DEVELOPMENT OF A HIGH PERFORMANCE SBS MODIFIED BINDER FOR PRODUCTION

Emery, S J[1] and O'Connell, J[2]

[1] Kubu Consultancy Pty Ltd, 68 Glenmore Avenue, Lynnwood Glen, Pretoria, South Africa, 0081 E-mail emery@iafrica.com (formerly with Colas Southern Africa Pty Ltd)

[2] Transportek, CSIR, PO Box 395, Pretoria, South Africa 0001 (formerly with Colas Southern Africa Pty Ltd)

Abstract

The paper describes a research programme undertaken to develop a high performance SBS modified bituminous binder for production in South Africa. The target performance specification included a softening point minimum of 80 ^{0}C, and an elastic recovery of 75%. Compatibility problems were experienced between the SBS polymer and the South African bitumen. Revisions to the 1994 SABITA SBS specification are suggested. The sampling and testing of SBS modified bitumen requires changes to the South African test methods. The use of a simple recipe specification for SBS modified bitumens is strongly cautioned against. The viscosity of SBS bitumen at the asphalt plant pugmill is only slightly increased over unmodified bitumen, despite laboratory indications otherwise.

1 INTRODUCTION

The modification of penetration grade bitumen by Styrene-Butadiene-Styrene (SBS) has been widely investigated, and such modified bitumens are in common use in several countries. In South Africa, most modification of penetration grade bitumen has historically been done using Styrene-Butadiene-Rubber (SBR) or crumb tyre rubber. The use of SBS has been limited. There is an existing specification for SBS modification (SABITA, 1994) which encompasses the lower performance modified bitumens (softening point minimum of 47-49°C; elastic recovery minimum of 60% at 10°C). This research is aimed at high performance SBS modified bitumens (softening point minimum of 80°C; elastic recovery minimum of 75% at 13°C).

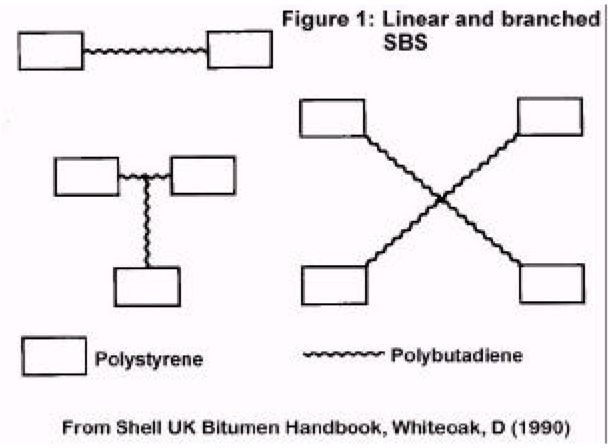


Figure 1: Linear and branched SBS

From Shell UK Bitumen Handbook, Whiteoak, D (1990)

1.1 SBS Polymer

SBS is a block co-polymer. In the case of a linear polymer, it consists of a block of butadiene monomer (ranging in length from 10 000 to 100 000 units) in the center and tipped by two blocks of styrene monomers at the end. By introducing linkages during the polymerization process, a branched form of SBS can be formed (the various forms are shown in Figure 1).

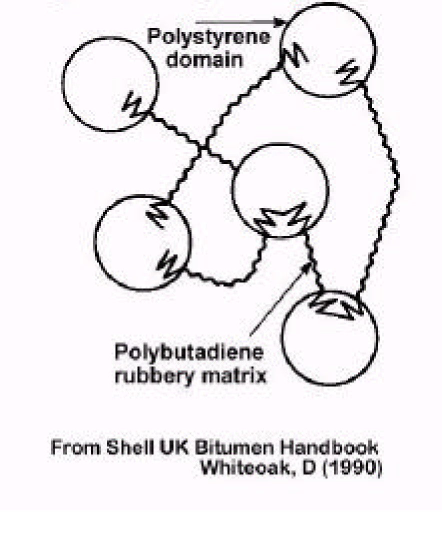


Figure 2: SBS phase structure

From Shell UK Bitumen Handbook Whiteoak, D (1990)

The chemical nature of butadiene and styrene differ markedly, and the block polymerization process allows the setting up of separate regions of differing polarity, one being hard and glassy (styrene) and the other being rubbery in nature (butadiene).

The incompatibility between the regions allows for a phase separation within the polymer, resulting in a network of hard polystyrene domains inter-connected by a rubbery matrix (Figure 2).

1.2 SBS modification of penetration grade bitumen

SBS modification of bitumen has widely investigated. It has been reported to be effective in preventing thermal cracking, delaying fatigue cracking and reducing permanent deformation in hot mix asphalts as well reducing or preventing crack reflection through chip seals.

The resultant properties of the SBS modified binder are strongly dependent on the properties of the SBS, such as degree of branching, butadiene/styrene ratio as well as effective molecular mass (chain length).

