Binder performance and testing

Impact of the Production Process on the Thermorheological Properties of Pure and Polymer Modified Asphalt

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Abstract

Bitumens used as a binder in bituminous pavements are complex materials and Polymer Modified-Bitumens (PMB) were developed to improve their thermomechanical performances. Styrene-Butadiene-Styrene copolymers (SBS) are commonly used for this purpose but their efficiency largely depends on crude oil origin and refinery process. To better understand the impact of the refinery process on PMB thermorheological properties, four bitumens obtained by various refinery processes (direct distillation, propane deasphalting, air-blowing rectification and visbreaking reduction) have been used as base material for PMB. Pure bitumens and PMB performances containing up to 5 wt-% SBS have been evaluated by fluorescent microscopy, differential scanning calorimetry (DSC), dynamic shear rheology (DSR) and dynamical mechanical analysis (DMA). Empirical tests (softening point, needle penetration and FRAASS breaking point) were also accessed. Neat bitumens were first characterized and only slight differences were observed for empirical tests and thermorheological behaviors. High-temperature rheological behaviors are linked to the bitumen colloidal structure and in accordance with (i) the asphaltene content after bitumen refining and (ii) the presence of a yield stress rheological behavior quantified using a specific Carreau-Yasuda model. Concerning glass-state properties at low temperature, correlations were found with the bitumen glass transition and the maltene composition (in particular aromatic fraction content). The use of SBS could largely improve empirical properties and thermorheological behaviors of neat bitumens. However, the impact of SBS content on softening points and elasticity of PMB revealed several trends. Propane deasphalting and air-blowing rectification are clearly detrimental to SBS efficiency whereas direct distillation and visbreaking reduction could favor co-continuous morphologies in PMB at low SBS content. Relationships between morphology and thermorheological behavior are finally discussed together with the role of SBS swelling behavior in aromatic oil of neat bitumen.

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4. INTRODUCTION

Bitumens are complex materials obtained during crude oil distillation as a viscous/solid residue and these materials are widely used in building applications such as binders for mineral aggregates for road pavements Despite the low bitumen content in road pavements (approx. 3 – 6% by weight), the use of bitumen has a great influence on the global thermorheological performances of road pavements. As it is well-know the choice of the binder will be critical in regards to their resistance to thermal cracking and rutting [1], [2], [3], [4], [5], [6].

The geographical origin of the crude oil primarily governs the chemical composition of bitumens [7]. Bitumens are originally produced from a direct vacuum distillation process. However, additional treatments can be applied to bitumens due to extraction optimization reasons and/or an actual will to produce a specific material. Among these additional modifications are (i) propane deasphalting process [8]; (ii) visbreaking reduction [9]; (iii) air-blowing process [10]. In other words, commercial bitumens are clearly composed of diverse chemical components altered by the refining process inducing chemical composition changes.

In this context, the proposed work attempts to clarify the impact of the refining process of neat bitumens on industrial properties and the consequences on the thermorheological properties of PmB. Four bitumens which have each undergone a unique refining process were selected (direct distillation, visbreaking reduction, air-blowing reduction and propane deasphalting). Their compositions and industrial performances were first investigated using SARA analysis and standardized tests followed by dynamic shear rheology and dynamic mechanical analysis. Then, PmB were produced with two contents of SBS and their industrial performances were accessed. Morphologies of PMA were carefully examined as well as thermomechanical properties to confirm and discuss the impact of refining process on PmB compatibility and performances.

5. MATERIALS AND METHODS

5.1 Materials

Four bitumens were selected with a similar 50/70 penetration grade and different refining process: direct distillation, propane deasphalting, air-blowing and visbreaking processes. In the following text, the bitumens will be respectively named: Direct, Deasphalted, Air-blown and Visbroken (according to their refinery process). For PmB production, a styrene-butadiene-styrene (SBS) block copolymer was provided by Sibur (Russia, grade DST-30-01).

5.2 PmB Preparation

PmB have been manufactured by heating bitumens at a temperature of 160 °C followed by the addition of SBS under stirring for 5 minutes using an Ultra Turrax T 50 (IKA, Germany). PmB were then stirred at 165°C (maximum) for another 1h30 and finally stored at 163°C in a 200 ml airtight container until characterizations.

5.3 Characterizations

5.3.1 Standardized tests

The Penetration, Ring&Ball and FRAASS Standardized test have been performed following the European standards NF EN 1426, NF EN 1427 and NF EN 12593 respectively.

5.3.2 SARA fractions

Chemical compositions of neat bitumens were carried using the IATROSCAN® process allowing the quantification of the SARA (saturated, aromatics, resins, asphaltenes) fractions. For each sample, a 1 µl a of 20 g/l solution of bitumen diluted in chloroform is applied on a silica rod (Chromarods SIII®). Then, the rod is successively emerged in three solvents: n-heptane, an 80/20 toluene/n-heptane and a dichloromethane/methanol. Eventually, the rods are placed in an IATROSCAN MK5 analyzer where burning is set at a speed of 30 seconds by chromarods with a hydrogen flow rate of 160 ml/min. Evaluation is done on the Chromstar ® software.

