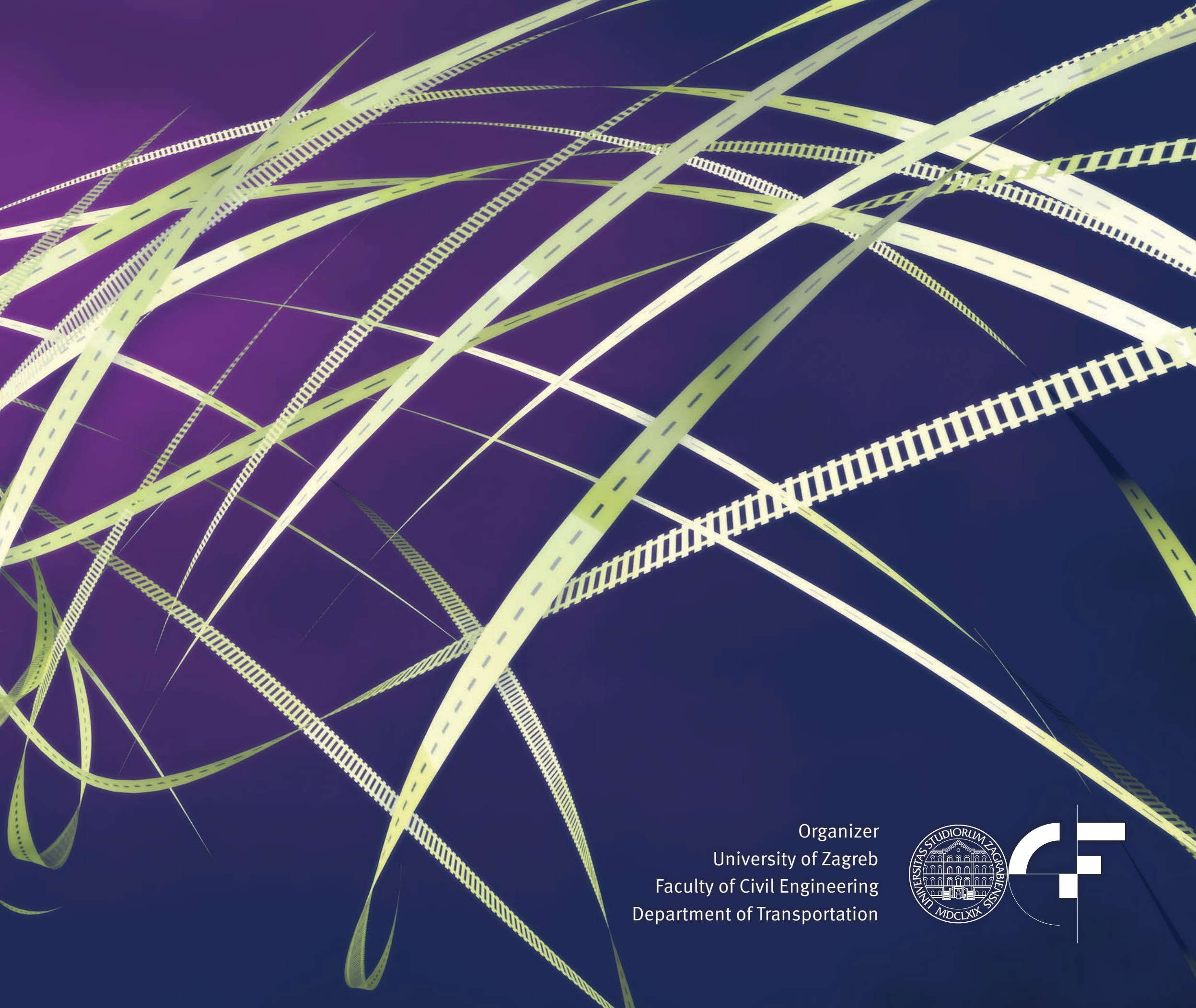
CETRA^{2014}

3rd International Conference on Road and Rail Infrastructure
28–30 April 2014, Split, Croatia

Road and Rail Infrastructure III

Stjepan Lakušić – **EDITOR**



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THE EFFECTS OF AGEING ON ROAD BITUMEN MODIFIED WITH THE ETHYLENE VINYL ACETATE POLYMER

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Abstract

The increase in axle loads, heavy traffic, severe climate conditions and construction failures has led to the enhancement of bitumen properties. There is a wide range of applications of polymer modified bitumens, PmBs, in road construction. Polymer modification significantly influences the rheological characteristics of the binder; therefore the use of fundamental rheological testing methods is required rather than the empirical methods.

