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Binder design for asphalt mixes with reduced temperature: EVA modified bitumen and its emulsions

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Abstract

High energy consumption and environmental risks are both associated to the use of hot asphalt mixes. In response to the need of more sustainable pavements, the modification of bitumen with low melting point EVA copolymers is investigated. Firstly, different modified binders containing EVA with varying VA contents (and so different crystalline fractions and melting temperatures) and Melt Flow Index (MFI) values were investigated. In the second stage, emulsification was implemented, in which the above EVA modified bitumen was suspended in the form of micro-size droplets in aqueous phase, in the presence of a surfactant. The results suggest that an optimum balance between VA content and MFI value will improve the binder rheological performance at medium-high in-service temperatures as well as its workability, and will facilitate its emulsification. Additionally, the binder viscosity is tremendously reduced after its emulsification, which allows mixing to be performed at much lower temperature, so reducing both energy consumption and environmental risks.

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1. Introduction

Bitumen, also found in natural deposits, is commonly a by-product of fractional distillation of crude oil, McNally (2011). Pavement is the top bitumen consumer, although other uses can be found in the roofing industry for this material. Bitumen is used as a binder to hold aggregates together in road pavement construction. Trend in the modification of bitumen arises as a consequence of the increasing demand of binders with improved resistance to permanent deformation, i.e. stiffer in the medium-high in-service temperature region, and more flexible at low in-service temperatures, i.e. preventing thermal cracking. In this sense, bitumen quality is often enhanced by polymer modification, to produce either physical or chemical interaction with the bituminous phase, Cuadri et al. (2015). The selection of the type of polymer is important, as various polymers provide unique characteristics in the final performance, and also during production, Zhu et al. (2014).

Handling of modified bitumen requires an elevated temperature to achieve optimum aggregate coating, and the energy spent negatively affects the environment. To overcome this issue, reduced temperature technologies are highly encouraged. On the one hand, polymer modified bitumens with lower viscosity that can be handled at lower temperatures without affecting their in-service performance represent a current concern. On the other hand, bitumen emulsions provide two joint benefits: 1) eliminating polymer-bitumen separation issue during storage; and 2) viscosity reduction. In fact, polymer modified bitumen emulsions have been successfully used for several decades by road industry due to their high performance in the application of chip seals and microsurfacing for heavy trafficked pavements, Lesueur (2011).

With the vision of greener development, reduced temperature technology such as emulsion is greatly considerable. However, to the recent literature, lack of information has been published in the field of bituminous emulsion, particularly for in-line emulsification of modified bitumen, in which EVA modified bitumen emulsion has been considered. This work offers a systematic study in exploring the effect of VA content, coupled with its melting point, and MFI value of EVA copolymer in the design of binders for reduced temperature technologies. Two differentiated parts are involved: 1) performance and processability of binders modified by EVA copolymer; and 2) their emulsions, concerning the ratio of bitumen to water phase.

Nomenclature

| | |
|-----------|----------------------------|
| $D_{3,2}$ | Sauter mean diameter |
| DSD | Droplet size distribution |
| EVA | Ethylene vinyl acetate |
| LVE | Linear viscoelastic region |
| G' | Storage modulus |
| G'' | Loss modulus |
| MFI | Melt flow index |
| PMB | Polymer Modified bitumen |

2. Experimental

2.1. Material and sample preparation

The bitumen selected for this study, supplied by Repsol (Spain) has a penetration grade of 70/100. EVA copolymer, also supplied by Repsol (Spain), was used as bitumen modifier by 5 wt.% addition into 150 °C molten bitumen. Dispersion process was done in two steps with the assistance of a Silverson L5M high shear homogenizer: 1) melting step at 3500 rpm for 15 minutes and 2) mixing step at 5000 rpm for 1 hour. Two varying VA contents, 18 and 28 wt.%, were studied. Additionally, the effect of the MFI value was also envisaged, by choosing two different MFI values of 2 and 500 for the 18 wt.% VA copolymer, and 7 and 400 for the 28 wt.% one. From this standpoint, the modified binder was then coded as 'Binder'-'VA content'-'MFI', for instance EVAMB-VA18-MFI2.

Based on the optimum performance, the selected binder was then emulsified into aqueous phase in the presence of 0.5 wt.% surfactant. The emulsification process was done in a colloid mill Denimotech DT03, and the emulsion collected in a pressurized vessel. Binder percentages chosen were 65 and 70 wt.% corresponding to typical applications of emulsion, such as microsurfacing and chip seals, respectively, Lesueur (2011).

