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This study focuses on morphological changes and micromechanical properties of bitumen and its components (maltenes and asphaltenes) under neat, laboratory short- and long-term, and long-term field ageing. The material was analysed by means of atomic force microscopy in pulsed force mode, allowing for material nano-mechanical measurements. It was concluded that the colloidal equilibrium of asphalt fractions is affected by a significant loss of low molecular weight components, and air oxidising the bitumen. In addition, stiffness and adhesion were measured for each condition. It was observed that the greatest contribution in stiffness is associated with polar components, while the adhesiveness is associated mainly with non-polar components. Finally, to relate the ageing process to chemical changes, Fourier transform infrared spectroscopy measurements were performed to quantify the functional groups associated with oxidation. Furthermore, thermodynamic analysis by means of differential scanning calorimetry was performed to explain some of the observed changes in micromechanical behaviour.

Keywords: atomic force microscopy; pulse force mode asphalt ageing; FTIR; thermodynamic properties

Introduction

Ageing of asphalt mixtures is one of the main factors associated with the decrease in pavement performance (Zhang, Yu, Feng, Xue, & Wu, 2012). Its consequences include a reduction in comfort and safety, as well as the financial impact associated with frequent maintenance and rehabilitation strategies. Ageing can occur from asphalt mix production to field service life, and can magnify in the latter due to oxidation, loss of lighter components in asphalt and a combination of several other processes (Masson, Leblond, & Margeson, 2006). The ageing process tends to be dominant due to the formation of functional groups: chemical compounds with some polarity and a high content of oxygen within the asphalt molecules, leading to an increase in molecular interaction resulting in a stiffer material that is more prone to fatigue (Pauli, Branthaver, Robertson, & Grimes, 2001; Pauli, Grimes, Beemer, Turner, & Branthaver, 2011).

In recent years, ageing has been widely characterised at laboratory scale by means of tests that attempt to accelerate the mechanisms that ultimately affect performance (Gamarra, 2014). The mechanisms have been associated with changes in molecular sizes, polarity and aromaticity that ultimately affect the colloidal balance of the bitumen (Siddiqui & Ali, 1999). Amongst the most typical ageing procedures are the rolling thin film oven (RTFO) (ASTM D2872, 2012) and

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pressurised ageing vessel (PAV) (ASTM D6521, 2013) methods, which have been widely used for simulating short- and long-term ageing, respectively, since the introduction of Superpave.

The present study uses atomic force microscopy (AFM) in pulsed force mode (PFM) to analyse the morphological and micromechanical changes of a PG64-22 bitumen, and its components (asphaltenes and maltenes), when subjected to accelerated ageing in the laboratory. Furthermore, the asphalt was also aged under field conditions (exposure to climate) for a period of 6 months to compare to laboratory ageing procedures. Additionally, the oxidation of samples was traced by means of Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC).

AFM measurements with PFM

The AFM technique was developed by Binnig, Quate, and Gerber (1986) and has been fundamental in analysing the microstructure and micromechanical behaviour of bitumen. AFM measured the interactions between a cantilever tip (generally composed of silicon) and the surface of a material. The method allows characterisation of the material surface in 3D. The AFM can be operated in several modes: contact mode (CM), non-contact or tapping mode (AC) and PFM. The PFM or intermittent contact mode aids in reducing the deterioration of viscous samples such as bitumen because of its fast exploration rate (Haugstad, 2012) and allows continuous measurement of micromechanical responses of the system.

In recent years, AFM has been widely used to understand the microstructure of bitumen. Loeber, Sutton, Morel, Valleton, and Muller (1996) observed a characteristic structure in bitumen that was named "bee structure". Pauli et al. (2011) suggested that the arrangement of asphaltenes or colloidal particles with polar functional groups can result in development of microstructures at the bitumen–air interface. Masson, Leblond, Margeson, and Bundalo-Perc (2007) suggested that the morphology of bitumen can be categorised into three distinct groups: fine dispersion (0.1–0.7 μm) in a homogeneous matrix, 0.1 µm domains or 4 distinct domains based on size and shape (one being the "bee structure"). Dourado, Simao, and Leite (2012) showed differences in the elasticity of bitumen in both the "bee structure" and the continuous domain.

Nazzal, Abu-Qtaish, Kaya, and Powers (2015) indicated that "bee-structures" are present in neat and modified bitumens. Aguiar-Moya, Salazar-Delgado, Bonilla-Mora, et al. (2015) observed the domains that are present in the different asphalt saturates, aromatics, resins, and asphaltene (SARA) fractions, and that the "bee-structures" were not related to the asphaltenes, recrystallised paraffinic waxes, thermal oxidation or polymer modification of bitumen. Furthermore, the authors found that "bee-structures" are related to the aromatic fraction of bitumen, and that their size, shape and topography are influenced by the thermal oxidation and by the combination of aromatics with the remaining SARA fractions of bitumen.

