ENSURING THE QUALITY OF SBS MODIFIED BINDERS

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ABSTRACT

SBS modification confers enhanced properties on bituminous binders, and will become increasingly important as freight loads and traffic stressing of surfacings increase. SBS bitumen blends exhibit complex phase behaviour and, unless this is taken account in the formulation, manufacture and handling of the binders, field failures can occasionally occur or the full potential of the binder may not be realised. Of key importance is the compatibility of the SBS polymer and bitumen. Segregation and other tests were carried out on twelve randomly selected, commercial SBS binders, and six of these were found to segregate, or degrade during storage at 180 °C. Issues identified during testing were: manufacturing and sampling, segregation and thermal stability. Practical measures were put forward to address these issues, and to ensure that the properties of SBS binders are satisfactory when delivered to the purchaser at the construction site.

INTRODUCTION

SBS thermoplastic rubber

The properties of bitumen binders used in road surfacings can be enhanced through the addition of polymers to create polymer modified binders (PMBs). The most common polymer type used in Australia and overseas for bitumen modification is styrene butadiene styrene (SBS) double ended block copolymer. SBS is a ‘thermoplastic rubber’ and this refers to the fact that the linking process between the rubber molecules is reversible through temperature change. Links are formed at close to ambient temperatures but are broken at elevated temperatures, only to reform again on cooling. This confers desirable properties on the polymer bitumen blend. Above about 90 °C the rubber molecules are mobile, and the material can be easily pumped and sprayed at elevated temperatures. Below 90 °C, however, the molecules tend to cross-link and the blend becomes more elastic in nature, resulting in improved properties such as enhanced fatigue and rut resistance at road service temperatures.

Morphology

Morphology describes the way in which the polymer-rich and bitumen-rich phases are distributed in a PMB. The properties of a particular SBS blend can vary considerably depending on the degree of dispersion of the SBS particles and whether a single phase structure is formed.

It is difficult to infer SBS morphology in a binder by measuring physical properties. However, it can be done by the use of ultraviolet (UV) fluorescence microscopy. This technique uses ultraviolet light to cause the polymer molecules (but not the bitumen) to fluoresce at a wavelength which can be detected by the eye. Thus polymer structures appear as bright objects against a dark (bitumen) background.

Figures 1 (a) and (b) are photographs of an SBS binder, taken using this technique. Hot binder samples were cooled very rapidly so that the structure at the elevated temperature was essentially ‘frozen’ in place and could thus be studied. In Figure 1 (a) the SBS phase is dominant and brightly coloured, while the darker areas represent occluded bitumen.
1 (b) is a picture of the same binder but, in this case, a change in storage temperature has caused the bitumen phase to become dominant. Information on the preparation of samples and the fluorescence microscope techniques are given in a paper by Oliver et al. (Austroads 2012).

![Fluorescence microscope images of a binder stored at two temperatures, 0.08 x 0.12 mm](image)

**Figure 1: Fluorescence microscope images of a binder stored at two temperatures,**

**Australian and overseas practice**

While PMBs can deliver improved performance, more care is needed in their manufacture, storage, transport and application than is the case for unmodified bitumens. Segregation and polymer degradation have been observed in SBS modified asphalt (Wegan et al. 2001) and significant failures of sprayed seals have been associated with PMBs based on SBS polymers (Neaylon et al. 2007). There have been concerns in Australia for a number of years with the difficulty of obtaining repeatable and consistent test results for PMBs, and a particular issue has been the relationship between manufactured and ‘as delivered’ properties of the binders. These problems have ramifications in terms of the control of test properties and thus field performance.

Such difficulties are related to the complex nature of SBS binders. Following manufacture at high temperature (around 180 °C – 200 °C), some SBS binders may show single phase behaviour (SBS ‘dissolves’ in the bitumen) but many form two phases. During cooling to service temperatures, virtually all SBS binders show two-phase behaviour, with phase separation becoming more distinct as cooling progresses (Soenen et al. 2008). The degree of separation, and thus morphology of the SBS blend, has an important effect on binder properties and field performance.

In overseas road applications, most SBS blends tend to be used at polymer concentrations of about 3% by mass of binder. However, in Australia, the concentration of SBS across the various grades covers a range from 3% to greater than 7% (Oliver et al. 2012). Furthermore, the main use of SBS blends overseas is in hot-mixed asphalt while, in Australia, the focus is more on
sprayed sealing binders. Thus overseas field experience and binder specifications cannot be relied on to provide guidance or help control performance in Australia.

