Effect of introduction of furfural on asphalt binder ageing characteristics

Article *in* Road Materials and Pavement Design · November 2015

DOI: 10.1080/14680629.2015.1108219

Taher Abu-Lebdeh
North Carolina Agricultural and Technical Sta…

Faisal Awadallah
Birzeit University

Road Materials and Pavement Design

ISSN: 1468-0629 (Print) 2164-7402 (Online) Journal homepage: http://www.tandfonline.com/loi/trmp20

Effect of introduction of furfural on asphalt binder ageing characteristics

Ellie H. Fini, Felix Smith Buabeng, Taher Abu-Lebdeh & Faisal Awadallah

Road Materials and Pavement Design, 2015
http://dx.doi.org/10.1080/14680629.2015.1108219

Taylor & Francis
Taylor & Francis Group

Effect of introduction of furfural on asphalt binder ageing characteristics

Ellie H. Fini[a*], Felix Smith Buabeng[a], Taher Abu-Lebdeh[a] and Faisal Awadallah[a,b]

[a]*Department of Civil Engineering, North Carolina A&T State University, Greensboro, NC 27411, USA;* [b]*Department of Civil and Environmental Engineering, Birzeit University, Birzeit, Palestine*

(*Received 23 March 2015; accepted 9 October 2015*)

Asphalt oxidative ageing and excessive hardening are known causes of premature pavement cracking. Asphalt ageing occurs mainly due to the oxidation of certain functional groups in asphalt as well as the loss of the maltene phase disturbing colloidal stability and increasing micellisation concentration. This in turn can cause large non-soluble asphaltene aggregates which are typically suspended in the maltene solution and are stabilised by resin molecules to flocculate. Flocculation can cause the asphalt to become stiffer and more brittle. It should be noted that excessive hardening and brittleness of asphalt caused by oxidation during pavement production and service life increase the susceptibility of asphalt pavements to cracking. Therefore, reducing the extent of asphalt oxidation could increase pavement service life. Therefore, it is imperative to reduce/delay asphalt oxidation in asphalt binder. There have been several studies on delaying asphalt oxidation by introducing modifiers and anti-ageing additives. Furfural, an organic compound derived from a variety of agricultural by-products, has been shown to be a promising modifier for petroleum asphalt binders used in asphalt pavement. Accordingly, this paper investigates the effect of introducing furfural as an antioxidant for asphalt by evaluating the extent of oxidation ageing in asphalt specimens modified by 1%, 2% and 5% furfural. To do so, furfural was introduced to asphalt and the level of change in physiochemical and rheological properties of asphalt after specimens were exposed to short- and long-term ageing was examined. Accordingly, performance characteristics of the base asphalt were compared with those of furfural-modified asphalts using a rotational viscometer, Fourier transform infrared spectroscopy and a dynamic shear rheometer to evaluate the rheological properties of asphalt modified with furfural at different percentages. The study results showed that the addition of furfural helped reduce the extent of oxidative ageing while enhancing high-temperature performance of asphalt binder. Specifically, it was found that the 2% furfural modification had the lowest ageing index after ageing, indicating an improvement in binder oxidative ageing.

Keywords: furfural; ageing; asphalt; oxidation; pavement performance; modifier

1. Introduction

Depleting crude oil resources and the need for petroleum-based asphalt resources have led to the research for alternative ways of acquiring chemicals and bio-additives to improve asphalt properties; such additives are typically made from residues from agriculture, forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste (Malinowski & Wardzinka, 2012; Tong, Ma, & Li, 2010; Xu et al., 2011). In conjunction with such efforts, the United States Departments of Transportation (US DOT) have also promoted sustainable

*Corresponding author. Email: efini@ncat.edu

asphalt and pavement practices. Implementation of sustainable asphalt production practices such as application of warm-mix technologies reduces carbon emissions and fuel consumption during construction while reducing asphalt ageing. Oxidative ageing is the irreversible chemical reaction of atmospheric oxygen with asphalt. Oxidative ageing occurs throughout the life of an asphalt pavement – during mixing, field placement and service life (Lau, Lunsford, Glover, Davison, & Bullin, 1992). It has been reported that high temperature, accessible voids, oxygen replenishment and its diffusion rate as well as propensity of asphalt components to oxidation control the extent of oxidation ageing in asphalt (Al-Azri et al., 2006). Regardless of the source of oxidation, this phenomenon causes asphalt binder to become stiffer, more brittle and prone to distresses referred to as age hardening (Bahia & Swiertz, 2011).

Asphalt ageing is a major factor affecting the durability of asphalt pavements (Bell, 1989; Woo et al., 2007). Excessive age hardening of the asphalt binder from oxidation during construction or later during its service life has been correlated to pavement distresses (Woo et al., 2007). Specially, excessive oxidation during hot-mix asphalt production causes the resulting asphalt pavements to be susceptible to cracking. Cracked pavements allow water to percolate into the pavement structure to weaken the pavement base and hasten pavement deterioration (Bahia & Swiertz, 2011). Thus, reduction of oxidative hardening could lead to longer lasting pavements, leading to substantial savings in pavement life cycle.

While there have been several studies on the effects of introduction of various additives and modifiers to asphalt binders, the complex nature of oxidative ageing has made it difficult to alleviate the aforementioned problems (Finn, 1967; Roberts, Kandhal, Brown, Lee, & Kennedy, 1996). Therefore, there is a need for fundamental understanding of oxidative ageing mechanisms as well as the interaction between the modifier and asphalt components in the presence of oxygen at high temperature. In addition, it is important to evaluate other potential additives and modifiers in order to determine the merits of their application while conducting a comparative study. Prior research by Apeagyei (2011) and Apeagyei, Buttlar, and Dempsey (2010) showed that combinations of dilauryl thiodipropionate (DLTDP) and furfural with a catalyst were highly effective in reducing asphalt oxidative ageing. In addition, it has been shown that furfural can be used to enhance surface reactivity of rubber particles in crumb rubber-modified asphalt (Shatanawi, Biro, Geiger, & Amirkhanian, 2012). Furthermore, studies show that furfural is a promising activation agent to improve the rheological properties of asphalt binders (Memon, Boone, & Chollar, 1995, Shashidhar, Needham, & Chollar, 1995). Considering the promising role of furfural on reducing asphalt oxidative ageing, there is a need for a comprehensive physiochemical and rheological evaluation of asphalt modified with furfural.

Therefore, this paper investigates the changes in performance characteristics of a control asphalt binder (PG 64-22) modified by various percentages (1%, 2% and 5%) of furfural while examining the changes in the chemical structure of the asphalt after modification. The performance characterisation involves determination of temperature susceptibility, shear susceptibility (SS) as well as rheology ageing index via measuring viscosity; complex shear modulus and phase angle. The study of chemical structure includes determination of carbonyl, ketones and sulphoxide. The ratio of ketones to sulphoxides is highly dependent on oxygen concentration, temperature and sulfur content. Accordingly, in this paper formation of carbonyl (C=O) band at 1600 cm^{-1}, ketones (C=O) band at 1680 cm^{-1}, sulphoxide (S=O) band at 1060 cm^{-1} as well as saturated (C–C) band at 1455 cm^{-1} was studied.

2. Background

Asphalt ageing is defined as the change in physical and rheological properties of asphalt due to the changes in its chemical composition as oxygen interacts with asphalt components. Pavement damage is promoted by volatilisation of light asphalt components, oxidation during service life as well as steric hardening (Fernández-Gómez, Quintana, & Lizcano, 2013). Among these factors, oxidation and volatilisation are generally considered as the most important factors affecting ageing in asphalt paving mixtures. An asphalt binder becomes stiffer and more brittle due to oxidative ageing (Finn, 1967; Roberts et al., 1996). Therefore, asphalt physiochemical properties are altered due to oxidative ageing which negatively impacts pavement's durability, while causing economic loss due to premature pavement deterioration.

Laboratory experiments to determine the effect of modifiers and additives in increasing asphalt binder ageing resistance have been conducted by several researchers. The modified binders were subjected to short-term and long-term ageing in the laboratory; then the effects of ageing on the modified binders were evaluated through comparison of rheological properties.