Effect of ageing on bitumen

The effect of ageing has also been analysed by means of AFM. Zhang et al. (2012) concluded that the surface stiffness of bitumen increased with ageing, but the changes were dependent on the ageing conditions. Rebelo et al. (2014) found that in aged bitumen samples, the micellar structure of asphalt can be easily identified, in both topography and phase images, as opposed to what was observed in a neat bitumen.

Lamontagne, Dumas, Mouillet, and Kister (2001) compared different ageing techniques to monitor the formation of carbonyl groups, concluding that ageing of bitumen results in changes to the microstructure mainly associated with aromatics. Lu and Isacsson (2002) and Yao et al. (2013) compared the effects of RTFO ageing by means of FTIR identifying changes in carbonyl and sulfoxide groups, changes in SARA fractions, and an increase in molecular weight. Shaopeng, Gang, and Zheng (2010) analysed the composition of bitumen before and after RTFO, RTFO + PAV and UV radiation by monitoring the increase in carbonyl and sulfoxide groups, as well as the reduction in aromatic groups. The measured increase in viscosity was associated with the effect of radiation and the thickness of the exposed film of bitumen, particularly when less than 150 μm.

Furthermore, Navarro, Partal, Martínez-Boza, and Gallegos (2005) found that the rheological response of neat and modified bitumen depends on the ageing conditions, and highlight that ageing occurring at high temperatures affects the rheological behaviour of bitumen differently from ageing occurring at service temperatures. Allen, Little, and Bhasin (2012) emphasise that prior to ageing, bitumen exhibits two distinct domains: continuous and disperse. By means of nanoindentation, the micromechanical properties of the domains were measured: stiffness, adhesion and visco-elastic behaviour. The properties were used to show that oxidative ageing results in microstructural changes in the bitumen such as phase dispersion, grouping and materialisation, suggesting that the "bee-structures" are the result of the latter.

Objective

The study focuses on determining the micromechanical properties of bitumen when subjected to different ageing conditions, using PFM. The effect of ageing as measured by AFM is then related to the thermodynamic behaviour of the bitumen and the occurrence of chemical changes due to oxidation.

Materials and AFM sample preparation

The neat bitumen corresponds to a PG64-22, with a viscosity grade of AC-30. The bitumen is composed of (15 ± 1)% asphaltenes and (85 ± 2)% maltenes. The bitumen was then aged by means of RTFO to simulate short-term ageing and RTFO + PAV to simulate long-term ageing. A minimum of 10 samples for each condition were prepared and analysed. Sample preparation consisted of applying a small piece of bitumen over a Si-wafer that was then placed in an oven at 163°C for 4 min, to ensure that the bitumen was liquid enough to be uniformly distributed into a thin film. The sample was then placed in the oven for 2 additional minutes to ensure that the film was uniform. Cooling of the samples was performed at room temperature for a 24-h period, while ensuring that no foreign contaminants would come in contact with the sample.

The asphalt fractions (asphaltenes and maltenes) were obtained by means of the chromatographic column method (ASTM D4124, 2009). The maltene sample was directly placed over the Si-wafer. The asphaltene sample was dissolved in trichloroethylene ACS prior to placement on the Si-wafer. The solvent was allowed to evaporate for a 24-h period, in a desiccator chamber at room temperature.

Finally, samples for field ageing were prepared. The samples correspond to 1 mm thick bitumen samples. Prior to exposing the samples to field conditions, the bitumen was aged by means of RTFO to simulate ageing during production and placement. After the samples were exposed to field conditions, a subset of the samples was collected every month for up to 6 months to be analysed.

Results and discussion

AFM results

Measurements were performed using a Witec Alpha 300 Atomic Force Microscope, in PFM. PFM is a non-resonant intermittent contact mode. Figure 1 shows the operation of the AFM

