Nonlinear rheological behavior of bitumen under LAOS stress

Liyan Shan*
School of Transportation Science and Engineering, Harbin Institute of Technology,
Harbin, Heilongjiang, China, 150090

Hongsen He
School of Transportation Science and Engineering, Harbin Institute of Technology,
Harbin, Heilongjiang, China, 150090

Norman J. Wagner
Center for Molecular and Engineering Thermodynamics, Department of Chemical and
Biomolecular Engineering, University of Delaware, Newark, Delaware, 19716

Zhuang Li
School of Transportation Science and Engineering, Harbin Institute of Technology,
Harbin, Heilongjiang, China, 150090

Synopsis

The linear viscoelasticity and steady shear properties of bitumen are established, however, bitumen used in pavement supports time-varying loading in the nonlinear regime that eventually leads to material failure. Consequently, recent research focuses on the nonlinear rheological behavior of bitumen under time-varying flows that may reveal information about its failure mechanisms. Here we propose a protocol to obtain the
The nonlinear rheological behavior of bitumen from such as under large amplitude oscillatory shear stress (LAOS stress). The LAOS stress rheological response of both a neat bitumen and a modified bitumen are analyzed by FT-rheology and strain decomposition to an orthogonal set of Chebyshev polynomials. We find that the relative nonlinearity of bitumen increases with increase in stress and decrease in frequency; the relationship between $I_3/I_1$ and stress amplitude can obey the sigmoidal function; the intrinsic nonlinearity $Q_0$ decreases with increase in frequency and decrease in temperature. Both the FT analysis results and decomposition results show that the nonlinearity of modified bitumen B is much more significant than neat bitumen A. Bitumen exhibits stress softening and stress thinning at all the studied test conditions.

I. INTRODUCTION

The rheological behavior of bitumen has always been of critical interest to paving technologists because it is linked to the in-service behavior of actual bituminous pavements. The rheological behavior of bitumen is typically measured under steady-state shear for its creep, relaxation or viscosity properties, where the bitumen sample was sheared in a same direction [1-4]. More recently, the rheological behavior of bitumen has been measured under small amplitude oscillatory shear (SAOS) to determine its dynamic rheological properties [5-9]. Application of the time-temperature superposition principle (TTSP) yields master curves for the modulus or phase angle [7,8,10,11]. The WLF
equation [12] and Arrhenius [13] equations are empirically employed to create master curves, enabling predictions of some rheological properties of bitumen over a wider frequency and temperature range. Differences between bitumen variants and the effects of additives as well as aging on the rheological behavior can be identified by comparing such master curves [9,14].

Based on these limited rheological measurements, constitutive equations have been proposed to describe the rheological behavior of bitumen. Some models used the glassy modulus, frequency at glassy modulus, together with a shape parameter to describe the master curve [15,16]. Other models utilized physical elements to describe the viscoelastic behavior of bitumen, such as Maxwell, generalized Maxwell, Burgers, Kelvin, generalized Kelvin and Huet–Sayegh, etc… [17-20]. Chang and Meegoda argued that Burger linear viscoelastic element is the most promising approach for modeling asphalt binder behavior [21]. Alternatively, the Huet-Sayegh model is proposed by Huet for characterizing the viscoelastic property of materials [22]. It has two parallel branches, one of which is the elastic spring, and the other is formed by three elements in series: one elastic spring, as the difference in instantaneous elastic modulus and long-term modulus and two parabolic dashpots. Olard and Benedetto extended the Huet-Sayegh model by adding on linear dashpot in series with the two variable dashpots and named it as 2S2P1D model (two spring, two variable dashpots and one linear dashpot) and applied it to successfully model aspects of bitumen viscoelasticity [23].

