MEASURING THE RHEOLOGICAL PROPERTIES OF BITUMINOUS BINDERS FINAL RESULTS FROM THE ROUND ROBIN TEST OF THE BNPÉ/P04/GE1 WORKING GROUP (FRANCE)

B. Eckmann [1], S. Largeaud [2], D. Chabert [3], G. Durand/M. Robert [4], R. Van Rooijen [5], E. Chailleux [6], V. Mouillet [7], H. Soenen [8], N. Clavel [9], L. Lapalu [10]

[1] EUROVIA, Direction Technique, 18, place de l'Europe, 92565 Rueil-Malmaison Cedex, France, bernard.eckmann@eurovia.com
[2] EUROVIA, Centre de Recherche de Mérignac,2, rue Thierry Sabine, BP 67, 33703 MERIGNAC Cedex, France, sabine.largeaud@eurovia.com
[3] EIFFAGE Travaux Publics, Centre d'études et de recherches, 8, rue du Dauphiné, 69960 Corbas Cedex, France, didier.chabert@eiffage.com
[4] COLAS, Direction Technique de la Recherche et du Développement, Campus Scientifique et Technique, 4, rue Jean Mermoz, Bât. A, 78772 Magny les Hameaux, France, durand@campus.colas.fr, robert@campus.colas.fr
[5] BP EUROPA SE, GFT BIT-FORM, Pawiker Strasse 30, 45896 Gelsenkirchen, Germany, ronald.vanrooijen@bpge.de
[6] IFSTTAR Nantes, Route de Bouaye, BP 4129, 44341 Bouguenais Cedex, France, emmanuel.chailleux@ifsttar.fr
[7] LRPC Aix en Provence, CETE Méditerranée, CS 70499, 13593 Aix-en-Provence Cedex 3, France, virginie.mouillet@developpement-durable.gouv.fr
[8] NYNAS NV, Product Technology, Noorderlaan 183, BE-2030 Antwerpen Belgium, hilde.soenen@nynas.com
[9] SHELL Bitumen, Société des Pétroles Shell, Immeuble « Les Portes de la Défense », 307 rue Estienne d'Orves, 92708 Colombes Cedex, France, norbert.clavel@shell.com
[10] Centre de Recherches TOTAL, Chemin du canal, BP 22, 69360 Solaize, France, laurence.lapalu@total.com

ABSTRACT

In a previous paper presented at the 2008 E&E Congress, the French mirror group (BNPé/P04/GE1) of the CEN/TC336 – WG1 committee (bituminous binder) has reported the results of a round robin test on DSR complex modulus measurements involving two paving grade bitumen (10/20 and 50/70 classes) and three modified binders (plastomer, elastomer and cross-linked elastomer). This paper presents the outcome of the follow-up studies which had been decided at the time. In a first step, a number of dedicated investigations have been made to identify the potential contribution of different factors to the variation in measurement results. In particular, the impact of waiting time after test sample preparation, gap setting procedure, bonding temperature, conditioning times and temperature sweep procedure have been investigated. How to establish the limits of the linear domain of visco-elasticity is another issue which has been dealt with. This has allowed to define more stringent operating conditions which have then been followed by the participating laboratories for a final round robin limited to a pure bitumen (50/70) and the "most difficult" PmB (high level of plastomer modified product). In comparison to the first round robin, reproducibility was indeed improved, even for the modified product. The BNPé/P04/GE1 work does thus further open the way for the definition of binder performance indicators based on DSR measurements. This will however only be possible (especially for modified binders) if operating conditions are strictly defined and followed.

Keywords : Complex Modulus, Polymer Modified Bitumen, Standardisation, Testing

1. INTRODUCTION

In 2003, the French mirror group of WG1 of the CEN TC336 committee (bituminous) had launched an extensive round robin test on the determination of the dynamic stiffness modulus of bituminous binders. Ten laboratories had been involved in a program which dealt with 5 types of binders (2 penetration grade bitumen and 3 modified binders). The equipment used mainly consisted in parallel plate "DSR" rheometers (European standard EN 14770) but the study also involved apparatus applying an oscillating linear loading, either in a tension-compression (TC) mode on cylindrical beams at low temperatures, or in an annular shear (AS) mode on samples poured in a cylindrical beaker (French standard NF T66-065). This study has been reported at the 2008 E&E Congress [1]. It confirmed earlier precision results on the determination of dynamic stiffness modulus and phase angle with "DSR" equipment [2] but also highlighted quite poor reproducibility in the case of certain polymer modified binders. This was more particularly the case for highly "plastomer" modified binders, at low frequencies and at test temperatures in the range going from 30°C to 50°C. These results had motivated GE1 to continue its investigations so as to find out possible ways of improving this situation. The outcome of these studies, which led to a new round robin test program, are the subject of this paper.

2. TEST PROGRAM

In a first step, a standard polydiméthylsiloxane (PDMS) reference product (PSTTD 1000VE 9696 by Anton Paar) has been used to evidence possible systematic off-sets between the various used equipments.

In a second step, focused on parallel plate rheometers, a number of small investigations have been conducted so as to quantify the potential impact of certain test parameters on the precision of test results. This work has been split between the different participating laboratories and essentially conducted on two binders already used for the first round robin test [1], i.e. a straight-run pure bitumen (50/70 pen. grade) and/or the "plastomer" polymer modified binder (referred to as "PmB2"). The investigated parameters are listed hereafter.

- Waiting time (at ambient temperature) between the casting of the binder sample and the start of the test procedure (only molded specimen have been used).
- Bonding temperature when loading the test sample onto the rheometer.
- Test preparation after loading the sample : "zero gap" temperature, sample trimming, gap setting.
- Thermal history of the sample once mounted on the rheometer

Based on these investigations as well as on the experience gained through the first round robin, the GE1 working group has then established more stringent operating conditions for a new circular test program. A particular emphasis has been laid on the control of sample preparation and on the verification that the rheometers were operated under the appropriate torque conditions as well as within the linear domain of viscoelastic behaviour. This new round robin has however been limited to a single straight-run bitumen (50/70) and the "most difficult" polymer modified binder (PmB2) which had already been used in the previous studies.

Although a few laboratories could only contribute to a limited extent, the participating laboratories have been essentially the same as for the first round robin (with one newcomer for the final round robin). Their coded designation (Lab. A, B, ….) has thus not been changed [1]. For several laboratories, the used equipment (see Table 1) has however changed.

