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# Influence of anti-ageing compounds on rheological properties of bitumen

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## Abstract:

The aim of this study was to investigate the effects of different anti-ageing compounds (AACs) on the oxidative stability, rheological and mechanical properties of bitumen. Modified bitumen samples containing six different AAC combinations, with five samples containing Irganox acid (3,5-di-tert-butyl-4-hydroxyphenylpropionic acid), a hindered phenol polymer-based antioxidant, were fabricated and aged under different conditions using a Rolling Thin Film Oven (RTFO) as well as a Pressure Aging Vessel (PAV). The oxidative stabilising performance (anti-ageing) of the AACs was examined using Fourier Transform Infrared (FTIR) Spectroscopy. The effect of the AAC-modified bitumen on different rheological and mechanical properties was investigated - complex viscosity, linear viscoelastic (LVE) properties, fatigue and rutting - using a Dynamic Shear Rheometer (DSR). The results illustrated that all the AAC-combinations examined afforded good oxidative stability to the base bitumen, with outstanding anti-ageing performance achieved by formulations C, D, E and F (Irganox acid:NaMMT, Irganox acid:furfural without or with DLTDP or NaMMT). The rheological results showed that the AAC-modified bitumen samples displayed non-Newtonian characteristics associated with simple thermo-rheological materials. The AAC formulations A (DLTDP:furfural), D (Irganox acid:furfural) and F (DLTDP:Irganox acid:furfural) were shown to significantly strengthen the resistance of the bitumen samples to fatigue cracking. In contrast to Irganox acid:furfural combination, the addition of the NaMMT nanofiller to this mixture was found to enhance the rutting resistance of the aged bitumen samples.

**Keywords:** Bitumen; Anti-ageing compounds; Rheological properties; Fatigue cracking; Rutting resistance

## 34 1. Introduction

35 Bitumen is a complex hydrocarbon produced from refining petroleum. When mixed and compacted with  
36 the graded mineral aggregates, the bitumen acts as a binder to fabricate asphalt mixtures used for paving  
37 the road surfaces. The bitumen is known to undergo oxidative ageing which leads to severe stiffness and  
38 brittleness of bitumen-based asphalt products in-service. Inherently, therefore, oxidation is one of the  
39 main processes that contribute to the chemical instability of bitumen in-service; water and other factors,  
40 e.g., volatilization, polymerization, syneresis and thixotropy, contribute considerably also to the loss of  
41 the adhesive attributes of the bitumen in asphalt products (Apeagyei, 2011; Gao et al., 2018; Omairey et  
42 al., 2021). The oxidative ageing of bitumen, which occurs throughout the service life of asphalt pavements,  
43 is caused by a complex set of irreversible chemical reactions in the bitumen initiated by atmospheric  
44 oxygen causing changes in its molecular structure leading to a build-up of carbonyl and sulfoxide  
45 functional groups (Petersen and Glaser, 2011; Petersen and Harnsberger, 1998).

46  
47 A correlation was found between the bitumen's hardening susceptibility and the carbonyl content (Glover  
48 et al., 2009). Thus, the oxidative ageing of bitumen can be quantified by the extent of build-up of the  
49 carbonyl functional groups. Researchers have developed different ways to evaluate the growth of the  
50 carbonyl functional groups using Fourier Transformation Infrared (FTIR) Spectroscopy (Hou et al., 2018).  
51 Carbonyl area (CA) is a parameter defined as the integral area within a wavelength range from 1820 to  
52 1650  $\text{cm}^{-1}$  under an absorbance curve from the FTIR test (Cui et al., 2018). Although the CA was widely  
53 used to characterise the ageing performance of the bitumen, it was shown that the fixed wavelength range  
54 (1820-1650  $\text{cm}^{-1}$ ) used for this parameter can lead to an inaccuracy in the CA calculation when the  
55 bitumen does not contain all the carbonyl functional groups determined from FTIR under this specific  
56 wavenumber range prior to ageing (Omairey et al., 2019). Herrington (2012) measured the normalized  
57 carbonyl area under the spectra from 1640 to 1810  $\text{cm}^{-1}$  for variations in sample concentration (using a  
58 baseline at 1810  $\text{cm}^{-1}$ ). To eliminate the effect of FTIR sample thickness, Liu et al. (2015) proposed a  
59 carbonyl index (CI) that was defined as the ratio of carbonyl area (under the peak at 1700  $\text{cm}^{-1}$ ) to the  
60 area of methylene group (under the peak at 1375  $\text{cm}^{-1}$ ).

61  
62 The build-up of various oxidation products (such as carbonyl and sulfoxides) causes an increase in the  
63 molecular size and cohesive energy density and a decrease of the fraction of the free volume which would  
64 eventually lead to the hardening of the bitumen (Gao, 2020; Gao et al., 2019). The age-hardening of  
65 bitumen has a detrimental effect on the durability of asphalt pavements as this would increase the  
66 susceptibility of the asphalt pavements to cracking leading to premature failure of pavements. In order  
67 to prolong the service life of asphalt pavements, research efforts have been made in which different anti-  
68 ageing compounds (AACs) have been used to reduce the bitumen's oxidative hardening (Apeagyei, 2006;  
69 Apeagyei, 2011; Gawel et al., 2016; Karnati et al., 2019; Omairey et al., 2019; Xu et al., 2017). Xu et al.  
70 (2017) used FTIR to investigate the anti-ageing performance of asphalt binder modified by wood lignin  
71 and found that the lignin improved the ageing resistance of asphalt binder through resisting the formation  
72 of carbonyl structure during the ageing process. Karnati et al. (2019) employed silica nanoparticles (SNPs)  
73 functionalised with (3-aminopropyl) triethoxysilane (APTES) to enhance the ageing resistance of asphalt  
74 binder. Ding et al. (2019) applied a mixed solvent of heptane and trichloroethylene (TCE) to dissolve and  
75 extract recycled asphalt shingle (RAS) binder. Results indicated that the extracted RAS presented a good  
76 anti-ageing performance. Omairey et al. (2019) developed a screening method to select potential AACs to  
77 combat the oxidative degradation of bitumen. They had used a normalized carbonyl index (NCI) to  
78 quantify the oxidative ageing of the AAC-modified bitumen and to evaluate the anti-ageing (stabilising)  
79 effectiveness of different compound types using FTIR. It was found that the samples containing AACs  
80 based on furfural:DLTDP, Irganox acid (10-15%), Irganox acid:sodium montmorillonite (NaMMT), and  
81 furfural had exhibited a high anti-ageing performance. Although the work of Omairey et al. (2020) had  
82 reported a preliminarily set of results on the resistance to fatigue cracking of some AAC-modified  
83 bitumen samples, a more comprehensive investigation of other potential AAC formulations on the  
84 rheological and mechanical properties are further investigated here.

85

86 The main objective of this study was therefore to investigate the effects of some anti-ageing compounds  
 87 (AACs) on the anti-ageing performance, rheological and mechanical properties of the AAC-modified  
 88 bitumen. Six AACs (five of which containing Irganox acid, both alone and in combination with other  
 89 compounds) were evaluated after fabrication in base bitumen (40/60). All the AAC-modified bitumen  
 90 samples, which were aged (using a Rolling Thin Film Oven, RTFO, and a Pressure Aging Vessel, PAV),  
 91 were evaluated for their effect on the oxidative stabilising (anti-ageing) performance (using FTIR  
 92 spectroscopy) and rheological and mechanical behaviour (using Dynamic Shear rheometry, DSR) with  
 93 respect to the complex viscosity, linear viscoelastic (LVE) properties, fatigue and rutting performance of  
 94 the bitumen formulations.

95

## 96 2. Materials and method

### 97 2.1 Materials and preparation of modified bitumen

98 A type of base bitumen with a penetration grade of 40/60 was used as a control binder for all the tests.  
 99 The base bitumen 40/60 has been employed to measure the effectiveness of anti-ageing additives (AACs)  
 100 in the authors' previous study (Omairey et al., 2019). Only one type of bitumen was examined in this  
 101 study in order to eliminate the binder-source effects (Omairey et al., 2019; Yao et al., 2013b; You et al.,  
 102 2011). The anti-ageing compounds (AACs) were selected based on the work by Omairey et al. (2019).  
 103 All the AACs used were commercial compounds except for Irganox acid which was synthesised in our  
 104 laboratories as a precursor for polymer antioxidant (Dintcheva et al., 2015). A list of the AACs  
 105 formulations and their concentrations used in this study are summarised in **Table 1**. Dilauryl  
 106 thiodipropionate (DLTDP) is typically used as a secondary antioxidant in polymers. Furfural is an organic  
 107 aldehyde. Irganox acid was synthesised by the following procedure: 1) a suspension of Irganox 1076 in a  
 108 solution of methanol/water (MeOH/H<sub>2</sub>O) and sodium methoxide (MeONa) was refluxed under N<sub>2</sub>  
 109 atmosphere; 2) the side product (stearyl alcohol) was removed from the resulting mixture; and 3) the  
 110 Irganox acid in the form of a white powder was obtained by washing with water and drying the product.  
 111 The synthesised Irganox acid is a hindered phenol typically used as a precursor for hindered phenol-based  
 112 antioxidants. Sodium montmorillonite (NaMMT) is an inorganic nano-clay nanomaterial usually used as  
 113 an additive to improve the resistance against permanent deformations of bitumen. The chemical structures  
 114 and physical characteristics of these additives are shown in **Table 2**.

115

116 **Table 1** Anti-ageing compounds (AACs) and their concentrations used in the bitumen.

