

DURABILITY OF POLYMER MODIFIED BINDERS IN ASPHALT PAVEMENTS

Xiaohu Lu¹, Hilde Soenen², Serge Heyrman³, Per Redelius⁴

^{1,4} Nynas AB, SE-149 82 Nynäshamn, Sweden

^{2,3} Nynas NV, 2030 Antwerp, Belgium

xiaohu.lu@nynas.com; hilde.soenen@nynas.com; serge.heyрман@nynas.com; per.redelius@nynas.com

Abstract: In sustainable asphalt road construction, proper selection of materials is of great importance. A durable material along with optimal mix and pavement design is crucial to a long lifetime of asphalt pavements. For bituminous binders, increased experience and knowledge has been seen on use of polymer modification. The main objective of this paper is to study the durability of polymer modified binders in terms of resistance to aging, rutting and cracking. Asphalt samples were taken from test roads where polymer modified binders were tested in different layers. Field samples were analysed with respect to binder contents and air void contents. In characterisation of recovered binders various tests were carried out, including time-temperature sweeps and multiple stress creep and recovery test (MSCR) using dynamic shear rheometer, gel permeation chromatography, Fourier transform infrared spectroscopy, fluorescence microscopy, as well as conventional tests such as penetration. The chemical and mechanical tests were also conducted on original binders and those aged at laboratory by RTFOT and PAV. It was found that the polymer modified binders demonstrate better rheological properties than unmodified pen bitumen, even after several years in asphalt pavements. These improvements include higher strain recovery and lower non-recoverable compliance (J_{nr}) at high temperatures, and lower stiffness at low temperatures. For the modified binders with styrene-butadiene-styrene (SBS) polymers, good aging resistance was also observed. The improved binder properties should be beneficial in terms of resistance to asphalt rutting and cracking. This is expected to be confirmed by a longer time of follow-up on the performance of the test road.

Keywords: Asphalt pavement, Test roads, Polymer modified binders, Durability

1. INTRODUCTION

In the last decade, increases in traffic density and axle loading in combination with a pressure to reduce material costs has created high performance requirements for asphalt pavements. To ensure long-term durability, thus minimizing maintenance cost and conserving resources, proper selection of paving materials along with optimal mix and pavement design is of great importance. There are numerous laboratory investigations that have shown various beneficial effects of adding polymers to bitumen and using polymer modified binders (PMB) in asphalt mixtures (Isacsson and Lu, 1995). Performance improvements are normally found with respect to permanent deformation or rutting, fatigue resistance and low temperature cracking, particularly for modified binders with styrene-butadiene-styrene block copolymer (SBS). These improvements are also confirmed in full-scale pavement tests using for example Heavy Vehicle Simulator (HVS) (Roque et al., 2005), and field trials, such as test sections included in the Long Term Pavement Performance (LTPP) program in North America (Von Quintus, 2007) and airfield runways (Aurstad et al., 2006). The American LTPP study indicated that test sections with PMB mixtures exhibited less fatigue cracking, transverse cracking and rutting compared to conventional companion sections. Thus, the use of PMBs extends the service life of flexible pavements and HMA overlays (Von Quintus, 2007).

Despite good performance, the application of PMB to asphalt paving has been quite limited in many countries mainly because of higher initial costs. In order to determine whether it is cost-effective to use PMB and to assess its sustainable benefits on heavy trafficked roads under Nordic conditions, a test road was built in Sweden during 2003 – 2006. The objective of constructing such a test road is also to validate if binder tests can quantify the functional properties of asphalt pavements. The test road is located in Geddeknippel – Kalsås and was built as part of highway E6 north of Uddevalla. The whole project consisted of ten south-bound sections and five north-bound sections. In the south-bound sections, various PMBs and bitumens were selected for the wearing course, binder course, as well as base course, whereas in the north-bound sections trials were only made for the

wearing course. The test road has been monitored continuously, and a follow-up research project, supported by the Swedish Transport Administration, has been carried out by the Swedish National Road and Transport Research Institute (VTI) and Nynas since 2010. The project includes field measurements, testing of asphalt cores, binder tests and evaluation, deterioration modeling, and life cycle cost analysis (LCCA). The present paper is to focus on binder durability in terms of resistance to aging, rutting and cracking. For this purpose, the south-bound test sections were studied.

2. EXPERIMENTAL

2.1 Materials and Test Roads

The test road (south-bound) consisted of two reference sections and eight sections where different PMBs were used, as illustrated in Figure 1. In constructing the test sections, 100 mm base course (50 mm over-layer and 50 mm under-layer, both with mixture type AG22) was laid on 80 mm unbound in 2003/2004, and followed by 50 mm binder course of ABb22 type between May and November 2004. After about two-year traffic and in September 2006, 40 mm wearing course (ABS16) was applied to the binder course. Technical requirements for these mixture types can be found in ref (The Swedish Transport Administration, 2011). Field sampling was made in September 2010 when asphalt cores were drilled from two different positions - the wheel path (or under track) and between the tracks, denoted as UT and BT, respectively.

