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Ageing Effect on Chemo-Mechanics of Bitumen

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Abstract. Ageing has a significant impact on the chemical and mechanical behavior of bituminous materials. In this study, Fourier Transform Infrared (FTIR) spectrometer and Dynamic Shear Rheometer (DSR) tests were utilized to investigate the effect of ageing on the chemical and mechanical 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 materials. 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 analyzed to determine the evolution of the 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.

Keywords: Bitumen · Ageing · FTIR spectroscopy · Rheology Chemo-mechanics

1 Introduction

In the Netherlands, raveling is the most common distress of porous asphalt pavements. Bitumen ageing is believed to be one of the main contributors to ravelling. It is well known that as bitumen ages its ductility and penetration index reduce while the softening point increases. Ultimately, the viscosity of the bitumen increases and bitumen becomes stiffer. This may cause the mixture to become excessively brittle and susceptible to damage (Saoula et al. 2013).

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 (Petersen and 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.

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2 Materials, Ageing Protocols and Test Methods

2.1 Materials

The tests were performed on a penetration bitumen 70/100 with no polymer or other chemical additive, a typical bitumen used in Netherlands.

2.2 Ageing Protocols

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 subjected to the standard ageing treatments: (i) RTFO at 163 °C for 75 min (EN 12607-1), which simulates bitumen after plant mixing, production, transportation and construction and (ii) PAV at 100 °C and 20 atm for 20 h (EN 14769), which simulates the state of bitumen after 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.

2.3 Test Methods

Fourier Transform Infrared Spectrometer. The tests were performed using the Spectrum 100 FT-IR spectrometer of Perkin-Elmer. A single-beam configuration was used. The sample was scanned 20 times, with a fixed instrument resolution of 4 cm^{-1}. The wavenumbers was set to vary from 600 to 4000 cm^{-1}.

Dynamic Shear Rheometer. DSR tests were performed using the Anton Paar MCR502. The bitumen samples were tested using the parallel-plates configuration. Initially, the linear viscoelastic (LVE) strain range of bitumen samples was determined using amplitude sweep tests. The frequency sweep tests were performed at five different temperatures (0, 10, 20, 30 and 40 °C). During the tests the frequency varied in a logarithmic manner from 50 Hz to 0.01 Hz.

3 Results and Discussion

3.1 Fourier Transform Infrared Spectrometer

At least three replicate samples were tested in FTIR at each condition. Using the obtained spectra, the ageing indices (carbonyl and sulfoxide index) of each sample were calculated. The calculation methodology is described in a previous study (Van den bergh 2011). Figure 1 shows the carbonyl and sulfoxide indices (average value of three measurements).

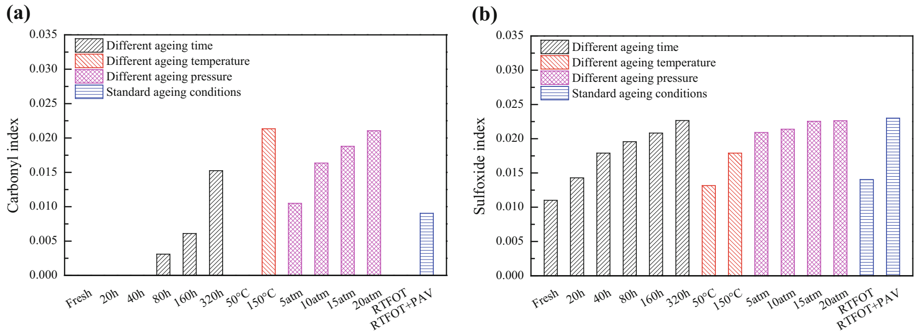

Fig. 1. Ageing indices of PEN 70/100 at different ageing conditions: (a) Carbonyl index, (b) Sulfoxide index

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 strong ageing conditions (long ageing time, high ageing temperature and pressure), whereas the sulfoxide index is stable probably due to the full consumption 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.

Moreover, comparing the results of different ageing protocols in Fig. 1, 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 and Schabron 2011).

