

Characterization of bitumens modified with SEBS, EVA and EBA polymers

ULF ISACSSON, XIAOHU LU

Division of Highway Engineering, Royal Institute of Technology, S-100 44, Stockholm, Sweden

E-mail: isacsson@ce.kth.se; xiaohu@infra.kth.se

A laboratory evaluation of the modified bitumens containing styrene-ethylene-butylene-styrene (SEBS), ethylene vinyl acetate (EVA) and ethylene butyl acrylate (EBA) copolymers is presented. The morphology, storage stability and rheological and ageing properties of the modified binders were studied using fluorescence microscopy, dynamic mechanical analysis, creep test (bending beam rheometer) and conventional methods. The results indicated that the morphology and storage stability of the modified binders were largely dependent on the polymer content and were influenced by the characteristics of the base bitumens and the polymers. At a low polymer content (3% by weight), the modified binders showed dispersed polymer particles in a continuous bitumen matrix. At a sufficiently high polymer content (6% by weight), a continuous polymer phase was observed. Regardless of the nature of the two phases, the storage stability of the modified binders decreased as polymer content increased. Polymer modification improved bitumen rheological properties such as increased elastic responses at high temperatures and reduced creep stiffness at low temperatures. The degree of improvement generally increased with polymer content, but varied with bitumen source/grade and polymer type. Polymer modification also influenced bitumen ageing properties. Evaluation of ageing effect was dependent on testing conditions (e.g. temperature and frequency). © 1999 Kluwer Academic Publishers

1. Introduction

Bitumen has been used in the construction of asphalt pavements for more than a century. Various types of crude source and refining process lead to extreme complexity in bitumen chemistry and rheology. Due to a large number of molecular species varying widely in polarity and molecular weight [1], no specifications for bitumen composition or structure are used today. Furthermore, the rheological behaviour of bitumen is also very complex, varying from purely viscous to elastic, depending on loading time and temperature. As a viscoelastic material, bitumen plays a prominent role in determining many aspects of road performance. For example, a bituminous mixture (asphalt) needs to be flexible enough at low service temperatures to prevent pavement cracking and to be stiff enough at high service temperatures to prevent rutting. These functional properties are required to enable pavements to accommodate increasing traffic loadings in varying climatic environments. Unfortunately, asphalt containing a conventional bitumen does not always perform as expected. In improving the properties of bitumens, several types of modification have been investigated. These include additive modification, polymer modification and chemical reaction modification [2].

Polymer modification of bitumens is not a new phenomenon, but interest of this technique has increased considerably during the past decade due to

the increased performance-related requirements on asphalt pavements. Despite the large number of polymeric products, there are relatively few types which are suitable for bitumen modification. When used as bitumen modifiers, polymers should be compatible with bitumen, resist degradation at asphalt mixing temperatures and be cost-effective. The degree of modification depends on the characteristics of bitumens, polymer type and content, as well as the process used for preparation of the modified bitumens.

The present paper characterizes the modified bitumens containing styrene-ethylene-butylene-styrene (SEBS), ethylene vinyl acetate (EVA) and ethylene butyl acrylate (EBA) copolymers. The morphology, storage stability, rheology and ageing properties of the modified binders are studied using fluorescence microscopy, dynamic mechanical analysis, creep test (bending beam rheometer) and conventional methods. The effects of base bitumen, polymer type and content on these properties are investigated.

2. Experimental

2.1. Materials

Three penetration-grade bitumens (one B85 and two B180) from two sources (Venezuela and Mexico) were used in this study. They are denoted by A, B and C, respectively. The physical properties and chemical characteristics of the base bitumens have been reported

elsewhere [3]. The polymers investigated are SEBS, EVA and EBA copolymers. The SEBS polymer is Kraton G 1650 (Shell), containing 29 wt % styrene. The two EVA copolymers used are Elvax 260 (coded as EVA 1) and Elvax 420 (coded as EVA 2), supplied by Du Pont. Melt indices (MI) of Elvax 260 and Elvax 420 are 6 and 158, and their vinyl acetate (VA) contents are 28 and 18 wt %, respectively. The EBA polymer was produced by Neste Chemicals and supplied by Nynas Petroleum.

The polymer modified bitumens were prepared using a low shear mixer (RW 20 DZM-P4, Janke and Kunkel) at 180 °C and a speed of 125 rpm. The mixing time was two hours. The process for preparing the modified binders exposed the bitumen to high temperature and air for an extended time, which led to hardening of the bitumen. For the accurate evaluation of polymer effects, the base bitumens were also subjected to the same treatment as the polymer-bitumen blends.

2.2. Test methods

2.2.1. Conventional binder tests

The standardized binder tests used to characterize base and polymer modified bitumens included softening point (R&B, ASTM D 36), penetration (25 °C, ASTM D 5), kinematic viscosity (135 °C, ASTM D 2170) and Fraass breaking point (IP 80).

2.2.2. Dynamic mechanical analysis (DMA)

DMA with frequency sweeps (from 0.1 to 100 rad/s) at 25 and 60 °C and temperature sweeps (from -30 to 135 °C) at 1 rad/s were performed using a rheometer (RDA II, Rheometrics). The test procedure has been described previously [4]. The DMA imposes a sinusoidally varying shear strain on the sample and the amplitude of the resulting shear stress is determined. The ratio of the peak stress to the peak strain is defined as the complex modulus (G^*). The in-phase and out-of-phase components of G^* are defined as the storage modulus (G') and the loss modulus (G''), respectively. The phase difference between the stress and strain in an oscillatory deformation is defined as phase angle (δ).

2.2.3. Low-temperature creep test

Creep tests were carried out at four different temperatures (-35, -25, -15 and -10 °C) using the bending beam rheometer (TE-BBR, Cannon Instrument Company). The rheometer was developed in the SHRP (*Strategic Highway Research Program*) [5]. The binder beam (125 mm long, 12.5 mm wide and 6.25 mm thick) was submerged in a constant-temperature bath at each test temperature (starting from -35 °C) for 30 min. A constant load of 100 g was then applied to the rectangular beam of the binder, which was supported at both ends by stainless steel half-rounds (102 mm apart), and the deflection of center point was measured continuously. Creep stiffness (S) and creep rate (m) of the binders were determined at different loading times ranging from 8 to 240 s.