All the abovementioned literature is concerned with the linear viscoelastic behavior
of bitumen. However, bitumen will undergo large loadings during its service life, which results in nonlinear deformation that can be quasi-periodic in time [24]. Rheological tests using LAOS have been proposed for studying construction materials, such as cements [25]. LAOS is a powerful method to independently measure rate or frequency effects independent of amplitude, and a number of methods have been proposed to interpret the results [26-28]. Consequently, there is a recent interest in the nonlinear rheological behavior of bitumen under large amplitude oscillatory shear (LAOS). For example, Padmarehka et al. studied the linear and nonlinear behavior of three different kinds of bitumen, and established a frame invariant nonlinear constitutive model [29]. Farrar et al. showed that the elasticity appeared dominant when the strain amplitude was less than 30% [30]. Jorshari et al. measured the nonlinear rheological behavior of SBS modified bitumen under LAOS and compared the first, the third and the fifth harmonic moduli [31, 32]. González et al. tested the rheological characterization of neat bitumen and EVA, HDPE polymer modified bitumen with the LAOS-FTR method, and showed that polymer modified bitumen exhibits higher harmonics (I_n/I_1 with 3≤n≤9), such that this method could quantitatively differentiate between the tested binders [33].

While these works demonstrate there is value in LAOS studies on bitumen, many aspects remain unexplored, such as whether LAOS can be used to understand the source of material failure under repeated loading. Importantly, as a road construction material, bitumen is definitely going to bear time-varying stress controlled loading. In the field of road engineering, the common practice is to employ controlled strain tests for bitumen
materials used in thin pavement and controlled stress tests for bitumen materials used in thick pavement [34]. Differences are noted between LAOS strain versus stress experiments on complex fluids [35]. Ewoldt and co-workers have proposed a method for analysis of LAOS stress experiments [36]. Consequently, it is necessary and important to study the rheological behavior of bitumen under LAOS stress, which is the novelty of the work presented here.

The goal of this work is to explore the nonlinear rheological behavior of bitumen under LAOS stress. In the following, we specify a protocol to measure the bitumen under LAOS stress for a neat bitumen and a modified bitumen at various frequencies and stress amplitudes. The nonlinearity ($I_3/I_1$) from FT-rheology as function of stress amplitude was investigated as a material metric. The dynamic strain was decomposed into elastic and viscous contributions. The Lissajous plots with the decomposed elastic/viscous strain at different stress levels were analyzed to investigate the stress thinning/thickening and stress softening/hardening behavior as a function of stress level.

II. MATERIALS AND METHODS

A. Materials

One neat bitumen and one bitumen modified with SBS (Styrene-Butadiene-Styrene) and crumb rubber were selected for this study. They are identified as bitumen A and bitumen B, respectively. The PG grade of bitumen A is PG64-22, and the PG grade of bitumen B is PG76-22. Based on the PG grading specification, the nomenclature of
PG64-22 bitumen means that the bitumen is suitable for the area where the highest temperature is lower than 64°C and the lowest temperature is higher than -22°C. So PG76-22 bitumen means that the bitumen is suitable for the area where the highest temperature is lower than 76°C and the lowest temperature is higher than -22°C. The components of these two types of bitumen are shown in Table 1. In the component theory of bitumen, the bitumen can be envisioned to be composed of asphaltene, resin, saturate and aromatic (SARA for short). Bitumen has a colloidal structure where the asphaltenes stabilized by resin are generally considered to be the dispersed phase, with the mixture of saturate plus aromatics acting as the dispersing medium phase [37]. Consequently, bitumen with higher percentage of dispersed phase is stiffer than the one with lower percentage of dispersed phase [38,39]. Based on this and the compositions listed in Table 1, it is anticipated that bitumen B is stiffer than bitumen A, which will also be shown in the following section.

<table>
<thead>
<tr>
<th>Bitumen type</th>
<th>Component (%)</th>
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<tbody>
<tr>
<td></td>
<td>Asphaltene</td>
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<tr>
<td>A</td>
<td>13.93</td>
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<tr>
<td>B</td>
<td>17.66</td>
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The SAOS master curves of the studied bitumen are shown in Figure 1. It can be seen from Figure 1(a) and 1(b) that the loss modulus is greater than the storage modulus for bitumen A and B in the studied frequency range (≤60 rad/s) at both 30°C and 60°C. It means that the viscous part is large than the elastic part for the studied bitumen at the
research test conditions, which is typical of suspensions [40]. The generalized Kelvin model (shown in Eq.(1)) was used to fit the tested modulus data, and the fitting results are also shown in Figure 1 (A table of the parameter values is provided in the Supplemental Information). As expected, the model can well describe the storage and loss modulus. These fitting results further prove our previous study that the generalized Kelvin model can well describe the modulus and phase angle if n is large enough [41]. Figure (c) shows that the shift factors for the different bitumens are similar to each other at the same temperature.

