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Styrene butadiene styrene polymer modification of road bitumens

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This paper describes the polymer modification of road bitumens with SBS. Six polymer modified bitumens (PMBs) were produced by mixing bitumen from two crude oil sources with an SBS copolymer at three polymer contents. The rheological characteristics of the SBS PMBs were analysed by means of dynamic mechanical analysis using a dynamic shear rheometer (DSR). The results of the investigation indicate that the degree of SBS modification is a function of bitumen source, bitumen-polymer compatibility and polymer concentration. When the polymer concentration and bitumen-polymer compatibility allow a continuous polymer network to be established, modification is provided by a highly elastic network which increases the viscosity, stiffness and elastic response of the PMB, particularly at high service temperatures. However, ageing of the SBS PMBs tends to result in a reduction of the molecular size of the SBS copolymer with a decrease in the elastic response of the modified road bitumen. © *2004 Kluwer Academic Publishers*

1. Introduction

Bitumen is a thermoplastic, viscoelastic liquid that behaves as a glass-like elastic solid at low temperatures and/or during rapid loading (short loading times—high loading frequencies) and as a viscous fluid at high temperatures and/or during slow loading (long loading times—low loading frequencies). As a viscoelastic material, bitumen exhibits both elastic and viscous components of response and displays both a temperature and time dependent relationship between applied stresses and resultant strains [1]. In addition, as bitumen is responsible for the viscoelastic behaviour of all bituminous materials, it plays a dominant part in determining many of the aspects of road performance, such as resistance to permanent deformation and cracking.

Polymer modification of bitumen in road paving applications has been growing rapidly over the last decade as government authorities and paving contractors seek to improve road life in the face of increasing traffic. Currently, the most commonly used polymer for bitumen modification is the elastomer styrene butadiene styrene (SBS) followed by other polymers such as styrene butadiene rubber, ethylene vinyl acetate and polyethylene. The use of synthetic polymers to modify the performance of conventional bituminous binders dates back to the early 1970s [2], with the binders having decreased temperature susceptibility, increased cohesion and modified rheological characteristics [3–12]. Globally, the distribution of the various types of modified binders can be estimated as 75 percent elastomeric, 15 percent plastomeric and 10 percent recycled crumb rubber and miscellaneous modifiers (e.g., sulphur) [13, 14]. Within the elastomeric group, styrenic block copolymers have shown the greatest potential when blended with bitumen [9, 10, 15]. Other examples of elastomers used in bitumen modification include natural rubber, polybutadiene, polyisoprene, isobutene isoprene copolymer, polychloroprene and styrene butadiene rubber.

Styrenic tri-block copolymers, commonly termed thermoplastic rubbers due to their ability to combine both elastic and thermoplastic properties, can be produced by a sequential operation of successive polymerisation of styrene butadiene styrene (SBS) [14]. Alternatively, a di-block precursor can be produced by successive polymerisation of styrene and the mid-block monomer butadiene, followed by a reaction with a coupling agent [16]. Therefore, not only linear copolymers but also multi-armed copolymers (known as star-shaped, radial or branched copolymers) can be produced. The structure of a SBS copolymer therefore consists of styrene butadiene styrene tri-block chains, having a two-phase morphology of spherical polystyrene block domains within a matrix of polybutadiene [5, 16].

SBS copolymers derive their strength and elasticity from physical cross-linking of the molecules into a three-dimensional network. The polystyrene end-blocks impart the strength to the polymer while the polybutadiene rubbery matrix mid-blocks give the material its exceptional elasticity. The effectiveness of these cross-links diminishes rapidly above the glass transition temperature of polystyrene (approximately 100°C), although the polystyrene domains will reform on cooling restoring the strength and elasticity of the copolymer [5, 9, 16].

In terms of its chemical composition, bitumen is a complex mixture of organic molecules. Both the chemical (constituent) and the physical (structural) part of bitumen comprise mainly hydrocarbons with minor amounts of functional groups such as oxygen, nitrogen and sulphur. As bitumen is extracted from crude oil with its variable composition according to its origin, the precise breakdown of hydrocarbon groups is difficult to determine. However, it is possible to separate bitumen into four main fractional groups, namely; saturates, aromatics, resins and asphaltenes (SARA) [5, 16]. Asphaltenes are considered as highly polar, complex aromatic materials, having the highest molecular weight of all the other groups present in the bitumen. They form micelles that are peptised by the polar resins and dispersed in a medium consisting primarily of aromatics and saturates, representing the fractions of the bitumen with the lowest molecular weight. Based on this structure, bitumen can be divided into two broad chemical groups, namely asphaltenes and a second group consisting of the resins, aromatics and saturates termed the maltenes. It is generally these low molecular weight maltenes (aromatic oils) that are absorbed by the synthetic or natural rubbers found in polymer modified and crumb rubber modified bitumens [17].