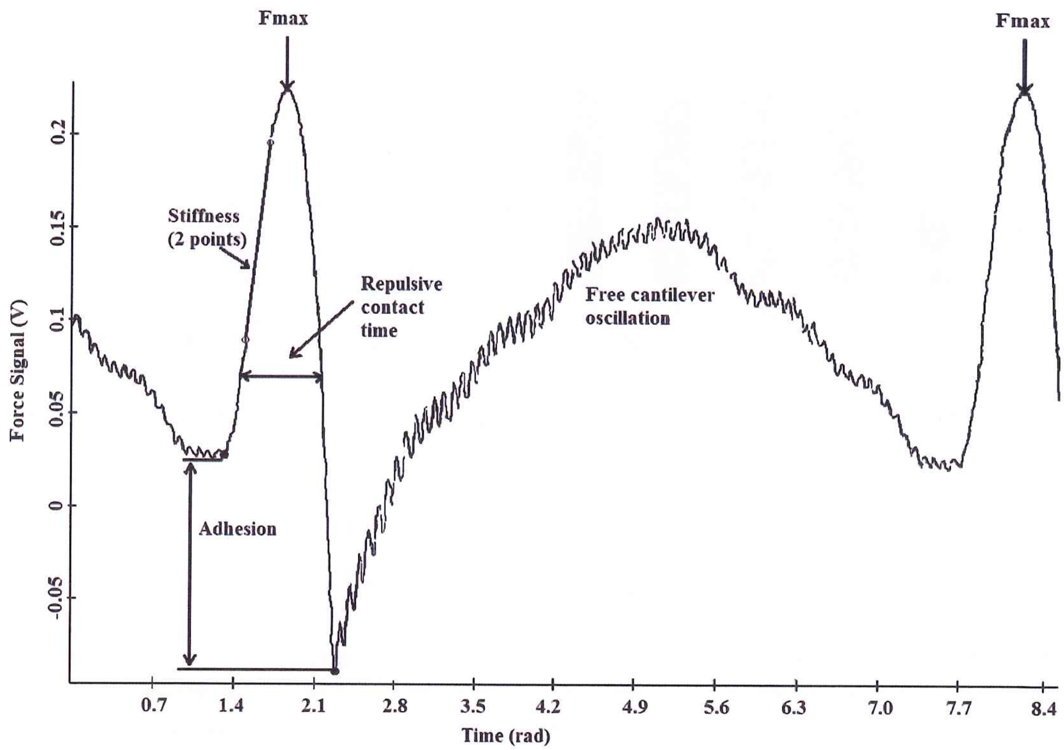

Figure 1. PFM sinusoidal modulation.

in PFM, where the cantilever oscillates in frequencies between 0.01 and 10 kHz, with amplitudes between 50 and 500 nm. The figure shows the same tip-sample characteristics as the force–distance curve.

The micromechanical behaviour of bitumen and its components prior to ageing is summarised in Figure 2. It can be verified from the data in Figure 2 that asphaltenes, corresponding to the bitumen's crystalline fraction, provide the stiffness to the overall structure. Inversely, maltenes contribute relatively less to stiffness but are responsible for the bitumen's adhesiveness.

The effects of ageing on adhesion and stiffness of the field-aged bitumens are shown in Figure 3. In general, the effects of ageing can be correlated to increases in both stiffness and

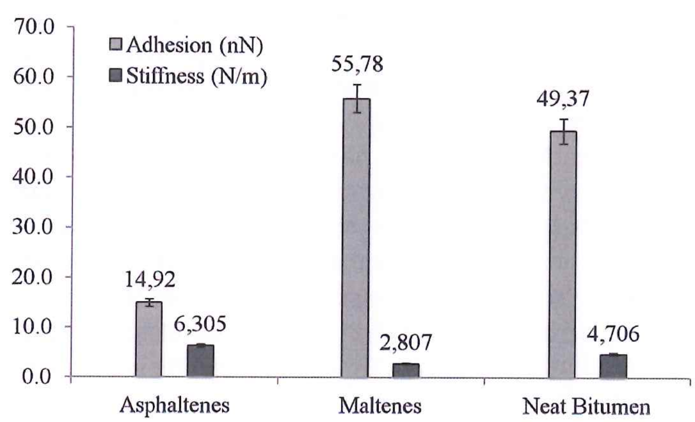

Figure 2. Micromechanical response of bitumen and its components.

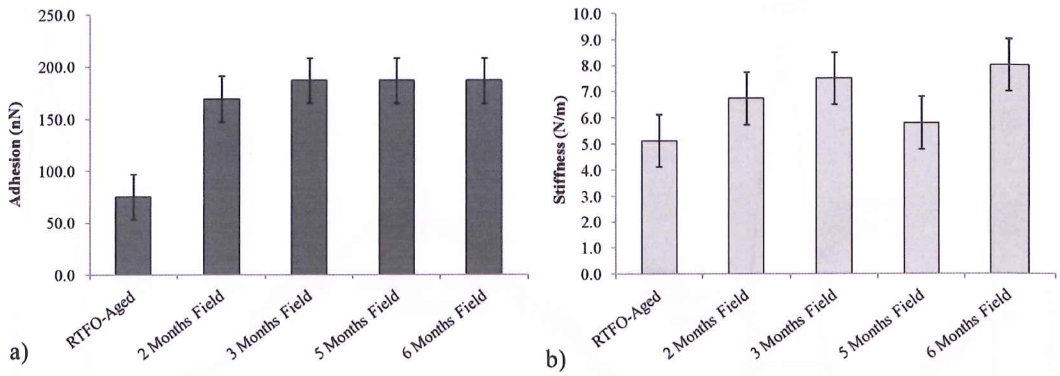

Figure 3. Micromechanical response of bitumen as a function of ageing, (a) stiffness and (b) adhesion measurements.

adhesiveness of bitumen. When the samples were subjected to field ageing, a significant increase in material adhesiveness was observed. The previous is expected due to chemical changes leading to the formation of carbonyl and sulfoxide groups, affecting the bitumen's components, polarity and molecular weight. A similar trend was observed regarding material stiffness: it was noticed that the hardening of samples increases with time of exposure to environmental conditions. The observed increase in stiffness can be related to UV radiation, which is believed to magnify the hardening of bitumen by means of photochemical reactions.

