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Ageing effect on chemo-mechanics of bitumen

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Ageing has a significant impact on the chemical and mechanical properties of bituminous materials. In this study, Fourier Transform Infrared (FTIR) spectrometer and Dynamic Shear Rheometer (DSR) tests were utilised to investigate the effect of ageing on the chemical and rheological properties of bitumen. Bitumen films with thickness of 2 mm were exposed to laboratory ageing at various conditions. Specifically, different combinations of ageing time, temperature and pressure were applied on the bitumen samples. The FTIR results were used to quantify the changes in the chemical functional groups and to calculate the combined ageing index (summation of carbonyl and sulfoxide indices) of bitumen. In addition, the DSR test results were analysed to determine the evolution of the black diagrams, crossover frequency and crossover modulus with ageing. A linear relationship was found between the combined ageing index and the distance in the crossover map, providing thus a chemo-mechanics framework to describe bitumen ageing. The results were validated by using data of field aged samples.

Keywords: bitumen; ageing; FTIR spectroscopy; rheology; chemo-mechanics

1. Introduction

Ageing of bitumen occurs during storage, mixing, transport, laying on the road, as well as during its service life (Ferrotti et al., 2018; Zargar, Ahmadinia, Asli, & Karim, 2012). The chemical and mechanical properties of bitumen, being an organic substance, evolve with time due to ageing. It is well known that as bitumen ages its ductility, penetration index and phase angle reduce while the softening point and complex shear modulus increases (Lesueur, 2009; Siddiqui & Ali, 1999). Ultimately, the viscosity of bitumen increases and it becomes stiffer. This may cause the mixture to become excessively brittle and susceptible to damage (Kliewer, Bell, & Sosnovske, 1995; Saoula, Soudani, Haddadi, Munoz, & Santamaria, 2013).

Early in time, researchers have recognised that typical physical parameters of bitumen such as viscosity, penetration, softening point and ductility have a good correlation with ageing (Benson, 1976; Oort, 1956). At that time, the level of ageing was expressed as a reduction in penetration, an increase in softening point or as the ratio of viscosities, always in relation with the unaged (fresh) condition (Petersen, 1989; Rostler & White, 1960). In recent years, more and more researchers use the Dynamic Shear Rheometer (DSR) to investigate the effects of ageing on the rheological properties of bitumen. Rheology involves the study and evaluation of the time-temperature dependent behaviour of materials and leads to a better knowledge of bitumen

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performance under different thermal and mechanical conditions (Behera, Singh, & Reddy, 2013; Kandhal & Chakraborty, 1996; Ruan, Davison, & Glover, 2003).

Chemical changes of bitumen before and after ageing include the formation of functional groups, transformation of generic fractions and changes in molecular weight. The Fourier Transform Infrared spectrometer (FTIR) is commonly used to determine the chemical characteristics of bitumen by identifying specific chemical functional groups. In the infrared spectrogram of bitumen, the absorbance bands corresponding to carbonyls and sulfoxides show a significant increase with ageing (Ahmed, 2016; Hofko et al., 2018; Kuang et al., 2014). The components of bitumen include four main classes of compounds: saturates, aromatics, resin and asphaltenes. It has been shown that ageing causes a decrease of the aromatics and at the same time increases the content of resins and asphaltenes. The content of saturates changes slightly due to their inert nature to oxygen (Feng, Yu, & Liang, 2012; Gamarra & Ossa, 2016). At the same time, ageing increases the molecular weight of bitumen, the amount of large molecules and polydispersity (Hofko et al., 2017; Lu & Isacsson, 2002). By comparing with other chemical characterisation methods, such as Gel Permeation Chromatography (GPC), and Atomic Force Microscope (AFM), FTIR is a more efficient, convenient and inexpensive tool to determine the chemical changes of bitumen due to ageing.

Recently, more and more researchers attempted to correlate the chemical composition of bituminous materials with their performance. Studies have indicated that the ageing mechanism affects the chemical composition of bitumen and it has been made clear that the rheological properties would change as well (Herrington, Patrick, & Ball, 1994; Petersen, 1984; Petersen & Glaser, 2011). Unfortunately, the specific relationship between the chemical properties and mechanical response of bitumen is still undefined.

The main objective of this study is to determine the changes in the chemical properties of bitumen due to ageing and link them to its mechanical response, by means of FTIR and DSR tests. For this, bitumen films were aged in the laboratory at various times, temperatures and pressures. On the basis of the experimental results, a chemo-mechanics relationship for aged bitumen is established and validated using results of field aged samples.

2. Materials, ageing protocols and test methods

2.1. *Materials*

The tests were performed on a penetration bitumen 70/100, typically used in the Netherlands, with no polymer or other chemical additive. Table 1 shows the main physical and rheological properties of the examined bitumen. The same bitumen type was used for the construction of test sections that were used to investigate the effect of field ageing on bitumen as explained in the following sections.

Table 1. Specifications of PEN 70/100 at fresh (unaged) state.

Property	Unit	PEN 70/100
Penetration at 25°C	0.1 mm	70–100
Softening point	°C	43–51
Dynamic viscosity at 60°C	Pa s	160
Complex shear modulus at 1.6 Hz & 60°C	kPa	1.8
Phase angle at 1.6 Hz & 60°C	°	88

Table 2. Ageing programme.

