# RHEOLOGY OF POLYMER MODIFIED BITUMEN: A COMPARATIVE STUDY OF THREE BINDERS AND THREE BINDER/FILLER SYSTEMS

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## Abstract

Polymer modified bitumen (PMB) is used extensively in thin asphalt surfacings and seals. PMB has to be characterised differently from penetration grade bitumen and the improved performance properties are difficult to demonstrate with conventional empirical rheological tests.

This paper gives an overview of a test programme that was followed to characterise bitumen-rubber and SBS modified bitumen using conventional as well as non-conventional methods. The effect that filler addition has on binder properties was also investigated. The characterisation was done through fundamental rheological tests. This paper focuses on the testing that was done using a state of the art dynamic shear rheometer at Natref's laboratory in Sasolburg.

In this study three binders were compared:

- 60/70 penetration grade bitumen
- SBS modified 60/70 bitumen
- Bitumen-Rubber

A mineral filler prevalent to the Western Cape was used with the binders in binder/filler mixes. The binder/filler ratio in all cases was 50/50 by % volume.

The dynamic shear rheometer was used to perform frequency sweeps on the binders and binder/filler systems in the temperature range of 5°C to 75°C. The results of the frequency sweeps were used to construct Master Curves and Black Diagrams. From the two types of curves, the influence of both rubber addition and filler addition was determined.

The high temperature behaviour of the binders was also studied.

The conclusions that could be drawn based on the results of this study include:

- Bitumen-Rubber and SBS binders show very different behaviour compared to the 60/70 bitumen in the Black Diagram: from the Black Diagram it is clear that PMB has better performance, especially when high temperatures/low frequencies are considered.
- The high temperature behaviour of SBS modified binders differs from normal penetration grade bitumen: the SBS exhibits shear thinning behaviour while the 60/70 exhibits normal Newtonian behaviour. Thus, the shear rate during mixing and compaction is very important when PMB is used.

## Introduction

Bitumen specifications that are used today are based on empirical tests. Binder properties are characterised by tests such as the penetration test and viscosity measurements. The results of these tests, in conjunction with tools such as the Bitumen Test Data Chart (BTDC) and Van Der Poel Nomogram, have been used extensively for the characterisation of binder behaviour and prediction of binder properties for use in asphalt design methods.

The empirical tests and viscosity measurements, however, fail to characterise the improved performance of polymer modified binders. The improved performance can be characterised by means of fundamental rheological characterisation of the binders. Test methods and apparatus for this type of fundamental characterisation have improved enormously over the past two decades. Due to the relative newness of these tests and the high initial cost for the acquisition of the testing apparatus, the binder industry is reluctant to use them. However, the benefits that can be gained from the fundamental characterisation of binder properties are high. For instance, by using a Black Diagram the increased resistance to permanent deformation is immediately characterised when a modified binder and unmodified binder are compared. (A Black Diagram gives the change in phase angle with the change in complex modulus.)

Rheology is a very important field of study for bitumen technologists. A thorough study of the behaviour of bitumen under different loading (load and frequency) and temperature domains can go a long way in the prediction of the binder's behaviour in the field.

When the empirical measures are used to characterise binder properties (e.g. penetration, softening point, ductility, etc.) a value is obtained at the end of the test. These results are difficult to correlate with binder performance. When, on the other hand, binder characterisation is done fundamentally, e.g. using the Dynamic Shear Rheometer (as was the case in this study), it is easier to correlate the property measured and binder performance, e.g. the Black Diagram shows phase angle at different complex moduli. The phase angle can be used directly to predict binder performance under different load and temperature regimes; high temperature viscosity measurements may show unusual behaviour for polymer modified binders – this knowledge can be used to determine mixing and compaction temperatures. It is for this reason that fundamental characterisation of binder properties is superior to conventional empirical characterisation. Figure 1 shows this graphically.

This paper gives an overview of a test programme that was followed to characterise and compare the influence of polymer and filler addition on binder properties with the interpretation of the results and discussion. This research forms part of a larger effort to correlate binder properties to mix performance – the first step to the mix being the binder/filler component. In the following section the test programme that was followed is described.

## Test Programme

This study focuses on the fundamental rheological characterisation of three binders: a 60/70 penetration grade bitumen; a 60/70 bitumen modified with 3% by mass SBS; and a bitumen-rubber binder.

The fundamental characterisation was done by means of the Dynamic Shear Rheometer.