Figure 4 shows the changes in microstructure due to laboratory ageing and 6 months field ageing. Each experimental condition was evaluated with a minimum of 10 samples to ensure repeatability of the results.

The images confirm that as the material ages, it gains adhesiveness and stiffness. The increase in stiffness can be related to changes in the microstructure of bitumen: a decrease in relative stiffness between the catana-phase ("bee structure") and remaining bitumen domains; the para-phase serving as a dispersing medium to catana-phase, the per-phase (area surrounding the catana-phase) and sal-phase (dispersed phase). Similarly, the increase in adhesion can be reflected in a reduction in the per-phase and a change in the size and intensity of the catana-phase: in the case of field-aged samples, an increase in elongation of the catana-phase is observed. From a chemical perspective, it has been recognised that as the bitumen oxidises, its surface energy changes in terms of an increase in both, polar and non-polar (dispersive) components. The dispersive component is related to adhesion and cohesion of bitumen: an increase in dispersivity results in a highly cohesive (probably stiffer) bitumen with improved adhesion properties (Baldi-Sevilla, Montero, Aguiar-Moya, & Loría-Salazar, 2016). Therefore, the increment in adhesion and stiffness observed with the AFM can be explained by means of the chemical transformations occurring in the bitumen, which influence the final microstructure of the material, as discussed previously. The differences with the PAV microstructures can be associated with a different ageing mechanism (temperature + pressure vs. temperature + solar radiation + humidity).

From Figure 5, it is also important to note that the part of the catana-phase domain that is associated with stiffness is also partly associated with adhesion: the stiffer structures are also highly adhesive; however, not all adhesive subdomains in the catana-phase are always stiff. The previous is most likely resulting from the combination of high molecular weight and polarity in the different bitumen components.

The changes that the bitumen experiences after 6 months of field ageing exceed those induced by RTFO + PAV.