Aims of the work

This paper describes studies which investigated the properties of a range of Australian commercial SBS blends in order to:

- understand field and laboratory performance, in particular where problems have been encountered
- identify tests which could be used to minimise the risk of field failures occurring.

BACKGROUND

Phase behaviour

When SBS polymer is added to a heated bitumen, it absorb oils from the bitumen and swells (Brule et al. 1988, Vonk et al.1989). How fast this occurs, and to what extent, depends on the temperature, the size of the polymer particles added, the mixing process and the composition of the polymer and bitumen. The reported degree of swelling of the SBS polymer is considerable, being in the range 500% to 700% by volume. Further information is given in a report by Oliver et al. (2012).

The idealised phase behaviour of an SBS binder, after equilibrium has been reached, is shown in Figure 2. The area above the curve is where the SBS ‘dissolves’ and a single phase structure is obtained. Below the curve the binder forms a two phase structure with either the polymer phase or the bitumen phase dominant, depending on the polymer concentration.

The location of the curve depends on the composition of the particular bitumen and SBS polymer used. Bitumens which are compatible with the selected SBS grade will result in a curve which is lower down the Y-axis than those which are not. That is to say, a compatible bitumen will show single phase behaviour at lower temperatures than an incompatible one.

![Figure 2: Idealised phase diagram for an SBS binder](image)
The normal range of concentration of Australian SBS binders is shown by the shaded area on the left of the diagram. It should be noted that this crosses a sharply rising section of the curve so that a small change in SBS concentration can have a large effect on the temperature at which a single phase structure is obtained (and thus on the likelihood of segregation).

Compatibility

As mentioned, a major influence on the properties of SBS modified paving bitumen blends is the compatibility between the bitumen and the SBS modifier. Essentially, the SBS polymer competes for solution in a bitumen with the asphaltene (large molecular size) fraction of the bitumen. High asphaltene contents tend to lead to SBS precipitation unless counteracted by increased aromaticity (ring based structures) in the bitumen. Manufacturers often add aromatic compatibilising oils for this purpose. The molecular size and particular composition of the SBS grade used will also have an important influence on compatibility.

To minimise the risk of segregation in an SBS blend, a bitumen of suitable compatibility should be used. Brûlé et al. (1988) proposed that a colloidal stability index, developed to characterise the stability of bitumens (Gaestel et al. 1971), might be useful in characterising their compatibility with polymers, as follows:

\[
\text{Gaestel Index} = \frac{\text{saturates} + \text{asphaltenes}}{\text{aromatics} + \text{resins}}
\]  

(1)

Table 1: Epifluorescence microscope photographs showing effect of bitumen compatibility on morphology at different temperatures, 0.08 x 0.12 mm

<table>
<thead>
<tr>
<th>Storage temperature</th>
<th>Poor compatibility bitumen (GI = 0.37)</th>
<th>Good compatibility bitumen (GI = 0.18)</th>
<th>Possibly grafted SBS binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 °C</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td></td>
</tr>
<tr>
<td>180 °C</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
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<tr>
<td>160 °C</td>
<td><img src="image5.png" alt="Image" /></td>
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<td>140 °C</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
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</tr>
<tr>
<td>120 °C</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td></td>
</tr>
<tr>
<td>100 °C</td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td></td>
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</tbody>
</table>
A study on compatibility was undertaken at ARRB, and details of the experimental techniques are given in a report by Oliver et al. (Austroads 2012). Two bitumens of widely differing Gaestel Index were identified and used to prepare blends containing 6% by mass of SBS polymer. Samples for microscopic examination were taken at intervals while the blends were subjected to an isothermal cooling regime.

Each sample container was first heated in an oven at 200 °C for 1 h. The container was removed from the oven, stirred and samples taken. The samples were cooled rapidly in order to ‘freeze’ the morphology at the storage temperature. The container was then returned to the oven which was now set at 180 °C. After a period of 1 h, samples were taken as before, and the process repeated, stepping down 20 °C each hour. The lowest isothermal storage temperature used was 100 °C.

Table 1 (columns 2 and 3) shows photographs of the samples taken with a fluorescence microscope. In the case of the good compatibility bitumen blend (low Gaestel Index), the polymer-rich phase was the continuous one from 200 °C to about 120 °C. In the case of the poor compatibility bitumen blend, the bitumen-rich phase appeared to be the continuous one at all temperatures. The two phase structure of the poor compatibility bitumen at transport and field storage temperatures would render it very liable to segregation. This occurs when a concentration gradient is established, with the less dense polymer phase tending to float to the surface.