Table 1 : Equipment used

Laboratory	"DSR" parallel plate	Linear loading (TC-AS)
A	Bohlin Gemini 200 ADS	
B1	Anton Paar MCR 501	
B2	Rheometrics ARES	
C	Haake RS 600	
D	Anton Paar MCR 500	
E	Haake MARS II	
F	TA Instr. AR 2000	
G	Rheometrics ARES	
I	Haake RS 150	METRAVIB DMA 450+
J	Anton Paar MCR 501	
K	Anton Paar MCR 501	METRAVIB VA 4000

3. TEST RESULTS OBTAINED WITH A REFERENCE PRODUCT

3.1 Parallel plate rheometers

In first instance, the tests with the reference product have been conducted at 25°C on DSR rheometers using 8mm plates, with a 1mm gap and a deformation of 1%. A good agreement has been obtained in-between the different laboratories and the results are also perfectly in line with the stiffness values (reference) indicated by the supplier of the PDMS product (Figure 1). At frequencies above 10Hz, and even more importantly above 50Hz, these results tend however to be slightly more scattered. Most of the laboratories have conducted these tests 3 to 5 times, which allows the calculation of a coefficient of variation (expressed as the ratio, in %, of the standard-deviation over the mean value). These values, which can be seen as an indicator for repeatability, are gathered in Table 2. One notices some differences depending on the type of equipment and frequency range.

Table 2 : Test results obtained with PDMS reference product - Coefficient of Variation (repeatability)

Laboratory	A	B1	D	E	F	F	I	J
Equipment	Bohlin 200	MCR 501	MCR 500	Haake Mars II	AR 2000	AR 2000	RS 150	MCR 501
Plate diameter (mm)	8	8	8	8	8	**25**	8	8
Strain (%)	1	1	1	1	1	**10**	1	1
Frequency range (Hz)	0.1 - 10	0.1 - 100	0.1 - 100	0.1 - 8	0.1 - 10	0.1 - 10	0.1 - 40	0.1 - 100
Number of repetitions	5	4	3	5	5	3	2*	3
Coefficient of Variation (%) on Modulus (|G*|)								
0.1 Hz - 10 Hz	1.7 - 4.6	0.2 - 1.6	0.2 - 1.7	~ 9.5	~ 10.5	**0.2 - 1.4**	0 - 2	~ 6.8
10 Hz - 50 Hz		0.3 - 5	0.3 - 4				0.5 - 1.5	6.8 - 20
Freq. for which CV > 10 %	-	≥ 60	≥ 80					≥ 20
50 Hz - 100 Hz	-	rapid increase	4 - 15					~ 20
Coefficient of Variation (%) onPhase Angle (δ)								
0.1 Hz - 10 Hz	0.1 - 5	0.2 - 0.5	0.1 - 2.4	0.1 - 2	0.1 - 1	< **0.1**	0 - 0.6	0.1 - 3
10 Hz - 50 Hz		0.4 - 10	0.5 - 4.5				0 - 2.5	rapid increase
Freq. for which CV > 10 %		≥ 50	≥ 80					≥ 20
50 Hz - 100 Hz		rapid increase	4.5 - 18					no data

* CV = 0.5*(MAX-MIN)/MEAN

One laboratory (Lab. F) repeated the test with a 25mm plate geometry and a strain of 10% and noticed a better repeatability. This is most likely due to the fact that the 25mm plate geometry is better suited for the relatively low stiffness of the PDMS product (indeed, the reference values indicated by the supplier are given for 25m plates !). This observation could be further supported by a few additional tests (although without repetitions) comparing results with 8mm and 25mm plates at different strain levels. Figure 2 shows that only the 25mm geometry allowed to obtain exactly the same stiffness ratio when changing the equipment (B1/B2) or when changing the applied strain level (1% vs 10%).

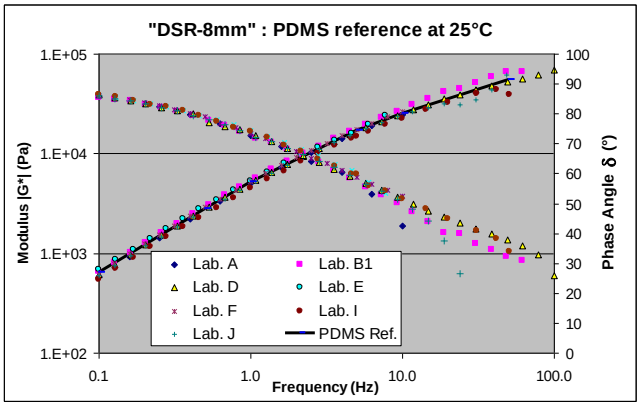


Figure 1 : tests on PDMS reference with 8mm plates

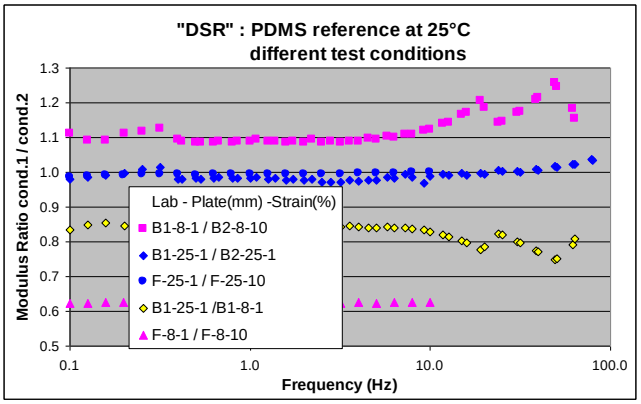


Figure 2 : compared tests on PDMS reference

These results illustrate that, also when using a reference product, care has to be taken to select the adequate test geometry and strain level. Comparing rheometers over a wide range of stiffness values may thus require to use several reference products !

When performing the final round robin (see § 5), the tests with the PDMS reference and the 25mm plates have been repeated by the different laboratories and the agreement proved to be excellent and better than with the 8mm plates (Figure 3). The coefficient of variation for the mean results obtained by each laboratory at, for instance, 1Hz, drops from 7% with the 8mm plates to 4% with the 25mm plates.

We could thus conclude that there was no bias between the different types of DSR equipment used for our investigations.

An important remark is however to be made concerning temperature regulation. If, as for the PDMS, the stiffness of the reference product is not or only slightly temperature dependent, off-sets between two pieces of equipment due to poor temperature regulation will not be detected on the basis of comparative testing !

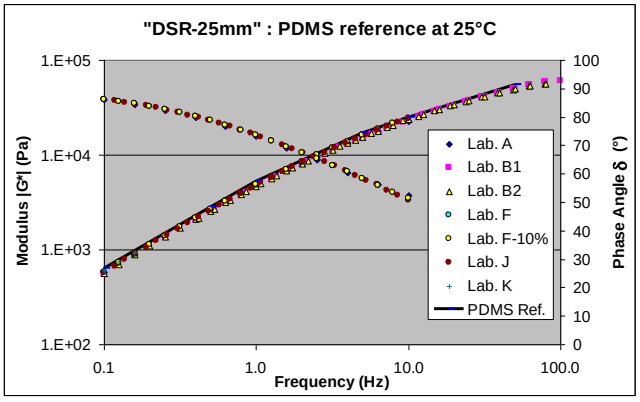


Figure 3 : tests on PDMS reference with 25mm plates

3.2 Test performed under annular shear conditions

In this case, tests with the PDMS product could only be performed under annular shear (AS) configuration. Since only two laboratories used this type of equipment, general conclusions cannot be drawn. A fairly good agreement with the DSR results is obtained by Lab. I. For Lab. K, however, we notice a systematic off-set of the stiffness modulus (Figure 4). A possible reason could be the difference in the gap between cylinder and plunger (1 mm for Lab. I vs. 0.5mm for Lab. K), but this point has not been further investigated. The off-set is not seen for the phase angle, but results are also less stable.

