CETRA^{2012}

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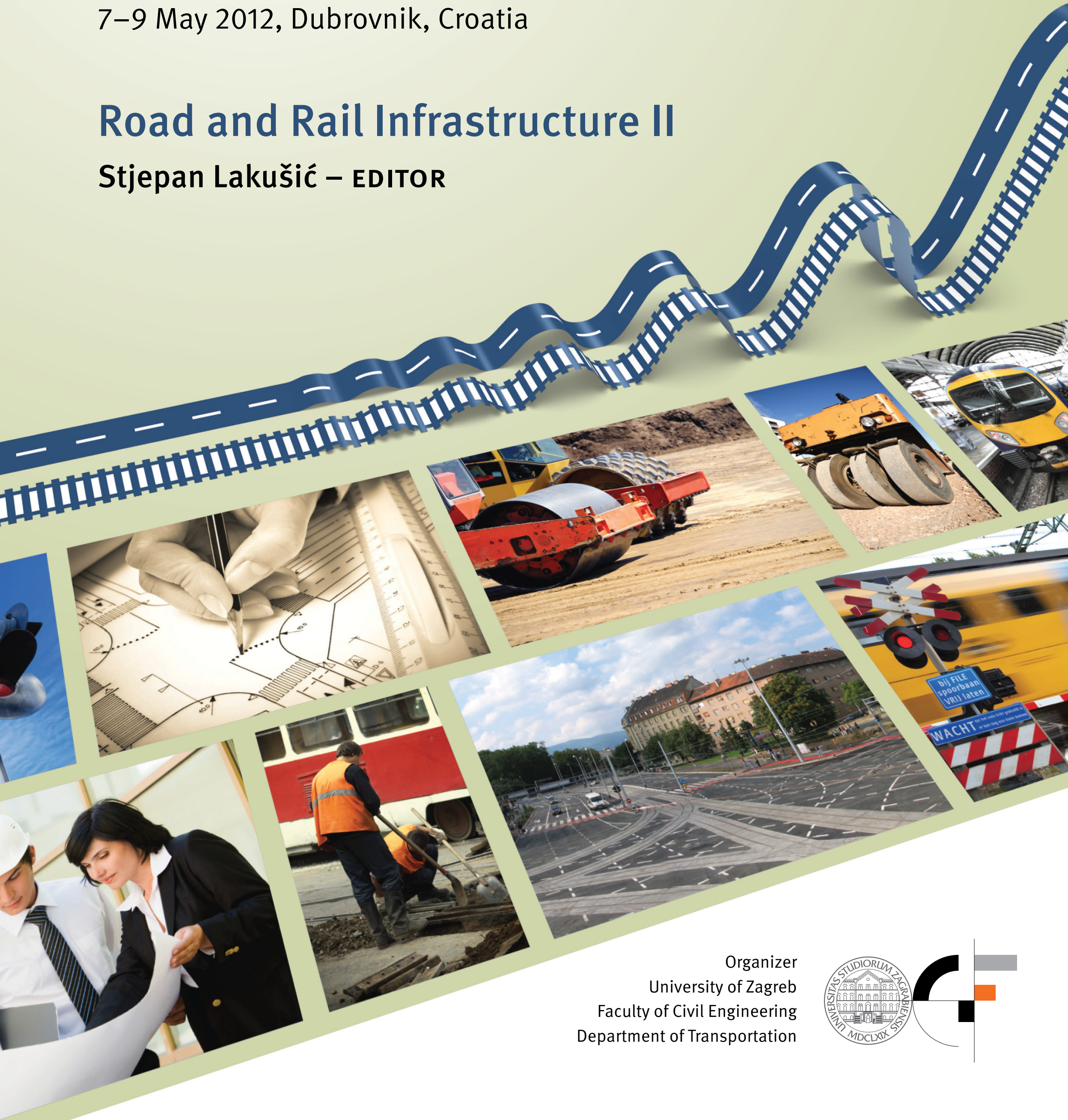
7–9 May 2012, Dubrovnik, Croatia

