ADHESION OF BITUMEN: SCREENING AND EVALUATING LABORATORY TESTING TECHNIQUES

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ABSTRACT

A huge number of laboratory testing techniques is known for assessing adhesion properties between bituminous materials and aggregates in laboratory. Besides simple empirical tests (usually established for binder specification and quality assurance), like Rolling Bottle Test or static immersion test, elaborate test methods are in use like contact angle measurement of either bitumen droplets on mineral aggregates or water droplets on bitumen surfaces. This paper presents latest results of a critical review of a number of laboratory testing techniques. Based on joint research work of Braunschweig Pavement Engineering Centre, Germany, and Vienna University of Technology, Austria, problems and limits of different techniques are discussed. Screening and evaluation of these techniques is based on data resulting from an extensive laboratory test program conducted in the frame of this research co-operation in recent years, including various aggregates and bitumen types. All testing techniques according to the European Standards have been taken into account. Furthermore, new approaches for adhesion testing have been investigated, like contact angle measurements especially adopted for bitumen-aggregate-systems, or like the static tensile test conducted on pins drilled out from aggregate rock and sticked together with bitumen film. The results from these laboratory testing campains are also presented in detail.

Keywords: adhesion, bitumen, aggregate, contact angle measurement, laboratory testing

1. Introduction

Adhesion between bitumen and aggregate is an important asphalt property which determines asphalt performance and in-service life. Research in this field has been active more than 100 years now, nevertheless identifying the fundamental mechanisms of adhesion in asphalt pavement materials is still a challenge [1, 2, 3]. Suitable models and laboratory testing methods are required for the assessment of adhesion properties of asphalt mixtures and for the prediction of long-term adhesion behaviour within the pavement are needed. Today, besides simple empirical tests, which are usually established for binder specification and quality assurance, like the Rolling Bottle Test (RBT) or the static immersion test, also elaborate test methods are in use like contact angle measurement of either bitumen droplets on mineral aggregates or water droplets on bitumen surfaces [4, 5, 6, 7]. Although a vast number of testing techniques has been developed so far - over 150 to this date [1], there are currently no satisfactory and universally accepted test methods. This paper presents first results of a critical review of a number of laboratory testing techniques addressing the adhesion between bitumen and aggregates, evaluating their suitability for routine laboratory testing. Screening and evaluation of these techniques is based on data resulting from a laboratory test program including various aggregates and bitumen types. All testing techniques conforming to the European Standards are taken into account. In addition, new approaches for adhesion testing are presented, like contact angle measurements especially adopted for bitumen-aggregate systems, or the static tensile test conducted on rods drilled out from aggregate rock and stuck together with bitumen film.

2. Test Methods Investigated

2.1. Contact Angle Measurements

Contact angle measurements were conducted on a DSA100 (KRÜSS Ltd., Hamburg, Germany), a goniometric setup including an automated sample dosing device [5]. The sample is illuminated by a strong light source and filmed and recorded with a high-resolution camera with manual zoom and focus (Figure 1). The software DSA1 (version 1.90.0.14) calculates mathematical functions to describe the boundaries of the liquid-solid and liquid-gaseous interfaces. While the liquid-solid boundary can be described as linear function, the fitting of the drop shape is a more elaborate matter. The method chosen for this study is a polynomial mathematical function to approximate the outline of the drop close to the baseline.

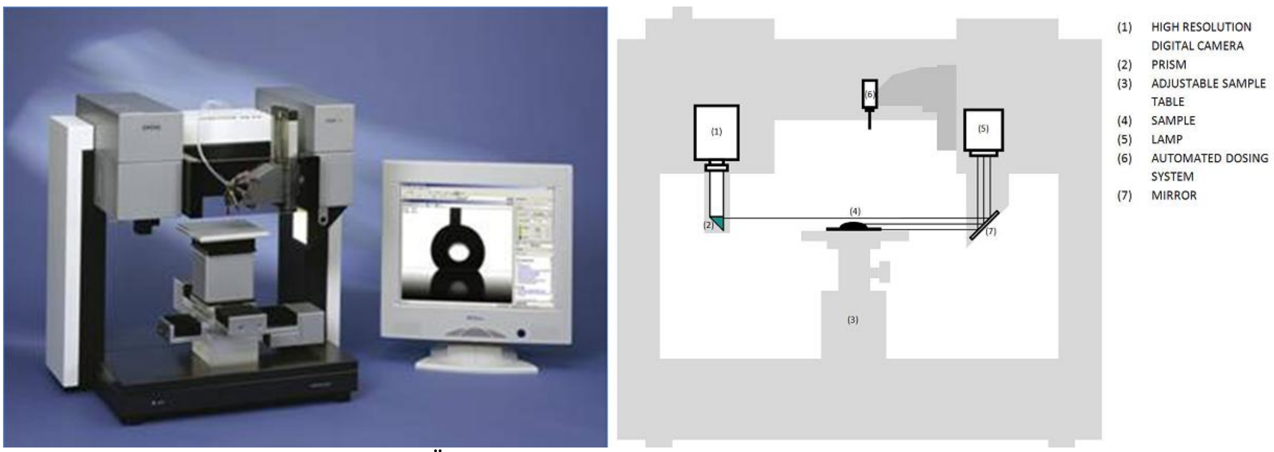


Figure 1: Photography of DSA100 (KRÜSS Ltd., Hamburg, Germany) (left) and schematics of the experimental setup (right)

For the analysis of bitumen, the contact angle measurement can be used in different fashions. Three different approaches were covered in this study:

2.1.1. Bitumen drop on glass

Since it is difficult to provide a perfectly smooth and chemically homogeneous surface using mineral aggregates, glass slides were used in a preliminary experiment. A small drop of bitumen was applied to a microscopic slide and then stored at 70°C for 30 minutes. Afterwards, the sample was cooled to room temperature and the drop was analysed using the DSA100 [5]. Additionally, the measurements were repeated after a short period (30 minutes) of water storage at 50°C.