5.3.3 Dynamic shear rheology (DSR) and dynamic mechanical analysis (DMA)

Within the temperature range from 15 to +60°C (high temperature domain), neat bitumens and PmB were analyzed by a dynamic shear rheometer (Anton Paar MCR302, Austria) equipped with parallel plates (diameter 25 mm, gap 2 mm) to perform frequency sweeps between 100 and 0.01 rad.s-1 (Figure 1-a). A constant strain of 1% (within the linear regime) was applied. Within the temperature range from -30 °C to 15 °C (low temperature domain), neat bitumens and PmB were analyzed by a dynamic mechanical analyzer (Metravib 150+, France) to perform either temperature sweeps (from -30°C to 15°C, frequency 10 Hz, heating rate 0,5 °C/min) or frequency sweeps between 100 and 0.1 Hz at various temperatures in mechanical compression conditions. The dynamic displacement has been set to 2.10^{-6} m. DMA experiments were carried out on cylindrical samples (⌀ = 16 mm; h = 38 ±2 mm) (Figure 1-b). In order to generate the master curves, the data were homogenized by considering the equivalence between Young's moduli (E) and shear moduli (G) expressed by the following equation: $|E^*| = 3 \times |G^*|$ [1].

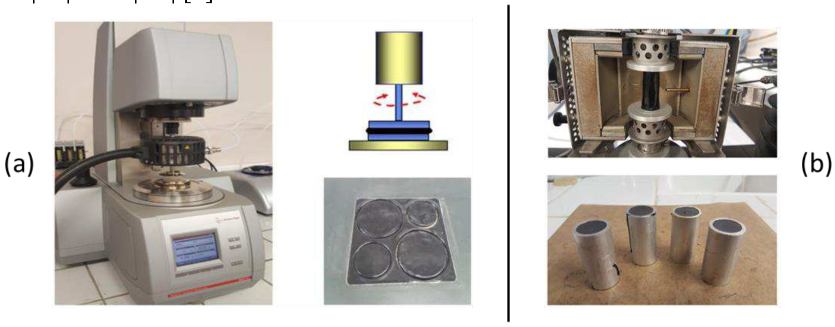

Figure 1. Apparatus and samples used for DSR (a) and DMA (b)

5.3.4 Thermal test

Temperature-Modulated Differential Calorimetry (TM-DSC) tests have been realized using a DSC 1 Metler Toledo (Switzerland). The mass of all pure and modified bitumens samples have been set to 15 ± 2 mg. The period has been set to 60 s and the amplitude to ± 0,5 °C. The thermal cycle used is represented in Figure 2.

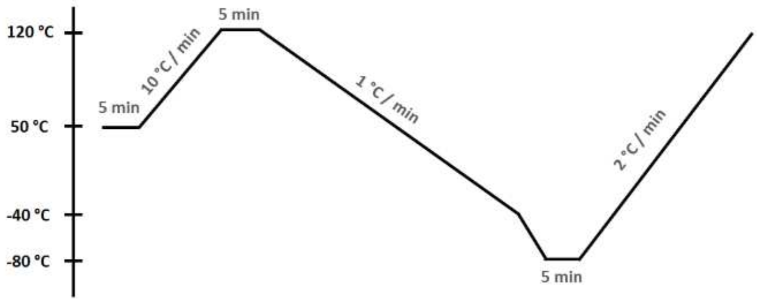

Figure 2. Thermal cycle used for DSC tests.

5.3.5 Fluorescent microscopy

Morphologies of PmB were revealed by fluorescence microscopy. A drop of PmB is placed between two glass slides and morphologies at x50 magnification are observed using a Axioscope (Zeiss, Canada) equipped with a high pressure mercury vapor lamp HBO 50 L1 (Zeiss, Canada).

5.4 Results and discussion

5.4.1 Composition and morphology

The evaluation of the SARA fractions has been carried using the IATROSCAN® process (Table 1). Compared to the “Direct” bitumen: the deasphalted one exhibits a clear reduction of the asphaltene (about 40%) and resins fractions; the visbroken present a decrease (about 20%) of the resins; the air-blown shows an important increase (90%) of the saturated and a decrease (30%) of the aromatic fractions. Considering the Colloidal index, the "deasphalted” present the most “sol” behavior and the air-blown the least.

Table 1. SARA Fractions of the four bitumens

Bitumen	Saturated	Aromatics	Resins	Asphaltenes	Colloidal Index (Ic)
	%	%	%	%	-
50/70 Direct	9	45	23	24	0,49
50/70 visbroken	8	48	18	26	0,52
50/70 Deasphalted	4	67	16	14	0,22
50/70 Air-blown	17	32	26	25	0,72

The Figure 3 shows the morphologies obtained with a 3 and 5% addition for the PmB. Among tested bitumens, two types

of morphologies can be observed. The first "nodular-like" morphology is found for the "Direct", "Deasphalted" and "Air-blown" bitumens. In those case, a greater concentration of SBS leads to a growth of the polymer-rich phase (brighter areas). The second "co-continuous" morphology is observed for the "Visbroken" one. In that case, a greater concentration of SBS leads to an even finer dispersion of the co-continuous phase.
On a structural aspect, the difference between those two morphologies could be related to the "phase inversion phenomena" [11]. In this case, one could assume that the "Visbroken" has a better compatibility with the polymer than the other bitumens.