2.2.4. Fluorescence microscopy

Fluorescence microscopy was used to study morphology of polymer modified binders. Photomicrographs

with a magnification of 250 were taken at room temperature. Squashed slides of binders were prepared using very small amounts of the heated sample. The instrument (Leitz, LABORLUX II) was equipped with a Polaroid camera and a blue filter system. A blue light (wavelength 390 to 490 nm) was used for binder excitation and the fluorescent yellow light was re-emitted by the swollen polymer phase.

3. Results and discussion

3.1. Conventional binder tests

Results of a number of conventional binder tests are given in Table I. As expected, polymer modification causes an increase in binder consistency (decrease in penetration and increase in viscosity and softening point). The modification also reduces temperature susceptibility of the bitumens, as indicated by increased penetration index (PI) [6] and increased penetration viscosity number (PVN) [7]. In addition, the modified binders generally display a lower Fraass breaking point than the corresponding plain bitumens. The effects are dependent on the base bitumen, the type of polymer and the proportion of the two components. For a given polymer content, the bitumens seem to be more susceptible to SEBS and EBA modification as compared to EVA modification. With increasing polymer content, enhanced changes are observed in the conventional parameters with the exception of Fraass breaking point.

3.2. Morphology

The morphology of polymer modified bitumens was investigated by means of fluorescence microscopy at room temperature. In the photomicrographs, the swollen polymer phase appears white (fluoresces yellow light) while the bitumen phase appears dark. As depicted in Fig. 1, the modified binders may show either a continuous bitumen phase with dispersed polymer particles or a continuous polymer phase with dispersed bitumen globules, depending on polymer content. In general, at a low polymer content (3%), the small polymer spheres, swollen by bitumen compatible fractions (e.g. aromatic oils), are spread homogeneously in a continuous bitumen phase. Compared with 3% SEBS modified binders, those containing EVA and EBA of the same polymer content reveal much finer dispersion of the polymers. However, in all cases, appearance of a continuous polymer structure begins at 6% polymer content. Furthermore, for a given polymer content, the characteristics of morphology of the modified binders are greatly dependent on the base bitumens and the type of polymers.

The morphology should also be influenced by testing temperature, which means that the morphology observed at ambient temperature does not necessarily reflect that at high temperatures. The differences in photomicrographs are mainly caused by the different structure of the polymers and varying degree of the molecular interactions between the bitumen and the polymer. As will be discussed later, the relative proportions of the two phases and their spatial configuration on microscopic scale (microstructure) may influence the rheological properties of the modified binders.

TABLE I Binder test results obtained using conventional methods

Binder	Viscosity @ 135 °C, (mm ² /s)	Penetration @25 °C, (dmm)	Softening point (°C)	Fraass breaking point (°C)	PI	PVN
A	370	77	47.3	-11	-0.86	-0.64
Bitumen A + 6% SEBS	2740	40	71.8	-16	2.55	1.38
Bitumen A + 6% EVA 1	1860	54	59.5	-14	1.12	1.24
Bitumen A + 6% EVA 2	1080	54	63.5	-12	1.90	0.49
Bitumen A + 6% EBA	2020	44	74.8	-13	3.25	1.09
B	224	165	39.5	-15	-1.10	-0.55
Bitumen B + 3% SEBS	577	111	58.0	-19	3.05	0.48
Bitumen B + 6% SEBS	1630	61	66.8	-18	2.84	1.22
Bitumen B + 9% SEBS	3950	46	78.5	-22	3.90	2.05
Bitumen B + 3% EVA 1	469	141	42.2	-17	-0.61	0.48
Bitumen B + 6% EVA 1	1140	97	53.4	-20	1.48	1.34
Bitumen B + 9% EVA 1	2970	76	59.8	-19	2.15	2.40
Bitumen B + 3% EVA 2	342	129	46.8	-17	0.64	-0.16
Bitumen B + 6% EVA 2	602	96	57.4	-20	2.39	0.35
Bitumen B + 9% EVA 2	1070	77	64.4	-17	3.10	0.93
Bitumen B + 3% EBA	472	121	51.6	-20	1.80	0.28
Bitumen B + 6% EBA	1180	82	70.2	-18	4.33	1.16
Bitumen B + 9% EBA	3040	61	77.8	-17	4.58	2.10
C	237	158	41.5	-16	-0.44	-0.51
Bitumen C + 6% SEBS	1490	67	70.5	-17	3.74	1.22
Bitumen C + 6% EVA 1	940	100	57.7	-17	2.60	1.09
Bitumen C + 6% EVA 2	584	88	59.8	-21	2.62	0.20
Bitumen C + 6% EBA	1080	72	71.1	-20	4.06	0.85

TABLE II Storage stability of polymer modified binders as evaluated by DMA at 25 °C and 1 and 10 rad/s

