An evaluation of aging of polymer-modified asphalts

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ABSTRACT

Due to budget constraints in Europe, sustainability of pavement materials is taking an increasing part in the construction and maintenance policy of road networks. The aging properties of bituminous binders are known to have a direct impact on the durability of road pavement and must be properly assessed.

The measurement of in-situ bituminous binder and asphalt mix performances is the most reliable way to appreciate and measure the consequence of aging and oxidation on materials. However, accelerated test methods provide a cost-efficient, predictive assessment of the aging behavior, provided that these methods are representative of the aging phenomenon in the field. The present study is focused on the low-temperature and the aging properties of various bituminous binders in relation to the corresponding properties of asphalt mixes. In a first publication, investigations were devoted to different binder’s characterization method (Fraass, BBR, ABCD) as potential predictive tool to thermal cracking of asphalt mixtures (TSRST). This paper focuses on analyzing the sensitivity of these test methods to the degree of aging of different binders (paving bitumen, crosslinked elastomer-modified binder and physical blend elastomer-modified binder) and asphalt mixes. Based on original investigations, noticeable trends are pointed out aging impact on binders and both methods.

Keywords: Ageing, Low-Temperature, Modified Binders, Polymers, Rheology
INTRODUCTION

Durability is a key issue and drives the research and innovation in the road industry. The budget crisis in Europe and Northern America has even more increased the need for sustainable, cost efficient, durable materials for long-lasting pavements. Amongst the technical indicators for durability, the aging of the bituminous binder is critical and must be properly assessed [1, 2]. Existing laboratory tests provide a fair approximation of the aging sensitivity of the bituminous binders, but their representativeness of the real aging in the asphalt mixture, and further in the pavement is questionable. The present study is focused on the low-temperature and the aging properties of various bituminous binders in relation to the corresponding properties of asphalt mixes. In a previous publication, investigations were devoted to different binder’s characterization method (Fraass, BBR, ABCD) as potential predictive tool to thermal cracking of asphalt mixtures (TSRST).

1- MATERIALS AND TEST METHODS PLAN

1.1 Binders and asphalt mixtures test methods

Test methods performed on asphalt binders and mixtures are the same as the ones performed in our previous article [3]: Thermal cracking of asphalt binders are performed through Thermal Stress Restrained Specimen Test (TSRST) [4]. In comparison, low temperature sensitiveness of binders is evaluated with Fraass breaking point [5], bending beam rheometer (BBR [6]) and the new Asphalt Binder Cracking Device (ABCD [7]) test method; details are reported on previous work [3, 23]. All binders/asphalt mixtures are reported on following Table 3.

1.2 Materials description

1.2.1 Asphalt mix

To minimize possible bias due to coating and compacting problems and to ensure a good homogeneity in the quality of the asphalt mixes prepared from the different bituminous binders, a continuously graded wearing course formulation, with a maximum aggregate size of 10 mm (AC 10 surf) and complying with NF EN 13108-1 [8] has been selected. Compositional data are given in Table 1.

Table 1: Asphalt Formulation

<table>
<thead>
<tr>
<th>AC 10 surf</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/10 Quartzite</td>
<td>33</td>
</tr>
<tr>
<td>4/6 Quartzite</td>
<td>11,3</td>
</tr>
<tr>
<td>0/4 Quartzite</td>
<td>46,2</td>
</tr>
<tr>
<td>Filler</td>
<td>3,8</td>
</tr>
<tr>
<td>Binder</td>
<td>5,7</td>
</tr>
<tr>
<td>Voids</td>
<td>5 - 8</td>
</tr>
</tbody>
</table>

1.2.2 Bituminous binders

In addition to previous works [3], the present investigations focus on the effect of aging procedure on test methods and on their ability to evaluate both binders and asphalt mixtures. In order to illustrate this approach, works are performed on three kind of bituminous binders, which are:

- PEN 35/50 A - Neat binder
- In-situ crosslinked elastomer modified binder with 3.5% polymer content and manufactured according to the « Styrelf® » process. Base bitumen is a 35/50 pen.

- Physical blend: PEN 35/50 A modified with 3.5% of copolymer. Added SBS displays higher molecular weight than the polymer used during « Styrelf® » process to obtain equal consistency for both PmB (cf Table 2).

