Rheological changes in the bitumen caused by heating and interaction with rubber during asphalt-rubber production

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Abstract

The demand for more safe and durable roads, combined with the need to preserve the environment, led to the production and application of asphalt-rubber (AR) on roads. Nevertheless, this complex material needs further study in order to better distinguish among the phenomena that take place during AR production, as they impact on the final product characteristics. Here, we effectively quantify the rheological changes related to bitumen aging due to diffusion of small molecules of bitumen into the rubber particles and to the release of fillers from rubber into the bitumen during AR production. "A sphere AR production simulator" was developed to assess AR aging independently. The comparison of the characteristic relaxation times of both AR and simulated AR shows that the aging alone cannot explain the rheological changes during AR production. The extent of the changes related to the combined effects of aging and filler release increases as the bitumen used to produce AR is softer.

Keywords Asphalt-rubber - Aging - Diffusion - Master curve · Relaxation time · Paving industry

Introduction

The structure and the mechanical properties of bitumen strongly depend on the origin of the crude oil (Stangl et al. 2007) and on the production method (Oyekunle 2006). Bitumen is a chemical continuum of many different molecules with a gradual increase of molar mass, aromatic content, and polarity, from saturates, aromatics, resins, and asphaltenes (Lesueur 2009). It is common to sort this chemical complexity into two groups of molecules, namely the maltenes, which comprise saturates, aromatics, and resins fractions, and the asphaltenes. However, in order to explain some of its physical and rheological behavior, bitumen has been approached as a colloidal dispersion. In the "bitumen colloidal model" (BCM) (Fig. 1), polar molecules (asphaltenes and resins) form weak "networks" of polar-polar associations which primarily give bitumen its elastic characteristics, and upon heating, these weak interactions are broken to yield a Newtonian fluid (Jones and Kennedy 1992).

Bitumen rheological behavior is reflected on pavements with bituminous mixtures, since those that deform and flow excessively may be susceptible to rutting and bleeding while those that are too stiff may be susceptible to fatigue or thermal cracking (Glover 2007).

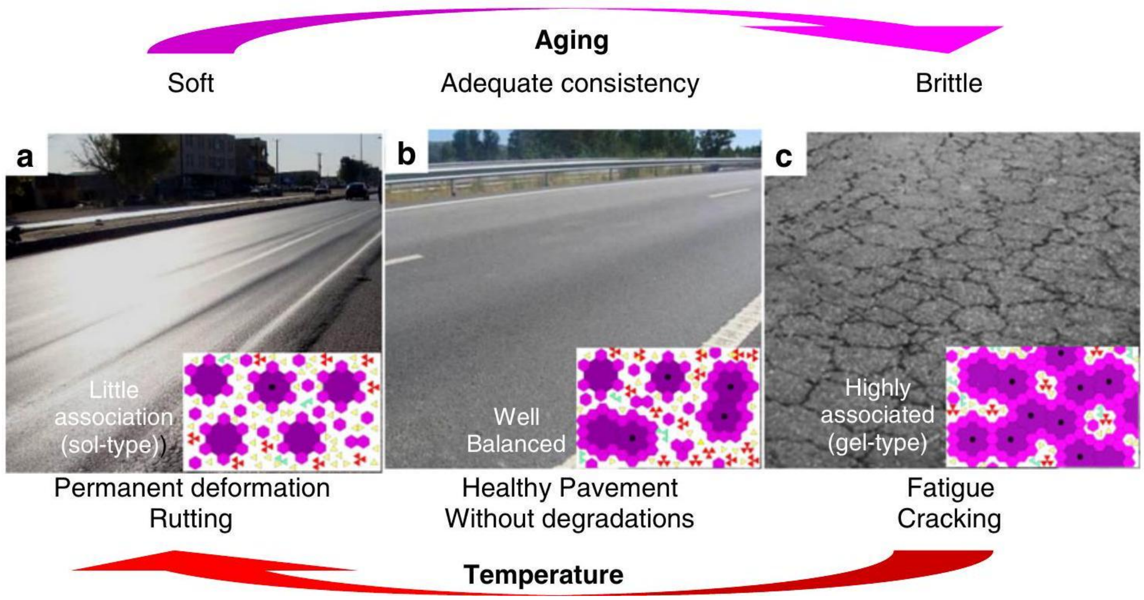


Fig. 1 Schematic relationship between bitumen colloidal model and the effects of aging and temperature in pavements (saturates are in single triangles, waxes in double triangles, aromatics in triple triangles, resins in single hexagons, asphaltenes in flower formed, and black dots symbolize the oxidized state)

When crumb rubber is mixed and heated with bitumen, the resulting modified binder (asphalt-rubber, AR) has significantly different properties than the raw bitumen. Property modification is due to physical and composition changes during the interaction process. Property modification depends on both material and interaction process variables (Shen et al. 2009; Jensen and Abdelrahman 2006; Neto et al. 2003).

Material variables include bitumen properties and crumb rubber properties: (1) Bitumen properties include stiffness and chemical composition, which depends on the amount of the aromatic fraction, temperature, and viscosity (Thodesen et al. 2009) and (2) crumb rubber properties include source and method of processing, namely the production method (ambient shredding or cryogenic grinding), size distribution, specific surface area (micromorphology), and chemical composition (i.e., amount of natural rubber). Another material factor affecting the binder properties is the crumb rubber concentration. Interaction process variables include curing temperature and duration, and mixing shear energy (Xiang et al. 2009; Ould-Henia and Dumont 2006; Jensen and Abdelrahman 2006; Putman and Amirkhanian 2006; Navarro et al. 2004).

During AR binder production, the main mechanism of interaction is the rubber particles swelling due to the absorption of bitumen light fractions into the rubber particles with the stiffening of the residual binder phase (Abdelrahman and Carpenter 1999; Airey et al.

2003; Shen and Amirkhanian 2005). In general, the best solvents or swelling agents for a given polymer are those whose chemical structure is similar to the polymer (Artamendi et al. 2006). Stroup-Gardiner et al. (1993) have concluded that asphalt-rubber interactions are a function of the molecular weight of bitumen components at AR storage temperatures, typically around 165°C. Gawel et al. (2006) stated that primarily lighter nonpolar fractions (n-alkanes and n-alkylbenzenes) are involved in the interaction, which have the highest propensity to penetrate into rubber particles. Preferential absorption of the compounds with linear aliphatic chains into the rubber suggests that these components have better skeletal compatibility with the linear polymeric skeleton of the rubber. On the other hand, bitumen with high asphaltene content is less prone to swelling rubber.

Interaction with rubber stiffens the residual bitumen (Khalid 2005), and the reduction in its aromatic oil content can produce an asphalt-rubber product with poor adhesive properties (Huff and Vallerga 1979). In addition, the volatilization of the lighter fractions and the oxidation of bitumen at high temperatures also occur during AR production. These phenomena are similar to the aging that occurs during the production and laydown of conventional bituminous mixtures. Consequently, residual bitumen is richer in higher molecular weight components (Rahman 2004).

The AR binder is a heterogeneous material, which can be separated in two different phases, the swelled rubber and the residual bitumen (Navarro et al. 2007). The swelled rubber, by itself, does not promote the adhesion between the aggregates in the production of AR mixtures. Thus, it is reasonable to consider the swelled rubber as a special category of aggregate (Airey et al. 2003; Thodesen et al. 2009), being the residual bitumen the final binder of the AR mixture. Therefore, it is essential to evaluate the behavior of this residual bitumen of the AR binder in order to optimize the performance of the AR mixtures (Peralta et al. 2012; Peralta 2009; Gawel et al. 2006; Airey et al. 2003).

In order to understand the characteristics of the residual bitumen of the AR, its aging process must be evaluated separately from the phenomenon of diffusion of lighter molecules of bitumen into the rubber cross-linked network. Thus, in order to assess the information about the aging and diffusion of the residual bitumen during AR production, some methods were proposed to obtain the adequate materials to study these phenomena, namely the "basket drainage method" (Airey et al. 2003) and the "Sphere AR production simulator" or SARPS method (Peralta et al. 2010c).

The aging phenomenon of bitumen has been broadly studied. However, multiple rheological indexes usually applied to quantify aging are generally less accurate than those typically used in pavement industry (Lu and Isacsson 2002; Mastrofini and Scarsella 2000). Recently, and among other rheological characterization studies of asphalt binders (Cuadri et al. 2013; Mouazen et al. 2011), a new rheological parameter was proposed by Peralta et al. (2010a) to study bitumen aging. This parameter is computed from the ratio of the aged and primary bitumen characteristic relaxation times measured from rheological characterization under small-amplitude oscillatory shear (SAOS) at low temperatures. This ratio was found to be a very useful and sensitive parameter to assess bitumen aging.

