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Microstructure and rheological response of laboratory-aged SBS-modified bitumens

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Microstructure and rheological response of laboratory-aged SBS-modified bitumens

Abstract

Polymer additives are widely used to improve the performance of road bitumens including their resistance to hardening during oxidation, although their oxidative inhibitor effect has not been well documented. This study aims to investigate the effect of laboratory-simulated ageing on the microstructure, and rheological properties of Polymer Modified Bitumens (PMBs) prepared with a Styrene-Butadiene-Styrene (SBS) copolymer and sulphur as a cross-linker. The laboratory ageing was conducted through the Rolling Thin Film Oven (RTFO) and the Pressure Aging Vessel (PAV) procedures. The unaged and aged binders were characterised using the Multiple Stress Creep and Recovery (MSCR) test, Gel Permeation Chromatography (GPC) and fluorescence microscopy. The MSCR test showed that the cross-linked polymer had a higher capability of mitigating the effect of bitumen hardening on the rheological response, while for the PMBs without cross-linking, the polymer effects decreased significantly after RTFOT ageing. The GPC results showed that the aromatics, resins and asphaltenes fractions of the unmodified bitumens shifted towards heavier molecules after one cycle of PAV ageing but showed limited variation with further ageing. Similar behaviour was observed for the uncross-linked polymer binders, while for the cross-linked polymer binder, the behaviour depended on the polymer concentration.

Key-words: polymer-modified bitumen, SBS, ageing, GPC, percent recovery, sulphur, MSCR.

Introduction

The modification of road bitumens with polymeric additives was developed through intense investigations which started decades ago and are still on-going (Airey, 2002, 2003; Goodrich, 1988; Lesueur, 2009; Lo Presti, 2013; Polacco, Filippi, Merusi, & Stastna, 2015; Yildrim, 2007; Zhu, Birgisson, & Kringos, 2014). The quality of the modification can be defined as the capability of small quantities of polymer in creating a product with improved performances compared to those of the base bitumen. In particular, such material is expected to be stiffer than the base bitumen at high pavement temperatures, to be softer than the base bitumen at low and intermediate pavement temperatures, and to maintain adequate levels of workability during the production and laying of asphalt mixtures. Different properties such as reduced moisture susceptibility, ageing resistance and storage stability need to be evaluated.

These properties represent the macroscopic result of complex chemical and thermodynamic interactions that occur at the microscopic level between the polymer and the bitumen. These interactions consist mainly of the polymer swelling in the bitumen phase by absorbing the most compatible fractions while maintaining its own structure. The complexity of such mechanisms is mostly due to the large variability in the composition of bitumens and polymers that affect their affinity, and therefore, the properties of modified bitumens (Polacco et al., 2015).

Although some of the advantages of polymer modification are clear, there are technical drawbacks and concerns that, besides cost, appear to limit the widening of the use of polymer additives with road bitumens. One of these aspects is the effect of polymers on the oxidative ageing mechanism occurring in bitumens. Even though several road agencies use polymers (e.g., SBS) as ageing inhibitors (Bahia et al., 2001), their beneficial effect on the resistance to hardening during oxidation of PMBs does not have a full consensus (Zhu et al., 2014). However, the understanding

of their contribution to the oxidative hardening mechanism of PMBs is of importance from several perspectives. Lowering the hardening of the asphalt mixtures in the field can contribute to delivering longer lasting and cost-efficient pavements. Furthermore, polymer modification might provide a higher quality Reclaimed Asphalt Pavement (RAP) by reducing the oxidative hardening of the binder in recycled mixtures.

This study aims to investigate the changes in the microstructure and rheological response of SBS modified bitumens subjected to laboratory-simulated ageing. Five PMBs were prepared by mixing a single base bitumen with different concentrations of a radial SBS copolymer. Sulphur was used as a cross-linker in three of the five PMBs. As a comparison, sulphur was also added to the unmodified bitumen.

The advantages of using sulphur in unmodified and elastomer modified bitumens have been investigated by several researchers (Das & Panda, 2017; Kumar, & Khan, 2013; Mandal, Sylla, Bahia, & Barmand, 2015; Masegosa et al., 2012; Zhang, Yu, Wu, 2010). Considering the procedures followed for bitumen modification in the referenced works, it appears that sulphur can be used as a modifier in bitumen with concentrations up to 5% by the weight of bitumen (Das & Panda, 2017). However, in the early ’70s, the use of sulphur in road bitumens received extra attention prompted by the abundance of this material from industrial processes. Several projects were conducted investigating the production of Sulphur Extended Asphalt (SEA) where the concentration of sulphur was higher than 35% by weight of bitumen (Bukowski, Youtcheff, & Harman, 2012; Nazarbeygi & Moeini, 2013). Among the potential benefits, the environmental impacts of processing the SEA at high temperatures were considered due to the potential emission of sulphur compounds. It appears that below 150°C the emission of sulphur compounds (e.g., H_2S, SO_2) remains within acceptable limits.

On the other hand, when sulphur has been used as a cross-linker, the concentration is considerably lower at 0.1% by the weight of bitumen or even lower (Mandal et al., 2015, Zhang et al., 2010). At such low concentrations, sulphur is not expected to improve (or extend) the properties of the bitumen. Its purpose is to improve the compatibility between the SBS and the bitumens. However, SBS modification is usually conducted at 180°C that is above the limit identified with the SEA to limit emissions. In this case, although the sulphur concentrations are lower, the use of temperatures above 150°C may represent a concern.

The modified bitumens were characterised by the Multiple Stress Creep and Recovery (MSCR) test (AASHTO T 350), fluorescence microscopy and Gel Permeation Chromatography (GPC). The MSCR test was developed explicitly for polymer-modified bitumens to overcome the shortcomings shown by the Superpave method (AASHTO M 320) in controlling the rutting resistance of Polymer Modified Mixes (D'Angelo & Kluttz, 2007). The advantage of using this test is that (at least for the unaged and the RTFO-aged conditions), the applied stress is capable of producing slippage in the polymer chain. The selected rheological indicators are the non-recoverable compliance (J_{nr}) and the average percent recovery (R), both measured at a stress level of 3.2 kPa as recommended by AASHTO M 332. The average percent recovery (R) at 3.2 kPa is a measure of the polymer elasticity that also depends on the flexibility of polymer chains, the presence of a structured network, and the molar mass (or molecular weight) of the polymer chains. Therefore, its value could be advocated as an indicator of polymer efficiency (Golalipour, 2011; Clopotel & Bahia, 2012).

On the other hand, the J_{nr} is representative of the response of the resistance to the accumulation of permanent deformation of the whole bitumen + polymer system. The GPC was used to measure the changes in the microstructure of the bitumens, at different levels of laboratory-simulated

ageing. Fluorescence microscopy was used to evaluate the effect of sulphur on the morphology of the PMBs. The binders were short-term aged by RTFO, and long-term aged by PAV according to the AASHTO R 28.

Background

The oxidation of bitumen is produced by the diffusion of atmospheric oxygen through a thin film of bitumen that coats the mineral aggregates. As with other hydrocarbon materials, the oxidative process originates the formation of carbonyl compounds characterised by strong associative forces whose concentration increases with the oxygen uptake (Liu et al., 1998). Four carbonyl compounds containing oxygen have been identified: ketones, anhydride, carboxylic acid and sulfoxides (Petersen, 1984). Ketones and sulfoxides are in the majority because their molecules are more sensitive to oxidation. Sulfoxides form at the start of bitumen ageing but only for a limited time, while the formation of ketones, carboxylic acid and anhydride occurs with time along with the oxygen uptake (Liu et al., 1998). The presence of such strong interactive forces contributes to increasing the content of heavy and polar groups of molecules also known as asphaltenes. The consequence is the reduction in the molecular mobility of the bitumen under shear stress which causes hardening. Macroscopically, this mechanism results in an increase in viscosity and stiffness, and in a reduced strain tolerance with the aged asphalt mixtures being more susceptible to cracking at low and intermediate temperatures (Corbett & Merz, 1975; Liu et al., 1998; Page, Murphy, Ruth, & Roque, 1985; Sisko & Brunstrum, 1968).

However, various questions remain unanswered. How do polymers affect this mechanism? How do polymers mitigate the formation of carbonyls? How do polymers contribute to reducing the formation of asphaltenes? Unfortunately, the large variety of polymers and bitumen sources

available on the market and the complexity of their interactions does not allow a general conclusion to be drawn.

For the reasons above, the study of oxidative ageing in PMBs has been of considerable academic and industrial interest (Airey & Brown, 1998; Cortizo, Larsen, Bianchetto, & Alessandrini, 2004; Ghavibazoo & Albdelrahman, 2014; Hao, Huang, Yuan, Tang, & Xiao, 2017; Kumbageri & Biligiri, 2015, 2016; Lu & Isacsson 1999, 2000; Lu, Sandman, & Redelius, 2010; Lucena, Soares S., & Soares J, 2004; Negulescu et al, 2006; Oliver & Tedrera, 1997; Ruan, 2003; Ruan, Davison, & Glover, 2003). The changes in the bitumen composition have been used as indicators to quantify the severity of the oxidative mechanism. For instance, Fourier Infrared Spectroscopy (FTIR) has been used to measure the formation of carbonyls at different levels of ageing (Lucena et al., 2004; Lu & Isacsson, 1999, 2000; Negulescu et al., 2006). Likewise, Gel Permeation Chromatography (GPC) has been used to evaluate the variation (with ageing) in the molecular weight distribution of the polymer and the bitumen phases (Airey & Brown 1998; Cortizo et al., 2004; Goodrich, 1988; Hao et al., 2017; Lu & Isacsson, 2000; Lu et al, 2010; Negulescu et al., 2006). Alternative approaches promote the use of the variation in the asphaltenes content as an indicator of the ageing susceptibility of bitumen (Kumbageri & Biligiri, 2015, 2016).

