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Thermo-oxidative aging of bitumen

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ABSTRACT

Thermo-oxidative bitumen ageing has been commonly recognised as the main cause of asphalt cracking. The effect of thermo-oxidative ageing level on bitumen has been studied in this work by means of a simple and effective mechanical stirring process. Physical characteristics of the material as Softening Point, Penetration and Viscosity were measured to samples with different ageing conditions. Chemical changes in the material were evaluated by means of SARA fractioning to measure the effect of ageing on the fundamental components of bitumen, and Infrared Spectroscopy in order to study the changes found on the oxidation-related compounds of the material. Microstructural changes on the material were evaluated using atomic force microscopy (AFM) finding that the ageing process on bitumen increases the number and size of the phases related to asphaltenes and resins, and decreases the amount of phases related to aromatics. The changes in chemical and physical characteristics of bitumen were found to be strongly dependent on the carbonyl formation. An extension to a previously proposed oxidation kinetics model was used to predict the fast rate (transient) and constant rate (steady-state) oxidation behaviour of bitumen and its relation to physical properties. The thermo-oxidative changes suffered by bitumen are associated with increasing hardening of the material, making it susceptible to cracking when in contact with aggregate as thin films in flexible pavements.

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Bitumen; ageing; thermo-oxidation; microstructure; chemical changes; carbonyl; asphalt

1. Introduction

Asphalt pavements are the most common road construction technique worldwide thanks to beneficial features as durability, being impervious to the bottom layers, rolling smoothness and comfort, among others. Despite these advantages, asphalt pavements suffer a series of failure mechanisms as cracking and permanent deformation (rutting) that have been usually attributed to the fundamental characteristics of the bitumen binder used on the aggregate–bitumen mixture placed on the upper layers.

Asphalt cracking has been associated with certain extent to a phenomenon known as thermo-oxidative bitumen ageing. This phenomenon is caused by the exposure of bitumen to oxygen-rich environments accompanied by high temperatures, which are common conditions during storage, mixing, transport and construction, as well as in service conditions due to environmental factors like exposure to oxygen, radiation, temperature or combination of these (Read and Whiteoak 2003). Between the main processes that contribute to ageing can be found: oxidative hardening, loss of volatile components and exudation, which is the migration of oily components from bitumen to aggregate. These processes appear in bitumen in an irreversible way and are caused by physical–chemical changes in its individual components (Loeber *et al.* 1998). Nonetheless, it is generally recognised that oxidation is probably the most important factor, working by forming polar chemical functions with oxygen content on bitumen molecules, causing a considerable increase in bitumen stiffness (and hardness), which can lead to cracking in service (Petersen 2009).

Several testing procedures have been proposed (and used) in order to study the thermo-oxidative ageing process of bitumen, seeking in all the cases to accelerate the ageing process, to get quantitative measurements on how the properties would change during mixing and while on service in the road (Airey 2003). The rolling thin film oven test (RTFOT) is one among the most common standardised ageing testing procedures that has been used to estimate short-term ageing which occurs during storage, mixing, transport and application on the road. Despite the widespread use of this test, there are several problems found when polymer modified bitumens are tested. The pressurised ageing vessel test (PAV) developed during the Strategic Highway Research Program (SHRP) (Jones and Kennedy 1993), on the other hand, was intended to estimate long-term ageing of bitumen during service. Lately, Farrar *et al.* (2012) at the WRI proposed the so-called simple aging test (SAT), which uses a thin film of bitumen (300 μm) to be thermo-oxidised in an oven along with dynamic shear rheometry (DSR) to study the rheological properties of the material at different temperatures. Recently, Steiner *et al.* (2016) proposed the so-called Viennese ageing procedure (VAPro), where HMA specimens inside of a triaxial cell with forced flow of a gaseous oxidant agent (ozone and nitric oxides)

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passes through the specimen at temperatures similar to those found during summer time (45–70 °C) to increase the rate of oxidation of the material, finding that their method accelerates the ageing of the material in shorter times than what can be achieved with RTFOT + PAV. Performing any of these ageing tests require specialised and expensive equipment, limiting their implementation and everyday use during pavement design and construction.

The effect of ageing on bitumen has been usually studied considering its changes in physical, chemical and rheological properties. Changes in physical properties have been generally studied by means of penetration and softening point tests, along with the use of indexes derived from these that allow for classifying the materials on different grades. Although, compositional analysis have shown that bitumens of the same 'grade' not necessarily have the same chemical composition or rheological behaviour (Loeber *et al.* 1998). Furthermore, pavement performance evaluations have shown that bitumen's source and nature of the materials with which it interact (e.g. polymers, acids, aggregates, etc.) form an important part of the oxidative ageing process (Petersen 2009).

SARA fractioning has been commonly used to study the chemical changes in bitumen due to oxidative ageing (Corbett 1969). Changes in SARA fractions due to oxidation have been interpreted as a movement of components from non-polar fractions up to the more polar fractions (i.e. from Aromatics to Asphaltenes), creating in this way oxygen-containing functional groups in bitumen's molecules. As these fractions have different reactivities with respect to oxidation, the result is usually a loss of aromatics and resins, with a consequent increase in the number of Asphaltenes. Due to its low reactivity, Saturates fraction is highly resistant to oxidation. The relative changes in SARA fractions due to oxidation provide a limited understanding of the ageing phenomenon, and the chemical changes are difficult to interpret due to the insufficient information obtained from mass variations in relation to chemical changes (Petersen 2009). Another analytical technique used to study chemical changes in bitumen due to oxidative ageing is infrared Spectroscopy, bringing information related to the distribution of aliphatic chains, aromatisation, substitution modes of aromatics and particularly giving important information related to functional groups and absorption of oxygen in bitumen. It has also been found that carbonyl (ketones) and sulfoxide functions are formed during the oxidative process, and particularly, the production of ketones during oxidation has been related to the increase in viscosity (Lu and Isacsson 2002, Petersen 2009, Jin *et al.* 2011). Based on rheological studies, it has been also found that bitumen ageing is responsible for reactions leading to increasing interaction forces between molecules, leading to increasing viscosity and moduli of the material (Read and Whiteoak 2003).

