

Applicability of time-temperature superposition for laboratory-aged unmodified and SBS-modified bitumens

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Abstract

The applicability of the time-temperature superposition principle (TTSP) is sometimes of concern for highly oxidized bitumens and polymer-modified bitumens (PMBs). This study investigates this in terms of binders modified with Styrene Butadiene Styrene (SBS) copolymers and subjected to high oxidative aging levels. The effects of aging were investigated by gel permeation chromatography (GPC), fluorescence microscopy (FM) and linear viscoelastic rheological characterization. As expected, the GPC and FM showed, respectively, an increase in the heavy fractions of bitumen and the degradation of the polymer morphology. Both the phenomena affected the rheological response provided in the form of black diagrams and isochrones of the loss tangent. The unmodified bitumens demonstrated thermorheologically simple behaviour irrespective of the laboratory-aging level. On the other hand, the applicability of TTSP to PMBs depends on the polymer content and the aging level. Low-medium and medium-high polymer contents PMBs produce minor concerns for TTSP irrespective of the aging level. However, high polymer contents may induce a TTSP breakdown mainly in unaged PMBs with the degradation of the polymer backbone due to oxidative aging progressively restoring a thermorheological simple configuration.

Introduction

Polymer additives are used to improve the performance and durability of road bitumens by producing Polymer Modified Bitumens (PMBs). However, the effect of polymers on the oxidative-aging of the binders remains relatively unclear (1-12). Polymer modification is a process that significantly depends on the compatibility between the polymer and the base bitumen. The more a polymer is capable of swelling into the bitumen phase without compromising its structure, the more evident is its effect on the final properties of PMBs (2, 13). This enhanced condition depends on the bitumen composition (i.e., crude source and refining method), on the polymer composition and characteristics, and finally may be strongly affected by the use of crosslinking additives (3, 14). Therefore, similar to other properties, the oxidative-aging resistance may depend on this polymer-bitumen compatibility. Aside from this, in PMBs, the two constituents undergo different aging mechanisms and each one affects the other. The bitumen experiences an increase in the heavy polar fractions with low molecular mobility (i.e., asphaltenes) which causes a higher stiffness and reduced strain tolerance (15-18). On the other hand, thermoplastic polymers commonly used in road applications (e.g., Styrene Butadiene Styrene (SBS) block copolymers) are subjected to oxidative degradation of the polymer backbone that causes a reduction in their molecular weight (3, 8-10). Both effects lead to a polymer de-swelling, which creates a decrease in volume of the polymer-rich phase, which probably desorbs that part of the maltenes whose polarity varies due to oxidation (19). Of course, in PMBs, the bitumen does not oxidize alone and the polymer does not degrade apart. Isolating the two mechanisms is not easy and a deep understanding of the phenomena is still to be achieved.

In the available literature, aged and unaged materials have been compared at both the compositional and physical scales (20). A few examples incorporate the monitoring of the carbonyl compounds (8, 21, and 22), the molecular weight distribution (MWD) (3, 9, and 23), the mechanical properties, i.e., linear viscoelastic functions (10, 25, and 35) and the morphology of the PMBs (4, 24). These methods have advantages and disadvantages; therefore, a combination of their results is critical to gather a comprehensive understanding of the mechanism.

A typical disadvantage of the compositional approach (i.e., Gel Permeation Chromatography (GPC)) is that the measurements are sometimes performed in diluted conditions, which inevitably alter the structure of bitumens and PMBs. For this reason, the MWD obtained by the GPC, may not be representative of the bulk structure. Moreover, the GPC results strongly depend on the operating conditions (i.e., column, solvent, sample concentration, flow rate, and so on) (3, 26, and 27). On the other hand, the bulk properties are representative of mechanical performance. However, these approaches are not easily linked to the effects of aging at the molecular level and a correlation between the microstructure and the physical response lacks a unique definition (2, 5, 13, 28-30). Despite this, rheological indicators (e.g., viscosity, linear and non-linear viscoelastic functions) have been used to substantiate results from compositional test methods to provide clear insights on the changes in bitumen microstructure and their effects on performance (3, 31-34). In the case of PMBs, the rheological analysis becomes even more complicated since the response is affected by non-Newtonian effects, strain dependency, thixotropy, and uncertainties about the applicability of the time-temperature superposition principle (TTSP) (37-44).

This paper focuses on the effects of laboratory aging on the linear viscoelastic response of PMBs prepared with SBS copolymer. The main points are the applicability of the TTSP at different levels of aging and the possibility of identifying the changes in the binder microstructure by using both black diagrams and the loss tangent in the temperature domain. The effects of aging were also evaluated by GPC and fluorescence microscopy.

Theoretical Background

In viscoelastic materials, stress-relaxation is a function of molecular rearrangement processes. The capability of the molecules to rearrange depends on their mobility (i.e., Brownian motion), of which temperature is a controlling factor (45, 46). If the molecular processes contributing to relaxation have the same temperature dependency, the relaxation (shear) modulus (G) can be given as a function of time (t) and temperature (T) in the form of Equation (1).

$$G(t, T) = G(\xi, T_0) \tag{1}$$

Where T_0 is the reference temperature, and ξ is the reduced time calculated by Equation (2).

$$\xi = \frac{t}{\alpha_T(T)} \quad (2)$$

Where $\alpha_T(T)$ is the shift factor, which is a function of the material and T_0 .

Materials that obey this principle are thermorheologically simple, and for them, the TTSP is applicable. In this case, the shift factor is applied to horizontally shift the experimental isotherms of viscoelastic functions into a single master curve calculated at T_0 in the reduced time (or frequency) domain. Concerning the TTSP applicability, there are some practical criteria (46). First, while calculating master curves, isotherms should superpose easily and within the tolerance limits. Second, the shift factor should be (when possible), equal for all viscoelastic functions. Third, the temperature dependency of α_T must have a form consistent with established literature. Whenever one of them is not verified, the TTSP breaks down (45). The TTSP applicability strongly depends on the absence of chemical and structural transitions in the material. For this reason, the glass transition is compatible with the TTSP, since it is simply related to the molecular mobility and does not involve changes in the material structure and amorphous polymers usually meet the TTSP (46). In contrast, melting, freezing, or changes in the chemical composition within the experimental interval, compromise the TTSP (46, 47). Moreover, materials constituted of multiple phases (i.e., composite materials) having different temperature susceptibilities of their viscoelastic response could not be thermorheologically simple. Based on these considerations, it is not easy to predict what would be the behavior of PMBs in terms of TTSP. The TTSP has been successfully applied to model the viscoelastic response of road bitumens (and bituminous mixtures) with a good approximation (43, 48-54, 62). Master curves of viscoelastic functions such as the loss and storage moduli and the phase angle are representative of stiffness, elasticity, temperature susceptibility, and, after some data manipulation, of the MWD of bitumens (34, 57-61, 64). However, the applicability of TTSP over the whole range of testing temperatures used for bitumens (indicatively between -20°C to 90°C) is a strong assumption, particularly within the high temperature region. Lesueur and co-workers refer to the colloidal model to describe the relaxation mode of neat bitumens in the Newtonian region (i.e., high temperatures) (43). In a general sense, a colloid deviates from a true suspension and is represented by two phases of which one is dispersed (solid-like

micelles) and the other one represents the dispersing matrix (63). Once these particles are sufficiently small, and the viscosity of the surrounding matrix is low, Brownian motion keeps particles suspended in the matrix. The viscoelastic effects arise when the temperature decreases (or the frequency increases). In this condition, the viscosity of the matrix is higher and the particle mobility depends on the applied shear rate while the effects of Brownian motion vanish. Moreover, the colloidal structure of bitumens depends on the equilibrium among the different functional groups (i.e., Saturates, Aromatics, Resins, and Asphaltenes (SARA)) with the resins having a peptizing action on the asphaltenes (17). This equilibrium is highly dependent on temperature and may cause the TTSP to fail in the high-temperature region. In contrast, in the low-temperature region, the oil matrix undergoes glass-transition preventing the structure from changing and this allows the applicability of the TTSP.

There are three cases representative of the TTSP breakdown in bituminous binders depending on their structure: highly-oxidized bitumens with a large asphaltene content; when crystalline waxes are used (the TTSP fails when the wax starts melting); and in the case of PMBs (43, 44). However, there is not an unanimous consensus on the latter point. Nevertheless, it is well known that the TTSP becomes less applicable at high temperatures and for heavily polymer modified bitumens.

