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

Sun, Zhaojie; Yi, Junyan; Chen, Zining; Xie, Sainan; Xu, Meng; Feng, Decheng

**DOI**
10.1617/s11527-019-1400-7

**Publication date**
2019

**Document Version**
Accepted author manuscript

**Published in**
Materials and Structures/Materiaux et Constructions

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

Zhaojie Sun[1,2], Junyan Yi[1,*], Zining Chen[1], Sainan Xie[1], Meng Xu[1], Decheng Feng[1,*]

1. School of Transportation Science and Engineering, Harbin Institute of Technology, Harbin, 150090, China
2. Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, 2628 CN, the Netherlands

Corresponding authors:

Junyan Yi, yijunyan@hit.edu.cn, +86-13936524780

Decheng Feng, fengdecheng@hit.edu.cn, +86-13703652113

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

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

## 1 Introduction

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

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

Recently, the potential application of waste cooking oil (WCO)-based bio-oil for bio-bitumen preparation is under investigation by different researchers [14-16]. This idea originates from the fact that a large amount of WCO is generated worldwide each year, such as the amount of WCO produced by the restaurants and hotels in the United States is about 3 billion gallons per year [17]. One commonly used method to deal with the WCO is to prepare biodiesel, with producing a kind of bio-oil by-product that accounts for about 10 wt% of the biodiesel production [18-20]. The processing of the bio-oil by-product is costly, so most of this by-product is left in the plants. Hence, it is necessary to develop a sustainable approach to use this bio-oil by-product, which is significant to both environment and economy.

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

## 2 Materials and methods

### 2.1 Bitumen

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

Table 1 Basic properties of the SBS modified bitumen

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

## 2.2 Bio-oil

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

## 2.3 Materials preparation

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

## 2.4 Methods

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

***FT-IR test***

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

***RV test***

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

***DSR test***

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

***BBR test***

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

## 3 Results and discussions

### 3.1 Chemical properties

3.1.1 Chemical composition

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

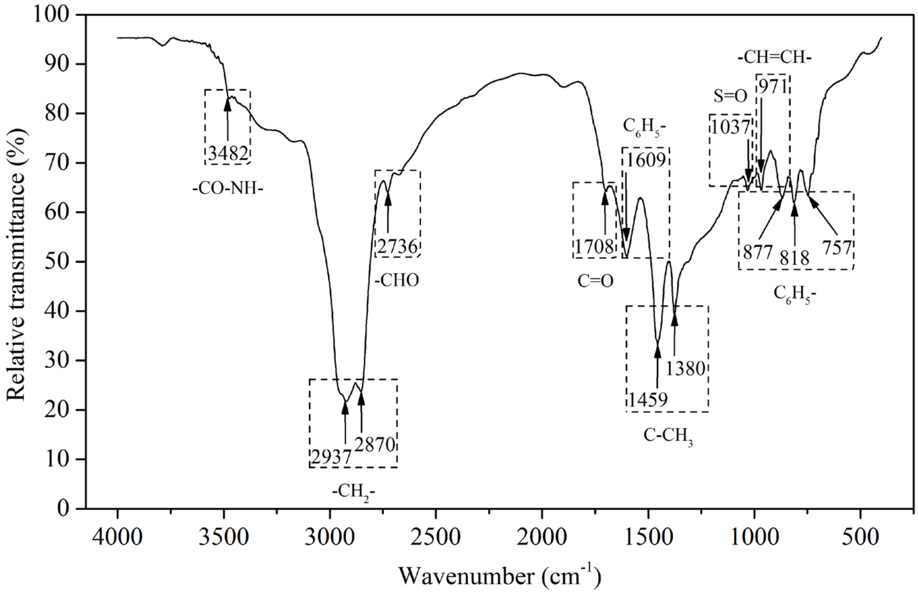


Figure 1 IR spectrum of S0 sample

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.