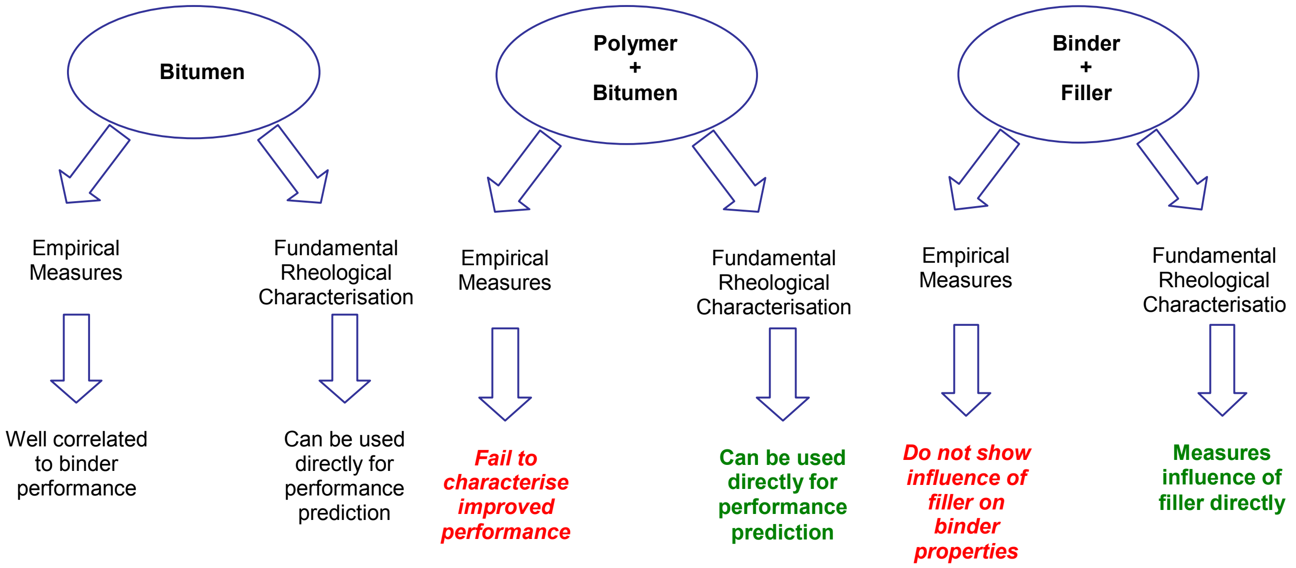

**Figure 1: Fundamental characterisation versus empirical measures.**

The Dynamic Shear Rheometer was used for three types of testing: strain sweeps; frequency sweeps and high temperature viscosity testing. Details of these tests include:

- Strain sweeps: to determine the linear limits of the binders at the temperatures at which the frequency sweeps were performed.
- Frequency sweeps: performed below the linear limits of the binders at eight different temperatures. These frequency sweep results were used to construct Master Curves and Black Diagrams for the three binders.
- High temperature viscosity tests: to gain insight into the high temperature and high shear rate behaviour of the binders used in the study.

Binder/filler mixes were included in the test programme in order to characterise the influence of filler addition on both normal and polymer modified bitumen properties. Similar testing has not been done previously.

The test programme that was followed in this study is summarised in Table 1. The test programme summarised here was used for the purpose of the rheological characterisation of the three binders and binder/filler systems. The results of the tests were compared for the different binders and on this basis conclusions could be drawn on the effect of polymer modification on binder properties as well as the effect that the filler has on the binder properties.

**Table 1: Summary test programme for the three binders.**

| Rheometer | Test | Temperature | Material | | Purpose |
|---|---|---|---|---|---|
| | | | Binder | Binder/Filler | |
| DSR | SS | 5 °C – 75 °C | ✔ | ✔ | Determine linear visco-elastic limits |
| | FS | 5 °C – 75 °C | ✔ | ✔ | Collect data for drawing of Master Curves and Black Diagrams |
| | VT | 105 °C, 135 °C, 165 °C | ✔* | ✔* | Characterise binder behaviour at high temperatures and high shear rates |

SS: Strain Sweeps
FS: Frequency Sweeps
VT: Viscosity Tests
* Tests performed only 60/70 & SBS

A filler content of 50% bulk volume filler was used throughout the study. The optimum filler content of the filler that was used in this study, was found to be between 50% to 55% bulk volume. [6] This translates into a filler/binder ratio of 1.1 by mass for the 50% bulk volume filler case.

The filler/binder ratio is calculated as follows:

- The masses of filler and binder in a binder/filler mix are calculated from the phase diagram (Figure 2). The filler used in this study has 42% Rigden Voids and a bulk density of 2 709 kg/m$^3$.