Arega, Bhasin, Motamed, and Turner (2011) reported that asphalt binder undergoes reduced short-term ageing when combined with warm-mix asphalt additive. These results were consistent with the findings reported by Kim, Lee, Amirkhanian, and Jeong (2012) who showed that application of lower mixing and compaction temperature significantly reduces asphalt ageing. According to Jamshidi, Hamzah, and You (2013), reduced volatilisation and oxidation due to lower construction temperatures result in reduced binder ageing. Furthermore, studies by other researchers showed that application of crumb rubber reduces the rate of oxidative ageing during laboratory short-term ageing (Ali & Sadek, 2013; Dong & Tan, 2011; Punith, Suresha, Raju, Bose, & Veeraragavan, 2011). Yu, Feng, Zhang, and Wu (2009) studied the effect of organo-montmorillonite (OMMT) on the thermo-oxidative and ultraviolet (UV) ageing properties of asphalt. It was shown than the viscosity ageing indexes of modified asphalt were all lower than that of non-modified specimens, indicating that addition of OMMT reduces oxidative ageing of asphalt (Yu et al., 2009). Huang et al. (2010) found that addition of hydrated lime slows down the oxidative ageing process of both unmodified asphalt and poly phosphoric acid-modified asphalt binders. Studying the effect of several antioxidants on asphalt binder properties, Apeagyei (2011) showed that combinations of DLTDP and furfural with a catalyst were effective in reducing oxidative ageing.

Huang, Claine Petersen, Robertson, and Branthaver (2002) blended hydrated lime with two different control asphalts and found that hydrated lime absorbed naturally occurring oxidation catalysts, this in turn reduced asphalt's propensity for ageing. The study of introducing electronic waste (e-waste) powders to asphalt binder showed that such modifications typically increase viscosity and mixing temperatures, but there is no effect on ageing properties (Colbert & You, 2012).

In another study, the high-temperature storage stability and ageing properties of asphalts modified with diatomite powder indicated that diatomite cannot improve the thermo-oxidative ageing resistance of asphalt binder (Cong, Chen, & Chen, 2012). Wasiuddin, Fogle, Zaman, and O' Rear (2007) studied the impact of anti-strip additives on asphalt binders after it was exposed to oxidative ageing and found that anti-strip effectiveness is significantly reduced after rolling thin film oven (RTFO) and pressure ageing vessel (PAV) ageing (Wasiuddin et al., 2007).

The merits of applying agriculture and food by-products such as dried grape pomace, lignin and bio-binder were studied by several researchers (Calabi-Floody & Thenoux, 2012; Fini, Al-Qadi, Zada, & Mills-Beale (2011); Fini, Kalberer, et al., 2011) and showed that some bio-based products could be promising antioxidants. However, the level of reducing oxidation was found to be dependent on the percentage of the antioxidant used, application temperature and processing methods (Calabi-Floody & Thenoux, 2012; McCready & Williams, 2008). This paper focuses on the application of furfural as another agricultural by-product to reduce asphalt oxidation.

3. Materials and methods

This section describes materials used in this study as well as the sources of each material and its preparation method.

3.1. *Furfural*

Furfural is an organic compound derived from a variety of agricultural by-products, including corncobs, oat, wheat bran and sawdust. It is also called 2-furancarboxaldehyde, furaldehyde, 2-furanaldehyde, 2-furfuraldehyde, fural and furfurol (Win 2005). Nearly 90% of all furfural production takes place in China, South Africa and the Dominican Republic, with China producing 74% of the entire production; worldwide market for furfural is about 300,000 tons per year at approximately $1800 per ton (Ong & Sashikala, 2007).

Furfural is a colourless oily liquid which quickly turns yellow upon exposure to air. Furfural as known by the chemical formula $C_5H_4O_2$ is a heterocyclic aldehyde (Hoydonckx, Van Rhijn, Van Rhijn, De Vos, & Jacobs, 2007; Ong & Sashikala, 2007; Win, 2005). It is represented by the ring structure and spectra shown in Figure 1.

Furfural participates in the same kinds of chemical reactions as other aldehydes and aromatic compounds (Malinowski & Wardzinka, 2012). According to Apeagyei et al. (2010), aldehydes are capable of lowering oxidative ageing of various materials. They reported that aromatic phenols present in asphalt binders undergo a chemical reaction with furfural (Apeagyei et al., 2010). Further studies attribute this chemical reaction to the carbonyl group (C=O) found in aldehydes and many other organic functional groups. Studies of the Fourier transform infrared spectra of furfural produced from rice husk showed a very strong absorption around wavenumber of 1600 cm^{-1}, indicating the presence of the conjugated carbonyl (C=O) group. The presence of the aldehyde was proven by two peaks attained at 3019 cm^{-1} and 2881 cm^{-1} and C=O band at 1714.46 cm^{-1} in furfural produced from rice husk (Ong & Sashikala, 2007). Carbonyl compounds are polar and contain a dipole along the carbon–oxygen double bond. This creates attractive forces between carbonyl compounds, but these attractions are not as strong as those in hydrogen bonding. Adams and Voorhees (1921) illustrated a laboratory production of furfural from corncob, while Ong and Sashikala (2007) studied furfural synthesis from rice husks using reflux with dilute sulphuric acid. The properties of the furfural used in this study are listed in Table 1.

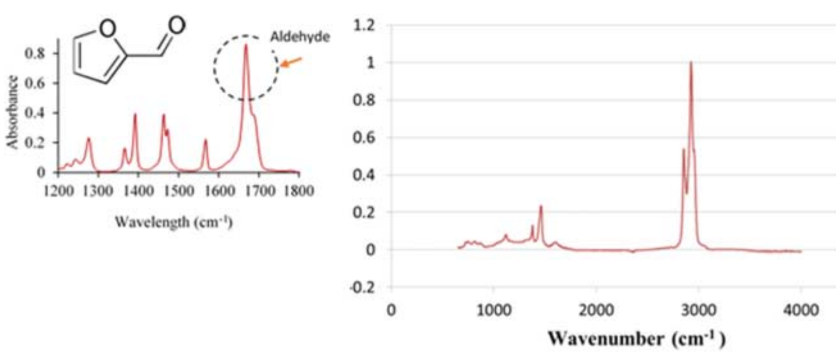

Figure 1. Furfural's (a) chemical structure and (b) asphalt spectra.

Table 1. Properties of furfural.

Physical property	Value
Molecular weight (g mol^{-1})	96.08
Boiling Point (°C)	162
Density at 25°C (g cm^{-3})	1.16

Table 2. Summary of experimental design.

No	Test	Code
1	Base binder	Control
2	Base binder + 1% furfural	FMA-1%
3	Base binder + 2% furfural	FMA-2%
4	Base binder + 5% furfural	FMA-5%

3.2. *Materials and sample preparation*

In order to investigate the effect of incorporation of furfural on the asphalt binder properties, furfural was added to 100 g of control asphalt binder. The control asphalt binder used in this study was PG64-22 provided by Asphalt Associate Inc. (Greensboro, NC, USA). To do so, furfural was blended with the base binder (PG 64-22) at 1%, 2% and 5% by weight of the base binder. The binder was mixed thoroughly with furfural at a shear rate of 800 rpm for 30 min, while the temperature was kept constant at 135°C. The furfural (2-furaldehyde) used in this study was provided by Sigma-Aldrich Co. LLC (St. Louis, MO, USA). Table 2 shows the modified specimens and their acronyms. Each of the modified asphalts was then exposed to two different ageing scenarios to simulate short- and long-term ageing; short-term ageing was conducted using a RTFO and long-term ageing was conducted utilising PAV. The extent of change in rheological and chemical properties of each specimen before and after each ageing process was studied.

3.3. *Ageing procedure*

Ageing of the binders was performed using RTFO according to ASTM D2872. The RTFO test was carried out at a temperature of 163°C for a period of 85 min to simulate the short-term ageing that occurs in asphalt binder during mixing and compaction (Bahia, Hislop, Zhai, & Rangel, 1998).

The PAV simulates in-service ageing of asphalt binder that may occur during seven to ten years (Bahia & Anderson, 1995). In this test, the asphalt binder is exposed to high pressure and temperature for 20 h to simulate the effect of long-term oxidative ageing (PAV) according to ASTM D6521. In this study, 50 g of each RTFO-aged sample is placed in the PAV at 2.1 MPa air pressure at 100°C for 20 h. At the end of the ageing period, each sample was scraped into different containers and placed in a vacuum oven at a temperature of 170°C for 30 min to remove entrapped air from the samples.