\[
G'(\omega) = \sum_{i=1}^{n} \frac{G_i}{G_i^2 + \eta_i^2 \omega^2} + \frac{1}{G_0}, \quad G''(\omega) = \sum_{i=1}^{n} \frac{\eta_i \omega}{G_i^2 + \eta_i^2 \omega^2} + \frac{1}{\eta_0 \omega} \tag{1}
\]
FIG. 1. Dynamic shear moduli for (a) bitumen A and (b) bitumen B, and the corresponding shift factors (c). Data were collected at different temperature and shifted in frequency to a reference state of 30 and 60 °C. These two temperatures are used for the LAOS tests. Lines calculated from $G(t)$ using eqs. (1). $G'$ are indicated with closed and $G''$ with open symbols. The shift factors are fit to the WFL equation.

The steady shear viscosity of bitumen A and B at 30 °C and 60 °C are shown in Figure 2. In contrast with more traditional colloidal suspensions, it is difficult to obtain the infinite shear viscosity of bitumen by shear rheometry. As expected, the bitumen viscosity at 30 °C is greater than that at 60 °C. The viscosities of bitumen B is greater than that of bitumen A at both 30 °C and 60 °C, such that bitumen B is stiffer than bitumen A as expected from the bitumen components given in Table 1.
B. Rheological measurements

The rheological behavior of the bitumen was tested using a TA Instruments ARG-2 stress controlled rheometer operated in native mode using disposable fixtures and the oven for temperature control. The tests were conducted with an 8-mm diameter parallel plate geometry and 2-mm gap setting at 30 °C, and with a 25-mm diameter parallel plate geometry and 1-mm gap setting at 60 °C. The frequency series were chosen as 1 rad/s, 2 rad/s, 5 rad/s, 10 rad/s and 60 rad/s. Stress sweep tests were conducted at each temperature and frequency to choose the stress levels for the oscillatory shear test. As shown in Figure 3, the loss modulus is greater than the storage modulus, which illustrates that the bitumen behaves as a viscous suspension. For all bitumen samples at both 30 and 60 °C, a significant linear regime is found. Bitumen A exhibits a near catastrophic failure at a critical stress amplitude at 30 °C, such that the sample was visibly broken. Increasing the temperature leads to a more plastic response, but with a lower critical stress amplitude. The modified bitumen B exhibits a similar range of linearity, but is less
“brittle” at 30 °C than bitumen A. A significant difference is observed for the modified bitumen B at 60 °C, where stress hardening is observed prior to material failure for the lower frequencies. These features and differences will be manifest in the LAOS results.

FIG.3. Stress sweep test results of the bitumen: (a) Bitumen A at 30 °C; (b) Bitumen A at 60 °C; (c) Bitumen B at 30 °C; (d) Bitumen B at 60 °C.

To test the bitumen at both linear range and nonlinear range at each frequency and temperature, the stress levels were chosen in the range between the two dotted lines, as shown in Figure 3. All the stress levels are summarized in Table 2 and Table 3. “L” in the tables means that the stress level is in the linear range, meanwhile “N” in the tables
means that the stress level is in the nonlinear range.

<table>
<thead>
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<th>TABLE 2. Selected stress levels of bitumen A.</th>
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<tr>
<td>Frequency (rad/s)</td>
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</tr>
<tr>
<td>10</td>
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<td>20</td>
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<td>50</td>
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<td>60</td>
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<table>
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<tr>
<th>TABLE 3. Selected stress levels of bitumen B.</th>
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<td>Frequency (rad/s)</td>
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<td>------------------</td>
</tr>
<tr>
<td>10</td>
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<tr>
<td>20</td>
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<tr>
<td>30</td>
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<tr>
<td>40</td>
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<tr>
<td>50</td>
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Note: L means that this stress level is in linear range and N stands for nonlinear range.

