

## Chemical and rheological properties of polymer modified bitumen incorporating bio-oil derived from waste cooking oil

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1           Chemical and rheological properties of polymer modified bitumen  
2                   incorporating bio-oil derived from waste cooking oil

3  
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37 **Abstract:** The chemical and rheological properties of polymer modified bitumen  
38 incorporating bio-oil derived from waste cooking oil (WCO) were investigated in  
39 this paper. At first, the chemical composition and mixing mechanism of the  
40 experimental materials were analysed from the perspective of functional group, and  
41 the influence of bio-oil on the activation energy was also researched. Then, the effect  
42 of bio-oil on the rotational viscosities of polymer modified bitumen and construction  
43 temperatures of corresponding mixtures was studied. Finally, the shear and bending  
44 rheological properties of polymer modified bitumen containing bio-oil were  
45 investigated. The results show that the bio-oil and styrene-butadiene-styrene (SBS)  
46 modified bitumen is mainly physically mixed, the addition of bio-oil decreases the  
47 activation energy of SBS modified bitumen. Additionally, the SBS modified bitumen  
48 containing bio-oil has lower viscosity values, and corresponding mixtures also have  
49 lower construction temperatures. Furthermore, the addition of bio-oil in SBS  
50 modified bitumen reduces the shear modulus and increases the bending creep  
51 compliance, which means bio-oil has positive effect on the low-temperature thermal  
52 cracking resistance performance while sacrificing the high-temperature rutting  
53 resistance performance to some extent. Therefore, the incorporation of WCO-based  
54 bio-oil in polymer modified bitumen is a promising technique to be used in cold  
55 regions where the low-temperature problems are more crucial.

56  
57 **Keywords:** Chemo-rheological property; Bio-oil; Polymer modified bitumen; Waste  
58 cooking oil; Huet-Such model

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## 72 **1 Introduction**

73 Petroleum is the main source of the bitumen commonly used in pavement  
74 engineering. Nevertheless, the use of bitumen is unsustainable because the petroleum  
75 is a kind of non-renewable resource. Hence, it is necessary to develop a promising  
76 substitute for traditional petroleum bitumen to ensure the sustainable development of  
77 pavement construction industry. Bio-bitumen, which refers to binding materials  
78 produced from renewable biomass resources, has been proposed by researchers as a  
79 sustainable substitute for traditional petroleum bitumen [1-3].

80 In reality, the sources of bio-bitumen preparation vary a lot, which consequently  
81 results in products with different properties [4-6]. The materials used for bio-bitumen  
82 preparation can be roughly divided into two categories according to their physical  
83 state. One category is powder-like material. For example, Zofka and Yut modified  
84 the petroleum bitumen with waste coffee grounds and investigated the rheological  
85 and ageing properties of resulting products [7]. Sobolev et al. partially replaced the  
86 petroleum bitumen with fly ash and researched corresponding rheological properties  
87 [8]. Zhao et al. produced bio-char products from the pyrolysis of switchgrass and  
88 investigated their potential application as bio-modifiers for petroleum bitumen [9].  
89 However, the physical state and components of the materials in this category are  
90 different from traditional petroleum bitumen, which limits their application in  
91 preparing high-performance bio-bitumen. The other category is oil-like material,  
92 which can be termed as bio-oil. For instance, Wu and Muhunthan studied the  
93 feasibility of partially replacing petroleum bitumen with waste engine oil [10]. Yang  
94 et al. obtained bio-binders from the fast pyrolysis of waste wood feedstock, and  
95 studied the ageing mechanism and rheological properties of petroleum bitumen  
96 containing bio-binders [11]. Fini et al. prepared a kind of bio-binder from the  
97 thermochemical liquefaction of swine manure and researched the characteristics of  
98 petroleum bitumen partially replaced by the bio-binder [12]. Audo et al. generated a  
99 kind of bio-binder from microalgae residues via subcritical hydrothermal  
100 liquefaction, and showed the potential of this product for substituting petroleum  
101 bitumen [13]. The materials in this category have more similarities with traditional  
102 petroleum bitumen, so they are more promising to be used to produce  
103 high-performance bio-bitumen.

104 Recently, the potential application of waste cooking oil (WCO)-based bio-oil  
105 for bio-bitumen preparation is under investigation by different researchers [14-16].  
106 This idea originates from the fact that a large amount of WCO is generated

107 worldwide each year, such as the amount of WCO produced by the restaurants and  
 108 hotels in the United States is about 3 billion gallons per year [17]. One commonly  
 109 used method to deal with the WCO is to prepare biodiesel, with producing a kind of  
 110 bio-oil by-product that accounts for about 10 wt% of the biodiesel production  
 111 [18-20]. The processing of the bio-oil by-product is costly, so most of this  
 112 by-product is left in the plants. Hence, it is necessary to develop a sustainable  
 113 approach to use this bio-oil by-product, which is significant to both environment and  
 114 economy.