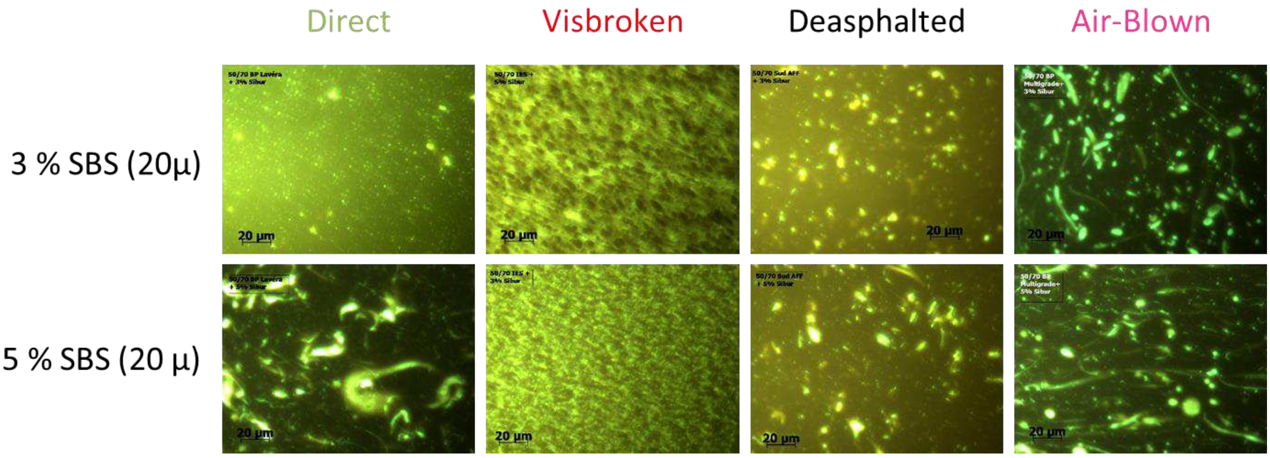

Figure 3. PmB morphologies with 3% and 5% SBS.

5.4.2 Global rheological behavior

In order to represent the global rheological behavior of the bitumens, master curves combining DSR and DMA data have been represented (Figure 4). The data were homogenized by considering the equivalence between the Young's modulus (E) and the conservation modulus (G) expressed by the following equation: $| E^* | = 3 \times | G^* |$.

In the case of pure bitumens (represented in black), the glass transition (Tg) is detected at high frequencies (> 10^4 Hz) equivalent to low temperatures) directly followed by viscous flow at low frequencies (> 10^{-3} Hz) equivalent to high temperatures). It should be noted that in the transition zone between the vitreous state and the molten state, a more or less marked shoulder probably linked to an additional relaxation is clearly detected as a function of the bitumens. This shoulder is more visible on the bitumens that have undergone heat treatment (Visbroken and Air-blown).

The addition of the SBS has two major effect on the rheological behavior of the bitumens. Firstly, a general increase in modulus value for frequencies lower than 10^4 Hz. Secondly, an emphasis of the shoulder effect creating a pseudo-plateau between the range 10^{-1} - 10^3 Hz for the "Visbroken" and the "Airblown" to a lesser extent. Some authors suggest the emergence of this pseudo-plateau could be linked to the formation of a small three-dimensional network [12], [13].