| Test sections | Ref 1 | 1a | 1b | 2a | 2b | 3a | 3b | 4a | 4b | Ref 2 |
|---------------------|---------|----------------|---------------|---------|---------|---------|---------|--------------|---------|---------|
| Wearing course | 70/100 | 70/100 | 50/100-75 SBS | | | 70/100 | | | 70/100 | |
| Binder course | 50/70 | 50/70 | 50/70-53 EVA | | | | | 50/70-53 SBS | | 50/70 |
| Base course - over | 100/150 | 100/150-75 SBS | | 100/150 | | | | | | 100/150 |
| Base course - under | 100/150 | 100/150-75 SBS | | 100/150 | 160/220 | 160/220 | 100/150 | 160/220 | 100/150 | 100/150 |

Figure 1. Illustration of the test sections and the binders used in different asphalt layers

Table 1 shows conventional properties of the binders selected. The modified binders were produced using different polymers and different concentrations. The 50/70-53 SBS, 50/100-75 SBS and 100/150-75 SBS contains 3, 4 and 6% SBS (by weight), respectively. In 50/70-53 EVA (ethylene vinyl acetate), the polymer content is 6%. All the modified binders are storage stable according to tube tests at 180°C and EN 14023 ($\Delta_{R\&B} \leq 5^\circ\text{C}$). Selection of the binders was based on intensive laboratory investigations on binder properties and asphalt mixture performance, including fatigue, rutting, water sensitivity, and wear resistance, etc. (Nordgren, 2004; Stenberg, 2007).

Table 1. Conventional properties of the binders used in the test road

| Asphalt layers | Binder types | Penetration, 1/mm | Softening point, °C | Tube test, $\Delta_{R\&B}$, °C |
|----------------|----------------|-------------------|---------------------|---------------------------------|
| Wearing course | 70/100 | 77 | 46 | -- |
| | 50/100-75 SBS | 58 | 98 | -1 |
| Binder course | 50/70 | 55 | 50 | -- |
| | 50/70-53 SBS | 58 | 58 | 0 |
| | 50/70-53 EVA | 52 | 66 | 3 |
| Base course | 100/150 | 127 | 43 | -- |
| | 160/220 | 190 | 38 | -- |
| | 100/150-75 SBS | 123 | 90 | -2 |

2.2 Binder Tests and Evaluation

A rather comprehensive testing and evaluation program (see Figure 2) was carried out, including various tests on binders, laboratory aging according to the Rolling Thin Film Oven Test (RTFOT, EN 12607-1) and the Pressure Aging Vessel (PAV, EN 14769), and extraction of binders from asphalt pavements. For binder extraction and recovery, the European standards EN 12697-1 and EN 12697-3 were followed. The solvent used was dichloromethane. In addition, air void contents of the field samples were determined in accordance with EN 12697-8.

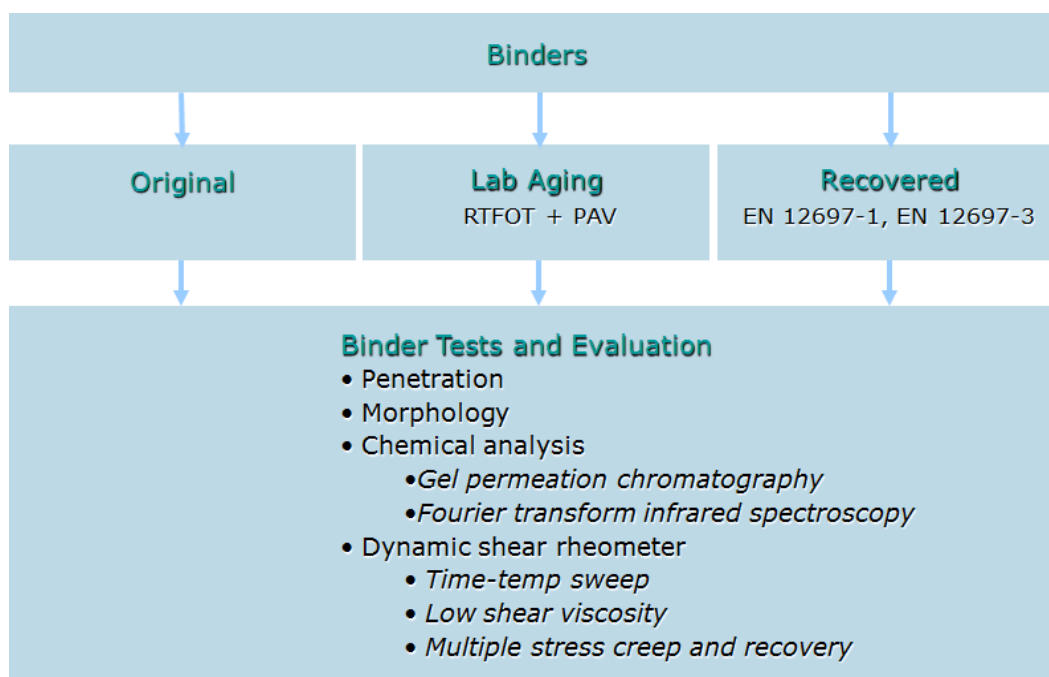


Figure 2. Outline of test program

Binders were tested by penetration, fluorescence microscope (morphology), gel permeation chromatography (GPC), Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR), and dynamic shear rheometer (DSR).