115 Current studies show that this WCO-based bio-oil can be used as modifier and  
 116 rejuvenator of base bitumen [14, 21]. However, the amount of bio-oil used in base  
 117 bitumen is very limited because the light components in bio-oil are not beneficial to  
 118 the high-temperature performance of bitumen. In order to deal with this problem, the  
 119 incorporation of polymer might be more promising because of the good performance  
 120 of polymer modification shown in pavement engineering. Therefore, this paper  
 121 focuses on the possible application of the WCO-based bio-oil in polymer modified  
 122 bitumen by investigating corresponding chemical and rheological properties.  
 123 Furthermore, the suitability of a promising model for predicting the performance of  
 124 polymer modified bitumen incorporating bio-oil is examined. The presented work is  
 125 helpful for the preparation of high-performance bio-bitumen by using polymer  
 126 modification and the sustainable development of pavement construction industry.

127

## 128 **2 Materials and methods**

### 129 **2.1 Bitumen**

130 A kind of styrene-butadiene-styrene (SBS) modified bitumen was used in this  
 131 paper as control bitumen, its basic properties were shown in Table 1. This bitumen is  
 132 prepared by base bitumen of PG 64-22 and star-shaped styrene-butadiene-styrene  
 133 (SBS) copolymer.

134

Table 1 Basic properties of the SBS modified bitumen

	Properties	Units	Test results
	Penetration @ 25 °C	0.1 mm	67.2
	Softening point	°C	59.4
	Ductility @ 5 °C	cm	39.4
	Rotational viscosity @ 135 °C	mPa·s	789.6
	Mass loss	%	0.25
After RTFOT	Retained penetration ratio @ 25 °C	%	85
	Retained ductility @ 5 °C	cm	35

135

136

## 137 **2.2 Bio-oil**

138 The bio-oil used in this paper is a kind of black oily liquid produced from the  
139 process of WCO refining for biodiesel. The density of this bio-oil at 15 °C is 0.95  
140 g/cm<sup>3</sup>, the rotational viscosity at 25 °C is 146.3 mPa·s, the pH value is 6.1. In  
141 addition, the content of aromatics is the highest in this bio-oil, while the content of  
142 asphaltenes is the lowest. More details can be found in reference [22].

143

## 144 **2.3 Materials preparation**

145 In this paper, the SBS modified bitumen and bio-oil were blended uniformly by  
146 a laboratory high shear mixer at 160 °C for 40 minutes with constant stirring speed  
147 of 5000 r/min to obtain a homogeneous mixture, the content of bio-oil ranged from 0  
148 to 16 wt% of the mixture with the increment of 4 wt%. In this paper, the mixed  
149 products with different bio-oil contents are respectively labelled as S0, S4, S8, S12,  
150 and S16. In addition, BP means the bio-oil by-product, and SMB stands for all the  
151 products prepared by SBS modified bitumen and bio-oil.

152

## 153 **2.4 Methods**

154 In this paper, Fourier transform infrared spectroscopy (FT-IR) tests were used  
155 to investigate the functional groups of the experimental materials. In addition,  
156 rotational viscosity (RV) tests were conducted to analyse the influence of bio-oil on  
157 the activation energy and viscosity of SBS modified bitumen. Moreover, dynamic  
158 shear rheometer (DSR) tests and bending beam rheometer (BBR) tests were carried  
159 out to research the shear and bending rheological properties of SBS modified  
160 bitumen containing bio-oil, respectively. The test methods used in this paper are  
161 consistent with the standard methods proposed by the American Association of State  
162 Highway and Transportation Officials (AASHTO).

### 163 ***FT-IR test***

164 The FT-IR tests were used to obtain the IR spectra of experimental materials,  
165 which were further analysed to investigate the chemical components and mixing  
166 mechanism from the functional group point of view. In the test process, the samples  
167 were dissolved in carbon disulphide and then dropped onto KBr pellets. After  
168 solvent evaporating, sample films were generated on the KBr pellets, which were  
169 scanned by FT-IR spectrometer to obtain the IR spectra. In this research, the  
170 scanning times were 32, the resolution was 1 cm<sup>-1</sup>, and the recorded wavenumber  
171 range was from 4000 to 400 cm<sup>-1</sup>.

172

173 ***RV test***

174 The RV tests were performed to measure the rotational viscosity of  
175 experimental materials, which could represent the flowing resistance. In this paper,  
176 the rotational viscosities of SMB were tested at 135 °C, 155 °C, and 175 °C. The  
177 measurements were used to evaluate the effect of bio-oil on the activation energy  
178 and rotational viscosities of SMB, and also the suitable construction temperature  
179 ranges of corresponding asphalt mixture.

180

181 ***DSR test***

182 The DSR tests were conducted to measure the shear modulus values of  
183 experimental materials without considering the ageing effect. The test temperatures  
184 were from 0 to 40 °C with increment of 10°C, the frequency sweep range was from  
185 0.1 to 60 Hz. In order to ensure the linear viscoelastic response of experimental  
186 materials, the strain amplitude sweep tests were conducted beforehand to determine  
187 suitable strain ranges. In this study, the applied strain was controlled to be 0.5 %,  
188 which can guarantee the linear viscoelastic behaviour of all the experimental samples.  
189 The shear modulus master curves were constructed based on the time-temperature  
190 superposition principle (TTSP) and the Huet-Such model to investigate the effect of  
191 bio-oil on the shear rheological properties of SBS modified bitumen.

