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Aging of bituminous binders in asphalt pavements and laboratory tests

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ABSTRACT: Aging of bituminous binders is one of the key factors affecting the performance and durability of asphalt pavements. To simulate binder aging in laboratory, a number of methods are available. In this paper, RTFOT (Rolling Thin-Film Oven Test), PAV (Pressure Aging Vessel) and RCAT (Rotating Cylinder Aging Test) using different aging times and temperatures were employed to age two straight-run bitumens and a styrene-butadiene-butadiene (SBS) polymer modified binder. For field aging, a number of asphalt pavements of different years in service were investigated. The binders (virgin, laboratory aged, and extracted from asphalt pavements) were evaluated by penetration and softening point tests, rheological measurements with a dynamic shear rheometer (DSR), as well as chemical analyses using Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC). It was confirmed that the rheological changes upon laboratory aging and the formation of chemical functionalities were strongly temperature dependent. Great differences were found between the unmodified and SBS polymer modified binders in the rheological response upon aging. For the modified bitumen, different chemical reactions of the two components (bitumen and polymer) may compensate each other in some ways, making the binder less age-hardening and more durable. Apparently, the standardized PAV and RCAT simulate about 10 years of field aging for the unmodified bitumens when used in a dense asphalt surface layer, but for open graded mixes a longer PAV or RCAT aging time is necessary. However, for polymer modified bitumen the relationship between laboratory and field ageing when studying both mechanical and chemical compositional changes is less trivial.

1 INTRODUCTION

As one of the key factors affecting the performance and durability of asphalt pavements, the aging behavior of bitumen has been investigated intensively for a long time. Usually, aging makes the binder harder and more brittle, thus increasing risk of pavement failure, such as surface cracking and raveling (Francken 1997, Leech & Nunn 1997, King et al. 2012). In reducing the potential for low temperature cracking, less aging of bitumen will be beneficial (Page et al. 1985). It has also been shown that on the long lasting asphalt pavements, the slow aging of the binder keeps asphalt layers flexible enough to resist cracking (Lu et al. 2011). A low degree of bitumen aging also minimizes the effects of moisture, thus retaining a high strength for the pavement structures (Thomas et al. 2006).

For a hot mix asphalt (HMA) pavement, aging takes place at high temperatures during asphalt production and road construction (short-term aging) and at ambient temperature during the service life of an asphalt pavement (long-term aging). The main mechanism of bitumen aging is oxidation, or called

oxidative aging. Oxidative aging is highly temperature dependent, and also largely affected by the chemical nature of the bitumen (Tuffour et al 1989, Branthaver et al. 1993, Petersen 2009). For certain type of bitumen, high aging resistance has been observed (Soenen et al. 2016).

In the field, important factor affecting bitumen aging also include the air voids content of asphalt mixtures. Much work has indicated that asphalt mixtures of low voids show a low degree of bitumen aging while higher void content facilitates the aging process (Dickinson 1980, Kemp & Predoehl 1981, Kemp & Sherman 1984, Leech & Nunn 1997, Oliver 1992, Lu et al. 2011). It is believed that air voids content determines the rate of aging by controlling oxygen access to the bitumen. Consequently, the oxidative aging of bitumen as function of depth in the pavement is closely linked to the air voids content of the mixture. Regardless of pavement structure, asphalt surface or top thin layer is aged more than the asphalt layers at lower depths (Coons & Wright 1968, Mirza & Witczak 1995).

To simulate bitumen aging in laboratory, different types of test methods may be used, including con-

duction of accelerated aging on bituminous binders, on loose asphalt mixtures, or on compacted asphalt specimens. For bituminous binders, there are three European standardized tests for the short-term aging at high temperatures, namely Rolling Thin-Film Oven Test (RTFOT, EN 12607-1), Thin Film Oven Test (TFOT, EN 12607-2), and Rotating Flask Test (RFT, EN 12607-3). These tests reasonably simulate aging particularly during mixing process in an asphalt mixing plant. As for the long-term aging during in-service, laboratory simulation is rather difficult. Ideally, such a test should be able to predict the chemical and physical property changes of the binder after certain years in asphalt pavement. This may be achieved by conducting a test under artificially severe conditions, for example, at a temperature higher than pavement service temperature and at a pressure higher than ambient pressure. Two European standardized long-term aging tests are Pressure Aging Vessel (PAV, EN 14769) and Rotating Cylinder Aging Test (RCAT, EN 15323). Although numerous investigations have been carried out on these test methods, field data for different types of binders under different climatic conditions are still needed to further demonstrate if these test methods are relevant enough or if natural aging occurred in the pavement can be properly predicted.