C. Data selection method

The LAOS stress response of these materials were observed to be time-dependent, as shown for some select conditions in Figure 4. As noted by Ewoldt and co-workers [42] the LAOS can yield a drift in the average strain/stress, which is observed in Figure 4 and tabulated in the appendix. Further, the LAOS stress response evolves with cycling to a time-stable regime, which was identified for each condition as indicated in Figure 4. This time-stable oscillatory response is termed alternance. Note that continued oscillation will lead to material failure, as illustrated in Figure 4.
FIG. 4. Strain response of the bitumen A at (a) 30 °C and (b) 60 °C. The marked time regime is identified as the alternance state and used for further analysis.

D. Data pre-treatment method

The strain-stress waveform obtained by the rheometer is shifted prior to analysis to zero average strain, as shown in Figure 5. All the shifting factors are summarized in the appendix.

FIG. 5. Schematic of the waveform shift.

III. Theory
A. FT-rheology

The theoretical aspects of FT-rheology are documented in more detail elsewhere [43-45]. Therefore, only the most pertinent mathematical relations are repeated here. The input shear stress is represented using cosine function, as shown in Eq.(2).

\[ \sigma(t) = \sigma_0 \cos \omega t \]  

(2)

The nonlinear shear strain response under LAOS stress can be expressed using a Fourier series expansion with either strain amplitude or stress amplitude with odd higher terms as follows [45].

\[ \gamma(t) = \sum_{n=1, \text{odd}} \gamma_n \cos(n\omega t - \delta_n) \]  

(3)

\[ \gamma(t) = \sum_{n \text{ odd}} \left\{ f_n'(\omega, \sigma_0) \sigma_0 \cos n\omega t + f_n''(\omega, \sigma_0) \sigma_0 \sin n\omega t \right\} \]  

(4)

Symmetry shows that the shear strain curve contains only odd higher harmonic contributions under LAOS flow. FT-rheology decomposes the shear strain in the time domain into the frequency domain.

From Eq.(3), the shear strain from nonlinear oscillatory shear flow by FT-rheology can be describe as

\[ \gamma(t) = \gamma_1 \cos(\omega t - \delta_1) + \gamma_3 \cos(3\omega t - \delta_3) + \gamma_5 \cos(5\omega t - \delta_5) + \cdots \]

\[ = \gamma_1 \cos \delta_1 \cos \omega t + \gamma_1 \sin \delta_1 \sin \omega t + \gamma_3 \cos \delta_3 \cos 3\omega t + \gamma_3 \cos \delta_3 \cos 3\omega t + \cdots \]  

(5)

From the above equation, the relative intensity of higher-harmonics \([I(n\omega)/I(\omega) = I_n/I_1, \text{ where } \omega \text{ is the excitation frequency}]\) from FT-rheology can be calculated as follows:
Any measured response from the tested system at frequencies other than $\omega$ is associated with nonlinearity in the system response. Therefore, the relative intensity $I_n/I_1$ is usually used to evaluate the degree of non-linearity of the material’s response.

The ratio of $I_3/I_1$ is the most common index used by the FT-rheology method. In a log-log plot, the ratio $I_3/I_1$ shows a linear relationship with strain amplitude at small and medium strain amplitude, expressed as Eq.(7) [46,47]. Some researchers focused on analyzing the intercept “a” and slope “b”, where they observed that the slope b equals two [48-50], as expected from theory in the limit of small amplitudes. However, at large strain amplitude, Wilhelm an co-workers showed that $I_3/I_1$ is often observed to be a sigmoidal function that can empirically be described via Eq.(8) [51]. In bitumen research, there is no prior report on the functionality of $I_3/I_1$.