During the AR production, there are two main phenomena occurring simultaneously that change the chemistry and the rheology of bitumen: bitumen aging due to heating and oxidation, and diffusion of the smallest molecules of bitumen into the rubber particles.

Thus, the main aim of this work is to determine, among the several rheological parameters obtained from SAOS experiments, the most effective ones to quantify the mentioned phenomena, namely to check if the previously proposed index based on the relaxation time is able to characterize the residual bitumen of AR binders. The rheological indexes are then compared with other indexes obtained from empirical parameters currently used in the paving industry, in order to validate the methodology. Another motivation of this work is the need for a sensitive rheological parameter to quantify and discriminate the stiffening effect of aging and diffusion of maltenes into the rubber, in order to define future actions that are able to reduce the combined effect of both phenomena (e.g., selection of bitumen and rubber and production conditions to be used).

Materials and methods

Materials

In order to minimize any variability in the characteristics of materials due to their source and processing, bitumens were collected from the same batch of the La Rábida Refinery of CEPSA in Huelva, Spain. The bitumens were from the same crude. After cracking, the residues in the bottom of the column were aged and oxidized, in different extents, to obtain bitumen with different penetration grades. Different paving grade bitumens were selected for testing: B10/20 (A), B40/50 (E), B60/70 (I), and B150/200 (M). The designations for the bitumen grades are defined in the EN 12591 standard, where the bitumens are classified in predefined penetration ranges (e.g., a bitumen with a penetration grade of 46×0.1 mm, which is between 40 and 50×0.1 mm, is classified as B40/50).

The crumb rubber used in this work was produced by the cryogenic process and, according to the supplier, RECIPNEU, was obtained by the grinding of 30% of used truck tires and 70% of used car tires. It was sieved so as to select and use only the fraction passing the ASTM #20(0.850 mm) sieve and retained on the ASTM #40 (0.425 mm) sieve. As a result, the crumb rubber particle size ranges between 0.18 and 0.60 mm (ASTM #30 to #80 sieves). These sizes represent the AR mixtures typically produced and applied in Portuguese roads.

The most important component of a tire is the elastomers, mainly a combination of styrene-butadiene rubber and natural rubber (Gawel et al. 2006). The proportion of natural and synthetic rubber varies according to the size and type of the tire. The generally accepted rule of thumb is that the larger the tire and the more rugged its intended use, the greater will be the ratio of natural to synthetic rubber (Rahman 2004). In general, truck tire rubber contains larger percentages of natural rubber compared to that from car tires (Artamendi and Khalid 2006). The second most important component of a tire is carbon black, mainly used to enhance rigidity in tire treads (to improve traction, control abrasion and reduce aquaplaning) and to add flexibility and reduce heat buildup in sidewalls (Shulman 2000). Also, to improve the mechanical and chemical properties of rubber (e.g., tire) further, different compounds and additives are blended into raw rubber, namely activators (e.g., ZnO_2), accelerators (e.g., MgO , fatty acids, amines), aging retardant (e.g., metal oxides, polychloroprene), fillers (e.g., $BaSO_4, MgCO_3, CaCO_3$), and others. Generally metal oxides, fatty acids, amines, and different glycols are used as activators and accelerators (Miskolczi et al. 2008). Each producer has his own recipe which varies for each of his tire brands.

Methods

Production and separation of the asphalt-rubber binder

The method used to produce AR and collect the desired samples of AR binder, of recovered swelled rubber, and of residual bitumen was the basket drainage method (Rahman 2004). The asphalt-rubber production facility consists of several pieces of equipment (Fig. 2) assembled in a laboratory ventilation chamber. The wire basket used in the AR production facility was manufactured with a steel wire mesh, which was previously observed in an optical microscope (Fig. 2c) to measure its average opening dimension (0.370 mm).

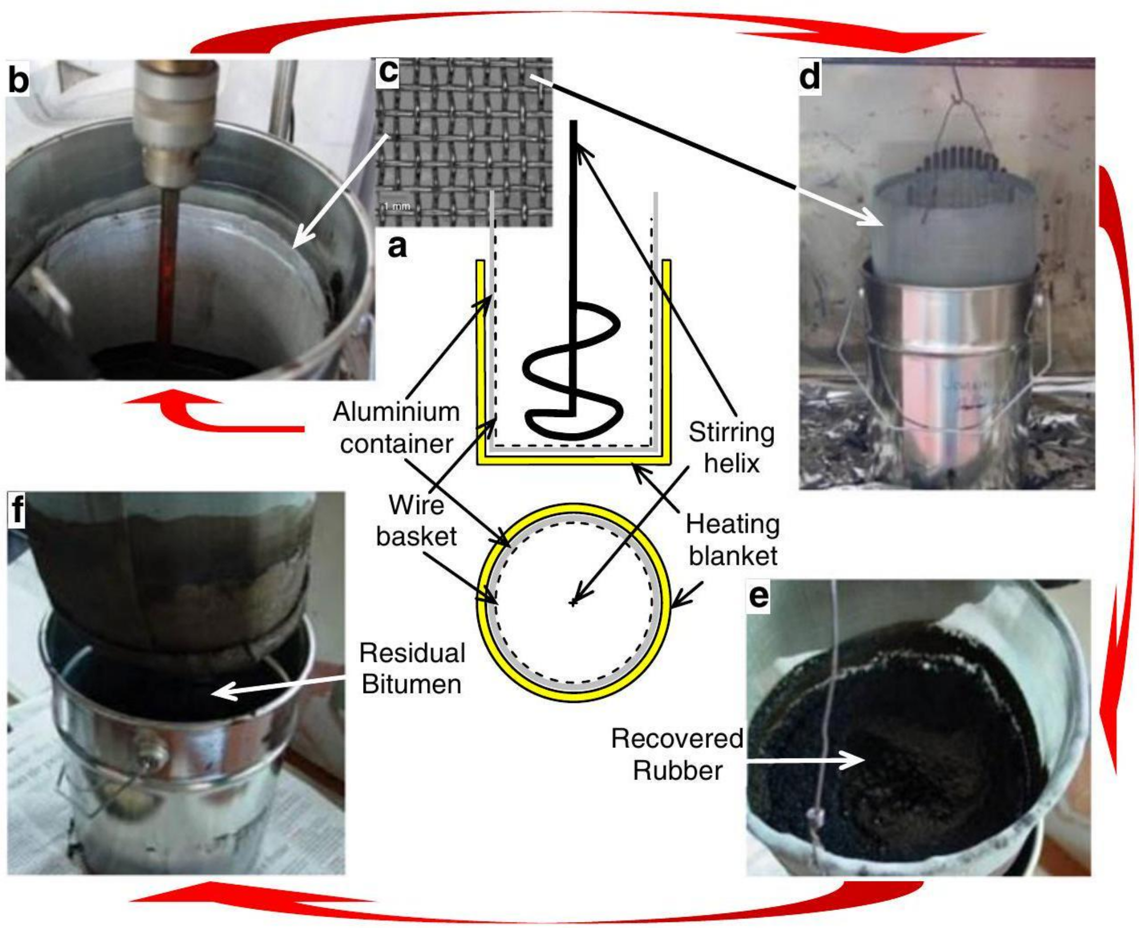
The process used to produce and collect the several samples of AR binder, of recovered swelled rubber, and of residual bitumen consisted of heating 1 kg of each base bitumen at 180°C (collecting a sample). Then, 17.5% (by weight of AR) of crumb rubber was added to the bitumen, and the resulting AR binder was continuously heated at 180°C for 60 min (interaction time) while stirring the binder at 230 rpm (Fig. 2b). The choice for such rubber concentration stems from an intensive study where three different rubber contents were tested (Peralta 2009). Results showed that the changes in the rheological and empiricalmechanical measurements are directly related to the content of rubber and are easier to assess when a rubber content of as large as 17.5wt% is used (Peralta et al. 2013). A sample of the produced AR was collected, and finally, the wire basket with the AR binder was suspended in an oven at 180°C for 15 min (Fig. 2d), to separate its constituents (Fig. 2e) and collect a sample of residual bitumen (Res) (Fig. 2f).

During AR production, the changes in bitumen density, AR, and rubber was assessed every 5 min . At the end of the interaction time, the changes in the recovered rubber weight were measured as well. These results allowed the indirect measurement of the increase in the rubber volume (Peralta 2009; Peralta et al. 2010b, c). These data showed that the interaction with bitumen produces an increase in the rubber weight and a decrease in its density; thus, a significant increase in the total volume of the recovered rubber was observed.