3.4. *Viscosity measurements*

A series of viscosity measurements were conducted on all three modified binders. Shearing was applied using spindle SC4-27 at a speed of 5, 10, 20, 25, 50 and 100 rpm. Viscosity measurement was conducted using Brookfield Viscometer (ASTM D4402). In this test, viscosity, torque and shear stress are determined while applying a rotational shear on the specimens. To prepare specimens, 10.5 g of each sample was poured into aluminium chambers. The chambers were then placed into a preheated thermosel to reach thermal equilibrium. The thermosel was preheated at its designated temperature for at least 20 min. Samples and the spindle were preheated in an oven for 30 min before being placed into the aluminium chamber in the thermosel. After loading the sample, an additional 20 min waiting time was used to ensure thermal equilibrium. Three replicates were used for each test and the average of the three values was recorded as the viscosity at the specified temperature and speed.

3.5. *Temperature susceptibility*

Temperature susceptibility is a measure of how fast the properties of the binder change with temperature (Claudy, Létoffé, Martin, & Planche, 1998). Thus, if a sample of binder has a high susceptibility to temperature, its viscosity changes rapidly as the temperature changes. Asphalt binders with high-temperature susceptibility are not desirable since they are prone to thermal and UV oxidation (Firoozifar, Foroutan, & Foroutan, 2011). The following equation has been commonly used to calculate the viscosity–temperature susceptibility (VTS) (Rasmussen, Lytton, & Chang, 2002).

$$\mathrm{VTS} = \frac{\log\log(\eta T_2) - \log\log(\eta T_1)}{\log(T_2) - \log(T_1)}, \tag{1}$$

where T_1 and T_2 are the temperatures of the binder at known points (in degrees Rankine) and ηT_1 and ηT_2 are the respective viscosities of the binder at known points (cP).

The magnitude of the VTS is directly proportional to the temperature susceptibility of the binder (Rasmussen et al., 2002). In one study, the VTS values were reported to range from -3.35 to -3.84 (US DOT 2011), which is almost consistent with values of -3.36 to -3.98 reported by (Puzinauskas, 1967; Rasmussen et al., 2002).

3.6. *Shear susceptibility*

Shear susceptibility is the rate of change in viscosity with the shear rate (Roberts et al., 1996). The SS, also known as the shear index, is determined by calculating the slope of the line formed by a log of shear rate versus the log viscosity graph by using the following equation (Raouf & Williams 2010). Shear susceptibility as calculated in Equation (2) is a commonly used indicator which is shown to be correlated with the extent of ageing (Fini, Oldham, & Abu-Lebdeh, 2013).

$$\mathrm{SS} = \frac{\log(\text{Viscosity})}{\log(\text{Shear rate})}. \tag{2}$$

3.7. *Dynamic shear rheometer (DSR) characterisation*

The DSR is used to evaluate the elastic and viscous behaviour of asphalt (it should be noted that the test method employs only a small strain measurement within the linear viscoelastic region of the binder) through tracking the shear stress and shear strain while applying a specified oscillation rate; an oscillation rate of 10 rad s^{-1} is typically used to represent the shearing action caused by a traffic speed of 90 km/h. Unaged and aged binder samples were tested in a DSR in accordance with the ASTM D7175 procedure. The complex shear modulus, G^*, and the phase angle, δ, at various temperatures and loading frequencies were measured. The complex modulus is a measure of total resistance of the binder to deformation when repeatedly sheared, and the phase angle is the lag between the applied shear stress and the resulting shear strain. Superpave uses the parameter $G^*/\sin\delta$ as a measure of resistance to rutting at high pavement temperatures. At high temperatures, rutting resistance increases as $G^*/\sin\delta$ increases. The asphalt binder with the highest $G^*/\sin\delta$ should have the most resistance to rutting.

3.8. *Ageing index*

To quantify the effect of ageing on viscosity, an ageing index was calculated based on the change in the viscosity before and after ageing. The viscosity ageing index (VAI) is defined as the ratio of the change in viscosity due to ageing divided by unaged viscosity (Zhang, Yu, & Wu, 2012).

$$\mathrm{VAI} = \frac{\text{Aged viscosity value} - \text{Unaged viscosity value}}{\text{Unaged viscosity value}} \times 100. \tag{3}$$

Furthermore, another ageing index was calculated based on the change in the complex modulus and phase angle for aged and unaged samples. The data were collected at 64°C and 10 rad s^{-1}, and the RAI is defined using Equation (5).

$$\mathrm{RAI} = \frac{G^*_{\mathrm{Aged}}}{G^*_{\mathrm{Unaged}}} \exp(\delta_{\mathrm{Aged}} - \delta_{\mathrm{Unaged}}), \tag{4}$$

where G^*_{Unaged} and G^*_{Aged} are the complex modulus of the samples at unaged and aged statues, respectively, and δ_{Unaged} and δ_{Aged} are phase angles of the samples before and after ageing.

3.9. *Fourier transform infrared spectroscopy*

Fourier transform infrared spectroscopy (FTIR) is an important technique used to identify the presence of certain functional groups in a medium. Functional groups are responsible for different properties of a compound. In this study, the Thermo Scientific Nicolet iS10 set-up was used to record the FTIR spectra. The set-up measures absorbance versus wavelength (cm^{-1}) for each sample tested. The apparent peaks that develop at each wavelength represent the absorbed frequencies corresponding to different functional groups in the sample (Bowers, 2013).

The carbonyl (C=O) bond found at the 1600 cm^{-1} peak and the sulphoxide (S–O) band found at the 1030 cm^{-1} peak are typically tracked in FTIR spectra analysis with respect to oxidative ageing. It has been reported that the carbonyl (C=O) bond shows a consistent increase during oxidation in asphalt binder. The increase is due to the presence of oxygen causing maltenes to become asphaltenes in asphalt binder (Liu, Ferry, Davison, Glover, & Bullin, 1998; Lu and Isacsson, 2002). Within a binder of the same source and grade, Negulescu et al. (2006) found that the saturated C–C bond at approximately 1455 cm^{-1} was relatively constant before and after ageing. A chemical ageing index (CAI), which is the ratio of the area under the carbonyl (C=O) peak at 1600 cm^{-1} divided by the area under the saturated C–C band at 1455 cm^{-1} (Bowers, Huang, & Shu, 2014; Bowers, Huang, Shu, & Miller, 2014; Jia, Huang, Bowers, & Zhao, 2014; Negulescu et al., 2006), was developed as shown in Equation (5).

$$\mathrm{CAI} = \frac{\text{Area of carbonyl (C = O) band} \sim 1600\,\mathrm{cm}^{-1}}{\text{Area of saturated C} - \text{C stretch band at} \sim 1455\ \mathrm{cm}^{-1}} \times 100. \tag{5}$$

An increase in the CAI corresponds to an increase in the area of the carbonyl group, which indicates an increase in oxidation. An increase in oxidation is correlated to an increase in viscosity (Huang & Grimes, 2010).

4. Experimental results and data analysis

4.1. *Viscosity measurement*

The viscosity results for all three modified samples are shown in Figure 2. It can be observed that the introduction of furfural leads to the increase in viscosity of the control asphalt binder, except for 5% furfural which led to the reduction of viscosity. The lowest increment in viscosity value compared to the control asphalt was found to be 6% at 135°C which occurred with the addition of 2% furfural to the control asphalt. This was when viscosity reduction due to the addition of 5% furfural was 10% compared to the control binder. The largest reduction in viscosity value with the addition of 5% furfural was about 11% at 105°C.

As mentioned earlier, to compare the susceptibility of the modified samples to ageing, each specimen was first aged using the RTFO ageing method (ASTM D2872) and then PAV aged (ASTM D6521). The viscosity of each specimen was then measured after each ageing phase and compared with those of unaged specimens. The results of viscosity measurement for all RTFO- and PAV-aged samples are given in Figures 3 and 4, respectively.

As it can be seen for all RTFO-aged samples, viscosity values increased in comparison to the unaged specimens. It can be further observed that all modified samples had viscosity values

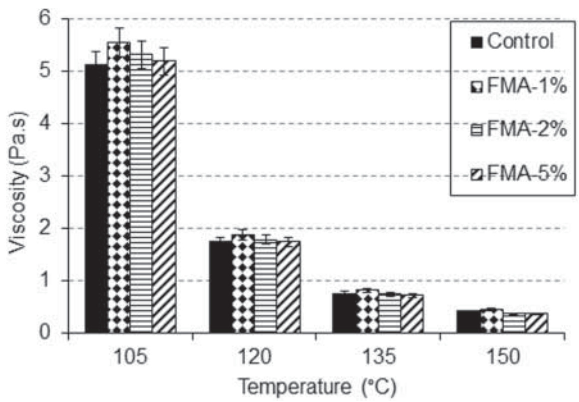

Figure 2. Viscosity results for all unaged samples.