Glass and secondary transitions represent quite complex molecular mechanisms. However, dynamic test methods associate the rheological response with different kinds of molecular responses depending on the mode of loading and on the time-temperature interval considered (46). In the case of polymers, these regions correspond to the transition zone from the glass-like to the rubbery-like consistencies, the plateau zone, the pseudo-equilibrium zones (cross-linked polymers), and the terminal zone (uncrosslinked polymers). Based on their MWD, bitumens can be considered as low-molecular-weight polymers (2, 36, 59, 60). In the low-temperature region, the glass transition temperature ($T_g \sim -20^\circ\text{C}$) is associated with the maximum of the loss modulus (G''). In the high-temperature region, where the behavior is Newtonian, the response is controlled by zero-shear viscosity (η_0) (44). Finally, in the intermediate temperature interval, viscoelastic effects become evident with the cross-over of the storage (G') and loss (G'') moduli. The latter zone represents the time (or temperature) interval in which the

transition between the response varies from solid-like (low temperature) to fluid (high temperature). Of course, polymer modification strongly affects the properties in this transition (6, 10, 35, 44, and 62).

This paper focuses on the effects of laboratory-aging on the rheological response of SBS modified bitumens between 0 and 88°C. The rheological response is measured through black diagrams (i.e., curves of the phase angle (δ) versus the magnitude of the complex shear modulus $|G^*|$) and isochrones of the loss tangent (i.e., $\tan \delta$) in the temperature domain. The phase angle is considered as the rheological parameter representative of the equilibrium between energy loss and storage under cyclic loadings and, in the case of unmodified bitumens, δ is representative of the MWD (34, 45). Aside from this, the loss tangent is inversely proportional to the relaxation time (τ) that can be expressed, based on the Maxwell model, according to Equation (3) (45, 46).

$$\tau = \frac{1}{\omega \cdot \tan \delta} \quad (3)$$

Where ω is the loading frequency. Black diagrams are handy when evaluating the TTSP applicability because they do not require time-temperature manipulation of data. In other words, when the TTSP is applicable, different isotherms constitute a relatively continuous curve in the $\delta - |G^*|$ plane. A lack of smoothness in the shape of the black diagram curve gives an immediate indication of either inconsistency in the data or breakdown of the TTSP (53).

The loss tangent is typically used in polymer technology to study molecular rearrangement processes (relaxation). In this case, it is used to evaluate the effect of the polymer-rich phase (at different levels of aging) in the intermediate temperature region. Data from GPC and fluorescence microscopy are used to show a direct quantitative (GPC) and qualitative (fluorescence microscopy) measure of the aging effects on the bitumen microstructure.

Materials and methods

Materials

Three different PMB were prepared by modifying one base bitumen (penetration grade 70/100) with three concentrations (i.e., 2%, 4% and 6%) of a radial SBS copolymer (polystyrene content 29-31%)

and sulphur (S) as a cross-linking agent (0.1% w/w). The preparation of the PMBs was discussed with the polymer supplier in advance. The PMBs were prepared using a Silversone® high shear mixer. The polymer was added to the bitumen at 180°C and the mix was blended for one hour at high shear rate (i.e., 5,000 RPM). Afterwards, sulphur was added and the mix was blended for additional two hours at 180°C at lower shear rate (~2,800 RPM).

Methods

Bitumen aging

The bitumens were short-term aged (STA) by the Rolling Thin Film Oven (RTFO) as per the UNI EN 12607-1 standard, and long-term aged (LTA) by Pressure Aging Vessel (PAV) as per AASHTO R 28. Multiple cycles of PAV were applied to simulate different levels of oxidation (i.e., 20 hours – 1PAV; 40 hours – 2PAV; 80 hours – 4PAV). Prolonged aging exposures (i.e., 2PAV and 4PAV) were used to obtain additional monitoring points of the progress of the PAV oxidation in the bitumens. In addition, the use of the traditional PAV procedure with PMBs raises some concerns due to their high viscosity at the PAV temperature (66).

Fluorescence microscopy

A Leica® DM LB microscope was used to capture images of the PMB morphology at 10X magnification. The microscope is connected to a camera to gather pictures of the various samples. The samples were prepared to gather the bulk morphology that is not affected by the contact with cold surfaces during cooling. Small stripes of bitumen at room temperature were refrigerated for 10 hours at -18°C. Afterwards, the stripes (now brittle) were cut in the middle and the surface corresponding to the cut was attached to the glass for microscope observation. The use of refrigerated samples was needed to avoid any disturbance of the cut on the PMBs morphology.

Gel Permeation Chromatography

The experimental aspects of the GPC are detailed in Cuciniello et al. (3). In a preliminary test, base bitumen and SBS copolymer were analysed separately. The uncross-linked SBS resulted in a retention time interval between 10 and 12 minutes, while the neat bitumen was found between 12 and 20 minutes. However, in the case of PMBs, the presence of the cross-linker determines the formation of a covalent-

bonded polymer network that does not dissolve in tetrahydrofuran (THF). Therefore, the results of the GPC analysis in the paper only refer to the portion of chromatogram between 12 and 20 minutes, representative of the entire MWD of the bitumen (light + heavy fractions). Nevertheless, in PMBs a portion of the polymer chain undergoes thermo-oxidative degradation during blending, STA or LTA with a consequent molecular weight reduction. Therefore, the bitumen signal may include some fragment of polymer molecules. The 10-12 minutes interval was not considered because the sulphur promotes the cross-linking of the polymer, which is then insoluble in THF and cannot be injected in the column. In other words, the GPC analysis provides information about MW changes in the bitumen and the bitumen-rich phase, which is not useful when considering polymer aging.

Frequency sweep test

The test was conducted as per the UNI EN 14770-2012 standard using a Dynamic Shear Rheometer (Anton Paar MCR 301) in a parallel plate configuration. The testing conditions are given in Table 1.

Table 1. Frequency sweep test conditions.

T [°C]	0	4	16	28	40	52	64	76	88
DSR Geometry	8 mm plate (2mm gap)				8mm-25mm	25 mm plate (1mm gap)			
f [Hz]	20 ÷ 0.1 (log ramp)								

The test temperatures were not equally applied to all the bitumens (and levels of aging). The temperature intervals were selected for each combination of bitumen-aging to be compatible with the DSR compliance and to cover the widest range of δ -values. Before conducting the test, the equilibrium temperature and the linear strain interval were determined for each bitumen-aging combination and for each geometry. At the overlapping temperature (40°C), the effect of the geometry was controlled according to UNI EN 14770:2012. Three replicates were used for each test.

Calculation of the temperature domain

The correspondence between temperature and frequency entails the applicability of the TTSP. The horizontal shift factors were calculated at a reference temperature of 4°C, on the isotherms of the loss tangent ($\tan \delta$) by minimizing the horizontal geometrical distance between two adjacent curves. In this

way, the shift factors depend more genuinely on relaxation properties (using the same DSR geometry), with the effect of density being excluded (46).

The values of $\alpha(T)$ were fitted with the William-Landel and Ferry (WLF) equation (Equation (4)) (46, 51, 64).

$$\log \alpha(T) = \frac{-C_1 \cdot (T - T_{ref})}{C_2 + (T - T_{ref})} \quad (4)$$

Where T is test temperature [$^{\circ}\text{C}$], T_{ref} is reference temperature [$^{\circ}\text{C}$], C_1 , and C_2 are model coefficients. The model parameters C_1 and C_2 were calculated at the reference temperature of 4°C by minimizing the error (ε) given in Equation (5).

$$\varepsilon = \sum_{i=1}^T (\log(\alpha(T_i)_{tan\delta}) - \log(\alpha(T_i)_{WLF}))^2 \quad (5)$$

Where T_i is the i -test temperature, $\alpha(T_i)_{tan\delta}$ is the shift factor calculated minimizing the geometrical distance between the isotherms, and $\alpha(T_i)_{WLF}$ is the shift factor calculated with the WLF equation. Then, the WLF was rearranged, Equation (6), and used to build the isochrones (at 0.5 Hz) of $\tan \delta$ in the domain of temperature (65).

$$T = \frac{C_2 \cdot \log\left(\frac{f}{f_{red}}\right)}{C_1 + \log\left(\frac{f}{f_{red}}\right)} + T_{ref} \quad (6)$$

Results and discussion

Fluorescence microscopy

Images of the fluorescence microscopy of the PMBs are given in Figure 1.