The SBS concentration in the bitumen is also critical, with three effective groups (Table 1).

Table 1: SBS concentration levels found in practice

SBS Polymer level	Use
below 3%	Bitumen dominates properties, limited modification benefit (benefits similar to SBR).
3 - 8%	Distinct network formation. Both bitumen and SBS influence properties. Usual range for modification of seal and asphalt bitumens
above 8%	SBS dominates properties. Typical levels for crack sealant

1.3 Common SBS polymers in South Africa

The SBS polymers that have been commonly used in South Africa to date are listed in Table 2.

Table 2: SBS polymers commonly used in South Africa

SBS	Linearity	Styrene Content	Supplier
Kraton D 1101	Linear	31 %	Shell
Kraton D 1184	Branched	30 %	Shell
Vector 2518	Linear	31 %	Exxon
Vector 2411	Branched	30 %	Exxon

Note: the D series Kraton polymers were previously trademarked as the TR or Cariflex series.

The linear polymers tend to have lesser increases in softening point, are recommended for asphalt by Shell (Vonk, 1998) and for seals by Exxon (Exxon, 1992). The branched polymers tend to have the greater increase in softening point. These are recommended for seals by Shell and for asphalt by Exxon. It is common in the literature to find modification by a mixture of linear and branched polymers, and an example used in this research was a blend of 50% 1101 and 50% 1184.

1.4 Historical Investigations

1.4.1 Introduction

A wealth of information exists with regards to properties of SBS modified binders as well as their use in hot mix asphalt (such as Van Gooswilligen et al, 1994). Typical results are:

- lower ductility values occur at higher testing temperatures (10-25 °C), but higher ductility values occur at lower temperatures (4 °C)
- elastic recoveries are substantially increased
- generally small decreases occur in penetration values, though increases have been reported (Rogge et al, 1992) which were assumed to be as a result of the addition of aromatic oils (often called extender oils or diluents)
- softening points (R&B) can increase drastically with increasing SBS content. A graph displaying softening points vs. SBS content shows a typically S-shaped curve with a drastic increase in softening point around the 2,5 to 4,0 % levels. This corresponds to the setting up of the network as mentioned earlier. A branched SBS polymer also indicates a larger increase in softening point than a linear one. This effect is well illustrated by work done by Serfass et al (1992).
- Viscosities show large increases in the region of 40-70°C (improved rut resistance at service temperatures), relatively small increases at the handling temperatures at around 140°C and a decrease in viscosity below 0 °C (improved Fraas brittle point).
- Penetration Index (PI) values indicate a significant decrease in temperature susceptibility of the modified binder at SBS concentrations from as low as 3%.

The influence of SBS on the properties of SBS modified binders are dependent on many things:

- nature and concentration of SBS polymer,
- nature of the bitumen,
- aging,
- thermal and mechanical history of the blend, and
- temperature at which the properties are tested.

Typical results are shown in Table 3 (from Boudin and Collins, 1992). However despite the ready availability of typical results, it was found that publications often omit crucial information, so that results cannot easily be compared.

Table 3: Typical properties of SBS modified bitumen

Test	**AR 1000**	**AR 1000 + 3% TR 1101**
Penetration (dmm) 100g,5s,25°C	103	95
Ring and Ball (°C)	41	63
Ductility (cm) @ 4°C	23	74
Elastic Recovery 1 hr, 4 °C (%)	8	66
Absolute Viscosity (Ps) @ 60 °C	745	23 000
Kinematic Viscosity (cSt) @ 135 °C	154	385

Note: AR1000 is an American bitumen specification that is not-dissimilar to 80/100

1.4.2 Testing of SBS-modified Bitumen Binders

There is broad agreement that traditional binder tests are poor predictive tools for field performance. Notwithstanding the results shown in table 3, Rogge et al (1992) found SBS-modified binders that had poor ductility values at 25 °C, which is in total contradiction of field performance. They found that they could use none of the normal binder tests as predictive tools with the possible exception of ductility at 4 °C. They echoed what is a general call for performance based tests for SBS modified binders.

1.4.3 Performance related testing

Several approaches have been used for performance testing. Srivastave et al (1992) related the deformation energy (product of force and displacement during tensile strength testing) of the binder to the performance of asphalt mixes and have been able to discriminate between modified and unmodified binders in performance.

Bouldin and Collins (1992) measured the storage modulus (portion of deformation energy which is stored elastically), G’, and loss modulus (portion of deformation energy which is dissipated in the form of viscous flow), G”, for a 3% TR 1101 modified AR 1000. The overall resistance to deformation can be described in term of the complex modulus, G*, where

$$G^* = (G'^2 + G''^2)^{1/2} \qquad (1)$$

Values for G* and G’ at 60 °C are given in Table 4. Unlike the unmodified bitumen, G* of the SBS modified bitumen remained constant over a large temperature range. The relationship of G* to performance was tested using a TRRL wheel tracking apparatus (also Table 4).