Modified binders are thus based on the same neat binder but differ by their manufacturing process.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Brookfield dynamic viscosity (mPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NF EN 13302</td>
</tr>
<tr>
<td></td>
<td>Styrelf</td>
</tr>
<tr>
<td></td>
<td>PB</td>
</tr>
<tr>
<td>120</td>
<td>2938</td>
</tr>
<tr>
<td>140</td>
<td>1027</td>
</tr>
<tr>
<td>160</td>
<td>413</td>
</tr>
<tr>
<td>180</td>
<td>211</td>
</tr>
</tbody>
</table>

Table 2 : Viscosity of Styrelf® and physical blend binders as a function of temperature.

2- EXPERIMENTAL PROGRAM

2.1 Binders and asphalt mixtures laboratory aging procedures

Binders have been aged using classical aging protocols:

- The Rolling Thin Film Oven Test (RTFOT) [9] is simulating short-term aging related to the asphalt production at high temperature, it involves a « dynamic » aging conditions induced by the rotation of glass bottles containing the binder. In this way, during 75 minutes and at 163°C, a thin film of binder is systematically renewed and the film is continually in contact with a constant air inflow.

- The Pressure Aging Vessel (PAV) [10] is simulating long-term aging of the binder during the service life of the pavement. It provides « static » aging conditions, done by heating a homogeneous thin layer of binder (previously hardened by RTFOT) during 20 hours at 100°C and under 2.1MPa.

Alternative laboratory aging protocols have also been used to simulate the aging of the asphalt. In these protocols it is the asphalt mixture that is directly aged as described below:

- A short term aging procedure which involves mixing the binder and the aggregates at high temperature, just like in the asphalt mixing plant. After the mixing step, the loose asphalt mixture is compacted to obtain a slab. This kind of asphalt mixture aging procedure is well correlated to the RTFOT short term aging procedure on the binder.

- A long term aging procedure which corresponds to the life cycle of the asphalt mixture in a pavement. This aging procedure is based on the one designed by RILEM TC-ATB Task Group 5 [11]. After the mixing step, loose asphalt mixture is deposited as a homogeneous thin layer on suitable plates. These plates are then kept inside a first ventilated oven during 4 hours at 135°C. After this period, plates are kept inside a second ventilated oven during around 7 days at 80°C (instead of 85°C as mentioned by RLIEM TC-ATB task). Once this aging procedure is complete, the loose asphalt mixture is heated and compacted to obtain slabs for the preparation of TSRST samples. This kind of long term aging procedure is correlated to the PAV test method.

In our paper, following references will be used:

- « -O » in relation to neat, unaged, binder
- « -R » in relation to short term aging
- « -P » in relation to long term aging.

Samples, aging procedure status and test method references are reported on Table 3.

Table 3 : binders and asphalt mixtures descriptions and aging step references
2.2 Limiting artefacts in RTFOT

It is well known that one remarkable effect of adding polymer to bitumen is a dramatic increase in viscosity. This increase is particularly significant as the polymer content is important; the other components being equal. Thus, binder viscosity is easily correlated to polymer ratio (see Table 4).

As expected the binder characteristics change during the RTFOT aging. However, the rate of change differs greatly depending on the type of binder. Indeed, when looking at Softening Point, we notice a significant change (ΔTBA = 5.8°C) for the virgin binder (viscosity around 200 mPa.s) whereas this evolution is much smaller (ΔTBA = 1.2°C) for the high polymer modified bitumen (5% polymer content - viscosity of 650 mPa.s).

Table 4: Binders characteristics change between unaged step and RTFOT aged step for different polymer content

<table>
<thead>
<tr>
<th>Bitumen</th>
<th>Polymer content (%)</th>
<th>Fraass-O</th>
<th>Fraass-R</th>
<th>Fraass-P</th>
<th>ABCD-O</th>
<th>ABCD-R</th>
<th>ABCD-P</th>
<th>BBR-O</th>
<th>BBR-R</th>
<th>BBR-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Bitume</td>
<td>0</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Styrelf®️</td>
<td>3,5</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>PB</td>
<td>3,5</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Styrelf: crosslinked PmB "Styrelf" - O: unaged binder
PB: "Physical blend" with an SBS elastomer - R: after RTFOT aging (EN 12607-1) - P: after RTFOT+PAV aging (EN 12607-1 followed by EN 14769)

