DYNAMIC VISCOSITY MEASURING ROUND ROBIN TESTS ON BITUMEN FLUXED WITH VEGETABLE OIL BY THE GE2 WORKING GROUP

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ABSTRACT

The viscosity measurement is an essential parameter for classifying fluxed bitumens in the framework of the CE marking of these binders which is being put in place at the European level. Straight bitumens and polymer-modified bitumens that have been fluxed with vegetable oils often exhibit complex rheological behaviour at the temperatures recommended for the standardized STV pseudo-viscosity test.

The goals of the study of bitumens that have been fluxed with a vegetable oil are to classify these products which have a high viscosity (>10 Pa.s at 60 °C) on the basis of the specifications laid down in the standard NF EN 15322 of April 2010, to conduct a critical analysis of the test procedure and the limits of the test for measuring dynamic viscosity and to appraise measurement methods which are easier to transpose to our factories for the purposes of day-to-day monitoring.

Keywords: bitumen, vegetable oil, standard, viscosity, measurement

1. INTRODUCTION

In recent years, the replacement of oil-based fluxes with plant-based fluxes in order to limit greenhouse gas (GHG) emissions has led firms to develop increasingly viscous fluxed bitumens to compensate for the slowing down of the cohesion build-up kinetic and take account of the fact that part of the flux no longer evaporates during laying. In the case of some highly viscous products, the rheological behaviour can nevertheless become complex and conventional flow-based pseudo-viscosity measurements are difficult to reproduce (flow time with a 10 mm orifice at 40 °C > 500s).

In the specification standard and for CE markings, viscosity is a key point for the classification of fluxed bituminous binders [1]. In the case of cutback and fluxed bitumens of the "conventional" type (viscosity classes 2 to 4), the standard relies on pseudo-viscosity measurements based on flow times at 25 or 40 °C [2]. In the case of the most viscous products, the standard lays down that a dynamic viscosity measurement should be made at 60 °C with a low shear rate (2 s^{-1}), using a coaxial cylinder rheometer [3]. These products correspond to viscosity classes 5 to 7, whose viscosity at 60° C is greater than 10 Pa.s (i.e. a pseudo-viscosity of more than 500s with a 10 mm orifice at 40 °C). The viscosity measurements are made with a low rate of shear to assess the properties of the fluxed bitumen after it has been sprayed onto the pavement in terms of its ability to wet aggregate in the case of surface dressings.

The work undertaken by the French expert group P04/GE2 which deals with bitumen emulsions and anhydrous binders sets out to classify highly viscous fluxed bitumens on the basis of the specifications laid down in the standard NF EN 15322, to conduct a critical analysis of the test procedure and the limits of the test for measuring the dynamic viscosity and to appraise measurement methods which are easier to transpose to our factories for the purposes of day-to-day monitoring.

It is important to note that the limited number of laboratories has meant that it was not possible to identify precisely the reproducibility of these tests, but simply obtain an initial estimate of their accuracy. In order to determine a reproducibility value, additional tests in the framework of genuine inter-laboratory comparison tests will be necessary.

2. THE BINDERS USED IN THE STUDY

The base bitumen used in the study was a 70/100 pen straight or elastomer-modified (SBS) bitumen. The vegetable flux oil was a methyl ester sunflower oil. Five fluxed bitumens (BF) and five polymer-modified fluxed bitumens (BPF) with different flux contents in order to obtain different dynamic viscosities at 60 °C were manufactured at the Corbas Study and Research Centre (Eiffage Travaux Publics).
The binders were designated as follows :

- Fluxed bitumens : BF 1, BF 2, BF 3, BF 7 and BF 8
- Polymer-modified fluxed bitumens: BPF 4, BPF 5, BPF 6, BPF 9 and BPF 10.

The binders were analyzed by the three following laboratories: the Colas scientific and technical campus, the Eiffage Travaux Publics Studies and Research Centre and the Eurovia Research Centre.

3. EXPERIMENTAL METHODS FOR MEASURING VISCOSITY

3. 1 Viscosity by flow (NF EN 12846-2)

The pseudo-viscosity tests on the fluxed bituminous binders were performed as specified in the standard NF EN 12846-2 where the cups used for the binders had a 10 mm orifice and the temperature was defined at 25 or 40 °C depending on the viscosity.

