Influence of polymer melting point and melt flow index on the performance of ethylene-vinyl-acetate modified bitumen for reduced-temperature application

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ABSTRACT

The paving industry is currently demanding polymer modified bitumens (PMBs) with enhanced in-service performance and low enough viscosity at lower application temperatures. With this aim, this study focuses on the use of ethylene vinyl acetate (EVA) copolymers with low melting temperatures and explores the effect on the desired properties of the vinyl acetate (VA) content and Melt Flow Index (MFI). To that end, binders were prepared from EVA copolymers having varying VA contents from 7 to 33 wt.%, and MFI from 2 to 800. A comprehensive characterization based on viscous flow curves, dynamic shear temperature sweeps, standardized technological tests, differential scanning calorimetry (DSC) and optical microscopy analysis was conducted on EVA-binders with 5 and 7.5 wt.% EVA. Low VA contents proved to endow bitumen with improved performance at medium-high in-service temperatures. Interestingly, binder viscosity at 135ºC decreased with increasing the MFI, regardless the selected VA content. This means that tailored PMBs can be designed with both improved in-service performance at medium-high temperatures and reduced viscosity to facilitate polymer-bitumen mixing, mineral coating and asphalt mix laydown/compaction at lower temperatures.

Keywords: modified bitumen, ethylene vinyl acetate, rheology, reduced-temperature paving, product design.

1. INTRODUCTION

Bitumen, by-product from crude oil distillation, has been largely used as binder of mineral aggregates in road paving [1]. Even though its content in the asphalt mixtures (composed of mineral aggregates and bitumen) never exceeds 5 wt.%, its contribution to the road performance is decisive [2]. In that sense, it is the only deformable component in the mixtures and actually constitutes their continuous matrix.

Consequently, the viscoelastic properties of bitumen, over a wide range of temperatures and loadings, are of special importance when predicting roads performance [3]. For certain applications, bitumen quality needs to be enhanced, commonly by its modification with polymers [4]. Depending on the requirements demanded, a bitumen additive should improve the binder properties at the in-service temperature range expected [5]. Thus, in the warmest climate countries, it should withstand the traffic loads which cause the so-called permanent deformation at high temperature. Moreover, if harsh winters are expected, high flexibility at low temperature is certain to help mitigate thermal fracturing. In addition to that, a modifying agent of bitumen should also meet the following features: (a) easy to incorporate; (b) homogeneously dispersed during storage; and (c) low viscosity at the mix asphalt temperatures, which assures the correct coating of the arids and laydown/compaction operations.

Traditional asphalt mixtures, also termed as hot mix asphalt (HMA), have been always produced and applied at very high temperatures, never below 150 ºC. Moreover, the use of polymer modified bitumens (PMBs) in HMA requires temperatures that normally exceed 160ºC and very frequently approaches 180-190 ºC. Otherwise, the viscosity of a PMB is not low enough so that coating of aggregates and further operations are performed adequately. Concerns with the environment impact and the health consequences of exposure to asphalt fumes have resulted in a major effort to develop alternative paving practices [6]. In this sense, reduced-temperature technologies represent a number of processes and additives that allow the production of asphalt mixes to be conducted at significantly lower temperatures than HMAs, reducing energy consumption and asphalt fumes emissions [7-9]. So, whilst HMAs are produced and applied at temperatures never below 150ºC, the more recent reduced-temperature technologies have been classified as follows: 100-140 °C, for warm mix asphalt (WMA); 60-100 °C, for half warm mix asphalt (HWMA); and 25-60 °C, for cold mix asphalt (CMA) [7]. With that purpose, novel additives and/or processes are required in order to achieve the desired lower viscosity at the mix production [10]. For instance, the selection of low melting point polymers may provide an advantage if compared to traditional SBS-modified binders that normally require very high temperatures of mixing with the aggregates [11]. So, as far as warm climate countries are concerned, the success of WMA technologies involving PMBs relies on the development of binders with low viscosity in the 100-140ºC temperature range which, instead, offer a high degree of modification at the highest in-service temperatures expected. Furthermore, for an even more substantial energy saving, the use of CMA technologies is also encouraged [12].

On this basis, excellent efforts have been so far done to study EVA (ethylene vinyl acetate)-modified bitumen in performance related concern. In this sense, they mainly focused on obtaining the optimum blending conditions (these are, mixing temperature, blending time and shear rate) for preparing EVA bituminous binders [13] or their morphology, thermal and rheological properties depending of the EVA copolymers characteristics and concentration [14-17]. Other researchers reported the use of recycled EVA polymers as bitumen modifying agent [18-19] and even the blend into ternary formulations with other polymer or clay [20-21]. Still, not so many in-depth investigations have been conducted on the potential of EVA as modifier in reduced-temperature technologies for asphalt roads.

The present paper explores the development of PMBs binders with enhanced in-service performance and low viscosity at reduced working temperatures. This objective is addressed through the use of EVA copolymers with melting temperatures substantially lower than other traditional polyolefins, which exhibit low viscosity at their molten state, but which impart a reinforcing effect on the bitumen matrix when they re-crystallize. With that purpose, a selection of PMBs derived from different EVA copolymers with varying vinyl acetate (VA) content and Melt Flow Index (MFI) value was studied. From their comprehensive characterization, it was proved that the optimal selection of VA content and MFI value may yield promising bituminous binders with the above desired properties.

2. EXPERIMENTAL

2.1. Materials

Two different types of neat bitumen supplied by Repsol S.A. (Spain), with penetration grades within the intervals 70/100 and 160/220 (EN 12591:2009), were used as base material for the modification.

Ethylene vinyl acetate (EVA) copolymers, also kindly donated by Repsol S.A. (Spain) under commercial names of Alcudia®, with different VA contents ranging 7 to 33 wt.%, and MFI between 2 and 800 were used as modifying agents (Table 1). VA contents relate to EVA melting point (Table 3) and the MFI is a measure of mass of polymer flowing under specific temperature and loading in a standard measuring device for 10 minutes. For EVA, the temperature is specifically set at 190 °C and the loading at 2.16 kg, according to ASTM D1238. For sake of clarity, these EVA copolymers will be identified attending both their VA and MFI values, e.g. EVA-VA7-MFI2 refers to a EVA with VA of 7 wt.% and MFI of 2 g/10min. Furthermore, a Styrene-Butadiene-Styrene (SBS) Calprene® C501 (Dynasol) and a wax Sasobit® (Salsol Wax) were selected as reference modifying agents, for sake of comparison.

2.2. Bituminous sample preparation

EVA/bitumen blends (referred to as EVA-binders) and reference systems (SBS and wax modified bitumens) were processed with a Silverson L5M (Silverson Machines Ltd., U.K.) homogenizer equipped with a J.P. Selecta (Spain) controlled heating system. The processing protocol consisted in mixing neat bitumen with 5 or 7.5 wt.% EVA polymer at 150°C in a cylindrical vessel (110 mm diameter and 130 mm height). Pre-blending of bitumen and EVA pellets was performed at 3500 rpm for 15 min, before the speed was increased up to a final value of 5000 rpm and maintained for 1 hour. Alternatively, other two binders were also prepared: (a) one with 1.5 wt.% wax following the same processing protocol and; (b) a 3 wt.% SBS modified bitumen processed at 180ºC, for 1 h and 6000 rpm. Immediately after mixing, all binders were poured on aluminium foil and cooled down to room temperature, in order to prevent polymer phase separation and, so, sample heterogeneity.

2.3. Tests and measurements

Two selected technological tests, penetration and ring-and-ball softening temperature, were performed on neat and modified binders according to EN 1426:2007 and EN 1427:2007 standards, respectively.

