

Evaluation of Rheological and Image Properties of Styrene-Butadiene-Styrene and Ethylene-Vinyl Acetate Polymer Modified Bitumens

Ali Topal,¹ Mehmet Yilmaz,² Baha Vural Kok,² Necati Kuloglu,² Burak Sengoz¹

¹Faculty of Engineering, Department of Civil Engineering, Dokuz Eylul University, 35160 Buca, Izmir, Turkey

²Faculty of Engineering, Department of Civil Engineering, Firat University, 23119 Elazig, Turkey

Received 6 March 2010; accepted 28 January 2011

DOI 10.1002/app.34282

Published online 7 July 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: This article presents a laboratory evaluation of conventional, fundamental, rheological, and morphological characteristics of styrene-butadiene-styrene (SBS) and ethylene vinyl acetate (EVA) polymer modified bitumens. Polymer modified bitumen (PMB) samples have been produced by mixing a 50/70 penetration grade unmodified (base) bitumen with SBS and EVA copolymer at different polymer contents. The fundamental viscoelastic properties of the PMBs were determined using dynamic (oscillatory) mechanical analysis and presented in the form of temperature and frequency-dependent rheological parameters. The morphology of the samples as well as the percent area distribution of polymers throughout the base bitumen have been characterized and determined by means of fluorescent light optic microscopy and Qwin Plus image

analysis software, respectively. The results indicated that polymer modification improved the conventional and rheological properties of the base bitumen. It was also concluded that the temperature and frequency had a significant effect on complex modulus of PMBs. The behavior of EVA and SBS PMBs had exhibited quite difference at 50°C. Moreover, it was found out that at low polymer contents, the samples revealed the existence of dispersed polymer particles in a continuous bitumen phase, whereas at high polymer contents a continuous polymer phase has been observed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3122–3132, 2011

Key words: asphalt; polymer modification; rheology; image analysis

INTRODUCTION

Bitumen has been widely used as an adhesive material in pavement mixtures, surface dressing, bridge deck waterproofing, overlays, and the protection of buildings, for example waterproofing roof and joint and crack seals. This is because asphalt is strong, readily adhesive, highly waterproof, and durable.¹ Bituminous binders used in pavement mixtures must perform adequately under a wide temperature regime. The binder must remain flexible enough to withstand sudden stresses without cracking at low temperatures during winter, but remain cohesive at high summer temperatures.²

The rheological behavior of bitumen is very complex phenomenon, varying from purely viscous to elastic, depending on loading time and temperature. Bitumen modification offers one solution to overcome the deficiencies of bitumen and thereby improves the performance of asphalt mixtures. The best known form of modification is by means

of polymer modification, traditionally used to improve the temperature susceptibility of bitumen by increasing binder stiffness at high service temperatures and reducing stiffness at low service temperatures.³

Currently, the most commonly used polymer for bitumen modification is the styrene-butadiene-styrene (SBS) followed by other polymers such as ethylene vinyl acetate EVA, styrene butadiene rubber (SBR) and polyethylene.⁴ SBS block copolymers are classified as elastomers that increase the elasticity of bitumen and they are probably the most appropriate polymers for bitumen modification. SBS copolymers derive their strength and elasticity from physical and crosslinking of the molecules into a three dimensional network. The polystyrene end blocks impart the strength to the polymer while the polybutadiene rubbery matrix blocks give the material its exceptional viscosity.⁵ When SBS is blended with bitumen, the elastomeric phase of the SBS copolymer absorbs the oil fractions from the bitumen and swells up to nine times as much as its initial volume. At suitable SBS concentration, a continuous polymer phase is formed throughout the polymer modified bitumen (PMB) and significantly modifies the base bitumen properties.⁶

Correspondence to: B. V. Kok (bahavural@firat.edu.tr).

TABLE I
Properties of the Base Bitumen

Test	Specification	Results	Specification limits
Penetration (25°C, 0.1 mm)	ASTM D5 EN 1426	63	50–70
Softening point (°C)	ASTM D36 EN 1427	49	46–54
Viscosity at 135°C (Pa s)	ASTM D4402	0.51	–
Thin film oven test (TFOT) (163°C, 5 h)	ASTM D1754 EN 12607–1		
Change of mass (%)		0.07	0.5 (max)
Retained penetration (%)	ASTM D5 EN 1426	51	50 (min)
Softening point after TFOT (°C)	ASTM D36 EN 1427	51	48 (min)
Ductility (25°C) (cm)	ASTM D113	100	–
Specific gravity (gr/cm ³)	ASTM D70	1.030	–
Flash point (°C)	ASTM D92 EN 22592	+260	230 (min)

EVA based polymers are classified as plastomer that modify bitumen by forming a tough, rigid, three-dimensional network to resist deformation. Their characteristics lie between those of low density polyethylene, semirigid, translucent product and those of a transparent and rubbery material similar to plasticized polyvinyl chloride (PVC) and certain types of rubbers.⁷ This type of polymers has revealed as good modifiers, which improve permanent deformation and thermal cracking.⁸

In spite of the significant research which has been carried out related to the SBS and EVA modified PMBs in road applications, more studies have to be undertaken on the compatibility and in the interaction between the SBS, EVA polymer and the base bitumen. This article aims to characterize the fundamental properties of the SBS and EVA based PMBs by using conventional test methods and dynamic (oscillatory) mechanical analysis as well as to evaluate the morphology by assessing the state of dispersion of elastomeric and plastomeric polymers and bitumen phases. The distribution of polymers in the base bitumen on the area basis has also been evaluated by Qwin-Plus image analysis software.

EXPERIMENTAL

Materials

The base bitumen with a 50/70 penetration grade was procured from Aliaga/Izmir Oil Terminal of the Turkish Petroleum Refinery. To characterize the properties of the base bitumen, conventional test methods such as; penetration test, softening point test, ductility test, etc. were performed. These tests were conducted in conformity with the relevant test methods that are presented in Table I.