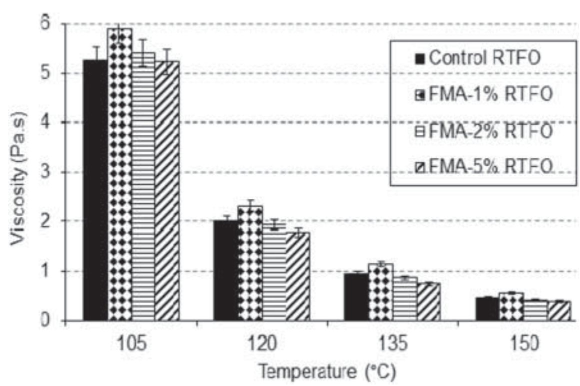

Figure 3. Viscosity results for all RTFO-aged samples.

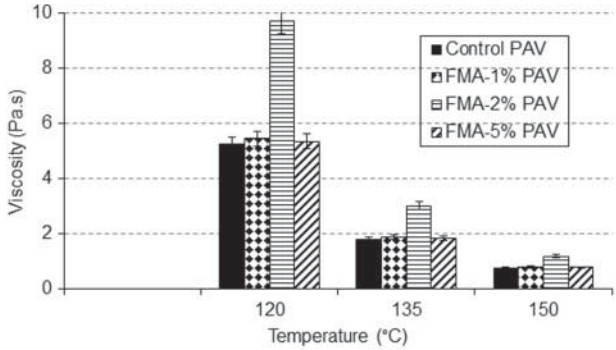

Figure 4. Viscosity results for all PAV-aged samples.

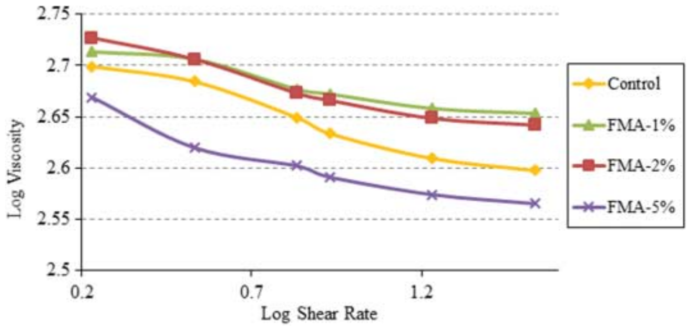

Figure 5. Shear susceptibility for all unaged samples at 135°C.

greater than that of the aged control asphalt. The only exception was 2% and 5% furfural RTFO-aged samples which had slightly lower values than that of the RTFO-aged control binder. This trend was seen at 135°C and 150°C.

Furthermore, comparing PAV-aged control asphalt with PAV-aged furfural-modified samples, it can be seen that all modified samples showed increase in viscosity values (Figure 4). The only exception was 2% and 5% furfural PAV-aged samples which had slightly lower values than that of the PAV-aged control binder at 135°C and 150°C. This is similar to the trend observed with RTFO-aged samples. The largest reduction in viscosity value with the addition of 5% furfural was around 4% which was observed at 150°C. In addition, 5% furfural-modified asphalt also showed a small increase in viscosity of 1% and 2.5% at 105°C and 120°C, respectively. Overall, with the increase in the furfural percentage above 1% in the control asphalt, the rotational viscosity decreased after RTFO ageing. It was also observed that the difference between the viscosity values of the furfural-modified binders becomes less significant at high temperatures.

To investigate the SS of each binder, the SS values were calculated using Equation (2) before and after ageing. The results were plotted for all furfural-modified samples and control binder at 120°C, 135°C and 150°C in logarithmic scale. Figures 5 and 6 show the SS plots for unaged and PAV-aged samples at 135°C, respectively. The SS of the samples was higher at 120°C than at 135°C and 150°C. Also, SS values were higher for the aged samples than the unaged at all temperatures. In addition, the 5% furfural-modified sample displayed less susceptibility to shear than all other samples. This was more evident when comparing samples before ageing and after long-term ageing (Figure 5), in which asphalt containing 5% furfural showed a significantly lower

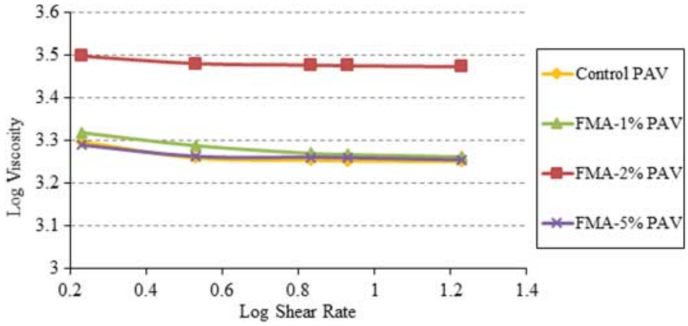

Figure 6. Shear susceptibility for PAV-aged samples at 135°C.

susceptibility to shear than those containing 1% and 2% furfural, respectively. The reduction of SS could be attributed to interactions between furfural and accessible oxygen within the matrix.

Shear susceptibility is a commonly used indicator that is shown to be correlated with the extent of ageing (Fini et al., 2013). As oxidation occurs, polarity of the asphaltene molecules increases, while resin and saturates convert to asphaltene promoting their aggregation and flocculation. The presence of such flocculation can lead to an increase in the SS of the matrix. It should be noted that Petersen, Barbour, and Dorrence (1974) have documented the relative affinity for oxidation of asphalt components to be the highest for asphaltenes (40%), followed by polar aromatics (32%), with naphthene aromatics and saturates showing the least reactivity of 7% and 1% to oxidation, respectively). The increased amount of asphaltene in oxidised asphalt compared to virgin binder could further increase the propensity of asphaltene for micellisation. At high micellisation concentration, asphaltene in the solution will self-associate, leading to flocculation (Priyanto, Mansoori, & Suwono, 2001). This in turn separates the asphalt matrix to two distinguishable phases, giving rise to asphalt susceptibility to the changes in shear rate.

However, furfural having more affinity for oxidation than asphalt components as well as chemical reactions among aromatic phenols of asphalt binders and furfural (Apeagyei et al., 2010) could reduce the oxidation rate of asphaltene and resin inside asphaltene micelles, reducing their affinity for flocculation. These findings are shown to be in agreement with previous studies where authors reported that introduction of certain bio-oils to asphalt binder could change the oxidation susceptibility of the base asphalt (Fini, 2015).

Tables 3 and 4 present the modified sample results for SS, VTS and viscosity measurements at various rotational speeds (5, 10, 20 and 25) for specimens containing various furfural percentages (1%, 2% and 5%). Measurements were conducted at temperatures ranging from 105°C to 150°C. Table 4 shows similar data for PAV-aged samples. Both tables show that viscosity decreases with increasing temperature for all samples at the same shear rate.

From the viscosity temperature susceptibility values in Table 4, it was observed that increasing shear rate led to a decrease in VTS values for the control and furfural-modified samples. Furthermore, the viscosity temperature susceptibility values for aged specimens were lower for modified samples than the control samples at each shear rate analysed, except for 5% furfural. This demonstrates that the furfural-modified samples are less susceptible to temperature than the control asphalt after ageing, with the 2% furfural sample showing the least susceptibility. This is further demonstrated in Figure 7 at 5 rpm.

4.2. *Dynamic rheological characterisation*

Complex shear modulus master curves were plotted from DSR test data. As shown in Figure 8, the G^* of all furfural-modified binders were increased when compared to the control asphalt

Table 3. Temperature effects on various furfural-modified asphalt for unaged samples.