**Commercial manufacture of SBS blends**

In order to satisfactorily blend SBS polymer with bitumen, a three stage process is recommended (Shell Chemicals 1994) and includes:

- A predispersion step where the polymer is added to the stirred bitumen at around 180 °C.
- A disintegration stage to break down the polymer particles, normally with a high shear mill. The shearing process can cause a rapid rise in temperature and measures need to be taken to avoid temperatures above 190 °C which can cause rapid degradation of the SBS polymer.
- A final soaking period. This is normally carried out using low shear mixing at 180 °C. Polymer swelling and incorporation of the polymer into the bitumen occurs during this stage.

Manufacturers may vary the above process. For example, a concentrate could be prepared and diluted with bitumen as needed in order to produce a range of PMB grades. This was the procedure used when SBS was first introduced into Australia. The properties of diluted blends can take some time to reach equilibrium.

Another process used to improve the stability of SBS blends is sulphur addition. The original process was patented (Maldonado et al. 1979) but now that patents have expired it is becoming more widely used. Addition of sulphur causes links to be established between the SBS and bitumen molecules, rather than between SBS molecules, as occurs during normal rubber vulcanisation. The increased stability may be because the SBS has ‘cloaked’ itself with bitumen components so it ‘looks’ more like bitumen than it did before, i.e. it is more compatible.

The fourth column of Table 1 shows photographs of a sample of a commercial SBS binder, believed to be grafted, which was used in an asphalt road trial (Austroads 2012). A strong sulphur smell during asphalt mixing was observed. This binder was unusual in that it exhibited an almost homogeneous appearance at 140 °C and above, as shown in the figure. This blend appeared to be very stable, and would be expected to have a much reduced tendency to segregate with storage, compared to most other SBS binders.
STUDY OF COMMERCIALLY AVAILABLE SBS BINDERS

Overview

In order to study the segregation resistance of Australian SBS binders, a range of commercially manufactured binders was obtained. A number of the binders were observed to segregate during the process of splitting of bulk samples into sub-samples, even before segregation testing began. This raises sampling issues which are discussed later.

The binders were subjected to the European storage stability test which involves storage of binder samples at 180 °C for three days. Some of the binders segregated and some degraded during storage. Degradation was indicated by a reduction in Softening Point, and the rheological properties of the original and degraded binders were measured. A summary of the segregation and degradation results is presented in this section, and measures to ensure that future binder quality is maintained are discussed in a later section.

Materials

<table>
<thead>
<tr>
<th>Grade</th>
<th>Manufacturer</th>
<th>Softening point (°C)</th>
<th>T190 specification S. Pt. range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A10E</td>
<td>Z</td>
<td>95 – sub-sample 1 70 – sub-sample 2</td>
<td>88–110</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>A15E</td>
<td>X1</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td></td>
<td>X2</td>
<td>91</td>
<td>82–105</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>93 – sub-sample 1 76 – sub-sample 2 80 – sub-sample 3</td>
<td></td>
</tr>
<tr>
<td>A20E</td>
<td>V</td>
<td>87</td>
<td>65–95</td>
</tr>
<tr>
<td>S20E</td>
<td>Z</td>
<td>97</td>
<td>62–88</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>S15E</td>
<td>Y</td>
<td>73</td>
<td>55–75</td>
</tr>
<tr>
<td>S10E</td>
<td>Z</td>
<td>58 – sub-sample 1 77 – sub-sample 2</td>
<td>48–64</td>
</tr>
</tbody>
</table>

Twelve commercial SBS binders, covering both sealing and asphalt grades and five different manufacturers, were obtained for testing. The specification requirements for the different polymer grades are given in the Austroads Specification Framework for PMBs and Multigrade Bitumens (Austroads 2010a), and the Softening Point ranges from this latest specification are shown in column four of the table. It should be noted that an upper limit for the Softening Point
value was only introduced into the specification in December 2010, and many of the binders in Table 2 were manufactured before this date.

The manufacturers have been identified in Table 2 by the letters ‘V’ to ‘Z’. The two A15E samples from manufacturer X (X1 and X2) came from different batches manufactured approximately a year apart. They were included to obtain an indication of the degree of variation in properties which might be expected between different batches of the same PMB grade from one manufacturer.

Normally, a bulk supply of each sample was provided to ARRB and this was split into smaller sub-samples for later use. Splitting was performed according to the Austroads test method (Austroads 2008) but a mechanical stirrer was used instead of a spatula to ensure good mixing was achieved. Testing of nominally identical sub-samples showed that, in three cases (A10E Z, A15E Y and S10E Z), the Softening Points of sub-samples derived from the same original sample were substantially different, as shown in Table 2. This was attributed to segregation occurring during the splitting process and is discussed further later.