Road and Rail Infrastructure II

Stjepan Lakušić – EDITOR



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PERMANENT DEFORMATION OF POLYMER MODIFIED BITUMEN

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Abstract

Bitumen (BIT) has been used in most road applications for many decades as the binder for asphalt. The most common distresses directly associated with the binder phase in road are a permanent deformation known as rutting and thermal cracking. This has resulted in the need to improve the properties of existing bitumen. In order to produce BIT with improved properties, polymers are used. It is known that the modified binders vary significantly in their sensitivity to traffic speed, to traffic volume, and to stress or strain level that varies according to the pavement structure, which has indicated the importance of investigations into rheological properties. The investigation into rheological properties of polymer modified bitumens (PmBs), with various polymers as potential modifiers, as well as of bitumens, makes it possible to characterize and evaluate PmBs as binders.
The Strategic Highway Research Program (SHRP), a research program in the field of road construction, includes the investigation into rheological properties at a traffic frequency and a temperature, which gives an insight into a permanent deformation known as rutting and into the effect of thermo–oxidative ageing.
In this paper, the following polymers are used as bitumen modifiers: styrenebutadiene–styrene block copolymers, linear and radial structure (SBS–L, SBS–R), plastomer ethylene–vinyl acetate (EVA) and reactive polymer ethylene butylacrylate glycidylmethacrylate (Elvaloy AM). Resistance to permanent deformation includes investigations into rheological properties of BIT and PmB performed by a dynamic shear rheometer (DSR) in a broad temperature range at a traffic frequency before and after ageing. The ageing of the investigated materials and their thermo–oxidative stability are determined by the Rolling Thin Film Oven Test (RTFOT).
Polymer modified bitumens are less sensitive to temperature and traffic speed than bitumen. They have a higher critical temperature, i.e. better resistance to permanent deformation. The critical temperature depends on the polymer type and content.

Keywords: PmB, DSR, rheological properties, permanent deformation, SHRP

1 Introduction

Natural bitumen (BIT) started to go out of use in road construction in the 1910s [1]. The highest percentages of bitumens that are produced worldwide each year are applied in the paving industry where they essentially act as binders for mineral aggregates to form asphalt mixes. In order to make sure that the mixture resists the climate and traffic, specifications of bitumen have become quite strict. The properties that are needed to obtain suitable bitumen are mostly rheological. Bitumen has to be fluid enough at high temperature to be pumpable and workable [2, 3]. Further, it has to be stiff enough at the highest pavement temperature to resist rutting and it must remain soft enough at the lowest pavement temperatures to resist cracking. All these properties are of conflicting nature and it is therefore difficult to obtain bitumen that would work under all possible climates. The current traffic loads and volume of vehicles considerably reduce the lifetime of pavements. In order to get longer periods between repairs and to reduce the total cost of road pavements new bituminous materials have to be developed. This has contributed to a large increase in the use of polymers as bitumen modifiers [2]. Two types of polymers are typically used in bitumen modifications, i.e. non–reactive plastomers and elastomers and reactive polymers. Non reactive plastomers and elastomers form a physical network between the bitumen and a polymer. The polymer is swollen by light aromatic components from the bitumen, i.e. by maltenes. Consequently, the polymer rich phase occupies between 4 to 10 times higher volume than that of the added polymer [4, 5]. This formation increases the complex modulus. It is an indication of resistance to rutting and a contribution to good elastic properties of the modified bitumen [4, 6]. Reactive polymers containing functional groups are able to form chemical bonds with certain bitumen compounds, thus improving the mechanical behaviour, rigidity, storage stability and temperature susceptibility of the bitumen [1,2, 7–9].

Generally, polymer modified bitumens (PmBs) are considered to have a longer life or higher pavement performance than bitumens [3, 10]. Polymers increase the resistance of the bitumen to traffic loading by reducing the permanent deformation at high temperature and thermal cracking at low temperature. They also prevent the phase separation and improve storage stability [2]. Characterization of bitumen and polymer modified bitumen as good binders for pavements should be based on rheological properties [1]. The properties of bitumen–polymer blends depend on the concentration and the type of polymer used.