This paper presents the polymer modification of road bitumen, BIT, with different contents of semi-crystalline thermoplastic copolymer ethylene- vinyl acetate, EVA, before and after thermo-oxidative ageing. The effects of EVA on the conventional, rheological and thermal properties of the modified bitumens were studied. The rheological characteristics of the EVA PmBs were analyzed by a dynamic shear rheometer, DSR. The primary viscoelastic functions were determined in dependence as a function of the frequency at temperatures in BIT use. The master curves were designed at a reference temperature of 30°C.

The results indicated that the thermoplastic copolymer EVA improves the viscoelastic properties of PmBs. EVA PmBs increase stiffness and elasticity at high service temperatures and low loading frequencies. The increased stiffness compared to the conventional bitumen enhances the performance characteristics of the modified bitumen and provides better protection against increased traffic loads and adverse climate conditions. The process of ageing increased the complex modulus and phase angle, and reduced temperature susceptibility. These changes were mainly due to the chemical processes, such as degradation reactions, oxidation as well as secondary processes of cross-linking which take place during the ageing of BIT and EVA PmBs. PmBs modified with EVA significantly reduce the permanent deformation under loads compared to the unmodified bitumen.

Keywords: polymer modified bitumen, rheological properties, thermal properties, thermo-oxidative ageing, permanent deformation

1 Introduction

Bitumen has been widely used for road paving applications [1]. Although it is added in a very low concentration (5 wt. %), bitumen controls the final properties and the performance of the asphalt mixture, since it is the only deformable component and forms a continuous matrix [2]. From a material engineer's point of view, bitumen can be classified as a thermoplastic material with thermally reversible properties [3]. Thus, at high temperatures, bitumen melts and solidifies so that asphalt mixtures can sustain the stress brought on by traffic. Two main limitations that were observed in pavements, yielding poor road performance, are directly associated to the bitumen matrix that surrounds the mineral aggregates at high and low temperatures. The first problem, permanent deformation (rutting), occurs at service temperatures higher than 40°C, leading to ruts in the direction of travel, and can be related to the

viscosity of the bitumen matrix. The second appears at lower temperatures (below 0°C) and can produce cracking of the road pavement, as a result of the brittle fracture of the bituminous component of the asphalt [2, 4]. Presently, the tightening of binder specifications, in order to get longer repairing periods and the reduction of the total cost of road maintenance, factors such as increased traffic, heavier loads, etc., have led to the development of new bituminous materials. The performance of road surface can be improved by modifying the bitumen with polymers, PmB [5-8]. One of the important modifiers of bitumen, which belong to the plastomers, is semi-crystalline copolymers ethylene vinyl acetate, EVA. This type of polymer is easily dispersed in and has good compatibility with generally available bitumens, as well as being thermally stable at normal mixing and handling temperatures [8, 9].
The aim of this paper is to study the effects of EVA, as a modifier of BIT in regard to the viscoelastic properties. Rheological characterization was carried out at different temperatures and frequencies before and after thermo-oxidative ageing. The frequency dependence of rheological parameters is shown by producing rheological master curves at reference temperatures of 30°C using the time-temperature superposition principle.

2 Experiment

2.1 Materials

The bitumen used in this paper was the 70/100 penetration grade base bitumen, INA Refinery Croatia, Rijeka. The polymer used as a modifier is a semi-crystalline copolymer, ethylene vinyl acetate, EVA, commercial grade Elvax 265, containing 28 wt. % of vinyl acetate with a melt index of 6, manufactured by DuPont, USA.

2.2 Sample preparation

EVA PmBs was prepared by melt blending with a high shear mixer, Silverson L4R. The EVA copolymer was mixed with the bitumen by using a preparation method developed in the laboratory to maximize the rheological properties and to minimize bitumen degradation. 500 g of bitumen was added to the container and heated to 160°C and continuously stirred for about 2h to obtain homogeneity and then was poured into 1 L aluminum cans. The cans of bitumen were then heated to 180-185°C and stirred for 10 min before adding a polymer. Upon reaching 180°C, a weighed amount of polymer was slowly added to the bitumen. The EVA contents used were 3, 4, 5 and 7 % by weight of blend. Mixing then continued at 180°C for 4h to produce homogeneous mixtures. After completion, the EVA PmBs were removed from the aluminum cans and divided into small containers covered with aluminum foil and stored for further testing at ambient temperature.

3 Measurements

3.1 Conventional tests

The traditional, conventional tests, such as penetration (HRN EN 1426), softening point (HRN EN 1427) and elastic recovery (HRN EN 13398), were first conducted for bitumen and EVA PmBs samples according to standards.