The SBS polymer used was Kraton D-1101 supplied by the Shell Chemicals Company. Kraton D-1101 is a linear SBS polymer in powder form that consists of different combinations made from blocks polystyrene (31%) and polybutadiene of a very precise molecular weight.⁹ These blocks are either sequentially polymerized from styrene and butadiene and/or coupled to produce a mixture of these chained blocks.

The EVA polymer used was Evatane® 2805 supplied in pellet form by the Arkema Company, Turkey. Evatane® 2805, which contains vinyl acetate content of 27–29% is a highly flexible plastomer designed for bitumen modification and especially for road paving.¹⁰ The properties of the Kraton D-1101 and Evatane® 2805 polymers are presented in Table II.

Preparation of SBS and EVA modified bitumens

The SBS and EVA modified bitumen samples were prepared by means of a high and a low shear laboratory type mixer rotating at 1100 and 125 rpm, respectively. In preparation, the base bitumen was heated to fluid condition (180–185°C), and has been poured into a 2000 mL spherical flask. The SBS and EVA polymers were then added slowly to the base bitumen.

The concentrations of SBS Kraton D-1101 in the base bitumen were chosen as 2–6% by weight. The utilization of this content is based on past research made by Isacson and Lu.¹¹ They concluded that, a significant improvement in the properties of base bitumen was observed when the SBS content was increased from 2 to 6% by weight. On the other hand, the Evatane® 2805 concentrations were chosen as 3–7% according to the manufacturers.

The temperature was kept constant at 185°C, and the mixing process continued for 2 h. The uniformity

TABLE II
The Properties of Kraton D-1101 and Evatane® 2805 Polymer

Composition	Specification	Kraton D-1101	Evatane® 2805
Molecular structure	–	Linear	Linear
Physical properties			
Specific gravity (gr/cm ³)	ASTM D792	0.94	0.92
Tensile strength at break (Mpa)	ASTM D412	31.8	33.0
Shore hardness (A)	ASTM D2240	71	82
Physical form	–	Powder, pellet	Powder, pellet
Melt flow rate	ASTM D1238	<1	5–8
Processing temperature (°C)	–	150–170	65–80
Elongation at break (%)	ASTM D 412	875	700–1000

of dispersion of SBS and EVA in the base bitumen was confirmed by passing the mixture through an ASTM 100 sieve. After completion, the samples were removed from the flask and divided into small containers, covered with aluminum foil and stored for testing.

Test method

Following the determination of the properties of the materials used in this study and preparation of the PMB samples, conventional test methods, differential scanning calorimetry test, dynamic mechanical analysis, fluorescence microscopy, and Qwin Plus image analysis were performed on each of the PMB samples.

Conventional tests

The base, SBS and EVA PMBs were subjected to the following conventional bitumen tests; penetration, softening point, thin film oven test (TFOT), penetration, and softening point after TFOT and storage stability test (EN 13399). Six replicates of each PMB sample containing different polymer contents were prepared for bitumen testing. The storage stability value was determined by the difference of softening point temperatures of PMB samples taken from the top and bottom of cylindrical mold (32 mm diameter and 160 mm height) after they were stored vertically at 163°C in an oven for 72 h. In addition, the temperature susceptibility of the modified bitumen samples was calculated in terms of penetration index (PI) using the results obtained from penetration and softening point tests. Temperature susceptibility is defined as the change in the consistency parameter as a function of temperature. A classical approach related to PI was given in the Shell Bitumen Handbook¹ as shown in the following equation:

$$PI = \frac{1952 - 500 \cdot \log(\text{Pen}_{25}) - 20 \cdot \text{SP}}{50 \cdot \log(\text{Pen}_{25}) - \text{SP} - 120} \quad (1)$$

where, Pen₂₅ is the penetration at 25°C and SP is the softening point temperature of PMB.

Dynamic mechanical analysis

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 linear viscoelastic (LVE) response. These oscillatory tests are undertaken using dynamic shear rheometers (DSRs).

The DSR test was performed on SBS and EVA PMBs by using a Bohlin DSR II rheometer. The test was performed under controlled-stress loading conditions using frequency sweeps between 0.01 and 10 Hz at temperature between 10 and 80°C. The tests were carried out with 8 mm diameter, 2 mm gap parallel plate testing geometry between 10 and 30°C, and with 25 mm diameter, 1 mm gap geometry between 30 and 80°C. Dynamic shear rheometer test configuration is given in Figure 1.³ The stress amplitude for all the tests was confined within the linear viscoelastic response of the bitumen.

The principal viscoelastic parameters obtained from the DSR are magnitude of the complex shear modulus (G^*) and 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.¹² The complex modulus consists of the storage modulus, G' and the loss modulus, G'' .

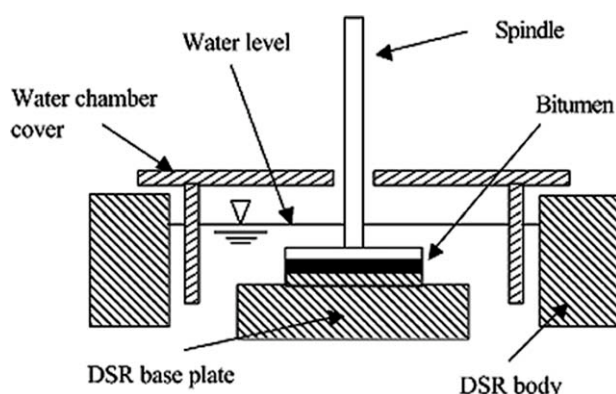


Figure 1 Dynamic shear rheometer testing configuration.³

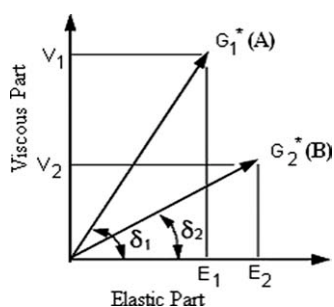


Figure 2 Relationship between complex modulus and phase angle.¹²

The storage modulus, which is the elastic (recoverable) component, represents the amount of energy stored in the sample during each loading cycle. The loss modulus, which is the viscous (nonrecoverable) component, represents the amount of energy lost during each loading cycle. When the phase angle is zero degrees, elastic behavior, the complex modulus consists solely of the storage modulus. Likewise, when the phase angle is 90°, viscous behavior, the complex modulus consists solely of the loss modulus.^{12,13} A graphical description of the phase angle with respect to the complex modulus is shown in Figure 2.

