Binder performance and testing

Which are the best rheological criteria for characterization of PMB ?

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Abstract

The classification standard for polymer modified bitumens (PMB) is currently under CEN/TC336/WG1 revision work, an opportunity to take a step towards classifying binders based on their performance. The first attempts were based in particular on the recent evolution of the EN12591 standard for the classification of pure bitumens, for which the declaration of values of certain rheological criteria obtained at the DSR are now compulsory. The selected DSR rheological criteria on RTFOT aged binder are relevant for pure bitumens. They have been chosen to take into account both: - relation with the fatigue behavior (to be in the temperature range such that the elastic component becomes preponderant versus the viscous component i.e phase angle δ> 45 °), and the rutting behavior (within the typical R&B temperature range) - measuring the probable ranges of G* with the same geometry device The first project to change the specification standard for PMB naturally relied on these same criteria at the DSR, also extending it to long-term aging, but are they still relevant for PMB? It was also based on criteria from the MSCR test after RTFOT (repeated creep test behavior at 60 ° C) and the cold behavior BBR test The investigation of a panel of different industrial SBS modified bitumens led us to identify which are among all these rheological tests the most relevant to rely with performance.

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1. INTRODUCTION

The classification standard for polymer modified bitumens (PMBs) -EN14023- is currently under revision. This work, under the responsibility of CEN/TC336/WG1 is an opportunity to take a step towards classifying binders based on their performance.
The first attempts were based on the draft elaborated in the framework of the evolution of the EN12591 standard for the classification of pure bitumens [1]. Some rheological criteria on short aged pure binder have been introduced in this draft, taken into account:
- the possible correlations with both the fatigue behavior (to be in the temperature range such that the elastic component becomes preponderant versus the viscous component i.e phase angle δ < 45 °) and the rutting behavior (within the typical softening point range)
- the ability to use the same equipment and same geometry assembly device for all the rheological criteria

The first EN14023 project [2] naturally relied on these criteria, also extending them to long-term aging. But are these criteria still relevant for PMBs ? The project was also based on criteria from the “Multiple Stress Creep Recovery (MSCR) test” and from the ‘’Bending Beam Rheometer (BBR) test’’.

Unfortunately, revision project of key specification standard EN 12591 has been negatively assessed by NAC consultant. The TC 336, willing to avoid additional confusion among the market players by publishing a revision that will not be harmonized, decided in 2019 to forgo the revision project. As a result, the revision project of PMBs specification standard EN14023 has been postponed too.

Regardless of these normative considerations, the target of this paper is to investigate which are the rheological criteria able to best differentiate between pure and modified bitumens and to highlight PMBs performances.

2. EXPERIMENTAL RHEOLOGICAL ASSESSMENT OF PURE AND MODIFIED BITUMENS

2.1. Materials

For the purpose of the study we have selected:
- 12 pure bitumens from 2 origins (refineries A and B) and 6 grades for each origin (10/20 – 20/30 -35/50 - 50/70 -70/100 - 160/220)
- 17 SBS modified bitumens, coming from 8 different industrial plants. They are all ‘PMB 25/55’. Their softening points are all above 60°C: 60.8°C for the lowest, 83.6°C for the highest.

The basic properties of all the binders are reported respectively in **Tables 4 & 5**.

2.2. Laboratory tests methods

Aging methodology
The laboratory ageing methodology is based on a combination of 2 tests conducted on thin films of binders: RTFOT (Rolling Thin Film Oven Test) aging according to EN 12607-1 and PAV (Pressure Aging Vessel) long term aging according to EN 14769.

Rheology methodology
Dynamic Shear Rheometer (DSR) is used to monitor the rheological viscous and elastic properties characteristics of the binder. All testing is carried out according to the EN14770 with an Anton Paar rheometer MCR501. The DSR geometry assembly is composed of 2 steel parallel plates of 8mm diameter. The gap is 2mm. All the tests are conducted within the linear viscoelastic region as defined by the EN 14770.
Both complex shear modulus G* (MPa) and phase angle δ are determined.
δ reflects the viscous/elastic character of the binder because: if δ → 0, more elastic is the binder; if δ → 90°more viscous is it.
The following critical temperatures are then obtained by logarithmic intrapolation from two temperatures, one leading to a modulus below and one above the target modulus:
- **T1**: temperature for which G* = 5MPa, after RTFOT
- **T2**: temperature for which G* = 50kPa, after RTFOT
- **T3**: temperature for which G* = 5MPa, after RTFOT + PAV
- **T4**: temperature for which G* = 50kPa, after RTFOT + PAV

The risks of using binders outside the temperature ranges delimited by these critical values are identified schematically on **Figure 1**.