2.2. Characterization

The binders were subjected to steady shear viscous flow tests at 60 and 135 °C. These measurements were performed in a controlled-stress rheometer Physica MCR 301 by Anton Paar, equipped with an electrically heated chamber. Serrated parallel plate geometry with 25 mm diameter was used. In addition, the viscoelastic properties of the binders, between 30-100 °C, were characterized by oscillatory shear temperature sweep tests in a controlled-stress Haake RS600, equipped with a TC501 temperature controller, at the heating rate of 1 °C/min. Serrated parallel plate geometry with 20 mm diameter was used. In order to determine the LVE region, stress sweeps were previously performed.

With regard to the emulsions, droplet size distribution was measured using laser diffraction technique in a Malvern mastersizer 2000. To characterize the droplet surface charge, zeta potential value was tested in a Malvern zetasizer through electrophoresis method. The rheological analysis for emulsion has been done by means of steady shear viscous flow tests at 30 °C, also performed in Physica MCR 301, but now equipped with 27 mm diameter serrated coaxial cylinder geometry.

3. Result and Discussion

3.1. Performance and processability of binder modified by EVA copolymer

The influence of EVA copolymer on the binder viscosity has been studied by means of steady shear flow tests at 60 °C and 135 °C (Fig. 1). The selection of 60 °C was based on the average asphalt temperature expected in a warm climate region, and 135 °C is a reference value for laydown and compaction operations and emulsification.

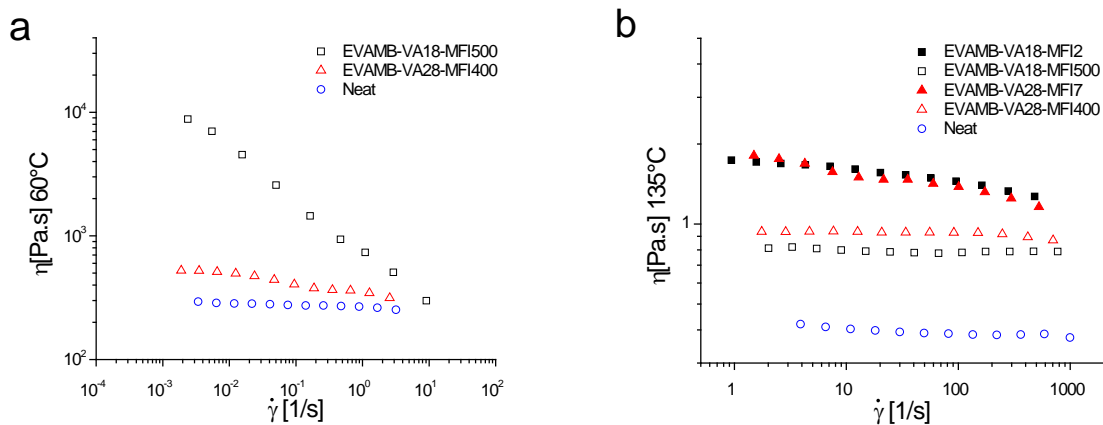


Fig. 1. Flow behavior of EVAMB at (a) 60 °C; and (b) 135 °C.

Binders modified with EVA copolymer exhibited improved resistance, as may be deduced from their viscosity increases observed at 60 °C, if compared to the neat 70/100 bitumen. The enhancement seemed to be significantly affected by VA content, so that the system VA18 was one order of magnitude more viscous than the PMB formulated with VA28 at low shear rates (Fig. 1a). In contrast, flow behavior at 135 °C did not appear to follow similar dependence on VA. At that temperature, MFI turned out to be the most relevant parameter. For instance,

EVAMB-VA18-MFI2 exhibits a viscosity close to the EVAMB-VA28-MFI7 one, which also applies for the other two cases (Fig. 1b). Knowing that molecular weight and MFI of polymer are inversely proportional, the chain entanglement and internal friction affect polymer flow behavior (and, therefore, PMB viscosity), Ravve (2012). As a result, binder viscosity decreases as EVA MFI value is higher, no matter the VA concentration studied (Fig. 1b).

Binder thermomechanical properties have been measured through temperature sweep measurements in oscillatory shear in a wide temperature range, 30 - 100 °C. Fig. 2 shows the evolution of the storage modulus, G' , as a function of temperature. PMB viscoelastic moduli increased by the development of EVA copolymer in bitumen matrix. Such an increase in G' would lead to an improved elastic performance at medium to high in-service temperatures. Moreover, the influence of VA content in binder is reflected on the G' comparison between VA18 and VA28 that demonstrates greater elastic response in VA18 case, which is more apparent as temperature rises. Interestingly, at 65 °C, a sudden change in this slope appears for binder VA-18 cases, indicating a polymer molecular rearrangement inside bituminous matrix as a consequence of EVA crystallites melting, Airey (2002); García-Morales et al. (2004). Conversely, a similar event is hardly seen for binder VA-28, due to a lower percentage of EVA crystalline fraction. The difference in percentage of crystal is related to the amount of non-crystallizable fraction in EVA, acetate pendant group, thereby, formation of crystal is more difficult in the case of binder with greater amount of VA content, Somrang et al. (2004).