Ageing method	Temperature (°C)	Pressure (atm)	Ageing time (h)
Oven	100	1	20, 40, 80, 160, 320
Oven	50,150	1	40
PAV	100	5,10, 15, 20	40
RTFOT (STA)	163	1	1.25
RTFOT + PAV (LTA)	163 (RTFOT), 100 (PAV)	1 (RTFOT), 20 (PAV)	1.25 (RTFOT), 20 (PAV)

2.2. *Ageing protocols*

2.2.1. *Laboratory ageing*

In this study, bitumen films with 2 mm thickness were aged using two different ageing methods: oven ageing and PAV (Pressure Ageing Vessel) ageing. Part of the samples were aged in the oven for 20, 40, 80, 160, 320 h at 100°C and atmospheric pressure. To investigate the effect of temperature, other subsets of the samples were oven aged at 50°C and 150°C for 40 h.

Moreover, the samples were aged by means of RTFOT and PAV. Short-term ageing (STA) was simulated by using the RTFOT at 163°C for 75 min, in accordance with the EN 12607-1 test standard. This ageing step is considered to represent the ageing of bitumen during plant mixing, production, transportation and construction. Long-term ageing (LTA) was simulated by using PAV at 100°C and 2.1 MPa (20 atm) for 20 h, according to the EN 14769 ageing standard. This protocol is thought to mimic age hardening of bitumen during the first 5–10 years of pavement service life. Finally, the standard PAV protocol was modified and bitumen was subjected to ageing for 40 h at 100°C and at four different pressures of 5, 10, 15, 20 atm. Table 2 summarises the various ageing processes that were considered in this study.

2.2.2. *Field ageing*

The pavement sections were constructed in October 2014 and since then they have been continuously exposed to the environment. The Netherlands has a temperature maritime climate influenced by the North Sea and the Atlantic Ocean, with cool summer and moderate winter. Daytime temperatures varies from 2°C to 7°C in the winter and 15–20°C in the summer. Rainfall is distributed throughout the year with a dryer period from April to September. The layers of the full-depth pavement structure are shown in Figure 1. The top layer is porous asphalt (PA), which is the main asphalt type used in the highways network in the Netherlands. The PA layer thickness was 50 mm and the layer was paved in one lift.

Asphalt cores (diameter is 100 mm) were taken from the PA layer every year until now. Then the samples were cut into three slices (each slice with 12–14 mm thickness), to investigate whether there is a gradient in the ageing level along the depth profile of the pavement. The slices are denoted with T (Top), M (Middle), and B (Bottom), respectively, Figure 2. The bitumen from each slices was extracted and recovered, and its chemical and rheological properties were evaluated.

Bitumen was extracted from the slices according to the EN 12697-1 European standard. Dichloromethane was used as a solvent during bitumen extraction. After the recovery of bitumen, DSR and FTIR tests were performed to check if the solvent was fully evaporated. If the solvent was still present in the sample, this would appear in the FTIR results as a special peak in the spectrum, Figure 3(a). Moreover, the DSR results showed that materials were much softer than the actual fresh materials, Figure 3(b).

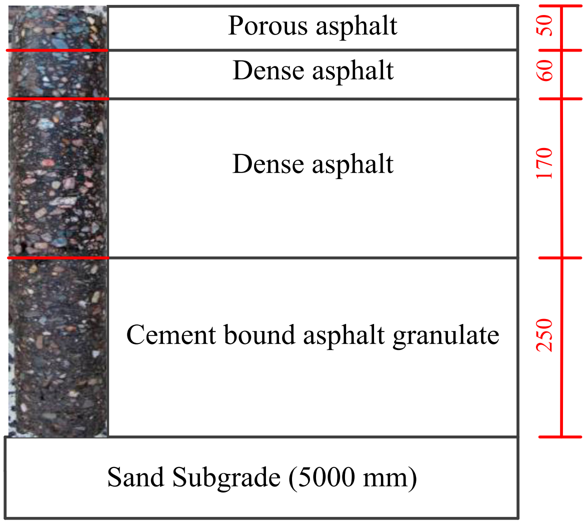


Figure 1. Structure of field test section (length unit: mm).

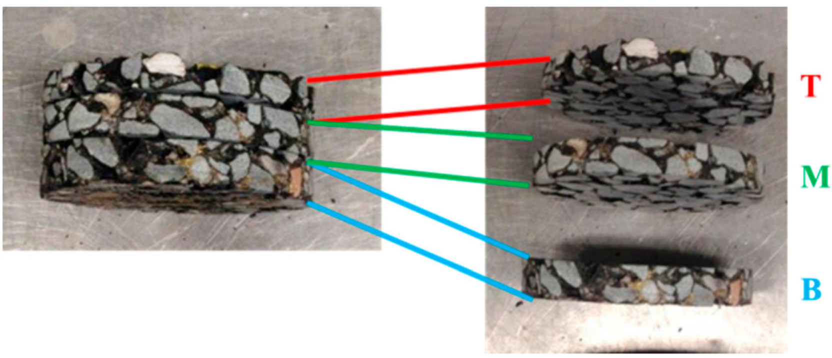


Figure 2. Slices description.