Blend	*T* (°C)	*T* (°R)	Shear rate (rpm)/log Viscosity (cP)				SS
			5RPM	10RPM	20RPM	25RPM	
Control	105	680.7	1.47	2.95	5.92	7.41	
	120	707.7	1.66	3.35	6.76	8.46	– 0.055
	135	734.7	1.85	3.73	7.55	9.49	– 0.085
	150	761.7	2.06	4.15	8.39	10.59	– 0.099
		VTS	– 3.00	– 2.98	– 3.07	– 3.14	
FMA-1%	105	680.7	1.44	2.89	5.79	7.24	
	120	707.7	1.63	3.30	6.61	8.27	– 0.030
	135	734.7	1.84	3.70	7.47	9.36	– 0.051
	150	761.7	2.09	4.20	8.42	10.56	– 0.037
		VTS	– 3.30	– 3.27	– 3.29	– 3.31	
FMA-2%	105	680.7	1.43	2.88	5.78	7.23	
	120	707.7	1.63	3.30	6.63	8.30	– 0.050
	135	734.7	1.83	3.70	7.48	9.38	– 0.069
	150	761.7	2.06	4.12	8.34	10.50	– 0.067
		VTS	– 3.24	– 3.13	– 3.22	– 3.27	
FMA-5%	105	680.7	1.49	3.00	6.01	7.52	
	120	707.7	1.67	3.39	6.84	8.57	– 0.060
	135	734.7	1.87	3.82	7.69	9.65	– 0.077
	150	761.7	2.09	4.20	8.42	10.77	– 0.090
		VTS	– 2.97	– 2.96	– 2.97	– 3.18	

Table 4. Temperature effects on various furfural-modified asphalt for PAV-aged samples.

Blend	*T* (°C)	*T* (°R)	Shear rate (rpm)/log Viscosity (cP)				SS
			5RPM	10RPM	20RPM	25RPM	
Control	105	680.7	1.16	2.33	–	–	
	120	707.7	1.34	2.69	5.38	6.72	
	135	734.7	1.52	3.07	6.15	7.69	– 0.031
	150	761.7	1.71	3.45	6.94	8.71	– 0.053
		VTS	– 3.40	– 3.25	–	–	
FMA-1% PAV	105	680.7	1.16	2.32	–	–	
	120	707.7	1.33	2.67	5.35	6.70	
	135	734.7	1.51	3.04	6.12	7.65	– 0.044
	150	761.7	1.69	3.40	6.91	8.66	– 0.070
		VTS	– 3.36	– 3.17	–	–	
FMA-2% PAV	105	680.7	1.14	–	–	–	
	120	707.7	1.25	2.51	5.02	6.27	
	135	734.7	1.43	2.87	5.75	7.19	– 0.024
	150	761.7	1.60	3.25	6.52	8.18	– 0.054
		VTS	– 3.01	–	–	–	
FMA-5% PAV	105	680.7	1.16	2.33	–	–	
	120	707.7	1.34	2.68	5.37	6.71	
	135	734.7	1.52	3.06	6.13	7.67	– 0.025
	150	761.7	1.72	3.46	6.94	8.70	– 0.037
		VTS	– 3.47	– 3.29	–	–	

binder. At lower frequency, it was observed that 2% furfural-modified binder showed higher G^* compared to all other samples. This observation was even more evident after PAV ageing (Figure 9).

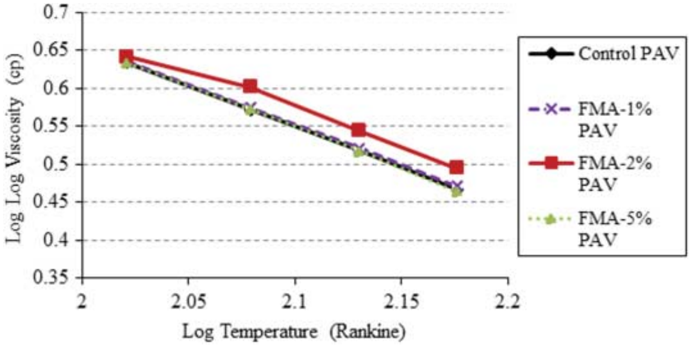

Figure 7. Viscosity versus temperature for all PAV-aged samples.

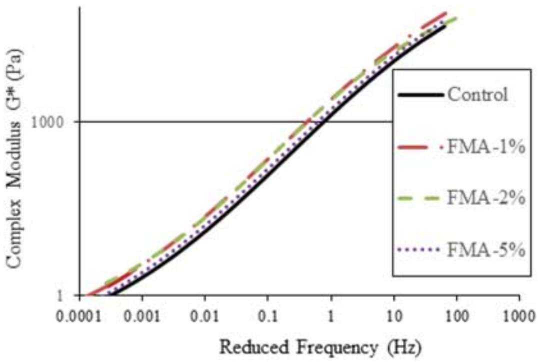

Figure 8. Complex shear modulus master curves for unaged samples at 64°C.

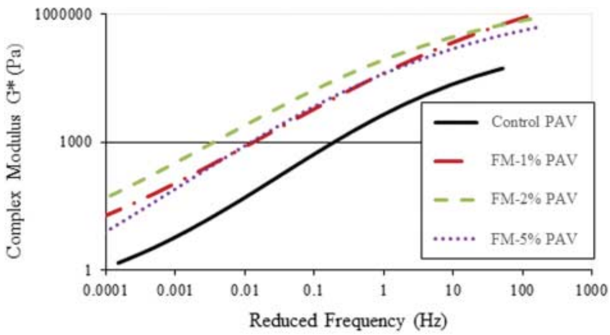

Figure 9. Complex shear modulus master curves for PAV-aged samples at 64°C.

Figure 9 shows the complex shear modulus master curve plots after PAV ageing. It is observed that all furfural-modified binders had higher *G** values compared to the control asphalt binder. At low frequency, 2% furfural performed significantly better by showing higher *G** compared to the control. This indicates better resistance to deformation at low frequency which would be equivalent to traffic loading at high temperature and slow traffic. This in turn could indicate better rutting resistance at highway intersections at which vehicles slow down and typically pavements are more susceptible to rutting at such slow traffic.

Studying the phase angle versus complex modulus diagram at 64°C for each of the specimens, it can be observed that at lower frequency furfural-modified samples showed lower phase angle compared to the control asphalt (Figure 10); however, the difference was insignificant. At the same complex modulus, 1% and 2% furfural appear to show the least phase angle. This trend indicates less time delay between stress and strain response, indicating more elastic behaviour. As it can be seen in Figure 10, 1% furfural had the lowest phase angle and the highest complex modulus among all specimens at frequencies below 1 Hz, while it shows behaviour similar to the control asphalt at higher frequencies. This effect is further illustrated in Figure 10 which indicates that furfural-modified samples could have better rutting resistance than control asphalt.

4.2.1. *Rutting resistance*

To compare various furfural-modified binders in terms of their rutting resistance, $G^*/\sin\delta$ was calculated for aged specimens and plotted in Figure 11. Superpave specification recommends a lower limit of 2200 Pa for $G^*/\sin\delta$ to ensure adequate resistance to rutting is achieved. This in turn indicates that having a higher $G^*/\sin\delta$ is advantageous to improve rutting resistance.

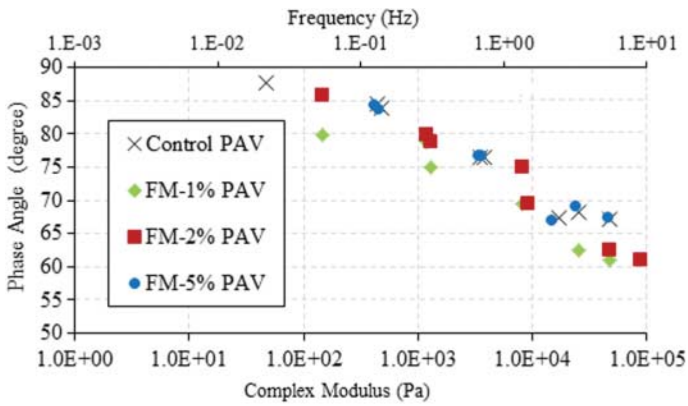

Figure 10. Complex shear modulus versus phase angle for aged samples.