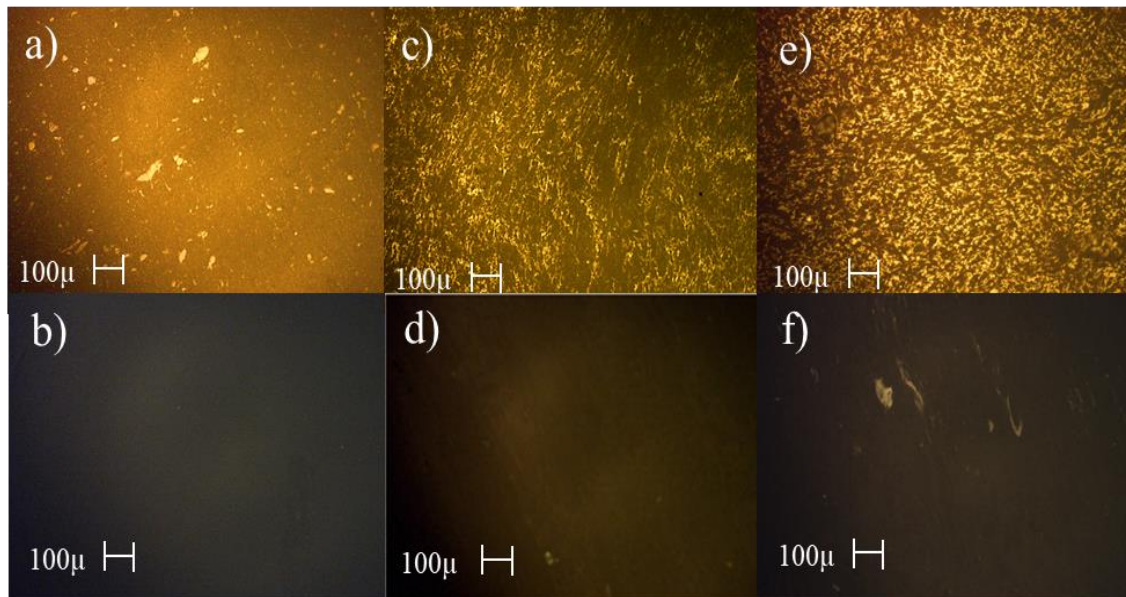


Figure 1. Morphology of PMBs at Unaged (U) and 4PAV-aged conditions (4P). a – SBS 2/S (U); b – SBS 2/S (4P); c – SBS 4/S (U); d – SBS 4/S (4P); e – SBS 6/S (U); f – SBS 6/S (4P).

The effects of bitumen-polymer compatibility and aging on the morphology have been discussed in Cuciniello et al. (4). The SBS PMBs show good compatibility (prompted by the use of sulphur as a cross-linking agent), and the unaged binders are either homogeneous (low polymer content) or with the so-called ‘orange-skin morphology’. After long-term aging, the images appear dark and homogeneous irrespective of the polymer content. This indicates that the polymeric network, initially swollen by the more fluorescent aromatic molecules, disappeared. Considering the highly unsaturated composition of the polymer, it is reasonable to suppose that the polymer underwent a degradation that at least partially destroyed the cross-linked network.

GPC

The GPC chromatograms between 12 and 20 minutes of retention time are given in Figure 2 (a to d).

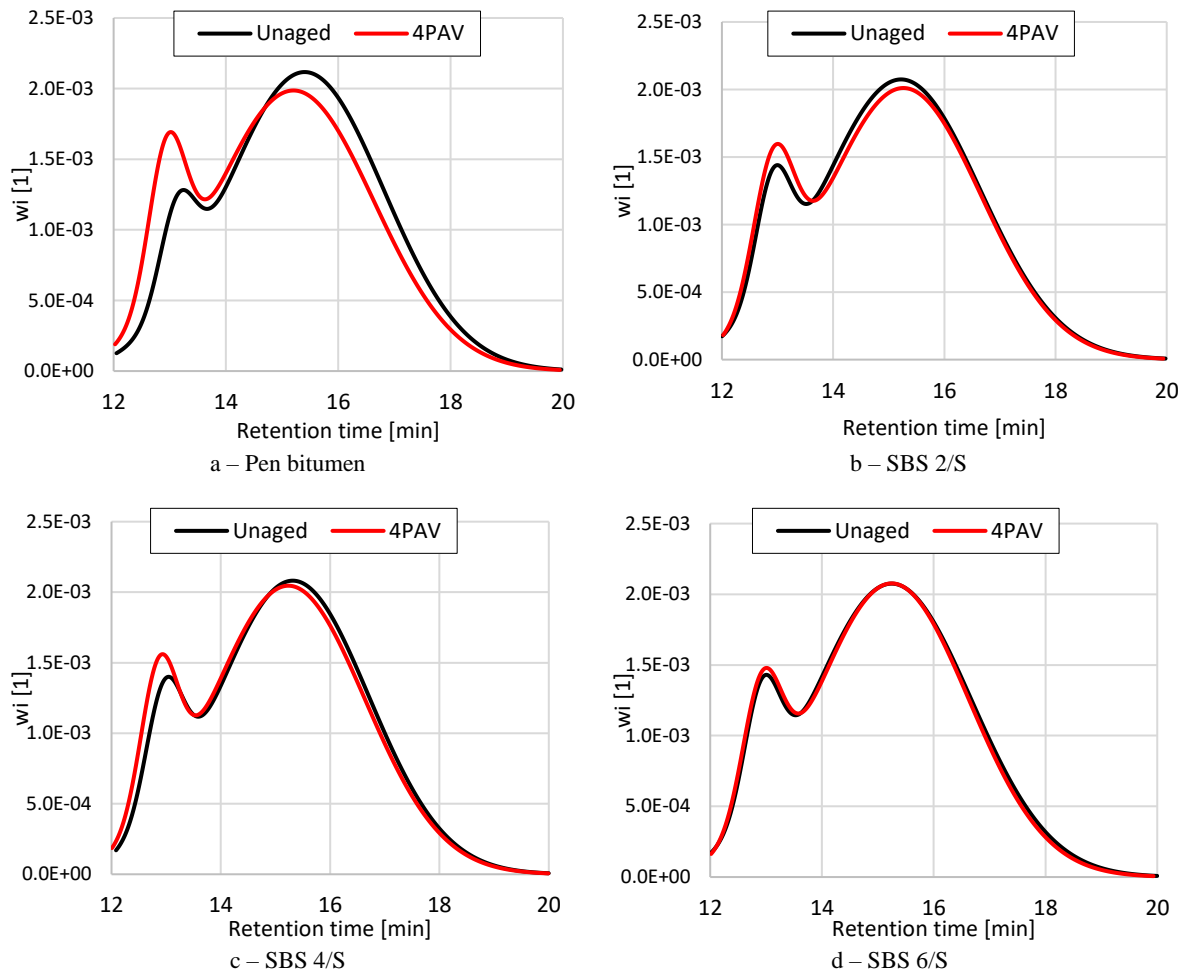


Figure 2. Chromatograms of bitumens at unaged and 4PAV-aged conditions.

It is worth noting that the chromatograms are reported as the raw data obtained from the instrument. The only data manipulation is a normalization of the y-axis so that the ordinate represents a weight fraction, but no time-molecular weight conversion was applied. The reason for this is that the use of a standard like polystyrene would give unreliable molecular weights. Therefore, the distributions reported in the graphs need to be interpreted as high (low retention times) and low (high retention times) molecular weights. Figure 2 shows that for all binders, there is a shift towards lower retention times (heavier molecules) with aging. This is well known since oxidative aging increases the heavier (and polar) fractions (i.e., asphaltenes). However, it is interesting to observe that the shift is lower in the case of modified binders. This could be surprising since polymer degradation is expected to contribute to increasing the heavier fraction. The most straightforward interpretation is that in this case, the oxygen diffusion during RTFOT and PAV is limited by the high viscosity of the binder (66). This is consistent with the observation that the SBS 6/S binder is the one that shows the smallest variation due to aging

(Figure 2 – d). Another possibility is a sort of sacrificial effect exerted by the polymer that, during the artificial aging procedures, preferentially captures the free radicals responsible for the aging reactions.

Given these preliminary results, it is interesting to evaluate how they parallel the effects on the molecular relaxation of the binders.

Black diagrams

Pen bitumen

The black diagrams of the Pen bitumen at unaged, 1PAV, and 4PAV-aged conditions are given in Figure 3.