2.1.2. Pendant drop

The pendant drop method is a most convenient, versatile and popular method to measure the interfacial tension of liquid matter. This method involves the profile determination of a suspended liquid drop at mechanical equilibrium, and due to the balance between gravity and surface tension the latter can be determined. The surface tension has been studied as a function of temperature. The surface free energy was calculated at different temperatures, and by linear regression the surface free energy at ambient temperature was extrapolated. Bitumen is taken up with a syringe fixed to the DSA100. Then the bitumen is extruded through the needle into a chamber prethermostatted at the desired temperature. The liquid drop of bitumen, formed as large as possible, is hanging down from the needle tip and a picture is gathered as described above. The software determines the drop profile, and the surface tension of the bitumen can be calculated using a Young-Laplace equation (Figure 2).

2.1.3. Water drop on bitumen surface

The surface wetting of bitumen is an interesting aspect [4] and can be examined by measuring the contact angle of a water drop on a bitumen surface. The interaction between water and bitumen is suspected to cause ablation. As a starting point, the experiences from the winning of crude bitumen from oil sands [6, 7] was used. Wetting experiments were conducted on six different samples ranging from air-blown bitumen to vacuum residue. Each bitumen was heated to 100°C and then applied to a microscopic slide. To allow surface relaxation and smoothing of the bitumen surface, the sample was held at 50°C for 24 hours. Preliminary experiments have shown that the storage under N_2 atmosphere does not significantly influence the test results. The samples were then cooled to room temperature and the contact angle of a water drop on the bitumen surface was measured. The needle of the dosage system was moved to a distance of just 3mm above the sample surface. 5µl of deionised water was then extruded at 1µl/min. The needle was then lifted so that it remained just visible in the picture, as the standardized diameter of the needle is needed by the software as a size calibration (Figure 2).

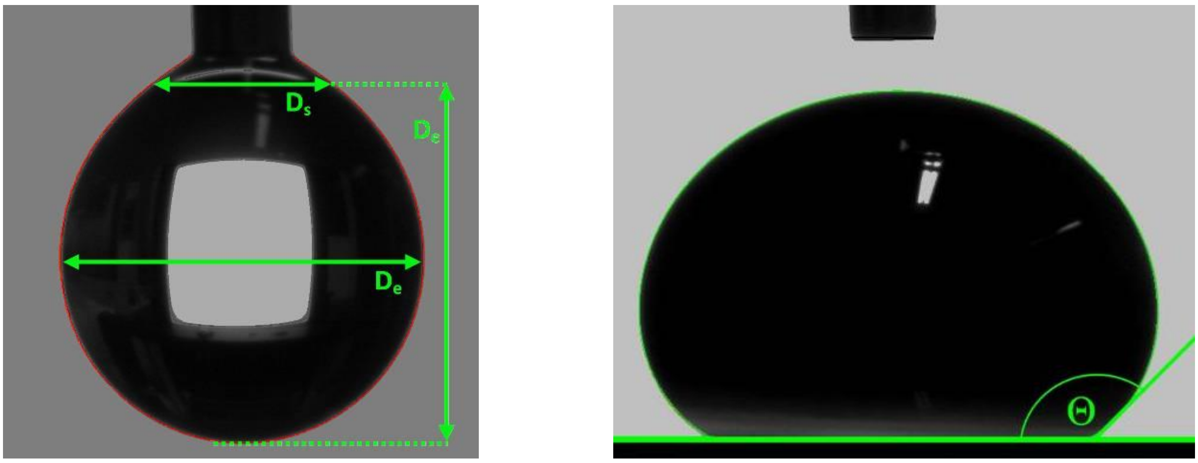


Figure 2: Image analysis of a hanging drop (left), and image analysis of a sessile drop (right): D_e maximum drop width, D_s parameter for drop shape (D_s = 0 for exactly spherical drops), Θ contact angle

2.2. Rolling Bottle Test

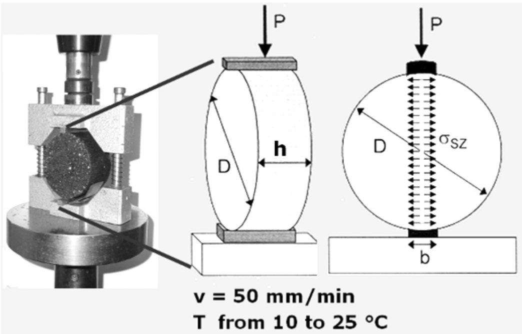
The adhesion between aggregate stones and bitumen is assessed by the Rolling Bottle Test (according to EN 12697-11A) through exposing bitumen-covered aggregate stones to mechanical abrasion under water. Subsequently, a visual estimation of the residual wrapping degree of the bitumen coated single grain after the abrasion test is conducted. 150 g of bitumen-coated single grains are placed in 500ml bottles then 5°C cold, distilled or deionised water and a stirrer are added. The bottles are turned automatically at a speed of 40 rotations per minute. After 6 hours and after 24 hours (the rolling time can be expanded up to 72 hours) the bitumen-coated grains are put in a white bowl for evaluation.

2.3. Static Water Storage Test

For the static water storage test (according to EN 12697-11B), a bowl is filled with 150 bitumen-coated single grains, which should not touch one another. Afterwards, the bowl rests for a predefined period under constant temperature conditions. Finally, the grains are dried and the number of grains is determined, which are not coated completely any more. In this study, additional tests were performed under varying temperatures and durations of exposure.

