DYNAMIC SHEAR RHEOMETRY, FLUORESCENT MICROSCOPY, PHYSICAL AND CHEMICAL EVALUATION OF POLYMER MODIFIED BITUMENS

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Abstract

The task of characterising the performance of binders has become increasingly more complicated with the escalating use of polymer modified bitumens in the asphalt paving industry. However, the combined use of fundamental rheological testing, by means of dynamic shear rheometry, morphological analysis, using fluorescent microscopy, physical evaluation, by means of differential scanning calorimetry, and chemical evaluation, using gel permeation chromatography, do provide a means to characterise the modification process. These methods have demonstrated the considerable variation in the chemistry, structure and particularly the rheology of a number of plastomeric and elastomeric polymer modified bitumens at various degrees of modification. The changes in the chemical and physical structure and rheological characteristics after ageing have also been shown to differ considerably amongst penetration grade bitumens, plastomeric and elastomeric PMBs.

1. INTRODUCTION

Conventional bituminous materials have tended to perform satisfactorily in most highway pavement and airfield runway applications. However, in recent years, increased traffic levels, larger and heavier loads, new axle designs and increased tyre pressures have added to the already severe demands of load and environment on the pavement structure. This has facilitated the need to enhance the properties of existing asphalt material, with bitumen modification, particularly polymer modification, offering one solution by improving the properties of bitumen and, thereby, improving the performance of asphalt mixtures. The improvements of the asphalt mixture, in terms of retarding fatigue crack initiation and propagation, and reducing the accumulation of permanent deformation, have been shown to decrease the whole life cycle costs of the asphalt pavement (Brown et al, 1990; Isacsson and Lu, 1995).

While conventional methods such as penetration, viscosity, ductility and ring-and-ball softening point may still adequately describe the rheological characteristics of conventional bitumens; they have limited ability at accurately predicting the relative performance of modified materials. In addition to rheological characterisation, it has also become increasingly common to investigate the polymer structure (morphology) of modified bitumen by means of fluorescent microscopy. This method of investigation is used extensively in research as well as for quality control purposes during modified bitumen production.

This paper presents a rheological, morphological, chemical and physical evaluation of various plastomeric and elastomeric polymer modified bitumens (PMBs) before and after laboratory ageing. The rheological investigation has been confined to small strain, oscillatory-type, dynamic shear rheometer (DSR) testing within the linear visco-elastic range of the PMBs. The morphology of the PMBs has been determined by means of fluorescent microscopy. The physical evaluation consisted of thermal characterisation of ethylene copolymer PMBs by means of differential scanning calorimetry (DSC) and the chemical evaluation of the molecular size analysis of styrenic block copolymer PMBs was by means of gel permeation chromatography (GPC).

The combined usage of physical and chemical analysis, fluorescent imaging and fundamental rheological testing has been used in the paper to provide a comprehensive evaluation of the modification processes associated with different physically blended PMBs. These tools have also been used to investigate the physical, chemical, morphological and rheological changes associated with laboratory simulated ageing of laboratory mixed PMB products.

2. EXPERIMENTAL PROGRAMME

2.1 Materials

Three base bitumens (A, B and C) from different crude sources, were used to produce a number of laboratory blended, semi-crystalline, ethylene vinyl acetate (EVA) PMBs and block copolymer, styrene butadiene styrene (SBS) PMBs. All three base bitumen had similar consistencies (penetration [60 to 81 dmm] and softening points [46.8 to 48.8°C]) and differed only slightly in their chemical composition (saturates, aromatics, resins and asphaltenes (SARA) fractions).

The EVA copolymer (EVA 20/20) was blended (mixed) with each of the 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%. The SBS copolymer (SBS Cariflex linear) was only mixed with two of the base bitumens, due to limitations in the supply of base bitumen A, again at the three polymer contents.

2.2 Dynamic Shear Rheometry

Traditionally, empirical specifications are based on measurements of viscosity, penetration, ductility and softening point temperature. These measurements are generally not sufficient to thoroughly describe the linear visco-elastic (LVE) and failure properties of bitumen needed to relate bitumen properties to mixture properties and to pavement performance. In order to begin to relate binder properties to pavement performance it is necessary to undertake more fundamental testing of bitumen.

At present the most commonly used method of fundamental rheological testing of bitumen is by means of dynamic mechanical methods using oscillatory-type testing, generally conducted within the region of LVE response. These oscillatory tests are undertaken using dynamic shear rheometers (DSRs) which apply oscillating shear stresses and strains to samples of bitumen, sandwiched between parallel plates, at different loading frequencies and temperatures (Goodrich, 1988).

The DSR tests reported in this paper were performed under the following test conditions:

☐	Mode of loading:	Controlled-strain,
☐	Temperatures:	10, 15, 25, 35, 45, 55, 65 and 75°C,
☐	Frequencies:	0.01, 0.015, 0.02, 0.05, 0.1, 0.15, 0.2, 0.5, 1, 1.5, 2, 5, 10 and 15 Hz,
☐	Strain amplitude:	Within LVE response (0.5 to 10%) dependent on G*.

The rheological properties of the binders were measured in terms of their complex (shear) modulus (stiffness), G*, and phase angle (visco-elastic balance of rheological behaviour), δ.

As bitumen is a good thermal insulator and also highly temperature susceptible, it is important that the whole sample is at the same temperature and that the temperature is tightly controlled to ensure accurate and consistent rheological measurements. The temperature control was obtained by using the testing arrangement shown in Figure 1, where the whole environment around the bitumen is submerged in a fluid bath. This testing arrangement has been found to provide uniform and constant temperature control over a range of 5°C to 90°C (Cointe and Monnoye, 1995). The temperature control unit used with this testing arrangement is capable of maintaining a temperature to within ± 0.1°C, as recommended by the Strategic Highways Research Program (SHRP) (Petersen et al, 1994). This ± 0.1°C change in temperature corresponds to a ± 2 percent error in measured complex modulus (Anderson and Knechtel, 1997).

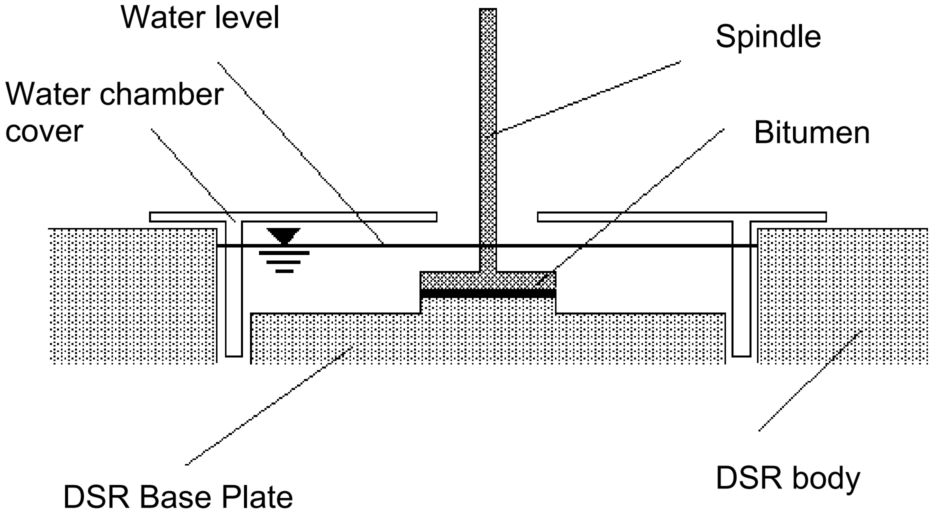


Figure 1: Testing arrangement in dynamic shear rheometer

The DSR rheological data for the base bitumens and PMBs were presented in the form of master curves of complex modulus, G*, and phase angle, δ, at a reference temperature of 25°C, isochronal plots of G* and δ at a loading frequency of 0.02 Hz and Black diagrams of G* versus δ.

2.3 Fluorescent Microscopy

Fluorescent microscopy is probably the most frequently used technique for assessing the state of dispersion of a polymer in a PMB (Brion and Brule, 1986). The technique is, therefore, extremely useful and well validated for studying the morphology of PMBs and, thereby, determining the quality and nature of the dispersion of the polymer within the modified binder.