In Europe, the characterization of bitumen and PmBs is still limited to conventional tests such as penetration and ring and ball softening temperature. The US characterization adopted the Strategic Highway Research Program (SHRP) which is based on rheological behaviour. Within the SHRP, the permanent deformation of BIT and PmB is correlated to viscoelastic functions, the shear complex modulus G* and the phase angle δ by means of the equation G*/sinδ [1, 11–12]. Thus, bitumens with a high complex modulus and a high degree of elasticity produced pavements with a low tendency for permanent deformation. The most commonly used method of rheological testing of BIT and PmB, which was included in the SHRP, is a dynamic mechanical method using the oscillatory type testing with dynamic shear rheometers, DSRs [2–4, 6].

The aim of this research is to compare the modification ability of two different types of bitumen modifiers, i.e. non–reactive plastomers and elastomers and reactive polymers, with respect to the rheological properties of PmBs. The testing was carried out in a set range of temperatures under defined traffic frequencies using a DSR. The group of non–reactive polymers included a thermoplastic block copolymer (SBS) with two different structures, a linear and a branched one, and the plastomer ethylene–vinyl acetate random copolymers (EVA). In the second group, reactive polymers included a therpolymer ethylene butylacrylate glycidylmethacrylate (GMA), commercial name Elvaloy. Due to their composition, they are often called reactive ethylene therpolymers (RET). These types of polymers have proved themselves as good modifiers which reduce permanent deformation and thermal cracking. This paper presents the characterization of the properties of PMBs modified with the above mentioned polymers, carried out by using conventional and empirical test methods as well as rheological measurements with reference to the SHRP to prove the permanent deformation.

Bitumen ageing during production, application and service life is one of the principal factors causing the deterioration of asphalt pavements. [10]. Ageing is a very complex process in BIT and even more complex when polymer bitumens are involved. Oxidation and physical hardening are present in BIT ageing [5]. The factors affecting the ageing of BIT and PmB include characteristics of BIT, the composition of BIT and PmB, the polymer content, and structure and phase interactions [13].

The rheological properties of unaged PmBs and of PmBs after artificial thermo–oxidative ageing were determined by the Rolling Thin Film Oven Test (RTFOT).

2 Experiment

2.1 Materials

The investigations were conducted with:

- BIT 70/100, INA Refinery Croatia, Rijeka.

The polymers used as modifiers were:

1. Thermoplastic styrene–butadiene–styrene block copolymers
   - SBS-L – linear with a content of polystyrene of 31 wt%, commercial grade Kraton D 1101
   - SBS-R – radial, with a content of polystyrene of 30 wt%, commercial grade Kraton D 1184, manufactured by Shell Chemicals Company, Germany.
2. Plastomer semi–crystalline copolymer ethylene–vinyl acetate
   - EVA – containing 28 wt % vinyl acetate, commercial grade Elvax 265
3. Thermopolymer ethylene – butylacrylate – glycidylmethacrylate
   - Elvaloy AM – containing butylacrylate 28 wt%, glycidylmethacrylate 5.3 wt%, manufactured by DuPont, USA.

2.2 Sample preparation

All PmBs were prepared by using a Silverson L4R mixer. First, the base bitumen was adequately heated (160°C) and stirred for about 2h to obtain homogeneity and was then poured into 1 L aluminium cans. The cans of bitumen were then heated to 180–185°C and stirred for 10 min before adding a polymer. The polymer content was 2 wt%, with the exception of Elvaloy AM where the content was 1.9% because of gel formation at higher polymer content. Polymers were then added slowly into the bitumen, under high speed stirring for 4h until the blend became thoroughly homogenous. A constant temperature was kept while the mixing process continued. For the preparation of PmB modified with Elvaloy AM, the softening point was checked after 1h of stirring to make sure that the reaction between the polymer and bitumen had started. When the reaction started, the cans were transferred to an oven and were kept at 180°C for 24 h under static conditions and in an oxygen–free environment to ensure a complete reaction.

After completion, the blends were removed from the aluminium cans and divided into small containers covered with aluminium foil and stored for testing at ambient temperature.

