)	Bit 3 (%)
Rolling bottle results after 48 h												
Lab 2	10	5	5	10	20	15	55	35	35	55	55	70
Lab 4							15	40	35	50	75	80
Lab 10	0	0	5	5	30	30	15	5	10	50	65	80
Average	5	3	5	8	25	23	28	27	27	52	65	77
Rolling bottle results after 72 h												
Lab 2	0	0	0	0	20	15	55	25	25	55	55	65
Lab 4								15	20	50	70	80
Lab 10	0	0	0	0	30	30	5	0	5	40	50	70
Average	0	0	0	0	25	23	30	13	17	48	58	72

Reproducibility was difficult within this round robin test as the number of laboratories was not enough to determine a reliable statistical analysis. For a probability of 95%, this led to reject five values over 100, in other words it requires at least 20 data points to reject one. When considering a probability of 95% resulting in twice the standard deviation, the reproducibility could be assessed as follows (Table 2.5).

The graphs display the results after 6 and 24 h for each aggregate and each bituminous binder. The error bars provide the variability of the results and are equal to minimum and maximum values from the eight laboratories.

Figure 2.8 displays the result after 6 h. The scattering of the results between laboratories was high. Granite aggregates displayed the worst results with values between 25 and 75%. Limestone aggregates displayed good results with limited variability, between 80 and 95%. However it was not discriminating enough to clearly distinguish between basalt and greywacke with values between 50 and 100%. When considering the different binders, the polymer modified binder might display slightly better results, but it was still within the variability of the results.

Figure 2.9 displays the results after 24 h. The scattering of the results was still high but the outcomes become more selective between aggregates. The extreme results, bad results for granite and good results for limestone, were more pronounced. Intermediate aggregates, basalt and greywacke, had intermediate values with a high variation between 10 and 75%. And again the polymer modified binder might display better results but the variability overlaps that of the standard bitumen.

The results after 48 and 72 h were recorded by 3 laboratories and are relevant for the aggregates which remained coated after 24 h. Figure 2.10 presents the results.

Table 2.5 Assessment of the rolling bottle test reproducibility

Value	<25%	>25% < 75%	>75% < 90%	>90%
R	20%	40%	20%	10%

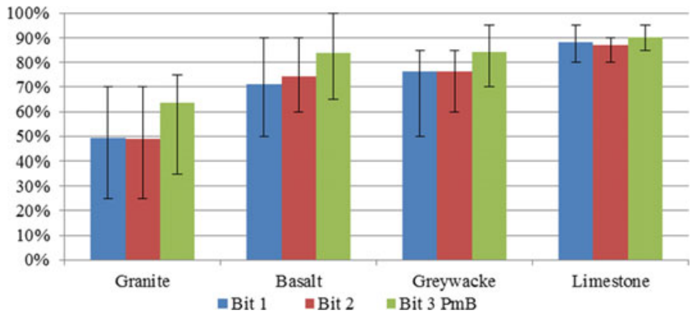

Fig. 2.8 Results of the rolling bottle test after 6 h

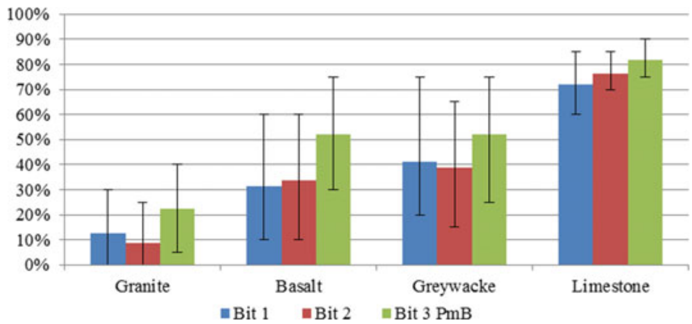

Fig. 2.9 Results of the rolling bottle test after 24 h

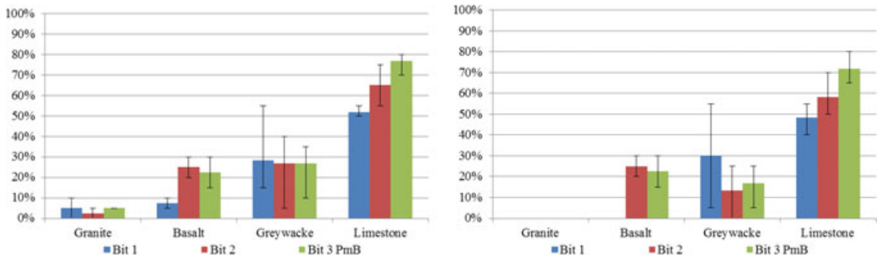

Fig. 2.10 Rolling bottle test results after 48 and 72 h

Each participant of this round robin test used the same standard test method. While the standard describes the different conditions to prepare the sample, to run the test and to interpret the results, there is still some freedom to conduct the test. Six laboratories over the eight reported precisely the test conditions, Table 2.6 summarises the main testing conditions that were reported.

Table 2.6 Rolling bottle test conditions

Laboratory	EN 12-697	Lab 3	Lab 4	Lab 5	Lab 6	Lab 10	Lab 13
Aggregate size	6/10 or 8/11	6/10	8/11	8/11	8/11	8/11	8/11
Washed or not	Washed	Washed		Washed	Washed	Washed	Washed
Factor for agg. density	Eventually	No	Yes	Yes	No	No	Yes
Mixing temperature	For 50/70, 150 °C					150 °C for 50/70 180 °C for PmB	140 °C for 50/70 180 °C for PmB
Waiting time before test	12–64 h at 20 °C					@ 18 h	
Rolling speed	60 rpm	60	40	40 50/70 60 PmB	60	60	60
Temperature at beginning	5 °C			5 °C		5 °C	5 °C
Test temperature	15–25 °C	17 °C		21 ± 2 °C	21 °C	21–25 °C	23 ± 2 °C

Aggregate size is either 6/10 or 8/11, most of laboratories used the 8/11 gradation, only one used the 6/10. In all cases, aggregates were washed before the test. One reported they removed the flat and elongated aggregates from basalt.

As the aggregate density may be different due to the petrographic nature of the stone, the standard advises to adjust the quantity of binder with a density factor, however only 3 laboratories reported they did so.

The mixing, temperature was in accordance with the one required by bitumen grade, 150 °C for the 50/70 pen grade bitumen and 180 °C for the PmB.

After mixing, the coated aggregates have to be kept between 12 and 64 h at 20 °C. However the exact time was not specifically reported by the laboratories.

The speed of the rolling bottle is adjustable according to the grade of the binder; the softer the bituminous binder, the lower the speed is. For the 50/70, only two laboratories used 40 rpm while the others used 60 rpm as recommended by the standard.

Finally the test temperature has to be between 15 and 25 °C. As the test is done at room temperature, there were some variations between laboratories but the temperature was reported between 17 and 23 °C with half of participants running the test at 21 °C.

2.4.2 Boiling Water Stripping Test

Only 2 laboratories conducted the boiling water stripping test according to EN 12697-11 clause 7 and one according to the French XP T 066-043 standard (066-043).

Table 2.7 displays the results for both test methods. The results of the test run according to EN 12697-11 are presented, with the corresponding average values, standard deviation and min/max values. Latter relative deviations permit a comparison with the precision data stated in the current European standard EN 12697-11 clause 7.8.

In this study, no repeated tests were carried out; consequently the determination of the repeatability is not possible. Moreover, as for the EN method, only two sets of data are available, a valid statistical analysis in order to assess the reproducibility of the test method by calculating R-values is also not conceivable (at present no reproducibility data are recorded in EN 12697-11 clause 7.8). Therefore, in order to evaluate the results summarised in Table 2.7, relative differences between the average values and individual laboratories were matched against the repeatability coefficient of variation of 15% as indicated in the European standard, although the latter criterion is based on results generated by one laboratory. However, by performing such an exercise, the limited data available can be discussed in terms of precision. The findings of the latter comparison include:

- All relative maximal differences between a test result obtained by one laboratory and the average result are smaller than 15%, except for one case (combination of granite and bitumen 2). Therefore, the results as reported by both laboratories are very consistent and consequently no differences in terms of ranking were observed.

Table 2.7 Results of the boiling water stripping tests

	Granite			Basalt			Greywacke			Limestone		
	Bit 1 (%)	Bit 2 (%)	Bit 3 (%)	Bit 1 (%)	Bit 2 (%)	Bit 3 (%)	Bit 1 (%)	Bit 2 (%)	Bit 3 (%)	Bit 1 (%)	Bit 2 (%)	Bit 3 (%)
Boiling water test according to EN 12697-11												
Lab 6	23	44	57	76	87	97	nd	81	77	91	85	91
Lab 7	23	17	44	94	92	96	49	66	82	85	86	96
Average	23	31	51	85	90	97	49	74	80	88	86	94
Std. dev.	0	19	9	13	4	1	–	11	4	4	1	4
Max	23	44	57	94	92	97		81	82	91	86	96
Min	23	17	44	76	87	96		66	77	85	85	91
Boiling water test according to XP T66-043												
Lab 11	0	0	<50	75	90	100	<50	<50	90	75	75	90

nd not determined

- It is worthwhile noting that for neither laboratory a difference between the test result (average of two runs) and an individual value exceeded 5% in absolute terms (data not shown).
- As anticipated, the scattering of test results increased in cases where aggregate was more prone to stripping and consequently the degree of bitumen coverage decreased (e.g. granite/bitumen combinations).

In Fig. 2.11 the average results of EN 12697-11 for the water boiling stripping test are plotted together with their spread. The error bars provide the variability of the results and are equal to minimum and maximum values from the two laboratories.

The granite displayed the worst results with residual equivalent coating between 20 and 50%, while both limestone and basalt have the best results above 80% coating. Greywacke had somewhat intermediate results between 50 and 80%. In the case of this test it is worth to notice a recordable difference between binders especially the neat unmodified bituminous binder when affinity is not above 80% coating. However, surprisingly the PmB, having a higher softening point than the neat binders, does not show significantly higher values.

The outcome of the boiling water stripping tests using the EN standard was compared to the result of the French test XP T66-043. Table 2.7 summarised the results for both test methods. As only one laboratory carried out this latter test, no statistical analysis could be done.