Despite the opaque nature of bitumen, microscopic techniques such as fluorescence microscopy (Handle *et al.* 2016) and atomic force microscopy (AFM) have been used to characterise its microstructural characteristics (Bardon *et al.* 1996). AFM is a microscopic technique where a small tip is used to scan and interact with the surface of the sample, being able to show topographic and phase characteristics in bitumen (Loeber *et al.* 1996). Probably the first reported works on AFM to study bitumen described the presence of a phase characteristic of asphalt matrix defined by a series of dark and clear lines, called 'Bee structure' (Loeber *et al.* 1996). This phase is created by undulations, giving a specific texture to bitumen's surface. Later, Pauli *et al.* (2001) attributed this structure to asphaltenes. Pauli and Grimes (2003) on the other hand, doped bitumen with asphaltenes finding an increase in bee structures density, confirming Pauli *et al.*'s (2001) theory.

By means of phase detection mode on AFM, Masson *et al.* (2006) were able to describe four fundamental phases on bitumen, which they called Cathane phase (bee structure), Periphase (surrounding the Cathane phase), Paraphase (dissolved phases) and Salphase (higher contrast regions). Further, they found a poor relation between asphaltene content and SARA fractions. In opposition to Pauli *et al.* (2001, 2003), they related the bee structures to Nickel and Vanadium content in bitumen. De Moraes *et al.* (2010) using AFM at different temperatures found that the bee structures completely disappear at temperatures above 70 °C, and even found that the topography of the samples was highly dependent on time and temperature of storage.

Pauli *et al.* (2011) on the other hand, argued that previous interpretations, even their own, were wrong at least in part, giving a new hypothesis where they established that the bee structure was mainly wax. They found the lack of this kind of structure on samples of bitumen with low wax content, leading to conclude that the interaction between paraffin wax and the remaining bitumen components were responsible for its microstructure, including the bee structures. Wu *et al.* (2009) and Zhang *et al.* (2012) reported a substantial increase in the amount of bee structures on bitumen samples exposed to thermo-oxidative processes, which leads to the conclusion that the formation of these structures was not directly related to the presence of wax or metallic atoms in the material, as reported by previous researchers. Recently, Eberhardsteiner *et al.* (2015) and Hofko *et al.* (2015) by means of artificially composed bitumen with varying asphaltene contents also concluded that the bee structures correspond to asphaltenes in bitumen microstructure.

Despite the different theories and hypothesis about the nature and formation of bitumen structures, AFM studies have shown that there is nocomplete understanding of the formation mechanisms of these structures on bitumen. Even so, bitumen can be considered as a material with certain tendency to separation of its phases under certain conditions and is recognised the need of relations between microstructure and its volumetric or macroscopic behaviour.

This work aims at studying the effect of thermo-oxidative ageing on the microstructural, chemical and physical characteristics of a bitumen commonly used for road construction in Colombia. A new and simple to implement thermo-oxidative ageing procedure based on mechanical stirring was proposed and used to extend a previously proposed oxidation kinetics model to predict the effect of ageing on different properties of the material, leading to an understanding of the main factors affecting ageing of the material.

2. Experimental procedure

2.1. Materials

A base bitumen with 80/100 penetration grade obtained from Ecopetrol Barrancabermeja's refinery was used in this study. This bitumen had the constituents listed in Table 1.

Table 1. SARA fractioning results for base and selected aged bitumen samples.

Sample	Saturates	Aromatics	Resins	Asphaltenes	CI
Base bitumen	14.96	38.96	35.01	11.10	0.35
5S	15.40	27.26	42.15	15.20	0.44
10S	15.40	21.10	49.06	14.74	0.43

2.2. Ageing procedure

A suggested procedure based on mechanical stirring of bitumen was used to study the effect of thermo-oxidative ageing on the microstructural, physical and chemical properties of bitumen. By applying mechanical stirring to bitumen it is possible to continuously remove the surface bitumen layer in contact with environmental oxygen, accelerating in this way the ageing process on all the material and not only in the surface layer.

Approximately 150 g of bitumen were placed inside of a metallic vessel of 88 mm in diameter, which was further heated to a temperature of 163 °C, which is a temperature higher than the softening point of the material (and the same used in ageing tests like TFOT and RTFOT), reducing its viscosity to approximately 100 Pa.s and allowing easy stirring. Once the material reached this temperature, the stirring process started using a conventional mechanical stirrer with a helical propeller shape impeller of diameter 55 mm at an approximate speed of 1800 rpm. The stirring process was continued for time periods of 2.5, 5.0, 7.5 and 10 h, respectively, for the different samples studied. The thermo-oxidised samples by this method will be subsequently referred to as 2.5S, 5S, 7.5S and 10S, to represent aged samples by mechanical stirring for 2.5, 5.0, 7.5 and 10 h, respectively. It is worth mentioning that each of the tests was prepared by triplicate in order to establish repeatability of the results.

2.3. Microstructural analysis

Microstructural changes in thermo-oxidised samples relative to unaged bitumen were studied by means of Atomic Force Microscopy (AFM), using an equipment Nanosurf (Switzerland), model Easyscan 2. Approximately 1 g of bitumen for each of the samples (base and aged) were placed on glass cover slips which were later left on a convective oven at a temperature of 140 °C for approximately 5 min in order to soften the bitumen samples and get surfaces smooth enough to allow measurements. The samples were then allowed to cool down at room temperature inside an hermetic container to avoid surface contamination by dust or external agents. The samples were then kept at room temperature for at least 24 h prior to testing, in order to allow reaching thermodynamic balance in bitumen structures.