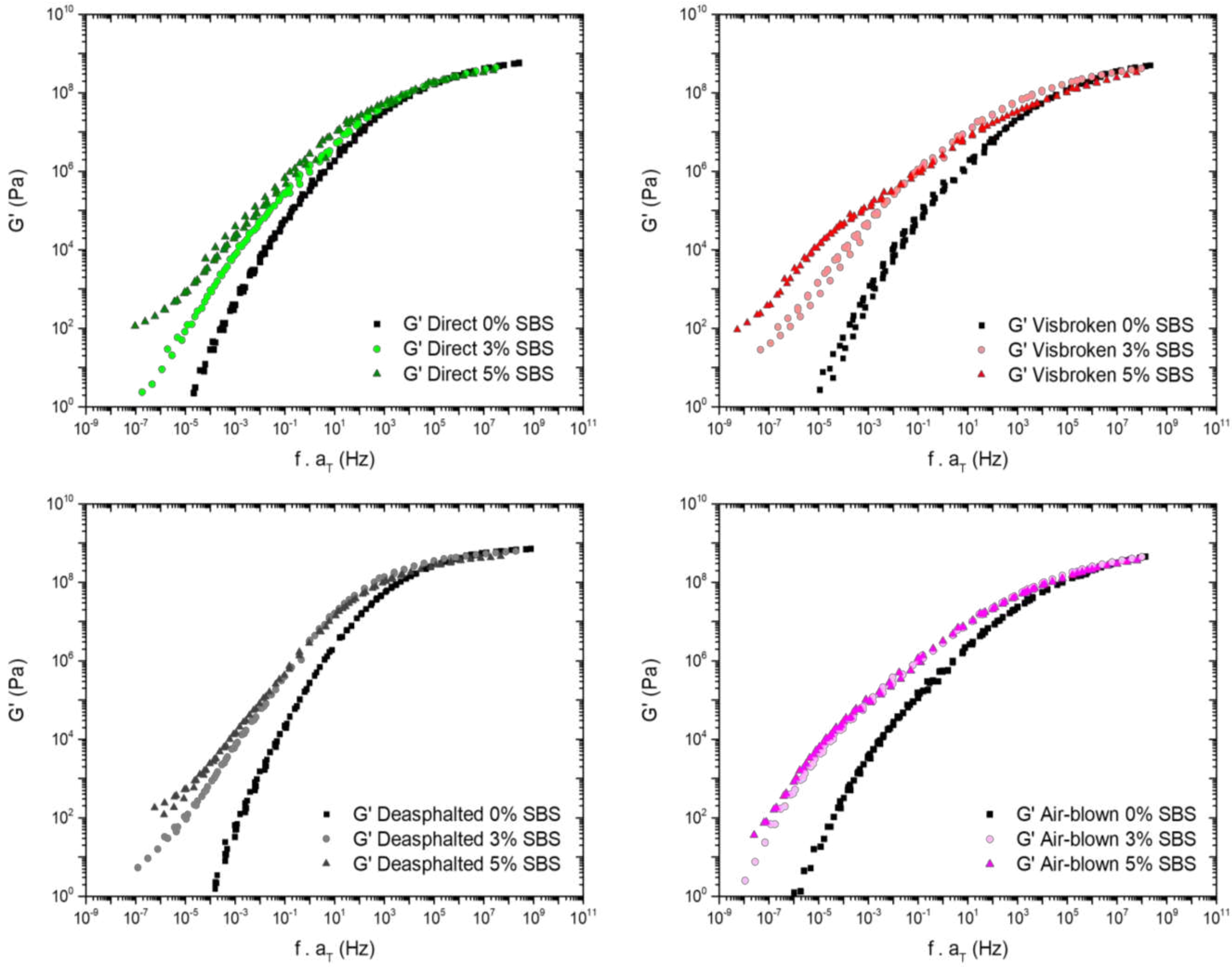

Figure 4. Conservation Modulus (G') Master curves of the pure bitumens (0 % SBS) and their respective 3% and 5% PmB.

The Black diagrams of the bitumen and their PmB are represented (Figure 5). They represent the evolution of the complex modulus (G*) as a function of the phase angle (δ). They are an indicator of the "Time Temperature Superposition Principle" (TTSP) quality, as they do not resort to a translation factor that are necessary for the master curves of the modulus. Indeed, for all the samples, curve superposition tends to degrade towards higher phase angles associated with high temperatures. It can be noticed that the poorest superpositions are observed for the "air-blown" and "visbroken" bitumen. It has been proposed that this effect could be related to the aging of the material [14]. In this case this could more or less severe conditions of thermal treatments cause by the refinery process. Except for this observation, all the pure bitumens reach a phase angle of 90 °, which makes it possible to confirm that the purely viscous terminal flow is obtained for a temperature of 60 ° C and above [15].

In the cases of the PmB, black diagrams make it possible to clearly highlight the elastic contribution of the polymer phase. In general, a reduction of the phase angle is observed towards the lowest modules with the addition of SBS. In other words, the greater the elastic effect of the polymer, the lower the phase angle will be [16].

In terms of phase angle, two successive "comma-like" reduction are found at 10^6 and 10^3 Pa. It appears that the "comma" situated around 10^3 Pa is susceptible to the polymer concentration. One reason could be related to the flow of binder which is more or less modified because of the elasticity of the polymer phase. Indeed, in this domain, the SBS the δ-value are decreasing significantly as the SBS concentration increased. At a 5% SBS concentration, this leads to two possible configurations for the two "commas": aligned and shifted. The aligned one is found for "Direct" and "Deasphalted". The shifted is found for the "Visbroken" and "Air-blown". It is interesting to note that the shifted configuration is obtained for the bitumens that have undergone additional heat treatment.

Based on the results given by the master curves and the Black diagrams, it seems that more information could be extract by studying the" above room temperature" and "cold" behaviors separately.