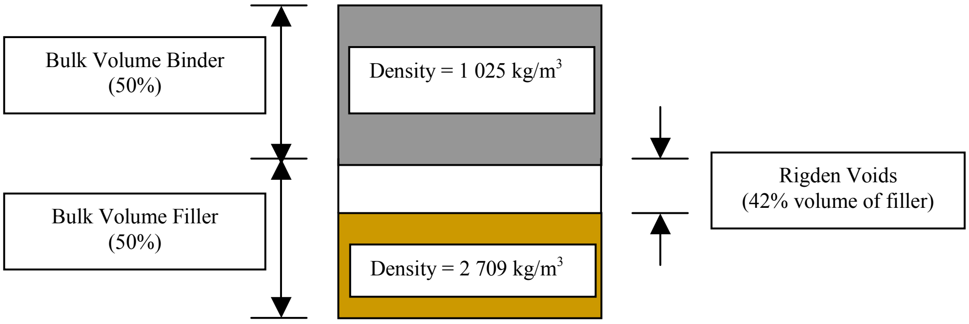

**Figure 2: Phase diagram of binder/filler mix.**

- Mass of filler:
$$MassFiller(g) = 0{,}5 \times (1 - 0{,}42) \times 2709 = 786g$$
- Mass of binder:
$$MassBinder(g) = (1 - [0{,}5 \times (1 - 0{,}42)]) \times 1025 = 728g$$
- The filler/binder ratio (mass/mass) is therefore 1,08 or approximately 1,1.

## Bitumen as a Visco-Elastic Material in terms of Dynamic Mechanical Analysis

A material that has time dependence in its elastic response to deformation is classified as a visco-elastic material. Bitumen is classified as such a material. Bitumen response to loading and unloading in a creep test is shown graphically in Figure 3.

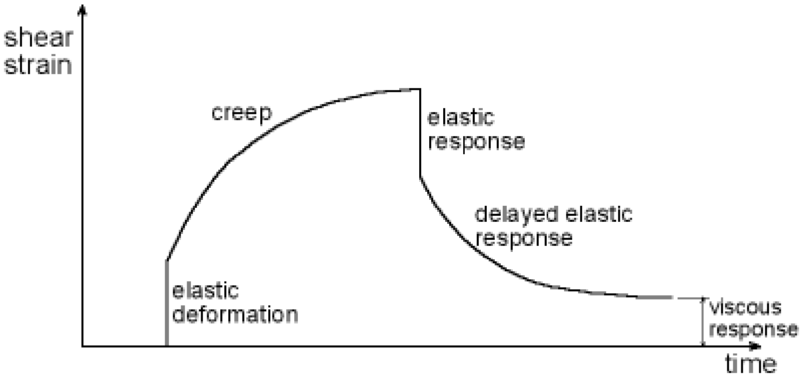

**Figure 3: Deformation response of visco-elastic material when loaded (constant shear load).**

Bitumen is a material characterised by a time of loading and temperature dependence of the mechanical response to loading. Bitumen is also characterised by time-frequency inter-dependence. This inter-dependency is characterised by the shift factor. The form of the shift factor is unique for every bitumen. A typical shift factor is shown graphically in Figure 4. There are several types of functions that are used to fit the shift factor curve. [3] The Arrhenius function is used in this research.

The Arrhenius function:

$$\ln a(T) = \frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)$$

| | | |
|---|---|---|
| a(T) | – | shift factor |
| E | – | activation energy of the binder |
| R | – | universal gas constant |
| T | – | temperature of the measurement being shifted |
| $T_r$ | – | reference temperature at which the Master Curve is constructed |

Using the shift factor it is possible to construct a Master Curve for binder stiffness at one temperature from measurements at different temperatures.

At any combination of time and temperature, the behaviour of the bitumen must be characterised by at least two properties: the total resistance to deformation (complex modulus G*) and the relative distribution of that response between an elastic part and a viscous part (phase angle δ).

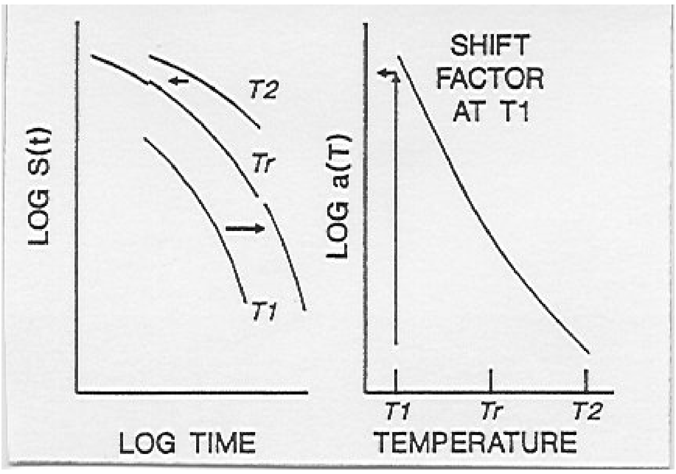

**Figure 4: Graphical representation of shift factor. [3]**

The complex modulus is the primary response of interest in dynamic testing [2, 3]:

$$G^* = \frac{\tau(\omega)}{\gamma(\omega)}$$

The phase angle is the measured lag between the application of the strain and the response of the material and it varies between 0º and 90º (purely elastic response to purely viscous response).

The in-phase component of the complex modulus ($G'$ - storage modulus) is the elastic component and it is a measure of the recoverable energy stored in the material with every loading cycle. The out-of-phase component ($G''$- loss modulus) is the viscous component and is a measure of the dissipated (lost) energy for every loading cycle.