When SBS is blended with bitumen, the elastomeric phase of the SBS copolymer absorbs the maltenes (oil fractions) from the bitumen and swells up to nine times its initial volume [5, 14, 18]. At suitable SBS concentrations, a continuous polymer network (phase) is formed throughout the PMB, significantly modifying the bitumen properties. As thermoplastic rubbers have molecular weights similar to or higher than that of the asphaltenes, they compete for the solvency power of the maltene phase and phase separation can occur if insufficient maltenes are available. This phase separation is an indication of the incompatibility of the base bitumen and polymer and care should be taken when blending thermoplastic rubber PMBs. The compatibility of the SBS—bitumen blend can be improved through the addition of aromatic oils. However, too high an aromatic content in the blend will dissolve the polystyrene blocks and destroy the benefits of the SBS copolymer.

Ageing of conventional bitumen, as well as PMBs, is induced by chemical and/or physical changes that occur during the production of the pavement and throughout its service life. Ageing (hardening) is primarily associated with the loss of volatile components and oxidation of the bitumen during asphalt mixture construction (short-term ageing) and progressive oxidation of the in-place material in the field (long-term ageing). Both processes are usually accompanied by hardening of the binder, which general influences the deterioration of the asphalt pavement. Other factors may also contribute to ageing, such as molecular structuring over time (steric hardening) and actinic light (primarily ultraviolet radiation, particularly in desert conditions) [19].

Although considerable research has been undertaken in this area, SBS PMBs have still to be comprehensively characterised, due to the complex nature and interaction of the bitumen and polymer system [3, 20]. This paper presents a laboratory evaluation of the fundamental rheological characteristics of a number of unaged and laboratory aged base bitumens and SBS PMBs. The SBS PMBs have been produced by laboratory mixing two different base bitumens with a SBS copolymer at three polymer contents. The effects of bitumen source, polymer content, bitumen-polymer compatibility and ageing on the fundamental rheological (viscoelastic) properties of the PMBs have been determined using dynamic (oscillatory) mechanical analysis and presented in the form of temperature and frequency dependent rheological parameters.

2. Experimental

2.1. Materials

A paraffinic (Russian crude source) bitumen, "Bitumen A", and a naphthenic (non-paraffinic) (Venezuelan crude source) bitumen, "Bitumen B", were used to produce a number of laboratory blended, block copolymer SBS PMBs. The conventional bitumen properties of penetration (25°C, BS 2000: Part 49), softening point (BS 2000: Part 58), Fraass breaking point (IP 80), and rotational viscosity (ASTM D4402) were used to characterise the two bitumens. Although both base bitumens have similar consistencies (penetrations of 73 and 81 dmm and softening points of 47.0 and 46.8°C), they differ in terms of their chemical composition (saturates, aromatics, resins and asphaltenes (SARA) fractions), as shown in Table I, and high and low temperature properties (viscosity and Fraass breaking point), as shown in Table II.

The Colloidal Indices (CIs) of the two bitumens were calculated in order to determine the potential compatibility of the base bitumens to polymer modification. Serfass *et al.* [21] are of the opinion that no precise CI borderline exists between what will be a "compatible" and what will be an "incompatible" bitumen. However, it is clear that the different percentages of the SARA fractions allow the CIs of the two base bitumens to differ considerably. Inevitably this will result in differences in the compatibility and rheological performance of the two sets of SBS PMBs.

TABLE I SARA analysis of base bitumens

Binder	Saturates (%)[a]	Aromatics (%)[a]	Resins (%)[a]	Asphaltenes (%)[a]	Colloidal index[b]
Bitumen A	4	68	19	9	0.149
Bitumen B	11	58	17	14	0.333

[a] Iatroscan thin film chromatography SARA analysis.

[b] Colloidal Index (I_c) = (asphaltenes + saturates)/(resins + aromatics).

TABLE II Conventional physical properties of the base bitumens

Binder	Pen @ 25°C (dmm)	Softening point (°C)	Penetration index (PI)[a]	Fraass (°C)	Viscosity @ 60°C (Pa.s)	Viscosity @ 135°C (Pa.s)
Bitumen A	73	47.0	−1.08	−12	165	0.370
Bitumen B	81	46.8	−0.86	−28	213	0.380

[a] $PI = (1952 - 500 \log Pen_{25^\circ C} - 20\,SP)/(50 \log Pen_{25^\circ C} - SP - 120)$.

The chemical dissimilarity between the two components (bitumen and SBS polymer) will generally result in two distinct phases following mechanical mixing [22]. This two-phase structure of the SBS PMB consists of a polymer-rich phase and an asphaltene-rich phase, also known as the polymer and bitumen phases. The polymer phase consists of the polymer swollen by the light, compatible fractions of the bitumen (e.g., aromatic oils), while the heavy fractions (mainly asphaltenes) are concentrated to form the bitumen phase.

Six SBS PMBs were produced by mixing a linear SBS copolymer (31% styrene content with a molecular weight of 120,000 and a toluene solution viscosity of 11.0 cSt (11×10^{-3} Pa·s)) with both base bitumens at three polymer contents by mass. The polymer contents ranged from low polymer modification at 3% to higher degrees of modification at 5 and 7%. All the PMBs were prepared with a Silverson high shear laboratory mill at temperatures between 170 and 185°C (depending on the viscosity of the PMB) until steady state conditions were achieved.

The different SBS PMBs were coded as "base bitumen," "polymer content" such as "A5" for the SBS PMB produced with Bitumen A and 5% polymer content or "B7" for the SBS PMB produced with Bitumen B and 7% polymer content.