2.3. *Test methods*

2.3.1. *Fourier transform infrared spectrometry*

The chemical composition of bitumen was evaluated by means of FTIR. A Perkin Elmer Spectrum 100 FTIR spectrometer was used in the attenuated total reflectance (ATR) mode to identify the chemical functional groups of the bitumen. The sample was scanned 20 times, with a fixed instrument resolution of 4 cm^{-1}. The wavenumbers range was set to vary from 600 to 4000 cm^{-1}. At least three repetition tests were done for each ageing condition.

In the previous studies of FTIR, researchers have identified mainly two important functional chemical groups which contain oxidation products, such as carbonyls (wavenumber from 1753 to 1660 cm^{-1}) and sulfoxides (wavenumber from 1047 to 995 cm^{-1}). In this study, the effects of ageing were analysed considering specific bands of wavenumber as defined by Lamontagne, Dumas, Mouillet, and Kister (2001) and the corresponding area under those bands, Figure 4.

The peak areas were evaluated using quantitative analysis and then the carbonyl and the sulfoxide indices were determined by dividing the area under a specific location of the spectrum by the sum of specific areas, Equations (1) to (3). The vertical limit bands with the corresponding

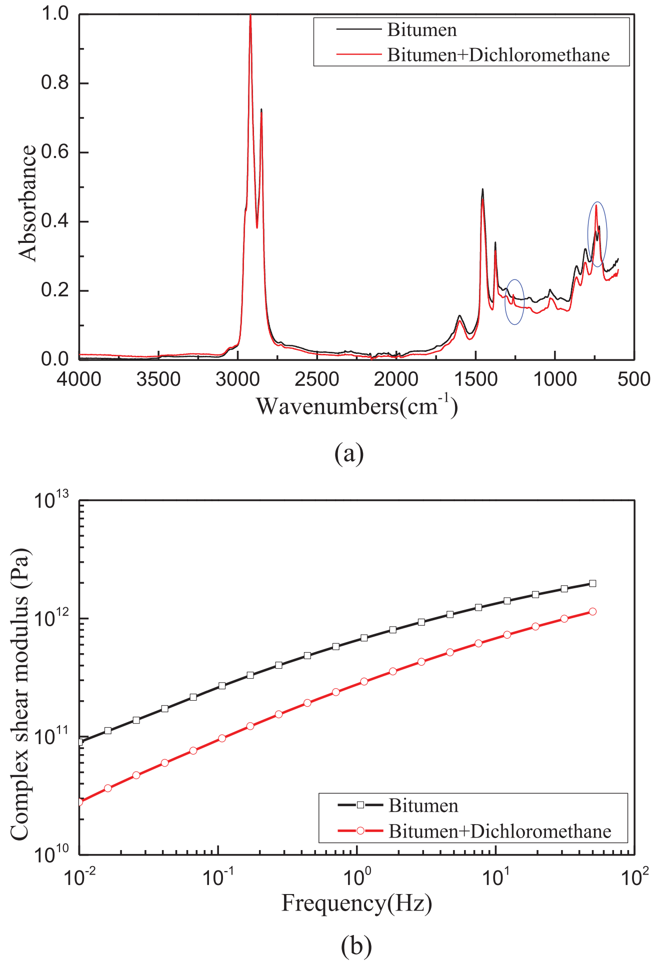


Figure 3. Results of pure bitumen vs bitumen with residual Dichloromethane. (a) FTIR results. (b) DSR results.

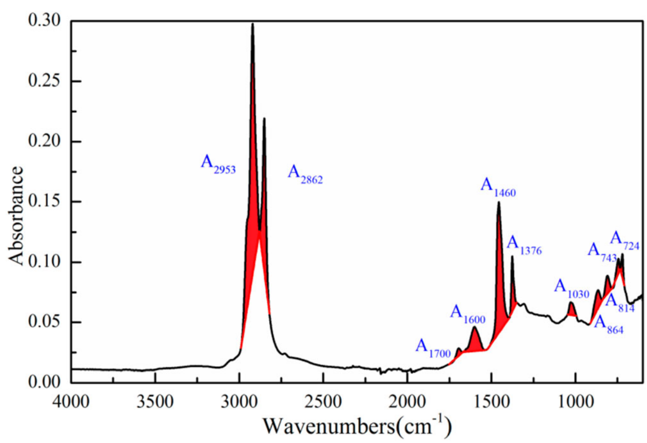


Figure 4. Schematic of bitumen infrared spectrum.

functional groups are present in a previous study (Van den bergh, 2011).

$$\text{Carbonyl index} = \frac{A_{1700}}{\sum A} \tag{1}$$

$$\text{Sulfoxide index} = \frac{A_{1030}}{\sum A} \tag{2}$$

$$\sum A = A_{(2953,2862)} + A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} \tag{3}$$

2.3.2. *Dynamic shear rheometer*

The rheological properties of bitumen were characterised by means of DSR tests according to NEN-EN 14770. An Anton Paar MCR 502 device was used to analyse the materials' response over a wide range of temperatures and frequencies. The bitumen samples were tested using a parallel-plates configuration in a stress-controlled model. Initially, the linear viscoelastic (LVE) range of bitumen samples was determined using amplitude sweep tests. The maximum strain value within the LVE range was 1%. The frequency sweep tests were performed at five different temperatures (0°C, 10°C, 20°C, 30°C and 40°C). During the tests the frequency varied in a logarithmic manner from 50 to 0.01 Hz. At least three repetition tests were done for each ageing condition. The complex shear modulus and phase angle values were collected during the tests. Master curves were constructed at the reference temperature of 20°C, in order to determine the visco-elastic behaviour in a wider range of frequencies.

