Asphalt mixture performance and testing

Advantages of polymer additives ready to be used at the asphalt mixing plant

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Abstract

In many countries, the major sources of flexible pavement distress are still cracking and rutting. The latter, caused by the repeated application of traffic loads, may become an even more widespread phenomenon as significant global warming is apparently already taking place now. Cracking can have several origins, mechanical (traffic), thermal and solar radiation. A number of polymer brands are used in Polymer Modified Bitumen to mitigate these issues. For the same purpose, it is also possible to use polymer compounds such as PR FLEX 20® which has been formulated to allow a direct introduction into the drum or pug mill of the mixing plant. This approach known as the “dry process” brings a number of advantages when compared with the more classical PMB approach. The paper shows how quickly the ready-to-use compounds are dispersed in the base bitumen. It also describes the improvement of the binder properties (mainly softening point, elastic recovery and dynamic shear rheometry properties) obtained when polymers and ready-to-use additives are used. Fluorescent microscopy was useful for the interpretation of the measured properties. The paper also shows the influence of the bitumen nature on the binder properties.

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1. INTRODUCTION TO THE "WET" AND "DRY" PROCESSES

When a road has to undergo heavy traffic, the solution provided by a Polymer Modified Bitumen (PMB) is often favoured in the countries where these products are available. The interest of this type of binder, whether based on elastomer or plastomer, is well established. In general, there is a dense network of binder plants and the PMB will not have to be transported long distances before reaching its destination, the asphalt mixing plant.

In some circumstances, however, another approach may be appropriate, that of additivation at the mixing plant [1]. In this case, a granule based on polymer(s) is introduced during the mixing phase. This is known as the "dry process", as opposed to the "wet process" represented by the PMB technology (see Figure 1). The granulated product, also called "compound" consists of several ingredients each having an active role. The finished product is a Polymer Modified Asphalt concrete (PMA). We will detail below the conditions that must be met for this process to work properly.

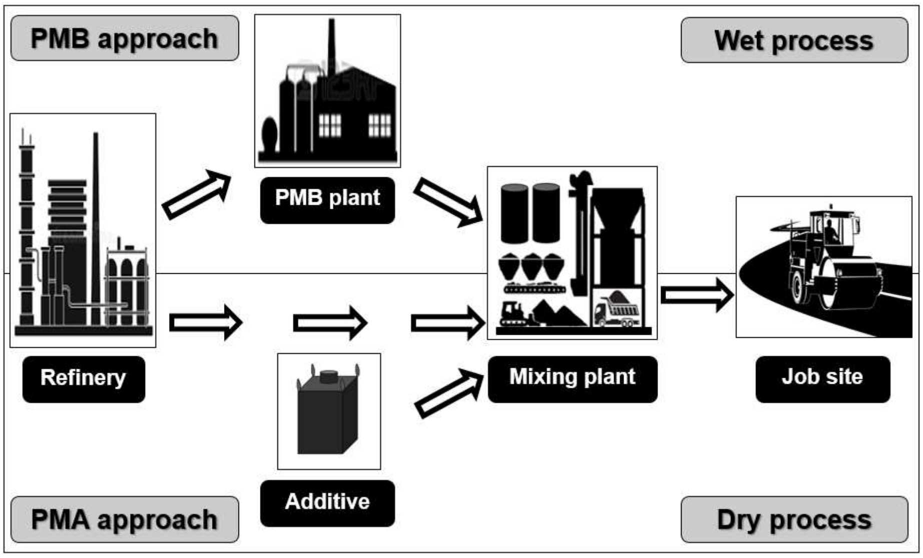


Figure 1: Presentation of the "Dry" and "Wet" processes

The dry process is generally justified in four particular cases.
The first one is when PMB technology is not yet well established in the region of the project. This is the case in areas with low population density where the presence of PMB plants is economically meaningless or in developing countries where the density of binder plants is still low.

The second case where the dry process will work perfectly, is for large projects requiring high production rates that can't usually be followed by mobile binder plants. The granulated polymer can, in turn, be delivered in part or in full before the start of the project. The logistical constraints are thus much less complicated than those related to the PMB, which always requires a very precise delivery time.

The third case where the dry approach is of interest is the opposite situation, that of small productions. If the production schedule indicates a small isolated production of a few hundred tons of modified mixture, it is necessary either to bring a compartmentalized bitumen carrier or to order a complete carrier and quickly find another site for the remainder of PMB. The reader will understand that the "dry process" brings a level of flexibility which justifies its use. Any unused big bag of additive can be stored in a cool and dry place for many months without altering the quality of the product. The material is almost insensitive to moisture, frost and heat. It is rather the packaging (bag or big bag) that may suffer from long exposure to weather and sunlight.

The last case where the "dry process" will be used occurs whenever the pure bitumen or PMB does not reach the properties required by the specifications. For special or niche markets, particularly high properties such as resistance to indentation under static loads, hydrocarbon resistance or high modulus must be achieved. It is also possible to reinforce a locally available PMB by adding polymeric compounds.

2. MATERIALS AND METHODS

2.1. Materials

Six different bitumen grades were investigated. They are all 50/70 grades with very similar penetration values (Table 1). They were obtained from Western and Easter Europe, from North and South Africa, from Latin America and Eastern Asia.

