Impact of the bitumen quality on the asphalt mixes performances

Frédéric Delfosse[1, a], Ivan Drouadaine[1, b], Stéphane Faucon-Dumont[1], Sabine Largeaud[1, c], Bernard Eckmann[2], Jean Pascal Planche[3, d], Fred Turner[3], Ron Glaser[3]

[1] *Eurovia, Mérignac, France*
[2] *Eurovia, Rueil Malmaison, France*
[3] *Western Research Institute, Wyoming, United States*

[a] frederic.delfosse@eurovia.com
[b] ivan.drouadaine@eurovia.com
[c] sabine.largeaud@eurovia.com
[d] jplanche@uwyo.edu

Digital Object Identifier (DOI): dx.doi.org/10.14311/EE.2016.049

ABSTRACT

European refining, French in particular, is currently going through a phase of rationalization and search for maximum flexibility in crude supplies. For users of bitumen, this creates concerns about the quality and consistency of products delivered, especially as the European standard EN 12591 appears to them as insufficient to ensure satisfactory performance of the finished products, particularly in the case of specialty products such as high modulus asphalt, polymer modified bitumen, and bitumen emulsions.
In this context, the search for correlations between bitumen properties and the performance of the finished product is more relevant than ever. The study presented here is focused on asphalt made with pure bitumen. It was based on a standard design, but with two different types of aggregates. After a preliminary selection, 8 bitumen (20/30, 35/50 and 50/70 pen. grades) were selected. The characterization of asphalt mixes covers all the usual characteristics (stiffness modulus, resistance to rutting and fatigue, resistance to thermal cracking, water sensitivity). The characterization of binders, besides conventional testing, includes the rheological properties (DSR, MSCR, and BBR tests) and the compositional analysis, particularly infra-red spectroscopy and SARA analysis. These tests were performed on the original binders, after RTFO, after RFFO + PAV as well as on the binders recovered from asphalt.
This project was conducted as a collaboration between Eurovia and the Western Research Institute (WRI) which performed the compositional analysis of binders, including the SAR-AD™ (WRI improved SARA separation technique) and the chemometrics analysis using their software ExpliFit™.

Keywords: Ageing, Asphalt, Chemical properties, Low-Temperature, Rheology

1. INTRODUCTION

In recent years, a significant evolution on the European bitumen market has been observed. French and European refining is currently in a phase of rationalization and search for maximum flexibility in crude supplies.

Road contractors such as Eurovia are worried about bitumen quality and have observed new problems on field.

The current European standard EN 12591 appears insufficient to ensure satisfactory performance of the finished products, particularly in case of specialty products such as high modulus asphalt (modulus, fatigue), polymer modified bitumen, and bitumen emulsions (settling tendency, viscosity).

The paving industry is therefore more and more confronted with the same problem: how to evaluate the quality of a given bitumen in relation to its intended use.

The search and validation of performance-related bituminous binder properties continues to be a key issue for the paving industry in Europe, as well as in the rest of the world. With the Superpave system implementation in the US, important progress has been achieved and is still on-going. In Europe, the development of 2nd generation product standards appears to be more necessary than ever.

In this context, Eurovia and the Western Research Institute (WRI) in Laramie, Wyoming (USA) launched a research program in 2013 to search for correlations between bitumen properties and the performance of the finished product.

2. RESEARCH PROGRAM

The research program was based on a carefully selected experimental matrix.

Eight bitumen samples (all unmodified) were selected: B1 to B8. With these binders, 12 asphalts were manufactured (8 with diorite and 4 with limestone aggregates). Each asphalt had a 4.9% bitumen content.

Table 1 presents the main characteristics of these bitumen samples and the different asphalt designs.

Table 1: Bitumen characteristics and asphalt designs

	B1	B2	B3	B4	B5	B6	B7	B8
Penetration (1/10 mm) : NF EN 1426	40	37	40	22	26	28	55	57
Rind and Ball Temperature (°C) : NF EN 1427	53.4	53	52	59	57.2	61	49	49.2
Superpave performance grading (PG)	70-22	70-16	70-16	76-16	76-16	76-10	64-22	64-16
HMA with diorite	X	X	X	X	X	X	X	X
HMA with limestone	X		X	X			X	

The analysis program for the bitumens (neat, after RTFO, recovered, after RTFO + PAV) included:

1- Chemical analysis: infrared, SAR-AD: Saturates, Aromatics, Resins and Asphaltene Determinator [1], SEC: Size exclusion chromatography, DSC: Differential Scanning Calorimetry (glass transition, wax content)

2- Superpave rheological tests: Bending Beam Rheometer (BBR), DSR: master curves, crossover, R parameter [2]…

3- Advanced rheological tests (LAS tests [3]…)

4- Asphalt Binder Cracking Device (ABCD) test [4],

5- Conventional European tests: penetration, ring and ball temperature, Fraass breaking point [5],,…

Table 2 presents the different tests performed to analyze asphalts.

Table 2: Asphalt tests performed

Test	Standard
Gyratory shear compactor	NF EN 12697-31
Water sensitivity	NF EN 12697-12 A
	AASHTO T283
Wheel tracking test	NF EN 12697-22
Stiffness modulus	NF EN 12697-26 E
	NF EN 12697-26 C
	LC 26/700
Fatigue	NF EN12697-24
Thermal Stress Restrained Specimen (TSRST)	AASHTO TP 10
Void content/sample	Gamma bench

From the overall research program launched in 2013, this article will present only some chemometric results [6], and the correlation between bitumen properties at low temperature (BBR, ABCD test, glass transition, Fraass breaking point) and asphalt properties at low temperature (Thermal Stress Restrained Specimen Test) with diorite aggregates. Other articles will be published in the future to present more results in detail.

3. BITUMEN SELECTION

The key starting point in a chemometric correlation is based on the quality of bitumen selection. The first step of the program before launching the analyses was to verify that the chemical composition and rheological properties of the selected bitumen samples were significantly different.