In the framework of the study, tests were conducted at 40 °C (as requested by the standard) , and also extended to 50 and 60° C in order to evaluate the limits of the test and define viscosity correlations according to the temperature.

3.2. Dynamic viscosity (NF EN 13302)

The dynamic viscosity tests were conducted as specified in the standard NF EN 13302 (April 2010) by all the laboratories which owned coaxial cylinder rheometers of the Brookfield RV DV type, as shown in Figure 1. The corresponding geometries all correspond to those specified in the standard : $R_2/R_1 \geq 1.1$ and 1 mm $\leq R_2\text{-}R_1 \leq 6$ mm.

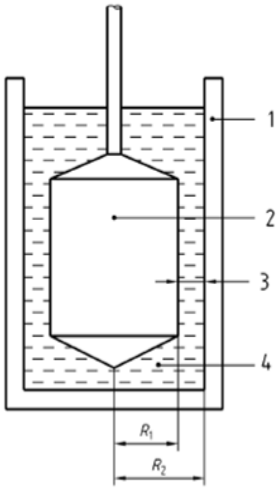

Figure 1. Coaxial viscosimeter (according to NF EN 13302, 2010)
1 Sample container, 2 : Spindle, 3 : Gap 4 : Sample R_1 : Inner radius (spindle), R_2 Inner radius (container)

The test standard specifies a shear rate of 2 s^{-1}. In the case of non-Newtonian behaviour, it is permissible to measure the viscosity at other shear rates. For samples which exhibit shear thinning behaviour of this type, it is particularly important to state the rate of shear applied as requested in the standard. Failure to do this is doubtless responsible for a large number of the sometimes major disparities that have been noted between different laboratories. Comparisons between viscosity measurements made in different laboratories are meaningless if they have not been obtained with the same shear rate and a similar stress application procedure (shear scanning).

The nature of the spindle must be optimized in accordance with the viscosity of the binder and therefore the temperature to ensure that measurement is conducted in the operating range prescribed by the supplier and thus guarantee accuracy. Typically, this value should be between 10 and 90 % of the full measurement scale (maximum torque for the sensor) which is specific for each spindle/speed combination. In the case of a Brookfield viscometer, the accuracy of measurement is 1 % at full scale and inversely proportional to the relative value of the applied torque. With torque of 50 %, the relative accuracy will be 1/50 i.e. 2 %.

When the limits of the various devices and tools are known, it is easy to plot theoretical viscosity graphs for different shear rates (Figure 2) in order to guarantee that the measurement is accurate to within 1 and 10 %.