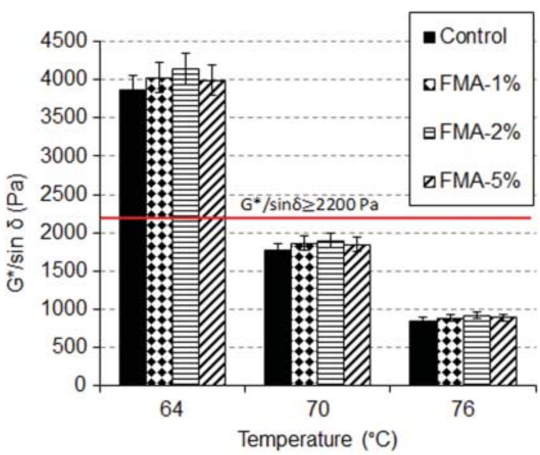

Figure 11. $G^*/\sin\delta$ of RTFO aged samples at 64°C, 70°C and 76°C (at 1.67 Hz).

Figure 11 illustrates the $G^*/\sin\delta$ for RFTO-aged samples at 64°C, 70°C and 76°C. It is shown that with the addition of furfural into asphalt binder, the $G^*/\sin\delta$ increases. Additionally, it can be seen that $G^*/\sin\delta$ for all furfural-modified samples were higher than that of control asphalt, indicating potential improvement in rutting resistance. Furthermore, the specimen containing 2% furfural had the highest $G^*/\sin\delta$ across the three temperatures. It should be noted that all furfural-modified binders meet the specification limit at 64°C for which the control binder is graded. However, they all failed at higher temperatures of 70°C and 76°C. This indicates that even though rutting resistance is improved due to the introduction of furfural, adding furfural up to 5% percent was not adequate to extend the binder grade by a full grade to become 70°C from that of control binder (64°C). Further study of higher percentages of furfural modification could provide insights on the possibility of extending the grade. Such study should be followed by comprehensive low temperature characterisation to ensure that furfural modification will not compromise low temperature properties of base asphalt.

4.3. *Ageing index*

4.3.1. *Viscosity ageing index*

To further study ageing susceptibility of each modified specimen, VAI was calculated and plotted for all samples at three different temperatures as shown in Figure 12. From the results, it appears that the largest VAI was observed for the 5% furfural-modified binder at 105°C and 135°C, indicating the highest susceptibility to ageing. Overall, the 2% furfural-modified binder showed the least VAI values at the temperature range incorporated in this study. This in turn indicates that asphalt modified with 2% furfural would have the least susceptibility to ageing. Accordingly, the VAI of 2% furfural-modified binder was reduced by 23%, 18% and 35% at 120°C, 135°C and 150°C, respectively, compared to that of control asphalt.

4.3.2. *Rheological ageing index*

Rheology ageing index was calculated and plotted for all samples at 64°C and 1.67 Hz (Figure 13) using Equation (4). The largest RAI value was observed for the control followed by FMA-2%, FMA-5% and FMA-1% after RTFO ageing. As shown in Figure 13, the RAI values of FMA-1%, FMA-2% and FMA-5% reduced by 63%, 56% and 59%, respectively, compared to the control. After PAV ageing, the RAI values for all tested samples had almost the same value except FMA-2%, which showed a significantly lower value. As it can be seen, the ageing indexes after short-term ageing is much more significant that those after long-term ageing; this could be attributed to the loss of majority of volatiles during short-term ageing.

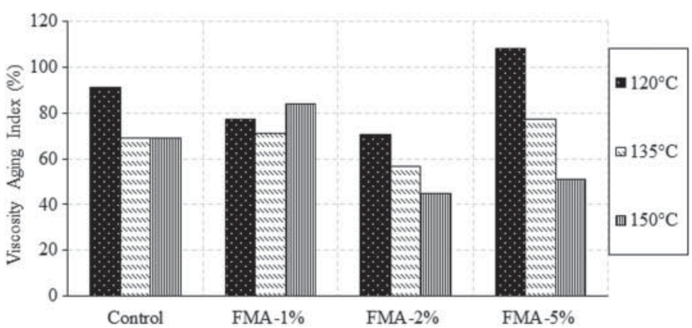

Figure 12. Viscosity ageing index for different samples at different temperatures.

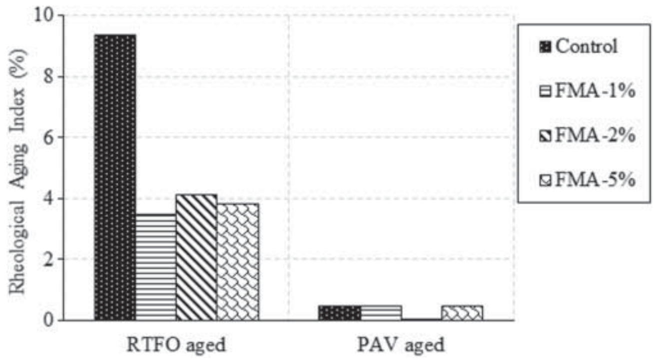

Figure 13. Rheological ageing index results for samples at 64°C at 1.67 Hz.

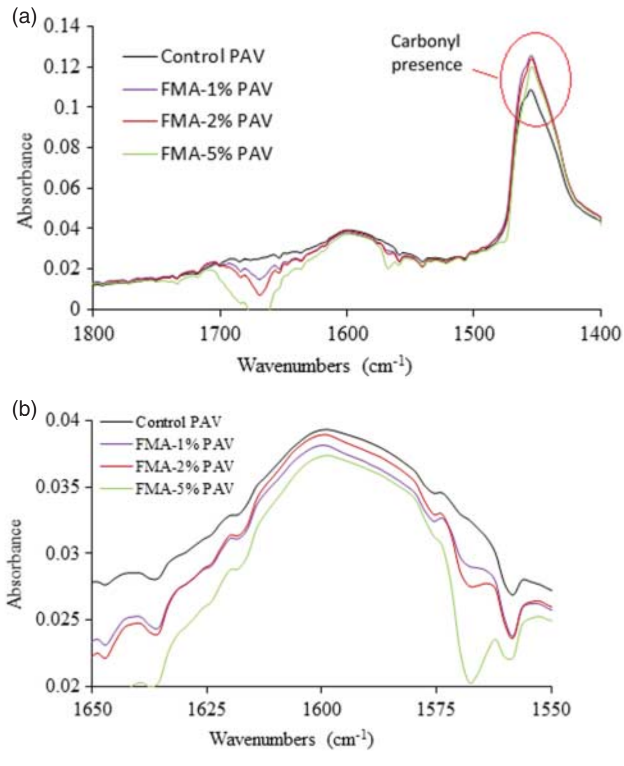

Figure 14. FTIR evaluation of samples (a) showing carbonyl presence and (b) comparing peak intensities in the carbonyl region.

4.3.3. *Chemical ageing index*

The FTIR results show that the introduction of furfural can improve the ageing susceptibility of the base binder. This is evidenced by the lower carbonyl area formation in furfural-modified specimens compared to those of non-modified specimens. It has been reported that the carbonyl (C=O) bond shows a consistent increase during oxidation in the asphalt binder. The increase is due to the presence of oxygen causing maltenes to become asphaltenes in the asphalt

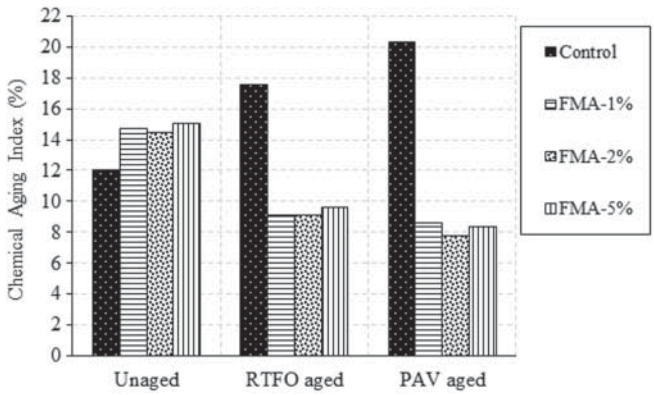

Figure 15. Chemical ageing index results for both modified and non-modified samples.

binder (Liu et al., 1998; Lu & Isacsson, 2002). Thus, appearance of the C=O bond in the FTIR spectra can be used as a reliable indicator to compare oxidative ageing behaviour in modified and non-modified asphalts. From Figure 14(a),(b), the extent of formation of carbonyl bond in modified samples was lower than that in the control binder. The carbonyl peak intensity was found to be the lowest for FMA-5%, while the control binder (without furfural) showed the highest peak intensity, representing the most carbonyl formation at the same ageing condition.