Besides compositional methods, mechanical characterisation has also been contemplated to quantify bitumen oxidation. The majority of these works aim to assess the role of the polymers in the oxidative mechanism through the comparison of physical parameters (i.e., penetration, softening point, viscosity, complex modulus and phase angle) of unmodified and polymer modified bitumens under the same level of ageing. The findings from these studies do not seem to converge towards the definition of a unique ageing mechanism. Nevertheless, some general conclusions can be drawn for some polymers.

The SBS copolymer appears to reduce the formation of sulfoxide while producing a negligible effect on the rest of the carbonyls (Lu & Isacsson, 2000). Additionally, results from the GPC show that the polymer chain undergoes thermo-oxidative degradation during the short-term and the long-term ageing (Airey & Brown, 1998; Cortizo et al., 2004; Lu & Isacsson 1999, 2000; Lu et al., 2010; Negulescu et al., 2006, Xu, J., Zhang, A., Zhou, T., Cao, and Xie, Z. 2007; Xu, X., 2017). Such deterioration seems to induce a more viscous response of the PMBs mitigating the hardening of the bitumen phase. However, the conclusions related to the compositional changes occurring in PMBs with ageing, are often generic and sometimes conflicting even when different studies focus on the same polymer (e.g., SBS). This aspect depends probably on the fact that the study of the interactions between polymer and bitumen is very complicated since both the constituents show considerable variability in their constitution and their interactions.

Although the problem appears to be complicated, in this study some shortcomings in the existing work have been identified. In the majority of the studies, the Job Mix Formula (JMF) of the PMBs is given in terms of polymer concentration only. No details on the use of a cross-linker, stability or level of dispersion of the polymer (morphology) are given. Furthermore, in most of the studies, the bitumens are laboratory-aged up to a single cycle of the Pressure Ageing Vessel (PAV) with no additional or intermediate ageing exposure. In the case of PMBs, such ageing conditions might not be severe enough to produce significant changes in the microstructures of the PMBs due to their high consistency at the PAV conditions (Anderson & Bonaquist, 2012).

Furthermore, the Dynamic Mechanical Analysis (DMA) of PMBs is conducted in the linear viscoelastic region (LVE) where the low strain level used in the tests does not allow the stress dependency of polymers to be considered and therefore may provide a weak correlation with asphalt mixture performance (D'Angelo & Kluttz, 2007). The strain dependency of polymers

depends on the fact that when their chains are extended, glassy or crystalline regions and chain entanglement can produce the distortion of the morphology with a consequent change in their physical response (Airey, Rahimzadeh, & Collop, 2004; Bahia, Zhai, Onnetti, & Kose, 1999; D'Angelo & Kluttz, 2007; Kose, Guler, Bahia, & Masad, 2000; Masad & Somadevan, 2002). Therefore, the effect of the thermo-oxidative degradation of the polymer chain on the physical response of PMB should be determined at stress levels higher than those used for LVE characterisation (Cuciniello et al., 2018; Hintz, Velasquez, Li, & Bahia, 2011; Singh, Saboo, & Kumar, 2017).

Materials and methods

Materials

Six types of bitumen were prepared by combining one base bitumen (Penetration grade –70/100 pen) with a radial SBS copolymer (polystyrene content 29-31%), and sulphur (S) used as a cross-linker. The details of the composition of the bitumens are given in Table 1.

Table 1 – Bitumens used in the experimental study

Bitumen	SBS [%]	Sulphur [%]	Mixing T. [°C]	Mixing t. [min]
Pen 70-100 (Pen)	-	-	-	-
Pen/S	0	0.1	180	180
SBS 2/S	2	0.1		
SBS 4/S	4	0.1		
SBS 4	4	0		
SBS 6/S	6	0.1		
SBS 6	6	0		

Methods

Preparation of SBS modified bitumens

Three PMBs were prepared by mixing the base bitumen with three SBS concentrations respectively of 2% (medium-low content), 4% (high content) and 6% (very high content). In this case, sulphur was used at a concentration of 0.1% with respect to the polymer + bitumen weight as a cross-linker. Therefore, PMB/S with different polymer contents have a different cross-link density of the polymer network (weight ratio between cross-linker and polymer). Future works might consider the use of a constant cross-link density. Two additional SBS modified bitumens were prepared by mixing the base bitumen with two concentrations of SBS (4% and 6%) without the addition of sulphur (i.e., SBS 4, SBS 6). Finally, the sixth bitumen was produced by mixing

the base bitumen with 0.1% of sulphur by weight (Pen/S). A high shear mixer was used in the preparation of the bitumens.

Storage stability

The stability of the SBS modified bitumens was determined as per the ASTM D 7173 'Tuben Test' on the SBS 6/S and the SBS 6 bitumens. Only the SBS 6/S bitumen was found to be stable at storage.

Fluorescence Microscopy

A Leica® DM LB fluorescence microscope was used to capture images of the PMB morphology at 10x magnification. The sample preparation consisted of producing at room temperature bitumen stripes of about 10 mm x 50 mm x 2 mm. Afterwards, these stripes were refrigerated at -18 °C for 10 hours. Then, once the stripes were solid and brittle, they were cut, and the surface corresponding to the cut was attached to a glass microscope slide. To obtain representative images of the morphology, nine surfaces per bitumen were prepared.

The sample preparation method was followed to obtain the bulk morphology that is not affected by the contact with cold surfaces. More details on the effects of the sample preparation on the morphology of the SBS modified bitumens are given in Soenen et al. (2008).

Laboratory Simulated Ageing

The bitumens were short-term laboratory aged (STA) in the Rolling Thin Film Oven (RTFO) and long-term aged (LTA) in the Pressure Ageing Vessel (PAV) by following AASHTO R 28. Besides the PAV exposure of 20 hours (1 PAV), additional PAV exposures were included: 40 hours (2 PAV) and 80 hours (4 PAV). The PAV ageing was conducted at 100°C.

Gel Permeation Chromatography

The molecular weight distributions of the samples were measured from solution in Tetrahydrofuran (THF) (10 mg/mL) by using a Gel Permeation Chromatography (GPC) apparatus Perkin Elmer 200 Series. The apparatus was equipped with two columns in series: a Resipore column, 3µm, 300x7.5 mm from Agilent (M_w operating range up to 500.000 Da); and a Phenogel column, 5 µm 50 Å, 300x7.5 mm, from Phenomenex (M_w operating range from 100 to 3000 Da). The system was maintained at 40°C by a Peltier column oven Perkin Elmer 200 Series, and a Flexar UV/VIS Perkin Elmer was used as a detector. The volume of solution injected was 15 µL. The flow rate of the solvent was 1 mL/min. Samples containing SBS and sulphur were filtered before injection using a 0.45 µm PTFE filter. Filtering the solution before its injection in the column represents a practice conducted to prevent the column from clogging.

Before testing the PMBs, the base bitumen and the SBS copolymer were tested separately to identify their retention time interval. The polymer resulted in a retention time interval between 10 and 12 minutes, while the neat bitumen was found between 12 and 20 minutes. Nevertheless, in the case of PMBs, a partial overlapping of the signals was observed because a portion of the polymer chain undergoes thermo-oxidative degradation during blending, STA or LTA with a consequent weight reduction. This overlap indicates that GPC cannot entirely separate base bitumen and SBS polymer.

In the subsequent analysis, the results of the GPC refer to the portion of chromatogram comprised between 12 and 20 minutes. In the case of Pen and Pen/S bitumen, this portion is representative of the whole microstructure of the bitumen (light + heavy fractions). In the case of SBS modified bitumens, this portion may include both bitumen and polymer molecules. Therefore, this portion can be defined as the ‘bitumen-rich phase’. The polymer phase (10-12 minutes) was not considered

because it is not visible in the chromatograms of the PMB/S bitumens. The reason for this is that the use of sulphur as a cross-linker promotes the reticulation of the polymer in the bitumen. At a high level of reticulation, the THF cannot dissolve the polymer phase, which remains in the filter used before injecting the solution into the column.

The bitumen and the bitumen-rich phases show a bimodal curve with two distinct peaks (Figure 1 – Curve 1 and Curve 2). Curve 1 is representative of the heavier fractions (possibly asphaltenes) that are characterised by lower retention times. Curve 2 represents the medium and lighter fractions with higher retention times (lower molecular weights). This fraction possibly consists of aromatics and resins. Saturates are not visible with the UV.

The chromatogram from the GPC device needs to be considered as the raw data from this test. Different types of parameters can be extracted from the 'raw chromatogram' by conducting the numerical analysis of such curves. In this study, the ageing indices indicative of the changes in the bitumen and PMBs microstructures were calculated by using the area beneath the curves of the heavy and the light fractions in the chromatograms. The first one is proportional to the weight fraction of heavy molecules (Curve 1). While the second one is proportional to the weight fraction of light molecules (Curve 2). In the case of PMBs, the heavy and light fractions include polymer and bitumen molecules. The curves related to the heavy fractions and the light fractions were extracted from the chromatograms through the baseline removal and the deconvolution of the biphasic curve of the bitumen. The process will not be detailed for the sake of brevity. However, the details on the mathematical deconvolution of GPC chromatograms can be found in Bartels et al. (2010) and Jenning et al. (2013). An example of the bimodal curve of bitumens' chromatogram is given in Figure 1.