2.4. Change of Indirect Tensile Strength After Water Storage

According to EN 12697-12, the durability and resistance of a compacted asphalt mix slice is checked by the indirect tensile strength test before and after water exposition. The change of indirect tensile strength is checked from six samples: three dry samples and three samples which have been exposed to water. During the indirect tensile strength test, the sample is attached between two load stripes and is loaded radially at a speed of 50mm/min. The maximum load at fracture is measured. The relation of the strength values before and after water storage is determined, and called Indirect Tensile Strength Ratio (ITSR) (Figure 3).



Indirect tensile strength (β_{SZ}, ITS)

$$\beta_{SZ} = \frac{2 \cdot F_{max}}{\pi \cdot h \cdot d} \quad [N/mm^2]$$

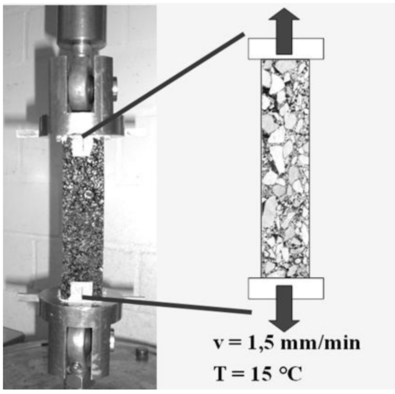
Indirect tensile strength ratio (ITSR)

$$ITSR = \frac{ITS_{wet}}{ITS_{dry}} \cdot 100 \quad [\%]$$

Figure 3: Indirect tensile strength test principle, and calculation of the ITSR

2.5. Direct Tensile Strength Test

In analogy to the indirect tensile strength test, the uni-axial direct tensile strength test was introduced for investigating adhesion strength properties in this study. Again, strength is determined before and after conditioning the test sample in a water bath according to EN 12697-12 B. Test samples used in this study included prismatic samples of asphalt mixture (Figure 4), as well as rods drilled out from aggregate rock and stuck together with bitumen film (Figure 5). For the tests on prismatic asphalt beams, always six beams are cut out from slabs of compacted asphalt mixture (three dry, three wet). Adaptors are attached with two-component adhesive to the face surfaces of the samples. This is necessary to load the samples into the machine. A tensile force is applied at a speed of 1.5mm/min at a temperature of 15°C. After the sample fractures, the tensile strength is determined from the maximum stress, and the direct tensile strength ratio (DTSR) according to Figure 4.



Direct tensile strength (DTS)

$$DTS = \frac{2 \cdot F_{max}}{\pi \cdot h \cdot d} \quad [N/mm^2]$$

Direct tensile strength ratio (DTSR)

$$DTSR = \frac{DTS_{wet}}{DTS_{dry}} \cdot 100 \quad [\%]$$

Figure 4: Direct tensile strength test principle, and calculation of the DTSR

Similarly, the direct tensile stress test was also applied on rods drilled out from aggregate rock and stuck together with bitumen film. The strength test was performed at different loading speeds and test temperatures. A fractured specimen is illustrated in Figure 5.

Figure 5: Aggregate pin drilled out from aggregate rock and stuck together with bitumen film: direct tensile test (left), and fractured pin after testing (right).

3. Selected test results

3.1. Materials

Materials investigated in this study included various types of plain bitumen (50/70, 70/100), of polymer modified bitumen (PmB 40/100-65H, PmB 45A), of natural aggregate ranging from poor adhesion to good adhesion characteristics (basalt, Taunusquarzite, limestone, granite, gabbro), and four types of asphalt mixtures (AC 11, AC 16, SMA 11, PA 8). Details of the bitumen, bitumen-aggregate combinations, asphalt mixture types and the related tests are given in Figure 6.