Assessment of bitumen aging during the AR production using the sphere AR production simulator method

When bitumen is heated, some smaller molecules are volatilized (aromatics), while other molecules may be associated with bigger ones (asphaltenes). Furthermore, when bitumen interacts with rubber, the rubber particles absorb the lighter parts of bitumen and swell. Also, antioxidants and other chemicals may diffuse in the bitumen phase, thus minimizing the extent of physical aging of the bitumen phase. Since these phenomena occur simultaneously during the AR production, it seems unfeasible to evaluate the changes in the bitumen structure caused by each

Fig. 2 (a) Scheme and (b) photo of the asphalt rubber production facility. (c) Optical microscopy photo of the wire mesh used to make the basket, (d) Separation between the crumb rubber and the residual bitumen of the AR, (e) recovered rubber, and (f) residual bitumen after separation



one of the previous phenomena. Hence, a new method was developed in order to quantify the changes induced in the bitumen exclusively by heating and stirring during the AR production, named sphere AR production simulator (SARPS).

The aim of this method is to simulate the AR production, by replacing the rubber particles with metallic spheres (roughly with the same dimensions of the crumb rubber particles) in order to reproduce the evaporation, linking, and oxidation processes occurring in the bitumen during the heating period used for AR production, independently from the interaction with rubber. Before the experimental procedure, the metallic spheres were observed and measured ($\emptyset_{eq} \approx 0.825\ \mathrm{mm}$) by optical microscopy (Fig. 3), using an Olympus BH-2 microscope and a magnification of 100 times, and their volumetric weight was evaluated ($7.75\ \mathrm{kg/dm^3}$). Bitumen treated with the SARPS is hereafter labelled "Sphere" bitumen.

The SARPS method was carried out in a reduced-scale AR production facility (similar to, but smaller than, that used for AR production), and the procedures used were also mimicking those applied in the AR binder production (Peralta et al. 2010c).

Penetration (Pen) test

The penetration test is an empirical method to measure the consistency of bitumens. The test method is described in EN 1426, in which penetration is defined as the distance that a standard needle loaded with a 100 g weight will penetrate into a bitumen sample for 5 s , at $25^{\circ}\mathrm{C}$. The penetration (Pen) grade is defined by the distance travelled by the needle ($\times 0.1$ mm) and, thus, smaller values indicate harder bitumens.

Softening point test (ring and ball, R&B)

The softening point (R&B) test measures the temperature at which the bitumen phase changes from semisolid to liquid. The test method is described in detail in EN 1427 standard
and essentially consists in two steel balls placed on two discs of bitumen contained within metal rings and these are heated at a constant rate ($5^{\circ}\mathrm{C}/\mathrm{min}$). The softening point is the temperature at which the bitumen softens enough to allow the balls placed on the bitumen discs to fall a distance of 25 mm into the bottom plate.

Apparent viscosity (AV)

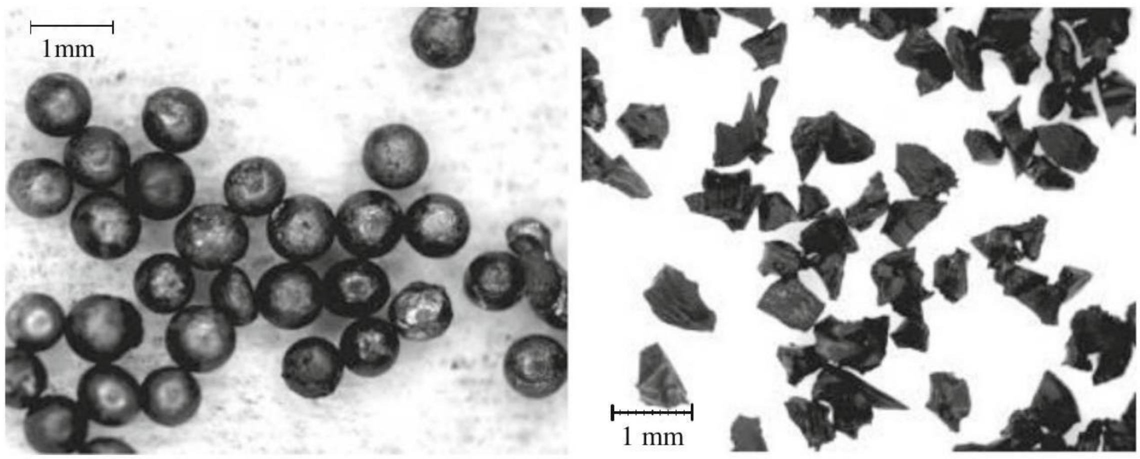
The apparent viscosity of the studied bitumen at $175^{\circ}\mathrm{C}$ was determined in accordance to EN 13302 standard, by means of a coaxial viscometer using a rotating spindle apparatus. The equipment used was a Brookfield viscometer (Programmable RVDV-II + viscometer) from the Brookfield Engineering Laboratories in Middleboro, MA 02346, USA.

The control device (Brookfield programmable temperature controller) was set and allowed to equilibrate at the test temperature, while the selected spindle (SC4-27, diameter of 11.76 mm) and the sample container (HT-2, internal diameter of 19.05 mm) were placed in an oven at $175^{\circ}\mathrm{C}$ for about 1 h . The gap between the selected spindle and the container is 3.645 mm , which is more than ten times the diameter of the rubber particles present in the residual bitumen (Peralta et al. 2010b).

The sample container was filled with the adequate volume of sample (about 10.5 ml) for the used spindle. The loaded container was placed in the controlled temperature environment device of the Brookfield equipment (Thermosel System). The spindle was then connected to the rotating spindle viscometer and lowered into the sample, and the system temperature was allowed to equilibrate for about 15 min .

The rotating spindle viscometer was switched on and allowed to stabilize at a speed of 20 rpm , corresponding to a shear rate of $6.8\ \mathrm{s}^{-1}$. Three readings were taken and recorded at $60-$ s intervals. The reported viscosity is the average of the three readings.

Fig. 3 Metallic spheres (left) used to simulate crumb rubber (right) in the SARPS method



Rheological characterization

The rheological properties were assessed using a stresscontrolled rotational rheometer (StressTech HR, Reologica). A parallel-plate geometry (diameter of 40 mm) and a gap of 1 mm were used. The experimental procedures for the rheological characterization of the bitumen were based on the European standard EN 14770 and were described in detail elsewhere (Peralta et al. 2010a).

Results and discussion

Master curves at service temperature

Construction of the master curves for the studied bitumen

The master curves of the four bitumens used at medium/high service temperatures (25,35,50, and 80 °C), before and after aging, were constructed using the Innovative Rheological Interface Software (IRIS, version 9.0) of Rheo-Hub Innovative Rheology Information Systems, IRIS Development LLC. Mechanical spectra obtained at temperatures below 80°C could not be superimposed on the mechanical spectra recorded at higher temperatures (Peralta et al. 2010a). However, master curves could be constructed for temperatures below 80°C by horizontal shifting of magnitude a_{T} of the corresponding curve onto the reference curve (at 80°C) and are displayed in Fig. 4 for conventional bitumen E . The master curves of the base and residual bitumen show a discontinuity in frequency due to the lack of experimental data between 50 and 80°C. Nevertheless, satisfactory master curves could be constructed as inferred from the temperature dependence of the horizontal shift factors a_{T} (see Fig. 6).

Rheological data in Fig. 4a indicate that the shear storage modulus G' reaches a high-frequency plateau. This plateau is assigned to the glassy behavior of the material (Lesueur 2009) and is not sensitive to the bitumen thermal history. Experimental pitfalls discussed elsewhere could explain the unchanged glassy mechanical behavior (Peralta et al. 2010a), since aged bitumen is expected to be stiffer, hence to show a larger glassy plateau (Huang and Grimes 2010; Anderson et al. 1994; Vinogradov et al. 1977).

The mechanical spectrum of the bitumen subjected to the SARPS method (Sphere bitumen) is qualitatively similar to the one of the aged bitumen (subjected to the rolling thin-film oven test (RTFOT) to simulate aging) presented elsewhere (Peralta et al. 2010a). Therefore, this complies with the structural picture of the BCM (see Fig. 1) and the assumption that during the production of AR, simulated by the SARPS method, bitumen ages as in RTFOT. This was expected since both methods rely on exposing bitumen to air and heat, inducing physical and oxidative aging of bitumen, thus leading to an increase in the volume fraction of asphaltenes/resins micelles (Peralta et al. 2010a).