3. Results and discussion

3.1. *Chemical results and analysis*

The FTIR spectra of bitumen at various ageing conditions (time, temperature and pressure) have been presented and discussed in a previous study (Jing, Varveri, Liu, Scarpas, & Erkens, 2018). Using the obtained spectra, the ageing indices (carbonyl and sulfoxide indices) of each sample were calculated based on Equations (1) to (3). Figure 5 shows the carbonyl and sulfoxide indices, that represent the average value of three measurements.

The results show that both indices increased with increasing ageing time, temperature and pressure. It is interesting to note that sulfoxides are formed earlier than carbonyls, because sulfur is more reactive than carbon in bitumen. It can be observed that, under weak ageing conditions (short ageing time, low ageing temperature and pressure), only sulfoxides are formed, and further increase, while no (or few) carbonyls are present in the aged bitumen samples. On the contrary, the formation of carbonyls starts under stronger ageing conditions (long ageing time, high ageing temperature and pressure), whereas the sulfoxide index becomes more stable probably due to the depletion of sulfur. In order to fully consider the chemical changes of bitumen due to ageing, a combined ageing index (the summation of carbonyl and sulfoxide indices) is used in this study, as shown in Figure 6.

Moreover, comparing the results of different ageing protocols in Figure 5, it can be observed that temperature is the most influential parameters for ageing, probably because of the fact that the ageing rate coefficient increases exponentially with temperature based on the Arrhenius equation (Boysen & Schabron, 2011; Han, Jin, & Glover, 2013; Juristyarini, Davison, & Glover, 2011), Equation (4).

$$k = Ae^{-(E_a/RT)} \tag{4}$$

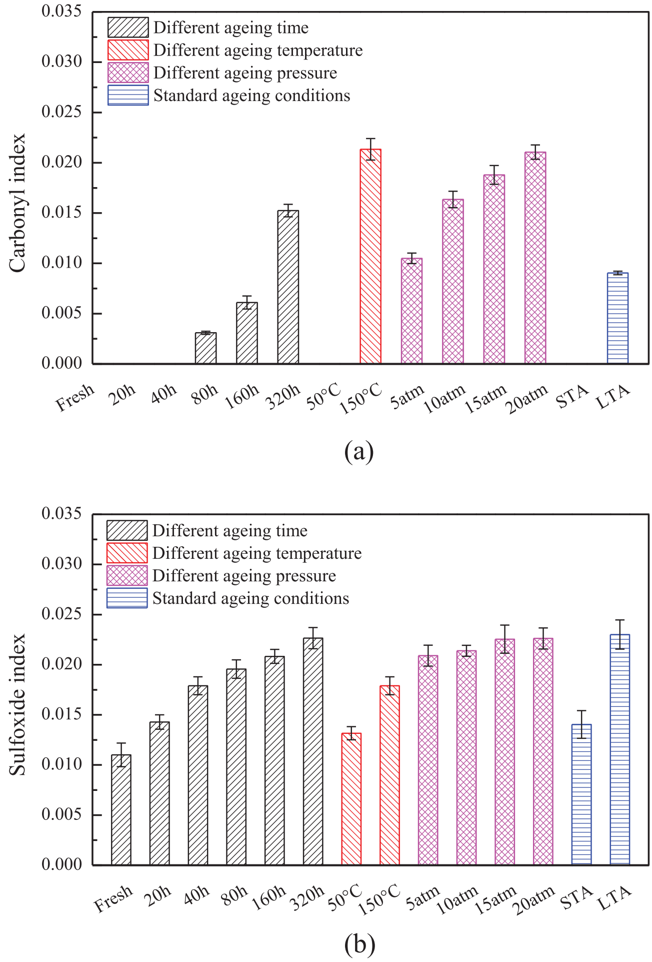


Figure 5. Ageing indices of PEN 70/100 at different ageing conditions. (a) Carbonyl index. (b) Sulfoxide index.

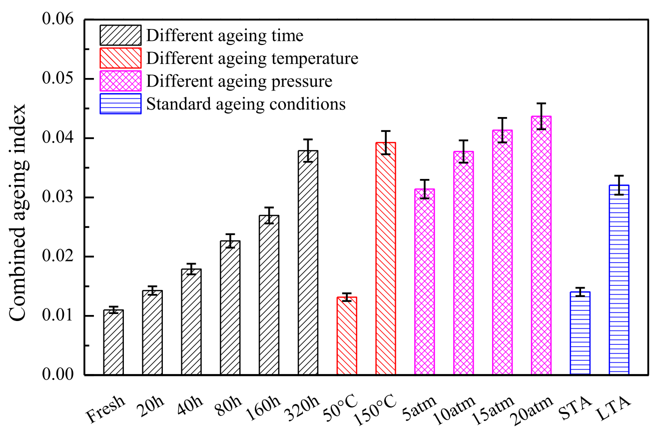


Figure 6. Combined ageing indices of PEN 70/100 at different ageing conditions.

where k is the rate coefficient, T is the absolute temperature, A is the pre-exponential factor, E_a is the activation energy of the reaction and R is the universal gas constant.