Table 4: Modulus and performance of SBS modified bitumen

Binder	**G* Pa**	**G' Pa**	**Rut rate mm/1000 cycles**
AR1000	15	0,02	0,320
AR1000+ 3% TR1101	205	112	0,075

1.4.4 SBS-Bitumen Compatibility

The issue of compatibility is confused in terms of the concept and its impact on binder performance properties. Some researchers measure compatibility as the difference between the softening point of the top half and bottom half of a modified binder. This is in a defined cylindrical vessel after standing at a defined temperature for a defined period of time; similar to the homogeneity test of SABITA Manual 15 (SABITA, 1994). However, a binder may be incompatible at one temperature and compatible at a slightly higher temperature. Thus the defined temperature is important, and this, together with time and vessel shape/size differs from researcher to researcher. It is therefore hard to extrapolate the compatibility findings of one researcher to another.

Other researchers define compatibility in terms of microscopic observation of the micro-morphology of the modified binder.

The importance of compatibility is contentious as well, with some researchers claiming that incompatibility has a deleterious effect on binder properties. Others claim that incompatibility has no significant effect on the final modified binder properties, as long as no separation of the binder and polymer has occurred.

The authors' opinion is based on their experience in the transition from laboratory research to production. In essence:

- some compatibility between bitumen and SBS is needed to cope with the variability in conditions during production.
  In one project, the SBS modified bitumen was manufactured in a tank at the asphalt plant and pumped into the plant's bitumen circuit. This was intended to reduce the storage time after manufacture to a minimum and bypass consideration of compatibility. In practice, the storage time varied from minutes to several days. On occasions, enough SBS modified bitumen was manufactured to meet the projected asphalt production, and only half the asphalt was in fact ordered. On other occasions, construction work was halted partway due to rain, and the SBS modified bitumen then stood in the tank for several days until the rain stopped.
- There are proven techniques that the manufacturer can use to deal with SBS modified bitumen that has separated. The fact is that in practice it will be exposed to a variety of handling conditions, usually without the benefit of a

chemist present. The system must be sufficiently compatible to cope with these.
- A totally compatible system is an inefficient utilization of the potential of the SBS polymer. Total compatibility means that the phase separation between the polystyrene and the butadiene does not occur, and thus the domain network does not establish. The result is low softening point and poor elasticity.
- A totally incompatible system is unacceptable for the production reasons outlined above.

The level of compatibility and thus network strength is determined by several factors such as base bitumen and polymer. It may be adjusted by the addition of additives such as aromatic oils that affect the compatibility of the modified binder (Srivastava et al, 1992)

Colloidal Instability Index, Ic, has been used by some researchers to predict compatibility between SBS and bitumen, where Ic is defined as the ratio of dispersed phase / dispersing phase:

$$Ic = \frac{(\text{Asphaltenes + Saturates})}{(\text{Resins +Aromatics})} \qquad (2)$$

Serfass et al (1992) found that no precise borderline exists between compatible and incompatible bitumen, but they found that bitumen with Ic values lower than 0,13 are definitely compatible, and bitumen with values higher than 0,28 are definitely incompatible. The molecular size distribution varies with refinery, grade and time, and it is not possible to definitively characterise South African bitumens. However some limited available data suggests Ic of 0,24 to 0,27 for 60/70 grade bitumen, which suggests that compatibility will need to be addressed by the use of aromatic oils.

2 RESEARCH PROGRAMME

The research programme that was reported on here was to enable production of a high performance SBS modified bituminous binder in South Africa. Such binders had been previously developed in the research laboratory, and this research was to establish tolerances and processes for full-scale production. The target performance specification is shown in Table 5.

Table 5: Production performance specification

Property	SBS modified bitumen
Softening point (°C)	80 minimum
Penetration (dmm)	50 minimum
Ductility @ 13 °C (mm)	650 minimum

Elastic Recovery @ 13°C (%)	75 minimum
Homogeneity (°C)	2 maximum

2.1 Previous research

Unpublished Colas research showed that such a specification could be met by a combination of 80/100 base bitumen from Refinery S (from a batch supplied in January 1997), with 3,5% aromatic oil (mass by mass: 3,5% oil in 100% modified bitumen), and 4% Polymer B SBS powder (mass/mass : 4% powder in 100% modified bitumen).

The literature search had shown that common tests for penetration bitumen were poor measures of performance improvements of SBS modified bitumen. In earlier unpublished research by Colas, penetration and ductility varied little or illogically with significant changes in formulation of SBS modified bitumen. In this research, the common tests that yielded the most useful information were softening point, elastic recovery, viscosity and homogeneity (Table 6). Further testing was planned using the shear rheometer and microscopic photographs.