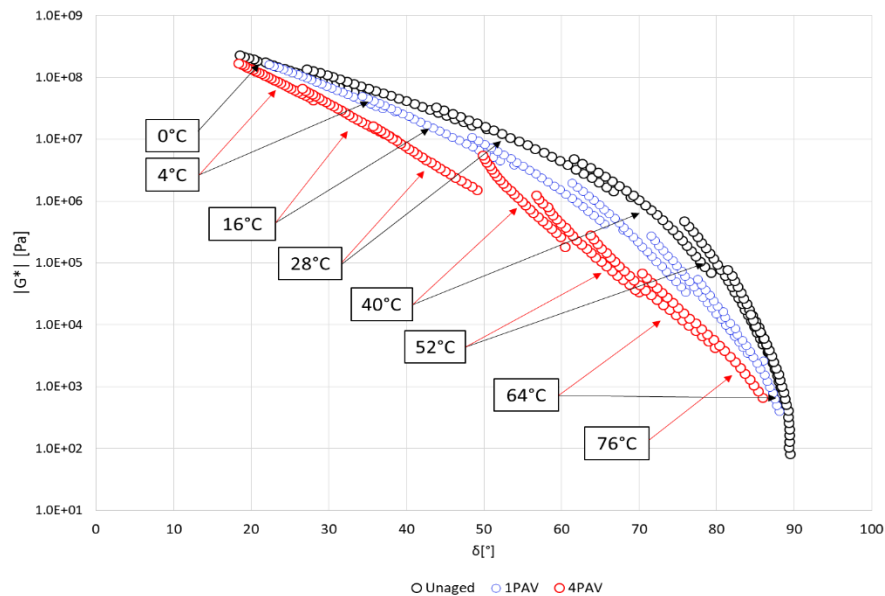


Figure 3. Black diagrams of Pen bitumen at unaged, 1PAV and 4PAV-aged conditions.

At unaged conditions, the curve shows a relatively smooth trend without relevant discontinuities. The pattern of the curve is typical of unmodified bitumens with the phase angle that increases while the material becomes softer. Laboratory aging produces an increase in the elastic response with the phase angle (δ) decreasing at the same level of stiffness (1PAV- curve - Figure 3). As mentioned above, the increase in heavy fractions depends on the growth of asphaltenes. Black curves at 1PAV aging still show a smooth trend, and thus no problems are expected for the applicability of the TTSP. However, prolonging the PAV exposure (i.e., 4PAV - Figure 3), the superposition of the isotherms, with respect to the unaged binder, is slightly reduced. Furthermore, the isotherms start showing a wavy pattern that could be ascribed to some initial “transition” in the bitumen microstructure that could affect the

temperature-dependency of the stress relaxation. Such a case belongs to one of the categories described by Lesueur (i.e., highly oxidized bitumens (43)), and confirms that aging may limit the TTSP applicability. In conclusion, for the unmodified binder, in the considered range of temperatures, the effects of PAV-aging on the microstructure are not significant enough to cause the breakdown of the TTSP. The black diagrams maintain an acceptable smoothness and only at a very high level of aging (probably non-compatible with road applications) are some symptoms of TTSP breakdown observed.

SBS modified bitumens

The black diagrams of the unaged modified binders (together with the Pen bitumen) are given in Figure 4.

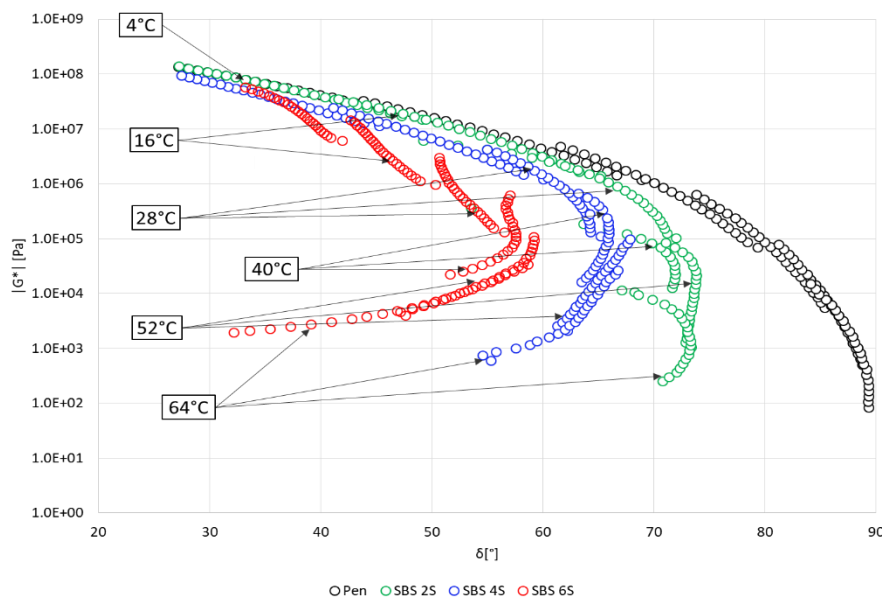


Figure 4. Black diagrams of SBS modified bitumens at unaged conditions. (Pen bitumen included as reference).

In the low-intermediate temperature region (i.e., 4-28°C), where the linear viscoelastic response is mainly controlled by the bitumen phase (62). The SBS 2/S and SBS 4/S have a behavior similar to that of the Pen bitumen. Different behavior is shown by the SBS 6/S bitumen, where the effect of the polymer network is more visible. It seems that this polymer concentration and the use of the cross-linker provides the SBS with such a high level of dispersion, swelling and structuring, to control the viscoelastic response even at low temperatures. The morphology supports this hypothesis. Figure 1- e indicates phase inversion; the polymer-rich phase is the dispersing phase, while the bitumen-rich phase is the dispersed one.

At higher temperatures (i.e., 40 to 64°C), the trend of the curves is a function of the polymer concentration. The SBS 2/S seems to reach a sort of plateau region that may indicate an elastic response determined by a weak polymer network (due to cross-linking and/or entanglements (47, 62)). At the same time, at higher SBS concentrations, the black diagrams tend towards lower phase angles. These trends confirm the formation of the polymer network, which resists viscous flow at higher temperatures and controls the rheological response.

As already mentioned the smoothness of the black diagram indicates that the relaxation spectrum depends uniformly on temperature variations and suggests the successful applicability of the TTSP. Therefore, Figure 4 does not raise concerns regarding the thermorheological simplicity of SBS 2/S and SBS 4/S but it does for SBS 6/S. In the latter case, something disturbs the internal structure of the binder. To understand the nature of this disturbance, it is useful to remember that in the case of polymers, the presence of a cross-linked structure completely alters the viscoelastic behavior and is responsible for the prevalence of the elastic component even at high temperatures. However, even uncross-linked polymers may show an elastic behavior, i.e., a “plateau” zone in the phase angle, thanks to the entanglement between the chains. These entanglements cause a significant delay in the molecular rearrangement process. Therefore, molecular relaxation is affected by both the cross-linking and the entanglements, and these effects may also be observed in SBS modified bitumens (44, 46, 62). The difference between the SBS 6/S and the other two bitumens is in the polymer content (and in the level of dispersion/cross-linking). In the first case, the polymer is the dominant phase, and its effects are visible at both low (i.e., the wavy shape of curves) and high temperatures (decrease in phase angle). However, in the low-temperature region, the relaxation spectrum depends also on the bitumen-rich phase, which has comparable stiffness. Therefore, in this range, the relaxation time seems to depend on both phases and this can result in the TTSP breakdown. From this point of view, we can classify this TTSP breakdown as included in the case mentioned above of composite materials. In contrast, in the two binders with lower polymer content, the effects of entanglements and polymer network are weaker and start to be disparate with bitumen only at higher temperatures, when the bitumen softens (10). Therefore, the relaxation spectrum is primarily governed by the bitumen-rich phase in the intermediate-

low temperature region (i.e., 4°C to 28°C) and by the polymer-rich phase in the high-temperature region (i.e., 40-64°C). In other words, the stiffness of the bitumen and polymer-rich phases become disparate at higher temperatures, where the bitumen has almost a liquid-like behavior. This could be the reason why the black diagram remains smooth over the whole temperature range.

The effects of aging are discussed at each polymer concentration.

SBS 2/S

The black diagrams of the SBS 2/S bitumen are given in Figure 5.