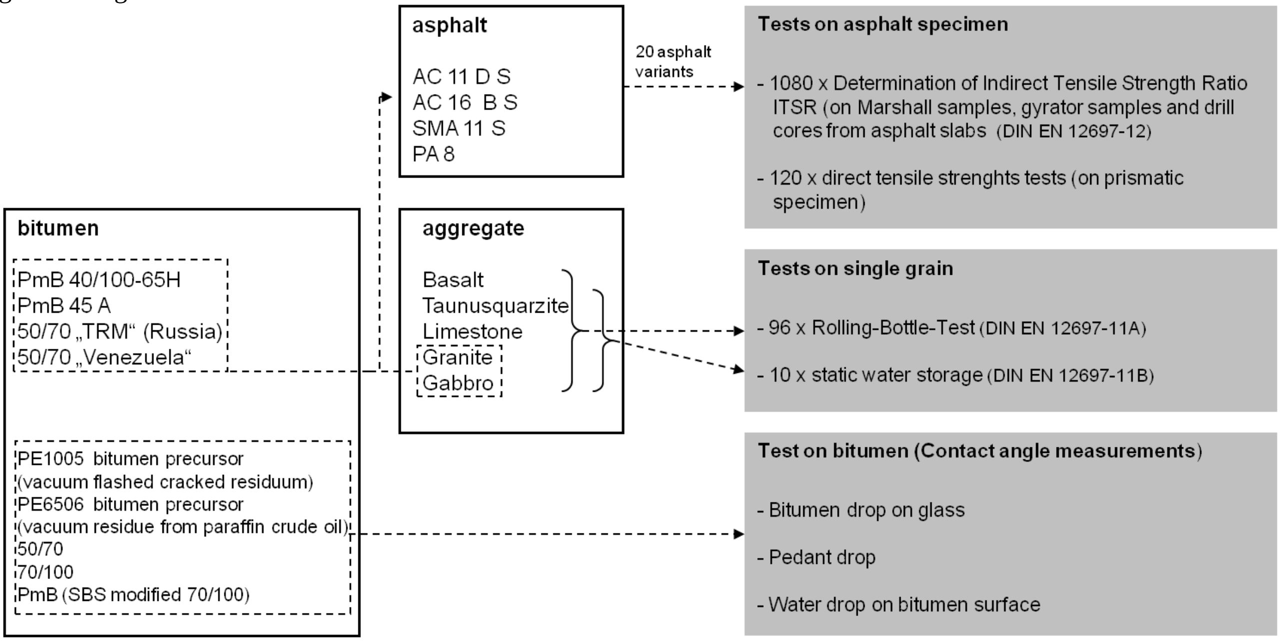


Figure 6: Bitumen, bitumen-aggregate combinations and asphalt mixture types assessed by the related test methods.

3.2. Contact Angle Measurements of Water Droplets on Bitumen Surfaces

Preliminary experiments have shown that a constant high quality of the pictures is of vital importance for the reproducibility, since both the fitting of the baseline and of the drop outline depend on the contrast and brightness of the image. Hence, picture quality was assured by the introduction of minimum standards for brightness, contrast, and image sharpness as measured by the DSA1 software. Around 10% of the generated images failed to meet these standards and were excluded from further analysis. The minimum count of viable measurements was defined to be 30 data points per bitumen type. The data shows only marginally different results for most samples, except for PE6506 (cp. Figure 6), and a high standard deviation (SD) of the method in general compared with the difference between the contact angles for the various surfaces. In order to determine whether contact angles are significantly different or not, statistical testing methods were applied. First the Shapiro-Wilk [8] test was used to test for normality. Table 1 confirms the normal distribution of the data. Then, analysis of variance (ANOVA) [8] was applied. Including all samples tested, the ANOVA rejected the null hypothesis that the average contact angles are not significantly different, i.e. the set of means and standard deviations are significantly different from one another. Since the mean values for PE6506 deviate greatly from the data of the other bitumina, the test was repeated excluding PE6506. The result shows that by means of this experiment only PE6506 can be differentiated from the bulk of the other samples, which in turn cannot be differentiated amongst each other (Figure 7).

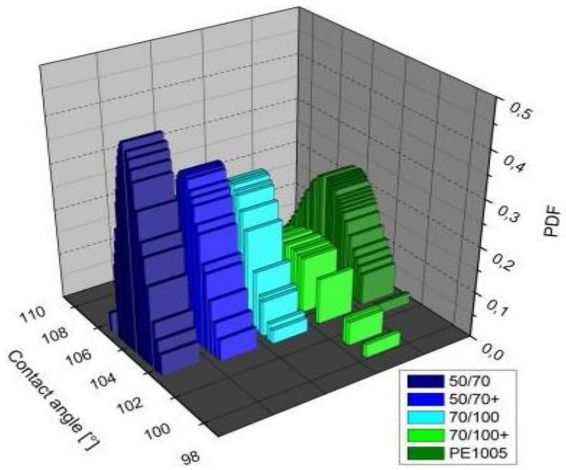


Figure 7: Contact angle of a water drop on bituminous surface - probability density function (PDF) plot of non-distinguishable samples

Table 1: Contact angle of water drops on coated surfaces - application of the Shapiro-Wilk test and ANOVA [8]

Sample	**avg. Contact Angle [°]**	**SD**	**Variance**	**W**	**p-value**	**α**	
50/70	104,53	0,91	0,82	0,98	0,86	0,05	**p > α**
50/70+	104,47	1,13	1,28	0,98	0,88		
70/100	105,02	1,36	1,85	0,97	0,54		
70/100+	104,48	3,07	9,42	0,95	0,27		
PE1005	105,15	1,70	2,87	0,98	0,64		
PE6506	115,07	3,95	14,81	0,93	0,11		

ANOVA (F-Test) for all tested samples

MSBG	**MSE**	**F-value**	**p-value**	**α**	
446,44	4,26	104,86	0	0,05	**p < α**

ANOVA (F-Test) for all tested samples excluding PE6506

MSBG	**MSE**	**F-value**	**p-value**	**α**	
4,83	2,74	1,76	0,14	0,05	**p > α**

3.3. Pendant Drop Measurements

The pendant drop measurements were carried out using five different bitumina and bitumina precursors. The surface energy was measured as a function of temperature. Linear regression analysis can be used to extrapolate to ambient conditions since the samples show very similar behaviour at high temperatures, but different tendencies toward lower temperatures [9]. Exemplary, two extrapolations are shown in Figure 8 including the confidence interval for a significance level of 95%. The areas overlap significantly. Figure 8 shows the results of the extrapolation for all studied bitumina including error bars, derived from the extrapolated confidence interval. The overlapping standard deviations indicate that this method is not capable of distinguishing between the tested samples. Thus, test improvements with regard to reproducibility are needed.

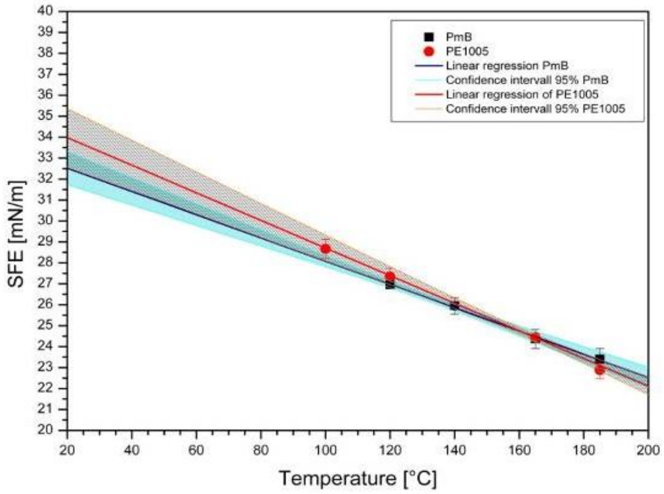


Figure 8: Extrapolation to 20°C of the SFE values of two bitumina measured at high temperatures including the respective confidence intervals of 95%.