ID	Anti-ageing compounds (AACs)	Concentration (% by weight of bitumen)
A	(3:4) DLTDP (Dilauryl thiodipropionate):furfural	3.5%
B	Irganox acid	10%
C	(3:2) Sodium montmorillonite (NaMMT):Irganox acid	25%
D	(2:1) Irganox acid:furfural	15%
E	(3:2:1) NaMMT:Irganox acid:furfural	12%
F	(2:2:1) DLTDP:Irganox acid:furfural	10%

117

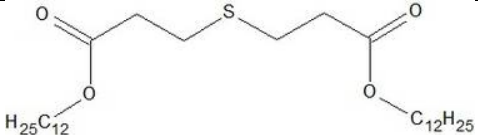
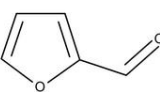
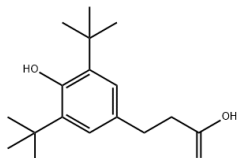
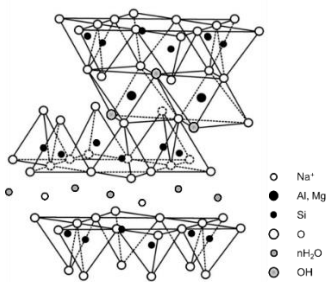
118 The AAC-modified bitumen samples were fabricated in the laboratory by mixing the AACs with the base  
 119 bitumen. The AACs formulations are presented in **Table 1**. For example, sample A comprises DLTDP  
 120 (1.5% by weight of base bitumen) and furfural (2%). A high-speed shear mixer was used to blend the  
 121 control bitumen and the AACs with the specific concentrations given in **Table 1**. The mixing was  
 122 conducted at 150 °C for 30 min and a shear speed of 500 rpm. After mixing, the modified sample was  
 123 slowly poured from the beaker to the container and its flow was observed to identify the dispersion of the  
 124 ingredients. For all modified samples, no block was seen in the samples, which indicates the ingredients  
 125 were completely dispersed in the base bitumen. This proved that the blending conditions including the  
 126 temperature, time and speed are suitable for different modified samples. It is noted that the control sample  
 127 (i.e., base bitumen) was also subjected to the same blending process in order to ensure that all the samples  
 128 underwent the same blend-induced ageing condition.

129

130 All control and modified bitumen samples were initially aged using a Rolling Thin Film Oven (RTFO) at  
 131 163 °C for 85 min (ASTM, 2012) to simulate the short-term ageing of the samples during the field mixing  
 132 and compaction stage of asphalt pavement construction. The RTFO aging was followed by further ageing  
 133 in a Pressure Aging Vessel (PAV) at 100 °C with air blow of 2.1 MPa (ASTM, 2013); to simulate different  
 134 levels of ageing, the PAV testing was conducted over 10 and 20 hours.

135

136 **Table 2** Chemical and physical characteristics of additives used in this study.

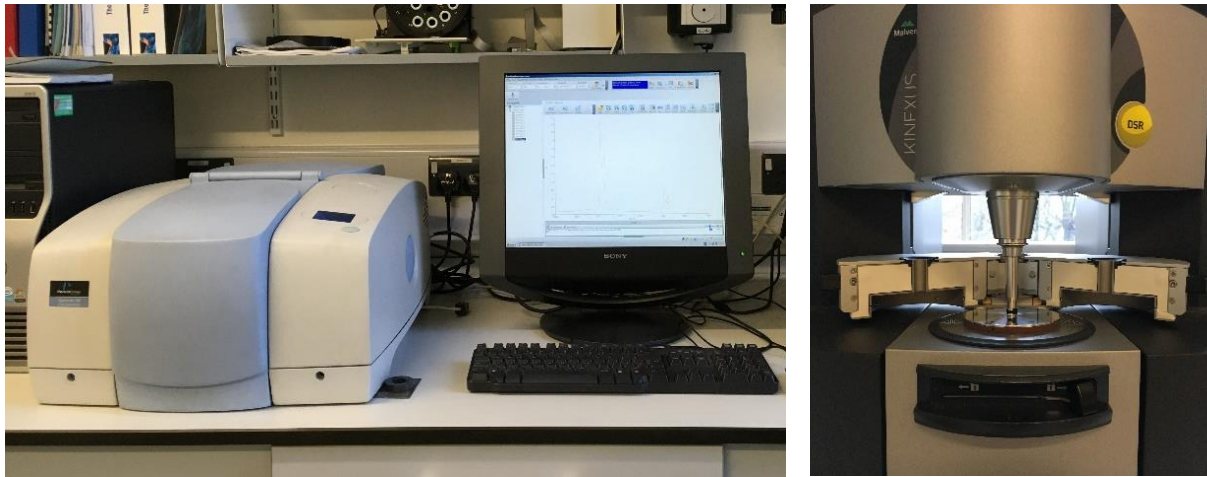
Name	Identity	State	Melting point (°C)	Solubility in water (% w/w)	Chemical structure
DLTDP	organic thioester	solid (white flakes)	39-42	< 0.01	
Furfural	organic aldehyde	liquid	-38	7.4	
Irganox acid	hindered phenol	solid (white crystals)	50-55	< 0.01	
NaMMT	inorganic clay nanomaterial	solid (yellow powder)	none	insoluble	

137

## 138 2.2 Fourier transform infrared (FTIR) spectroscopy test

139 Fourier transform infrared (FTIR) spectroscopy tests were conducted for all the unaged and aged bitumen  
 140 samples to measure the oxidative transformation and in particular the changes in the carbonyl functional  
 141 groups in these samples due to ageing. The AAC-modified bitumen was cast as a thin film (0.5 mm  
 142 thickness) by dissolving (at room temperature) in a small amount of dichloromethane used as a solvent  
 143 here due to its high bitumen dissolving ability followed by complete evaporation of the solvent under  
 144 nitrogen (Lamontagne et al., 2001; Omairey et al., 2019). The thin-film samples were then placed on a  
 145 sodium chloride disc in an infra-red cell holder. FTIR spectral measurements were carried out using a  
 146 Perkin-Elmer spectrum 100 instrument (resolution 4 cm<sup>-1</sup>, 32 scans, range 450-4000 cm<sup>-1</sup>), as shown in  
 147 **Fig. 1(a)**. Background scans were run first before scanning the samples, and all FTIR measurements were  
 148 carried out in duplicates. **Fig. 2** shows a representative transmission FTIR spectrum of the base bitumen.

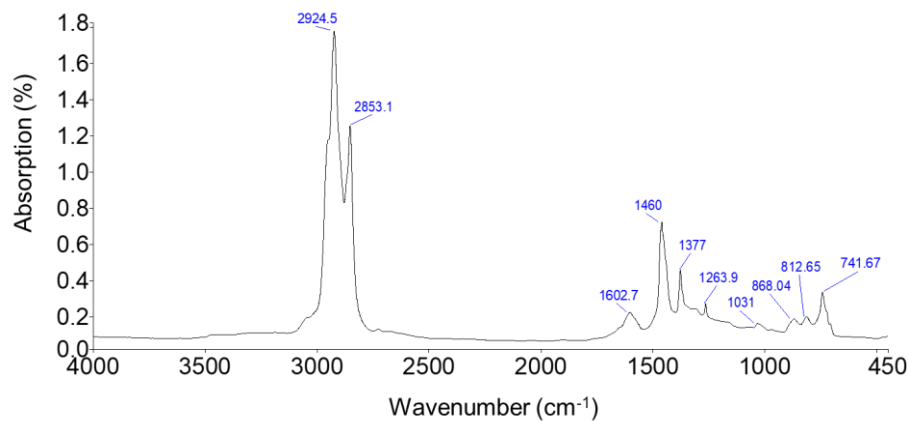
149



(a) FTIR

(b) DSR

**Fig. 1.** Instruments used in this study.



**Fig. 2.** FTIR spectrum of the unaged control bitumen sample 40/60.

### 2.3 Dynamic shear rheometer (DSR) tests

Dynamic shear rheometer (DSR) tests were conducted to evaluate the rheological and mechanical properties of the bitumen samples using a Kinexus Rheometer from Malvern Panalytical shown in **Fig. 1(b)**. A silicone mould was used to prepare the test samples with a diameter of 8 mm (2 mm in height) or 25 mm (1 mm in height). A series of DSR tests including frequency sweep test, time sweep fatigue test and multiple stress creep recovery (MSCR) test were conducted on unaged and aged bitumen samples. **Table 3** illustrates the testing schemes used in this study.

**Table 3** Testing schemes used in this study.

NO	Test method	Purpose	Test parameters	Bitumen tested
1	RTFO	Short term ageing	163 °C, 85min	Unaged
2	PAV	Long term ageing	100 °C, 2.1MPa, 10h, 20h	RTFO aged
3	FTIR	Anti-ageing evaluation	Room temperature	All samples
4	Frequency sweep	Viscosity/Stiffness	20, 30, 40, 50 and 60 °C	Unaged & PAV aged
5	Time sweep	Fatigue	20 °C, 10Hz, 5% strain	PAV aged
6	MSCR	Rutting	64 °C	RTFO aged

Note: RTFO, Rolling Thin Film Oven; PAV, Pressure Ageing Vessel; LVE, Linear Viscoelastic; and MSCR, Multiple Stress Creep and Recovery.