The measurements were performed using the non-contact dynamic mode, with a silicon cantilever aluminium coated on the reflective surface with a nominal stiffness constant of 48 N/m. The measurements were obtained on topographic and phase modes and were further processed using the free software WSxM, version 6.2.

2.4. Chemical tests

Chemical fractions changes in the material after thermo-oxidative ageing were measured by means of the Corbett (1969) method. The Iatroscan (Flame Ionisation Detector) was the method employed for separation of fractions (Saturates, Aromatics, Resins and Asphaltenes). This method can use the same solvents proposed in the ASTM standard D4124 (2009) or different solvents with successive dissolutions. The solvents used here were (i) n-heptane to separate asphaltenes from maltenes; (ii) a toluene–methanol solvent was used to separate aromatics; and finally (iii) trichloroethylene was used to separate resins. It is also important to mention that the Iatroscan method was preferred here as it is the standardised method used in Colombia to separate bitumen fractions.

Fourier Transform Infrared Spectroscopy FTIR (Perkin Elmer, model Spectrum One) was used to measure the chemical changes in the samples due to thermo-oxidative ageing. This technique allows detecting the presence of carbonyl and sulfoxide functional groups in order to establish oxidation levels of the samples. To quantify these functional groups, a selective solvent (Trichloroethylene) was used in order to allow breaking of hydrogen bonds, getting rid of superposition effects on absorption bands, which make difficult to obtain a quantitative measure of the functional groups related with the oxidation process. All spectra were obtained by means of 16 scans, with a wavelength resolution of 4 cm^{-1}, in a total range of wavelengths between 4000 and 400 cm^{-1}. The degree of oxidative ageing was studied following the changes in two characteristic bands of the infrared spectra: (i) Carbonyl group band, which is found between 1752 and 1653 cm^{-1} and centred at 1700 cm^{-1}, covering in this way the region containing carboxylic acids, ketones and anhydrides absorption bands; and (ii) Sulfoxide group band, which is found between 1065 and 1007 cm^{-1} and centred at 1030 cm^{-1}. These two functional groups are recognised as the most important in relation to oxidative ageing of bitumen. The areas of the absorption bands were measured and calculated for the analysis and quantification of these functional groups. Absorption bands were used instead of peaks in order to avoid possible effects of sample thicknesses in the analysis (Wu *et al.* 2010).

Carbonyl ($I_{C=O}$) and Sulfoxide ($I_{S=O}$) group indexes were calculated from the ratios between functional group area and the sum of the areas in the range of wave lengths between 2000 and 600 cm^{-1}, measured valley to valley, according to Wu *et al.* (2009), as:

$$I_{C=O} = \frac{\text{Carbonyl band area centred at 1700, cm}^{-1}}{\sum \text{Bands between 2000 and 600, cm}^{-1}} \quad (1)$$

$$I_{S=O} = \frac{\text{Sulfoxide band area centred at 1030, cm}^{-1}}{\sum \text{Bands between 2000 and 600, cm}^{-1}} \quad (2)$$

2.5. Physical properties tests

The samples were tested after the ageing processes to measure physical properties as penetration, softening point and Brookfield viscosity in order to quantify the level of change on these characteristics caused by the thermo-oxidative process.

The softening point test was performed following the ASTM standard D36 (1995), where the ring and ball apparatus was used in order to find the softening point temperature of bitumen. The penetration test (ASTM standard D5 (1997)) uses a standardised needle with a load of 100 g to measure its penetration in the material in a time period of 5 s. The depth of penetration of the needle expressed in units of 1/10 mm indicates the penetration (pen) for the analysed material.

Viscosity was measured by means of a Brookfield viscosimeter (Model DV-II+, Brookfield Engineering Laboratories Inc.) following the procedure described by the ASTM standard D4402 (2006), where after heating 8 gr of bitumen on a testing vessel the change in rotational viscosity due to thermal changes at temperatures of 100, 120, 140 and 160 °C was evaluated.

3. Results

3.1. Microstructure

Figure 1 shows the microstructure of base bitumen obtained by means of AFM on the phase mode. In this figure three fundamental phases of bitumen can be differentiated such as: (i) the phase commonly associated with asphaltenes or 'Bee structures'; (ii) the phase corresponding to resins, appearing as the most clear phase surrounding asphaltenes; and (iii) the darkest phase which corresponds to the matrix supporting the other two phases, which has been associated with aromatics and saturates altogether. The average size of these three phases for the different images analysed is of approximately 5 µm, with the bee structures having an average length of 1 µm.

Figure 2 shows bitumen's microstructure after thermo-oxidation by mechanical stirring. This figure shows phase images at the four times of ageing studied. It can be seen that the phase corresponding to asphaltenes (bee structures) increases in number as the ageing time increases (see also Figure 3). An increase in the amount of phase corresponding to resins and a reduction in the phase corresponding to aromatics was found as the ageing process was increased.