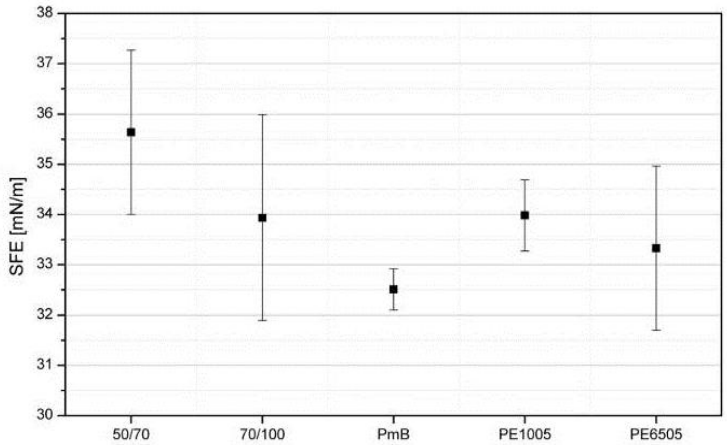


Figure 9: Results of the above extrapolations of SFE values down to 20°C, including error bars

3.4. Contact Angle of Bitumen Drops on Glass Slides – An Approach to Real Systems

The use of microscopic glass slides as a basic model system for the bitumen-mineral aggregate interface has several advantages [10]. Firstly, the surface is perfectly smooth and chemically homogeneous. Secondly, the chemical properties of glass are similar to the more acidic mineral aggregates, which usually have a very high content of SiO_2 [5]. In order to investigate the capabilities of this test, two bitumen samples (50/70 and 70/100) as well as mixtures of these bitumina with an adhesion-promoting agent were tested (50/70+ and 70/100+). The fresh droplets of bitumen on glass yield similar results for all bitumina, it was not possible to distinguish between them (Figure 9, top left). After storage at 70°C for 30 minutes, well above the softening points of the bitumina (50/70 and 50/70+: 48°C; 70/100 and 70/100+: 45°C) the results were rather different (Figure 9, top right). The contact angles differ significantly from each other. The contact angles of the pure bitumina are around 6° lower than of the mixtures. This means, that the wettabilities are worse for the additive-containing bitumina. The final variation of these experiments was the introduction of static water storage. The bitumen drop was applied to the glass slide and then stored at 70°C for 30 minutes (Figure 9, bottom left). Afterwards, the sample was immersed in water and left there for another 30 minutes at 70°C. The result is an increase in contact angle for all samples. The contact angle increased by 35-55°, but by a different value for each. The differences are significant according to an ANOVA performed (Figure 9, bottom right). The adhesion-promoting agent influenced the change of the contact angle differently for 50/70 and 70/100. While it seems advantageous to use the agent on 50/70, it worsens the stability towards water for 70/100. The worsening can be explained as the result of increased polar functionalities in the bitumen surface due to the admixture of the adhesion-promoting agent. As most agents are chemically active surfactants, it is hardly surprising that their use reduces the surface tension between water and bitumen as well.