Pressure is also a significant influential parameters for ageing. It is another way of expressing the concentration of gases. Under a higher pressure, or at a higher concentration, more oxygen molecules are dissolved in bitumen based on the Henry's law (Cui, Glover, Braziunas, & Sivilevicius, 2018; Herrington, 2012; Jin, Han, Cui, & Glover, 2011; Prapaitrakul, Han, Jin, & Glover, 2009), Equation (5).

$$c_0 = h\left(\frac{P_{O_2}}{RT}\right) \tag{5}$$

where, c_0 is the concentration of dissolved oxygen in bitumen, P_{O_2} is the oxygen gas phase partial pressure, T is the temperature, R is the universal gas constant and h is the Henry's law constant.

In short, ageing temperature dramatically changes the ageing rate, following an exponential growth trend following Arrhenius equation. And the ageing rate linearly with ageing pressure following Henry's law, which it decreases exponentially with ageing time due to the consumption of the bitumen during ageing.

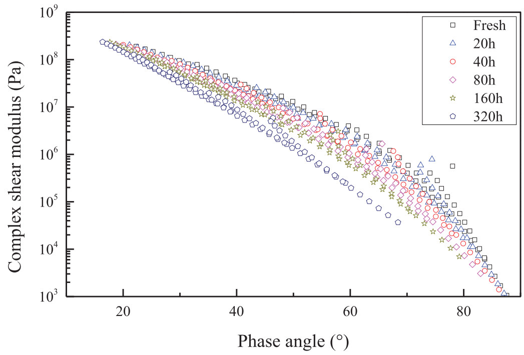
3.2. *Rheological results and analysis*

Similarly to the FTIR tests, at least three replicate samples at each condition were tested by means of the DSR. The evolution of the complex shear modulus and phase angle master curves of bitumen with increased ageing time, temperature and pressure was discussed in a previous study (Jing et al., 2018). In this study, the rheological changes of bitumen due to ageing were selected and plotted as Black diagrams (Airey, 2002) in Figure 7. The effect of ageing is seen as a shift of the Black diagram curves towards lower phase angles; while the shape of the curves changes to a straight line and the curvature reduces. These changes denote a tendency towards a more brittle material response.

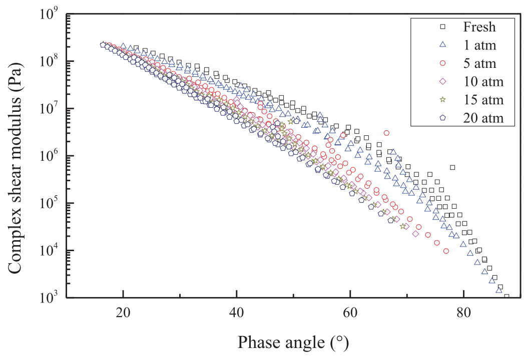
Figure 8 shows the effect of selected ageing conditioning protocols and the standard ageing protocols on bitumen rheology. It is evident that different ageing methods can be used to appropriately obtain similar rheological results with the RTFOT and PAV aged samples; similar results were obtained from the spectroscopy tests. For example, in Figures 6 and 8(a), STA and oven ageing at 100°C for 20 h give both similar combined ageing index (CAI) values and rheological results, and in Figures 6 and 8(b), LTA and PAV ageing at 5 atm and 100°C for 40 h give both CAI values and rheological results.

In this study the frequency when the storage shear modulus is equal to the loss shear modulus (phase angle is 45°) at the reference temperature, explicitly the crossover frequency, was used to characterise the viscoelastic fluid to solid transitory behaviour, Figure 9(a). The complex shear modulus corresponding to the phase angle of 45° or the crossover frequency is named the crossover modulus, Figure 9(b). Lower crossover frequency suggests higher molecular mass (Liu, He, Ruymbeke, Keunings, & Bailly, 2006), longer relaxation time and higher softening point (Nivitha & Krishnan, 2016), while lower crossover modulus denotes wider molecular mass distribution and higher polydispersity (Scarsella, Mastrofini, Barre, Espinat, & Fenistein, 1999). The crossover frequency and modulus for all samples are represented in Figure 10(a) and (b), respectively. The results shows that aged bitumen has lower crossover frequency and lower crossover modulus than the fresh bitumen at reference temperature.

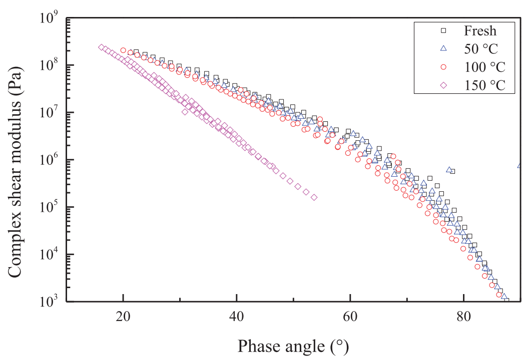
Chambon and Winter have shown that there exists a good logarithmic relationship between crossover frequency and crossover modulus for the same type of polymers (Chambon & Winter, 1985; Winter, 1987). Figure 11 shows that a good logarithmic relationship also holds for the studied bitumen, which is in good agreement with these findings.