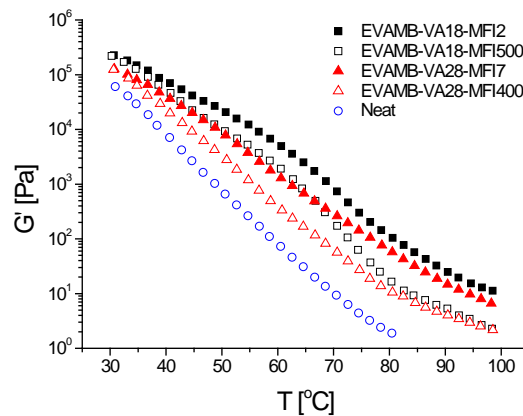


Fig. 2. Storage modulus dependence on temperature, ranging 30-100 °C.

For the same reason, the above commented higher viscosity at 60 °C of VA18 binder is closely linked to a higher percentage of EVA crystallites that leads to improved binder resistance to permanent deformation. Nevertheless, above the melting of the EVA crystalline fraction, e.g. 135°C, MFI is a key parameter to understand binder flow behavior (Fig. 1b). In this sense, EVAMB flowability was favored by selecting high MFI values, which would facilitate aggregate-binder mixing as well as other processes such as emulsification. On this ground, EVAMB-VA18-MFI500 was selected for being emulsified, due to its suitable balance between binder performance (i.e. high viscosity and elasticity at 60 °C) and processability (i.e. low viscosity at 135°C).

3.2. EVAMB emulsion

During emulsification, low viscosity of bituminous phase, as low as 200 mPas or less, is recommended to facilitate the breaking and dispersion process, Read and Whiteoak (2003) and with a water phase temperature at 50 °C, Salomon (2006). As seen in Fig.1b, viscosity of EVAMB-VA18-MFI500 at 135 °C laid around 782 mPas, beyond the recommendation. Therefore, a higher temperature, around 145°C, was required with an attention paid for compensating water phase evaporation in colloid mill. Thus, pressure during emulsification was maintained above saturated water pressure at its corresponding temperature, above 5 bar.

Bituminous emulsion DSD curves are shown in Fig. 3 as droplet size by volume fraction. Unimodal distributions were perceived for both modified bitumen emulsion cases, whilst neat emulsion appears as unimodal with a shoulder at low particle size. Conversion of DSD volume fraction to volume to surface mean diameter, the so called Sauter mean diameter, $D_{3,2}$, was carried out as follows:

$$D_{3,2} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \quad (1)$$

where n_i is the number of droplets with diameter d_i . As may be seen in Table 1, EVAMB-E-65 exhibited larger $D_{3,2}$ values than its corresponding neat emulsion (Neat-E, having 65% bitumen), as a consequence of a more difficult droplet breaking during process, Lesueur (2011), derived from a more viscous bituminous phase. Likewise, processing of the most concentrated emulsion was also hindered by the higher bulk viscosity of the resulting emulsion, as deduced from $D_{3,2}$ value of EVAMB-E-70 being larger than EVAMB-E-65.

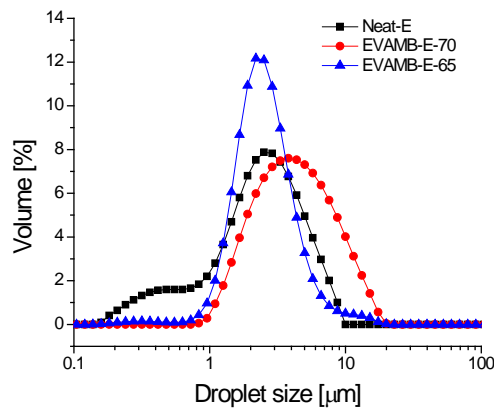


Fig. 3. Droplet size distribution of the emulsions obtained.

