

Rheological Quantification of Bitumen Aging: Definition of a New Sensitive Parameter

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Abstract

: Bitumen is undoubtedly the most important material in the construction and rehabilitation of flexible road pavements. By increasing the temperature, bitumen changes from brittle solid, to viscoelastic solid and finally to Newtonian fluid. The rheological characteristics of bitumen also vary greatly due to aging, which is a phenomenon initiated in the phases of production and application of bituminous (asphalt) mixtures and continued during the life of road pavements. The aim of this work is to study several rheological parameters in order to evaluate if they are able to quantify the aging of various types of bitumens. Four bitumens from the same distillation column in the refinery, but with different penetration grades, were aged by using the RTFOT method, which simulates the aging of the bitumen during the asphalt mixture production and pavement construction. The original (base) and aged bitumens were characterized with conventional tests used in the paving industry, and the results were compared with the rheological characteristics obtained with small amplitude oscillatory shear tests. Aging was assessed at high temperatures (110 to 180°C) through the activation energy computed from the temperature dependence of the Newtonian viscosity. However, the comparison of the characteristic relaxation times extracted from master curves measured at medium/low temperatures (between 25 to 80°C), proved to be the most sensitive indicator of bitumen aging.

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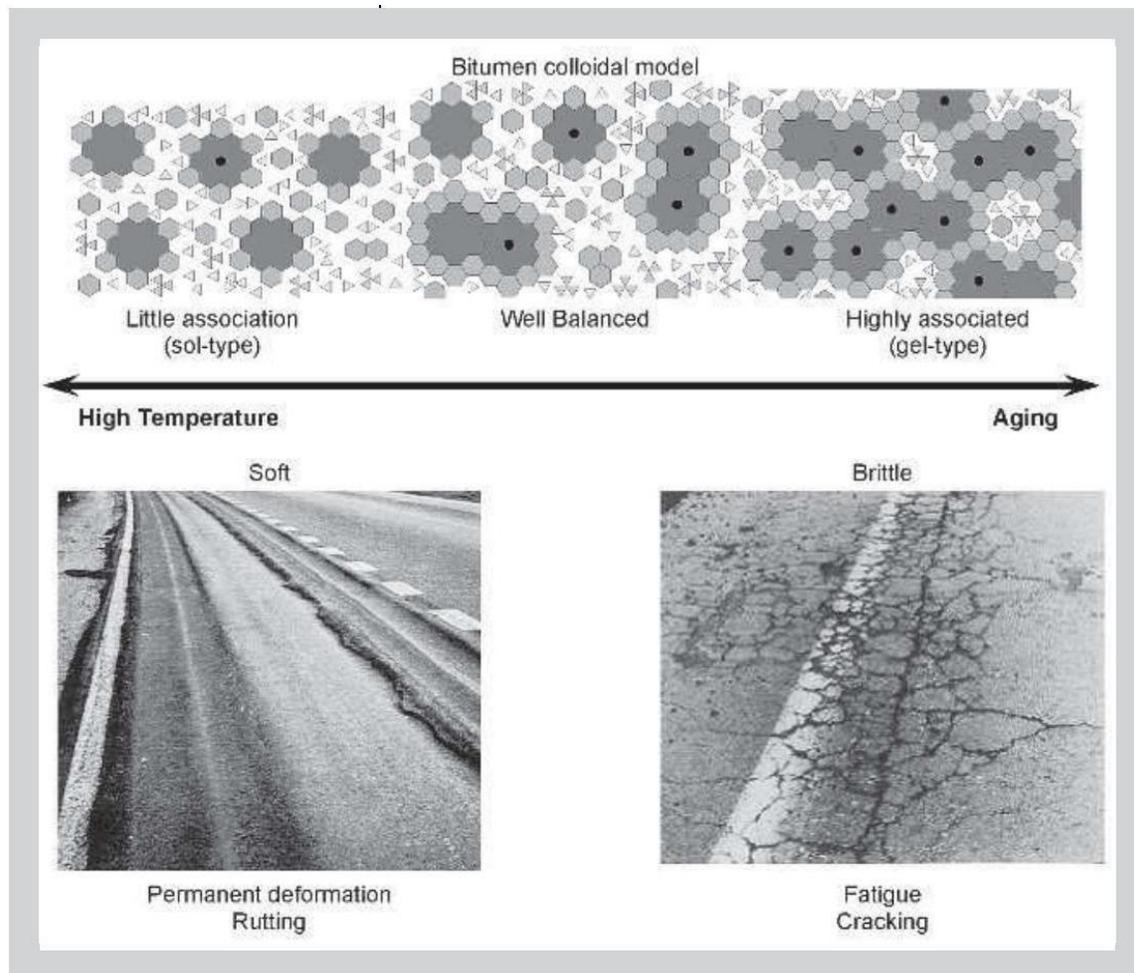
Asphalt ist unzweifelhaft das wichtigste Material bei der Konstruktion und Ausbesserung von flexiblen Straßenbelag. Durch Temperaturerhöhung geht Asphalt von einem spröden Festkörper, zu einem viskoelastischen Festkörper und schließlich zu einer Newtonschen Flüssigkeit über. Darüber hinaus verändern sich die rheologischen Eigenschaften von Asphalt durch Alterung. Dieses Phänomen wird während der Herstellung und Anwendung der Asphaltmischungen initiiert und setzt sich danach fort. Das Ziel dieser Arbeit ist, verschiedene rheologische Parameter zu untersuchen und ihre Eignung zur Charakterisierung des Alterungsverhalten von Asphalt zu evaluieren. Vier Asphaltmischungen aus derselben Destillationskolonne einer Raffinerie mit unterschiedlichen Eindringwerten wurden mit Hilfe der RTFOT-Methode gealtert. Diese Methode simuliert die Alterung von Asphalt während der Herstellung der Asphaltmischungen und des Straßenbelags. Der Ausgangs- und der gealterte Asphalt wurden mit den üblichen industriellen Versuchen getestet und ihre Resultate mit den Ergebnissen von linear-viskoelastischen Scheroszillationen verglichen. Das Alterungsverhalten wurde bei hohen Temperaturen (110°C bis 180°C) durch die Aktivierungsenergie ermittelt, die aus der Temperaturabhängigkeit der Newtonschen Viskosität bestimmt wurde. Es zeigte sich jedoch, dass der Vergleich der charakteristischen Relaxationszeiten, die aus den gemessenen Masterkurven bei niedrigen und mittleren Temperaturen (zwischen 25°C und 80°C) erhalten wurden, der beste Indikator für die Alterung von Asphalt ist.

RÉSUMÉ:

Le bitume est sans aucun doute le matériau le plus important pour la réhabilitation et la construction de revêtements routiers flexibles. En chauffant, le bitume passe d'un comportement de solide cassant, à celui d'un solide viscoélastique et finalement à celui d'un fluide Newtonien. Les caractéristiques rhéologiques du bitume varient grandement avec le vieillissement, qui est un phénomène initié dans les phases de production et d'application des mélanges bitumineux (asphalte), et qui continue durant la vie du revêtement routier. Le but de ce travail est d'étudier les paramètres rhéologiques du bitume qui sont les plus sensibles au vieillissement. Quatre bitumes provenant de la même colonne de distillation mais possédant des grades différents, ont été vieillis au moyen de la méthode RTFOT qui simule le vieillissement du bitume lors de la production du mélange d'asphalte et lors de la construction du revêtement. Les bitumes originaux (base) et âgés ont été caractérisés à l'aide de tests conventionnels utilisés dans l'industrie, et les résultats ont été comparés avec les caractéristiques rhéolo-

Figure 1:

Effects of aging and temperature in bitumen (top) and in pavements (bottom), where the symbols are organized in a grey scale: Saturates are in lighter grey followed by Waxes, Aromatics, Resins and Asphaltenes in darker grey (where the black dots symbolize the oxidised state).



giques obtenus au moyen de tests dynamiques de cisaillement. Le vieillissement est mis en évidence à haute températures (de 110 à 180°C) en considérant l'énergie d'activation calculée à partir de la dépendance thermique de la viscosité Newtonienne. Cependant, la comparaison des temps de relaxation caractéristiques obtenus à partir des courbes maîtresses construites pour des températures entre 25 et 80°C, se révèle être la méthode la plus sensible au vieillissement du bitume.

Key words: bitumen, aging, activation energy, master curve, relaxation time, paving industry

INTRODUCTION

Healthy economies require an appropriate transportation system, in which roadways are an essential part. Therefore, the construction and maintenance of road pavements should be long lasting and have a significant impact on the economic vitality of a nation. The primary reasons for the deteriorated conditions of roads include the increase in the overall traffic, climatic changes and, for flexible pavements, poor binder quality.

Bitumen is predominantly used as a binder to construct pavements for roads, highways, and airports. Most road pavements are constructed using a mixture of mineral

aggregates and a binder (usually bitumen), blended at high temperatures (135 – 163°C). In road construction, although it is added in a very low concentration (5%w/w), bitumen controls the final properties and performance of bituminous mixtures, since it is the only deformable component and forms a continuous matrix [1]. In fact, bitumen is the element that enrobes all the aggregates: i) at high temperatures, it acts as a lubricant to facilitate the mixing and compaction of the bituminous mixtures during the pavement construction phase, and ii) at service temperatures, bitumen binds the aggregates and confers the viscoelastic behaviour to the asphalt mixtures, waterproofing the pavement and preventing the ravelling of aggregates. Pavements with asphalt mixtures 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. Pavement deformation is closely related to bitumen rheology [2].