Table 1: Properties of the base bitumen grades

Binder	Bitumen A	Bitumen B	Bitumen C	Bitumen D	Bitumen E	Bitumen F
Penetration	68	67	64	64	66	65
Softening pt.	47.7	46.6	46.4	48.6	49.4	49.0

Many different polymers were analysed. Two of them were studied in depth:
- the SBS polymer mentioned in Sections 4 and 6 is a linear Styrene Butadiene Styrene block copolymer in the form of pellets characterised by a molecular weight of 180000 Dalton and a styrene content of 31%.
- the PR FLEX 20®, an optimised compound containing SBS, bitumen and other additives. It is a kind of extremely concentrated SBS modified bitumen, in the form of solid pellets. It makes it possible to reach high performance mixes (cracking, rutting, fatigue, etc).

With the two products mentioned above, physical blends were produced, i.e. without crosslinking agent. SBS chemical blends aren't considered in this paper.

2.2. Methods

As written previously, this paper focusses only on the binder properties as the performance of Polymer Modified Asphalt Concrete has been reported already [2, 3, 4].

Mixers
For the dispersion of the different polymers (including the PR FLEX 20® compound) in the bitumen, a High Shear Mixer L5M-A from SILVERSON was used. The initial rotational speed was set at 3000 RPM and the temperature at 180°C. After 30 min, the speed was reduced to 1000 RPM and the temperature lowered at 165°C. When not mentioned otherwise, the total mixing time was 90 min. In any case, agitation was stopped after 120 min.

Classical binder tests
The main properties used in this study are part of the EN 14023 standard [5] for polymer modified bitumen:
EN 1426 – Determination of needle penetration; result in tenth of mm.
EN 1427 – Determination of the softening point – Ring and ball method; result in degree Celsius.
EN 13498 – Determination of elastic recovery of modified bitumen; temperature at 25°C; result in %.

Dynamic Stress Rheometry
Rheological behaviour of the binders was characterised using a Dynamic Stress Rheometer (DSR). The equipment used was a Modular Advanced Rheometer System (MARS) from Thermo-Scientific equipped with a HAAKE RheoWin software. All measurements were performed in the oscillatory imposed stress mode with the 25 mm parallel plate configuration. All data points corresponding to a strain exceeding 50% were discarded to guarantee a measurement in the Linear Viscoelastic (LVE) domain. A few grams of binder were poured in silicon moulds. The day after sample preparation, the binder sample was positioned on the centre of the lower plate. After heating the sample to 90°C, the upper plate was lowered. The sample was trimmed and the final gap was adjusted to 1 mm. The frequency sweeps from 100 to 1 rad/s were performed at different temperatures ranging from 60 to 88°C. The data obtained at 10 rad/s made it possible to calculate the temperature at which $G^*/\sin(\delta)$ reaches the value of 1000 Pa. This temperature expressed in degrees Celsius is denoted PG OB below. G^* is the complex shear modulus and δ is the phase angle.
Fluorescence microscopy
Fluorescence microscopy was used to study the morphology of PMB samples. Very small amounts of hot binder were dropped on glass slides. Once cooled to room temperature, the glass side was illuminated by a blue light (wavelength of 470 nm). The fluorescent yellow light re-emitted by the polymer phase was captured by a LEICA DFC7000T cooled fluorescence colour camera. The magnification of the microscope was a factor 10.

3. COMPATIBILITY BITUMEN / SBS

A PMB formulator is often faced with the question of how much SBS needs to be added to a base bitumen to achieve a certain level of performance. It has been shown [6] that the rate of addition strongly depends on the SBS / bitumen pair. In the presence of a bitumen of unknown nature, the formulator will have no alternative but to perform laboratory tests.

To illustrate how much this effect is important, five 60/70 bitumen grades (rated A, B, C, D and E) but of different origins were selected. The SBS described above was tested at 4 different levels (0, 3, 4.25 and 5.5%). At first, we are interested in the value of the Softening Point of the different blends obtained.

The following trends are observed (Figure 2):
- Bitumen A: gradual but very small increase in Softening Point.
- Bitumen B and E: progressive and significant increase of the Softening Point.
- Bitumen C and D: significant but non progressive increase of the Softening Point.

While Bitumen B, C and D gain 23 to 24 ° C of SP with a 5.5% addition of SBS, Bitumen A only gains 6 ° C under the same conditions.

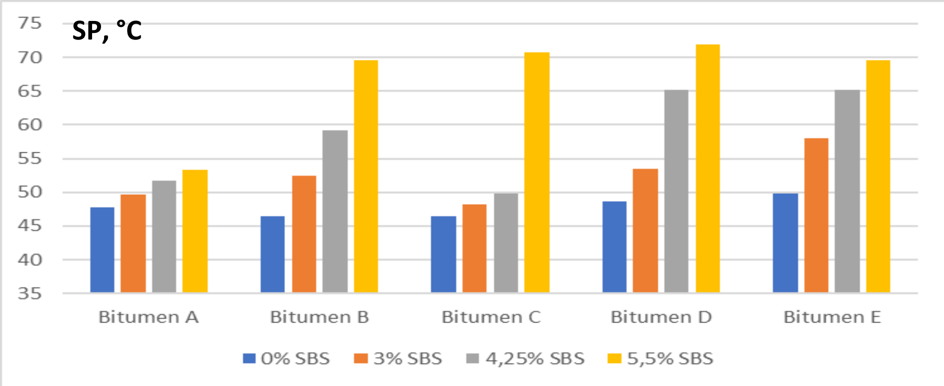


Figure 2: Evolution of the Softening Point with different base bitumen and different SBS loadings

The evolution of Elastic Recovery (Figure 3) follows fairly well the evolution of the Softening Point. Bitumen A is again distinguished by a particularly slow rise in the level of performance. At 5.5% of SBS, the Elastic Recovery does not reach 60% whereas the other 4 feeds give values exceeding 90%.