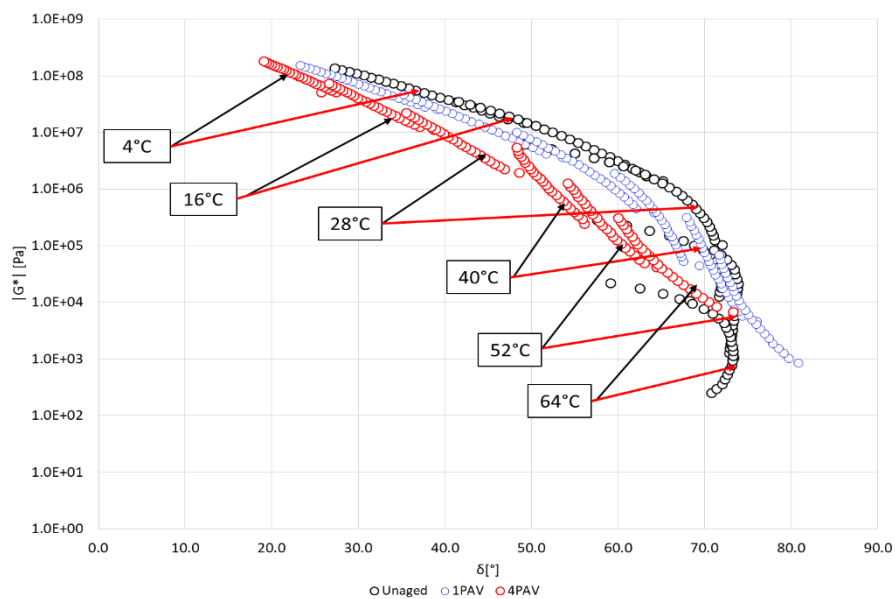


Figure 5. Black diagrams of SBS 2/S bitumen at unaged, 1PAV and 4PAV-aged conditions

Laboratory aging affects the viscoelastic response over the whole range of temperatures. However, based on the previous considerations, we can analyse the curves as if they are divided into two zones. At low temperatures, they mainly reflect the effect of the bitumen phase aging, while at high temperatures, the effects of the polymer phase aging are seen. Therefore, the shift towards lower phase angle and higher stiffness observed at 4, 16, and 28°C indicates the hardening of the bitumen-rich phase. In contrast, the 40-64°C region shows the changes in the polymer-rich phase. At unaged conditions, the presence of a weak polymer network contributes to the formation of a plateau region with the phase angle that remains constant while the bitumen softens. This plateau disappears after one cycle of PAV, and the isotherms tend to be disconnected and shift towards higher phase angles. Furthermore, the wavy pattern of the isotherms at 4PAV (Figure 5) is similar to what observed in the Pen bitumen (Figure 3).

All these results indicate that the SBS-rich phase has undergone extensive degradation and the bitumen phase has oxidized irrespective of the presence of the polymer. These observations are in agreement with other works in literature (10, 35). Concerning the applicability of the TTSP, the bitumen-rich phase maintains the same behavior observed for the unmodified binder. At the same time, the degradation of the polymer backbone reduces the smoothness of the curve in the high-temperature region (Figure 5 – 1PAV), whose trend varies from a plateau (i.e., unaged) to the one of a 4PAV-aged neat bitumen. Therefore, it seems that the relaxation spectrum ranges from a thermorheological simple (TS) unaged configuration, governed by the bitumen-rich phase and the polymer-rich phase (non-oxidised), to an oxidized TS configuration whose relaxation spectrum depends mainly on the oxidized bitumen. The degradation of the morphology of the SBS network is visible in the fluorescence microscope images (Figure 1).

SBS 4/S

The black diagrams of the SBS 4/S bitumen are given in Figure 6.

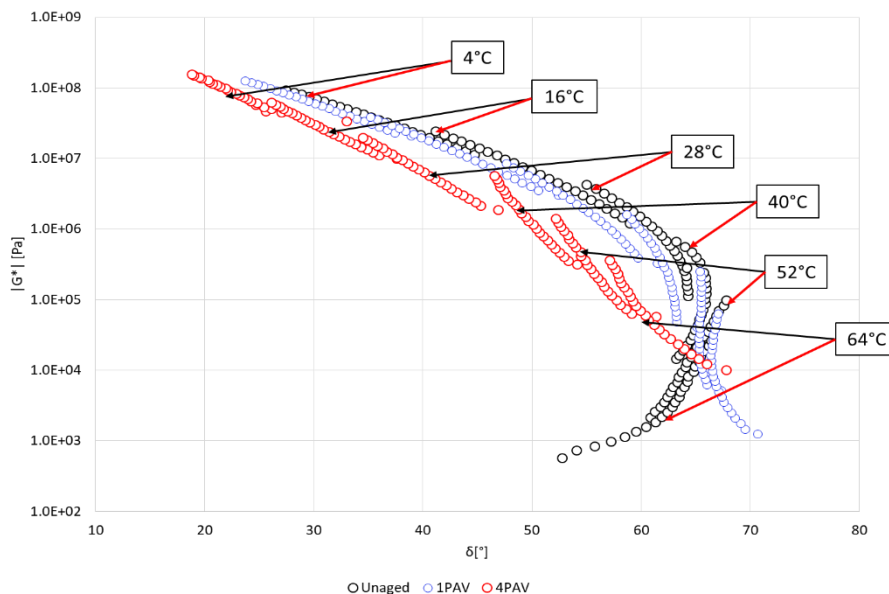


Figure 6. Black diagrams of SBS 4/S bitumen at unaged, 1PAV, and 4PAV-aged conditions

In the intermediate-high temperature range (i.e., 40 to 64°C), the effects of aging are similar to those observed at 2% SBS concentration with the polymer backbone showing degradation (i.e., unclear presence of plateau region). On the other hand, in the low-intermediate temperature region (i.e., 4 to 28°C), laboratory aging does not seem to alter the rheological response in one cycle of PAV (or even

after two cycles). Therefore, at high SBS concentrations, the degradation of the polymer backbone is likely to inhibit and delay the hardening of the bitumen phase. After four cycles of PAV, the response is similar to those observed in Figure 3 & Figure 5 (i.e., 4PAV conditions). The considerations provided for the SBS 2/S bitumen about the TTSP and morphology (Figure 1 - d) apply in this case as well.

SBS 6/S

The black diagrams of the SBS 6/S bitumen are given in Figure 7.

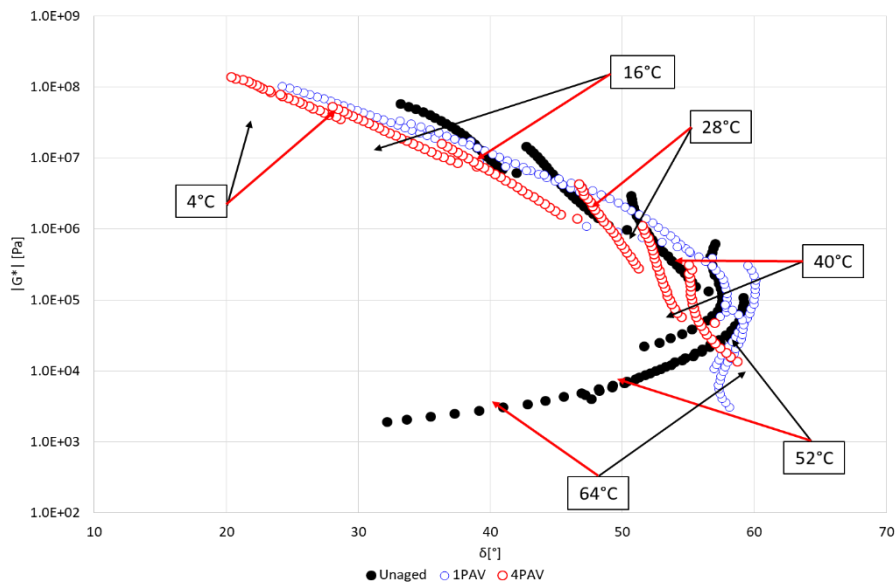


Figure 7. Black diagrams of SBS 6/S bitumen at unaged, 1PAV, and 4PAV-aged conditions.