3.1 Chemical composition

The SAR-AD [1] analysis is a novel approach, developed by the Western Research Institute. The main principle of this approach is an on-column precipitation followed by a sequence of re-dissolutions, using selected solvents and columns at the various stages of the separation. In practice, it combines the Automated Asphaltene Determinator (AD) separation with an automated SAR (saturates, aromatics and resins) separation to provide a fully integrated rapid automated SARA (saturated, aromatics, resins and asphaltenes) separation using milligram sample quantities. The combined SAR-AD separation utilizes high performance liquid chromatography (HPLC) equipment with multiple columns and solvents switching valves to conduct the highly complex automated separation. The solvents are selected on polarity and include n-heptane, cyclohexane, toluene, dichloromethane / methanol blend.

Figure 1 presents the chemical compositions of the 8 bitumens.

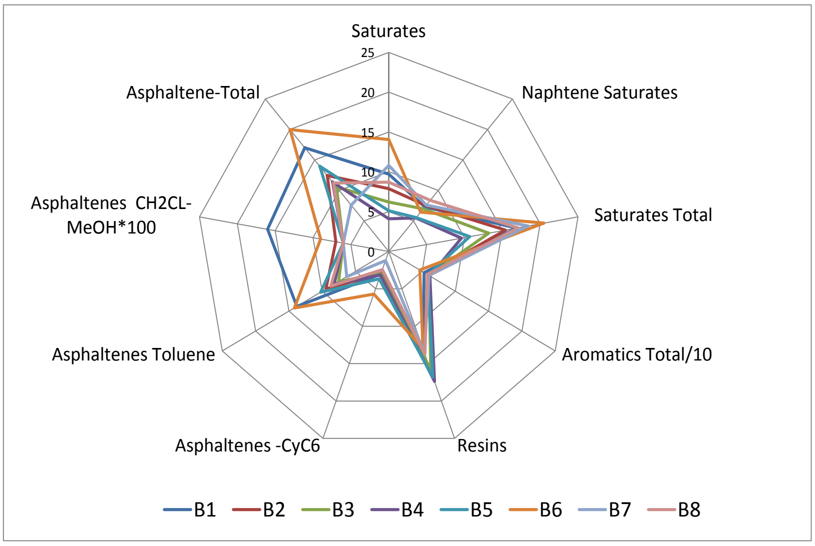


Figure 1: Bitumen composition for B1 to B8

3.2 Rheological properties

Figures 2a and 2b present the isotherms at 15°C from 1 to 30Hz.

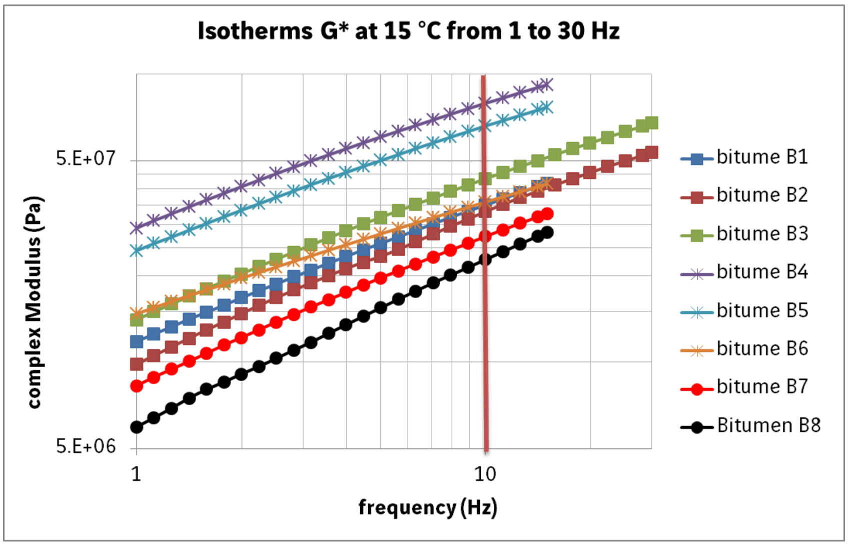


Figure 2a : Isotherms G* at 15°C from 1 to 30 Hz

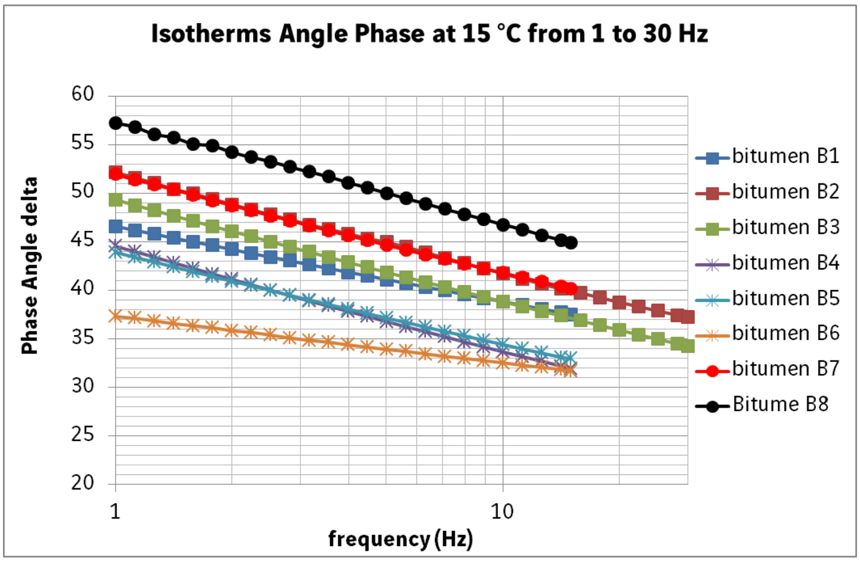


Figure 2b : Phase angle at 15°C from 1 to 30 Hz

3.3 Comments

These analyses enabled the validation of the bitumen choice, showing significant differences both in chemical composition and rheological properties. For example, the asphaltene content varies from 7 to 20 % and the saturate content from 9 to 21 %, whereas the bitumen rheological properties feature differences both in terms of stiffness level and thermal susceptibility. Thus, it is worth mentioning the atypical rheological behavior of sample B6, and of B1 to a lesser degree.