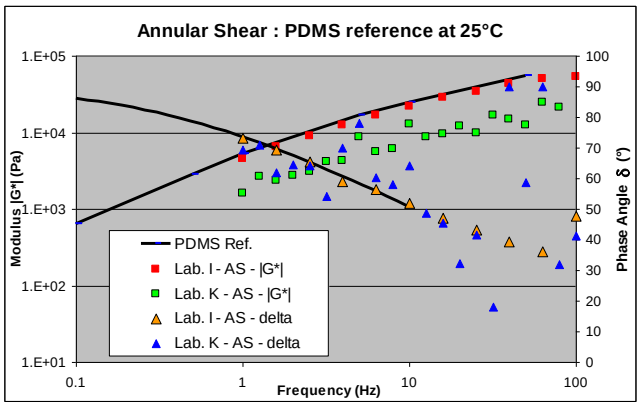


Figure 4 : annular shear tests on PDMS reference

4. INVESTIGATION OF SOME OPERATING PARAMETERS

4.1 Impact of waiting time between molding of test sample and beginning of test procedure

These tests have been performed by laboratory E with the 25mm parallel plate geometry, the test samples being cast in silicon molds. 30 minutes after casting, samples were trimmed, then either immediately tested or allowed to rest at room temperature for 1, 13, 17, 21 or 24 hours. Comparisons have been done on the basis of a frequency sweep (up and down) at 40°C. In the case of the 50/70 bitumen, rest time did not have any impact on the results. In the case of the plastomer modified binder (PmB2), no effect was seen for the modulus but, at low frequencies, differences of more than 6° could be observed for the phase angle (Figure 5). It is possible that the short waiting times (0h and 1h) correspond to a stage where the binder has not yet reached its full equilibrium and where the polymer phase has a stronger impact on the elastic component than under stabilized conditions (longer waiting times). This phenomenon would however be different from the structuring effect due to thermal history which has later been observed when performing the final round robin test (§ 5.2).

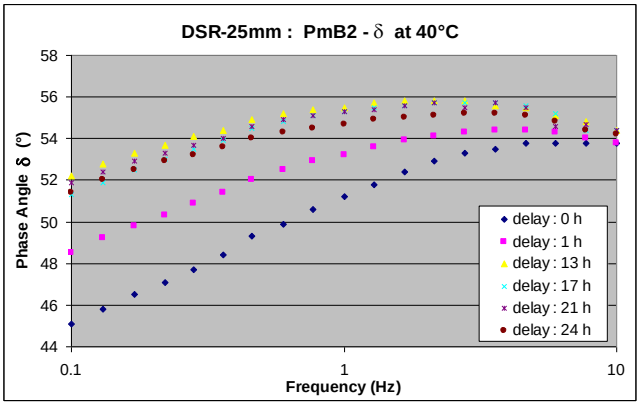


Figure 5 : DSR tests : impact of sample curing time

4.2 Loading the sample on the rheometer – Impact of bonding temperature

When loading a test sample on the rheometer, a sufficiently high temperature of the parallel plates is necessary to ensure proper bonding, especially in the case of viscous products such as polymer modified binders. This point has been investigated by laboratory I with PmB2, based on frequency sweeps performed at 40°C and 10°C with respectively 20mm (2mm gap) and 8mm (1.5mm gap) geometries. In each case, test samples have been bonded at either 80°C or 30°C. This did not have any significant impact on the measured stiffness modulus (|G*|) values. Again, differences appeared however in the case of the phase angle. Lower phase angles have been measured for the specimen bonded at 80°C, which could however not be readily explained. It is suspected that both the initial "reheating" of the sample and the time elapsed between bonding and actual testing, which has been longer for the specimen mounted at 80°C, may have affected differently the evolution of the internal structure of the binder.

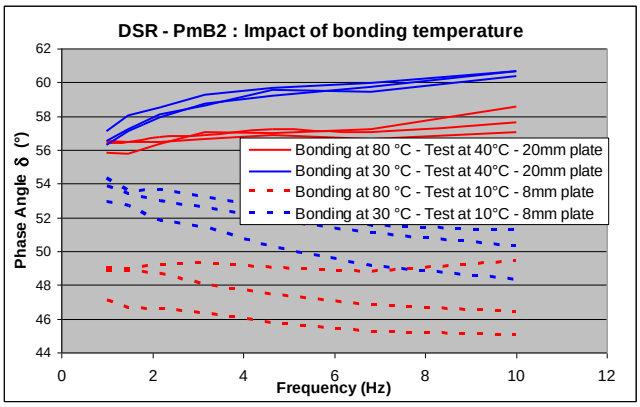


Figure 6 : DSR tests : impact of sample bonding temperature

4.3 Gap setting

Theoretically, during temperature changes, metal can expand or contract, which changes the exact value of the gap between the parallel plates and, hence, modifies the way it is filled by the test sample with a possible incidence on the test result. When performing a temperature sweep, eliminating this possibility would require to "zero" the gap at different temperatures before starting the test procedure. A small investigation on this issue has been made by Laboratory B with the 25mm plate geometry (B1-MCR501), using a 35/50 straight-run bitumen. Three different samples were set between the plates after the gap was zeroed at respectively 0°C, 60°C and 120°C. The modulus of each sample (gap of 2mm) was determined at 60°C following a frequency sweep from 0.1 Hz to 10 Hz. No differences in results were found, which support the idea that, in the case of temperature sweeps, zeroing of the gap may be done at a single temperature, which simplifies the test procedure.

On the same line, one may even more wonder about the possible incidence of the actual gap setting (sample thickness between the plate) on the measured values. This point has also been addressed by Laboratory B (B1-MCR501), again with a 25mm plate geometry, through tests conducted on the 35/50 bitumen at 40°C and 60°C, as well as on a PmB sample (this time of an elastomeric type) at 60°C, the gap being varied from 0.01mm to 3mm. As it can be seen on Figure 7, the gap setting only started to significantly affect the results below 0.5mm. This study is of course only partial and results may be different at lower test temperatures (minimum gap could be different due to the higher rigidity of the sample) and with a different geometry (8mm plates). But it may probably be concluded that, for the usual gap values such the ones used in the GE1 round robin (2mm for the 8mm plates and 1mm for the 25mm plates), a minor deviation from the nominal value should not be of any consequence.