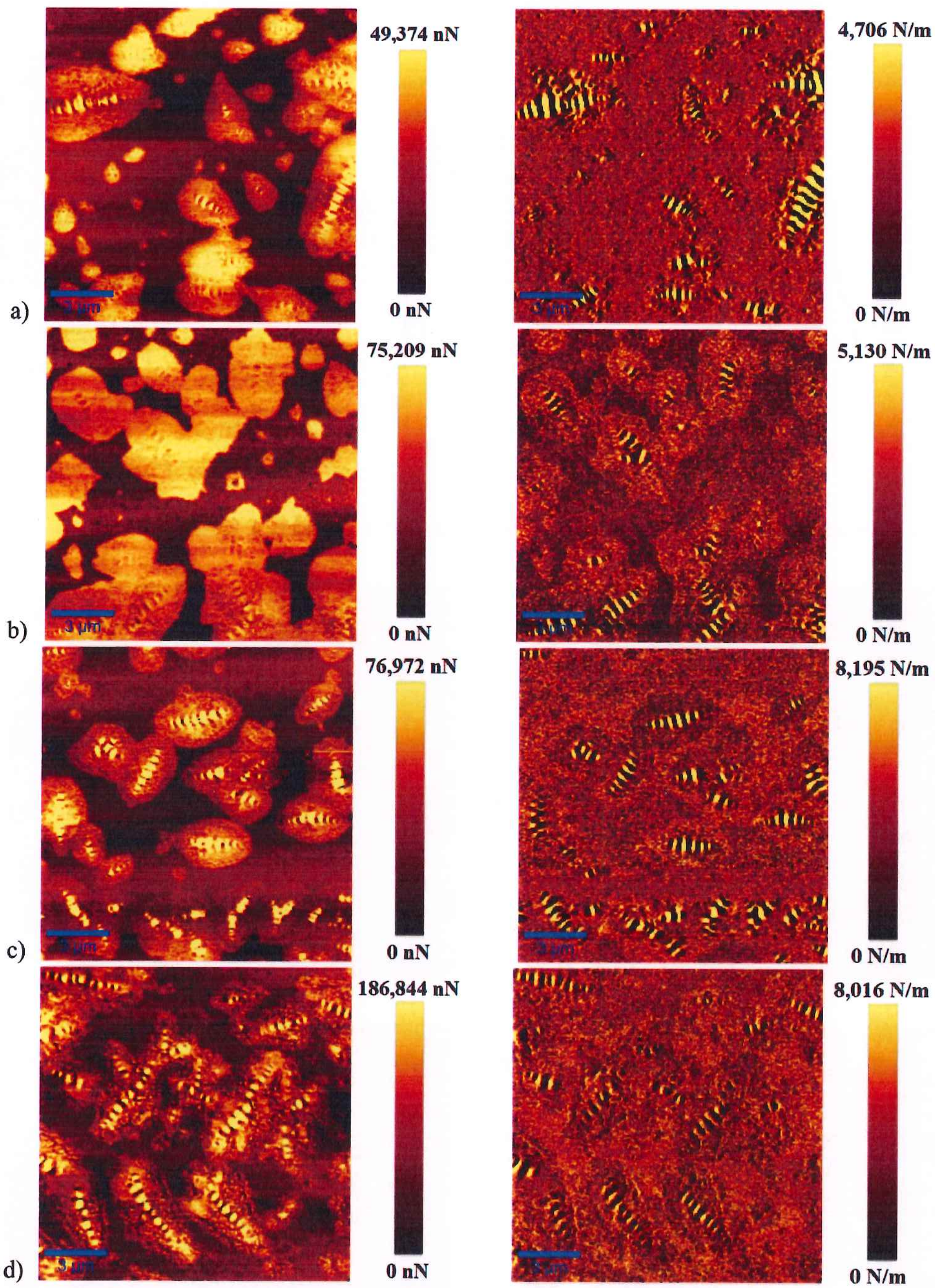

Figure 4. Changes in adhesion (left) and stiffness (right) in the bitumen's microstructure (a) neat bitumen, (b) RTFO-aged bitumen, (c) PAV-aged bitumen and (d) 6 months field-aged bitumen.

The changes in micromechanical response are directly associated with the composition of the bitumen. Figure 6 shows the morphology of the bitumen components for the case of a neat bitumen.

It can be observed that the highest contribution to adhesion is provided by the catana-phase precursor domain in the maltenes. However, the composition of the catana-phase is not uniform and also includes low depth areas with relatively low adhesiveness. The asphaltenes are relatively uniform in their contribution to stiffness. Finally, the catana-phase in the maltenes also provides

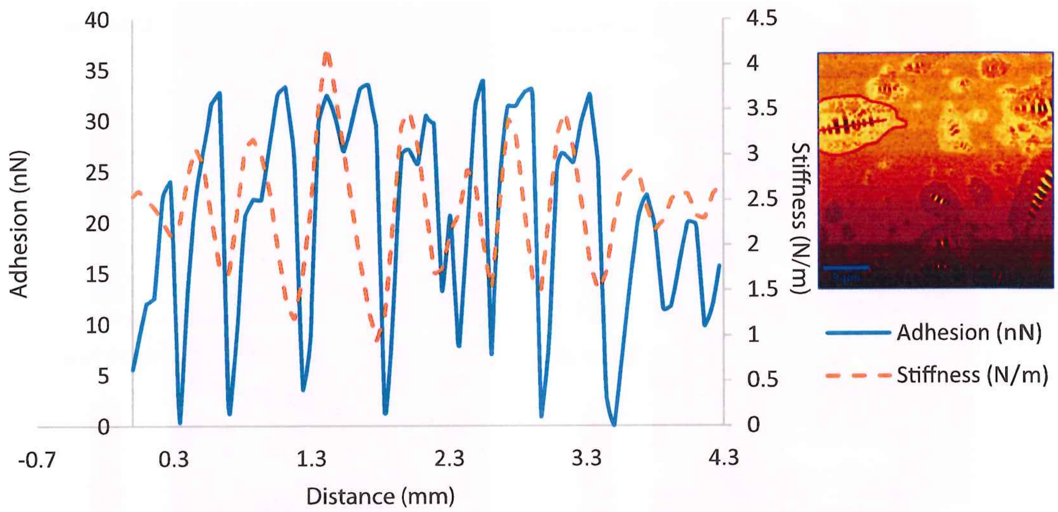

Figure 5. Adhesion/stiffness of highlighted catana-phase element in neat bitumen.