4. CHEMOMETRIC CORRELATIONS

4.1 Chemometric Software

A new software [5] has been used to investigate relationships between independent and depend variables using standard multivariable linear regression algorithms. This software was developed at Western Research Institute.

The dependent variables data are all analyses performed on bitumen or asphalt.

The independent variables data are typically measured to predict the dependent variables data. In this research program, the independent data include infrared (IR) spectra measurements, SAR-AD compositions, and distribution of the particle sizes by SEC.

Example: If we try to correlate bitumen IR measurements with bitumen penetration, in a first step, the software will find out which of the wavenumbers are significant when combined additively with other significant wavenumbers. This step will enable a reduction in the number of relevant wavenumbers. In a second step, the software will propose a correlation equation such as:

Bitumen penetration (1/10 mm) = $c_0 + c_1$ [Abs_1] + c_2 [Abs_2]+ + ….c_n [Abs_n]

c_1= Fit coefficient 1, Abs_1 = Absorbance to the wavenumber 1 …

In addition to the actual measurements, a precision file for each independent and dependent variables data set must also be prepared. The program requires these files to create the data clouds needed for computation. From these values, the software represents automatically the correlation between predicted values and measured values (figure 3): black dots represent the actual measurements, red dots are created data points.

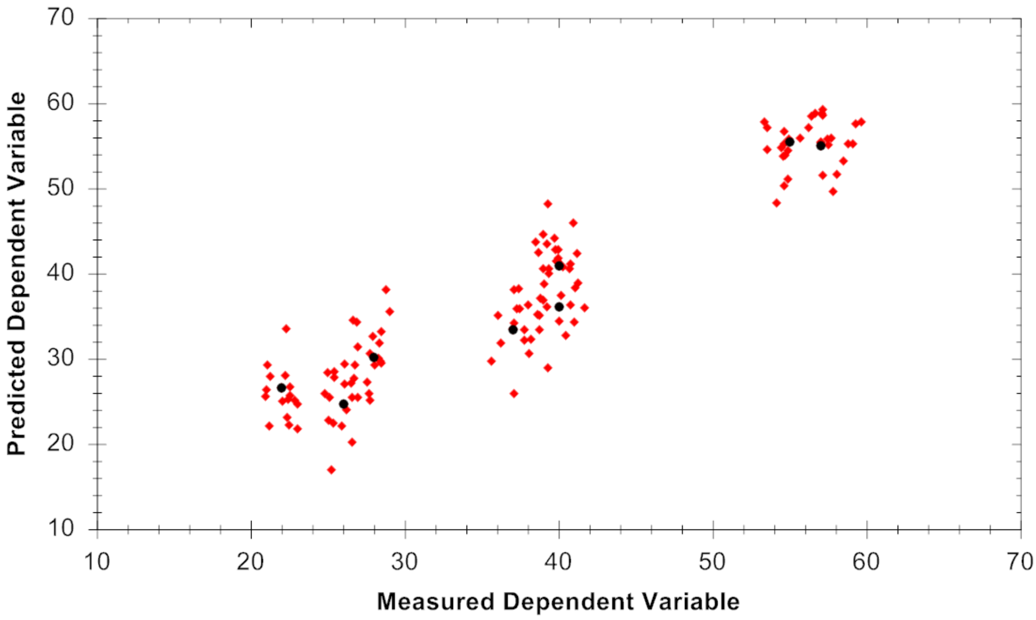


Figure 3 : Chemometric correlation obtained by Explifit® software.
Calculation of bitumen grade from IR measurements

In this case the software gives the following equation:

Bitumen penetration (1/10 mm) = 27.4 + 1211 [Abs $_{1035}$] -1363 [Abs $_{1570}$] +13.71 [Abs $_{2929}$]- 1053 [Abs $_{3854}$]

The linear regression coefficient (R^2) is 0.90.

4.2 Results

Different chemometric correlations are presented here:

4.2.1 Correlation between bitumen properties from Infrared measurements

All the IR measurements are performed using a PerkinElmer Spectrum 400 infrared spectrometer.

The bitumen concentration is 3 w% in perchloroethylene. For all the chemometric correlations, we determined the linear regression coefficient (R^2) and an equation of correlation with 2 to 4 (maximum) independent variables. Figure 4 features the R^2 correlation coefficient according to the different bitumen tests. From only 8 bitumen samples, interesting fair correlations are obtained with R^2 ranging from 0.55 to 0.88, most above 0.75.