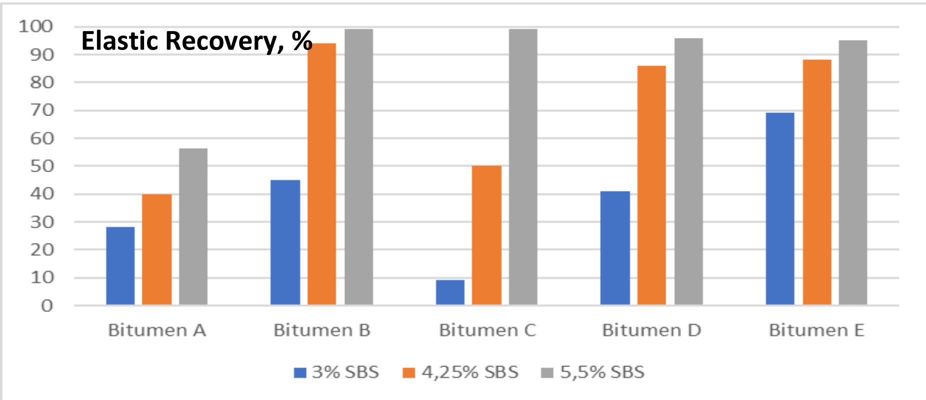


Figure 3: Evolution of the Elastic Recovery with different base bitumen and different SBS loadings

Fluorescent microscopy images from the different blends were taken. In general, one observes (Figure 4 on the left) a fine distribution of SBS droplets (Elastomer Rich Phase) in a darker medium (Asphaltene Rich Phase). In the SBS / Bitumen A blends, an apparently continuous medium can be seen (Figure 4 on the right).

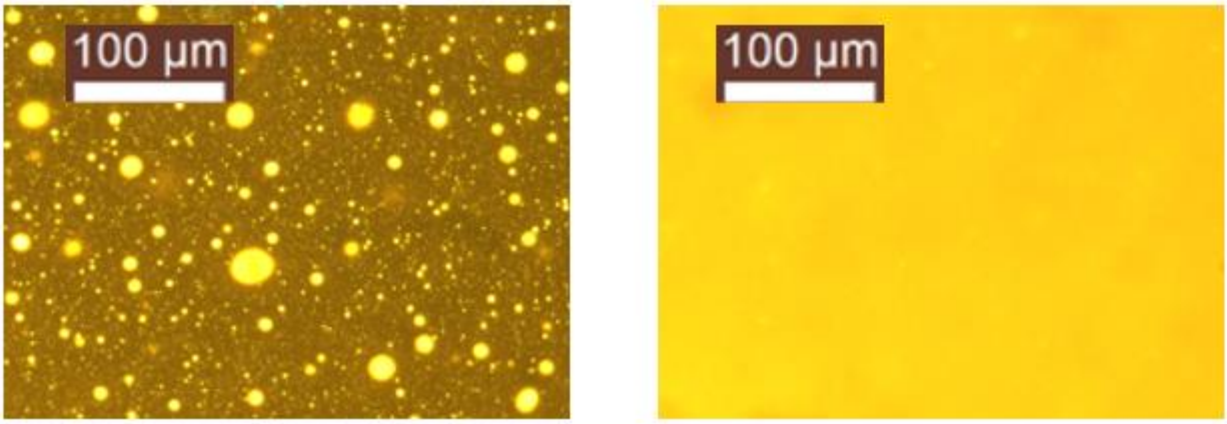


Figure 4: Blends with 4,25% SBS with Bitumen B (left) and Bitumen A (right)

To better understand the strange behaviour of Bitumen A, SARA analyses were performed (Table 2). SARA is an analysis method that divides bitumen components according to their polarizability and polarity. The Gaestel Colloidal Index, I_c was developed [7] to indicate the colloidal stability of bitumen:

Gaestel colloidal stability index = (saturates + asphaltenes) / (resins + aromatic oils)

Table 2: SARA characterisation of Bitumen A

Sample	Saturates %	Aromatics %	Resins %	Asphaltenes %	Gaestel Colloidal index, I_c
Bitumen A	5.0	69	18.3	7.8	0.14

SBS and asphaltenes compete to absorb the light oily components of the bitumen. Bitumen with high aromatics content can be helpful in producing a compatible and stable SBS modified bitumen. Too high aromatics content, however, may lead to the swelling and anti-plasticization of some PS blocks, which is not good for the resulting properties of the SBS modified bitumen [8]. The SBS modified binder still forms a homogenous medium as shown in Figure 4 (on the right) but loses elastic properties as illustrated in Figure 5. The Gaestel index of Bitumen A is equal to 0.14 which doesn't belong the typical I_c range for paving grades (say from 0,20 to 0,70). Bitumen A significantly differs in its chemical composition and seems too compatible to make a good feed for SBS modification.