Fluorescence microscopy and Q-win image analysis

In describing the microstructure interacting between bitumen and polymer, the term “morphology” is often used.¹⁴ A fluorescence microscopy has been used to investigate the morphology of the SBS and EVA PMBs by determining the state of dispersion of the polymer within the base bitumen as well as to characterize the nature of the continuous and discontinuous phase.

By far, fluorescent microscopy is the most valuable method for studying the phase morphology of polymer modified bitumen, as it allows the observation of the homogeneity and the structure in the raw state.¹⁵

Fluorescent microscopy is based on the principle that polymers swell due to the absorption of some of the constituents of the base bitumen and due to the fluorescence effect in ultraviolet light.³ The bitumen rich phase appears dark or black, whereas the polymer rich phase appears light.

Samples of each PMB were prepared (for imaging purposes) by using a standard sample preparation method. The method involves a heating and homogenizing procedure, a sample cooling regime as well as a surface preparation procedure over thin films of the samples.¹⁶

PMB samples were examined at room temperature under a Leica DM EP microscope with fluorescent light (generated from a high pressure Xenon lamp)

at magnification levels of 10×. Images were then taken by a 7.2 Mp Leica DFC 320 color camera (fitted in line with the optic axis of the microscope by means of an attachment to the trinocular observation head). The camera digitizes the image and stores the data as an image file in the permanent memory of workstation.

Digital image processing and analysis techniques were used in this study to quantify the polymer distribution area throughout the PMB samples. The polymer distribution area is expressed as the relative proportion of polymer phase to composite image based on each polymer content.

Along with the system mentioned in previous part, Qwin Plus image analysis program has been used to extract significant information from the captured images. The Qwin Plus image analyzer is versatile software capable of providing full measurements of polymer distribution. Although digital image processing has increasingly been used in characterizing a number of civil engineering materials, its use in quantifying the distribution of polymers in the base bitumen on the area basis has not been evaluated.

After the images had been captured by means of color camera, they were transformed to gray scale. Using the algorithms within the Qwin Plus program, operations including shading corrections, contrast/brightness optimizing, white tophat (function to enhance the white detail and to remove the unwanted art effects), and sharpen, enhancement were then applied to transform the original image to binary image which has a bit depth of only two, i.e., it consists of areas/features of either black (0) or white phases (1). The main purpose of this step is to isolate polymers from composite images, therefore to prepare the images that are ready for quantified measurements.

RESULTS AND DISCUSSION

Conventional binder test results

The effect of SBS and EVA polymer modification on the properties of the base bitumen can be seen in Table III as a decrease in penetration values and an increase in softening points with the increasing polymer contents. This trend is relatively uniform on the EVA modified samples, however there is a significant large decrease in the penetration values and a considerable increase in the softening point temperatures of SBS modified samples at polymer content of 3 and 5%, respectively. The increase in softening point (which is an indicator of the stiffening effect of PMBs) is favorable since bitumen with higher softening point is less susceptible to permanent deformation (rutting).¹⁷

TABLE III
Conventional Properties of Polymer Modified Bitumen

Property	Type	Content (%)						
		0	2	3	4	5	6	7
Penetration (1/10 mm)	SBS Kraton D-1101	63	61	51	49	48	48	–
Softening point (°C)		49	50	54	57	67	69	–
Penetration index (PI)		–0.92	–0.73	–0.16	0.35	2.18	2.46	–
Change of mass (%)		0.07	0.06	0.06	0.07	0.07	0.07	–
Retained penetration after TFOT (%)		51	41	31	24	21	21	–
Softening point difference after TFOT (°C)		2	4	4	2	3	2	–
Storage Stability (°C)	Evatane® 2805	–	3	3	2	3	2	–
Penetration (1/10 mm)		63	–	53	52	49	48	47
Softening point (°C)		49	–	54	57	59	61	62
Penetration index (PI)		–0.92	–	–0.13	0.49	0.79	1.14	1.24
Change of mass (%)		0.07	–	0.04	0.06	0.05	0.07	0.06
Retained penetration after TFOT (%)		51	–	30	31	32	33	34
Softening point difference after TFOT (°C)		2	–	6	6	5	4	5
Storage Stability (°C)		–	–	1	1	0	1	2

Polymer modification reduced temperature susceptibility (as determined by the PI) of the bitumen. Lower values of PI indicate higher temperature susceptibility. Asphalt mixtures containing bitumen with higher PI are more resistant to low temperature cracking as well as permanent deformation.¹⁸ As seen in Table III, both SBS and EVA modified PMB samples exhibit less temperature susceptibility compared to base bitumen with increasing of polymer content. SBS modified samples yield higher PI values compared to EVA modified samples especially at high polymer contents (5–6%).

The age hardening of the bitumen during bulk storage is evaluated by the mass loss, retained penetration, and softening point temperature difference in the TFOT. The mass losses corresponding to each SBS and EVA PMB samples are almost identical as seen in Table III. However, the retained penetration values and difference in the softening point temperature are higher for the EVA modified samples. This result indicates that, the EVA PMB samples are affected by aging in the TFOT which simulates the aging (hardening) of bitumen during the bulk storage period.