3.2 Dynamic Shear Rheometer

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 frequency when the storage shear modulus is equal to the loss shear modulus (phase angle is 45°), explicitly the crossover frequency was used to characterize the viscoelastic fluid to solid transitory behavior. The complex shear modulus corresponding to the crossover frequency is named crossover modulus. The crossover frequency and modulus for all samples are represented in Fig. 2(a) and (b), respectively.

Figure 2(a) shows that aged bitumen has lower crossover frequency than fresh bitumen. This suggests that aged bitumen has higher molecular mass (Liu et al. 2006). In the meanwhile, lower crossover frequency denotes longer relaxation time and higher

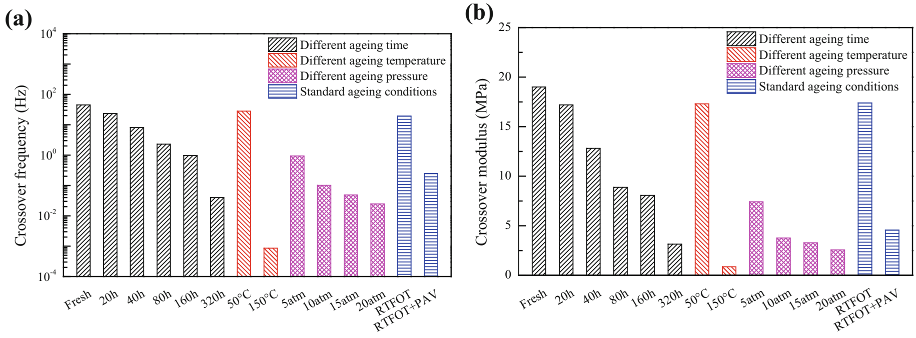

Fig. 2. Crossover frequencies and crossover modulus of bitumen at different ageing condition: (a) Crossover frequency, (b) Crossover modulus

softening point (Nivitha and Krishnan 2016). In Fig. 2(b), the crossover modulus of bitumen reduces due to ageing. This is indicative of wider molecular mass distribution and increased polydispersity of aged bitumen (Scarsella et al. 1999).

3.3 Chemo-Mechanics of Ageing

Chambon and Winter have shown that there was a good logarithmic relationship between crossover frequency and crossover modulus for the same type of polymers (Chambon and Winter 1985). The findings of this research validate this statement for studied bitumen. Figure 3(a) plots the crossover frequency against the crossover modulus of bitumen subjected to the various ageing protocols and, for the convenience of description, it is referred hereinafter as the crossover map.

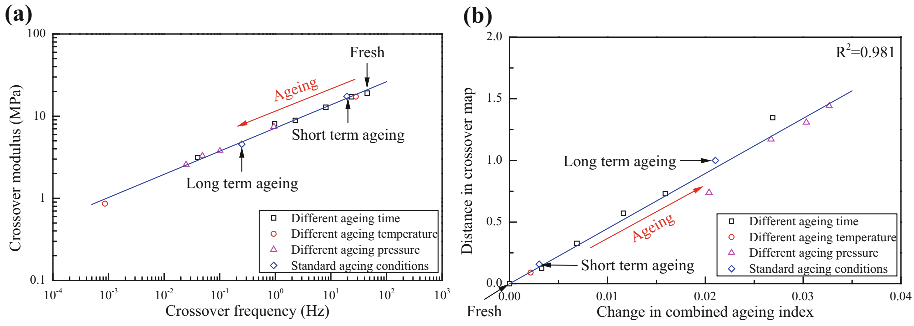

Fig. 3. Chemo-mechanics of ageing: (a) Crossover frequency vs crossover modulus of bitumen at different ageing condition, (b) Chemo-mechanical coupling of aged bitumen

In Fig. 3(a), 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). Figure 3(b) 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 methods. In another words, the results indicate that the different ageing conditions can be used interchangeably.

4 Conclusion

Given the strong relationship between the mechanical pavement response and ageing, which is a chemically-induced process, the knowledge of the evolution of the chemical 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, a series of FTIR and DSR tests were carried out to determine the changes in chemical properties and rheological response of aged bitumen. A linear relationship was found to exist between the combined ageing index and the distance in crossover map. The results suggest that different ageing conditions can yield the same ageing effect.

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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