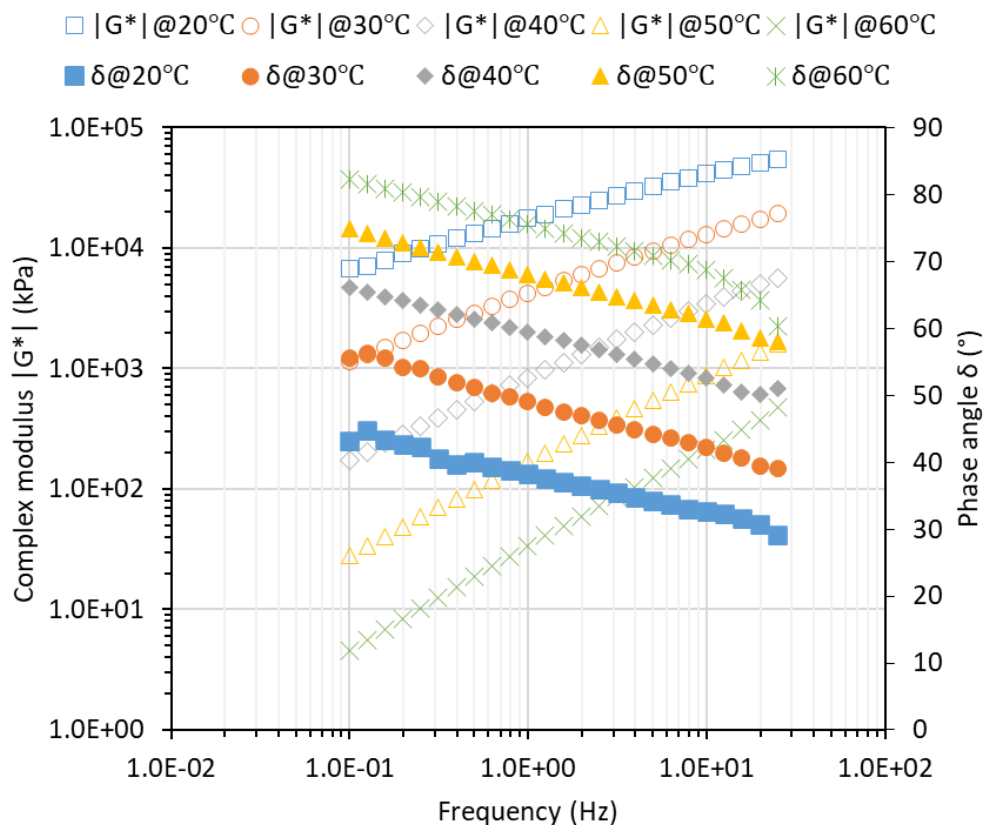


166

167 2.3.1 Frequency sweep test

168 Frequency sweep test was used to measure the linear viscoelastic (LVE) properties of the bitumen samples.  
 169 The tests were conducted on the unaged and 20-hour PAV aged samples from 0.1 to 25 Hz over a  
 170 temperature range of 20 °C ~ 60 °C with an increment of 10 °C to obtain the samples' complex shear  
 171 modulus, phase angle and complex viscosity. To ensure that the frequency sweep tests were run within  
 172 the LVE response of the materials, strain amplitude sweep tests were undertaken with the strain  
 173 amplitudes ranging from 0.1% to 30% to identify the LVE region and measure the damage tolerance of  
 174 different samples prior to the frequency sweep tests. **Fig. 3** presents an example for the results of  
 175 frequency sweep tests of the bitumen samples.

176



177

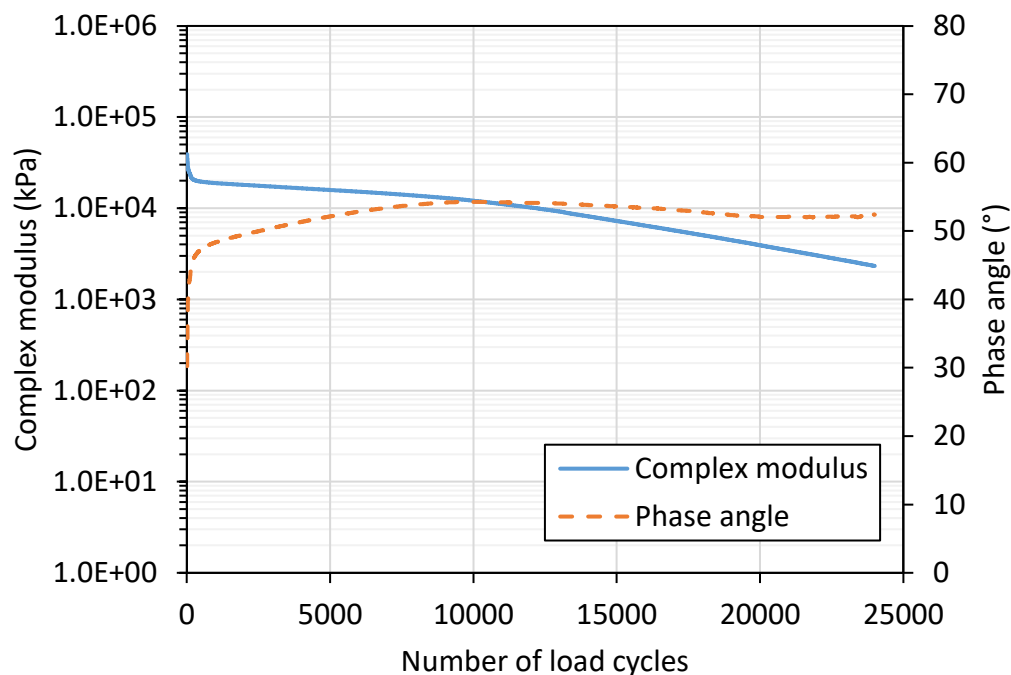
178 **Fig. 3.** Results of frequency sweep tests of the 20-hour PAV aged control bitumen sample 40/60.

179

180 2.3.2 Time sweep test

181 Time sweep test was performed to evaluate the fatigue performance of the 20-hour PAV aged bitumen  
 182 samples at an intermediate temperature. The parallel loading plates with 8 mm diameter (2 mm gap) were  
 183 used in this test. The tests with a 5% strain amplitude were carried out at temperature of 20 °C and  
 184 frequency of 10 Hz for 40 min (i.e., 24,000 load cycles) to determine the complex shear moduli and phase  
 185 angles of the samples in the damaged condition. **Fig. 4** illustrates an example for the results of time sweep  
 186 tests of the bitumen sample.

187



188

189 **Fig. 4.** Results of time sweep tests of the 20-hour PAV aged control bitumen sample 40/60.

190

191 

### 2.3.3 Multiple stress creep and recovery (MSCR) test

192 Multiple stress creep and recovery (MSCR) test was used to measure of the rutting performance of  
 193 different bitumen samples at elevated temperatures (ASTM, 2010); the loading plates used in this test  
 194 were disc-shapes of 25 mm diameter  $\times$  1 mm . The MSCR tests were performed on the RTFO aged  
 195 samples at temperature of 64 °C to obtain the non-recoverable creep compliance and the percent  
 196 recoverable strain of the samples. In this test, the samples were loaded at a constant stress level for 1s  
 197 and then allowed to recover for 9s. Following twenty creep and recovery cycles at 0.1 kPa creep stress, ten  
 198 creep and recovery cycles were run at 3.2 kPa creep stress.

199

200 

## 3. Results and discussion

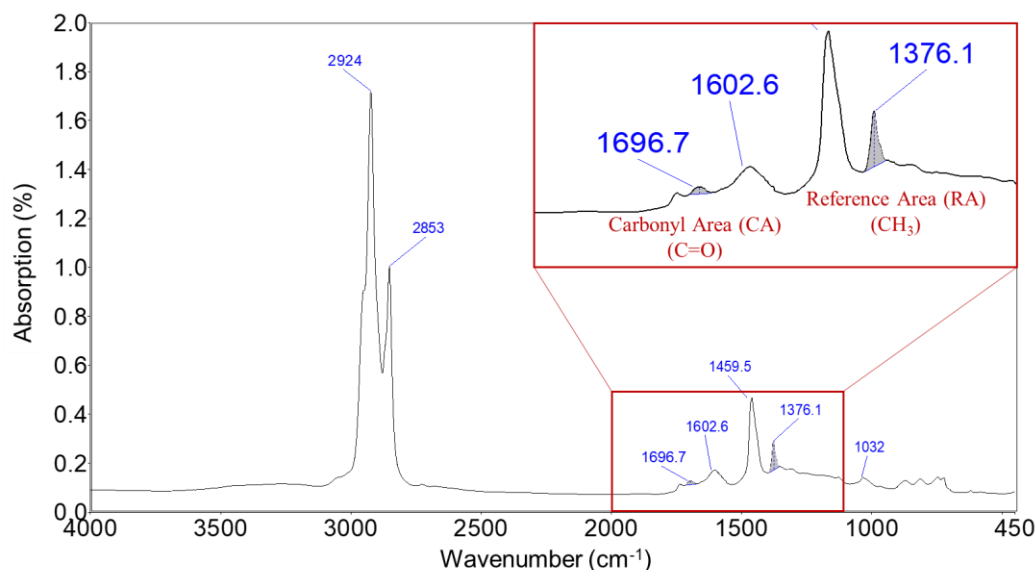
201 

### 3.1 Evaluation of AACs' stabilising effectiveness in bitumen after ageing

202 Prior to analysing the rheological properties of the AAC-modified bitumen samples, the stabilising (anti-  
 203 ageing) performance of the AACs was evaluated based on FTIR test results (conducted in duplicates) for  
 204 unaged, RTFO aged, 10-hour and 20-hour PAV aged samples by measuring the changes in the carbonyl-  
 205 forming oxidation products with ageing. **Fig. 5** shows the carbonyl region, where the build-up of the main  
 206 oxidation products are expected to appear, in the infrared spectra of the AAC-modified bitumen, in this  
 207 case it is shown for the 20-hour PAV aged bitumen sample modified by the formulation A  
 208 (DLTDP:furfural).

209





210  
 211 **Fig. 5.** FTIR spectrum of the bitumen sample modified by the formulation A (DLTDP:furfural) after 20-  
 212 hour PAV ageing.

213  
 214 A normalized carbonyl index (NCI) is used to quantify the samples' oxidative ageing performance. NCI  
 215 is defined as the ratio of the difference between the carbonyl index at any ageing time ( $CI_t$ ) and the  
 216 carbonyl index before ageing at time zero ( $CI_0$ ) to that of the initial carbonyl index  $CI_0$ , as shown in **Eq.**  
 217 **(1)**; the carbonyl index (CI) is calculated according to **Eq. (2)**. CI is the ratio of the areas under the C=O  
 218 region with a peak around  $1700\text{ cm}^{-1}$  to that of a reference  $\text{CH}_3$  peak around  $1377\text{ cm}^{-1}$ ; the reference peak  
 219 is assumed to be unaffected by ageing and hence allows one to compensate for differences in sample  
 220 thickness and the effect of changes in the film thickness on ageing. In this study, the two-point method  
 221 was used to calculate the peak areas. The baseline was created by connecting the lower and upper limits  
 222 on the two sides of the peak in the spectrum curve, as shown in **Fig. 5**.