Table 6: Test parameters used in this research

Test	Primary indication
Softening point	Extent of thermo-reversible styrene domain network
Elastic recovery	Flexible butadiene branches
Homogeneity / storage stability	Compatibility
Viscosity	Handling

Previous research had also addressed the issue of production mixing time. SBS polymer suppliers recommended mixing times around 2 hours at 180°C (Exxon, 1992; Bull and Vonk, 1984). A standard mixing time and temperature were established which avoided oxidation problems (Linde and Johannson, 1992). Temperatures above 180°C lead to rapidly increasing problems of oxidation of the polymer and, it was thought, a loss of modified binder performance. While the adhesive industry commonly uses very high production temperatures, they also provide nitrogen blanketing to avoid oxidation in their high percentage SBS bitumen production. The extra costs of such production would render road grade SBS bitumens uneconomic relative to SBR and bitumen-rubber.

2.2 This research programme

The research programme was aimed at investigating factors that affect production, and at establishing the optimum recipe for the product. The issues investigated in this programme were:

1. Effect of different polymers and base grade bitumens.
2. Effect of base bitumens from different crude oil/production routes (essentially from different refineries).
3. Effect of varying aromatic oil concentration.
4. Effect of storage at high temperature.
5. Mixing and compaction temperatures for an asphalt plant.
6. Degradation (mechanical/shearing) by gear pumps in an asphalt plant.
7. Reproducibility and repeatability of testing

Issues investigated in other research programmes, but not reported on here included the issues discussed above and the issues following:

- other test methods to characterise SBS bitumen, including the torsional recovery meter (locally termed the “Kangaroo Ductilometer”; kindly donated to Colas by Pioneer Road Services, Australia) to measure elastic recovery
- SBS modified bitumens for seal applications.
- Type of aromatic oil.
- Ongoing investigation into bitumen from different refineries.

2.3 Experimental design

The experimental design was a factorial design which covered constituents such as refinery, bitumen grade, aromatic oil concentration, type of SBS polymer, and concentration of SBS polymer.

3 ANALYSIS OF RESULTS

3.1 Effect of different SBS polymers and base bitumens

There was an effect of different SBS polymers and base bitumens on softening point, and the branched polymers had a greater effect on softening point than the linear polymers (Table 7).

This means that control over the base bitumen is needed to ensure uniformity of product with time. This means control over molecular distribution (the balance of asphaltenes, saturates, aromatic, and resins), and control over the propane de-asphaltened tar content. Since this can vary from day to day for a given crude and production route, effective control is more easily assured with large scale batching, especially if the modified bitumen is being produced by someone other than a refinery.

In the tests used to generate Table 7, the base bitumen came from a single refinery and from samples taken at one point in time. Yet still the effect of the different polymers varied, and there was no consistent trend.

Table 7: Effect of different SBS polymers and base bitumens on softening point

Softening point (^oC)			
	SBS polymer and type		
Added aromatic oil	Kraton D1184 *Branched*	Vectra 2411 *radial*	1101/1184 blend *linear/branched*
60/70 bitumen, refinery S			
3,5%	103	106	71
5%	87	104	72
80/100 bitumen, refinery S			
3,5%	92	93	70
5%	99	97	69

Note: results here are each the average of two tests, with only small differences between individual tests.

For the 1184 polymer, neither the base bitumen nor the level of added aromatic oil had a statistically significant effect (at a probability level of 95%) on softening point. This suggests that the base bitumen and the 1184 were partially compatible. It also suggests that there were also adequate aromatic fractions in the base bitumen to be absorbed by the styrene domains; thus a blend could be made using less added aromatic oils.

For the Vectra polymer, the base bitumen had a statistically significant effect (at a probability level of 99%), but the level of added aromatic oil had no statistically significant effect. This suggests that the 60/70 base bitumen was less compatible than the 80/100, and that there were adequate aromatic fractions in the base bitumen. It is interesting to note that there is a difference between the 1184 polymer and the Vectra polymer, since the 1184 and the Vectra have similar styrene/butadiene ratios and configuration. However their extent of branching differs and their molecular weight distribution differs. Clearly the interaction of SBS polymer with bitumen is a complex issue.

For the 1101/1184 blend, the base bitumen and level of aromatic oil had a negligible effect. With the relatively small changes in softening point, it is hypothesized that the 1101/1184 blend is showing compatibility with the base bitumen. This is probably influenced by the greater compatibility of the linear component (1101).

In view of the inconsistent results, this does need more research, especially into the role of bitumen molecular size distribution.

3.2 Effect of storage at high temperature

The storage stability of the SBS/bitumen blend is a prime indicator of compatibility. Storage at high temperature was defined here as 160^{o}C, which bracketed the temperature for onset of rapid oxidation (180^{o}C), the temperature of bitumen in an asphalt plant circuit (160^{o}C), and the commonly used long term storage temperature (140^{o}C).

The storage stability was checked using the 3 day, 160^{o}C test (SABITA, 1994), and is reported in Table 8. The SBS level used was 5% to ensure network formation and study trends without being near the network threshold.