192

193 ***BBR test***

194 The BBR tests were used to obtain the bending creep stiffness and m-value of  
195 experimental materials without considering the ageing effect. The test temperatures  
196 were -18 °C, -24 °C, and -30 °C. The bending creep compliance master curves  
197 were constructed based on the TTSP and the Huet-Such model to investigate the  
198 effect of bio-oil on the bending rheological properties of SBS modified bitumen.

199

200 **3 Results and discussions**

201 **3.1 Chemical properties**

202 **3.1.1 Chemical composition**

203 The IR spectrum and corresponding functional groups of S0 sample were  
204 shown in Figure 1. The results show that the SBS modified bitumen is mainly  
205 composed of saturated hydrocarbons, unsaturated hydrocarbons, aromatic  
206 compounds, sulfinyl compounds, amides, aldehydes, and ketones. As shown in the  
207 previous research, the BP mainly contains saturated hydrocarbons, unsaturated  
208 hydrocarbons, sulfinyl compounds, amides, and esters.

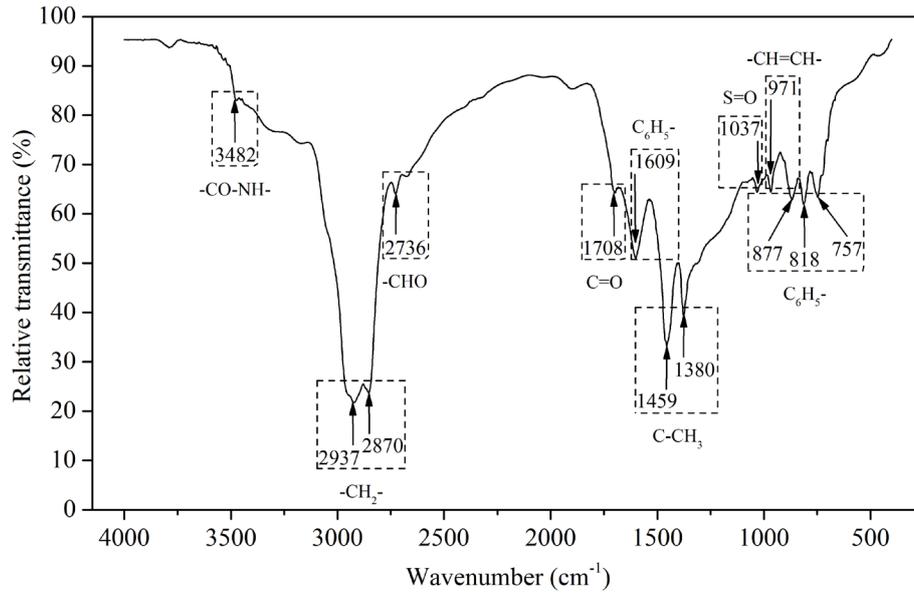


Figure 1 IR spectrum of S0 sample

### 3.1.2 Mixing mechanism

In order to have an insight into the mixing mechanism between BP and S0, the IR spectra of them and corresponding mixed materials were compared in Figure 2. The results show that the spectra of S8 and S16 include all the absorption peaks in the spectrum of S0, and also three extra absorption peaks which come from the spectrum of BP (see the dashed boxes in Figure 2). However, no new absorption peaks are found in the spectra of S8 and S16. Hence, the mixing process of bio-oil and SBS modified bitumen might be mainly physical.