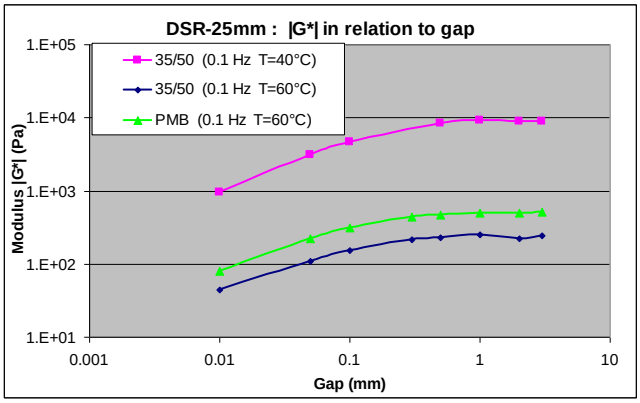
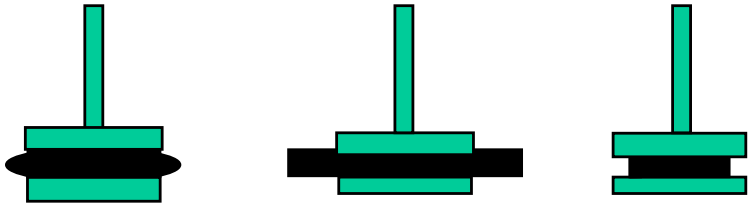


Figure 7 : DSR tests : impact of gap setting between both plates

4.4 Sample trimming



1 : levelled gap (barrel 2 : overfilled gap 3 : underfilled gap

Figure 8 : schematic representations of extreme gap filling conditions

Gap filling conditions, as shown in Figure 8, are known to influence test results. This point has been once more confirmed by laboratory B (B2-ARES) with the 35/50 bitumen and the 8mm plate geometry. At first, the sample was set between the two plates at a gap of 1.0 mm under "overfilled" conditions (configuration 2 in Figure 8) and G* was measured under a frequency sweep at 40°C. Then, the bitumen was levelled for a new G* measurement (config. 1); the bitumen being trimmed at gap +50 µm. After that, a gap of 1.1 mm was applied on the same sample (the gap is underfilled – config. 3) and a measurement of G* was done. Then a gap of 0.9 mm ("overfilled" – config. 2) was applied, and G* was measured. Finally, the bitumen was again levelled (config. 1), and G* was re-measured.

The "leveled" gaps (barrel effect) gave very similar G* modulus values with a coefficient of variation (defined as 0.5*(MAX-MIN)/MEAN) of about 3%. Overfilling or underfilling the gap by 10% lead to an artificial increase, respectively decrease, of the G* values by about 12%. Uncontrolled filling of gap may thus lead to an overall error of more than 20% on the modulus values. This highlights once more that proper trimming of the test sample is a key step in the operating process.

4.5 Thermal history

Because of its possible impact on the internal structure of the binder, be it due to the presence of crystallized fractions or of polymers, the thermal history of the sample may impact the measured stiffness and phase angle values [3]. In the frame of the preliminary studies to the second GE1 round robin test, Laboratory J has performed, on both the 50/70 penetration grade and the PmB2 modified bitumen, a temperature sweep from 70°C down to -30°C (8mm parallel plates, 2mm gap) and compared the results obtained while observing a stabilization time of either 15 min or 30 min. at

each test temperature. In the case of the 50/70 bitumen, no significant differences (compared to the general level of repeatability observed in the first round robin trials) have been observed. In the case of PmB2, differences became significant as from 0°C (hence after longer overall time on the rheometer), the stiffness values measured after 30 min. of stabilization being higher than those measured after only 15 min. Differences appeared even earlier (as from 40°C) for the phase angle. In certain cases, temperature equilibration time may thus have an incidence and it is not advised to extent this time above the minimum needed for temperature equilibrium (15 min. are felt to be adequate).

In the frame of a small study limited to PmB2, variations have also been observed by Laboratory A in relation to the applied temperature sequence. Directly after loading the sample onto the rheometer at 30°C (8mm plate, 1.5mm gap), frequency sweeps (0.1 Hz to 10 Hz) have been performed at 30°C, then at 10°C, again at 30°C, then at 50°C and finally a third time at 30°C. Especially at low frequencies, significantly lower stiffness and higher phase angle values where measured after the cooling down phase, these differences becoming close to nil towards 10 Hz.

4.6 Magnitude of applied strain – limit of the linear domain of behaviour

For the final round robin, all laboratories have been asked to determine, for each test geometry, test temperature and type of binder, the limits of the linear domain of viscoelasticity. For the sake of reproducibility, it is indeed important to ensure that the strain applied by each laboratory stays below these limits. Even if, for "conventional" products such as pure bitumen, experience rapidly tells which strain levels are not to be trespassed, such a verification should not be neglected in the case of unknown products. The procedure adopted by the working group consisted in "sacrificing" one test sample per test geometry. Strain sweeps are made at the highest foreseen test frequency (frequency at which the linear domain should be the shortest) and conducted over the full temperature range to be covered with the geometry, starting from the lowest. One gets thus a limiting strain at each temperature, from which "safe" strain levels (which may of course be common for several test temperatures) are then defined. Although there is some risk for premature damage of the sample, this procedure has been adopted since it is easier to proceed from low to high temperatures rather than the opposite. It is to be mentioned here that the limiting strain (defined as the value above which the modulus differs by more than 5% of its initial value) is not always easy to define due to the fluctuations observed during the first measurement cycles which may also affect the definition of a regression line. An interesting suggestion has been made by Laboratory D which observed that, in many cases, the deviation from a constant value is sharper and easier to detect for the phase angle than for the modulus. This point is illustrated in Figure 9 and should be kept in mind by practitioners.

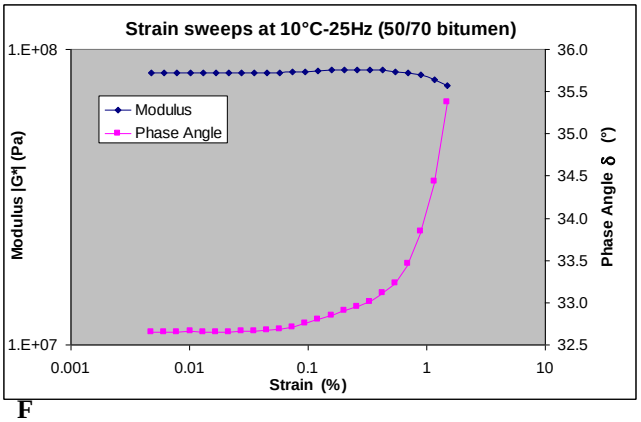


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Figure 9 : Definition of linear domain of viscoelasticity

Finally, it is to be further mentioned that adequate strain levels have not only to be defined for the sake of linearity, but also to ensure that the rheometer is working in an adequate torque range. At each test temperature and frequency, the strain must be such that the required torque stays within the proper working range. These limits (there is as well an upper as a lower limit) are specific to each apparatus and test geometry. As for the limits of the linear domain, they should be checked prior to the actual testing and further verified (by comparing the asked strain level to the strain actually delivered by the equipment) when analyzing the measurement results.