Fluorescent microscopy is based on the principle that the polymers swell due to absorption of some of the constituents of the base bitumen (primarily some of the light oil fractions found in the maltenes) and, subsequently, fluoresces in ultraviolet light. The bitumen-rich phase appears dark or black while the polymer-rich phase appears light or yellow-green. This fluorescence from the polymer-rich phase is due to the fluorescence of the aromatic oils that have been absorbed by the polymer during the swelling process.

Factors such as the homogeneity of the PMB, the sample preparation method (cooling rate, sample fracturing, etc) and the magnification of the image all have an influence on the structure that will appear in the fluorescent images. For this study, samples of each PMB where prepared using a standard sample preparation method incorporating a re-heating and homogenising procedure, a sample cooling regime, a surface preparation procedure and recommended magnifications (Wegan, 1996). All the samples were examined under a Leitz Medilux microscope with incident UV-light from a high-pressure 75 W Xenon lamp at 25x to 400x magnification depending on the polymer structure (Wegan and Brule, 1999).

2.4 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a technique used to characterise the thermal behaviour of pure bitumen (Shutt et al, 1993). The technique provides the values of temperature (°C) and enthalpy (J/g) corresponding to the following transitions:

- ☐ Glass transition (2nd order transition),
- ☐ Melting (fusion) (1st order transition), and
- ☐ Crystallisation (1st order transition).

DSC can be performed in either a heating mode to obtain melting peaks associated with endothermic reactions or in a cooling mode to obtain crystallisation peaks associated with exothermic reactions. In addition to characterising the thermal behaviour of pure bitumen, DSC can also be used to characterise the thermal behaviour of semi-crystalline, ethylene copolymer modified bitumens by indicating the presence of specific crystalline components in the PMBs. Using the heating mode of testing, the first-order transition, associated with the melting of the crystalline fractions of the copolymer, are accompanied by endothermic signals which are easily characterised by DSC analysis. The parameters recorded from these tests are the enthalpy associated with the endothermic reaction and the peak temperature at which these crystalline EVA components melt. DSC testing in this study was undertaken with a Mettler DSC 30 analyser using a heating rate of 5°C.min^{-1} from 0 to 120°C (Brule and Gazeau, 1996).

2.5 Gel Permeation Chromatography

Gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC), is a form of liquid chromatography where separation of the molecules is accomplished, in a column of porous gel material, by a simple classification process according to size (Isacsson and Lu, 1995; Ozdemir and Partl, 1993). GPC can, therefore, be considered as essentially a sieve-like analysis of the bitumen components (Stroup-Gardiner, 1996). A characteristic of the process is that the smaller molecules enter the pores of the gel structure, by diffusion and, therefore, remain longer in the column than the larger molecules, which are flushed rapidly through the large interstices. The molecules, which leave the columns at separate times, are detected by ultraviolet (UV) and/or refractive index (RI) detectors, with the measured data being recorded in the form of chromatograms of UV absorption or refractive index.

GPC can be used to determine the molecular mass distribution of components, polymer content in PMBs and the degradation of polymers during the ageing process (Isacsson and Lu, 1995). The actual molecular size of the components can be determined by correlation with the UV signals for a standard polystyrene solution of known molecular sizes (Ozdemir and Partl, 1993). GPC testing in this study was performed with a Waters chromatograph, operating at room temperature with a M6000A pump and a refractive index detector. The column set consisted of three μ-styragel columns with nominal exclusion limits of 1000, 500 and 100 μ respectively. The sample was dissolved in tetrahydrofuran (THF) and injected into the GPC at a flow rate of 1 ml/min.

3. POLYMER MODIFICATION

3.1 Conventional Properties

The effects of polymer modification for each of the five laboratory blended PMB sets are seen as a decrease in penetration @ 25°C (BS 2000, part 49) and an increase in softening point (BS 2000, part 58) with increasing modification (Table 1). The magnitude and extent of these changes do, however, vary as a function of the base bitumen – polymer type combination. In general, the SBS PMBs tend to show a larger increase in softening point than the EVA PMBs with the decreases in penetration being similar for both PMB types.

The decrease in penetration and increase in softening point indicate an increased hardness or stiffness of the modified binders. In addition to this increase in hardness, the penetration indices (PI's) (Pfeiffer and Van Doormal, 1936) generally indicate an improvement in temperature susceptibility with polymer modification.

The higher softening point temperatures obtained for the high SBS polymer content PMBs can be construed as an indication of superior high temperature permanent deformation performance. However, the extremely high softening point temperatures of highly modified SBS PMBs tend to overestimate the benefits of modification (Airey, 1997). Furthermore, the correlation between softening point and rutting resistance for highly modified SBS PMBs has been found to be extremely poor (King et al, 1993), particularly for "soft" base bitumen, highly polymer modified binders.

Table 1: Penetration, softening point and penetration index for PMBs

Binder	Penetration (dmm)	Softening Point (°C)	Penetration Index
Base bitumen A	60	48.8	-1.08
3% EVA – A	53	54.8	0.08
5% EVA – A	43	61.0	0.86
7% EVA – A	37	69.4	1.99
Base bitumen B	73	47.0	-1.08
3% EVA – B	61	59.5	1.45
5% EVA – B	51	66.6	2.31
7% EVA – B	47	69.2	2.54
Base bitumen C	81	46.8	-0.86
3% EVA – C	65	53.7	0.35
5% EVA – C	58	63.8	2.15
7% EVA – C	53	69.2	2.86
Base bitumen B	73	47.0	-1.08
3% SBS – B	63	52.4	-0.05
5% SBS – B	57	78.0	4.41
7% SBS – B	50	95.0	6.13
Base bitumen C	81	46.8	-0.86
3% SBS – C	63	52.2	-0.09
5% SBS – C	54	74.0	3.67
7% SBS – C	49	88.0	5.29

Table 2: Fraass breaking point, ductility and elastic recovery for PMBs

Binder	Fraass (°C)	Ductility (cm)	Elastic Recovery (%)
Base bitumen A	-18	21	-
3% EVA – A	-	13	-
5% EVA – A	-12	8	-
7% EVA – A	-11	5	-
Base bitumen B	-12	63	-
3% EVA – B	-	16	-
5% EVA – B	-13	20	-
7% EVA – B	-13	19	-
Base bitumen C	-18	130	-
3% EVA – C	-	22	-
5% EVA – C	-14	10	-
7% EVA – C	-10	12	-
Base bitumen B	-12	63	-
3% SBS – B	-16	95	68
5% SBS – B	-15	99	76
7% SBS – B	-14	101	81
Base bitumen C	-18	130	-
3% SBS – C	-18	81	71
5% SBS – C	-16	90	78
7% SBS – C	-14	81	80

The Fraass breaking point (IP 80) results (Table 2) for the EVA PMBs (EVA 20/20) show a reduction in low temperature flexibility with increasing modification, although the results for the base B – EVA PMBs show consistent Fraass results before and after modification. The results for the two elastomeric PMB (linear SBS) groups initially show opposite changes in Fraass temperature with modification. The SBS PMBs produced with base bitumen B show an initial increase in low temperature flexibility, while the base C - PMBs show a decrease in flexibility. However, both groups then show an increase in Fraass temperature with increasing polymer contents.

The same grouping can be seen for the ductility @ 10°C (DIN 52013) results (with the EVA PMBs and the base C – SBS PMBs showing a decrease in ductility with modification, while the base B – SBS PMBs show an increase in ductility with modification. In terms of elastic recovery, the results indicate the high elastic nature of the elastomeric SBS PMBs with the elastic recovery @ 10°C (CEN prEN FFF) increasing with increasing polymer content. The results for the Fraass, ductility and elastic recovery tests show the high degree of dependence of the intermediate and low temperature physical properties of the PMBs on the nature of the base bitumen, the chemical composition of the polymer, and base bitumen – polymer compatibility.

The rotational viscosities at 135°C (ASTM D4402) are presented in Table 3. As with the penetration and softening point tests the viscosities give a clear indication of the effect of the addition of either an EVA or SBS copolymer to bitumen, although the magnitude of the increase in viscosity differs between the plastomeric and elastomeric PMBs.