3 Measurements

3.1 Conventional tests

The base bitumen and PmBs were subjected to the following conventional bitumen tests according to standards: penetration test (HRN EN 1426), ring and ball technique to determine the softening point temperature (HRN EN 1427), elastic recovery test (HRN EN 13398) and the Frass breaking point test (HRN EN 12593/01). The storage stability of PMBs was determined according to standards HRN EN 13399. The results of these tests are listed in Table 2.

3.2 Rheological measurements

Rheological measurements to determine viscoelastic parameters such as complex modulus G*, complex viscosity n*, and phase angle δ were performed using a dynamic shear rheometer, DSR, MCR 301, Anton Paar with the Peltier temperature control system. The dynamic rheometer is a type of testing equipment applying oscillatory loading on a material sample. The DSR tests were performed under controlled strain loading conditions using temperature sweep tests. A temperature sweep was applied over the range of -5°C to 80 °C at a fixed traffic frequency of 10 rad/s (cca 85 km/h) and variable strain. Preliminary tests were carried out at different temperatures in order to determine the strain range within which the bitumen remains in the linear viscoelastic range (LVN) [14]. The temperature sweep tests for low 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 for medium and higher temperatures the tests 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 [1, 12]. The critical temperature is both the temperature at which G*/sinδ is equal to or less than 1 kPa at a frequency of 10 rad/s (strain is constant 10%) before ageing and that at which G*/sinδ is equal to or less than 2.2 kPa (strain value 12 %) after ageing. The critical temperature was determined automatically by the DSR software.

3.3 Ageing procedure

Accelerated thermo–oxidative ageing of base bitumen and PmBs was performed using the Rolling Thin Film Oven Test, RTFOT, according to ASTM D 2872. The RTFOT procedure simulated the short–term ageing of bitumen and PmBs. The bitumen and PmBs were exposed to elevated temperatures to simulate the conditions during the production, mixing and laying of asphalt mixes. Samples of a specific weight were placed into glass containers heated to 163°C for about 15 min and then they were placed into a rotating oven heated at 163°C for 85 min with the air on and with a flow rate of 4 L/min. All measurements were done before and after the simulated ageing in the laboratory, i.e. before and after the RTFO test.

4 Results and Discussion

Figs 1–6 show the results of rheological measurements of the base bitumen, BIT, and the polymer–modified bitumens, PmBs, modified with the styrene–butadiene–styrene (SBS) block copolymers, with a linear and a radial structure (SBS-L, SBS-R), the semi–crystalline copolymer ethylene–vinyl acetate (EVA) and reactive polymer ethylene butylacrylate glycidylmethacrylate (Elvaloy AM) in dependence on temperature. Changes in G*, n* and δ in the temperature range of -5°C to 80°C under the fixed traffic frequency of 10 rad/s are noted (Figs 1–3). The G* values of the base BIT and PmBs decrease as the temperature increases (Fig. 1). The G* and n* values of PmBs are higher than the same values of the base BIT (Figs 1 and 2). The PmB modified with the plastomer EVA and SBS-L shows higher values of G* and n* compared with other modifiers. It means that a polymer gives stiffness to the bitumen, particularly EVA and SBS-L. The modification with a reactive polymer and SBS-R shows significant changes at higher temperatures of above 50°C. The formation of elastic plateau is noted on the G*/T and n*/T curves of PmBs modified with Elvaloy AM and SBS-R (Figs 1 and 2). It indicates the formation of a physically cross–linked network in the BIT modified with SBS-R and also the reaction of epoxy group and the formation of chemical network in BIT modified with Elvaloy AM [7]. Comparison results on the G*/T and n*/T curves for SBS-L and SBS-R indicated that SBS-R shows an elastic plateau due to better various interactions between SBS-R and BIT. These interactions are more pronounced with a higher content of SBS-R in BIT, which was proved in the previous paper [6]. In Elvaloy AM, the elastic plateau is formed due to the formation of chemical bonds with bitumen. At lower temperatures in a range of -5°C to 15°C the PmB modified with EVA and SBS-R has the same values of G* and n* as the pure bitumen, while Elvaloy AM shows lower values and SBS-L higher values compared with BIT (Figs 1 and 2). The BIT modified with SBS-L has greater stiffness at low temperature areas than the BIT modified with Elvaloy AM, which indicates enhanced resistance to low temperature cracking [7]. The changes in the phase angle δ related to the changes in temperature (Fig. 3) are more expressed than the changes in G* in the same temperature range (Fig. 1). The phase angle is more sensitive to the chemical structure and its change is more expressed in PmBs than the changes in G* and n* (Figs 1 and 2) [15]. The base bitumen shows predominantly viscous behaviour with an increasing temperature, as can be seen at a fixed frequency and at temperatures exceeding some 50°C, and the phase angle of the base bitumen approaches 90° (Fig. 3). In this case the stored energy per cycle of deformation becomes negligible compared to that dissipated as heat [7]. The δ/T curves of PmBs are shifted to lower δ values (Fig. 3). Lower δ means that polymers significantly improve the elasticity of the modified bitumen. This higher elastic behaviour could indicate that PmBs have lower susceptibility to permanent deformation/ rutting [16]. At low temperatures (<10°C), there is no significant difference in the phase angle of pure bitumen and PmBs, except SBS-L. At intermediate temperatures (15°C – 60°C), one can note large differences in d/T of PmBs. EVA shows the lowest value of phase angle which rapidly increases with increased temperature, thus indicating the dominance of viscous behaviour. For SBS-L and SBS-R, the plateau formation is noted. It is related to the formation of polymer network as a consequence of SBS swelling in the maltene phase in BIT. For the Elvaloy AM, the values on the δ/T curves increase with temperature, and at 30°C reach an approximately constant value. This is related to the already mentioned formation of chemical bond, resulting in better behaviour at higher temperatures. This difference may be assigned to a different level of compatibility of a polymer with bitumen.