Softening point test results on SBS and EVA samples taken from the top and bottom of the tube in the storage stability test indicate that, the SBS tends to separate from bitumen at high temperatures and

thus SBS PMB is not storage stable compared to EVA samples.

The rotational viscosity values for both PMB samples together with the modification indices are presented in Table IV.

The results show a consistent increase in viscosity by polymer modification. As with the penetration and softening point results, the viscosities also give an indication of the stiffening effect of SBS and EVA modification. The viscosity values and modification indices related to EVA modified samples are higher than SBS modified samples as seen in Table IV. This may be due to the melting of EVA polymer at lower temperatures compared to SBS polymer, consequently it exists in liquid form at temperatures of 135°C and higher. The increment in viscosity is not favorable since it requires higher mixing, compaction and laying temperatures and thus more energy consumption. The results indicate that mixtures prepared with EVA PMB (due to high viscosity values) require more mixing and compaction temperatures compared to mixtures prepared with SBS PMB.

Dynamic mechanical analysis test results

The variation of complex modulus of the base, 6% SBS and 7% EVA polymer modified bitumens with frequency and temperature are presented in

TABLE IV
Rotational Viscosities Related to SBS and EVA Modification

Property	Type	Content (%)						
		0	2	3	4	5	6	7
Brookfield viscosity at 135°C (Pa s)	SBS Kraton D 1101	0.51	0.55	0.62	0.76	1.20	1.50	–
Modification index (η_{PMB}/η_{base})		1	1.08	1.22	1.49	2.35	2.94	–
Brookfield viscosity at 135°C (Pa s)	Evatane 2805	0.51	–	0.98	1.24	2.16	2.98	3.41
Modification index (η_{PMB}/η_{base})		1	–	1.92	2.43	4.24	5.84	6.69

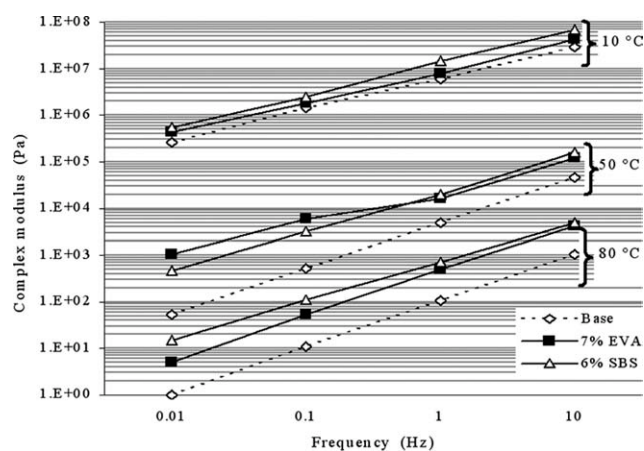


Figure 3 Complex modulus frequency relationship of base, SBS and EVA PMB.

Figure 3. Figure 4 also depicts the variation on phase angles of base and modified bitumens versus frequency at 50°C. It is seen that the phase angles decrease with the increase in frequency. An increment in the complex modulus with the decrease of phase angles indicates higher elastic part, thus an improved elastic behavior.

As depicted in Figure 3, which are drawn on log-log scale, for all samples as the frequency increases, the complex modulus increases as well. This is due to the rheologic behavior of the bitumens since bitumens under shorter loading times exhibit elastic behavior.

For the same frequency level, the increase in temperature decreases the complex modulus as presented in Figure 3. This indicates that, the temperature has a significant effect on the level of complex modulus. This effect is more obvious at low frequency level (0.01 Hz).

Also, the complex moduli of the PMB samples are greater than the complex modulus of base bitumen as seen in Figure 3. Among the PMB samples, the complex modulus of 6% SBS sample is greater than the complex modulus 7% EVA sample at all fre-

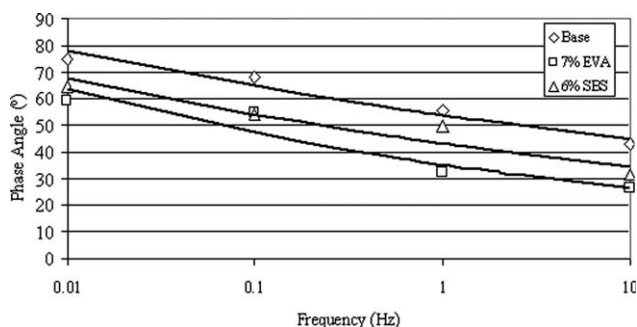


Figure 4 Phase angle frequency relationship of base, SBS and EVA PMB at 50°C.

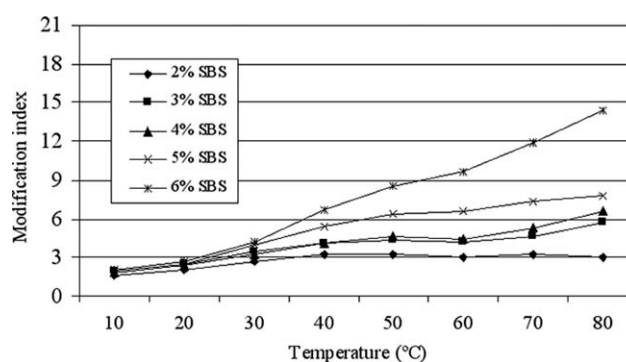


Figure 5 Modification index temperature relationship of SBS modified bitumen at 0.01 Hz.

quencies at 10 and 80°C. However at 50°C, the complex modulus of 7% EVA polymer modified bitumen sample is greater than the complex modulus of 6% SBS polymer modified bitumen sample at a frequency level lower than 1 Hz. This indicates that EVA polymer has a dominant polymer network within the modified bitumen at 50°C and at a frequency level lower than 1 Hz.

