A Study of the Low-Temperature Properties of Sulphur Extended Asphalt Mixtures

David Strickland
Shell Sulphur Solutions
Manchester, United Kingdom

Jacques Colange
Shell Sulphur Solutions
Petit Couronne, France

Pamela Shaw
Shell Sulphur Solutions
Calgary, Alberta, Canada

Norman Pugh
Shell Sulphur Solutions
Elk Grove, California, USA

ABSTRACT

Sulphur Extended Asphalt (SEA) mixtures were used commercially in the 1970s and 1980s. Increases in sulphur prices, however, rendered SEA mixes uneconomical. Handling and safety issues also were of concern, as molten sulphur was difficult to use and occasionally generated H_2S.

Interest in the use of SEA mixes has been renewed by the precipitous rise in bitumen prices and some recent innovations in sulphur technology. A sulphur mixture modifier is supplied in pellet form, allowing easy handling and storage. The modified sulphur pellets are at ambient temperature when added to the Hot Mix Asphalt (HMA) during the mixing process. By keeping the mix temperature to a range of 130°-145°C, H_2S emissions are virtually eliminated.

Although economic factors offer valid reasons to use SEA, recent laboratory studies have also shown that the addition of sulphur improves performance. Significantly enhanced performance in high temperature conditions has been well documented [2]. This study examines low temperature effects of SEA by using the Thermal Strength Restrained Specimen Test and also examines the effects of sulphur binder content as measured by stiffness modulus in both high and low temperatures. The study concludes that SEA can enhance the performance of HMA in both high and low temperature conditions.

1 INTRODUCTION

Sulphur Extended Asphalt (SEA) was originally developed and promoted in the 1970s and 80s by the US Bureau of Mines and Federal Highways. However, significant problems with storing hot sulphur at the asphalt mix plant as well as pre-blending the sulphur with the bitumen were encountered. Because sulphur is approximately twice as dense as bitumen, segregation within the bitumen/sulphur blend was frequently observed within the binder tank. This was an issue as the ratio of bitumen and sulphur was carefully designed to optimise the properties of the final asphalt mixture. When these issues were overcome, the asphalt mixture did perform well. Aside from the processing and handling challenges, there were health and safety concerns, which arose from the prolonged exposure of the sulphur to the bitumen at elevated temperatures. The bitumen can function as a hydrogen donor leading to hydrogen sulphide generation.

Over 100 test roads were built in the United States during the 70s and 80s. Experience from the trial roads led to SEA commercialisation. However, the product became uneconomical each time due to high sulphur cost and lower bitumen prices. With the reduced availability of bitumen leading to higher prices, the expectation is that the use of sulphur for asphalt mixes will become economically beneficial.

Whilst odour and vapour emissions from the hot paving mixtures during road construction were in compliance with legislated health standards, they were a regular source of worker complaints. In the late 1990s, the development began of solid sulphur pellets, which could be readily added to asphalt paving mixtures, eliminating the expense and hazards associated with hot, liquid sulphur use and significantly decreasing the fumes and odours emanating from the paving mixture. This is primarily due to the fact that the pellet is added to the HMA rather than the binder, thus ensuring that the sulphur is exposed for only a relatively short time to the hot bitumen. Fume mitigation is further enhanced by the incorporation of a hydrogen scavenger in the sulphur pellets. These modified sulphur pellets have been marketed as SEAM™ Asphalt Mix Modifier.

Laboratory and field mix testing indicate that the stability, deformation resistance, stiffness and fatigue performance of these sulphur-enhanced mixes are particularly suitable for high stress applications, such as heavy-duty pavements, high traffic intersections, container terminals and airports as well as full-depth pavements. In particular, the intermediate temperature stiffness and the rut resistance are significantly improved over standard or even polymer-modified HMAs. This study examines SEA performance in high and low temperatures.

2 THE APPLICATION OF MODIFIED SULPHUR PELLETS

Modified sulphur pellets are used as an additive in asphalt paving mixtures. The pellets are both a binder extender and an asphalt mixture modifier. These sulphur pellets are made using existing processes for forming sulphur pellets with the following modifications:

- **Pre-treatment of the elemental sulphur pellets to significantly reduce the formation of hydrogen sulphide gas.**
- **Incorporation of hydrogen sulphide scavengers in the pellets that reduce emissions from the paving mixture.**
- **Plastification of sulphur pellets to lower the solidification temperature. This has the benefit of lowering the compaction temperature of the paving mixtures.**

The resulting modified sulphur pellets, as shown in photograph 1, may be shipped in bulk, sacks or super sacks for storage at the asphalt plant.