The changes in rheological properties, i.e. in G* and n*, and in d are noted after ageing under the RTFOT conditions (Figs 4–6). After ageing, the G* and n* values of BIT are higher. This is related to the higher stiffness, which is a consequence of the oxidation process of BIT. Also, PmBs with EVA, SBS-L and SBS-R show a larger increase in G* after ageing (Fig. 4), which means that besides the oxidation process, degradation reactions as well as secondary processes of crosslinking are included. As for Elvaloy AM, no large increase in the values of G* and n* can be noted after ageing (Figs 4 and 5). This is associated with the resulting chemical bond which contributes to the retention of the properties and good stability.

After ageing, the δ values of BIT on the δ/T curve are evidently lower as well as the δ values of PmBs (Fig. 6).

The ageing effect is strongly temperature–dependent. At medium and high temperatures the aged samples are characterized by higher stiffness and elasticity, whereas at low temperatures, the rheological properties G* and δ are not affected by ageing.

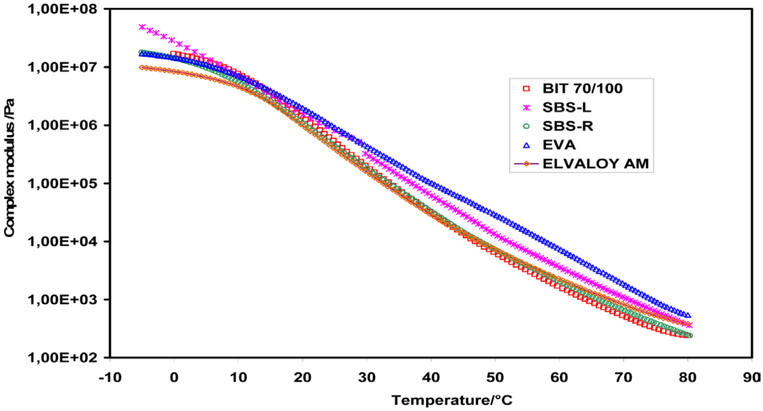

Figure 1 Complex modulus as a function of temperature for BIT 70/100 and PmBs

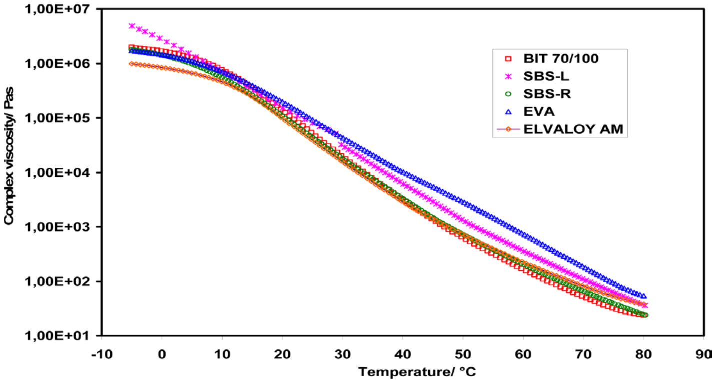

Figure 2 Complex viscosity as a function of temperature for BIT 70/100 and PmBs

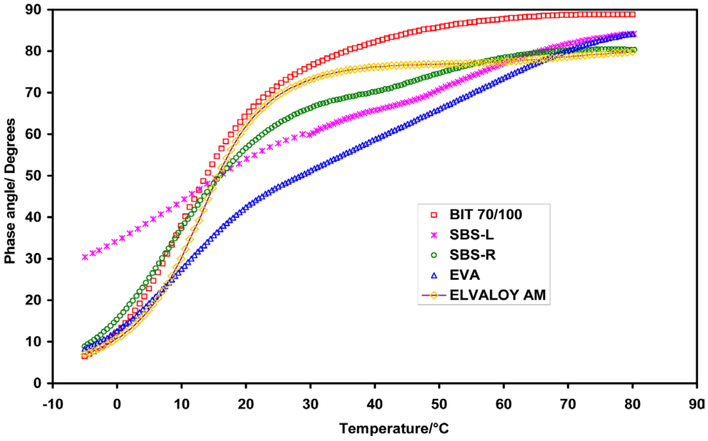

Figure 3 Phase angle as a function of temperature for BIT 70/100 and PmBs

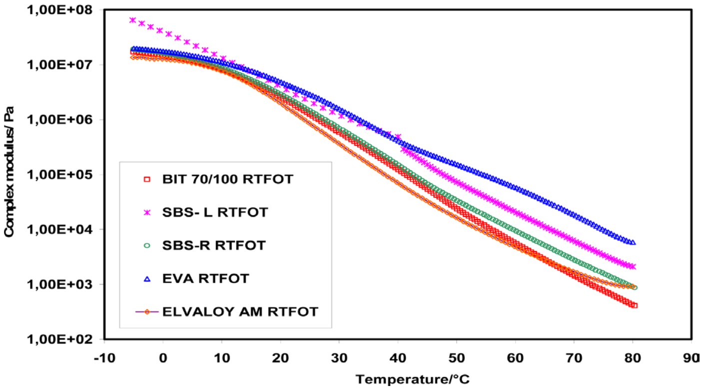

Figure 4 Complex modulus as a function of temperature for BIT 70/100 and PmBs after RTFOT

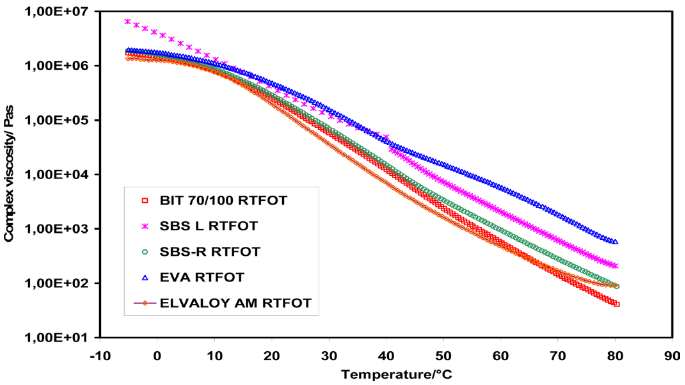

Figure 5 Complex viscosity as a function of temperature for BIT 70/100 and PmBs after RTFOT