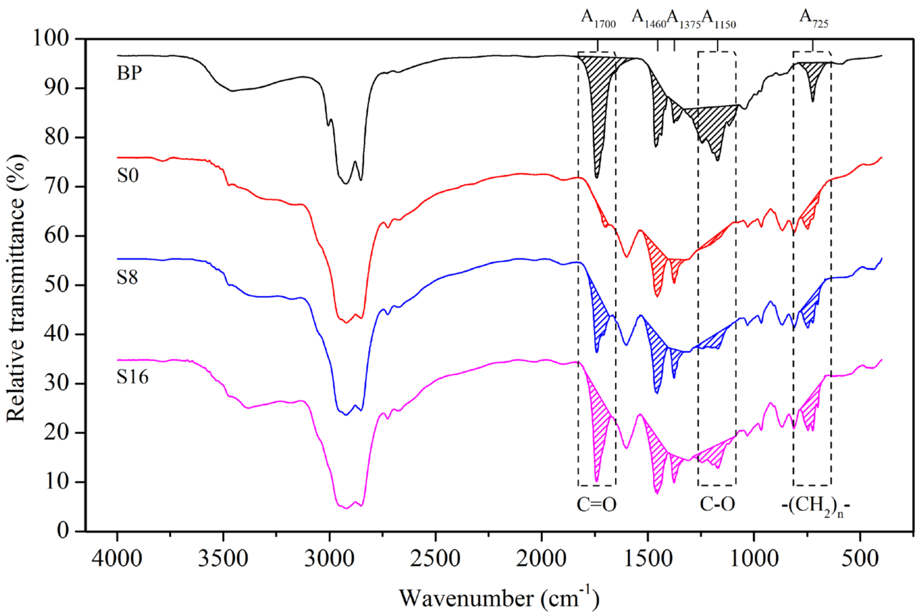


Figure 2 IR spectra comparison of different materials

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

$$I_{\mathrm{i}} = \frac{V_{\mathrm{i}}}{V_{\mathrm{r}}} \tag{1}$$

in which $V_{\mathrm{i}}$ is the value measured at wavenumber of interest and $V_{\mathrm{r}}$ is the corresponding value measured at reference wavenumber.

In this paper, the indices are calculated by using the area of absorption peak measured from valley to valley (see the shaded area in Figure 2). Based on the principle of normalisation, the wavenumbers of 1460 cm$^{-1}$ and 1375 cm$^{-1}$ are chosen as the reference wavenumbers. The wavenumbers of interest are 1700 cm$^{-1}$, 1150 cm$^{-1}$, and 725 cm$^{-1}$, which are corresponding to the absorption peaks in the dashed boxes in Figure 2. These three wavenumbers correspond to the functional groups of carbonyl (C=O), carbon-oxygen band (C-O), and methylene ($CH_2$), respectively. Hence, the indices for functional groups of interest can be expressed as follows:

$$I_{\mathrm{C=O}} = \frac{A_{1700}}{A_{1460} + A_{1375}} \tag{2}$$

$$I_{\mathrm{C\text{-}O}} = \frac{A_{1150}}{A_{1460} + A_{1375}} \tag{3}$$

$$I_{\mathrm{CH_2}} = \frac{A_{725}}{A_{1460} + A_{1375}} \tag{4}$$

where $A_{\mathrm{k}}$ means the area of absorption peak around wavenumber *k*.

The areas of absorption peaks in the vicinity of interested wavenumbers for different materials were measured. Then, corresponding index values for SBS modified bitumen with different bio-oil contents were calculated and shown in Figure 3. The results show that the indices of these three specific functional groups have approximately linear relationships with the bio-oil content, which means the areas of these three extra absorption peaks almost linearly increase with the addition of bio-oil. Therefore, it can be confirmed that the bio-oil and SBS modified bitumen are mainly physically mixed.