Table 3: Rotational viscosity at 135°C for PMBs

Binder	Viscosity (mPa.s)	Binder	Viscosity (mPa.s)
Base bitumen A	510	Base bitumen B	370
3% EVA – A	880	3% SBS – B	740
5% EVA – A	1380	5% SBS – B	1100
7% EVA – A	2050	7% SBS – B	1710
Base bitumen B	370	Base bitumen C	380
3% EVA – B	590	3% SBS – C	860
5% EVA – B	900	5% SBS – C	1390
7% EVA – B	1440	7% SBS – C	2120
Base bitumen C	380		
3% EVA – C	710		
5% EVA – C	1160		
7% EVA – C	1970		

3.2 Differential Scanning Calorimetry Analysis

The DSC parameters of enthalpy associated with the fusion of the EVA crystalline fractions and the peak temperature at which this occurs for the EVA PMBs are presented in Table 4. The peak temperature at which the first-order transition occurs depends on the type of ethylene copolymer and base bitumen but is generally considered to be insensitive to polymer content (Shutt et al, 1993; Gazeau et al, 1996). However, the copolymer content does have an effect on the enthalpy associated with the endothermic reaction, there being an increase in enthalpy with increasing polymer content (Gazeau et al, 1996).

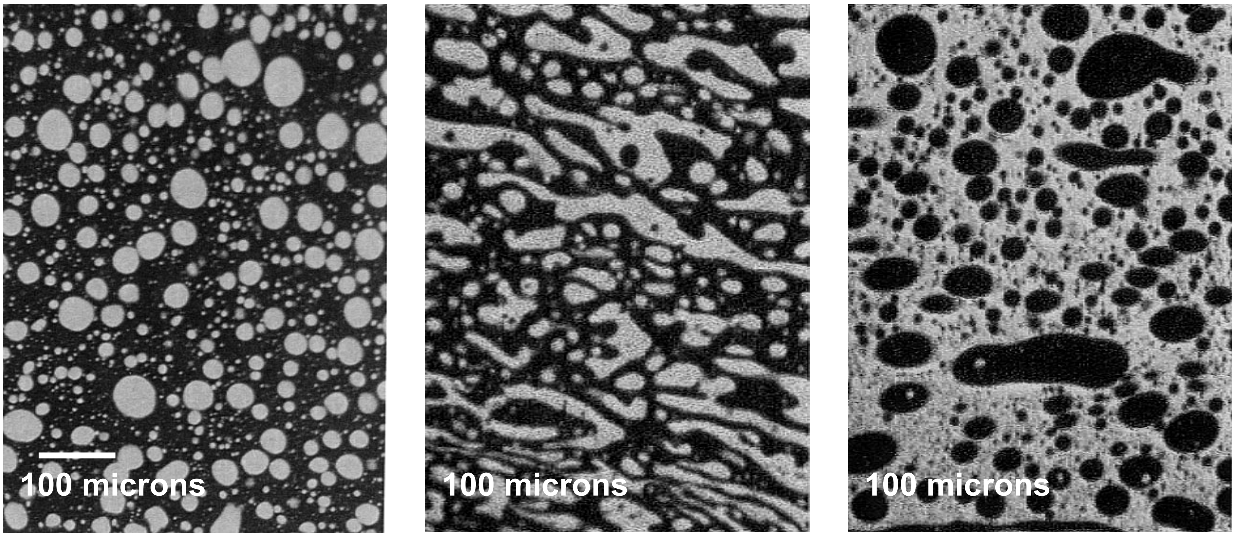
Table 4: Variations in DSC parameters due to modification of EVA PMBs

Binder	Enthalpy (J/g)	Peak Temperature (°C)
3% EVA – A	2.4	69.7
5% EVA – A	3.0	69.9
7% EVA – A	3.2	69.9
3% EVA – B	2.7	66.7
5% EVA – B	3.4	69.6
7% EVA – B	4.3	69.9
3% EVA – C	2.5	61.9
5% EVA – C	3.1	61.5
7% EVA – C	4.4	65.4

The results in Table 4 tend to confirm these previous findings with the peak temperature being relatively consistent within each EVA PMB group and there being an increase in enthalpy with increasing polymer content. On average the group B - EVA PMBs tend to have the highest value of enthalpy with the group A – PMBs having the lowest. If it is accepted that there is a relationship between enthalpy and degree of modification, the results would tend to suggest that the base B – EVA PMBs show the highest degree of modification, followed by base C - and then base A – EVA PMBs.

3.3 Fluorescent Microscopy

In addition to changing the rheological and chemical nature of a binder, polymer modification also alters the morphology (structure) of the PMB. Fluorescent microscopy images of the EVA and SBS PMBs were obtained at 100 x magnification. The fluorescent images for the 3% EVA – C, 5% EVA – C and 7% EVA – C PMBs are shown in Figures 2(a) to (c).



(a) (b) (c)

Figure 2: Fluorescent images of (a) 3% EVA – C, (b) 5% EVA – C and (c) 7% EVA - C

The fluorescent images show a change in the morphology of the PMBs as the polymer content increases. The image in Figure 2(a) shows a continuous bitumen-rich phase with a dispersed polymer-rich phase, while the image in Figure 2(c) shows the opposite with a continuous polymer phase with a dispersed bitumen phase. The image at 5% EVA polymer content displays a relatively unstable, intertwined phase structure with neither phase dominating the overall system. The relative proportion of bitumen to polymer phase has been determined by means of image analysis and shows an increase in the polymer phase from 29 percent for the 3% EVA PMB to 42 percent and, finally, to 59 percent for the 7% EVA PMB (Sundahl and Wegan, 1999). Similar results were seen for the other EVA and SBS PMBs.

The different morphologies seen in Figure 2 are a function of the swelling potential of the polymer (nature of the polymer), the nature of the base bitumen (composition of the maltenes fraction), the polymer content of the PMB and the bitumen-polymer compatibility. The different chemical and morphological nature of the PMBs will inevitably affect the rheological characteristics of these modified binders.

3.4 Fundamental Rheological Data

3.4.1 Base Bitumens

The rheological data obtained for base bitumen A has been presented in the form of isothermal plots of G*, which have been shifted in Figure 3 to produce a continuous master curve at a reference temperature of 25°C. The thermo-rheologically simple nature of the base bitumen allow the isotherms to be shifted using the time-temperature superposition principle (TTSP) (Ferry, 1971) to produce a smooth, continuous curve.

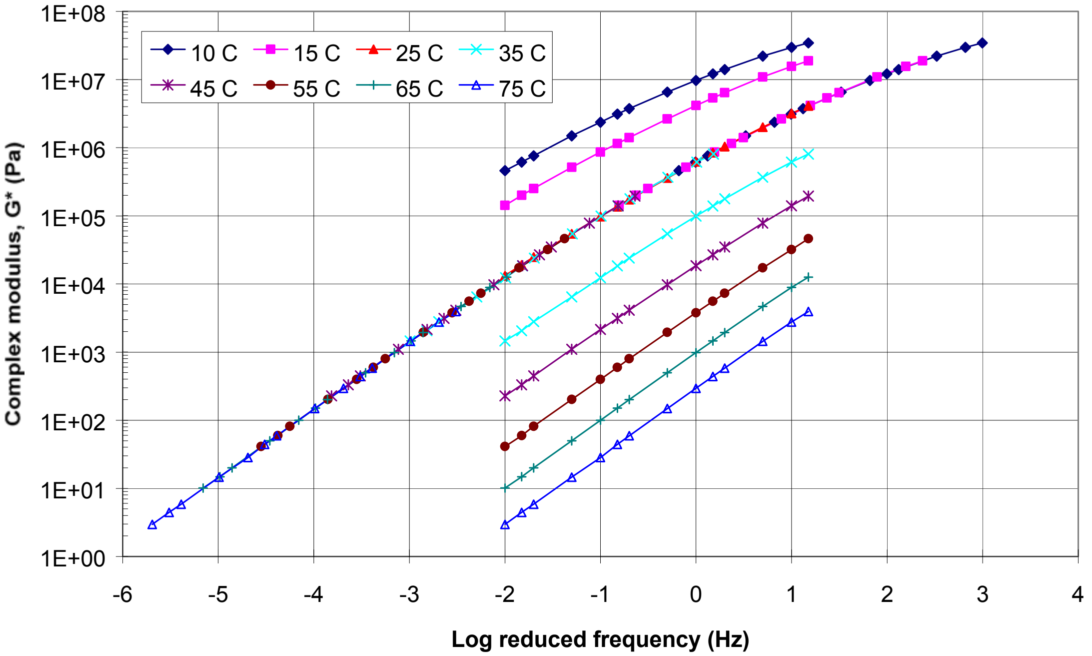


Figure 3: Master curve of complex modulus at 25°C for base bitumen A

In addition to the G* master curve, a phase angle master curve has been produced by shifting the δ isotherms in Figure 4. Again the thermo-rheologically simple nature of the penetration grade bitumen allows time-temperature equivalence to be applied with the production of a smooth master curve.