Table 8 : Storage stability

Base bitumen	**Polymer (5% m/m)**	**Added aromatic oil**	**Homogeneity (Refinery S) ^{o}C**	**Homogeneity (Refinery N) ^{o}C**
80/100	1184	3,5%	1,25	45,5
80/100	1184	5%	2,0	28,5
60/70	1184	3,5%	1,0	44,5
60/70	1184	5%	0,5	45,5
60/70	Vectra	3,5%	0	19,0
60/70	Vectra	5%	0	41,0
60/70	1101/1184	3,5%	0	43,2
60/70	1101/1184	5%	1,0	42,0

There was a clear difference between bitumen sourced from the two refineries. The authors' opinion, based on handling the material in the laboratory and experience during production, is that the magnitude of homogeneity using the refinery N bitumen is not acceptable in an asphalt production situation. More background to this opinion is given in section 1.4.4. Homogeneity is especially important because tests for the SBS properties in asphalt after manufacture have not yet been developed. Interestingly in other research, the highest homogeneity test result was 73,5^{o}C, obtained with a base bitumen from yet another refinery. Results of 30-40^{o}C were commonly obtained from other combinations deemed unacceptable.

The point must be made that "compatibility" is not necessarily a desirable property for all bitumen used on roads. The authors have considerable experience with the unmodified bitumen from refinery N, and are of the opinion that it is a first class road bitumen. Indeed, it may be preferable for some unmodified bitumen applications to the "compatible" bitumen. Consequently, it is felt that the focus should be increasingly on the end result of the product, and not on the recipe or pathway used to make it.

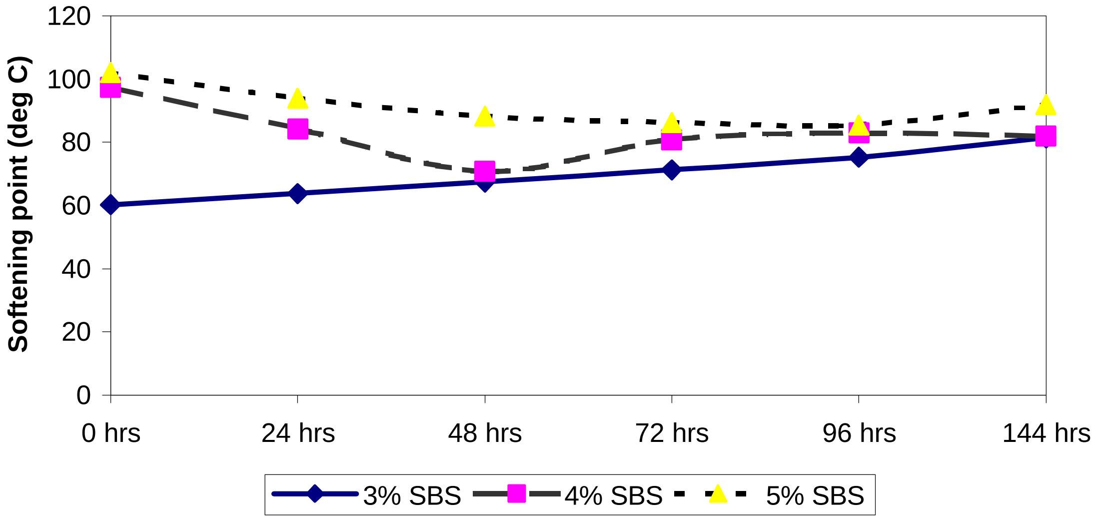
Control over mixing and circulation is an important demand on the manufacturer, and significant adjustment of recipe or raw materials may be required periodically for changing base bitumens. This makes a recipe approach even less desirable.

3.3 Aging during storage at high temperature

The effect of aging during storage of SBS modified bitumen was determined by storing samples at 180^{o}C in the oven, and observing the change in softening point (Figure 3) and viscosity at 150^{o}C (Figure 4). The samples were made from Refinery S 80/100, 3,5% aromatic oil, 1184M SBS powder, homogeneity test result of 1^{o}C.

There is an increase in softening point and viscosity with time, which should be recognised, although the bitumen used was partially compatible. This is due to gellation, rather than cross-linking between the butadienes. This has implications for the testing procedures (discussed later), but may be countered by the effect of pumping (discussed later).

Figure 3: Effect of ageing on softening point



Note: The 4% SBS result @ 48 hours is probably a testing error

3.4 Asphalt Mixing and Compaction Temperatures

In the design and manufacture of asphalt, the viscosity of the bitumen is controlled to ensure good mixing with the aggregate. For practical reasons, this is done by temperature control within limits set by the bitumen temperature/viscosity relationship. These limits differ for Marshall laboratory test and for the asphalt plant (Table 9).