2.2. Test methods

2.2.1. Conventional binder tests

The base bitumens and SBS PMBs were subjected to the following conventional binder tests: penetration, softening point, Fraass breaking point, ductility (10°C, ASTM D113), elastic recovery (10°C, modified ASTM D113) and rotational viscosity. The elastic recovery test was performed on the SBS PMBs to measure the binders' elasticity (the ability of the binder to stretch and recover elastically after 1 h). In addition, the penetration and softening point values were used to calculate the temperature susceptibility of the binders in terms of their penetration index (PI) [23].

2.2.2. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed on the base bitumens and SBS PMBs using a Bohlin DSR50 controlled stress rheometer [24–27]. The test procedure and sample preparation method that were used with the DSR have been described in detail previously [12, 28, 29]. The DSR tests reported in this paper were performed under controlled-strain loading conditions using frequency sweeps between 0.01 to 15 Hz at temperatures between 10 and 75°C. The tests between 10 and 35°C were undertaken with a 8 mm diameter—2 mm gap, parallel plate testing geometry and from 25 to 75°C with a 25 mm diameter—1 mm gap geometry. The strain amplitude for all the tests was confined within the linear viscoelastic (LVE) response of the binder [28].

The principal viscoelastic parameters obtained from the DSR were the complex shear modulus (G^*) and the phase angle (δ). G^* is defined as the ratio of maximum (shear) stress to maximum strain and provides a measure of the total resistance to deformation when the bitumen is subjected to shear loading. It is a combination of the (shear) storage modulus (G') and the (shear) loss modulus (G'') in the complex plane: $G^* = G' + iG''$. These two components are related to each other through the phase angle (δ), which is the phase shift between the applied shear stress and shear strain responses during a test. The phase angle is a measure of the viscoelastic balance of the material behaviour as $\tan \delta = G''/G'$. If δ equals 90° then the bituminous material can be considered to be purely viscous in nature, whereas δ of 0° corresponds to purely elastic behaviour. Between these two extremes the material behaviour can be considered to be viscoelastic in nature with a combination of viscous and elastic responses.

2.2.3. Ageing procedures

Short and long-term laboratory ageing of the base bitumens and SBS PMBs were performed using the Rolling Thin Film Oven Test (RTFOT, ASTM D 2872) and the pressure ageing vessel (PAV, AASHTO PP1), respectively. The standard ageing procedures of 163°C and 75 min for the RTFOT and 100°C, 2.1 MPa and 20 h for the PAV were used and the aged binders then subjected to dynamic mechanical analysis to evaluate changes in their rheological properties.

3. Results and discussion

3.1. Conventional binder properties

The effect of SBS polymer modification on the conventional binder properties of the two PMB groups can be seen in Table III as a decrease in penetration and an increase in softening point with increasing polymer content. Although the decrease in penetration is relatively uniform with increasing polymer content, there is a significantly large increase in softening point temperature at the high polymer contents of 5 and 7%. In addition to the increase in stiffness, the increased penetration indices (PIs) of the PMBs indicate a significant reduction in temperature susceptibility with polymer modification, particularly at the higher polymer contents.

In terms of low temperature performance, SBS modification of base Bitumen A has almost no effect on

TABLE III Changes in conventional binder properties following SBS modification

Binder	Pen @ 25°C (dmm)	Soft. Pt (°C)	Penetration index (PI)	Fraass (°C)	Ductility @ 10°C (cm)[a]	Elastic recovery @ 10°C (%)[b]
Bitumen A	73	47.0	−1.08	−12	63	—
PMB-AS3	63	52.4	−0.05	−16	95	68
PMB-AS5	57	78.0	4.41	−15	99	76
PMB-AS7	50	95.0	6.13	−14	101	81
Bitumen B	81	46.8	−0.86	−28	130	—
PMB-BS3	63	52.2	−0.09	−18	81	71
PMB-BS5	54	74.0	3.67	−16	90	78
PMB-BS7	49	88.0	5.29	−14	81	80

[a] ASTM D113.

[b] Modified ASTM D113.

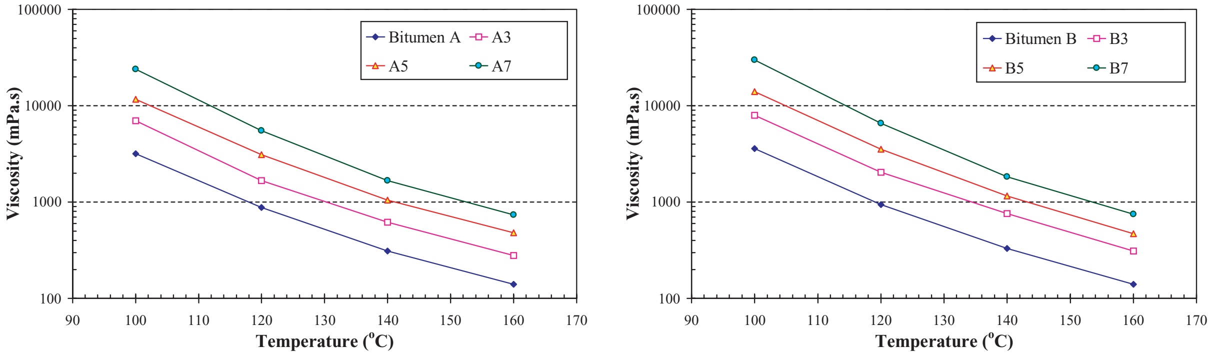

Figure 1 Rotational viscosities of SBS PMBs.