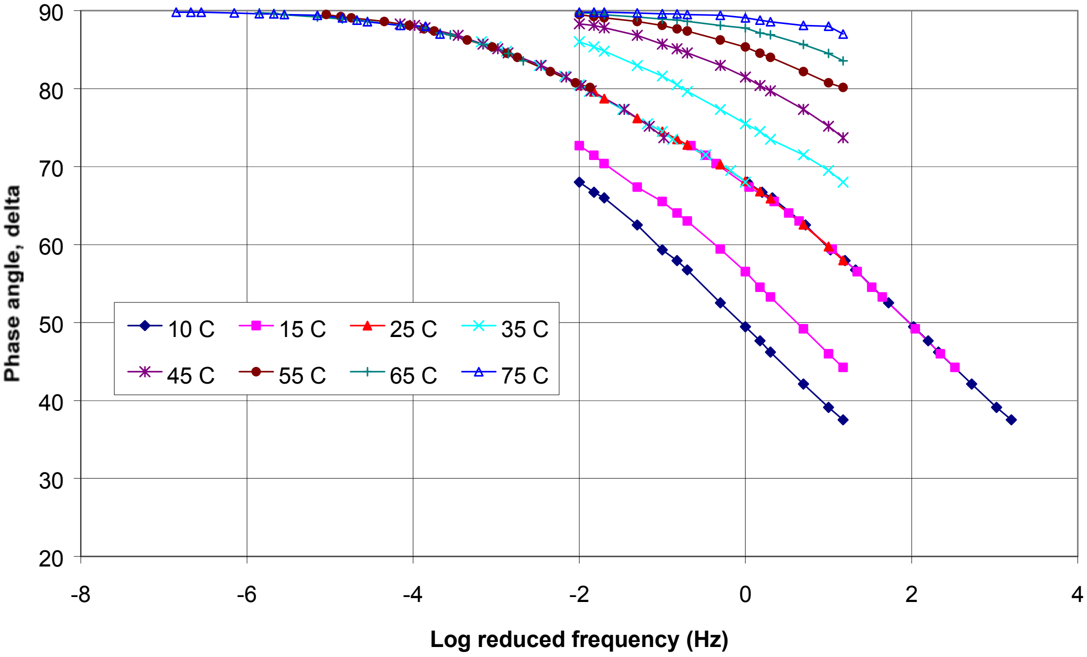


Figure 4: Master curve of phase angle at 25°C for base bitumen A

3.4.2 Ethylene Vinyl Acetate Polymer Modified Bitumens

The rheological data obtained for one of the EVA PMBs has been presented in the form of G* isotherms and then shifted to produce a master curve in Figure 5.

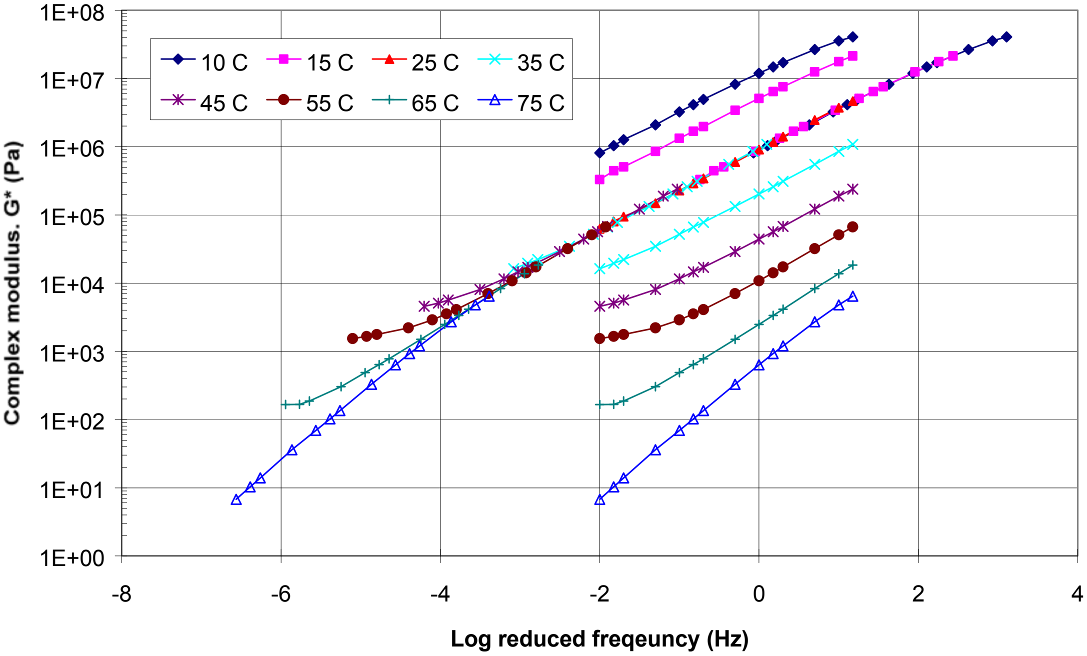


Figure 5: Master curve of complex modulus at 25°C for 7% EVA - B

The resulting master curve differs from that seen for the penetration grade bitumen in that there is evidence of a breakdown of time-temperature equivalence at the lower frequency end of the master curve. The breakdown of the smoothness of a master curve can be attributed to a number of factors. These include loss of LVE response due to DSR testing at strain levels outside the linear region, compliance errors associated with the testing apparatus and testing configuration and the presence of structural changes with temperature within the bitumen as found for waxy bitumens, highly structured 'GEL' type bitumens and some PMBs.

As the DSR testing was conducted in such a manner to try and ensure LVE response and appreciating that time-temperature equivalence does not hold across a phase transition such as crystallisation or glass transition (Phillips, 1997), the "branching" in the master curve can be attributed to the presence of the semi-crystalline EVA copolymer. The "branches" in the master curve are formed due to the occurrence of different EVA crystalline structures in the PMB at different temperatures, ranging from 35°C to 65°C. Once the EVA copolymer has melted at approximately 75°C, a temperature slightly higher than the DSC peak temperature associated with this first-order transition, the isotherm and low frequency portion of the master curve reverts back to a unit slope associated with the viscous asymptote found for unmodified bitumens.

The phase angle master curve for the base B – EVA PMB (Figure 6) differs considerably from that seen for the unmodified bitumen (Figure 4).

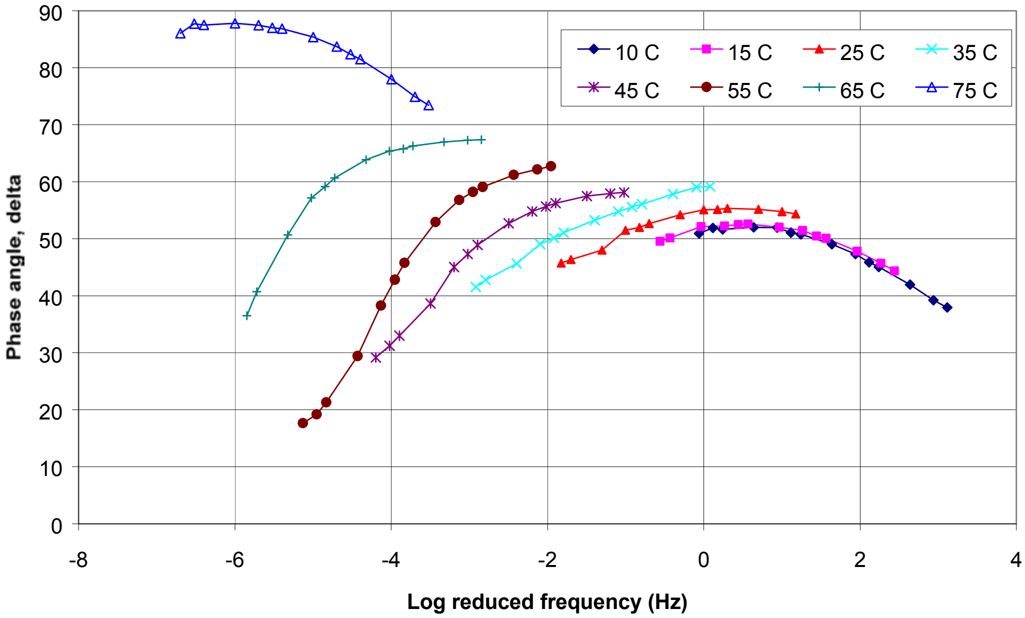


Figure 6: Master curve of phase angle at 25°C for 7% EVA - B

It is generally accepted that the phase angle is more sensitive to the modification of a binder than G*. This is evident in Figure 6 where the δ master curve, constructed using the shift factors derived for the G* master curve, clearly indicates the presence of different crystalline structures at each of the temperatures above approximately 25°C. The discontinuous "waves" of the master curve clearly demonstrate the breakdown of the time-temperature equivalence for highly modified, semi-crystalline PMBs. The only similarities with the δ master curve in Figure 4 occur at high frequencies were the bitumen-rich phase of the PMB is more dominant and at low frequencies (high temperatures) where the semi-crystalline polymer has melted (75°C).