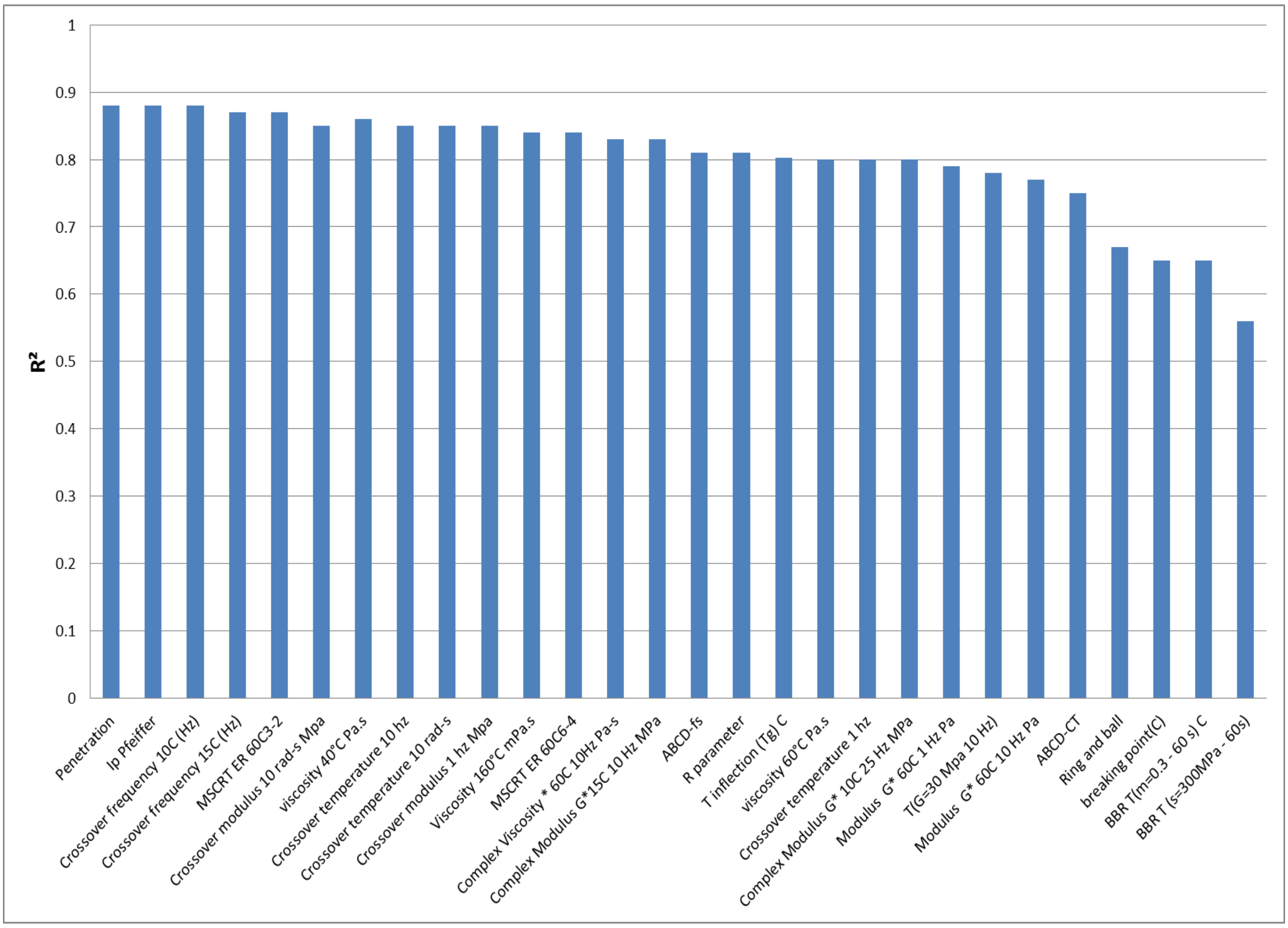


Figure 4 : Correlation between IR measurements and bitumen tests

4.2.2 Correlation between bitumen properties and SAR-AD compositions

Figure 5 presents correlations obtained between SAR-AD bitumen composition and bitumen tests.

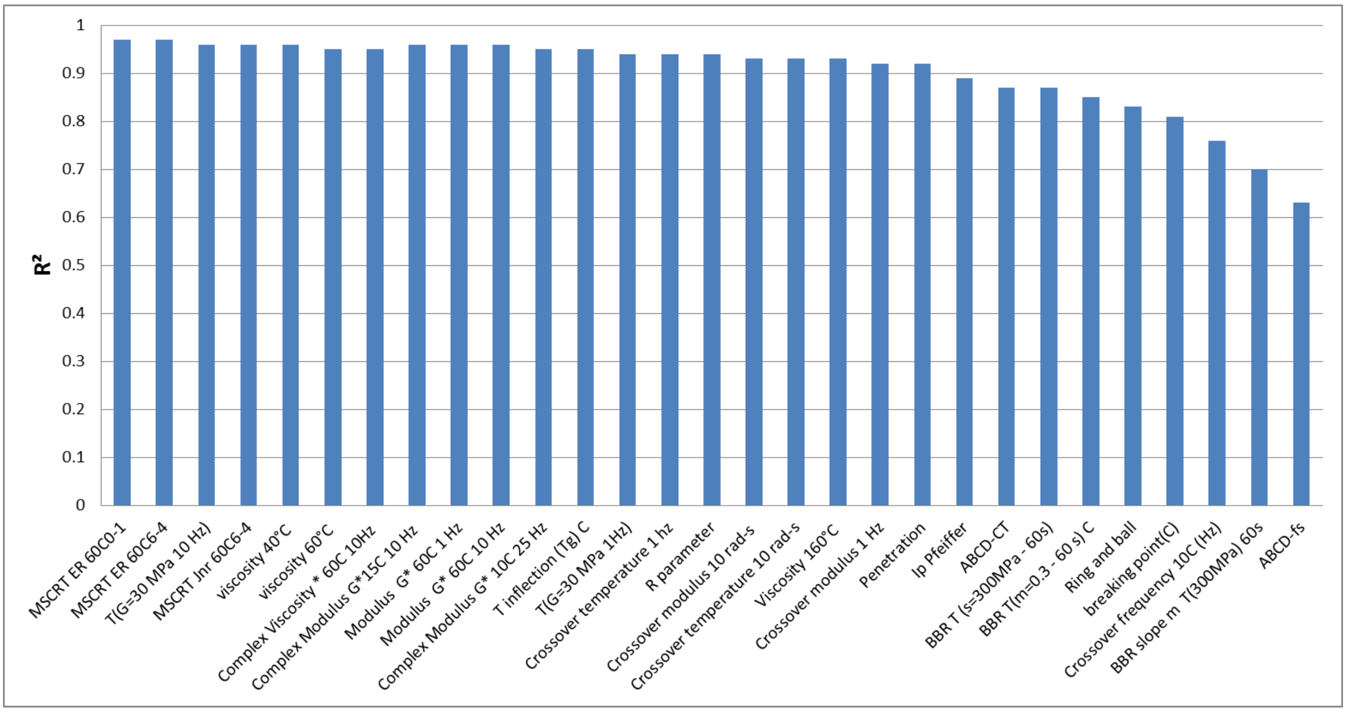


Figure 5 : Correlation between SAR-AD measurements and bitumen tests

From SAR-AD compositions, more interesting and stronger correlations are obtained with R^2 ranging from 0.62 to 0.98, most above 0.80, including very good correlations ($R^2 > 0.85$), using 3 or 4 independent variables, with a lot of tests such as MSCR, dynamic viscosity (40 to 160 °C), complex viscosity (60°C), complex modulus (10 to 60°C for different frequencies), crossover modulus, crossover temperature, R-parameter, penetration test, IP Pfeiffer…

For some tests, the correlation is less relevant (R^2 between 0.6 and 0.85): Ring and Ball temperature, Fraass breaking point, BBR results, ABCD results…

Among the various fractions determined by SAR-AD measurements, 2 fractions often appear in correlations: naphthene saturates and asphaltene soluble in cyclohexane.