In GPC, an Alliance 2690 Separation Module (Waters) with UV or refractive index detector was employed. Sample solutions of 0.4% were prepared using tetrahydrofuran (THF). The solvent was also used as mobile phase. Calibration was carried out with polystyrene standards of known molecular weights. This technique is used to assess changes in molecular weight and molecular weight distribution.

In FTIR-ATR, a very small amount of bitumen sample (without preparing a solution) was directly placed on an ATR crystal and IR reflection from the sample was measured. Spectra were recorded at wavelengths ranging from 500 to 4000 cm^{-1} . This technique can be used to characterize polymers e.g. SBS at 966 cm^{-1} (butadiene) and 699 cm^{-1} (styrene), and bitumen functional groups, such as carbonyl compounds at around 1700 cm^{-1} and sulfoxide at about 1030 cm^{-1} .

The conducted DSR tests include frequency sweeps (0.01 to 10 Hz) at different temperatures ranging from 0 to 90°C, and multiple stress creep and recovery test (MSCR) according to ASTM D7405. Depending on test temperature, parallel plates of 25 mm in diameter and 1 mm in gap or 8 mm in diameter and 2 mm in gap were used.

3. RESULTS AND DISCUSSION

3.1 Fluorescence Microscopy

The morphologies of the modified binders measured at room temperature are presented in Figure 3. In the microscopic test, specimens were prepared by taking a drop of sample at 180°C on a glass plate. As expected, at a low concentration (3 or 4% by weight in this case), the polymer exhibits dispersed phase in the binder. At a sufficiently high concentration of 6%, a continuous polymer phase is formed. The polymer morphology may significantly influence the rheological properties of the binder (Soenen et al., 2008; Lu et al., 2010). But for mixture performance, it is probably more important to know polymer structures in the mixture or mastics and understand their structural impact. Research on this aspect is on-going.

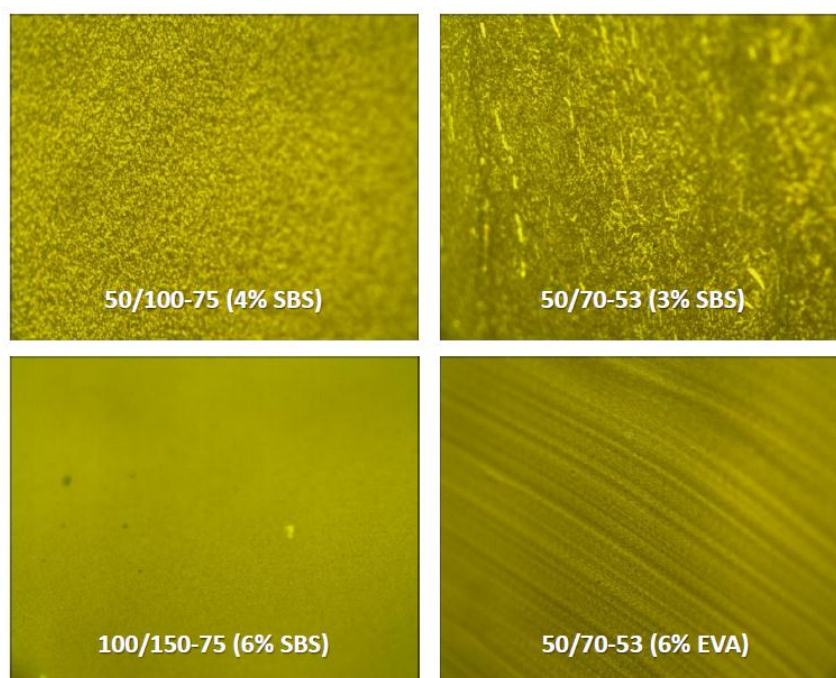


Figure 3. Fluorescence photomicrographs of PMBs (magnification 200x)

3.2 Retained Penetration

In assessing the age-hardening of bitumen or PMB over the time, an empirical parameter is retained penetration. It was found that after several years in the field, the modified binders used in the wearing course and base course generally showed higher retained penetration (i.e. less age-hardening) than the unmodified. The results are exemplified in Figure 4 for the binders extracted from the base course (AG22) which has been in the field for six years. On average, the degree of the age-hardening of 100/150-75 (SBS) is about half of that of bitumen 100/150 pen. This is probably due to polymer modification starting with soft bitumen and/or aged SBS acting as a softener in the bitumen. On the other hand, such improvement was not seen for the modified binders used in the binder course. It should be noticed that these binders were modified with EVA or with relatively low concentration SBS (3%).