The chemical composition, the structure and the mechanical properties of bitumen strongly depend on the origin of the crude oil [3], the method of production [4] the short term aging (handling, pumping and pavement construction process), and the long term aging (field service). 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 [5]. It is usual 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 behaviour, bitumen has been approached as a colloidal dispersion. In the Bitumen Colloidal Model (BCM), 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 [6]. Bitumens exhibit a complex rheological behaviour due to these constituents (Saturates, Aromatics, Resins and Asphaltenes) and their interactions [7] (Figure 1), and a clear structural picture of bitumen that supports the rheological behaviour is still to be documented.

It is generally assumed that bitumen is a thermorheologically simple material, i.e. the time-temperature superposition principle (TTS) applies to bitumen [8, 9]. However, this picture has been challenged by Lesueur [5], who proposes two fundamental transitions upon cooling: the Brownian/non-Brownian transition of the asphaltenes, which gives rise to a Newtonian/viscoelastic α' relaxation at temperatures around 50°C, and the glass transition of the maltenes, with a viscoelastic/elastic α relaxation at temperatures around -20°C [10].

Two types of mechanisms are involved in bitumen aging (Figure 1). The main aging mechanism is irreversible, being characterised by chemical changes of the binder. The processes contributing to this type of aging include oxidation, isomerisation and dehydrogenation reactions, polymerization, condensation, loss of volatile and exudation (migration of oily components from the bitumen into the aggregate) [11, 12]. Oxidation results in the formation of highly polar and strongly interacting oxygen containing functional groups [13], which are responsible for a more brittle structure and an increase in susceptibility to cracking. Oxidative hardening happens at a relatively slow rate and varies seasonally; it occurs faster at higher temperature as diffusion of oxygen increases. The second mechanism is a reversible process called physical hardening. Physical hardening may be attributed to molecular structuring, i.e. the reorganisation of bitumen molecules (orbitumen microstructures) to approach an optimum thermodynamic state

under a specific set of conditions [11]. Rheological testing of aged bitumen indicates that aging is strongly temperature-dependent. At medium-high temperature, the aged samples are characterised by higher stiffness and elasticity, resulting in an increase in the complex shear modulus G^* and a decrease in the phase shift angle δ [14]. However, at low temperatures, the rheological behaviour is not affected by aging [15].

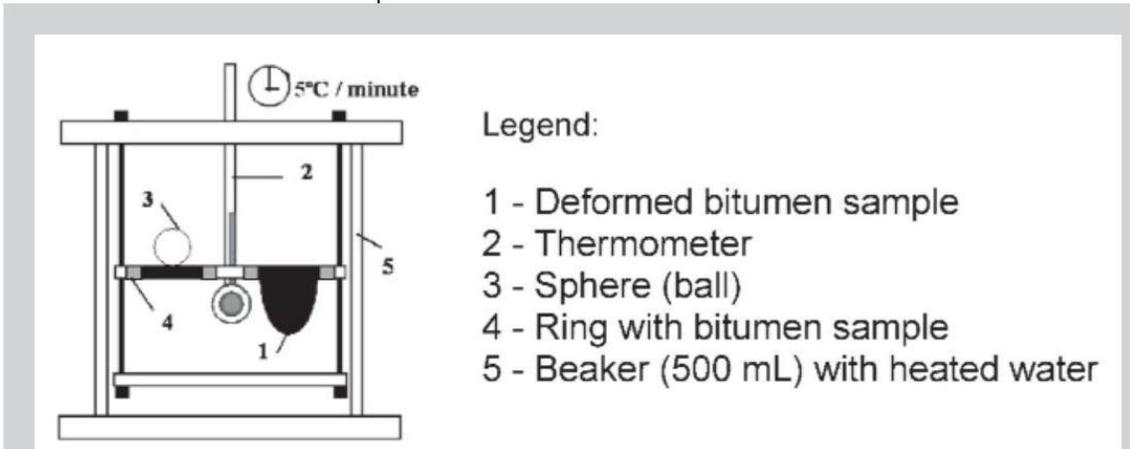
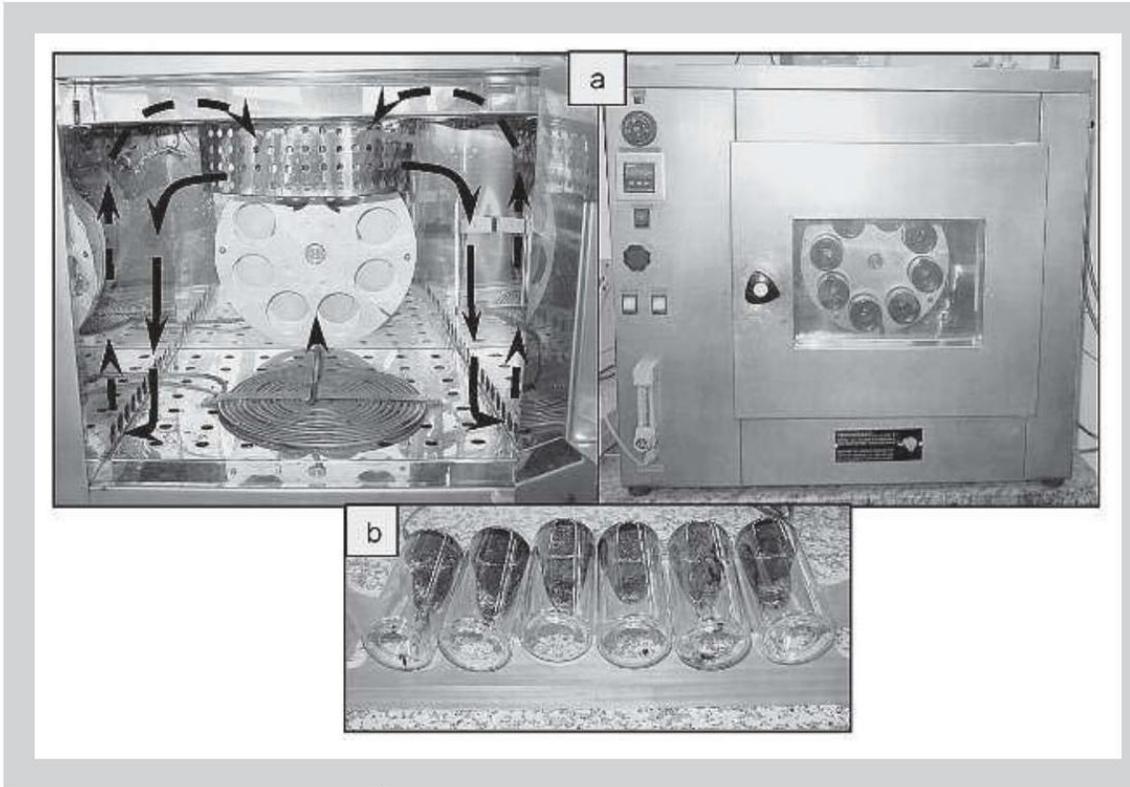
Several methods have been proposed to replicate the effect of aging and, therefore, to predict bitumen actual behaviour during application and in service. To simulate the age hardening occurring during plant mixing and application processes the most commonly used tests are the Thin Film

Oven Test (TFOT) and the Rolling Thin Film Oven Test (RTFOT). The results of the RTFOT are expressed as a percentage of the change of mass or as a change in the bituminous binder's characteristics such as penetration, softening point or dynamic viscosity before and after the aging period in the oven. These bitumen characteristics are obtained by performing normalized tests (see the experimental section below) [15] aimed at evaluating the physical properties of manufactured bitumens, namely the quality and consistency (degree of fluidity) [16].

After the bitumen hardening/aging process (RTFOT), an increase on the softening point and viscosity and a decrease on the penetration and mass can be usually observed. From the chemical point of view, the RTFOT method may induce an increase in the asphaltene content, as aromatics and saturates are converted into resins and resins become asphaltenes. The conversion gives rise to a light increase of the peptized material (asphaltenes) and a relative decrease in resins (peptizing material) content with respect to asphaltenes and in aromatics and saturates (solvent) content with respect to resins [15].

In terms of rheology, the parameters mostly used to study bitumen aging are the index of the kinematic or apparent viscosity measured in a capillary viscometer or in a rotating spindle apparatus respectively. Other approaches to quantify bitumen aging through rheological parameters can be done by assessing the aging index (ratio aged against unaged) for the complex modulus at the glass transition temperatures, the activation energies, E_a , from the Arrhenius equation or the C_1 and C_2 constants of the WLF equation. Finally, the shift factors, a_T , obtained in the construction of master curves can also be used to assess another bitumen aging index. Nevertheless, these rheological indexes are generally less accurate than those typically used in pavement industry [11, 15].

The main aim of this work is to determine, among the several rheological parameters extracted from small amplitude oscillatory shear experiments, the most effective one to quantify the bitumen aging. Then, rheological indexes are compared with the indexes of empirical parameters currently used in the paving industry. The output of this study is a new rheological index based on the relaxation times of bitumens which is found to be truly adequate to quantify bitumen aging.