Two different rheological tests were carried out on bituminous binders: a) viscous flow measurements at 60 and 135 °C; and b) temperature sweep tests under oscillatory shear between 30 and 100 °C. Viscous flow curves were conducted in a controlled-stress rheometer Physica MCR-301 (Anton Paar, Austria) using plate-plate geometry (25 mm diameter and 1 mm gap). Measurements were performed by ranging shear stress from 1 to 1000 Pa and collecting the viscosity data every 2 minutes, once apparent viscosity had reached steady state values at the applied stress. On the other hand, temperature sweep tests in oscillatory shear, from 30 to 100 ºC and using a continuous heating ramp of 1 ºC/min, a frequency of 10 rad/s and a shear stress of 100 Pa (within the linear viscoelasticity, LVE, interval), were conducted in a controlled-stress rheometer RheoStress RS600 (Haake, Germany). Previously to temperature sweep tests, shear stress tests, at the same frequency and at selected constant temperatures within the 30-100ºC interval, were performed in order to determine the limit value below which the material moduli did not show any stress dependence. Plate-and-plate geometry (20 mm diameter and 1 mm gap) was selected for these measurements. In order to ensure accurate results, at least two replicates were conducted for every sample.

DSC was conducted with a TA Q-100 (TA Instrument, USA) to provide any relevant thermal event information for the different EVA copolymers and their corresponding bituminous binders. Samples of 5-10 mg were always subjected to the following testing procedure: (a) a first heating ramp from room temperature to 20 ºC above its corresponding EVA melting point, in order to eliminate discrepancy in the molecular structure in response to a distinct thermal history; (b) cooling ramp, to -60 ºC; and (c) a second heating ramp, to the same final temperature used for the first one. The heating/cooling rate was set at 5 ºC/min, and N_2 was used as purge gas. The values of the melting temperatures were determined during the second heating ramps. Degree of crystallinity (χ_C) of each sample was calculated as follows:

$$\chi_C = \frac{\Delta H_C}{\Delta H_{100} \cdot C_{EVA}} \cdot 100 \qquad (1)$$

where ΔH_c and ΔH_{100} are the crystallization enthalpy obtained from integration peak in the cooling ramp and the melting enthalpy of 100 % crystalline polymer [22], respectively, and "C_{EVA}" represents the EVA weight fraction (0.05 or 0.075 in every case) in the bituminous binders.

Optical microscopy images, taken at room temperature, were used to study the morphology of the EVA modified binders. A LTS-350 Heating-Freezing Stage, manufactured by Linkam Scientific Instruments (U.K.), coupled with a standard Olympus BX51 microscope equipped with a pair of crossed polarisers, by Olympus Optical (Japan), was employed to that purpose. Samples were prepared by using standard microscope slides (76 x 26 mm). Very thin layers of the modified binders were set on them and prepared at temperature above its corresponding softening temperature, allowing them to be in-placed, excluding too high temperature causing a microstructural change.

3. RESULTS AND DISCUSSION

3.1. Effect of Vinyl Acetate content

With the aim of evaluating the effect of EVA vinyl acetate concentration on the in-service performance and morphology of the resulting modified bitumens, a rheological, technological, calorimetric and microstructural characterization was conducted on bituminous binders prepared from EVA copolymers with different VA contents, at selected concentrations of 5 and 7.5 wt. % EVA.

The viscous flow curves, at 60 ºC (usually considered as the maximum expectable temperature to be reached in a pavement exposed to ambient in warm climates), for the neat bitumens and their corresponding EVA-binders (5 and 7.5 wt.% EVA), as a function of VA content, are presented in Figure 1. A Newtonian behaviour over the whole range of shear rates tested is exhibited by both neat bitumens. On the contrary, modification with EVA copolymers leads to a shear-thinning behaviour that can be characterized by the Ostwald-De Waele model fairly well:

$$\eta = k(\dot{\gamma})^{n-1} \tag{2}$$

where “k” and “n” are the consistency and flow indexes, respectively. As can be seen in Table 2, much lower values of flow index, that is, more remarkable shear-thinning properties, are obtained for the EVA-binders having the lowest VA contents (7 and, mainly, 18 wt.%). On the contrary, EVA-binders with the highest VA contents (28 and 33 wt.%) present a much less pronounced shear-thinning behaviour, with flow index values (n) very close to 1, in the range of shear rates considered. On the other hand, a significant increase in the consistency index and, therefore, in the EVA-binder viscosity, is found as the VA content of the EVA copolymer decreases, which suggests enhanced properties for such EVA-binders at 60ºC. For these EVA copolymers, their corresponding binders viscosities also increased when the EVA polymer concentration was raised from 5 to 7.5 wt.%, mainly for the EVA copolymer with the lowest VA content. In addition to that, an increase in polymer concentration does not significantly alter the values of flow index, showing the EVA-binders similar shear-thinning properties.

Likewise, Table 1 presents the values of penetration and ring & ball softening temperature tests. The addition of polymer to bitumen is well-known to decrease its penetration value and increases its softening temperature [14, 23-24], which was also corroborated on the EVA-binders studied. As expected from the previous viscosity results, the lowest penetrations and highest softening temperatures correspond to the binders prepared with EVA copolymers containing 7 and 18 wt.% VA. If compared to the corresponding neat bitumens, the addition of EVA-VA7 produced a decrease of about 50 % in their penetration values, as well as increases of 19 and 22 ºC in their softening temperatures, for the base bitumen 70/100 and 160/220, respectively. It can be also noticed that, for the bitumen 70/100 EVA-binders, the parameter “k” of the Ostwald-De Waele model is in good agreement with the results of the technological tests (mainly, with binder penetration values). However, for the 160/220 neat bitumen, the highest consistency value corresponds to the modification with EVA-VA18, whilst the lowest penetration and highest softening temperature is found for EVA-VA7. However, Ostwald-De Waele model does not accurately described the flow behaviour of EVA-VA18, giving consistency index above the real one. Instead, if it is accepted that “k” represents binder viscosity at 1 s^{-1}, Figure 1b shows that there still exist a good correlation between rheological and technological results (i.e. EVA-VA18 shows a lower viscosity at 1 s^{-1} and is softer than binder EVA-VA7). On the whole, the results obtained from technological tests and viscosity curves indicate, in general terms, a larger degree of modification for bituminous binders prepared from EVA with 7 and 18 wt.% VA contents.

In addition to the viscous flow tests, Figure 2 shows the dynamic shear temperature sweeps for the neat bitumen 70/100 and their corresponding EVA-binders. It can be seen that storage modulus (G’) decreases with increasing testing temperature from 30 to 100 ºC (Figure 2a). Among all the EVA-binders studied, the one containing EVA-VA7 presents significantly higher G’ values in the medium-high temperature range (30-75 ºC) than the others. This reveals a better resistance to permanent deformation at that temperature interval. In addition, an enhancement in the temperature susceptibility is also observed after modification with EVA-VA7, if compared to the base bitumen 70/100, as deduced from a decreased value of the average slope of G’ (and also tan δ) vs. temperature, within the interval 30-75 ºC. Interestingly, an abrupt variation of slope in G’, starting at about 80 and 60 ºC for the EVA-binders with 7 and 18 % VA content, respectively, can be clearly observed. With regard to the EVA copolymers containing 28 and 33 wt.% VA this behaviour in G’ vanishes. This fact was also observed for polymer gels based on EVA with different VA content and vegetable oils [25]. Furthermore, Figure 2b shows values of loss tangent (tan δ=G”/G’) always higher than 1 in the entire temperature interval tested, which points out a prevailing viscous behaviour. In accordance with the previous viscous flow curves and technological results, addition of EVA containing low VA content (7 and 18 wt.%) yields an increase in storage modulus compared to the neat bitumen. Likewise, a decrease in VA content leads to lower values of loss tangent, which evidences improved elastic properties (enhanced performance) at medium-high in-service temperatures.

DSC runs and microstructural observations allowed shedding some light on these results. Figure 3 shows the thermograms corresponding to the second heating ramps for the EVA copolymers (Figure 3a) and their resultant EVA-binders (Figures 3b and 3c). The values of the melting temperature (T_m), crystallization enthalpy (ΔH_c) and crystallinity degree (χ_c) are shown in Table 3. Firstly, the DSC scans for some selected EVA copolymers (varying VA contents and MFI values) were studied. As can be observed in Figure 3a, they all display a broad shoulder followed by a unique endothermic event, which appears at temperature ranges typically found for this type of polyolefins [26]. It has been considered that the width of EVA melting peak can reflect the distribution of the lamellar thickness of its crystalline fraction [27-28]. Therefore, EVA-VA7 has the narrowest size distribution of crystallites (and highest melting temperature), followed by EVA-VA18, EVA-VA28 and EVA-VA33. In addition to that, the decrease in the crystallinity (please, see Table 3) can be explained based on the amount of total non-crystallizable, intra-molecular defects [28], such as acetate pendant groups. Thus, EVA copolymers with high VA content present a higher amount of pendant groups which partially hinder crystallization. In contrast, EVA copolymers with low VA content resemble the behaviour of LDPE.