low temperature flexibility. However, for the Bitumen B PMBs there is a significant increase in Fraass temperature with modification. Although the behaviour of the SBS PMBs relative to their respective base bitumens is different, the actual Fraass breaking point temperatures for each polymer content PMB pair are almost identical. With regard to ductility and elastic recovery at 10°C, the results are again similar for the SBS PMB pairs, although the ductilities of the Group A SBS PMBs are approximately 10 to 25 percent greater than those of Group B. Elastic recovery differs from the elastic response of the binder, which is a dynamic rheological property of the binder quantified by means of the material's phase angle. Whereas elasticity is usually associated solely with elastomeric PMBs, an improvement in the elastic response of a binder is usually evident in most PMBs (elastomeric and plastomeric).

The Fraass and ductility results show the considerable influence of the base bitumen, the nature of the polymer and the base bitumen-polymer compatibility on the intermediate and low temperature physical properties of PMBs. Although there are slight differences in the values of the conventional binder properties of the two PMB groups, overall these differences cannot be considered to be significant.

Rotational viscosities for the two PMB groups (100 to 160°C) are shown in Fig. 1. The results show a consistent increase in viscosity with polymer modification for both PMB groups. In addition, rotational viscosities (η) at 100 and 160°C for the base bitumens and SBS PMBs are presented in Table IV together with modification indices (η for PMB divided by η for the base bitumen) at these two temperatures. As with the penetration and softening point tests, the viscosities give a clear indication of the stiffening effect of SBS modification. The modification indices between the two groups are relatively similar but generally higher at 100°C than at 160°C as well as slightly higher for Bitumen B. However, other than requiring higher mixing and compaction temperatures, the results do not indicate any significant rheological differences between the base and modified bitumens or between the two SBS PMB groups at these elevated temperatures.

TABLE IV Rotational viscosities following SBS modification

Binder	Rotational viscosity @ 100°C (mPa · s)	Rotational viscosity @ 160°C (mPa · s)	$\eta_{\text{PMB}}/\eta_{\text{Bitumen}}$ @ 100°C	$\eta_{\text{PMB}}/\eta_{\text{Bitumen}}$ @ 160°C
Bitumen A	3,170	140	1.00	1.00
PMB-AS3	7,000	280	2.21	2.00
PMB-AS5	11,700	480	3.69	3.43
PMB-AS7	24,000	740	7.57	5.29
Bitumen B	3,600	140	1.00	1.00
PMB-BS3	7,950	310	2.21	2.21
PMB-BS5	14,000	470	3.89	3.36
PMB-BS7	30,000	750	8.33	5.36

3.2. Dynamic viscoelastic parameters

Isochronal plots of complex modulus (G^*) versus temperature at 0.02 and 1 Hz for both SBS PMB groups are shown in Figs 2 and 3. Unlike the conventional binder properties, the isochronal plots show a difference in the degree of modification between Bitumen A and B, particularly at the upper and lower ends of the temperature domain at the lower frequency of 0.02 Hz. For Bitumen A, although there are only minor increases in G^* at low temperatures due to SBS modification, there is considerable evidence of extreme polymeric modification at high temperatures with the approach of a plateau region indicative of a dominant polymer network. Compared to Bitumen A, the increase in G^* for the Group B SBS PMBs is not as marked at high temperatures. However, there is a more uniform increase in G^* over the entire temperature domain indicating a difference in the compatibility of the two PMB base bitumen-polymer systems and as a consequence a difference in their rheological characteristics. In addition, the differences between Figs 2 and 3 highlight the increased frequency-dependence of Group A compared to Group B. Whereas the isochronal plots for Group B are similar at 0.02 and 1 Hz, the isochronal plots for the Group A PMBs at 1 Hz show no evidence of a high temperature plateau region compared to that seen at 0.02 Hz.

Phase angle isochrones at 0.02 and 1 Hz for the SBS PMBs are presented in Figs 4 and 5. Measurements of δ are generally considered to be more sensitive to the chemical structure and therefore the modification of bitumen than complex modulus. The phase angle isochrones clearly illustrate the improved elastic response (reduced phase angles) of the modified binders compared to their respective base bitumens. What is noticeable is the considerable difference in the extent