- Legend:
- 1 - Deformed bitumen sample
 - 2 - Thermometer
 - 3 - Sphere (ball)
 - 4 - Ring with bitumen sample
 - 5 - Beaker (500 mL) with heated water

Figure 2 (above):
 Photos of the used rolling thin-film oven test (RTFOT) equipment showing the oven (a) with the black arrows representing the air flow in the oven and the glass containers (b).

Figure 3:
Schematic representation of the ring and ball method for determination of the softening point of a bitumen (adapted from ref. [17]).

MATERIALS AND METHODS

MATERIALS

In order to minimize any variability in the characteristics of the materials due to their source and processing, bitumens were collected from the same batch of the La Rábida Refinery of CEPSA in Huelva, Spain. Different paving grade bitumens were selected for testing: B10/20 (A), B40/50 (E), B60/70 (I) and B150/200 (M). The designations of the bitumen grades are defined in the standard EN 12591 (bitumen and bituminous binders - specifications to paving grade bitumens), where the bitumens are classified in pre-defined penetration ranges, e.g. a bitumen with a penetration of 45×0.1 mm is classified as a B40/50 (the penetration is between 40 and 50×0.1 mm). In this case, since the bitumens were supplied by a Spanish refinery, the grades are defined in accordance to the Spanish national version of the EN standard for commercialized bitumens.

METHODS

Rolling Thin-Film Oven Test (RTFOT) used to age bitumen samples

The Rolling Thin Film Oven Test (RTFOT) was developed in 1963 by the California Division of Highways and involves the rotation of glass containers with samples of 35 grams of bitumen, in an oven at 163°C for 75 minutes. Thin films of bitumen with a thickness of 1.25 mm are obtained in these conditions. This method measures the combined effects of heat and air on a moving thin film of bitumen, simulating the hardening that a bituminous binder undergoes during mixing in an asphalt plant and the application of the bituminous layers in the pavement (EN 12607-1:1999). The rolling thin-film oven test equipment was obtained from Tecnotest, s.n.c. di cuoghi & C., Modena, Italy. The RTF controller used in this test is shown in Figure 2, which is in accordance to EN 12607-1 standard (bitumen and bituminous mixtures - determination of the resistance to hardening under influence of heat and air - Part 1: RTFOT method) requirements. The RTFOT oven was preheated at 165°C. Then, eight bitumen samples with 35 ± 0.5 g were poured into the glass containers and the carriage was set to rotate at a speed of 15 ± 0.2 rpm. The air flow was started and maintained at a rate of 4000 ± 200 ml/min. The bitumen samples were maintained in the oven for 90 min (Figure 2).

Penetration test (Pen)

The penetration test is an empirical method to measure the consistency of the bitumen. The test method is described in EN 1426 (bitumen and bituminous binders - determination of needle penetration). According to EN 1426, penetration is defined as the distance that a standard needle loaded with a 100 g weight will penetrate into a bitumen sample for 5 seconds. Usually penetration is measured at 25°C, which also approximates the average service temperature of the hot mix asphalt (HMA) pavements.

The distance ($\times 0.1$ mm) is then labelled as penetration grade (Pen) and, thus, smaller values indicate harder bitumens.

Softening point test (R&B)

The softening point (ring and ball or R&B) test is also an empirical method to determine the consistency of penetration grade or oxidised bitumens. In this test two steel balls are placed on two discs of bitumen contained within metal rings and these are raised in temperature at a constant rate ($5^{\circ}\text{C}/\text{min}$). The softening point is the temperature at which the bitumen softens enough to allow the balls enveloped in bitumen to fall a distance of 25 mm into the bottom plate (Figure 3). In short, this test measures a temperature at which the bitumen phase changes from semi solid to liquid. The test method is described in detail in EN 1427 standard (bitumen and bituminous binders - determination of softening point - ring and ball method).

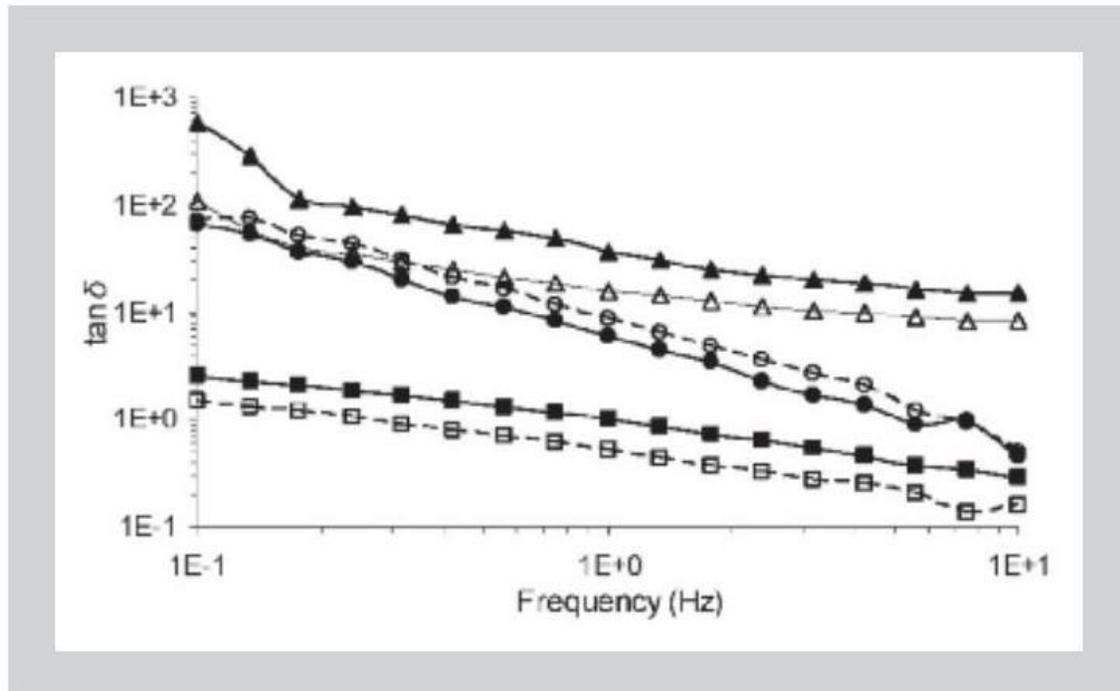
Apparent Viscosity (AV)

The apparent viscosity of the studied bitumens at 175°C was determined in accordance to EN 13302 (bitumen and bituminous binders - determination of viscosity of bitumen using a rotating spindle apparatus), by means of a coaxial viscometer using a rotating spindle apparatus. The used equipment was a Brookfield viscometer (Programmable RVDV-II+viscometer) from the Brookfield Engineering Laboratories, 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 1.18 cm) and the sample container (HT-2, internal diameter of 1.90 cm) were placed in an oven at 175°C for about 1 h .

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 systems). 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 stabilise at a speed of 20 rpm , corresponding to a shear rate of 6.8 s^{-1} . Three readings were taken and recorded at 60 s intervals. The reported viscosity is the average of the three readings.

Rheological characterization

The rheological properties were assessed using a stress controlled rotational rheometer (Stress-tech-HR, Reologica) equipped with 40 mm parallel plates and a gap of 1 mm . Small amplitude oscillatory shear (SAOS) tests were performed at various temperatures (25,35,50,80,110,140,160 and 180°C). In a preliminary set of experiments, stress sweep tests were performed at 1 Hz to determine the linear regime for each temperature and sample. As a result of these tests, frequency sweep tests recorded with stresses of about 1000 Pa (for tests at 25 and 35°C), 200, 40, 30, 20, 10 and 3 Pa for temperatures of 50,80,110,140,160 and 180°C ,



respectively, allowed obtaining the mechanical spectra of each sample at the corresponding temperatures. Prior to the record of the mechanical spectra, time sweeps were applied using a frequency of 1 Hz and the stresses mentioned above in order to check that samples reached both thermal and structural equilibrium conditions. The experimental procedures for the rheological characterization of the bitumens were based on the European standard EN 14770 (bitumen and bituminous binders-determination of complex shear modulus and phase angle - dynamic shear rheometer (DSR)).

RESULTS AND DISCUSSION

ISOTHERMS

In order to exemplify the rheological behaviour of the tested bitumens (before and after aging), the results of only one of them are presented, namely bitumen E (40/50), because this is the binder typically used in flexible road pavements and it presents the average characteristics among the studied bitumens. The best way to visualise any qualitative change in the structure of the material is to represent $\tan \delta$ versus test temperature and/or frequency. This rheological function directly reflects the relationship between the viscous and the elastic contributions to the rheological response of the material and gives a straightforward graphical comparison of aged and base bitumen samples for different selected temperatures (see Figure 4).

The isotherm plots show a decrease of $\tan \delta$ with increasing frequency for all tested temperatures. At higher temperatures (see the curves for $T = 160^\circ\text{C}$ in Figure 4), $\tan \delta$ shows almost a -1 slope with increasing frequency, which is indicative of a Newtonian fluid behaviour and contrasts with the viscoelastic behaviour probed at lower temperatures. The isotherms of base and aged bitumen have roughly the same shape,

indicating that the changes induced in the bitumen by the RTFOT do not significantly affect the overall viscoelastic behaviour of bitumen. In particular, for temperatures equal or lower than 80°C, the aged bitumen presents a slight reduction in the value of $\tan \delta$ when compared to the base one. Data at 160°C

Figure 4:
Isotherms of the $\tan \delta$ for bitumen E before (solid symbols) and after RTFOT (open symbols) at 25°C (squares), 80°C (triangles) and 160°C (circles).