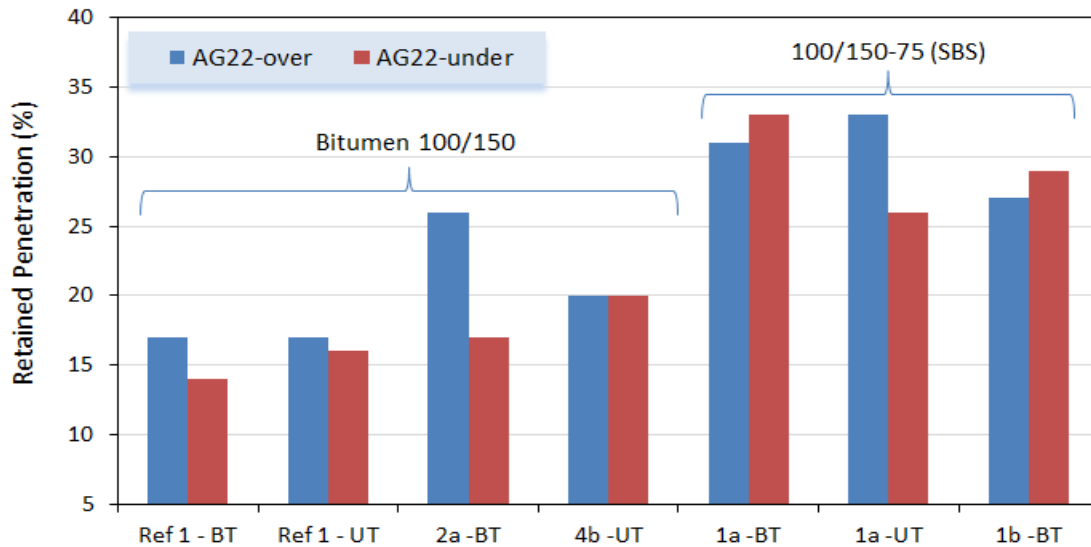


Figure 4. Retained penetration for the binders used in the base course

3.3 Rheological Characterization

Based on the DSR data obtained with frequency scans at various temperatures, master curves are constructed by applying the time–temperature superposition principle (Christensen and Anderson, 1992). Using master curves, bitumen rheological behavior and effect of aging may be characterized over wider ranges of time or frequency at a specified temperature. Examples of the master curves of complex modulus are shown in Figure 5 for the binders used in the wearing course. For both the modified and unmodified binders, the transition to the glassy state can be seen at high frequency. The differences between the binders, as well as the effect of aging, are more evident at low frequency range; the SBS modified binder exhibits higher modulus than the pen bitumen, which should be beneficial with respect to permanent deformation resistance. In addition, the master curves for the extracted binders from the wearing course (4 years on the test road) lie between the original and RTFOT-PAV aged samples, suggesting the laboratory aging test predict field aging quite well in this case.

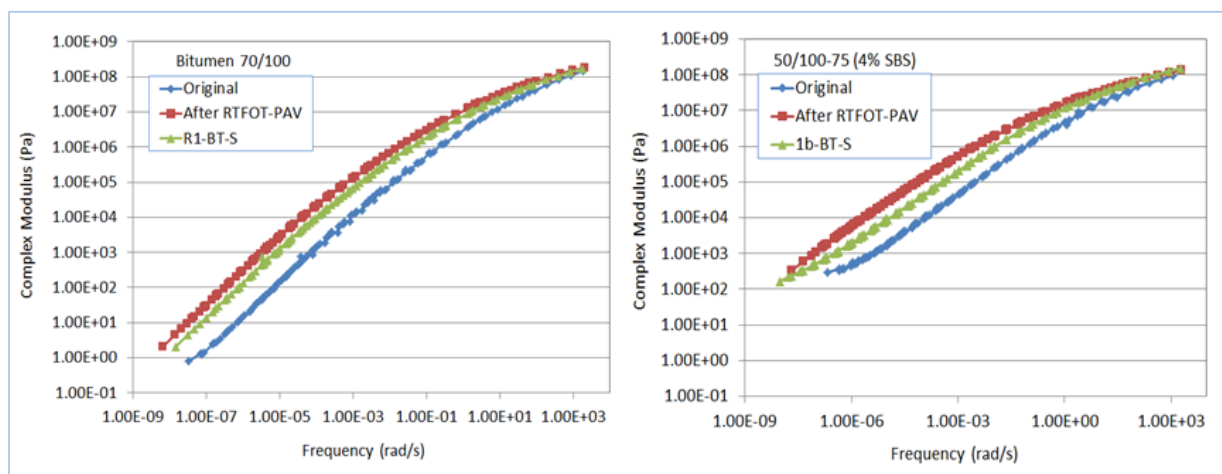


Figure 5. Complex modulus master curves at reference of 10°C for the wearing course binders (original, laboratory aged, and extracted from test road)

To quantify the aging sensitivity of the different binders in the test road, it was intended to use aging index based on the zero shear viscosity (ZSV) measurements. Unfortunately it was not possible to precisely define ZSV for most of the modified binders studied. Instead, the complex viscosities measured at a low frequency of 0.001 Hz and at 60°C are used to calculate the aging index (the low shear viscosity of the extracted binders divided by that of the original binders). The results averaged by test sections are shown in Table 2. As indicated, of the binders used in the test road, the SBS modified binders are the most resistant to aging. This was also confirmed by the stiffness measurements on asphalt mixtures (Said, 2013). It should be mentioned that the modified binders are two-phase systems where the polymer and the bitumen respond differently to oxidative aging and to dynamic loading. Thus, at a lower temperature and/or higher frequency that favours the response of bitumen, the SBS effect will decrease.