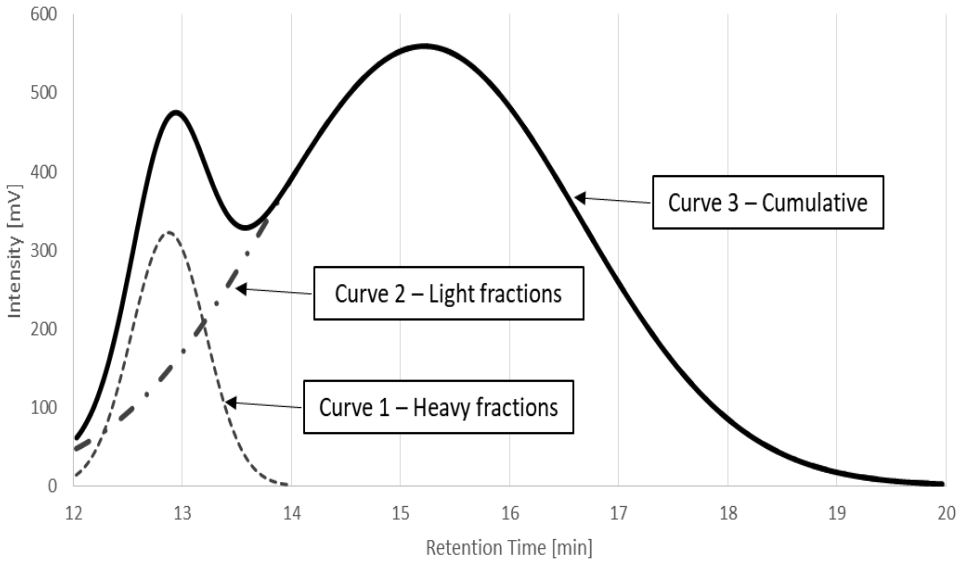


Figure 1. Chromatogram of Pen bitumen. Curve 3 – bimodal curve of the bitumen (cumulative); Curve 1 – curve of heavy fractions after deconvolution; Curve 2 - curve of light fractions after deconvolution.

The ageing indexes were calculated using the following equations:

The weight percentage of the heavy fraction (R_H)

$$R_h = \frac{\int Curve_1}{\int Curve_1 + \int Curve_2} \quad (1)$$

The weight percentage of the light fraction (R_L)

$$R_L = 1 - R_H \quad (2)$$

Multiple Stress Creep and Recovery (MSCR) Test

The MSCR was conducted as per AASHTO T-350 for the sake of consistency with the standards used for the PAV ageing (AASHTO R 28) and PG-grading (AASHTO M 320). The test was conducted at two stress levels: 0.1 kPa and 3.2 kPa. At each stress level, ten creep and recovery cycles were applied. The values of J_{nr} and R were calculated at each loading cycle and then averaged at each stress level. The non-recoverable compliance (J_{nr}) at the n-cycle was calculated using Equation (3).

$$J_{nr}^{n}(kPa^{-1}) = \frac{\varepsilon_r^n - \varepsilon_0^n}{\tau_0} \qquad (3)$$

Where:

- ε_r^n is the strain value at the end of the recovery phase;
- ε_0^n is the initial strain value at the beginning of the creep portion;
- τ_0 is the value of the stress level used in the loading cycle.

The percent recovery (R) at the n-cycle was calculated using Equation (4).

$$R^n(\%) = \frac{\varepsilon_c^n - \varepsilon_r^n}{\varepsilon_c^n - \varepsilon_0^n} \qquad (4)$$

Where ε_c^n is the strain value at the end of the creep portion (significance of other terms given in Equation (3)). According to AASHTO M 332, the traffic designation is determined as a function

of average J_{nr} value calculated at the stress level of 3.2 kPa. Therefore, the results incorporated in this paper refer to the stress level of 3.2 kPa.

The MSCR measures the rutting resistance of bitumens. It is known that rutting occurs at an early stage in the pavement life and therefore the use of very long-term aged bitumen might not be representative of field conditions. However, in this study, the MSCR has not been included for grading purposes but rather to provide rheological indicators (J_{nr} and R @3.2kPa) measured at strain levels higher than those considered in the LVE characterisation (G*, δ). In particular, the percent recovery (R) is considered an indicator of the integrity of the polymer network (Golalipour, 2011; Clopotel & Bahia, 2012). On the other hand, the J_{nr} that measures the resistance to the accumulation of permanent deformation might provide indications on the hardening of the bitumen (and on the degradation of the polymer). Additional considerations on the MSCR test are included in Cuciniello et al. (2018).

The MSCR testing temperatures (

Table 2) were selected as the temperature at which the parameter G*/sin δ measured on the RTFO residue is equal to 2.20 kPa (defined as the Continuous Grade High Temperature).

Table 2 – MSCR test temperatures

Bitumen	**MSCR Temperature [°C]**
Pen	64
Pen/S	64
SBS 2/S	70
SBS 4/S	75
SBS 4	75
SBS 6/S	87
SBS 6	87

This criterion was selected to compare the different bitumen at relatively similar levels of stiffness after short-term ageing. As mentioned above, the continuous grade high temperature was measured on the base bitumen and the PMB/S bitumens. Regarding the remaining bitumens (i.e., SBS 4, SBS 6) the MSCR test temperatures correspond to the ones determined on the PMB/S bitumens with the same polymer concentration. For the bitumen Pen/S, the MSCR temperature corresponds to the one determined on the Pen bitumen. This choice was made to highlight the effect of sulphur at the same temperature. It is worth clarifying that according to AASHTO M 332, the traffic designation should be measured at the Performance Grade temperature and not at the Continuous Grade High Temperature. However, the traffic designation is included to provide a synthetic indicator of the change in the resistance to the accumulation of permanent deformation and not for grading purposes.

Results and discussion

Fluorescence microscopy

After the Tuben Test, fluorescence microscopy was used to observe the polymer-bitumen separation of the SBS 6 bitumen (Figure 2 – a, b), and of the SBS 6/S bitumen (Figure 2 – c, d).

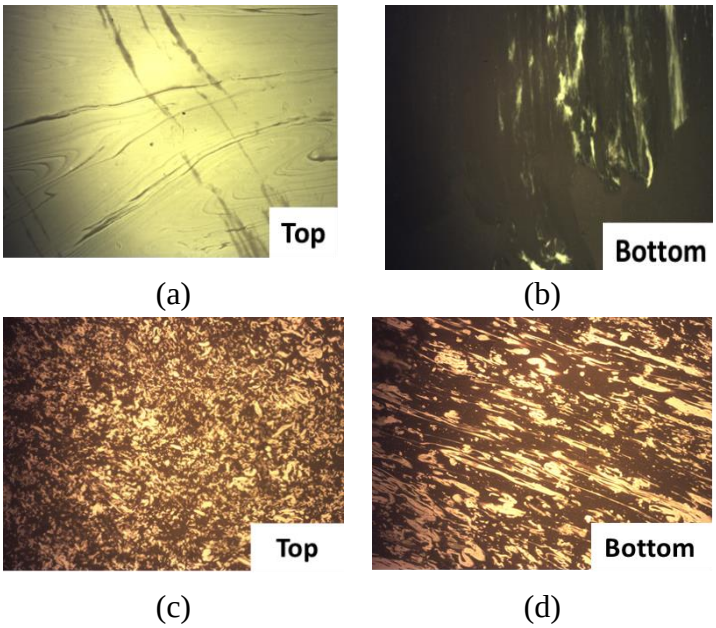


Figure 2. Images of Morphology (10x magnification) of SBS 6 after ASTM D 7173 Test (a – PMB in the top part of the tube; b – PMB in the bottom part of the tube); SBS 6/S after ASTM D 7173 Test (c – PMB in the top part of the tube; d – PMB in the bottom part of the tube).

The images show that in the case of SBS 6 bitumen due to the phase separation the SBS phase moves to the top part of the tube where a higher polymer concentration is shown. On the other hand, the SBS 6/S bitumen shows higher stability with the morphology of the PMB in the top and the bottom parts of the tube being very similar. These results are in agreement with other research published on the advantages of using sulphur as a cross-linking agent with PMBs (Mandal et al., 2015; Das & Panda, 2017; Zhang et al., 2010).

Besides stability, the use of a cross-linker enhances the level of dispersion of the polymer network in the bitumen phase during modification (Figure 3).

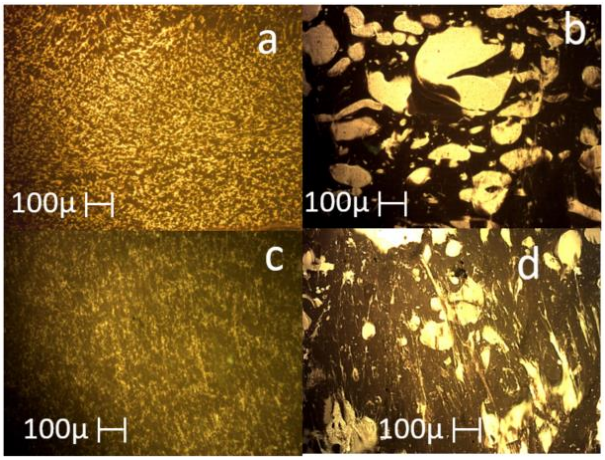


Figure 3. Morphologies (10x magnification) of SBS modified bitumens.

a) SBS 6/S; b) SBS 6; c) SBS 4/S; d) SBS 4

As shown in the images, in the PMB/S (Figure 3 – a, c), the polymer phase shows a higher dispersion compared to the PMB (Figure 3 – b, d). The reason behind this is that sulphur cross-links the chains of the SBS copolymer enhancing its level of reticulation. Furthermore, the shape of the SBS phase in the SBS 4 and SBS 6 bitumens highlights the fact that the polymer is more prone to remain separated in dispersed agglomerates (Figure 3 – b, d). This aspect might be indicative of low affinity.