5. FINAL ROUND ROBIN TEST

For the final Round Robin test program, each laboratory had to follow strict operating conditions. Those included precise sample re-heating and conditioning instructions, minimum and maximum delay to be observed between the casting of the sample and its placement onto the rheometer, bonding temperature (60°C for the 50/70 bitumen, 80°C for PmB2), stabilization time at each temperature (15 minutes for parallel plate and AS samples, 30 minutes for TC samples). For DSR and annular shear measurements, after installation of the sample, temperature was to be dropped to the lowest test temperature and temperature sweeps to be conducted from that temperature upwards. Tension-compression tests were conducted from upper to lowest temperature. All laboratories made a preliminary verification of the visco-elatic domain and the operational limits to be observed for their equipment. The measurements performed by each laboratory for the 50/70 bitumen and the PmB2 binder are shown in Table 3 and 4.

Table 3 : Overview of Final Round Robin measurements performed on the 50/70 bitumen

50/70	"DSR"												"TC - AS"			
	Lab. A		Lab. B1		Lab. D		Lab. F		Lab. G		Lab. J		Lab. K		Lab. I	Lab. K		
	BG-200 ADS		AP-MCR 501		AP-MCR 500		TA-AR2000		ARES		AP-MCR 501		AP-MCR 501		DMA 450+	VA 4000		
Geometry	8 - 2	25 - 1	8 - 2	25 - 1	8 - 2	25 - 1	8 - 2	25 - 1	8 - 1.8	25 - 1.8	8 - 2	25 - 1	8 - 2	25 - 1	9 - 16	10-8 - 5	8 - 16	10-9 - 5
Sample bonding temp. (°C)	60		60		60		40		60		60		60		T amb		T amb	
Test temperature																		
-30																		
-20																		
-10																		
0																		
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50																		
60																		
70																		
80																		

Parallel plate - Φ in mm, gap in mm
Parallel plate - Φ in mm, gap in mm
Tension - Compression - Φ in mm, height in mm
Annular Shear - Φext - Φint in mm, height in mm

Table 4 : Overview of Final Round Robin measurements performed on the PmB2 binder

PmB2	"DSR"															"TC - AS"	
	Lab. A		Lab. B		Lab. D-1		Lab. D-2	Lab. D-3		Lab. F		Lab. G		Lab. J	Lab. K	Lab. I	
	BG-200 ADS		AP-MCR 501		AP-MCR 500					TA-AR200		ARES		AP-MCR 501	AP-MCR 501	DMA 450+	
Geometry	8 - 2	25 - 1	8 - 2	25 - 1	8 - 2	25 - 1	8 - 2	8 - 2	25 - 1	8 - 2	25 - 1	8 - 1.8	25 - 1.8	8 - 2	8 - 2	25 - 1	9 - 16	10-8 - 5
Sample bonding temp. (°C)	80		80		80		80	40		40		60		80	80		T amb	
Test temperature																		
-30																		
-20																		
-10																		
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10																		
20																		
30																		
40																		
50																		
60																		
70																		
80																		

Parallel plate - Φ in mm, gap in mm
Parallel plate - Φ in mm, gap in mm
Tension - Compression - Φ in mm, height in mm
Annular Shear - Φext - Φint in mm, height in mm

5.1 Final Round Robin DSR results –50/70 bitumen.

After rejecting outliers (relatively few), reproducibility for DSR data has been evaluated by calculating a coefficient of variation (in %), defined as the standard deviation (**s**-value) divided by the mean (**m**-value). The comparison to the corresponding values obtained from the first Round Robin [1], is shown in Table 5. Reproducibility is significantly improved for |G*|, especially at the lower frequencies. The s/m values are now in a range of 10 to 15% with the 8mm plates and stay lower than 10% with the 25mm plates. Concerning the phase angle, the situation could not be significantly improved. This may be attributed to the fact that the results obtained in the first Round Robin were already quite good and that the impact of operating parameters such as waiting time and bonding temperature evidenced in § 4.1 and § 4.2 is probably not as significant in the case of pure bitumen than in the case of a highly modified PmB.

Table 5 : Comparison of Final Round Robin with First Round Robin [1] – 50/70 bitumen

Evaluation of reproducibility : values of s/m (%) (s = standard deviation, m = mean)

50/70	Modulus |G*| - 8mm plates							
Temp. (°C)	0.01 Hz		0.1 Hz		1 Hz		10 Hz	
-10	**15.0**		**11.9**		**13.1**		**14.6**	
0	**6.6**		**2.1**	12.5	**3.2**		**6.0**	
10	**11.8**	25.2	**11.4**	19.6	**10.7**	13.1	**12.5**	9.3
20	**16.7**	38.1	**16.1**	32.0	**13.8**	25.6	**11.8**	20.4
30	**12.3**	39.0	**12.0**	34.7	**11.2**	23.6	**10.1**	23.1
40	**12.1**	38.5	**13.6**	24.8	**13.7**	17.7	**12.9**	25.2

Phase Angle δ - 8mm plates							
0.01 Hz		0.1 Hz		1 Hz		10 Hz	
3.9		**4.5**		**6.5**		**7.3**	
3.5		**3.8**	3.9	**5.1**		**5.5**	
1.6	1.3	**2.3**	1.7	**1.8**	2.7	**1.4**	2.5
0.7	1.1	**1.3**	1.1	**1.1**	1.8	**2.2**	2.7
0.8	0.4	**0.8**	0.8	**1.1**	1.5	**2.3**	0.9
0.4	1.1	**0.4**	1.0	**1.0**	1.8	**2.1**	3.6

50/70	Modulus |G*| - 25mm plates							
Temp. (°C)	0.01 Hz		0.1 Hz		1 Hz		10 Hz	
40	**9.9**	31.4	**10.1**	26.6	**10.9**	24.1	**7.1**	19.4
50	**8.3**	30.8	**8.5**	14.6	**7.8**	13.1	**7.5**	4.8
60	**5.9**	24.2	**6.0**	12.8	**6.1**	13.8	**6.4**	9.4
70	**5.7**	25.8	**6.6**	10.3	**6.5**	15.3	**6.5**	12.3
80	**16.4**	31.1	**6.1**	9.0	**8.7**	15.6	**10.2**	11.5

Phase Angle δ - 25mm plates							
0.01 Hz		0.1 Hz		1 Hz		10 Hz	
1.0	0.6	**0.6**	0.9	**0.3**	1.4	**1.5**	2.8
0.3	0.5	**0.2**	0.4	**0.4**	0.8	**1.2**	1.0
0.7	0.3	**0.2**	0.5	**0.2**	0.5	**0.8**	1.2
0.8	0.2	**0.9**	0.9	**0.2**	0.6	**1.0**	2.1
1.7	0.4	**1.1**	0.2	**0.6**	0.7	**1.1**	2.4

Bold font **Values obtained in the final Round Robin**
Normal font Values obtained in the first Round Robin [1]

5.2 Final Round Robin DSR results – PmB2 binder.

The results proved to be less positive in the case of the modified binder. As it can be seen in Table 6, reproducibility for |G*| could only be improved at higher frequencies (1Hz and 10Hz). No improvement could be reached for the phase angle and results are even worse with the 25mm plates at low frequencies (0.01 Hz and 0.1 Hz). These dispersions are illustrated in Figure 10 for the 8mm plates (measurements at 10°C) and in Figure 11 for the 25mm plate. The improvements expected from the investigations reported under § 4 have thus been outbalanced by other factors which we tried to discover through a closer analysis of data in relation to operating conditions.