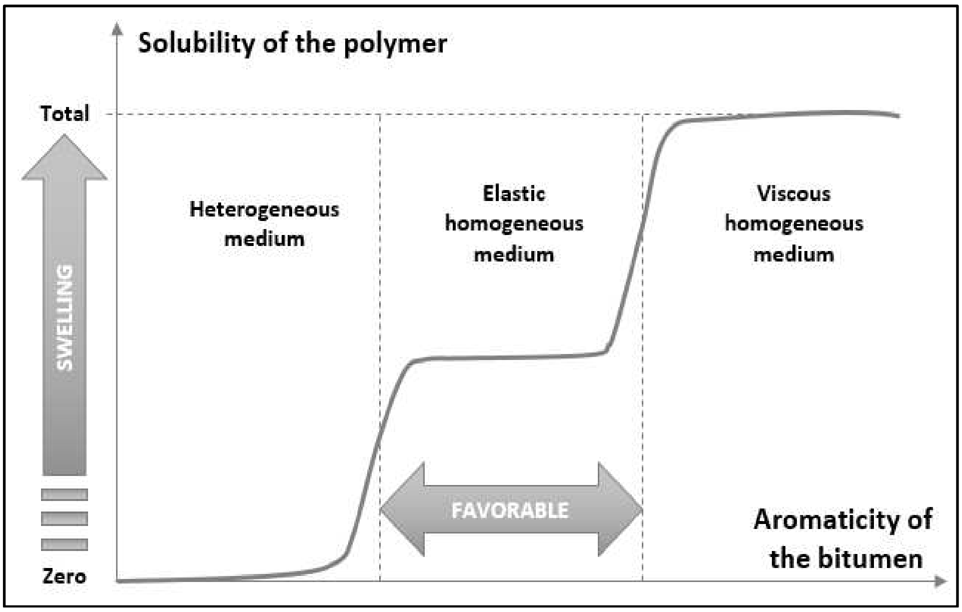


Figure 5: SBS / bitumen compatibility window [8]

4. OPTIMISATION OF THE BINDER PROPERTIES WITH PR FLEX 20®

In the previous paragraph, we have seen how much the SBS can be influenced by the nature of the bitumen. It may be interesting from an operational point of view to get away from the detrimental effects of the composition of some exotic bitumen. The ideal situation is to have an additive that minimizes the fluctuations that can be observed from one bitumen to another. If this is not achieved then it may be necessary to optimize the composition of the compound to the particular nature of the base bitumen.

This idea was the subject of a study where variants of PR FLEX 20® were tested with the same base bitumen. These variants of PR FLEX 20® are designed to be used according to the Dry Process. They still mainly contain SBS, some bitumen to compatibilise the elastomer and possibly some other additives. In this exercise, other polymeric ingredients and waxes were added or not. Different kinds of SBS (linear / radial, different proportions of Styrene and Butadiene, etc) were also tested. Bitumen C was selected because the Softening Point gain is low for SBS loadings less than 5%.

To facilitate the graphical representation, only the properties of Softening Point and Elastic Recovery are presented here. On the graphs, the minimum values to reach certain sets of specifications often used in Europe (Table3) have been represented:

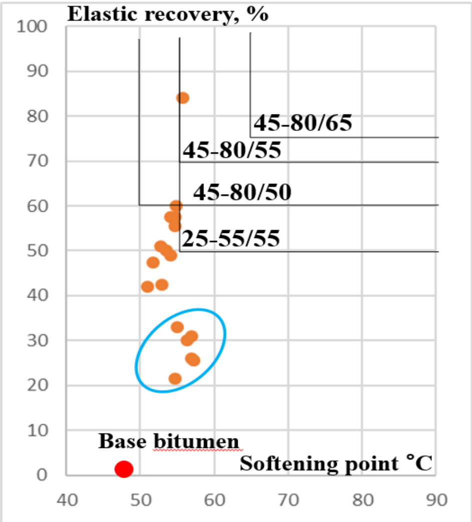
Table 3: Example of specification sets used for PMB (non exhaustive list)

Specification set	Penetration	Softening point	Elastic recovery
25-55/55	25 – 55	≥ 55	≥ 50
45-80/50	45 – 80	≥ 50	≥ 60
45-80/55	45 – 60	≥ 55	≥ 70
45-80/65	45 – 80	≥ 65	≥ 75

Blends containing 7.5% compound (Figure 6 on the right) cover a large area of the diagram. Many formulations seem promising for reaching the most demanding specification sets.

Blends containing 5.0% compound (Figure 6 on the left) cover a much smaller space. No formulation prepared with this bituminous bitumen does reach class 45-80/65. That said, not all formulations are equal: the points surrounded by the ellipse generally correspond to formulations containing waxes. These tend to improve the properties of Softening Point but often have a dramatic effect on the value of Elastic Recovery.

Other properties have also been measured but, for the sake of brevity, they won't be detailed in this paper. This study helped to improve the composition of PR FLEX 20®. The advantage of working with a compound is that the formulator has great freedom over choice of ingredients. Each of these must bring a desired property or, by synergy, must enhance the effect of another already present.