Along with the complex modulus, the effect of polymer addition was also evaluated by the modification index determined by the ratio of the complex modulus of PMB to the complex modulus of base bitumen. The effect of SBS content and temperature on modification index at low (0.01 Hz) and high (1 Hz) frequency is presented in Figures 5 and 6, respectively.

The modification indices increase regularly with the increase in temperatures at low and high frequency as seen in Figures 5 and 6. The complex modulus exhibits no significant variation at low temperatures (up to 30°C), however on reaching the high temperature region, significant difference in the increment of complex modulus is observed.

The PMB sample containing 6% SBS polymer exhibits a superior performance than other SBS involving PMB samples at 80°C as depicted in

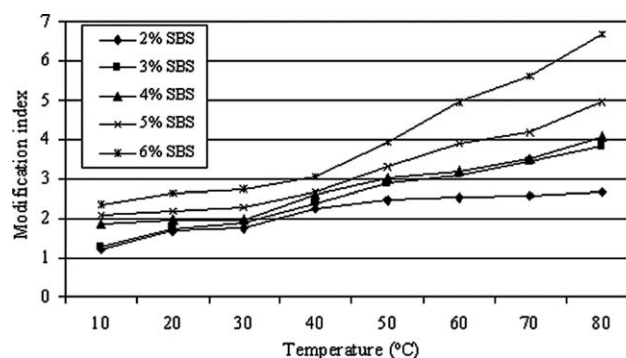


Figure 6 Modification index temperature relationship of SBS modified bitumen at 1 Hz.

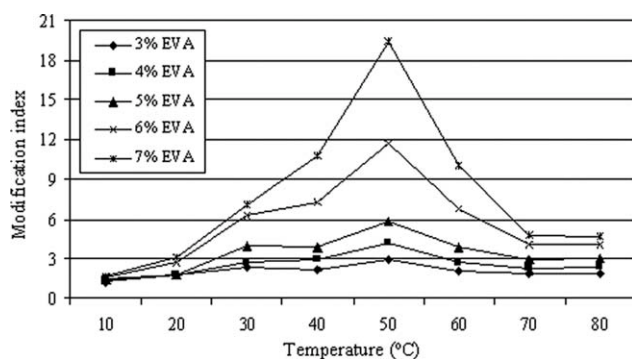


Figure 7 Modification index temperature relationship for base and EVA PMB at 0.01 Hz.

Figures 5 and 6. Utilization of 5 and 6% SBS, increases the complex modulus as ~ 8 and 15 times than those of the base bitumen at 80°C and at 0.01 Hz. However, the improvement effect of SBS content at high frequency at 80°C (Fig. 6) is not as high as it is at low frequency. So, it can be concluded that the frequency has a slight effect on the complex modulus at high temperatures and high frequency compared to complex modulus values at high temperature and low frequency.

The effect of EVA content and temperature on modification index at low (0.01 Hz) and high (1 Hz) frequency is presented in Figures 7 and 8, respectively.

As seen in Figure 7 for all contents of EVA PMB samples, the modification index increases with increasing temperature, the index reaches a peak at 50°C then decreases gradually. The complex modulus tends to be similar at low temperatures and there is not a significant difference in the increment of complex modulus on reaching high temperatures (80°C).

Among the modification index values at 50°C, as EVA content increases, the modification index increases as well. This indicates that PMB containing high proportion of EVA (7%) exhibits decreased thermal susceptibility compared to base bitumen at low frequency and especially at 50°C. Besides, the mixtures prepared by EVA modified binders with a high percentage can resist rutting at low traffic speeds and at high temperatures.

As seen in Figure 8, the modification index increases regularly between 10 and 80°C. Besides, the improvement effect of EVA at high frequency is not as high as it is at low frequency when considering the intermediate temperatures such as 50°C.

The increase in complex modulus at low and high frequency exhibits similar characteristics at 80°C as depicted in Figures 7 and 8. Utilization of 6 and 7% EVA, increases the complex modulus approximately four and five times than those of the base bitumen

at 80°C for both 0.01 and 1 Hz. Therefore, it can be concluded that the frequency does not effect on the complex modulus at high temperatures (80°C).

Among the modification index values related to 6% EVA and 6% SBS polymer modified bitumen samples at 50°C and at 0.01 Hz, it is seen that the improvement effect of EVA on complex modulus is much higher than the effect of SBS. However, when the comparison is made at 80°C the reverse situation is occurred, that is, the improvement effect of SBS on complex modulus is much higher than the effect of EVA.

Morphology and image analysis

Fluorescent microscopy images of PMBs captured by 7.2 Mp color camera are presented in Figures 9 and 10.

A distinction can be made between the PMBs whose continuous phase is bitumen matrix with dispersed polymer particles and samples whose continuous phase is a polymer matrix with dispersed bitumen globules. In the images, the swollen polymer phase appears (light) while the bitumen phase appears dark.

A clear distinction regarding the nature of the phases is observed between SBS- and EVA-based samples as seen in Figures 9 and 10. Among SBS- and EVA-based PMBs having the same polymer content (4%); EVA based samples reveal the finest dispersion of polymers whereas polymer distribution is more pronounced in SBS based samples. Nevertheless in all cases, the appearance of continuous polymer matrix begins at 5–6% polymer content.

As depicted in Figure 9, the images show a clear change in morphology of the SBS based PMBs as polymer content increases. At polymer content below 5%, the small polymer globules that are swollen by the base bitumen compatible fractions are spread homogeneously in a continuous bitumen phase.