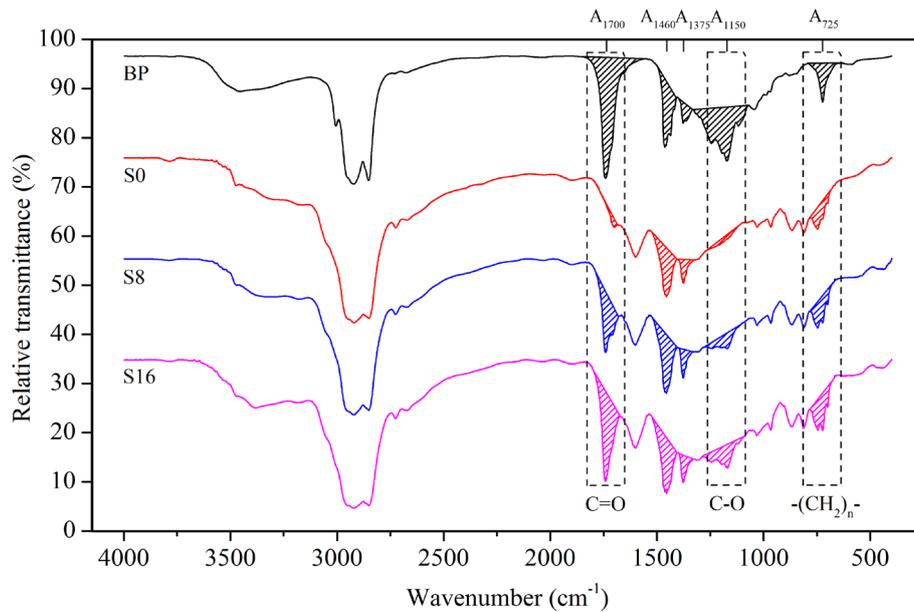


Figure 2 IR spectra comparison of different materials

In order to verify this idea, quantitative analysis of the IR spectrum is

222 conducted. In general, the measurements are affected by the sample thickness and  
 223 infrared radiation path length, so the relative values are more meaningful. Generally,  
 224 a normalisation procedure is used in the quantitative analysis, in which the value  
 225 (height or area of absorption peak) at wavenumber of interest is divided by the  
 226 corresponding value at reference wavenumber which does not change significantly  
 227 [23]. By referring to the definition of carbonyl index ( $I_{CO}$ ) and sulphoxide index  
 228 ( $I_{SO}$ ), which are usually used to analyse ageing evolution [24, 25], the general form  
 229 of index at wavenumber of interest ( $I_i$ ) can be expressed as follows:

$$230 \quad I_i = \frac{V_i}{V_r} \quad (1)$$

231 in which  $V_i$  is the value measured at wavenumber of interest and  $V_r$  is the  
 232 corresponding value measured at reference wavenumber.

233 In this paper, the indices are calculated by using the area of absorption peak  
 234 measured from valley to valley (see the shaded area in Figure 2). Based on the  
 235 principle of normalisation, the wavenumbers of 1460  $\text{cm}^{-1}$  and 1375  $\text{cm}^{-1}$  are chosen  
 236 as the reference wavenumbers. The wavenumbers of interest are 1700  $\text{cm}^{-1}$ , 1150  
 237  $\text{cm}^{-1}$ , and 725  $\text{cm}^{-1}$ , which are corresponding to the absorption peaks in the dashed  
 238 boxes in Figure 2. These three wavenumbers correspond to the functional groups of  
 239 carbonyl (C=O), carbon-oxygen band (C-O), and methylene (CH<sub>2</sub>), respectively.  
 240 Hence, the indices for functional groups of interest can be expressed as follows:

$$241 \quad I_{C=O} = \frac{A_{1700}}{A_{1460} + A_{1375}} \quad (2)$$

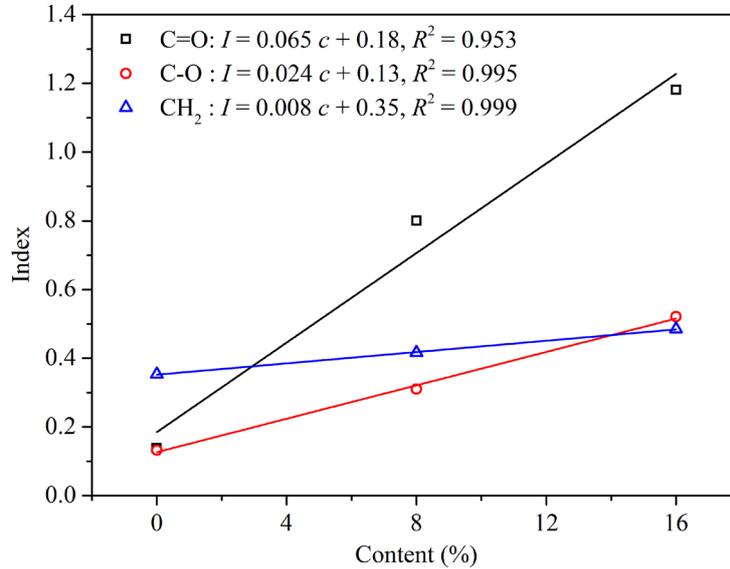
$$242 \quad I_{C-O} = \frac{A_{1150}}{A_{1460} + A_{1375}} \quad (3)$$

$$243 \quad I_{CH_2} = \frac{A_{725}}{A_{1460} + A_{1375}} \quad (4)$$

244 where  $A_k$  means the area of absorption peak around wavenumber  $k$ .

245 The areas of absorption peaks in the vicinity of interested wavenumbers for  
 246 different materials were measured. Then, corresponding index values for SBS  
 247 modified bitumen with different bio-oil contents were calculated and shown in  
 248 Figure 3. The results show that the indices of these three specific functional groups

249 have approximately linear relationships with the bio-oil content, which means the  
 250 areas of these three extra absorption peaks almost linearly increase with the addition  
 251 of bio-oil. Therefore, it can be confirmed that the bio-oil and SBS modified bitumen  
 252 are mainly physically mixed.