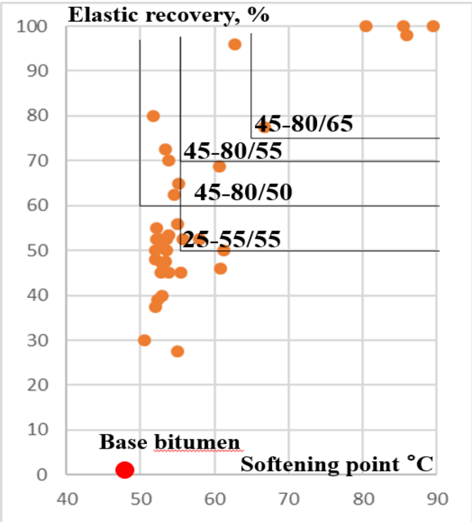


Figure 6: PR FLEX 20® formula optimisation
Blends prepared with 5.0% (left) and 7.5% (right) of compound in bitumen C

It seemed useful to refer to the same graph (Figure 7) the values of Softening Point and PG OB determined on all blends (all bitumen combined and different kinds of polymers) for which these two values have been measured. Note that the property called PG OB only takes into account the value obtained on the Original Binder.

It is found that the two properties are weakly correlated, in particular for the strong modifications (SP in excess of 60 °C). A high SP value obtained with the modified binders is an indication of increased resistance to permanent deformation. This is the reason why the SP is consistently part of the specification sets in Europe. However, it has already been shown [10] that very high values of the SP tend to overestimate the benefits of the modification.

From Figure 7, it is deduced that deviations of the order of 20°C between PG OB and SP are common at low modification. However, as the percentage of modifier increases, this gap tends to decrease and becomes negative in some cases (all points under the solid black parity curve).

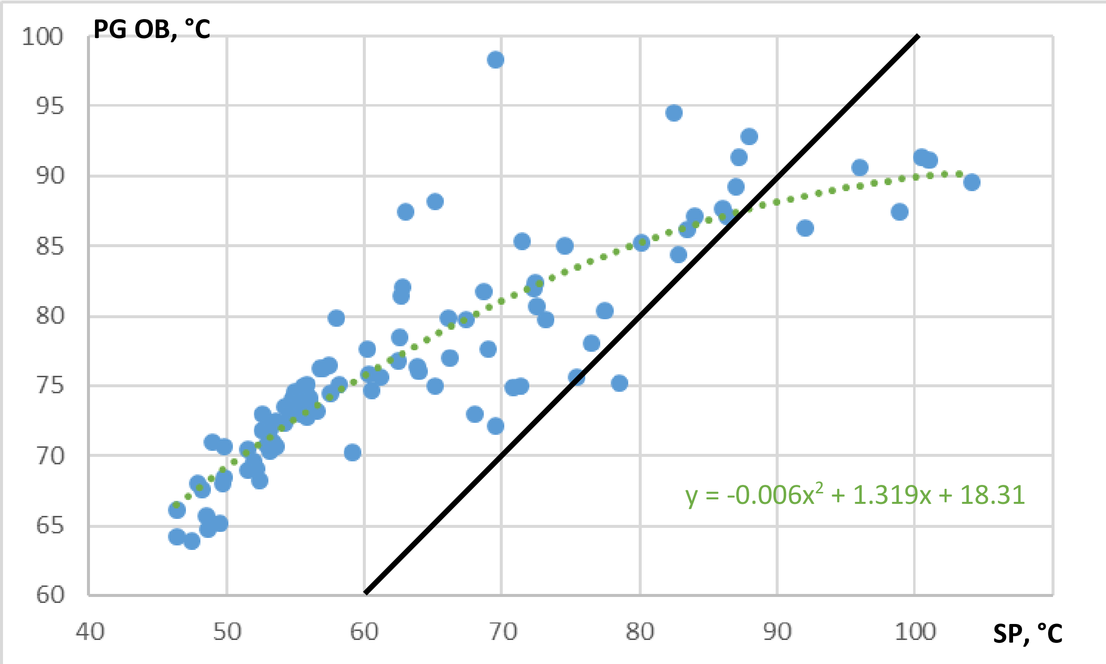


Figure 7: PG OB versus Softening Point for different modified binders.

5. EFFECT OF MIXING TIME

In the introduction, it has been explained that elastomeric polymers can be used via the "wet" or "dry" method. Beyond the differences in the industrial process, PMBs and ready-to-use additives can both be compared in the laboratory: the interest of their use can be demonstrated in tests on asphalt mixtures, in particular those described in the series of EN 12697 norms. But ready-to-use additives can also be assessed in the framework of the EN 14023 standard for Polymer Modified Bitumen if one condition is fulfilled: it must be proven that the elastomeric compound is quickly dispersed in the bitumen as the mixing time in the industrial "dry" process is short. It should be noted that, in the industrial process (both wet and dry), there are, between the mixing step and the compaction step, a long storage and transportation time during which the modified binder is still hot and allowed to mature.

The extent of the maturation process was investigated by applying different mixing times during the preparation of SBS or PR FLEX 20® modified bitumen samples in the laboratory. The quality of the dispersion was assessed in different ways: visual observation, fluorescence microscopy or indirectly by checking the performance of the blends.