Photograph 1. Modified sulphur pellets

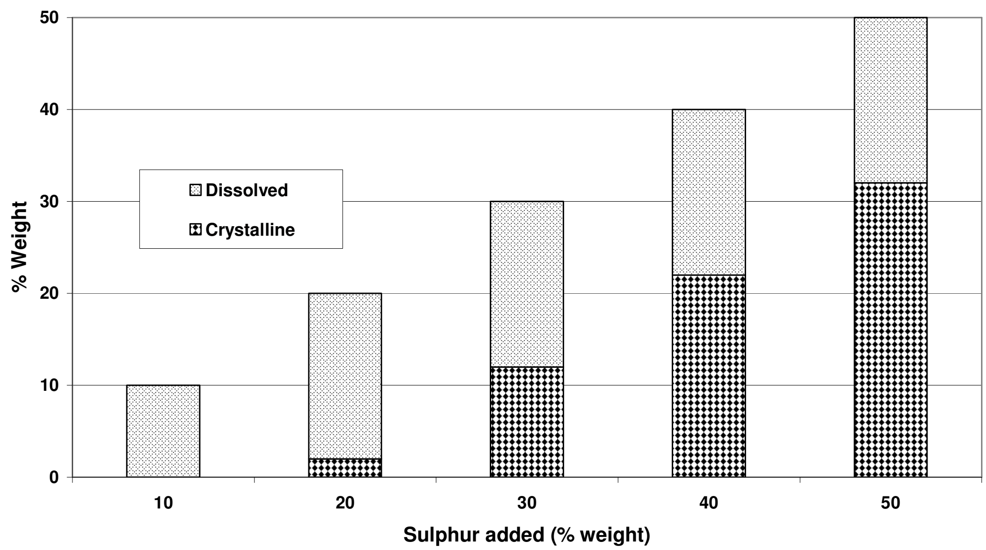


Figure 1. Sulphur added to bitumen (Kennepohl *et al*)

2.1 Maximizing the Benefit of Modified Sulphur Pellets in the Paving Mixture

The modified sulphur pellets are at ambient temperature when added to the HMA during the mixing process. They are not pre-blended with bitumen.

2.1.1 Effect of Modified Sulphur Pellets in the Bitumen and in the HMA

The addition of modified sulphur pellets into the bitumen mixture modifies the bitumen properties. Bitumen and sulphur combine at a temperature above the melting point of the modified sulphur pellets (120°C). Part of the sulphur is chemically combined with the bitumen and acts as an extender. This portion of sulphur is dissolved in the bitumen modifying the bitumen properties – the viscosity is lowered and the ductility is increased. Above a certain quantity of sulphur in the bitumen, the sulphur remains predominantly as free sulphur and when the blend cools, it solidifies. Depending on the amount of modified sulphur pellets added, the crystallisation results in different levels of strengthening. Sulphur crystallisation acts as a structuring agent in the asphalt mixture. Some previous studies e.g. [1] have shown the effect of sulphur combination in bitumen depending on the amount of sulphur added. This is shown in Figure 1.

2.1.2 Asphalt Mixture Design with Modified Sulphur Pellets Extension

The combination between sulphur and bitumen results in some of the bitumen being replaced by sulphur. As the specific gravity of the modified sulphur pellets is approximately 1.95 (virtually twice that of bitumen), the binder content by weight of total mix, made with modified sulphur pellets, is increased to ensure that the total volume of binder (bitumen + sulphur) remains constant. In the past, the replacement was sometimes carried at lower total volume of binder. Now, it is recommended, for good durability of the mixture, to maintain or increase the binder volume fraction of the HMA. The modified sulphur pellets addition rate depends on the type of mixture. In order to obtain a paving mixture with enhanced structural and rutting properties, which retains its flexiblity, the recommended ratio of bitumen and modified sulphur pellets is approximately 2:1 by mass. Generally, the HMA is not changed in any other aspect, i.e., the aggregate gradation is not changed.

The bitumen and sulphur content (total binder content) of the asphalt mixture is calculated as described in equation 1 which is adapted from a conventional asphalt mix design.

$$Sulphur + Bitumen\_weight\_\% = \frac{10000AR}{10000R - 100Ps(R-1) + APs(R-1)}$$

Equation 1. Calculation of the total binder content of sulphur extended asphalt mixture

Where:

A = Weight percentage of bitumen in conventional asphalt mixture design.
R = Sulphur substitution ratio, R, is around 1.9 for having equal volume of binder of the conventional HMA. R, in this case, is typically the ratio between the density of sulphur in pellets to the bitumen density.
P_S = Weight percentage of sulphur pellets in the total binder content.