253

254 Figure 3 Relationships between functional group indices and bio-oil content

254

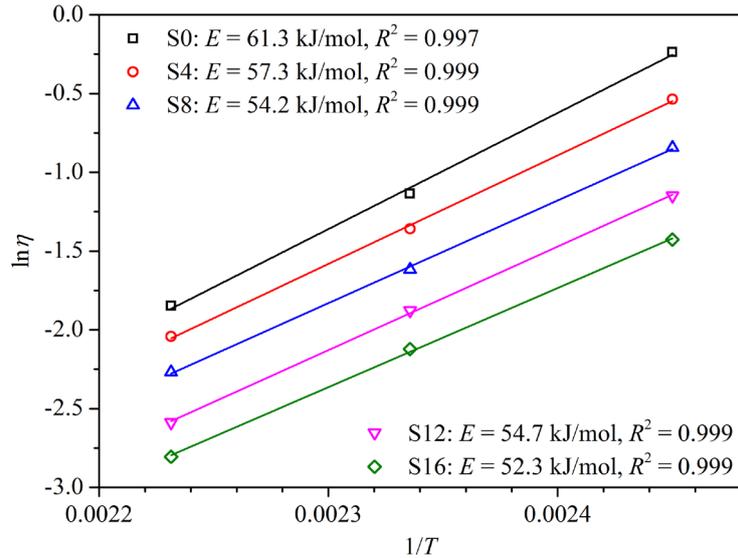
### 255 3.1.3 Activation energy

256 The activation energy of fluids means the energy barrier to be overtaken by  
 257 molecules to make the fluids flow. According to the Andrade equation, the activation  
 258 energy of fluids has the following relationship with viscosity and temperature:

$$259 \ln \eta = \frac{E}{RT} + \ln A \quad (5)$$

260 in which  $\eta$  is the viscosity (Pa·s),  $E$  is the activation energy (J/mol),  $R$  is the  
 261 universal gas constant which equals to 8.314 J/(mol·K),  $T$  is absolute temperature  
 262 (K),  $A$  is a constant related to material properties (Pa·s).

263 At high temperature or low loading frequency, the polymers (such as bitumen or  
 264 polymer modified bitumen) turn into viscous fluids, and corresponding viscosities  
 265 can be modelled by equation (5). This equation indicates that  $\ln \eta$  has linear  
 266 relationship with  $1/T$  if the activation energy is constant within the range of test  
 267 temperatures. Hence, the activation energy of bitumen can be obtained by parameter  
 268 fitting based on the testing results of viscosity at different temperatures. In this paper,  
 269 the RV test results were used to calculate the activation energy values of different  
 270 experimental materials. The fitting curves of viscosities at different temperatures  
 271 based on equation (5) and fitted activation energy values were shown in Figure 4.



272

273 Figure 4 Fitting results of viscosities at different temperatures based on the Andrade equation

274 Figure 4 shows that the test data are properly fitted, so the Andrade equation is  
 275 suitable to describe the viscosity-temperature relationships of SBS modified bitumen  
 276 incorporating bio-oil at high temperatures. In addition, the activation energy of SBS  
 277 modified bitumen is decreased with the addition of bio-oil, which means the  
 278 incorporation of bio-oil makes SBS modified bitumen easier to flow.

279

### 280 3.2 Rheological properties

#### 281 3.2.1 Rotational viscosity

282 Researchers have proposed different models to describe the  
 283 viscosity-temperature relationship of fluids, among which the most commonly used  
 284 model for bitumen is the Saal equation:

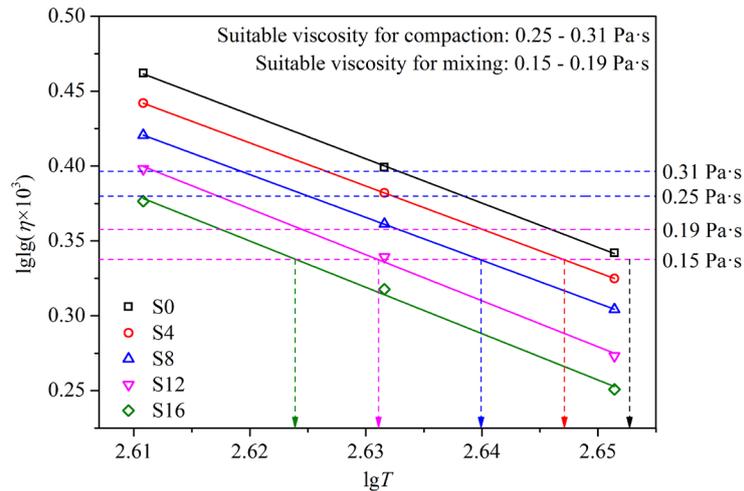
$$285 \lg \lg(\eta \times 10^3) = -m \lg T + n \quad (6)$$

286 where  $\eta$  is the viscosity (Pa·s),  $T$  is absolute temperature (K),  $m$  is a constant  
 287 which can reflect the temperature susceptibility of materials, and  $n$  is a constant  
 288 depends on material properties.

289 In this section, Equation (6) was used to fit the rotational viscosities of SMB at  
 290 different temperatures. The fitting results were shown in Figure 5, and corresponding  
 291 fitted parameter values were shown in Table 2. It can be seen that the Saal equation  
 292 can describe the test data properly. Additionally, the addition of bio-oil decreases the  
 293 viscosity and has slight influence on the temperature susceptibility of the SBS  
 294 modified bitumen.