3.4.3 Styrene Butadiene Styrene Polymer Modified Bitumens

The G* master curve for the SBS PMB in Figure 7, unlike the master curve for the EVA PMB (Figure 5), does not show any “branching” or discontinuities at the lower frequency end of the master curve where the polymer phase will tend to be dominant. The master curve illustrates the amorphous nature of the SBS PMB compared to the semi-crystalline nature of the EVA PMB, thereby, allowing the isotherms to be shifted to form a smooth, continuous curve. The dominance of the elastomeric SBS copolymer can, however, be seen at low frequencies (high temperatures) where the slope of the master curve deviates from the unit slope seen for the unmodified bitumen (Figure 3). As the testing temperature approaches 100°C and the polystyrene end blocks begin to melt, the slope of the master curve will revert back to the unit slope found for unmodified bitumens.

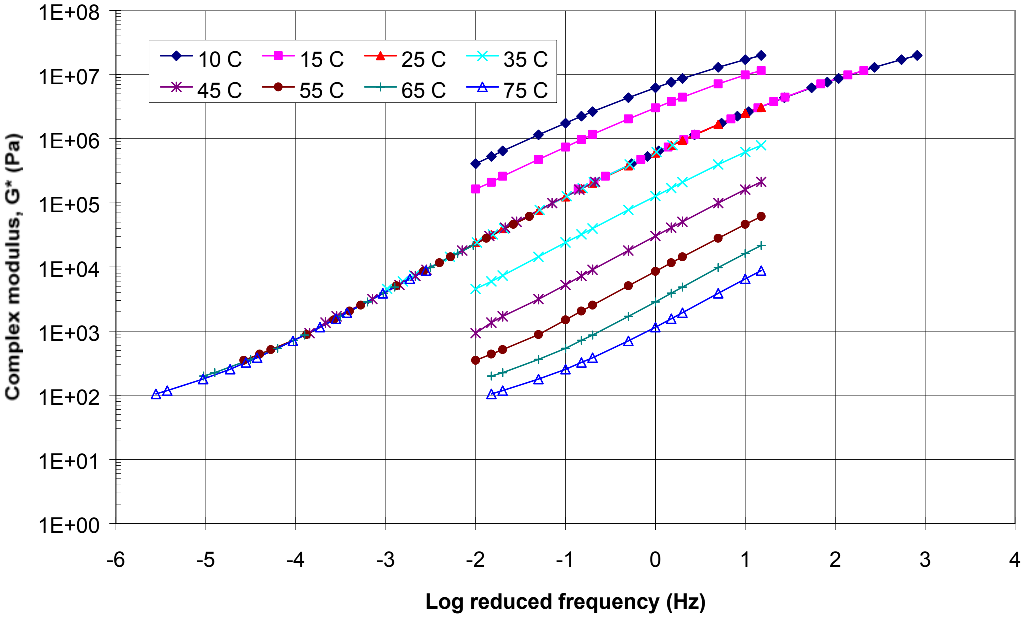


Figure 7: Master curve of complex modulus at 25°C for 7% SBS - B

A phase angle master curve for the SBS PMB has been constructed and presented in Figure 8. The curve differs from that seen for the EVA PMB in that, although it has a different shape compared to the penetration grade bitumen (Figure 4), is it still possible to produce a relatively smooth master curve. The phase angle master curve clearly indicates the elastomeric nature of the SBS PMB with the formation of a distinctive phase angle plateau region and increasing elastic behaviour at intermediate and low frequencies.

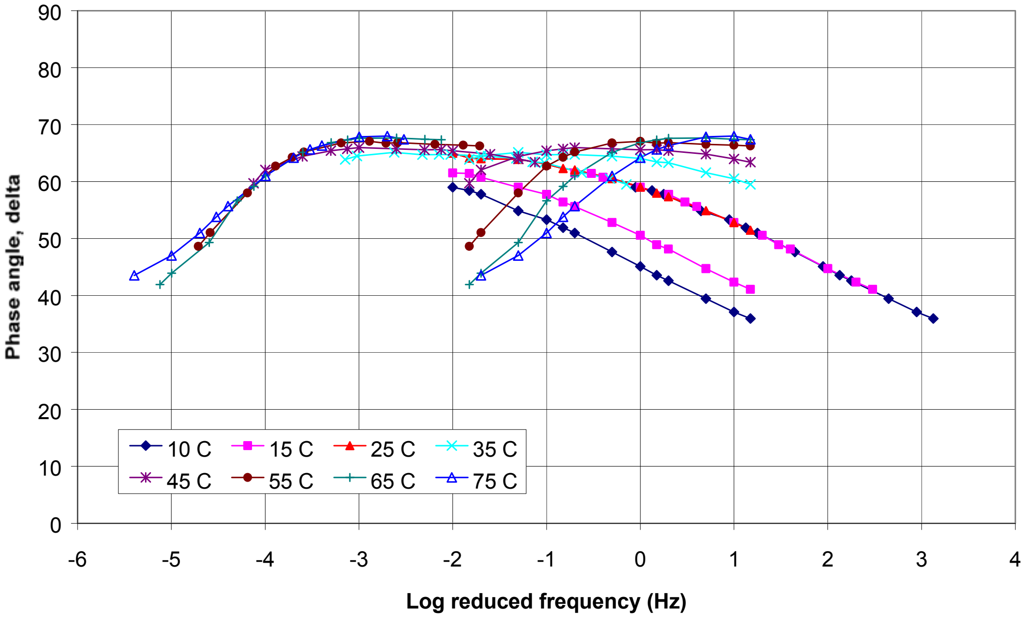


Figure 8: Master curve of phase angle at 25°C for 7% SBS - B

4 LABORATORY AGEING OF POLYMER MODIFIED BITUMENS

The base bitumens and PMBs were subjected to standard laboratory ageing procedures using the rolling thin film oven test (RTFOT) (ASTM D2872), to simulate short-term ageing, and the pressure ageing vessel (PAV) test (Anderson et al, 1994), to simulate long term ageing. Various researchers have questioned the appropriateness of these two laboratory ageing methods with regard to the ageing of PMBs. One of the main problems with the RTFOT procedure for modified bitumens is that due to their high viscosity at 163°C, they do not roll inside the glass bottles. A modified RTFOT method using steel rods in the glass bottles has been prescribed as a means to alleviate the rolling problem (Bahia et al, 1998). One of the main problems with the PAV procedure is the high temperature (90°C to 110°C) used with the test and the effect it may have on PMBs, particularly SBS modified products that undergo a phase transition (polystyrene block melting) at these temperatures (Phillips, 1997). An alternative long term ageing procedure, known as the high pressure ageing test (HiPAT), developed from the PAV but with a lower temperature of 85°C and a longer exposure at 2.1 MPa of 65 hours compared to 20 hours, has been recommended to overcome the high temperature problems of the PAV (Hayton et al, 1999). However, appreciating the shortcomings of the RTFOT and PAV tests, they have still been used in this study to investigate the physical, chemical, morphological and rheological changes associated with the ageing of PMBs.

4.1 Differential Scanning Calorimetry Analysis

In an attempt to quantify the changes associated with RTFOT and PAV ageing of the EVA PMBs, DSC thermal analysis was performed on the laboratory blended EVA PMBs before and after ageing (Table 5).