2.2 Mechanical Performances at High Temperature of Paving Mixtures Made with Modified Sulphur Pellets

In comparison with conventional HMA, the rheological and performance-related properties of the asphalt mixtures made with modified sulphur pellets are generally enhanced. An example of this is shown in Figure 2, which compares the Marshall stability of conventional asphalt mixture made with different Performance Grade (PG) bitumens and the same HMA formulation in which part of the PG bitumen has been replaced by modified sulphur pellets [2]. The replacement was made for achieving an equal volume of binder, compared to conventional asphalt mixture, containing 60 per cent by weight bitumen and 40 per cent by weight modified sulphur pellets. Figure 2 indicates that the stability obtained for a given high temperature PG for conventional asphalt is increased by 1 to 3 PG high temperature grades for the HMA made with modified sulphur pellets.

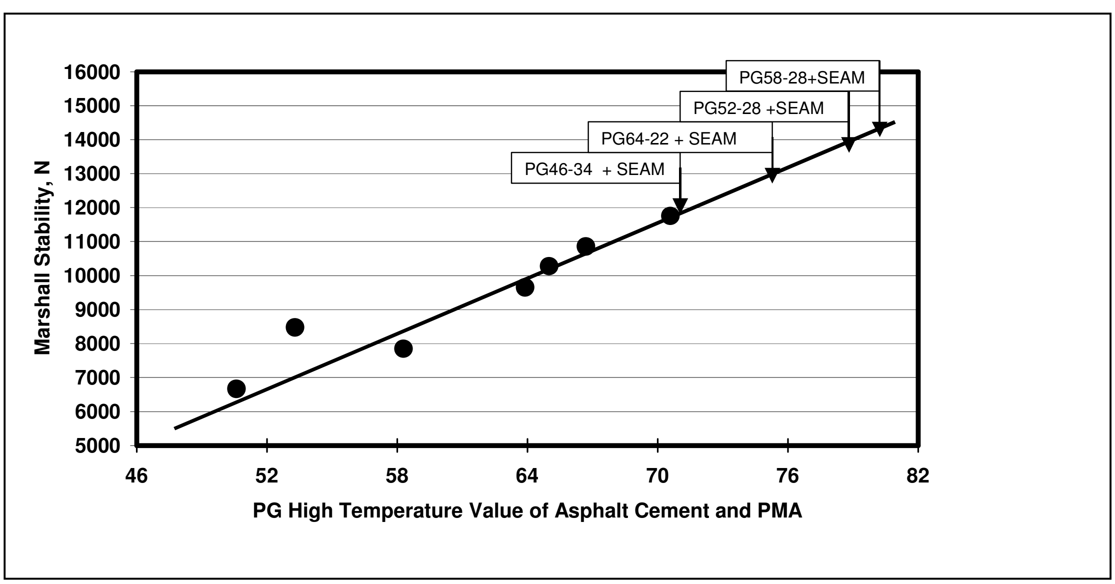
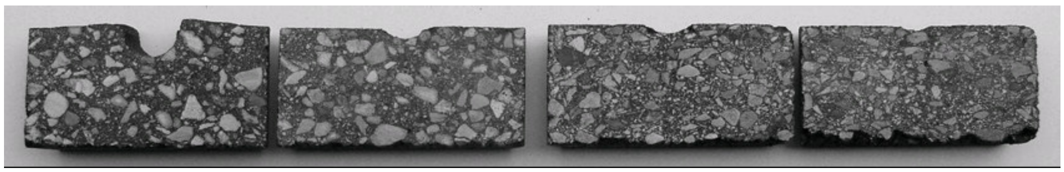


Figure 2. The effect of modified sulphur pellets on PG high temperature value. (Note: PMA stands for HMA made with a Polymer-Modified Bitumen (PMB).)

The performance improvements of HMA containing modified sulphur pellets can also be seen in other performance characteristics such as the resistance permanent deformation and stiffness modulus [2] as shown in Photograph 2 and Figure 3 respectively.



Sandy aggregates mixture		Highly crushed aggregates mixture	
HMA	Paving mixture with modified sulphur pellets	HMA	Paving mixture with modified sulphur pellets