Table 6 : Comparison of Final Round Robin with First Round Robin [1] – PmB2 binder

Evaluation of reproducibility : values of s/m (%) (s = standard deviation, m = mean)

PmB2	Modulus |G*| - 8mm plates							
Temp. (°C)	0.01 Hz		0.1 Hz		1 Hz		10 Hz	
-10	**23.0**		**14.4**		**7.5**		**4.5**	
0	**23.6**		**18.3**	13.5	**20.6**	9.0	**20.6**	
10	**30.8**	24.9	**20.4**	21.1	**16.5**	23.0	**17.0**	22.5
20	**28.1**	26.3	**23.9**	25.4	**18.0**	27.1	**13.1**	23.4
30	**26.7**	30.8	**23.1**	24.7	**19.4**	26.9	**14.8**	27.2
40	**31.7**	25.3	**27.2**	30.8	**14.4**	22.2	**17.4**	27.3

Phase Angle δ - 8mm plates							
0.01 Hz		0.1 Hz		1 Hz		10 Hz	
		9.0		**10.8**		**13.9**	
10.4		**3.6**	4.4	**5.2**	5.3	**4.1**	
6.3	6.7	**5.9**	3.7	**5.1**	3.0	**1.8**	4.5
6.8	10.4	**4.1**	4.1	**4.9**	3.1	**4.6**	3.3
8.6	8.1	**4.6**	9.0	**3.6**	3.3	**4.1**	2.8
11.7	15.0	**7.8**	6.6	**5.4**	5.3	**6.2**	3.0

PmB2	Modulus |G*| - 25mm plates							
Temp. (°C)	0.01 Hz		0.1 Hz		1 Hz		10 Hz	
40	**54.6**	52.2	**32.3**	35.0	**20.8**	30.0	**21.2**	24.9
50	**43.8**	32.3	**21.8**	16.2	**9.8**	18.7	**12.2**	18.1
60	**26.5**	15.5	**13.9**	16.7	**13.3**	24.2	**13.3**	21.5
70	**21.9**	51.2	**23.1**	40.5	**21.4**	38.8	**21.0**	27.5
80	**19.4**	32.6	**17.4**	34.7	**16.4**	0.0	**16.2**	23.7

Phase Angle δ - 25mm plates							
0.01 Hz		0.1 Hz		1 Hz		10 Hz	
35.5	17.2	**17.7**	8.1	**5.7**	4.0	**3.5**	4.4
36.8	12.6	**21.2**	6.5	**8.6**	5.0	**2.3**	2.0
22.3	6.8	**11.1**	9.5	**3.9**	3.2	**1.5**	1.9
1.6	2.8	**1.0**	2.2	**1.3**	1.5	**1.2**	2.1
2.5	1.1	**0.6**	1.2	**1.0**	1.6	**1.7**	2.3

Bold font **Values obtained in the final Round Robin**
Normal font Values obtained in the first Round Robin [1]

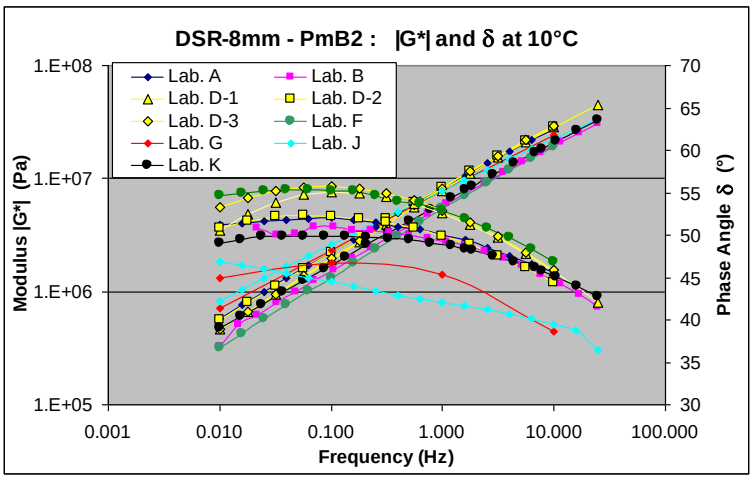

Figure 10 : Final Round Robin Test on PmB2 – 8mm plates

When observing the curves obtained for the phase angle at 40°C and 60°C (Figures 11-b and 11-c), one does indeed distinguish 2 families of curves. For Laboratories A, B and D-1, tests have been performed as prescribed : bonding of the samples at 80°C, then drop in temperature down to 40°C and performing the temperature sweep upwards. In this case, one may assume that after an initial partial "melting" of the polymer network due to the high bonding temperature, re-structuring of this network could not take place, the first testing temperature being still relatively high and being reached quickly. Hence the relatively high phase angle values. Laboratory K also applied this procedure, however the first testing temperature was far lower (10°C) and it took thus a much longer time to get there, giving the polymer network the opportunity to restructure itself. Laboratories D-3 and F did not follow the planned procedure and bonded their sample at 40°C (i.e. the first test temperature). In this case, there was probably no initial partial "melting" of the polymer network, which would explain the lower phase angle values, as for Lab. K. The same explanation could possibly also apply to Laboratory G which bonded its sample at 60°C. It seems further quite logical that at higher test temperatures, at which the polymer network starts to "melt" again, the differences due to the thermal history of the sample disappear (Figure 11-d).