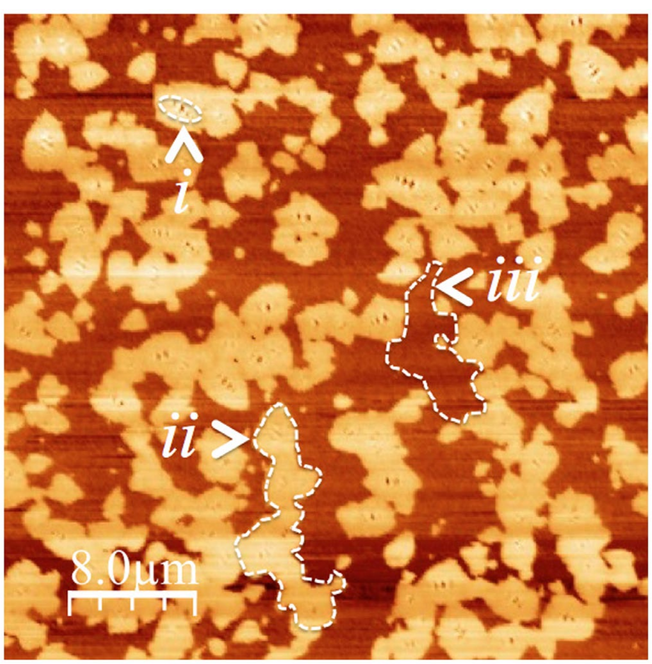

Figure 1. Phase contrast AFM image showing the microstructure of base bitumen. The phases associated to asphaltenes (i), resins (ii) and aromatics (iii) are indicated.

3.2. Chemical characteristics

Table 1 shows the results found by SARA fractioning for both, base bitumen and selected samples obtained from the thermo-oxidative process at 5 and 10 h. It was found that aged samples showed an increase in asphaltene and resin contents along with a reduction in the amount of aromatics, in line with the microstructural changes seen in Figures 2 and 3. A small increase in saturates content was also found, but it is not enough to be considered representative of the ageing process of the material.

Figure 4 shows the carbonyl Index measured for base and aged bitumens at the different ageing times. A fast-rate (transient) and constant-rate (steady-state) oxidation behaviours, commonly found for bitumen (Jin *et al.* 2011) are seen, clearly indicating the oxidation process of the material.

Figure 5 shows the Sulfoxide Index behaviour for base and aged bitumen with an approximately steady-state increase in $I_{S=O}$ as ageing progresses.

3.3. Physical characteristics

Figure 6 shows the change in the measured values of penetration for base and thermo-oxidised bitumens at different time exposures. The behaviour of bitumen under ageing shows an initial fast rate reduction on penetration followed by a steady-state behaviour, which makes evident the effect of ageing on the material, making it stiffer (harder) at longer thermo-oxidative periods of exposure.

Figure 7 shows the variation in softening point for the bitumen samples depending on the time of exposure to thermo-oxidative ageing. Bitumen displays the ageing effect by means of an initial fast rate increase on the softening point followed by a steady-state behaviour, which is consistent with the results obtained for penetration tests, making the material stiffer and difficult to deform as ageing progresses.

Figure 8 shows the Ageing Index, which was calculated as the ratio between viscosity of oxidised (aged) bitumen (η_a) with respect to base bitumen's viscosity (η_o), which gives an indication of the level of viscosity increase in the material due to the ageing process (Jones and Kennedy 1993). Changes in viscosity at 140 °C were considered in the calculation of this index (similar results were found for the other temperatures studied). It was found, as for the previous results, an initial fast rate increase in ageing index followed by a steady-state increase as ageing advances.

4. Discussion

The main advantage of the proposed stirring process for thermo-oxidative ageing of bitumen in comparison with other ageing tests resides in its ability to constantly remove the upper layer of the material in direct contact with atmospheric oxygen, allowing all of the material to be thermo-oxidised and not only a superficial thin layer as in most of the common tests. Furthermore, the

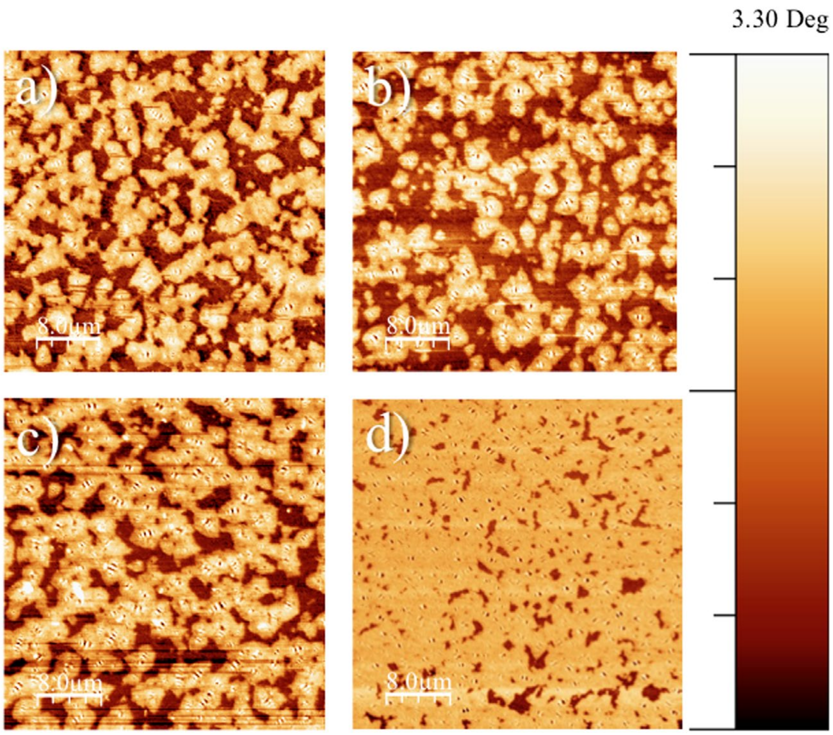

Figure 2. Phase contrast AFM microstructure of thermo-oxidised bitumen by mechanical stirring at (a) 2.5S; (b) 5S; (c) 7.5S; and (d) 10S.