**Test procedures**

**Segregation testing**

Segregation treatment was conducted according to the European storage stability test method (EN 13399:2010) which involves storing a binder sample vertically in a toothpaste tube in an oven at 180 °C for three days. The tube is then removed from the oven and cooled in a vertical position at room temperature followed by storage for several hours in a freezer at -20 °C. When solid, the tube is cut into three equal parts. The binder from the top third of the toothpaste tube is recovered and tested, and the same is done for the binder in the bottom third of the tube. In the case of the ARRB study, testing involved measurement of Softening Point.

**Softening point**

The Softening Point of the binder samples was determined using the ring and ball test (AS 2341.18–1992). The test method requires duplicate samples to be tested and a mean value to be reported provided the two results for a bitumen sample are within 1.2 °C. For the current investigation using PMBs, it was decided that two results would be acceptable if they were within 2 °C of each other. Otherwise the test would be repeated.

The value of 2 °C was based on the results of a small experimental program to examine the reproducibility and repeatability of the Softening Point of SBS PMBs. While the experiment was limited in nature, it suggested that the repeatability and reproducibility of storage stable and thermally stable PMBs are not too different to the values applicable to bitumen.

**Method**

The Softening Point of each of the 12 binders was measured. A sample of each was then stored for three days at 180 °C vertically in a tube, as described in the European test method for the determination of storage stability of modified bitumen (EN 13399:2010 ). The Softening Point of the binders in the top and bottom thirds of the tubes was then measured.
Results and discussion

Segregation during sample splitting

As indicated previously, nominally identical sub-samples of the same bulk sample were found to be different in three cases (A10E Z, A15E Y and S10E Z), as indicated by Softening Point measurements (Table 2).

One sample (A10E Z) had been found in other testing to be very prone to segregation. To try to ensure homogeneity before testing a sub-sample of this material for other work, the sub-sample was heated to a standard temperature of 180 °C and stirred with a high shear (Silverson) mixer before being poured into a fresh can. However, during cooling of the can, and before the binder reached room temperature, it was observed that the surface of the binder was becoming coarse and mottled, indicating polymer was concentrating there. Removal of material from the surface, and from beneath the surface, with a spatula confirmed that the surface material was much more polymer-modified than the interior material. Thus this sub-sample of A10E Z showed evidence of substantial segregation within a matter of minutes.

Another sub-sample of A10E Z which was used for segregation testing in an earlier study (Austroads 2010b) also showed a strong propensity to segregate but the particular sub-sample used in the current study did not. Thus different sub-samples from the same bulk sample of A10E Z showed different segregation propensities. This suggests that different layers in a container of binder (which may be a storage tank or a bulk sample) which is segregating may have different segregation propensities. This is probably related to the polymer concentration in the layer. A sample containing material taken from close to the surface of the container will have a higher polymer concentration (and greater tendency to segregate), while the polymer concentration in succeeding samples will reduce as material is taken from greater depths below the surface.

This raises the important point that a sample taken from a manufactured batch and tested for storage stability may yield a result indicating no segregation while the batch is, in reality, prone to segregation. Consideration should be given to developing procedures to ensure that a sample of SBS binder taken from a manufactured batch, or from a bulk sample for splitting, is representative of the batch. If an unrecognised SBS polymer concentration gradient is present in the batch then an erroneous test result may be obtained.

Storage stability testing and thermal stability

Prior to segregation treatment, the Softening Point of each sample was measured (termed 'initial Softening Point' and marked 'A' in Table 3). Following storage of the samples in a tube for three days at 180 °C, the Softening Points of the binder in the top third of the tube (marked 'B') and the bottom third of the tube (marked 'C') were determined.

A storage stability value, which indicated the segregation propensity of the binder, was calculated as the Softening Point of the top third of the binder in the tube minus the Softening Point of the bottom third of the binder in the tube (B – C). Examination of the results indicated that a substantial reduction in Softening Point had occurred in some samples following oven storage at 180 °C, and a thermal stability value was also calculated. This was defined as the initial Softening Point of the sample minus the average Softening Point of the top and bottom thirds of the binder in the tube following oven exposure (A – ((B+C)/2)).