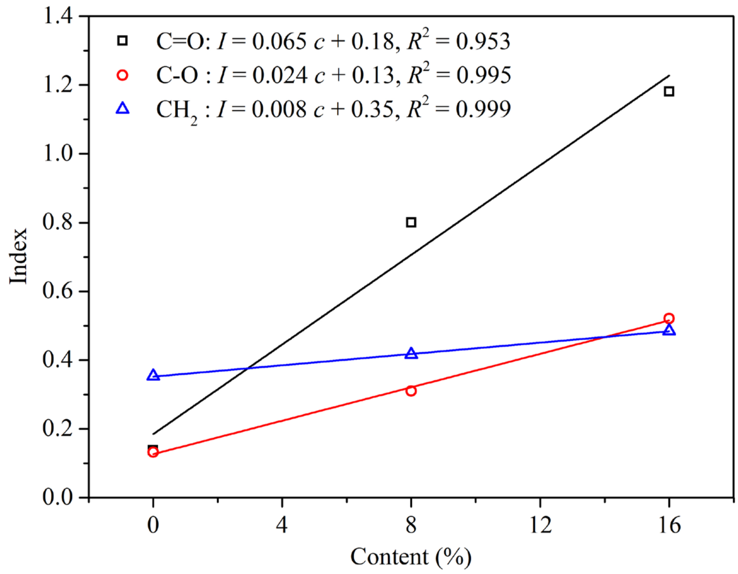


Figure 3 Relationships between functional group indices and bio-oil content

### 3.1.3 Activation energy

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

$$\ln \eta = \frac{E}{RT} + \ln A \tag{5}$$

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

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

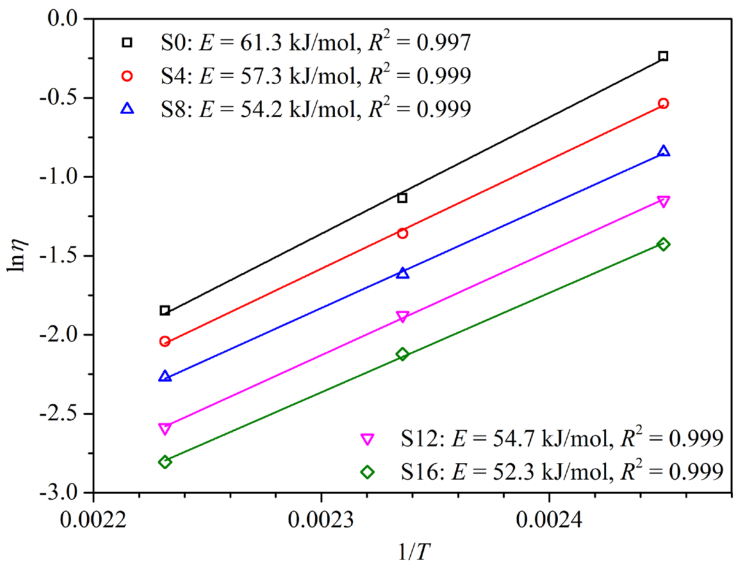


Figure 4 Fitting results of viscosities at different temperatures based on the Andrade equation

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

## 3.2 Rheological properties

### 3.2.1 Rotational viscosity

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

$$\lg\lg\left(\eta\times10^{3}\right)=-m\lg T+n \tag{6}$$

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

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

The fitted viscosity-temperature curve of a kind of bitumen can be used to determine the suitable construction temperatures of corresponding asphalt mixture. According to the Superpave$^{TM}$ mix design manual, the temperatures are suitable for the mixing of asphalt mixture if the viscosities of bitumen are in the range of 0.15 to 0.19 Pa·s, and the temperatures are suitable for the compaction of asphalt mixture if the viscosities of bitumen are in the range of 0.25 to 0.31 Pa·s. On the basis of these specifications and viscosity-temperature curves, the suitable mixing and compaction temperatures for SMB mixtures were shown in Table 3, including corresponding average construction temperatures. It can be found that the average construction temperatures of asphalt mixtures are decreased by about 1.8 ℃ with each 1 % increment of the content of bio-oil in SBS modified bitumen. Consequently, less energy consumption and smoke emission will be achieved for SMB mixtures in the construction process. However, the content of bio-oil in SBS modified bitumen should be controlled in a proper range to ensure its practical performance.

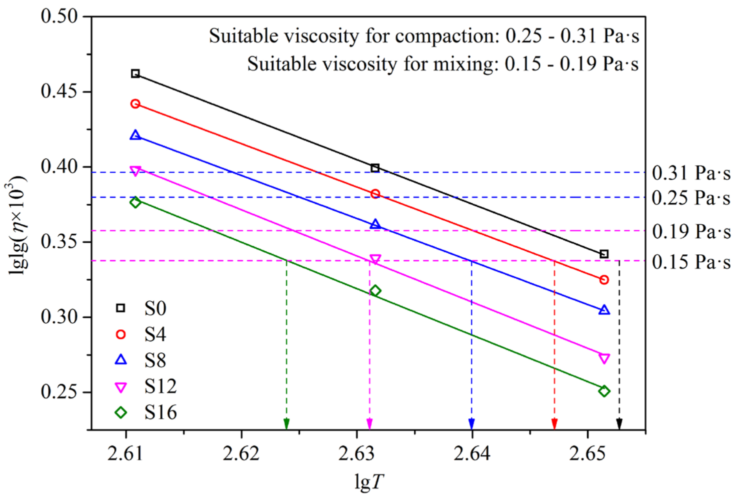


Figure 5 RV test results and viscosity-temperature curves of SMB

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 |

Table 3 Suitable mixing and compaction temperatures of SMB mixtures

| Materials | Mixing temperatures/℃ | | | Compaction temperatures/℃ | | |
|---|---|---|---|---|---|---|
| | 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 |