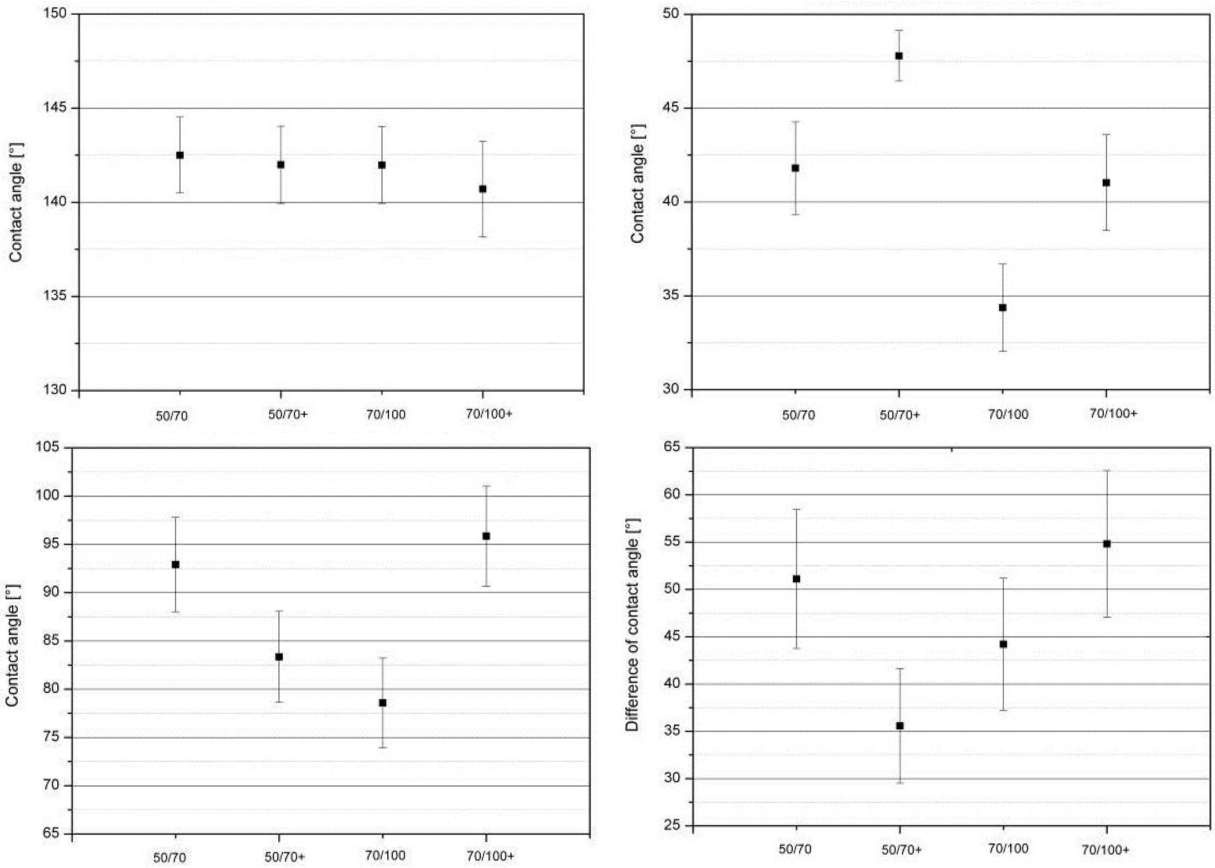


Figure 10: Contact angle of a bitumen drop on glass before (top left), after 30 minutes of dry storage at 70°C (top right), after water storage for 30 minutes at 70°C (bottom left), and the difference of contact angle (bottom right) for 20 samples each

3.5. Rolling Bottle Test

On the whole, test results obtained from the Rolling Bottle Test are plausible regarding the differentiation of the minerals in critical and uncritical to adhesion (Figure 10). The aggregates granite and Taunusquarzite - classified as critical to adhesion due to their mineralogical characteristics – yield the lowest wrapping degrees after rolling times of either 48 hours or 72 hours. Therefore, they rated worse in comparison to the aggregate types, which are uncritical to adhesion (overall the absolute values of "critical to adhesion" aggregates are more than 10 % below the absolute values of the "uncritical to adhesion" aggregates types.

The Rolling-Bottle-Test can therefore be rated qualitatively as a suitable procedure for addressing adhesion of the single grain. Due to the data structure a meaningful statistical evaluation is not possible. However, it is recommended to optimize the procedure while taking into account the following insights gained from the project: For visual estimation of the wrapping degree, 8/11 mm grain size is more suitable than 5/8 mm grain size. Also, a small grain size leads to agglomeration of bitumen-coated aggregates during the rolling process which generally results in a lower wrapping degree. The subjective influence by the visual estimation of the wrapping degree should be minimized by the indicated application of a computer-aided analysis technique (cp. [11]). For this technique, digital images of each sample are taken and the characteristic colour areas for the aggregate and bitumen coverage are classified by means of an imaging software. The wrapping degree is calculated from the fraction of each class.

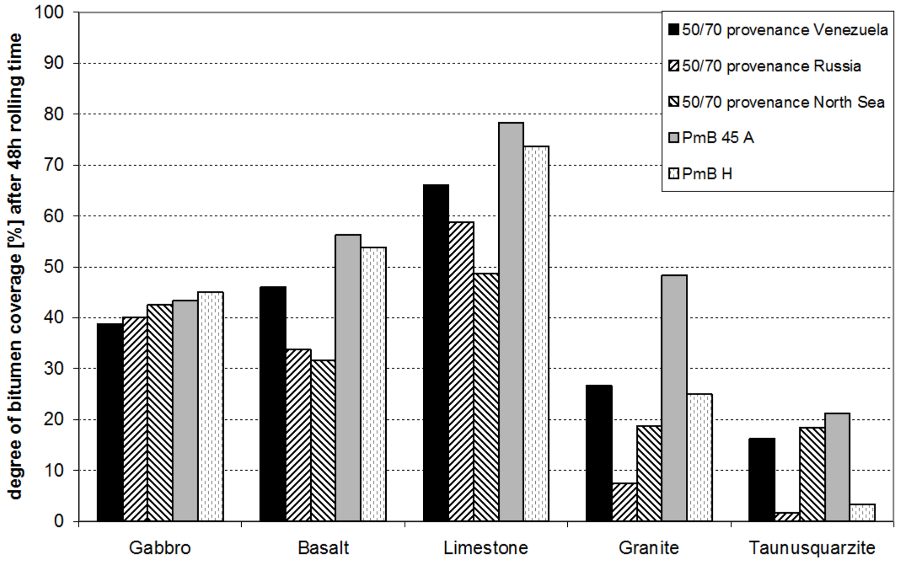


Figure 11: Rolling Bottle Test: degree of bitumen coverage [%] after 48 hours of rolling time

3.6. Static Water Storage Test

Static water storage according to EN 12697-11B (48 hours in water at 19°C) did not result in any detachment of bitumen. Thus, the standard test conditions were regarded as inappropriate for investigating the materials used in the study. A more distinguishing result was achieved after 72 hours exposure to water of 40°C temperature. An aggregate influence, as well as a (less significant) bitumen influence on adhesion behaviour was stated (Figure 12). However, experiments considering more severe test conditions to activate detachment did not result in better repeatability and results that distinguish significantly, neither by extending the exposure time in water, nor by rising water temperature (up to 60°C according to Swiss standard SN 671960).