$$log(I_3/I_1) = a + b log \gamma_0$$

$$I_3/I_1 (\gamma_0) = A \left(1 - \frac{1}{1+(B \gamma_0)^c}\right)$$

B. Strain decomposition method

FT-rheology can quantify the degree of nonlinearity of the shear strain response, but
the higher harmonics cannot provide all information about the nonlinear response. Therefore, the total strain is also analyzed with strain decomposition method. The viscoelastic strain measured in dynamic oscillatory shear flow can be decomposed into elastic and viscous parts in the linear regime. In the nonlinear regime, using the Fourier series representation of the strain signal represented in Eq.(4), the nonlinear strain can be decomposed into an apparent elastic strain, $\gamma'$, and an apparent plastic strain, $\gamma''$[36]:

$$
\gamma'(t) = \sigma_0 \sum_{n \text{ odd}} J_n'(\omega, \sigma_0) \cos n\omega t 
$$

$$
\gamma''(t) = \sigma_0 \sum_{n \text{ odd}} J_n''(\omega, \sigma_0) \sin n\omega t 
$$

The strain decomposition is based on the idea that we desire $\gamma'$ and $\gamma''$, such that over one cycle of oscillation $\gamma'$ is a single-valued function of $\sigma$ and the apparent plastic strain rate $\gamma''$ is a single-valued function of $\sigma$. The convention of naming $\gamma'$ an elastic strain and naming $\gamma''$ a plastic strain then follows because elastic strain typically depends only on imposed stress.

Following the reference of Ewoldt et al.(2008) [52] and Dimitriou et al. (2013)[36], The elastic strain and plastic strain can also be represented as a series of orthogonal Chebyshev polynomials $T_n(x)$, where $x$ is the scaled stress, $x = \sigma(t)/\sigma_0$:

$$
\gamma'(t) = \sigma_0 \sum_{n \text{ odd}} J_n'(\omega, \sigma_0) \cos n\omega t = \sigma_0 \sum_{n \text{ odd}} J_n'(\omega, \sigma_0) T_n(x)
$$
\[ y''(t) = \sigma_0 \sum_{n \text{ odd}} n \omega f_n^\omega(\omega, \sigma_0) \cos n \omega t = \sigma_0 \sum_{n \text{ odd}} n \omega f_n^\omega(\omega, \sigma_0) T_n(x) \] (12)

The above representation follows from the identity \( T_n(\cos \theta) = \cos n\theta \). The resulting material coefficients in Eq. (9) and (10) have units consistent with compliances \( c_n(\omega, \sigma_0) \) [Pa]\(^{-1}\) and fluidities \( f_n(\omega, \sigma_0) \) [Pa.s]\(^{-1}\), respectively. The Fourier coefficient can represent a complete mathematical description of the time-domain response, but the physical interpretation of the higher harmonics is revealed by considering the Chebyshev coefficients in the orthogonal space formed by the input stress/stain and strain-rate [52-54].

**IV. RESULTS AND DISCUSSION**

In this section, the nonlinear strains under LAOS stress for bitumen A and bitumen B were investigated using FT-rheology and stress decomposition method.

**A. FT-rheology analysis**

When the stress amplitude such that the sample is in the linear oscillatory shear regime, the strain is sinusoidal. Increasing the stress amplitude results in a nonlinear response such that the strain is no longer sinusoidal and has higher harmonic contributions. FT-rheology shows that the higher harmonics \( I_n/I_1 \) become significant and increase with the stress amplitude, as shown in Figure 6 and Figure 7. For bitumen A,
only $I_3/I_1$ and $I_5/I_1$ are measurable and they increase as the stress amplitude increases. However, for bitumen B, $I_7/I_1$ and $I_9/I_1$ are also measurable along with $I_3/I_1$ and $I_5/I_1$, and all of them increase as the stress amplitude increases. As bitumen A is neat and bitumen B is modified, these results also show that the nonlinearity of modified bitumen is much more significant than neat bitumen at the test conditions explored.
FIG. 6. The strain signal (shifted to zero average strain) as a function of time and corresponding Fourier spectra as a function of frequency at various stress amplitude (40kPa, 50kPa, 60kPa, and 70kPa) of bitumen A at 30°C and 1rad/s
FIG. 7. The strain signal (shifted to zero average strain) as a function of time and corresponding Fourier spectra as a function of frequency at various stress amplitude (20kPa, 100kPa, 180kPa, and 260kPa) of bitumen B at 30°C and 1rad/s.