The unaged curve, which has been described above, has been plotted with plain circles to improve the clarity of the image. On the other hand, the curves at different levels of ageing highlight that aging produces visible changes in their shape. In the range of temperature between 4 and 40°C, the curve is similar to the other bitumens at unaged conditions (i.e., smooth continuous curve). This indicates that, due to its degradation (visible in Figure 1 - f), the effects of the polymer backbone on the molecular relaxation (within this range of temperatures) has almost vanished. Therefore, the stress relaxation is now more controlled by the bitumen-rich phase that provides a smooth trend, which highlights that the changes in the bitumen microstructure cause a transition towards a more TS configuration. On the other hand, at higher temperatures (i.e., 52°C and 64°C), the degradation of the polymer backbone is visible with the phase angle that shows an unclear plateau. After four cycles of PAV, the presence of the polymer is almost undetectable and the curve is very similar to those of the other PMBs.

Isochrones of loss tangent in the temperature domain

The isochrones of the loss tangent in the temperature domain were calculated by applying the TTSP. Except for one case (i.e., SBS 6/S unaged), the black diagrams show the validity of the time-temperature superposition for all the cases investigated (although some of them require more caution than others). With this premise in mind, the loss tangent is used to investigate the effects of the SBS network on the stress relaxation at different levels of aging. The isochrones of the bitumens are given in Figure 8.

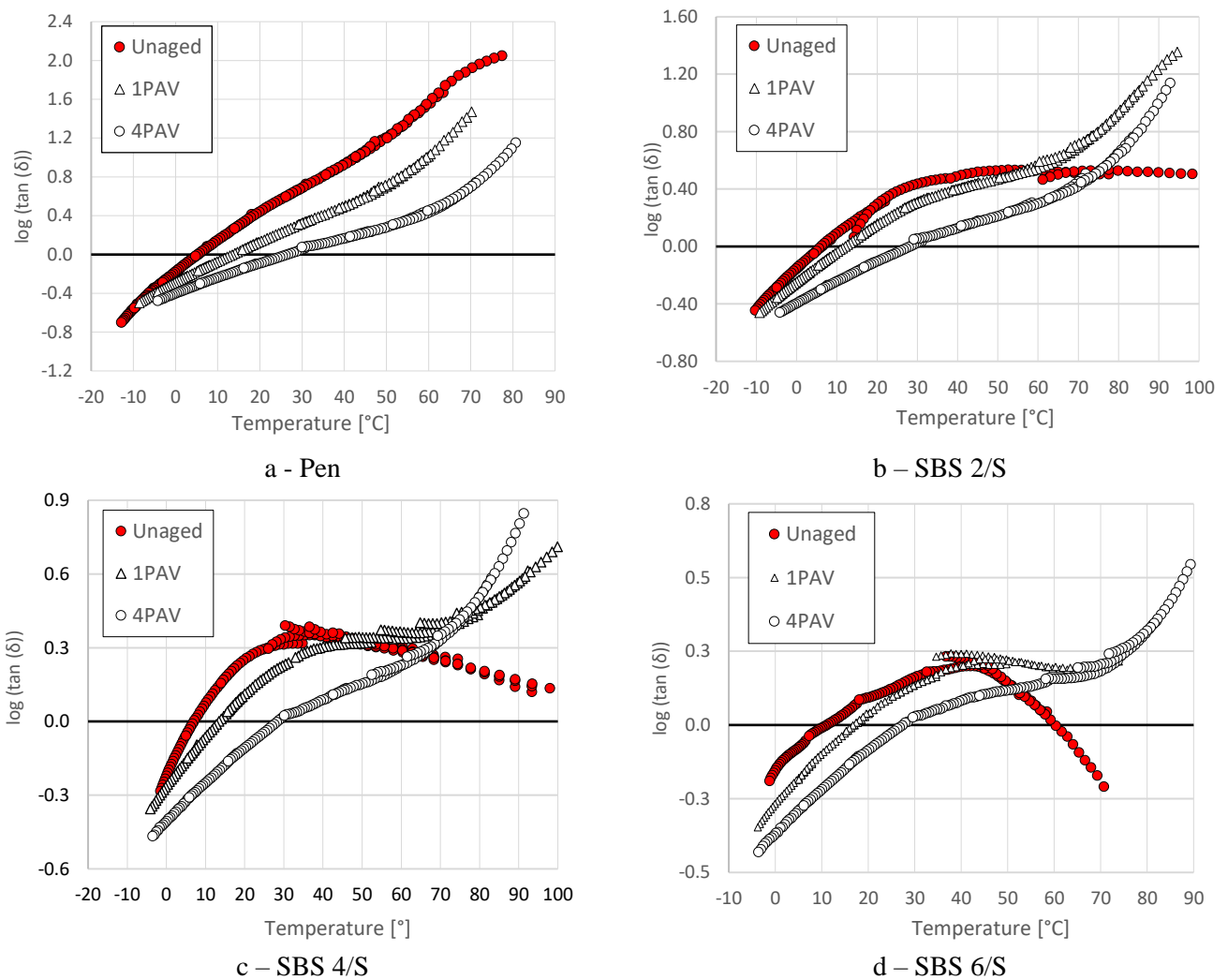


Figure 8. Isochrones (@0.5Hz) of the logarithm of the loss tangent versus temperature at unaged, 1PAV, and 4PAV aged conditions. (a – Pen bitumen; b – SBS 2/S; c – SBS 4/S; d – SBS 6/S)

Pen

The Pen bitumen (Figure 8 - a) shows a monotonic behavior without any intermediate (or secondary) transition. The loss tangent increases with temperature, indicating an increase in the relaxation time (Equation (3)). This behavior is similar to low-molecular-weight polymers between the terminal zones

of steady flow (high temperatures) to glasslike consistency (low temperature) without any rubbery transition (44, 46). As expected, aging produces a shift of the loss tangent curve towards lower values at higher temperatures with a consequential change of the cross-over temperature, which is the temperature at which $\tan \delta=1$ (i.e., $\log (\tan \delta) = 0$), towards higher temperature values. The curve at 4PAV is smooth and does not show any discontinuities. Therefore, the applicability of the TTSP over this range of temperatures provides satisfactory results.

The use of SBS polymer modifies the transition zone as a function of the polymer content.

SBS 2/S

At 2% SBS, the curve of the unaged bitumen shows a horizontal plateau of loss tangent which is maintained up to 100°C (Figure 8 - b). This behaviour depends on the formation of the network/entanglements as discussed previously. The effects of laboratory-aging are visible at higher temperatures, where the curves show a monotonic trend. After one cycle of PAV, the polymer network seems to have a residual effect between 30°C and 60°C, whilst after four cycles of PAV, the isochronal plot has the same trend as an unmodified bitumen. The cross-over temperature increases with aging. Again, in this case, the applicability of the TTSP provides smooth curves.

SBS 4/S

In the region of temperatures below 30°C, the isochrones do not show relevant deviations from those of the SBS 2/S (Figure 8 - c) since the rheological response is more controlled by the bitumen-rich phase. At unaged conditions, the curves show some scattering around 40°C, which might depend on the change in the DSR geometry, and on the fact that this temperature is where the phase angle starts decreasing (Figure 6). Increasing the temperature (>40°C), the unaged curve shows a slightly decreasing trend that indicates a more elastic response at higher temperatures. This is the effect of the polymer network (i.e., entanglements/cross-linking). Aging produces the same effects discussed for the SBS 2/S bitumen with the polymer backbone degrading progressively. The curve at 1PAV shows some scattering between 40°C and 70°C, caused by the degradation of the polymer backbone already discussed in the black diagrams (Figure 6). This case could represent one of those where the applicability of the TTSP

to the whole temperature interval may provide a lower accuracy in the results. However, the shape of the curve is consistent with that shown previously for the SBS 2/S bitumen.

SBS 6/S

The loss tangent isochrones of the unaged SBS 6/S bitumen (Figure 8 - d) show a smooth trend despite that seen in the black diagram (Figure 7). The downward concave shape of the isochrone at unaged condition has some similarities with the transition of high-MW polymers, where the drop at low temperatures is linked to the entrance into the glassy region. In contrast, the one at high temperatures is connected to entanglements. This is not surprising since, at this concentration, the SBS has become the dominant phase that controls the whole temperature interval. Another visible difference is the presence of two cross-over temperatures at approximately 10 and 60°C. This behavior is consistent with the strength of the polymer network and has already been described in master curves of similar binders (44). Once again, the effects of aging are similar to those discussed for the other two SBS concentrations.

Conclusions

This work investigated the changes in the microstructure of laboratory-aged unmodified and SBS modified bitumens with a close focus on the applicability of the TTSP. The following points summarize the main findings.