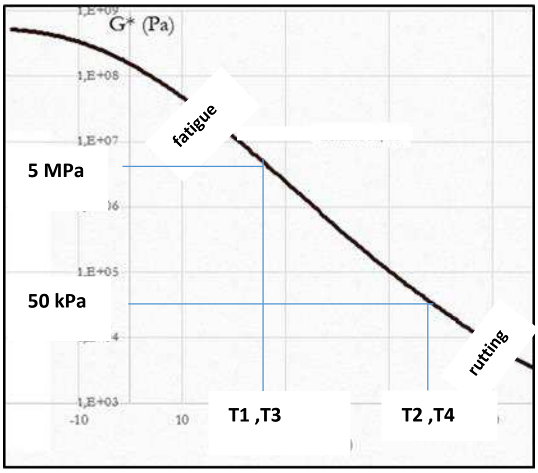

Figure 1: Determination of the critical temperatures T_1, T_2, T_3, T_4

Repeatability and reproducibility based on the results of two Round Robin Tests organized by the BnPé (Bureau de normalization du Pétrole – France) are reported in **Table 1**, for T_1 to T_4 and the determination of δ at T_1 to T_4.

Round Robin Tests (2018 - 2019)	Repeatability	Reproducibility
T_1, T_3 (G*=5MPa)	1.1°C	2.6°C
T_2, T_4 (G*=50kPa)	1.1°C	2.2°C
δ @ T_1, T_3	1.0°	3.1°
δ @ T_2, T_4	0.8°	1.3°

Table 1: Repeatability and reproducibility for T_1, T_2, T_3, T_4 determination

The **"Multiple Stress Creep Recovery (MSCR)** test" has been conducted according to EN16659. The MSCR test is performed using the same DSR equipment, with parallel plates of 25 mm diameter and a 1 mm gap, on RTFOT aged samples at 60°C. The binder specimen is subjected to series of ten creep/recovery cycles, with a 1 second creep period followed by a 9 seconds recovery period. Main parameters are:

- **Jnr**, the non-recoverable creep compliance, which is the ratio of the non-recovered strain to the applied stress;
- **R%**, the percent recovery, which is the ratio in percent of the recovered strain

The non-recoverable creep compliance 'Jnr' is an indicator for the sensitivity of bituminous binders to the permanent deformation under the repeated loading. A good correlation with asphalt rutting has been demonstrated by several researchers [3, 4, 5].
The capacity to recover from deformation is characterized specifically by the percent recovery 'R%'. The precision of the method is reported in **Table 2**.

EN 16659	Repeatability	Reproducibility
R%	1%	5%
Jnr	6%	33%

Table 2: Repeatability and reproducibility for R% and Jnr (MSCR test)

At low temperature, the test was conducted using the **Bending Beam Rheometer (BBR)** ''Cannon'' according to the EN14771 standard after RTFOT+PAV. The testing temperature gap was always 6°C. The precision of the method is reported in **Table 3**. Both critical temperature $T_{c,S}$ and $T_{c,m}$ are determined :

- **$T_{c,S}$** is the critical low temperature predicted using stiffness criterion of 300MPa
- **$T_{c,m}$** is the critical low temperature predicted using m-value criterion of 0.300

EN 14771	Repeatability	Reproducibility
S	9%	27%
m	4%	13%

Table 3: Repeatability and reproducibility for S modulus and m-value determination (BBR)

We have also calculated the coefficient ΔTc introcuced by ANDERSON et al.(2011) [6]:

- **ΔTc= $T_{c,S}$ - $T_{c,m}$** . If ΔTc < 0, it is the low stress relaxation capacity that induces cracking. More ΔTc is negative, more susceptible is the binder to stress relaxation. ANDERSON recommended a critical ΔTc threshold of -5°C for cracking to occur.

2.3. Laboratory results

2.3.1. Pure bitumens

The characteristics as defined in paragraph 2.2 are reported in **Table 4** for the 12 pure bitumens of the study.