The relative distribution of the elastic and viscous components, is a function of material composition, loading time and temperature. The relationship between the four parameters can be described graphically (Figure 5).

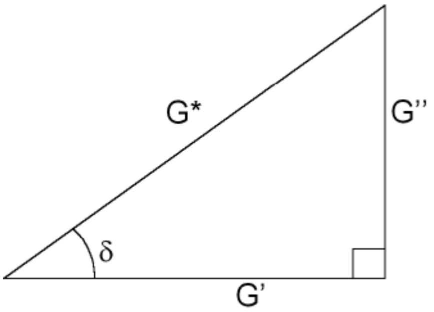

**Figure 5: Relationship between complex modulus components and δ [1].**

From Figure 5 the following relations can be written [2, 3]:

$$G' = G^*(\omega)\cos\delta$$

$$G'' = G^*(\omega)\sin\delta$$

$$\tan\delta = \frac{G''}{G'}$$

The rheological properties are represented in the following ways:

a) variation of G* and δ with frequency at a constant temperature (isothermal or "master" curve – Figure 6)
b) variation of G* and δ with temperature at a constant frequency (isochronal curve)

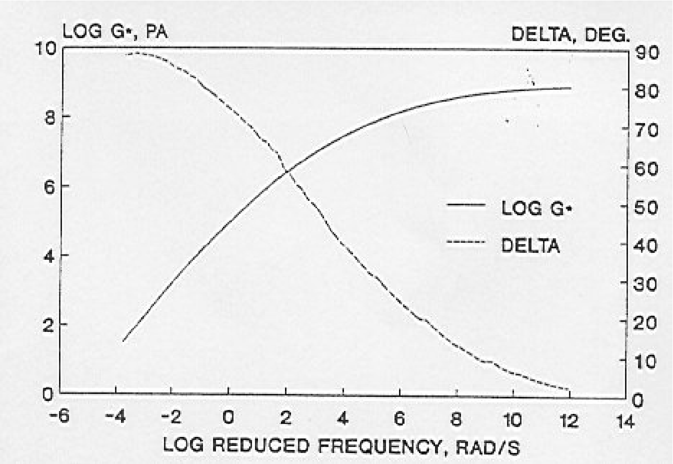

**Figure 6: Typical master curve. [3]**

At low temperatures and/or high frequencies, bitumen approaches a limiting value of 1 GPa for G*. δ tends toward 0º for the same conditions. An increase in temperature (or decrease in frequency) results in a decrease in the value of G* while the value of δ increases. At high temperatures and/or low frequencies, the slope of the master curve approaches 1:1. This signifies viscous flow, as the rate of deformation is directly proportional to the applied stress.

A decrease in the value of G* means a decrease in resistance to deformation. An increase in the value of δ means a decrease in elastic response. The rate of change of the properties (the form of the graph) is dependent on the bitumen composition. Some bitumens show a rapid decline, while others have a more gradual change.

At high temperatures and/or low frequencies, δ approaches a limiting value of 90º. This means that the material response is almost totally out of phase with the load and complete viscous behaviour (complete dissipation of energy) is approached. The bitumen tends toward Newtonian fluid behaviour and it is normally characterised in terms of dynamic viscosity. The value of G* varies due to the different consistency properties of the bitumens.

## Test Results

In this section the results of the tests are summarised in tabular and graphical form. The results are discussed in a separate section

### *Strain Sweeps*

The results of the strain sweeps are summarised in Table 2. The Bitumen-Rubber was not aged. This is because the modified Rolling Thin Film Oven Test (RTFOT) for Bitumen-Rubber was not available.

**Table 2: Combined linear limits (% strain at 10 Hz) for the three binders studied.**

| Temperature | 60/70 | | | SBS | | | B-R | |
|---|---|---|---|---|---|---|---|---|
| | unaged | aged | + Filler | unaged | aged | + Filler | unaged | + Filler |
| 75 °C | 21.10% | | | 56.50% | 65.40% | 2.56% | 12.00% | 2.96% |
| 65 °C | | 21.10% | | 57.60% | 37.50% | 1.27% | 13.90% | 2.57% |
| 55 °C | 32.50% | 28.30% | 0.83% | 37.60% | 18.60% | 2.96% | 12.10% | 1.46% |
| 45 °C | 18.50% | 12.20% | 0.47% | 14.00% | 7.97% | 1.69% | 9.18% | 0.55% |
| 35 °C | 5.60% | 4.50% | 0.36% | 4.65% | 2.52% | 0.84% | 6.95% | <0,1% |
| 25 °C | | 2.24% | <0,1% | 2.58% | 1.69% | 0.36% | 2.97% | <0,1% |
| 15 °C | 2.00% | 1.69% | <0,1% | 1.69% | 1.47% | <0,1% | 1.68% | <0,1% |
| 5 °C | 1.50% | 1.48% | <0,1% | 1.28% | 1.11% | <0,1% | 1.28% | <0,1% |

The strain levels that were used for the Frequency Sweeps (Table 3) were determined from the results of the strain sweeps reported in Table 2. The values reported in Table 2 were used as guideline for the selection of strain levels for the frequency sweeps.