Secondly, the DSC scans for the EVA-binders prepared from the two base bitumens 70/100 and 160/220 were studied in Figures 3b and 3c, respectively. As can be observed, the melting temperatures of EVA copolymers in the corresponding bituminous binders appear shifted to lower temperatures (Table 3). As a result, when EVA-VA7 is blended with the base bitumen 70/100, the melting temperature decreases from 105 ºC, for pure EVA, to 90 ºC, for its corresponding EVA-binder. For the EVA-VA18, a reduction of 19 ºC in the melting temperature is observed. Furthermore, the magnitude of this reduction is not affected by the hardness (or penetration) of the neat bitumen used (70/100 and 160/220). This fact can be explained on the basis of the swelling experienced by the polymer-rich phase by migration of compounds from the bitumen [4]. The bitumen-rich phase is artificially enriched in asphaltenes by a "physical distillation" of the lighter species from the original bitumen (e.g. paraffinic and aromatic compounds). Thus, their inclusion in the polymer-rich phase prevents the formation of larger crystallites and, as observed for EVA-VA18, yields an eventual broader size distribution (or broader melting peak) [29-30]. In consequence, the decrease in the EVA melting points after its blending with bitumen would result from the presence of crystallites with smaller size. Moreover, for each EVA-binder, its addition to bitumen reduces the extent of crystallization of the polymer (Table 3) due either to migrated bitumen species hindering crystallization or even to a fraction of crystallizable molecules retained within the amorphous bitumen-rich phase [29]. Finally, the EVA melting events for the binders prepared with EVA-VA28 and EVA-VA33 cannot be observed on DSC thermograms.

Further microstructural considerations may be drawn from the optical microscopy images (Figure 4), taken at 25 ºC, for neat bitumen 70/100 and their EVA-binders, as a function of VA content. Compared to the neat bitumen, its modification with EVA copolymers yields a new morphology in the resulting binders, where two phases are clearly distinguished. The lightly toned regions were assigned to a polymer-rich phase, whereas the bitumen-rich phase appears as a darker background. As expected from previous DSC results, the formation of a polymer-rich phase becomes more evident for EVA-binders prepared with polymer containing the lowest VA contents, mainly for the EVA-VA7 (Figure 4). Instead, high VA contents lead to a highly dispersed polymer phase and a very homogeneous binary blend at the micro-scale. The presence of crystals in the EVA-binder prepared with the EVA-VA7 copolymer was corroborated by a polarized light microscopy imagen, which is also included in the Figure 4.

Figure 2a demonstrates for EVA-binders with low VA contents (7 and 18 wt.%) a sudden decay in G’ (or the end of the loss tangent plateau) as temperature approaches the EVA melting point determined by DSC scans. However, this evidence is hardly noticed in the EVA-binders prepared with 28 and 33 % VA content, which is in accordance with their poorer crystals contents. In consequence, their melting process results more evident from the abrupt increase observed in the tan δ curve (Figure 2b).

Consequently, uniformly distributed polymer-rich domains (optical microscopy observations) including larger and more crystals (DSC scans) exert a reinforcing effect on the bitumen-rich matrix that enhances rheological behaviour of the EVA-binders with the lowest VA contents, at temperature below EVA melting (ie. at medium-high in-service temperatures). Additionally, the observed sudden decrease in G’ upon melting of the binder polymer-rich phase would facilitate its final application. In this sense, EVA-binder viscosity at 135 ºC is of particular interest in evaluating its pumpability (between storage facilities and into the HMA manufacturing plant), mixability (mixing with and coating of aggregates in the HMA manufacturing plant) and workability (ease with which a HMA can be placed, worked by hand, and compacted) [31]. According to the standard AASHTO MP320, viscosity must be maintained below 3 Pa·s at 135ºC for the binder to be adequately pumped, mixed with the mineral aggregates, and the resulting mix to be properly laid down and compacted [32]. Figure 5 displays the viscosity flow curves for base bitumen 70/100 and their corresponding EVA-binders, as a function of VA content, at 135 ºC. Despite the increases in viscosity (Figure 1) and elastic modules (Figure 2) found, all the 5 wt. % EVA-binders studied fulfil this specification. However, if the EVA-VA7-MFI2 copolymer is used, its corresponding EVA-binder exceeds this limit viscosity when the EVA polymer concentration is increased up to 7.5 wt.%. Interestingly, this fact is not observed for the EVA-VA18-MFI500 copolymer, since its 7.5 wt.% EVA-binder displays viscosity value lower than 3 Pa·s. Surprisingly, there does not exist a good correlation between the VA content and the viscosity at this temperature (Figure 5), suggesting that VA content is not the only parameter controlling the binder viscous behaviour at temperatures well above the EVA copolymer melting point.

3.2. Effect of Melt Flow Index

Previous results suggest that additional EVA properties, other than the VA content, may also affect the binder's quality. In order to study the effect of MFI on the in-service performance and workability of EVA-binders containing 5 wt.% polymer , different EVA polymers with 18 and 28 % VA content and varying MFI values have been considered.

Table 3 displays the melting temperatures (T_m), crystallization enthalpy (ΔH_c) and crystallinity degree (χ_c) for EVA copolymers, and their corresponding EVA-binders prepared from neat bitumen 70/100, as a function of MFI values. It can be clearly observed that, for every type of EVA copolymer studied, varying MFI values do not produce significant differences in none of the three measured parameters. If further attention is paid to EVA-binders prepared from EVA-VA18, a very similar reduction in both EVA copolymer melting point and crystallinity degree is observed. Likewise, the optical microscopy images (results not shown) for the binders prepared with EVA copolymer having the same VA content but differing MFI values displayed very similar morphology in terms of size and distribution of their polymer-rich phases. Consequently, the swelling process experienced by the polymer-rich phase of the EVA-binders, which is the responsible for the decreases in T_m and χ_c values, depends only on the VA content. Finally, as expected, the EVA-binders prepared with the three different EVA-VA28s do not show any measurable endothermic peak on the DSC thermograms.

In addition to this, the presence of a significant amount of crystals can be also corroborated by the dynamic shear temperature sweeps displayed in Figure 6, which shows the evolution with the temperature of complex shear modulus (|G*|) and tan δ for EVA-binders, as function of MFI values. It can be seen that the EVA-VA18-MFI500 binder shows an abrupt decay in |G*| at about 60 ºC (Figure 6a), similar to that found in G' (Figure 2a) when approaching the polymer-rich phase melting point. Interestingly, this event in |G*| does not occurred in the modified binders prepared with neither EVA-18-MFI2 nor EVA-VA28s. Furthermore, Figure 6b demonstrates lower values of the loss tangent, between 30 and 50 ºC, imparted by the EVA copolymers with the lowest MFIs, revealing an enhancement in the in-service elastic properties with respect to the viscous ones and leading to a highly structured binder for EVA-VA18-MFI2 with a trend to predominantly elastic response (being tan δ slightly below 1) between 30 and 50 °C. For sake of comparison, two modified binders, containing 3 wt.% SBS and 1.5 wt.% wax, respectively, have been included in Figure 6. If attention is paid to Figure 6a, the SBS modified bitumen presents values of the complex shear modulus very similar to that shown by the EVA-VA18-MFI500 binder at the medium-to-high in-service temperatures (30 to 60 ºC), but much higher values at higher temperatures, at which its application is expected. In contrast, the wax modified binder shows |G*| values quite close to those exhibited by the bitumen modified with EVA-VA28-MFI400. On the whole, EVA modification imparts better elastic properties and improved thermal susceptibility (loss tangent much less temperature-dependent and with presence, in some cases, of a pronounced plateau up to about 60 ºC) if compared to the wax. SBS modification also yields a plateau in tan δ up to even higher temperatures than EVA does, but with poorer elastic properties than the two EVA-binders with the lowest MFIs (e.g., 2 and 7).