At polymer content above 5%, a continuous polymer phase with dispersed bitumen phase is

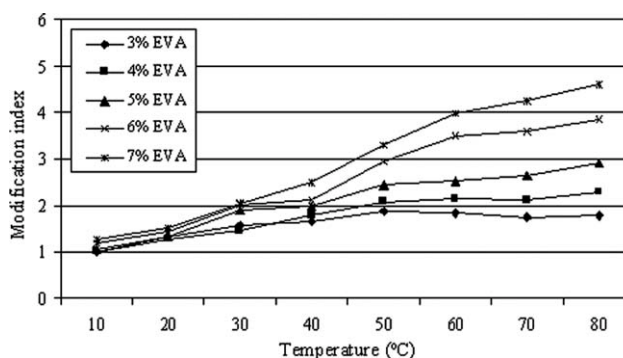


Figure 8 Modification index temperature relationship for base and EVA PMB at 1 Hz.

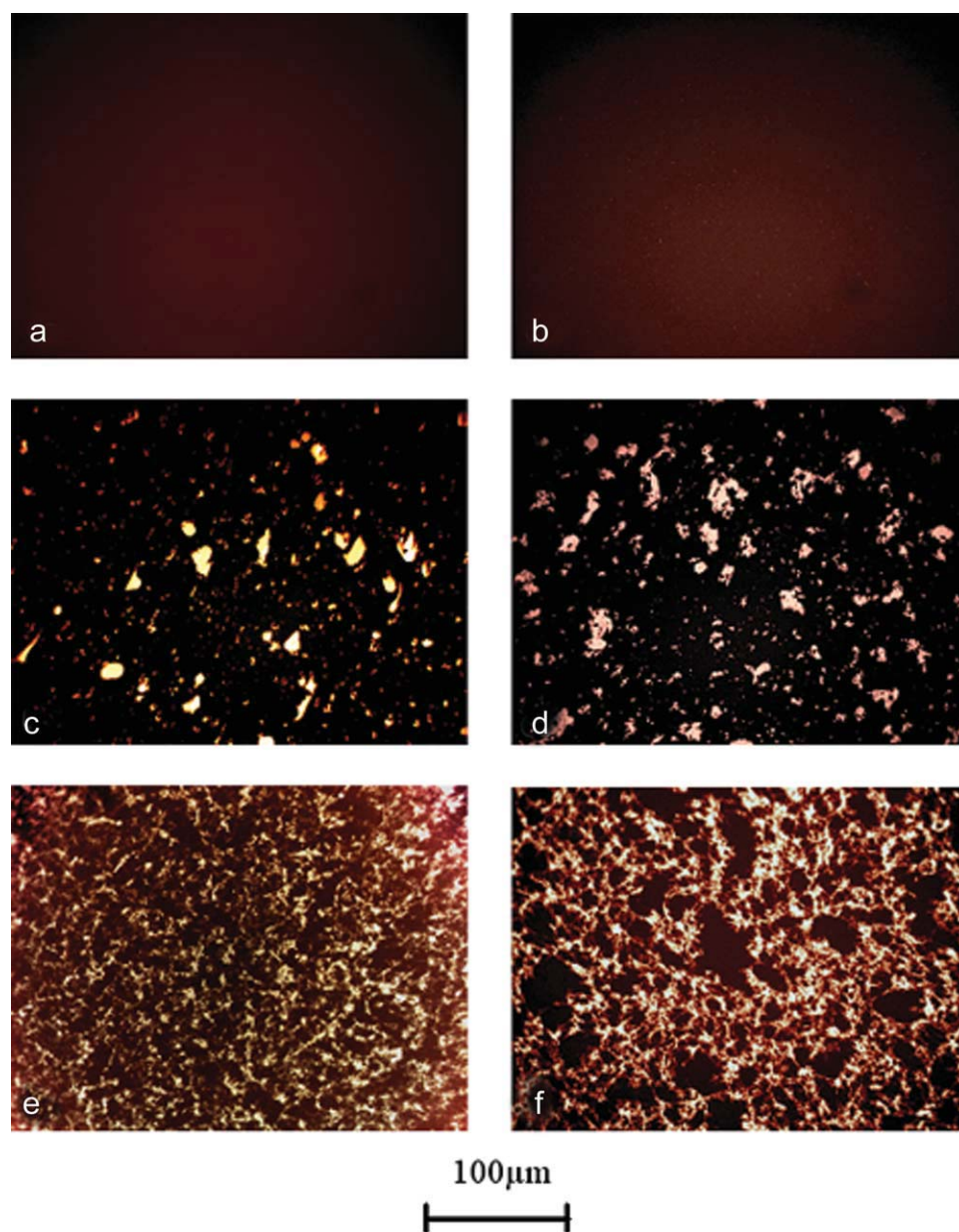


Figure 9 Fluorescent images of SBS PMB samples with 100X magnification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

observed. In this situation, the properties of the mixture are mainly determined by the polymer phase, therefore by the type of the polymer. The PMB samples with this phase morphology have the properties of high softening point and viscosity.

At about 5% polymer content, two twisted continuous phases are observed. The two interlocked phases form a network structure which could enhance the properties of the bitumen. Brule et al. found that the phase morphology of two interlocked continuous phases was an ideal microstructure for polymer modified road asphalt, and the optimum polymer content was determined based on the for-

mation of the critical network between asphalt and polymer.¹⁷

As indicated in Figure 10, no significant variation in morphology is observed with the EVA PMBs especially at polymer contents below 5%. The dispersion of the polymers begins at a polymer content of 5%. However, at the polymer content of 6–7%, a continuous polymer phase with a dispersed bitumen phase is observed.