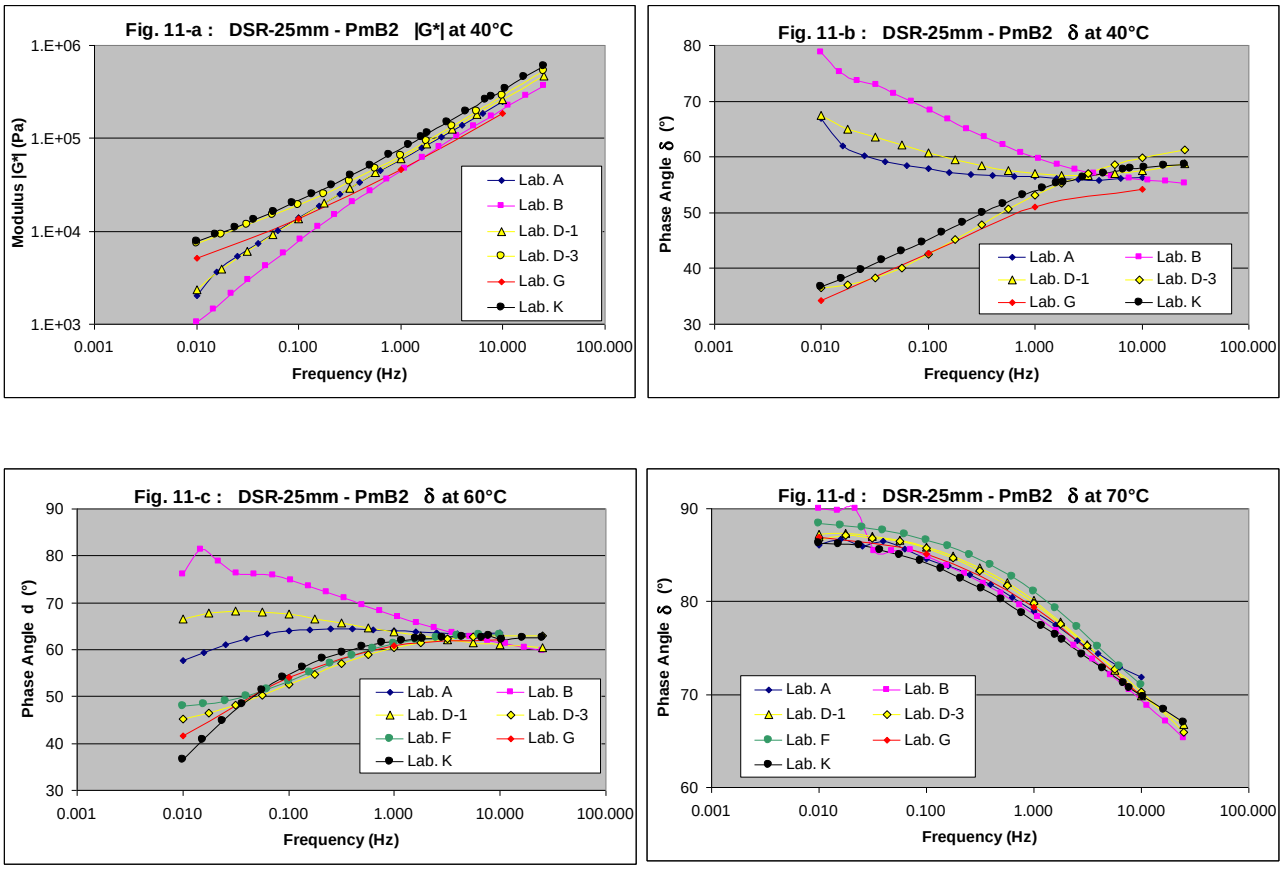

Figure 11 : Final Round Robin Test on PmB2 – 25mm plates

5.3 Complementary DSR tests – PmB2 binder.

To support the above exposed analysis, the GE1 working group decided to conduct a small complementary study with the 25mm plates at a single (most problematic) temperature of 40°C. Thermal history of the sample has been set such as to allow the polymer network structure to recover in exactly the same way at all laboratories. More precisely, after the initial bonding at 80°C, the sample has been cooled down to 10°C at a fixed rate of 2°C/min. and maintained at this temperature for 15 minutes. It has then been reheated at a rate of 1°C/min. to the test temperature of 40°C and maintained for 15 min. before starting the frequency sweep. The calculated coefficients of variation, as compared to the first round robin test, are given in Table 7. As it can be seen, the results are markedly improved. This is further illustrated in Figure 12-a and 12-b. Stiffness values stay much closer at low frequencies. With the exception of Lab. B (for which the values obtained at frequencies lower than 1 Hz have been withdrawn from the calculation of the coefficient of variation), all phase angle values follow the same trend. It is also important to mention that both stiffness and phase angle are now very close to the values obtained at 40°C with the 8mm plate geometry (Figure 13-a and 13-b).

Table 7 : Comparison of Final Round Robin with First Round Robin [1] – Complementary DSR tests with the PmB2 binder

Evaluation of reproducibility : values of s/m (%) (s = standard deviation, m = mean)

PmB2	Measurements at 40°C - 25mm plates							
	0.01 Hz		0.1 Hz		1 Hz		10 Hz	
Modulus |G*|	**9.6**	52.2	**15.3**	35.0	**14.7**	30.0	**16.1**	24.9
Phase Angle δ	**4.2**	17.2	**4.3**	8.1	**2.8**	4.0	**2.0**	4.4

Bold font **Values obtained in the final Round Robin**
Normal font Values obtained in the first Round Robin [1]

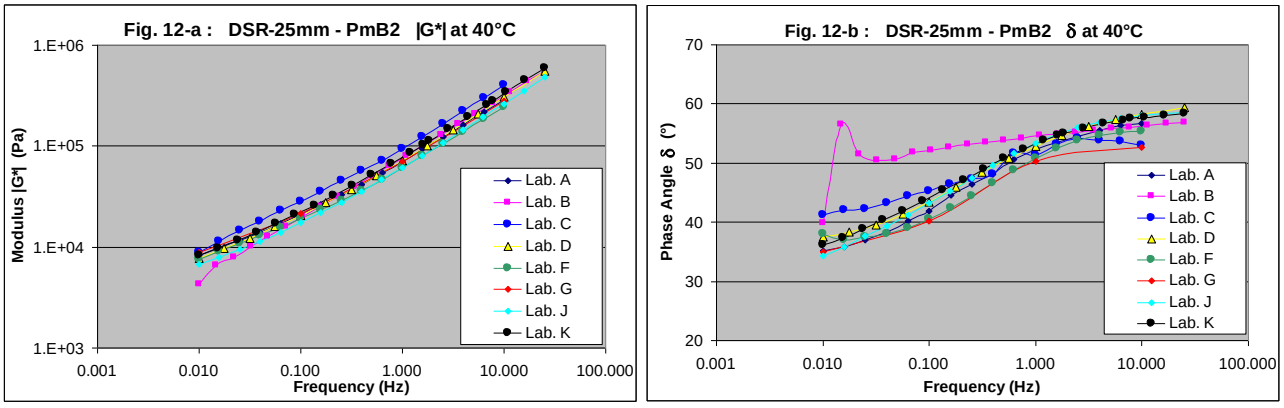

Figure 12 : Final Round Robin Test on PmB2 – complementary tests with 25mm plates