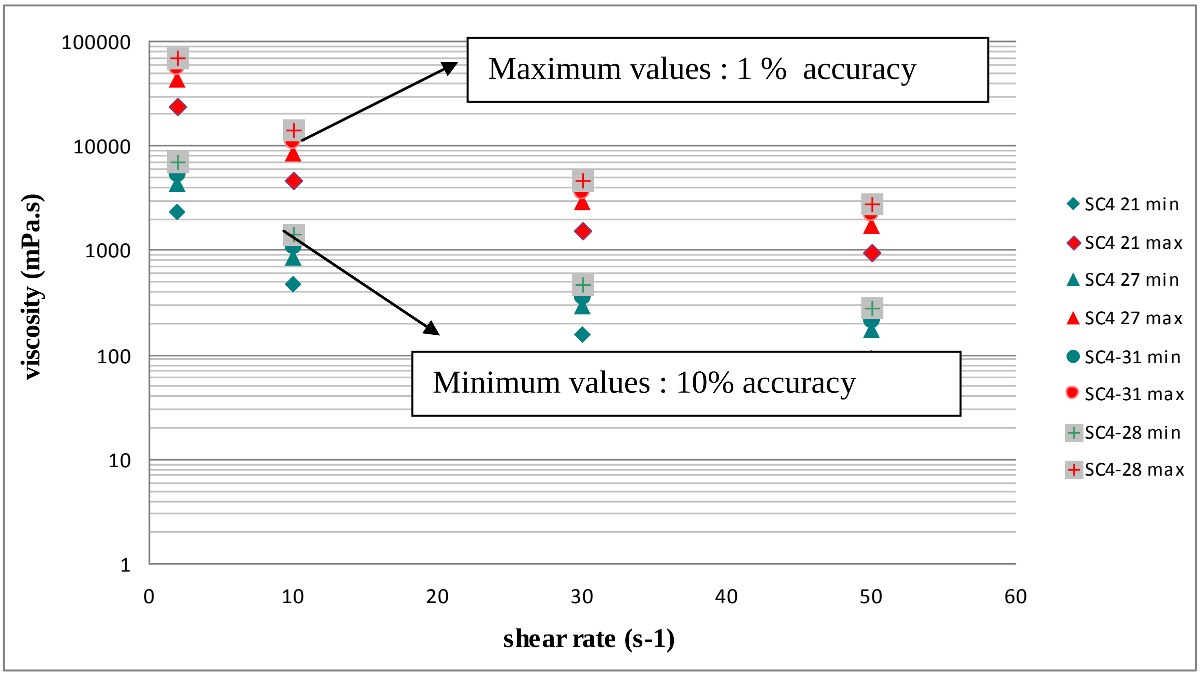

Figure 2. Theoretical plot of the limits of the viscosity measurements for 4 spindles depending on the rate of shear – Brookfield RV

The choice of spindle is therefore a key parameter for this dynamic viscosity measurement. Each viscosity measurement must be carried out under static (as opposed to transient) conditions in order to guarantee the representativity of the measurement. The suppliers consider that the viscosity readout is stable after 5 revolutions of the spindle. The current standard specifies that the measurement should be taken after 30s. The reproducibility of this test is not specified in the standard for fluxed bitumens but in the case of bituminous binders it is given as 15% of the mean value for hot coating binders

When the aim is to measure the viscosity at 2 s^{-1} of class 5 binders (10 to 50 Pa.s according to the standard NF EN 15322, the blue zone in Figure 3, only spindles SC4-28 and SC4-31 are suitable for the entire range of class 5 binders (Table 1).

Table 1 : Viscosity ranges according to the spindle with the Brookfield RV DV II+ or III.

Spindle	Viscosity range at 2 s^{-1}
SC4 -21	2.3 to 23.2 Pa.s
SC4-27	4.2 to 42.5 Pa.s
SC4-28	7 to 70 Pa.s
SC4-31	5.4 to 54.4 Pa.s
SC4-34	8.9 to 89 Pa.s

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4. RESULTS

4. 1. Flow viscosity measurements at 40, 50 and 60 °C

The pseudo-viscosities at 40, 50 and 60° C were measured on the fluxed bitumens (Table 2) and the fluxed polymer-modified bitumens (Table 3) on the basis of an average of two tests.

Table 2. STV pseudo-viscosities with a 10 mm orifice (in s) for fluxed bitumens at different temperatures (ND : not determined)

Temperature	Laboratory	BF1	BF2	BF3	BF7	BF8
40 °C	A	ND	ND	ND	1010*	255
	B	1988*	568	241	931*	229
	C	1840*	581	218	1009*	265
	Mean value	***1914***	***575***	***230***	***983***	***250***
	(Maximum- Minimum) Value	148	13	23	79	36
	(Max-Min) mean (%)	8	2	10	8	15
50 °C	A	ND	ND	ND	247	80
	B	ND	ND	ND	254	72
	C	426	155	70	271	73
	Mean value	***ND***	***ND***	***ND***	***257***	***75***
	(Maximum- Minimum) Value	ND	ND	ND	24	8
	(Max-Min) mean (%)	ND	ND	ND	9	10
60 °C	A	100	53	21	71	29
	B	95	46	23	61	23
	C	ND	ND	ND	70	27
	Mean value	***98***	***50***	***22***	***67***	***26***
	(Maximum- Minimum) Value	5	7	2	10	6
	(Max-Min) mean (%)	5	14	9	15	23

Table 3. STV pseudo-viscosities with a 10 mm orifice (in s) for polymer-modified fluxed bitumens at different temperatures (ND : not determined)