Table 2. Aging index of different binders averaged by test sections

| Test sections | Asphalt layers | Binder types | Aging index |
|----------------|----------------|--------------------|-------------|
| ref 1, 1a & 4b | Wearing course | 70/100 | 6.75 |
| 1b & 2a | | 50/100-75 (4% SBS) | 0.91 |
| ref 1 & 1a | Binder course | 50/70 | 4.28 |
| 1b & 2a | | 50/70-53 (6% EVA) | 5.05 |
| 4b | | 50/70-53 (3% SBS) | 1.02 |

Using DSR several rheological parameters are used to assess rutting resistance. One test which can distinguish the difference in rutting potential between various binders is the MSCR test (D’Angelo, 2010). The measured rutting-related parameters include strain recovery and non-recoverable compliance (Jnr). Typical examples of binder response to repeated loading during the MSCR test are shown in Figure 6, and differences in the strain recovery between the binders and the effect of aging are compared in Figure 7. Obviously, the SBS modified binders display much higher strain recovery than other binders. With 4 or 6% SBS, the shear deformation of the modified binders are almost 100% recovered.

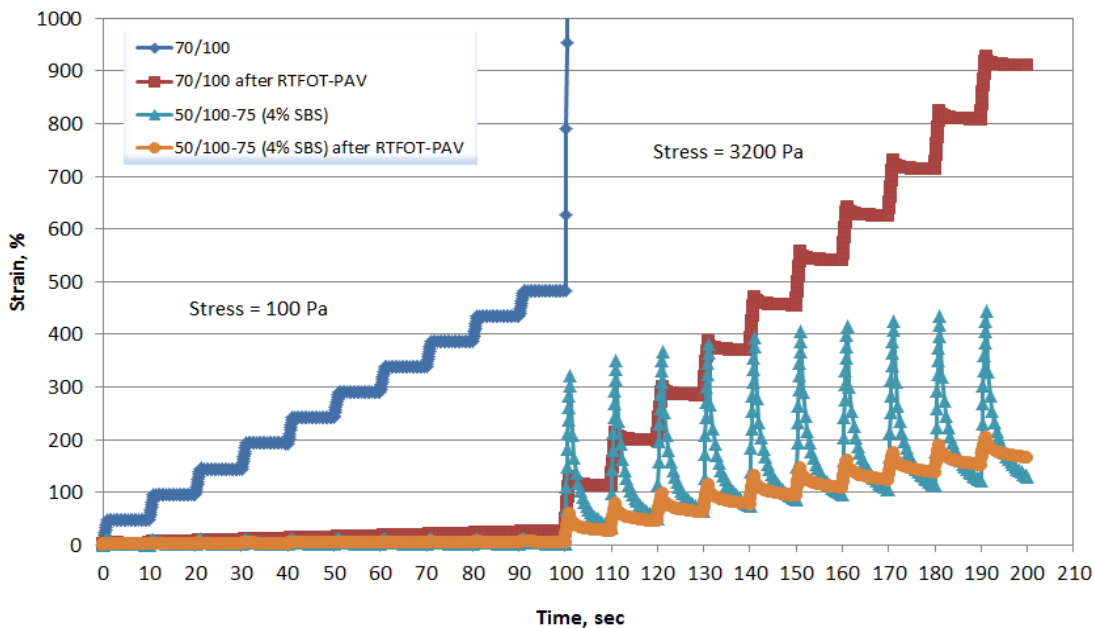


Figure 6. Strain response to repeated loading at 60°C for unmodified and SBS modified binders

As can also be seen in Figure 7, the effect of aging on the strain recovery follows the same trend for the unmodified and EVA modified binders. For these binders, the strain recovery increases after aging, and this is due to bitumen oxidation that makes the binders more elastic. In the case of SBS modification, aging may reduce the strain recovery of the binders because of oxidation of the polymer. However, even after laboratory aging or several years in the field, the SBS modified binders, especially for those containing 4 or 6% SBS, still retain higher potential for the rutting resistance as compared to other binders.