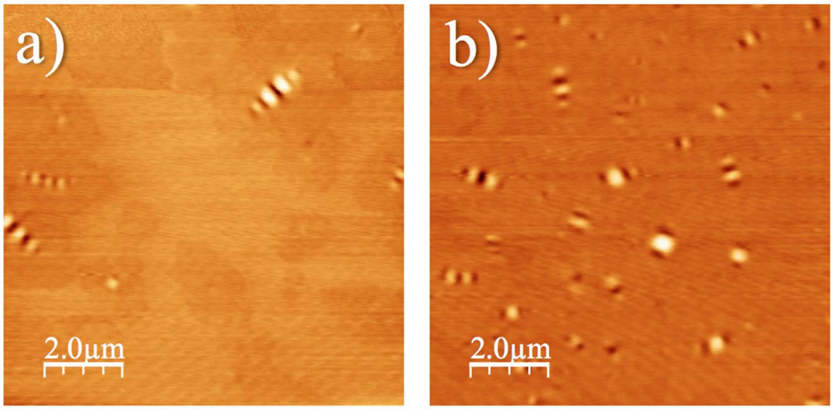

Figure 3. Topographic AFM microstructure of: (a) base bitumen; and (b) thermo-oxidised bitumen by mechanical stirring 10S.

constant movement of the material in the vessel allows testing of polymer-modified bitumen without the common separation problems occurring during static ageing procedures.

The quality of blending processes based on the characteristics of the blended fluid and impellers has been extensively studied in order to understand and improve the stirring mixing for the chemical industry (e.g. Kramers *et al.* 1953, Calabrese and Stoots 1989, Nienow 1997, Szoplik and Karcz 2005, Takahashi *et al.* 2012, Ascanio 2015). Mixing time (θ_m) is deemed to be the main parameter in the analysis of the hydrodynamic performance of a stirred vessel. This parameter is defined as the time required to get all points in the vessel uniformly distributed, and can be calculated as (Ascanio, 2015):

$$\theta_m = \frac{1}{N}\left(\frac{\rho N D^2}{\mu}\right)^n, \tag{3}$$

where N is the impeller speed in revolutions per second, ρ is the fluid density (kg/m^3), D is the impeller diameter (m), μ is the fluid viscosity (Pa.s) and n is dependent on the type of impeller (n = 2.2 for the propeller type (Tatterson 1991)).

Using Equation (3) it was possible to estimate the mixing time for the ageing tests performed as θ_m = 0.027 s. This can be regarded as a change in the external layer of material in direct contact with atmospheric oxygen every 0.027s. The thickness of this layer can be assumed as the average size of the main structures found in bitumen (i.e. bee structures, resins and aromatics), which were found to have an approximately size of B_l = 5 µm for base bitumen (Figure 1). Consequently, the time required for all the material placed in the vessel to be thermo-oxidised (aged) can be expressed as:

$$\alpha = \frac{V\theta_m}{\pi r^2 B_l}, \tag{4}$$

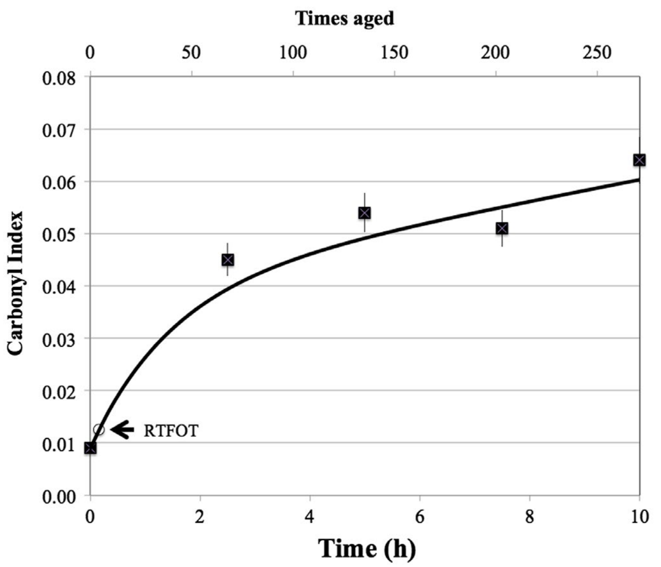

Figure 4. Effect of thermo-oxidative aging time on Carbonyl functional group formation. The solid line represents the prediction of the model for oxidation kinetics of bitumen (Equation 5). The circle indicates the predicted value for a RTFO test.

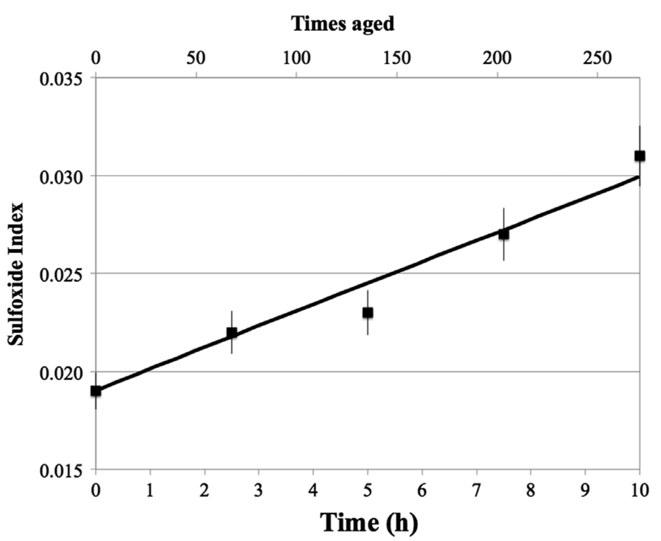

Figure 5. Effect of thermo-oxidative aging time on Sulfoxide functional group formation. The solid line represents the prediction of the model for oxidation kinetics of bitumen (Equation 7).