The additional effect of the rubber-bitumen interaction on the rheological behavior of residual bitumen is detected in the low-frequency regime, which shows a departure from the terminal behavior of both base and Sphere bitumen. Several studies reported that rubber absorbs the lighter fractions of bitumen and swells, whereas other light fractions are volatilized in the aging process (Peralta et al. 2010b; Gawel et al. 2006; Airey et al. 2003). Thus, physical distillation of bitumen reminiscent from the addition of polymers to bitumen can be invoked to rationalize the change in AR viscoelasticity (Lesueur 2009). No oxidative hardening happens in the rubber-bitumen interaction process, as long as it does not involve any contact with an oxygen source. Therefore, an alternative mechanism can be advanced to

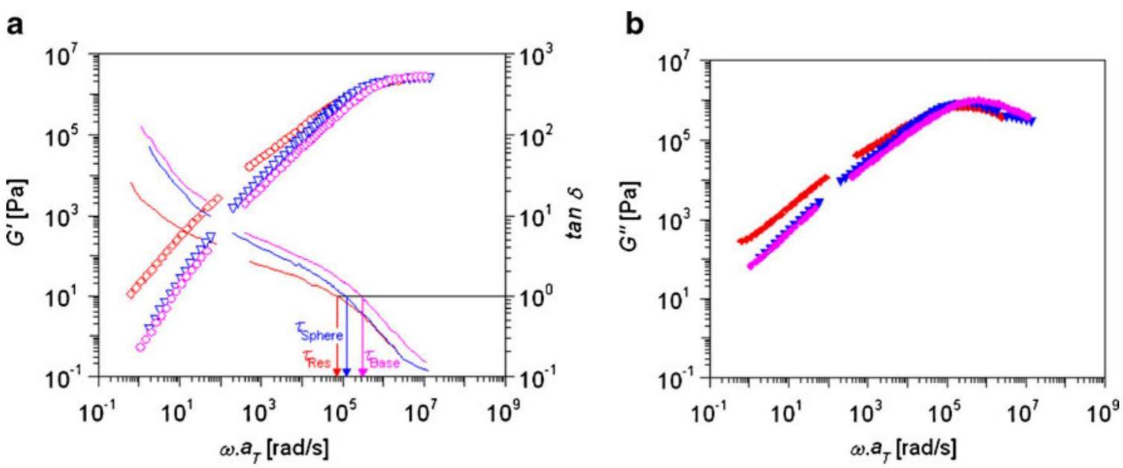


Fig. 4 Master curves ($T_{\mathrm{ref.}} = 80°\mathrm{C}$) of (a) elastic modulus, tan δ, and (b) loss modulus for base (pink circles), Sphere (blue inverted triangles), and residual (red diamonds) bitumen E

explain the overall increase in elasticity at low frequencies and the concomitant decrease in tan δ. First, it has been reported that the growing of the asphaltenes/resins micelles is due to their polarity, and the rate of growth depends on the concentration of polar molecules. The increase of the concentration of those molecules occurs as bitumen ages, due to the volatilization of the nonpolar molecules (that are simultaneously the smallest ones). Second, tire rubber contains considerable amounts of carbon black and other mineral fillers (Continental 2008). These inert materials may disperse into the residual bitumen during AR production. The splitting and depolymerization of the rubber particles, occurring during the hot production of AR, favors the release of the fillers into the bitumen (Peralta et al. 2010b). This leads to an increase in the effective fraction of such reinforcing components with sizes ranging from 1μ m to 100Å (Hamed 1992).

The spectrum of residual bitumen highlights the different phenomena described above. Thus, on the one hand, the effects of aging, explained by the BCM approach, can be compared with the results from the model of the hard sphere colloidal suspensions (Larson 1999)-in these systems, an increase in particle volume fraction results in a shift of the spectrum of relaxation times towards lower frequencies (slow down), whereas the width of the spectrum remains constant, for volume fractions between 0.30 and 0.55 . On the other hand, when compared with the Sphere bitumen, no shift is observed in the frequency spectrum of the residual bitumen, but rather a delay for times slower than the relaxation time, consistent with the presence of fillers (released from the swollen rubber) into a viscoelastic matrix.

Analysis of the relaxation times obtained from the master curves

A characteristic relaxation time (τ), corresponding to the inverse of the frequency where tan $\delta = 1$, can be extracted from the master curve for the base, Sphere, and residual bitumens (frequencies corresponding to the relaxation times are indicated with vertical arrows in Fig. 4). In model hard sphere colloidal suspensions, the relaxation time relates to the relaxation of the largest particle in the colloidal system, which depends on both particle size and volume fraction (Larson 1999). In contrast to this, the longest relaxation time in the material can be extracted from the terminal regime which shows up in the low-frequency range of the mechanical spectra displayed in Fig. 4.

Data in Fig. 4 clearly show that the relaxation time increases from the base bitumen (shortest relaxation time), followed by the Sphere bitumen and the residual bitumen (longest relaxation time). This phenomenon of increasing relaxation time was reported to be a consequence of bitumen aging (Peralta et al. 2010a). In terms of the colloidal approach, and assuming that no change in the viscoelastic properties of the suspending matrix occurs, a longer relaxation time is related to larger particles resulting from the aggregation of more asphaltenes peptized by resin molecules and, concurrently, to the reduction of the maltene phase in the bitumen colloidal structure (Mastrofini and Scarsella 2000). The increased relaxation time from the base to the Sphere bitumen is an expected result, as a consequence of the previously mentioned aging process.

However, the increase of τ of the residual bitumen (in comparison with the Sphere bitumen) is not solely due to the aging process, but rather results primarily from the diffusion of the lighter molecules (Airey et al. 2003) into the rubber particles, mostly saturates (Gawel et al. 2006), and subsequent swelling of rubber particles. Once again, building on the colloidal model, the loss of the bitumen saturate fraction contributes to the increase in the concentration of other bitumen fractions. This increased concentration promotes the aggregation between the polar molecules, as some of the aromatic molecules merge into resins, and these into the asphaltene bitumen fractions (Isacsson and Zeng 1997). Indeed, the increase in the aggregate size has been detected by gel permeation chromatography (GPC): the larger molecular size (LMS) assessed with this technique increases with bitumen aging, and an additional slight increase in the LMS has been observed in the corresponding residual bitumen (Lee et al. 2011; Jeong et al. 2010). This result is consistent with the further slowing down of the largest relaxation time described in Fig. 4.

In order to analyze the response of different paving grade bitumens to the AR production process, the values of the base bitumen relaxation times were plotted against the relaxation times of the corresponding Sphere and residual bitumens (Fig. 5).

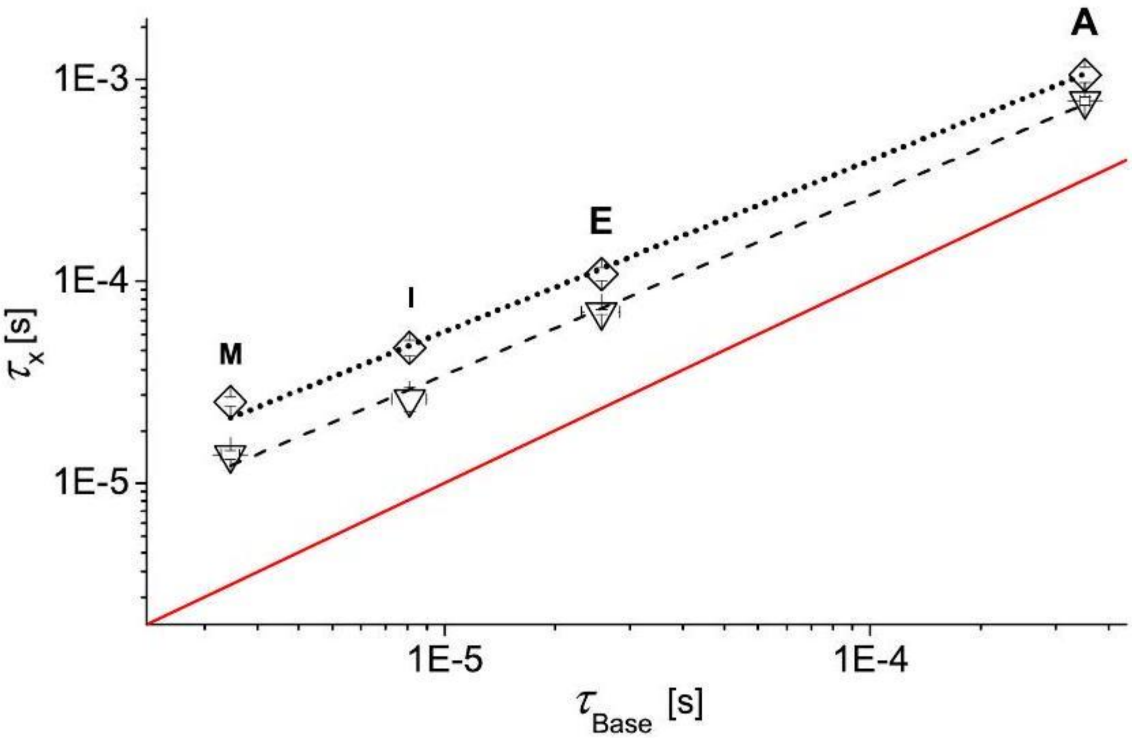


Fig. 5 Relaxation times extracted from the master curves of the Sphere (triangles) and residual (diamonds) vs. their base bitumen relaxation times for four different bitumen grades (M to A), with the equality continuous line in red

Figure 5 shows an increase of the relaxation times with the increase of bitumen stiffness (see also the reference for paving grade bitumen in Table 1). This is consistent with previous studies (Stastna et al. 1994), since it is known that the relaxation time is proportional to the bitumen viscosity and the cube of the size of the asphaltenes/resins micelles. The increase of those two rheological parameters is induced by aging processes (Lesueur 2009), such as the SARPS method used in this work. The depletion of the lighter molecules of bitumen by the rubber particles in AR also causes an increase in the size of the asphaltenes/resins micelles, and the corresponding effect observed in the relaxation times is similar to that of SARPS aging.