Although the test result of the French method XP T66-043 is expressed while making use of 6 different classes of residual coating, quantitative results are in correlation with the results obtained in the boiling water stripping test. Not only a similar ranking is observed, but for some cases the visual appreciation is very close to the quantitative result as obtained by titration according to EN 12697-11 clause 7 especially for limestone and basalt.

It should also be noted that by using a class <50% for all test results corresponding to a stripping percentage lower than 50%, the possible variability in the test result, as obtained by visual appreciation of the remaining area coated with bitumen, is, to some extent, strongly reduced. This approach is of particular interest

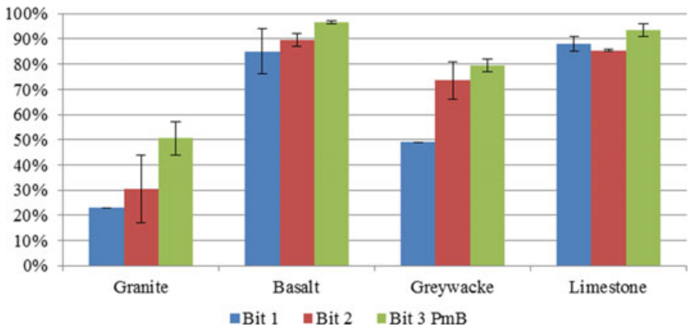

Fig. 2.11 Results of the boiling water stripping test

for aggregates showing a rather intermediate or even low affinity with bituminous binders in the presence of water such as granite. Applying such methodology also circumvents the high spread in test results as observed for instance in the rolling bottle test.

It is worth to notice that the softening point of the PmB was around 60 °C in the same magnitude of range as the test temperature, while for the unmodified binders the softening point was about 50 °C. A viscosity effect of the binders may be induced with better results for the PmB as can be seen systematically for the four different aggregate types.

2.4.3 *Bitumen Bond Strength*

For the bitumen bond strength, three laboratories performed the test, two using the same protocol, lab 8 and lab 9 and the third one, lab 10, using the developed protocol for mastic. For the conventional BBS test, the dry samples were tested first at temperatures of 15, 22 and 30 °C with the four different aggregate types (granite, basalt, greywacke and limestone), the same temperature range being used to evaluate early ravelling. Different moisture conditioning regimes (time and temperature conditioning) were used by the three laboratories.

2.4.3.1 BBS Results with Dry Strength Measurements

Table 2.8 provides the overall results for the standard BBS test, as performed by the two laboratories with calculated average and standard deviation values even if this latter value is not really meaningful as there were only two test results.

The graphs in Fig. 2.12 display the dry results at 15 °C, Fig. 2.13 at 22 °C and Fig. 2.14 at 30 °C. The average values are displayed while the error bars are for the two max and min values.

When considering the binder types, differences were within the variability of the measurements. For the aggregates types, except for granite displaying slightly lower strength, they all had the same values. The differences were even lower at 22 and 30 °C. The polymer modified binder showed lowest POTS in all temperatures and aggregate types relative to unmodified binders. It is also worth to notice that for both laboratories the failure was reported as cohesion failure and not adhesion failure.

Overall the dry bond strength decreased with increasing test temperature. At 15 °C, the strength was about 4–5 MPa, at 22 °C it decreased to 3 MPa and at 30 °C to 2 MPa. Results demonstrate the sensitivity of the pull-off tensile strength (POTs) parameters to test temperature and then to the bitumen stiffness.

This outcome is not unexpected as the stiffness of the bituminous binder changes significantly over this range of temperatures. Temperature susceptibility for all asphalt binder types was relatively close in the range of 50–63%. This observation

Table 2.8 Results of the bitumen bond test, dry measurements

	Granite			Basalt			Greywacke			Limestone		
	Bit 1	Bit 2	Bit 3	Bit 1	Bit 2	Bit 3	Bit 1	Bit 2	Bit 3	Bit 1	Bit 2	Bit 3
Bitumen bond strength (MPa), dry measurement at 15 °C												
Lab 8	4.08	4.94	4.54	4.80	4.51	5.16	5.21	5.11	3.51	4.58	4.62	4.24
Lab 9	3.73	4.83	4.94	4.61	3.87	4.47	4.58	3.94	4.06	4.04	4.22	4.21
Average	3.91	4.88	4.74	4.71	4.19	4.81	4.90	4.52	3.78	4.31	4.42	4.22
Std. dev.	0.25	0.08	0.28	0.13	0.45	0.49	0.44	0.83	0.39	0.38	0.28	0.02
Bitumen bond strength (MPa), dry measurement at 22 °C												
Lab 8	3.34	3.25	3.70	3.31	3.30	3.21	3.42	3.42	2.32	2.89	2.77	2.96
Lab 9	3.12	3.28	3.25	3.11	2.80	2.95	2.94	2.99	2.57	2.80	2.68	2.72
Average	3.23	3.27	3.47	3.21	3.05	3.08	3.18	3.20	2.45	2.85	2.73	2.84
Std. dev.	0.16	0.02	0.32	0.14	0.35	0.18	0.34	0.30	0.18	0.06	0.06	0.17
Bitumen bond strength (MPa), dry measurement at 30 °C												
Lab 8	1.94	2.31	2.36	1.84	2.17	2.45	2.41	2.15	1.83	2.30	2.29	2.15
Lab 9	1.85	1.76	2.13	1.98	1.85	1.68	2.04	1.68	1.68	1.66	1.79	1.66
Average	1.89	2.04	2.25	1.91	2.01	2.07	2.22	1.91	1.75	1.98	2.04	1.90
Std. dev.	0.06	0.39	0.16	0.10	0.23	0.54	0.26	0.33	0.11	0.45	0.36	0.35

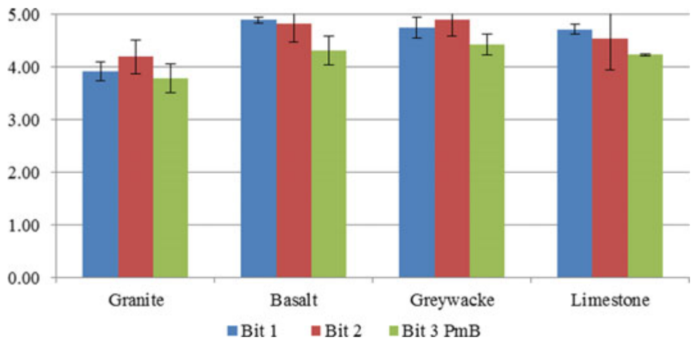

Fig. 2.12 Bitumen bond strength results at 15 °C in MPa

emphasises the significance of climatic conditions on asphalt binder selection to prevent in-service ravelling and justifies the use of three test temperatures to fully capture the bond strength vs. temperature relationship.

The dry strength is not able to address the differences in either binder or in aggregate types. For each temperature, the dry results had not statistically independent values towards aggregate types of binders. Thus the average calculation of the standard deviation is about 10% which provides an indication of the test accuracy.

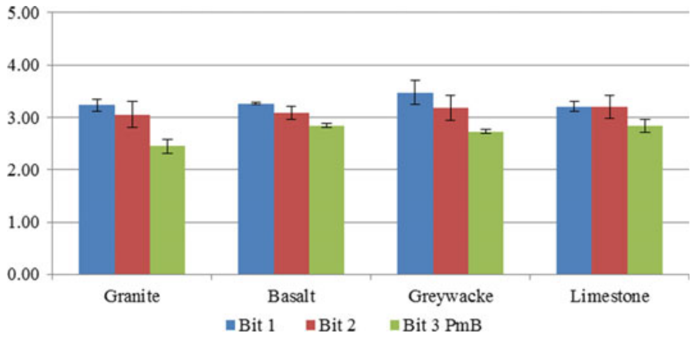

Fig. 2.13 Bitumen bond strength results at 22 °C in MPa

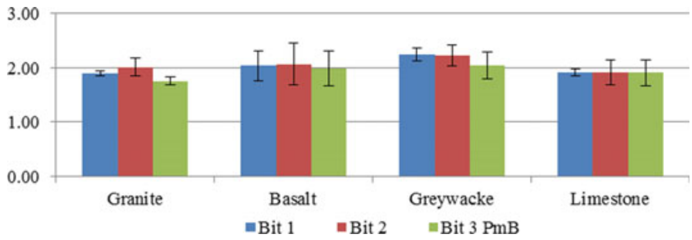

Fig. 2.14 Bitumen bond strength results at 30 °C in MPa

2.4.3.2 Results of Moisture Damage Evaluation

The moisture damage was evaluated using the Bond Strength Ratio (BSR) defined as the ratio between wet and dry bond strength at 22 °C. Table 2.9 provides the results of the wet bond strength at 22 °C and the calculated BSR. The failure mode is recorded as A for adhesion and C for cohesion.

It is worth to notice that except for granite which was adhesion failure, the failure mode was cohesion failure similarly to the dry results. This can either means that the water did not reach the binder aggregate bond and the failure is still cohesive or the water did reach the bond, but the adhesion is still stronger than the cohesion. Particularly for greywacke and limestone the difference between dry and wet strength is negligible and in the accuracy of the test.

Figure 2.15 displays the bitumen bond strength under wet conditions at 22 °C with average values and error bars being for the values of both laboratories. While for greywacke and limestone the measurements for both labs displayed a low variability, for granite and basalt, the variation was much higher. In addition for wet

Table 2.9 Results of the bitumen bond test, wet measurements

	Granite			Basalt			Greywacke			Limestone		
	Bit 1	Bit 2	Bit 3	Bit 1	Bit 2	Bit 3	Bit 1	Bit 2	Bit 3	Bit 1	Bit 2	Bit 3
Bitumen bond strength (MPa), wet measurement at 22 °C												
Lab 8	0.85	0.47	0.53	1.92	1.77	1.45	3.51	2.79	2.79	3.13	2.91	2.91
	A	A	A	C	C	C	C	C	C	C	C	C
Lab 9	1.82	1.33	1.30	2.90	1.27	2.46	3.17	2.90	2.80	3.07	2.67	2.52
	A	A	A	C	C	C	C	C	C	C	C	C
Average	1.34	0.90	0.92	2.41	1.52	1.96	3.34	2.85	2.80	3.10	2.79	2.72
Std. dev.	0.69	0.61	0.54	0.69	0.35	0.71	0.24	0.08	0.01	0.04	0.17	0.28
Bitumen bond strength ratio (at 22 °C)												
Lab 8	25	14	23	59	55	50	95	82	101	95	85	98
Lab 9	58	47	51	88	43	88	98	98	104	99	89	93
Average	42	31	37	74	49	69	96	90	103	97	87	96
Std. dev.	23	23	20	21	9	27	2	12	3	3	3	4

measurements, after water conditioning, the results were sensitive to the aggregate types with lower values for granite, around 1 MPa and also for basalt around 1.5–2 MPa. greywacke and limestone values were in the same range of magnitude as the dry measurements, around 3 MPa.