Temperature	Laboratory	BPF4	BPF5	BPF6	BPF9	BPF10
40 °C	A	ND	ND	ND	4082*	694*
	B	2357*	1114*	859*	3030*	627*
	C	3432*	1925*	1047*	2240*	998*
	Mean value	***2895***	***1520***	***953***	***3117***	***773***
	(Maximum- Minimum) Value	1066	811	188	1842	371
	(Max-Min) mean (%)	37	53,	20	58	46
50 °C	A	ND	ND	ND	783*	307
	B	ND	ND	ND	534	207
	C	493	353	262	583	238
	Mean value	***ND***	***ND***	***ND***	***633***	***251***
	(Maximum- Minimum) Value	ND	ND	ND	249	100
	(Max-Min) mean (%)	ND	ND	ND	38	39
60 °C	A	230	124	96	195	84
	B	162	108	64	149	75
	C	ND	ND	ND	207	74
	Mean value	***196***	***116***	***80***	***184***	***78***
	(Maximum- Minimum) Value	68	16	32	58	10
	(Max-Min) mean (%)	35	14	40	33	13

*It is important to note that the standard NF EN 12846-2 limits the validity of the measurement, whatever the temperature for the test with a given orifice, to a duration of flow of 600s on condition that flow is continuous. Beyond this duration and/or if flow is interrupted, the instruction is to increase the duration of the test. It should also be remembered that for flow durations in excess of 20 s, the standard gives a mean reproducibility of 10%.

At 40 °C, only 3 of the 10 studied binders (BF2, BF3 and BF8) had a pseudo-viscosity of less than 600 s and can therefore be characterized by a psuedo-viscosity in the strict sense according to the standard EN 12846-2. All the other studied binders, particularly the polymer-modified fluxed bitumens, had very much longer flow times. When we calculated the ratio (in %) between the observed maximum and minimum values and the mean of the results, it was apparent that only the straight fluxed bitumens gave values that were compatible with the 2 % reproducibility stated in the standard. The values obtained for the polymer-modified fluxed bitumens were often considerably greater than 20 %, which suggests that the pseudo-viscosity of these binders at 40 °C is not only unsuitable (excessively long flow times) but also not reproducible.

At 50 °C, the STV pseudo-viscosities with a 10 mm orifice were measured by the three laboratories on only 4 binders (2 fluxed bitumens, BF 7 and BF8 and 2 polymer-modified fluxed bitumens, BPF 9 and BPF 10). While in general, the flow times became lower than the 600 s limit value, the differences observed for the two polymer-modified fluxed bitumens were smaller, but nevertheless still considerable.

At 60 °C, the 10 binders all had pseudo-viscosities of less than 250 s. The differences between the laboratories (as a percentage of the mean) were however not improved in the case of the straight fluxed bitumens (values between 5 % and 25 %). In the case of the polymer-modified fluxed bitumens, these relative differences were admittedly better than the results at 40 °C, but in some cases they still exceeded 30 %. This suggests that for these binders increasing the test temperatures would probably not be enough to guarantee satisfactory reproducibility.

This result may be the outcome of the more pronouced non-Newtonian behaviour of these produicts, but also possible problems with regard to sampling and preparation of the tests (instability of the product…).

4.2. Dynamic viscosity measurements

Measurements at 60 °C

The dynamic viscosity was measured by the 3 laboratories for both the fluxed bitumens and the polymer-modified fluxed bitumens (Tables 4 a and b).

Tables 4. Dynamic viscosity measurement at 60 °C (in Pa.s) performed with coaxial viscometers by the 3 laboratories with a shear rate of 2 s^{-1} (a- straight fluxed bitumen, b- polymer-modified fluxed bitumen) (ND* = * Not determined as not performed at 2 s^{-1})

4a- Laboratory	BF1	BF2	BF3	BF7	BF8
A	39.8	22.5	9.5	26.5	9.5
B	ND*	19.5	9.7	24.9	10
C	43.2	19.5	9.7	28.8	10.5
Mean value	***42***	***21***	***10***	***27***	***10***
Maximum - Minimum	3.4	3	0.2	3.9	1
Max-Min/Mean (%)	8.1	14.3	2.1	14.1	10

4b- Laboratory	BPF4	BPF5	BPF6	BPF9	BPF10
A	46.2	27.6	19.4	45.6	19.2
B	ND*	31.5	21.9	45.2	19.9
C	44.1	31.1	23.3	52.2	24.9
Mean value	***45***	***30***	***22***	***48***	***21***
Maximum - Minimum	2.1	3.9	3.9	7	5.7
Max-Min/Mean (%)	4.7	13.2	18.3	14.4	25.9