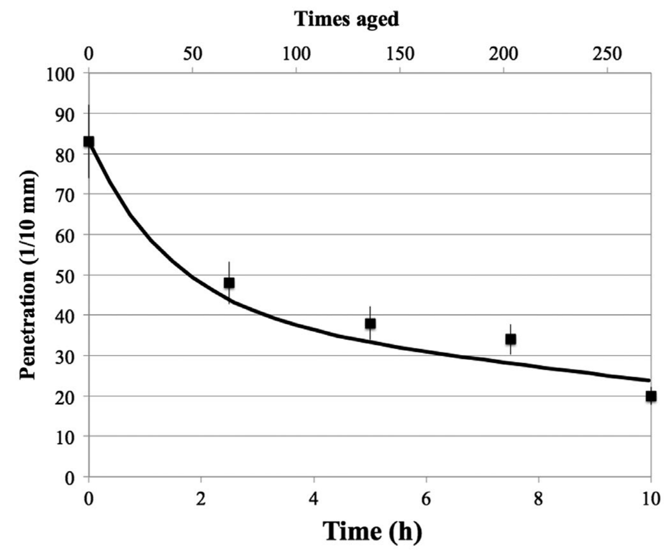

Figure 6. Effect of thermo-oxidative aging time on penetration of bitumen. The solid line represents the prediction of the model for oxidation kinetics of bitumen (Equation 7).

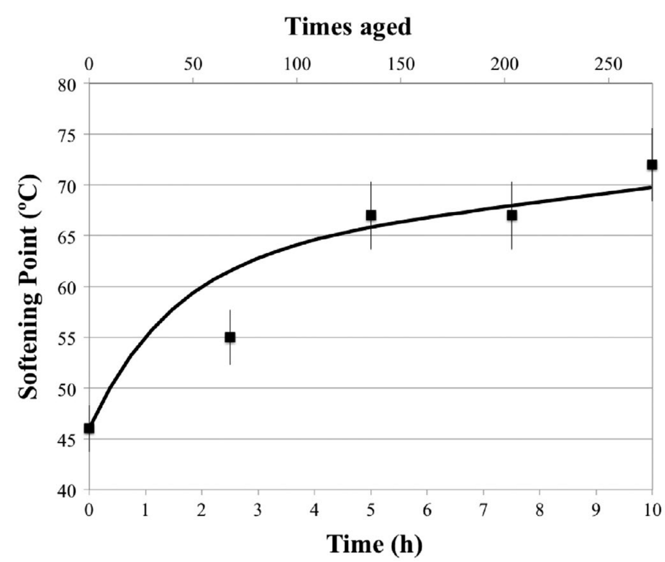

Figure 7. Effect of thermo-oxidative aging time on Softening Point of bitumen. The solid line represents the prediction of the model for oxidation kinetics of bitumen (Equation 7).

where V is the volume of the material and r is the internal radius of the vessel.

This analysis of the stirring process allows the test to be easily repeatable and adjusted to specific testing conditions available in a given laboratory, like different vessel sizes, impeller types, amount of bitumen tested, stirring speeds, etc. Furthermore, as the stirring time is dependent on these specific testing conditions, it is preferred to consider how many times the material in the vessel has been aged instead of the stirring time, which will be dependent on testing conditions. Figures 4–8 show secondary axis with information on how many times the material was aged (times aged) in the test, allowing in this way comparison to other tests and making it independent of testing conditions.

One of the fundamental drawbacks found on the methods to evaluate ageing of bitumen resides on the need of specialised equipment, with the usual high costs involved, making in some cases prohibitive its everyday plant use. Using mechanical stirring it is possible to accelerate the ageing process of bitumen in a simple and economic way, which can make this technique of everyday use in engineering practice.

4.1. Effect of ageing on microstructure

AFM results showed that there is a progressive increase in the amount of phases corresponding to asphaltenes (bee structures) as the level of ageing was increased in bitumen (see Figures. 1–3). Ageing has been commonly associated with an increase in

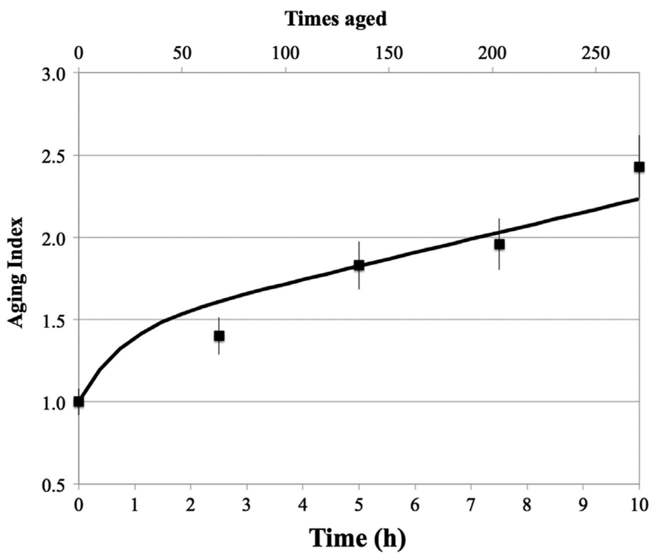

Figure 8. Effect of thermo-oxidative aging time on the Aging Index of bitumen. The solid line represents the prediction of the model for oxidation kinetics of bitumen (Equation 7).

the asphaltene content (Wu *et al.* 2009, Eberhardsteiner *et al.* 2015). According to SARA fractioning (Table 1), the amount of asphaltenes increases up to approximately 36% with the ageing processes followed, consistent with the microstructure observed using AFM, which is also coherent with other parameters measured after ageing. The increase in number of structures corresponding to asphaltenes in the bitumen studied is opposite to the results reported by Zhang *et al.* (2012), who suggested the absence of the bee structures on aged bitumens, as these structures were believed to be dissolved by the other domains present, which would make its visualisation impossible. This hypothesis turns out to be incorrect, because based on the measured results of carbonyl and sulfoxide functional groups, there is evidence that these groups form part of the heavier molecules, which in this case are the asphaltenes, increasing in number and size the structures corresponding to these. Indeed, asphaltenes are responsible for material hardening and its increase in viscosity even at high temperatures, as also suggested by Eberhardsteiner *et al.* (2015) who after creep recovery tests on artificially composed bitumens with varying fractions of asphaltenes found that these phases trigger an increase in stiffness and decrease of creep rate and ductility on the material.