The main objectives of this paper are to study how different binders behave under different aging tests and to assess how laboratory aging tests are related to field aging. Two straight-run and one polymer modified bitumens were investigated. Characterization of the binders (virgin, laboratory aged, and extracted from asphalt pavements) was performed using conventional test methods, fundamental rheological measurements, as well as chemical analyses.

2 LABORATORY AGING

2.1 Bituminous binders

Three types of binders were selected for this study, including a penetration-grade bitumen B1, a viscosity-grade bitumen B2, and a highly polymer modified bitumen PMB with styrene-butadiene-styrene (SBS) block copolymer. Conventional properties of the binders are shown in Table 1. According to the current European binder specifications, the polymer modified binder is classified as 90/150-75, while unmodified bitumen B1 and B2 are classified as 70/100 and 160/220, respectively.

Table 1. Properties of bituminous binders

Binders	Penetration, 1/10 mm	Softening point, °C	Viscosity at 135°C, mm ² /s
B1	76	45.5	381
B2	220	35.3	170
PMB	98	95.0	1700

2.2 Aging test methods

Aging of the binders was performed by different methods under different conditions. Those include RTFOT, followed by PAV at 100°C (PAV 100) for 8h, 20h, and 48h; RTFOT, followed by PAV at 75°C (PAV 75) for 48 h, 120 h, and 220 h; and RCAT at 163°C for 4 h, then at 90°C for 17 h, 65 h, and 140 h. The use of different temperatures and aging times in PAV is to study aging kinetics, which is believed to be binder specific. RCAT is another standard long-term aging test method. It was also claimed that RCAT at 163°C for 4 h (used as the first step of RCAT) can simulate short-term aging (Verhasselt 2003).

2.3 Evaluation of aging by conventional and rheological measurements

Various conventional, rheological and chemical property measurements were carried out to evaluate bitumen aging. Those are softening point, complex viscosity by a dynamic shear rheometer (DSR), functional groups (sulfoxides and carbonyls) by Fourier transform infrared spectroscopy (FTIR), and molecular weight distributions by gel permeation chromatography (GPC). Detailed procedures for these tests can be found elsewhere (Lu et al. 2011).

In Figure 1, the complex viscosities measured at 60°C and 10 rad/s are plotted versus the aging time in PAV and RCAT. The starting points at zero hour are corresponding to those after the short-term aging, i.e. RTFOT or RCAT at 163°C. According to literature (Verhasselt 2003), the short-term aging tests by RTFOT and RCAT at 163°C are quite similar. This is confirmed in this study both for the unmodified and SBS polymer modified binders. In the long-term aging, as expected, the temperature is shown as a factor significantly affecting aging kinetics, and the temperature effect is strongly binder-specific. For the unmodified bitumen B1 and B2, under the tested durations, the complex viscosity gradually increases with the aging time, both in PAV and RCAT. The general rule that increasing temperature by 10°C doubles the rate of aging is also likely followed in the PAV. For example, to reach the same level of complex viscosity of 1000 Pa.s at 60°C, for B1, aging time in the PAV at 100°C is estimated to be 12h, which is about 1/8 of the time (90h) required in PAV at 75°C. However, the rule is not valid when PAV and RCAT are compared to each other. To obtain a similar level of aging, RCAT will take much longer time than PAV if the temperature is the same. The DSR data, as well as softening point and penetration (Figure 2), show that for the unmodified bitumens, aging of 140h in RCAT at 90°C is more or less equivalent to 20h PAV at 100°C, or 120h PAV at 75°C.

Figure 1. Evolution of complex viscosity during PAV and RCAT under different conditions.

Figure 2. Comparison of the long-term aging methods by penetration and softening point.