5. CORRELATION BETWEEN ASPHALT PROPERTIES (AC 10) AND SAR-AD COMPOSITIONS OF THE CORRESPONDING BITUMEN

A lot of asphalt tests are impacted by the mix design and the nature of the aggregates (shape, petrography…): gyratory shear compactor, rutting, sensitivity to water or stiffness modulus according to test procedure.

To be able to predict the impact of the chemical composition of bitumen, the mix design was fixed in terms of void content, bitumen content, and aggregate nature (diorite). This research was based on the following tests: rutting, various stiffness modulus tests all using cylindrical specimens (NF EN 12697-26 C, applying indirect tension at 10 °C for 124ms application time, NF EN 12697-26 E applying direct tension at 15°C, for 0.02 s, LC 26/700 applying direct tension compression at 15 °C, 10 Hz), fatigue and TSRST.

Figure 6 presents the chemometric correlations obtained from SAR-AD composition of neat bitumen and bitumen after RTFO.

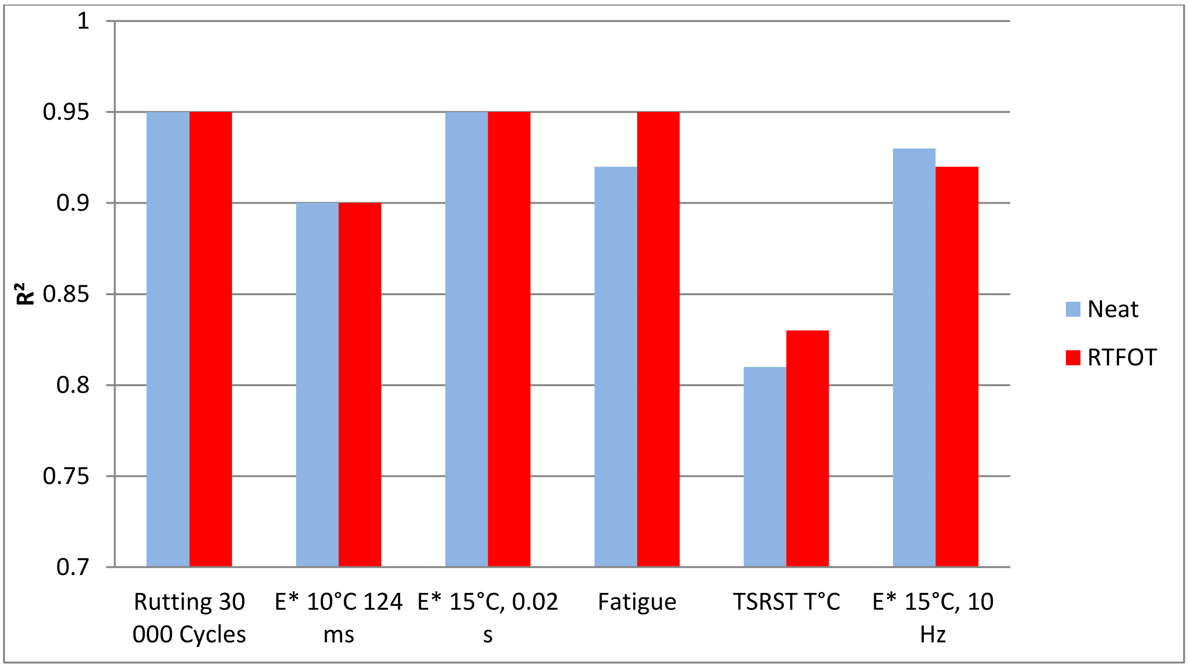


Figure 6 : Correlation between chemical composition of bitumens (SAR-AD) with asphalt performances

Very good correlations are obtained from SAR-AD composition except for the TSRST tests. Concerning low temperature performance as measured by TSRST, the lower quality of the correlation may be connected to the lower quality of the correlations obtained for low temperature tests (Fraass, ABCD, BBR) on bitumen (Figure 5).

6. RELATIONSHIPS BETWEEN LOW TEMPERATURE BEHAVIOR OF BITUMEN AND ASPHALT PERFORMANCE (TSRST)

The Fraass test is the common test in Europe to qualify bitumen at low temperature. This test is known for its poor reproducibility and its use for PmB characterization is often disputed [7]. The bending beam Rheometer (BBR) [8], developed during the SHRP program, enables the determination of two criteria: the stiffness modulus and the ability of stress relaxation of the bitumen (m-value = - d(logS)/d(log t)). The relaxation rate is a function of the loading time dependency of the stiffness and directly related to the creep rate. The higher the creep rate, the faster the relaxation of stresses. These two parameters are numerically called:

- $T_{S=300\ MPa}$ = temperature at which the stiffness modulus (S) equals 300 MPa for the loading time of 60 s
- $T_{m=0.3}$ = temperature at which m = 0.3 for the loading time of 60 s

In the literature, the correlation between BBR test results on bitumen and polymer modified bitumen with the TSRS test on asphalt are contrasted [9,10]. Other authors found interesting correlations between BBR results and field behavior after several years [11] or validated that linear viscoelastic properties play an important role in the energy dissipation during crack opening but highlighted that this test is insufficient to predict the temperature of brittleness of bitumen [12].

In order to have an overall view of the different tests used to characterize the low temperature behavior we added two other tests in this research program: the ABCD test [4,13] and DSC to determine the glass transition [14].