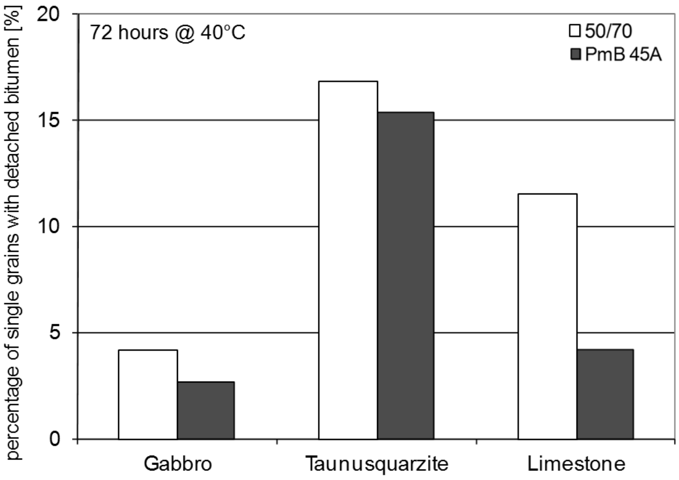


Figure 12: Static water storage: percentage of single grains showing detachment of bitumen

3.7. Indirect Tensile Strength Test

Regarding the indirect tensile strength test at 15°C test temperature, an influence of the bitumen type on water susceptibility was determined for all asphalt mixtures and aggregate types, as exemplarily illustrated in Figure 13.

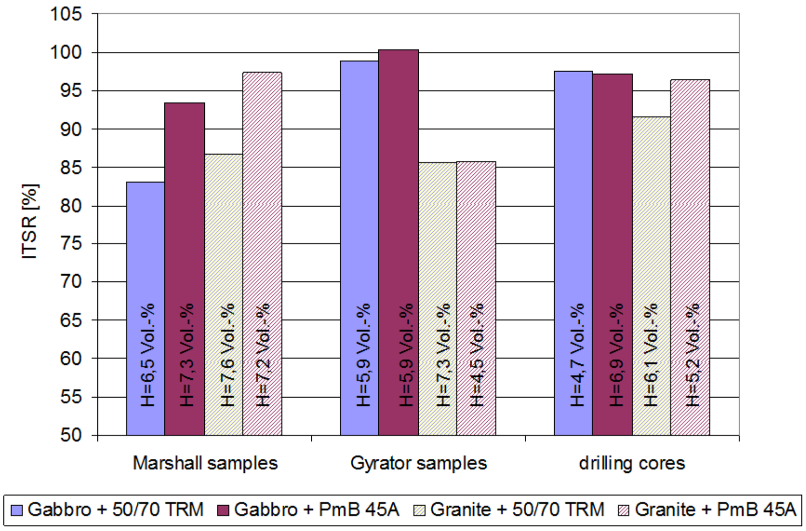


Figure 13: Indirect tensile strength test results for AC 16 at 15°C temperature: influence of bitumen type

The void content of the asphalt mix specimen (H) was found to influence the test results significantly. Specimens with lower void content (gyratory-compacted, drilling cores) led to higher strength ratios (Figure 14). This relation could not be verified for all tested variants though.

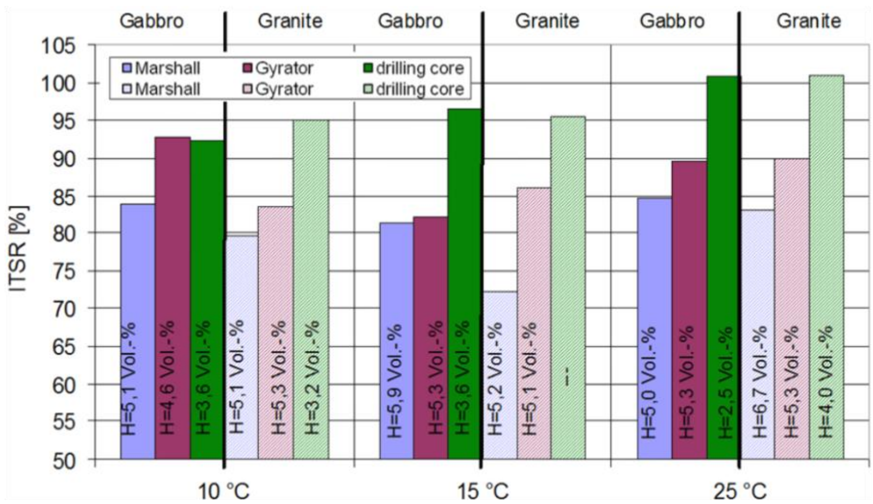


Figure 14: Indirect tensile strength test results for AC 16 at 15°C temperature: influence of void content

3.8. Direct Tensile Strength Test on Asphalt Mix Samples

Results of the direct tensile strength tests for asphalt mix types AC 11 and AC 16 are exemplarily presented in Figure 15. It is clearly shown, that the strength decreases after exposition of the prismatic specimen to water. The most extreme losses were found for samples containing granite.

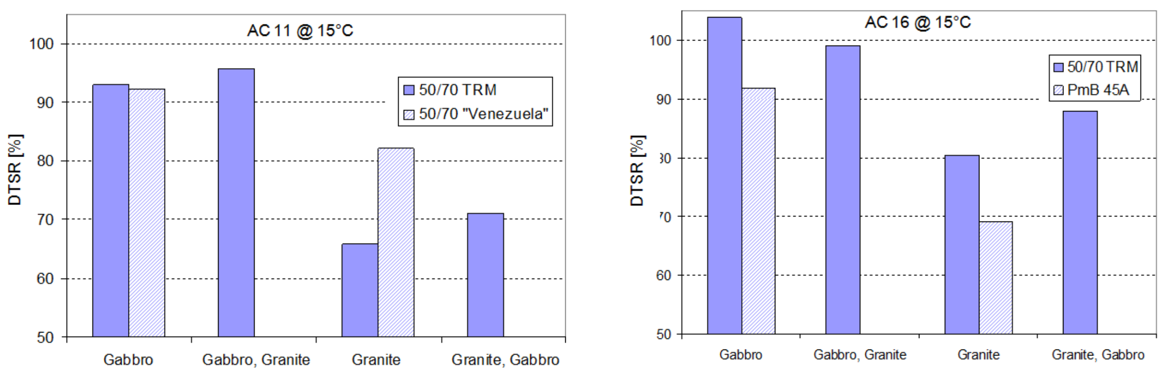


Figure 15: Influence of aggregate and bitumen type on remaining tensile strength after water storage.