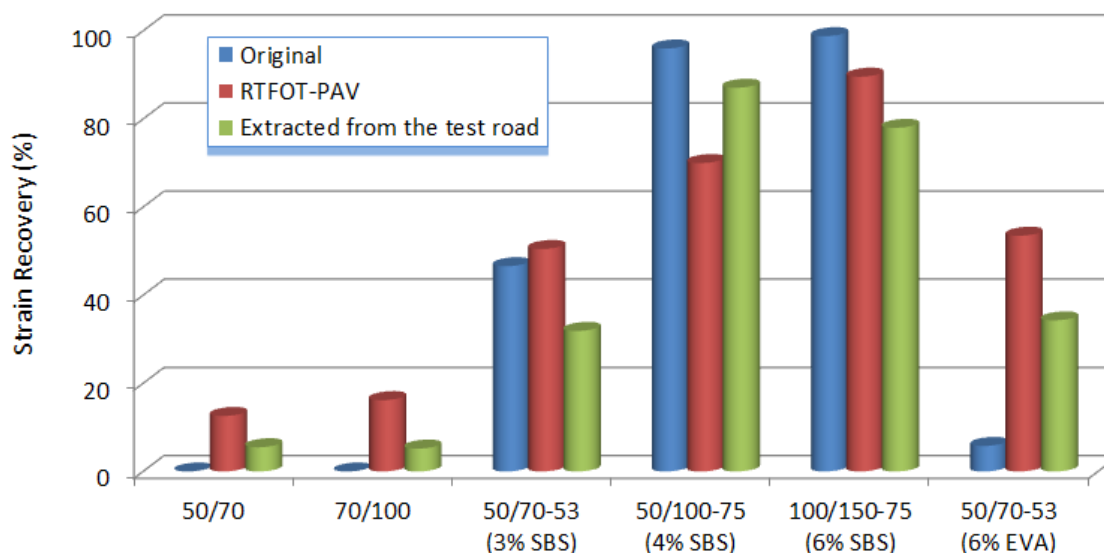


Figure 7. Comparison of strain recovery at 3.2 KPa and 60°C

The differences between the binders, as well as the effect of aging, are also evident when the non-recoverable compliances (J_{nr} 3200) are compared (see Table 3). Regardless of sample state (original, laboratory aged, or extracted from the test road), the polymer modified binders always show lower values of J_{nr} 3200 or higher rutting resistance than the reference bitumens.

Table 3. Non-recoverable compliances (J_{nr}) measured at 60°C

| Asphalt layers | Binder types | J_{nr} 3200, kPa-1 | | |
|----------------|---------------------|----------------------|-----------|-----------|
| | | Original | RTFOT-PAV | Recovered |
| Wearing course | 70/100 | 5.16 | 0.28 | 0.69 |
| | 50/100-75 (4% SBS) | 0.04 | 0.05 | 0.04 |
| Binder course | 50/70 | 3.55 | 0.41 | 0.84 |
| | 50/70-53 (6% EVA) | 1.76 | 0.04 | 0.15 |
| | 50/70-53 (3% SBS) | 1.00 | 0.09 | 0.34 |
| Base course | 100/150 | -- | -- | 0.51 |
| | 100/150-75 (6% SBS) | 0.01 | 0.08 | 0.34 |

Another aspect of particular importance to Nordic countries is low temperature cracking. This was assessed by measuring binder stiffness (complex modulus) at 0°C and 10 Hz using the 8-mm parallel plate geometry. The results obtained for the binders used in the wearing course are presented in Figure 8. Compared to the reference bitumen, the SBS modified binder remains softer at the low temperature even after several years in the test road, and this should be beneficial in terms of resistance to low temperature cracking.

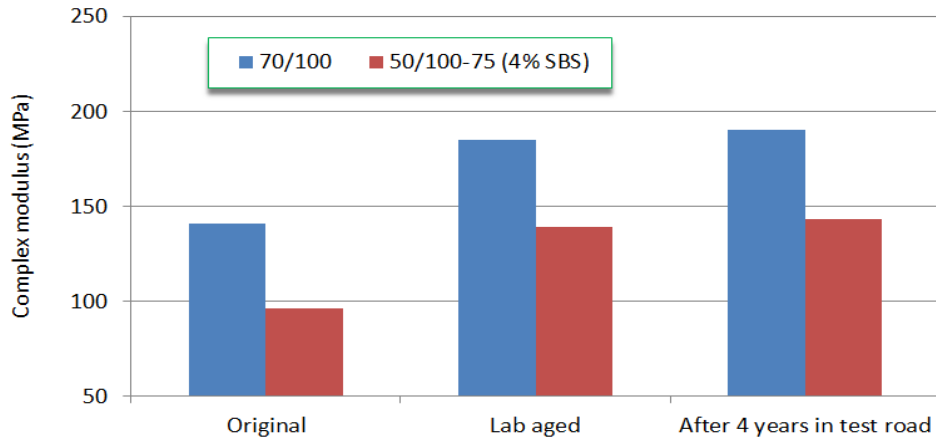


Figure 8. Complex modulus measured at 0°C and 10 Hz

As for the pavement performance of the test road, field measurements and inspection showed that all the sections are in good conditions (Carlsson, 2013). After 6 years traffic (2012), the rut depth measured on the wearing course was less than 7 mm, and differences between the different sections were small (around 2 mm). In addition, other deteriorations, such as stripping and low temperature cracking, have not been seen on the test road. To make definite comparison on performance, a longer time of follow-up on the test road is needed.