Such a detailed description of the materials highlights the fact that when the composition of PMBs is studied, the use of the polymer concentration alone might not be indicative of the polymer-bitumen interactions. The same polymer mixed at different conditions (e.g., with or without cross-linker) shows a different interaction with the bitumen. However, the Job Mix Formula of PMB is not always available because suppliers are often reluctant to disclose the details of the modification.

Gel Permeation Chromatography (GPC)

Two significant effects appear to occur with regard to the Molecular Weight Distribution (MWD) of the unmodified bitumens during laboratory-simulated ageing. The first is the volatilisation of the light fractions during the RTFO; while the second seems to be a relative increase in the heavier fractions during the PAV oxidation. As shown by Equations (1) and (2), that refer to Figure 1, the weight proportion of each fraction depends on the ratio between the area representative of the fraction considered versus the cumulative area. In this regard, the loss in the light fractions during the RTFO will be defined as 'Volatilization of the light fractions'. While the changes in the MWD during the PAV ageing will be defined as 'PAV oxidative hardening'.

On the other hand, once PMBs are exposed to laboratory-simulated ageing, the polymer phase undergoes thermo-oxidative degradation. In the case of SBS modified bitumen, this mechanism should correspond to the scission of the SBS chains with a consequential reduction in their molecular weight (Cortizo et al., 2004; Negulescu et al., 2006). In particular, researchers have observed that the chain scission occurs due to the reaction between the allyl group (CH_2) adjacent to the C=C double bond within the polybutadiene segment that readily reacts with oxygen. The higher sensitivity of the polybutadiene segment to oxidation, heat and solar radiation is well known (Xu, J. et al., 2007; Xu, X. et al., 2017).

The more the polymer chains are exposed to thermo-oxidative processes, the more their molecular weight (MW) is reduced, and the fragments of the polymer chains can be detected at retention times characteristic of the bitumen fractions. At low oxidative levels, the fragments of the polymer have retention times comparable to that of the heavy fractions (increase in R_H – Equation(2)), while at higher oxidative levels they undergo a further degradation and have retention times comparable to that of the light fractions (increase in R_L – Equation (2)). This mechanism will be defined as

‘polymer degradation’ and is visible in the three chromatograms related to the SBS 2/S bitumen within the unaged condition, after 1 PAV and after 2 PAV (Figure 4).

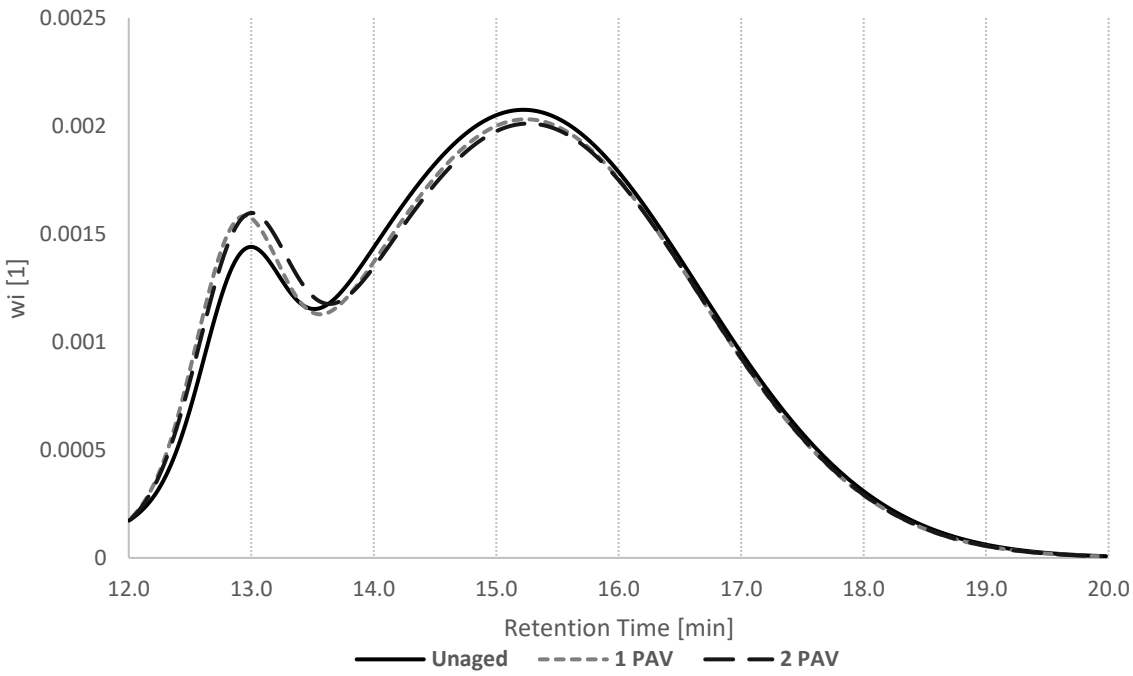


Figure 4 – Chromatograms of SBS 2/S bitumen at the unaged condition and after one and two cycles of PAV.

The portion of the chromatogram between 12 and ~13.5 minutes increases with ageing and shifts to lower retention times (higher molecular weight) with ageing. On the other hand, the portion of the chromatogram approximately between 14 and 16 minutes shows a slight shift downward and towards higher retention times (lower molecular weight). Therefore, this fraction does not seem to undergo significant structuring. As a consequence, the increase in the 12 to 13.5 minutes portion might depend on the polymer fragments formed during the RTFO and the PAV oxidation.

Once the mechanisms that seem to occur at the molecular level have been described, the expected findings from the GPC test are organised in 'Investigated Areas' whose content is summarised in Table 3.

Table 3. GPC test investigated areas

Investigated areas	**Compared bitumens**		**Focus on**
Area 1	Pen	Pen/S	Isolate the effect of 0.1% of sulphur on the variation in the bitumen composition at different levels of Laboratory-Simulated Ageing (LSA).
Area 2	Pen	SBS 2/S	Effect of SBS copolymer modification with the use of cross-linker on the variation in the bitumen-rich phase composition at different levels of LSA.
		SBS 4/S	
		SBS 6/S	
Area 3	SBS 4/S	SBS 4	Comparing the effects of LSA between SBS modified bitumens prepared with sulphur as a cross-linker and SBS modified bitumens without cross-linker.
	SBS 6/S	SBS 6	

Results of Investigated Areas

The results of the *Investigated Areas 1, 2,* and *3* are given in terms of Equation (1) (R_H – portion of heavy fractions), respectively in Figure 5 to 7.

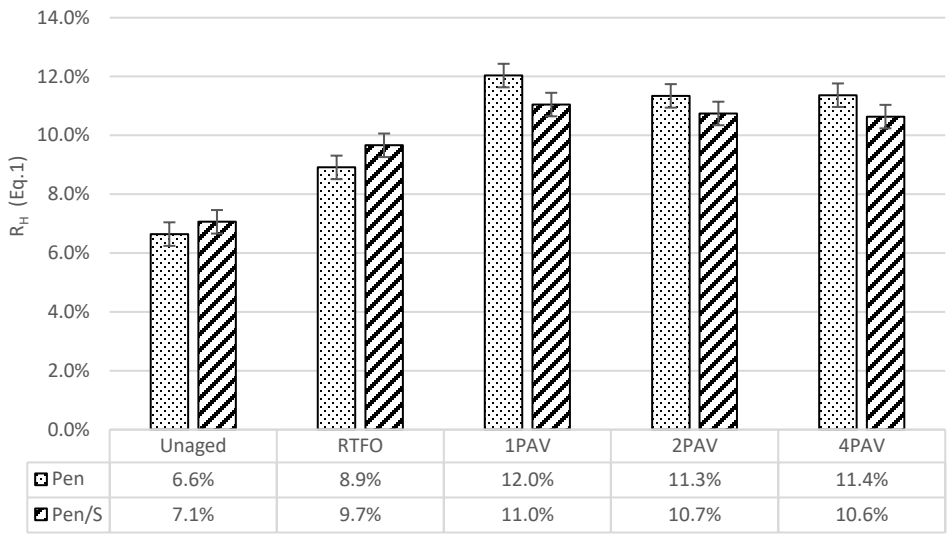


Figure 5. Values of R_H of the Pen and the Pen/S bitumens at different levels of LSA