Figure 4: Effect of ageing on viscosity @ 150 degC

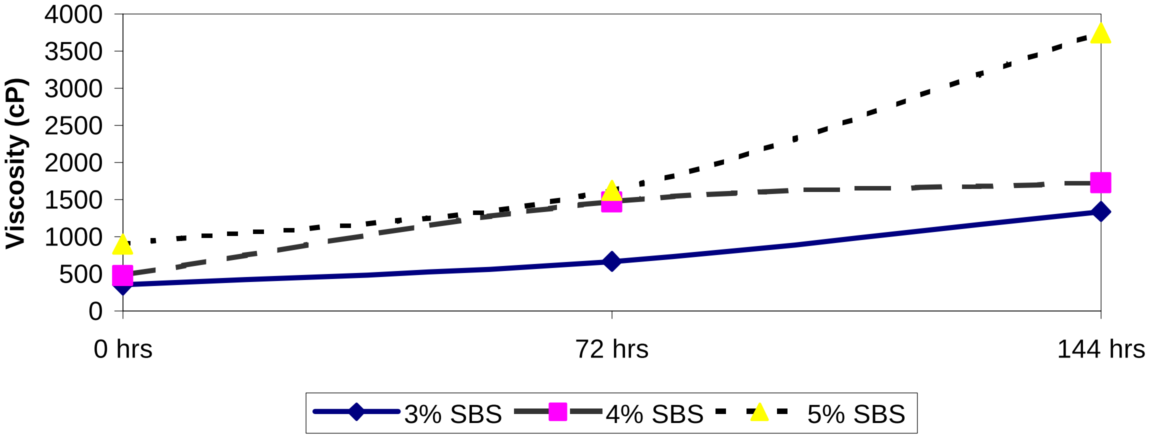


Table 9: Marshall test and asphalt mixing viscosities

	Mixing viscosity	**Compaction viscosity**
Laboratory Marshall test (note 1)	150-190 cSt	250-310 cSt
Asphalt plant (note 2)	200-500 cSt 0,2-0,5 Pa.s (note 3)	2000 - 20000 cSt 2 - 20 Pa.s.

Note 1: test limits from TMH 1 (CSRA, 1986)
Note 2: asphalt plant limits from Shell (Whiteoak, 1990). The ideal mixing viscosity is 200 cSt.
Note 3: conversion from kinematic to dynamic viscosity assumes a specific gravity of 1.00

Table 10: Viscosity/temperature relationship for SBS modified bitumen

Kinematic viscosity (cSt)	**3 % 1184**	**4 % 1184**	**5 % 1184**
@ 110 °C	7650	23 300	44 000
@ 120 °C	1960	3 690	6 300
@ 130 °C	685	1 715	2 120
@ 140 °C	435	615	860
@ 150 °C	320	430	605

@ 160 °C	235	315	420
@ 180 °C	130	170	220

Note: test was by Brookfield viscosity, and results converted to kinematic. The viscosity/temperature relationship for SBS modified bitumen (Refinery S, 1184 at various levels, 3,5% added aromatic oil) is shown in Table 10. This was similar to published results (Serfass et al, 1992).

The interpretation of the data in Table 10 is that for 4% SBS bitumen, the asphalt plant temperature for optimum mixing (200 cSt) should be about 175°C. The compaction temperature range should be about 110-130°C.

This was not supported by experience in practice however. There were problems with mixing and compaction that gave some concern about the temperature limits being used. It appears that the mixing and compaction temperature / viscosity limits for modified bitumen are not directly comparable with those of unmodified binders.

Shell (1998) recommends an increase of 2,5°C in normal mixing and compaction temperatures for every 1% of TR1101 added. The relationship between TR1101 and 1184 is not known, but assuming it to be equal (which is unlikely and a topic for further research), this would suggest the following:

Table 11: Asphalt plant mixing temperature

Binder	**Temperature (°C)**	
	60/70	80/100
Unmodified bitumen	140	150
Shell recommendation SBS modified	150	160
Temperature/viscosity graphs SBS modified	n.a.	175

Table 12: Asphalt compaction temperature

Binder	**Temperature (°C)**
Unmodified 80/100	100 - 130
Shell recommendation SBS modified 80/100	110 - 140
Temperature/viscosity graphs SBS modified 80/100	110 - 130

More research was done to understand the differences, and it uncovered the effect of gear pumps in the asphalt plant, which is discussed below.

3.5 Degradation (shearing) by gear pumps in the asphalt plant

The manufacturing process and the laboratory research on SBS here used low shear stirrers with SBS in the powder form. Full-scale manufacturing facilities commonly use high shear stirrers, where the capital cost of the high shear plant can be offset by the savings in SBS type. Medium or high shear stirrers are also more effective in dispersing the SBS in the bitumen. In the asphalt plant, the SBS modified binder was to be circulated, transferred and injected transferred via a gear pump (which is a high shear condition). The effect of the high shear on the SBS domain structure was of concern, both in terms of cutting the network chains and changing the properties, so it was investigated. The low shear manufactured SBS modified binder was passed through two passes of a high-shear gear pump. The SBS modified binder was Refinery S 80/100, with varying polymer B, and 3,5% aromatic oil). The results are shown in Tables 13a and 13b.