The $\log - \log$ plot in Fig. 5 indicates a power law relationship between the relaxation times of the Sphere and residual bitumens and those of the corresponding base bitumen. This strong correlation between relaxation times from all samples suggests that the same SARPS-induced aging process occurs for all types of bitumen studied. Although the relaxation times of the residual bitumen are higher than those of SARPS, the slopes of both curves are mostly the same, showing that the effects of the aging due to the SARPS and the absorption of some molecular faction of bitumen by rubber (residual bitumen) are similar for all the bitumens studied.

The ratios of the relaxation times of the Sphere and residual bitumens to their initial base bitumen ($\tau_{\text{Sphere}}/\tau_{\text{Base}}$, $\tau_{\text{Residual}}/\tau_{\text{Base}}$, and $\tau_{\text{Residual}}/\tau_{\text{Sphere}}$), shown in Fig. 5, are presented in Table 1.

The ratio gathered in Table 1 ranges between 2.46 and 8.06. The rather wide range of variation (roughly four fold) shows that these ratios are a sensitive index to quantify the changes that occur in bitumen during AR production for a wide range of penetration grade bitumens (since the tested bitumen had penetrations between 10 and 200×0.1 mm).

Additionally, the values of the indexes determined between the Sphere and residual bitumens range between 1.35 and 1.83 . This variation is related to the changes in bitumen induced solely by rubber and shows smaller ratios for harder bitumens than for softer ones. These observations suggest that the interaction between bitumen and rubber clearly depends on the bitumen characteristics, as reported by Airey et al. (2003). The higher values of the ratios computed from the dada obtained by Airey et al. (2003) relate to the much longer time of interaction between bitumen and rubber and aging time (48 h vs 60 min in the present study). This index is larger and thus more sensitive for softer bitumen than for harder bitumen. However, since aging is not incorporated in $\tau_{\text{Residual}}/\tau_{\text{Sphere}}$, these results can also be attributed to the release of fillers into the bitumen aged matrix. Therefore, a larger reinforcing effect is expected when the base bitumen is softer, and thus, a larger index is measured. Airey et al. (2003) also computed the ratios of the asphaltene content of similar asphalt binder materials, achieving values of 1.16 for the ratio between the aged and base bitumen, 1.56 for the ratio between the residual and base bitumen, and 1.35 for the ratio between the residual and aged bitumen.

Comparing the relaxation time ratios of the different bitumens, it becomes clear that the changes observed in the residual bitumen during AR production are induced by both aging and rubber effect, as both ratios are significantly larger than 1. Additionally, the mechanical spectrum for residual bitumen is not simply a horizontal shift from base or SARPS aged bitumen, and thus, additional filler effects are clearly occurring due to the interaction with rubber. We also computed the relaxation time ratios with the graphical data presented by Lee et al. (2011) for different bitumens, for an interaction time with rubber of 60 min . Thus, it was possible to calculate the estimated values of the ratios aged/base bitumen (1.07), residual/base bitumen (2.22), and residual/aged bitumen (2.07), confirming the trend of the results of the present study, despite the fact that no SARPS method was used by Lee et al. (2011) to differentiate the various aging and particle release effects. We draw similar conclusions from the ratios computed with the relaxation times reported in Christensen and Anderson (1992).

Table 1 Ratio between the relaxation times of the Sphere and residual bitumens with base bitumen

Paving grade bitumen	Bitumen	$\tau_{\text{Sphere}}/\tau_{\text{Base}}$	$\tau_{\text{Residual}}/\tau_{\text{Base}}$	$\tau_{\text{Residual}}/\tau_{\text{Sphere}}$
10/20	A	2.46 ± 0.13	3.31 ± 0.30	1.35 ± 0.13

40/50	E	3.02 ± 0.33	4.65 ± 0.60	1.54 ± 0.13
60/70	I	3.16 ± 0.52	5.67 ± 0.75	1.80 ± 0.29
150/200	M	4.40 ± 0.31	8.06 ± 0.60	1.83 ± 0.14
40/60	M3	9.03 [a]	28.05 [a]	3.16 [a]

Temperature dependence of shift factor a_T

The Arrhenius equation or the Williams-Landel-Ferry (WLF) equation (Williams et al. 1955) can be used to describe the temperature dependence of the horizontal shift factors a_T used to construct the master curves for bitumen. For polymer melts, the temperature dependence of viscoelastic functions, such as viscosity, can be modelled by the Arrhenius equation in a temperature regime well above the glass transition temperature. This is also the case for bitumen at higher temperatures. On the other hand, at lower temperatures (near the glass transition temperature, T_g), associative processes of molecules dominate and temperature dependence is better described using the WLF equation (Vijay et al. 2008). This equation was reported to adequately describe the thermal properties of bitumen for temperatures lower than $100^\circ\mathrm{C}$ (Zanzotto et al. 2000). Usually, the WLF coefficients of bitumens present values close to the expected universal values of $17\ ^\circ\mathrm{C}(\mathrm{C}_1)$ and $52^\circ\mathrm{C}(\mathrm{C}_2)$, and Marasteanu and Anderson (1996) mentioned values of 14.0 to $24.6^\circ\mathrm{C}$ for C_1 and 69 to $230^\circ\mathrm{C}$ for C_2.

Results from the WLF fits were not satisfactory, as errors as large as 40% on both C_1 and C_2, which stem from the poor quality of the fits to the data (see inset in Fig. 6), were found.

Alternatively, the Arrhenius equation gave better fitting results, and this is in agreement with earlier reports for the same range of low/medium temperatures (Partal et al. 1999; Martínez-Boza et al. 2001; Navarro et al. 2007). Arrhenius plots are presented in Fig. 6 for bitumen E, and the activation energies (E_a) obtained from the fits are gathered for all samples in Table 2.

The E_a values vary in the range of approximately 160.0 to 210.0 kJ/mol for all tested bitumens. In spite of the better quality of the Arrhenius fits with respect to WLF fits,

