

# SBS Modified Bitumens: Does Their Morphology and Storage Stability Influence Asphalt Mix Performance?

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**ABSTRACT:** This paper studies the influence of morphology and storage stability of polymer modified binders on the mechanical performance of asphalt mixes, in particular permanent deformation and fatigue characteristics. Four 70/100 pen bitumens of different crude origins and a linear SBS were selected to prepare polymer modified binders (PmBs). The binders showed differences in morphology, storage stability and in phase separation diagram; their rheological properties were found to be strongly morphology-related. To study the asphalt mix, a dense graded asphalt was selected. Mixing was conducted at 180°C, and asphalt specimens were prepared at the same temperature using a gyratory compactor. Permanent deformation and fatigue were characterised by triaxial test at 50°C and indirect tensile test at 10°C, respectively. It was shown in loose mixes and in compacted specimens that all PmBs displayed a similar morphology and that the polymer was seen as a discontinuous phase. In the triaxial test, little differences were found in final accumulated strains between the different mixes. The mixes also behaved similarly with respect to the amount of recoverable strain. However, the mixes differed largely in the fatigue performance. The fatigue and permanent deformation of the mixes had no relation to the differences in the storage stability and morphology of the modified binders. The present study also suggests that mix performance will not be properly predicted by testing PmBs if the morphology in the binder deviates from that in the mix.

**KEY WORDS:** Polymer modified bitumen, morphology, storage stability, permanent deformation, fatigue.

## 1 INTRODUCTION

The functionality of a polymer modified binder (PmB) is often believed to depend on the compatibility between the bitumen and the polymer. In this case compatibility is defined as the tendency not to separate on storage. The compatibility property is generally assessed by microscopy (morphology) and a storage stability test. In literature, it has been shown that PmB morphology and storage stability depend on the chemical nature of the base bitumen, the characteristics and contents of the polymer, as well as the manufacturing process (Masson et al. 2003, Pérez-Lepe et al. 2007, Wilson et al. 2000). It has also been demonstrated that for a given PmB, morphology and storage stability are influenced by the temperature and the thermal history of the binder (Soenen et al. 2009). Modified binders of “unfavourable”

morphology may show small or non improvement in mechanical properties while poor storage stability may lead to phase separation during storage and inconsistent binder quality.

The purpose of this paper is to study if the morphology and storage stability of polymer modified binders influence the mechanical performance of asphalt mixes. By a careful selection of various base bitumens and an SBS polymer, modified binders of varying storage stability and morphology were prepared. Asphalt mixes made of different PmBs were studied by microscopy for morphology, triaxial test for permanent deformation, and indirect tensile test for fatigue characteristics.

## 2 EXPERIMENTAL

### 2.1 Materials and Sample Preparation

Four 70/100 pen bitumens of different origins and a linear SBS polymer (Kraton D-1101CU) were selected to prepare PmBs. Typical parameters of the base bitumens are shown in Table 1. The weight average molecular weight of the polymer is 189000 and the styrene content is about 30%. PmBs were prepared at 180°C using a low shear mixer at 500 rpm. The mixing time was 3 hours. Polymer content was 5% by weight of the blend. Conventional test results of the PmBs are shown in Table 2. According to EN 14023, the modified binders PmB2 and PmB3 are storage stable ( $\Delta_{R\&B} \leq 5^\circ\text{C}$ ) while PmB1 and PmB4 are not stable ( $\Delta_{R\&B} > 5^\circ\text{C}$ ) at 180°C.

Table 1: Typical parameters of the base bitumens

Bitumen	Pen, dmm	R&B, °C	Iatrosan SARA analysis (%)			
			Saturates	Aromatics	Resins	Asphaltenes
B1	99	43.0	8	52	20	20
B2	93	43.2	7	55	22	16
B3	86	43.4	8	55	22	15
B4	93	45.5	4	62	18	16

Table 2: Conventional tests of polymer modified binders

Modified binders	Penetration, dmm	Softening point (R&B), °C	Storage stability (diff. in R&B), °C
PmB1	57	76.0	45.2
PmB2	52	85.0	0.0
PmB3	56	77.8	-1.0
PmB4	52	65.0	32.0