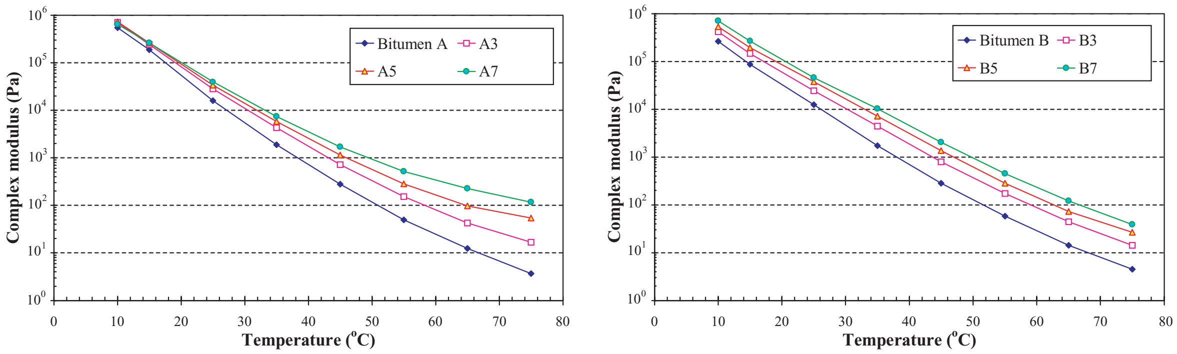

Figure 2 Isochronal plots of complex modulus at 0.02 Hz for SBS modified bitumens.

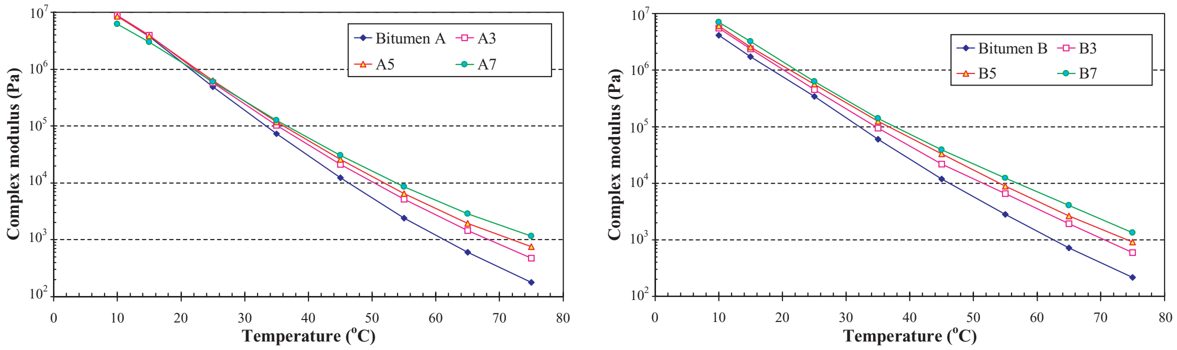

Figure 3 Isochronal plots of complex modulus at 1 Hz for SBS modified bitumens.

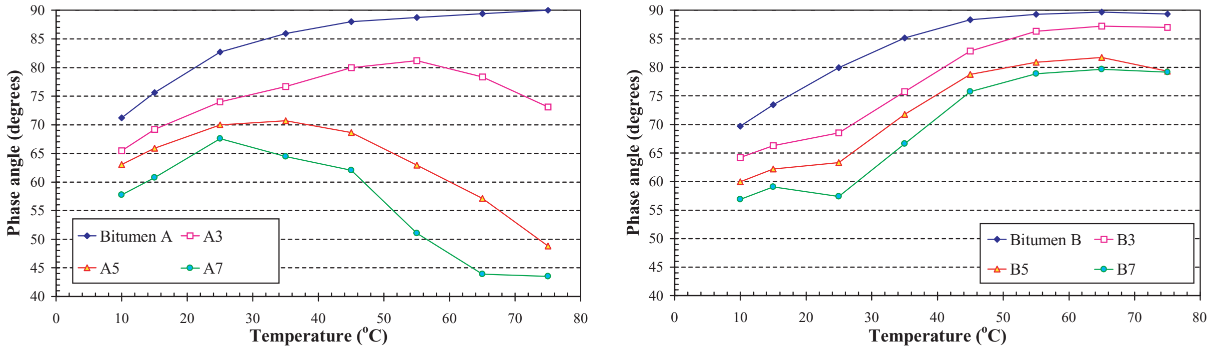

Figure 4 Isochronal plots of phase angle at 0.02 Hz for SBS modified bitumens.

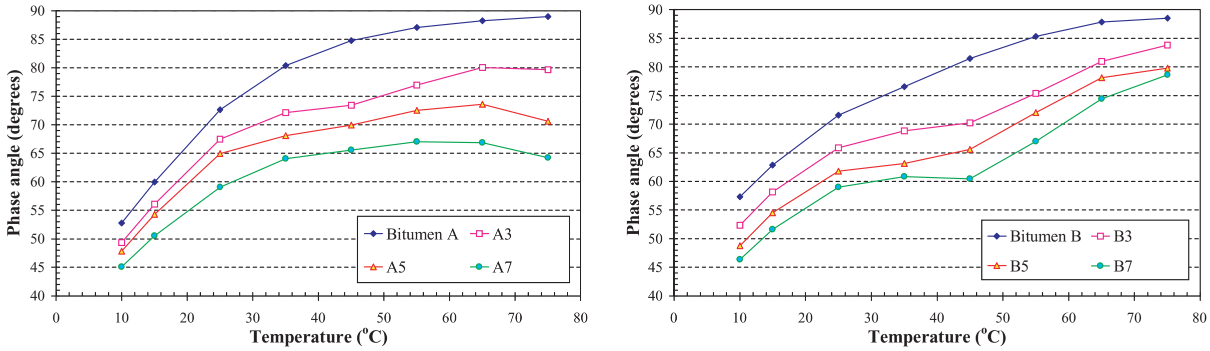

Figure 5 Isochronal plots of phase angle at 1 Hz for SBS modified bitumens.

of the modification for the two groups particularly at high temperatures (>35°C) at the lower frequency of 0.02 Hz. Whereas the phase angles of the two base bitumens approach 90° and therefore predominantly viscous behaviour with increasing temperatures, the SBS polymer significantly improves the elastic response of the modified binders. This increase in elastic response at high temperatures can be attributed to the viscosity of the base bitumens being low enough to allow the elastic network of the polymer to influence the mechanical properties of the modified binders [7]. At the higher frequency of 1 Hz (Fig. 5), the increased viscosity of the base bitumens reduces the effect of the polymer network.