To analyze the change of relative intensity with stress amplitude, frequency and
temperature, Eq.(13) was used to fit the relationship between stress and the relative third intensity of the studied bitumen. Based on the $Q$ parameter theory in the references of Hyun et al. (2009) [55] and Abbasi et al. (2013) [56], the $Q$ parameter under LAOS stress can be described by Eq.(14). The relationships between $Q$ and stress amplitude at various conditions are plotted in Figure 8 and Figure 9. The dotted lines in each figures are the fitting curves by Eq.(14). Because the data is limited, the shapes of the curves among different conditions are qualitative, however, some trends are evident. It can be seen that $Q$ values decrease with increases in frequency. For the neat bitumen A, the $Q$ value changes little during the test conditions, and it is predicted to decrease with increase in stress based on the modeling results. For the modified bitumen B, the $Q$ decreases with increases in stress amplitude.

$$I_3/I_1(\sigma_0) = A \left(1 - \frac{1}{1+B\sigma_0\gamma} \right)$$

$$\log Q = \log \frac{I_3/I_1(\sigma_0)}{\sigma_0^2} = \log A + \log B + C\log\sigma_0 + \log(1 + B\sigma_0^\gamma) - 2\log\sigma_0$$

**FIG.8.** $Q = I_3/I_1/\sigma_0^2$ as a function of stress amplitude of bitumen A at various frequencies and different temperatures: (a) 30°C; (b) 60°C
FIG. 9. $Q = l_3/l_1/\sigma_0^2$ as a function of stress amplitude of bitumen B at various frequencies and different temperatures: (a) 30°C; (b) 60°C

It can also be seen from Figure 8 and Figure 9 that, at relatively small stress amplitude, $Q$ had a constant value ($Q_0$) that changes with frequency. Figure 11 shows the trend of $Q_0$ increasing with frequency and decreasing with temperature. The $Q_0$ value of bitumen A is less than that of bitumen B at the same frequency and temperature.

FIG. 10. $Q_0$ of the studied bitumen at various frequencies and different temperatures.
B. Strain decomposition

As described above, the use of Chebyshev polynomials allows decomposition of the strain response into purely elastic and viscous components, represented by $c_n$ and $f_n$. Here we are focusing at $c_3$ and $f_3$ since they are significantly larger than the higher order contributions in all cases.

Examples of strain decomposition with Chebyshev polynomials are presented in Figure 11. Both the elastic $[\gamma(t) \text{ vs } \tau(t)]$ and viscous representation $[\dot{\gamma}(t) \text{ vs } \tau(t)]$ are shown together with the Lissajous curve. For the same bitumen, the shapes of the Lissajous curves are similar at different stress levels. The elastic Lissajous loop is an ellipse as expected, and the nonlinearity of the dotted line [in Figure11 (a),(e),(c) and (g)] becomes more and more obvious with increase in stress level. The viscous Lissajous loop of bitumen A at 30°C is also elliptical but is linear line at 60°C, which shows that bitumen A is viscoelastic at 30°C, and becomes a purely viscous material at 60°C. For bitumen B, the nonlinearity is much more obvious because of a visual inspection of distorted Lissajous loops. The elastic and viscous strain depart from linearity with increasing stress, revealing a rich material response with softening/hardening and thinning/thickening contributions depending on the frequency as will be discussed below.
FIG. 11. Decomposition of shear strain into elastic and viscous part for bitumen A and bitumen B at 10 rad/s and different temperatures. For bitumen A (a) strain vs. stress at 30°C, (b) shear rate vs. stress at 30°C, (c) strain vs. stress at 60°C and (d) shear rate vs. stress at 60°C. For bitumen B (e) strain vs. stress at 30°C, (f) shear rate vs. stress at 30°C, (g) strain vs. stress at 60°C and (h) shear rate vs. stress at 60°C.