In the literature, there are a multitude of protocols for preparing a PMB. Generally, the preparation is in two parts: a step with a high shear rate (typically 30 to 60 min) followed by a step with a low shear rate of longer duration (1 to 4 hours, or even a night). Voluntarily, it was decided to take samples at very short mixing times (8, 15, 30, 60 min, 2 and 10 h).

Two mixtures were compared:
- 95.75% Bitumen C and 4.25% of the SBS described above
- 94.50% of Bitumen C and 5.50% of PR FLEX 20®.
The blend ratios were selected to get approximately the same polymer content in each blend.

The first blend appears lumpy after 8 minutes of mixing. The sample breaks prematurely at the stretching stage of the Elastic Recovery test. Finally, an unusual response was measured in the DSR (Figure 8 left) suggesting that clusters of non-dispersed SBS come into contact with the walls of the parallel plate geometry. As expected, the dispersion of the SBS is not complete at this stage.

After 30 minutes of mixing, the dispersion of the first mixture seems more homogeneous. The results of the DSR and Elastic Recovery are more consistent (Figure 8 left).

By increasing the mixing time from 1 hour to 10 hours, the Softening Point and Elastic Recovery properties improve. The sample had time to mature. In this stage, the polymer can absorb the oily aromatic fractions of the bitumen and occupy a larger volume in the binder. By this swelling mechanism (swelling of more than 500% is possible for elastomers), the Elastomer Rich Phase (ERP) can occupy a large space even at relatively low polymer loadings [11].

The second blend appears smooth and homogeneous from the beginning of the experiment. Photos of Fluorescent Microscopy are shown in Figure 9 and show relatively little evolution at the different maturation times. The sample taken after 8 minutes of mixing does not present any particular weakness. On the contrary, it seems to give, from the beginning, excellent properties (see Figure 8 right).

Between 1 and 2 hours, there is a slight decrease in properties associated with a post-maturation stage. We are talking here about post-maturation because during the manufacturing process of PR FLEX 20® in the extruder, the SBS is mixed under high shear and high pressure with a special bitumen. This "pre-digestion" step allows to reach the required property level more quickly (Figure 8 right).

Beyond the "pre-digestion" stage, other aspects increase the efficiency of the dispersion process such as the type of polymer, the polymer particle size, the temperature of the process, the dispersion system, … During the PR FLEX 20® design stage, these considerations were of course kept in mind.

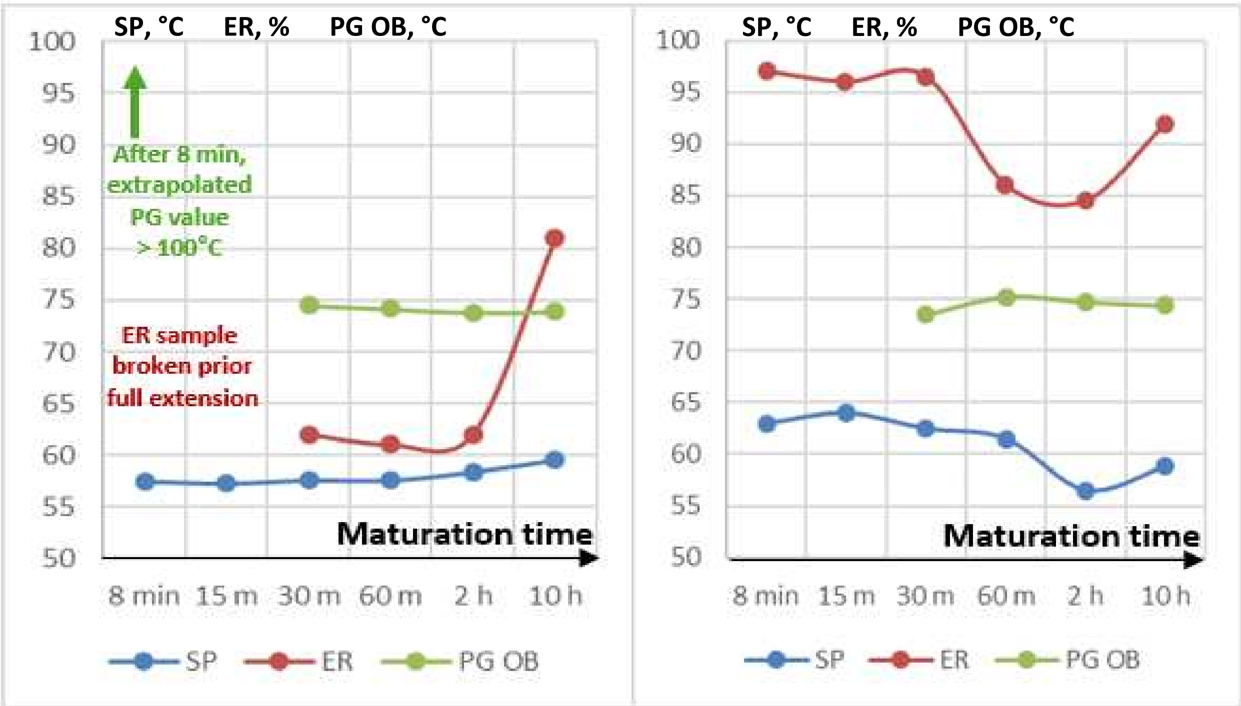


Figure 8: Properties of Bitumen C
with 4.25% of SBS (left) and 5.5% of PR FLEX 20® (right)