Considering binder types, there was a slight difference with Bitumen 1, unmodified bitumen having higher wet strength values compared to the others and even the modified binder did not show better values (Fig. 2.15).

Figure 2.16 displays the Bitumen Bond Strength Ratio (BSR) at 22 °C with average values while the error bars are for the two max and min values.

The results presented indicate a significant variation in resistance to moisture damage as measured by the bonding strength ratio due to changing asphalt binder and aggregate types. Results range from no moisture damage (BSR > 100%) to significant moisture damage (BSR < 50%). The BSR value can be considered to be similar to the wet to dry Tensile Strength Ratio (TSR) for hot mix asphalt, where a limiting value of 80% is commonly used to evaluate sensitivity. If a limiting BSR of 80% is used as a criterion to indicate failure, it appears that greywacke and limestone with BSR > 80% can be considered moisture resistant, while granite and basalt can be considered as moisture sensitive with BSR < 80%. Six combinations out of twelve will pass this criterion.

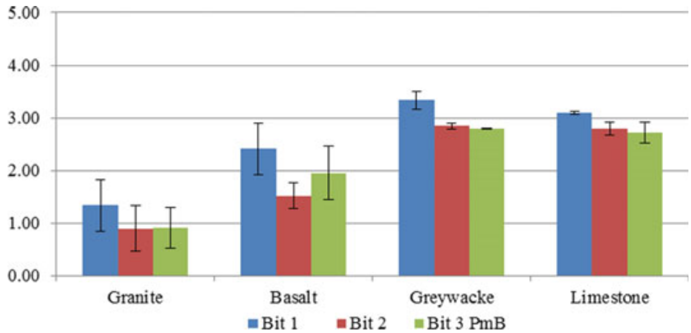

Fig. 2.15 Bitumen bond strength wet measurements at 22 °C (MPa)

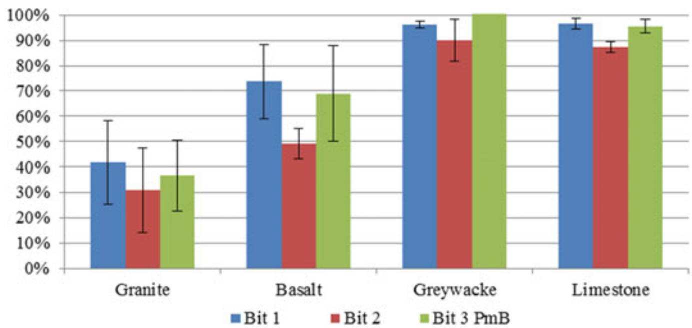

Fig. 2.16 Bitumen bond strength ratio at 22 °C (%)

Based on the BSR results, the BBS test is able to discriminate aggregate/bituminous binder combinations that are highly moisture sensitive such as granite. For the other case, as the failure is on cohesive bond, some other factors certainly affect the outcomes like water absorption of the stone, conditioning process or even size and shape of the sample.

2.4.3.3 Results of the New Pull-off Test

The effect of moisture for three different conditioning times (0, 3 and 7 days) on aggregate-mastic interfacial bond strength was determined by using a new pull-off test, called NOPTS (Zhang et al. 2015; Apeagyei et al. 2014). All the tensile tests were conducted at the same testing temperature of 25 °C using a constant cross-head speed of 20 mm/min. Three replicate specimens were tested. The results were used to estimate aggregate-mastic bond strength as a function of aggregate type and conditioning time. Some of the advantages of the NOPTS are the ability to precisely measure the loading rate, film thickness of both bitumen and mastics and simulate moisture diffusion at the aggregate-binder interface.

Due to lack of material and time only one binder, the Bit 2 50/70 pen bitumen was tested. The results for three replicate specimens conditioned in water and tested at 25 °C are summarised in Table 2.10 and Fig. 2.17.

The results showed that in the dry state, the difference between granite and limestone bond strength are not statistically significant. The effect of moisture was aggregate dependent. The effect of moisture on limestone bonds was not statistically significant even after 7 days of conditioning. However, significant degradation of strength can be seen in granite bonds as bond strength decreased after 7 days of moisture conditioning.

Table 2.10 New pull-off test results (MPa)

Conditioning time (days)		Granite	Basalt	Greywacke	Limestone
0 day	Mean value	2.18	4.71	4.20	3.43
	Std. dev.	0.64	0.62	1.01	0.48
3 days	Mean value	0.36	4.37	5.04	3.38
	Std. dev.	0.23	0.18	0.46	0.61
7 days	Mean value	0.22	5.32	4.56	3.96
	Std. dev.	0.16	1.02	0.61	0.48

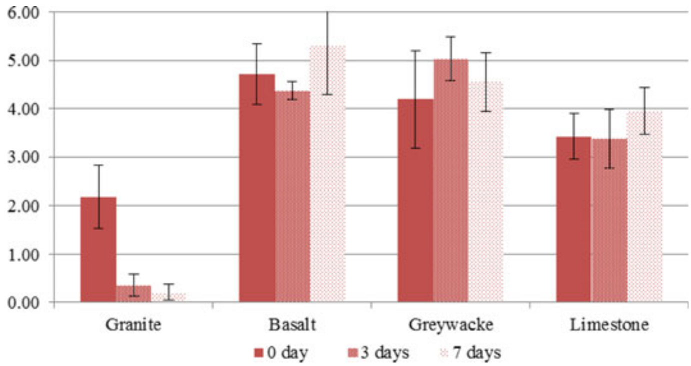

Fig. 2.17 NOPTS bond strength after 0, 3, 7 days water conditioning (MPa)

2.5 Surface and Adhesion Intrinsic Properties

2.5.1 Theoretical Background on Surface Properties

The surface free energy 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 as in asphalt mixture are mainly comprised of an apolar (nonpolar) component and an acid-base component (Fowkes 1962; Good and van Oss 1991; Good 1992). Equation (2.1) is used to describe the total surface energy and its components:

$$\gamma = \gamma^{LW} + \gamma^{AB} \tag{2.1}$$

where

γ surface energy of bitumen or aggregate (mJ/m2);

γ_{LW} Dispersive part of Lifshitz–van der Waals interaction of the surface energy (mJ/m2); and

γ_{AB} Polar part of Lifshitz–van der Waals interaction and 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 (Good and van Oss 1991) postulated a resolution of the acid-base term, γ^{P} into a Lewis acidic surface parameter and a Lewis basic surface parameter. The relationship between the γ^{P} and its components is shown in Eq. (2.2):

$$\gamma^{AB} = 2\sqrt{\gamma^{+}\gamma^{-}} \tag{2.2}$$

where

γ^{+} Lewis acid component of surface interaction, and
γ^{-} Lewis base component of surface interaction.

Surface tension is the work necessary to create a surface of a unit area. In terms of vocabulary, surface tension is referred to the liquid/vapour interface. For the solid/vapour interface, the term surface energy is used. The energy needed to separate two immiscible media is called interfacial tension.

Liquid surface tension and substrate surface energy can be divided into a polar γ_P and a dispersive component γ_D. This dispersive component corresponds to Van der Waals interactions and is present in every molecule (Miller et al. 2012). According to Good-Van Oss theory, the polar component can be separated into electron donor γ^{+} (Lewis acid) and electron acceptor γ^{-} (Lewis base) components (Miller et al. 2012). The overall surface energy or surface tension is:

$$\gamma = \gamma^{D} + \gamma^{P} = \gamma^{D} + 2\sqrt{\gamma^{+}\gamma^{-}} \tag{2.3}$$

Liquid/substrate adhesion work W_{adh} can be expressed as a function of the substrate surface energy γ_S, the liquid surface tension γ_L and the liquid/substrate interfacial tension γ_{SL}:

$$W_{adh} = \gamma_S + \gamma_L - \gamma_{SL} \tag{2.4}$$

W_{adh} can also be divided into two components to deduce the polar and non-polar interactions occurring at the interface:

$$W_{adh} = W^{P}_{adh} + W^{D}_{adh} \tag{2.5}$$

where W^{P}_{adh} and W^{D}_{adh} are the polar and the dispersive components of adhesion work respectively.

Surface energy of substrates and binder/substrate interfacial tension is strongly correlated to binder wetting. For a liquid drop deposition onto a solid surface, several wetting regimes can be observed:

- The liquid spreads completely; contact angle close to zero
- The liquid partially wets the surface. At equilibrium, the liquid presents a hemispherical shape and forms a contact angle θ with the surface; $0 < \theta < 180°$
- The liquid does not wet the solid. In this case, the contact angle is close to 180°.

In the partial wetting regime and at equilibrium, the summation of the forces applied at the liquid/solid contact line equals zero. Surface energy of the solid is then determined following Young's equation which is valid for pure liquids and “ideal” surfaces, i.e. plane, rigid, smooth, chemically homogeneous and non-reactive surfaces (Beatty and Smith 2010):

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \tag{2.6}$$

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 adhesion work (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. 2.7 and 2.8). For an asphalt mixture to be durable and less sensitive to moisture, it is desirable that the adhesion work between the bitumen and the aggregate be as high as possible.