### 3.2.2 Shear rheological properties

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

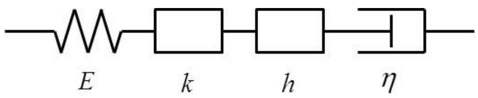


Figure 6 Schematic representation of the Huet-Such model

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

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

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

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

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

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

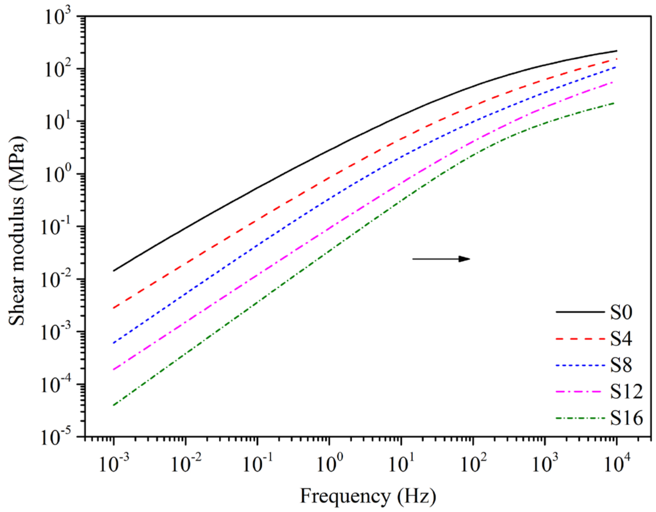


Figure 7 Shear modulus master curves of SMB (@ 20 ℃)

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

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

| Materials | Fitted parameter values (@ 20 ℃) | | | | | |
|---|---|---|---|---|---|---|
| | $E$ (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 |

### 3.2.3 Bending rheological properties

The bending creep stiffness and m-value results of SMB obtained from BBR tests were shown in Figures 8 and 9, respectively. It can be seen that the bending creep stiffness values are decreased and m-values are increased with the addition of bio-oil, which means that bio-oil can improve the stress relaxation ability of SBS modified bitumen. In addition, the bending creep stiffness has an approximately linear relationship with the bio-oil content in the semi-logarithmic coordinate system, and the m-value has an approximate linear relationship with the bio-oil content in normal coordinate system at a certain temperature. The regression equations of these relationships are also included in these Figures, where $s$ means bending creep stiffness, $m$ means m-value, and $c$ means bio-oil content. The reason of the missing data for specimens with higher bio-oil contents at higher temperatures is that corresponding measurements exceed the measuring range of BBR test.