The results are shown in Table 3. Where substantial segregation occurred during sample splitting, (i.e. nominally identical sub-samples of the binder had different Softening Points), the appropriate box in the column headed ‘Manufacturer’ has been shaded. Where substantial changes in storage stability (segregation) or thermal stability occurred after testing, the corresponding boxes have been shaded in columns six and seven of the table.
It should be noted that a small change in SBS concentration can lead to a large change in Softening Point at a concentration of about 5% by mass SBS in the binder, the exact figure depending on the properties of the SBS and the bituminous fraction (Valkering & Vonk 1990). This concentration corresponds to a Softening Point range of about 50 °C to 80 °C. Sample S15E Y is within this range so a drop in the Softening Point of this binder would represent a smaller change in effective SBS concentration than for many of the other binders. However, the Softening Point vs SBS concentration plots reported by Valkering and Vonk (1990) indicate that the 19 °C Softening Point drop experienced by S15E Y corresponds to an approximate 2% reduction in ‘effective’ SBS concentration (i.e. not a small change in concentration).

Table 3: Segregation test results for 12 commercial PMBs

<table>
<thead>
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<tbody>
<tr>
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</tr>
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</table>

**Degradation of SBS binders**

The large reduction in Softening Point results following storage at 180 °C is believed to be due to chain scission (cutting) of long SBS molecules. This was studied by Johansson and Linde (1991) who used gel permeation chromatography (GPC), supplemented by mechanical testing. GPC can give the molecular size distribution of a binder i.e. it produces a plot of the amount of material of each molecular size (molecular weight). This is very useful for evaluating polymers like SBS, where the length of the polymer chain which influences the properties of the PMB binder.

Johansson and Linde looked at several SBS types, and the results below are for the same SBS grade as used in ARRB work. A blend of a B180 bitumen (45 Pa.s at 60 °C) and 8% by mass of SBS polymer was stirred in a vessel heated at 200 °C for up to 27 h. GPC analyses showed that after a few hours there was a pronounced change in the polymer phase, and after 24 h almost all the original SBS had degraded to lower molecular weight fractions (i.e. chain scission had occurred).

To determine how the reduction in polymer molecular weight affected the low temperature mechanical properties of the binder, samples were evaluated using a tensile test rig. This was equipped with a climate chamber which kept the sample at -10 °C while tensile measurements were carried out at a crosshead speed of 50 mm/min. Dumb-bell shaped specimens were fitted into an aluminium holder with epoxy adhesive.
A summary of the elongation at break results is shown in Figure 3 for samples taken at 0, 3, 5 and 7 h. The tensile strength and the elongation at break had decreased drastically after 7 h at 200 °C. Even longer exposure times resulted in almost no tensile strength or elasticity at all in the blend (Johansson & Linde 1991).

![Figure 3: Tensile test of TR 1101 binder stored at 200 °C, 50 mm/min, -10 °C (data from Johansson & Linde 1991)](image)

ARRB testing with a dynamic shear rheometer (DSR) of a thermally unstable binder (A15E Y), (Table 3) supported this finding. The thermally unstable PMB showed a large increase in phase angle at low rates of loading, following oven exposure (3 days at 180 °C). This indicated a substantial loss in elasticity.

Johansson and Linde repeated their 200 °C storage study in a vessel with an inert (nitrogen) atmosphere. They found almost no difference in the molecular weight distribution of the polymer even after 24 hours. This indicated that the chain scission reaction was oxygen initiated. While it is possible to provide PMB field storage tanks with an inert atmosphere, this is not the practice in Australia.

The degradation reaction rate increases rapidly with increase in temperature, and it is therefore important to minimise the time an SBS PMB is exposed to high temperature. The AAPA code of practice for the manufacture, storage and handling of PMBs (AAPA 2004) seeks to do this by limiting the temperature at which SBS binder is stored in the medium term (up to 14 days) to a maximum of 160 °C. However sprayed seal binders can be held at point of spraying at a maximum temperature of 190 °C (one manufacturer specifies 200 °C) for one or two days. The results in Figure 3 suggest that exposure for this period could be deleterious to the binder.

**GENERAL DISCUSSION**

**Issues identified**

**Manufacturing and sampling**

The formulation and manufacture of SBS PMBs requires a high level of technical expertise and the use of suitable manufacturing and storage equipment. Most grades of SBS require high shear milling in order to reduce the particle size to the degree that swelling of the SBS occurs sufficiently quickly, and the swollen SBS is incorporated into the bitumen.
Manufacturing may not always be up to the necessary standards. An example is an A20E binder sampled at a Melbourne road trial. When the sample was heated in the laboratory to 200 °C to examine binder morphology, it was apparent that the SBS particles had not been adequately milled and mixed. In Figure 4, individual polymer particles can be identified and the largest has an indent on the side which probably occurred during the mixing process. The presence of discrete, irregularly shaped SBS particles at 200 °C, when the binder should have a single phase structure, indicates a high likelihood of segregation. It also indicates likely reduced field performance due to the lack of incorporation of the SBS polymer into the bitumen.