Photograph 2. Rutting behaviour of different asphalt mixtures

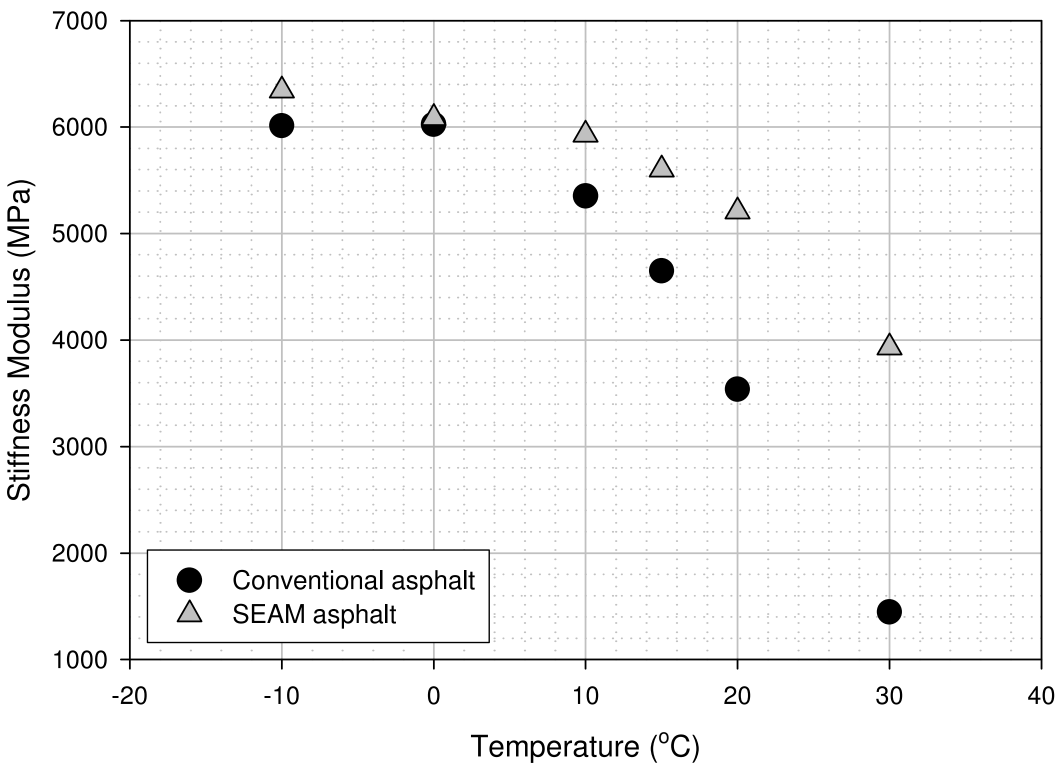


Figure 3. Stiffness modulus of HMA vs. temperature.

All of the improved mechanical properties shown above are measured at the expected in-service high temperatures. The Marshall stability was measured at 60ºC, the resistance to permanent deformation was measured using the Asphalt Pavement Analyser (APA) at 58ºC and the stiffness modulus was measured up to 30ºC. As these high temperature properties have been extensively studied in the past, the aim of this paper is to examine the effects of the modified sulphur pellets on the low-temperature properties of the asphalt mixtures made with modified sulphur pellets.

3 EXPERIMENTAL

3.1 Low-temperature Properties of Chinese Asphalt Mixtures

Since 2002, the modified sulphur pellets have been used in more than twenty projects in China where there are extreme variations in temperatures both summer and winter. In the summer, in Southern China, the weather conditions can be almost tropical, whilst in Northern China; the winter temperatures can be extremely low. The resistance of single event thermal cracking of various asphalt mixtures was studied to ensure that the sulphur modifier did not adversely affect the relative performance.

For experimental work in the laboratory, the TSRST was used. The temperature condition of TSRST does not attempt to simulate the in-situ temperature cycling condition, which causes low temperature fatigue cracking. Moreover, it monotonically decreases temperature until the specimen fails in tension (single event thermal cracking). However, some studies have shown that low-temperature behavior of asphalt concrete pavements can be predicted by TSRST e.g. [4], [5].

A typical Chinese asphalt mixture AC 20mm (Asphalt Concrete) was manufactured in the laboratory with a Chinese limestone aggregate and a 60/80pen (penetration grade) Chinese bitumen. The bitumen content of this HMA was 4.1 per cent. An equivalent asphalt mixture was manufactured with the same aggregates and bitumen, as described above, together with the modified sulphur pellets. In order to have equivalent volumetric characteristics of both mixtures, the amount of the modified sulphur pellets added to the modified mixture was calculated using equation (1) given in chapter 2.12. The bitumen and sulphur ratio was respectively 60 per cent and 40 per cent by mass and the sulphur substitution ratio, R, was 1.9.

The low-temperature performance of both mixtures was assessed using the TSRST according to the AASHTO TP10-93 [6]. The principle of the test is that the length of the cylindrical specimens (250 mm length and 60 mm diameter) is kept constant when the specimen is cooled at a temperature rate of 10°C per hour. The stress, induced in the specimen, and the temperature are recorded up to the temperature at which the specimen fails in tension, called the fracture temperature. The build up of stress and the subsequent failure of the specimens are shown in Figure 4 comparing both mixtures.

Figure 4 shows that the fracture temperature of the Chinese asphalt mixture containing the modified sulphur pellets are equivalent to the Chinese conventional asphalt mixture, with the results of both formulations being around -25ºC in terms of the fracture temperature.