Asphalt mixes were prepared in accordance with the Swedish ABT11, a dense graded asphalt concrete with a maximum aggregate size of 11 mm, with a binder content of 6.5% by weight and an air void content of 3%. The selected aggregates were crushed granite. The temperature of asphalt mixing was 180°C, and the mixing time was about 2 minutes. After mixing, each loose mix was divided into several equal portions and stored at the same temperature of 180°C. Cylindrical specimens of 100 mm in diameter and 65 mm in height were prepared using a gyratory compactor. Density and air voids of the specimens were measured. The obtained mixes with four modified binders were coded as M-PmB1, M-PmB2, M-PmB3, and M-PmB4, respectively.

For each mix, at least 20 gyratory specimens were prepared; three were used directly in the triaxial test. For the fatigue test, 15 specimens of 50 mm in height were prepared by cutting off the top and bottom of the gyratory samples. From the compacted specimens (one for each mix), plane and thin sections were also prepared (Wegan and Brule 1999) to study microstructure of the modified binders in the asphalt mixes.

## 2.2 Binder Tests

The storage stability of PmBs was measured according to EN 13399 in which an aluminium foil tube filled with the binders was stored vertically at 180°C for three days. The samples taken from the top and bottom of the tube were used for measuring difference in softening point. For certain PmBs, the storage stability was also tested at other temperatures ranging from 130°C to 160°C. In addition, polymer concentrations of top and bottom parts after the tube storage were determined by means of Fourier transform infrared spectroscopy (FTIR). To determine the polymer concentration from FTIR, a calibration curve was developed using a series of standards of known polymer concentrations ranging from 1% to 11%.

Fluorescence microscopy was used to study morphology of PmBs at different temperatures and of different thermal histories. This was conducted by using different sample preparation methods including a drop method and freeze fracture method (Soenen et al. 2009). In the drop method, samples were prepared by taking a small drop from a hot can, and by letting this drop fall on a glass plate at ambient temperature. In the freeze fracture method, sample specimens were prepared by fracturing the binders which were cooled in a mould.

In the DSR tests, frequency sweeps were carried out from 0.01 to 10 Hz and at different temperatures ranging from -10°C to 90°C. Parallel plates of 8 mm or 25 mm in diameter were used, depending on the stiffness level of the binders.

## 2.3 Asphalt Mix Tests

A fluorescence microscope was used to visualise PmB structure in the asphalt mix. The observations were conducted on plane and thin sections of gyratory compacted specimens, the fractured surface of a broken compacted specimen, as well as on loose mixes.

Triaxial test was selected to evaluate permanent deformation. It was performed basically in accordance with EN 12697-25 “Cyclic compression test: Test method B - Triaxial cyclic compression test”. Test control and data acquisition were conducted using a MTS Teststar II system. Asphalt specimen (100 mm in diameter, 65 mm in height) was mounted in a triaxial cell, which was subsequently filled with silicon oil. The test temperature was 50°C and asphalt specimen was conditioned at this temperature for 3 h before testing. Test procedure comprised a pre-loading and a conditioning period followed by the main cyclic loading. Initially, a small contact load of approximately 5 kPa was maintained. Then the deviator stress was increased to 22 kPa over a period of 10 s. This stress level was held constant for an additional 110 s then the confining stress was raised to 150 kPa over a period of 5 s. After an additional 5 s, the cyclic loading test started under sinusoidal deviator stress (3 Hz) with a maximum of 1000 kPa and a minimum of approximately 20 kPa, and under a constant confining pressure of 150 kPa. The number of loading cycles was 15000. The selection of above stress conditions was based on a series of tentative tests. After the axial cycling, the confining stress was gradually reduced to zero during 30 s. The axial strain was monitored for an additional 10 minutes (recovery period). In determining the amount of strain accumulation, the accumulated strain after the axial pre-loading (i.e. 120 s) was used as a reference or zero level.