![Epifluorescence microscope photograph of commercial A20E binder at 200 °C, 0.08 x 0.12 mm](image)

Where a concentrated batch of SBS is diluted with bitumen to prepare particular specification grades, it may take a considerable time for a diluted batch to reach equilibrium. For example, Remtulla and Tait (1986) reported that the Softening Points of diluted batches of SBS binder continued to increase after seven days storage at 180 °C.

When a sample is taken by a manufacturer to determine whether a batch is suitable for release it is necessary to ensure that the batch has reached equilibrium before the sample is taken, and that the sample is a representative one. As indicated in a previous section, if a concentration gradient is present in a storage tank, a sample may incorrectly indicate that a material is storage stable while in fact the opposite is true.

**Segregation**

Segregation can occur when a binder forms a two phase structure. Figure 2 shows an idealised phase diagram of an SBS binder. Above the curve, the SBS ‘dissolves’ in the bitumen and a single phase is obtained. This is the desirable condition. If storage conditions are such that the binder is in the area below the curve then two phases are formed. The lower density SBS then tends to migrate upwards and a concentration gradient is formed.

If a binder with a concentration gradient is sprayed, for example, there will be a low concentration of SBS at the start of the run (as binder is sprayed from the bottom of the tank) and a high concentration at the end of the run. Depending on how severe the concentration gradient is, the performance of the binder may be severely compromised. It could be too soft and lacking in elastic properties at the start of the run, and too elastic to adhere to the cover aggregate particles at the end of the run.

A similar situation can occur in road tankers or vertical storage tanks. In both cases, when a concentration gradient exists, product drawn off first will tend to have a lower concentration of SBS then product drawn off last.
Degradation

Butadiene based rubbers, such as SBS, maintained at elevated temperatures are subject to three competing reactions: increase in molecular size due to cross-linking, oxygen induced polymerisation, and breakdown reactions (Bull & Vonk 1994). Cross-linking can lead to a considerable increase in the viscosity of the blend leading to gelation but this has not been reported as happening in Australia.

As has been known for some time (Kraus 1982), and discussed earlier in this paper, the most common effect is that the unsaturated butadiene rubber portion of the SBS molecule undergoes chain scission in the presence of oxygen. Chain scission reduces the length of the rubber chains and thus the effectiveness of the polymer. The free radicals formed as a result of the chain scission process may react with bitumen which will improve SBS compatibility, and this was observed in the current study.

It is likely that the large (≈ 20 °C) reduction in Softening Point shown in Figure 2 for three of the binders was due to chain scission resulting in a reduction in the molecular weight of the polymer, and reduced physical properties. Since the rate of the reaction tends to increase rapidly with temperature, it is important to minimise exposure at elevated temperatures and to avoid temperatures above the recommended range. There is a temptation for field personnel to utilise higher temperatures since this makes the materials easier to pump and spray, and this should be avoided.

Chain scission is a free radical reaction. Only small amounts of oxygen are needed to start the process, which then continues as a chain reaction without the need for further oxygen (though the overall process is complex, and materials such as antioxidants can slow or stop the reaction). Thus the amount of oxygen in the head space of a storage tank may be enough to initiate the reaction or even, possibly, oxygen dissolved in the binder during earlier processing.

As discussed, SBS binders which have substantially degraded show reduced elasticity and reduced elongation to break at low service temperatures. Such materials would be expected to have poorer field performance in terms of reduced fatigue resistance for asphalts and reduced cracking resistance for seals.

MEASURES TO ENSURE QUALITY IS OBTAINED

Improved performance of PMB binders

Rising freight loads and ever greater traffic stressing of road surfacings continue to put increasing demands on paving binders. In certain conditions these demands exceed the capabilities of conventional bitumens, and only modified binders can provide the necessary performance. It is, therefore, important that when PMBs are used that they reliably deliver the expected performance improvement.

This can best be done by ensuring that PMBs meet appropriate specification requirements when manufactured, and that the properties do not alter, or only alter to an acceptable extent, during storage and transport to the end user. To purchasers, it is the ‘as delivered’ properties of the binder which are important. The following sections discuss specification clauses which aim to ensure that the ‘as delivered’ properties of SBS PMBs are acceptable.

Storage stability test

The European storage stability test used in this study was developed to identify binders which are at risk of segregation. If a binder fails the test then this is an indication that at 180 °C the binder forms a two phase structure (Figure 2).
A summary of manufacturer’s information, published as an appendix to the AAPA code of practice for the manufacture, storage and handling of PMBs (AAPA 2004), specifies a range of temperatures for medium term storage. Medium term storage for SBS binders is generally up to 14 days but some manufacturers specify shorter or longer periods. The specified storage temperatures vary between manufacturers but the overall range is between 120 °C and 160 °C. Thus a binder which passes the storage stability test i.e. has a single phase structure at 180 °C could well have a two-phase structure in the temperature range 120 °C to 160 °C, and be liable to segregate.