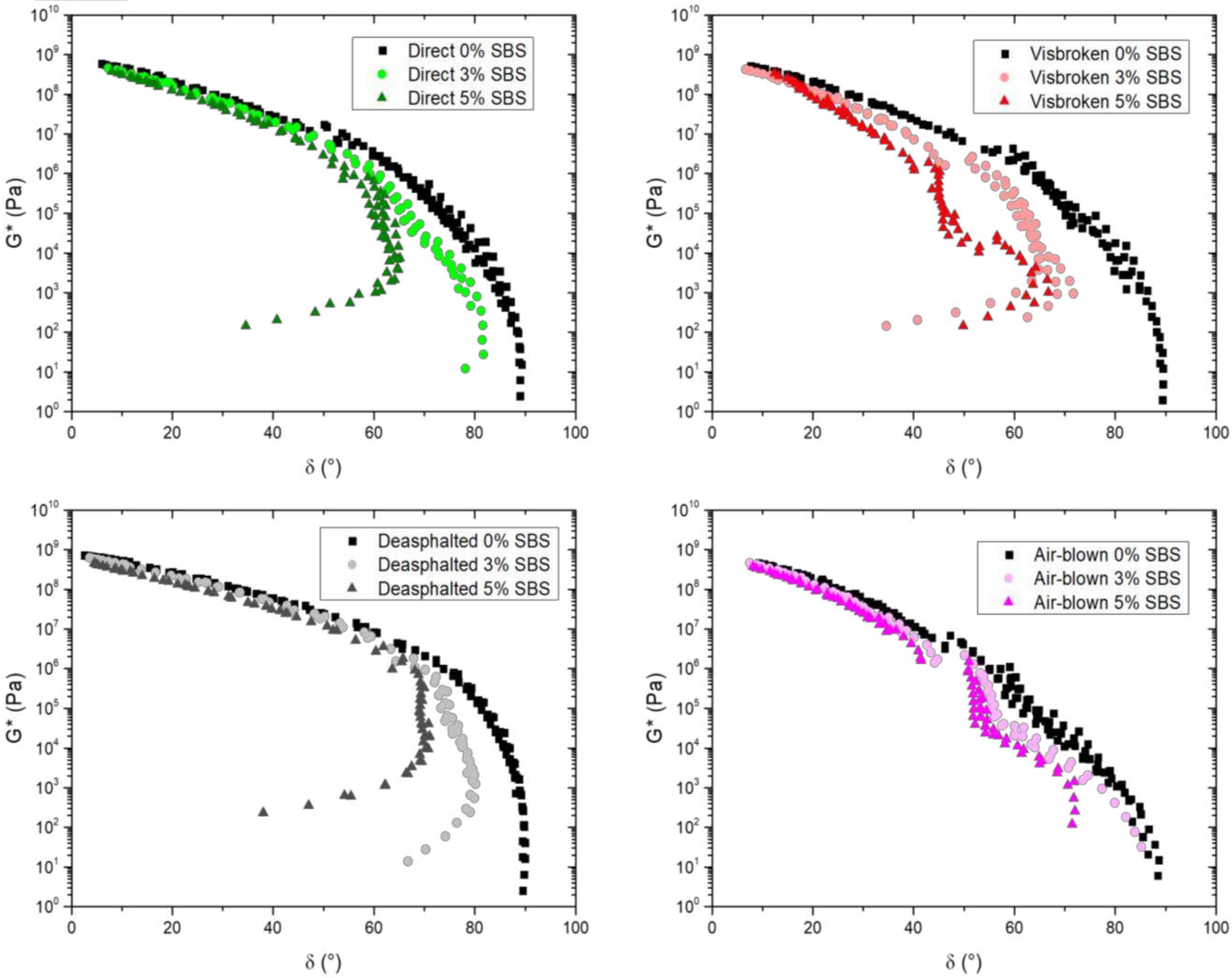

Figure 5. Black diagrams of the pure bitumens (0% SBS) and their respective 3% and 5% PmB.

5.4.3 Properties above 15 °C

5.4.3.1 Ring and ball temperature

The most practical way to evaluate the standardized performance over room temperature of a bitumen is the ring & ball (R&B) temperature. The evolution of the R&B temperatures of the base bitumen and their PmB are represented Figure 6. As all the base bitumens are the same 50/70 grade, they naturally have a rather close R&B value. Differences start to appear when SBS is added. Indeed, three kind of evolution of this parameter are found:

- In the case of the "visbroken" A significant increase of the R&B is observed with a low SBS concentration (70 °C for 2,5% SBS). It should be noted, however, that optimal performance is achieved for 4% of SBS as it seems to reach a plateau under the test conditions.
- In the cases of the "Direct" and "Deasphalted", significant enhancement of the R&B value only appears after a threshold. The value of this threshold seems to be lower for the "Direct" (around 3% SBS) than for the "Deasphalted" (around 4% SBS).
- In the case of the "Air-blown", the increase of the R&B is minor but steady. Also, as it is the case for the others, a notion of threshold seems to be applied (around 4 % SBS).

These differences could be related to the more or less ability of the polymer to swell with the lightest fractions of the bitumen (mostly aromatics). However, the impact of the source of the bitumen should also be taken into account to better understand those results.