Table 5: Variations in DSC parameters for unaged, RTFOT and PAV aged EVA PMBs

Binder	Enthalpy (J/g)			Peak Temperature (°C)		
	Unaged	RTFOT	PAV	Unaged	RTFOT	PAV
3% EVA – A	2.4	1.4	1.2	69.7	69.0	69.6
5% EVA – A	3.0	2.9	2.1	69.9	70.5	71.5
7% EVA – A	3.2	3.1	3.0	69.9	71.9	70.5
3% EVA – B	2.7	1.6	-	66.7	70.0	-
5% EVA – B	3.4	3.3	2.1	69.6	67.4	72.5
7% EVA – B	4.3	3.9	3.6	69.9	72.2	72.8
3% EVA – C	2.5	1.4	-	61.9	64.2	-
5% EVA – C	3.1	2.5	2.0	61.5	65.8	66.0
7% EVA – C	4.4	3.8	3.3	65.4	66.6	63.6

The results in Table 5 indicate that the peak temperatures obtained during DSC testing remain relatively constant for the unaged and aged PMBs. However, there is a reduction in enthalpy for the RTFOT aged binders compared to the unaged binders with a further reduction for the PAV aged binders. As the enthalpy associated with DSC testing can be broadly related to the degree of modification, the reduction in enthalpy would suggest that there might be some loss of the effect of modification associated with the change in the crystallising nature of the EVA PMBs.

4.2 Gel Permeation Chromatography Analysis

GPC analysis was performed on the six laboratory blended SBS PMBs in their unaged, RTFOT and PAV aged conditions in order to quantify the changes in the molecular mass distribution with laboratory-simulated ageing. An example of the GPC chromatograms obtained for one of the SBS PMBs is shown in Figure 9.

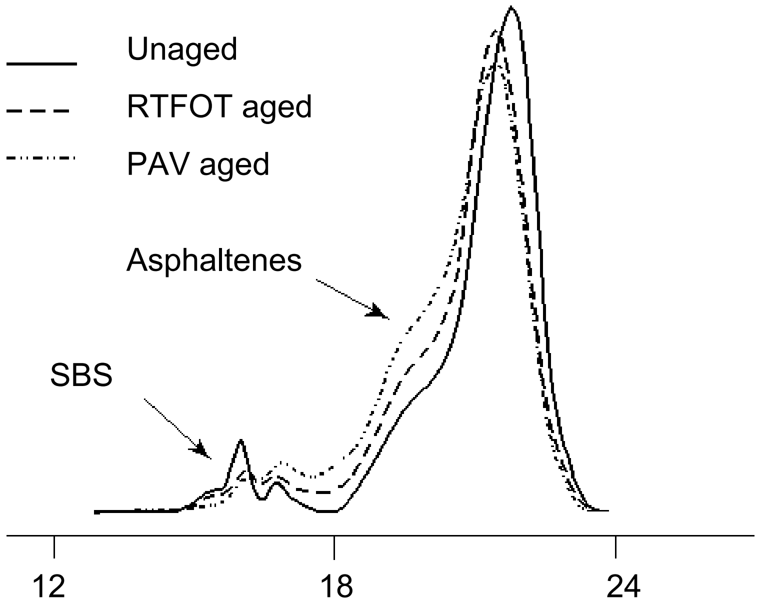


Figure 9: GPC plots for unaged, RTFOT and PAV aged 7% SBS - C

The GPC analysis shows changes in the molecular size distribution of both the polymer and bitumen phases. The SBS copolymer has degraded to a lower molecular size after RTFOT, with a further degradation after PAV ageing. This degradation, or change in the molecular size of the SBS copolymer has been seen by other researchers (Airey and Brown, 1998; Linde and Johansson, 1992; Kuppens, 1995) and is associated with the oxidation of the sensitive double bonds in the butadiene part of the polymer. The opposite is true for the bitumen phase, which shows an increase in the larger molecular size fractions (asphaltenes) after ageing.

4.3 Fluorescent Microscopy

Fluorescent images for unaged, RTFOT and PAV aged 7% EVA – B PMB samples are presented in Figure 10. The images show the considerable change in the morphology of the PMB with ageing. The image of the unaged sample (a) shows a continuous polymer matrix with a dispersed bitumen phase consisting of spherical globules with the polymer phase making up 79 percent of the image. The RTFOT sample shows a structure with a less dominant but still continuous polymer phase (57 percent), while the PAV sample shows a continuous bitumen phase with a dispersed polymer phase (36 percent) (Sundahl and Korsgaard, 1999). Similar results were seen for the SBS PMBs.

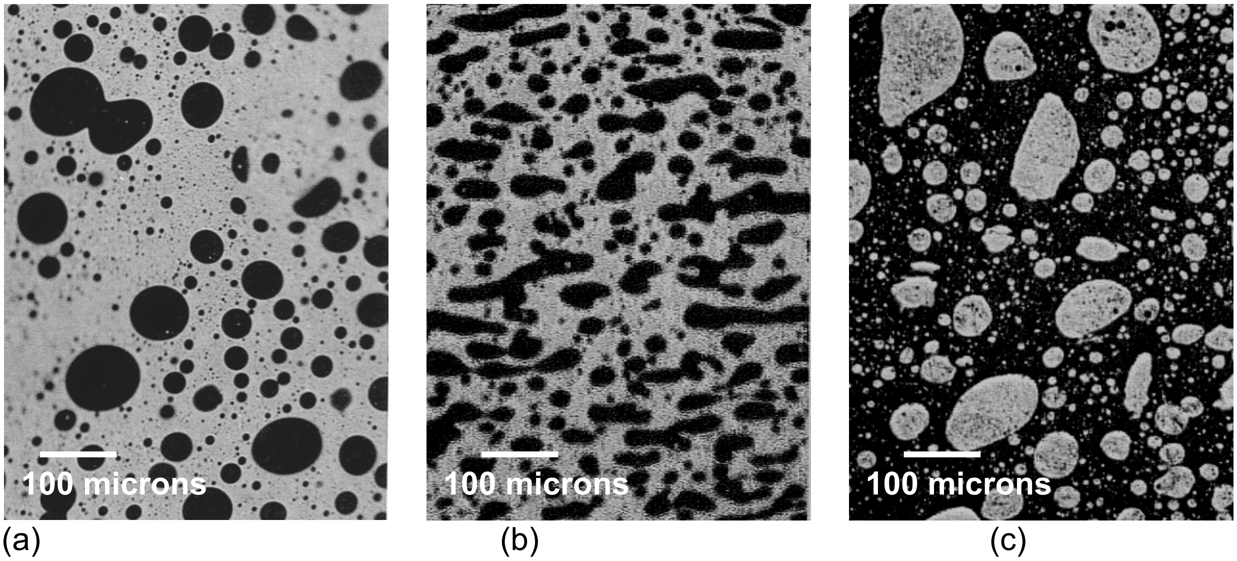


Figure 10: Fluorescent images of (a) unaged 7% EVA – B, (b) RTFOT aged 7% EVA – B and (c) PAV aged 7% EVA - B

If there are changes in the crystalline nature (EVA PMBs), molecular size distribution (SBS PMBs) and morphology of the aged PMBs this will inevitably result in changes in the rheological characteristics of the aged product. However, it is important to appreciate that these changes may also be associated with the separation of the base bitumen and polymer during the laboratory ageing procedures as well as being a consequence of PMB ageing.

4.4 Fundamental Rheological Parameters

4.4.1 Base Bitumens

The isochronal plot for the unaged and aged base bitumen in Figure 11 shows a consistent increase in G* after RTFOT with a further increase after PAV ageing. There is also a regular decrease in phase angle over the temperature domain after ageing.