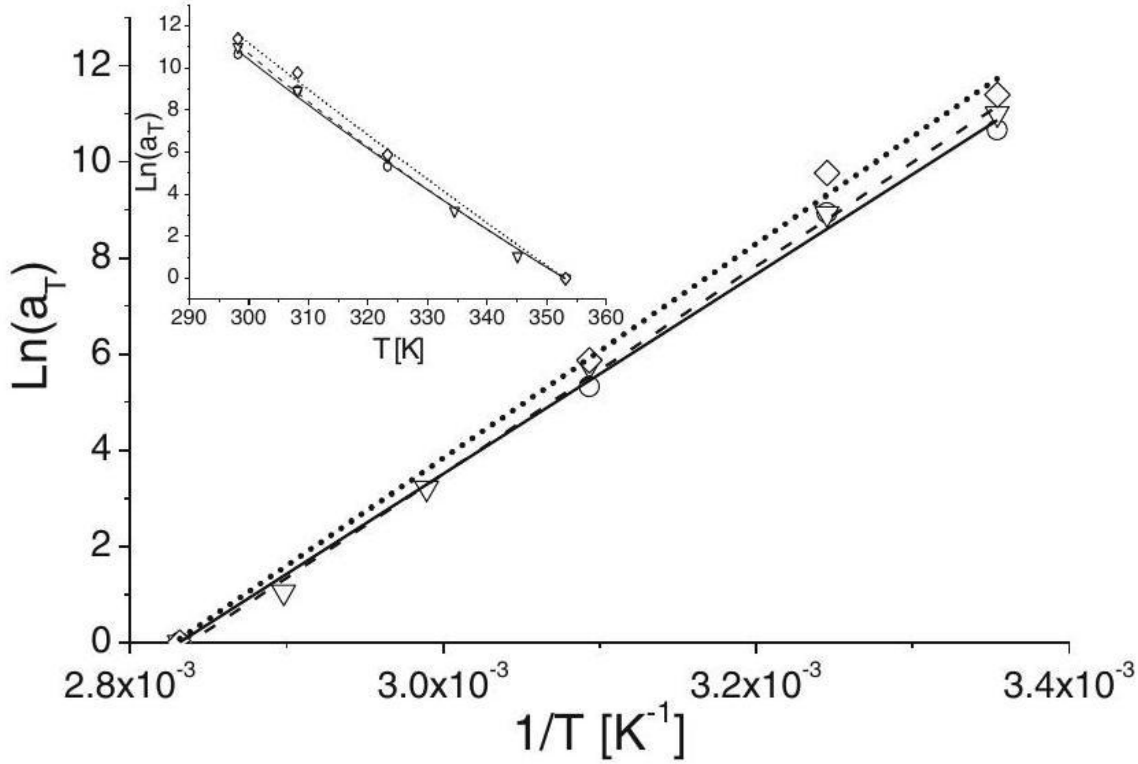


Fig. 6 Fit of Arrhenius equation to the temperature dependence of shift factors a_{T} computed for the base (circles), Sphere (inverted triangles), and residual (diamonds) bitumen E. Insert: Fit of WLF equation to the temperature dependence of shift factors a_T the values of E_{a} obtained for aged or AR samples, corresponding to the same base bitumen, are not significantly different (see ratios $E_{\mathrm{a\,(Sphere)}}/E_{\mathrm{a\,(Base)}}$, $E_{\mathrm{a\,(Residual)}}/E_{\mathrm{a\,(Base)}}$, and $E_{\mathrm{a(Residual)}}/E_{\mathrm{a(Sphere)}}$ in Table 2). Thus, the temperature dependence of the rheological properties is not sensitive enough to bitumen changes during AR production. This result is not a surprise since other authors already reported on the poor sensitivity of the temperature dependence of a_{T} on chemical and structural differences in a set of penetration grade bitumens (Zanzotto et al. 2000). Such weak temperature dependence might also explain why master curves could be obtained for all bitumen using TTS. As a result, any index built on the ratio of rheological parameters, such as the one proposed here, should be a better indicator of the changes that occur in bitumen during AR production.

Previous research (Lesueur 2009) showed that the increase in the values of the E_{a} is directly related to the increase in the asphaltene content. However, the elevated values of E_{a} found for bitumens A to M , together with the very slight increase of asphaltenes (Mastrofini and Scarsella 2000) during AR binder production and in the SARPS method, have an almost unnoticeable impact on the corresponding computed ratio presented in Table 2.

Thus, to summarize the rheological characterization of bitumen at service temperatures (between 25 and 80°C), results suggest that the changes that occur during AR production and the SARPS method can be essentially quantified by computing an index from the relaxation times observed in the master curves of the raw, residual, and Sphere bitumens. In fact, this index was previously designed to quantify bitumen aging (Peralta et al. 2010a).

In addition, the qualitative analysis of mechanical spectra suggests that small molecules are diffusing from bitumen into the rubber particles and that fillers are released from the swollen rubber to reinforce the bitumen matrix.

Thermorheological behavior at production and application temperatures

Figure 7 presents the frequency dependence of the dynamic viscosity (η^*) measured at different temperatures for bitumen E, before and after aging, and after interaction with rubber. Similar results were obtained for all bitumen samples evaluated.

The dynamic viscosity displayed in Fig. 7 is independent of the frequency, which is indicative of a Newtonian behavior at high temperatures. In this range of temperatures (110 to 180°C), the waxes that constitute the paraffinic part of the saturate fraction of bitumen, which crystallize at low temperatures (Lesueur 2009; Soenen et al. 2006), are no longer in a crystalline state and the compact structure constituted by asphaltenes surrounded by resins (Romera

Table 2 Activation energies E_a computed for the different base, Sphere, and residual bitumens at service temperatures, and respective activation energy ratios

Bitumen		E_a (kJ /mol)	R^2	$E_{a\,(Sphere)}/E_{a\,(Base)}$	$E_{a\,(Residual)}/E_{a\,(Base)}$	$E_{a\,(Residual)}/E_{a\,(Sphere)}$
A	Base	172.8 ± 1.5	0.999	1.159 ± 0.024	1.051 ± 0.050	0.906 ± 0.046
	Sphere	200.3 ± 3.8	0.998			
	Residual	181.6 ± 8.5	0.994			
E	Base	172.7 ± 6.3	0.999	1.040 ± 0.044	1.075 ± 0.064	1.033 ± 0.054
	Sphere	179.7 ± 3.9	0.998			
	Residual	185.6 ± 8.7	0.993			
I	Base	180.0 ± 7.8	0.998	1.004 ± 0.062	1.047 ± 0.065	1.043 ± 0.065
	Sphere	180.7 ± 7.8	0.991			
	Residual	188.5 ± 8.4	0.994			
M	Base	171.9 ± 1.3	0.999	1.031 ± 0.039	1.101 ± 0.052	1.067 ± 0.063

	Sphere	177.3 $\pm$ 6.5	0.993			
	Residual	189.2 $\pm$ 8.5	0.994			

et al. 2006) is almost collapsed. The shifts to larger viscosities after interaction with rubber and spheres are consistent with the rheological data measured at lower temperatures and thus relate to the same AR production effects outlined above and also documented elsewhere (Romera et al. 2006; Artamendi et al. 2006; Gawel et al. 2006; Airey et al. 2003; Palade et al. 2000).

The horizontal lines in Fig. 7a are linear fits to the experimental data, from which the Newtonian viscosity (zero shear viscosity or η_0) has been computed. The changes in bitumen due to AR production are expressed by an increase of the Newtonian viscosity, as demonstrated in Fig. 7b, where the temperature dependence of η_0 has been recast in an Arrhenius plot. The good quality of the fits (see R^2 for the computed E_a in Table 3) shows that the temperature dependence of η_0 can be described by an Arrhenius-like equation, as reported in earlier rheological studies (Martínez-Boza

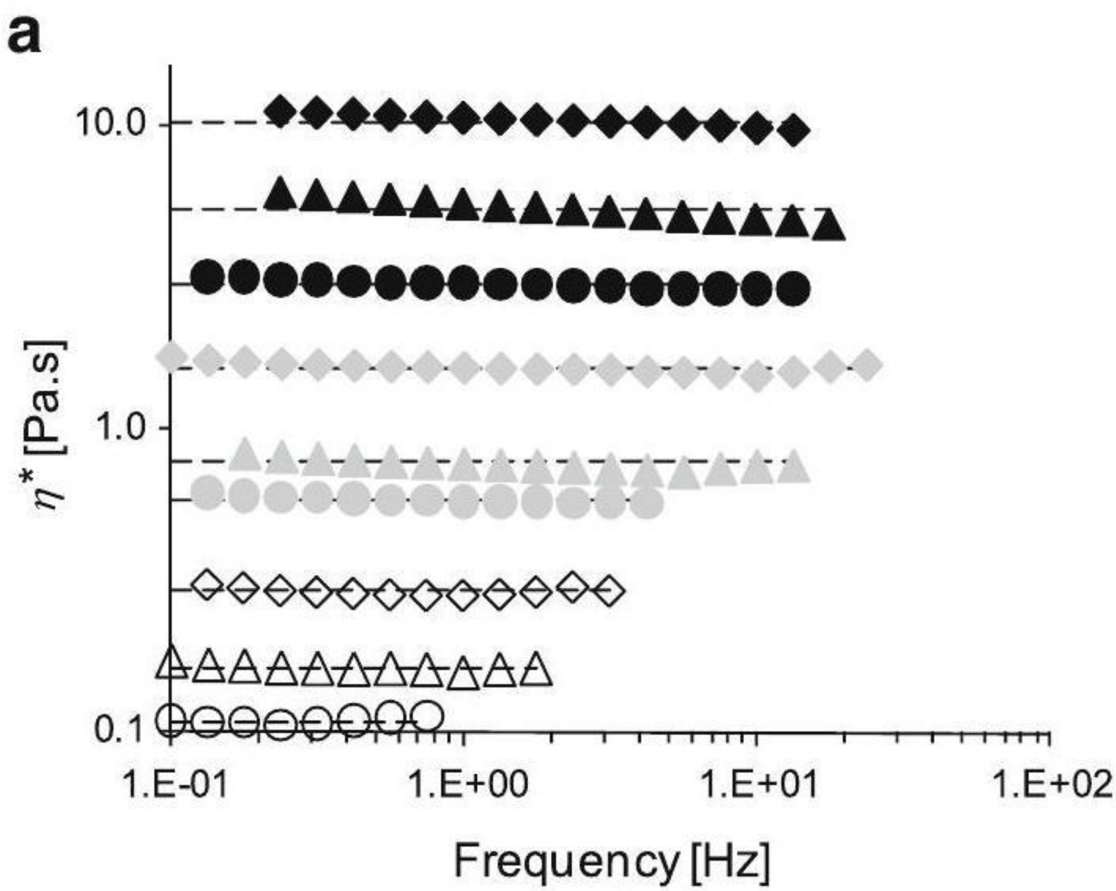
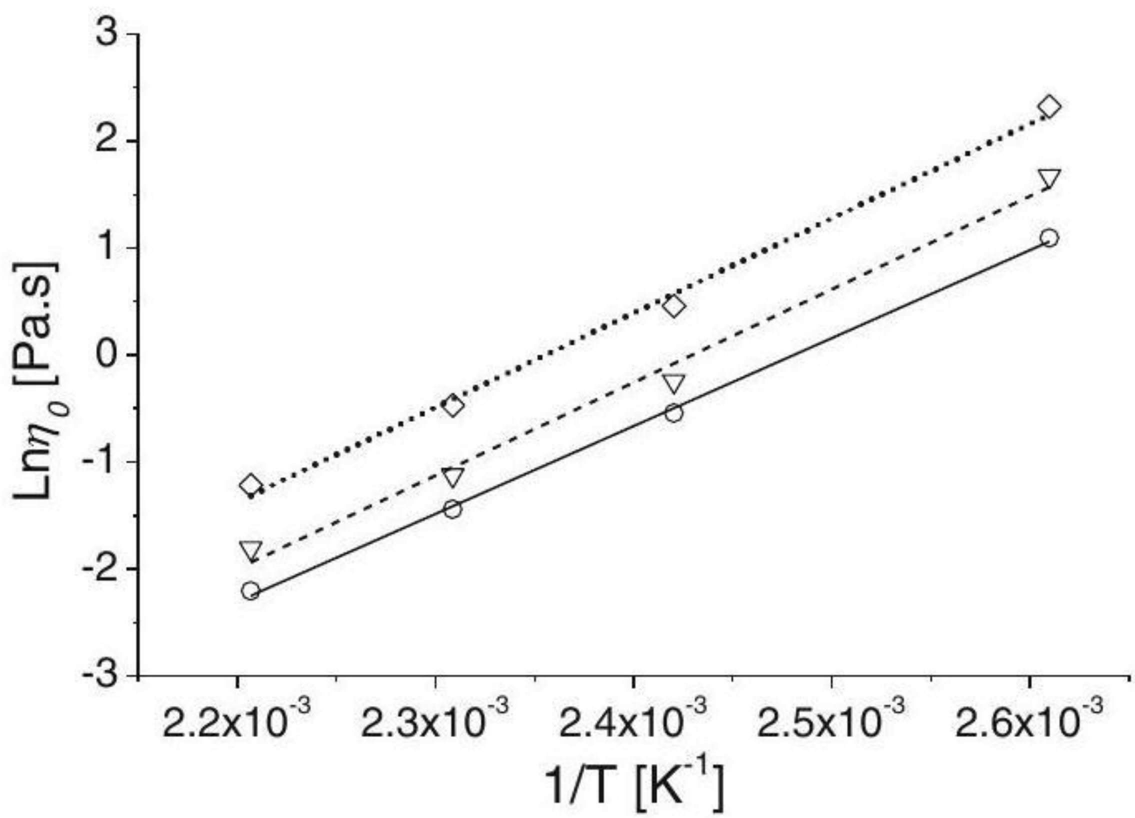