On the other hand, for the PMB, aging kinetics is very different from those of unmodified bitumens. As shown in Figure 1, using PAV at 75°C, the complex viscosity of the modified binder increases gradually with the aging time. However, when the temperature is raised from 75°C to 100°C in PAV or 90°C in RCAT, such trends in the viscosity change are not seen. The different behaviors are also reflected in softening points (Figure 3). Unlike the unmodified bitumens, the softening point of the modified binder does not increase with the aging time. This is attributed to a combined effect of bitumen oxidation and polymer degradation, and to changes in the compatibility or polymer networks of the system. The degradation of the polymer apparently compensates for bitumen oxidative hardening. As a consequence, the equivalences between the long-term aging tests observed for the unmodified bitumens are not valid for the PMB (Figure 2). The strong temperature dependence of aging mechanisms and kinetics also means that it will be difficult to predict PMB aging properly in the field by a laboratory simulation at a high temperature.

Figure 3. Penetration vs softening point after different long-term aging tests.

2.4 Evaluation of aging by FTIR

Chemical changes during aging have been studied extensively in the past years. It is well-known that oxidation of bitumen produces carbonyls (C=O) and sulfoxides (S=O) and increases aromaticity, causing increases in bitumen viscosity and elasticity. The chemical changes may differ largely between different bituminous binders, especially between polymer modified and unmodified. From infrared (IR) spectrograms, absorbance bands (peak areas) at about 1705 and 1030 cm^{-1} were measured for carbonyl compounds (e.g. ketones, carboxylic acids and anhydrides) and sulfoxides, respectively.

In Figure 4, the IR absorbance ratios of aged to unaged bitumen are plotted against the aging time in PAV. Again, the samples of zero-hour aging are

those after RTFOT. As indicated, at both low (75°C) and high (100°C) aging temperatures, the formation of sulfoxides is significant. With increasing aging time, the rate of sulfoxides formation tends to decrease. Unlike sulfoxides, carbonyl compounds are formed at a more constant rate, which is much higher at 100°C than at 75°C. The observations agree well with those findings reported in the literature (Branthaver et al. 1993).

Figure 4 also indicates that the formation of sulfoxides in the modified binder is lower than that in the unmodified ones, while an opposite trend is seen for carbonyl compounds. Notice that the base bitumen used for the modified binder is very similar to B2. The inhibiting effect of the polymer on sulfoxide formation has also been observed earlier (Lu & Isacson 2000). It is suspected that the SBS polymers may compete with sulfur compounds in the bitumen for oxidants. As for carbonyls, the higher increase is contributed by oxidation of the polymer (or polymer degradation).

Figure 4. FTIR analysis of bitumen aging – effect of temperature.

For a given bitumen, correlation may be expected between rheological and compositional changes, and this was the case for the three binders investigated in this paper. The correlation coefficients were found between 0.68 and 0.91 for the complex viscosity *versus* carbonyls, and between 0.61 and 0.96 for the complex viscosity *versus* sulfoxides. However, such correlations did not exist when different binders

were examined together because of differences in the temperature dependence of oxidation and other contributing factors.

3 FIELD AGING IN ASPHALT PAVEMENTS

3.1 Road sections

Three pavement sections were selected for field aging study (Table 2). They are coded as B1-E6, B2-RV53 and PMB-E4, representing the different binders (B1, B2 and PMB) used. The section B1-E6 was selected from a test road on the highway E6, Geddekippe – Kalsås, in Sweden. It was a reference section of the test road constructed in 2006, where B1 was used in a 40 mm stone mastic asphalt ABS16 (SMA16) as the wearing course. Asphalt cores were taken from the road section after nine years of service in October 2015.