On top of that, Figure 7 shows the viscosity flow curves, at 60 ºC, for the EVA-binders prepared from the neat bitumen 70/100, as a function of the MFI values. For the both VA contents studied, the binder's viscosity always increased with decreasing MFI value, what is in accordance with the values of the complex shear modulus, at 60ºC, observed in Figure 6a. It has been reported [33] that EVA copolymer molecular weight and MFI values are inversely proportional, as the chain entanglement and the friction increase the viscosity of the EVA copolymer. Consequently, EVA copolymers with the same VA content but lower MFI values endow EVA-binders with increased viscosity. However, a significant reduction in the MFI value, from 500 to 2, did not modify its shear thinning behaviour, as deduced from their similar flow indexes (Figure 7a). Moreover, with a view to their application, Figure 8 presents the effect of MFI values on the EVA-binders viscosity at 135 ºC. For both VA contents, an increase in MFI yielded a decrease in the binder viscosity and, interestingly, EVA-binders with MFIs above 400 present lower viscosities than the SBS-modified bitumen. Likewise, it is worth noting that binder EVA-VA18-MFI500 containing 7.5 wt. % polymer (Figure 5) shows lower viscosity at 135ºC than system EVA-VA18-MFI2 with 5 wt.% polymer (Figure 8A), confirming the importance of the EVA MFI parameter. Consequently, if these EVA PMBs present reduced viscosity at 135ºC, if compared to standard PMBs, we may also expect reduced working temperatures, with respect to standard PMBs. However, they are more viscous than the binder modified with the wax, a well-known viscosity reducer.

Moreover, no matter the selected VA content, Figure 8 has revealed the flow behaviour of EVA-binders at 135 ºC to be dependent on MFI values. Thus, Figure 9 shows the viscosity at 135ºC and two different shear rates (10 and 100 s^{-1}) of all the EVA-binders formulated with the 70/100 bitumen. As may be seen, bitumen viscosity undergoes a power law decrease, as MFI is raised, with the slope of the fitting curve being just slightly dependent on the shear rate, which evidences their nearly Newtonian behaviour at 135ºC. In any case, all the viscosity values at 135 ºC satisfy the limiting value required (3 Pa·s) and are lower than SBS-binder’s for MFIs above 45. Furthermore, the relevance of the MFI on the binder performance, at in-service conditions, is confirmed by Figure 10, which shows a power-law correlation between penetration of EVA-binders and their MFI, so that binder becomes softer with increasing the MFI values, no matter which VA content and neat bitumen are selected. Similarly, an acceptable dependence of R&B softening point with MFI has been found, obtaining a lower value of this parameter as MFI becomes higher. However, this parameter also seems to be affected by the VA content.

4. CONCLUDING REMARKS

The objective of this research was to develop EVA modified bitumens with in-service performance comparable to traditional PMBs but lower viscosity than these at the application temperatures, so enabling their use in reduced-temperature technologies. To that end, two EVA characteristics (vinyl acetate content and Melt Flow Index) need to be optimized.

On the one hand, bitumen modification with the EVA copolymers having the lowest VA contents (7 and 18 wt.%) yielded higher viscosity at 60ºC, and improved elasticity and thermal susceptibility at the medium-to-high in-service temperatures, if compared to their corresponding unmodified bitumens. Likewise, optical microscopy observations demonstrated the existence of large and uniformly distributed polymer-rich domains. Interestingly, these formulations showed reduced viscosity once the EVA melting point was exceeded and the reinforcing effect of the crystals disappeared. On the other hand, it was also found that the MFI strongly affects some of the binders’ properties. Hence, a power-law correlation between the viscosity at 135ºC and the MFI values was found, regardless the VA content.

We conclude that EVA modified bitumens with both improved in-service properties and reduced application temperature can be obtained by balancing VA content and MFI for a selected polymer concentration. In our case, for example, the results proved an optimum balance with a VA content of 18 wt.% and a MFI of 500 g/10 min. This formulation gave rise to a binder with similar performance at medium-to-high in-services temperatures to a reference modified bitumen with 3 wt.% SBS, but with lower viscosity at 135 ºC. If compared to 1.5 wt.% wax-modified bitumen, the reduction in viscosity at 135 ºC was not so significant, but it exhibited much higher elasticity.

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Table 1. Penetration values and ring & ball softening temperatures for neat and modified bitumens with wax, SBS and EVA with varying VA content and MFI.

Neat bitumen	**Modifying agent**		**Binder**	
			Penetration (dmm)^{a}	**R&B softening point (°C)^{b}**
70/100	Unmodified		73	46
	SBS		45	63
	wax		57	58
	EVA Polymer		**EVA Binder**	
	VA (wt. %)	**MFI (g/10min)**	**Penetration (dmm)^{a}**	**R&B softening point (°C)^{b}**
	7	2	39	65
	18	2	40	69
		500	53	64
	28	7	44	60
		400	58	54
		800	58	51
	33	45	54	54
160/220	Unmodified		190	39
	7	2	99	61
	18	500	124	57
	28	400	135	44
	33	45	149	44

[a] According to EN 1426:2007.

[b] According to EN 1427:2007.

Table 2. Fitting parameters of the Ostwald-De Waele model, at 60 ºC, for the EVA-binders, as a function of VA content and polymer concentration.

Polymer concentration	EVA copolymer	Base bitumen 70/100		Base bitumen 160/220	
		k (Pa.s^n)	n	k (Pa.s^n)	n
5 wt. %	EVA-VA7-MFI2	1443.15	0.65	407.44	0.79
	EVA-VA18-MFI500	745.38	0.58	473.19	0.35
	EVA-VA28-MFI400	343.27	0.92	77.50	0.96
	EVA-VA33-MFI45	361.05	0.91	89.77	0.96
7.5 wt. %	EVA-VA7-MFI2	3025.01	0.53	n.p.	n.p.
	EVA-VA18-MFI500	1003.72	0.49	n.p.	n.p.

n.p. not performed

Table 3. Melting temperatures (T_m), crystallization enthalpy (ΔH_c) and crystallization degree (χ_c) for EVA copolymers and EVA-binders, as a function of the VA content and MFI.

EVA		EVA polymer data			EVA Binder data					
VA (wt.%)	MFI (g/10 min)	T_m (^{o}C)	ΔH_c (J/g)	χ_c (%)	Neat bitumen 70/100			Neat bitumen 160/220		
					T_m (^{o}C)	ΔH_c (J/g)	χ_c (%)	T_m (^{o}C)	ΔH_c (J/g)	χ_c (%)
7	2	105.3	110.8	37.8	89.7	4.5	30.9	90.5	4.4	30.1
18	2	84.5	75.8	25.9	65.0	3.5	23.7	n.p.		
	500	84.1	76.5	26.1	64.7	3.3	22.7	64.9	3.1	21.3
28	7	69.5	51.7	17.6	n.m.			n.p.		
	400	68.8	51.5	17.6				n.m.		
	800	69.3	49.3	16.8						
33	45	60.7	36.7	12.5						

n.m. not measureable
n.p. not performed

FIGURE CAPTIONS

Figure 1. Viscous flow curves, at 60 ºC, for EVA-binders prepared from (a) the base bitumen 70/100 and (b) the base bitumen 160/220, as a function of the vinyl acetate (VA) content and polymer concentration. Neat bitumens are included.

Figure 2. Evolution with temperature of the storage modulus and loss tangent for the EVA-binders prepared from base bitumen 70/100, as a function of the vinyl acetate (VA) content. Neat bitumen is included.

Figure 3. Heat flow curve for (a) neat EVA copolymers; (b) EVA-binders from bitumen 70/100; and (c) EVA-binders from bitumen 160/220.

Figure 4. Optical microscopy images, at 25ºC, for base bitumen 70/100 and their corresponding EVA-binders, as a function of the vinyl acetate (VA) content.

Figure 5. Viscous flow curves, at 135 ºC, for base bitumen 70/100 and their corresponding EVA-binders, as a function of the vinyl acetate (VA) content and polymer concentration.