3.2 Rheological measurements

The rheological properties of neat bitumen and EVA modified bitumen were measured by a dynamic shear rheometer (DSR), MCR 301, Anton Paar. The tests were conducted over a range of temperatures and loading frequencies in order to provide a complete characterization of the viscoelastic properties of the binder [7, 8, 10, 11]. The DSR tests were performed under controlled strain loading conditions using frequency sweep tests. The frequency sweep was applied over the range from 0.1 to 100 rad/s at temperatures between -5°C and 60 °C. The strain was kept low enough so that all tests were performed within the linear viscoelastic range (LVE) [10, 12]. The tests at temperatures between -5°C and 30°C were carried out with a parallel plate testing geometry of 8 mm diameter and 2 mm gap, and from 30°C to 60°C were done with a parallel plate testing geometry of 25 mm diameter and 1 mm gap. To provide a more profound insight into rheological properties, the critical temperature without permanent deformation (rutting) was determined according to the SHRP [9, 12, 13]. The critical SHRP temperature, T_C/°C, is the temperature at which $G^*/\sin\delta \geq 1$ kPa before ageing and $G^*/\sin\delta \geq 2.2$ kPa after ageing at a frequency of 10 rad/s. The critical temperature was determined automatically by the DSR software.

3.3 Ageing procedure

Thermo-oxidative ageing of base bitumen and EVA PmBs was performed using the Rolling Thin Film Oven Test, RTFOT, according to ASTM D 2872. The bitumen and PmBs were exposed to elevated temperatures (163°C) to simulate the conditions during the production, mixing and laying of asphalt mixtures.

3.4 Differential scanning calorimetry, DSC

In an attempt to quantify the ageing mechanism associated with RTFOT ageing of the EVA PmBs, DSC thermal behavior was studied with a Mettler Toledo DSC 822e in a nitrogen atmosphere at a heating rate of 10°C/min. In the first heating and cooling scans, the samples were heated from 25°C to 150°C and held at that temperature for 10 min in order to eliminate any previous thermal history. Then, the samples were cooled with liquid nitrogen from 150°C to -120°C.

4 Results and discussion

The DSC studies have been carried out to understand the thermal behavior of the EVA PmBs before and after RTFOT ageing and the results are presented in Table 1. Changes of the super molecular structure with the addition of the EVA polymer were followed. As the content of the EVA polymer increased the increase of the crystal structure was obtained, visible through the increment of melting enthalpy. After ageing, temperatures associated with the fusion of the EVA PmBs shifted toward lower values. Also, the melting enthalpy was reduced, indicating the distortion of the crystal structure and degradation of EVA PmBs after thermo-oxidative ageing [8-10].

Table 1 DSC parameters of EVA PmBs before and after RTFOT

Samples	Conditions	Temperature Fusion Range [°C]	ΔH_m [J/g]	T_m [°C]
EVA-3	Unaged	40.4-82.8	1.78	64.9
	RTFOT	41.3-82.0	1.05	64.5
EVA-4	Unaged	39.7-82.1	2.68	65.9
	RTFOT	42.3-80.9	2.32	65.4
EVA-5	Unaged	34.9-89.5	5.21	66.8
	RTFOT	35.3-90.2	4.98	65.2
EVA-7	Unaged	30.5-87.6	7.24	67.6
	RTFOT	31.9-79.8	5.46	59.8