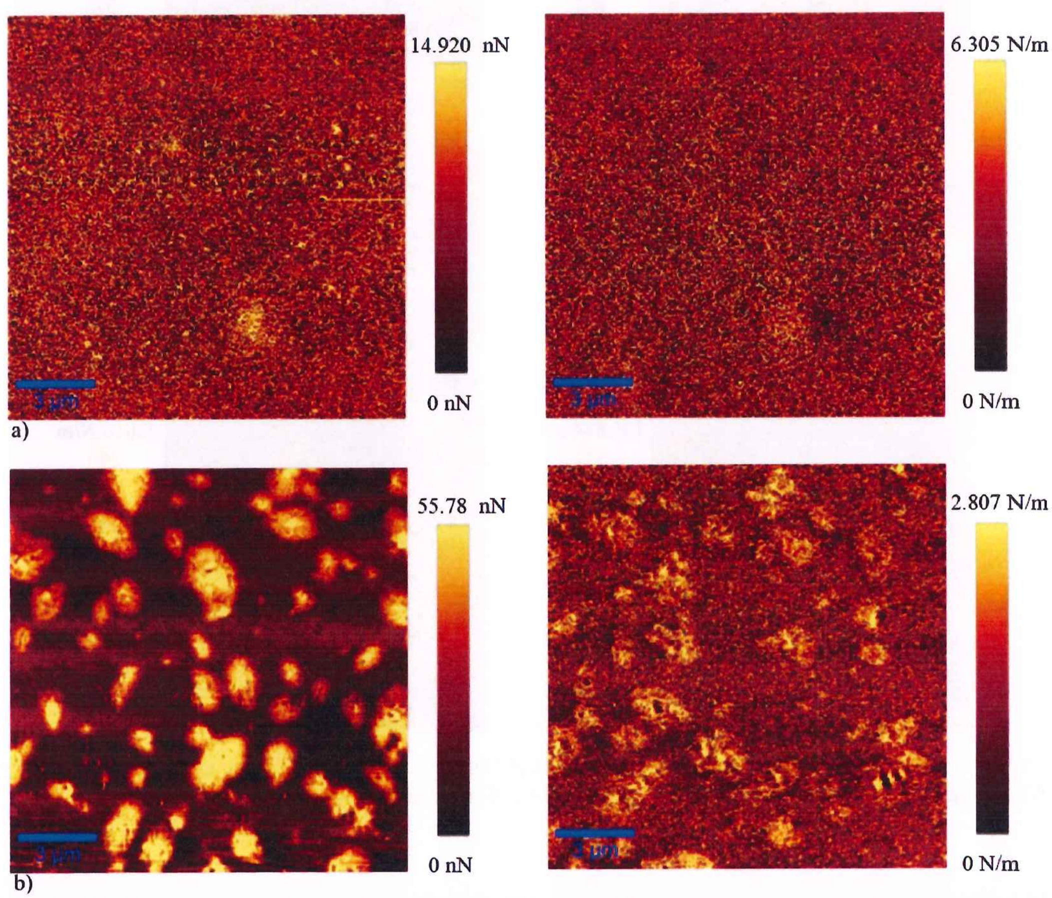

Figure 6. Adhesion (left) and stiffness (right) associated with the neat bitumen's components (a) asphaltenes and (b) maltenes.

significant stiffness to the bitumen. The observation is consistent with the possibility that the "bee structure" is polar in nature and therefore associated with the more polar components in maltenes (i.e. aromatics and resins) (Aguiar-Moya, Salazar-Delgado, Bonilla-Mora, et al., 2015).

The topographic and phase detection by AFM images allowed to determine the different phases present within the different components of asphalt. The observation of the possible source of the type structures “bee” was emphasised. The obtained measurements indicate that in the case of evaluated asphalt type, the “bee structure” are not related to asphaltenes, because no such structures were identified in the asphaltene image by PFM. In addition, the hypothesis that the “bee structures” are the result of oxidation processes, modification of asphalt with polymers or crystallisation of paraffin waxes within the asphalt does not seem to be feasible, since the structures are present in the morphology of the neat bitumen. However, there is clear evidence that ageing temperature influences asphalt morphology, and as such, in each of the phases present in the various components SARA (Aguiar-Moya, Salazar-Delgado, Bonilla-Mora, et al., 2015).

Phase detection of the different components indicates that the type “bee structures” are correlated to the aromatic component of asphalt. Both AFM images at 20 × 20 μm and optical imaging at 100x corroborate their presence in naphthenic aromatics. Overall, although the source of the “bee structure” seems to be directly related to the aromatic (aromatics naphthenics), the shape, size and topography of the structure is associated with the combination of the different bitumen components. This could be verified by enrichment of asphalt with 50% of each of the fractions SARA (saturated and aromatic resins) and analysing each combination simultaneously. These findings are summarised in Aguiar-Moya, Salazar-Delgado, Bonilla-Mora, et al. (2015).

DSC analysis

DSC is widely used for estimation of thermal transitions, that is, first-order transitions, such as melting and crystallisation of crystallisable species (Elseifi et al., 2010). The glass transition, T_g, a second-order phenomenon taking place in the amorphous region of the sample, can also be achieved by means of DSC analysis. T_g is related to the energy required to break and re-form covalent bonds in an amorphous or random network (Ojovan, 2008). However, T_g depends largely on the nature of the material and its content of crystallisable fractions. Below the glass transition temperature, bitumen behaves like a glass and appears brittle, affecting the fatigue performance and tensile strength of the binder and the mix. The thermograms of the analysed bitumens are shown in Figure 7.

The onset temperature denotes the temperature at which the glass transition begins, near −34°C. The parameter T_m represents the peak melting temperature, near 31°C. As per Figure 7, the bitumen clearly exhibits these properties within the range of −90°C to 200°C (Leiva-Villacorta, Aguiar-Moya, Salazar-Delgado, & Loria-Salazar, 2015).

The DSC analysis in this study was conducted using a TA Q2000 system. Approximately 10 mg of bitumen was weighed in the sample holder and placed in the DSC cell under a nitrogen blanket. The sample was heated to 200°C and then cooled reach −90°C at a rate of 20°C min^{-1}, to remove all traces of the thermal history. The sample was then heated at 10°C min^{-1} to 200°C to allow the wax and other chemical species to crystallise. A baseline between the temperature at the end of the glass transition and 90°C was established (i.e. the line above the heat flow curve). The area between the baseline and the heat flow curve could then be calculated and compared to melting enthalpy so as to derive the crystallised fraction content.