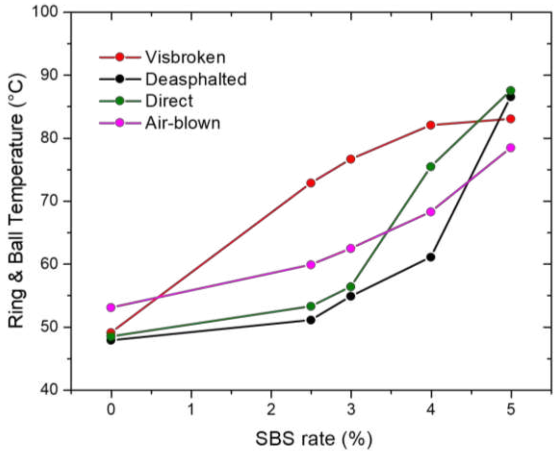

Figure 6. Ring and ball temperatures for pure and SBS-modified bitumens with SBS concentrations between 2,5% and 5 %.

5.4.3.2 Potential use of the yield stress to describe the bitumen rheological behavior

Frequency sweeps at temperature between 15 and 60 °C for the "deasphalted" and the "visbroken" pure bitumen are shown in Figure 7(a-b). For temperatures near 60 ° C, quasi-Newtonian behavior is observed over the frequency range studied. With decreasing temperature, a clear shear-thinning behavior appears. A slight increase of the complex viscosity is also noted for temperature below 30 °C A modeling of the rheological behaviors was tested using the Carreau-Yasuda (C-Y) model in order to fully fit those rheological responses. This model has been able fit faithfully all pure bitumens rheological behaviors.

In this study, a Carreau-Yasuda law with a yield stress has been used to fit the complex viscosity (η^*) over the shear rate range (ω) [16]. This law is defined as follow:

$$\eta^*(\varpi) = \frac{\sigma_0}{\varpi} + \eta_0 \, . [1 + (\lambda . \varpi)^a]^{\frac{m-1}{a}}$$

Where σ_0 (Pa) is the melt yield stress, η_0 (Pa.s) the zero shear rate or Newtonian viscosity, λ (s) a characteristic time, "m" power law or shear thinning index and "a" the Yasuda parameter. Note that "a" is set to 2 as in the Carreau's law in order to simplify calculations.

As it is shown Figure 7(c) the yield stress parameter (σ_0) appears for temperatures below 30°C and increases exponentially as the temperature drops. The "Visbroken" exhibits a higher value than the "Deasphalted". It is worth mentioning that σ_0 does not correspond to a yield stress as it is commonly defined. It can still be said that the bitumen has a "yield stress fluid-like" behavior under these test conditions.

One of the possible origins of this phenomenon could be the evolution of the colloidal structure with the temperature schematized in Figure 8. As it has been proposed in another work the resins fraction is can be found in a solid or a liquid state depending on the temperature [18]. Based on the asphaltenes and resins contents, two structures can be imagined during cooling. The first structure would be a more or less dispersed colloidal system of resin-asphaltene micelles embed in a viscoelastic fluid. The second, in the case of a sufficiently high amount of asphaltenes and resins, a compact structure caused by the growth of the micelle resin could be formed.

Interestingly, the C-Y model with a yield stress has been previously used for the quantification of state of exfoliation in polymer-clay nano-composites thanks to evaluation of the yield stress [19]. By the way, the bigger the networks of clay, the higher the yield stress was. If the same methodology is applied to the PmB it can be assumed that the increasing yield stress could somehow be linked to the state of structuration of the material. Indeed, both thermally treated bitumens ended up giving the highest σ_0 values. Due to their particular refinery processes and their opposite rheological behaviour, the "Desalphalted" and "Visbroken" bitumens σ0 evolutions are only presented in Figure 9-a.

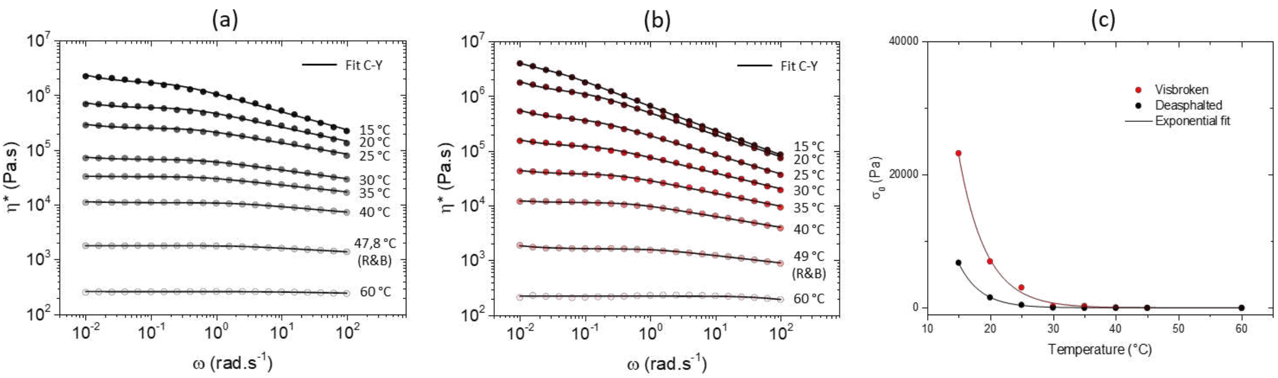

Figure 7. Frequency sweeps and their C-Y fit of the deasphalted (a) and visbroken (b) pure bitumens, and the resulting evolution of the yield stress over the temperature (c).