3.9. Direct Tensile Strength Test on Aggregate Rods

First results obtained from direct tensile strength tests on aggregate rods showed that contact strength between bitumen and aggregate can be assessed in a fast and simple way. However, it was found, that the choice of test conditions is of utmost importance for the scattering of test results. Further investigations are needed to specify the most suitable test conditions.

4. Conclusions

The ranking of bitumen-aggregate interaction properties is usually investigated on the bitumen level, and on the asphalt mix level. The following test methods were comparatively analyzed in this study (i) at the bitumen level: contact angle measurement (in various ways), Rolling Bottle Test, static water storage, and the direct tensile strength test performed on rods drilled out from aggregate rock and stuck together with bitumen film; and (ii) at the asphalt mix level: the indirect tensile strength test and the direct tensile strength test.
From this study the following conclusions can be drawn:
All tests were found to be of limited appropriateness for routine testing. A number of disadvantages were identified depending on the test method, like test complexity, inappropriate methods for sample conditioning, high rate of scatter in test results, and/or difficulties to separate interrelated factors influencing the test results.
Strength tests do not allow distinguishing clearly between adhesion and cohesion properties, but are intended for quality assessment of different bitumen products.
The contact angle measurement is an intriguing method to study bitumen and the method has given rise to great expectations due to the prospect of obtaining information about adhesive interactions and surface effects between bitumen, mineral aggregates, and water, respectively. Some researchers have even mentioned the perspective that this method might give access to the forecast of the adhesive qualities of bitumen-mineral aggregate mixtures. However, poor reproducibility and high standard deviations impose severe limits. By introducing minimum standards for image quality, the reproducibility can be increased significantly.
Wetting of bitumen surfaces was found to be inappropriate for distinguishing bitumen samples. The experimental data indicate that the tested bitumina have similar surface free energies, and the pendant drop method alone is not suitable to differentiate between the bitumen samples.
The experiments involving the bitumen drop on glass slides provided intriguing results and did not fail to differentiate the bitumina if the right storage time and resting temperature was chosen.

5. REFERENCES

[1] Renken, P. 1992. Untersuchungen zum Haftverhalten zwischen Bindemittel und Gestein. Straße + Autobahn, 1/1992, Kirschbaum Verlag, Bonn.

[2] Renken, P., Wistuba, M., Grönniger, J. und Schindler, K. 2010. Adhäsion von Bitumen am Gestein. Verfahren der quantitativen Bestimmung auf Grundlage der Europäischen Normung. Schlussbericht zum Forschungsprojekt des Instituts für Straßenwesen der TU Braunschweig, erschienen in: Forschung Straßenbau und Straßenverkehrstechnik, Bundesministerium für Verkehr, Bau und Stadtentwicklung, Heft 1043.

[3] CEN, Comité Européen de Normalisation. 2009. Activity Report of the CEN Ad-hoc Group „Adhesion/Durability". Forschungsbericht 2009/TC/012-N090, Brüssel.

[4] Basu, A., Nandakumar, K., Masliyah, J.H. 1996. Study of Oil Displacement on Model Surfaces. Journal of Colloid and Interface Science, 182, Elsevier Science Ltd., UK, p. 82ff.

[5] Hirsch, V., Friemel-Göttlich, B. 2004. Bestimmung des adhäsiven Potentials von Bitumen und Gesteinsoberflächen mit Hilfe der Kontaktwinkelmessmethode. Bundesanstalt für Straßenwesen, Bergisch Gladbach.

[6] Dang-Vu, T., Jha, R., Wu, S.-Y., Tannant, D.D., Masliyah, J., Xu, Z. 2009. Effect of Solid Wettability on Processability of Oil Sands Ores. Energy & Fuels, Vol. 23, American Chemical Society, US, p. 2628ff.

[7] Ren, S., Dang-Vu, T., Zhao, H., Long, J., Xu, Z., Masliyah, J. 2009. Effect of Weathering on Surface Characteristics of Solids and Bitumen from Oil Sands. Energy & Fuels, Vol. 23, American Chemical Society, US, p. 334ff.

[8] Neter J., Kutner M., Nachtsheim C., and Wasserman W. 1996. Applied Linear Statistical Models, The McGraw-Hill Companies, Inc., Boston, MA., cp. chapter 16,8 and 16,9.

[9] Hefer, A.W., Bhasin, A., Little, D.N. 2006. Bitumen Surface Energy Characterization Using a Contact Angle Approach. Journal of Materials in Civil Engineering, Vol. November/December 2006, American Society of Civil Engineers, US, p. 759ff.

[10] Jada, A., Salou, M. 2002. Effects of the asphaltene and resin contents of the bitumens on the water–bitumen interface properties. Journal of Petroleum Science & Engineering, Vol. 33, p. 185ff.

[11] Grönniger, J., Wistuba, M. and Renken, P. 2010. Adhesion in bitumen-aggregate systems – new technique for automated interpretation of Rolling Bottle Tests. Int. J. of Road Materials and Pavement Design, ISSN 1468-0629, Vol. 11, No. 4/2010, Lavoisier, Paris.