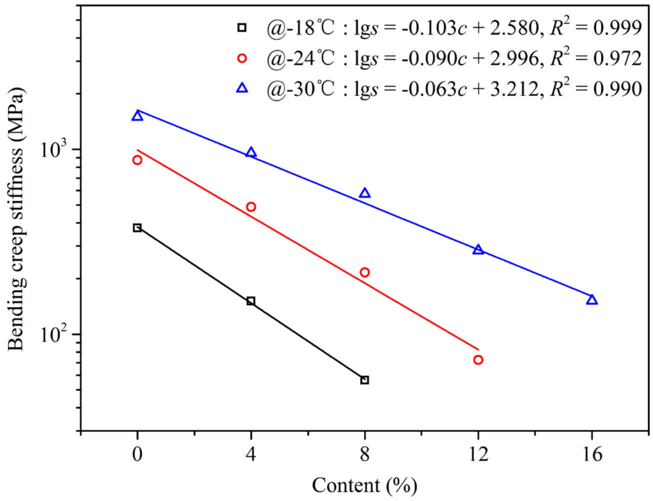


Figure 8 Bending creep stiffness test results of SMB

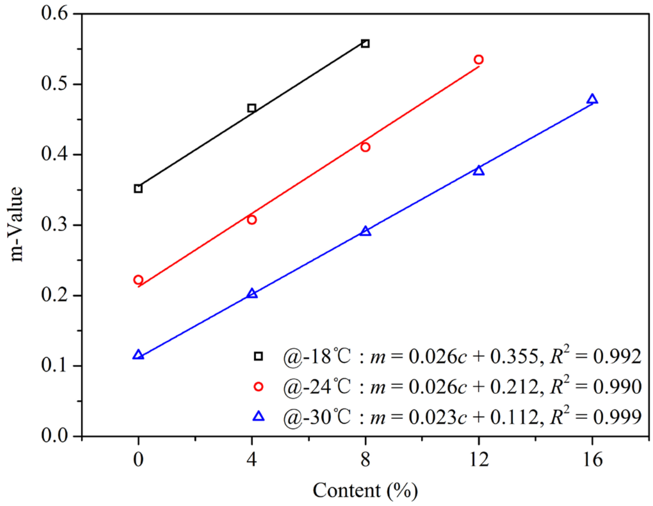


Figure 9 m-Value test results of SMB

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

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

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

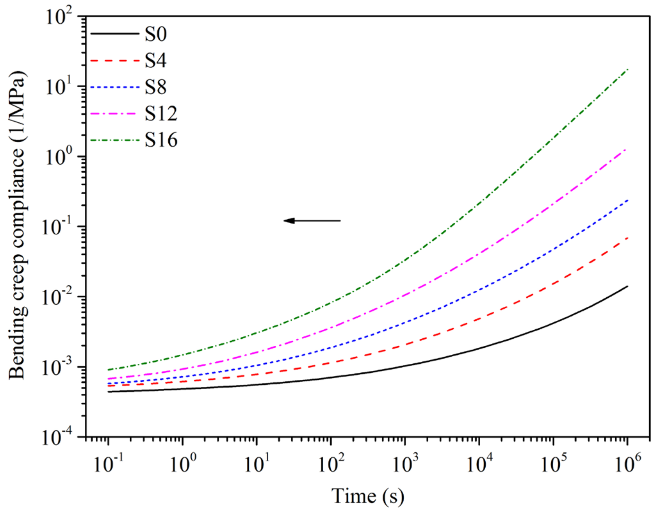


Figure 10 Bending creep compliance master curves of SMB @ -30 ℃

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

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

| Materials | Fitted parameter values (@ -30 ℃) | | | | | |
|---|---|---|---|---|---|---|
| | $E$ (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 |

## 4 Conclusions

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

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

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

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

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

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

## 5 Recommendations

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

## Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (No. 51878229), the China Postdoctoral Science Foundation (No. 2013M541393), and the China Scholarship Council (No. 201608230114).

## References


[1] Raouf M, Williams R (2010) Temperature and shear susceptibility of a nonpetroleum binder as a pavement material. Transp Res Rec: J Transp Res Board 2180: 9-18

[2] Fini EH, Kalberer EW, Shahbazi A, Basti M, You Z, Ozer H, Aurangzeb Q (2011) Chemical characterization of biobinder from swine manure: sustainable modifier for asphalt binder. J Mater Civ Eng 23(11): 1506-1513

[3] You Z, Mills-Beale J, Fini E, Goh SW, Colbert B (2011) Evaluation of low-temperature binder properties of warm-mix asphalt, extracted and recovered RAP and RAS, and bioasphalt. J Mater Civ Eng 23(11): 1569-1574

[4] Dong Z, Zhou T, Wang H, Luan H (2018) Performance comparison between different sourced bioasphalts and asphalt mixtures. J Mater Civ Eng 30(5): 04018063

[5] Yang X, You Z (2015) High temperature performance evaluation of bio-oil modified asphalt binders using the DSR and MSCR tests. Constr Build Mater 76: 380-387

[6] Zhang R, Wang H, You Z, Jiang X, Yang X (2017) Optimization of bio-asphalt using bio-oil and distilled water. J Cleaner Prod 165: 281-289

[7] Zofka A, Yut I (2012) Investigation of rheology and aging properties of asphalt binder modified with waste coffee grounds. Transp Res E-Circular: 61-72