Table 2. List of pavement sections

Road sections	Mix types	Binder content, %	Air voids, %	Years in the field (and as top layer)
B1-E6	SMA16	6.0	3.0	9 (9)
B2-RV53	AC16	6.2	3.5	26 (5)
PMB-E4	SMA11	6.5	3.5	15 (15)

For bitumen B2, a pavement section was selected from the national road RV53 based on the Swedish LTPP (Long Term Pavement Performance) database. The section (B2-RV53) was located in Kvicksund, and was built in 1977 with a 25 mm MAB16T (AC16). According to the technical requirements of that time, MAB16T was a dense graded asphalt mixture with maximum aggregate size of 16 mm and with about 6.2% (by weight) binder and 3-5% air voids. The layer was on the top of the pavement for about five years, and a surface treatment was then carried out in 1982. In total the asphalt had been in the field for 26 years when samples were taken.

The field object PMB-E4 was a bridge deck pavement on the High Coast Bridge on the highway E4. The bridge was constructed between 1993 and 1997, and the surface layer was 35 mm ABS11 (SMA11) produced with the studied PMB. The asphalt mixture contained about 6.5% binder (by weight) and 3.5% air voids. After nearly 15 years of service, asphalt samples were collected. For this PMB, field data from literature were also used for laboratory aging comparison.

For binder extraction and recovery, the European standards EN 12697-1 and EN 12697-3 were followed. The solvent used was dichloromethane.

3.2 Conventional and rheological tests

The results of penetration and softening point tests for the field aged binders are summarized in Table 3.

The binders were also characterized using DSR at different temperatures and frequencies. For simplicity, only the complex viscosities measured at 60°C and 10 rad/s are shown in Table 3. These data will be used for comparing with laboratory aging tests later.

Table 3. Conventional and viscosity measurements of the field aged binders

Recovered binders	Penetration, 1/10 mm	Softening point, °C	Complex viscosity at 60°C, Pa.s
B1-E6	NM*	56.4	1091
B2-RV53	101	44.0	114
PMB-E4	54	81.0	686

*not measured due to insufficient amount of sample

3.3 FTIR analysis

The chemical compositions (functional groups) of the field aged binders were analyzed by FTIR. By comparing with unaged samples, absorbance ratios were calculated for carbonyls and sulfoxides. Results are shown in Table 4. Unexpectedly, for B1-E6, the IR absorbance ratio of carbonyls is less than 1. This might indicate that carbonyl compounds probably were not completely extracted from the asphalt material due to e.g. certain active aggregates.

Table 4. IR absorbance ratio (field aged/unaged)

Recovered binders	Carbonyls	Sulfoxides
B1-E6	0.56	3.32
B2-RV53	1.57	26.3
PMB-E4	1.27	2.73

4 FIELD AGING VERSUS LABORATORY AGING TESTS

To compare with field aging, laboratory aging tests with PAV at 100°C and RCAT at 90°C are used. Figure 5 shows the viscosity changes of the different binders during PAV and RCAT, as well as the viscosities of the field aged samples. As can be seen from Figure 5, the standardized PAV conditions (100°C and 20 h) predicts about 10-year field aging of the unmodified bitumen (B1) in the surface layer. However, for the binder extracted from RV53, very low aging is observed, and to produce the same level of aging as in the field, only about 8 hours are required for the PAV. It should be noticed that this binder had been in the pavement for more than 25 years, but only 5 years as top layer. The results imply that oxidation of bitumen may be slowed down when the asphalt layer was overlaid, due to a limited access of oxygen (and UV) and lower temperature as compared to that in the top layer. The asphalt mixture itself also had a low air voids content (1.9%)

when field cores were taken. Taking these into account, for this binder, PAV seems also give a quite good prediction of field aging (around 10 years).

For polymer modified binders, the prediction of field aging by PAV generally becomes difficult due to more complicated chemical reactions. As shown in Figure 5, a very low degree of aging is observed for the PMB studied even after a long time (15 years) in the bridge deck pavement. The equivalent aging time in PAV 100°C is estimated to about 9 h, which is considerably lower than the standardized aging time of 20h. The smaller viscosity change or less age-hardening of the field aged PMB could be due to more degraded polymers that act as a kind of softening agents, which then compensate for the oxidative hardening of the bitumen. This is illustrated by the GPC analysis of the laboratory and field aged samples in Figure 6.

Similar observations can also be made with RCAT. For these field aged samples, the equivalent aging times with this test method are estimated to be 107 h for B1-E6, 37 h for B2-RV53, and 56 h for PMB-E4; the last two are considerably shorter than 140h.