<table>
<thead>
<tr>
<th>Asphalt mix</th>
<th>Polymer content (%)</th>
<th>TSRST-R</th>
<th>TSRST-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitume pur</td>
<td>0</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Styrelf®️</td>
<td>3,5</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>MP</td>
<td>3,5</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Styrelf: crosslinked PmB "Styrelf" - R: after aging related to mixing with aggregates
PB: "Physical blend" with an SBS elastomer - P: after aging related to RILEM TC-ATB Task Group 5 procedure

As described previously, the RTFOT aging procedure is based on air contact with a constantly renewed thin film of binder in rotating glass containers. For paving grade bitumens according to EN 12591: 2010 [9], the testing temperature of 163°C is suitable to obtain and properly renew such a thin film.

On the other hand, for highly viscous, polymer-modified binders, tested in the same conditions of temperature, the renewal of the thin film might be hindered and modified binder might not undergo the full RTFOT aging impact. This effect, already reported in previous studies [24], might lead to an underestimation of aging and to results that are not fully reliable. Analyzing the RTFOT impact for such kind of highly modified binders becomes then more difficult.
This point of view led us to focus on PmB with moderate modification (3.5% ratio), so as to reduce the artifact due to viscosity. We also focused only on binders after full aging (RTFOT+ PAV).

3- TEST RESULTS

First of all, the sensitiveness of the TSRST method to the mixture aging protocol described in section 2.1 is discussed.

These results are then compared to binder low temperature characteristics (Fraass breaking point, BBR and ABCD test) obtained after RTFOT+PAV [1, 2, 12-21].

3.1 Aging procedure impact on TSRST asphalt mixtures performances

As depicted in figure 1, TSRST results for asphalt mixtures aged through mixing binder with aggregates (TSRST-R) show that the one based on crosslinked PMB binder displays lower cracking temperature (Tc) in comparison with asphalt mixture made from neat bitumen (ΔTc reaches almost 3°C).

Nevertheless, the variation seems to be slight in comparison with standard deviation (+/-2°C).

In addition, it is clear that, at same polymer content, asphalt mixture made from polymer physical blend modified binder presents lower performance than crosslinked PMB binder. Moreover, its cracking temperature is equal to that of the asphalt mixture with neat bitumen, despite the addition of polymer.

![Figure 1: TSRST critical temperature of asphalt mixtures related to aging procedures - standard deviation +/- 2°C](image)

TSRST results for asphalt mixtures after long term aging procedure (TSRST-P) show the same tendency. The crosslinked PMB mixture still displays the best TSRST cracking temperature in comparison with the two others asphalts mixtures. The latter ones present equal cracking temperatures at this stage.

Moreover, based on cracking temperature variation between short term aging procedure and long term aging procedure, crosslinked PMB mixture clearly displays also a lower sensitiveness to aging, thus potentially a better material durability than the two others asphalt mixtures. Indeed, critical temperature change between short and long term aging is significantly lower (increased by about 2.6°C) in the case of crosslinked PMB than for the two others binders (increased by around 5°C). This good resistance to aging was investigated in the literature and related to a better resistance of the polymer network [25, 26].

TSRST can be considered as the reference method to evaluate low temperature performance of different binders. In following sections, the ability of binder test methods to evaluate the impact of aging on low temperature performance will thus be discussed in comparison to the TSRST test results.
### 3.2 Aging procedure impact on binder low temperature performance

#### 3.2.1 Fraass breaking point

*NB: Polymer physical blend modified bitumen is not evaluated in this part due to lack of results*

Fraass breaking point results (fig. 2) show a large gap between neat bitumen and crosslinked PmB, as expected. Whatever the short term or long term aging procedure, the crosslinked PMB displays a lower breaking temperature (9°C and 6°C better than neat bitumen, respectively for Fraass-R and Fraass-P) suggesting a better resistance against cracking.

![Figure 2: Fraass breaking temperature of binders related to aging procedures - standard deviation +/- 2°C](image)

However, as depicted in figure 2, according to Fraass breaking point, neat bitumen would be more resistant to long term aging impact (Fraass breaking point increased by 3°C) than the crosslinked PMB binder (Fraass breaking point increased by 6°C), although this variation is in the range of test reproducibility (+/- 6°C). This observation doesn’t match with the previously discussed asphalt mixtures TRSRT results.