Indirect tensile test (ITT) was selected to characterise the fatigue properties of asphalt mixes and to measure their stiffness. Tests were carried out at 10°C in accordance with EN 12697-26 annex C for stiffness and EN 12697-24 annex E for fatigue. Specimens of 100 mm in diameter and 50 mm in height were prepared by trimming the gyratory compacted samples, as described in Section 2.1. In the indirect tensile fatigue test, the cylindrical specimens were exposed to a repeated haversine loading with a loading duration of 0.1 s followed by a 0.4 s rest period (i.e. a frequency of 2 Hz) through the vertical diametral plane. The resulting horizontal deformation of the specimen was measured and used to calculate tensile strain at the centre of the specimen. The initial strain was calculated after stabilisation of the horizontal deformation, which normally occurred after 60 load repetitions. In this study, the initial strain was calculated from the average horizontal deformations of five load applications from 98 to 102. Fatigue life was defined as the total number of load repetitions when complete fracture of the specimen occurred (Cf. Section 3.5).

### 3 RESULTS AND DISCUSSION

#### 3.1 Polymer Modified Binders – Morphology and Storage Stability

Morphologies of the PmB samples at different temperatures are shown in Figure 1. It is evident that the morphology of the selected PmBs is very temperature-dependent, and the temperature for achieving a homogenous system is binder specific. For the storage stable samples PmB2 and PmB3 (Table 2), a fine dispersion of the polymer is seen at temperatures equal to or higher than 160°C, whereas the storage unstable samples PmB1 and PmB4 show heterogeneous phases up to and above 180°C. At 120°C, all the PmBs show a very similar appearance of phase separated structure even though the samples were stirred.

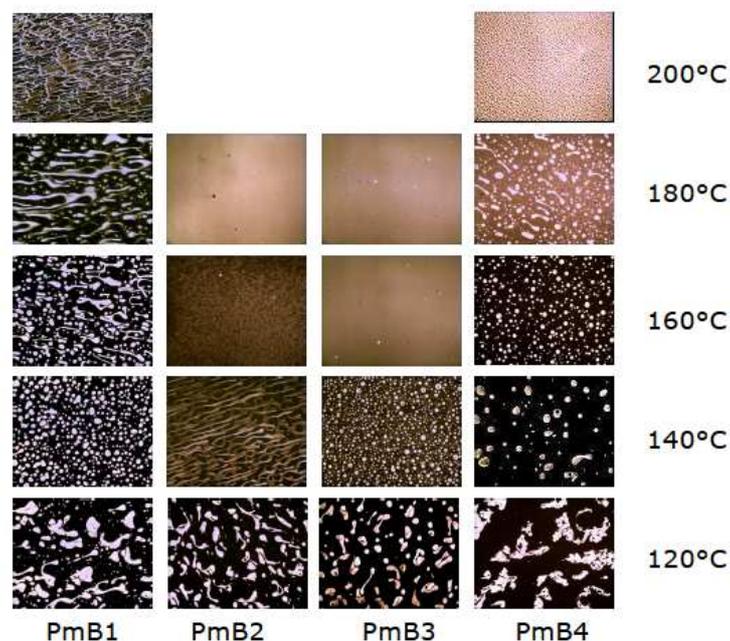


Figure 1: Morphologies of the PmB samples taken at 200°C and after 1 hour isothermal annealing at different temperatures (magnification = 50x)

The morphologies shown in Figure 1 give indications about the storage stability of the modified binders and the temperature dependence of the storage stability. For example, a fine and homogeneous dispersion of polymer indicates storage stability. On the contrary, a coarse polymer phase is not storage stable. At a temperature lower than 140°C, all the PmBs are expected to be unstable ( $\Delta_{R\&B} > 5^\circ\text{C}$ ) because of their phase-separated structures. This has been confirmed by the storage stability tests made for the selected binders in Table 3.

Table 3: Storage stability tests of PmB1 and PmB2 at different temperatures

Temp. (°C)	PmB1 (R&B, °C)			PmB2 (R&B, °C)		
	Top	Bottom	$\Delta$ R&B	Top	Bottom	$\Delta$ R&B
200	82.8	58.8	24.0	--	--	--
180	99.6	54.4	45.2	86.5	86.0	0.5
160	101.0	53.7	46.3	91.9	90.6	1.3
140	99.6	54.3	45.3	97.5	62.3	35.2
130	101.2	54.3	46.9	103.9	54.5	49.4

Since in the tube test, it is possible to physically separate the polymer-rich phase from the bitumen-rich phase, in this study these phases were investigated further using FTIR. The so-determined phase separation diagrams for PmB1 and PmB2 are shown in Figure 2. As expected both diagrams show an upper critical solution temperature, meaning that compatibility decreases upon cooling. The phase separation diagrams also show differences between the two binders tested. PmB2 shows a better compatibility than PmB1 at high temperatures; however, at lower temperatures (< 140°C) the difference between the two binders is much less. This is in agreement with microscopic observations.