Fig. 7 a Frequency dependence of the dynamic shear viscosity of bitumen E base (circles), Sphere (triangles), and residual (diamonds) measured at 110 °C (open symbols), 140 °C (gray symbols), and et al. 2001). Figure 7b also shows that the activation energies E_a extracted from the Arrhenius fits are affected by the aging due to heating/oxygenation (Sphere) and due to the diffusion of bitumen molecules into rubber during AR production (different slopes in the different materials obtained before and after AR production). However, the ratios computed from E_a for the different bitumen samples (i.e., base, Sphere, and residual bitumens) are analogous (see Table 3) and hence are not a valuable quantifying index. Nevertheless, the changes that occur in bitumen during AR production are reflected in the activation energy computed from the temperature dependence of the zero shear viscosity, as E_a values (Table 3) for residual bitumen, Sphere bitumen, and base bitumen samples are consecutively lower.

In this range of temperatures (110 to 180°C), E_a varies between 57 and 87 kJ/mol, which are values very different from those obtained at lower temperatures using the shift b



180°C (solid symbols). b Adjustment of Arrhenius equation to the temperature dependence of the Newtonian viscosity η_0 for bitumen E

Table 3 E_a values computed from Arrhenius fits to viscosity data for the different base, Sphere, and residual bitumens at production and application temperatures, and respective ratios

Bitumen		E_a (kJ /mol)	R^2	$E_{a\,(Sphere)}$ $/E_{a\,(Base)}$	$E_{a\,(Residual)}$ $/E_{a\,(Base)}$	$E_{a\,(Residual)}$ $/E_{a\,(Sphere)}$
A	Base	75.8 $\pm$ 2.4	0.999	1.046 $\pm$ 0.059	1.156 $\pm$ 0.076	1.077 $\pm$ 0.080
	Sphere	81.4 $\pm$ 3.8	0.993			
	Residual	87.6 $\pm$ 5.1	0.990			
E	Base	68.2 $\pm$ 1.5	0.999	1.052 $\pm$ 0.062	1.076 $\pm$ 0.057	0.988 $\pm$ 0.071
	Sphere	74.3 $\pm$ 4.0	0.994			
	Residual	73.4 $\pm$ 3.5	0.993			
I	Base	63.3 $\pm$ 2.0	0.999	1.034 $\pm$ 0.082	1.148 $\pm$ 0.056	1.077 $\pm$ 0.088
	Sphere	67.5 $\pm$ 4.9	0.984			
	Residual	72.7 $\pm$ 2.7	0.996			
M	Base	56.9 $\pm$ 2.6	0.998	1.130 $\pm$ 0.065	1.309 $\pm$ 0.083	1.103 $\pm$ 0.062
	Sphere	67.5 $\pm$ 2.3	0.996			
	Residual	74.5 $\pm$ 3.3	0.994			

factors. Smaller activation energy values may be explained by a transition to a Newtonian fluid behavior. The increase in the content of asphaltenes, which have the lowest temperature susceptibility among the four separated fractions of bitumen (saturates, aromatics, resins, and asphaltenes), may explain these results (Lesueur 2009).

With respect to the quest for a best index to quantify the changes that occur in the bitumen binder during AR production, the ratios of residual and Sphere over base bitumen zero shear viscosity (see Table 4) are able to do a better job than the activation energy since they span a 1.3 to 2.6 range. However, the zero shear viscosity ratios do not allow distinguishing between the different base bitumens in the AR binder (e.g., the ratios of bitumens E and M are similar).

Besides the changes in bitumen previously described, the composition and characteristics of bitumen during AR production can also be changed by the dissolution/suspension of extender oils, fillers (e.g., carbon black, silica, carbon, chalk, etc.) and other rubber compounding agents into bitumen. These fillers actually constitute approximately 30% of the total weight of the tire rubber (Continental 2008) and are imbedded in the rubber matrix. When tire rubber is milled, the carbon black and other fillers are exposed and can be suspended in hot bitumen. Additional amount of fillers is available as rubber particles split and depolymerize during the AR production (Peralta et al. 2010c). The presence of these fillers in the residual bitumen also contributes to the increase of the viscosity of the residual bitumen (Palade et al. 2000). The release of filler from rubber into the bitumen is thus mirrored by the ratios computed with η_0 for comparing the Sphere and residual bitumens. Therefore, this ratio is an index as good as that computed from the ratio of relaxation times at service temperatures. In agreement with the conclusion drawn from the rheological data at service temperatures, most of the viscous enhancement observed at

Table 4 Ratio between the η_0 values for the different base, Sphere, and residual bitumens at production and application temperatures

Bitumen		η_0 at 175°C(Pas)	$\eta_{0\,(\text{Sphere})}/\eta_{0\,(\text{Base})}$	$\eta_{0\,(\text{Residual})}/\eta_{0\,(\text{Base})}$	$\eta_{0\,(\text{Residual})}/\eta_{0\,(\text{Sphere})}$
A	Base	0.262 ± 0.012	1.343 ± 0.126	1.707 ± 0.162	1.271 ± 0.121
	Sphere	0.351 ± 0.029			
	Residual	0.446 ± 0.037			
E	Base	0.128 ± 0.004	1.495 ± 0.144	2.607 ± 0.195	1.744 ± 0.130
	Sphere	0.192 ± 0.017			
	Residual	0.334 ± 0.023			
I	Base	0.128 ± 0.006	1.372 ± 0.099	2.043 ± 0.141	1.499 ± 0.102
	Sphere	0.176 ± 0.010			
	Residual	0.262 ± 0.014			
M	Base	0.086 ± 0.005	1.466 ± 0.130	2.504 ± 0.221	1.708 ± 0.151
	Sphere	0.126 ± 0.079			

	Residual	0.215 $\pm$ 0.013			

high temperatures for AR bitumen is due to the AR process rather than the bitumen aging.