295 The fitted viscosity-temperature curve of a kind of bitumen can be used to

296 determine the suitable construction temperatures of corresponding asphalt mixture.  
 297 According to the Superpave™ mix design manual, the temperatures are suitable for  
 298 the mixing of asphalt mixture if the viscosities of bitumen are in the range of 0.15 to  
 299 0.19 Pa·s, and the temperatures are suitable for the compaction of asphalt mixture if  
 300 the viscosities of bitumen are in the range of 0.25 to 0.31 Pa·s. On the basis of these  
 301 specifications and viscosity-temperature curves, the suitable mixing and compaction  
 302 temperatures for SMB mixtures were shown in Table 3, including corresponding  
 303 average construction temperatures. It can be found that the average construction  
 304 temperatures of asphalt mixtures are decreased by about 1.8 °C with each 1 %  
 305 increment of the content of bio-oil in SBS modified bitumen. Consequently, less  
 306 energy consumption and smoke emission will be achieved for SMB mixtures in the  
 307 construction process. However, the content of bio-oil in SBS modified bitumen  
 308 should be controlled in a proper range to ensure its practical performance.



309 Figure 5 RV test results and viscosity-temperature curves of SMB

310 Table 2 Fitted parameter values for viscosity-temperature curves of SMB

Materials	Fitted parameter values		
	$m$	$n$	$R^2$
S0	2.956	8.180	1.000
S4	2.883	7.970	1.000
S8	2.864	7.898	1.000
S12	3.074	8.424	0.995
S16	3.094	8.455	0.995

311 Table 3 Suitable mixing and compaction temperatures of SMB mixtures

Materials	Mixing temperatures/°C			Compaction temperatures/°C		
	Lower	Upper	Average	Lower	Upper	Average
S0	169.4	176.3	172.9	156.2	161.8	159.0
S4	163.4	170.5	167.0	150.1	155.8	153.0
S8	156.2	163.2	159.7	143.1	148.7	145.9

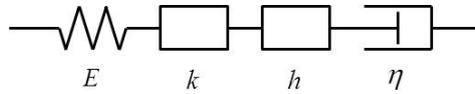
S12	148.1	154.4	151.3	136.0	141.1	138.6
S16	141.3	147.5	144.4	129.5	134.5	132.0

314

### 315 3.2.2 Shear rheological properties

316 The frequency sweep results of the shear modulus of SMB at different  
317 temperatures measured by DSR tests were shifted horizontally to a reference  
318 temperature based on the TTSP, and then fitted by the absolute value of the complex  
319 shear modulus of the Huet-Such model to obtain corresponding master curves. The  
320 master curve can characterise the rheological behaviours of a material in a broader  
321 frequency range.

322



323

324 Figure 6 Schematic representation of the Huet-Such model

325 The Huet-Such model is a combination of the Huet model with a dashpot in  
326 series, as shown in Figure 6. On the basis of the expressions shown in reference [26,  
327 27], the complex shear modulus  $G^*(\omega)$  of the Huet-Such model can be expressed  
328 as follows:

$$329 \quad G^*(\omega) = E \left( \frac{\kappa_1}{\kappa_1^2 + \kappa_2^2} + i \frac{\kappa_2}{\kappa_1^2 + \kappa_2^2} \right) \quad (7)$$

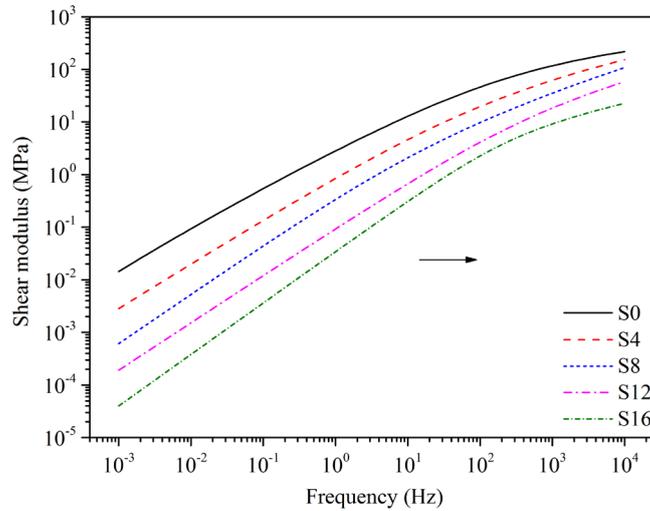
330 with the definitions of  $\kappa_1$  and  $\kappa_2$  as follows:

$$331 \quad \kappa_1 = 1 + \delta (\omega\tau)^{-k} \cos\left(\frac{k\pi}{2}\right) + (\omega\tau)^{-h} \cos\left(\frac{h\pi}{2}\right)$$

$$332 \quad \kappa_2 = \delta (\omega\tau)^{-k} \sin\left(\frac{k\pi}{2}\right) + (\omega\tau)^{-h} \sin\left(\frac{h\pi}{2}\right) + (\beta\omega\tau)^{-1}$$

333 in which  $i$  is the imaginary unit satisfying  $i^2 = -1$ ,  $\omega = 2\pi f$  with  $\omega$  being the  
334 loading angular frequency and  $f$  being the loading frequency,  $\tau$  is the  
335 characteristic time depends only on temperature,  $E$  is the Hookean constant of the  
336 spring element,  $\delta$  is a positive dimensionless constant,  $k$  and  $h$  are dimensionless  
337 exponents of the two parabolic elements with relationship  $0 < k < h < 1$ ,  $\beta$  is a  
338 dimensionless constant related to the Newtonian viscosity  $\eta$  of the dashpot element

339 by equation  $\eta = \beta\tau E$ .