[8] Sobolev K, Vivian IF, Saha R, Wasiuddin NM, Saltibus NE (2014) The effect of fly ash on the rheological properties of bituminous materials. Fuel 116: 471-477

[9] Zhao S, Huang B, Ye XP, Shu X, Jia X (2014) Utilizing bio-char as a bio-modifier for asphalt cement: A sustainable application of bio-fuel by-product. Fuel 133: 52-62

[10] Wu S, Muhunthan B (2017) Evaluation of the effects of waste engine oil on the rheological properties of asphalt binders. J Mater Civ Eng 30(3): 06017020

[11] Yang X, You Z, Mills-Beale J (2014) Asphalt binders blended with a high percentage of biobinders: aging mechanism using FTIR and rheology. J Mater Civ Eng 27(4): 04014157

[12] Fini EH, Al-Qadi IL, You Z, Zada B, Mills-Beale J (2012) Partial replacement of asphalt binder with bio-binder: characterisation and modification. Int J Pavement Eng 13(6): 515-522

[13] Audo M, Paraschiv M, Queffélec C, Louvet I, Hémez J, Fayon F, Lépine O, Legrand J, Tazerout M, Chailleux E, Bujoli B (2015) Subcritical hydrothermal liquefaction of microalgae residues as a green route to alternative road binders. ACS Sustainable Chem Eng 3(4): 583-590

[14] Sun Z, Yi J, Huang Y, Feng D, Guo C (2016) Properties of asphalt binder modified by bio-oil derived from waste cooking oil. Constr Build Mater 102: 496-504

[15] Wang C, Xue L, Xie W, You Z, Yang X (2018) Laboratory investigation on chemical and rheological properties of bio-asphalt binders incorporating waste cooking oil. Constr Build Mater 167: 348-358

[16] Qu X, Liu Q, Wang C, Wang D, Oeser M (2018) Effect of co-production of renewable biomaterials on the performance of asphalt binder in macro and micro perspectives. Materials 11(2): 244

[17] Sun D, Sun G, Du Y, Zhu X, Lu T, Pang Q, Shi S, Dai Z (2017) Evaluation of optimized bio-asphalt containing high content waste cooking oil residues. Fuel 202: 529-540

[18] Yang F, Hanna MA, Sun R (2012) Value-added uses for crude glycerol--a

byproduct of biodiesel production. Biotechnol Biofuels 5(1): 13

[19] Dang Y, Luo X, Wang F, Li Y (2016) Value-added conversion of waste cooking oil and post-consumer PET bottles into biodiesel and polyurethane foams. Waste Manage 52: 360-366

[20] Sun Z, Yi J, Feng D, Kasbergen C, Scarpas A, Zhu Y (2018) Preparation of bio-bitumen by bio-oil based on free radical polymerization and production process optimization. J Cleaner Prod 189: 21-29

[21] Zhang R, You Z, Wang H, Ye M, Yap YK, Si C (2019) The impact of bio-oil as rejuvenator for aged asphalt binder. Constr Build Mater 196: 134-143

[22] Sun Z, Yi J, Huang Y, Feng D, Guo C (2016) Investigation of the potential application of biodiesel by-product as asphalt modifier. Road Mater Pavement Des 17(3): 737-752

[23] Marsac P, Piérard N, Porot L, Van den bergh W, Grenfell J, Mouillet V, Pouget S, Besamusca J, Farcas F, Gabet T, Hugener M (2014) Potential and limits of FTIR methods for reclaimed asphalt characterisation. Mater Struct 47(8): 1273-1286

[24] Lamontagne J, Dumas P, Mouillet V, Kister J (2001) Comparison by Fourier transform infrared (FTIR) spectroscopy of different ageing techniques: application to road bitumens. Fuel 80(4): 483-488

[25] Yut I, Zofka A (2014) Correlation between rheology and chemical composition of aged polymer-modified asphalts. Constr Build Mater 62: 109-117.

[26] Olard F, Di Benedetto H (2003) General “2S2P1D” model and relation between the linear viscoelastic behaviours of bituminous binders and mixes. Road Mater Pavement Des 4(2): 185-224

[27] Di Benedetto H, Olard F, Sauzéat C, Delaporte B (2004) Linear viscoelastic behaviour of bituminous materials: from binders to mixes. Road Mater Pavement Des 5(sup1): 163-202