Table 1 shows the calculated parameters for all ageing conditions. The onset temperature for the neat bitumen was −33.85°C. The glass transition temperature for field-aged samples did not show significant differences with respect to the neat bitumen. However, a decrease in T_g was observed for thermal-aged samples. The PAV-aged sample exhibited two transitions related to crystallisation. This indicates that the PAV-oxidised sample has a larger crystalline fraction which can be related to the larger stiffness value found with AFM. In the case of the 6-month field-aged bitumen, a small increase in T_g was observed, which can also be related to

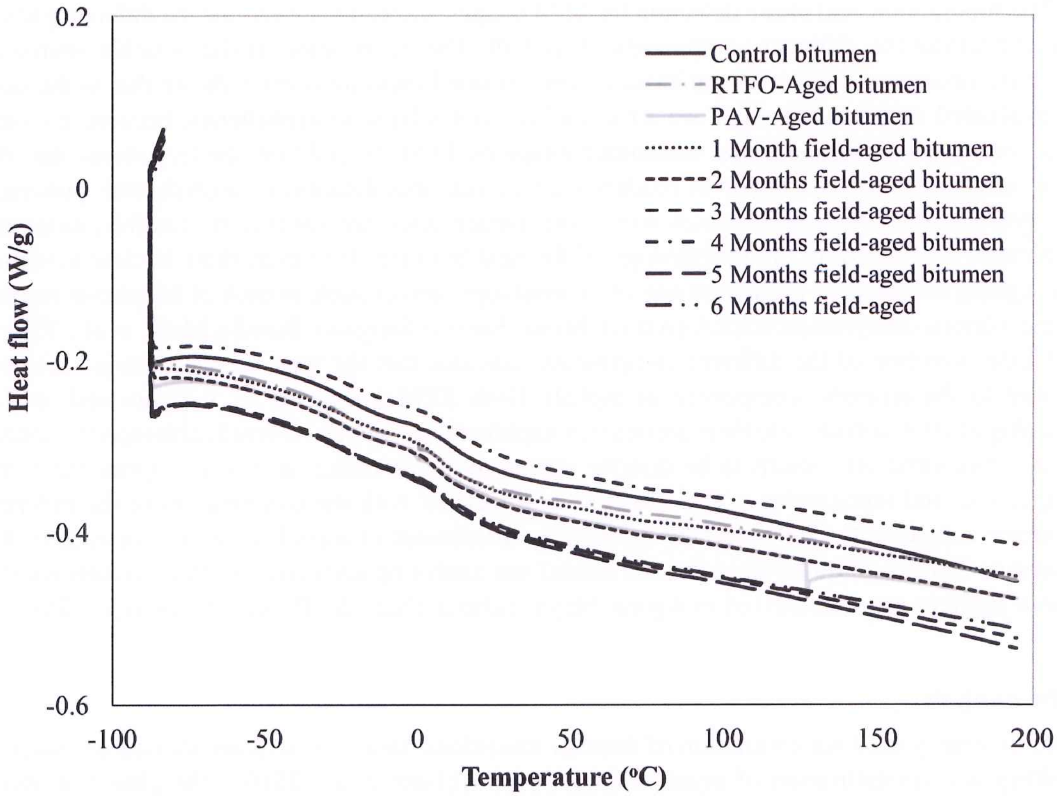

Figure 7. DSC analysis for laboratory and field-aged bitumen samples.

Table 1. Thermal properties of the aged bitumens.

Bitumen	T_{gOnset} (°C)	T_g (°C)	T_m (°C)	ΔH (J g^{-1})
Neat	− 33.85	− 23.34	30.68	6.988
RTFO-aged	− 34.21	− 24.55	29.46	7.706
PAV-Aged[a]	− 35.34	− 26.39	33.04	8.090
	–	–	127.2	1.616
1 Month field	− 35.20	− 23.13	27.43	9.384
2 Months field	− 34.62	− 23.75	28.64	9.299
3 Months field	− 35.36	− 23.99	29.08	8.647
4 Months field	− 34.76	− 22.89	32.43	7.514
5 Months field	− 34.08	− 23.73	29.06	8.418
6 Months field	− 34.78	− 22.54	30.65	8.518

[a]Two transitions related with crystallisation.

the increase in stiffness (compared to the neat bitumen) observed in the AFM measurements. The small increase in the melting peak of PAV-aged bitumen when compared to neat bitumen is also indicative that more energy is required to produce molecular motion as the material is more rigid. No significant differences were observed in terms of the melting peak between neat bitumen and field-aged bitumen.

The total enthalpy of the melting transition of the aged bitumens increased compared to the neat bitumen. This suggests that both oxidation processes, thermal and field ageing, increased the bitumen crystallinity. Based on Harrison, Wang, and Hsu (1992), an increase in hardness, tensile strength, a more rubber-like consistency and a better resistance to flow at high temperatures can

Table 2. Carbonyl and sulfoxide areas for the aged bitumens.