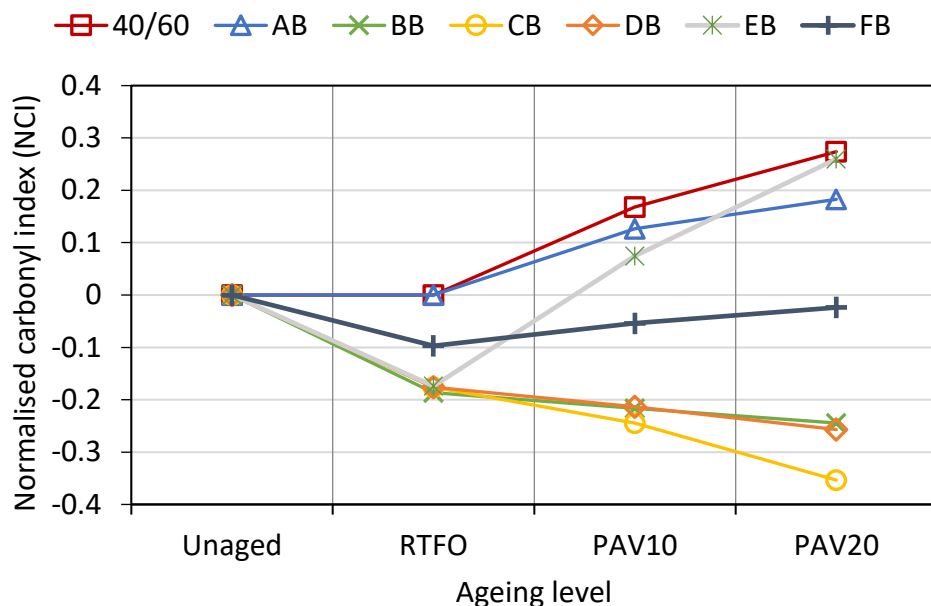
$$223 \quad NCI = \frac{CI_t - CI_0}{CI_0} \quad (1)$$

$$224 \quad CI = \frac{CA}{RA} \quad (2)$$

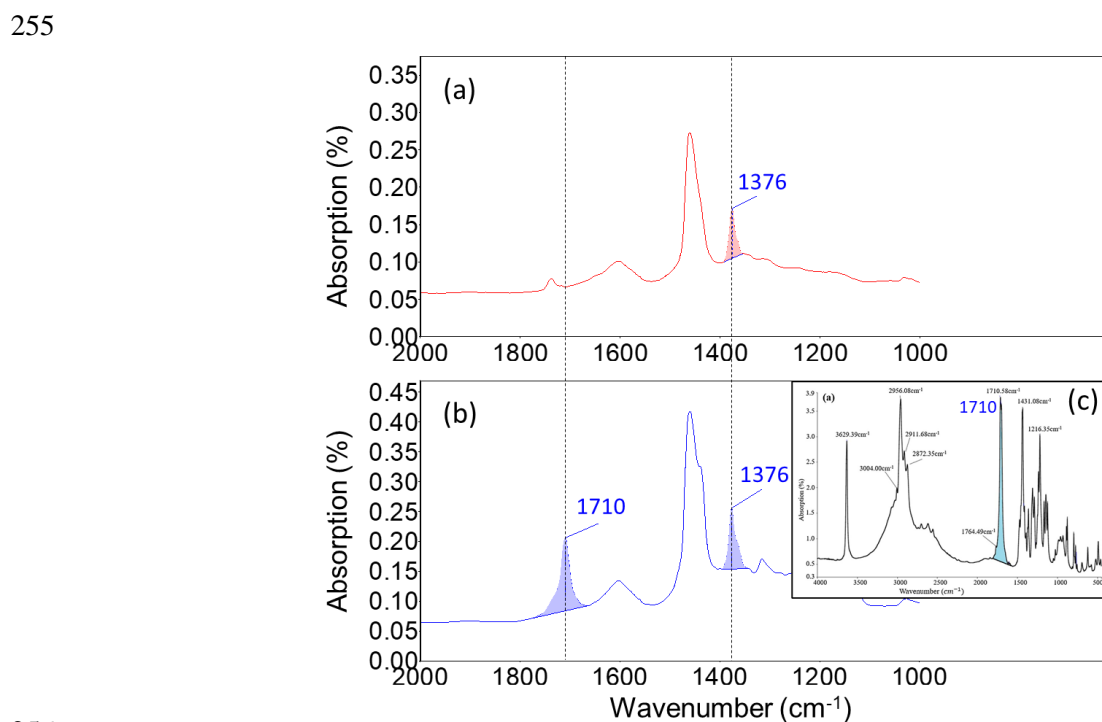
225 where  $NCI$  is the normalized carbonyl index;  $CI_t$  is the carbonyl index for the samples with different  
 226 ageing times (i.e., unaged, RTFO aged, 10-hour PAV aged and 20-hour PAV aged);  $CI_0$  is the initial  
 227 carbonyl index for the unaged samples;  $CA$  is the carbonyl area centred around  $1700\text{ cm}^{-1}$ ; and  $RA$  is the  
 228 reference area centred around  $1377\text{ cm}^{-1}$ .

229  
 230 **Fig. 6** shows the NCI values with different ageing regimes and times for all the tested bitumen samples.  
 231 It can be seen that all the modified samples with the AACs have lower values of NCI compared to that of  
 232 the control bitumen sample 40/60 thus all the six AAC formulations used in this study tend to improve  
 233 the oxidative ageing of the bitumen. It is interesting to note that all the samples containing Irganox acid,  
 234 except that of sample EB (NaMMT:Irganox acid:furfural modified bitumen), show a negative NCI value  
 235 under all ageing regimes tested here, which contrasts to the behaviour of the non-Irganox acid containing  
 236 sample AB (DLTDP:furfural modified bitumen) and sample E (NaMMT:furfural:Irganox acid modified  
 237 bitumen) where their NCI increases sharply after the 10-hour and 20-hour PAV ageing, see **Fig. 6**. It is  
 238 important to point out here that while the unaged bitumen modified with DLTDP:furfural, sample AB,  
 239 has no significant absorption in the carbonyl region, see **Fig. 7(a)**, all the unaged samples containing  
 240 Irganox acid show a significant absorption in this region which is due to the carboxylic acid carbonyl  
 241 absorption peak centred around  $1710\text{ cm}^{-1}$  characteristic of Irganox acid itself, see **Fig. 7(b)** (bitumen

242 containing Irganox acid, sample BB) and **inset, Fig. 7(c)** (Irganox acid, (Omairey et al., 2019)). It is clear  
 243 from **Fig. 6** that all the samples containing Irganox acid, except for sample EB, show an excellent  
 244 stabilising performance and in excess of that afforded by the AAC combination DLTDP:furfural (sample  
 245 AB). The reason for the negative carbonyl index observed after the PAV ageing for the Irganox acid-  
 246 containing samples (samples BB, CB, DB and FB) is attributable to the sacrificial loss of Irganox acid  
 247 with ageing (see **Fig. 8** as an example) as a result of its mode of action as an antioxidant (as evidenced  
 248 from the decrease in the intensity of its characteristic carboxylic acid function, & the decrease of NCI  
 249 during ageing, see **Fig. 6**) in preventing the oxidation of bitumen.

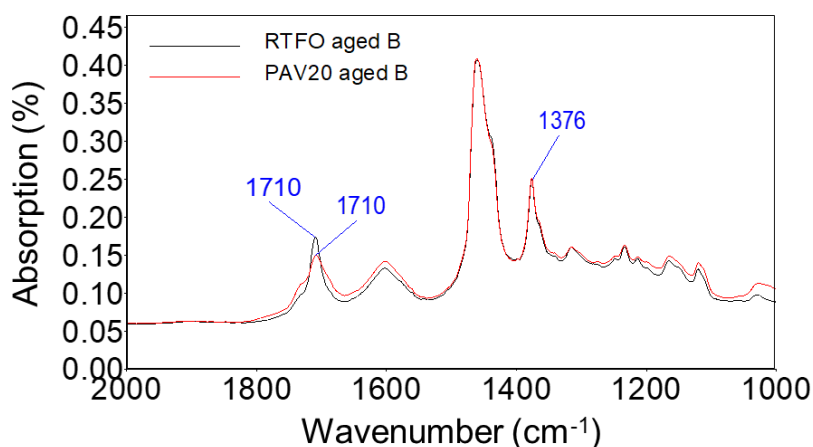


250  
 251 **Fig. 6.** Normalized carbonyl index (NCI) with different ageing levels for all the bitumen samples. (Note:  
 252 in the legend, the first letter stands for the ID of AACs shown in Table 1 and the second one is the initial letter of  
 253 the word ‘Bitumen’. For example, AB means the bitumen sample modified by the additive A. In the horizontal axis,  
 254 PAV10 and PAV20 stand for 10-hour PAV and 20-hour PAV ageing levels, respectively.)



257 **Fig. 7.** FTIR spectra in the region 2000-1000  $\text{cm}^{-1}$  of (a) unaged bitumen containing DLTDTP:furfural  
 258 (sample AB) and (b) unaged bitumen containing Irganox acid (sample BB). (c) The inset in (b) is the  
 259 FTIR spectral region of Irganox acid showing its carboxylic carbonyl absorption at 1710  $\text{cm}^{-1}$ .

260



261

262 **Fig. 8.** FTIR spectra in the region 2000-1000  $\text{cm}^{-1}$  of RTFO and 20-hour PAV aged bitumens containing  
 263 Irganox acid (sample BB).