The influence of the SBS polymer network is more noticeable for the Bitumen A PMBs where the elastic response (decreased phase angle) is greater, particularly at the lower frequency of 0.02 Hz. The decreased phase angles demonstrate the tendency of the polymer to form a continuous elastic network when dissolved/dispersed in the bitumen [30]. The presence and nature of the plateau and the polymer network is a function of the chemical and physical properties of the SBS polymer and base bitumen and the compatibility of these two components.

3.3. Rheological master curves and Black diagrams

The frequency dependence of complex modulus and phase angle for the SBS PMBs has been assessed in Figs 6 and 7 by producing rheological master curves at a reference temperature of 25°C using the time-temperature superposition principle (TTSP) [30] and shift factors determined for the G^* master curves. The complex modulus master curves in Fig. 6 show slightly different trends between the two PMB groups. For the base bitumen A PMBs there is a significant increase in G^* at low frequencies where the SBS polymer network is particularly dominant with a plateau being approached for the 5 and 7% polymer content PMBs. Although the Group B PMBs show a similar increase in complex modulus with increasing polymer content, no plateau can be recognised.

The phase angle master curves for the SBS PMBs (Fig. 7) show a reduction in phase angle with modification and the presence of a phase angle plateau at intermediate loading frequencies. The phase angle plateau is an indication of the presence of polymer elastic networks or entanglements in the modified binders. In the case of SBS PMBs, this polymer network is formed by the physical cross-linking of polystyrene blocks. The significant difference between the two bitumen groups occurs at low frequencies where the nature of the polymer network is dependent on the properties of the base bitumen (maltenes composition) and the compatibility of the bitumen-polymer system. Whereas the polymer network for the Group A PMBs results in a continued reduction in phase angle (increased elastic response) at low frequencies, the opposite is true for the Group B PMBs where there is an increase in phase angle (decreased elastic response). The differences in the plots of phase angle versus frequency may be related to differences in the molecular interaction (e.g., dispersion, swelling and compatibility) between the two base bitumens and the SBS polymer.

The effect of SBS modification on the rheological parameters (complex modulus and phase angle) has been combined in the form of Black diagrams (complex modulus versus phase angle [31]) in Fig. 8. The enhanced polymer modification for the Group A PMBs compared to the Group B PMBs can be clearly seen in the figure and is more significant at the higher polymer contents. The morphology and therefore the rheological characteristics of the PMBs are functions of the mutual interaction of polymer and bitumen and consequently are influenced by bitumen composition and polymer nature and content. At the lower polymer content (3%) the behaviour of the modified binder remains closer to that of the base bitumen. For optimum performance

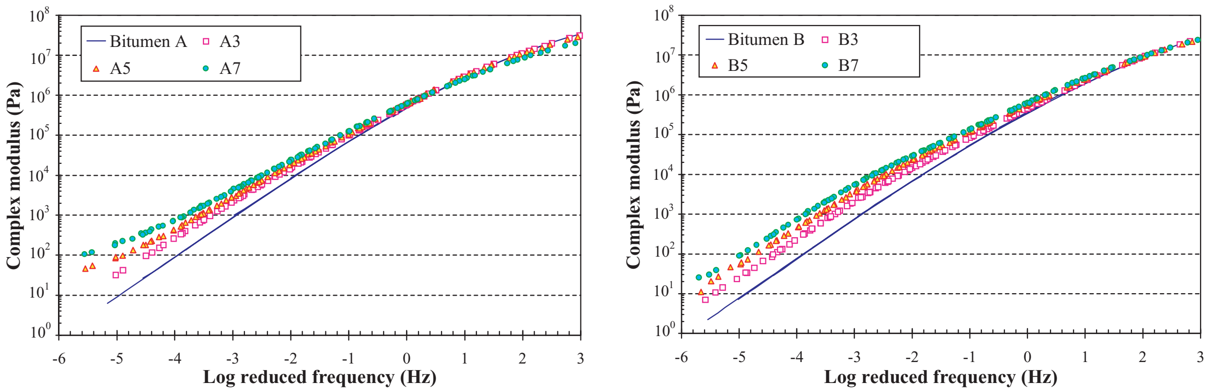

Figure 6 Master curves of complex modulus at 25°C for SBS PMBs.