Binder ^a	G^* (Pa) at 25 °C, 1 rad/s			G^* (Pa) at 25 °C, 10 rad/s			I_s at 25 °C	
	Original sample	Top section	Bottom section	Original sample	Top section	Bottom section	1 rad/s	10 rad/s
Bitumen A + 6% SEBS	2.37E5	4.59E4	7.56E5	9.94E5	1.72E5	3.43E6	1.22	1.30
Bitumen A + 6% EVA 1	6.60E4	2.31E4	6.05E5	2.91E5	1.04E5	2.48E6	1.42	1.37
Bitumen A + 6% EVA 2	8.77E4	3.32E4	5.66E5	4.23E5	1.49E5	2.38E6	1.23	1.20
Bitumen A + 6% EBA	7.75E4	1.68E4	9.10E5	3.40E5	6.85E4	3.59E6	1.73	1.72
Bitumen B + 3% SEBS	3.84E4	4.53E4	4.54E4	2.16E5	2.51E5	2.54E5	0.00	0.01
Bitumen B + 6% SEBS	7.52E4	8.62E4	2.92E5	3.36E5	4.01E5	1.38E6	0.53	0.54
Bitumen B + 9% SEBS	1.20E5	4.35E4	7.58E5	4.19E5	1.13E5	3.11E6	1.24	1.44
Bitumen B + 3% EVA 1	2.11E4	2.25E4	2.20E4	1.32E5	1.40E5	1.38E5	0.00	-0.01
Bitumen B + 6% EVA 1	3.00E4	9.50E3	2.80E5	1.44E5	4.51E4	1.20E6	1.47	1.43
Bitumen B + 9% EVA 1	4.79E4	1.82E4	1.49E6	1.77E5	5.92E4	4.86E6	1.91	1.91
Bitumen B + 3% EVA 2	2.51E4	3.15E4	3.03E4	1.59E5	1.86E5	1.81E5	-0.02	-0.01
Bitumen B + 6% EVA 2	3.10E4	2.04E4	1.57E5	1.59E5	9.29E4	7.27E5	0.89	0.89
Bitumen B + 9% EVA 2	5.61E4	2.70E4	1.17E6	2.18E5	7.59E4	3.99E6	1.64	1.72
Bitumen B + 3% EBA	2.56E4	3.21E4	3.21E4	1.58E5	1.90E5	1.89E5	0.00	0.00
Bitumen B + 6% EBA	2.92E4	1.20E4	3.49E5	1.37E5	4.92E4	1.53E6	1.46	1.49
Bitumen B + 9% EBA	6.23E4	1.84E4	1.57E6	2.25E5	5.10E4	5.19E6	1.93	2.00
Bitumen C + 6% SEBS	7.50E4	4.08E4	2.33E5	3.43E5	1.66E5	1.16E6	0.76	0.84
Bitumen C + 6% EVA 1	3.32E4	1.81E4	1.28E5	1.70E5	7.47E4	6.49E5	0.85	0.94
Bitumen C + 6% EVA 2	4.77E4	3.93E4	1.21E5	2.35E5	1.61E5	5.87E5	0.49	0.56
Bitumen C + 6% EBA	5.66E4	2.24E4	2.81E5	2.45E5	7.40E4	1.29E6	1.10	1.24

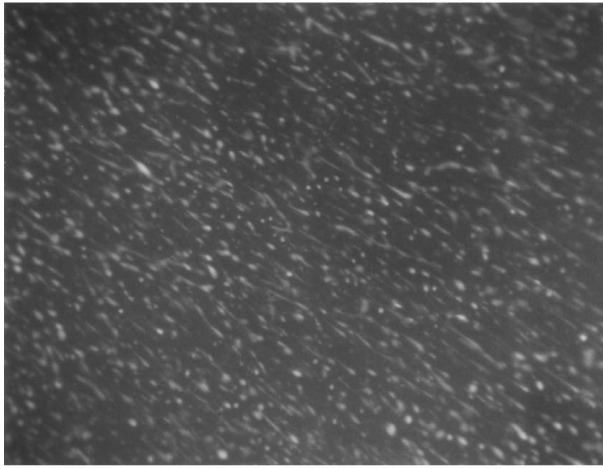
^aThe modified binders were stored at 180 °C for three days

3.3. Storage stability

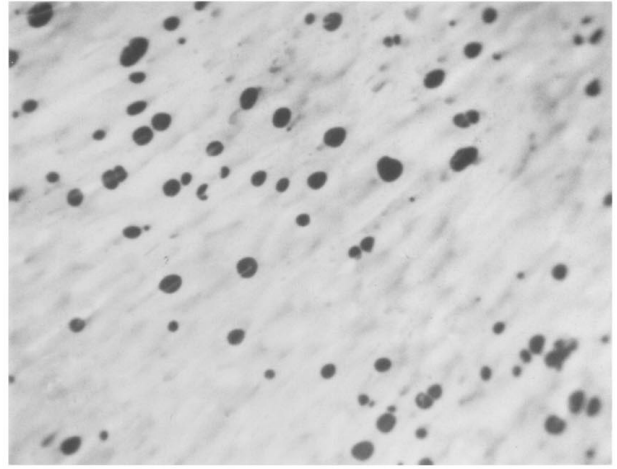
As described previously [3], a tube test was used to determine the storage stability of polymer modified bitumens. After vertically storing the tube at 180 °C for three days, DMA (frequency sweeps between 0.1 and 100 rad/s) at 25 °C and fluorescence microscopy were carried out on the samples taken from the top and bottom of the tube. The measurements were also performed on the corresponding original binders. The fluorescence micrographs indicated that the top samples of the tube were rich in polymers and bottom sam-

ples of the tube were rich in asphaltenes, and therefore defined as polymer-rich and asphaltene-rich phases, respectively. The two phases differ widely in their rheological properties. An example of complex modulus (G^*) as a function of frequency for a polymer modified binder before and after hot storage is given in Fig. 2.

The logarithm of the ratio of G^* of the asphaltene-rich phase to G^* of the polymer-rich phase is defined as the separation index, I_s . DMA results obtained at 1 and 10 rad/s are summarized in Table II. As can be seen, the storage stability of the modified binders decreases with