264

265 It should be noted here that although sample EB (NaMMT:Irganox acid:furfural modified bitumen) shows  
 266 a negative NCI after RTFO ageing (**Fig. 6**), its NCI value shows a substantial increase after the PAV  
 267 ageing at both 10 h and 20 h. This suggests that furfural is affecting negatively the oxidative stability of  
 268 the bitumen substrate, and may be acting antagonistically with the Irganox acid in the presence of the  
 269 NaMMT. This suggestion is supported by the fact that both samples DB (furfural:Irganox acid modified  
 270 bitumen) without NaMMT, and CB (NaMMT:Irganox acid modified bitumen) without furfural, have  
 271 shown very effective stabilisation which is clearly illustrated by the sacrificial loss of the Irganox acid  
 272 (and reduction in its carbonyl signature on ageing, hence the negative NCI observed) in affording  
 273 protection to the bitumen. Clearly, furfural is an ineffective AAC when compared to that of the other  
 274 AAC candidates investigated here. Moreover, the fact that the addition of Irganox acid to the same  
 275 combination of DLTDTP:furfural (i.e. F, DLTDTP:Irganox acid:furfural) results in a considerably enhanced  
 276 stabilising performance when compared to that shown by the combination DLTDTP:furfural (A) is a further  
 277 support to the above suggestion about the negative stabilising effect of furfural.

278

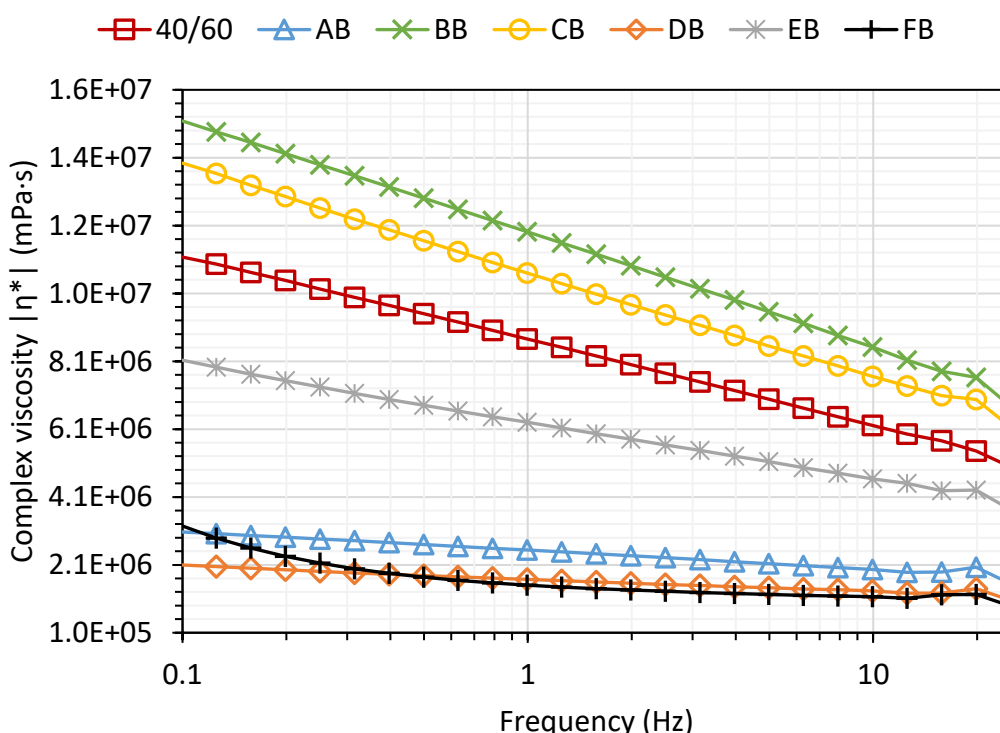
### 279 3.2 Effect of AACs on complex viscosity of bitumen

280 The complex shear viscosity of all the unaged bitumen samples was obtained from the frequency sweep  
 281 tests at different temperature, as shown in **Fig. 9**. **Fig. 9(a)** illustrates the complex viscosity versus the  
 282 frequency at the temperature of 40 °C. It can be seen that the viscosity is dependent on the frequency,  
 283 which decreases with increasing frequency (shear rate). At 40 °C, the control bitumen sample 40/60 and  
 284 all the AAC-modified samples exhibit non-Newtonian (shear thinning) behaviour since the viscosity  
 285 decreases as the shear rate increases. **Fig. 9(b)** shows the complex viscosity versus temperature at a  
 286 frequency of 0.1 Hz. It is found that the viscosity decreases as the temperature increases, which indicates  
 287 the viscosity is also dependent on the temperature.

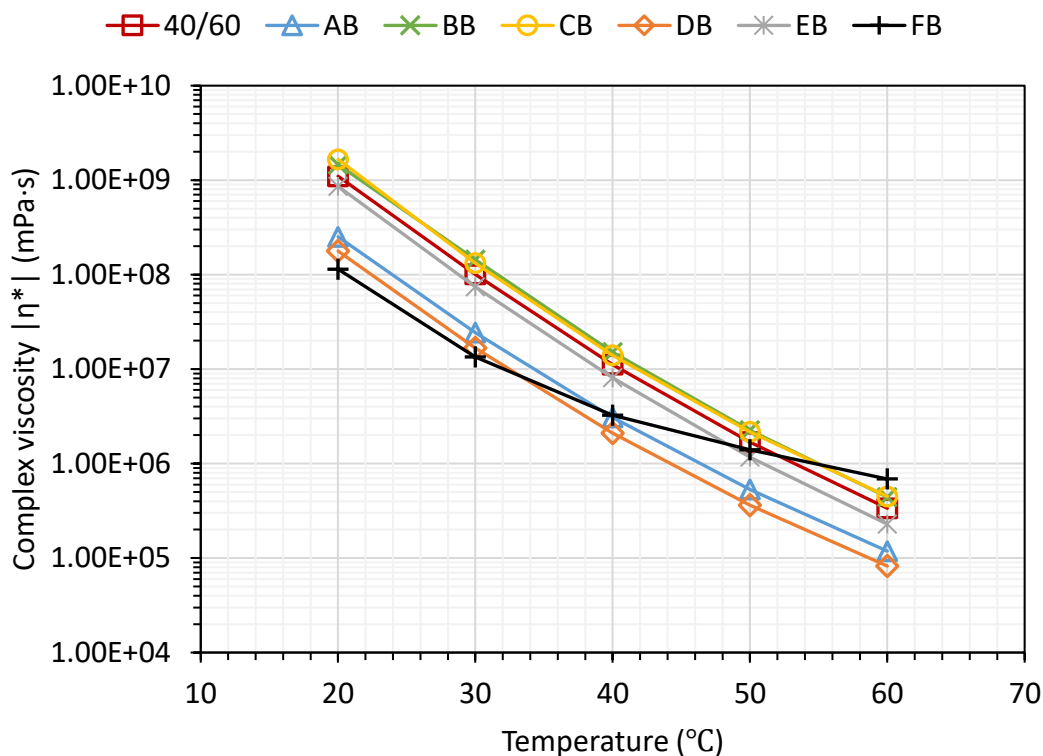
288

289 It can be seen also from **Fig. 9** that samples BB (containing Irganox acid) and CB (the combination  
 290 Irganox acid:NaMMT modified bitumen) have a slightly greater complex viscosity than the control  
 291 bitumen sample 40/60. This is because that they contain a high concentration (10%) of Irganox acid.  
 292 However, the bitumen sample modified by Irganox acid:furfural (DB) show a lower viscosity than that  
 293 of the control sample due to the low viscosity liquid-nature of the furfural. The effect of furfural on the

294 complex viscosity is further supported by the lower viscosity of samples AB (DLTDP:furfural modified  
 295 bitumen) and EB (NaMMT:Irganox acid:furfural modified bitumen). Thus, it is concluded that the  
 296 Irganox acid enhances the complex viscosity of the samples while the furfural can be used to reduce the  
 297 viscosity. The sample modified by DLTDP:Irganox acid:furfural (FB) has a smaller viscosity than the  
 298 control sample (40/60 bitumen) at different temperatures (except 60 °C) and frequencies. It is noted that  
 299 the polymer network of this formulation DLTDP:Irganox acid:furfural can be formed by cross-linking of  
 300 molecular chains of the ingredients within the bitumen matrix. Thus, a weak polymer network of FB  
 301 sample reduces its complex viscosity due to the presence of furfural (liquid) in the combination  
 302 DLTDP:Irganox acid:furfural. However, at the temperature of 60 °C, the complex viscosity of FB sample  
 303 is slightly larger than that of the control sample, indicating that the network of FB sample enhances its  
 304 complex viscosity at higher temperature (i.e., 60 °C). The temperature of 60 °C has exceeded the melting  
 305 points of DLTDP (39-42 °C) and Irganox acid (50-55 °C) shown in **Table 2**. Therefore, DLTDP with  
 306 long molecular hydrocarbon chains, Irganox acid and furfural in bitumen matrix form a strong  
 307 crosslinking and/or entanglement, leading to an increase in complex viscosity of FB sample.  
 308



309  
 310 (a) Complex viscosity versus frequency at 40 °C



311

312 (b) Complex viscosity versus temperature at 0.1 Hz

313 **Fig. 9.** Complex viscosity of all the unaged samples versus (a) frequency at 40 °C and (b) temperature at  
 314 0.1 Hz.

315

316 3.3 Complex modulus and phase angle of the modified bitumen

317 3.3.1 Black diagram

318 A black diagram is a graph of the complex modulus versus the phase angle obtained from the frequency  
 319 sweep tests at different temperatures. In the black diagram, the frequency and the temperature are  
 320 eliminated, which allows the viscoelastic properties of the bitumen to be analysed without performing the  
 321 time-temperature superposition principle (TTSP) manipulations of the raw dynamic data. A smooth curve  
 322 in the black diagram indicates the time-temperature equivalency. The black diagram has been widely used  
 323 to identify possible errors in the measurements, thermo-rheological simplicity of the samples, and  
 324 different types of binders (Airey, 2002; Wang et al., 2018).