Table 1. Sauter mean diameter and zeta potential of emulsions at pH of 1 and ambient temperature

| Emulsion | $D_{3,2}$ [μm] | ζ_{AVG} [mV] |
|------------|-----------------------------|---------------------------|
| Neat-E | 1.443 | 74.68 |
| EVAMB-E-65 | 2.287 | 68.15 |
| EVAMB-E-70 | 3.641 | 82.45 |

N-tallow alkyl tri-methylene diamine has been used as surfactant (cationic type). The lipophilic (apolar) part interact with bituminous phase resulting the other end of diamine group (polar) available for water, Salager (2002). Surfactant has been prepared in acidic water phase to allow amine as a proton receptor being positively charged. In this sense, zeta potential measurement was performed to estimate the charged value, and the results are shown in Table 1. All emulsion studied present positive charge value higher than 65, suggesting a high electrophoretic mobility that is equivalent to the estimated surface charge value, hence providing excellent stability.

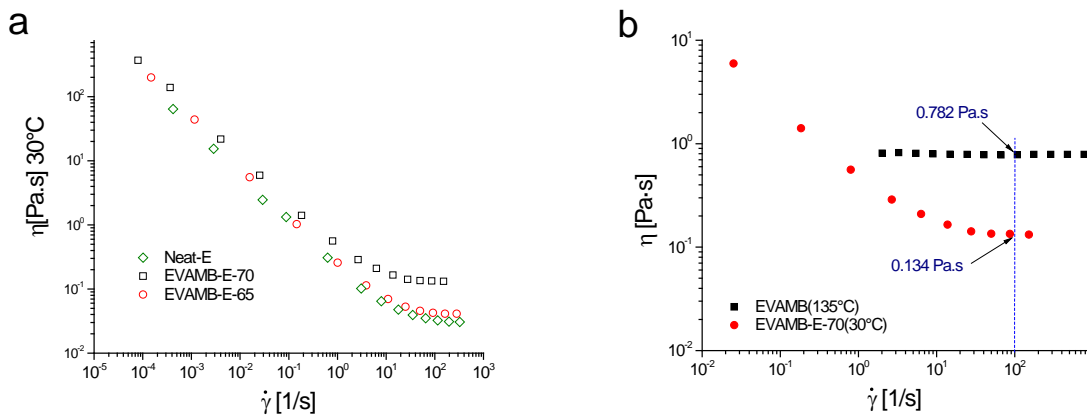


Fig. 4. (a) Viscosity curve of emulsion at 30 °C and (b) Viscosity comparison between EVAMB at 135 °C & EVAMB emulsion at 30 °C.

Viscosity curves of emulsion for neat and both EVAMB cases at 30 °C are displayed in Fig.4a. The selection of 30 °C was based on emulsion application temperature, for cold mixes technology, typically from 25 to 60 °C, Rubio et al. (2012). For all emulsions tested, a shear thinning behavior was noticed from 10^{-4} s $^{-1}$ to 10 s $^{-1}$, followed by a constant viscosity. Neat emulsion with 65 % suspended bituminous phase and EVAMB-E-65 gave a close value of high-shear-rate limiting viscosity, around 35 mPa·s, whilst EVAMB-E-70 has a value about 134 mPa·s. This result agrees with the larger volume fraction of disperse phase of system EVAMB-E-70, which leads to a higher packing density and, therefore, to a higher viscosity of the expected deflocculated emulsion at high shear rate, Otsubo and Prud'homme (1994); Carrera et al. (2015); Read and Whiteoak (2003).

In the interest of comparing the two tested methods, binder viscosity curve at 135 °C (elevated temperature method) and its emulsion with 70% bituminous phase (reduced temperature method) were shown in Fig.4b. In that particular case, emulsion technology presented a viscosity difference by 6 times lower than the elevated temperature method for a more effective flowability.

4. Conclusion

The study of binder rheological behavior, through steady shear viscosity and oscillatory shear measurements, suggests that EVA copolymer containing lower VA content, 18%, affects more the viscoelastic parameter and thermal susceptibility of modified binder within its in-service temperature. Whilst, binder flow resistance was seen to decrease by increasing MFI after crystalline fraction vanished, suggesting better flowability for binder with higher MFI. The necessity of enhanced fluidity is to promote a milder processing condition for the production of EVA modified bitumen emulsion. Thus, EVAMB-VA18-MFI500 was selected for emulsion process.

Bituminous to water phase ratio affects DSD and, mainly, high-shear-rate limiting viscosity of the emulsion. Coarser droplet size, as perceived in $D_{3,2}$, was reported for higher bitumen concentrations and/or for more viscous binders. In the interest of underlining the involvement of emulsion technology, emulsion viscosity at 30 °C was reported 6 times lower than binder viscosity at 135 °C, regardless the temperature difference that could suppress the energy consumption and environmental risk.

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