Thus while the storage stability test will identify binders which are likely to segregate, some of the binders which pass the test could still segregate. Whether a particular binder segregates or not will depend on the degree of incompatibility of the bitumen and polymer components, the transport and storage temperature regime, the degree of agitation during transport and storage, and the length of time the binder is stored. It takes a finite time for a binder to segregate and it is likely that the most incompatible binders will segregate most rapidly.

It is proposed that the Australian PMB specification be modified so that the acceptance criteria for the European storage stability test are used. The difference in Softening Point between binder in the top and bottom thirds of the tube, following storage at 180 °C for three days, should be ≤ 5 °C. The European Standard Specification Framework for Polymer Modified Binders (EN 14023:2010) applies to 31 countries including France, Germany and the United Kingdom. The major European PMB producers have internal specifications which mirror the storage stability requirement in the European specification.

Currently, the Austroads segregation (beer can) test (Austroads 2006a) is specified in Australia. This test specifies storage at 180 °C for two days and the can is cut in half rather than thirds. Stoke’s law indicates that a difference in the diameter of the containers used in the two tests should have no effect on segregation rate. The longer storage time in the European test, and the use of thirds of the container, rather than halves, should make this test more sensitive than the Austroads one. However, either test should be suitable for identifying highly segregation susceptible binders.

### Ease of remixing test

The clause in the current Australian PMB specification (Austroads 2010a), that permits acceptance of a binder which has failed the storage stability test if it passes the ease of remixing test, should not be included the specification. The ease of remixing test (Austroads 2006b) requires the binder to be stored at 180°C for two days and then thoroughly mixed (100 movements/minute) for 10 minutes before being immediately frozen. The Softening Points of the binder in the top and bottom halves of the can are then compared.

The laboratory ease of remixing test does not give the remixed binder any opportunity to again segregate before it is immediately frozen. The mixing procedure in the laboratory test is very different from the field situation. Because a binder can be easily remixed in the laboratory does not mean that it will be satisfactorily remixed in the field. Field storage mixing may be limited to comparatively slow circulation of a binder in a tank by means of a pump, or there may be no facility for mixing in some tanks.

If the binder has failed the segregation test at 180°C then this means it has a two phase structure at that temperature. A remixing procedure might temporarily homogenise the binder but it will still consist of a two phase structure and the SBS will not be incorporated into the bitumen. If the binder is subsequently stored at this temperature or below (as recommended in the AAPA guide) it will again segregate.
Thermal stability test

Previously discussed work has shown that the low temperature properties of SBS binders can be substantially reduced if thermal degradation occurs. It is, therefore, important to identify those binders at particular risk of thermal degradation.

A thermal stability test has been proposed for this purpose. It utilises the Softening Point results from the storage stability tests in conjunction with the Softening Point result for the untreated binder, and thus does not require any extra testing effort. It is suggested that the difference between the Softening Point of the untreated binder and the average Softening Point of the binders in the top and bottom thirds of tubes stored at 180 °C for three days should be ≤ 5 °C. Nine of the 12 binders tested had little difficulty in meeting this requirement.

However, as indicated previously, Softening Point changes more rapidly with change in SBS concentration for binders with Softening Points in the range 50 °C to 80 °C, than for binders outside this range. It may, therefore, be desirable to increase the permitted Softening Point reduction for binders in this range to say ≤ 10 °C (representing an approximate 1% reduction in effective SBS content).

It has been suggested that if the average Softening Point of a sample, after oven treatment of the binder, is above the minimum requirement for the binder grade in the Australian PMB framework specification, then the sample should be accepted. However, the proposed thermal stability test is intended to identify samples susceptible to degradation, and does not simulate the full range of conditions to which binders may be subject. Operational requirements may sometimes result in extended storage periods for binders and there are advantages, in terms of ease of transport and pumping, in keeping binders at as high a temperature as possible. Thus a binder which has an average Softening Point above the specification requirement in the laboratory test may well degrade much more under field storage conditions and have a much lower Softening Point.

The most satisfactory situation for a PMB purchaser is to be supplied with a binder which is not degradation susceptible and which will, therefore, be likely to give good field performance under most transport and storage conditions.