325

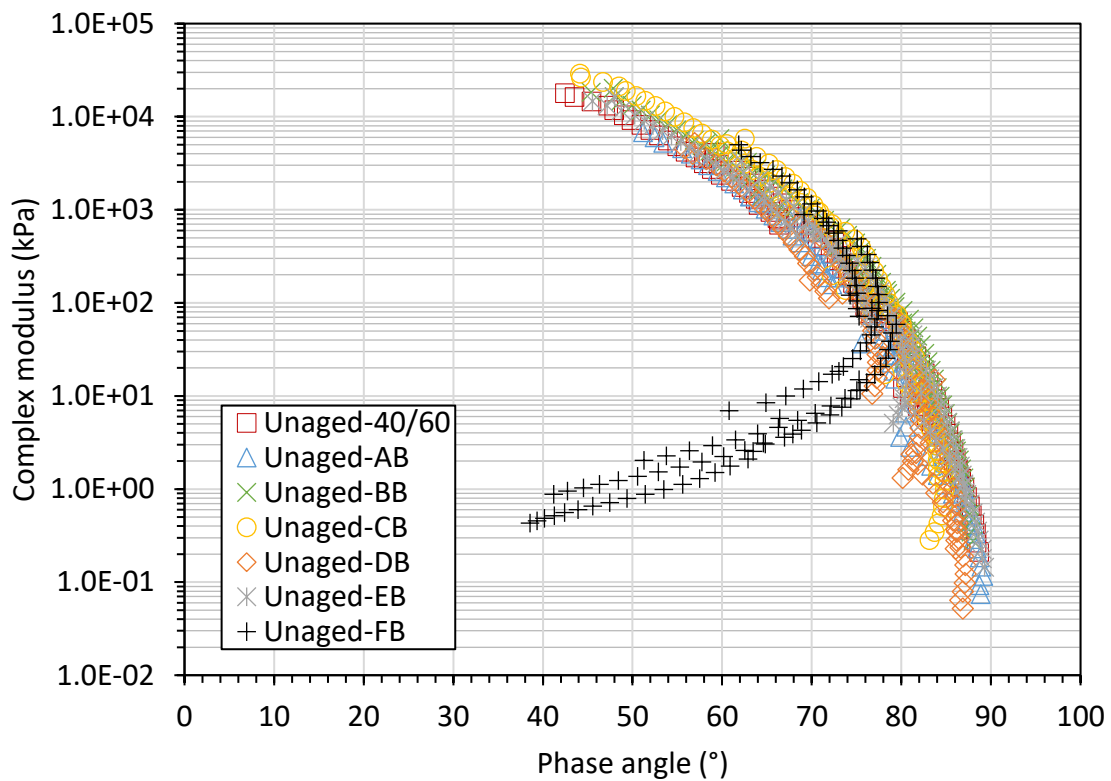
326 The black diagrams of all the bitumen samples at the unaged and 20-hour PAV aged conditions are shown  
 327 in **Fig. 10**. It is seen that the dynamic data of all the samples present a relatively smooth trend. This  
 328 indicates that the unaged and aged samples can be considered as thermo-rheologically simple materials.  
 329 The black diagrams of all the unaged samples are shown in **Fig. 10(a)**. In the black diagram, the curves  
 330 of samples AB, BB, CB, DB and EB have a trend similar to that of the control sample 40/60. These curves  
 331 are overlapping in black space. However, the curve of the sample FB exhibits an inverse “C” pattern,  
 332 which is significantly different from that of the control sample. This inverse “C” pattern was also  
 333 reported in the literature for the SBS modified bitumen (Airey, 2002; Wang et al., 2018). At the low  
 334 temperature (i.e., 20 °C), the sample FB has a behaviour similar to that of the control sample as the linear  
 335 viscoelastic response is mainly dominated by the bitumen phase (Cuciniello et al., 2020). At the higher  
 336 temperatures (i.e., 30 to 60 °C), the curve of the sample FB tends towards lower phase angles. The trend  
 337 may be caused by the polymer network of the combination F (DLTDP:Irganox acid:furfural) formed by

338 cross-linking of molecular chains of its ingredients within the bitumen matrix, which resists viscous flow  
 339 and controls the rheological response at higher temperatures.

340

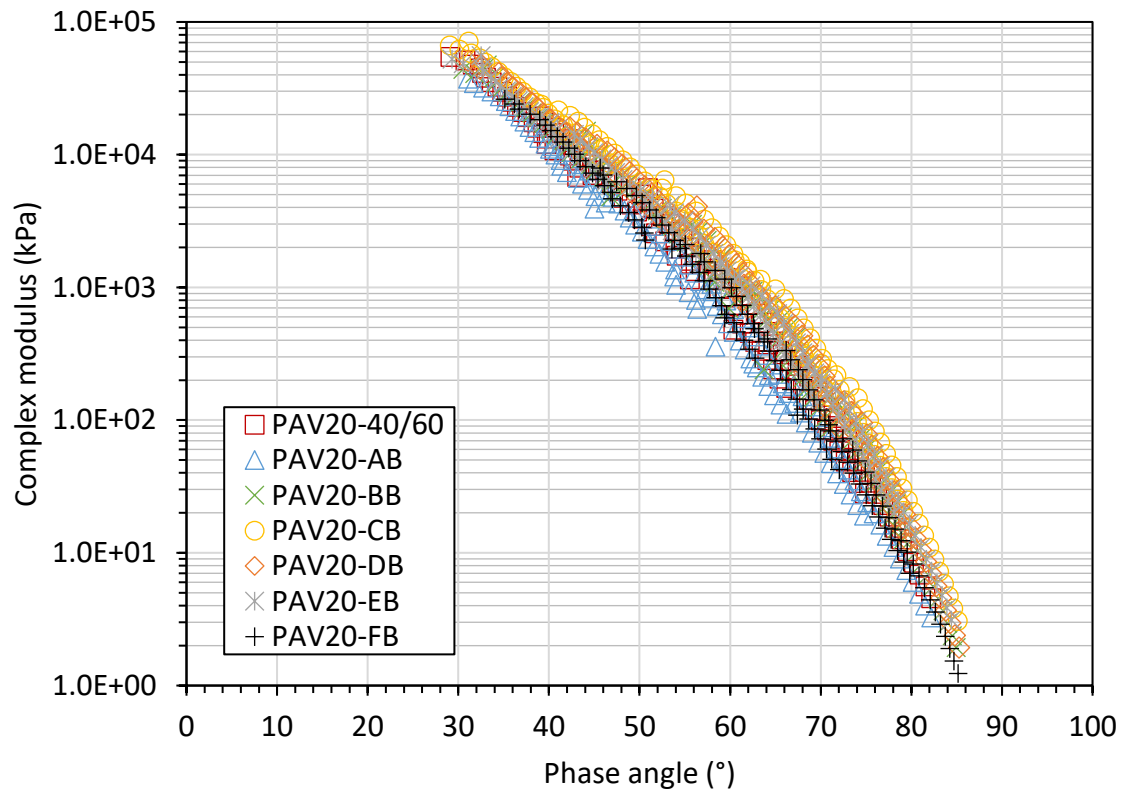
341 **Fig. 10(b)** illustrates the black diagrams of all the 20-hour PAV aged samples. Laboratory aging affects  
 342 the viscoelastic response of the samples. Compared to the unaged dynamic data shown in **Fig. 10(a)**, it  
 343 can be seen that the black diagrams at the aged condition shift towards the left (a lower phase angle) for  
 344 the samples 40/60, AB, BB, CB, DB and EB, which means these 20-hour PAV aged samples have more  
 345 elastic behaviour. At the low temperatures (i.e., 20 and 30 °C), the same trend can be found for the sample  
 346 FB. However, at the higher temperatures (i.e., 50 and 60 °C), the black diagram of the aged sample FB  
 347 tends towards a greater phase angle (right), which indicates more viscous behaviours. This could result  
 348 from the viscoelastic response being mainly dominated by the bitumen phase at the high temperatures  
 349 due to the sacrificial loss of the combination F (DLTDP:Irganox acid:furfural) after 20-hour PAV ageing.  
 350 This phenomenon was also observed in other works (Airey and Brown, 1998; Cuciniello et al., 2020).  
 351 Thus, the curve of the aged sample FB has a trend similar to that of the remaining samples rather than an  
 352 inverse “C” pattern at the unaged condition. These curves of all the samples are overlapping in the black  
 353 diagram, as shown in **Fig. 10(b)**.

354



355

356 (a) Black diagrams for the unaged samples



357

358 (b) Black diagrams for the 20-hour PAV (PAV20) aged samples

359 **Fig. 10.** Black diagrams of all the samples at (a) unaged and (b) 20-hour PAV aged conditions.