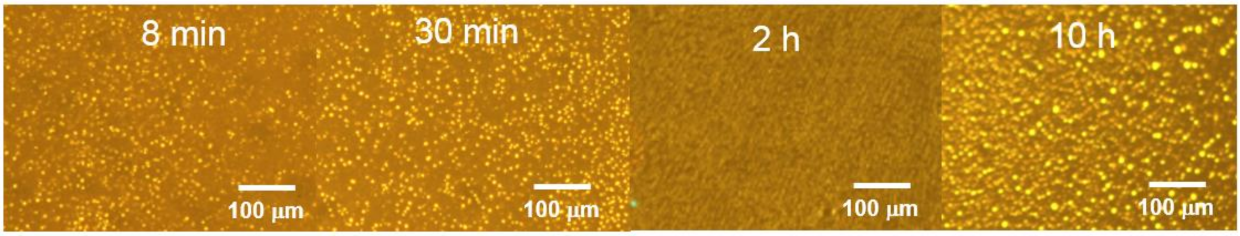


Figure 9: Fluorescent Microscopy pictures of blends of Bitumen C with PR FLEX 20®.

The Dynamic Shear Rheometer was used to generate Black diagrams. The measurements were made at different temperatures (from 60 to 88 ° C) and different frequencies (from 100 to 1 rad/s). In a Black diagram, the shear modulus G * is displayed as a function of the phase angle δ. This space provides a fingerprint of the binder behaviour. Indeed, all data points corresponding to all frequencies and temperatures are represented. If the binder exhibits thermo-rheologically simple behaviour, all data points fall on a single curve. It is generally the case for SBS modified binders [6, 12]. The curves displayed on Figure 10 and 11 follow the same rule.

However, it appears that, after 8 minutes of mixing, the Black curve shown in Figure 10 is nothing like those obtained at higher maturation times. This is not the case of the curves shown in Figure 11.

In the light of this study, it appears that SBS granules require a certain mixing time to achieve an acceptable and stable performance. For this reason, it does not seem desirable to add them as such directly into the pug mill of the mixing plant. In the field, this practice seems to be little or not applied at all.

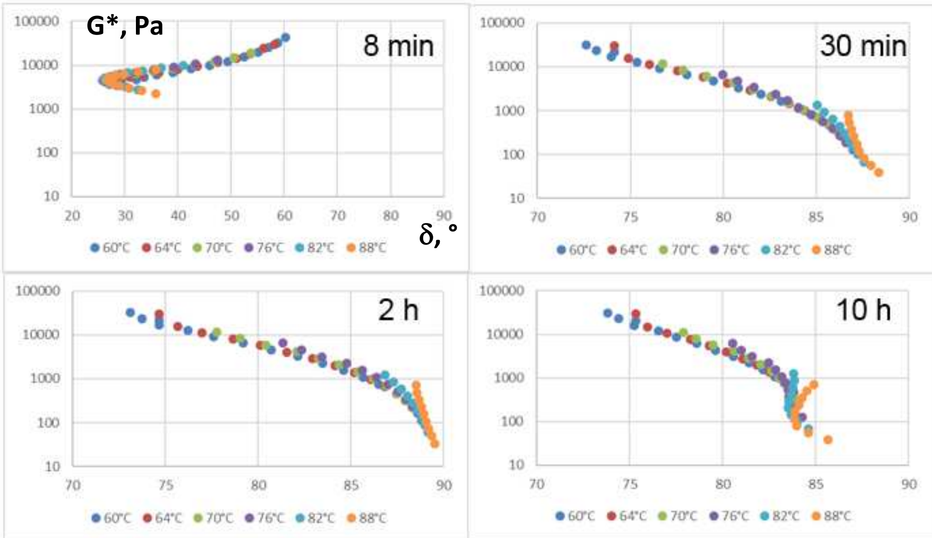


Figure 10: Black plot of a blend of Bitumen C with 4.25% of SBS after different maturation times.

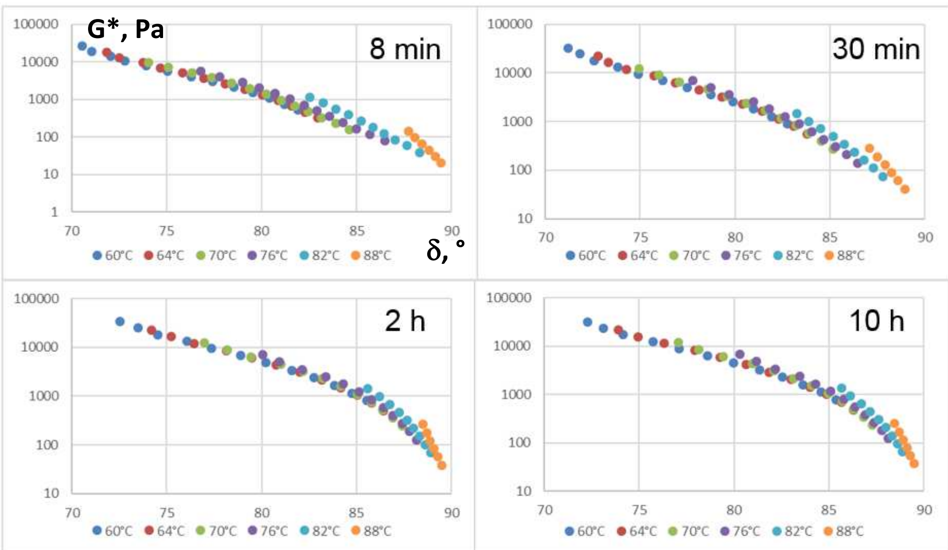


Fig. 11: Black plot of a blend of Bitumen C with 5.5% of PR FLEX20® after different maturation times.