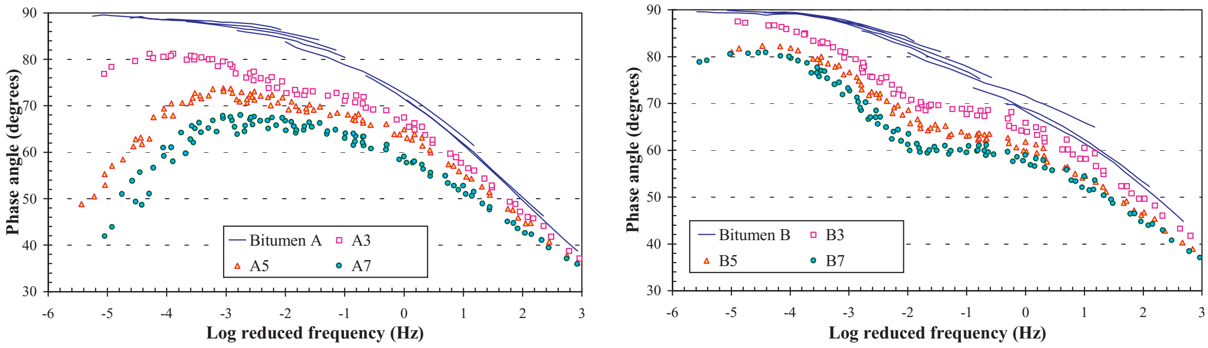

Figure 7 Master curves of phase angle at 25°C for SBS PMBs.

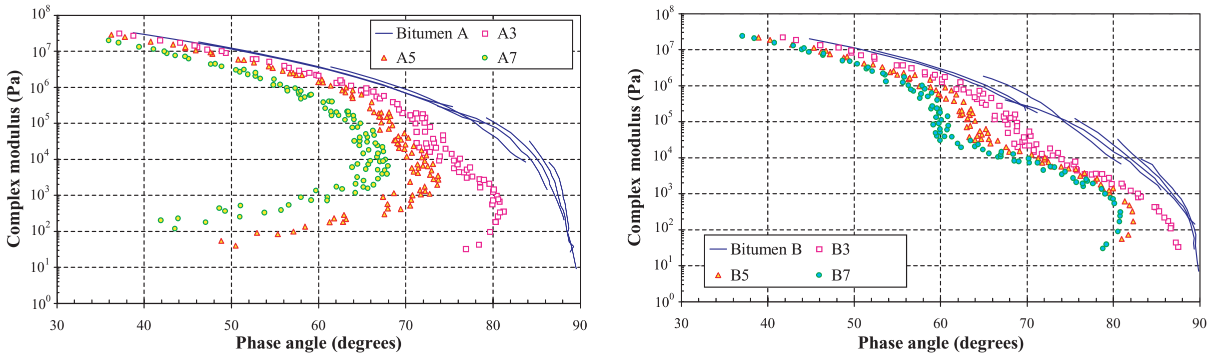

Figure 8 Black diagrams of SBS modified bitumens.

at elevated temperatures and low frequencies, the SBS polymer needs to form a continuous rubber-elastic network when dissolved/dispersed in the bitumen, as discussed above.

3.4. Changes in rheological properties after laboratory ageing

3.4.1. Dynamic viscoelastic parameters

Isochronal plots of complex modulus and phase angle at 0.02 Hz for A7 and B7 in their unaged, RTFOT and PAV aged conditions are shown in Fig. 9. As with the SBS modication of the different base bitumen groups, there are distinct differences in the rheological characteristics of the two PMBs after ageing. Although both binders show an increase in G^* between 10 and 55°C, identical to that seen for penetration grade bitumens [27, 32, 33], the behaviour at temperatures greater than 55°C differs between the two PMB groups. For A7 instead of an increase there is a decrease in G^* after ageing, which might be attributed to be a rearrangement (degradation) of the SBS copolymer into lower molecular weight fragments after ageing leading to a "softening" of the PMB [32–35]. This phenomenon is not evident for B7, as the rubber-elastic network does not dominate the rheological behaviour of the PMB to the same degree as that seen for A7.

The changes in δ after RTFOT and PAV ageing are the same as those shown for an unmodified bitumen (decrease in δ) within the temperature domain of 10°C to approximately 35°C. This region corresponds to conditions where the base bitumen is dominant and, therefore, this correlation with the behaviour shown for unmodified bitumens is expected. In the temperature domain greater than 40°C, where the SBS polymer network is rheologically dominant, the changes after RTFOT and PAV ageing are different from those experienced for unmodified bitumens. Again the rheological behaviour for the Group A PMBs differs from that of Group B particularly above 45°C. At these elevated service temperatures there is an increase in phase angle after RTFOT and PAV ageing indicating a more viscous response for A7. This increase in viscous response after ageing (where the polymer network is dominant) is not evident for B7, although δ does increase slightly after RTFOT at temperatures greater than 65°C.