- The GPC analysis confirms that aging produces an increase in the heavy fractions of the bitumens, but suggests that the SBS could inhibit this mechanism. The higher the polymer content, the greater is the effect. The fluorescence microscopy images indicate that the SBS-rich phase disappears with aging, thus suggesting polymer degradation.
- The unmodified bitumen is thermorheologically simple even after a prolonged PAV exposure. Only at 4 PAV aging do some symptoms of TTSP failure seem to show up in the black diagrams.
- The applicability of the TTSP to SBS modified bitumens is highly dependent on the capability of the polymer to form a structured network in the bitumen phase. The network

could include chemical cross-linking and/or the presence of entanglements and increase the elasticity at high temperatures. Moreover, the network causes a delay in the molecular relaxation time that may induce a TTSP breakdown.

- In the case of low-medium and medium-high polymer contents, the applicability of the TTSP is not challenged since the rheological response is distinctively controlled by the bitumen-rich phase at low temperatures and by the polymer-rich phase at high temperatures. Aging causes the degradation primarily of the SBS network, and the response of the whole systems shifts progressively under the control of the bitumen-rich phase with no concerns for the validity of the TTSP.
- At high polymer contents, the polymer becomes the dominant phase affecting both the high and the low temperature regions challenging the applicability of the TTSP. That is, if at high temperatures the polymer-rich phase is more evident in the response, at low temperatures the concomitant effects of the polymer network (that is not weak in this case) and of the bitumen phase, results in a biphasic structure, which might not be TS. Aging produces effects similar to the other two concentrations, but with different magnitudes.
- The isochrones of the loss tangent in the temperature domain are a valid representation of the effects of the polymer network and of its oxidative-degradation on the elasticity and the stress relaxation of PMBs.

References

1. Zhu, J., Birgisson, B., Kringos, N. (2014). Polymer modification of bitumen: Advances and challenges. *European Polymer Journal*. Vol. 54, pp. 18-38.
2. Lesueur, D. (2009). The colloidal structure of bitumen: Consequences on the Rheology and on the Mechanisms of Bitumen Modification. *Advances in Colloid and Interface Science*, 145(1-2), 42-82.
3. Cuciniello, G., Leandri, P., Filippi, S., Lo Presti, D., Polacco, G., Losa, M., & Airey, G. (2019). Microstructure and rheological response of laboratory-aged SBS-modified bitumens. *Road Materials and Pavement Design*, 1-25.
4. Cuciniello, G., Leandri, P., Filippi, S., Lo Presti, D., Losa, M., & Airey, G. D. (2018). Effect of ageing on the morphology and creep and recovery of polymer-modified bitumens. *Materials and Structures*, 51, 136.
5. Goodrich J.L, Goodrich J.E., Kari, W.J., Asphalt Composition Tests: Their Application and Relation to Field Performance. *Transportation Research Record: Journal of the Transportation Research Board*, Vol. 1096, pp. 146-167, 1986.
6. Lu, X., Isacson, U. (1999). Chemical and Rheological Characteristics of Styrene-Butadiene-Styrene Polymer-Modified Bitumen. *Transportation Research Record: Journal of the Transportation Research Board*, Vol. 1661, pp. 83-92.
7. Lu, X., Isacson, U. (2000) Artificial Ageing of Polymer-modified Bitumen. *Journal of Applied Polymer Science*, Vol. 76, pp. 1811-1824.
8. Negulescu, I., Muhammad, L., Daly, W., Abadie, C., Cuero, R., Daranga, C., and Glover, I., Chemical and rheological characterization of Wet and Dry Ageing of SBS Copolymer-modified Asphalt Cement: Laboratory and Field Evaluation. *Journal of the Association of Asphalt Paving Technologists*, Volume: 75, pp. 267 – 296, 2006.
9. Cortizo M.S., Larsen, D.O., Bianchetto, H., Alessandrini, J.L., Effect of the Thermal Degradation of SBS Copolymers during the Ageing of Modified Asphalts. *Polymer Degradation and Stability*, Vol. 86, pp. 275 282, 2004.

10. Airey G.D, Brown S. F., Rheological Performance of Aged Polymer Modified Bitumens. *Journal of Association of Asphalt Pavement Technologists*, Vol. 67, pp. 66-100, 1998.
11. Kumbargeri, Y., and Biligiri K.. A Novel Approach to Understanding Asphalt Binder Aging Behavior Using Asphaltene Proportion as a Performance Indicator. *Journal of Testing and Evaluation*, Vol. 44, No. 1, p. 20140490, 2015.
12. Kumbargeri, Y., and Biligiri K.. Rational Performance Indicators to Evaluate Asphalt Materials' Aging Characteristics. *Journal of Materials in Civil Engineering*, Vol. 28, No. 12, pp. 04016157, 2016.
13. Polacco G., Filippi S., Merusi F., & Stastna G. (2015). A Review of the Fundamentals of Polymer-Modified Asphalts: Asphalt/polymer Interactions and Principles of Compatibility. *Advances in Colloid and Interface Science*, 224, 72–112.
14. Mandal, T., Sylla, R., Bahia, H. U., & Barmand, S. (2015). Effect of cross-linking agents on the rheological properties of polymer-modified bitumen. *Road Materials and Pavement Design*, 16(1), 349–361.
15. Petersen, J. C.. Chemical Composition of Asphalt as Related to Asphalt Durability: State of the Art. Transportation Research Record 999 Transportation Research Board, 13-30 1984.
16. Petersen, J., and R. Glaser. Asphalt Oxidation Mechanisms and the Role of Oxidation Products on Age Hardening Revisited. *Road Materials and Pavement Design*, Vol. 12, No. 4 pp. 795-819, 2011.
17. Petersen J. C.. A Review of the Fundamentals of Asphalt Oxidation. Transportation Research Board Circular E-C140, 2009.
18. Page G.C., Murphy K.H., Ruth B.E., and Roque R.. Asphalt binder Hardening-Causes and Effects. *Journal of Association of Asphalt Paving Technologists*, pp. 140-167, 1985.
19. Mouillet, V., Lamontagne, J., Durrieu, F., Planche, J.P., & Lapalu, L. (2008). Infrared Microscopy Investigation of Oxidation and Phase Evolution in Bitumen Modified With Polymers. *Fuel* 87 (7): 1270-1280.

20. Cuciniello, G. (2019). Study of the effect of laboratory-simulated ageing on the damage resistance of polymer-modified bitumens in intermediate climates. PhD thesis, University of Nottingham.
21. Lucena, M., S. Soares, and J. Soares. Characterization and thermal behavior of polymer-modified asphalt. *Materials Research*, Vol. 7, No. 4, 2004, pp. 529-534.
22. Hofko B, Porot L, Falchetto Cannone A, Poulikakos L, Huber L, Lu X et al (2018) FTIR spectral analysis of bituminous binders: reproducibility and impact of ageing temperature. *Mater Struct* 51(2):45.
23. Hao, G., Huang, W., Yuan, J., Tang, N., Xiao, F. Effect of aging on chemical and rheological properties of SBS modified asphalt with different compositions. *Construction and Building Materials*, Vol. 156, pp. 902-910, 2017.
24. Handle, F., Füssl, J., Neudl, S., Grosseegger, D., Eberhardsteiner, L., Hofko, B., Hospodka, M., Blab, R. and Grothe, H. 2014, The Bitumen Microstructure: A Fluorescent Approach. *Materials And Structures* 49 (1-2): 167-180.
25. Ruan, Y., Davison, R.R., Glover, C.J. The effect of long-term oxidation on the rheological properties of polymer-modified asphalts. *Fuel*, Vol. 82, Issue 14, pp. 1763-1773, 2003.
26. Cuciniello, G., Filippi, S., Cappello, M., Leandri, P., & Polacco, G. A revised relationship between molecular weight and reduced angular frequency in δ -method applied to unmodified petroleum bitumens. Submitted to *Road Materials and Pavement Design* for publication. Under Review.
27. Le Guern, M., Chailleux, E., Farcas, F., Dreessen, S., and Mabilille, I. (2010). "Physico-Chemical Analysis of Five Hard Bitumens: Identification of Chemical Species And Molecular Organization Before And After Artificial Aging". *Fuel* 89 (11): 3330-3339.
28. Bahia, H. U., Perdomo, D. Current practices for modification of paving asphalts, *Fuel*, 1996, 41, 4.
29. Zhang, Feng, Jianying Yu, and Shaopeng Wu. 2010. Effect Of Ageing On Rheological Properties Of Storage-Stable SBS/Sulfur-Modified Asphalts. *Journal of Hazardous Materials* 182 (1-3): 507-517.