			BITUMEN refinery A						BITUMEN refinery B					
Characteristics	units	testing method	10/20	20/30	35/50	50/70	70/100	160/220	10/20	20/30	35/50	50/70	70/100	160/220
Penetration	1/10mm	EN1426	14	23	42	62	84	175	12	24	35	61	77	157
Softening point	°C	EN1427	65,0	59,4	52,0	48,8	45,4	40,2	71,6	61,0	52,6	49,0	46,2	41,0
Resistance to ageing RTFOT acc. to EN 12607-1														
MSCR Jnr at shear stress 3,2 kPa at 60°C	kPa-1	EN 16659	0,05	0,18	0,76	1,53	2,83	12,32	0,01	0,06	0,52	1,81	2,38	9,80
MSCR R% at shear stress 3,2 kPa at 60°C	%	EN 16659	29,9	18,3	4,7	1,4	0,2	0,1	57,3	46,9	7,6	2,0	0,5	0,0
DSR T1 - equivalent G*= 5MPa	°C	EN 14770	34,6	29,1	23,7	20,4	18,3	13,1	35	26	26	20	18,9	15
phase angle at T1	°		49,8	50,6	50,3	52,4	52,6	54,5	42,5	40,5	50	48,4	50,8	52,5
DSR T2- equivalent G*= 50kPa	°C	EN 14770	64,2	57,8	50,3	46,2	43,1	36	69	61	52	45	43,9	37
phase angle at T2	°		73,5	74,1	75,3	76,4	77,8	79,4	65,4	63,1	75,2	73,8	75,8	78,3
Resistance to ageing RTFOT + PAV acc. to EN 12607-1 +														
DSR T3- equivalent G*= 5Mpa	°C	EN 14770	40,2	34,1	30	25,9	23,7	17,5	41	31,6	27,2	25,7	21,3	15,8
phase angle at T3	°		45,4	46,1	45,5	46,7	48,1	50,2	37,8	36,4	45,3	40,5	45,3	46,9
DSR T4- equivalent G*= 50kPa	°C	EN 14770	72,6	65,8	59,4	54,8	51	41,9	79	71	58,4	54	51,6	43
phase angle at T4	°		71	71,5	71,9	73,2	74,2	76,5	62,1	58,6	71,5	69,6	71,6	75,3
BBR Tc,S (S=300MPa)	°C	EN 14771	-5,6	-9	-12,4	-14,8	-15,5	-19,6	-9,0	-14,3	-13,8	-15,9	-17,6	-20,3
Tc,m (m=0,300)	°C		-2,4	-7,3	-9,5	-12,4	-13,9	-18,8	4,6	1,1	-8,5	-13,4	-13,8	-19
ΔTc = Tc,S - Tc,m	°C		-3,2	-1,7	-2,9	-2,4	-1,6	-0,8	-13,6	-15,4	-5,3	-2,5	-3,8	-1,3

Table 4: Rheological characteristics of pure bitumen samples

DSR

The critical temperatures T_1 to T_4 have been plotted according to the penetration on **Figure 2**. Logically, they all decrease when bitumens penetration increases, and it is important to notice that the difference between each grade is significant according to the precision of the test.

The correlation coefficients are all good (> 0.95) and for penetration higher than 60 1/10 mm, the relation with critical temperatures seem to be independent of bitumens origin. For the hardest bitumens (with penetration values around or lower than 60 1/10 mm), the critical temperatures T_2 and T_4 depend mainly on consistency but also on the origin of bitumen. These temperatures are clearly influenced by the chemical structure of bitumen which may differ according to the crude oil selection and the manufacturing process used to produce the hard bases . Long-term PAV ageing causes an increase of the critical temperatures, with a Δ_{T4-T2} value slightly higher than the Δ_{T3-T1} value.