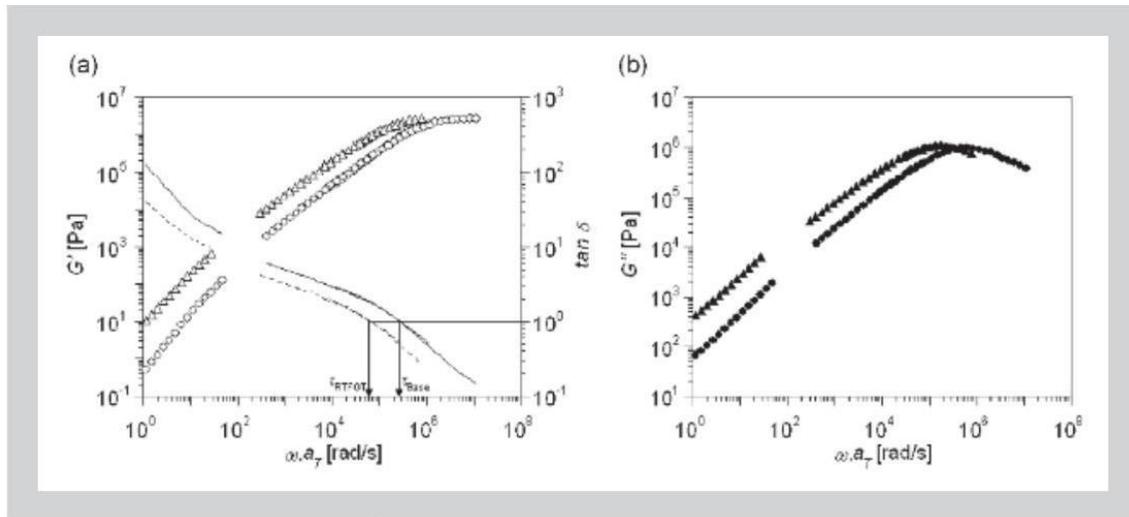


Figure 5 (left):
Master curves ($T_{ref} = 80^\circ\text{C}$) of (a) elastic modulus, $\tan \delta$ and (b) loss modulus for bitumen E before (circles) and after (triangles) aging.

Figure 6:
Relation between the relaxation times extracted from the master curves of the different bitumens before and after RTFOT.

Table 1:
Ratio between the relaxation times of the different bitumens after and before aging. suggest that aging relates to higher values of $\tan \delta$. However this result is difficult to reconcile with the simultaneous increase in the Newtonian viscosity of the aged bitumen (see Figure 8 below). As such, we suspect that limitations in the rheometer sensitivity impede any quantitative distinction in the phase shift angle of such poorly viscous fluids.

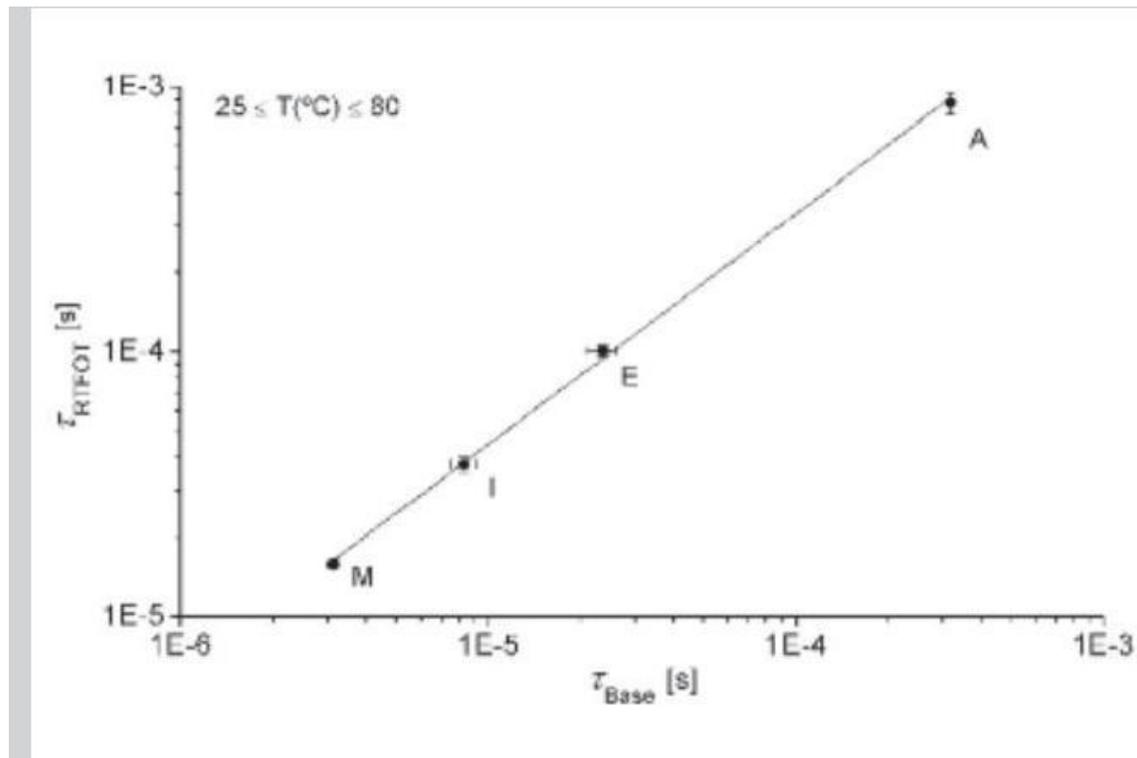
MASTER CURVES

The procedure of superposing curves at different times (frequencies) and temperatures is known as the time-temperature superposition (TTS) and the resulting curves (master curves) cover large time or frequency domains well beyond the frequency range experimentally accessed by the rheometer. An important criterion for the use of the method of reduced variables is that the shapes of the original curves at different temperatures must match over a substantial range of frequencies or times. An equally important criterion to evaluate the applicability of the method of reduced variables is the

requirement that the same values of the horizontal shifting factor must superpose all viscoelastic functions [18].

Construction of the master curves for the studied bitumens

The master curves of the four bitumens before and after aging at medium/high service temperatures (25,35,50 and 80°C) were constructed using the IRIS software - Innovative Rheological Interface Software (version 9.0, copyright 1990-2005) 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. This indicates that bitumens are not thermorheologically simple over the whole range of temperatures spanning from service temperatures (25 to 80°C) to production and application temperatures (from 100 to 180°C). We note here that different models were in fact proposed in the literature to describe the rheological behaviour of bitumens at high or low temperatures [5]. Therefore, this complies with the structural transition evidenced in Figure 4



between 80 and 160°C, which is the cause of the failure of the time-temperature equivalence principle for the bitumens studied here. Indeed, such transition has been highlighted in Dynamic Mechanical Thermal Analysis where a peak in the temperature dependence of $\tan \delta$ was assigned to the collapse of the glassy structure [14]. However, master curves could be constructed for temperatures below that transition, and are displayed in Figure 5 for the representative bitumen E. Evidently, the master curves show a discontinuity in frequency due to the lack of experimental data between 50 and 80°C. However, satisfactory master curves could be constructed as inferred from the temperature dependence of the horizontal shift factors a_T (see Figures 7 and 8).

Rheological data in Figure 5a indicate that the shear storage modulus G' reaches a high frequency plateau. This glassy plateau reads values of 2.629 GPa for the base bitumen, and of 2.742 GPa for the aged (RTFOT) bitumen at 25°C. This behaviour and the corresponding values for the elastic modulus are in agreement with the values reported in the literature, which point towards the formation of a glassy plateau between 1 GPa [5, 8] and 5 GPa [10]. However, instrument compliance affects the results at high frequency [19], especially at temperatures below 50°C, where sample rigidity is higher. Nevertheless, Equation 1 in reference [19] suggests that the rheometer compliance will equally affect the mechanical response of all bitumens. As such, we conjecture that this inherent experimental pitfall has a negligible effect on the analysis proposed below (see also table 1) for the quantitative indexing of bitumen aging.