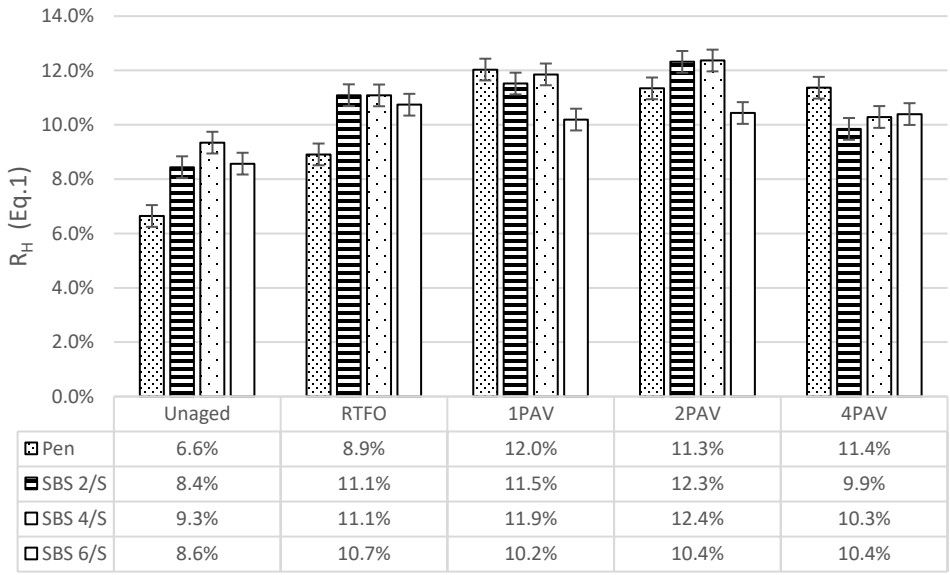


Figure 6. Values of R_H of the Pen and the PMB/S bitumens at different levels of LSA

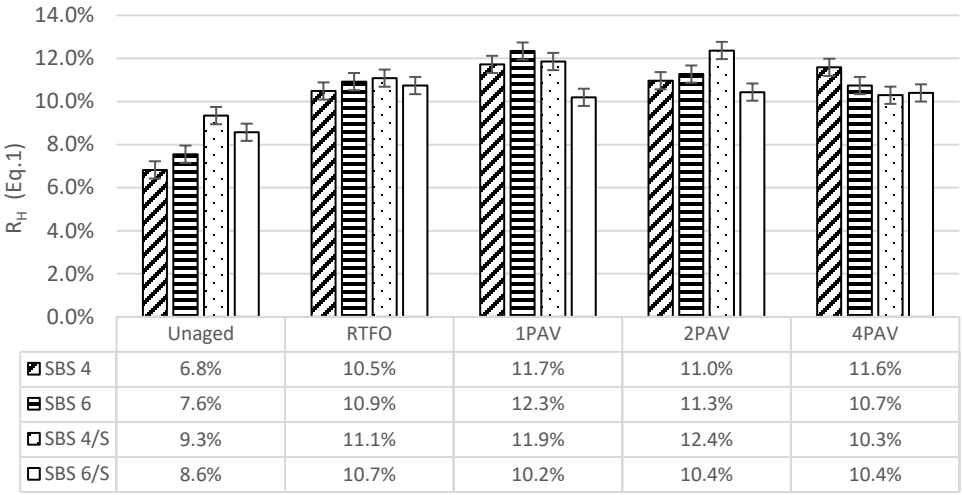


Figure 7. Values of R_H at different levels of LSA of bitumens SBS 4, SBS 6, SBS 4/S, SBS 6/S.

A detailed discussion of the results is given in the following sections organised as per Investigated Areas. However, it is worth mentioning that the proposed mechanism of the changes in the MWD of bitumens with ageing (in particular for PMB/S) represents a plausible interpretation of the results developed at this stage of the research that might need additional verification.

Results of Investigated Area 1 (Figure 5)

- *Pen bitumen* - The heavy fraction increases during both the RTFO and the first cycle of PAV. In the RTFO, such an increase might depend on the volatilisation of the lighter fractions, while during the first cycle of PAV it depends on the PAV-oxidative hardening. At higher oxidative levels (i.e., 2 PAV, 4 PAV), the R_H values tend to reduce although remain within the test variability (±0.4%).

- *Pen/S bitumen* - Results show a similar trend as the Pen bitumen, but sulphur mitigates, to some extent, the formation of the heavy bitumen molecules. The R_H values after one cycle

of PAV of the Pen and the Pen/S bitumens differ by 1%. However, the mitigated oxidative kinetics of the Pen/S bitumen might depend on the blending process (3 hours at 180°C). During this stage, part of the oxidative products might be formed causing a subsequent lower PAV oxidative susceptibility. Nevertheless, the evaluation of the effects of the bitumen-sulphur interactions on the oxidation of the base bitumen deserves further investigation.

Results of Investigated Area 2 (Figure 6)

In this case, the Pen bitumen has been included as a reference and shows the lowest R_H value at the unaged condition (Figure 6). The higher values of R_H for the PMB/S bitumens compared to the Pen at the unaged condition, may depend on the 'Polymer Degradation' that occurs during blending. It is true that some changes in the molecular distribution might have occurred during blending, but the magnitude of the differences (+ 1.8% for SBS 2/S bitumen and +2.7% for SBS 4/S bitumen) suggests the presence of polymer fragments. This aspect is supported by the slightly higher R_H value of the Pen/S bitumen (Figure 5), that although having a similar thermal history (3 hours at 180°C) shows an increase of +0.5% with respect to the Pen bitumen at the unaged conditions. In the RTFO, the increase in the R_H value is slightly dependent on the polymer concentration, due to the simultaneous effect of the 'Volatilization of the light fractions' and 'Polymer degradation'. The variation of the R_H values with PAV ageing depends on the polymer concentration. A discussion on the variation of the R_H values with laboratory-ageing of the PMB/S bitumens is given below.

- *SBS 2/S and SBS 4/S bitumens* - The increase in the portion of the heavy fractions of the bitumen-rich phase occurs within two cycles of PAV with the R_H values achieving the

maximum values at 2 PAV ageing. Therefore, the variation of R_H takes longer before it becomes stable or, as seen in this case, to decrease. Based on this point, it seems that the SBS cross-linked by the sulphur results in a delay in the growth of the heavy fractions. However, the reduction of heavier compounds might also be due to some asphaltenes being retained in the filter together with the polymer network. The growth in the R_H values could depend on the combined effect of 'Polymer degradation' and 'PAV-oxidative hardening'. However, these two contributions cannot be recorded separately in the GPC since this test only provides information on the molecular weight. The mechanism of 'Polymer degradation' contributes to understanding the reduction in R_H at 4 PAV ageing. That is, after four PAV cycles, the polymer chains are no longer detected within the interval of the heavy fractions, but instead, they are detected in the interval of the light fractions with a consequent reduction in the proportion of the heavy fractions (Equation (2)). An alternative explanation of the results at 4 PAV is that, at such high oxidative levels, the polarity of the bitumen molecules could increase their affinity, and thus solubility, with THF. In other words, the solvent could be more capable of dissolving the heavy fractions causing a decrease in their proportion. If this is the case, the GPC might show some limitations when used at high oxidative levels.

- *SBS 6/S bitumen* - The variation of the R_H remains within the test variability. The low PAV-susceptibility of R_H might depend on the high consistency of the modified bitumen at the PAV temperature (100°C) which could prevent the oxygen from diffusing throughout the layer of bitumen in the PAV pan as discussed in Anderson & Bonaquist (2012).

Results of Investigated Area 3 (Figure 7)

The combination of the sulphur (*Investigated Area 1*) and the SBS copolymer produces more relevant effects than the two constituents in isolation. These effects depend on the polymer concentration. Although it is difficult to identify whether this is the effect of the sulphur or the polymer, what appears to be clear is that the two additives (SBS and sulphur) alone do not achieve the results of their combination. Therefore, the polymer type alone might not be indicative of anti-oxidative properties, and other factors such as stability and morphology must be taken into account. However, a detailed discussion per each polymer concentration is given below.

- *SBS 4/S bitumen* - The R_H value achieves the maximum after two cycles of PAV and then starts to decrease. The contribution of the polymer to this mechanism has been clarified in Investigated Area 2.

- *SBS 4 bitumen* - The maximum R_H value is achieved after one cycle of PAV and then becomes stable as observed in the unmodified bitumens.

- *SBS 6/S bitumen* - The PAV susceptibility of the R_H values is negligible.

- *SBS 6 bitumen* - R_H value is susceptible to RTFO and PAV. The R_H value shows an increase in the portion of the heavy fractions between the Unaged to the 1 PAV aged conditions and a subsequent decrease between 1 PAV and 4 PAV aged conditions.

Multiple Stress Creep and Recovery (MSCR)

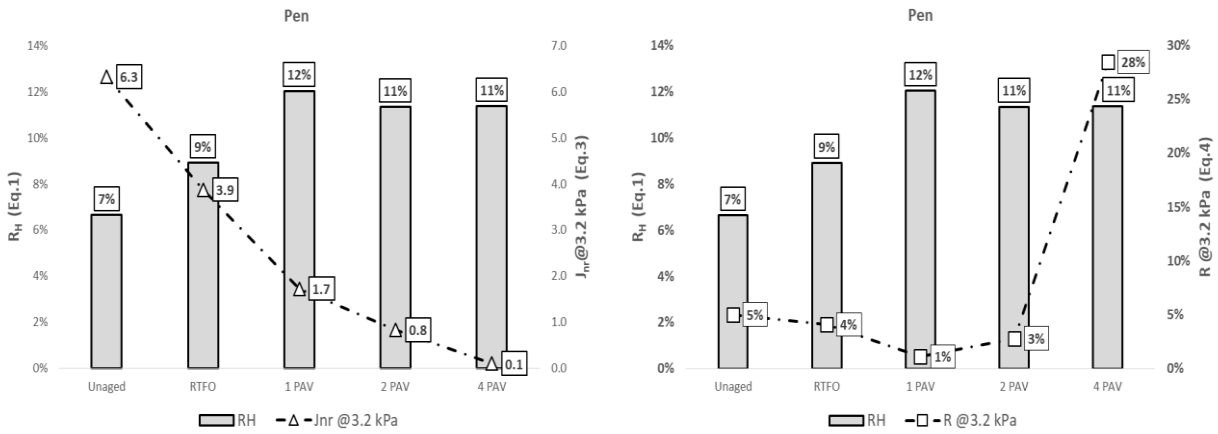
In this study, the MSCR was used to provide rheological indicators to evaluate the effect of different levels of LSA on SBS modified bitumens prepared with and without a cross-linker. Furthermore, the comparison between the MSCR test results and the GPC test results was undertaken to establish whether there is any correspondence between the mechanical response and the constitutive changes with ageing.