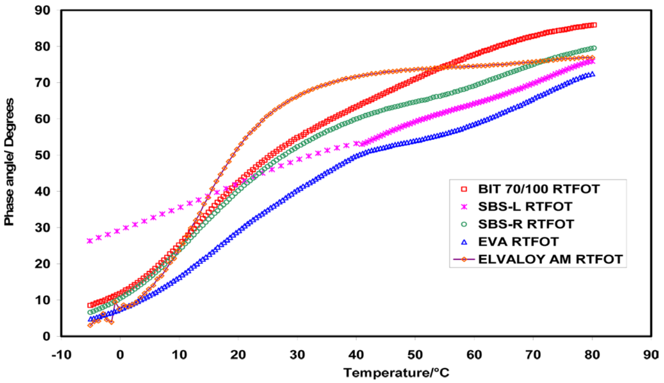

Figure 6 Phase angle as a function of temperature for BIT 70/100 and PmBs after RTFOT

The critical SHRP temperature values for permanent deformation, when the value of G*/sinδ ≥ 1 kPa before ageing, and the value of G*/sinδ ≥ 2.2 kPa after ageing, are presented in Table 1. The critical temperatures of PmBs are higher than that of the base bitumen. The BIT modified with EVA exhibits the highest value of critical temperature for permanent deformation, i.e. rutting, but it also exhibits a great difference in critical temperatures before and after ageing. Comparing the obtained results it is evident that SBS-R and Elvaloy AM show the same values of critical temperature for rutting, i.e. 70°C. The same temperature was determined after ageing. The higher critical temperature of BIT/SBS-R is related to a better interaction between the polymer and bitumen, resulting in a physical network. On the other hand, the higher critical temperature in BIT/Elvaloy AM is a result of a chemical bond between BIT and the polymer.

Table 1 The critical SHRP temperature for permanent deformation

Sample	Before RTFOT T/°C	 (G*/sinδ)/kPa	After RTFOT T/°C	 (G*/sinδ)/kPa
BIT 70/100	64	1.44	64	3.60
SBS-L	64	1.70	70	4.35
SBS-R	70	1.74	70	3.83
EVA	76	1.73	88	2.44
Elvaloy AM	70	1.26	70	3.68

Better rheological properties of PmBs and better resistance to temperature can be also noted in conventional tests (Table 2). For better understanding, Figures 7 and 8 show graphically the results of the softening point (R&B), penetration, and elastic recovery tests carried out on PmBs with a content of 2% added polymers, and on bitumen. To improve the PmB performance, a polymer should be able to increase the softening point value and the elastic behaviour of the bitumen without decreasing the penetration range too much [17]. The best compromise between these parameters is reached by the PmBs modified with SBS-R and Elvaloy AM. Also, it is very important to find the best compromise between these parameters after thermo–oxidative ageing. Figure 8 shows the same parameters after RTFO tests. Elvaloy AM exhibits the smallest changes in these properties. EVA, SBS-L and SBS-R showed significant changes after ageing. It indicates that hardening occurs during ageing as a consequence of a secondary reaction of degradation [5,18]. These changes are in agreement with the changes in rheological properties of BIT and PmBs after ageing.

Storage stability is one of the most critical aspects of modifying bitumen with polymers. Polymers contribute to the improvement of the rheological properties of bitumen, but on the other hand, create the multiphase nature of bitumen–polymer blends witch are thermodynamically unstable and tend to separate macroscopically during storage at high temperatures [20]. Figure 8 shows the results of ring and ball temperatures of the top and the bottom part of PmBs after three days at 180°C. The softening points between the top and the bottom of the samples after the storage stability test are not higher than 4°C.These results indicate that there is no substantial phase separation, which results in good storage stability of all PmBs [11, 21].