**Table 3: Table of strain levels used for frequency sweeps at different temperatures.**

| Temperature | 60/70 | | | SBS | | | Bitumen-Rubber | |
|---|---|---|---|---|---|---|---|---|
| | unaged | aged | + Filler | unaged | aged | + Filler | unaged | + Filler |
| 75 °C | 5% | 1% | 0,2% | 2% | 1% | 0,2% | 1% | 0,2% |
| 65 °C | 5% | 1% | 0,2% | 2% | 1% | 0,2% | 1% | 0,2% |
| 55 °C | 5% | 1% | 0,2% | 1% | 1% | 0,2% | 1% | 0,2% |
| 45 °C | 5% | 1% | 0,2% | 1% | 1% | 0,2% | 1% | 0,2% |
| 35 °C | 5% | 1% | 0,1% | 1% | 1% | 0,1% | 1% | 0,1% |
| 25 °C | 5% | 1% | 0,1% | 1% | 1% | 0,1% | 1% | 0,1% |
| 15 °C | 2% | 0,5% | 0,1% | 1% | 0,5% | 0,1% | 1% | 0,1% |
| 5 °C | 1% | 0,5% | 0,1% | 1% | 0,5% | 0,1% | 1% | 0,1% |

## Frequency sweeps

In this section the results of the frequency sweeps on the binders and binder/filler systems are presented. Typical Master Curves and Black Diagrams are shown for one of the binders and the Black Diagrams of the different binders are shown on comparative figures.