In addition to the two parameters: dry bond strength and debonding work, 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 debonding work) 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 $\left(W_{BA}^{a}\right)$ is defined as given in Eq. (2.7) as the interfacial adhesion work between the bitumen (B) and aggregate (A). A bigger value of dry bond strength suggests greater adhesion between the two materials and hence more resistance against debonding in the absence of moisture.

$$W_{BA}^{a} = 2\sqrt{\gamma_B^{LW}\gamma_A^{LW}} + 2\sqrt{\gamma_B^{+}\gamma_A^{-}} + 2\sqrt{\gamma_B^{-}\gamma_A^{+}} \tag{2.7}$$

Equation (2.8) gives the debonding work $\left(W_{BWA}^{a}\right)$ which is considered as the reduction in bond strength of a bitumen-aggregate system when water is introduced into the system or when water displaces the bitumen from the aggregate surface. A smaller value of this parameter for a given bitumen-aggregate system is indicative of a better moisture damage performance of that system.

$$\begin{aligned} W_{BWA}^{a} = & \left\{\left(\left(\sqrt{\gamma_A^{LW}} - 4.67\right)^2\right) + \left(2\times\left(\sqrt{\gamma_A^{+}} - 5.05\right)\times\left(\sqrt{\gamma_A^{-}} - 5.05\right)\right)\right\} \\ & + \left\{\left(\left(\sqrt{\gamma_B^{LW}} - 4.67\right)^2\right) + \left(2\times\left(\sqrt{\gamma_B^{+}} - 5.05\right)\times\left(\sqrt{\gamma_B^{-}} - 5.05\right)\right)\right\} \\ & - \left\{\left(\left(\sqrt{\gamma_B^{LW}} - \sqrt{\gamma_A^{LW}}\right)^2\right) + \left(2\times\left(\sqrt{\gamma_B^{+}} - \sqrt{\gamma_A^{+}}\right)\times\left(\sqrt{\gamma_B^{-}} - \sqrt{\gamma_A^{-}}\right)\right)\right\} \end{aligned} \tag{2.8}$$

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

$$ER_1 = \left| \frac{W^a_{BA}}{W^a_{BWA}} \right| \tag{2.9}$$

Aggregates with higher surface roughness and greater surface area are supposed to bond better with bitumen by providing more bond area and better interlocking. In order to accommodate this effect, a second bond energy parameter (ER1*SSA) obtained by multiplying the bond energy ratio ER_1 with specific surface area (SSA) has been proposed in addition to ER_1 to predict moisture sensitivity of asphalt mixtures.

Wetting/coating of an aggregate with bitumen is not only affected by the surface properties of the two materials; the viscosity or cohesion of the bitumen itself also plays a very important role. Bituminous binder with lesser cohesion and greater affinity for the aggregates will have a higher wettability and will coat the aggregate surface more than bitumen having less wettability characteristics. However, softer bituminous binder having lesser cohesion may be more prone to stripping (decrease in cohesion) in the presence of water. The effects of cohesion and wettability on moisture resistance can be accounted for by modifying the ER_1 parameter by replacing the bond strength in the dry condition $\left(W^a_{BA}\right)$ with a wettability relationship $\left(W^a_{BA} - W_{BB}\right)$. This new moisture sensitivity assessment parameter (ER_2) is given by Eq. (2.10). In order to accommodate the effects of aggregate micro-texture on the bitumen-aggregate bond strength in the presence of moisture, the bond parameter ER_2 can be multiplied by specific surface area of the aggregates to obtain a fourth bond energy parameter (ER_2*SSA).

$$ER_2 = \left| \frac{W^a_{BA} - W_{BB}}{W^a_{BWA}} \right| \tag{2.10}$$

where $\left(W^a_{BA}\right)$ and $\left(W_{BB}\right)$ represent bitumen-aggregate dry bond strength and bitumen cohesion respectively.

These four bitumen-aggregate bond energy parameters (ER_1, ER_1*SSA, ER_2 and ER_2*SSA) can be used to assess the moisture susceptibility of the asphalt mixtures. In all cases, higher energy ratios are associated with mixtures with better moisture resistance (Grenfell et al. 2014).

2.5.2 Methods

Three experimental devices were used to determine the surface energy of the aggregate and bitumen samples. The devices included a Dynamic Contact Angle (DCA) analyser, a Dynamic Vapour Sorption (DVS) system and a Drop Shape Analyser (DSA). The DSA, a pendant drop method, was used to determine surface energy of both aggregates and binder at different temperatures while the DCA and DVS were used to determine surface energy of binder and aggregates, respectively, at room temperature. Carefully selected probe liquids (Table 2.11) were used depending on material and device type. A brief description of the procedures used for each device is provided next.

A Thermo Scientific CAHN Radian dynamic contact angle (DCA) analyser was used to determine the surface energy components of the binders. The DCA uses the Wilhemy plate method to determine surface energy of binders. Surface energy components of each binders was estimated using the contact angles that a set of three probe liquids with known surface energy components make with bitumen (in solid state) under dynamic conditions. The probe liquids used were water, glycerol and diiodomethane. The probe liquids were selected because of their purity, their low chemical interactions with bitumen and their known surface energy components. The results of the DCA test can be used to estimate the total surface energy of bitumen as well as its cohesive bond strength (Liu et al. 2014).

During the DCA test, a clean 40 mm × 24 mm × 0.45 mm No. 15 microscope glass slide is 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 is placed on a movable stage positioned under the glass slide (Fig. 2.18). The bitumen-coated glass slide is 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 µm/s while continuously recording the change in

Table 2.11 Properties of probe liquids used for surface energy measurements

Probe liquid	γL (mN/m)	γLP (mN/m)	γL^{+} (mN/m)	γL^{-} (mN/m)	γLD (mN/m)	Device
Water	72.8	51.0	25.5	25.5	21.8	DCA
Glycerol	64.0	29.9	3.92	57.4	34.0	
Diiodomethane	50.8	0.0	0.00	0.00	50.8	
Octane	21.6	0.0	0.00	0.00	21.6	DVS
Ethyl Acetate	23.9	0.0	0.00	19.2	23.9	
Chloroform	27.2	0.0	3.80	0.00	27.2	
Water	72.8	51.0	25.5	25.5	21.8	DSA
Glycerol	64.0	29.9	3.92	57.4	34.0	
Ethylene glycol	47.7	16.8			30.9	

γL total surface energy; γLP polar component; γLD dispersive component mass of the bitumen-coated slide with depth of immersion. The results are used to compute the contact angle between the bitumen and the probe liquid. All the DCA contact angle measurements were obtained at room temperature (23 ± 2 °C and 50 ± 5% relative humidity). Three replicates of each bitumen-probe liquid combination were tested.

The DCA approach for estimating surface energy of bitumen uses measured mass-depth relationships to estimate the forces acting on a bitumen-coated slide as it is being immersed or removed from a probe liquid to determine contact angles between the binder and at least three probe liquids. The contact angle results from the three probe liquids are used in Eq. (2.11) to obtain three simultaneous equations from which the three surface energy components (γ^D, γ^+, and γ^-) can be estimated. The estimated surface energy components are then used to determine the total surface energy $\left(\gamma_B^T\right)$ of the binders using Eq. (2.12) from which the cohesive bond strength (equal to twice γ_B^T) of the binder could also be obtained.

Fig. 2.18 Dynamic contact angle analyser test set-up

$$W_{BL} = \gamma_L(1+\cos\theta) = 2\sqrt{\gamma_B^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_B^{-}\gamma_L^{+}} + 2\sqrt{\gamma_B^{+}\gamma_L^{-}} \tag{2.11}$$

where

W_{BL} adhesion work between the bitumen (B) and a probe liquid (L)
γ_L total surface energy of the probe liquid
θ contact angle between bitumen and probe liquid

$$\gamma_B^T = \gamma_B^{LW} + 2\sqrt{\gamma_B^{-}\gamma_B^{+}} \tag{2.12}$$

A DVS Advantage 2 system (Surface Measurement Systems, Middlesex, UK) was used to determine the surface energy components of the aggregates using sorption isotherms obtained at 25 °C as shown in Fig. 2.19.

The DVS tests were conducted using aggregates passing the 5 mm sieve and retained on the 2.36 mm sieve that had been cleaned with deionised water and dried in an oven at 115 °C to a constant mass. During the adsorption test, a pre-heating step was conducted combined with dry nitrogen run into the system for 800 min to ensure that any trace of moisture is removed from the sample surface. Three carefully

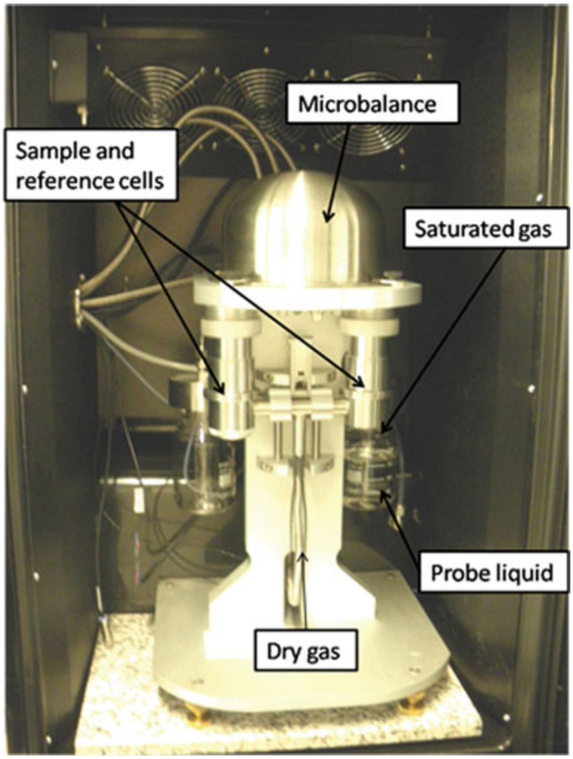

Fig. 2.19 Dynamic vapour sorption device (DVS Advantage 2)

selected probe liquids - octane, ethyl acetate, and chloroform were used. The probe liquids were selected because they have low chemical interactions with aggregates and because their surface energy components are known. The DVS approach for determining surface energy properties of aggregates involves measuring the weight gain of an aggregate sample (usually less than about 10 g in weight) kept in a sealed DVS sample chamber containing a probe liquid vapour (at partial pressures ranging from 0 to 95%). Only a single replicate of each aggregate-probe liquid combination was tested as each sorption isotherm took more than a day to complete. It is worth to notice that the instrument itself is more precise than the influence of the aggregates can have on the results. The device combines precise partial pressure control of probe liquid and unique real time vapour concentration monitoring with a high resolution (1 µg) microbalance to monitor aggregate weight gain.