Figure 6. Evolution with temperature of (a) the complex modulus and (b) loss tangent for the 5 wt. % EVA-binders prepared with either EVA-VA18 or EVA-VA28 and neat bitumen 70/100, as a function of the Melt Flow Index value.

Figure 7. Viscous flow curves, at 60 ºC, for the 5 wt. % EVA-binders prepared with either (a) EVA-VA18 or (b) EVA-VA28 and neat bitumen 70/100, as a function of the Melt Flow Index value.

Figure 8. Viscous flow curves, at 135 ºC, for the 5 wt. % EVA-binders prepared with either (a) EVA-VA18 or (b) EVA-VA28 and neat bitumen 70/100, as a function of the Melt Flow Index value.

Figure 9. Viscosity evolution (at 10 and 100 s^{-1}) for 5 wt. % EVA-binders, as a function of EVA MFI value used for the modification of a 70/100 bitumen. Comparison with SBS and wax modified binders formulated with the same bitumen.

Figure 10. Dependence on MFI of EVA-binders (5 wt. % polymer) penetrations and ring & ball softening points.

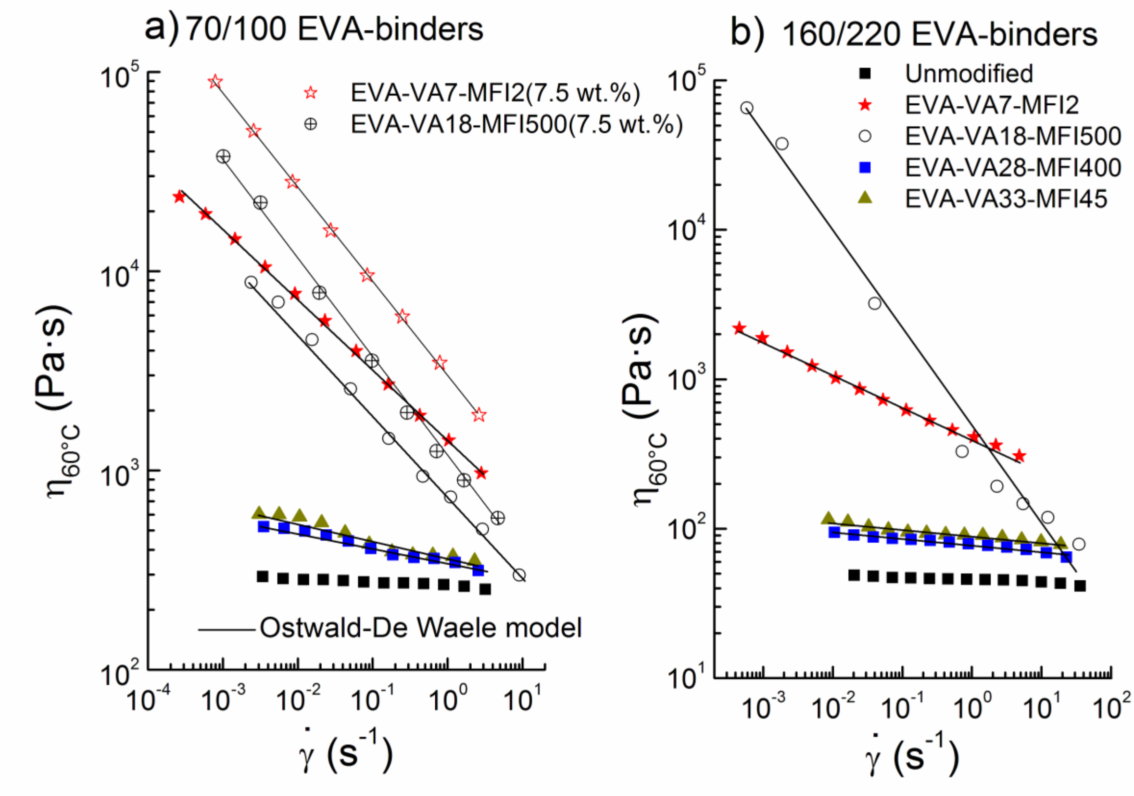
a) 70/100 EVA-binders
b) 160/220 EVA-binders
EVA-VA7-MFI2(7.5 wt.%)
EVA-VA18-MFI500(7.5 wt.%)
Ostwald-De Waele model
Unmodified
EVA-VA7-MFI2
EVA-VA18-MFI500
EVA-VA28-MFI400
EVA-VA33-MFI45
$\eta_{60°C}$ (Pa·s)
$\dot{\gamma}$ (s^{-1})
10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2}
10^{1} 10^{2} 10^{3} 10^{4} 10^{5}

Figure 1

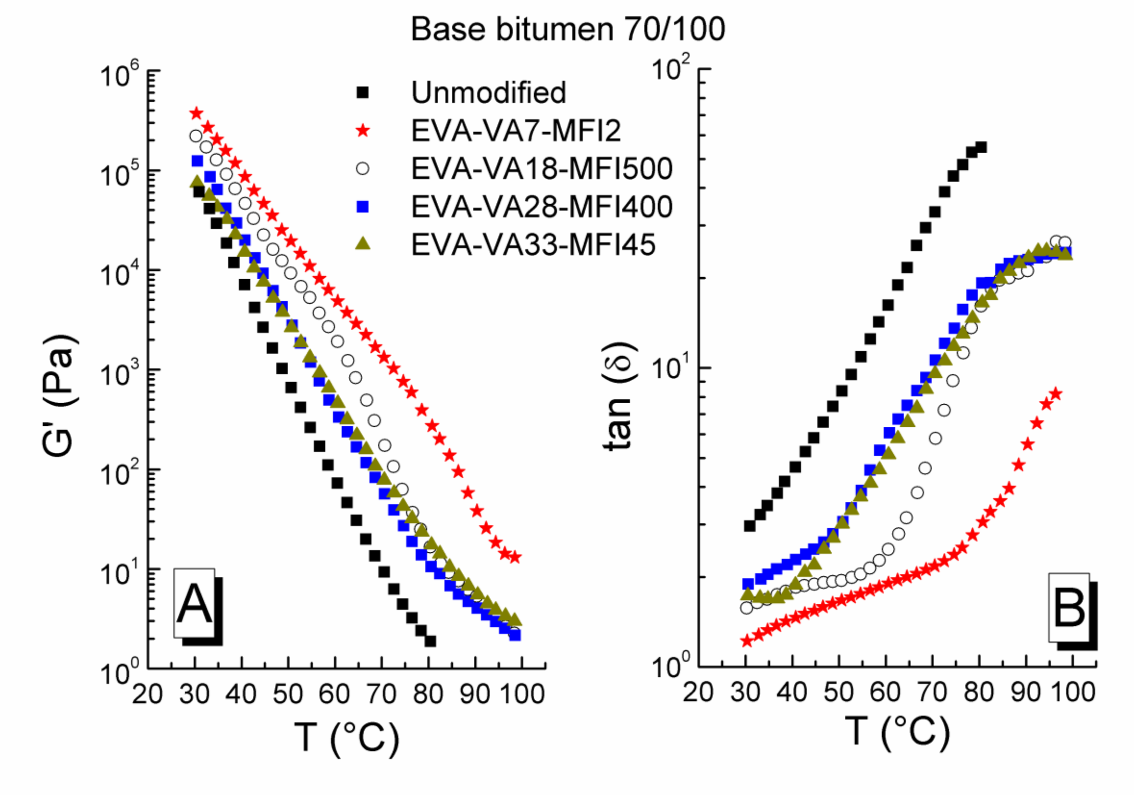
Base bitumen 70/100
Unmodified
EVA-VA7-MFI2
EVA-VA18-MFI500
EVA-VA28-MFI400
EVA-VA33-MFI45
G' (Pa)
10^0
10^1
10^2
10^3
10^4
10^5
10^6
T (°C)
20 30 40 50 60 70 80 90 100
A
tan (δ)
10^0
10^1
10^2
T (°C)
20 30 40 50 60 70 80 90 100
B