In particular, the Percent Recovery (R) measured at 3.2 kPa (Equation (4)) was selected to evaluate the changes in the polymer phase integrity (Golalipour, 2011; Clopotel & Bahia, 2012). While the J_{nr} measured at 3.2 kPa (Equation (3)) was used to focus on the combination of bitumen hardening and polymer degradation. It is evident that in the case of unmodified bitumen (i.e., Pen, Pen/S) only the bitumen hardening is considered. It is worth mentioning that part of the results from the MSCR test conducted in this work is already published in Cuciniello et al. (2018). However, this paper extends these results by including different materials and one additional level of ageing (4 PAV).

To facilitate the understanding of the comparison between the GPC results and the MSCR results, the MSCR results for each bitumen are superimposed over the R_H values as shown in Figure 8 to Figure 14**Error! Reference source not found.**. In the following charts, the R_H values are displayed as histograms, while the MSCR parameters are represented as dashed lines.

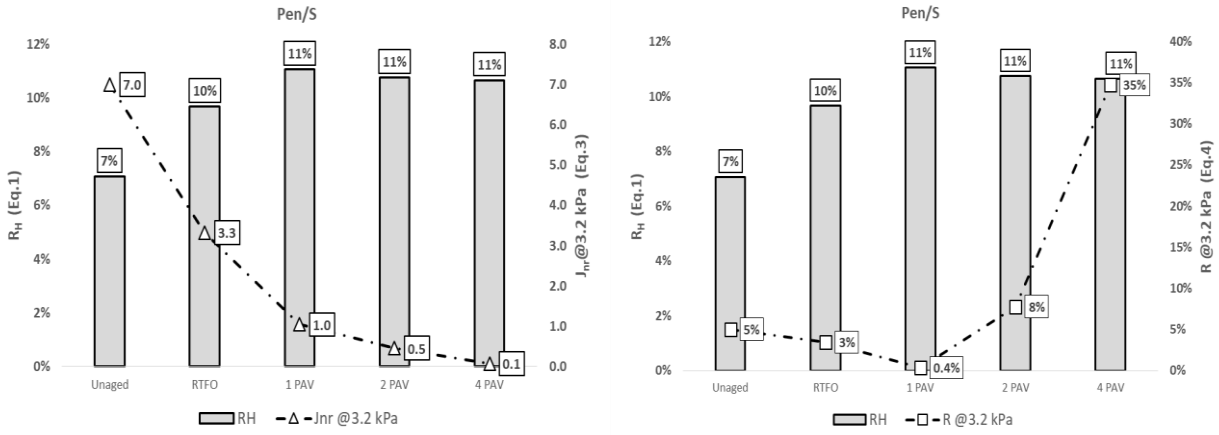
MSCR test results – Pen and Pen/S

The MSCR test results of the Pen and the Pen/S bitumens are given respectively in Figure 8 and Figure 9.



(a) (b)

Figure 8. MSCR test results overlapped with R_H values of the Pen bitumen at different LSA. (a) – Non-recoverable compliance@ 3.2kPa (J_{nr} - kPa^{-1}); (b) – Average Percent Recovery@ 3.2 kPa (R - %).



(a) (b)

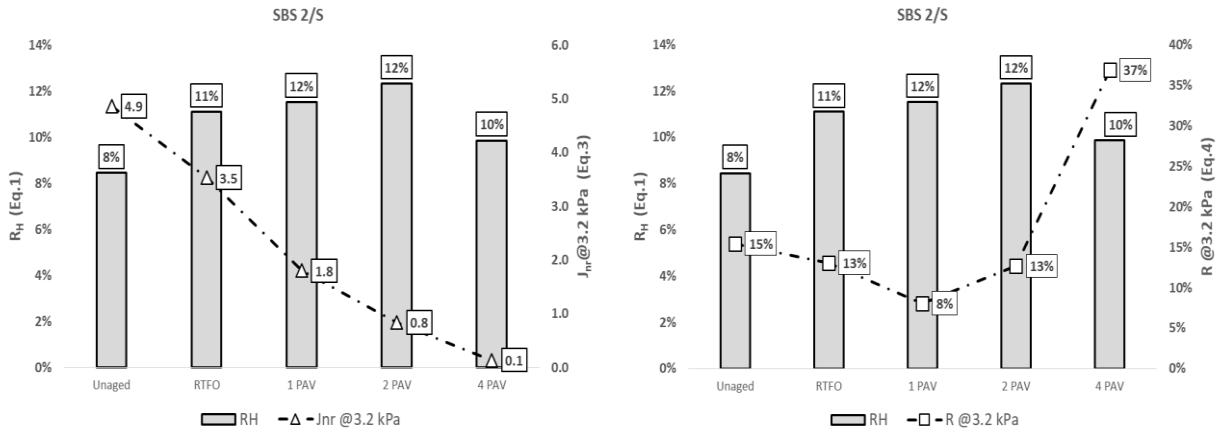
Figure 9. MSCR test results overlapped with R_H values of the Pen/S bitumen at different LSA. (a) – Non-recoverable compliance@ 3.2kPa (J_{nr} - kPa^{-1}); (b) – Average Percent Recovery@ 3.2 kPa (R - %).

For the Pen and Pen/S bitumens, the value of J_{nr} decreases with ageing due to the hardening of the bitumen (Figure 8, 9 - a). These results were expected, and no remarkable effects are provided by the use of 0.1% sulphur. Results from the GPC analysis (Figure 8, 9 - a (R_H)) show that after the first cycle of PAV, in both bitumens, the portion of the heavy fractions becomes stable. However, the results from the MSCR show that the rheological response still changes even after one cycle of PAV. Therefore, although the R_H becomes stable, changes in the polarity and the molecular bonds still occur.

Results of the Average Percent Recovery of the Pen and Pen/S bitumens are given in Figure 8, 9 – b. No particular considerations need to be made on the percent recovery since these bitumens do not contain the polymer. However, the increase in the percent recovery at 4 PAV may depend on the hardening of the bitumen with the consequent decrease in the strain level of the test (especially in the creep portion). As discussed for the J_{nr}, the R values also show that although the variations in the light and heavy fractions appear to be reduced (Figure 8, 9 - b (R_H)), the rheological response still shows visible variations. This aspect confirms the previous statement detailing the importance of the type of molecules in addition to their size.

MSCR test results – PMB/S bitumens (SBS 2/S)

The MSCR test results of the SBS 2/S bitumen are given in Figure 10.



(a) (b)

Figure 10. MSCR test results overlapped with R_H values of the SBS 2/S bitumen at different LSA. (a) – Non-recoverable compliance@ 3.2kPa (J_{nr} - kPa^{-1}); (b) – Average Percent Recovery@ 3.2 kPa (R - %).

The variation in J_{nr} with the ageing of the PMB/S bitumens up to 2 PAV ageing has been discussed in Cuciniello et al. (2018). At medium-low SBS content (2%), the trend is similar to the Pen bitumen even after 4 PAV cycles (Figure 10 - a).

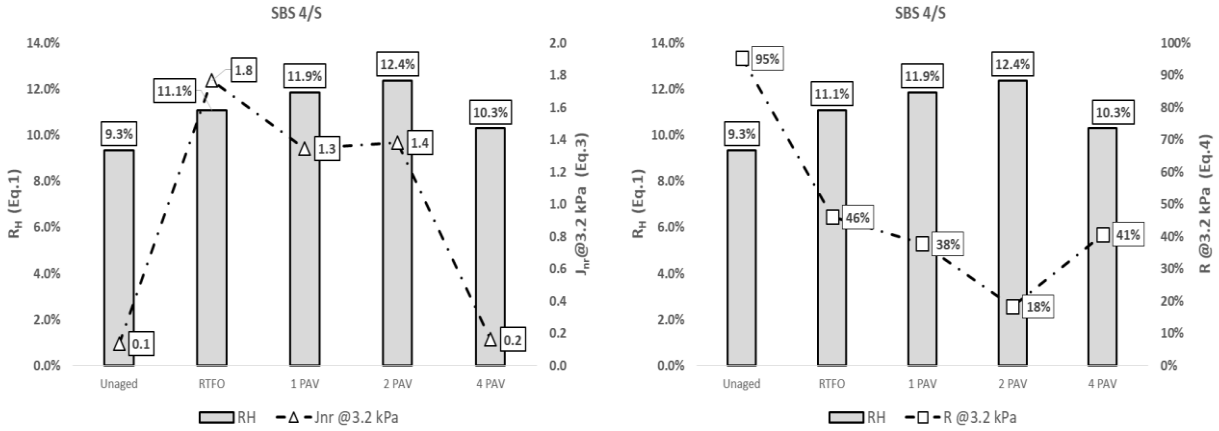
As shown in Figure 10 – b, the percent recovery of the SBS 2/S shows a relatively reduced variation between the unaged condition to 2 PAV ageing. Then, between two and four cycles of PAV, the average percent recovery increases up to 37%. The use of the GPC data (Figure 10 – b (R_H)), supports the interpretation of these results by considering that the trend of R depends on the integrity of the polymer chains. Between the unaged and the 2 PAV-aged conditions, the polymer chains have sufficient integrity to mitigate the effects of the bitumen hardening on the rheological response measured at 70°C (Table 2). Therefore, within this ageing interval, the average percent

recovery (R) shows a limited variation. Then at 4 PAV, the chains undergo more significant damage, and the hardened bitumen becomes dominant on the response with the value of R increasing (Figure 10 – b). Based on these considerations, the PAV seems to have an important effect on the integrity of the polymer chains.