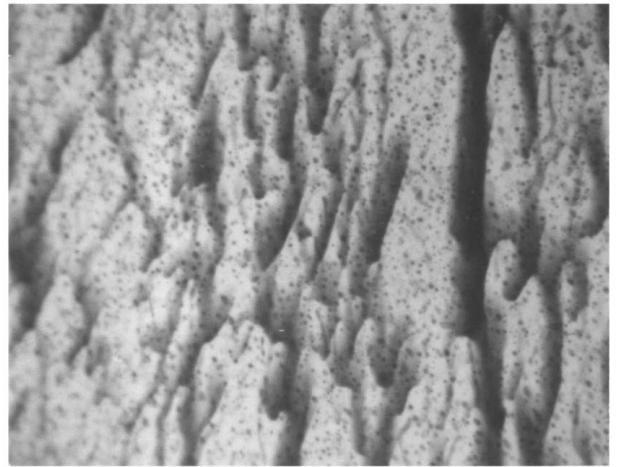
Bitumen B + 3% SEBS



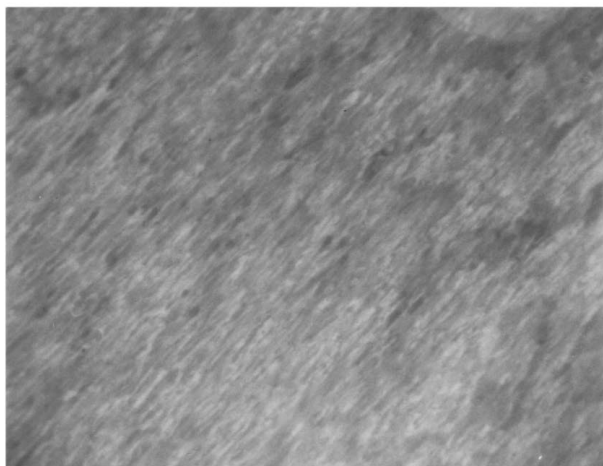
Bitumen B + 9% SEBS



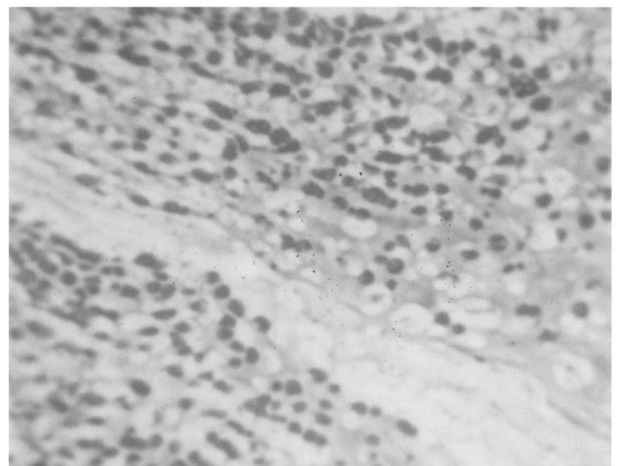
Bitumen B + 3% EVA 1



Bitumen B + 9% EVA 1



Bitumen C + 6% EVA 2



Bitumen C + 6% EBA

Figure 1 Influence of base bitumen and polymer type and content on microstructure of polymer modified bitumens.

increasing polymer content. For the modified binders with 3% polymer, no phase separation (I_s close to 0) is observed. The storage stability is also dependent on the base bitumen and the type of polymer. Among all the modified binders prepared, those containing EBA display the lowest storage stability. For EVA modified binders, better storage stability is observed for those containing the polymer with lower VA content and higher MI (EVA 2). On the other hand, for a given

polymer, the modified binders produced from bitumen C generally demonstrate higher storage stability than those produced from bitumens A and B. Also the use of harder bitumen seems less favourable with regard to storage stability as compared to softer bitumen (cf. A and B). The results are consistent with those obtained previously [3]. The base bitumens with higher aromatic content and/or lower asphaltene content may result in higher storage stability of polymer modified binders.

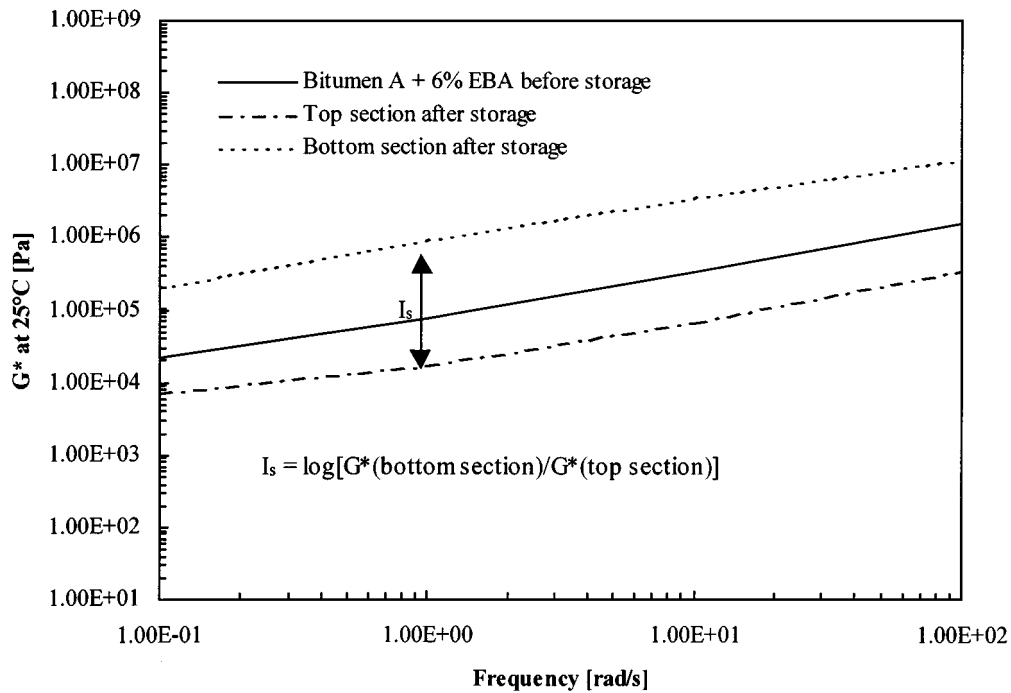


Figure 2 G^* as a function of frequency at 25 °C for 6% EBA modified bitumen A before and after storage at 180 °C for three days.