Figure 2

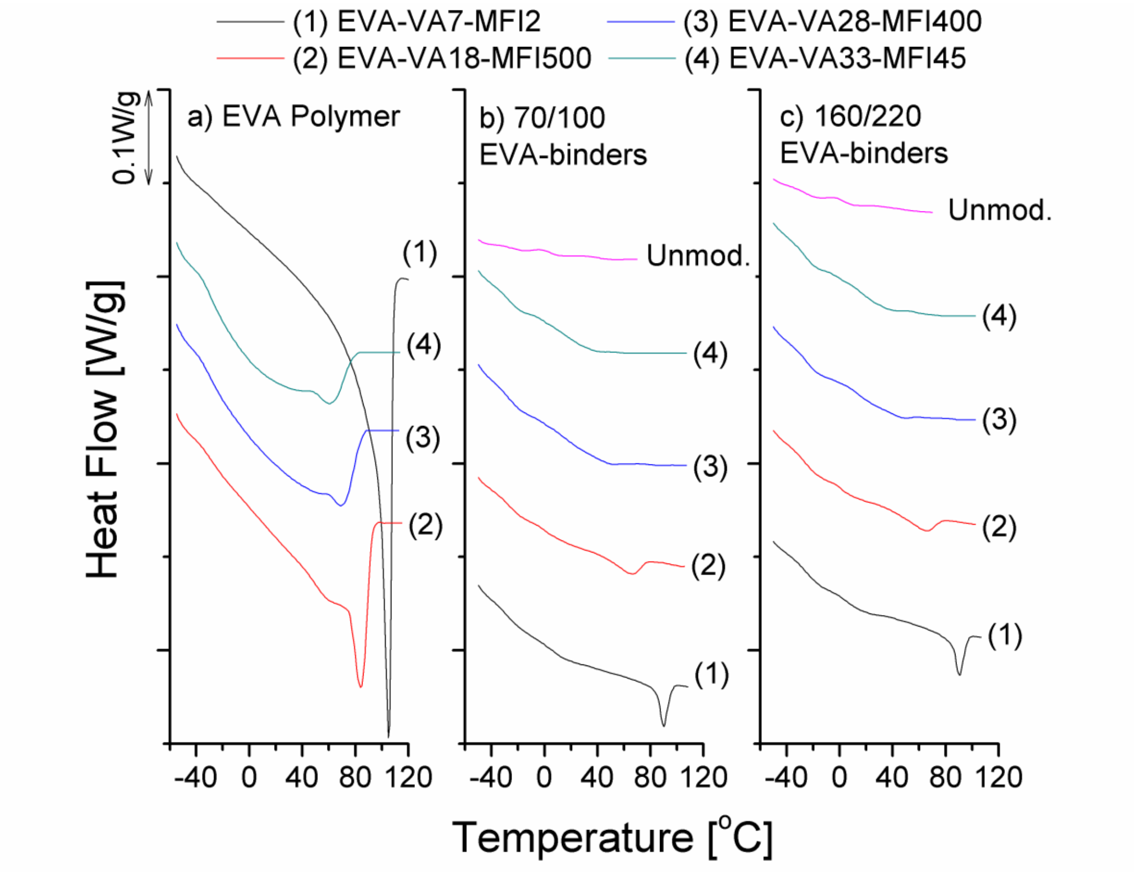
(1) EVA-VA7-MFI2
(3) EVA-VA28-MFI400
(2) EVA-VA18-MFI500
(4) EVA-VA33-MFI45
0.1W/g
Heat Flow [W/g]
a) EVA Polymer
b) 70/100
EVA-binders
c) 160/220
EVA-binders
Unmod.
(1)
(2)
(3)
(4)
-40
0
40
80
120
Temperature [°C]

Figure 3

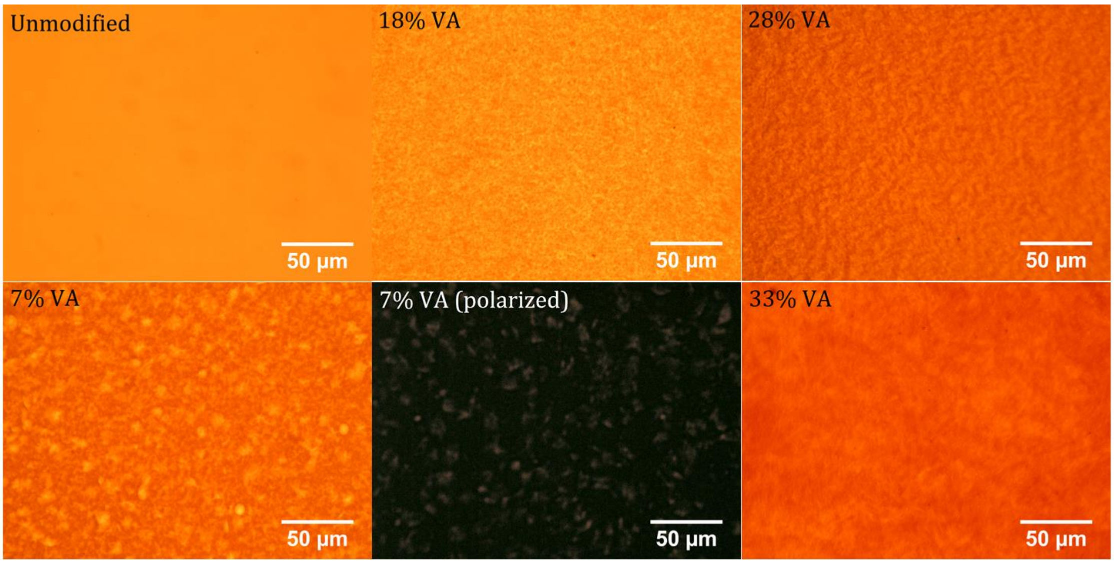

Figure 4

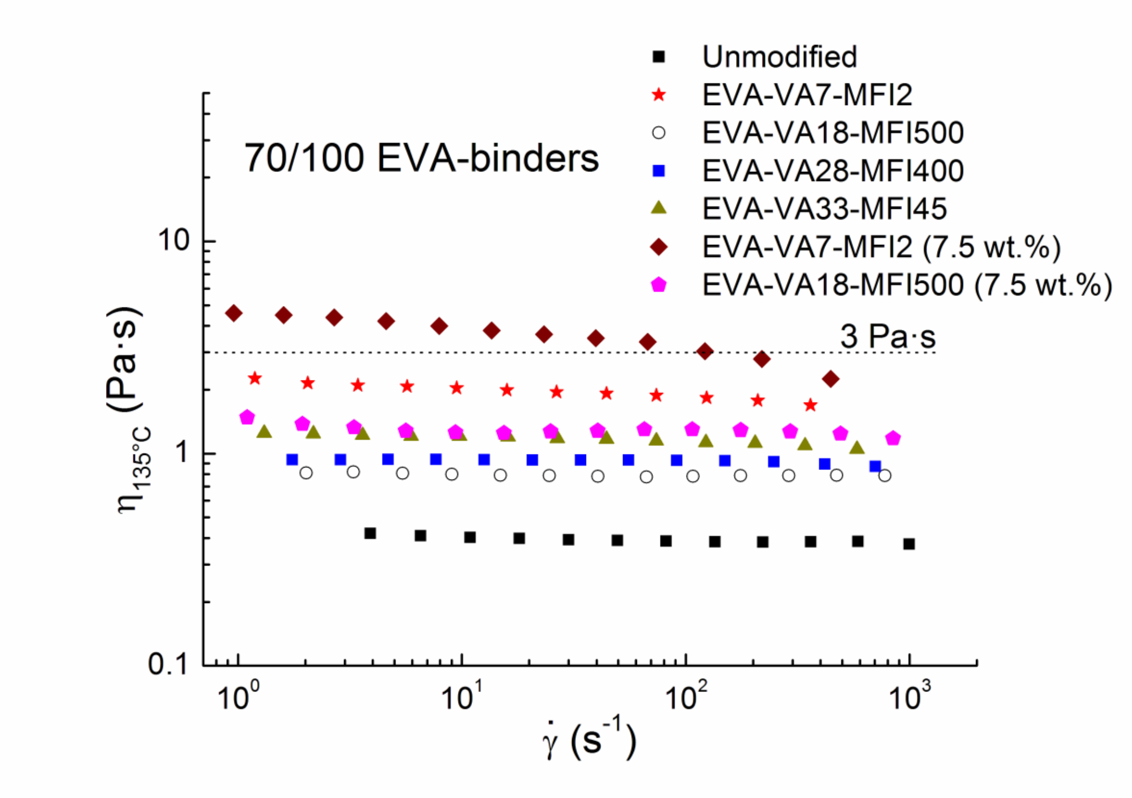
70/100 EVA-binders
Unmodified
EVA-VA7-MFI2
EVA-VA18-MFI500
EVA-VA28-MFI400
EVA-VA33-MFI45
EVA-VA7-MFI2 (7.5 wt.%)
EVA-VA18-MFI500 (7.5 wt.%)
3 Pa·s
$\eta_{135°C}$ (Pa·s)
10
1
0.1
10^0
10^1
10^2
10^3
$\dot{\gamma}$ (s^{-1})