For each aggregate-probe liquid combination, mass gain in the aggregates is monitored, using an ultra-sensitive balance, at 14 different partial pressures until equilibrium mass is reached at each partial pressure stage. The results (i.e. equilibrium mass) are plotted against partial pressure to generate sorption isotherms from which the SSA and spreading equilibrium pressures (Bhasin 2006) for each of the three probe liquids could be estimated. The results are then used to estimate the surface energy components of the aggregates as discussed below. Similar to Eq. (2.11) for determining surface energy of binders, Eq. (2.13) was used to generate three simultaneous equations which could be solved to obtain the three surface energy components by utilising the total surface energy and the spreading pressure of each probe liquid. The total surface energy of the aggregates is given by Eq. (2.14), using the surface energy components of the aggregates.

$$W_{AL} = 2\gamma_L + \prod\nolimits_e = 2\sqrt{\gamma_B^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_B^{+}\gamma_L^{-}} + 2\sqrt{\gamma_B^{-}\gamma_L^{+}} \tag{2.13}$$

where

W_{AL} adhesion work between an aggregate (A) and a probe liquid (L)
γ_L total surface energy of the probe liquid
π_e spreading pressure of probe liquid aggregateAggregate

$$\gamma_A^T = \gamma_A^{LW} + 2\sqrt{\gamma_A^{-}\gamma_A^{+}} \tag{2.14}$$

The Drop Shape Analyser (DSA) was used for characterising the surface properties of materials and for assessment of bitumen/mineral substrate adhesion. Surface tension of the bituminous binder was assessed using a drop tensiometer (DSA 100, Krüss GmbH) via the pendant drop method. Binder was introduced in a brass syringe, itself placed in a dosing cell heated at the target temperature. Droplets were formed automatically using DSA software below the syringe. Figure 2.20 shows the DSA equipment.

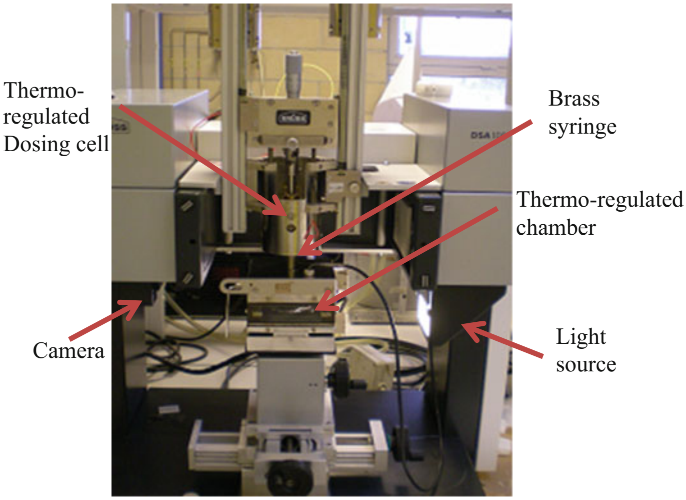

Fig. 2.20 The drop shape analyser (DSA)

The surface tension is the average value from five measurements. Surface tension, in the air, was performed at the same temperature, 120 °C, than the contact angle between the binder drop and the aggregate substrate. It is determined using equations taking into account the geometrical form of the droplet and the binder density. Dispersive and polar components of surface energy (γ_L^D and γ_L^P respectively) allow characterising the chemical interactions inside the binder. Both components are determined from a contact angle measurement of a bitumen drop on a PTFE substrate (pure dispersive material, γ_S = 20.5 mJ/m^2). They were calculated using the following Eqs. (2.15) and (2.16):

$$\gamma_L^D = \frac{\gamma_L^2(1 + \cos\theta)^2}{4\,\gamma_S} \tag{2.15}$$

$$\gamma_L^P = \gamma_L - \gamma_L^D \tag{2.16}$$

The surface energy of substrates is assessed by measuring contact angles in hot conditions (at 120 °C in this study) using a thermoregulated syringe and chamber to heat binder and aggregates. Rocks were obtained from quarries and drilled to obtain 40 mm diameter cores. Then cores are sawn in water to have 5–15 mm thick slices which have been ground to low roughness. Samples are stored in a cool place away from dust six days before the contact angle tests. Concerning the contact angle measurements, three reference liquids with different polar properties are used. They include water, glycerol and ethylene glycol. Their surface properties are presented in Table 2.11.

Liquid droplets were created automatically using a multi-dosing cell. Contact angles are determined with the software, which fits the angle with an ellipsoidal equation. The drop diameter on the slide was 3–8 mm. Contact angles are taken just after drop stabilisation. They are the average value of, at least, five measurements. The surface energy is deduced from the contact angle via the Owens-Wendt-Rabel-Kaelble:

$$\frac{\gamma_L(1+\cos\theta)}{2(\gamma_L^D)^{1/2}} = \left(\gamma_S^D\right)^{1/2} + \left(\gamma_S^P\right)^{1/2}\frac{(\gamma_L^P)^{1/2}}{(\gamma_L^D)^{1/2}} \quad (2.17)$$

γ_S^D and γ_S^P are the dispersive and the polar component of the mineral substrate respectively, γ_L^D and γ_L^P are the dispersive and the polar component of the reference liquid respectively, γ_L is the surface tension of the reference liquid, θ is the reference liquid/mineral substrate contact angle.

Finally, bitumen binder/mineral substrate adhesion work W_{adh} is theoretically determined using Eq. (2.18):

$$W_{adh} = 2\left[\left(\gamma_L^D\gamma_S^D\right)^{1/2} + \left(\gamma_L^P\gamma_S^P\right)^{1/2}\right] \quad (2.18)$$

According to contact angle measurements between binder droplets on mineral substrate, adhesion work W_{adh} could be also determined using the Dupre equation:

$$W_{adh} = \gamma_L(1+\cos\theta) \quad (2.19)$$

In this case, contact angle measurements are performed using a binder and a substrate heated at the same temperature.

2.5.3 *Results of Intrinsic Adhesion Properties*

2.5.3.1 Binders Surface Tension

Surface tension of the binders has been measured using the Dynamic Contact Angle (DCA) analyser with Wilhelmy plate and the Drop Shape analyser (DSA) in pendant drop configuration. Results are reported on Table 2.12. It has to be noted that the temperature of measurements are different, 23 °C for the DCA and 120 °C for the DSA.

Table 2.12 Surface tension of three binders by the DCA and the DSA method

Binder ID	Summary—SE components (mN/m)						
	DCA method (T = 23 °C)				DSA method (T = 120 °C)		
	γ^D	γ^+	γ^-	γT	γD	γP	γT
Bit 1	18.82	0.34	5.08	**21.44**	16.64	10.81	**27.46**
Bit 2	20.75	0.06	2.90	**21.57**	16.34	10.55	**26.89**
Bit 3	26.63	0.00	4.86	**26.64**	17.18	9.69	**26.87**

The same order of magnitude was found when considering the total surface tensions of the three binders using both methodologies, DCA and DSA. The values of Table 2.12 appear to be between 19 and 27 mN/m. Values generally reported in the literature (Lytton and Flumerfelt 1998; Shell et al. 1979; Saal 1933) are between 24 and 33 mN/m. Surface tensions from the DCA method on the unmodified binders appear, by consequence, lower than expected. However, DCA and DSA methods give the same values for the PmB binder (γ^T = 26.6 mN/m for DCA and γ^T = 26.9 mN/m for DSA).

Surface tension is generally found to be independent of binder nature. The DSA method agrees with this observation. Moreover, both methods show that bituminous binder surface tension is more dispersive than polar, while there is polar difference reported between DCA and DSA.

2.5.3.2 Aggregates Surface Energy

Surface energy of aggregates, measured with the Dynamic Vapour Sorption Test (DVS) and the Contact Angle Measurement (CAM), are reported on Table 2.13. Small particles (5–2.36 mm) are used for the DVS method whereas bulk and not polished flat samples are used for the CAM method.

Whatever the method, surface energy appears to be dependent on aggregate nature. Considering the total surface energy, both methods give the same value for the greywacke (71 mN/m). However, a difference of 10 mN/m is found for the granite while a difference of 20 mN/m is found for the limestone. What is very curious is the repartition between the polar and dispersive components. The DVS method always gives a dispersive component of the surface energy superior to the polar component. This is quite unexpected when comparing to literature values. On the contrary, the CAM method shows a polar component superior to the dispersive one, except for the limestone.

These total surface energies differences could be explained by the surface characteristic of the aggregates. In the DVS method, crushed particles are used whereas sawed blocks are used for the CAM method. It has to be noted that these differences between methods have already been observed during the NCHRP program (Little and Bhassin 2006).

Table 2.13 Surface energy of the four aggregates

Aggregate type	Summary—SE components (mJ/m^2)						
	Method 1 (DVS)				Method 2 (CAM)		
	γ_{LW}	γ^+	γ^-	γT	γD	γP	γT
Granite	56.4	0.28	12.7	**60.17**	9.30	59.88	**69.18**
Basalt	–	–	–	–	13.85	45.11	**58.96**
Greywacke	56.53	2.22	22.27	**70.58**	6.15	64.90	**71.05**
Limestone	56.74	0.39	14.78	**61.56**	24.07	16.87	**40.94**

2.5.3.3 Adhesion Work Between Aggregates and Binders

Adhesion work is calculated using two approaches. The first uses bitumen surface tension and aggregate surface energy measurements through a theoretical calculation: Eq. (2.7) (associated with DCA and DVS methods) and Eq. (2.18) (associated with DSA and CAM method). Results using this approach are reported in Table 2.14. It should be noted that Eqs. (2.7) and (2.18) are equivalent in theory and should therefore result in similar results. However, in practice, Eq. (2.7) has been found to be more accurate.

The second uses the contact angle measurements at 120 °C between bitumen and aggregate (CAM method) and the bitumen surface tension measurements (from DSA method) to calculate the work of adhesion of the binder on the aggregate and the interfacial tension at the interface. Results using this approach are reported in Table 2.15.

Concerning the first approach, whatever the method used, values of adhesion work were between 66 and 84 mJ/m^2. Obviously, differences between both methods reflect the observations made on the surface tension and surface energy measurements. By consequence, both methods give adhesion work values very sensitive to aggregate nature. If we consider only greywacke, granite and limestone, method 1 gives the greywacke as the best and granite as the worst aggregate; method 2 gives the granite as the best and the limestone as the worst aggregate.