Table 13a: Effect of high-shear gear pump on 3% SBS properties

Property	Initial Values	After high shear circulation
Softening Point (°C)	60,3	53,5
Viscosity @ 120 °C (cP)	1 960	320
Viscosity @ 150 °C (cP)	1 170	305

Table 13b: Effect of high-shear gear pump on 5% SBS properties

Property	Initial Values	After high shear circulation
Softening Point (°C)	102	96,3
Viscosity @ 120 °C (cP)	6 300	605
Viscosity @ 150 °C (cP)	3 100	450

These results show a significant decrease in viscosity after the binder passes through a gear pump. In practice, the binder will pass through several pumps between manufacturing and the asphalt plant pugmill. These may include transfer pumps, re-circulation pumps in the asphalt plant bitumen circuit, and finally the injection pump into the pugmill. Consequently, a decrease in viscosity between laboratory and manufacturing is inevitable. This supports the Shell approach, and suggests that the laboratory measured viscosity of SBS modified binder cannot be compared to that experienced in the pugmill.

3.6 Reproducibility and repeatability of tests

With SBS modified bitumen, the SBS network which forms upon cooling must be completely broken down on re-heating SBS bitumen to pour into test moulds to ensure that reproducibility and repeatability are possible (Dony and Durrieu, 1991). During construction on one project, problems were experienced in correlating results between different laboratories when testing retained samples of SBS modified binder (reproducibility). A short investigation into repeatability (the same operator), in the Coltech laboratory found differing results for the same sample. The thermal history (length and duration of heating) of the retained sample was investigated because it was felt that this has a direct influence on the test results obtained (Table 14). What was surprising was the magnitude of the influence and the fact that the laboratories showing poor reproducibility were experienced in bitumen testing. Clearly handling SBS modified samples in the same manner as unmodified bitumen samples is not acceptable. Later informal testing found penetration and elastic recovery to be somewhat less influenced by the thermal history.

Table 14: Effect of thermal history on repeatability of softening point

Binder	**Softening point (°C)**			
	Poured directly after manu-facture	Retained sample reheated to 120°C and stirred for 5 minutes	Retained sample reheated to 160°C and stirred for 15 minutes	Retained sample reheated to 180°C and stirred for 20 minutes
Refinery S, 60/70 + 6% SBS	98	67	81	105
Refinery N, 60/70 + 6% SBS	106	n.a.	n.a.	97
Refinery S, 80/100 + 4% SBS +3,5 % oil	90	68	n.a.	n.a.

Table 15: Effect of compatibility on repeatability of softening point (Dony and Durrieu, 1991)

Thermal history	**Softening point (°C)**		
	Fully Compatible Bitumen	**Semi-compatible Bitumen**	**Least Compatible Bitumen**
Sample poured just after manufacture	80 °C	87 °C	88 °C
Retained sample reheated to 120°C	69 °C	60 °C	63 °C
Retained sample reheated to 140°C	79 °C	67 °C	70 °C
Retained sample	79 °C	87 °C	78 °C

reheated to 160°C			
Retained sample reheated to 180°C	79 °C	88 °C	87 °C

Note: 5% TR1101 in bitumen of varying compatibility.

The thermal history depends in part on the re-heating process and a minimum re-heating temperature and time is needed to get repeatable results. This is directly influenced by the degree of compatibility between SBS and bitumen, where compatibility is determined by the microscopic observation of the micro-morphology.

Based on this work and that of Dony and Durrieu (1991), the authors support the SABITA Manual 15 recommendation that the minimum re-heating of samples be at 180°C for 15 minutes before retained samples are tested for softening point. However it is further recommended by SABITA that re-heated samples should undergo controlled cooling in air at 15°C +/- 3°C as it is believed that the rate of cooling influences the formation of the three dimensional structure. The authors believe that there should also be time controls on the storage of hot samples, due to the effect of aging.

4 CONCLUSIONS

I. The compatibility of SBS with bitumen available in South Africa was found to vary widely, from highly compatible through partially compatible through not compatible. The highly to partially-compatible blends are recommended for use in road applications.
   A. These are characterised by homogeneity test results in the range 0 to 6 °C.
   B. There should be little difference in performance of these acceptable bitumens if the SBS/bitumen is in a single phase at the time of application. This may require specialist techniques in terms of mixing and circulation.
   C. The incompatible mixtures are too difficult to keep in a one-phase solution in practice. These are characterised by high homogeneity test results (>20 °C).
   D. The SABS penetration grade specification provides no guide as to the compatibility of bitumen with SBS.