Table 2 Conventional properties of modified bitumen

Properties	Bitumen 70/100	SBS-L	SBS-R	EVA	Elvaloy AM
Penetration (1/10 mm)	71.1	56.9	64.1	63	66.7
Softening point, R&B(°C)	46.7	53.3	55.4	56.7	55
Penetration index (PI)*	-0.83	-0.11	0.70	0.26	0.72
Change in mass (%)	-0.21	-0.23	-0.20	0.17	0.1
Retained penetration (%)	62	54	53	48	61
Variation of softening point (°C)	0.5	11	12	14	4
Stability ΔT (°C)	/	0	0.1	0.1	0.4
Elastic recovery before RTFOT (%)	/	47	71	25	69
Elastic recovery after RTFOT (%)	/	54	75	16	62.5
Frass breaking point before RTFOT(°C)	-12	-14	-15	-7	-11
Frass breaking point after RTFOT(°C)	-13	-12	-17	-6	-14.5

*PI= 1952- 500*log(pen_{25})-20*SP/ 50*log(pen_{25})-SP-120 [19];

pen_{25} is the penetration at 25°C and SP is the softening point temperature of PmB

5 Conclusions

The rheological properties and resistance to permanent deformation of road BIT are improved by means of SBS-L, SBS-R, EVA and Elvaloy AM polymer modification. This has been proven by both conventional and rheological parameters G*, h* and d obtained by DSR measurements. Furthermore, acceptable properties were obtained in this investigation by using a small amount of polymer, i.e. 2% wt. With the addition of polymer, G* and h* are increased and the elastic response is improved. All PmBs samples show good storage stability. Modification with the reactive polymer Elvaloy AM and SBS-R shows the elastic plateau, which indicates the formation of a physical network in BIT/SBS-R and a chemical network in BIT/Elvaloy AM. All PmB samples have higher critical temperatures, i.e. better resistance to permanent deformation/ rutting. After ageing, the hardening of BIT and PmBs occurred and the elastic response decreased as a consequence of degradation. The hardening is more pronounced in BIT and in BIT modified with EVA and the changes are less pronounced in the PmB modified with Elvaloy AM. PmBs modified with SBS-R and Elvaloy AM have the best relation between softening point, elastic behaviour and penetration value before and after thermo–oxidative ageing.

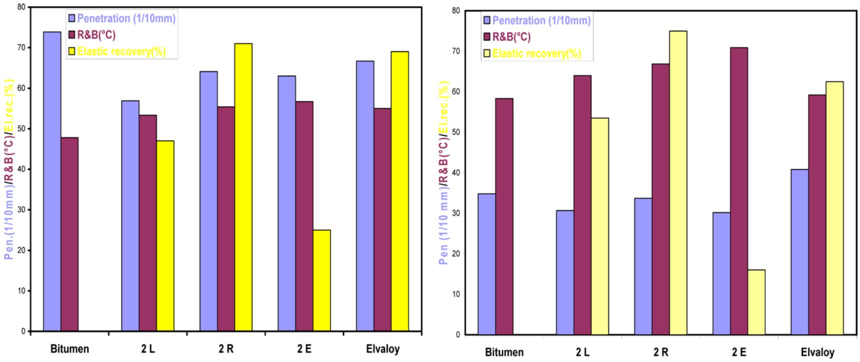

Figure 7 Softening point (R&B), penetration and elastic recovery for all before (left) and after (right) RTFOT

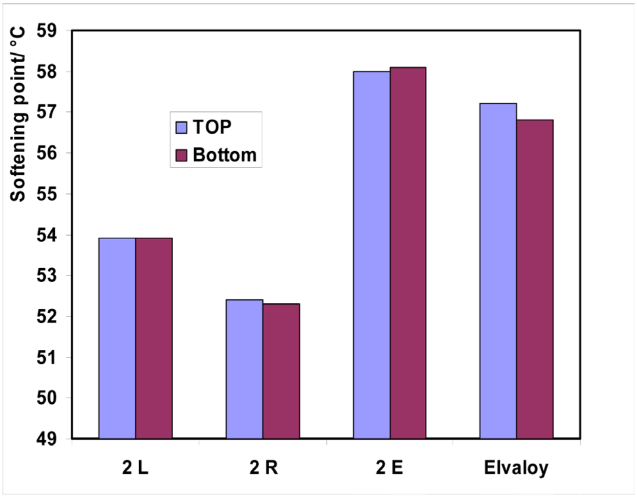

Figure 8 Storage stability

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