Table 2.14 Calculated adhesion work (Wa_{th}) between aggregate and bitumen from measured dispersive and polar components of γ_L and γ_S

Aggregate ID	Summary Wa (mJ/m^2)					
	Method 1 (Eq. 2.7)			Method 2 (Eq. 2.18)		
	Bit 1	Bit 2	Bit 3	Bit 1	Bit 2	Bit 3
Granite	71.69	71.94	79.86	75.79	74.93	73.47
Basalt	–	–	–	74.55	73.73	72.68
Greywacke	77.44	75.86	84.20	73.23	72.39	70.72
Limestone	72.65	72.62	80.52	67.05	66.35	66.25

Table 2.15 Experimental method: Adhesion work (Wa_{exp}) between aggregate and bitumen and interfacial tension (γSL) from contact angle measurement (T = 120 °C)

	Bit 1			Bit 2			Bit 3		
	θ (°)	Wa_{exp} (mJ/m^2)	γ_{SL} (mN/m)	θ (°)	Wa_{exp} (mJ/m^2)	γ_{SL} (mN/m)	θ (°)	Wa_{exp} (mJ/m^2)	γ_{SL} (mN/m)
Granite	8.4	54.62	42.02	8.8	53.47	42.61	15.0	52.85	43.22
Basalt	10.1	54.49	31.94	9.4	53.43	32.44	15.3	52.81	33.04
Greywacke	10.1	54.49	44.02	9.1	53.45	44.50	11.9	53.18	44.76
Limestone	9.8	54.52	13.88	8.4	53.50	14.33	15.0	52.84	14.98

The highest adhesion works were found for Bit 3 using method 1. On the contrary, the lowest adhesion works were found for the Bit 3 using method 2.

The second approach, as shown in the Table 2.15, gives adhesion work (Wa_{exp}) between 53 and 55 mJ/m^2, being very insensitive to aggregate nature. Whatever the aggregates, the lowest adhesion works (associated with higher contact angle) were found for Bit 3, which is consistent with the semi-theoretical approach, method 2 (Table 2.14). The interfacial tension has also been calculated ($\gamma_{SL} = \gamma s + \gamma_L - Wa_{exp}$) and reported in Table 2.15. The interfacial tension appeared to be strongly influenced by the surface energy of the aggregate (γs). In comparison to other aggregates, a very low value of interfacial tension was found for the limestone. Considering the Wa_{exp}, they were similar for all aggregates; the interfacial tension could be interesting to rank aggregates. In this case, it would distinguish limestone as a good aggregate for binding according to the low interfacial tension value measured.

2.5.3.4 Debonding Work, Compatibility Ratio

Debonding work is considered as the reduction in bond strength of a binder-aggregate system when water is introduced into the system or when water displaces the binder from the aggregate surface. A smaller value of this parameter for a given binder-aggregate system is indicative of a better moisture damage performance of that system. Furthermore, in theory, a negative work of debonding between an aggregate and a bitumen bond may be indicative of spontaneous de-bonding in water. Debonding work was calculated from Eq. (2.3) using the dispersive part of the Lifshitz–van der Waals component of the surface energy (and tension) and Lewis acid and base components of surface energy (and tension), for aggregates (DVS method) and bitumen (DCA method). The results are reported in Table 2.16 where each aggregate-bitumen combination resulted in a positive work of debonding; even though work of debonding alone cannot be used to conclusively rank the moisture resistance of an asphalt mixture. In this case, however, as the work of debonding is positive, it means that energy is needed to break the bitumen aggregate bond in water. It also means that a higher value would relate to a stronger bond compared to a lower value. The preceding criterion (lower work of debonding is worse than higher work of debonding) can be used to rank the materials, i.e. aggregate ranking: Greywacke < Limestone < Granite; bitumen ranking: Bit 1 < Bit 2 = Bit 3 (Table 2.16).

Table 2.16 Debonding work of aggregate-binder bond in presence of water

Aggregate	Binder		
	Bit 1	Bit 2	Bit 3
Granite	36.7	43.9	43.5
Greywacke	21.0	26.4	26.4
Limestone	33.6	40.5	40.1

The ratio (ER_1) between the adhesive bond energy values in the dry condition, adhesion work, and in the presence of water, debonding work, can be used to predict the moisture sensitivity of asphalt mixtures. In addition to ER_1, three other parameters ER_2, ER_1*SSA and ER_2*SSA, as previously defined, could be used to quantify moisture sensitivity. A higher value of energy ratio indicates better resistance to moisture damage for that binder-aggregate combination. For example, Bhasin et al. (2006) applied the ratio ER_1 to study different types of asphalt mixtures and concluded that mixtures with a ratio higher than 0.8 were more moisture resistant than the ones with ratios lower than 0.8. In addition, mixtures with ER_2 greater than 0.5 performed better than those with ER_2 less than 0.5. However, it is questionable if these threshold values still hold if the work of debonding results in a positive value. Results using values from Table 2.14 (method 1) and Table 2.16 are shown in Tables 2.17 and 2.18. Following the criteria proposed by Bhasin et al., none of the aggregate-bitumen combinations considered in this study appears to be poor performing mixtures in terms of moisture sensitivity.

2.5.4 Outcomes of Surface Energy Measurements

Surface tension of the bituminous binders and surface energy of the aggregates has been measured using different methodologies. Both methods show more differences for aggregates than for binders. For binders, surface tension values from both methods are close to each other and highlight a more dispersive than polar behaviour. This finding is in line with usual data in the literature. For aggregates, even if the same value is found for the greywacke, other surface energy values appear to be significantly different. Moreover, the DVS method gives for all aggregates a more dispersive behaviour whereas the CAM gives a more polar behaviour (except for limestone). There is no explanation for this at the moment. This effect could be the

Table 2.17 Compatibility ratios, ER_1 and ER_2

Aggregate	ER_1			ER_2		
	Bit 1	Bit 2	Bit 3	Bit 1	Bit 2	Bit 3
Granite	1.95	1.64	1.84	0.79	0.66	0.61
Greywacke	3.68	2.87	3.18	1.64	1.24	1.17
Limestone	2.16	1.79	2.01	0.89	0.73	0.68

Table 2.18 Compatibility ratios ER_1*SSA and ER_2*SSA

Aggregate	SSA (m^2/g)	ER_1*SSA			ER_2*SSA		
		Bit 1	Bit 2	Bit 3	Bit 1	Bit 2	Bit 3
Granite	2.2812	4.46	3.74	4.19	1.79	1.50	1.39
Greywacke	1.3978	5.15	4.02	4.45	2.30	1.73	1.63
Limestone	0.6199	1.34	1.11	1.24	0.55	0.45	0.42

consequence of the geometrical surface properties of the bulk flat and not polished sample used in the CAM method.

Adhesion works between bitumen and aggregate are first calculated from the dispersive and polar component of surface energy and surface tension, from both methods (DVS and CAM). Obviously, differences between the two methods reflect the observations made on the surface tension and surface energy measurements. Regarding the DVS method, greywacke has the highest adhesion work and the granite and limestone has the lowest. Regarding the CAM method, granite, basalt and greywacke (very close values) have the highest adhesion work, limestone the lowest.

Adhesion works were also determined from a more direct method; the contact angle between binder and aggregate. There is no aggregate influence on the adhesion work from this direct method. There is a small influence of binder on the adhesion work; the PmB Bit 3 appeared to give the lowest values. It has to be noted that, in each case, the contact angle was quite low, between 8° and 15°, which is the consequence of good wettability.

Both methods, used to get the adhesion work, do not give the same results. The first, by calculation, is able to find differences between aggregates; the second appears to be more sensitive to the binder.

The compatibility ratio allows taking into account, theoretically, the water effect which leads to the debonding phenomena. It has been calculated using the binder surface tension from the DCA method and the aggregate surface energy (dispersive and polar component). This compatibility ratio is more sensitive to aggregate than to binder type. none of the aggregate-bitumen combinations considered in this study appears to be poor performing mixtures in terms of moisture sensitivity regarding Bhasin criteria.

Knowing the on field performance of the aggregates used in bituminous mixtures for pavement, adhesion work from surface energy measurements cannot be used alone as a criteria for moisture resistance. Indeed, low adhesion work was calculated for limestone whereas this aggregate is generally associated with a good resistance to debonding. The compatibility ratio appears to be a more accurate criterion and the interfacial tension calculated from the contact angle measurement could also be a good indicator and allows ranking aggregate-bitumen combinations.

In order to have a more accurate comparison of the surface energy and adhesion work from the different methods, a first recommendation could be to work on the same theoretical framework or model. For example, it could be interesting to re-calculate all data using the energy decomposition in Lifshitz–van der Waals and Lewis acid-base components of surface energy. Another recommendation is to assess the influence of the surface state; roughness and porosity in the CAM method and cleanliness of the aggregate in the DVS method. Finally, in order to increase the debonding phemonenon knowledge, it could be interesting to assess the contact angle evolution (CAM method) for aggregate-bitumen samples immerged in water.

2.6 Discussion and Recommendation

2.6.1 Discussion of the Rolling Bottle Test Results

Based on the raw results, the first outcomes are:

- the results are more discriminating after 24 h compared to 6 h
- the type of aggregates has a significant influence
- the type of bituminous binder has limited influence, with slightly better results for the polymer modified binder compared to the pen grade binders.

However, the overall results of this test do not appear really accurate and a lot of variability is observed from the different laboratories. The highest variation being for basalt and greywacke aggregates which displayed intermediate values, regardless the bituminous binder. To some extent this is aligned with the precision statement of the EN 12697-11. A reproducibility of 30% is given in the standard with the note: *"The obtainable precision may depend on the level of the result as determinations close to 0 or 100 are easier visually to determine than 'mid-range' results between 25 and 75%"*. Also it has to be noted that these aggregates were dark aggregates and it was difficult to qualify the remaining coating of bituminous binder.

Analysing in detail the results, the first thought explaining such a difference, was the visual interpretation of the coverage. The standard provides some reference scale to "quantify" the coating degree. The final value has to be an average of observation from at least two different technicians on three samples. Some laboratories provided the full observation. Mostly the variation between two observers and samples was no more than 10% coating. Some laboratories also provided pictures of samples. Examples are given in Fig. 2.21, for the granite aggregates with Bit 3, polymer modified bitumen after 24 h. As granite is a light coloured aggregate, the pictures are easier to interpret. One laboratory recorded only 5% remaining coating, another 20% and the other 40%. From the pictures, the difference is still recordable.

Both assumptions, of the variation between technicians and the visual interpretation cannot alone explain the variability of the results. So far, the test results are not always consistent within the same test method. The reproducibility is not as good, and does not seem to come fully from the visual observation, maybe there are some underlining reasons. Another possible reason could come from the test conditions themselves. The EN standard still leaves some freedom for the test conditions such as the test temperature, if the bottles are already used or are brand new etc. This certainly needs more attention.