II. The properties of SBS modified bitumen change inconsistently upon varying the hardness of base bitumen, varying the type of SBS polymer used, and varying the amount of added aromatic oil.

III. Revision of SABITA Manual 15 (1994) is suggested for SBS modified bitumens:

A. There is general acceptance now that the unmodified bitumen tests/specifications should not be applied to SBS modified bitumens.
B. Softening point, elastic recovery and homogeneity were found very useful for characterising the modified bitumen.
C. Homogeneity test should be retained, but the range modified to 0-6°C.
D. The addition of performance testing is suggested.

IV. **The use of a simple recipe specification for SBS modified bitumens in South Africa is strongly cautioned against.** The successful production manufacture of high-performance SBS modified bitumen is possible using bitumen available in South Africa, but it requires attention to several factors:
A. Control over the base bitumen molecular distribution; balance of asphaltenes, saturates, aromatic, and resins; and control over propane de-asphaltened tar content. Since this can vary from day to day for a given crude and production route, effective control is more easily assured with large scale batching.
B. Control over mixing and circulation is required by the manufacturer at the time of application.
C. Significant adjustment of the raw materials may be required periodically for changing base bitumens.

V. The implications of the application temperature/viscosity relationship for SBS modified bitumen are different to unmodified bitumen.
A. SBS modified bitumen has a higher viscosity than unmodified bitumen. This viscosity can increase on standing at high temperature.
B. Gear pumps, which are typically used for pumping, circulation and asphalt plant injection in South Africa, reduce the viscosity of SBS modified bitumen, probably by disturbing the SBS network chains.
C. The net effect at the asphalt plant pugmill is that the SBS bitumen viscosity is only slightly increased over unmodified bitumen. Shell recommends that the asphalt plant mixing temperature should be increased by only 2,5 °C for every percentage point of 1101 polymer added, and this is supported by the research here.

VI. The testing and sample preparation for SBS modified bitumen requires close control and this should be reflected in the test method; the present test methods may need re-writing to incorporate this. The SBS network which forms upon cooling must be completely broken down on re-heating SBS bitumen to pour into test moulds.
A. The SBS bitumen sample should be reheated to 180°C and stirred for 15 minutes before pouring into test moulds and cooling at a specific rate.
B. Limits should be placed on time of storage at high temperature.

ACKNOWLEDGMENTS

This work forms part of the research programme of Colas Southern Africa Pty Ltd, and was done while the authors were employed there. The permission of Colas to use their research data is gratefully acknowledged.

REFERENCES

Bouldin, M.G. and Collins, J.H. (1992) **Influence of Binder Rheology on Rut Resistance of Polymer Modified and Unmodified Hot Mix Asphalt** in Polymer Modified Asphalt Binders, ASTM STP 1108, Philadelphia

Bull, A.L. and Vonk,W.C. (1984) **Thermoplastic Rubber / Bitumen Blends for Roof and Road** Shell Technical Note TR8.15, London

CSRA (formerly NITRR) (1986) **Standard test methods for road building materials** Manual TMH 1, CSIR, Pretoria

Dony, A. and Durrieu, F (1991) **Characterization of Bitumen-Polymers: The Effect of the Sample preparation Method on Test Results** Bulletin de Liaison, LCPC, No 175, Sept-Oct 1991, pp 7-11, Paris.

Exxon (1992) **Polymer-Modified Bitumen for Pavements** Polymers Group, Exxon Chemicals, Belgium

Linde,S. and Johannson, U. (1992) **Thermo-oxidative Degradation of Polymer Modified Bitumen** in Polymer Modified Asphalt Binders, ASTM STP 1108, Philadelphia

Rogge, D.F., Terrel, R.L., and George A.J**.** (1992) **Polymer modified Hot Mix Asphalt – Oregon Experience** in Polymer Modified Asphalt Binders, ASTM STP 1108, Philadelphia

SABITA (1994) **Technical Guidelines for Seals Using Homogeneous Modified Binders** Manual 15, Cape Town.

Serfass, J.P., Joly, A. and Samanos, J. (1992) **SBS-modified asphalts for surface dressing** in Polymer Modified Asphalt Binders, ASTM STP 1108, Philadelphia.

Srivastava, A., Hopman, P.C., and Molenaar, A.A.A. (1992) **SBS Polymer Modified Asphalt binder and its Implications on Overlay Design** in Polymer Modified Asphalt Binders, ASTM STP 1108, Philadelphia

Van Gooswilligen, G., de Hilster, E., and Robertus, C. (1994) **Changing needs and requirements for bitumen and asphalts** Session IV, pp189-209, CAPSA, Cape Town

Vonk, W. (1998) **Styrene-Butadiene-Styrene (SBS) Block Copolymers: Asphalt Mix Improvers for Severe Climatic Conditions** Lecture Delivered at the CSIR Conference Centre, Pretoria

Whiteoak, D (1990) **The Shell Bitumen Handbook** Shell Bitumen UK, London