(a)



(b)



(c)

Figure 7. Black diagram for bitumen at different aging conditions. (a) Different ageing time (oven ageing at 100°C and 1 atm). (b) Different ageing pressures (PAV ageing for 40 h at 100°C). (c) Different ageing temperatures (oven ageing for 40 h at 1 atm).

4. Chemo-mechanics of ageing

4.1. *Model development*

In a previous study (Jing et al., 2018), an empirical model was proposed, which describes the linear relationship between the complex shear modulus (at 10 Hz, 20°C) and the combined ageing

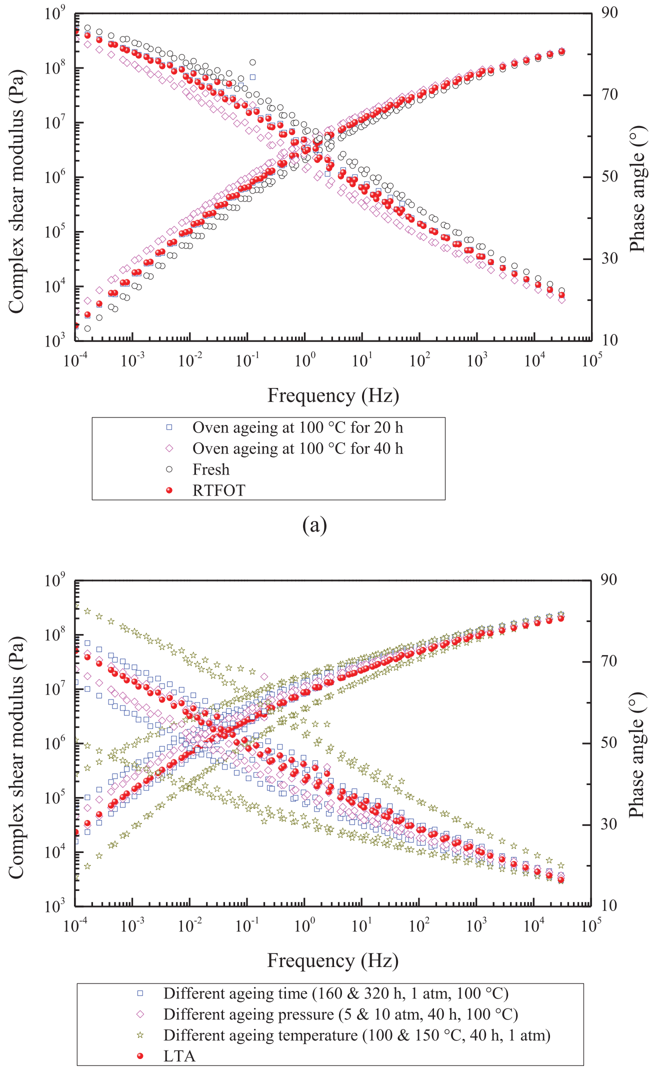


Figure 8. Comparison between standard STA/LTA with various ageing conditions. (a) STA. (b) LTA.

index. However, this model is limited to consider only the complex shear modulus at a specific frequency and temperature. In this study, an new model was developed to correlate the phase change behaviour (bitumen change from viscoelastic fluid to solid) with ageing.

As described in Figure 11(hereinafter referred as the crossover map), there was a good logarithmic relationship between crossover frequency and crossover modulus for the studied bitumen. In the crossover map, the points move from the top right corner to the down left corner along the blue line due to ageing. The ageing state of bitumen, which can be described by the changes in the values of the combined ageing index, would determine how far one point can move. Then the relationship between chemical and mechanical properties of aged bitumen (for each ageing condition) can be described by using this distance in the crossover map and the combined ageing index (carbonyl index + sulfoxide index). The unit distance is defined as the length between