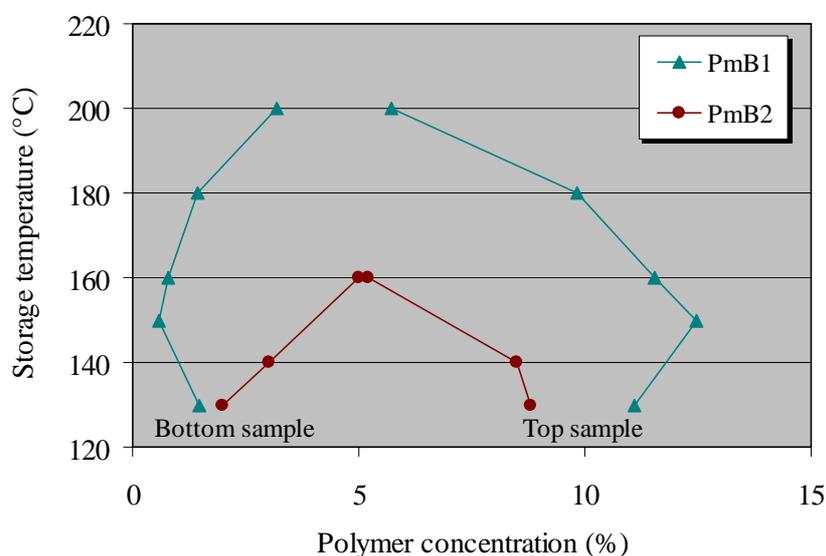


Figure 2: Phase separation diagrams of PmBs based on FTIR determined SBS concentrations

### 3.2 Polymer Modified Binders - Effect of Morphology on Rheological Properties

The rheological properties of the modified binders are largely influenced by their morphology. An example showing such influence is illustrated by black diagrams (i.e. complex modulus vs phase angle) together with the corresponding morphologies in Figure 3. In the left figure of Figure 3, the black diagram of unmodified bitumen is also shown as a

reference. For the same modified binder PmB2, one sample was prepared by quick cooling to the testing temperature and another sample was isothermally conditioned at 120°C for 30 min before further cooling to the testing temperature. By the quick cooling, the homogenous morphology was retained at the lower temperatures. As can be seen, the specimen of a homogeneous morphology and of a polymer network displays a rubbery-like behaviour at a phase angle of 40 – 60° and stiffness around 10<sup>3</sup> – 10<sup>4</sup> Pa. However, for the sample of polymer as a separated phase, the rubbery-like behaviour is much weaker. Similar observations are also made for other PmBs as shown in the right figure of Figure 3.