The frequency dependence of the rheological viscoelastic parameters, master curves of complex modulus, G*, complex viscosity, η*, and phase angle,δ, for BIT and EVA PmBs before and after thermo-oxidative ageing are presented in Figure 1 to 3. The figures indicate that improved viscoelastic properties of EVA PmB can be observed over a wide frequency range. The curves of G*/f and η*/f show different behavioral trends at high and low frequencies. All EVA PmBs show a similar shifting of the complex modulus master curves towards higher values as the polymer content increases, particularly at low frequencies. At low frequencies, the differences in G*/f and η*/f curves are more evident in all EVA PmBs, which means the EVA modification has a stronger influence at lower frequencies. The complex viscosity master curves continuously decrease with the increase in frequency. The curve of η*/f develops higher values at lower frequencies, but it remains similar to that of unmodified BIT from intermediate to high frequencies. EVA PmBs shows an apparent increase in complex viscosity with increasing polymer content (Figure 2). It is evident that the η* BIT value approaches a constant value of 10^4 Pas at low frequencies. The BIT shows viscous behavior, the phase angle approaches 90°C at low frequencies (Figure 3) [7-10]. The values of phase angle master curves decrease with EVA modification. We can see evidence of a breakdown of time-temperature equivalence from the master curves of phase angle for EVA PmBs, particularly at intermediate and low frequencies and with a high content of added EVA (Figure 3). The breakdown of the smoothness of the master curve can be attributed to the structural changes of EVA with temperature which is evident from the DSC measurements (Table 1) [10]. The crystalline portions (packed polyethylene segments) of the EVA polymers may melt and networks weaken at a temperature of about 50°C [6, 9, 10]. The discontinuous “waves” on the phase angle master curve are more evident for highly modified, semi-crystalline EVA PmBs. The PmB with a 3 wt. % EVA polymer shows good master curves with small “branching” at temperatures of 50°C and 60°C, which is related to the start of semi- crystalline EVA polymer melting, as confirmed by the DSC measurement (Table 1). Despite the complex picture of phase angle master curve of EVA PmBs, the modification contributes to the decrease of the phase angle and the presence of a slight phase angle plateau. Lower δ and plateau formation mean that PmBs have better elastic behavior [7, 8, 10]. The changes in rheological master curves of EVA PmBs are noted after ageing under RTFOT conditions. The values of G* and η* increase after ageing, which is more evident at very low frequencies (Figure 1 and 2). This is related to the higher stiffness, which is a consequence of the oxidation process of BIT which is evident from the microphotography [12]. As the content of EVA increases the influence of ageing is reduced. After ageing the values of δ decrease, indicating lower elasticity (Figure 3) [3, 7, 9]. Discontinuous “waves” and “branching” on the phase angle master curves are reduced after ageing. This is more evident as the content of the EVA polymer increases. This is related to the destruction of the crystal structure of EVA PmB, as can be seen from the results of DSC (Table 1) and from the microphotography [12]. The crystal structure is disrupted and leads to a phase angle towards higher values, indicating the viscous behavior after ageing (Figure 3).

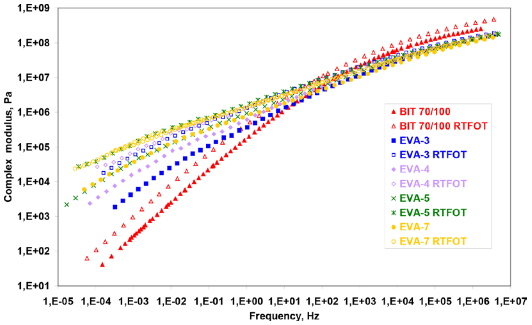

Figure 1 Complex modulus master curves for BIT and EVA PmBs

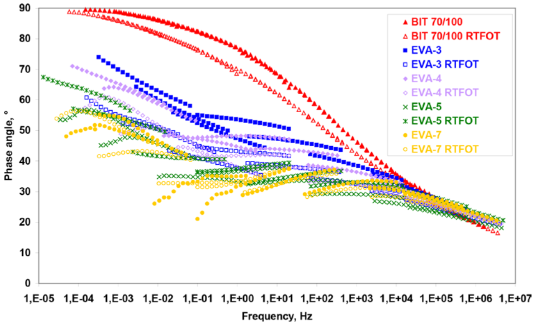

Figure 2 Complex viscosity master curves for BIT and EVA PmBs

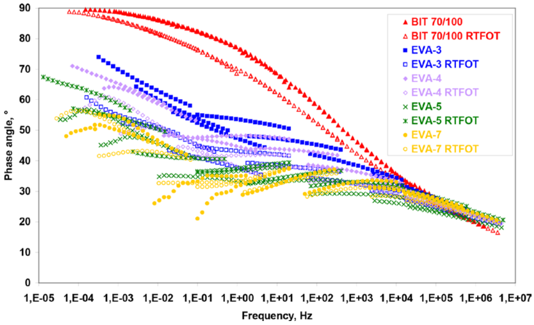

Figure 3 Phase angle master curves for BIT and EVA PmBs

Better rheological properties of EVA PmBs and better resistance to temperature can also be noted from the conventional tests results. The EVA addition in BIT increases the softening point value and the elastic behavior of the bitumen without a significant decrease of the penetration value. The best compromise between softening point, elastic recovery and penetration value, before and after RTFOT is reached by the EVA PmBs modified with 5 wt. % EVA polymer. These changes are in agreement with the changes in rheological properties of EVA PmBs.