The binary representation of the distribution of the polymers within the composite image is determined using the functions in Qwin Plus image analysis software. An example of the binary

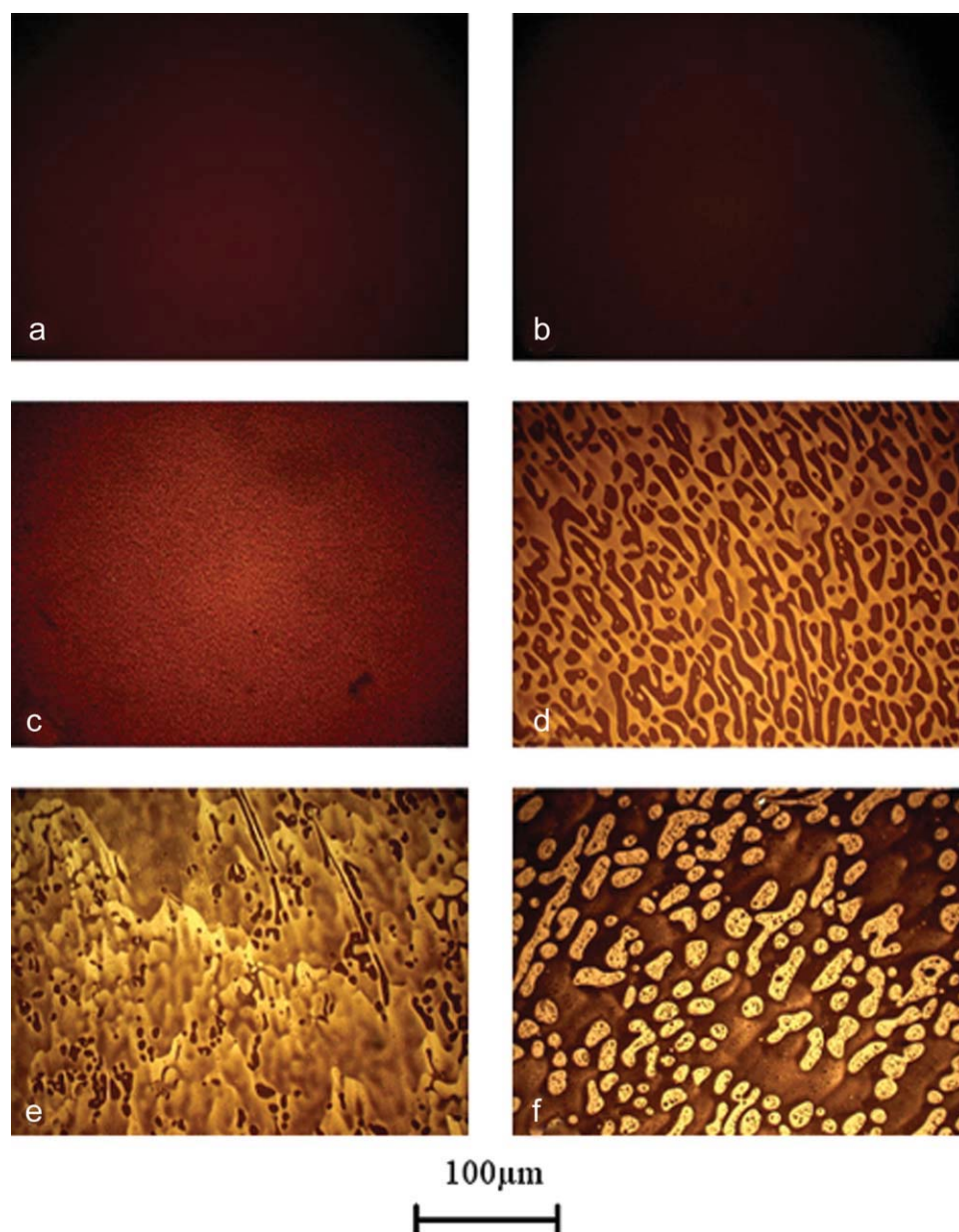


Figure 10 Fluorescent images of EVA PMB samples with 100 \times magnification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conversion of the resulting image is presented in Figure 11.

As shown in Figure 11, the white spots represent the region of interest—the polymer phase—and the black constitutes the bitumen phase. The determination of the region of interest (ROI) is significant as it is recognized by the software based on color depth (either black or white).

Having identified the region of interest, the mathematical parameter related to the ROI, based on predefined criteria (which is the polymer distribution area in this study), is calculated for each polymer content.

Figure 12 presents the relationship between the polymer content and polymer distribution area (%) of SBS and EVA polymers. It should be noted that the calculated polymer distribution areas are the average values taken from the measured ROI's per each polymer content.

Based on the evaluation shown in Figure 12, it can be concluded that a relationship exists between the polymer content and polymer distribution area related to SBS Kraton® D1101 and Evatane® 2805. It should be noted that, the relationships illustrated in Figure 12 are valid only for SBS content of 2–6% and EVA content of 2–7%. It should be also mentioned

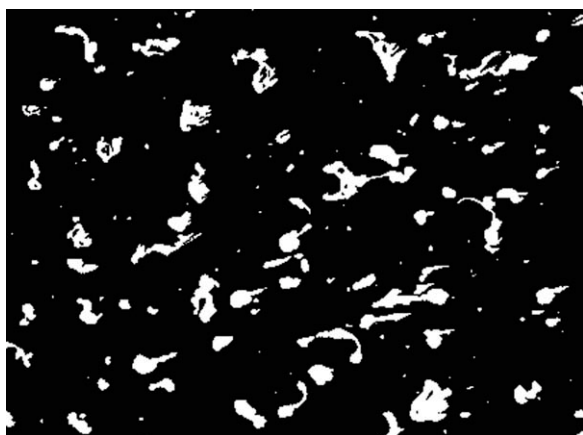


Figure 11 An example of an image transformed to binary image of black and white phases.

that the phase properties of the PMB samples is not totally dependent on the polymer dispersion area, which means the high values of polymer dispersion area does not always reflect the continuous polymer phase.

CONCLUSION AND RECOMMENDATIONS

The properties of road bitumens are improved by means of SBS and EVA polymer modification as identified by both conventional and dynamic mechanical analysis.

Conventional tests have demonstrated the increased stiffness (hardness) and improved temperature susceptibility of the SBS and EVA modified PMBs. In terms of this article, the conventional bitumen tests can quantify the differences in the properties of SBS and EVA PMBs produced with different contents for the same base bitumen.