#### 3.2.2 Asphalt Binder Cracking Device - ABCD

As expected, ABCD cracking temperature results show a significant gap between studied binders, as neat bitumen presents the highest critical temperatures at each aging status (see figure 3). On the other hand, whatever the aging procedure applied, the cracking temperatures for the physical blended binder are systematically slightly lower than for the corresponding crosslinked PMB binder (around 1-2°C). However, this gap is in the range of the test reproducibility. Also this observation is not consistent with the asphalt mixture TSRST method results.

Besides, for all the investigated binders in our present works, the impact of RTFOT and RTFOT+PAV aging on the ABCD failure temperatures appear as quite limited, especially for the neat bitumen, as expected to be the more sensitive to aging (cf fig. 3 and fig. 5-b). This result is surprising since the binder aging protocols, particularly PAV step, is quite intensive and usually induces very significant changes in for the binder characteristics, especially at low temperatures [16-18, 20-22].
Figure 3: ABCD failure temperature of binders related to aging procedures - standard deviation +/- 1.5°C

3.2.3 Bending Beam Rheometer - BBR

BBR test method (critical temperature $T_{S}=300$ MPa, and $T_{m}=0.3$) allows to discriminate binder characteristics whatever aging status. It also differentiates binders according to their ability to resist aging (see figure 4). The crosslinked PMB binder shows outstanding performance on both items: critical temperature is lower and the effect of aging is reduced. These trends are particularly visible after applying PAV (long term aging).

As an example, based on the $S$ criterion, crosslinked PMB BBR-P critical temperature is 2.6°C lower than for both the neat bitumen and the physical blend binder. This gap is also noted for the $m$ criterion since the BBR-P critical temperature is 5°C lower for crosslinked PMB than for the physical blend modified binder. Furthermore, it is surprising that physical polymer modified bitumen show equal ($S$ criteria) or worse ($m$ criteria) critical temperatures than pure bitumen.

Besides, BBR critical temperature variation during long term aging procedure (between BBR-R and BBR-P values), in other word the aging sensitiveness, is reduced in the case of crosslinked PMB binder in comparison to the two others binders, with gap values significantly higher than the standard deviation of the BBR test method (+/- 2°C). This is however more particularly true for the $m$ criterion.

It is interesting to point out that these results are confirmed by the asphalt mixture TSRST results (see part 3.1).

Figure 4: BBR critical temperature of binders related to aging procedures - standard deviation +/- 1.5°C

4. Binder Test Methods as Predicting Tool to Capture Aging Impact on the Low Temperature Cracking Behaviour of Asphalt Mixes

4.1 Trend criterion analysis procedure

In this part, the relation between binder aging and asphalt mixture aging methods is discussed. The goal is to identify the binder test method that best predicts the aging impact on asphalt mixture cracking performance as measured by the TSRST method.
For such investigations, both binder and asphalt mixture characteristics have been displayed as vectors in a binder test method = f (TSRST asphalt mixture) plot, as depicted in following figures. Thus, figures 5-a, 5-b, 5-c, 5-d display respectively Fraass breaking point, ABCD cracking temperature and BBR critical temperatures (vertical axis) as a function of TSRST cracking temperature (horizontal axis) with the same scale on each axis. To be consistent, only equally aged characteristic values between binder and asphalt mixture have been plotted: short term aging status (“-R”) and long term aging status (“-P”) are assigned respectively to the origin and the end of each vector. Thus, both binder and asphalt mixture characteristics variation under aging impact could be shown as a vector (arrow) which is to be interpreted as follows:

- The amplitude of the horizontal projection of the vector displays the variation with aging of the asphalt mixture TSRST cracking temperature.
- The amplitude of the vertical projection of the vector displays the variation with aging of the binder test method cracking or critical temperature.
- The slope p of the vector is a measure of the relevance of the binder test method property for evaluating the impact of aging on asphalt mixture TSRST performance:
  - p=1 corresponds to an accurate capture of the impact of aging on asphalt mixture TSRST performance by the binder test method.
  - p < 1 means that the variations of binder characteristics with aging are lower (thus underestimate) than the corresponding variations of the TSRST cracking temperature. In opposite way, p > 1 means that the variations of binder characteristics with aging are larger (thus overestimate) than the corresponding variations of the TSRST cracking temperature.