Figure 5

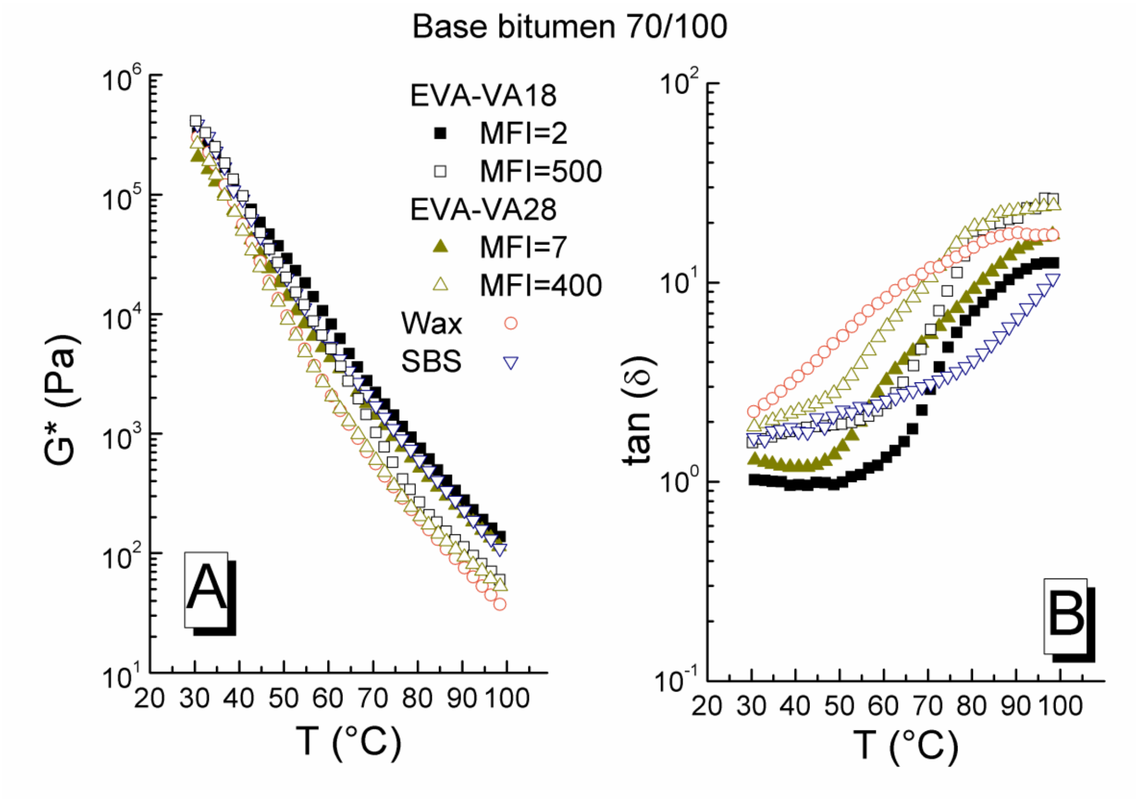
Base bitumen 70/100
G* (Pa)
tan (δ)
T (°C)
EVA-VA18
■ MFI=2
□ MFI=500
EVA-VA28
▲ MFI=7
△ MFI=400
Wax ○
SBS ▽
A
B
10^1
10^2
10^3
10^4
10^5
10^6
10^{-1}
10^0
20 30 40 50 60 70 80 90 100

Figure 6

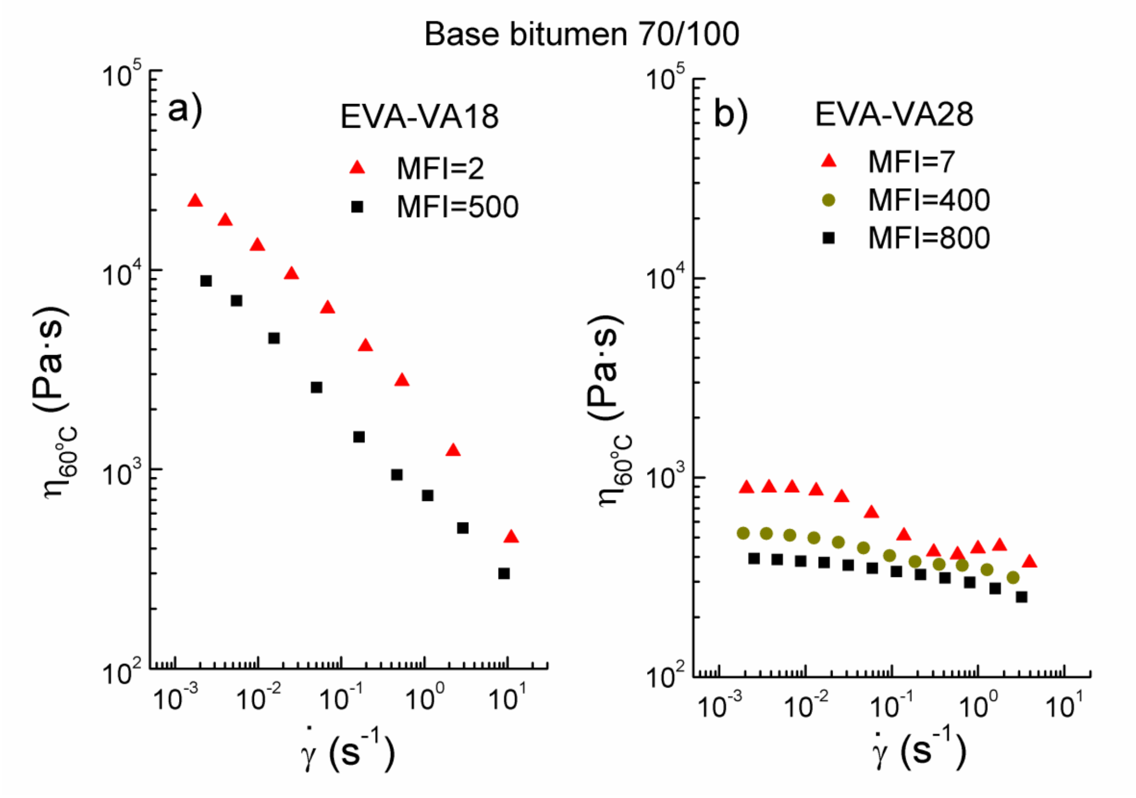
Base bitumen 70/100
a)
EVA-VA18
▲ MFI=2
■ MFI=500
b)
EVA-VA28
▲ MFI=7
● MFI=400
■ MFI=800
$\eta_{60^\circ C}$ (Pa·s)
$\dot{\gamma}$ (s^{-1})
10^2
10^3
10^4
10^5
10^{-3}
10^{-2}
10^{-1}
10^0
10^1