340

341 Figure 7 Shear modulus master curves of SMB (@ 20 °C)

342

343 In this study, 20 °C was selected as the reference temperature. The shear  
 344 modulus master curves of SMB were constructed based on the TTSP and the  
 345 Huet-Such model, as shown in Figure 7. The fitted values of parameters in the  
 346 Huet-Such model for different materials were presented in Table 4. Figure 7 shows  
 347 that the whole master curve is right shifted with the increasing content of bio-oil,  
 348 which means the addition of bio-oil decreases the shear modulus in the whole  
 349 frequency domain. Therefore, bio-oil has a negative effect on the shear/rutting  
 resistance performance of SBS modified bitumen.

350

Table 4 Fitted values of parameters in the Huet-Such model for different materials

Materials	Fitted parameter values (@ 20 °C)					
	$E$ (MPa)	$\delta$	$k$	$h$	$\beta$	$\lg(\tau)$
S0	700	3.10	0.264	0.701	87.7	-4.11
S4	700	5.87	0.396	0.827	69.8	-4.23
S8	700	10.9	0.492	0.943	60.8	-4.20
S12	700	7.43	0.412	0.895	67.2	-5.10
S16	700	21.4	0.327	0.979	64.2	-5.19

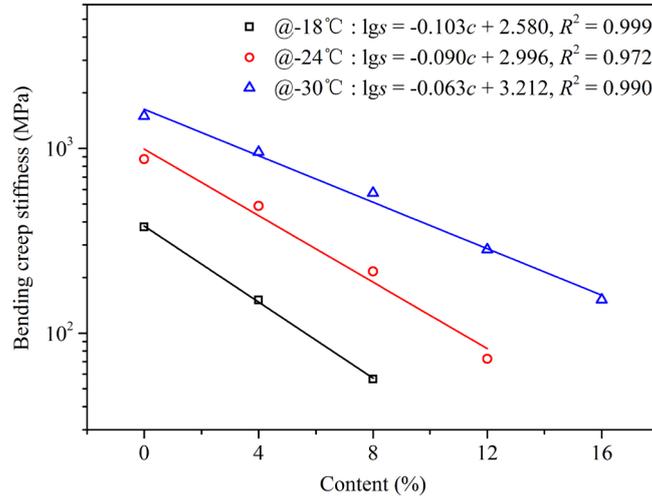
351

### 352 3.2.3 Bending rheological properties

353

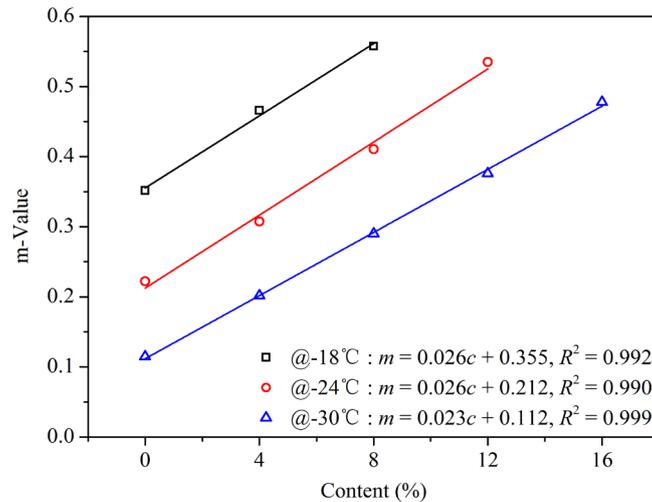
354 The bending creep stiffness and m-value results of SMB obtained from BBR  
 355 tests were shown in Figures 8 and 9, respectively. It can be seen that the bending  
 356 creep stiffness values are decreased and m-values are increased with the addition of  
 357 bio-oil, which means that bio-oil can improve the stress relaxation ability of SBS  
 358 modified bitumen. In addition, the bending creep stiffness has an approximately  
 linear relationship with the bio-oil content in the semi-logarithmic coordinate system,

359 and the  $m$ -value has an approximate linear relationship with the bio-oil content in  
 360 normal coordinate system at a certain temperature. The regression equations of these  
 361 relationships are also included in these Figures, where  $s$  means bending creep  
 362 stiffness,  $m$  means  $m$ -value, and  $c$  means bio-oil content. The reason of the missing  
 363 data for specimens with higher bio-oil contents at higher temperatures is that  
 364 corresponding measurements exceed the measuring range of BBR test.