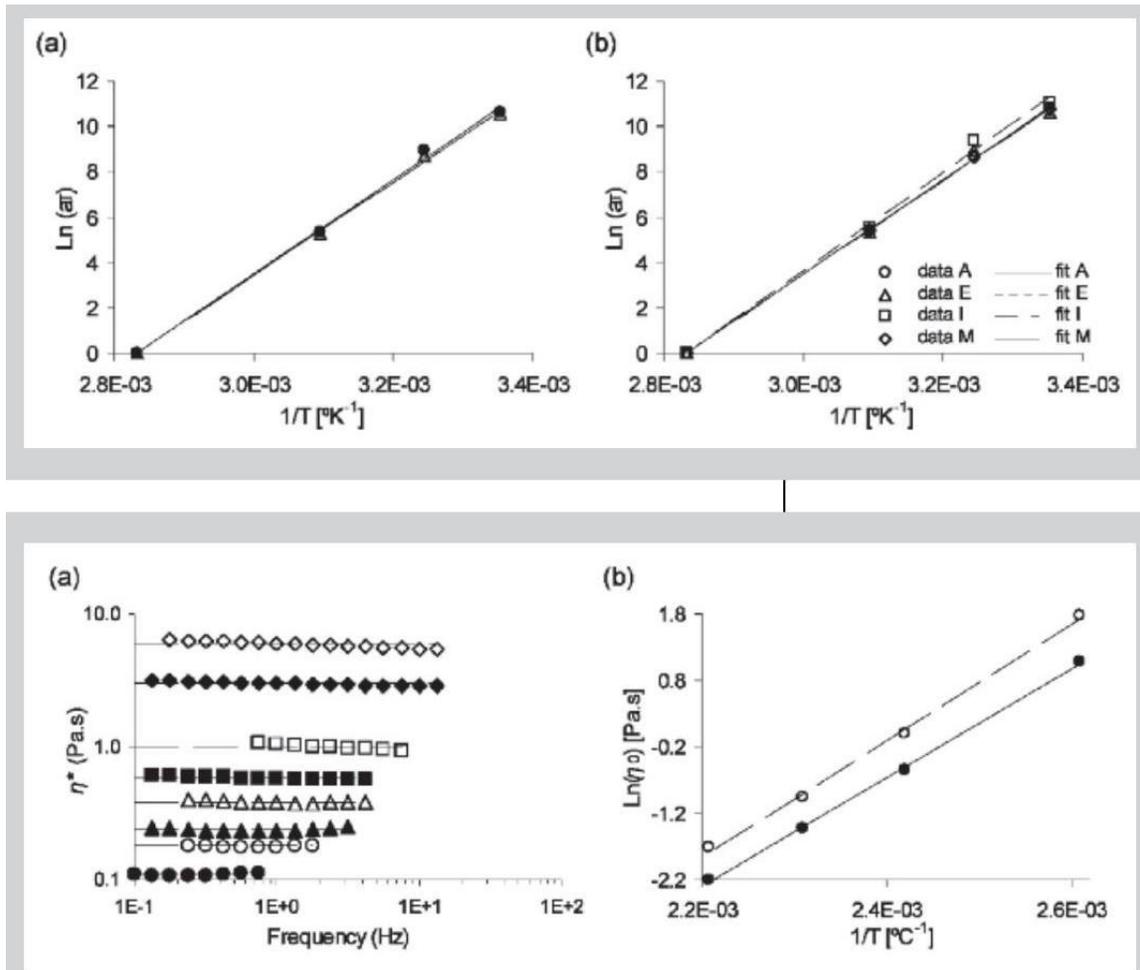
Paving Grade Bitumens	Bitumen	$\tau_{\text{RTFOT}} / \tau_{\text{Base}}$	Ref.
10/20	A	2.72 ± 0.25	
40/50	E	4.30 ± 0.50	
60/70	I	4.60 ± 0.53	
150/200	M	5.01 ± 0.37	
133	AAD-1	1.86	[8]
109	AAC-1	2.69	[8]
94	AAB-1	2.14	[8]
70	AAK-1	1.90	[8]
63	AAM-1	2.08	[8]
58	AAF-1	1.95	[8]
53	AAG-1	1.48	[8]

The mechanical spectra displayed in Figure 5 are indicative of a broad distribution of relaxation times. Following the structural picture of the BCM (see Figure 1), one may correlate the distribution of relaxation times with the size distribution of resin and asphaltene aggregates. The fact that the TTS is valid below 80°C both before and after aging implies that all relaxation times show similar temperature dependence, and that aging did not affect this rheological simplicity. No structural transition resulting in a failure of the TTS is observed in the aged sample, which is in harmony with both physical aging and oxidative aging. Alternatively, this could also mean that the thermal dependence of the rheological functions measured between 25 and 80°C, is not sensitive to the structural changes induced by the RTFOT aging.

Analysis of the relaxation times obtained from the master curves

The structural complexity of bitumens is usually mirrored in the broad distribution of relaxation times inferred from mechanical spectra such as the ones displayed in Figure 5. The distribution can be roughly characterized by picking up one characteristic relaxation

time and quantifying the width of the distribution. For asphalts, an index has been proposed to quantify such width, namely the rheological index R [8,20], which is the difference between two values of the complex shear modulus C^* picked at two different characteristic frequencies in the spectrum: the frequency range corresponding to the glassy behaviour and the frequency at which $\tan \delta = 1$. This index showed to be very effective in specifying different types of bitumen. A characteristic relaxation time corresponding to the inverse of the frequency where $\tan \delta = 1$ can be extracted from the master curve for both base and aged bitumens (frequencies corresponding to the relaxation times are indicated with vertical arrows in Figure 5). This characteristic time can be seen as the longest relaxation time in the distribution. In model hard sphere suspensions, the longest relaxation time relates to the characteristic sphere relaxation time which depends on both particle size and volume fraction [21]. Data in Figure 5 clearly show that the relaxation time increases with aging. In terms of the colloidal approach, a longer relaxation time relates to larger particles resulting from the aggregation of more asphaltene peptized by resin molecules and, concurrently, to the reduction of the maltenes phase in the bitumen colloidal structure [15].



In order to analyse the response of different paving grade bitumens to the aging process, the values of their relaxation times before RTFOT (base) were plotted against the relaxation times of the aged bitumens (Figure 6). Figure 6 shows an increase of the relaxation times with the increase of bitumen stiffness (see also the reference for paving

grade bitumens in Table 1). This is coherent with previous studies, 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. Indeed, aging induces the increase of those two rheological parameters [5]. The log-log plot in Figure 6 suggests a power law relationship between the relaxation times before and after aging (base and RTFOT). This strong correlation between relaxation times from all samples suggests that the same aging process occurs for all types of bitumens studied here.

The ratio $\tau_{RTFOT} / \tau_{Base}$ between the relaxation times of the different bitumens after and before aging, obtained from the master curves, are presented in Table 1. Other values of this ratio, computed from values referred in literature [8], are also presented as reference in the last seven lines of Table 1. These values were obtained from master curves constructed at a reference temperature of 25°C using torsion bar and parallel plates (the classification of these paving grade bitumens is based on their effective values of penetration). The aging index based on the ratio of bitumen relaxation times, determined in this work, ranges between 2.47 and 5.38. The quite high values of the aging index, along with the rather wide range of variation (roughly two fold) show that this is a sensitive parameter to quantify aging for a wide

Figure 7 (above):

Fit of Arrhenius equation to the temperature dependence of shift factors a_T for (a) bitumen E before (solid symbols) after aging (open symbols) and for (b) the base bitumens.

Figure 8:

a) Frequency dependence of the dynamic shear viscosity before (solid symbols) and after (open symbols) aging of bitumen E measured at 110°C (diamonds), 140°C (squares), 160°C (triangles) and 180°C (circles); b) Adjustment of Arrhenius equation to the temperature dependence of the Newtonian viscosity η_0 for bitumen E before (solid symbols) and after aging (open symbols).

Table 2 (above):

Constants of the WLF equation (C_1 and C_2) for the different bitumens before and after aging.

Table 3 (middle):

Activation energies E_a computed for the different bitumens before and after aging at service temperatures.

Table 4 (below): Ratio between the η_0 and E_a values for the different bitumens before and after aging at production and application temperatures.

Bitumen	C_1	C_2
A Base	32.0 ± 7.6	318.3 ± 89.5 0.999
E RTFOT	43.1 ± 29.3	460.1 ± 347.10 .998
I RTFOT	91.3 ± 53.2	836.6 ± 523.70 .998
M Base	32.9 ± 4.4	331.1 ± 50.90 .999

Bitumen	E_a (kJ/mol)	R^2
A Base	172.8 ± 1.5	$0.9991.084 \pm 0.049$
RTFOT	187.3 ± 8.4	0.998
E Base	172.7 ± 6.3	$0.9990.986 \pm 0.044$
RTFOT	170.2 ± 4.5	0.999
I Base	180.0 ± 7.8	0.998
RTFOT	213.5 ± 5.8	0.999
M Base	171.9 ± 1.3	$0.9991.047 \pm 0.054$
RTFOT	180.1 ± 9.3	0.998

Bitumen	η_0 at 175°C(Pa · s)	η_0 (RTFOT)/ η_0 (Base)	E_a (kJ /mol)	R^2	E_a (RTFOT)/ E_a (Base)
A Base	0.262	1.299	75.8	0.999	1.186 ± 0.107
RTFOT	± 0.012	± 0.168	± 2.4		
	0.340		89.9	0.993	1.062 ± 0.044
	± 0.041		± 7.6		
E Base	0.128	1.600	68.2	0.999	
	± 0.004	± 0.093	± 1.5		
RTFOT	0.205		72.5	0.999	
	± 0.01		± 2.5		
I Base	0.128	1.302	63.3	0.999	1.110 ± 0.063
	± 0.006	± 0.102	± 2.0		
RTFOT	0.167		70.2	0.998	
	± 0.011		± 3.3		
M Base	0.134	1.517	56.9	0.998	1.201 ± 0.073
	± 0.005	± 0.127	± 2.6		
RTFOT	1.071		68.3	0.998	
	± 0.007		± 2.7		

confirm that a sensitive parameter to quantify aging, independently from bitumen origin, can be derived from the rheological relaxation times. Additionally, the tendency of the aging index to increase when softer bitumens are analysed is confirmed by the results of both studies.