It has to be mentioned that the level of impact on the physical response (referred to as 'dominance') between the polymer and the bitumen phases also depends on the testing temperature with the polymer effect being more relevant at high temperatures (Airey & Brown, 1998).

MSCR test results – PMB/S bitumens (SBS 4/S)

The MSCR test results of the SBS 4/S bitumen are given in Figure 11.



(a) (b)

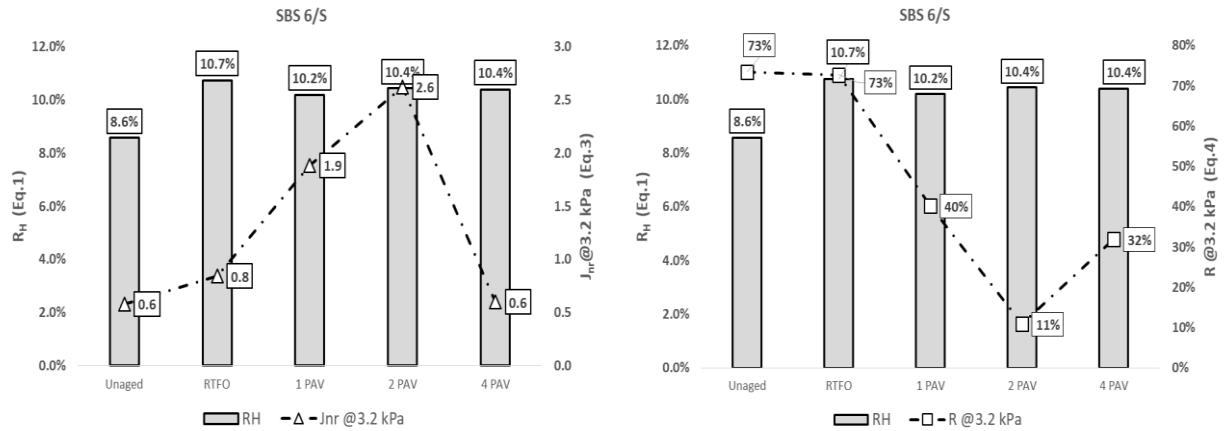
Figure 11. MSCR test results overlapped with R_H values of the SBS 4/S bitumen at different LSA. (a) – Non-recoverable compliance@ 3.2kPa (J_{nr} - kPa^{-1}); (b) – Average Percent Recovery@ 3.2 kPa (R - %).

The SBS 4/S modified bitumen represents a stable configuration (defined as 'optimum' polymer content) with the J_{nr} being stable between the RTFO and 2 PAV (Cuciniello et al., 2018). Then at

4 PAV, as shown by all the other bitumens, the J_{nr} of the SBS 4/S modified bitumen decreases to lower values (E- Grade) (Figure 11 - a). The low variability of the J_{nr} value between the RTFO and the 2 PAV ageing, might depend on the balance between the bitumen hardening and the polymer degradation (observed through the increase in R_H values in Figure 11 - a). Therefore, in the case of high polymer concentrations (SBS 4/S), within two cycles of PAV, the fragments of the polymer chains, whose weight is similar to the heavy bitumen fractions, are capable of mitigating the hardening of the bitumen to such an extent to maintain the J_{nr} value to be almost constant (at the MSCR test temperature). Probably, at 2% SBS content, the polymer fragments do not have a sufficient concentration to mitigate the bitumen hardening resulting in the J_{nr} values decreasing. Then at 4 PAV, the weight fragments of the polymer chains are reduced due to the thermo-oxidative process occurring in the PAV (R_H decreases from 12.4 to 10.3% - Figure 11 - a), and bitumen molecules become dominant with the J_{nr} value decreasing. The trend of the Percent Recovery (Figure 11 - b) is representative of the degradation of the polymer chains (R_{unaged}=95%, R_{2PAV}=18%). As shown in Figure 11 - b, the decrease in the Percent Recovery occurs concurrently with the increase in the R_H values that, as mentioned previously, depends on the contribution of the fragments of the polymer chains and the bitumen hardening. Since the hardening of the bitumen should produce an increase in percent recovery, the decrease in R between the unaged to the 2 PAV aged condition highlights that, at the testing temperature (Table 2 – 75°C), the polymer chains are dominant on the R values and decrease with polymer degradation. At 4 PAV, as seen with the J_{nr} values, the hardened bitumen becomes dominant (polymer fragment excessively degraded), and the percent recovery increases.

MSCR test results – PMB/S bitumens (SBS 6/S)

The MSCR test results of the SBS 6/S bitumen are given in Figure 12.



(a) (b)

Figure 12. MSCR test results overlapped with R_H values of the SBS 4/S bitumen at different LSA. (a) – Non-recoverable compliance@ 3.2kPa (J_{nr} - kPa^{-1}); (b) – Average Percent Recovery@ 3.2 kPa (R - %).

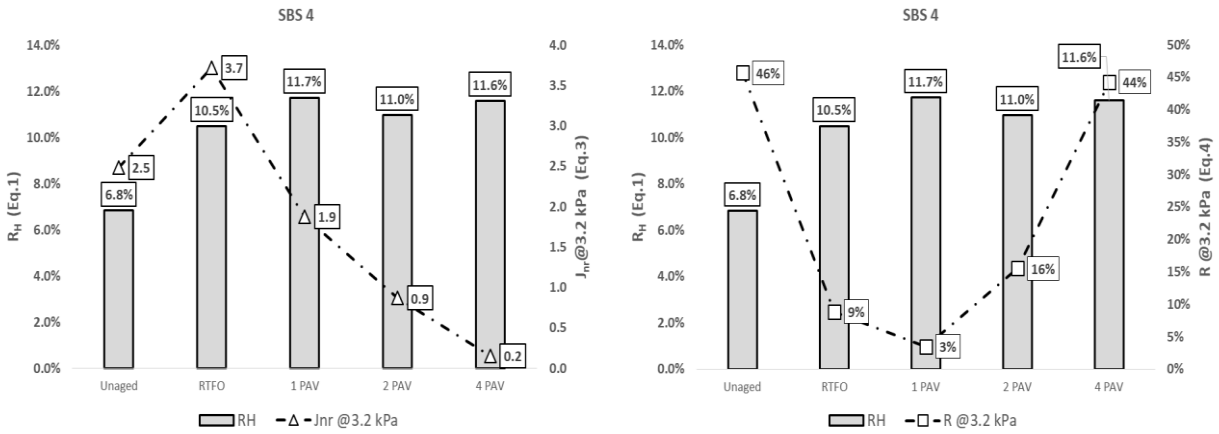
Although the results from the GPC of the SBS 6/S modified bitumen show a reduced PAV susceptibility, the rheological indexes show variations (Figure 12 – a, b). The J_{nr} values increase with ageing between the unaged and the 2 PAV aged conditions (Figure 12 - a). This aspect is counterintuitive since hardening should be expected. However, what might happen in this case, corresponds to what was observed in SBS 4/S modified bitumen (Figure 11 - a), with the difference that at very high polymer concentration (6% - with the use of a cross-linker), the polymer fragments are dominant over the bitumen molecules as shown in the J_{nr} values (at 4% there is potentially a balance). Therefore, the J_{nr} values increase as the polymer undergoes degradation. Moreover, the degradation of the polymer chains is also observed through the percent recovery (R) that reduces between the unaged and the 2 PAV aged conditions (Figure 12 - b). As shown by

the results, the RTFO does not appear to produce significant damage to the polymer chains with the value of R being very similar for the unaged and RTFO aged conditions (Figure 12 - b). Despite this, the R_H value increases by about 2.1% (R_H Figure 12 - b). In this case, the change in the R_H might be due to the volatilisation of the light fractions with the polymer chain remaining undamaged. The mechanism for which the J_{nr} decreases and the R increases at 4 PAV is the same as that detailed in the bitumens SBS 2/S and SBS 4/S. In this case, the GPC results are not helpful since the heavy fractions do not vary throughout the PAV ageing (Figure 12 - a, b (R_H)).

However, the MSCR – GPC comparison helps to raise some considerations, such as that besides the size of the polymer chains, there are other properties of the polymer that change with ageing even though the weight distribution of the molecules does not vary. Therefore, the effect of the polymer on the rheological response of PMBs (in this case the MSCR) depends on various polymer properties although the molar mass is one of the most important (Young & Lovell, 2011). It appears that these properties begin to degrade in the PAV before the molar mass of the polymer starts changing.