Binder changes quantified by standard methods

In the road paving industry, changes in bitumen are traditionally quantified by comparing the results of empirical tests (Pen, R&B, AV). The Pen, R&B, and AV test results of the base bitumen were plotted against those of the corresponding residual and Sphere bitumens, as shown in Fig. 8.

The three tests show a different impact of the AR production on the four studied bitumens. While the R&B and Pen test results show a higher range of variation for the base bitumens, as compared to those of the sphere and residual bitumen, the AV test results have the opposite tendency (comparison of slopes in Fig. 8). The greatest variation is observed in the results of the AV test (e.g., see also ratios in Table 5).

By carrying out the European standardized characterization tests for paving grade bitumens, the main objective of the road paving industry is to determine its consistency. It is important to study the consistency of binder because it establishes the development of distresses in pavements. The ratios of the parameters traditionally used to quantify the changes in bitumen characteristics were computed to compare the base, Sphere, and residual bitumens and are presented in Table 5.

The ratios of R&B are quite insensitive to changes related to AR production, as they do not differ much from 1 (although they are, in general, higher for softer than for harder bitumens). The ratio index obtained with the penetration test results is lower than 1.0 and presents some sensitivity to the changes observed in the materials during AR production, especially for softer bitumen (the ratio of 0.332 for bitumen M is equivalent to an index of 3.012, the inverse of 0.332). Nevertheless, this index, along with its range of variation, remains less sensitive than the one computed from the relaxation times (see the factor 4 index in Table 1). The parameter that shows the higher sensitivity to bitumen changes during AR production is the AV, once again for the softer bitumen M, with an index of 4.24, but the associated error is significant (1.131).

Comparing the indexes presented in Table 5 to those based on the relaxation times (Table 1), the greater expression and sensitivity of the indexes calculated from the relaxation times and the higher influence of errors for the indexes listed in Table 5 suggest that the index proposed in this work (relaxation times) has a better performance than that commonly used to quantify the changes in the binder during AR production. When compared with the relaxation times, the data computed from the empirical tests, namely penetration and ring and ball results, present higher errors because they are mostly performed in a nonlinear regime. On the other hand, the use of the relaxation times is directly related to the changes of the bitumen structure caused by aging, which is similar to the changes in the chemical composition of bitumen during AR production (Peralta et al. 2010a).

The same range of values were approximately obtained when comparing the values of the ratios of the different parameters studied in this work, for a wide range of temperatures, with a previous rheological study on bitumen aging (Airey et al. 2003). The present results indicate that the index based on the relaxation times observed in the master curves (base, Sphere, and residual) is the most sensitive parameter to quantify bitumen aging, since the computed values exceed the ratio of 8 (Table 1), and 28 when computed from rheological data available in Airey et al. (2003). However, indexes obtained from the linear viscoelasticity regime could show shortcomings in quantifying nonlinear properties such as cracking and rutting, even though parameters such $G^*/\sin\,\delta$ and $G^*.\,\sin\,\delta$, combined with aging, are being broadly used in the USA to design pavements that do not develop rutting and fatigue cracking prematurely (Asphalt Institute 2003). Nevertheless, efforts are still needed to design rheologically sound indexes to quantify and predict such properties.

Conclusions

Any study of bitumen composition and behavior is a very complex task per se, since bitumen varies significantly according to its origin and processing of the crude oil. Ground tire rubber is also a very intricate material, as different polymers and additives may be used according to different applications and suppliers. Additionally, the interaction between bitumen and rubber depends on many production factors. Therefore, the results presented above may not be applicable to all asphalt-rubber binders. Bearing that in mind, the main conclusions drawn from this study are the following:

- According to the relationship between the relaxation times determined from the master curves of the base, Sphere (SARPS), and residual asphalts, it was possible to observe that the developed SARPS method is able to simulate the aging of bitumen during AR production without the influence of rubber interaction (this method was also important to quantify the changes due to the interaction between bitumen and rubber during AR production, beyond those caused by aging, by comparing the relaxation times of residual and Sphere bitumens);
- Changes in the residual binder are caused by a combination of aging and bitumen-rubber interaction (diffusion

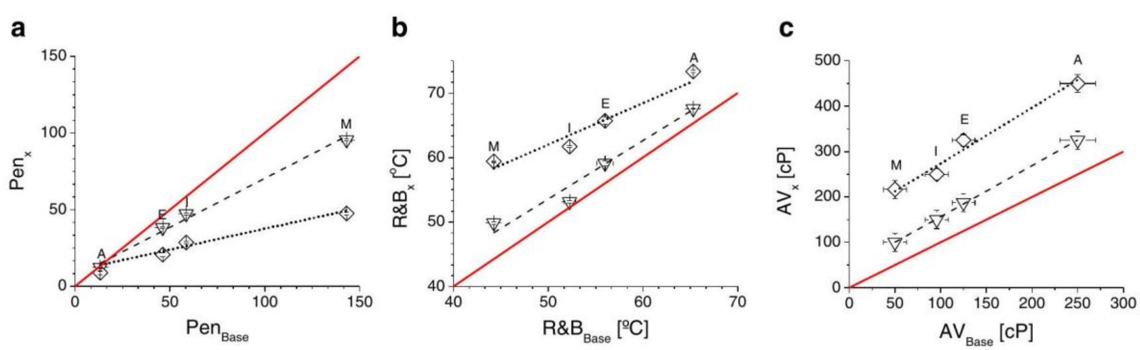


Fig. 8 Parameters (a Pen, b R&B, c AV) usually applied for binder characterization obtained for Sphere (inverted triangles) and residual bitumens (diamonds) vs. their corresponding base bitumens, with the equality continuous lines in red

of lower weight bitumen molecules into swollen rubber and release of fillers from swollen rubber into the aged bitumen);

- The most sensitive indexes that are able to quantify the changes (aging and the rubber interaction phenomena) in the bitumen during AR production are the ratio of relaxation times at service temperatures and the ratio of Newtonian viscosities assessed by SAOS at high temperatures;
- The effect of released filler from swollen rubber during AR binder production can explain why the Newtonian viscosity index assessed by SAOS at high temperatures is efficient in assessing the interaction between bitumen and rubber, but not so capable when used only for aging evaluations (Peralta et al. 2010a);
- Concerning the empirical tests typically used by road paving industry to characterize bitumens (penetration, ring and ball, and apparent viscosity), the most sensitive parameter that should be used to measure the changes in the bitumen during AR production is the ratio of the apparent viscosity;
- Generally, it was also observed that the most significant changes in the binder properties are obtained when a softer base bitumen (M) is used for AR binder production;

Table 5 Ratios of the conventional characteristics of studied base, Sphere, and residual bitumens

Bitumen	Ratio between properties	Penetration at 25 °C	R&B softening point	Apparent viscosity at 175 °C
A	Sphere/base	0.921 ± 0.044	1.034 ± 0.004	1.300 ± 0.129
	Residual/base	0.668 ± 0.085	1.123 ± 0.006	1.800 ± 0.162
	Residual/Sphere	0.726 ± 0.097	1.086 ± 0.003	1.385 ± 0.104
E	Sphere/base	0.830 ± 0.021	1.055 ± 0.018	1.500 ± 0.217
	Residual/base	0.447 ± 0.031	1.173 ± 0.020	2.400 ± 0.260
	Residual/Sphere	0.539 ± 0.036	1.112 ± 0.012	1.600 ± 0.181
I	Sphere/base	0.806 ± 0.016	1.017 ± 0.013	1.565 ± 0.290
	Residual/base	0.488 ± 0.012	1.181 ± 0.015	2.421 ± 0.342

	Residual/Sphere	0.606 ± 0.014	1.161 ± 0.005	1.547 ± 0.220
M	Sphere/base	0.667 ± 0.013	1.127 ± 0.010	2.000 ± 0.637^{a}
	Residual/base	0.332 ± 0.009	1.342 ± 0.011	4.240 ± 1.131^{a}
	Residual/Sphere	0.498 ± 0.010	1.192 ± 0.006	2.120 ± 0.462^{a}
M3	Aged/base			1.14^{b}
	Residual/base			3.03^{b}
	Residual/aged			2.66^{b}

- The proposed indexes were also computed with data taken from different literature sources (necessary for bitumens from different origins), confirming the trend of the results obtained for the materials evaluated in this study and suggesting the universality of the proposed rheological indexes.

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[a] These values were computed from the data presented by Airey et al. (2003), determined at interaction times of 48 h , and the aging of bitumen did not include the spheres to simulate the rubber particles

[a] These ratios are computed from values of apparent viscosity inferior to 125 cP , which is the minimum value with suitable accuracy in the used equipment. Therefore, the computed error is much larger
[b] These AV ratios were computed with apparent viscosities measured at 160°C and reported in Airey et al. (2003). The bitumen aging was performed in the absence of any spheres or other rubber substitution inert material