Besides the relaxation time, other rheological parameters have been used to quantify indexes of bitumen aging, namely the zero shear viscosity [5] (with aging indexes

between 1.5 and 4.0) and the complex shear modulus (G^*) [11], with aging indexes ranging from 1.0 to 2.3. The values of these indices are lower than the ones obtained in this work, however the zero shear viscosity shows a wide range of variation, which enables to capture small changes effectively. As mentioned above, the rheological index R is an alternative to quantify the broad distribution of relaxation times. In reference [8], the values of R range from 1.24 to 2.21 for all aged and based bitumens listed in Table 1. Consequently, the ratio $R_{\text{RTFOT}}/R_{\text{Base}}$ shows a little range of variation (from 1.08 to range of penetration grade bitumens (since the tested bitumen had penetrations between 10 and 200×0.1 mm)).

Christensen and Anderson [8] reported bitumens relaxation times obtained from experiments carried out with a torsion bar and with parallel plates geometries, for base and aged (TFOT) bitumens from different origins, freeing the results from experimental artefact (rheometer compliance). In spite of this, the aging indexes displayed in Table 1 were not computed by these authors. The ratios calculated from the relaxation times measured by Christensen and Anderson [8],

of $E_{\text{obtained for aged samples}}$ do not differ significantly from those determined for base samples (see ratios $E_a(\text{RTFOT})/E_a(\text{Base})$ in Table 3). Thus, the temperature dependence of the rheological properties is not sensitive enough toward bitumen aging. This result comes as no surprise since other authors already reported on the poor sensitivity of the 1.17) which is not effective in quantifying the aging. This result comes as no surprise if one compares the BCM approach with results from model hard sphere colloidal suspensions [21]. 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.

Temperature dependence of shift factor a_T

Arrhenius equation or Williams-Landel-Ferry (WLF) equation [22] can be used to describe the temperature dependence of the horizontal shift factors a_T used to construct the master curves. For polymer melts, the temperature dependence of viscoelastic functions such as viscosity can be modelled by an Arrhenius equation, if barriers in terms of molecular interactions are dominant. This is usually the case of bitumen at higher temperatures. On the other hand, at lower temperatures (near glass transition temperature - T_g), associative processes of molecules dominate and temperature dependence is better described using WLF equation [7]. This equation was reported to adequately describe the thermal properties of bitumen for temperatures lower than 100°C [9]. Therefore, the temperature dependence of shift factors a_T was first analyzed with the WLF equation. Results from the fits were not satisfactory. Only four bitumens could be rationalized with the WLF equations, but with large errors on both C_1 and C_2 (see Table 2), which stem from the poor quality of the fits to the data. Indeed, this analysis did not allow the comparison between aged and base bitumens.

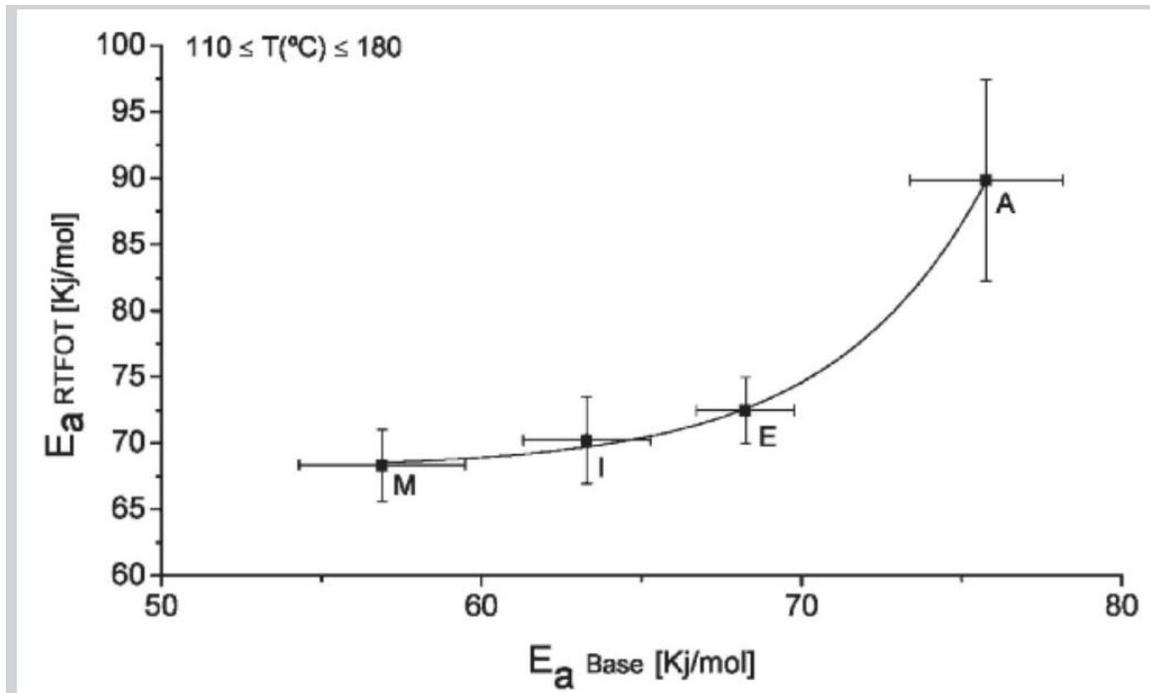
Alternatively, the Arrhenius equation gave better fitting results, and this is in harmony with earlier reports for the same range of low/medium temperatures [10]. Arrhenius plots are presented in Figure 7 for all samples, and the corresponding activation energies, E_a , are shown in Table 3. The E_a values vary in the range of approximately 170 to 190 kJ/mol for all tested bitumens. In spite of the better quality of the fits with respect to WLF fits m m s -

temperature dependence of a_T towards chemical and structural differences in a set of penetration grade bitumens [9]. Such weak temperature dependence might also explain why master curves could be obtained for all bitumens using TTS. As a result, any index built on the ratio of rheological parameters obtained before and after aging should be a better aging indicator.

Previous investigation [5] showed that the increase in the values of the E_a is directly related to the increase in the asphaltenes content. However, the rather elevated E_a values found for bitumens A to M, together with the very slight increase of asphaltenes during RTFOT [15] have an almost imperceptible impact on the computed ratio in Table 3. So, to summarize the rheological characterization of bitumens at service temperatures (between 25 and 80°C), results suggest that bitumen aging can be essentially quantified by computing an aging index from the relaxation times observed in the master curves of the bitumens after and before aging. In fact, this was the only sensitive parameter capable of evaluating the aging of the different bitumens tested.

THERMORHEOLOGICAL BEHAVIOUR AT PRODUCTION AND APPLICATION TEMPERATURES

Figure 8 presents the frequency dependence of the dynamic viscosity (η^*) measured at different temperatures for Bitumen E before and after aging. Similar results were obtained with all remaining bitumen samples. The dynamic viscosity of the studied bitumens was independent of the frequency, which is indicative of their Newtonian behaviour at high temperatures. In this range of temperatures (110 to 180°C) the waxes (which are a constituent of the paraffinic part of the saturate fraction of bitumens, which crystallize at low temperatures [5]) are no longer in a crystalline state and the compact structure constituted by asphaltenes surrounded by resins [14] is almost collapsed. The shifts to higher viscosities after aging are associated with the relative increase of asphaltene volume fraction caused by short and longterm aging. Short-term aging is mainly due to oxidation and volatilization, an outcome of heating during mixing and construction [14]. Overall, viscosity data at high temperatures are consistent with results reported elsewhere and obtained with similar rheometrical set-up [5, 14].



Horizontal lines in Figure 8a are linear fits to the experimental data, from which the Newtonian viscosity (zero shear viscosity or η_0) has been computed. The aging of bitumens is expressed by an increase of the Newtonian viscosity, as demonstrated in Figure 8b, where the temperature dependence of η_0 has been recast in an Arrhenius plot. The good quality of the fits (see errors reported in Table 4 for the computed E_a) shows that η_0 can be described by an Arrhenius-like equation, as reported in earlier rheological studies [10]. Figure 8b also shows that the activation energies E_a extracted from the Arrhenius fits are affected by aging (different slopes before and after aging). However, the ratios computed from E_a for base and aged bitumen samples are close to one, and hence are not a valuable aging index (see Table 4). Aging does reflect in the activation energy computed from the temperature dependence of the zero shear viscosity, as E_a values listed in Table 4 for RTFOT samples are larger than E_a energies obtained for base samples. In this range of temperatures (110 to 180°C), E_a vary between 57 and 90 kJ/mol, which are values very different from those obtained at lower temperatures using the shift factors. Smaller activation energy values may be explained by a transition to a Newtonian fluid behaviour. 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 [5].