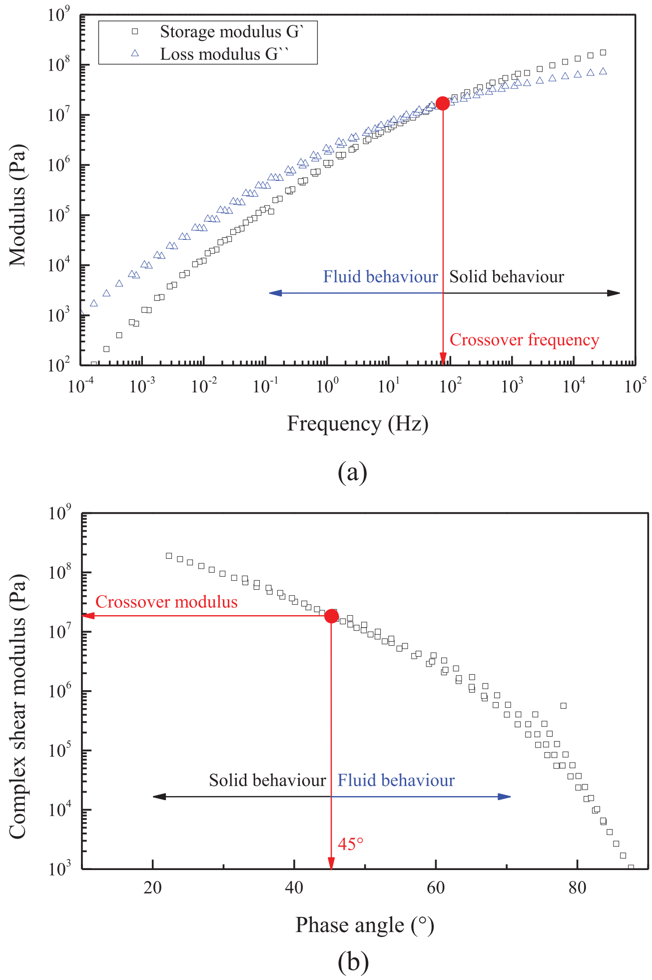


Figure 9. Schematic of crossover frequency and crossover modulus. (a) Crossover frequency. (b) Crossover modulus.

the point for the fresh bitumen and the point for the results of long-term ageing in Figure 11. Figure 12 shows that there is a good linear relationship between the two parameters for the specific bitumen type. Interestingly it appears that this relationship does not depend on the ageing method. In another words, the results indicate that the different ageing conditions can be used interchangeably.

4.2. *Model validation*

In order to correlate laboratory ageing to field ageing, bitumen was recovered from the field cores collected from the pavement test sections and was tested for its rheological and chemical properties.

The crossover frequency and crossover modulus of the recovered bitumen are shown in Figure 13. The black symbols in the graph are the results from the laboratory aged samples and the coloured symbols are the ones from the field aged samples. The field ageing data follow in a logical way the logarithmic relationship between crossover frequency and crossover

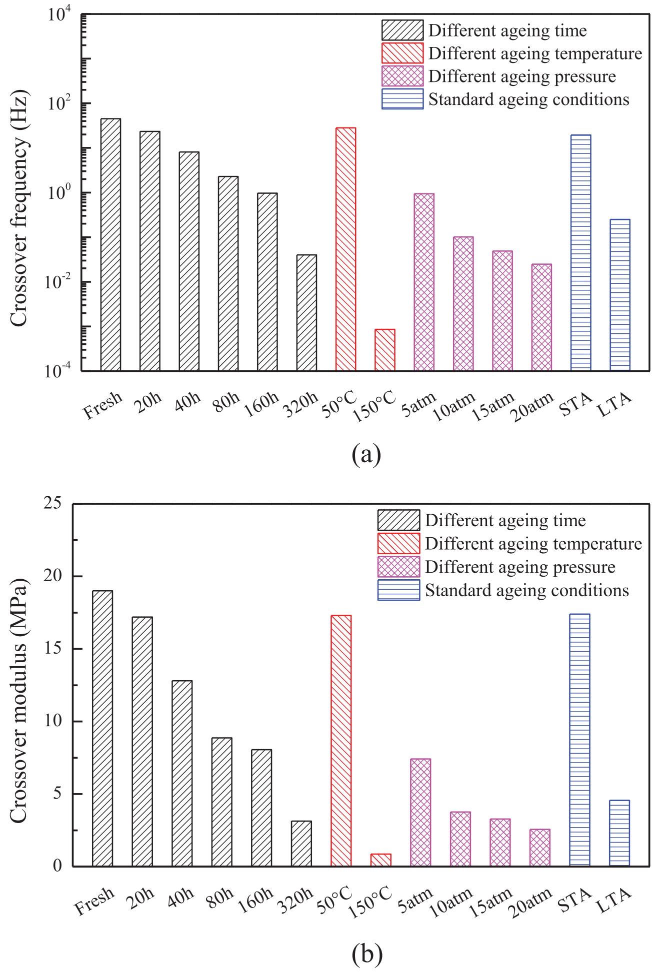


Figure 10. Crossover frequencies and crossover modulus of bitumen at different ageing conditions. (a) Crossover frequency. (b) Crossover modulus.

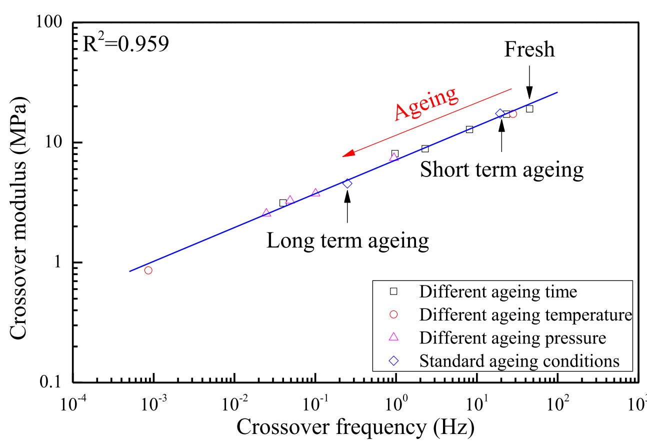


Figure 11. Crossover modulus vs crossover frequency of bitumen at different ageing conditions.