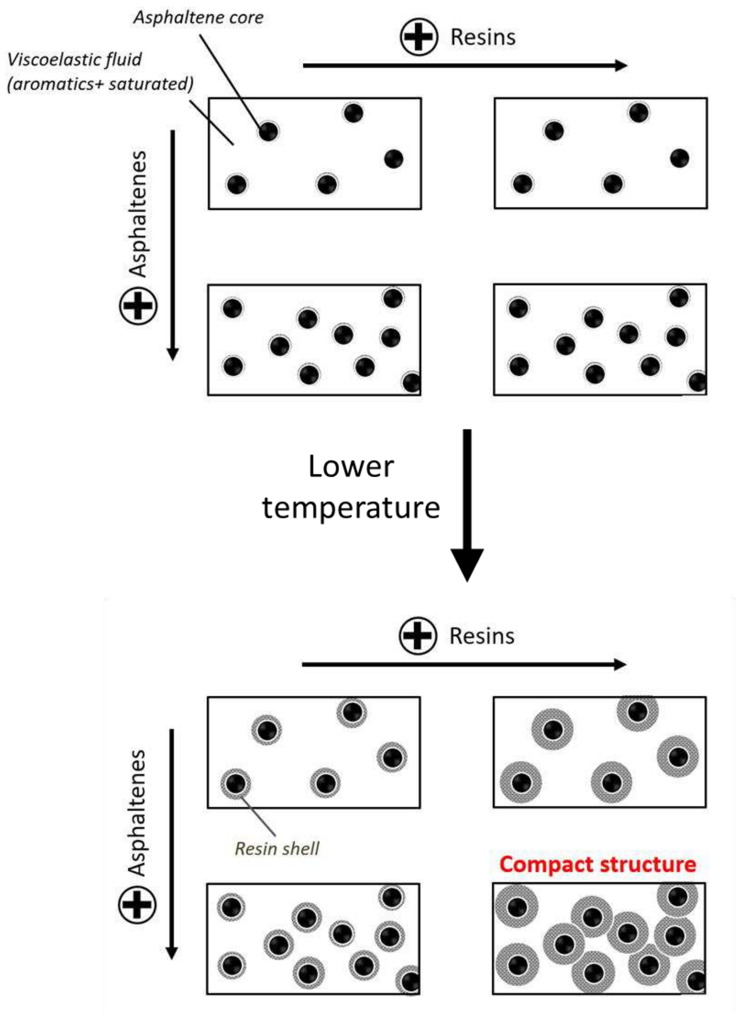

Figure 8. Evolution of the colloidal structure of the pure bitumen with decreasing temperatures.

The Figure 9 shows the evolution of the yield stress for all pure and modified bitumen with an SBS content of 3 and 5%. Regardless of the SBS content the highest and lowest value are observed for the "Air-blown" and "Deasphalted" respectively. The "Direct" and the "Visbroken are within the same range. However, with the current data it is not possible to attribute this phenomenon to a particular physico-chemical aspect.

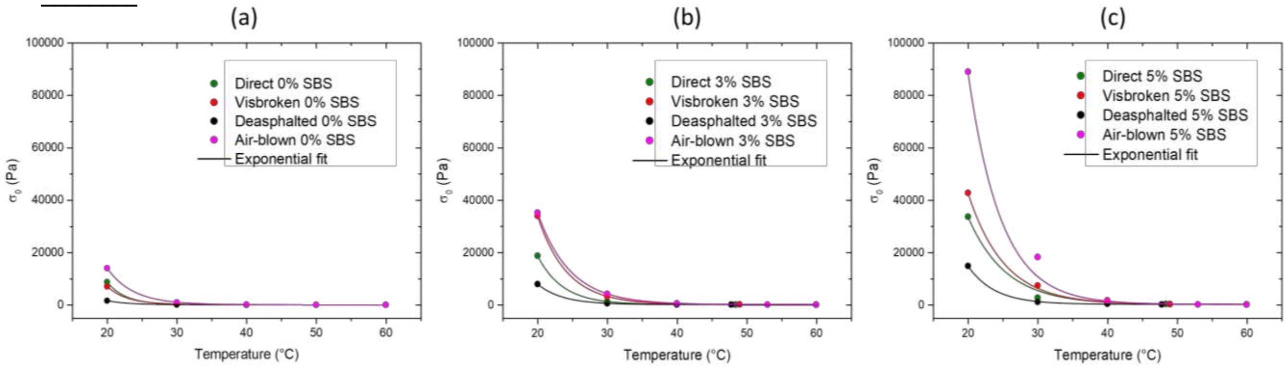

Figure 9. Evaluation of the C-Y model's yield stress pure bitumen (a) and PmB with SBS concentrations of 3% (b) and 5% (c).