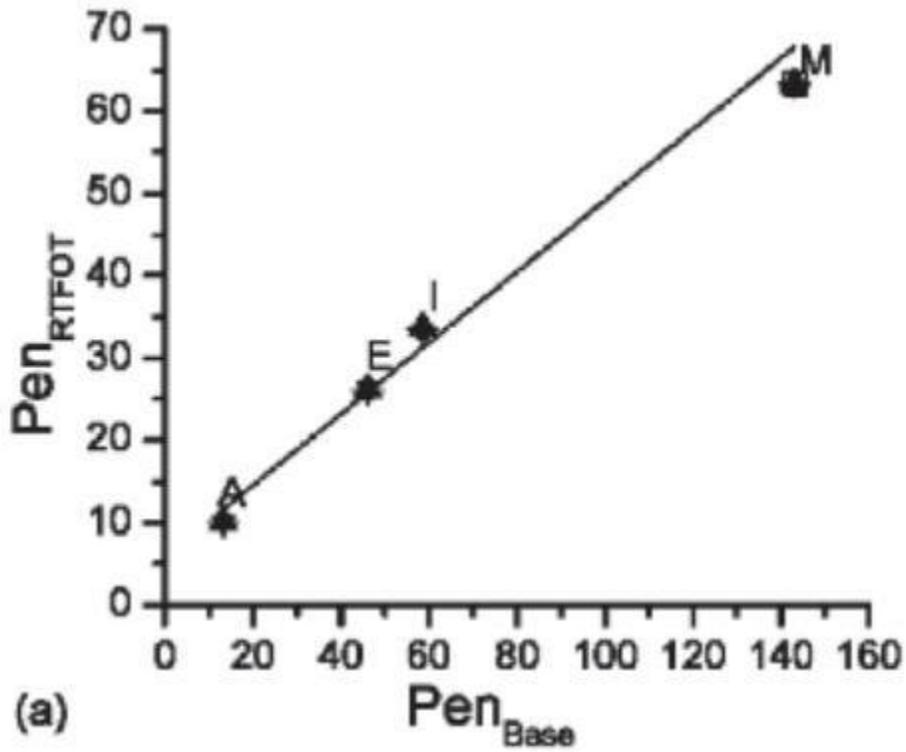
In Figure 9, the Arrhenius energies of the aged bitumens are plotted against those of the base bitumens, in order to find possible correlations. First, it can be noticed that harder bitumens (e.g., bitumen A) present higher E_a values, which is consistent with the literature review. However, the resulting ratio of activation energies does not allow to distinguishing between the different grades of bitumen. This aging index, namely the ratio shown in the last column of Table 4, is not

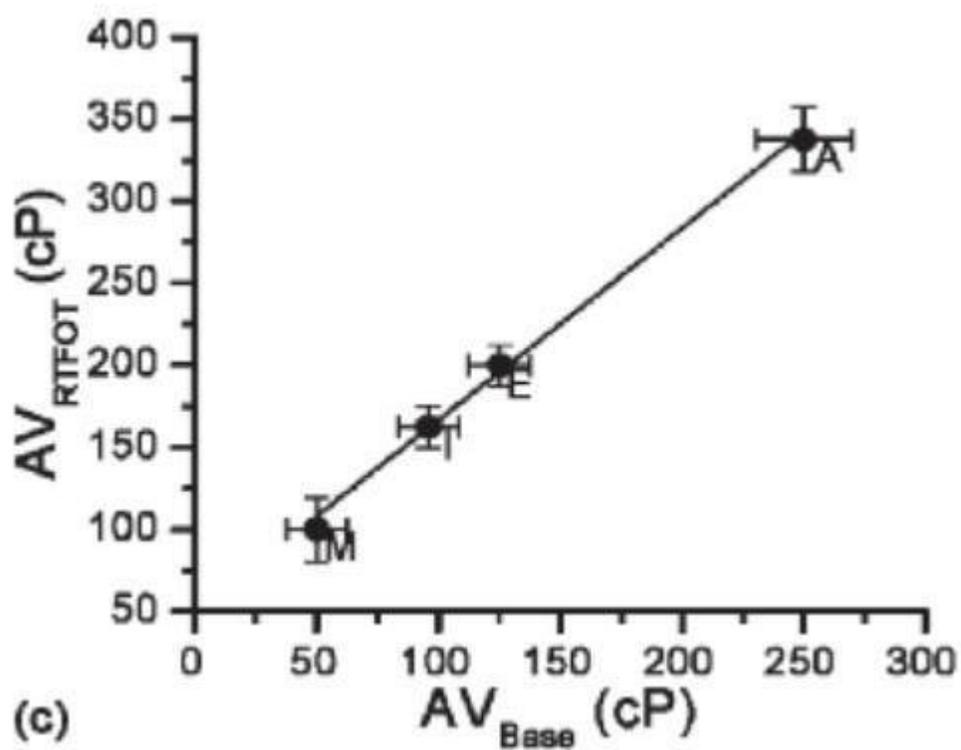
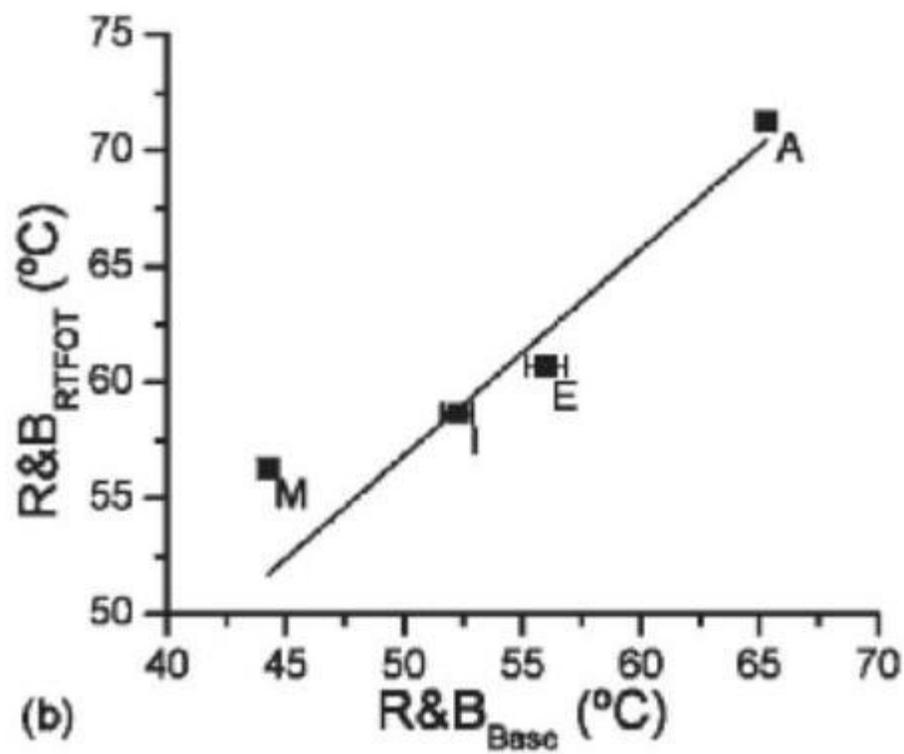
Figure 9:

Relation between the activation energies extracted from the η_0 of the different bitumens before and after RTFOT, fitted by an exponential trend line.

Figure 10:
Relation between the parameters usually applied to characterize paving grade bitumens before and after aging (a. Pen, b. R&B, c. AV).

Table 5:
Ratios between the conventional characteristics of studied bitumens before and after aging and percent mass loss during RTFOT aging.





significantly differentiating the aging of a RTFOT processed hard bitumen from a RTFOT processed softer bitumen (compare sample A and B). The observed results are consistent with those of the relaxation times at lower temperatures and with those of literature review, which show an increase in the E_a as the asphaltene content of bitumen increases during the production of harder bitumens or during the simulation of the aging phenomenon with the RTFOT [5, 15]. Nevertheless, the earlier observations were more noticeable in what refers to aging.

With respect to the quest for a best aging index, the ratio of RTOFT over base zero shear viscosity does not do a better job than the activation energy for this range of temperatures. Although aging does impact on η_0 , as larger Newtonian viscosities correlate with aged samples, the ratio of viscosities is not able to significantly distinguish sample A aging from sample E aging.

AGING AS QUANTIFIED BY CURRENTLY USED STANDARD METHODS

In the road paving industry, the bitumen aging is traditionally quantified by comparing the results of empirical tests (penetration-Pen; ring and ball - R&B; apparent viscosity - AV) commonly used to characterize bitumen before and after RTFOT. Additionally, the mass loss of the bitumen sample during the RTFOT aging procedure is also determined. The Pen, R&B and AV test results of the base bitumens were plotted against those of the corresponding aged bitumens, as shown in Figure 10. The three tests show a different impact of RTFOT aging on the four studied bitumens. While the R&B and Pen test results show a higher range of variation for the base bitumens, compared to those of the aged bitumens, the AV test results show the

Bitumen	Ratio between the properties of RTFOT/Base bitumen			
	Penetration at 25°C	R&B Softening Point	Apparent Viscosity	Mass Loss [%]
A	0.754 ± 0.051	1.091 ± 0.006	1.35 ± 0.13	0.000 ± 0.000
E	0.566 ± 0.022	1.084 ± 0.018	1.60 ± 0.19	0.3131 ± 0.0006
I	0.573 ± 0.014	1.123 ± 0.014	1.70 ± 0.25	0.3033 ± 0.0205
M	0.443 ± 0.013	1.272 ± 0.014	2.00 ± 0.50*	0.9063 ± 0.0983
*This ratio was computed from values of apparent viscosity inferior to 125 cP , which is the minimum value with suitable accuracy in the used equipment. Therefore, the indicated error may be quite higher.				

opposite tendency. The greatest variation is observed in the results of the penetration test.

By carrying out RTFOT aging and further characterization tests in paving grade bitumens, the main objective of the road paving industry is to determine its rate of hardening, i.e. in the paving industry aging is equivalent to hardening. It is important to study the aging/hardening of bitumen because it becomes more brittle, thus leading to premature cracking failure of the pavement. The ratios traditionally used as indexes to quantify the aging phenomenon during the bituminous mixture production and application, and the bitumen mass loss during RTFOT aging, are presented in Table 5.