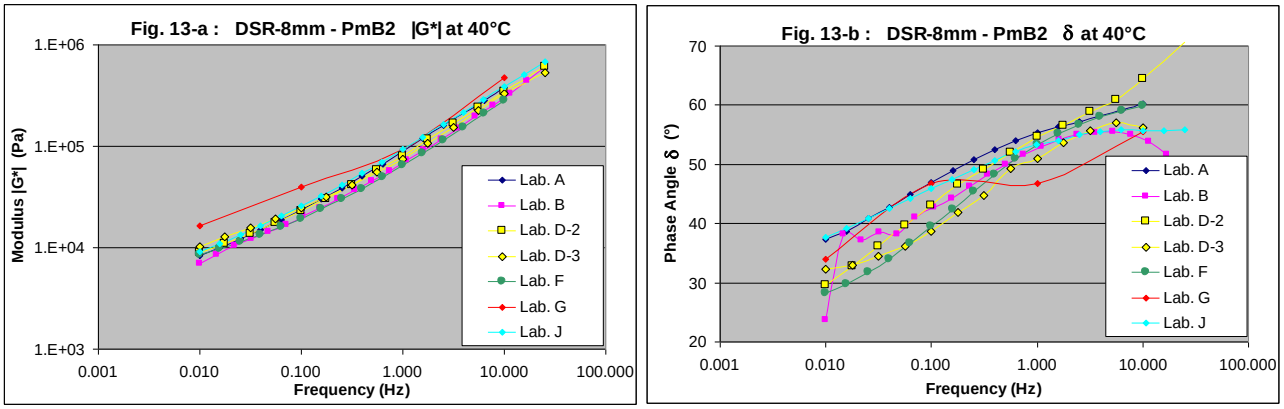

Figure 13 : Final Round Robin Test on PmB2 –8mm plates

5.4 Comparison to results obtained under annular shear and tension-compression mode of loading

As it can be inferred from Tables 3 and 4, the number of results obtained under linear mode of loading was far too limited for any statistical treatment. A comparison to DSR data is however still of interest. Tests under linear mode of loading were performed at frequencies ranging from 7.8 Hz to 200 Hz (Lab. I) and from 1.6 Hz to 250 Hz (Lab. K), thus at the higher end and in the continuation of the frequencies used for DSR testing (up to 25 Hz). Figures 14 and 15 show a comparison at 10 Hz. In Tension-Compression, a good agreement is obtained, for both |G*| and δ by both laboratories. Concerning the Annular Shear mode, results are also in line for Laboratory I whereas, for Laboratory K, we observe a similar off-set as the one already evidenced when using the PDMS reference (see § 3.2 and Figure 4).

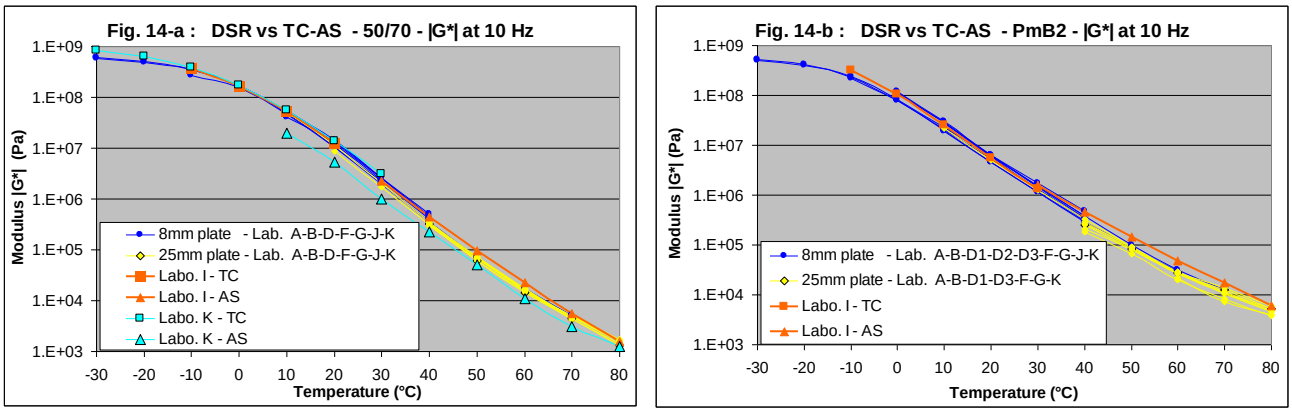

Figure 14 : Comparison of DSR data to TC-AS data : isochrones of |G*| at 10 Hz

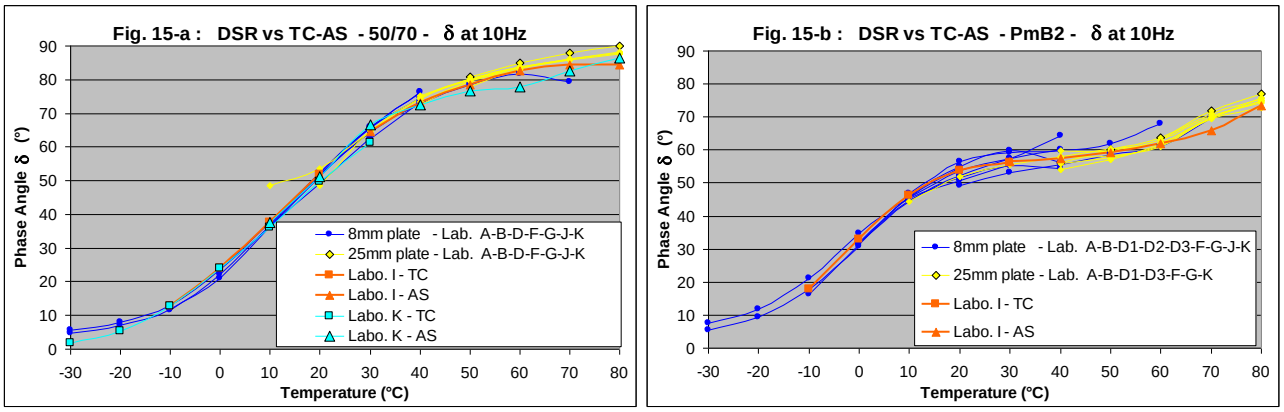

Figure 15 : Comparison of DSR data to TC-AS data : isochrones of δ at 10 Hz

6. CONCLUSION

It is envisaged that rheological properties from DSR measurements will be included in future performance related binder specifications. Achieving acceptable repeatability and reproducibility for "simple" binders such as straight-run bitumen is, in that respect, not good enough. Indeed, it is essentially for non-conventional binders, such as polymer modified binders, that rheological properties are more particularly needed. Unfortunately, it is also for these binders that acceptable precision is most difficult to achieve. This has once more been experienced by the GE1 working group with the PmB2 binder.

Rheology testing does however not suffer from any evil spell. Possible causes for discrepancies being well known, rigorously defined and applied test procedures allow reproducibility to be improved to a great extent. For binders prone to structural changes in relation to time and temperature, and as it has already been demonstrated by others [3,4], thermal history of the sample is of paramount importance. For comparisons to be meaningful and precision acceptable, this history has to be strictly defined and controlled, not only during the sample preparation phase, but also during the testing procedure itself. Furthermore, if DSR data are to be used as performance indicators, the procedure should be such that the binder tested in the rheometer is in the same state as the binder that is incorporated in the asphalt.

The very positive outcome of the second GE1 Round Robin test program is that reproducibility data then do become comparable to those achievable with "simple" plain bitumen. Even for "complex" binders, there is thus a future for performance specifications with rheological parameters from DSR tests. But there will also be a high price to it, i.e. strictly controlled equipment, strictly defined and applied test procedures and, above all, well trained operators !

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