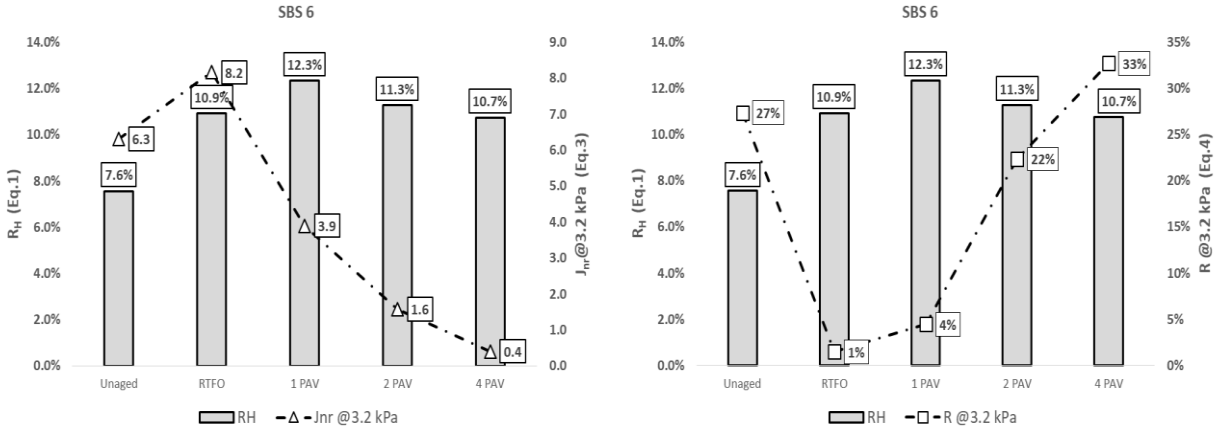
MSCR test results – SBS 4 and SBS 6 bitumens

The MSCR test results of the SBS 4 and the SBS 6 bitumens are shown respectively in Figure 13 and 14.



(a) (b)

Figure 13. MSCR test results overlapped with R_H values of the SBS 4 bitumen at different LSA. (a) – Non-recoverable compliance@ 3.2kPa (J_{nr} - kPa^{-1}); (b) – Average Percent Recovery@ 3.2 kPa (R - %).



(a) (b)

Figure 14. MSCR test results overlapped with R_H values of the SBS 6 bitumen at different LSA. (a) – Non-recoverable compliance@ 3.2kPa (J_{nr} - kPa^{-1}); (b) – Average Percent Recovery@ 3.2 kPa (R - %).

The MSCR findings for the SBS 4 and SBS 6 bitumens highlight that the use of sulphur as a cross-linker plays a fundamental role in the ageing susceptibility of the PMBs. Both bitumens show an increase in the J_{nr} values between the unaged condition and the RTFO (Figure 13, 14 - a) and a decrease in the percent recovery (R) within the same interval (Figure 13, 14 - b). After the RTFO, the trend throughout the PAV ageing highlights the dominance of the bitumen phase on the rheological response: J_{nr} decreases (Figure 13, 14 – a) and percent recovery increases after one cycle of PAV (Figure 13, 14 – b). Such behaviour is in agreement with what was observed in the Pen, Pen/S, and in the SBS 2/S bitumens. The rheological response indicates that after the RTFO, the polymer phase is degraded and does not provide a remarkable effect on the hardening of the PMB. In the case of low reticulation, the presence of the fragments of the polymer chains at the different levels of ageing (R_H values in Figure 13, 14 – a, b) is not capable of controlling the rheological response with ageing for the same polymer concentration.

The comparison of the results between the PMB (without sulphur) and the PMB/S needs to be conducted keeping in mind that the two modified bitumens in each pair differ only in terms of the cross-linker. However, the advantages provided by the cross-linker (sulphur) are remarkable in terms of stability (Figure 2) and morphology (Figure 3). Therefore, mentioning that the bitumens differ in the cross-linker only is misleading. The correct statement should be that ‘the bitumens in each pair differ in terms of the cross-linker content, the polymer dispersion and their stability’. Keeping this in mind, the comparison of the two PMB groups can be conducted.

Before discussing the differences, it is worth mentioning that the effects of the sulphur alone on this mechanism need further investigation. However, at such a low concentration, sulphur does not appear to influence the rheological response. What can be concluded is that the use of sulphur as a cross-linker provides the polymer with such a high level of dispersion (and stability) to make the polymer more capable of mitigating the hardening of the bitumen. Therefore, it seems that a well-dispersed morphology and storage stability, besides being indicators of good quality of modification, can also be advocated as indicators of adequate ageing resistance.

Conclusions

Five SBS modified bitumens were prepared by mixing different concentrations of SBS copolymer with one base bitumen (Pen) and sulphur as a cross-linker. Three PMBs were prepared by mixing 2%, 4% and 6% SBS with the base bitumen and using 0.1% sulphur as a cross-linker (i.e., PMB/S). Two SBS modified bitumens were prepared by mixing 4% and 6% SBS with the base bitumen without the use of sulphur (i.e., PMB). The use of sulphur enhances the storage stability of the SBS modified bitumens (PMB/S), with the PMBs becoming stable at storage. Besides this, the use of the cross-linker is likely to improve the level of dispersion of the polymer in the bitumen providing a more homogeneous structure. One unmodified bitumen was modified with 0.1% sulphur to isolate its effect (Pen/S). The bitumens were RTFO and PAV aged up to 4 PAV cycles (80 hours). Results from the GPC and the MSCR were collected on unmodified bitumens and PMBs at different levels of LSA. The GPC analysis was conducted on the portion of the chromatograms between 12 and 20 minutes. In the case of unmodified bitumens, this interval is representative of the whole microstructure of pure bitumen (heavy and light fractions). In the case of SBS modified bitumens, this time interval is representative of the bitumen-rich phase that includes the heavy and light bitumen fractions and the fragments of the polymer chains having

similar molecular weight to that of the bitumen fractions. The polymer phase of the SBS modified bitumens (10-12 minutes) was not visible in the chromatograms because the high level of reticulation does not allow the THF solvent to dissolve this phase.

The following conclusions can be drawn from the study:

- The comparative analysis of MSCR and GPC data of the cross-linked SBS modified bitumens (i.e., PMB/S) helps to raise some considerations. The variation with LSA of the J_{nr} and the percent recovery (R) at 3.2 kPa is a function of the polymer concentration. The higher the polymer content, the more the fragments of the polymer chains of a specific size (and molecular weight) are capable of mitigating the oxidative hardening of the bitumen. In the case of 2% and 4% SBS, the correspondence between the size of the fragments of the polymer chains and the MSCR response is visible when comparing the GPC and the MSCR results. In the case of the 6% SBS the GPC findings are not helpful since the limited variation of R_H during PAV ageing does not support the macroscopic changes observed in the rheological response.

- In the case of the SBS modified bitumens without cross-linker (i.e., SBS 4, and SBS 6), the variation of R_H is similar to the one shown for the unmodified bitumens with the microstructure being less resistant to RTFO and PAV ageing than the cross-linked SBS modified bitumens.

- In the SBS modified bitumens without cross-linker, the variation in the MSCR response with PAV-ageing is similar to that of the unmodified bitumens (decrease in J_{nr} values and increase in percent recovery R). The effect of the polymer seems to disappear after the RTFO.

- The comparative results between cross-linked SBS bitumens and un-linked SBS bitumens highlight the fact that the combined use of sulphur and SBS changes the resistance to hardening during artificial ageing of the SBS modified bitumens considered in this work. The available data does not allow the contribution of sulphur to be isolated. However, the cross-linked SBS modified bitumens (SBS + sulphur) are likely to have different resistance to hardening during artificial ageing than un-linked SBS modified bitumens at the same polymer concentration. Therefore, in the study of the anti-oxidative properties of SBS, properties such as polymer stability and level of dispersion (using morphology) should be taken into consideration.

- The Pen and Pen/S bitumen showed an increase in the portion of the heavy fractions up to 1 cycle of PAV. Afterwards, the R_H appears to remain stable within the test variability. The addition of 0.1% sulphur appears to mitigate the formation of the heavy fractions slightly. Despite the constant trend of R_H at high oxidative levels, the rheological indicators measured by means of the MSCR test highlight a further hardening of the bitumen. As a consequence, a further investigation focusing on the changes in functional groups by infrared spectroscopy is needed.

- The results of the GPC on the PMB/S modified binders highlight the fact that the changes in R_H at different levels of ageing depend on the polymer concentration and can be caused by three mechanisms: volatilization of the light fractions during RTFO ageing; polymer degradation (during blending, RTFO and PAV ageing); bitumen oxidative hardening in the PAV. The GPC test is unlikely to isolate the contribution of each mechanism. The first and the third are well-known ageing mechanisms while the second corresponds to the degradation of the polymer chains that reduce their size (and MW) with ageing. The reduction in MW causes an increase in retention time. In the case of the SBS 6/S bitumen, only the effect of the RTFO ageing is visible in the GPC with the PAV ageing has a reduced effect due (probably) to the high consistency of the bitumen at the PAV temperature (100°C). In the case of the SBS 2/S and SBS 4/S, the three mechanisms are all visible. The degraded polymer fragments are detected in the region of the heavy bitumen fractions between the unaged and 2 PAV aged conditions. Their amount seems to increase with ageing up to 2 PAV. Then, after 4 PAV, the degradation of the polymer chains is so high that they are detected with the light bitumen fractions with a consequent reduction in the proportion of the heavy fractions. At this stage of the research, this mechanism is considered as a hypothesis.

Disclosure statement

No Potential conflict of interest was reported by the authors.

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