The CAI was calculated and plotted using Equation (6) to further demonstrate the oxidative ageing reduction effect of furfural. The index measures the area beneath the carbonyl (C=O) group at 1600 cm^{-1} divided by the area beneath the saturated C–C band at 1455 cm^{-1} (Bowers, Huang, & Shu, 2014; Bowers, Huang, Shu, & Miller, 2014; Jia et al., 2014; Negulescu et al., 2006). Oxidative ageing increases the carbonyl band, while the saturated C–C band remains relatively unchanged and unaffected during ageing (Bowers, 2013). Figure 15 shows the CAI plot for all samples under different ageing processes. At the same ageing condition, the CAI of the control binder was found to be higher than that of furfural-modified samples. As it can be seen in Figure 15, after RTFO ageing, furfural-modified binder shows 38% reduction in ageing index for FMA-1%, followed by 37% for FMA-2% and 36% for FMA-5%.

After PAV ageing, CAI of FMA-1%, FMA-2% and FMA-5% decreased by 42%, 46% and 44%, respectively. These results indicate that furfural-modified samples are less susceptible to oxidative ageing than the control, with FMA-2% showing the least susceptibility.

5. Conclusion

This paper evaluates the effect of introduction of furfural on the rheological characteristics and chemical structure of an asphalt binder. This paper presents the result of a comparative study of an asphalt binder modified with three different percentages of furfural (1%, 2% and 5%) before and after they are exposed to oxidative ageing. This was done through the application of several rheological laboratory characterisation tests, resulting in the following conclusions:

- Study of viscosity results for aged specimens showed that ageing leads to continuous increase in viscosity value. However, the extent of increase in viscosity was found to be less for modified specimens, with FMA-5% showing the least viscosity value among all samples.

- The VTS values show that the furfural-modified samples have lower slopes than the control binder, indicating that the temperature susceptibility of the binder was reduced due to modification with furfural.
- The SS of furfural-modified samples was found to be significantly lower than the control asphalt after ageing. This can be attributed to the reduced extent of flocculation due to the presence of furfural. Due to furfural having more affinity for oxidation than asphalt components as well as the chemical reactions among aromatic phenols of asphalt binders and furfural, the presence of furfural could lead to the reduction of asphaltene and resin oxidation within the micelles structures and reduce the extent of their flocculation.
- Study of VAI showed that specimens containing 2% furfural are most resistant to ageing. The VAI value for FMA-2% was found to be still 18% lower than that of control asphalt even after being exposed to long-term ageing.
- The RAI after RTFO ageing showed that furfural-modified samples were more resistant to ageing. The RAI decreased by 63% for FMA-1%, 56% for FMA-2% and 59% for FMA-5% after RTFO ageing. After PAV ageing, RAI values of all tested samples were almost the same except for FMA-2%, which was 49% lower than the control asphalt, indicating that FMA-2% shows the least susceptibility to oxidative ageing even after long-term ageing.
- Study of chemical functional groups, specifically the formation of carbonyl (C=O) at 1600 cm^{-1}, as well as calculation of the CAI showed that furfural-modified samples have better resistance to oxidative ageing. After PAV ageing, CAI of FMA-1%, FMA-2% and FMA-5% decreased by 42%, 46% and 44%, respectively. It should be noted that FMA-2% showed the least susceptibility to oxidative ageing after PAV ageing.

Acknowledgement

The authors would like to acknowledge the invaluable assistance provided by Daniel Oldham of North Carolina A&T State University.

Disclosure statement

The contents of this paper reflect the view of the authors, who are responsible for the facts and the accuracy of the data presented. This paper does not constitute a standard, specification or regulation.

Funding

This research is sponsored by the National Science Foundation [Award No: 1150695].

References

Adams, R., & Voorhees, V. (1921). Furfural. *Organic Syntheses*, 49. doi:10.15227/orgsyn.001.0049

Al-Azri, N. A., Jung, S. H., Lunsford, K. M., Ferry, A., Bullin, J. A., Davison, R. R., & Glover, C. J. (2006). Binder oxidative aging in Texas pavements: Hardening rates, hardening susceptibilities, and impact of pavement depth. *Transportation Research Record: Journal of the Transportation Research Board*, *1962*(1), 12–20.

Ali, B., & Sadek, M. (2013). Experimental analysis of the influence of crumb rubber addition on the short-term aging of Syrian asphalt. *Arabian Journal of Geosciences*, *6*(1), 85–90.

Apeagyei, A. K. (2011). Laboratory evaluation of antioxidants for asphalt binders. *Construction and Building Materials*, *25*(1), 47–53.

Apeagyei, A. K., Buttlar, W. G., & Dempsey, B. J. (2010). *Antioxidant treatment of asphalt binders*. Google Patents.

Arega, Z., Bhasin, A., Motamed, A., & Turner, F. (2011). Influence of warm-mix additives and reduced aging on the rheology of asphalt binders with different natural wax contents. *Journal of Materials in Civil Engineering*, *23*(10), 1453–1459.

ASTM. D2872. (2005). *Standard test method for effect of heat and air on a moving film of asphalt (rolling thin-film oven test)*. West Conshohocken, PA: Author.

ASTM. D6521. (2008). *Standard practice for accelerated aging of asphalt binder using a pressurized aging vessel (PAV)*. West Conshohocken, PA: Author.

ASTM. D7175. (2008). *Standard test method for determining the rheological properties of asphalt binder using a dynamic shear rheometer*. West Conshohocken, PA: Author. doi:10.1520/D7175-08.

ASTM. D4402. (2013). *Standard test method for viscosity determination of asphalt at elevated temperatures using a rotational viscometer*. West Conshohocken, PA: Author.

Bahia, H. U., & Anderson, D. A. (1995). The pressure aging vessel (PAV): A test to simulate rheological changes due to field aging. *ASTM Special Technical Publication*, *1241*, 67–88.

Bahia, H. U., Hislop, W. P., Zhai, H., & Rangel, A. (1998). Classification of asphalt binders into simple and complex binders. *Journal of the Association of Asphalt Paving Technologists*, *67*, 1–41.

Bahia, H. U., & Swiertz, D. (2011). Design system for HMA containing a high percentage of RAS material. Retrieved October 26, 2015, from http://rmrc.wisc.edu/wp-content/uploads/2012/12/Bahia-No.-66-Design-System-for-HMA-Containing-a-High-Percentage-of-RAS-Material-.pdf.

Bell, C. A. (1989). Summary report on aging of asphalt-aggregate systems. SR-OSU-A-003A-89-2. Retrieved from https://ntrl.ntis.gov/NTRL/dashboard/searchResults/titleDetail/PB91122523.xhtml.

Bowers, B. F. (2013). *Investigation of asphalt pavement mixture blending utilizing analytical chemistry techniques* (Ph.D. dissertation). University of Tennessee, Knoxville.

Bowers, B. F., Huang, B., & Shu, X. (2014). Refining laboratory procedure for artificial RAP: A comparative study. *Construction and Building Materials*, *52*, 385–390.

Bowers, B. F., Huang, B., Shu, X., & Miller, B. C. (2014). Investigation of reclaimed asphalt pavement blending efficiency through GPC and FTIR. *Construction and Building Materials*, *50*, 517–523.

Calabi-Floody, A., & Thenoux, G. (2012). Controlling asphalt aging by inclusion of byproducts from red wine industry. *Construction and Building Materials*, *28*(1), 616–623.

Claudy, P. M., Létoffé, J. M., Martin, D., & Planche, J. P. (1998). Thermal behavior of asphalt cements. *Thermochimica Acta*, *324*(1), 203–213.

Colbert, B. W., & You, Z. (2012). Properties of Modified Asphalt Binders Blended with Electronic Waste Powders. *Journal of Materials in Civil Engineering*, *24*(10), 1261–1267.

Cong, P., Chen, S., & Chen, H. (2012). Effects of diatomite on the properties of asphalt binder. *Construction and Building Materials*, *30*, 495–499.

Dong, Y., & Tan, Yi. (2011). Mix design and performance of crumb rubber modified asphalt SMA. *Geotechnical Special Publication*, *212*, 78–86.

Fernández-Gómez, W. D., Quintana, H. R., & Lizcano, F. R. (2013). A review of asphalt and asphalt mixture aging. *Ingeniería e Investigación*, *33*(1), 5–12.

Fini, E. (2015). *Susceptibility of bio-modified asphalts*. Paper presented at the International Airfireld and Highway Pavemnets Conference, Miami, FL, June 7–9, 2015.