The ratios of AV and R & B are quite insensitive to aging, because their values are not very different from 1 (although they are, in general, higher for softer bitumens than for harder ones). The percent mass loss of the studied bitumens also increases for softer bitumens, being null for bitumen A (the harder bitumen). The aging index obtained with the results of the penetration test is lower than 1.0, but it is more sensitive to aging than the other parameters, especially for softer bitumens (the ratio of 0.44 for bitumen *M* is equivalent to an index of 2.3, the inverse of 0.44). Nevertheless, this aging index, along with its range of variation, is also lower than the ones previously observed for the relaxation times (see Table 1).

One of the indexes used to quantify the bitumen aging is based on the evaluation of viscosities. The literature [5] reports that RTFOT may result in a ratio of viscosities between 1.5 and 4.0, which is in harmony with the results displayed in Table 5. However, in the present work, this aging index was not the most expressive one among those usually applied to characterize paving grade bitumens (when comparing penetration, R&B and apparent viscosity tests). In fact, the aging index obtained with the penetration results presents a slightly higher value (2.3) than with the apparent viscosity results (2.0). Comparing the aging indexes presented in Table 5 to those based in 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 both suggest that the index proposed here performs better in quantifying bitumen aging. What will be the reason for this?

The characteristics of a viscoelastic liquid material change with the frequency at which a load is applied. Under a load applied at high frequencies it behaves as a solid, while at low frequencies it may behave as a liquid. A simple example of this viscoelastic behaviour is the Maxwell model [23]. When the penetration test is performed in a bitumen sample, a load (100 g) is applied during a pre-defined period of time (5 s). Consequently, the sample is submitted to a load applied at an equivalent frequency of 0.2 Hz which will capture the material's mechanical intrinsic property at this frequency, provided that linear mechanical excitation, namely small load, is respected. Alternatively, the applied load may result in a non linear mechanical response which will turn any experimental comparison between bitumens a more complex task than simply computing an index from a mechanical response. Regarding the ring and ball test, the deformation of the sample also occurs under stress controlled conditions (the weight of the sphere), and this is obviously performed in the non linear regime since a total strain of 25 mm/4.4 mm (disk thickness) occurs during the test. In addition, both tests involve a combination of shear and elongational deformations, which contrast with the simple shear field of rotational rheometry (SAOS), thus justifying the higher errors of these empirical tests.

On the other hand, the use of the relaxation times to quantify the aging phenomenon is fully justified and coherent, since this parameter is clearly related to the changes in the colloidal structure of bitumen and stability of asphaltenes, which depends directly on bitumen aging [15]. Lu and Isacsson [11] used traditional, rheological and chemical

indexes to quantify bitumen aging and obtained different values, although the bitumen hardening mirrored in the increase in mechanical properties was the result of the chemical changes induced by aging. Hence, the aging susceptibility of bitumen may be ranked differently when different evaluation methods are used. 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 [11]. The aging index, proposed in that study (based in other rheological and empirical parameters [11]), was usually lower than 2. Thus, the present results indicate that the aging index based on the relaxation times observed in the master curves (after and before aging) is the most sensitive parameter to quantify bitumen aging, since the computed values exceed the ratio of 5 (Table 1).

Finally, the parameters that should be used to quantify aging must be based on the mechanical dependence rather than on the thermal dependence of any viscoelastic function, since the objective of the aging study is to determine the behaviour of the bituminous mixtures in the pavement. Actually, bituminous mixtures applied in road pavements are subjected to significantly larger ranges of applied loads and frequencies than to temperature variations, and generally viscoelastic parameters have low sensitivity to thermal variations.

CONCLUSIONS

Any study of bitumen composition and behaviour is a very complex task, since bitumen varies significantly according to its origin and processing of the crude oil. Therefore, the results presented above may not be applicable to all paving grade bitumens. As such, the present study should be applied to a wider set of bitumens (especially materials for which TTS is not valid) as to definitely claim about the usefulness of the proposed aging index. The chemical analysis of bitumens used here before and after aging is also under way, in order to seek for correlations between the proposed aging index and the asphaltene content or, to a larger extent, between the aging index and variations in the content of saturates, aromatics, resins and asphaltenes. Such analysis will help rationalizing the efficiency of the aging index. The main conclusions drawn from this study are the following:

□ For the bitumen studied in the temperature ranges tested, it was found that the Arrhenius equation is the one that best describes the thermal dependence of rheological functions, both at service temperatures, using shift factors, a_T , and at production and application temperatures, using the zero shear viscosity, η_0 . The changes in the temperature dependence of the rheology of bitumen after aging, measured by comparing the activation energy, E_a , values of the studied bitumens (determined by analysis of η_0), before and after aging, were significant. However, these changes were quantitatively very similar for all tested bitumen (both aged and base). As such, using the thermal dependence of any viscoelastic function will not be an efficient method to quantify the aging.

- The most significant changes in the rheological behaviour due to aging were observed when comparing the relaxation times, τ , obtained from master curves of bitumen before and after aging, at service temperatures. The aging index assessed by the relaxation times is also more effective than the indexes obtained through the empirical tests (penetration, ring and ball and

apparent viscosity) typically used by the road paving industry to characterize bitumen aging.

Data taken from the literature and encompassing bitumens from a different origin, also show the same trend, namely that the proposed index for aging is effective in quantifying and discriminating between bitumens (see Table 1). We note here that the aging index was computed at a single temperature (25°C), without relying on TTS.

REFERENCES

- [1] Dongré R, Youtcheff J, Anderson DA: Better roads through rheology, *Appl. Rheol.* 6 (1996) 75-82.
- [2] Glover IC: Wet and Dry Aging of polymer-asphalt blends: chemistry and performance, PhD Thesis, Louisiana State University and Agricultural and Mechanical College - Department of Chemistry (2007).
- [3] Stangl K, Jäger A, Lackner R: The effect of styrene-butadiene-styrene modification on the characteristics and performance of bitumen, *Chem. Monthly* 138 (2007) 301307.
- [4] Oyekunle, LO: Certain relationships between chemical composition and properties of petroleum asphalts from different origin, *Oil & Gas Sci. Technol. - Rev. IFP* 61:3 (2006) 433-441.
- [5] Lesueur D: The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification, *Adv. Colloid Interface Sci.* 145 (2009) 42-82.
- [6] Jones DR IV, Kennedy TW: The asphalt model: Results of the SHRP Asphalt Research Program, SHRP A-001, Center for Transportation Research University of Texas (1992).
- [7] Vijay R, Deshpande AP, Varughese S: Nonlinear rheological modelling of asphalt using White-Metzner model with structural parameter variation based asphaltene structural build-up and breakage, *Appl. Rheol.* 18 (2008) 23214.
- [8] Christensen Jr DW, Anderson DA: Interpretation of dynamic mechanical test data for paving grade asphalt cements, *Proceedings of the Association of Asphalt Paving Technologists* 61 (1992) 67-99.
- [9] Zanzotto L, Stastna J, Vacin OJ: Thermomechanical Properties of Several Modified Asphalts, *Appl. Rheol.* 10 (2000) 185-191.
- [10] Martínez-Boza F, Partal P, Navarro FJ, Gallegos C: Rheology and microstructure of asphalt binders, *Rheol. Acta* 40 (2001) 135-141.
- [11] Lu X, Isacsson U: Effect of ageing on bitumen chemistry and rheology, *Const. Build. Mater.* 16 (2002) 15-22.
- [12] Siddiqui MN: NMR finger printing of chemical changes in asphalt fractions on oxidation, *Petrol. Sci. Technol.* 27 (2009) 2033-2045.
- [13] Mouillet V, Farcas F, Besson S: Ageing by UV radiation of an elastomer modified bitumen, *Fuel* 87 (2008) 2408-2419.
- [14] Romera R, Santamaría A, Peña JJ, Muñoz ME, Barral M, García E, Jañez V: Rheological aspects of the rejuvenation of aged bitumen, *Rheol. Acta* 45 (2006) 474478.
- [15] Mastrofini D, Scarsella M: The application of rheology to the evaluation of bitumen ageing, *Fuel* 79 (2000) 1005-1015.
- [16] Rahman MM: Characterisation of Dry Process Crumb Rubber Modified Asphalt Mixtures, PhD Thesis, University of Nottingham, School of Civil Engineering (2004).
- [17] Branco F, Pereira P, Picado-Santos L: Pavimentos Rodoviários, Edições Almedina, Coimbra (2005).
- [18] Polacco G, Vacin OJ, Biondi D, Stastna J, Zanzotto L: Dynamic master curves of

polymer modified asphalt from three different geometries, *Appl. Rheol.* 13 (2003) 118-124.

[19] Schröter K, Hutcheson SA, Shi S, Mandanici A, McKenna GB: Dynamic shear modulus of glycerol: Corrections due to instrument compliance, *J. Chem. Phys.* 125 (2006) 1-4.

[20] Anderson AD, Christensen DW, Bahia HU, Dongre R, Sharma MG, Antle CE, Button J: Binder Characterization & Evaluation, Vol. 3, Physical Characterization, SHRP-A-369, National Academy of Science, Washington DC (1994).

[21] Larson RG: The structure and rheology of complex fluids, Oxford University Press, New York (1990).

[22] Williams ML, Landel RF, Ferry JD: The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids, *J. Am. Chem. Soc.* 77 (1955) 3701-3707.

[23] Ferry JD: Viscoelastic properties of polymers, Wiley, New York (1980).