CONCLUSIONS

1. Australian PMB manufacturers can produce segregation and degradation resistant SBS binders. However, not all compositions tested in the recent study were satisfactory. Of the 12 randomly selected SBS binders subjected to the storage stability test, Softening Point measurements indicated that:
   - 3 samples segregated during splitting of bulk samples
   - 2 samples segregated in the toothpaste tube test
   - 3 samples degraded after exposure in an oven at 180 °C
   - 2 samples both segregated and degraded.

   Thus six out of 12 randomly selected commercial SBS samples segregated or degraded, suggesting that specifications need to be improved.

2. The European storage stability test identified binders that were prone to segregation. The Austroads segregation test would be expected to give similar results though the European test should be more sensitive.

3. Results from the storage stability test combined with the Softening Point result for the untreated binder were used to calculate a thermal stability value, and this identified binders at risk of degradation. The work of Johansson and Linde (1991) showed that the elastic behaviour and elongation to break at low temperature of thermally degraded binders was
much reduced. This suggests that fatigue and crack resistance performance would be compromised.

4. Samples taken from a batch or bulk sample which is segregating can yield storage stability results indicating that the binder is not prone to segregation. This is because an unrecognised composition gradient can exist in a batch or bulk sample of already segregating SBS binder, resulting in samples drawn from it having a range of compositions. Some of the samples in this range may possibly have a composition which is storage stable.

RECOMMENDATIONS

1. The clause in the Austroads Specification Framework for PMBs and Multigrade Bitumens (Austroads 2010a) which permits a binder sample which fails the segregation test to be accepted if it passes the ease of remixing test should be deleted. The ease of remixing test is unrepresentative of field practice and does not take into account whether field remixing actually occurs. If a sample was stored after remixing it would be likely to segregate.

2. The European storage stability test and specification limits should be adopted. If the Austroads segregation test is retained then the European specification limits should be used.

3. A thermal stability test should be introduced. Nine of the 12 randomly selected binders passed the requirements of the proposed test.

4. Sampling practice should be reviewed to address the issue raised in conclusion 4.

5. Consideration should be given to updating the AAPA PMB guide to limit the time for which SBS binders are exposed to elevated temperatures.

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REFERENCES


Austroads (2006b), Ease of remixing of polymer modified binders, AG:PT/T109Austroads, Sydney, NSW.

Austroads (2008), Protocol for handling modified binders in preparation for laboratory testing, AG:PT/T102, Austroads, Sydney, NSW.

Austroads (2010a), Specification framework for polymer modified binders and multigrade bitumens, AG:PT/T190, Austroads, Sydney, NSW.

Austroads (2010b), Measurement of Changes in PMBs during Transport and Storage: a Pilot Study, by JWH Oliver & KY Khoo, AP-T166/10, Austroads, Sydney, NSW.

Austroads (2012), The Effect of styrene butadiene styrene (SBS) morphology on field performance and test results: an initial study, by JWH Oliver, KY Khoo & K Waldron, AP-T197-12, Austroads, Sydney, NSW.


**Standards**

**European Committee for Standardization**


**Standards Australia**

AS 2341.18-1992, *Methods of testing bituminous and related roadmaking products: determination of softening point (ring and ball method).*
AUTHOR BIOGRAPHIES

Dr. Oliver graduated from Strathclyde University in Scotland with a Bachelor of Science (Hons) and a Ph. D. in Applied Chemistry. He joined ARRB Group Limited in 1969 and now holds the position of Chief Research Scientist. He is the author of over 150 papers and reports, and has wide experience in binder characterisation, bitumen durability and anti-oxidants, scrap rubber and polymer modified binders, asphalt and sprayed seal design procedures, and skid resistance. He has presented papers and lectured extensively both in Australia and overseas. Dr. Oliver received the inaugural Eldon J Yoder award from the U.S. Transportation Research Board (TRB) and was awarded the John Shaw Medal by the Australian Road Federation. He has served on expert advisory panels for the U.S. Strategic Highway Research Program (SHRP) projects, was the Australian SHRP Co-ordinator and chaired the Australian Standards bitumen committee.

Dr Khoo was awarded a B. Eng. (Hons) degree and followed this with a PhD in Biochemical Engineering, both from the University of Adelaide. She worked as a process engineer with OGS before moving to Constellation wines where she was responsible for the performance of wine separation equipment. She joined ARRB as a Research Scientist in the bituminous materials group in 2008. Dr Khoo was technical secretary for the 2nd International Sprayed Sealing Conference held in Melbourne in 2010. While at ARRB she has worked on a number of projects in the binders and sprayed sealing areas, and is currently concerned with the chemical and physical properties of bitumen, and the performance of polymer modified binders.

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