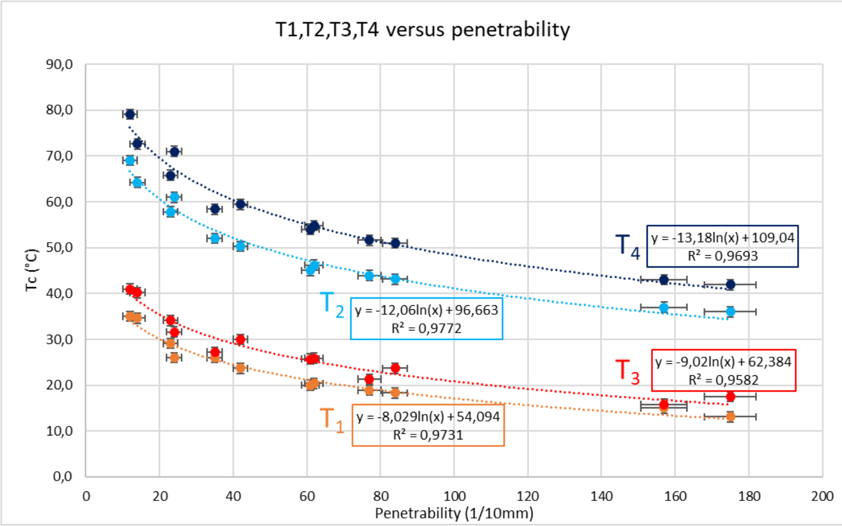

Figure 2: Critical Temperatures T_1 to T_4 for all the pure bitumens

It can nevertheless be seen from the values of phase angles δ shown in Table that the bitumens from refinery A get higher δ than those from refinery B, which reflects a more viscous behavior.

MSCR

From the MSCR test, the Jnr (kPa^{-1}) at 3.2kPa has been plotted according to the penetration on **Figure 3**. The correlation coefficient is greater than 0.99, regardless of the origin of bitumen.

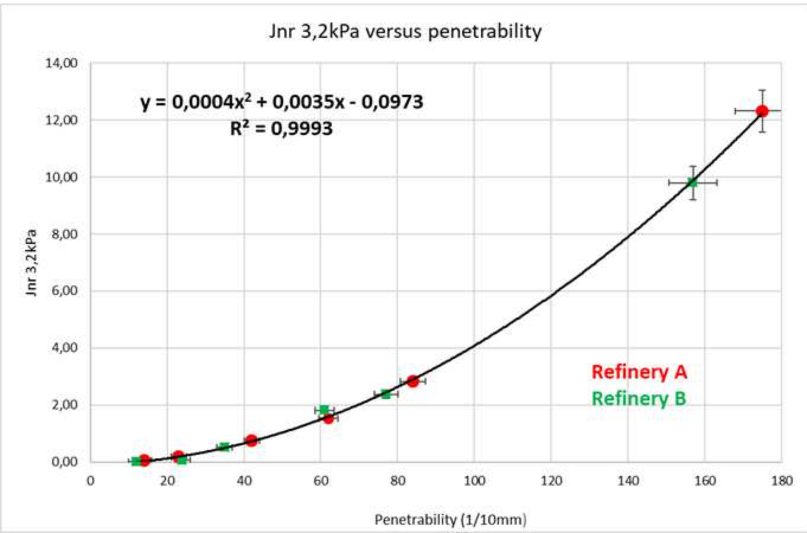

Figure 3: Correlation between Jnr at 3.2kPa (MSCR) and penetration, for all the pure bitumens

Since the Jnr and T_2 criteria (measured after RTFOT) are both intended to reflect the binder's rutting behavior, we checked the level of correlation between these two parameters. **Figure 4** shows that the correlation coefficient is higher than 0.99, regardless of the nature of the pure bitumen.

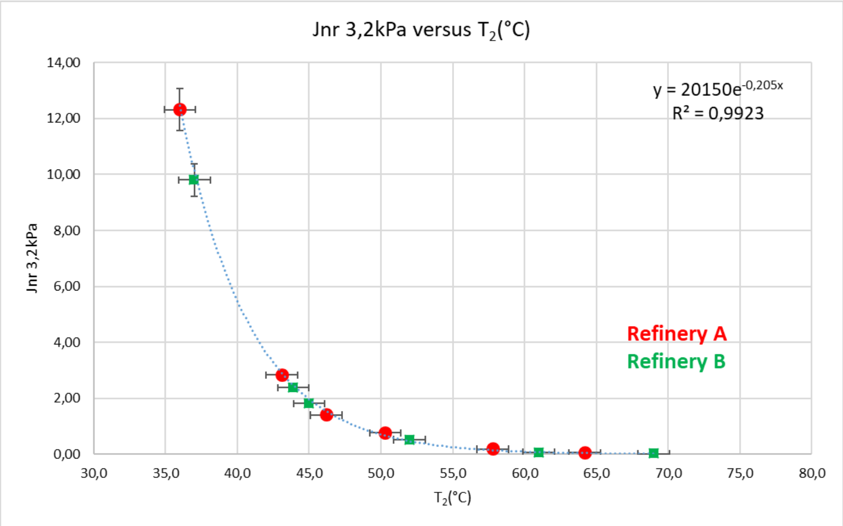

Figure 4: Correlation between Jnr (MSCR) and T_2 critical temperature

BBR

The BBR results are shown in **Figure 5**:

- All binders (Refineries A and B) are m-controlled, it means that the low stress relaxation capacity is the cause of thermal cracking
- The softer binders logically have a better behavior towards thermal cracking.
- Bitumens of origin A exhibit a good correlation between the Tc and the penetration; it is not the case for bitumens of origin B.
- All the ΔTc values are in the acceptable range except for the two hardest bitumens of origin B for which ΔTc are far below -5°C. They would present a proven risk of thermal cracking if applied as a wearing course

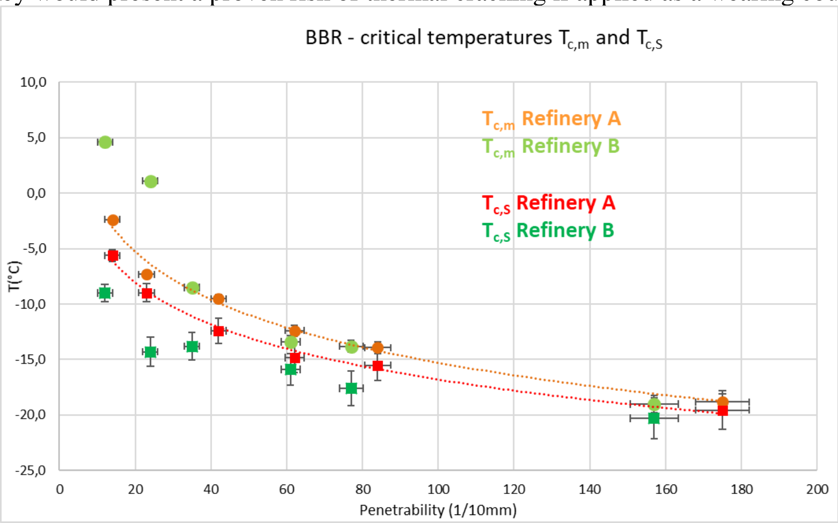

Figure 5 : BBR critical temperatures : Tc,S and Tc,m

In conclusion, all the rheological criteria seem relevant for pure bitumens because they can highlight significant differences between the bitumen grades. The MSCR criteria are independent of the bitumen origin, at least for refineries A and B. The DSR critical temperatures T_2 and T_4 depends on the bitumen origin and structure at least for hardest grades. BBR results exhibit cold behavior differences for the hardest grades and gives indications about cracking tendency that could not be deducted from other characteristics.

The correlations identified during the analysis of binders from refineries A and B may be verified in future work on pure binders from other refineries.

Following the study, the implementation of these same tests in the case of PMBs will be examined.

2.3.2. Polymer modified bitumens

The characteristics defined in 2.2 are reported in **Table 5** for the 17 SBS based PMBs. Samples were taken from plants A to H. As they are all 'PMB 25/55'; they will be compared to a 35/50 pure bitumen grade. The 35/50 bitumen from refinery A was used as a reference purpose but this is not necessarily the bitumen used to manufacture the PMBs.