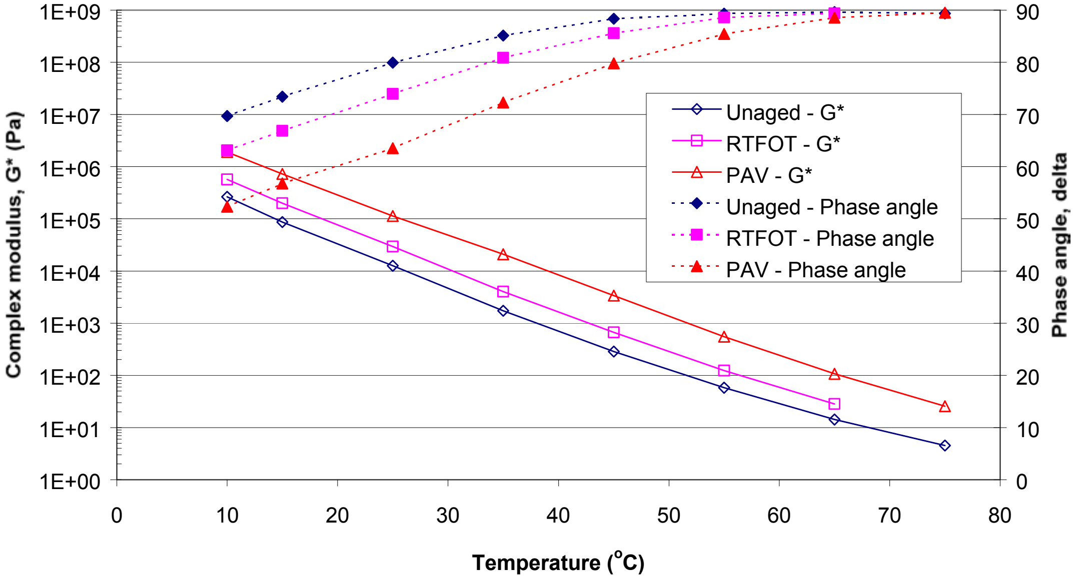


Figure 11: Isochronal plot at 0.02 Hz for unaged, RTFOT and PAV aged base C

The effect of oxidative ageing of the penetration grade bitumen is seen as a shift of the Black diagram curves towards lower phase angles after ageing (Figure 12). The rheological changes after ageing, therefore, consist of an increase in stiffness and a greater proportion of elastic behaviour compared to the unaged binder.

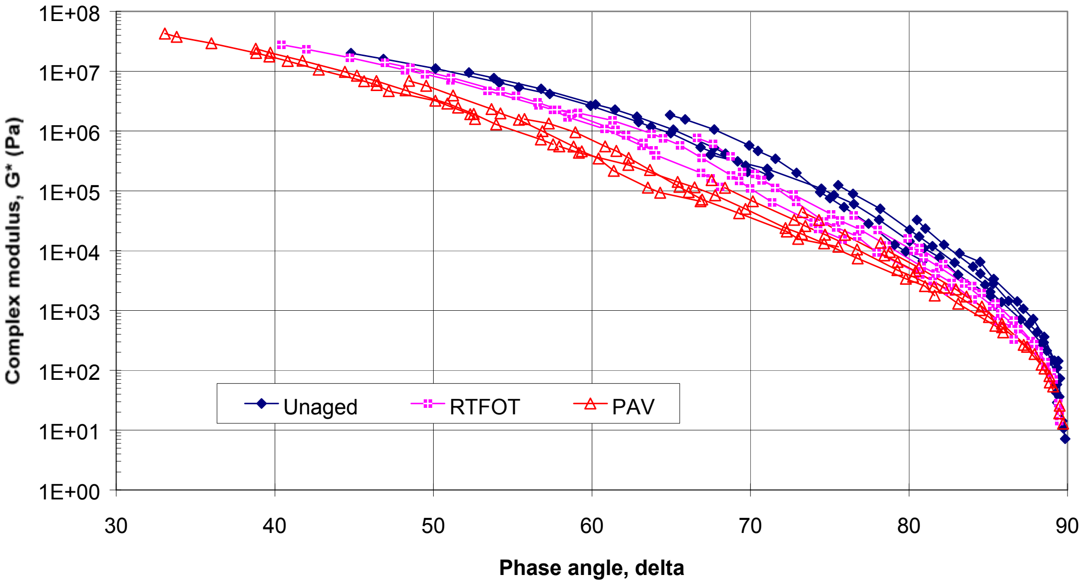


Figure 12: Black diagram for unaged, RTFOT and PAV aged base C

4.4.2 Ethylene Vinyl Acetate Polymer Modified Bitumens

The DSC and morphological evaluation of the EVA PMBs before and after ageing have shown significant changes both in the crystalline nature and the physical structure (morphology) of PMBs. The rheological changes for the unaged and aged 7% EVA – B PMB can be seen in the isochronal plot of G* and δ at 0.02 Hz in Figure 13. The G* isochrones show an increase in G* with ageing similar to the trend seen for a penetration grade bitumen. However, the changes shown for phase angle with ageing differ considerably from that seen for penetration grade bitumens. Within the temperature range of 35°C to 65°C, where the EVA polymer phase can be considered to have the greatest influence on the rheological behaviour of the PMB, there is an increase in phase angle with ageing, opposite to the decrease seen for penetration grade bitumens.

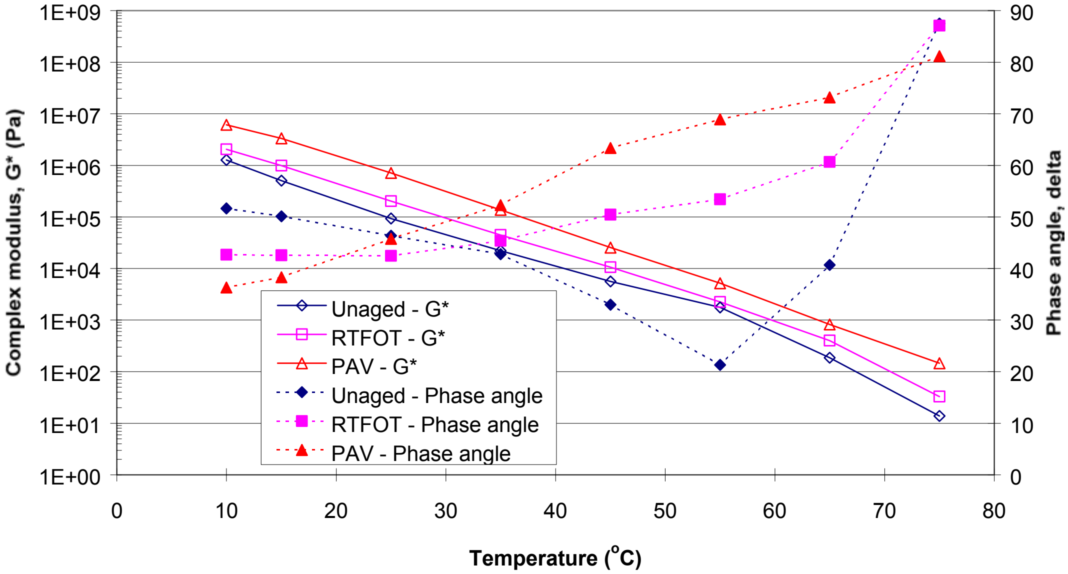


Figure 13: Isochronal plot at 0.02 Hz for unaged, RTFOT and PAV aged 7% EVA - B

The rheological data has also been presented as a Black diagram in Figure 14. Unlike the regular shifting of the Black diagram curves towards lower phase angles for the unmodified bitumens after ageing, the changes in the Black diagram with ageing for the EVA PMB are considerably more complex. Similar shifts towards lower phase angles after ageing do occur at G* values greater than 10^7 Pa where the bitumen phase can be considered to have a greater influence on the rheological character of the PMB. However, at G* values less than 10^7 Pa, the Black diagram curves show a significant alteration in the rheological behaviour of the EVA PMB. These rheological changes consist of the G* versus δ waves, associated with different EVA crystalline structures at different temperatures, altering their shape and orientation with ageing. The DSC analysis and fluorescent microscopy images have shown changes in the morphology of the EVA PMBs with laboratory ageing. These changes seem to have manifested themselves as alterations in the rheological characteristics of the aged EVA PMBs which differs from that seen for penetration grade bitumens. The rheological changes associated with ageing for the other EVA PMBs have been presented in a previous paper (Airey and Brown, 1998).