The ABCD test is a fairly new test method, using a simple testing device that can provide the overall low temperature cracking potential of a bitumen. A circular bitumen specimen is prepared on the outside of an Invar ring. Invar is a steel alloy with near zero coefficient of thermal expansion/contraction. As the temperature is lowered, the thermal stress within the bitumen increases until fracture. For the tests, the cooling rate was fixed at 10°C/h.

Figure 7 presents the results obtained on the 8 neat bitumen samples.

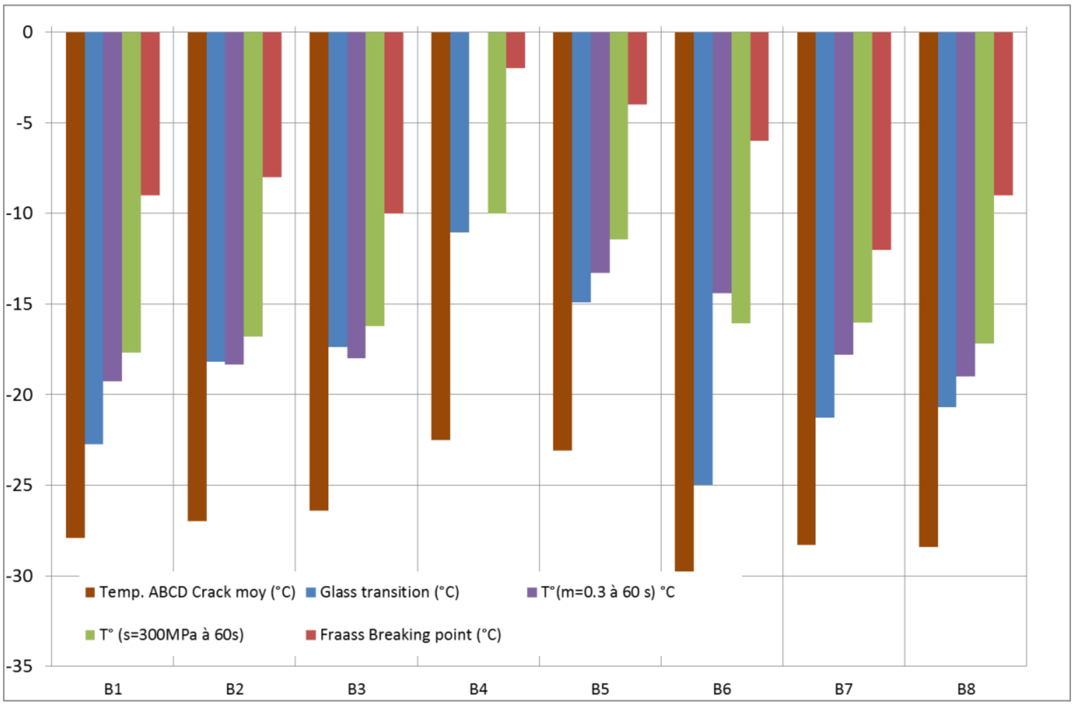


Figure 7 : Comparison of different tests to qualify the low temperature behavior of bitumens

Taking into account the reproducibility of the ABCD test (R=3), the bitumen classification in ascending order of temperature gives the following result : B6 (-30°C) <B7, B8, B1 (-28°C) <B2, B3 (-27°C) < B4, B5 (-22.5°C). The glass transition measurement, gives a temperature between 5 and 11 °C higher. The bitumen ranking remains the same except for sample B4 which becomes the most brittle. The BBR test results do not show significant difference according to either $T_{S=300MPa}$ or $T_{m=0.3}$. The main difference in comparison to the glass transition or ABCD test concerns sample B6. With the BBR test, this sample seems to be more brittle than samples B7, B8, B1, B2 and B3. The level of temperature with this test is close to the glass transition temperature. The Fraass breaking point ranks bitumen according to their grade at a significantly higher level of temperature: 20°C vs. the ABCD test, and 5 to 10°C vs. BBR or the glass transition. Figure 8 compares these results with TSRST critical temperature values.

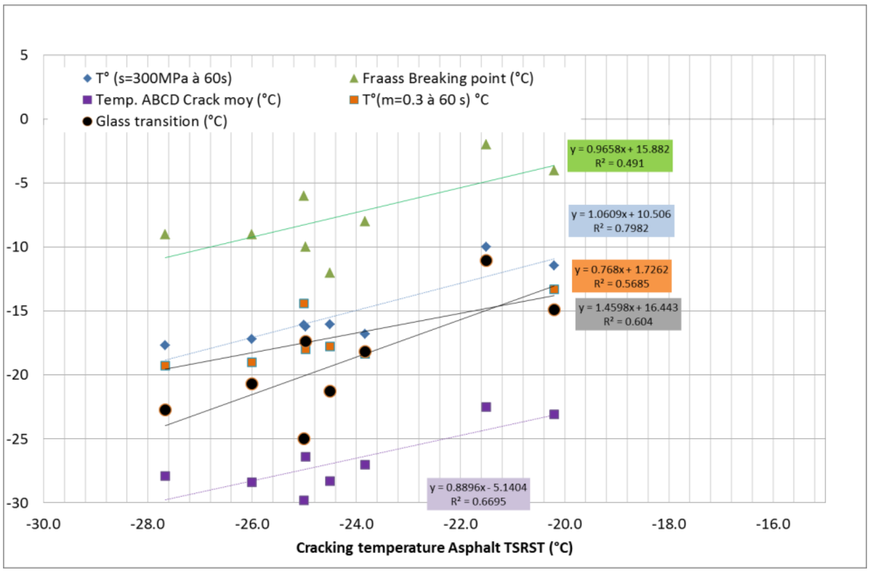


Figure 8: Correlation between TSRST test and different bitumen tests before aging

The best correlation is obtained with the BBR test on the S criterion ($T_{S=300MPa}$) but the ABCD test gives cracking temperatures closest to the TSRS test critical ones. Subtracting 10 °C to the BBR temperatures as applied in the Superpave specifications, the gap with the TSRST values becomes very low.