		PMB 25/55																
Characteristics	units	PMB A1	PMB A2	PMB B1	PMB B2	PMB C1	PMB C2	PMB C3	PMB C4	PMB D1	PMB D2	PMB E1	PMB E2	PMB F1	PMB F2	PMB G1	PMB G2	PMB H1
Penetration	1/10mm	45	39	49	50	40	35	43	39	46	45	41	45	44	37	47	45	42
Softening point	°C	66,8	67,0	63,6	83,6	60,8	79,0	77,6	77,6	71,0	70,8	65,4	66,6	70,1	74,6	82,0	74,4	69,6
		Resistance to ageing RTFOT acc. to EN 12607-1																
MSCR Jnr at shear stress 3,2 kPa at 60°C	kPa-1	0,40	0,19	0,21	0,05	0,07	0,05	0,10	0,17	0,08	0,05	0,15	0,10	0,27	0,08	0,27	0,35	0,09
MSCR R% at shear stress 3,2 kPa at 60°C	%	36,90	39,70	61,50	87,50	64,20	64,30	55,50	49,60	69,10	75,40	58,20	71,30	43,40	58,70	40.00	38,80	75,30
DSR	.																	
T1 - equivalent G*= 5MPa	°C	21,2	23,3	20,7	19,5	23,8	21,9	19,5	21,2	20,4	18,6	23,7	21,1	22,5	22,5	20	20,8	20,1
phase angle at T1	°	48,2	47,2	50,4	45,2	44	43,4	44,6	47,1	44,9	41,9	47,7	45,5	45,5	45,5	43,6	46,6	47
DSR	.																	
T2- equivalent G*= 50kPa	°C	49,6	53,8	48,9	49,5	56,2	56,3	53,3	51	51,5	53,1	50,3	51,2	51,7	51,7	50,7	49,7	50,2
phase angle at T2	°	66,3	66,6	66,4	59,1	58,9	56,1	58,7	57,7	58,4	58,6	65,5	62,8	63,8	63,8	62,9	65,7	62,6
		Resistance to ageing RTFOT + PAV acc. to EN 12607-1 + EN 14679																
DSR	.																	
T3- equivalent G*= 5Mpa	°C	27	28,1	24,2	23,7	28,9	28,2	24,7	26,6	24,4	24,9	28,3	26,8	30	30	25,4	26,5	24,8
phase angle at T3	°	42,5	43,8	45,4	41,4	38,3	39,1	39,2	43,7	38,3	37,6	43,6	41,4	40,2	40,2	40,1	43,8	44,5
DSR	.																	
T4- equivalent G*= 50kPa	°C	56	60,3	55,2	57,4	65,7	66,9	62,9	59,9	62,4	62,1	55,3	60,1	62,1	62,1	60,1	57,4	57,1
phase angle at T4	°	64,5	64,2	63,9	55,9	54,6	53,4	53	58,3	54	47,4	61,2	61	61,1	61,1	60,6	60,1	61,2
BBR																		
Tc,S (S=300MPa)	°C	-15,2	-14	-16,3	-18	-15,7	-14,9	-16,6	-15,7	-19,3	-18,4	-13,3	-16,4	-15,2	-16,3	-16,5	-16,1	-17,1
Tc,m (m=0,300)	°C	-11,5	-10	-15,3	-14,4	-12,0	-10	-12,5	-10,8	-14	-12,8	-11,8	-12,6	-12,9	-9	-12,9	-10,3	-14,4
ΔTc = Tc,S - Tc,m	°C	-3,7	-4,0	-1,0	-3,6	-3,7	-4,9	-4,1	-4,9	-5,3	-5,6	-1,5	-3,8	-2,3	-7,3	-3,6	-5,8	-2,7

Table 5: Rheological characteristics of PMBs 25/55

DSR

The critical temperatures T_1 to T_4 have been compared to those of pure bitumens of same penetration grade. None of these critical temperatures makes it possible to differentiate modified bitumen from pure bitumen in a sufficiently relevant way. For example, **Figure 6** allow us to assess T_2 et T_4 criteria (T_2: temperature for which G* = 50kPa, after RTFOT, T_4: temperature for which G* = 50 kPa, after RTFOT + PAV): for nearly 50% of the PMBs, there is no improvement comparatively to the 35/50 pure bitumen. Long-term PAV ageing causes a similar increase of the critical temperatures for PMBs and pure bitumen.

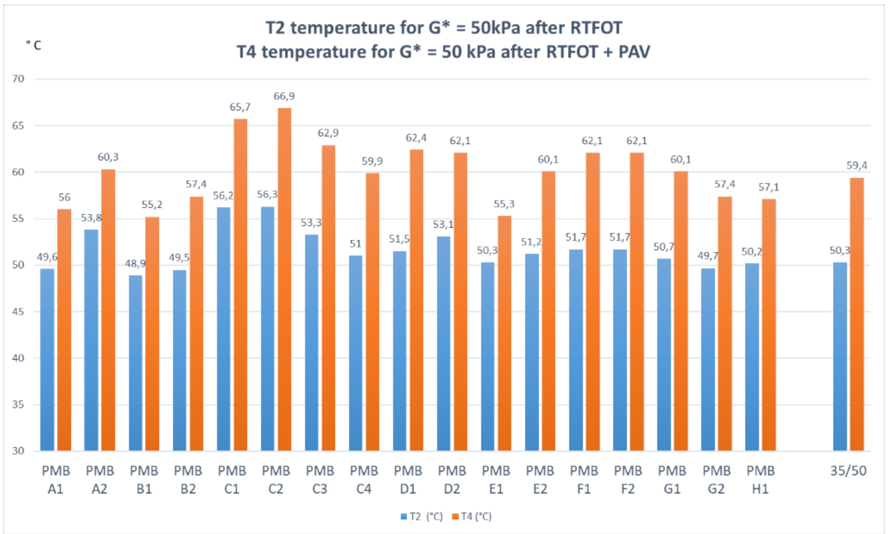

Figure 6: T_2 and T_4(°C) criteria for PMBs compared to 35/50 pure bitumen

But we can observe that the phase angle δ at T_2 reflects clearly the fact that the binder is more elastic than the pure bitumen. In Table 4, while δ is 75° for pure bitumen, δ is within the range [56° - 67 °] for the PMBs. According to the precision of the test, this difference in δ can be considered as significant.