5.5 Properties under 0 °C

In this study, the properties of the pure and modified bitumens at low temperature have been quantified with three parameters (Figure 10): the standardized FRAASS temperature, the α relaxation by DMA; the glass transition (Tg) by DSC. Different trends are found depending on the method of characterization.

The evolution of the FRAASS temperature as the SBS concentration increases confirm that the addition of SBS enhanced the viability of the binders at low temperature. However, this enhancement seems to be related to the the properties of the base bitumen and thus its refinery process. Indeed, with a higher SBS content, the "Visbroken" exhibits the best improvements, the "Air-blown" almost none, and the other two shows a consistent decrease of the FRAASS temperature.

The α relaxation is determined by the maximum value of E'' during the temperature sweep. Except for the "Deasphalted", the addition of SBS tends to decrease the α temperature implying better low temperature properties. It has not been found a concrete explanation for the "Deasphalted" particular behavior.

The Tg appears to be the less sensible test of the three as it shows little to no evolution in most cases with various SBS concentration in all cases except for the "Deasphalted".

In conclusion, the results between those techniques are consistent if the case of the "Deasphalted" is omitted. Regarding the impact of the refinery process, it seems that the visbreaking process offers the best improvement and the air-blowing should be avoided.

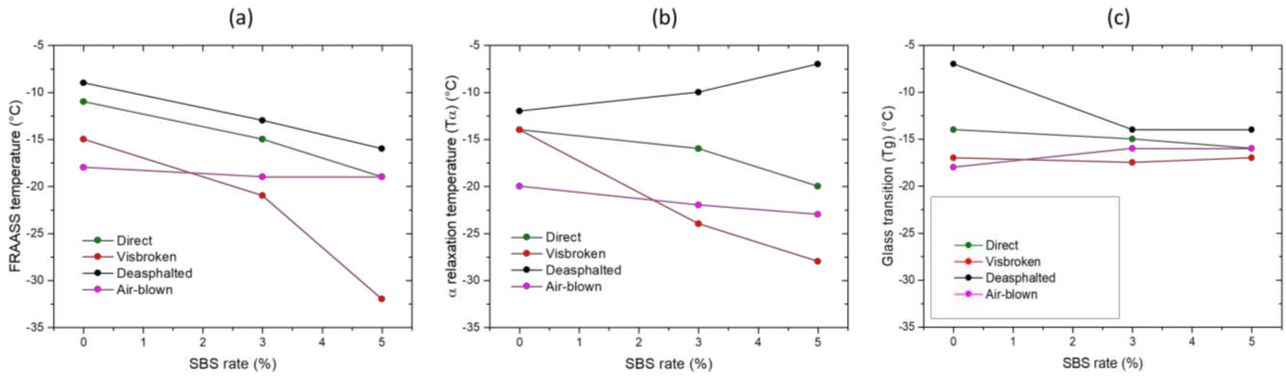

Figure 10. Evolution of the FRAASS temperature (a), α relaxation (b) and the glass transition (c) for pure and SBS-modified bitumens with SBS concentrations between 3% and 5 %.

6 CONCLUSIONS

Pure bitumens from four refining processes (direct distillation, propane deasphalting, visbreaking and air-blowing) were selected to manufacture Polymer Modified Bitumens (PmB) with SBS contents between 2.5 and 5%. These materials were then analyzed using various analytical techniques to assess their standardized properties used industrially as well as their thermorheological properties. For PmB, an additional morphological analysis was also conducted.

The global rheological behavior is obtained through the drawing of master curves over a wide range of frequencies / temperatures. The rheological behavior of pure bitumens is characteristic of a low molecular weight fluid with a unique transition between vitrous domain and viscous flow (similar to the behaviour ot a Newtonian fluid at high temperature). The rheological behavior of the PmB differs from pure bitumens by the more or less marked appearance of a pseudoplastic plateau attributed to the presence of the polymer-rich phase. This phenomenon is also found on the diagrams of Black in the form of a drop in the phase angle (δ) around 10^6 Pa.

Concerning the rheological behavior in the molten state (for temperatures between 15 and 60 ° C), it has been shown that it can be fitted by a Carreau-Yasuda (C-Y) model with a yield stress. This model has made it possible, in particular, thanks to the yield stress parameter (σ_0) to highlight the more or less "structured" nature (in terms of colloidal structure) of the binders. It is interesting to note within the perimeter of this study, trends observed for pure binders are kept for modified binders.

Regarding properties at low temperatures. It has been shown that the evaluation of these properties is very susceptible to the characterization technique although the general trends are the same. Indeed, propane rectification seems to induce higher average temperatures (leading to a weaker material at low temperature) and air-blowing seems to inhibit the improvement of low temperatures properties. The best performances are obtained for the visbroken. Finally, the direct distillation presents intermediate results.

In summary, the impact of the process on the industrial properties of pure bitumens is obvious and some parameters (such as σ_0 or FRAASS temperature) make it possible to discriminate relatively easily bitumen which has undergone additional treatment (air-blowing and propane rectification). In addition, the PmB show developments coherent with the origin of their pure base bitumen. As a result, once the refining process has been identified, it might be then possible to predict to some extent the performance of the PmB.

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