Figure 5. Comparison of laboratory aging and field aging by the complex viscosity.

5 DISCUSSION AND CONCLUSIONS

Figure 6. GPC chromatograms of the laboratory aged PMB and that extracted from the pavement section.

To further examine the relevance of PAV for the modified binders, the same PMB used in other mix types and in other road sections are compared. In this case, the binder is assessed by age-hardening through penetration measurements. In Figure 7, the percent retained penetrations, i.e. (penetration of aged binder / penetration of unaged binder) $\times 100$, are calculated partly based on literature data (Jacobson & Hornwall, 2000). It is evident that the prediction of the PMB field aging is strongly dependent on air voids content of the asphalt mixtures. For the porous asphalt (PA) of 15% air voids, the age-hardening of 10-year in the field is not predictable by the PAV. On the other hand, in the SMA containing 3% or 5% air voids, the extent of binder age-hardening after 8 to 15 years in service is rather low, for which a corresponding aging time in PAV will be much shorter than that being standardized.

Figure 7. Retained penetration of PMB – comparison of laboratory aging and field aging.

During the production and service life of an asphalt pavement, the rheological changes of bituminous binders are mainly due to oxidative aging. As already mentioned, oxidative aging has been studied extensively for a long time by monitoring changes both in the chemistry and in the mechanical properties of bitumen. It is well-known that the oxidation of bitumen increases its viscosity and elasticity, and this is normally attributed to the formation of polar, oxygen-containing chemical functionalities and/or aromaticity on bitumen molecules, resulting in stronger molecular interactions (Petersen 2009). The importance of chemical functionality to bitumen rheological properties was also very much emphasized in the American SHRP investigations. The present study confirms that, for a given bitumen and during aging, correlation exists between changes in viscosity and in chemical functionalities. However, such relationship has not been seen when different binders were examined together, indicating other chemical parameters also contributing to viscosity.

Regarding chemical reactions of bitumen upon aging, Petersen and Harnsberger (1998) proposed a two-step mechanism; in a first rapid step oxygen reacts with a limited amount of highly reactive hydrocarbons, most likely polycyclic hydroaromatics which form hydroperoxides and which in turn react with sulfides to form sulfoxides and aromatized rings. During this first reaction, a much slower oxidation of benzylic carbons involving formation of benzyl free radicals is initiated, which produces both ketones and sulfoxides. This dual oxidation mechanism explains well the viscosity changes during the aging, which is normally a larger increase during RTFOT followed by a slower increase during PAV. The magnitude and duration of the different steps in the viscosity change are bitumen specific, and these characteristics are believed to be critical to asphalt durability in the field. Considering polymer modified binders, aging-induced mechanical property changes will be complicated also by the chemical changes of the polymer.

It can be speculated that chemical reactions during asphalt production and in-service are not necessarily the same as those occurring during laboratory aging tests, because of differences in temperature and in reaction environments (e.g. presence/absence of aggregates, fillers, water, and UV etc.). The oxidative aging of bitumen in the field is also affected by asphalt air voids and layer thickness and position. And as already mentioned, the surface or top thin layer of asphalt pavement is aged more than that at lower depths. All these factors make it rather difficult to predict field aging by a laboratory method, especially for polymer modified binders. In spite of this, selection of an aging-resistant binder based on

these laboratory tests is still of great importance to ensure long-term durability of asphalt pavements.

From the results obtained in this study, the following conclusions can be drawn. The rheological changes upon laboratory aging and the formation of functionalities are strongly temperature dependent. There are great differences between unmodified and SBS polymer modified binders in the rheological response upon aging. For modified bitumen, different chemical reactions of the two components (bitumen and polymer) may compensate each other in some ways, making the binder less age-hardening and more durable. Apparently, the standardized PAV and RCAT simulate about 10 years of field aging for the unmodified straight-run bitumens when used in a dense asphalt surface layer. However, for polymer modified bitumen, the relationship between laboratory and field ageing when studying both mechanical and chemical compositional changes is less trivial. It should also be noticed that, for more open asphalt mixes, longer PAV or RCAT aging times will be necessary in order to predict the service life time.

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