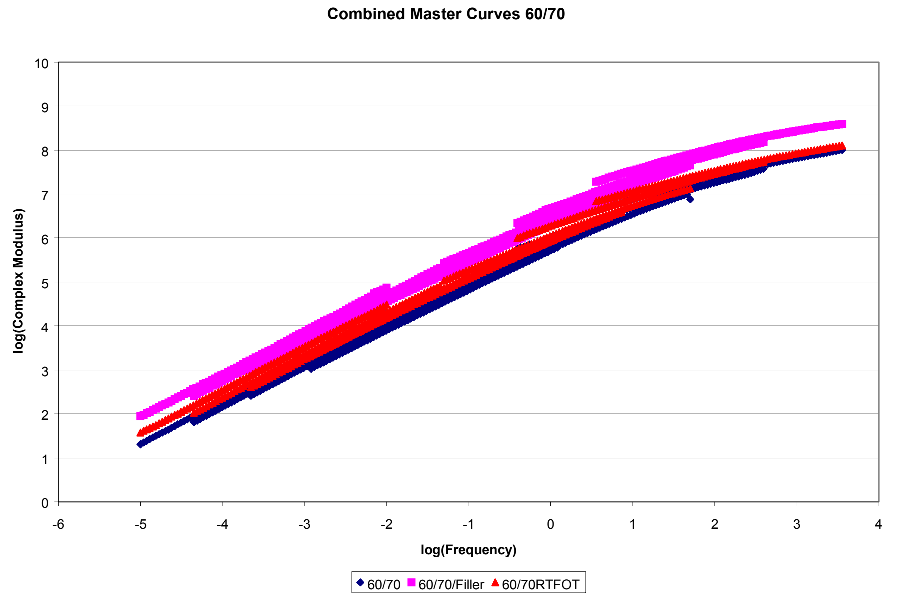

**Figure 7: Master Curves at 25 °C of the three 60/70 binders.**

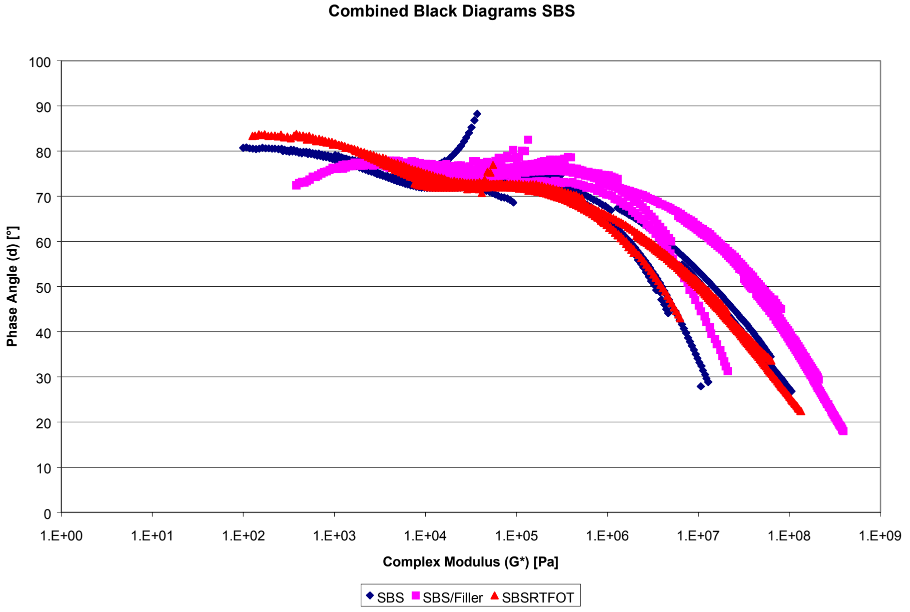

**Figure 8: Black Diagrams for the SBS modfifed binders.**

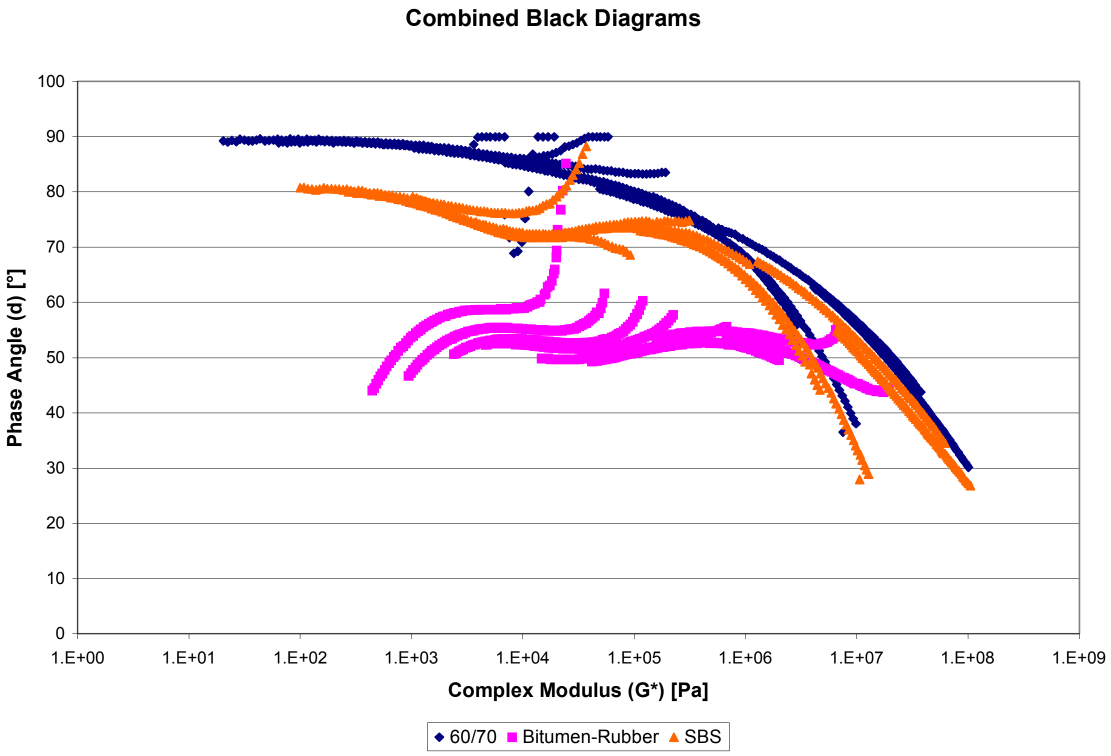

**Figure 9: Black Diagrams for the three unaged binders.**

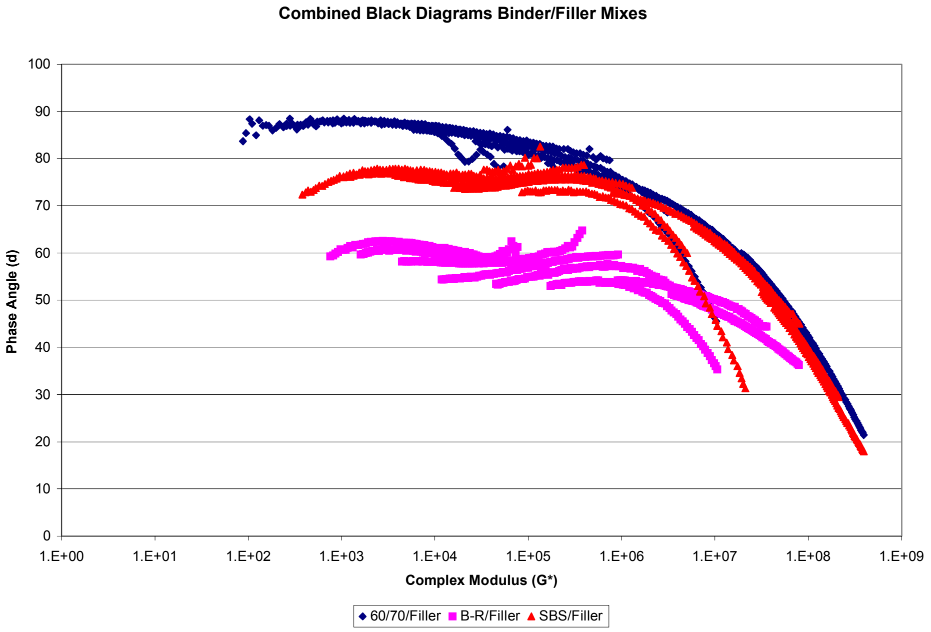

**Figure 10: Combined Black Diagrams for the binder/filler systems.**

# *High Temperature Viscosity Tests*

In this section the results of the High temperature viscosity tests are shown.