There is no correlation between the TSRS test and the Fraass values (between 10 to 20°C of difference).

Figure 9 presents the correlation between the bitumen tests after aging (RTFOT + PAV) with the TSRS test.

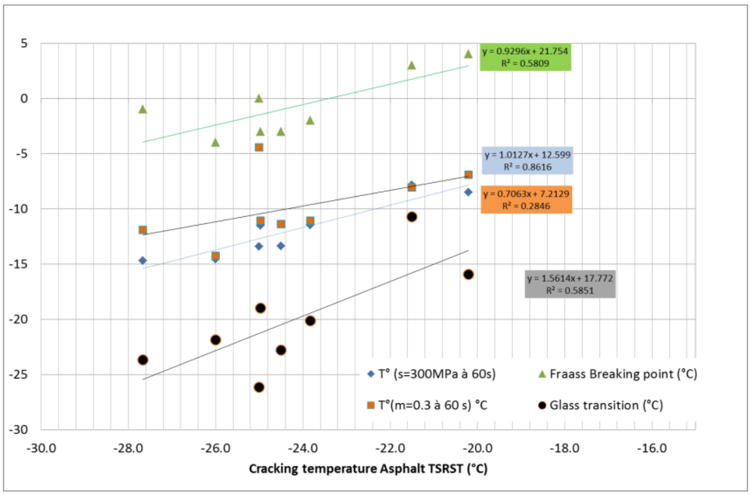
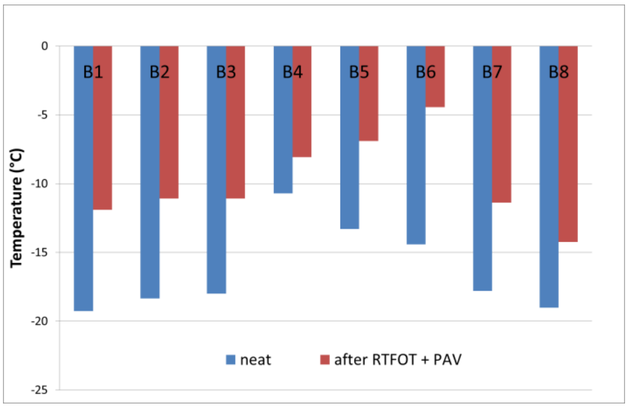


Figure 9: Correlation between TSRST test and different bitumen tests after RTFOT+ PAV aging

PAV aging does not have the same impact on the different BBR criteria. $T_{S=300\ MPa}$ correlates well with the TSRS test; the evolution of temperature (after PAV versus unaged) is between 15 to 30% for all bitumen samples. $T_{m=0.3}$ on neat bitumen and even more on bitumen after RTFO + PAV doesn't correlate with the TSRS critical temperature.

Figures 10 a and 10 b present the difference for all bitumen samples after aging on the BBR tests.



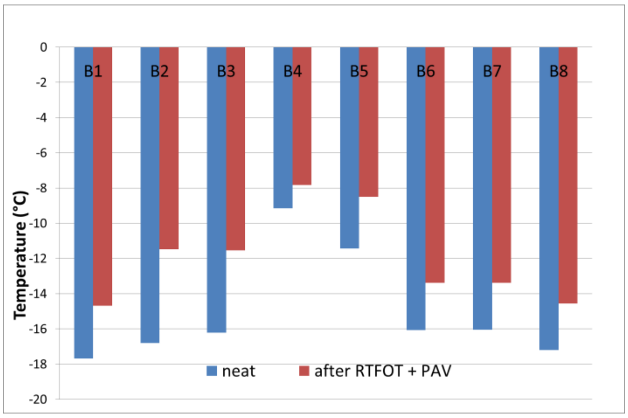


Figure 10a : $T_{m=0.3}$ before and after RTFOT + PAV **Figure 10b : $T_{S=300\ MPa}$ before and after RTFOT + PAV**

These results highlight the importance of analyzing the low temperature properties of bitumen after aging. Some bitumen are sensitive to oxidation phenomena and their low temperature characteristics are strongly impacted. According to bitumen origin, aging reduces greatly the relaxation potential of bitumen while the effect on the low temperature stiffness is only moderate. This is particularly the case of bitumen B6 [15].

The difference of temperature (ΔT) between $T_{S=300\ MPa}$ and $T_{m=0.3}$ after PAV could be a good indicator to illustrate this bitumen oxidation sensitivity (figure 11). The higher the |ΔT| value, the higher the sensitivity to oxidation and lesser the durability of the road could possibly be.

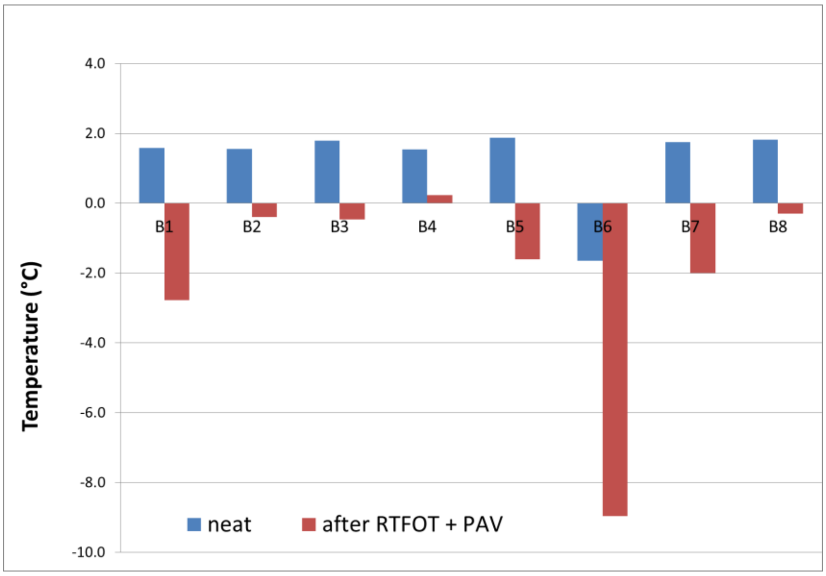


Figure 11: Evaluation of the bitumen oxidation ΔT ($T_{S=300\ MPa}$ - $T_{m=0.3}$)

The PG (Superpave Performance Grade) of the bitumen B6 is conditioned by its property after PAV; B1 also shows some of the same behavior but to a lesser extent. This is not reflected by the mechanical properties measured on laboratory made asphalt which lead to very good results (fatigue, TSRST…). However, these asphalt properties are measured with no long term aging conditioning. This is likely to explain this discrepancy.