3.4 Chemical Characterization

Using FTIR-ATR, the compositional information can be obtained directly on the binders without preparation of sample solution. It was observed that aging did not change EVA as reflected by more or less unchanged absorbance at 1241 cm^{-1} for the polymer. For the SBS modified binders, and as expected, the butadiene signal at 966 cm^{-1} decreased slightly while the styrene at 699 cm^{-1} remained unchanged after aging (see example in Figure 9). It was also observed that a very small amount of filler left in the extracted binders makes it not possible to integrate peak area for the polybutadiene, as well as for 1030 cm^{-1} which is normally assigned to sulfoxides.

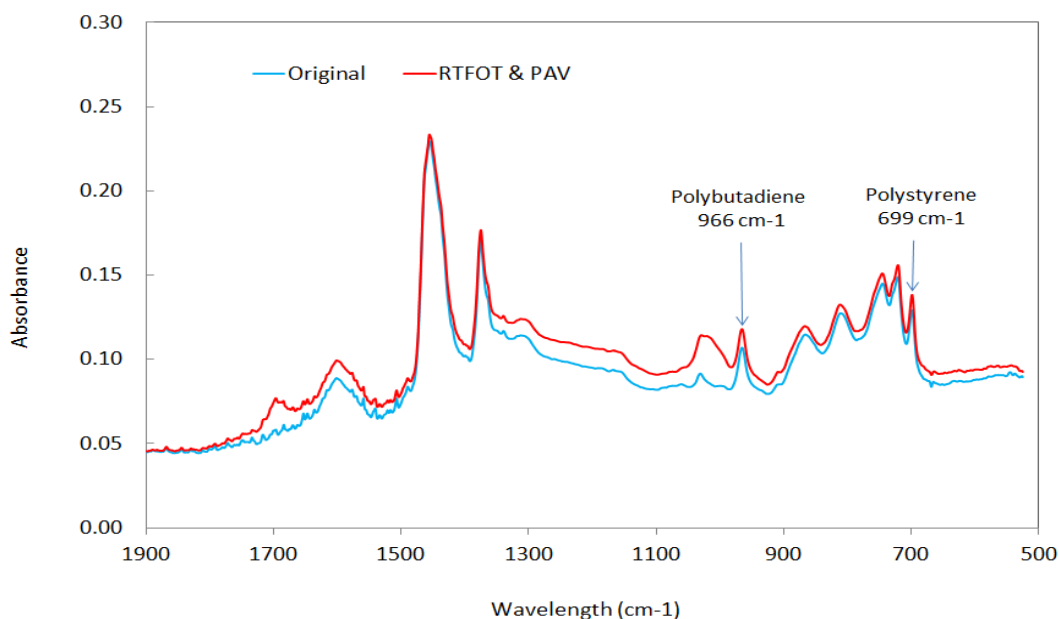


Figure 9. FTIR spectra of 50/100-75 (4% SBS) before and after aging

Although the SBS polymers take part in chemical reactions and degradation of the polymers may occur during aging, the fragments formed are still a kind of polymers that are large enough to affect the binders beneficially. This can be shown by using GPC with UV detector and estimating the contents of SBS polymer (and its fragments) via chromatogram at a polystyrene-related wavelength 210 nm (see Figure 10). As illustrated in Figure 11, the laboratory aging or field aging seems not to change the polymer contents.

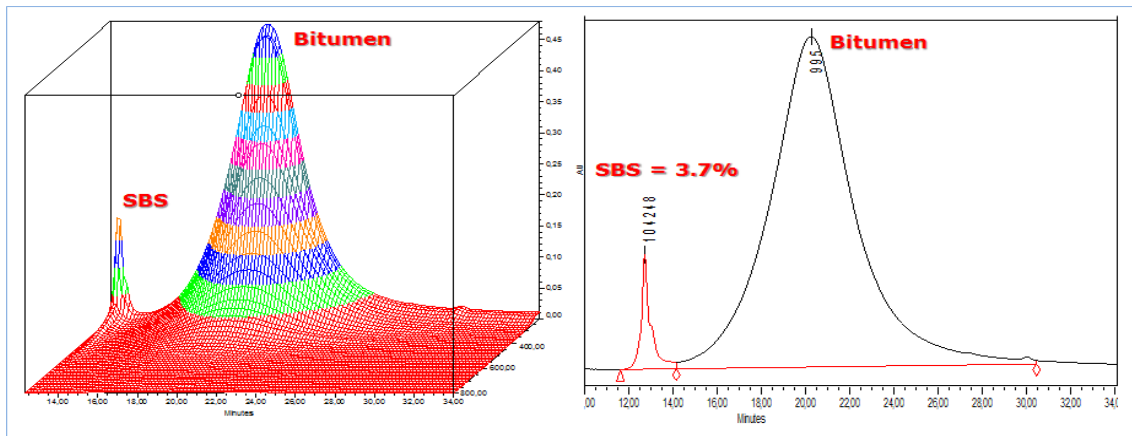


Figure 10. GPC analysis of a polymer modified binder (50/100-75, 4% SBS)