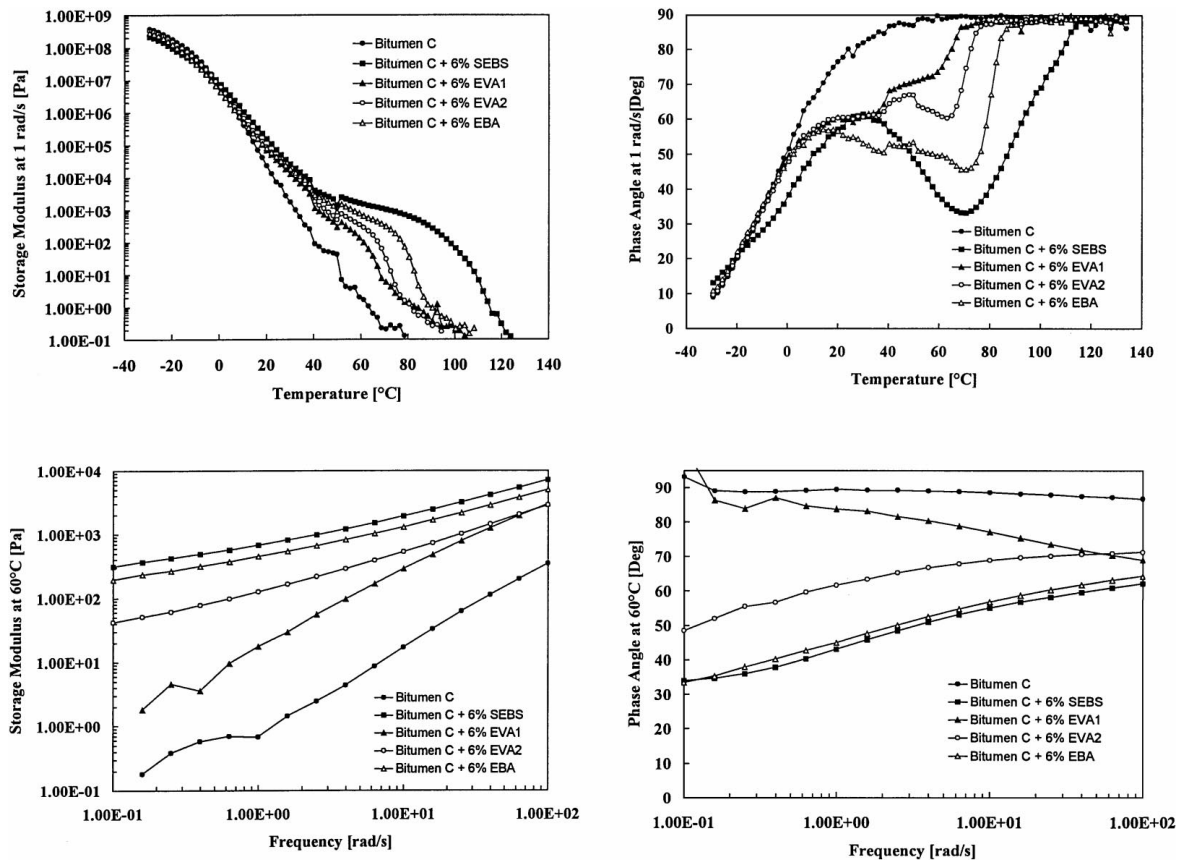


Figure 3 Storage modulus and phase angle as a function of temperature and frequency.

3.4. Rheological properties

In DMA, G^* is a measure of the overall resistance to deformation of a material, while G' and G'' provide information on the elastic and viscous responses of a material, respectively. The viscoelastic character of the material is characterized by δ . A purely viscous liquid and an ideal elastic solid demonstrate δ of 90° and 0°,

respectively. The rheological parameters of bitumens are functions of temperature and frequency, which may be modified significantly by the addition of polymers (Fig. 3). The increased elastic responses (increased G' and decreased δ) are mainly due to polymer networks (cross-links and entanglements) and/or polymer crystallinity. When sufficient polymer networks are formed

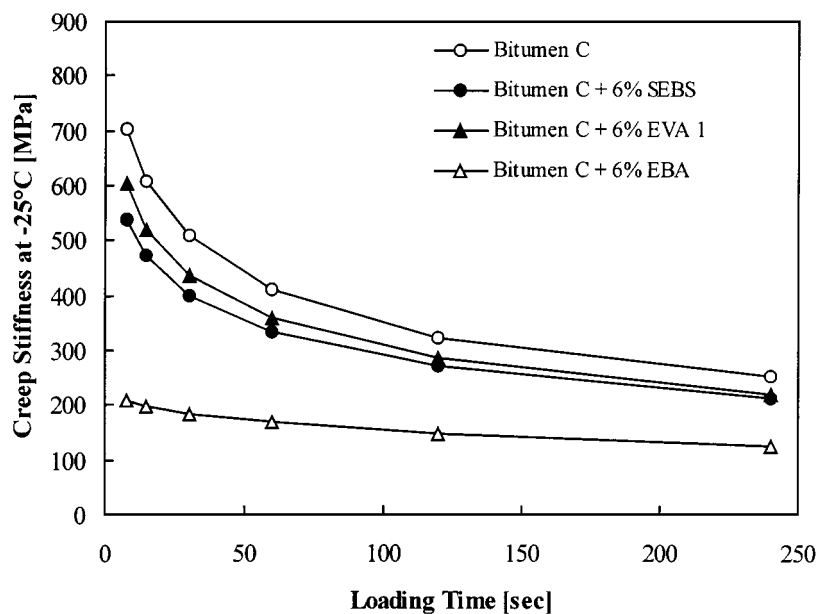
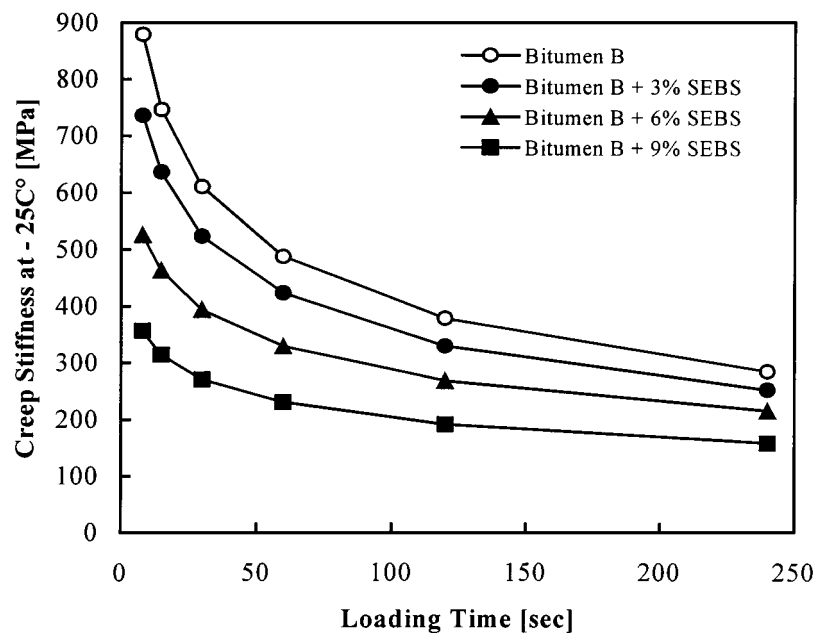