30. Wang, P., Dong, Z., Tan, Y., & Liu, Z. Investigating the interactions of the saturate, aromatic, resin, and asphaltene four fractions in asphalt binders by molecular simulations. *Energy & Fuels*, 29(1), 2015.
31. M. Liu, M. A. Ferry, R. R. Davison, C.J. Glover, J. A. Bullin, Oxygen Uptake As Correlated to Carbonyl Growth in Aged Asphalts and Asphalt Corbett Fractions, *Industrial Engineering and Chemical Research*, Vol. 37, pp. 4669-4674, 1998.
32. Pérez-Martínez, M., Marsac, P., Gabet, T., Pouget, S., & Hammoum, F. (2017). Ageing evolution of foamed warm mix asphalt combined with reclaimed asphalt pavement. *Mater. Constr.*, 67 (327), p. e125.
33. Themeli, A., Chailleux, E., Farcas, F., Chazallon, C., Migault, B., & Buisson, N. (2017). "Molecular Structure Evolution Of Asphaltite-Modified Bitumens During Ageing; Comparisons With Equivalent Petroleum Bitumens". *International Journal Of Pavement Research And Technology* 10 (1): 75-83.
34. Themeli, A., Chailleux, E., Farcas, F., Chazallon, C., & Migault, B. (2015) Molecular weight distribution of asphaltic paving binders from phase-angle measurements. *Road Materials and Pavement Design*, 16, 228–244.
35. Cotte C., Such C., Influence of RTFOT Ageing on the Rheological Behavior of Polymer Modified Bitumen and Their Associated Phases.” Proceedings of the Euraspalt & Eurobitume Congress, E&E.5.105, Strasbourg, May 1996.
36. Masson, J., and Polomark, G. Bitumen Microstructure by modulated differential scanning calorimetry. *Thermochimica Acta*, Vol. 374, No. 2, pp. 105-114, 2001.
37. D'Angelo, J., R. Kluttz, R. (2007). Revision of the Superpave high temperature binder specification: the multiple stress creep recovery test (with discussion). *Journal of the Association of Asphalt Paving Technologists*, Vol. 76, 123–162.
38. Bahia, H. U., Zhai, H., Bonnetti, K., & Kose, S. (1999) Non-Linear Viscoelastic and Fatigue Properties of Asphalt Binders. *Journal of the Association of Asphalt Paving Technologists*, Vol. 68, 1-34.

39. Bahia, H., D. Perdomo, and P. Turner. (1999). Applicability of Superpave Binder Testing Protocols to Modified Binders. *Transportation Research Record: Journal of the Transportation Research Board*, Vol. 1586, pp. 16-23.
40. Kose, S., M. Guler, H. Bahia, and E. Masad. (2000). Distribution of Strains Within Hot-Mix Asphalt Binders: Applying Imaging and Finite-Element Techniques. *Transportation Research Record: Journal of the Transportation Research Board*, Vol. 1728, pp. 21-27.
41. Masad, E., and N. Somadevan. Microstructural Finite-Element Analysis of Influence of Localized Strain Distribution on Asphalt Mix Properties. *Journal of Engineering Mechanics*, Vol. 128, No. 10, pp. 1105-1114, 2002.
42. Airey, G., Rahimzadeh B., and Collop A. Linear Rheological Behavior of Bituminous Paving Materials. *Journal of Materials in Civil Engineering*, Vol. 16, No. 3, pp. 212-220, 2004.
43. Lesueur, D., Gerard, J. F., Claudy, P., Letoffe, J. M., Planche, J. P., & Martin, D. (1996). A structure-related model to describe asphalt linear viscoelasticity. *Journal of Rheology*, 40(5), 813-836.
44. Polacco, G., Stastna, J., Biondi, D., & Zanzotto, L. (2006). Relation between polymer architecture and nonlinear viscoelastic behavior of modified asphalts. *Current opinion in colloid & interface science*, 11(4), 230-245.
45. Lakes, Roderick. *Viscoelastic Materials*, Cambridge University Press, 2009.
46. Ferry, John D. *Viscoelastic Properties of Polymers*, 3rd Edition. New York: Wiley, 1980.
47. Young, R. J. & Lovell, PA. *Introduction to Polymers: Third Edition*. 3 edn, CRC Press, Inc., Boca Raton, FL, USA, 1991.
48. Yusoff, M. D., Izzi, N., Chailleux, E., and Airey, G. (2011). A comparative study of the influence of shift factor equations on master curve construction. *International Journal of Pavement Research and Technology*, 4.
49. Chailleux, E., Ramond, G., Such, C., and De La Roche, C. (2006). A Mathematical-Based Master-Curve Construction Method Applied To Complex Modulus Of Bituminous Materials. *Road Materials and Pavement Design* 7 (sup1): 75-92, 2006.

50. Rowe, G.M., & Sharrock, M.J. Alternate Shift Factor Relationship for Describing Temperature Dependency of Viscoelastic Behavior of Asphalt Materials. (2011) *Transportation Research Record: Journal of The Transportation Research Board* 2207 (1).
51. Yusoff, N.I.M., Shaw, M.T., and Airey, G.D. Modelling the linear viscoelastic rheological properties of bituminous bitumen. *Constr. Build. Mater.*, vol. 25, 2011, no. 5, pp. 2171–2189.
52. Airey, G. D., Grenfell, J. R. A., Apegyei, A., Subhy, A., & Presti, D. L. (2016). Time dependent viscoelastic rheological response of pure, modified and synthetic bituminous binders. *Mechanics of time-dependent materials*, 20(3), 455-480.
53. Airey, G. D. (2002). Use of black diagrams to identify inconsistencies in rheological data. *Road Materials and Pavement Design*, 3(4), 403-424.
54. Di Benedetto, H., Sauzeat, C., Bilodeau, K., Buannic, M., Mangiafico, S., Nguyen, Q. T., ... & Van Rompu, J. (2011). General overview of the time-temperature superposition principle validity for materials containing bituminous binder. *Int. J. Roads Airports*, 1(1), 35-52.
55. Petersen, J. C. (2009). A Review of the Fundamentals of Asphalt Oxidation. Transportation Research Board Circular E-C140.
56. Petersen, J. C. Chemical Composition of Asphalt as Related to Asphalt Durability: State of the Art. (1984). *Transportation Research Record: Journal of the Transportation Research Board*, 999, 13-30.
57. Tuminello, W. H., & Mauroux, N. C. (1991). Determining molecular weight distributions from viscosity versus shear rate flow curves. *Polymer Engineering & Science*, 31, 1496–1507.
58. Tuminello, W. H. (1986). Molecular weight and molecular weight distribution from dynamic measurements of polymer melts. *Polymer Engineering & Science*, 26, 1339–1347.
59. Zanzotto, L., J. Stastna, S. Ho. (1999). Molecular weight distribution of regular asphalts from dynamic material functions. *Materials and Structures* 32, 224–229.

60. Zanzotto, L., Stastna, J., & Ho, K. (1996). Characterization of regular and modified bitumens via their complex modulus. *Journal of Applied Polymer Science*, 59(12), 1897–1905.
61. McGrory, W. J., & Tuminello, W. H. (1990). Determining the molecular weight distribution from the stress relaxation properties of a melt. *Journal of Rheology (1978-present)*, 34(6), 867–890.
62. Airey, G. Rheological properties of styrene butadiene styrene polymer modified road bitumens. *Fuel*, 2003, Vol. 82, No. 14, pp. 1709-1719.
63. MEYERS Drew. *Surfaces, Interfaces and Colloids: Principles and Applications*. Wiley VCH, 1999.
64. Zeng, M., Bahia, H. U., Zhai, H., Anderson, M. R., & Turner, P. (2001). Rheological modeling of modified asphalt binders and mixtures (with discussion). *Journal of the Association of Asphalt Paving Technologists*, 70.
65. Losa, M., & Di Natale, A. (2012). Evaluation of representative loading frequency for linear elastic analysis of asphalt pavements. *Transportation research record*, 2305(1), 150-161.
66. Anderson D. A., & Bonaquist R. (2012). Investigation of Short-Term Laboratory Aging of Neat and Modified Asphalt Binder (NCHRP Report No. 709). National Highway Research Programme (US).