(A) Pictures of granite aggregate with PmB after 24 h from lab1 with 5% coating

(B) Pictures of granite aggregate with PmB after 24 h from lab 4 with 20% coating

(C) Pictures of granite aggregate with PmB after 24 h from lab 3 with 40% coating

Fig. 2.21 Pictures of different rolling bottle test results

2.6.2 Blind Test for Visual Interpretation

For assessing the accuracy of visual inspection, a “blind test” was run using the pictures provided by one laboratory. The pictures came from the results of the boiling water stripping test according to XP T 066-043 test method. This method consists of bitumen coated aggregates left for 16 h in water maintained at 60 °C during the whole test duration.

The pictures from the combination of the four aggregates and the three bituminous binders were visually ranked by each experienced technician of the laboratories. Figure 2.22 displays the different pictures for each combination.

For Greywacke and Basalt, the darkness of the stone didn’t help the visual interpretation. But clearly some differences are recordable between aggregate types. For bitumen type, differences are noticeable for the modified binder Bit 3 having a softening point temperature around the test temperature, while the other having lower softening point.

A total of 10 laboratories participated to this additional “blind test”. The results are displayed in Table 2.19 and Fig. 2.23 with the mean values and the errors bars with the standard deviation.

The overall standard deviation across the different values is about 6% for 10 laboratories; this means a reproducibility of 12%. The variability of the measurements is lower for either very low or high values. While for intermediate values it is slightly higher variability.

The results are slightly different from the rolling bottle test but in line with the boiling water results. The interpretation is selective enough for aggregates. Granite gave the worst results and limestone was still good. However, basalt became one of the best regardless the binder. Regarding the different binders, there were significant differences with the modified binder, especially for the greywacke, displaying better results for the Bit 3 PmB.

2.6.3 Discussion Bitumen Bond Strength Results

In the field, ravelling can be the main problem in asphalt pavements. This failure needs to be taken into account to optimise the material used. Several factors are related to the deterioration of aggregate and bituminous binder resulting in ravelling. In the study, it focused on three main effects causing the bonding deterioration between aggregate and bituminous binder: temperature, binder and its modification and aggregate mineralogy. The samples were cured in dry conditions at different temperatures and were tested by BBS to determine the dry pull-off tensile strength. The dry results show a significant decrease in POTS with increasing temperature, however independent to bitumen types or aggregate types. This indicates that in-service temperature is important to control the bond strength of aggregate and asphalt binder.

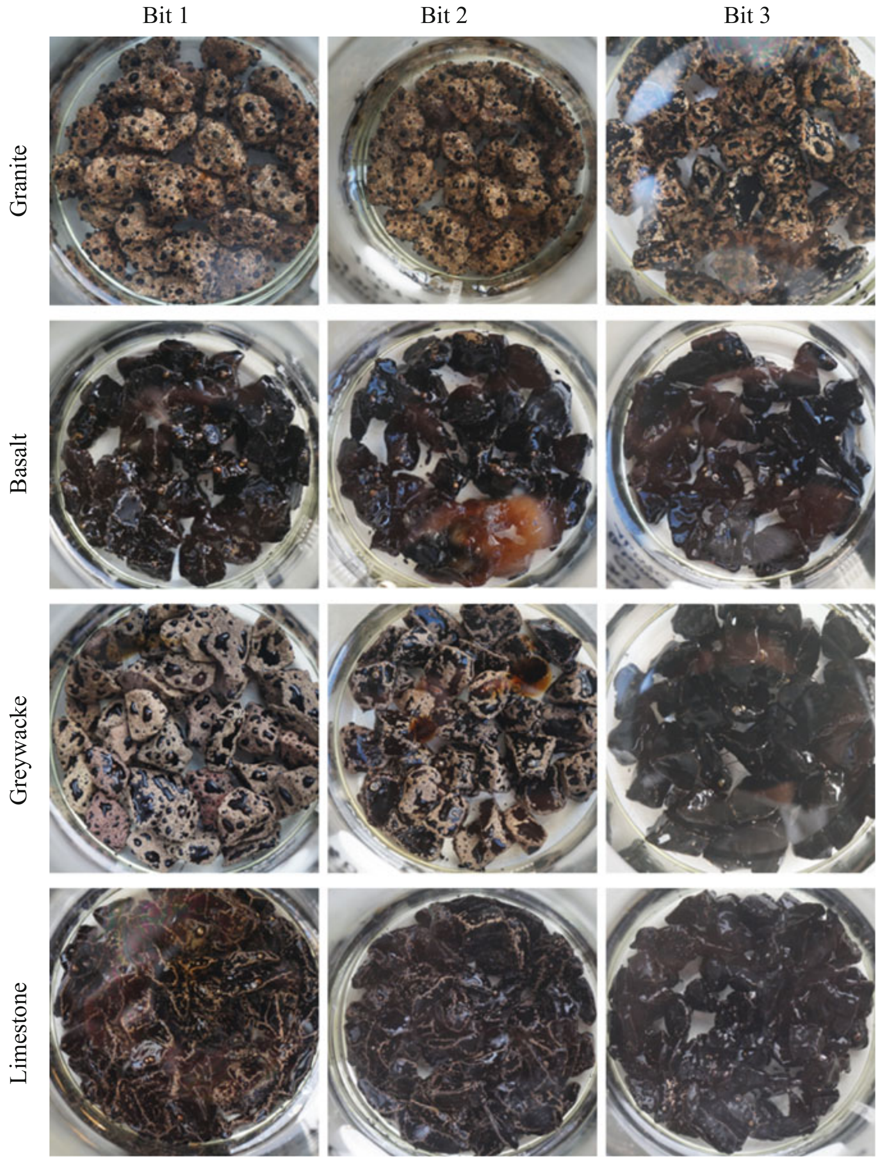

Fig. 2.22 Pictures for “blind test” addressing visual inspection reproducibility

The dry results had shown only significant different results for granite where the failure mode was in adhesion rather than cohesion. The failure mode is one predominant parameter to interpret the results.

For the polymer modified binder, the results show that in this case, where binders are selected with a similar penetration value at 25 °C and are tested under

Table 2.19 Assessment of the visual interpretation (% residual coating)

	Granite			Basalt			Greywacke			Limestone		
	Bit 1	Bit 2	Bit 3	Bit 1	Bit 2	Bit 3	Bit 1	Bit 2	Bit 3	Bit 1	Bit 2	Bit 3
Lab 2	10	10	35	95	100	100	15	60	100	85	90	100
Lab 3	10	10	25	85	95	100	15	50	95	75	85	95
Lab 4	10	10	20	90	90	100	15	30	100	80	80	95
Lab 5	20	20	35	85	90	100	30	40	95	55	70	90
Lab 6	10	10	30	85	95	100	15	40	100	75	85	95
Lab 7	15	20	50	90	85	95	25	40	100	80	85	90
Lab 10	15	15	30	85	85	95	15	30	95	50	60	95
Lab 11	10	10	25	95	95	100	20	60	100	85	90	95
Lab 13	20	15	25	80	90	95	25	35	95	65	80	85
Lab 14	20	20	40	80	90	100	30	40	100	65	80	90
Lab 15	10	10	25	95	100	100	15	35	100	85	85	100
Average	14	14	31	88	92	99	20	42	98	73	81	94
Std. dev.	5	5	9	6	5	2	6	11	3	12	9	5
Min	10	10	20	80	85	95	15	30	95	50	60	85
Max	20	20	50	95	100	100	30	60	100	85	90	100

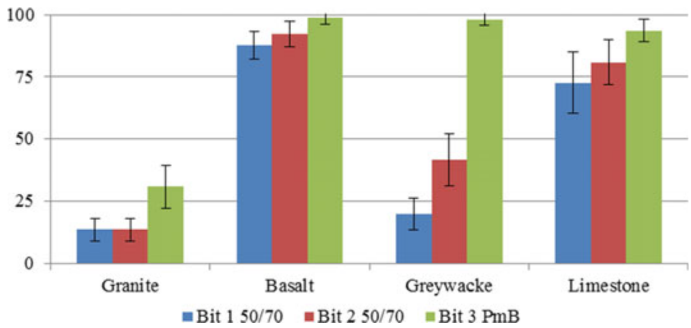

Fig. 2.23 Blind test results for residual coating

temperature and loading conditions similar to the penetration test, the modified binder did not show a difference in the cohesive strength of the material, which was the case when it was tested in the dry case.

The evaluation of bituminous binder moisture damage on BBS used the same criterion as for the Tensile Strength Ratio (TSR) used for asphalt mixture. If a value of a TSR ratio of 70% is used as a criterion to indicate failure, it appears that the same 70% criterion can be used with the BSR. This can rank the effect of combination of aggregate mineralogy and bituminous binder on moisture damage. Granite has the worst compatibility with the bituminous binder to prevent moisture damage. Greywacke showed the greatest potential for aggregate use, in preventing moisture damage.

2.6.4 Comparison Between Test Methods

From the different test methods used, the rolling bottle test, the water boiling test or the bitumen bond strength, the results are mostly affected by aggregate type. The binder impacts the results significantly, mostly with the boiling water when the temperature is raised at least to the softening point level of the binder. In this condition, the modified binder, having higher softening point, shows better results than the unmodified binder. In this condition, it was of interest to make a ranking comparison of the different aggregates.

For the rolling bottle test, there is a clear trend that granite displays the worst results and limestone the best, but for greywacke and basalt the ranking is equally balanced between laboratories.

However, for the boiling water stripping test, the ranking is slightly different. The granite aggregates are still the worst, but the ranking changes with basalt being the best, then limestone and finally greywacke.

Finally for the bitumen bond strength, granite is still the worst followed by basalt, and limestone and greywacke being very similar.

From this comparison, it is not obvious to conclude that the three test methods are equal and provide similar results. They all discriminate granite to have the worst affinity with bituminous binder in presence of water. For limestone, considering the absolute values, they all rank it as having good results in terms of affinity. However for intermediate values, the ranking from test to test is not consistent and the absolute values are not comparable.

Table 2.20 summarises the results for the pen grade bitumen with 1 being the highest remaining coating and 4 the lowest.