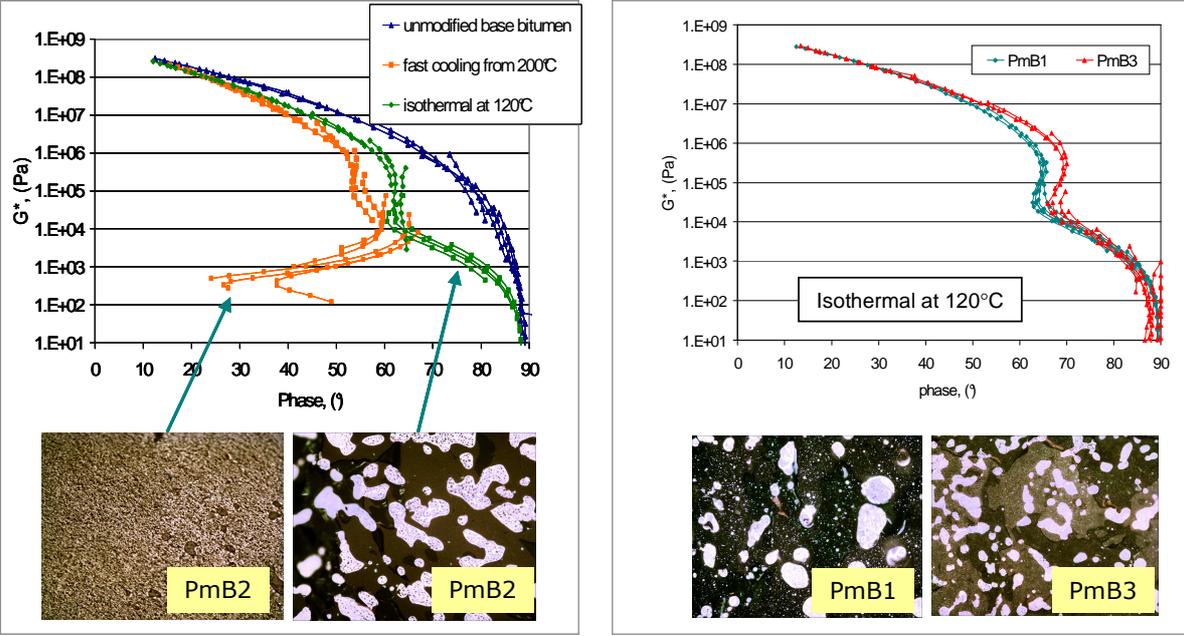


Figure 3: Binder rheology as related to thermal history and morphology

### 3.3 Asphalt Mixes - Microscopic Observations

Morphology of the modified binders in asphalt mix was studied by using different forms of samples, including thin section, freeze fractured surfaces, and loose mix. Typical examples of the microscopic pictures taken on thin sections (20 µm) are shown in Figure 4 along with an unmodified mix as a reference. For the four mixes studied in this paper, the observed morphologies are very similar and can be described as distinct polymer-rich phases (seen as small yellow spots in Figure 4) which are randomly dispersed in a continuous bitumen-rich matrix. A more detailed discussion on the morphology of binders and mixes can be found elsewhere (Soenen et al. 2009).

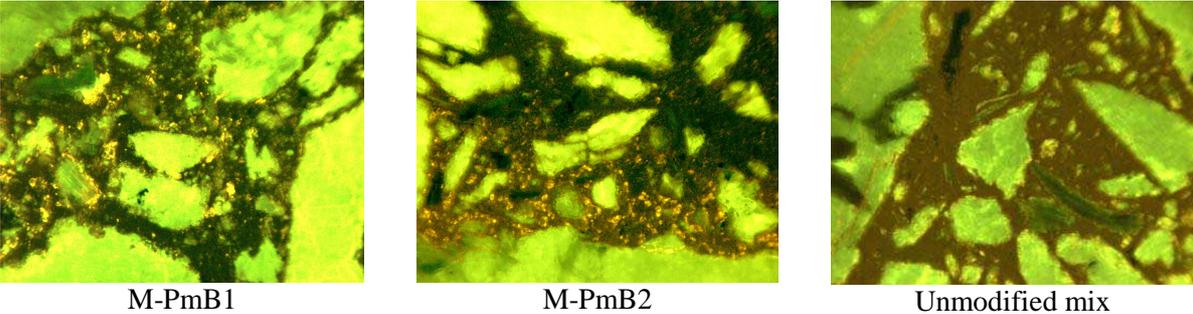


Figure 4: Microscopic pictures taken on thin asphalt sections (magnification = 100x)

### 3.4 Asphalt Mixes - Permanent Deformation

Permanent deformation of asphalt mixes was studied by the triaxial test at 50°C. For each mix, three specimens were tested. Results are exemplified in Figure 5, in which the acquired data are fitted to power-law functions. In Figure 5, a strain recovery phase is also shown. This is intended to examine the viscoelastic recovery of the mixes after 15000 loading cycles.