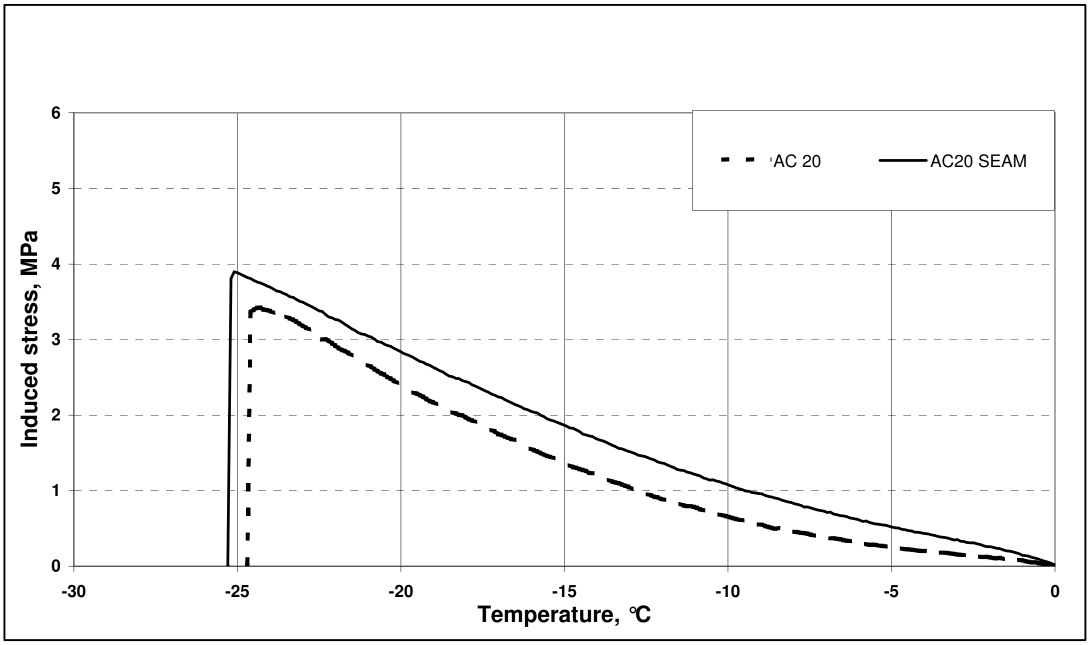


Figure 4. TSRST tests at a temperature decrease rate of 10°C per hour

3.2 3.2 Low temperature property of other asphalt mixture and bitumen grades

In order to support the TSRST findings from the Chinese asphalt mixture, a new investigation was started with the aim of confirming that the low-temperature property of the asphalt mixture containing the modified sulphur pellets are dictated by the bitumen low-temperature property rather than the sulphur affect.

French dense asphalt mixtures were manufactured in the laboratory with and without the modified sulphur pellets. The mix formulations contained 70/100pen, 100/150pen, 160/220pen and 250/330pen bitumen. All of the mixtures produced had the same volumetric composition in terms of aggregates, voids and binder contents. The amount of the modified sulphur pellets added to the mix was calculated using Equation 1 in chapter 2.12, with a bitumen and sulphur ratio of 60:40 by mass and the sulphur substitution ratio of 1.9. The TSRST results of the French asphalt mixes are shown below in Figure 5 below.