MSCR

From the MSCR test, the Jnr (kPa^{-1}) and %R at 3.2kPa criteria for PMBs both exhibit strong differences compared to pure bitumens, as it can be seen on **Figures 7 and 8**. The range of Jnr values for the polymer modified bitumens in **Figure 7** is significantly smaller than for the paving grade bitumen. Polymer modified bitumens are thus, as expected, clearly superior in this test related to the resistance to rutting. There is a strong impact of the presence of polymer on %R in **Figure 8**; it clearly discriminates binders with different degrees of SBS modification.

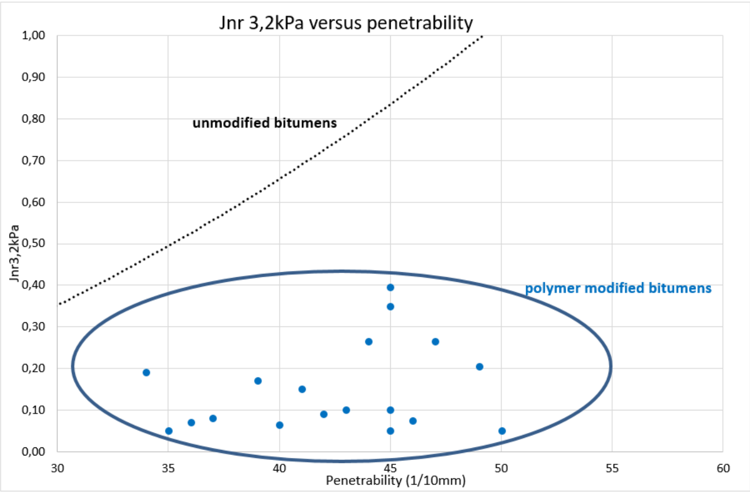

Figure 7: Jnr at 3.2 kPa (MSCR test) for PMBs compared to pure bitumens versus penetration

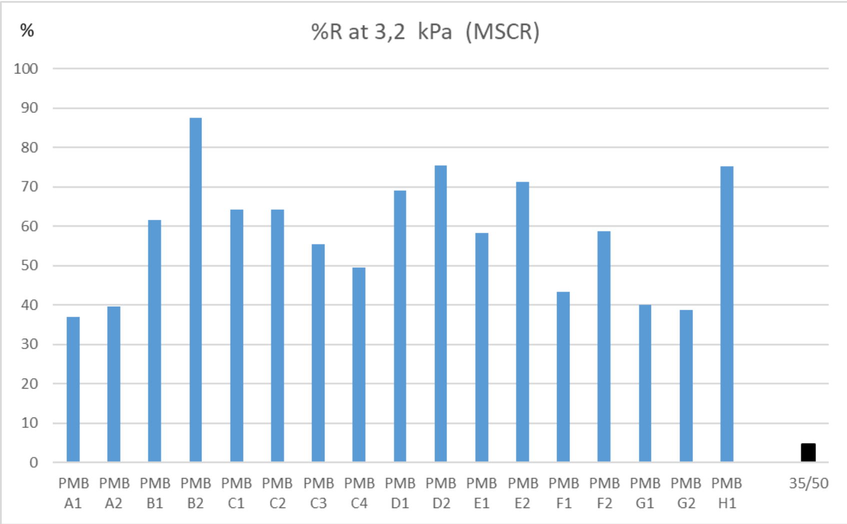

Figure 8: %R at 3.2 kPa (MSCR test) for PMBs compared to 35/50 pure bitumen

BBR

The BBR results (after RTFOT+PAV) are shown in **Figure 9**:
- All binders are m-controlled, it means that the low stress relaxation capacity is the cause of thermal cracking
- For all the PMBs, Tc (S= 300MPa) is improved compared to the reference pure bitumen, in good agreement with the property of the SBS polymer that remains flexible at low temperature
- But for some of them, Tc (m=0.300) is in the same range as pure bitumen. The impact of SBS on this criterion seems lower. It certainly comes from the fact that PMBs have a higher elastic component (lower phase angle δ as shown before) at a given stiffness. Direct consequence is that the value of ΔTc appear to be lower (more negative) than unmodified binder for most of them, with increased potential of cracking, which is not relevant for this kind of binders. Thresholds defined for pure bitumens do not seem to be adapted for PMBs [7]. Consequently, in this paper, ΔTc will not be discussed for PMBs.