The viscosity values given by the different laboratories were obtained by calculating the average for the two tests. All the tests were conducted at a speed of 2 s^{-1}. The spindles were selected to obtain a measurement accuracy of between 1 and 10 % as specified in the standard NF EN 13302.
The differences between the laboratories (as a percentage of the mean) were below 15 % for the straight fluxed bitumens. It is particularly interesting that in the case of the polymer-modified fluxed bitumens these relative differences (which nevertheless sometimes attained a level of 25 %) were considerably better that the results obtained during the pseudo-viscosity test at 60 °C.

Measurements at 100 °C

Following this first series of measurements, additional tests were conducted at 100 °C. At this temperature, it was however often impossible to conduct measurements at a shear rate of 2 s^{-1} by using the same apparatus with a different spindle as the measurement was outside the torque measurement scale of the apparatus. The laboratories therefore had to alter the shear rate in order to achieve precise measurements without making prior judgments about the Newtonian nor non-Newtonian behaviour of the product.
The values presented in Tables 5a and 5b below were given for a shear rate of 30 to 50 s^{-1} for the pure fluxed bitumens and between 20 and 50 s^{-1} for the polymer-modified fluxed bitumens.

Table 5. Dynamic viscosity measurement at 100 °C (in Pa.s) performed with coaxial viscometers by the 3 laboratories with a shear rate of 2 s^{-1} (a- straight fluxed bitumen, b- polymer-modified fluxed bitumen) (ND* = * Not determined as not performed at 2 s^{-1})

5a - Laboratory	BF1	BF2	BF3	BF7	BF8
A	1.36	0.83	0.55	0.98	0.52
B	1.3	0.84	0.56	ND	ND
C	1.29	0.80	0.51	1.02	0.56
Mean value	***1.32***	***0.82***	***0.54***	***1.00***	***0.54***
Maximum - Minimum	0.07	0.03	0.05	0.04	0.04
Max-Min/Mean (%)	5.3	4.0	9.3	4.3	6.6

5b - Laboratory	BPF4	BPF5	BPF6	BPF9	BPF10

A	2.17	1.35	1.15	2.07	1.01
B	1.55	1.23	0.99	ND	ND
C	1.73	1.35	1	1.95	1.05
Mean value	***1.82***	***1.31***	***1.05***	***2.01***	***1.03***
Maximum - Minimum	0.62	0.12	0.16	0.12	0.04
Max-Min/Mean (%)	33.3	9.3	14.9	6.0	3.6

While the repeatability for each laboratory and the differences between the laboratories generally improved when the temperature was raised from 60 to 100 °C, the differences between the binders were reduced and it was no longer possible to distinguish between the types of product. Furthermore, as mentioned above, in the case of low viscosities, the apparatus which is available on the market is generally unable to perform precise measurements at low shear rates. In the context of comparisons and standardization, a shear rate of 2 s^{-1} which is currently recommended by the standard EN 13302 should be revised. Based on our results, these shear rates could be 50 s^{-1} for products with a viscosity of between 0 and 1.5 Pa.s and 20 s^{-1} for products with a viscosity of between 1.5 and 3 Pa.s.

4.3. Relationship between the dynamic viscosity measurements and the flow viscosity measurements (STV)

Figure 3 shows the STV viscosity with a 10 mm orifice at 40 °C on the basis of the dynamic viscosity at 60 °C, using the mean value obtained by the laboratory. This graph shows the good continuity between class 4 (50 to 500s with the STV apparatus and a 10 mm orifice at 40 °C) and class 5 (10 to 50 Pa.s at 60 °C) as specified in the standard NF EN 15322. Similar correlations were achieved with the STV pseudo-viscosity measurements at 60 °C (Figure 4) and with the dynamic viscosity at 100 °C (Figure 5) for the straight fluxed bitumens and polymer-modified bitumens.

Dynamic viscosity measurements are a more reliable way of characterizing the viscosity of a polymer-modified fluxed bitumen. Performing the test at 60 °C strikes us as being a good compromise (Figure 4). If the test temperature is increased to 100 °C (Figure 5), the difference between the classes of binder is reduced and it is no longer possible to meet requirements, particularly in the framework of manufacturing monitoring.