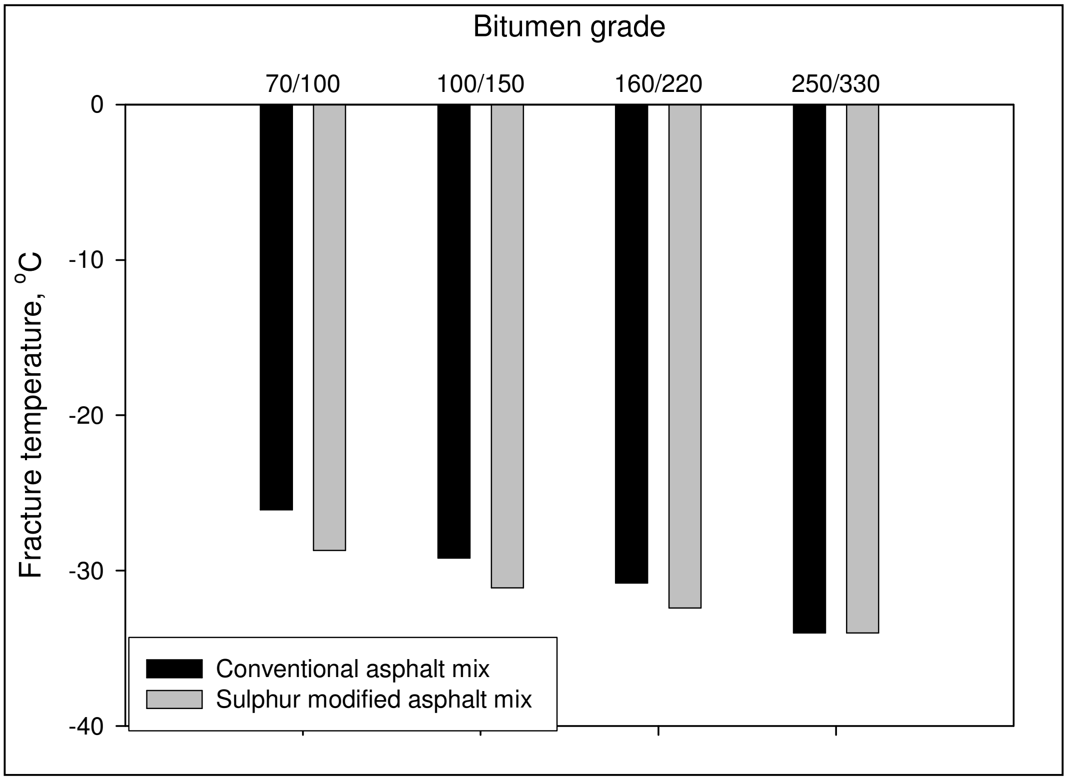


Figure 5. TSRST measurements with a range of penetration grade bitumens

This figure shows the following:

The results show that the fracture temperature measured in the TSRST reduces as the bitumen becomes softer. This was expected as softer grades are more flexible with decreasing temperature therefore more suitable for combating low-temperature cracking in colder climates.

It can also be seen that with the conventional asphalt mix with 250/330pen bitumen and the asphalt mix containing modified sulphur pellets and 250/330pen bitumen, there is no difference in terms of fracture temperature. In fact for these two asphalt mixtures, the limit of test was reached (-34ºC) and the specimens did not fail in tension. The limit of the test is in fact due to the climate chamber capabilities

The fracture temperatures of the conventional asphalt mixes were always slightly higher than the fracture temperatures of asphalt mixes manufactured with the modified sulphur pellets. The repeatability of the test being ±1°C, the difference shown is realistic

The conclusion from this work is that with the French asphalt mixtures, the properties of the bitumen dictates the low-temperature properties of the asphalt mixture and that these low-temperature properties are not affected by the inclusion of the modified sulphur pellets. This also confirms the previous findings from the results of the TSRST with the Chinese asphalt mixtures.

3.3 *The effects of Sulphur Content in the Binder on the Fracture Temperature of Asphalt Mixtures.*

With the same aggregates, same binder contents, in terms of volume, and same asphalt mixture type as described in chapter 3.2, asphalt mixtures with varying ratios of modified sulphur pellets and bitumen were manufactured and their fracture temperatures measured using the TSRST. The base bitumen used for this exercise was 70/100pen bitumen of the same batch as for the previous study. The binder content of the different asphalt mixture tested was as defined in Table 1 below.

Table 1. Binder formulation of sulphur extended asphalt mixtures (in weight)

% of bitumen	% of modified sulphur pellets
100	0
90	10
80	20
70	30
60	40

The fracture temperatures, as obtained in the TSRST, of the asphalt mixtures with the different amounts of modified sulphur pellets are shown in Figure 6.

The figure 6 indicates that, whatever the sulphur content of the binder, no detrimental effect on the low-temperature fracture, as measured in the TSRST, has been observed, up to 40 per cent sulphur in weight in the binder. Again, as measured in this test, it shows that the fracture temperature is slightly decreased. This confirms the findings of sections 3.1 and 3.2.