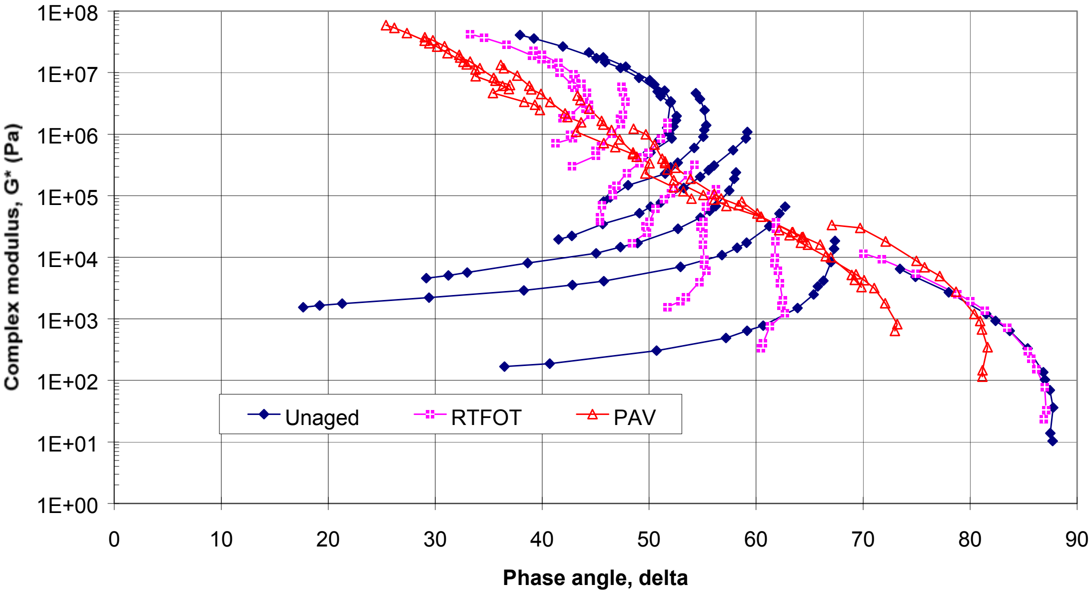


Figure 14: Black diagram for unaged, RTFOT and PAV aged 7% EVA - B

4.4.3 Styrene Butadiene Styrene Polymer Modified Bitumens

The isochronal plot for the SBS PMB (Figure 15) shows a similar increase in G* after RTFOT and PAV ageing to that seen for the unmodified bitumen. However, there is a slight decrease in G* after ageing between 65°C and 75°C which is probably associated with the degradation in the molecular size of the SBS copolymer leading to a “softening” of the PMB in the region where the polymer phase is most dominant.

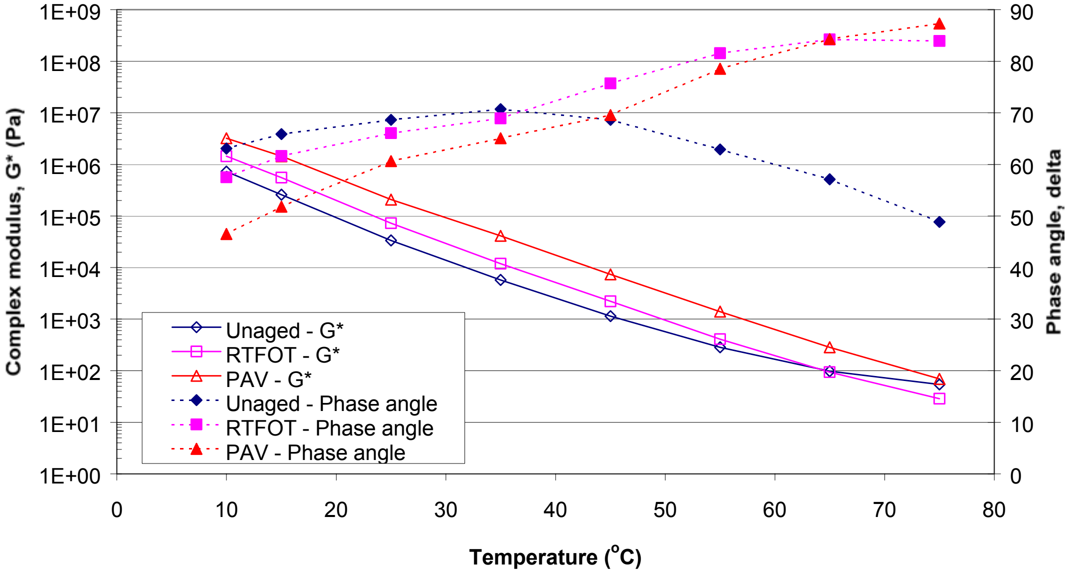


Figure 15: Isochronal plot at 0.02 Hz for unaged, RTFOT and PAV aged 5% SBS - B

The changes in δ with ageing show two different trends, being similar to that seen for the base bitumen at temperatures less than 40°C but different in the higher temperature region where the polymer phase is dominant. It is within this polymer dominant region that there is an increase in δ (increased viscous response) after ageing, again probably linked to the reduction in SBS molecular size fractions with ageing.

These two regions of behaviour are can also be seen in Figure 16. At G* values greater than 10^4 Pa, the behaviour is similar to that seen for the base bitumens (increased stiffness and elastic response) but below 10^4 Pa the Black diagram shows decreased stiffness and increased viscous response.

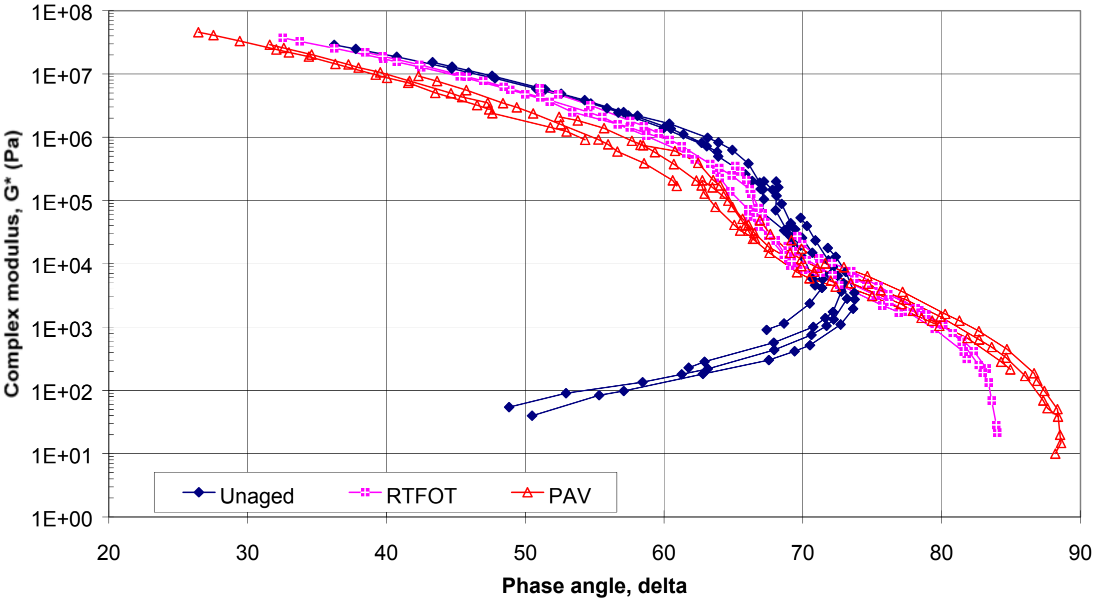


Figure 16: Black diagram for unaged, RTFOT and PAV aged 5% SBS - B

5 CONCLUDING SUMMARY

Fundamental rheological testing, physical and chemical analysis and fluorescent imaging have been used in this paper to quantify the changes in a binder associated with modification and laboratory simulated ageing. These methods have demonstrated their usefulness in showing the considerable changes that can occur in the physical, chemical, morphological and rheological properties of different PMBs as a function of polymer type, base bitumen type, polymer-bitumen compatibility and polymer content.

The conventional penetration, softening point, Fraass, ductility, elastic recovery and high temperature viscosity tests have indicated the increased stiffness and improved temperature susceptibility of both elastomeric and plastomeric PMBs. However, dynamic shear rheometry, differential scanning calorimetry, gel permeation chromatography and fluorescent imaging have been required to identify the complex changes in morphology, chemistry and rheology associated with the semi-crystalline EVA PMBs and the styrenic block SBS PMBs. With regard to polymer modification, the results have shown the changes in morphology with increasing modification from bitumen phase dominant systems to polymer phase dominant systems. The DSR results have identified the formation of different crystalline structures at different temperatures for the semi-crystalline EVA PMBs and the enhanced high temperature / low frequency elastic response of the SBS PMBs.

The effects of laboratory simulated ageing has been shown to differ amongst the penetration grade bitumens, EVA and SBS PMBs. The effect of oxidative ageing for the penetration grade bitumens has been seen as an increase in stiffness and elastic response. However, the effects of laboratory ageing for the EVA and SBS PMBs consist of a considerably more complex change in the binder's chemical nature, morphology and, consequently, rheological characteristics.

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