Figure 2 shows how the phase corresponding to resins occupies a bigger region of material as the thermo-oxidative condition increases, leading to a noticeable reduction in the phase corresponding to aromatics (darkest phase). It is well known that harder phases correspond to asphaltenes, followed by resins, which surround the later. Having an increase in area of the harder phases makes the viscous movement of the material difficult, reaching this with increased levels of ageing the material becomes stiffer and brittle, leading to possible fractures in service of the material.

4.2. Effect of ageing on chemical characteristics

The results from SARA fractioning (Table 1) are consistent with results reported by other researchers (i.e. Read and Whiteoak 2003, Lesueur 2009, Petersen 2009), who argued that these changes represent the movement of components from non-polar up to more polar states. Indeed, a fraction of aromatics went to be part of the resins, which along passed to form asphaltenes due to the thermo-oxidative process. A small increase in saturates content was found but cannot be considered representative of the ageing process of the material. The Colloidal Instability Index (*CI*) proposed by Gaestel *et al.* (1971), calculated for the samples studied, increased from 0.35 to 0.44, which is not considered as a significant change. This behaviour can be explained by the fact that this index relates dispersed constituents (aromatics and resins) with flocculated components (saturates and asphaltenes). According to Table 1, due to the ageing process, bitumen shows an increase in aromatics molecular weight, which is confirmed by a 46% reduction of this fraction, an increase of 40% in resins and 36% in asphaltenes, indicating colloidal changes due to a sequential transformation from aromatics to resins and in lower amount to asphaltenes (Siddiqui and Ali 1999).

Bitumen has been commonly found to oxidise in two stages, a nonlinear fast-rate (transient) period and a linear steady-state period (Van Oort 1956, Liu *et al.* 1996, Petersen and Harnsberger 1998, Petersen 2009). Recently, Jin *et al.* (2011) proposed an oxidation kinetics model that includes both fast-rate and constant-rate parameters as a function of the Carbonyl content of the material. The model can be described as (Jin *et al.* 2011):

$$I_{C=O} = \left(I_{C=O}\right)_b + M\left(1 - exp\left(-k_f t\right)\right) + k_c t, \tag{5}$$

$$M = \left(\left(I_{C=O}\right)_o - \left(I_{C=O}\right)_b\right), \tag{6}$$

where t is the number of times the material has been thermo-oxidised (in contact with atmospheric oxygen), $(I_{C=O})_b$ is the carbonyl index of the base bitumen, $(I_{C=O})_o$ is the intercept of the steady-state line; while k_f and k_c are two reaction constants that are temperature dependent following an Arrhenius behaviour.

Jin *et al.* argued that the terms in Equation (5) incorporate the three elements important to the ageing process. The first term being the initial carbonyl index for the base bitumen, giving an ageing starting point. The second term characterises the transient ageing process that follows a first-order reaction that terminates on the depletion of reactants. These parameters also determine the transition from transient to steady-state behaviour. The third term characterises the steady-state reaction. Although the first-order and steady-state reactions are not fixed to specific or identified reaction mechanisms, rather they are phenomenological descriptors of the overall reaction kinetics, the model shows a reasonable agreement with experimental results even for a complex material like bitumen as shown in Figure 4, where the model shows to have a good agreement with experimental results. The oxidation kinetics model parameters obtained are shown in Table 2.

Table 2. Oxidation kinetics model parameters (Equation 5) for the bitumen studied.

Parameter	Value
$(I_{C=O})_b$	0.009
$(I_{C=O})_o$	0.04
k_c	7.5×10^{-5}
k_f	0.025

The approach followed to study the stirring oxidation kinetics based on whole material oxidation can be extended to analyse other tests like RTFOT, where rotating glass bottles containing 35 g of bitumen are placed in a vertically rotating shelf. During the test, the bitumen flows continuously around the inner surface of each container in films of approximately 1.25 mm at a temperature of 163 °C for 75 min. The vertical circular carriage rotating at a rate of 15 revolutions/min leads to approximately 4.5 complete exposures of the material to oxygen during the entire test. Figure 4 shows the value predicted by the oxidation kinetics model for the RTFO test, which is placed in the transient regime of the oxidation behaviour. The conditions in the RTFO test are not considered identical to those found in practice, but experience has shown that the amount of hardening in the RTFOT correlates reasonably well with that observed in a conventional batch mixer (Read and Whiteoak 2003). This experimental evidence is consistent with the predicted values of the oxidation model in the sense that at such level of exposure the oxidation reaction of the material is at the initial transient stage, while at field ageing levels at the end of a mixture service life have been found at steady-state oxidation regime (Liu *et al.* 1996) which are well reached by the stirring method proposed. Recently, Soenen *et al.* (2016) studied the oxidation of bitumen by means of RTFOT followed by different time exposures under pressure ageing vessel (PAV) finding also increases on the Carbonyl and Sulfoxide indexes.