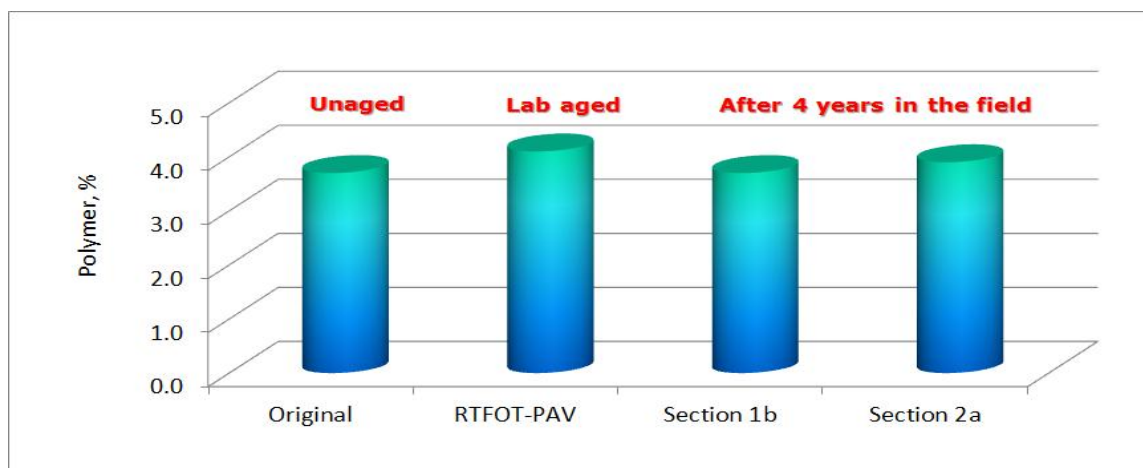


Figure 11. SBS polymer contents estimated by GPC for a wearing course binder 50/100-75

4. CONCLUSIONS

The polymer modified binders studied in this paper demonstrate better rheological properties than the unmodified bitumens, even after several years in the test road. These include higher strain recovery and lower non-recoverable compliance (J_{nr}) at high temperatures, and lower stiffness at low temperatures. For the SBS modified binders, good aging resistance is shown; and this is also supported by stiffness measurement on asphalt mixtures. The present study suggests that by a chemical compensation to the oxidative age-hardening of bitumen components, the polymer modified binders are able to retain proper rheological properties that are desired for asphalt performance. The improved binder properties should be beneficial in terms of resistance to asphalt rutting and cracking. This is expected to be confirmed by a longer time of follow-up on the performance of the test road.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Carl-Gösta Enocksson (The Swedish Transport Administration) for supporting this research, and Safwat Said and Håkan Carlsson (VTI) for their collaboration in the project. The authors also wish to thank Orjan Otterstrom (Nynas Bitumen Nordic) for his assistance in the laboratory.

REFERENCES

Aurstad J., Lange G. and Sturm D., 2006. Long term pavement performance on Norwegian asphalt runways – A field and laboratory study, in *Proc of the 10th ISAP Conference on Asphalt Pavements*, August 12-17, 2006, Quebec, Canada.

Carlsson H., 2013. E6 Uddevalla – Tillståndsutveckling PMB-provväg, *Transportforum*, January 9-10, 2013, Linköping, Sweden.

Christensen Jr D. W. and Anderson D. A., 1992. Interpretation of dynamic mechanical test data for paving grade asphalt cements, *Proc. of AAPT*, Vol. 61, pp. 67-115.

D'Angelo J., 2010. New high-temperature binder specification using multistress creep and recovery, *Transportation Research Circular E-C147*, December 2010, pp. 1-13.

Isacson U. and Lu X., 1995. Testing and appraisal of polymer modified road bitumens – state of the art, *Materials and Structures*, Vol. 28, pp. 139-159.

Lu X., Soenen H. and Redelius, 2010. SBS modified bitumens: does their morphology and storage stability influence asphalt mix performance, in *Proc of the 11th ISAP Conference on Asphalt Pavements*, August 1-6, 2010, Nagoya, Japan.

Nordgren T., 2004. PMB identifiering av egenskaper i bitumen som ger rätt egenskaper i beläggning, *SBUF Rapport (projekt 11138, 11400)*.

Roque R., Birgisson B., Drakos C. and Sholar G., 2005. Guidelines for use of modified binders, *Final Report 4910-4504-964-12*, University of Florida.

Said S., 2013, Asfaltmassans funktion E6 PMB – provväg, *Transportforum*, January 9-10, 2013, Linköping, Sweden.

Soenen H., Lu X. and Redelius P., 2008. The morphology of bitumen-SBS blends by UV microscopy - An evaluation of preparation methods, *Road Materials and Pavement Design*, Vol. 9, pp. 97-110.

Stenberg N., 2007. PMB – Inverkan på asfaltbelägningens funktionella egenskaper, *SBUF Projekt 11692*.

The Swedish Transport Administration, 2011, TRVKB 10 Bitumenbundna lager, TRV 2011:082.

Von Quintus H. L., Mallela J. and Buncher M., 2007. Quantification of effect of polymer-modified asphalt on flexible pavement performance, *Transport Research Record*, No. 2001, pp. 141-154.