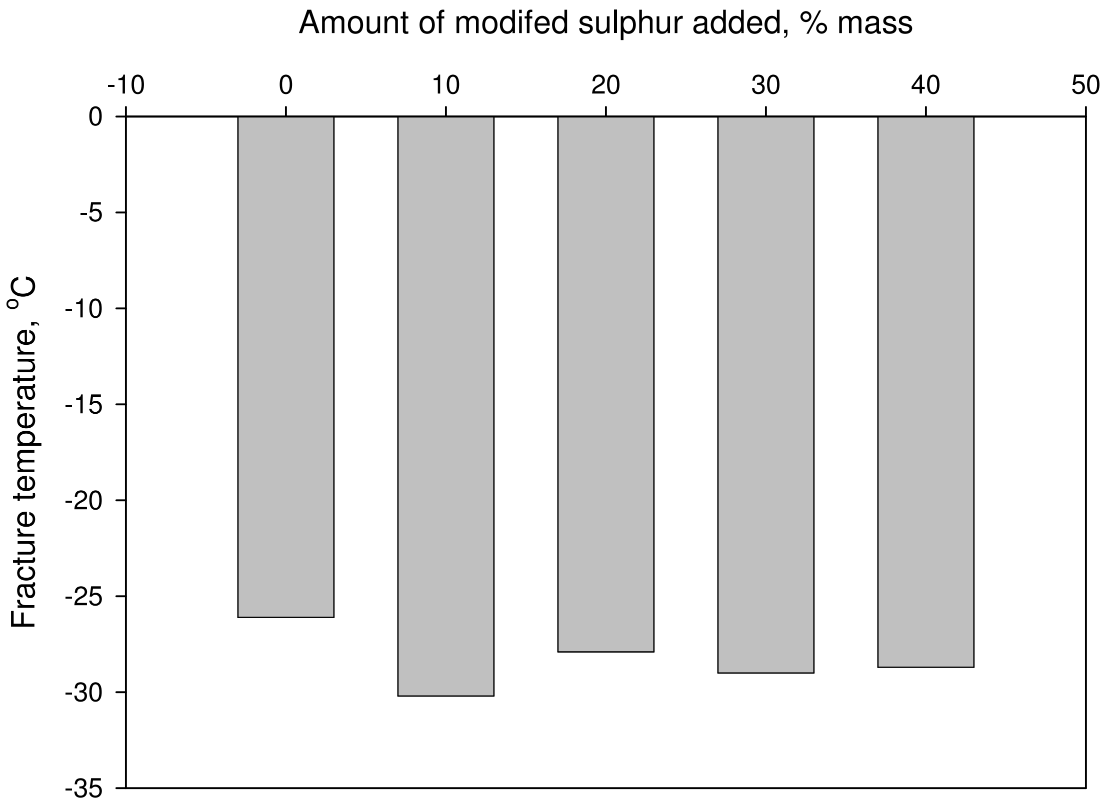


Figure 6. Fracture temperatures of the asphalt mixtures with a range of modified sulphur contents.

3.4 The Effects of Sulphur Content in the Binder on the Stiffness Modulus

It has been reported in previous papers, e.g. [2], that the modified sulphur pellets give paving mixtures enhanced structural properties. As it has been determined that the modified sulphur pellets enhance high temperature properties and do not affect the cold temperature properties, complex modulus (also referred to as stiffness modulus) measurements were made at various loading frequencies and temperatures to obtain a full understanding of the in-service temperatures. This type of measurement has been carried out on a typical dense asphalt concrete formulation, as used in chapter 3.2, with different sulphur concentrations as described in Table 1. Stiffness modulus determination was carried out with an electro-hydraulic machine, in accordance with standard EN 12697-26 (annex D) [7].

The temperature and frequency sweeps allow a master curve to be constructed in order to get an overview of the whole performance of the paving mixture made with modified sulphur pellets. The master curves obtained with the same asphalt formulation having the same volume characteristics, but different bitumen and sulphur concentration are shown in Figure 7.

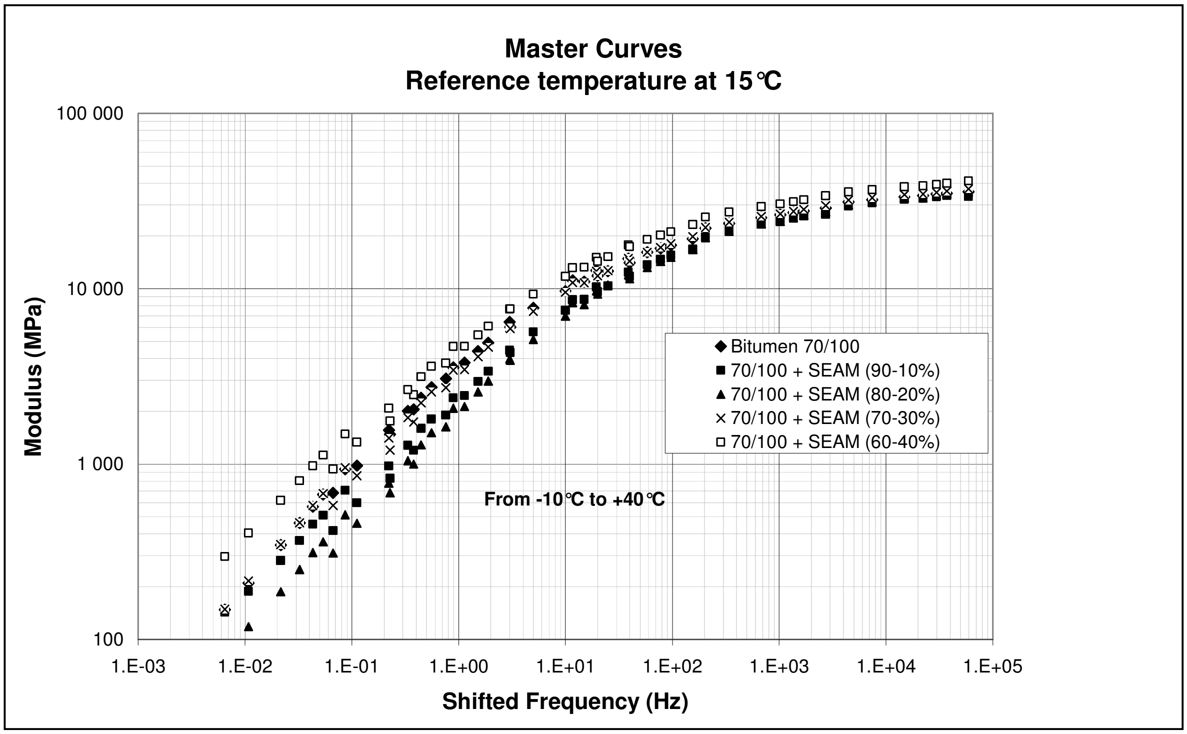


Figure 7. Modulus master curves at 15°C

Figure 7 shows the following:

At low reduced frequencies (long loading times/high temperatures), the asphalt with the modified sulphur pellets at 40 per cent of the binder content by mass, had significantly higher stiffness modulus than the conventional asphalt. As the frequency increases (shorter loading times/lower temperatures), the relative difference in the stiffness modulus between the 60 per cent bitumen, 40 per cent modified sulphur pellets asphalt mixture and the conventional asphalt mixture reduces. This explains why these paving mixes made with modified sulphur pellets have been targeted to improve resistance to rutting in high temperature climates and in pavements with high traffic densities e.g. [1]

At low reduced frequencies (long loading times/high temperatures), the asphalt with the modified sulphur pellets at 30 per cent of the binder content in mass, had equivalent stiffness modulus to the conventional asphalt. As the frequency increases (shorter loading times/lower temperatures), the stiffness modulus remains equal

At low reduced frequencies (long loading times/high temperatures), the asphalt with the modified sulphur pellets at 10 and 20 per cent of the binder content by mass, had significantly reduced stiffness modulus than the conventional asphalt. As the frequency increases (shorter loading times/lower temperatures), the difference in the stiffness modulus between these asphalt mixes reduces until they are almost equal.

In summary, with higher temperatures, the amount of sulphur within the asphalt mix affects the stiffness modulus. Above 30 per cent of the modified sulphur pellets of the binder content, the stiffness modulus is increased above the stiffness modulus of the conventional asphalt mixture. Below 30 per cent, the stiffness modulus is reduced as compared to the conventional asphalt mixture.

With the colder temperatures, the influence caused by amount of the modified sulphur pellets contained within the asphalt mix is insignificant, as it is the bitumen that dominates the low temperature characteristics. This means that SEA mixtures, made with these sulphur pellets, are less susceptible to temperature and frequency than conventional asphalt mixtures made with bitumen only.

4 DISCUSSION

It can be seen from the data presented above, that the incorporation of the modified sulphur pellets has not affected the low temperature properties of the Chinese or French asphalt mixtures. The data above also shows that the low temperature properties of the bitumen dominates the low temperature properties of the asphalt mixture made with modified sulphur pellet contents of up to 40 per cent by mass of the total binder content. This might also be the case for modified sulphur contents above 40 per cent, but this was not tested as 40 per cent sulphur provides enough strengthening of the asphalt mixtures.

Although this was expected for conventional asphalt mixture, this study has also shown that the fracture temperature of the asphalt mixture, as measured using the TSRST, decreases as the bitumen grade becomes softer with and without the inclusion of the modified sulphur pellets.

Whilst the modified sulphur pellets do not affect the cold temperature properties, they do affect the warmer in-service temperatures. The master curves above show that with a sulphur content of 40 per cent by mass of the total binder content, the asphalt mixture properties are significantly enhanced. At the 30 per cent level, the properties of the asphalt mixture are approximately equal to the conventional asphalt and lower sulphur contents reduce the performance characteristics at high temperatures. This data confirms why the modified sulphur pellets have been used recently in projects at 40 per cent mass and why excellent results have been achieved in hot climates and in pavements that carry high amounts of traffic.

This work shows that in climates with extremes, the use of 40 per cent modified sulphur pellets of the overall binder mass can reconcile low temperature cracking resistance and permanent deformation resistance.

5 CONCLUSIONS

The main conclusions of this study are:

The incorporation of the modified sulphur pellets, up to 40 per cent by mass of the total binder volume, does not have any affect on the low-temperature cracking property of the asphalt mixture, as measured in the Thermal Strength Restrained Specimen Test (TSRST).

The low-temperature property of the asphalt mixtures that contain the modified sulphur pellets are dominated by the bitumen, with softer grades giving better resistance to thermal fracture.

The warmer in-service performance characteristics of the asphalt mix are significantly enhanced by the inclusion of 40 per cent modified sulphur pellets of the overall binder content.

The low-temperature property of the asphalt can be significantly improved by using a soft grade of bitumen with 40 per cent modified sulphur pellets to improve the performance characteristics when the climate becomes warmer in the summer months.

The sulphur extended asphalt mixtures, made with sulphur pellets as described in this study, show less thermal and loading-time susceptibility than the conventional asphalt mixture made with bitumen only.

6 REFERENCES

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