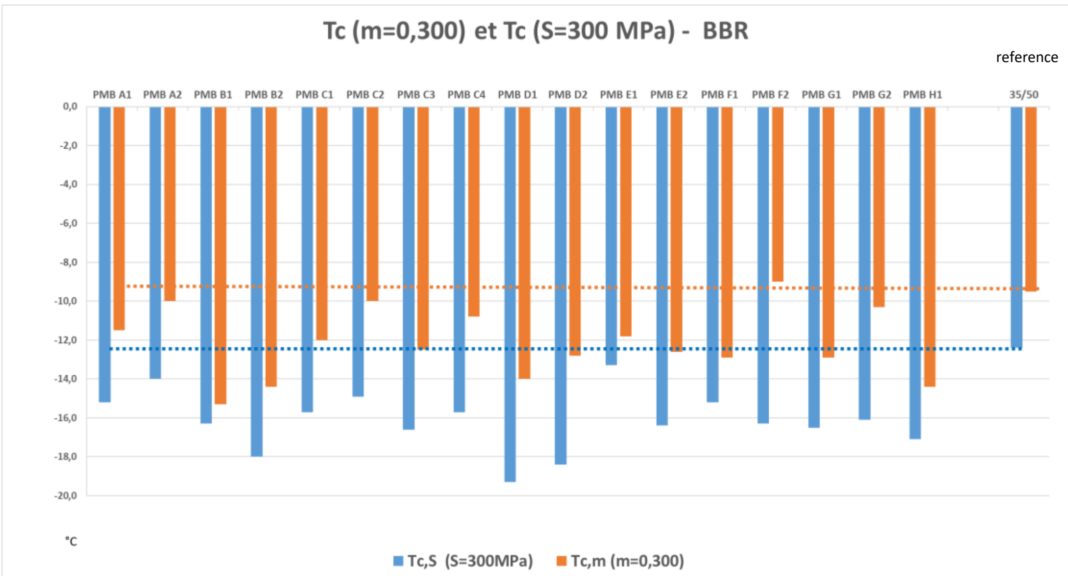

Figure 9: Tc,m and Tc,S (BBR test after RTFOT+PAV) for PMBs compared to 35/50 pure bitumen

In conclusion, the rheological criteria that best highlight the benefits of polymer modified bitumens compared to unmodified bitumens are MSCR criteria: Jnr and R% at 3.2 kPa.

T_1, T_2, T_3 and T_4 are not relevant for SBS modified bitumens. Only phase angle values reflect the fact that the binders are significantly more elastic than pure bitumen.

If BBR is certainly a better test in terms of reproducibility than Fraass test, Tc (m=0.300) and ΔTc values are biased due to the elastic component of the PMBs.

3. CONCLUSION

The purpose of this study was to determine the rheological criteria that best highlight the impact of polymer modified bitumens compared to unmodified bitumens.

The first part was dedicated to pure bitumens. All the rheological criteria seem relevant for pure bitumens because they can highlight significant differences between the bitumen grades. The MSCR criteria are independent of the bitumen origin, at least for refineries A and B. The DSR critical temperatures T2 and T4 depends on the bitumen origin and structure at least for hardest grades. BBR results exhibit cold behavior differences for the hardest grades and gives indications about cracking tendency that could not be deducted from other characteristics.

On the other hand, for polymer modified bitumens, only MSCR criteria, Jnr and R% at 3.2 kPa, are particularly relevant: PMBs exhibit significantly lower Jnr and higher R% than pure bitumen of the same penetration grade.
Critical temperatures at which G*=50kPa, or G*=5MPa after aging cannot be differentiated from those obtained with a pure bitumen of the same penetration grade.
And because of the elastic behavior of PMBs, BBR criteria such as Tc (m= 0.300) and ΔTc are biased.

We have carried out this investigation on modified binders formulated with different types of raw materials and from different processes, and we will continue to complete the database. The study of all the generated data will be an opportunity to optimize COLFLEX® formulas with regard to these rheological criteria.

We also hope that this work will be useful for further standardization work within the TC336/WG1 working group.

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