Fini, E., Al-Qadi, I. Y., Zada, B., & Mills-Beale, J. (2011). Partial replacement of asphalt binder with bio-binder: characterisation and modification. *International Journal of Pavement Engineering*, *6*(13), 515–522. doi:10.1080/10298436.2011.596937

Fini, E. H., Kalberer, E. W., Shahbazi, A., Basti, M., You, Z., Ozer, H., & Aurangzeb, Q. (2011). Chemical characterization of biobinder from swine manure: Sustainable modifier for asphalt binder. *Journal of Materials in Civil Engineering*, *23*(11), 1506–1513.

Fini, E., Oldham, D., & Abu-Lebdeh, T. (2013). Synthesis and characterization of biomodified rubber asphalt: Sustainable waste management solution for scrap tire and swine manure. *ASCE Journal of Environmental Engineering*, *139*(12), 1454–1461.

Finn, F. N. (1967). *Factors involved in the design of asphaltic pavement surfaces* (Report No. 39). Washington, DC: NCHRP.

Firoozifar, S. H., Foroutan, S., & Foroutan, S. (2011). The effect of asphaltene on thermal properties of bitumen. *Chemical Engineering Research and Design*, *89*(10), 2044–2048.

Hoydonckx, H. E., Van Rhijn, W. M., Van Rhijn W., De Vos, D. E., & Jacobs, P. A. (2007). Furfural and derivatives. In *Ullmann's encyclopedia of industrial chemistry* (pp.20–32). Weinheim: Wiley-VCH. doi:10.1002/14356007.

Huang, S.-C., Claine Petersen, J., Robertson, R. E., & Branthaver, J. F. (2002). Effect of hydrated lime on long-term oxidative aging characteristics of asphalt. *Transportation Research Record: Journal of the Transportation Research Board*, *1810*(1), 17–24.

Huang, S.-C., & Grimes, W. (2010). Influence of aging temperature on rheological and chemical properties of asphalt binders. *Transportation Research Record: Journal of the Transportation Research Board*, *2179*(1), 39–48.

Huang, S.-C., Miknis, F. P., Schuster, W., Salmans, S., Farrar, M., & Boysen, R. (2010). Rheological and chemical properties of hydrated lime and polyphosphoric acid–modified asphalts with long-term aging. *Journal of Materials in Civil Engineering*, *23*(5), 628–637.

Jamshidi, A., Hamzah, M. O., & You, Z. (2013). Performance of warm mix asphalt containing Sasobit®: State-of-the-art. *Construction and Building Materials*, *38*, 530–553.

Jia, X., Huang, B., Bowers, B. F., & Zhao, S. (2014). Infrared spectra and rheological properties of asphalt cement containing waste engine oil residues. *Construction and Building Materials*, *50*, 683–691.

Kim, H., Lee, S.-J., Amirkhanian, S. N., & Jeong, K.-D. (2012). Quantification of oxidative aging of polymer-modified asphalt mixes made with warm mix technologies. *Journal of Materials in Civil Engineering*, *25*(1), 1–8.

Lau, C. K., Lunsford, K. M., Glover, C. J., Davison, R. R., & Bullin, J. A. (1992). Reaction rates and hardening susceptibilities as determined from pressure oxygen vessel aging of asphalts. *Transportation Research Record: Journal of the Transportation Research Board*, (1342), 50–57.

Liu, M., Ferry, M. A., Davison, R. R., Glover, C. J., & Bullin, J. A. (1998). Oxygen uptake as correlated to carbonyl growth in aged asphalts and asphalt Corbett fractions. *Industrial & Engineering Chemistry Research*, *37*(12), 4669–4674.

Lu, X., & Isacsson, U. (2002). Effect of ageing on bitumen chemistry and rheology. *Construction and Building Materials*, *16*(1), 15–22.

Malinowski, A., & Wardzinka, D. (2012). Catalytic conversion of furfural towards fuel biocomponents. *Chemik*, *66*(9), 982–990.

McCready, N. S., & Williams, R. C. (2008). Utilization of biofuel coproducts as performance enhancers in asphalt binder. *Transportation Research Record: Journal of the Transportation Research Board*, *2051*(1), 8–14.

Memon, G. M., Boone, J. G., & Chollar, B. H. (1995). Furfural substitutes for chemical modification of asphalt. *ASTM Special Technical Publication*, *1241*, 186–204.

Negulescu, I., Mohammad, L., Daly, W., Abadie, C., Cueto, R., Daranga, C., & Glover, I. (2006). Chemical and rheological characterization of wet and dry aging of SBS copolymer modified asphalt cements: Laboratory and field evaluation (with discussion). *Journal of the Association of Asphalt Paving Technologists*, *75*, 267–296.

Ong, H. K., & Sashikala, M. (2007). Identification of furfural synthesized from pentosan in rice husk. *Journal of Tropical Agriculture and Food Science*, *35*(2), 305–312.

Petersen, J. C., Barbour, F. A., & Dorrence, S. M. (1974). Catalysis of asphalt oxidation by mineral aggregate surfaces and asphalt components. *Proceedings of Association of Asphalt Paving Technologists*, *43*, 162–177.

Priyanto, S., Mansoori, G. A., & Suwono, A. (2001). Measurement of property relationships of nano-structure micelles and coacervates of asphaltene in a pure solvent. *Chemical Engineering Science*, *56*, 6933–6939.

Punith, V. S., Suresha, S. N., Raju, S., Bose, S., & Veeraragavan, A. (2011). Laboratory investigation of open-graded friction-course mixtures containing polymers and cellulose fibers. *Journal of Transportation Engineering*, *138*(1), 67–74.

Puzinauskas, V. P. (1967). *Evaluation of properties of asphalt cements with emphasis on consistencies at low temperatures*. Lexington: Asphalt Institute.

Raouf, M. A., & Williams, R. C. (2010). Temperature and shear susceptibility of a nonpetroleum binder as a pavement material. *Transportation Research Record: Journal of the Transportation Research Board*, *2180*(1), 9–18.

Rasmussen, R. O., Lytton, R. L., & Chang, G. K. (2002). Method to predict temperature susceptibility of an asphalt binder. *Journal of materials in civil engineering*, *14*(3), 246–252.

Roberts, F. L., Kandhal, P. S., Brown, E. R., Lee, D-Y., & Kennedy, T. W. (1996). *Hot mix asphalt materials, mixture design and construction*. Lanham, MD: National Asphalt Pavement Association Research and Education Foundation.

Shashidhar, N., Needham, S. P., & Chollar, B. H. (1995). Rheological properties of chemically modified asphalts. *Transportation Research Record: Journal of the Transportation Research Board*, *1488*, 89–95.

Shatanawi, K. M., Biro, S., Geiger, A., & Amirkhanian, S. N. (2012). Effects of furfural activated crumb rubber on the properties of rubberized asphalt. *Construction and Building Materials*, *28*(1), 96–103.

Tong, X., Ma, Y., & Li, Y. (2010). Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes. *Applied Catalysis A: General*, *385*(1), 1–13.

Wasiuddin, N. M., Fogle, C. M., Zaman, M. M., & O' Rear, E. A. (2007). Characterization of thermal degradation of liquid amine anti-strip additives in asphalt binders due to RTFO and PAV-aging. *Journal of Testing and Evaluation*, *35*(4), 387.

Win, D. T. (2005). Furfural-gold from garbage. *Au Journal of Technology*, *8*, 185–190.

Woo, W. J., Ofori-Abebresse, E., Chowdhury, A., Hilbrich, J. M., Kraus, Z., Martin, A. E., & Glover, C. J. (2007). *Polymer modified asphalt durability in pavements*. (Report No. FHWA/TX-07/0-4688-1). Austin, TX: Texas Department of Transportation.

Xu, W., Xia, Q., Zhang, Y., Guo, Y., Wang, Y., & Lu, G. (2011). Effective production of octane from biomass derivatives under mild conditions. *ChemSusChem*, *4*(12), 1758–1761.

Yu, J-Y., Feng, P-C., Zhang, H-L., & Wu, S-P. (2009). Effect of organo-montmorillonite on aging properties of asphalt. *Construction and Building Materials*, *23*(7), 2636–2640.

Zhang, H., Yu, J., & Wu, S. (2012). Effect of montmorillonite organic modification on ultraviolet aging properties of SBS modified bitumen. *Construction and Building Materials*, *27*(1), 553–559.