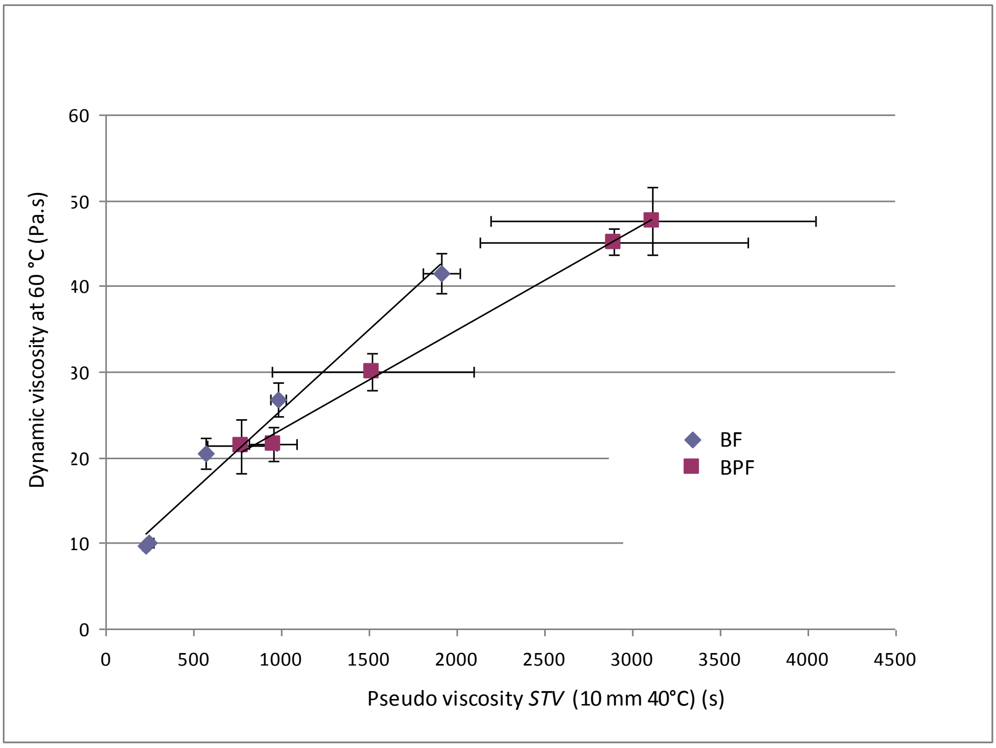

Figure 3. Correlation between the dynamic viscosity at 60 °C and the STV pseudo-viscosity at 40 °C for straight fluxed bitumens and polymer-modified fluxed bitumens