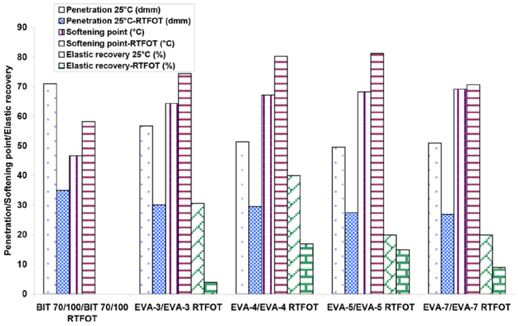

Figure 4 The relationships between the softening point, penetration and elastic recovery for BIT and EVA PmBs; before and after RTFOT

Critical SHRP temperature, T_C/°C, values for permanent deformation (rutting) are presented in Table 2. The critical temperatures of EVA PmBs are higher than that of the base bitumen. EVA PmBs with higher polymer contents have higher critical temperatures. This means better temperature resistance to permanent deformation, i.e. rutting [7, 8, 13].

Table 2 The critical SHRP temperature

SHRP	Samples				
	BIT 70/100	EVA-3	EVA-4	EVA-5	EVA-7
$T_{C,\text{before RTFOT}}$/°C where G*/sin≥1 kPa	65.1	86.0	93.5	91.1	85.9
$T_{C,\text{after RTFOT}}$/°C where G*/sin≥2.2 kPa	64.4	91.9	95.9	92.1	89.4
T_C/°C	64.0	82.0	88.0	88.0	82.0

5 Conclusions

The rheological properties of road bitumen are improved with EVA polymer modification as proven by the rheological master curves of G*, h*, d and by resistance to permanent deformation. EVA PmBs have better temperature resistance to permanent deformation under traffic frequencies than BIT which means better properties when used in road construction at high temperatures. The phase angle master curves have “branching” and “waves” due to the structural changes of EVA with temperature. After ageing the penetration values and the elasticity of EVA PmBs are decreased, while the softening point temperature is increased. This indicates that thermo-oxidative degradation is present. The rheological changes of EVA PmBs that occur after ageing are linked to a chemical change of the copolymer due to fusion of the crystallites. This leads to the reduction of discontinuous “branching” and “waves” on the phase angle master curve and an increase in viscous behavior after ageing.

References

[1] Carera, V., García-Morales, M., Gallegos, C. & Pérez-Lepe, A.: Bitumen chemical foaming for asphalt paving applications, Industrial & Engineering Chemistry Research, 49, pp. 8538-8543, 2010.

[2] Adedeji, A., Grunfelder, T., Bates, F. S., Macosko, C. W., Stroup-Gardiner, M. & Newcomb, D. E.: Asphalt modified by SBS triblock copolymer: structures and properties, Polymer Engineering and Science, 36, pp. 1707-1723, 1996.

[3] Carreau, P. J., Bousmina, M. & Bonniot F.: The viscoelastic properties of polymer modified asphalts, The Canadian Journal of Chemical Engineering, 78, pp. 495-502, 2000.

[4] Navarro, F. J., Partal, P., Martinez-Boza, F. J., Valencia, C. & Gallegos, C.: Rheological characteristics of groundtyre rubber-modified bitumens, Chemical Engineering Journal, 89, pp. 53-61, 2002.

[5] Kalantar, Z. N, Karim, M. R. & Mahrez, A.: A review of using waste and virgin polymer in pavement, Construction and Building Materials, 33, pp. 55-62, 2012.

[6] Polacco, G., Stastna, J., Vlachovicova, Z., Biondi, D. & Zanzotto, L.:Temporary Networks in Polymer-Modified Asphalts, Polymer Engineering and Science, 44, pp. 2185-2193, 2004.

[7] Bulatović, O. V., Rek, V., Marković, J. K.: Polymer Modified Bitumen, Materials Research Innovations, 16, pp. 1-6, 2012.

[8] Bulatović, V. O., Rek, V. & Marković, K. J.: Effect of polymer modifiers on the bitumen properties, Journal of Elastomers and Plastic, DOI: 10.1177/0095244312469964, 2013.

[9] McNally, T.: Polymer modified bitumen, Woodhead, UK, 2011.

[10] Airey, G. D.: Rheological characteristics of Polymer Modified and Aged Bitumens, Doctoral Thesis, Nottingham, 1997.

[11] Mezger, T. G.: The Rheology Handbook, Vincentz Network, Hannover, Germany, 2006.

[12] Bulatović, V. O., Rek, V. & Marković, K. J.: Rheological properties and stability of ethylene vinyl acetate polymer-modified bitumen, Polymer Engineering and Science, DOI: 10.1002/pen.23462, 2013.

[13] Nejad, F. M., Aghajani, P., Modarres, A. & Firoozifar, H.: Investigating the properties of crumb rubber modified using classic and SHRP testing method, Construction and Building Materials, 26, pp. 481-489, 2012.