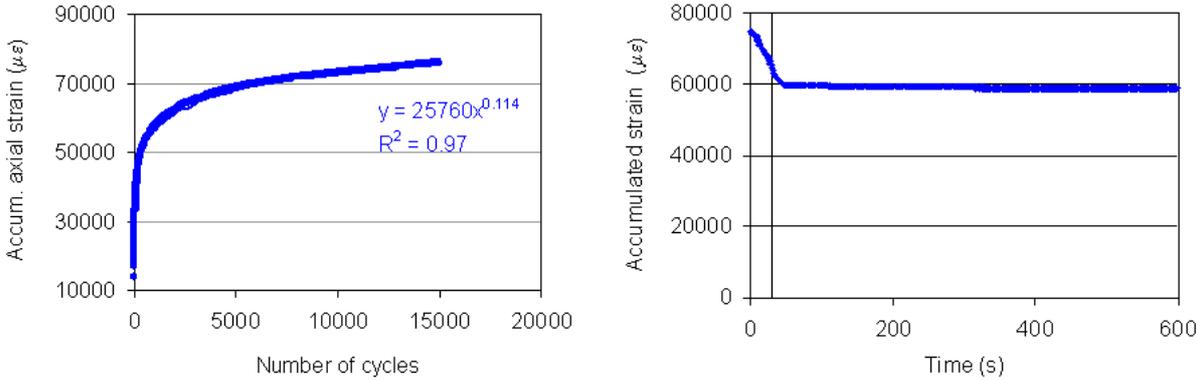


Figure 5: Typical triaxial test result (left) and strain recovery (right) for the mix M-PmB1

The averaged values of permanent deformation together with maximum and minimum points and the recovered strains are compared in Figure 6. As a reference, testing of a mix with an unmodified 70/100 bitumen is also shown. Figure 6 indicates that the mixes made with the modified binders perform better than the one with unmodified bitumen. However, the mixes with different PmBs behave fairly similar not only in the amount of the permanent strain but also in the strain recovery. In fact, after an unloading sequence (first 30 s), only a minor viscoelastic recovery is observed during approximately 20 s, and subsequently further recovery is very small (see Figure 5). The total strain recovery was found to be 20 – 25% for all the mixes tested.

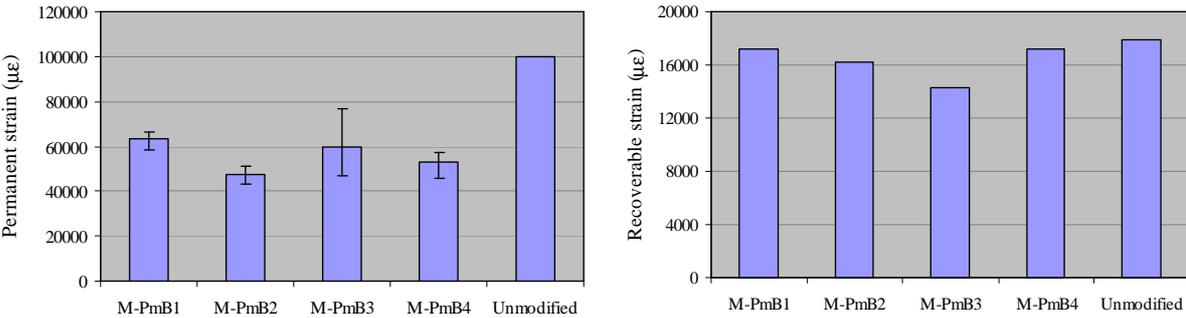


Figure 6: Permanent and recovered strains for different mixes

Regarding the slopes of log-log curves between 1 – 15000 cycles, statistical analysis showed no significant differences between the different PmB mixes. The average slope was found to be 0.121, which is less than that for the unmodified mix (0.192).

The small differences between the mixes are not surprising if the morphologies of the PmBs in the respective mixes are considered. As already exemplified in Figure 4, in all the investigated mixes the polymer is concentrated in the distinct phases in a continuous bitumen-rich matrix. Consequently, it can be expected that main deformation is borne by the

continuous bitumen-rich phase. The improvement as compared to unmodified binder could be due to the fact that the polymer-rich domains are acting as reinforcement and that bitumen-rich matrix contains certain amount of polymer. Based on the storage stability tests made at lower temperatures and the phase separation diagrams in Figure 2, the polymer content in the bitumen-rich phase is around 1.5%.