Figure 4 Creep stiffness at -25°C as a function of loading time.

in the modified binders, e.g. in a continuous polymer phase (cf. Fig. 1), four regions, glassy, transition, plateau, and terminal or flow, are observed in plots of G' against temperature, and correspondingly, a maximum and a minimum are observed in δ . Different degrees of prominence may be observed in the four regions. This is dependent on the chemical and physical nature of the binders. For EVA and EBA modified binders, the crystalline portions (packed polyethylene segments) of the polymers may melt and networks weaken at temperatures higher than about 60°C (EVA) or 80°C (EBA), leading to a pronounced decrease in G' and a sharp increase in δ . In the case of SEBS modified binders, the dramatic changes in G' (decrease) and δ (increase) are observed at temperatures higher than about 100°C , where the physical cross-links of polystyrene diminish rapidly.

A parameter previously proposed for quantitative comparison of the elastic response of the binders is $T_{75^{\circ}}$ [4]. This is the temperature above which δ is higher than 75° . It was observed that polymer modification increased $T_{75^{\circ}}$ of the binders; the improvement generally increased with polymer content and was also influenced by bitumen source/grade and polymer type [8]. The effectiveness regarding the elastic response of the polymers tested may be ranked as SEBS, EBA, EVA 2 and EVA 1, SEBS being the best. The temperature was observed to correlate with softening point (risk level 5%). The correlation coefficient is 0.88. However, at the softening point, all the base bitumens are purely viscous, as indicated by phase angles of 90° , while the modified binders still display considerable elasticity. It should be noted that softening point is generally valid for conventional bitumens, but

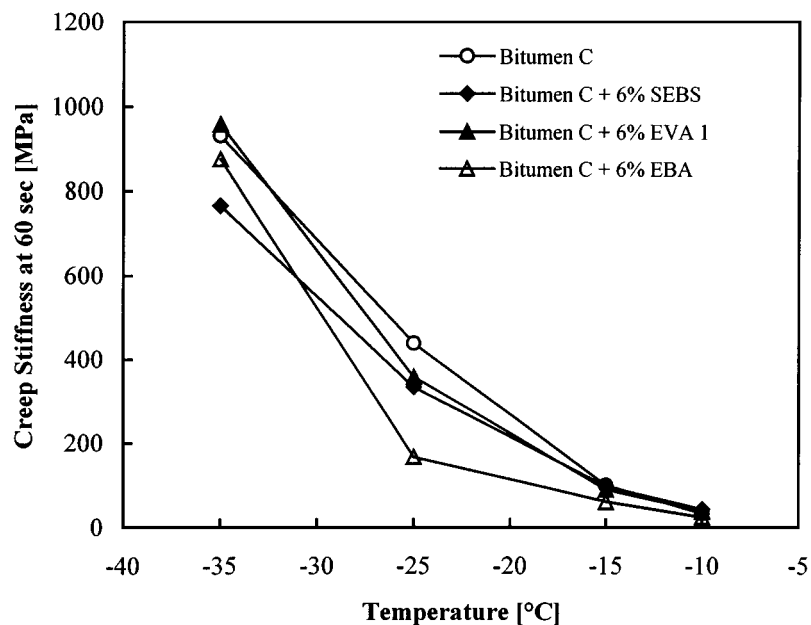
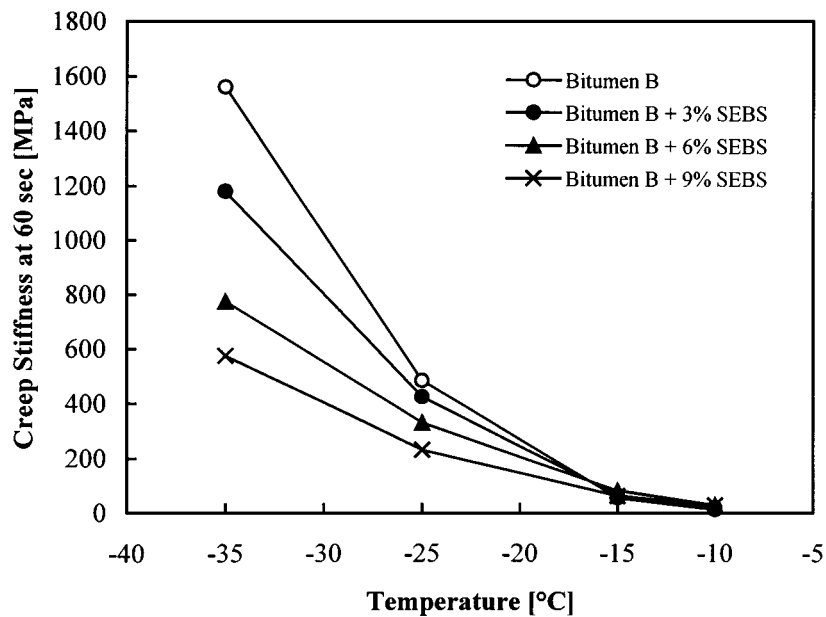


Figure 5 Creep stiffness at 60 s as a function of temperature.