The reasons for the different ranking should be discussed in relation to the specific properties that are tested and also to differences in how the water is affecting the adhesion. For example in the rolling bottle test and the water boiling the rough aggregate is used, while in the BBS it is controlled-polished; so one parameter, stone roughness is not included in the BBS while it is playing a role in the other two tests. Furthermore, in the rolling bottle and the boiling water test, the coated stones are immersed in water, while in the BBS test water needs to penetrate through the aggregate to reach the interface; this introduces at least one extra parameter. For aggregates that absorb water very slowly the bond may not be attached within the experimental set up in the BBS test. This effect is not playing a role in the two other tests. Moreover, in the BBS test the failure can take place in the bitumen film or at the interface, where a coating below 50% is used as the adhesive failure; in the rolling bottle test only adhesive failure occurring in the interface is counted. And in the boiling water test, finally, the temperature conditions are very different, so the binder viscosity may have a more pronounced effect.

Table 2.20 Ranking between laboratories for each test methods

	Granite	Basalt	Greywacke	Limestone
Rolling bottle test after 24 h				
Average coating	10%	30%	40%	75%
Lab 1	4	3	2	1
Lab 2	4	3	2	1
Lab 3	4	3	2	1
Lab 4	4	3	2	1
Lab 5	4	2	3	1
Lab 6	4	2	3	1
Lab 10	4	2	3	1
Lab 13	4	2	3	1
Average	4	2.5	2.5	1
Boiling water stripping test				
Average coating	0–25%	75%	50%	75–85%
Lab 6	4	1	3	2
Lab 7	4	1	3	2
Lab 11	4	1	3	2
Average	4	1	3	2
Bonding bond strength test				
BSR	30–40%	50–90%	100%	85–100%
Lab 8	4	3	1	2
Lab 9	4	3	1	2
Lab 10				
Average	4	3	1	2

Nevertheless, it is interesting to see that with all these differences, all labs found the same worst aggregate.

The test conditions, especially in the case of the boiling water test play an important role in the results. Thus, the choice of one test should depend on climate conditions and/or viscosity of the binder.

When comparing the surface energy of aggregates independently to binder types, as determined in Table 2.13, it is not obvious there is a good correlation. Even the debonding work of aggregate/binder in presence of water, as shown in 0 cannot explain the results from the other tests; limestone and granite having similar values compared to greywacke.

Another important topic is how to correlate these test conditions to field behaviour. As bituminous binder viscosity is temperature dependent, it automatically affects the adhesion/cohesion properties of the binder. There is still limited research at this point of time to understand how the temperature influences the affinity or adhesion. If lowering the temperature will affect the adhesion: is there a linear relation or is there a temperature where the adhesion is worst? And finally this test is performed on fresh bituminous binder, while on the road the binder was already processed through the mix plant and is already aged. The behaviour could be influenced by ageing.

2.6.5 Recommendation

The activities around this Task Group were mostly focused on having a better understanding of the adhesion and cohesion between bituminous binder and aggregates especially in presence of water. The number of laboratories participating to this study clearly shows the interest of this subject as confirmed by the numerous bibliographies available. Even with 13 laboratories in total there were seven different test methods or deviations from standard test methods used. As stated in the introduction, the adhesion theme is more than complex and within the scientific community there is no or not yet consensus on how to address that in a unique way. The end results certainly depend on many different factors which will fit more with one test method rather than another one.

Considering ravelling as the ultimate visible effect of loss of adhesion for hot climates; the bitumen bond strength with dry strength will certainly address pavement degradation. When ravelling occurs, most likely during summer time in presence of water, like in tropical or hot oceanic climate, the boiling water test is more appropriate for addressing good combinations of aggregate and binder. And for temperate climate conditions, the rolling bottle test could give a good indication of good vs. bad aggregate affinity.

Despite the reasonably good level of participation, the number of final results was not enough to determine statically valid repeatability and reproducibility. However, some recommendations can be made to consider values in terms of class rather than absolute value. Typically, it can be suggested four different classes as described in Table 2.21.

Considering the rolling bottle test, the test can be run by many laboratories, requires limited equipment and is easy to run. The test conditions are multiple and certainly need to be more accurately used and recorded. The overall reproducibility can be assessed in the magnitude of 15%, maybe higher for intermediate values between classes 2 and 3. The results after 24 h are already discriminating for combinations of aggregates and binders. The aggregates are the affecting parameter towards adhesion at equi-penetration values. However softness of binder could certainly affect the results.

Table 2.21 Proposed classes for affinity between aggregate and binders

Class	1	2	3	4
Ratio	100–75%	75–50%	50–25%	25–0%

For the boiling water test, the method is more accurate and quick to run (10 min) provided the calibration curve is done. It is less used than the rolling bottle and may use aggressive acid. The French standard is maybe more aggressive due to longer test duration, but to some extent more relevant to the normal temperature conditions of a pavement. The reproducibility is relatively good and can be assessed in the range of 10–15%, but this would require more data points.

For both of the above tests, automatic image analysis can improve accuracy but the main variability of results still remains in the test conditions and the preparation and conditioning of the samples.

The bitumen bond test may be a promising test method although it requires significant preparation of the stone, using a bulk piece of stone that can be different from the aggregates used in the final asphalt mixture. The test provides a comprehensive set of information from dry conditions and in presence of water. Its use has become more common in North America and so far not yet implemented in Europe. Reproducibility is not yet straight forward. The new protocol including mastic combination is promising and could improve reproducibility while addressing better control of load and sample shape.

In terms of recommendation, to improve reproducibility, additional work and effort have to be made on accurately defining and recording the test conditions.

2.7 Conclusions

As water damage is one important part of asphalt pavement durability. RILEM TC 237-SIB, Task Group 1 (TG1) worked on the affinity between aggregates and bituminous binder especially in presence of water. A round robin test was conducted with 13 laboratories and various test methods using four different aggregate types and three bituminous binders.

Water damage is more than a complex phenomenon and involves, amongst other things, wetting effect, adhesion and cohesion of bituminous binder over various conditions of use with climate, materials composition and loading.

The rolling bottle test consists of recording the remaining percentage of bituminous binder coating aggregates after being rolled in a water bottle. Whilst the test is run for 6, 24, 48 and 72 h, the outcomes start to be really discriminating after 24 h.

The analysis of these results shows that the reproducibility of the rolling bottle test is to date rather fair; one reason may be related to the visual interpretation of the percentage of coating, but blind analysis has shown relatively good repeatability. Other possible causes are more on the test conditions and sample preparation. The reproducibility of the rolling bottle test with the limited data available depends on the degree of coating. For poor, <25%, and excellent values, >75%, the reproducibility is relatively good with 15% while for intermediate values it is only 40%.

The boiling water test consists of more accurately measuring remaining coated bitumen on aggregates after being left in boiling water for 10 min. The test results are discriminating towards aggregate type and start to be dependent of bitumen type as far as there are differences in the softening point. The number of data was not enough to technically determine reproducibility, but can be estimated to be 10–15%, again depending of the absolute results.

The bitumen bond strength test consists of measuring the bonding strength of bitumen on a block of stone aggregate. Results in dry conditions made at different temperatures are independent to aggregates and binders. The bonding strength ratio of wet over dry strength values at 22 °C has been shown to be in the same range of interpretation as the tensile strength ratio as measured on asphalt mixtures. Again with a limited amount of laboratories the reproducibility is difficult to determine and absolute results have shown a wide variability between laboratories.

The final recommendations from this study are that the different tests display similar results for extreme values, worst or best combinations of aggregate binder. But for intermediate values, the correlation between tests is less obvious. While reproducibility was difficult to determine due to insufficient data sets, it is in line with what is reported in the literature and the current standard. In order to better improve the accuracy of the results, it is suggested to provide results within four classes; from class 1 being best results to class 4 being the worst results.

When comparing rankings as obtained by each participant, the results are much more consistent. Most of the results have ranked the limestone aggregate as the best and granite the worst; the intermediate greywacke and basalt are more difficult to distinguish. The ranking of the stone types is rather independent of the binder type. Regarding the binders, the polymer modified binder ranks slightly better for all stone types, compared to the two unmodified binders, which perform similarly especially at high temperature test conditions.

In order to validate the affinity test method to experience from field behaviour; the effect of the variations in the field temperature and the effect of aged binder need to be taken into account.

Glossary

RILEM Réunion internationale des laboratoires et experts en matériaux

SIB Testing and characterization of sustainable innovative bituminous materials and systems

TG1 Task group 1

SHRP Strategic highway research program

ITS Indirect tensile strength

ITSR Indirect tensile strength ratio

CAST Coaxial shear test

APA Asphalt pavement analyser

EAPA European asphalt pavement association

FEHRL Federal highway agencies

CEN European committee on standardization

BBS Bitumen bond strength

AASHTO American association of state highway and transportation officials

RRT Round robin test

IFSTTAR Institut français des sciences et technologies des transports, de l'aménagement et des réseaux

NTEC Nottingham transportation engineering centre

XRF X-ray fluorescence

RBT Rolling bottle test

PmB Polymer modified bitumen

PATTI® Pneumatic adhesion tensile testing instrument

POTS Pull-off tensile strength

Ag Contact area of gasket with reaction plate (mm^2)

BP Burst pressure (kPa)

Aps Area of pull stub (mm^2)

C Piston constant

BSR Bond strength ratio

NOPTS New pull-off test

γ surface energy of bitumen or aggregate (mJ/m^2)

γ_{LW} Dispersive part of Lifshitz–van der Waals interaction of the surface energy (mJ/m^2)

γ_{AB} Polar part of Lifshitz–van der Waals interaction and acid-base component of the surface energy (mJ/m^2)

$\gamma+$ Lewis acid component of surface interaction

$\gamma-$ Lewis base component of surface interaction

γ_P Polar component of surface tension energy

γ_D Dispersive component of surface tension energy

γ_S Substrate surface energy

γ_L Liquid surface tension

γ_{SL} Liquid/substrate interfacial tension

W_{adh} Adhesion work

W_{adh}^P Polar components of adhesion work

W_{adh}^D Dispersive component of adhesion work

W_{BA}^a Dry bond strength, interfacial adhesion work between the bitumen (B) and aggregate (A)

W_{BWA}^a Interfacial adhesion work between the bitumen (B) and aggregate (A) in presence of water

W_{BB} Bitumen cohesion

W_{BL} Adhesion work between bitumen (B) and a probe liquid (L)

DCA Dynamic contact angle

DVS Dynamic vapour sorption

DSA Drop shape analyser

CAM Contact angle measurement

SSA Specific surface area

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