Additional tests are ongoing at the Eurovia research centre. More asphalts will be laboratory manufactured and aged according to the procedure defined by the RILEM ATB/SIB technical committee [16] using some of the same bitumen samples, keeping the same VMA and VFA. The TSRS test will be then performed to correlate with the BBR results after PAV.

7. CONCLUSION

The collaboration Eurovia/Western Research Institute enabled to evaluate the potential of applying chemometric correlations to predict bitumen or asphalt properties from the infrared spectrum or /and the SAR-AD generic composition.

Correlations to date are more relevant for SAR-AD composition than Infrared data. An Infrared spectrum contains more than 3400 wavelengths, the selection of 3 or 4 wavelengths from only 8 bitumens is too complex. Additional investigations on a wider bitumen population may enable to improve some of these correlations.

From SAR-AD compositions, good correlations were found with several bitumen viscosity or rheological tests ($R^2 >$ 0.85), including the viscoelastic behavior characterized by the R-parameter, crossover modulus, and penetration. For BBR or ABCD low temperature properties, the correlations are less relevant ($R^2 < 0.8$).

Chemometric correlations with asphalt properties are obviously more complicated. For many tests, the aggregate impact is significant (sensitivity to water, gyratory shear compactor…). From the SAR-AD test limited to 2 or 3 fractions, very interesting and significant correlations are obtained to predict fatigue, stiffness modulus…

Additional analyses are ongoing to improve or validate these correlations but also to search for new correlations to understand the impact of bitumen origins on their mechanical performances after long term aging…. About 10 new bitumen samples are going to be added to this study.

The second part of this collaboration is devoted to the comparison between bitumen tests and asphalt tests to propose new and more relevant performance indicators for product standards in Europe. In this filed, the present article has been focused on low temperature properties.

The results highlight the importance of analyzing the low temperature behavior of bitumen after aging to take into account the impact of oxidation. According to bitumen origin, aging can greatly reduce the relaxation potential of bitumen while the effect on the low temperature stiffness is only moderate. It is to be reminded here that some publications correlate indeed stress relaxation to the cracking phenomenon on field.

The fact that asphalt tests are always done at the early stage could explain the bad correlation with the BBR results after PAV. Additional tests will be performed on asphalt after aging to evaluate the ability to correlate with BBR results after PAV.

These trials may enable to answer recurring questions related to low temperature performance, such as the possibility to correlate a stiffness test on bitumen with a thermal stress restrained test on asphalt, and the selection of more relevant test methods to predict cracking phenomena in the field after aging.

REFERENCES

[1] *The Automated Asphaltene Determinator Coupled with Saturates,Aromatics, and Resins Separation for Petroleum Residua Characterization*, Ryan B. Boysen and John F. Schabron, Energy Fuels 2013, 27, 4654−4661

[2] *Interpretation of Dynamic Mechanical Test Data for Paving Grade Asphalt* , Christensen, D.W. and Anderson, D.A. Journal of the Association of Asphalt Paving Technologists, 61, 67-116, 1992

[3] AASHTO TP 101-12-UL, *Estimating Damage Tolerance of Asphalt Binders Using the Linear Amplitude Sweep*, available on the MARC website: http://uwmarc.wisc.edu/linear-amplitude-sweep

[4] *Asphalt Binder Cracking Device to Reduce Low-Temperature Asphalt Pavement Cracking*, S. Kim, Final Report, FHWA-HIF-11-029, 2010

[5] NF EN 12593: *Determination of the Fraass breaking point*

[6] *Chemo- mechanical software, Fundamental properties of asphalts and modified asphalts product*, R. Glaser, A. Beemer, T.F. Turner, march 2015

[7] *Checking low temperature properties of polymer modified bitumen – is there a future for Fraass Breaking point ?*, B. Eckmann, M. Mazé, Y. Le Hir, O. Harders, G. Gautier, B. Brulé, 3rd Eurasphalt & Eurobitume congress, Vienne, 2004

[8] NF EN 14771: *Determination of the flexural creep stiffness: Bending beam rheometer* (BBR)

[9] *Caractérisation du comportement à basse température des liants bitumineux*, S. Largeaud, B.Eckmann, S. Faucon Dumont, Y. Hung, L. Lapalu, G. Gauthier, Revue générale des routes et de l'aménagement, n° 928, juin 2015

[10] *Combined traffic and climate effects on durability of pavement mixture with polymer modified binder*, M. Ould-Henia, A.G Dumont, M. Pittet, J.P Planche, S. Dreessen, Proceedings ISAP 2010 congress, Nagoya, JP, p 1594.

[11] *Durability study: Field aging of conventional and polymer modified binders*, S; Dreessen, M. Ponsardin, JP. Planche M. Pittet, A.G Dumont, TRB, 2010

[12] *Relationships between low temperature properties of asphalt binders*, Babadopoulos, Le Guern, Chailleux, Dreesen, ISAP 2012

[13] *Determination of low temperature thermal cracking of asphalt binder by ABCD*, S.S Kim, Z.D. Wysong, J. Kovach, TRB, 2006

[14] *Characterization of paving asphalt by differential scanning calorimetry*, P. Claudy, J.M Létoffé, G.N King, J.P Planche, B. Brulé, Fuel science and technology international 9, 1991.

[15] *Performance indicators for low temperature cracking*, H. Soenen, A. Vanelstraete, Rilem, 2003

[16] *Advances in interlaboratory testing and evaluation of bituminous materials*, M.N. Partl et al., Rilem state of art report 9, 2013