Dynamic mechanical analysis indicated that the degree of modification generally increases with polymer content. It also varies with test conditions such as temperature and frequency. Based on all PMB samples, the complex modulus increases with increasing frequency and decreasing temperature.

The effect of polymer addition is also evaluated by the modification indices. In terms of modification index values, the frequency has a slight effect on the complex modulus at high temperatures (80°C) for SBS based PMB, however, same conclusion cannot be made for EVA PMB. A clear distinction between the two polymer types is observed at 50°C and at frequencies lower than 1 Hz. In the light of findings from modification index values, it is possible to consider that the utilization of EVA polymer under heavy traffic conditions (low frequency) and at intermediate temperature (50°C) whereas the utilization of SBS polymer at high temperatures is suitable.

Fluorescent microscopy can be used to group SBS and EVA type PMBs either by displaying a continuous polymer rich phase with dispersed bitumen phase, or by displaying a continuous bitumen rich phase with dispersed polymer phase or displaying two interlocked phases. For the investigated PMBs, phase inversion from a continuous bitumen phase to continuous polymer phase occurs when polymer content is around 5%. This content can be accepted as intertwined phase which is an ideal microstructure for polymer modified road asphalt. A clear distinction between the images indicates that at a given polymer content of 4%, the EVA based PMB sample exhibits the finest polymer dispersion whereas the dispersion of polymers is more pronounced with the SBS based samples.

The conclusion of this study covers the utilization of one type of SBS and EVA polymer and

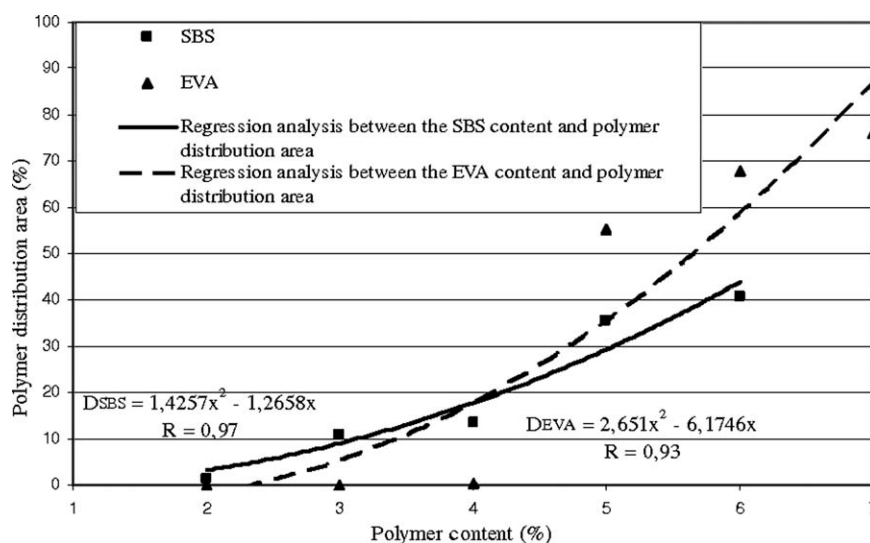


Figure 12 Area of distribution of SBS and EVA based polymers in base bitumen.

penetration grade bitumen. More research should be carried out by using different kinds of polymers such as linear, radial, diblock as well as the base bitumen obtained from different crudes.

References

1. Whiteoak, D.; Read, J. M. *The Shell Bitumen Handbook*; Thomas Telford Services: London, 2003.
2. Herrington, P. R.; Wu, Y.; Forbes, M. C. *Fuel* 1999, 78, 101.
3. Airey, G. D. *J Constr Build Mater* 2002, 16, 473.
4. Airey, G. D. *J Mater Sci* 2004, 99, 951.
5. Isacsson, U.; Lu, X. *Mater Struct* 1995, 28, 139.
6. Cavaliere, M. G.; Diani, E.; Dia, M. D. *Proceedings of 1st Euroasphalt and Eurobitume Congress*, Strasbourg, France, 1996.
7. Mahabir, P.; Mazumdar, M. *J Mater Civil Eng* 1999, 11, 13.
8. Gonzales, O.; Munoz, M. E.; Santamaria, A.; Garcia-Morales, M.; Navarro, F. J.; Partal, P. *Eur Polym Sci* 2004, 40, 2365.
9. Shell Technical Bulletin. *Preparing Blends of Kraton D Polymers and Bitumen*; Shell Technical Bull., London, England, 1995.
10. Booklet by Resinex Company. *Polymers as Additives*; Resinex Company, Izmir, Turkey, 2004.
11. Lu, X.; Isacsson, U. *J Constr Build Mater* 1997, 11, 23.
12. Zaniwski, J. P.; Pumphrey, M. E. *Evaluation of Performance Graded Asphalt Binder Equipment and Testing Protocol*, Asphalt Technology Program, 2004; p 107.
13. McGennis, R. B.; Shuler, S.; Bahia, H. U. *Background of Superpave Asphalt Binder Test Methods*, National Asphalt Training Center, Demonstration Project 101, 1994; p 104.
14. Chen, J.; Liao, M.; Shiah, M. *J Mater Civil Eng* 2002, 14, 224.
15. Brule, B.; Brion, Y.; Tanguy, A. *J Assoc. Asphalt Paving Technol* 1998, 57, 41.
16. Wegan, V. *Sampling for Microscopy-Test Procedure*; Danish Road Institute, Denmark, 1996.
17. Mohammed, L. N.; Negulescu, I. I.; Wu, Z. C.; Daranga, W. H.; Daly, C. *J Assoc Asphalt Paving Technol.*, 2003, 72, 551.
18. Lu, X.; Isacsson, U. *J Test Eval* 1997, 25, 383.