The above observations on the mixes agree well with the rheological tests performed on the PmB binders of phase separated morphologies (see Section 3.2). Being isothermally conditioned at 120°C, all the PmBs are phase separated and behave very similarly in rheology; however, improvement is still seen as compared to the unmodified binder.

### 3.5 Asphalt Mixes – Stiffness and Fatigue Characteristics

The fatigue properties, as well as stiffness, of the asphalt mixes were measured using the indirect tensile test (ITT) at 10°C. For stiffness measurement, five specimens were tested. Average of test results and standard deviations are summarised in Table 4. For comparison, results of the corresponding unmodified mixes are also shown in Table 4. As can be seen, the differences in stiffness between the mixes are mainly attributed to the use of different base bitumens. This is consistent with the rheological observation on the binder that stiffness at a temperature around 10°C is determined by the corresponding based bitumen (data not shown).

Table 4: Mix stiffness measured using ITT at 10°C

Modified mixes	M-PmB1	M-PmB2	M-PmB3	M-PmB4
Stiffness (MPa)	7274	9987	11086	9287
Sdv	280	287	1243	726
Unmodified mixes	M1	M2	M3	M4
Stiffness (MPa)	7274	10357	10870	8073
Sdv	212	710	425	594

There are a number of tests available for the fatigue characterisation of asphalt mixes. The selection of ITT is mainly because of its simplicity, and its good correlation with more fundamental tests such as the uniaxial tension-compression and trapezoidal tests (Cocurullo et al. 2008). As a type of constant-loading test, fatigue life ( $N_f$ ) is normally defined as the total number of load repetitions when complete fracture of the specimen occurs (Figure 7). The strain is computed from the total horizontal deformation during a loading period. The total deformation may consist of both elastic part and viscoplastic part (permanent deformation). The accumulation of permanent deformation can be significant, which causes a large error in measurement of the fatigue life if a continuous haversine loading is applied (Di Benedetto et al. 2004; Said and Wahlström 2000). However, by using a cyclic loading with rest periods, which is the case in this study, the effect of permanent deformation is negligible. Moreover, the cyclic loading with rest periods is believed to be more representative of field conditions than that without rest periods.

In order to establish the fatigue relationship at the test temperature, 12 specimens of each mix were tested under a range of loading levels. The load levels were selected to ensure reasonable initial strains (in most cases 100 to 400 micro strains, or  $\mu\epsilon$ ). The developed fatigue line is expressed as  $N_f = K (1/\epsilon)^n$ , where  $K$  and  $n$  are mix-dependent constants.