360

### 361 3.3.2 Master curve

362 Master curve has been widely employed to investigate the stiffness (flow) properties of bitumen samples  
 363 over a wide range of frequency and temperature (Tang et al., 2018; Wang et al., 2018; Yusoff et al., 2013).  
 364 Based on the measured dynamic data (i.e., complex modulus and phase angle) at different temperatures  
 365 and loading frequencies, the master curves can be constructed at a reference temperature using the TTSP.  
 366 In this study, the master curve of complex modulus is developed using the sigmoidal model expressed in  
 367 **Eq. (3)** (Tang et al., 2018; Yusoff et al., 2013; Zhang et al., 2016).

$$368 \log|G^*| = \nu + \frac{\alpha}{1 + e^{\beta + \gamma \log(f_r)}} \quad (3)$$

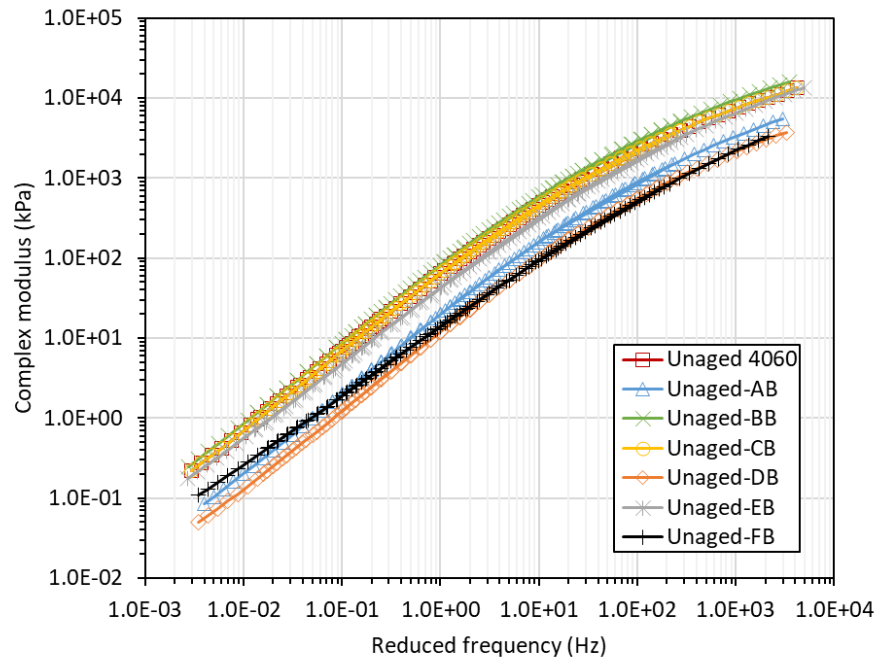
369 where  $|G^*|$  is complex modulus;  $\nu$  is the lower asymptote;  $\alpha$  is the difference between the values of the  
 370 upper and lower asymptotes;  $\beta$  and  $\gamma$  are the shape parameters; and  $f_r$  is the reduced frequency that can  
 371 be obtained by the loading frequency  $f$   $\times$  the time-temperature shift factor  $\alpha_T$ .

372

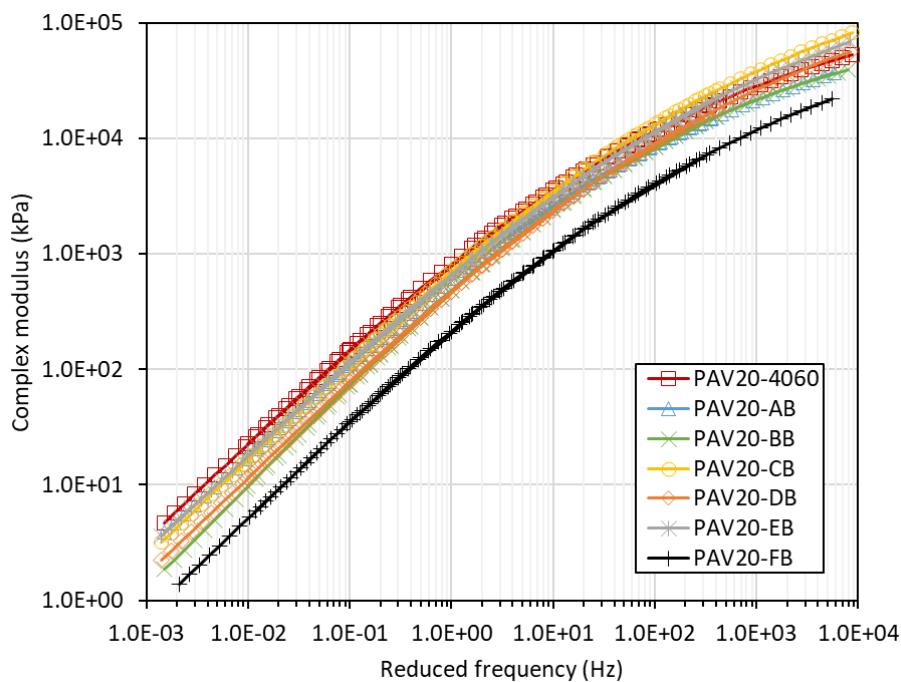
373 **Fig. 11** shows the master curves of complex modulus for all the unaged and 20-hour PAV aged bitumen  
 374 samples at the reference temperature of 40 °C. The complex modulus for all the samples increases with  
 375 the increasing reduced frequency at the unaged and aged conditions. It is found from **Fig. 11 (a)** that the  
 376 addition of the additives B (Irganox acid) and C (NaMMT:Irganox acid) leads to a slight increase in the  
 377 complex modulus of the samples at the unaged condition. This means that the samples BB and CB are a  
 378 little stiffer than the control sample 40/60 due to the presence of a high concentration (10%) of Irganox  
 379 acid. However, the samples AB, DB, EB and FB containing the furfural exhibit a lower complex modulus  
 380 than the control sample, indicating that they become softer because of the addition of the furfural.



381 Compared to the unaged samples, all the 20-hour PAV aged samples have a greater complex modulus, as  
 382 shown in **Fig. 11 (b)**. The master curves of all the samples (except for the sample FB) are close to that of  
 383 the control sample 40/60 at the aged condition, which demonstrates that the stiffness of these aged  
 384 samples is not significantly changed by the AACs, resulted from the sacrificial loss of the additives after  
 385 20-hour PAV ageing. It is noted that the complex modulus of the aged sample FB is much smaller than  
 386 that of the aged control sample. This indicates that the addition of the formulation F (DLTDP:Irganox  
 387 acid:furfural) makes the bitumen softer at the aged condition.



388  
 389 (a) Master curves for the unaged samples



390  
 391 (b) Master curves for the 20-hour PAV (PAV20) aged samples

392 **Fig. 11.** Master curves of complex modulus for all the samples at (a) unaged and (b) 20-hour PAV aged  
 393 conditions.

394

## 395 3.4 Effect of AACs on fatigue performance of bitumen

396 The fatigue resistance potential of the 20-hour PAV aged bitumen samples at the intermediate temperature  
 397 (20 °C) is evaluated using a DSR-based cracking (DSR-C) model developed by the authors based on  
 398 damage mechanics in the previous work (Gao et al., 2020a, b; Li et al., 2020; Zhang and Gao, 2019). In  
 399 the DSR-C model, the crack length in the bitumen during a time weep fatigue test is predicted by the  
 400 samples' shear moduli and phase angles in the undamaged and damaged conditions, as shown in **Eq. (4)**.  
 401 The shear modulus ( $|G_0^*|$ ) and the phase angle ( $\delta_0$ ) in the undamaged condition were obtained from the  
 402 frequency sweep tests. The shear modulus ( $|G_N^*|$ ) and the phase angle ( $\delta_N$ ) at the  $N$ th load cycle in the  
 403 damaged condition were recorded up to 24,000 load cycles in the time sweep tests. It is noted that the  
 404 fatigue crack length predicted from the DSR-C model has been validated by comparing with the measured  
 405 crack length using a digital visualisation approach for unmodified and modified bitumen at different  
 406 temperatures, frequencies and strain levels in the previous work (Zhang and Gao, 2019).

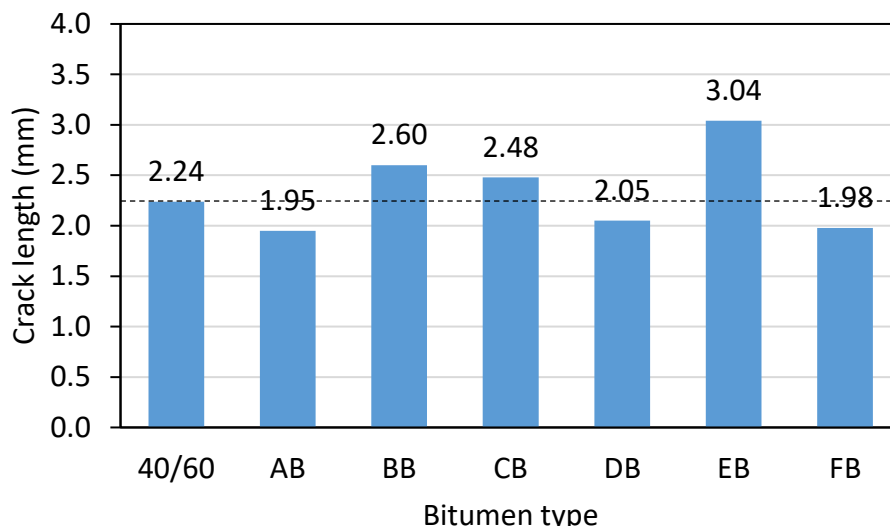
$$407 \quad c = \left[ 1 - \left( \frac{|G_N^*| / \sin(\delta_N)}{|G_0^*| / \sin(\delta_0)} \right)^4 \right]^{1/4} r_0 \quad (4)$$

408 where  $c$  is the crack length in the cylindrical bitumen sample;  $r_0$  is the original radius of the bitumen  
 409 sample;  $|G_0^*|$  and  $\delta_0$  are the shear modulus and the phase angle in the undamaged condition, respectively;  
 410 and  $|G_N^*|$  and  $\delta_N$  are the shear modulus and the phase angle at the  $N$ th load cycle in the damaged  
 411 condition, respectively.