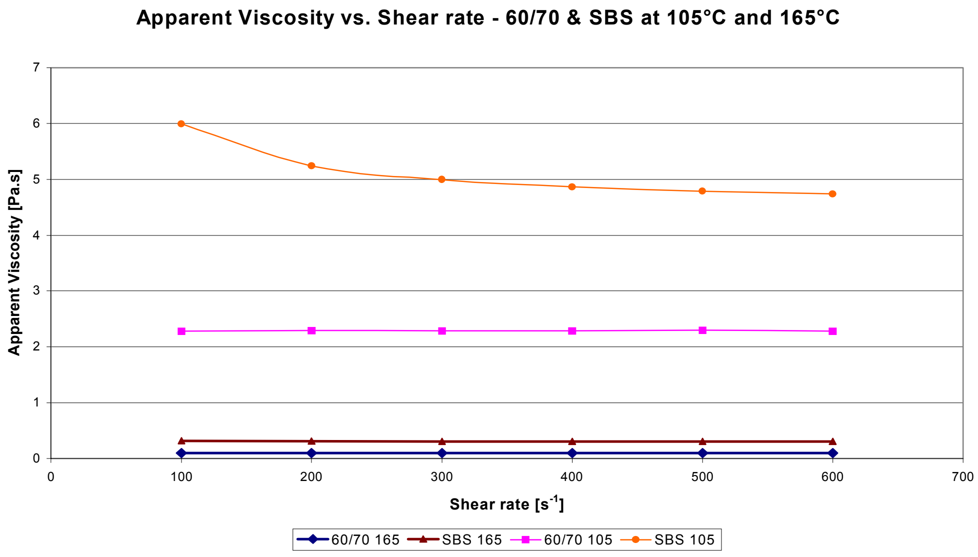

**Figure 11: Apparent viscosity versus shear rate for binders at 105°C and 165°C.**

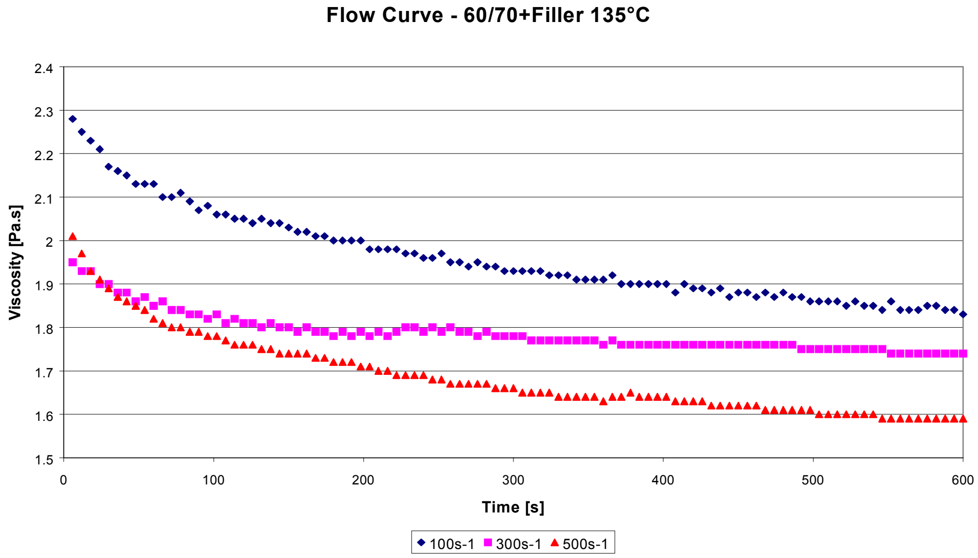

**Figure 12: Viscosity vs. time curve for 60/70+Filler at 135 °C.**

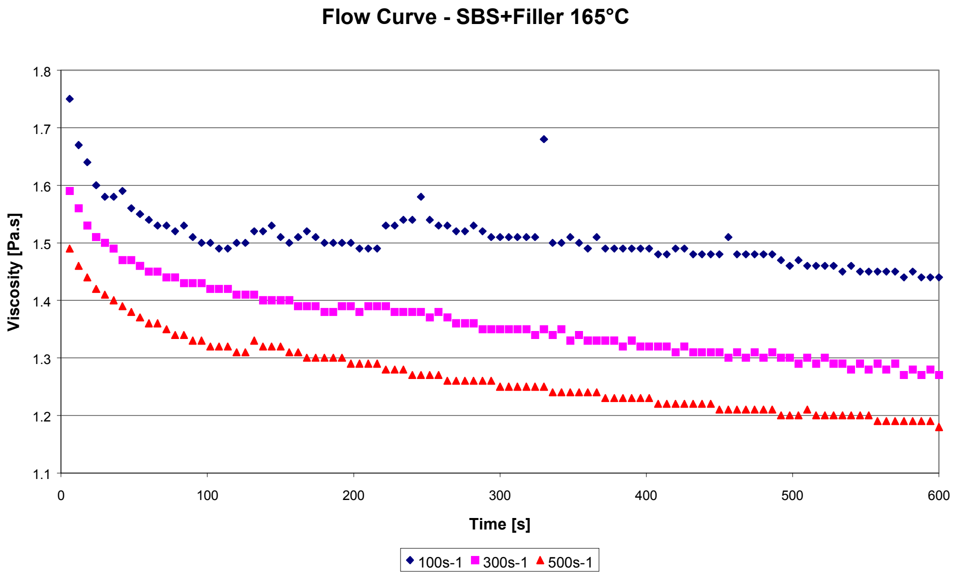

**Figure 13: Viscosity vs. time curve for SBS+Filler at 165 °C.**

## Discussion of results

### *Linear visco-elastic limits (Strain Sweeps)*

It is clear that temperature has a definite influence on the linear visco-elastic limits of the materials tested – results in Table 2. It can also be seen that the binder/filler systems have much lower linear limits compared to the binders.

### *Frequency sweeps*

The frequency sweeps produced good results that could be used for the construction of both Master Curves and Black Diagrams. From the two types of curves the effect of polymer addition, ageing and filler addition were determined. Two typical results that were obtained for the binders are shown (Figure 7 and Figure 8). It is clear from these figures that ageing and the addition of filler leads to stiffer response to loading – the curves are shifted vertically (Master Curves) or horizontally (Black Diagrams).

The Black Diagrams (Figure 9 and Figure 10) are very useful for the characterisation of binder properties. It can be seen that the addition of polymer leads to a binder that performs better under high temperatures/low frequencies (lower values of G*) compared to unmodified bitumen – the polymer modified binders had a more elastic response under these conditions. It is also apparent that filler addition does not alter binder response to loading in terms of the relative distribution between elastic and viscous response – the form of the Black Diagrams is the same for the unaged binders and binder/filler systems.

## *High (Mixing and Compaction) Temperature viscosity tests*

The 60/70 bitumen has Newtonian behaviour at the temperatures used and the SBS has shear thinning behaviour at 105°C – this is seen in Figure 11. At the high temperature (165°C), the SBS and 60/70 binders show similar behaviour. The SBS could be exhibiting shear thinning behaviour. It should be stressed that this research did not cover the region of shear rates below $100s^{-1}$. Therefore, it is difficult to say with certainty whether it is shear thinning behaviour or not. However, based on recent research that covered the region below $100s^{-1}$, it is reasonable to assume that the SBS binder is exhibiting shear thinning behaviour. [4] [5]