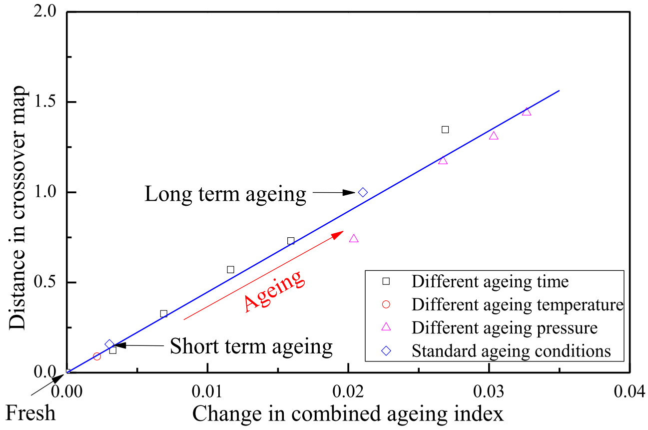


Figure 12. Distance in the crossover map vs change in combined ageing index (summation of carbonyl and sulfoxide indices) of bitumen at different ageing conditions.

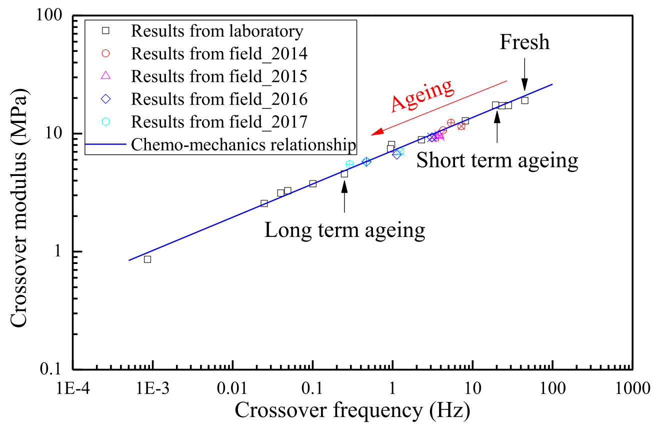


Figure 13. Crossover frequency vs crossover modulus of bitumen at laboratory and field ageing conditions.

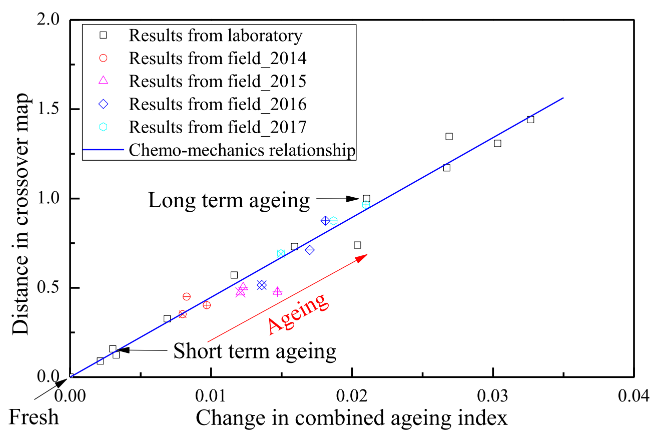


Figure 14. Distance in the crossover map vs change in combined ageing index (summation of carbonyl and sulfoxide indices) of bitumen at laboratory and field ageing conditions.

modulus that was established for the studied bitumen. It can be observed that the results for the field aged samples move down the curve with ageing time. The symbols with ' + ', ' − ' and ' × ' correspond to the results of recovered bitumen from the top, middle and bottom slices of the field cores respectively. It can be observed that the effect of ageing is more pronounced on the top part of the pavement and decreases with increasing pavement depth. Also, the points that represent the results for the three sample slices are closer in the first year of field ageing and spread more along the curve for subsequent years, indicating thus that the differences in ageing along the pavement depth increase with ageing time.

Following the aforementioned methodology, the relationship between the combined ageing index and the distance in crossover map was found. The results after laboratory and field ageing are plotted in Figure 14. Considering the test error, Figure 14 shows an overall agreement between field results and the predictions of the chemo-mechanics of ageing relationship.

5. Conclusions

Given the strong relationship between ageing, which affects bitumen chemistry and rheology, and mechanical pavement response, the knowledge of the evolution of the chemo-rheological properties in bituminous materials is of uppermost importance. For this reason, a series of ageing experiments were conducted on bitumen films at different times, temperatures, and pressures.

In order to develop a chemo-mechanics model of ageing, FTIR and DSR tests were carried out to determine the changes in chemical properties and the rheological response of aged bitumen. The analysis of the chemical properties showed the high variability of the carbonyl and sulfoxide functional groups with ageing. Furthermore, it confirmed two distinct phases of ageing, with an initial increase of sulfoxides and a second phase in which carbonyls formation occurs. The analysis of rheological properties showed that the effect of ageing is seen as a shift of the Black diagram curves towards lower phase angles; moreover the shape of the curves changes to a straight line and the curvature reduces. In addition, both crossover frequency and crossover modulus reduce with ageing. On the basis of chemical and rheological results, a linear relationship was found to exist between the combined ageing index and the distance in crossover map. The model was developed on the basis of the results of laboratory aged samples and was validated by using data of field aged samples. The results suggest that different ageing conditions can yield the same ageing effect on bitumen properties.

As a continuation of this research, the chemo-mechanics relationship will be validated for other bitumen types and a mathematical model will be develop to describe this relationship.

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Disclosure statement

No potential conflict of interest was reported by the author.

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