Bitumen	Carbonyl area	Sulfoxide area
Neat	0.009	0.107
RTFO-aged	0.019	0.194
PAV-aged	0.129	0.672
1 Month field	0.054	0.498
2 Months field	0.049	0.516
3 Months field	0.084	0.670
4 Months field	0.080	0.645
5 Months field	0.087	0.684
6 Months field	0.106	0.738

be consequences of an increase in crystallinity. The previous is in agreement with the increase in stiffness observed by means of AFM. In this case, the higher content of fractional crystallisation was obtained from field-aged samples after several months of exposure to the environment. The transition temperature corresponds to the breakdown temperature of the molecular association that might be due to polar associations between molecules.

FTIR analysis

The FTIR technique allows the study of the molecular structure of certain sample based on a transmittance spectrum. Typically, the obtained results are compared to a previously developed database of similar materials in order to determine the nature of the analysed material and to allow for interpretation of the spectrum bands (Aguiar-Moya, Salazar-Delgado, Baldi-Sevilla, Leiva-Villacorta, & Loría-Salazar, 2015). The chemical oxidation of asphalt binder produces oxygenated functional groups, such as carbonyl and sulfoxide (Liu, Ferry, Davison, Glover, & Bullin, 1998; Yang, You, & Mills-Beale, 2015). These groups can be found in an infrared spectrum of the oxidised material since they appear around 1700 and 1030 cm^{-1}, respectively. By measuring the corresponding peak area, it is possible to quantify the level of oxidation in bitumen (Le Guern, Chailleux, Farcas, Dreessen, & Mabille, 2010). The results for the analysed bitumens are shown in Table 2. Sixty-four replicas of the FTIR spectrum were measured per sample using a Thermo Nicolet iS50 ATR system.

When the bitumen is thermally aged according to RTFO and PAV procedures, the peak areas of carbonyl and sulfoxide increase significantly from the neat condition to the RTFO + PAV-aged condition. This behaviour is expected since the ageing procedure involves the exposure of samples to high levels of oxygen and severe conditions of temperature and pressure. In the case of the field-aged samples, the results show that the carbonyl and sulfoxide content also increases significantly. The increase in carbonyl and sulfoxide functional groups is related to an increase in viscosity of the bitumen due to an increase in polarity and molecular interactions within the bitumen structure.

It can also be seen that both, the PAV-ageing procedure and field ageing, result in a larger production of carbonyl groups rather than sulfoxide groups, since the observed increment in the peak areas of the former is significantly larger. In the case of RTFO + PAV-ageing, the carbonyl content increases by 579% and the sulfoxide content increases by 344%, with respect to the neat bitumen. For field-aged samples, the carbonyl area increases by 458% and the sulfoxide area increases by 378%, with respect to RTFO aged samples. These findings are related to an increase in molecular interactions due to oxidation. In turn, these interactions increase the viscosity and stiffness of the aged bitumens, which is consistent with the results obtained in the AFM and DSC measurements discussed previously.

Finally, it is important to remark that the carbonyl and sulfoxide content produced during field ageing in a short period of time (6 months) is close to that produced with the PAV-ageing procedure. This suggests that the PAV-ageing might not be efficiently simulating the oxidation of bitumen. The previous is probably associated with the absence of UV radiation in the process: it has been found that UV light significantly affects the mechanical performance of asphalt mixtures due to the chemical changes associated with oxidation (Petersen, 2009; Xiao, Amirkhanian, Karakouzian, & Khalili, 2015; Xiao, Newton, Putman, Punith, & Amirkhanian, 2013).

Concluding remarks

AFM by means of PFM allowed estimation of micromechanical response associated with bitumen morphology. An increase in both adhesion and stiffness was identified as the result of the ageing process. However, the changes in adhesion and rigidity were also related to the morphology of the bitumen and its components.

The higher adhesion and stiffness values found for the PAV and field-aged bitumens correspond to chemical transformations, such as introduction of oxygenated functional groups, detected by means of FTIR. It was found that the aged bitumens exhibited a significant increase in carbonyl and sulfoxide content, compared to the neat bitumen. Furthermore, these changes might be translated into a larger occurrence of chemical interactions along the molecules, which influence on the resulting thermal behaviour of bitumen, as observed in the DSC analysis. The PAV-aged samples exhibited a secondary crystallisation enthalpy at 127.2°C, a phenomenon that is not present in field-aged samples, probably due to a higher content of crystallisation fractions. In the case of the field-aged samples, the longer the bitumen is subjected to field ageing conditions, the calorimetric curves tend to become more endothermic, which means that a greater energy is required to activate the structural changes associated with crystallisation. In other words, the bitumen becomes more rigid after field ageing.

In summary, the observed differences between laboratory and field-aged bitumens can be related to differences in the oxidation compounds produced during ageing: the occurrence of double bonds and aromatisation of molecules can also be determining the behaviour of the aged bitumen. In general, the increase in molecular weight, molecular interactions and the consequent increase in bitumen stiffness can lead to a state of fragility affecting the long-term performance of the asphalt mixture.

Disclosure statement

No potential conflict of interest was reported by the authors.

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