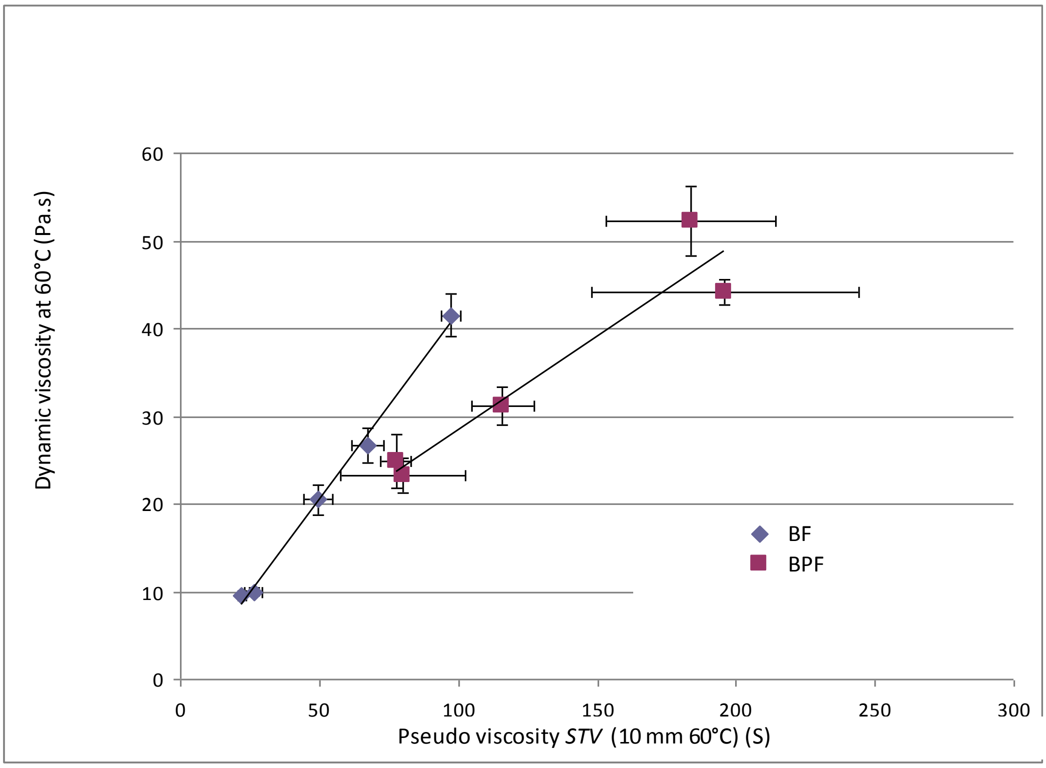

Figure 4. Correlation between the dynamic viscosity at 60 °C and the STV pseudo-viscosity at 60 °C for straight fluxed bitumens and polymer-modified fluxed bitumens

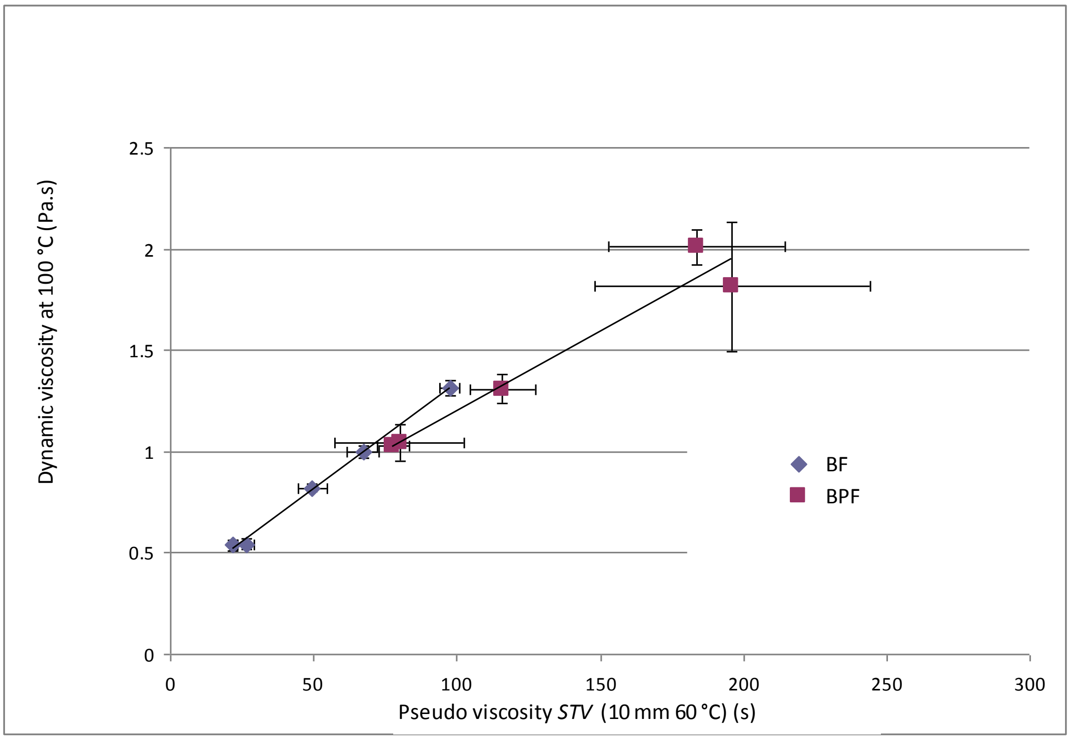

Figure 5. Correlation between the dynamic viscosity at 100 °C and the STV pseudo-viscosity at 60 °C for straight fluxed bitumens and polymer-modified fluxed bitumens

4.4. Dynamic viscosity measurements with plate-cone rotating viscometers

In order to assess the accuracy of plate-cone viscometers, additional tests were conducted by laboratories B and C (Brookfield CAP 2000 viscometer). The aim of these measurements was to appraise potentially simpler tests for monitoring binders in our factories. The theory is similar to that we have described for dynamic viscosity using a coaxial apparatus. The cone is modified according to the viscosity of the product in order to obtain a measurement accuracy of between 1 and 10%.