3.4.2. Rheological Black diagrams

The changes in the rheological characteristics of A7 and B7 after ageing are also shown in the form of Black diagrams in Fig. 10. For A7, the rheological behaviour can be divided into two areas above and below a complex modulus value of 10^4 Pa. At high stiffness values, corresponding to low temperature and high frequency tests, the Black diagram curves show a shift towards lower phase angles indicating the hardening (ageing) of the PMB. The phenomenon is similar to the hardening effect seen for penetration grade bitumens [27]. The second area occurs below the complex modulus value of 10^4 Pa and shows an opposite shift of the curve towards higher phase angles rather than lower phase angles, thereby indicating a change towards a more viscous rather than more elastic response after ageing. This change is a further illustration of the findings of 3.4.1. Once again the changes in the rheological

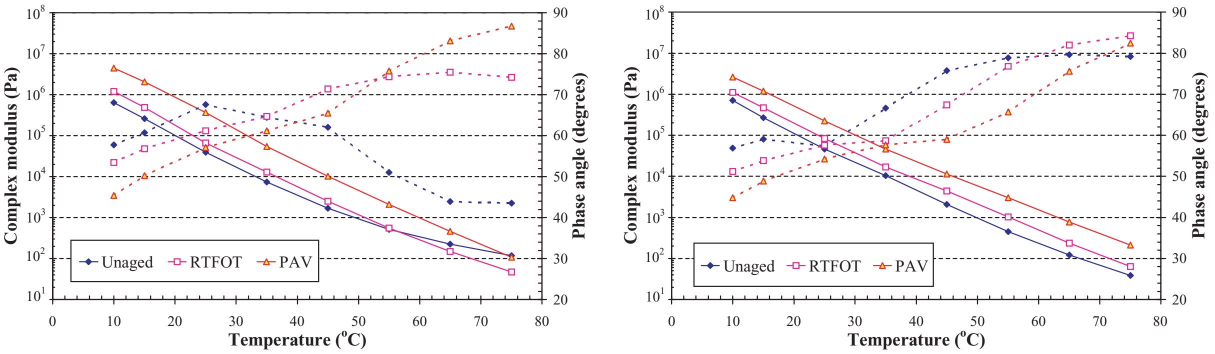

Figure 9 Isochronal plots at 0.02 Hz for unaged, RTFOT and PAV aged A7 and B7 (complex modulus: solid lines; phase angle: dashed lines).

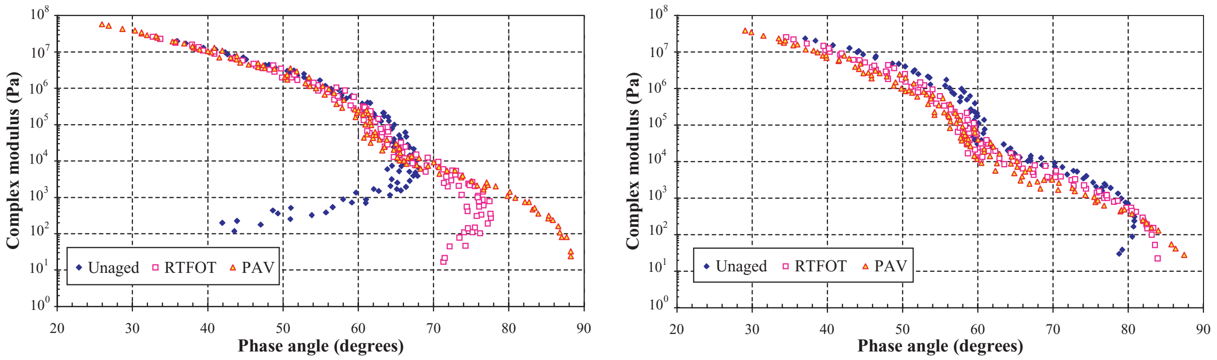

Figure 10 Black diagrams for unaged, RTFOT and PAV aged A7 and B7.

characteristics of B7, as depicted in the Black diagram in Fig. 10, are not as marked as those seen for the Group A PMB. However, there is a shift towards higher phase angles, as seen for the A7, at G^* values below 10^4 Pa.

4. Conclusions

The rheological properties of road bitumens are improved by means of SBS polymer modification as identified by both conventional and more fundamental rheological parameters. Tentatively one may suggest that the mechanism associated with SBS polymer modification consists of a swelling of the polymer through the absorption of the light fractions of the base bitumen and the establishing of a rubber-elastic network within the modified binder. The nature of the network and its influence on polymer modification is a function of the nature of the base bitumen, the nature and content of the polymer and the bitumen-polymer compatibility. In addition to conventional binder properties, such as softening point, penetration index and Fraass temperature, which are generally unable to quantify the unique rheological characteristics of different PMB groups, dynamic mechanical analysis has been used to determine the rheological parameters of complex modulus and phase angle. SBS polymer modification has increased the complex modulus of the two base bitumens, particularly at high temperatures and low frequencies. The extent of polymer modification has also differed depending on the nature of the base bitumen and subsequently the compatibility of the bitumen-polymer system. In general, the paraffinic bitumen has shown a greater degree of polymer modification compared to the naphthenic bitumen PMBs with the differences being more pronounced at higher polymer contents, higher temperatures and lower frequencies. It is under these conditions that the lower viscosity of the base bitumen allows the polymeric nature of the SBS polymer network to dominate the rheological properties of the modified binder.

Laboratory simulative short and long-term ageing of the SBS PMBs has shown differences in the rheological characteristics of the modified binders after ageing compared to those experienced for penetration grade bitumens. The high polymer content modified binders have shown some shift towards more viscous behaviour after ageing.

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