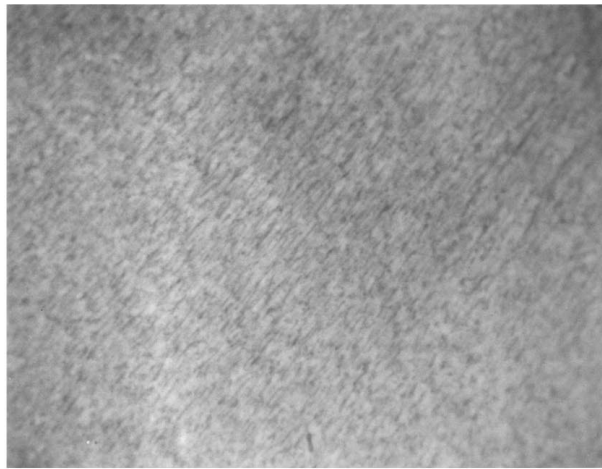
may lose its relevance in the case of polymer modified binders.

To study influence of polymer modification on the low-temperature creep responses of bitumens, the SHRP bending beam rheometer was employed at different loading times (8, 15, 30, 60, 120 and 240 s) and temperatures (-35 , -25 , -15 and -10 °C). Figs 4 and 5 indicate that the polymer modified binders generally display a lower creep stiffness than the corresponding base bitumen, especially at temperatures lower than -15 °C. The improvement increases with polymer content, but varies with the base bitumen and polymer type. It is also influenced by loading time and test temperature. For all the binders tested, the creep stiffness was observed to statistically (risk level 5%) correlate with complex modulus [8]. The reduced creep stiffness should be favourable for asphalt cracking resistance at low temperatures.

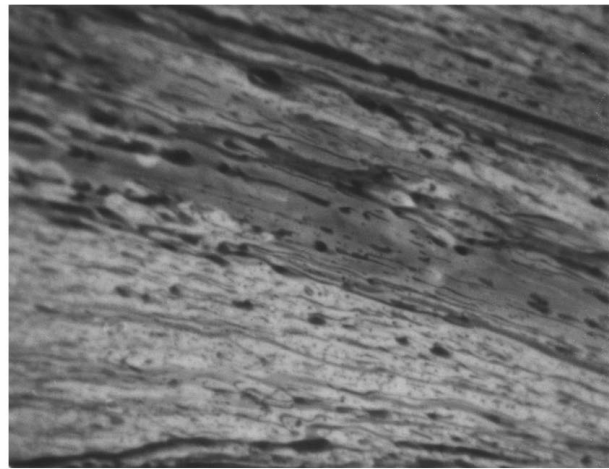
3.5. Ageing properties

Oxidative ageing causes hardening of bitumen and degradation of polymer, and consequently, changes in the rheological properties of polymer modified binders. In this investigation, ageing of a number of typical binders was conducted using the Rolling Thin Film Oven Test (RTFOT). The RTFOT glass containers were heated to 160 °C prior to loading the sample. The sample holders were horizontally kept in an oven at 160 °C for about 15 min and then aged at 163 °C for 75 min. As illustrated in Fig. 6, after the RTFOT, the modified binders still show two distinct phases, but the microstructure is significantly changed. The microstructural change is probably caused by an increase in asphaltenes and a decrease in aromatics, or by the mechanical work during the RTFOT.

Figs 7 and 8 depict the influence of the RTFOT on the rheological properties of the binders. It is evident



Bitumen B + 6% EBA before RTFOT



Bitumen B + 6% EBA after RTFOT

Figure 6 Influence of RTFOT ageing on the microstructure of polymer modified binders.

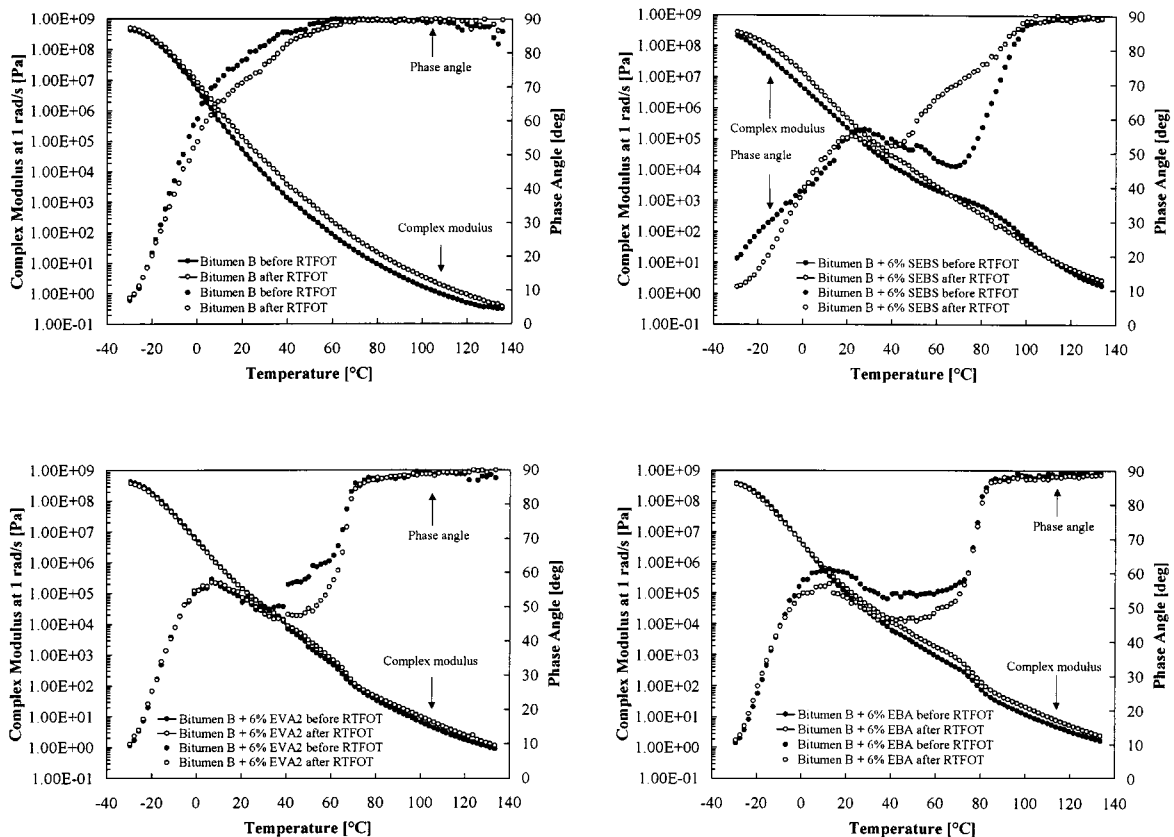


Figure 7 Complex modulus and phase angle at 1 rad/s as a function of temperature for base and polymer modified bitumen B before and after RTFOT.