Measurements were conducted at 60 °C (1 laboratory), 90 °C (2 laboratories) and 100 °C (2 laboratories) and are set out in Table 6.

Table 6. "Plate-cone" dynamic viscosity (in Pa.s) as a function of temperature for straight fluxed bitumens and polymer-modified fluxed bitumens (ND : not determined)

Temperature	Laboratory	BF7	BF8	BPF9	BPF10
100 °C	B	1.08	0.58	1.58	ND
	C	1.13	0.63	1.6	1.0
	Mean	***1.1***	***0.6***	***1.6***	***1.0***
90 °C	B	1.91	1.0	2.5	1.7
	C	2	1.0	3.0	1.6
	Mean	***2.0***	***1.0***	***2.8***	***1.7***
60 °C	B	ND	ND	ND	ND
	C	28.2	9.9	44.1	18.8
	Mean	*ND*	*ND*	*ND*	*ND*

At 90 and 100 °C, the results from the two laboratories were very similar. The Newtonian behaviour of the tested products meant it was possible to work to apply different shear rates according to the procedures implemented in each laboratory. In order to work within a zone of accuracy of between 1 and 10 %, the required shear rate for the different binders is 2500 s^{-1}.

At 60 °C, the non-Newtonian behaviour of some of the binders and the measurement limits of some of the equipment meant the shear rates had to be fixed on the basis of the viscosity. For example :

- a shear rate of 100 s^{-1} if the viscosity was above 20 Pa.s
- a shear rate of 1000 s^{-1} if the viscosity was below 20 Pa.s

5. CONCLUSIONS

The study conducted on the measurement of the viscosity of fluxed bituminous binders in the framework of the introduction of CE marking for these binders (the standard NF EN 15322) has revealed a considerable number of points :

- STV flow viscosity measurements with a 10 mm orifice at 40 °C will not be able to characterize the full range of fluxed bitumens on the market, in particular those with high viscosities. In the case of straight fluxed bitumens, increasing the temperature to 50 or even 60 °C is therefore possible, while retaining an acceptable degree of reliability for the test. However, this approach does not seem possible in the case of polymer-modified fluxed bitumens for which the observed differences between the different laboratories are much greater.
- Dynamic viscosity measurements with coaxial cylinders at 60 °C provide results with more acceptable differences between the different laboratories. It is important to emphasize that when dynamic tests are conducted, the apparatus and the spindle must be selected on the basis of the level of viscosity that is to be measured. Based on the characteristics of the existing apparatus, it is possible to plot graphs for selecting the appropriate spindle for measuring a given level of viscosity with the required accuracy. In this context, we have been able to demonstrated that it is feasible to make binder viscosity measurements in the 10 to 90 Pa.s range with the shear rate of 2 s^{-1} required by the standard NF EN 15322. In addition, as far as the continuity of viscosity classes is concerned, this standard seems to have a good level of consistency. It should be borne in mind that the non-Newtonian nature of some of the products makes it necessary to decide on a shear rate. Increasing the temperature of the test (to 100 °C) will probably improve the reproducibility, but it will also reduce the differences between different binders, which could have an adverse impact on the identification of classes.
- Some modifications of the test standard NF EN 13302 are necessary in order to refine the test procedure (sample preparation, introduction of the spindle into the tube, homogenization of the binder before measurements are begun). The conditions under which the applied shear rates can differ from the reference value of (2 s^{-1}) should also in our view be clarified.
- Dynamic viscosity measurements with a plate-cone system have good potential. For binders with Newtonian behaviour from low rates of shear, dynamic viscosity measurements are very close to those obtained with coaxial cylinders. However the limited number of tests conducted means that we cannot reach a categorical conclusion in this area.

Last, it should be borne in mind that the tests described here are too limited to permit an estimate of reproducibility. Much larger inter-laboratory tests are required for this.

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