Figure 7

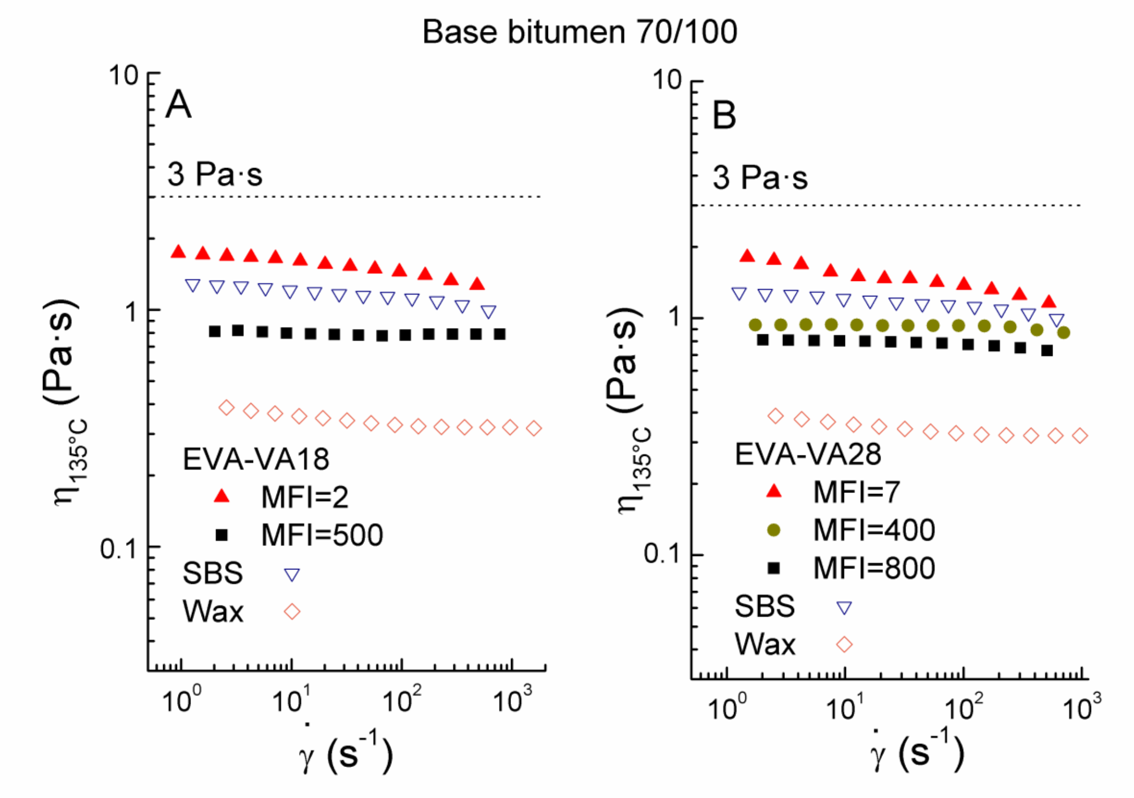
Base bitumen 70/100
A
B
3 Pa·s
3 Pa·s
$\eta_{135°C}$ (Pa·s)
$\eta_{135°C}$ (Pa·s)
10
1
0.1
EVA-VA18
MFI=2
MFI=500
SBS
Wax
EVA-VA28
MFI=7
MFI=400
MFI=800
SBS
Wax
10^0
10^1
10^2
10^3
$\dot{\gamma}$ (s^{-1})
$\dot{\gamma}$ (s^{-1})

Figure 8

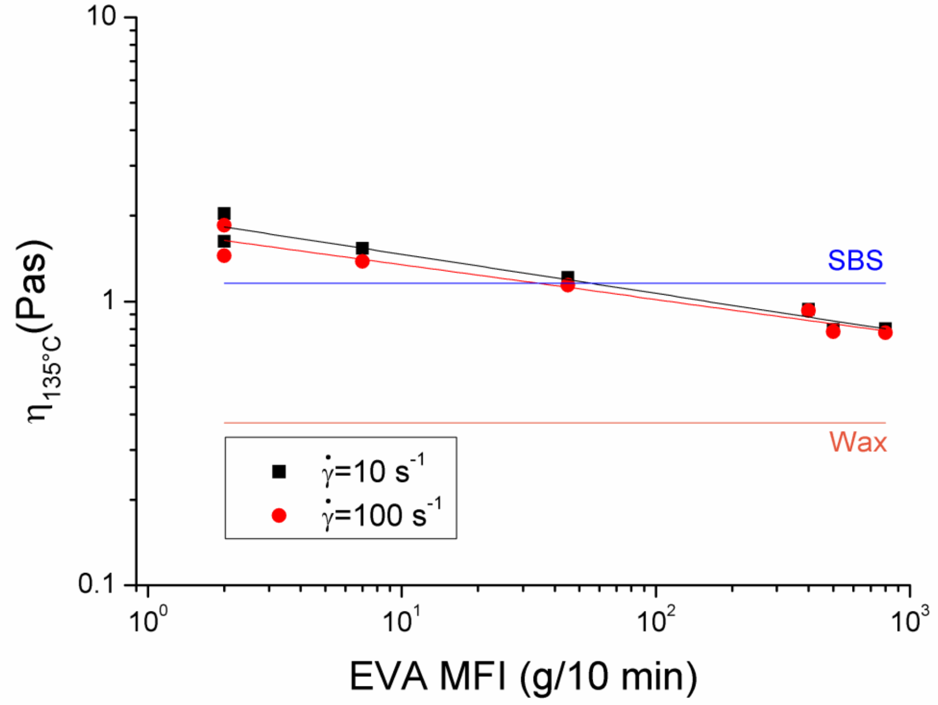
10
1
0.1
$\eta_{135°C}$(Pas)
10^0
10^1
10^2
10^3
EVA MFI (g/10 min)
SBS
Wax
■ $\dot{\gamma}$=10 s^{-1}
● $\dot{\gamma}$=100 s^{-1}

Figure 9

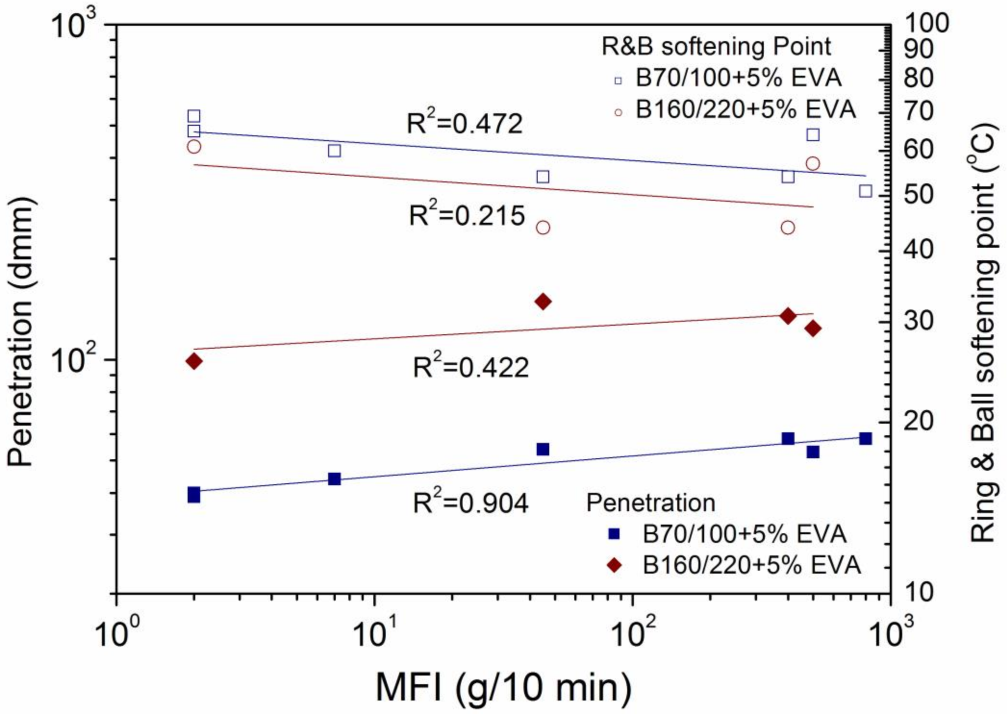
R&B softening Point
□ B70/100+5% EVA
○ B160/220+5% EVA
R^2=0.472
R^2=0.215
R^2=0.422
R^2=0.904
Penetration
■ B70/100+5% EVA
◆ B160/220+5% EVA
Penetration (dmm)
Ring & Ball softening point (°C)
MFI (g/10 min)
10^0
10^1
10^2
10^3
100
90
80
70
60
50
40
30
20
10

Figure 10