412

413 The crack length in the bitumen was calculated at the 24,000<sup>th</sup> load cycle for all the 20-hour PAV aged  
 414 samples using the DSR-C model in **Eq. (4)** to evaluate their fatigue performance, as shown in **Fig. 12**. It  
 415 is seen that the crack length values of the samples AB (1.95 mm) and FB (1.98 mm) are smaller than that  
 416 of the control sample 40/60 (2.24 mm). This indicates that the addition of the formulations A and F  
 417 containing DLTDP and furfural can enhance the resistance of the bitumen to fatigue cracking, which  
 418 agrees well with the findings reported in the literature (Omairey et al., 2020). In contrast, the samples BB  
 419 and CB present greater crack length (2.60 mm and 2.48 mm) than the control sample, which means that  
 420 the fatigue resistance of the bitumen is weakened by the additives B (Irganox acid) and C  
 421 (NaMMT:Irganox acid). Compared to the sample BB containing Irganox acid, the sample DB with  
 422 Irganox acid:furfural has a lower crack length (2.05 mm), indicating that furfural improves the fatigue  
 423 performance of the bitumen modified by the additive B (Irganox acid). However, the furfural becomes  
 424 ineffective in the fatigue improvement due to the addition of NaMMT, which is demonstrated by the  
 425 higher crack length (3.04 mm) of the sample EB with NaMMT:Irganox acid:furfural. In conclusion,  
 426 among the six types of the anti-ageing compounds, A (DLTDP:furfural), D (Irganox acid:furfural) and F  
 427 (DLTDP:Irganox acid:furfural) can significantly strengthen the fatigue performance of the bitumen  
 428 samples.

429



430

431 **Fig. 12.** Fatigue crack length calculated for all the 20-hour PAV aged samples.

432

433 3.5 Effect of AACs on rutting performance of bitumen

434 The rutting resistance potential of the RTFO aged bitumen samples at the high temperature is evaluated  
 435 by the non-recoverable creep compliance and the percent recoverable strain that can be obtained by **Eqs.**  
 436 **(5)** and **(6)** based on the results from the MSCR tests. The non-recoverable creep compliance and the  
 437 percent recoverable strain are employed to characterise the deformation resistance and the elastic property  
 438 of bitumen samples, respectively. A smaller non-recoverable creep compliance with a higher percent  
 439 recoverable strain is desirable, which means a better resistance to rutting for the bitumen at the high  
 440 temperature.

$$441 \quad J_{nr} = \frac{\varepsilon_{nr}}{\sigma} \quad (5)$$

442 where  $J_{nr}$  is non-recoverable creep compliance ( $\text{kPa}^{-1}$ ),  $\varepsilon_{nr}$  is non-recoverable strain at end of rest period  
 443 of 9 s, and  $\sigma$  is stress level (kPa) applied during creep phase.

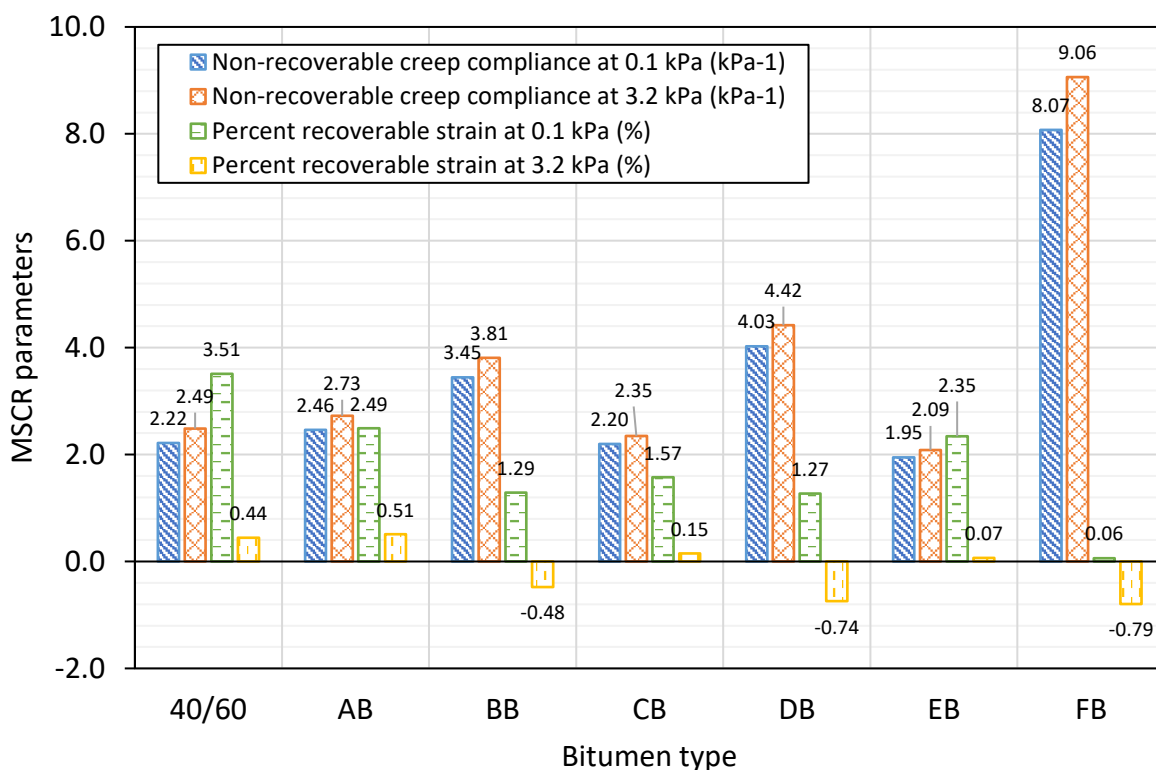
$$444 \quad \varepsilon_r = \frac{\varepsilon_1 - \varepsilon_{10}}{\varepsilon_1} \times 100\% \quad (6)$$

445 where  $\varepsilon_r$  is percent recoverable strain,  $\varepsilon_1$  is strain at the end of 1 s creep phase, and  $\varepsilon_{10}$  is strain at the end  
 446 of 10 s creep phase.

447

448 **Fig. 13** illustrates the MSCR parameters (i.e., the non-recoverable creep compliance and the percent  
 449 recoverable strain) for all the RTFO aged bitumen samples. It can be seen that the MSCR parameters of  
 450 sample AB are close to that of the control sample 40/60, which means that the rutting performance of the  
 451 bitumen is not significantly changed by the formulation A (DLTDP:furfural). However, the sample FB  
 452 shows the highest non-recoverable creep compliance with the lowest percent recoverable strain due to the  
 453 presence of Irganox acid. The sample BB with the additive Irganox acid also has a higher non-recoverable  
 454 creep compliance with a lower percent recoverable strain than that of the control sample. This  
 455 demonstrates that the addition of Irganox acid reduces the rutting resistance of the samples. Compared to  
 456 the sample BB, the MSCR parameters of the samples DB and CB indicates that the furfural weakens its  
 457 rutting performance while the NaMMT strengthens its rutting resistance, respectively. The role of  
 458 NaMMT in improving the rutting performance is also found by the MSCR parameter comparison of the  
 459 samples DB and EB. This finding is consistent with the previous research on the effects of the  
 460 nanomaterials on the rutting resistance of bitumen (Yao et al., 2013a). In summary, it is concluded that

461 the anti-ageing compounds B (Irganox acid), D (Irganox acid:furfural) and F (DLTDP:Irganox  
 462 acid:furfural) reduce the rutting resistance of the bitumen samples that is not significantly changed by the  
 463 formulations A (DLTDP:furfural), C (NaMMT:Irganox acid) and E (NaMMT:Irganox acid:furfural).  
 464



465  
 466 **Fig. 13.** MSCR parameters for all the RTFO aged samples.  
 467

468 **4. Conclusions**

469 In this study, the effects of anti-ageing compounds (AACs) on the rheological and mechanical properties  
 470 of the bitumen were investigated using the Dynamic Shear Rheometer (DSR) tests. The anti-ageing  
 471 performance of all the AACs was evaluated by Fourier Transform Infrared (FTIR) Spectroscopy test. All  
 472 the AAC modified bitumen samples were examined by a series of rheological tests to analyse their  
 473 complex viscosity, linear viscoelastic (LVE) properties, fatigue and rutting performances. The main  
 474 findings from this research are as follows:

- 475 (1) All the AACs that contained Irganox acid, with the exception of the formulation NaMMT:Irganox  
 476 acid:furfural (E), resulted in highly effective stabilisation of the bitumen substrate (anti-ageing  
 477 performance); the presence of furfural in the AAC compositions, on the other hand, displayed adverse  
 478 effects.  
 479 (2) All the AAC modified bitumen samples exhibited a non-Newtonian behaviour. Irganox acid is shown  
 480 to enhance the complex viscosity of the bitumen while the furfural reduces the viscosity.  
 481 (3) The unaged and 20-hour PAV-aged bitumen samples modified by the AACs can be considered as  
 482 thermo-rheologically simple materials. The black diagram of the unaged sample FB with the  
 483 formulation F (DLTDP:Irganox acid:furfural) showed an inverse “C” pattern, which is significantly  
 484 different from that of the remaining AAC modified bitumen samples.  
 485 (4) The samples BB with Irganox acid and CB with NaMMT:Irganox acid are somewhat stiffer than the  
 486 control sample 40/60 due to the presence of a high concentration (10%) of Irganox acid. However,  
 487 the samples AB (with DLTDP:furfural), DB (with Irganox acid:furfural), EB (with NaMMT:Irganox

488 acid:furfural) and FB (with DLTDP:Irganox acid:furfural) became softer because of the addition of  
489 the furfural.

490 (5) The anti-ageing compounds A (DLTDP:furfural), D (Irganox acid:furfural) and F (DLTDP:Irganox  
491 acid:furfural) have significantly strengthened the resistance of the bitumen samples to fatigue  
492 cracking.

493 (6) NaMMT enhanced the rutting resistance of bitumen samples while Irganox acid and furfural  
494 weakened the rutting performance of the samples.

495 This study evaluated the oxidative stability (anti-ageing), rheological and mechanical performances of  
496 bitumen modified with different anti-ageing compounds (AACs). Future study will be continued to  
497 investigate the low temperature performance of the AAC-modified bitumen. In addition, different base  
498 bitumen will be examined to further evaluate the influence of the AACs on the rheological and mechanical  
499 performances of bitumen.

500

### 501 **Conflict of interest**

502 The authors declare that there are no conflicts of interest.

503

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508 No 101030767.

509

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