365  
366

Figure 8 Bending creep stiffness test results of SMB



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368  
369

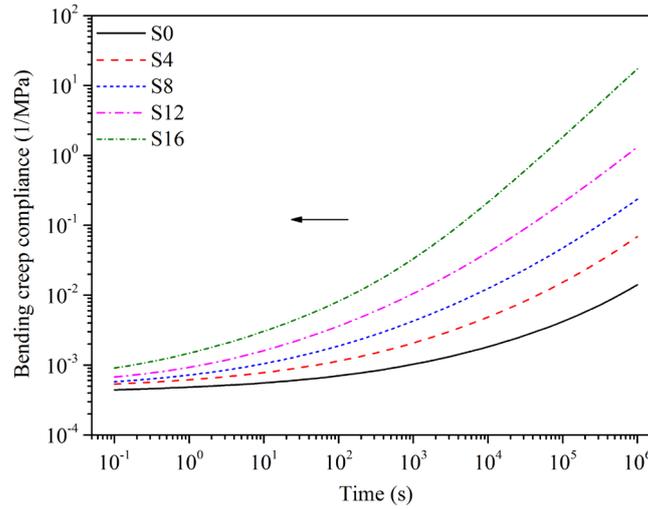
Figure 9 m-Value test results of SMB

370 The bending rheological properties of SMB were analysed in a broader time  
 371 range by constructing their bending creep compliance master curves. At first, the  
 372 bending creep compliance values of SMB were calculated by taking the reciprocals  
 373 of corresponding bending creep stiffness values. Then, the bending creep compliance  
 374 data at different temperatures were horizontally shifted to a reference temperature  
 375 based on the TTSP. Finally, the data in the reference temperature were fitted by the  
 376 creep compliance  $J(t)$  of the Huet-Such model, which can be expressed as

377 follows:

$$378 \quad J(t) = \frac{1}{E} \left[ 1 + \delta \frac{(t/\tau)^k}{\Gamma(k+1)} + \frac{(t/\tau)^h}{\Gamma(h+1)} + \frac{t}{\beta\tau} \right] \quad (8)$$

379 where  $t$  is the loading time,  $\Gamma(\cdot)$  is the Gamma function, and other parameters are  
 380 the same as those defined in the previous section.



381

382 Figure 10 Bending creep compliance master curves of SMB @ -30 °C

383 The obtained bending creep compliance master curves of SMB at reference  
 384 temperature of -30 °C were shown in Figure 10. The fitted values of different  
 385 parameters in the Huet-Such model for different materials were shown in Table 5.  
 386 Figure 10 shows that the bending creep compliance master curves are left  
 387 horizontally shifted in the whole time domain with the increasing content of bio-oil,  
 388 which implies the enhanced bending creep compliance and consequently improved  
 389 thermal cracking resistance property. The decreasing trend of  $E$  with the addition of  
 390 bio-oil also supports this conclusion. Hence, adding bio-oil into SBS modified  
 391 bitumen is an effective method to improve the low-temperature cracking resistance  
 392 property.

393

394 Table 5 Fitted values of parameters in the Huet-Such model for different materials

Materials	Fitted parameter values (@ -30 °C)					
	$E$ (MPa)	$\delta$	$k$	$h$	$\beta$	$\tau$ (s)
S0	2967	0.6498	0.1015	0.4064	82.90	686.6
S4	2354	1.224	0.2145	0.5163	40.41	309.1
S8	2201	2.482	0.3172	0.6292	26.31	174.6
S12	1921	5.054	0.4117	0.8489	37.25	131.3
S16	1850	5.962	0.4018	0.9923	21.45	30.86

## 395 **4 Conclusions**

396 This paper investigated the chemical and rheological properties of SBS  
397 modified bitumen containing WCO-based bio-oil. Based on the analyses above, the  
398 following conclusions can be drawn:

399 (1) The mixing process of bio-oil and SBS modified bitumen is mainly physical  
400 reaction, and the incorporation of bio-oil makes bitumen easier to flow.

401 (2) Adding bio-oil into SBS modified bitumen decreases its viscosity, and  
402 consequently lowers the suitable construction temperatures of corresponding asphalt  
403 mixture.

404 (3) Increasing the content of bio-oil in SBS modified bitumen reduces the shear  
405 modulus and bending creep stiffness, while increases the m-value. Hence, the  
406 addition of bio-oil is beneficial to improve the low-temperature thermal cracking  
407 resistance performance of SBS modified bitumen, but it has a negative effect on the  
408 shear/rutting resistance performance.

409 (4) The Huet-Such model can properly predict the rheological properties of SBS  
410 modified bitumen incorporating bio-oil derived from WCO.

411 In conclusion, considering the improved low-temperature performance and  
412 moderate high-temperature performance, the incorporation of WCO-based bio-oil in  
413 polymer modified bitumen is promising, especially in cold regions where the  
414 low-temperature property of bitumen is the main concern. Additionally, the bio-oil  
415 also has the potential to be used as softening agent for reclaimed/aged polymer  
416 modified bitumen.

## 417 **5 Recommendations**

418 According to the research in this paper, more attention should be paid on the  
419 high-temperature performance of the polymer modified bitumen containing  
420 WCO-based bio-oil. In addition, the similarity of the chemical components should  
421 be taken into account when preparing high-performance bio-bitumen by different  
422 materials.

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