The binder/filler systems did not give results similar to the binders. In fact, viscosity tests show that the viscosity is decreasing with time (Figure 12 and Figure 13). The binder/filler systems show unusual behaviour and this could be attributed to the rearrangement of the filler particles during testing.

## Conclusions

The following conclusions may be drawn:

- Polymer addition improves binder response to loading at service temperatures – and thus the expected performance of the polymer modified binders. Ageing and filler addition does not affect this result.
- At high temperatures, care has to be taken when use is made of polymer modified binders as it was shown that these binders exhibit shear rate dependent behaviour.
- Filler addition results in the creation of a stiffer mastic compared to the binder, while binder response to loading remains unchanged – this is true for the one filler that was tested with both penetration grade bitumen and modified bitumen.

This study showed that the fundamental rheological characterisation of binder properties is superior to the conventional empirical measures. For example, the empirical measures report a value such as penetration and the increase thereof with ageing or it prescribes a value for ductility. These empirical measures cannot be directly related to the improved binder properties resulting from polymer modification. However, the fundamental rheological characterisation could be used directly to predict binder performance (e.g. the Black Diagrams comparing normal bitumen with SBS and rubber modified bitumen).

Through the use of fundamental rheological characterisation, knowledge regarding the effect of ageing on polymer modified binders and the influence of filler addition on binder properties was gained. Both ageing and filler addition did not alter binder response to loading. It was also shown that the shear rate during mixing and compaction of asphalt pavements containing polymer modified binders is an important factor – the shear rate should also be considered when mixing and compaction temperatures are determined for polymer modified binders.

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Johan Muller
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Professor Kim Jenkins

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