4.2 Fraass test method as trend criterion for TSRST results

As described in figure 5-a, it seems that the Fraass test underestimates aging in the case of neat binder (vector slope p= 0,65 < 1) and it overestimates aging in the case of crosslinked PMB (p=2,31 > 1).

Consequently, Fraass test method would not be a relevant criterion to catch the impact of aging on asphalt mixture TSRST performance since the relationship depends on the type of binder. Its poor reproducibility (+/-6°C) adds to the difficulty of interpretation. To further validate this observation, it might be interesting to extend this study to a wider binder database, in particular with polymer physical blend modified binders.

![Figure 5-a: Fraass breaking temperature change of binders as function of TSRST temperature change related to aging procedures](image)

4.2 ABCD test method as trend criterion for TSRST results

Similar plots are presented in figure 5-b for ABCD test results. Plotted vectors show that both variation of ABCD cracking temperature and variation of asphalt mixture TSRST cracking temperature due to aging impact are clearly similar for crosslinked PMB binder as revealed by the slope (p= 0,92 ≈ 1).
On the other hand, for neat bitumen and polymer physical blend modified binder, ABCD cracking temperature variation due to aging is very small in comparison with asphalt mixture TSRST temperature variation (p slope = 0.09 and 0.24 respectively for bitumen and polymer physical blend modified binder). This points out that also the ABCD test method is not relevant as a universal (independent from the type of binder) binder test to catch the evolution with aging of asphalt mixture TSRST cracking temperature.

Moreover, as discussed in section 3.2.2 and also noticeable in extended database [3], the impact of aging, and more particularly of PAV aging on ABCD cracking temperature is quite small for all investigated binders (not more than 1 to 2°C change). Although test mechanisms for ABCD and TSRST are similar (based on thermal stress on restrained sample), some further investigations have to be made in order to better understand the mechanical stress field induced by both test methods and possible aggregates effect on it. So, based on these results, the ABCD test cannot yet be considered as a relevant method for predicting the impact of aging on TSRST performance.

### 4.3 BBR test method as trend criterion for TSRST results

Similar plots are presented in figure 5-c and 5-d for BBR test results. It is noticeable that the binder aging effect on BBR is well correlated to the mixture aging effect on TSRST. Indeed, for all binders, p slope values are closely similar and are providing the same variation effect for a same BBR criterion:

**S criterion:** p slope values are 0.39; 0.54; 0.61 respectively for pure bitumen, crosslinked PMB binder and polymer physical blend modified binder. Nevertheless, this criterion underestimates real amplitude of performance variation of asphalt mixture because p slope is below 1.

**m criterion:** p slope values are 0.93; 1.35 et 0.84 respectively for pure bitumen, crosslinked PMB binder and polymer physical blend modified binder. This binder test method criterion seems to be the one that best catches the aging impact of asphalt mixture on TSRST cracking temperature. Further investigations have to be made on others kinds of binders to extend the validation of this analysis.

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Figure 5-b: ABCD failure temperature change of binders as function of TSRST temperature change related to aging procedures
CONCLUSION AND RECOMMENDATION

The compared analysis three binder test methods (Fraass breaking point, ABCD cracking temperature, BBR criteria) suggests that BBR, and more specifically the m-criterion, is the most appropriate to adequately predict the evolution with aging of the low temperature performance of asphalt mixtures as seen by the TSRST procedure. These findings are consistent with previous works based on the in-situ monitoring of materials on actual jobsites. In earlier studies [1, 2], the authors showed on both aged binders from pavement cores and laboratory artificially aged binders that crosslinked elastomer binders like Styrel® present a better resistance to oxidative aging. As a matter of fact, and although three different types of binders have been investigated, these findings are based on a still limited amount of data. They need thus to be confirmed on a wider product slate.

Figure 5-c : BBR critical temperature - S criterion - change of binders as function of TSRST temperature change related to aging procedures

Figure 5-d : BBR critical temperature - m criterion - change of binders as function of TSRST temperature change related to aging procedures
To evaluate the potential of binder test methods to correctly evaluate performance, our study has not only looked at binder properties at different states of aging, but also compared those to laboratory aged asphalt mixture properties. This is not current practice. In our case, it has triggered a number of questions concerning the behavior of a binder as such or when inside a mix. We believe thus that this kind of approach is likely to be extremely fruitful and that it should be pursued in the future.

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