The effect of reactive oxygen species (ROS) on the long-term ageing behaviour of bitumen is well known and reported (see for instance Hofko *et al.* 2015). These species, like nitric oxides and ozone, are usually related to exhaust gases that promote their formation. The ageing procedure proposed here can lead to future work into the effect of ROS's into the oxidation behaviour of bitumen and possibly lead to the establishment of correlations between this method and long term ageing of asphalt.

4.3. Effect of ageing on physical characteristics

Martin *et al.* (1990) and Jin *et al.* (2011) found that changes in viscosity of bitumens during thermo-oxidative processes show a fast-rate transient behaviour followed by a steady-state behaviour with level of ageing. This behaviour was further related to the carbonyl index, leading to directly link the carbonyl content with physical properties of the material. The three parameters model proposed by Jin *et al.* (2011) to predict the oxidation kinetics of bitumen (Equation 5) can be extended to predict the different physical parameters studied as:

$$\zeta = \zeta_b + M\left(1 - \exp\left(-\kappa_f t\right)\right) + \kappa_c t, \tag{7}$$

$$M = \left(\zeta_o - \zeta_b\right), \tag{8}$$

where t is the number of times the material has been thermo-oxidised (in contact with atmospheric oxygen), ζ_b is the physical parameter measured for base bitumen, ζ_o is the intercept of the steady-state line for the given parameter; while κ_f and κ_c correspond to two material constants.

Equation 7 was used in Figures 5–8 to model the ageing behaviour of bitumen showing a reasonable agreement with experimental results (Table 3 shows the values of the different model parameters depending on the property measured). It was found that the value of the first reaction constant (κ_f) on the oxidation kinetics model (Equation 5), which controls the exponential rate behaviour of the different measured parameters, remains constant independent of the measured property. This is an indication that the carbonyl content controls the ageing behaviour of the material and if this parameter is measured, the behaviour of bitumen during mixing and service life can be predicted and included in asphalt mixture models previously proposed (see for instance: Glover *et al.* 2005, Ossa *et al.* 2010, McCarthy and Liang 2011, Jin *et al.* 2013, Hofko *et al.* 2016). This parameter controls the fast-rate transient behaviour of the material and is related with the initial fast formation of carbonyl functions, increasing the hardness and stiffness of the material as evidenced by the penetration, softening point and viscosity measurements performed in this study.

Table 3. Oxidation kinetics model parameters (Equation 7) used to predict penetration, softening point, ageing index and sulfoxide index.

Parameter	Penetration	Softening point	Aging index	Sulfoxide index
ζ_b	83	46	1.0	0.019
ζ_o	40	63	1.42	0.0191
κ_c	6.0×10^{-2}	2.5×10^{-2}	3.0×10^{-3}	4.0×10^{-5}
κ_f	-2.5×10^{-2}	2.5×10^{-2}	2.5×10^{-2}	2.5×10^{-2}

It is worth mentioning that the stirring model (Equations 3 and 4) assumed constant values of the surface thin layer of material (corresponding to the size of the three main bitumen structures) and the viscosity. Experimental results have shown that both parameters increase upon exposure to thermo-oxidative ageing, leading to possible changes in the stirring model parameters. Inclusion of these changes into the model was not attempted in this study in order to keep the model as simple as possible, but the need for further study and improvement of the model in order to account for these material changes is recognised.

5. Concluding remarks

The effect of thermo-oxidative ageing on the microstructural, chemical and physical characteristics of a 80–100 pen bitumen commonly used in Colombia was studied experimentally by means of a proposed method where bitumen was exposed to mechanical stirring at high revolutions and temperature. Using mechanical stirring it was possible to accelerate the ageing process of bitumen in a simple and economic way, showing a potential of this technique to be adopted for every day use on the engineering practice.

The stirring thermo-oxidative test is easily repeatable and independent of individual testing parameters (e.g. propeller type, rotational speed, amount of material, etc.). Further, the test can be related to the number of total exposures of the material to ageing instead of time of exposure as in most of the common ageing tests.

The stirring ageing procedure continuously removes the upper layer of the material in contact with oxygen, allowing increased interaction between bitumen and oxygen, enabling the creation of new carbonyl and sulfoxide groups on all the material and not only on the surface of the material. The formation of these functional groups leads to a molecular weight increase in the phases or fundamental components of bitumen, making that part of the aromatics get transformed into resins and, in the same way, part of the resins change to form asphaltenes. In this manner, the thermo-oxidative process increases the number of asphaltenes and resins, increasing hardness and brittleness of the material, which is the detrimental effect of bitumen ageing on flexible pavements, leading in some cases to failure of the material in service.

AFM microstructural analysis showed that the amount and size of bee structures (associated to asphaltenes) increased as the ageing process was further applied. This technique allowed establishing the change in shape and distribution of bitumen's phases as the thermo-oxidative process was increased. Despite the results obtained in this study, which revealed the microstructural changes suffered by bitumen due to the ageing process, it is clear that a more detailed study on the effect of ageing on specific properties of each of the phases and their distribution on the material is needed. This will lead to fully understand the effect of these phases on the macroscopic properties of the material.

An oxidation kinetics model previously proposed by Jin *et al.* (2011) was used to predict the carbonyl formation of the material during ageing, showing a fast-rate transient and constant steady-state increase in carbonyl functionalities. Furthermore, an extension of the model was used to predict the physical properties variations with level of ageing, finding that the same parameter governing the carbonyl formation controls the changes on properties, which confirms that the main mechanism controlling ageing of bitumen is the carbonyl formation.

It is worth mentioning that the study carried out had no intention to correlate the levels of ageing achieved with stirring thermo-oxidative tests to time periods of exposure of the material on the road. A long-term study will be necessary to propose such a correlation.

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