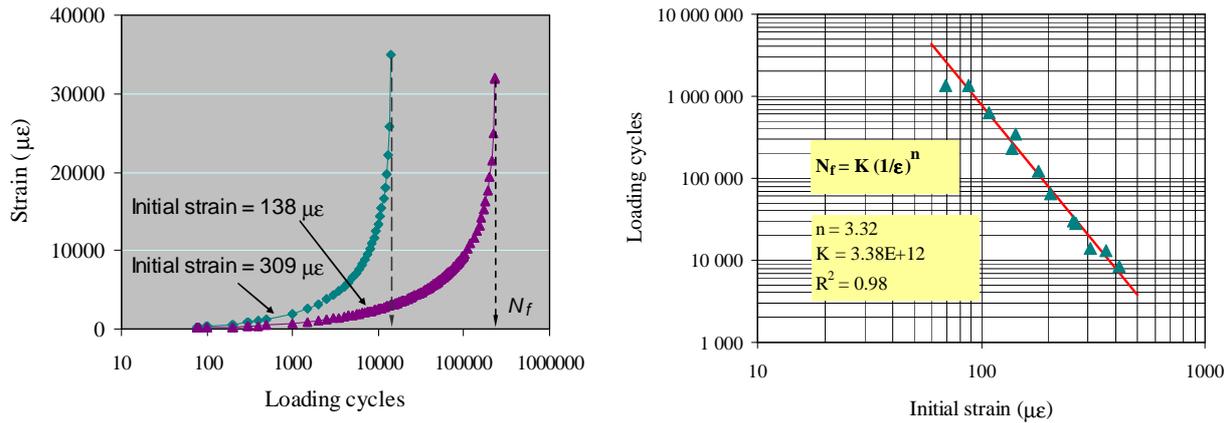


Figure 7: Examples of fatigue tests and fatigue line for the mix M-PmB1

The fatigue lines developed for the four modified mixes are shown in Figure 8. As indicated, the mixes differ in the strain (stress) dependence of the fatigue life. Consequently, they may be ranked differently depending on strain levels. For a simple comparison, the initial strains for one million cycles ( $\epsilon_6$ ) are calculated. Those are  $93 \mu\epsilon$  for M-PmB1,  $84 \mu\epsilon$  for M-PmB2,  $88 \mu\epsilon$  for M-PmB3, and  $100 \mu\epsilon$  for M-PmB4. On the other hand, at a high tensile strain level of  $300 \mu\epsilon$ , the loading cycles to failure for the four mixes are 20670, 6060, 12770, and 9320, respectively.

The varying fatigue performance of the mixes is not dependent on the storage stability of the modified binders. As a cyclic haversine loading with rest periods is applied in the fatigue test, the observed differences in the strain (stress) dependency may reflect different self-healing potentials that the modified binders have. This could be verified by tests of continuous loading or changing ratios of loading and rest periods, which is outside the scope of this study.

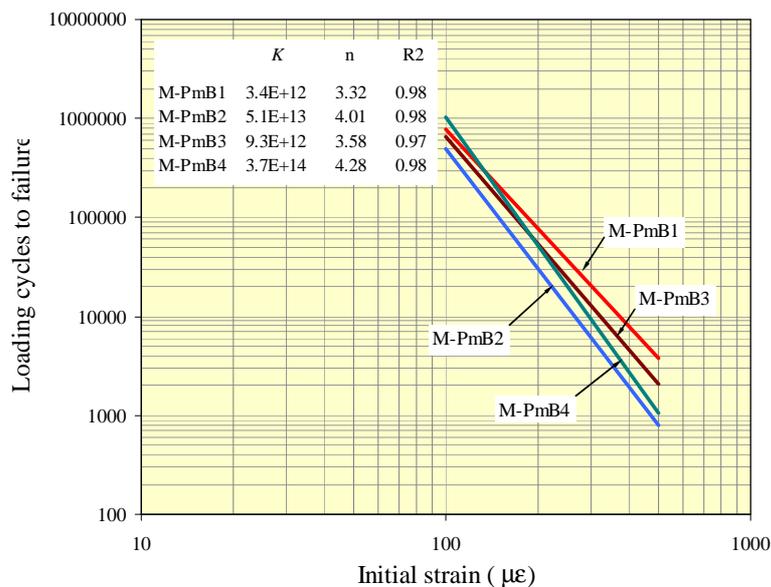


Figure 8: Fatigue lines – comparison of the mixes produced with different PmBs

## 4 CONCLUSIONS

Based on the results and discussion presented above, the following conclusions can be drawn:

As expected, the morphology and storage stability of the SBS modified binders are base bitumen dependent. They are also greatly influenced by the temperature and thermal history.

The storage stability of polymer modified binders is only relevant at the temperature where it is tested. It can be very different at different temperatures.

The morphology of polymer modified binders strongly influences the rheological properties. Even for one and the same binder, large differences may be introduced through for example different procedures of sample preparation or thermal treatments.

All the modified binders display similar microstructures in loose asphalt mixes and in compacted specimens, both showing a discontinued polymer-rich phase in a continuous bitumen-rich phase.

The performance of the polymer modified mixes has no relation to the storage stability and compatibility of the modified binders. In spite of the polymer modified binders with varying storage stability at 180°C, the triaxial test shows little difference in the final accumulated strain and almost no difference in the recoverable strain between the mixes. The mixes differ in the fatigue performance; however, these differences cannot be attributed to the differences in morphology and storage stability between the different binders.

The study also implies that the mechanical performance of asphalt mixes will not be properly predicted by testing of the modified binders if the morphology in the binder deviates from that in the mix.

The above conclusions are based on the investigated samples, in which the main parameter that was varied was the type of base bitumen. Effects of other variables, such as polymer type, polymer concentration, and asphalt mix type, still need to be investigated.

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