that, for the base bitumen and the modified binders with thermoplastics (EVA and EBA), the RTFOT increases complex modulus and elastic response (decreased phase angle). These changes are mainly due to the oxidative hardening of the bitumen. However, for the aged SEBS modified binders, decreased complex modulus and increased phase angle are observed at certain temperatures and frequencies. A possible reason for that is the thermal degradation of the SEBS polymer. Figs 7 and 8 also indicate that evaluation of ageing effect depends on testing conditions. This may be attributed to the difference in temperature and frequency dependence of flow exhibited by the pure and polymer modified bitumens.

4. Conclusions

The morphology and storage stability of the modified binders depend greatly on polymer content and are also influenced by the characteristics of base bitumens and polymers. For all the modified binders, two distinct phases (polymer phase and bitumen phase) are observed. At a low polymer content (3% by weight), the modified binders show dispersed polymer particles in the continuous bitumen matrix. On mixing a high quantity ($\geq 6\%$ by weight) of polymer with bitumen, a continuous polymer phase is observed. Regardless of the nature of the two phases, the storage stability of the modified binders decreases with increasing polymer content. Among the modified binders

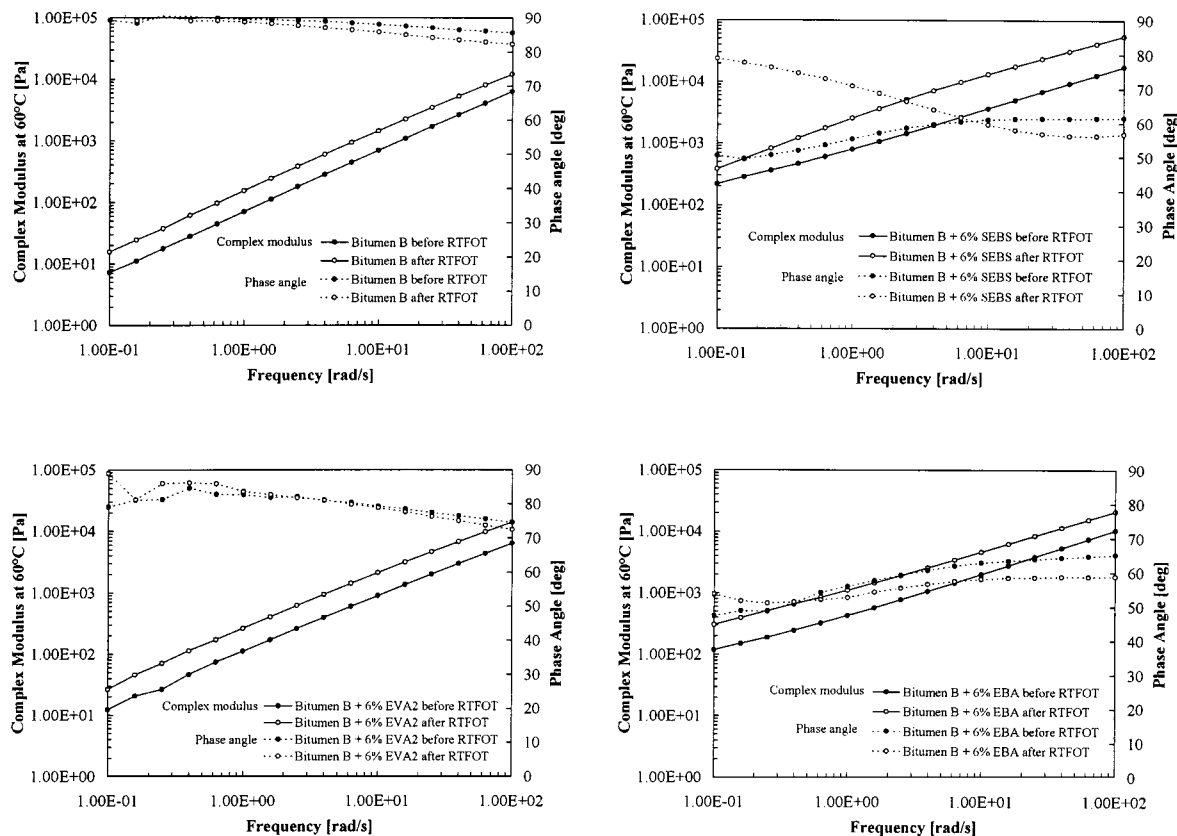


Figure 8 Complex modulus and phase angle at 60 °C as a function of frequency for base and polymer modified bitumen B before and after RTFOT.

prepared, the binders containing EBA display the lowest storage stability. For the EVA modified binders, better storage stability is observed for those containing the polymer with a lower VA content and a higher MI (EVA 2). Higher storage stability may be also achieved by using a base bitumen with a higher content of aromatics and/or a lower content of asphaltenes.

Polymer modification improves the rheological properties of bitumens, such as increased elastic responses (increased storage modulus and decreased phase angle) at high temperatures and reduced complex modulus and creep stiffness at low temperatures. The degree of modification generally increases with polymer content and is influenced by the characteristics of the base bitumen and the polymer. It also varies with test conditions such as temperature and frequency (or loading time).

The RTFOT ageing may cause oxidation of bitumen and degradation of polymer, and consequently, change the microstructure and rheological properties of the modified binders. These changes largely depend on the characteristics of the polymer used. For the modified binders with thermoplastics (EVA and EBA), the RTFOT increases complex modulus and elastic response (decreased phase angle). However, for the SEBS modified binders, the influence of RTFOT on complex modulus and phase angle is dependent on testing temperature and frequency.

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