6. EFFECT OF PHASE INVERSION

Fluorescence microscopy is the most frequently used technique for studying the morphology of PMBs. It is a useful and well validated approach to determine the quality and nature of the dispersion of the polymer within the modified binder [6].

Various mixtures with Bitumen F and PR FLEX 20® were made using the High Shear Mixer. Temperature sweeps were performed at different temperatures (60, 64, 70, 76, 82 and 88°C) and 10 rad/s using the DSR. Fluorescent microscopy images were also obtained for each blend at room temperature.

The addition of PR FLEX 20® shifts the curves upwards and especially to the left of Figure 12. It is well known [6] that the phase angle is more sensitive to the modification of a binder than G*. However, in the current example, there is sudden jump to lower phase angle values when the loading of PR FLEX 20® is increased from 7 to 9%. The fluorescent microscopy images help understand the phenomenon: at a concentration of 9% of PR FLEX 20®, phase inversion has taken place, which gives the binder a more elastic character than at lower concentrations of the additive. Indeed, at 5 and 7% of PR FLEX 20®, Figure 12 shows a continuous asphaltene-rich phase (ARP) with a dispersed elastomer-rich phase (ERP), while the image at 9% of PR FLEX 20® shows the opposite.

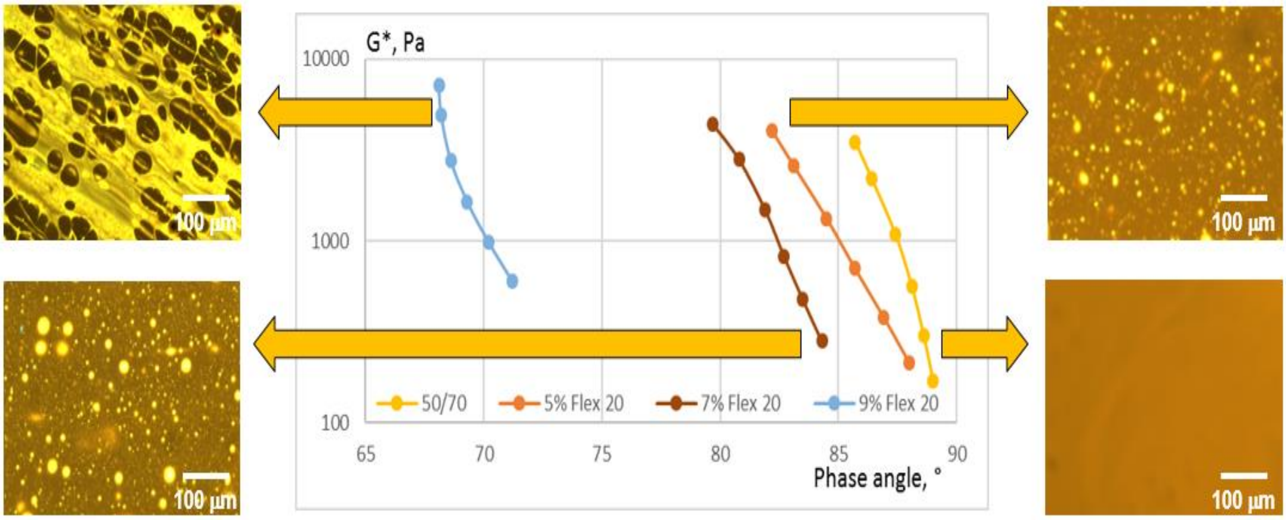


Figure 12: Black plot and Fluorescent Microscopy pictures of blends of Bitumen F with PR FLEX 20®.

7. CONCLUSIONS

Conventional testing (penetration, softening point, elastic recovery), fundamental rheological testing, chemical analysis (SARA) and fluorescent imaging have been used in this study to assess the change in properties associated with polymer modification. The addition of SBS has the effect of stiffening the binder and giving it a more elastic character, which are known to reduce the risk of rutting. However, the chemical composition of the base bitumen has a huge influence on the evolution of PMB performance. A base bitumen characterized by extreme aromatic fraction values is not a good choice for SBS modification. A non-uniform evolution of the properties (in particular of the phase angle) as a function of the SBS addition rate may be the sign of a phase inversion (bitumen in polymer matrix instead of polymer in a bitumen matrix).

Due to its particular composition and pre-digestion during the granule production step, PR FLEX 20® is particularly soluble in bitumen. Unlike most polymers that are not treated in this way, PR FLEX 20® is ready for use for direct introduction into the mixers of asphalt mixing plants. This high-quality product offers new perspectives for engineers responsible for building roads with severe traffic or weather conditions.

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