By decomposing the elastic and viscous strain signal into the orthogonal set of Chebyshev polynomial, we may determine quantitatively the stress softening/hardening and shear thinning/thickening response of the material. Due to the convexity of the third Chebyshev polynomial values of $c_3$ result in stress softening of the apparent elastic stress-strain curve, while positive values of $f_3$ result in stress thinning of the apparent plastic strain-rate vs shear stress curve. Conversely, negative values of $c_3$ imply stress stiffening of the elastic material, while negative values of $f_3$ imply stress thickening.
Figure 12 and Figure 13 depict $c_3/c_1$ and $f_3/f_1$ as a function of the applied stress at different frequencies and temperatures in the nonlinear regime. With increasing stress, both $c_3/c_1$ and $f_3/f_1$ increase. Both $c_3$ and $f_3$ are larger than zero, which reveal a stress softening and stress thinning. It means that both bitumen A and bitumen B will reveal stress softening and stress thinning at all the studied test conditions.

**FIG.12.** Relative third order elastic, $c_3/c_1$, and viscous, $f_3/f_1$ Chebyshev coefficients as a function of stress for bitumen A at different frequency and temperatures: (a) and (b) 30°C; (c) and (d) 60°C
FIG.13. Relative third order elastic, $c_3/c_1$, and viscous, $f_3/f_1$ Chebyshev coefficients as a function of stress for bitumen B at different frequency and temperatures: (a) and (b) 30°C; (c) and (d) 60°C.

V. CONCLUSIONS

We have presented a protocol to obtain the nonlinear rheological behavior of bitumen under LAOS stress. Both FT-rheology and stress decomposition methods are applied to analyze the nonlinear rheological behavior of one kind of neat bitumen and one kind of modified bitumen. Distinct differences are observed between the neat and modified bitumen. Our results show that the relative intensity of the nonlinear parameter...
of bitumen increases with increase in stress and decrease in frequency. Furthermore the nonlinearity of modified bitumen B is much more significant than neat bitumen A. The relationship between $I_3/I_1$ and stress amplitude obeys a sigmoidal function. The $Q$ parameter, which equals to $\frac{I_3/I_1(\sigma_0)}{\sigma_0^2}$, is a nonlinear material property that identifies property differences between neat and modified bitumen. The intrinsic nonlinearity $Q_0$ decreases with increase in frequency and decrease in temperature. The $Q_0$ value of bitumen A is less than that of bitumen B at the same frequency and temperature, which also slows that the nonlinearity of bitumen B is more obvious than A. The strain decomposition results show that bitumen A is viscoelastic material at 30°C and pure viscous at 60°C; bitumen B is viscoelastic at both 30°C and 60°C. In general, analysis of the LAOS stress results show bitumen exhibits stress softening and stress thinning at all the studied test conditions. These results illustrate useful information distinguishing bitumen samples can be rapidly and accurately obtained from LAOS stress measurements, suggesting it is meaningful to perform further studies of the nonlinear rheological characteristics of bitumen under LAOS, especially with respect to identifying failure mechanisms that limit material lifetime in practical applications.

**SUPPLEMENTARY MATERIAL**

See supplementary material for the generalized Kelvin model parameters for bitumen A and bitumen B at 30°C and 60°C.
ACKNOWLEDGEMENTS

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Appendix

All the strain factors for LAOS stress for bitumen A and bitumen B at different conditions are summarized in Table 4 and Table 5. It can be seen from the tables that there is no obvious trends of the shift factors, except that the shift factors at 30 °C are larger than the factors at 60 °C

| TABLE 4. The shift factors of bitumen A at different conditions. |
|-----------------------------|-------|-------|-------|-------|-------|
| Frequency (rad/s) | 1     | 2     | 5     | 10    | 60    |
| 10 kPa          | 4.8   | 1.5   | 0.6   | 0.2   | -0.1  |
| 20 kPa          | 8.1   | 3.0   | 1.4   | 0.9   | -0.2  |
| 30 kPa          | 10.4  | 5.2   | 2.5   | 1.5   | -0.3  |
| 40 kPa          | 1.4   | 5.3   | 3.0   | 2.0   | -0.2  |
| 50 kPa          | -27.4 | 4.7   | 3.6   | 2.4   | -0.1  |
| 60 kPa          | -5.1  | -6.7  | 2.2   | 1.2   | 0     |
| 70 kPa          | -18.8 | -4.9  | -0.6  | -0.2  | -0.2  |
| 8 kPa           | -366.9| -40.3 | 57.4  | 0     | 0.2   |
| 9 kPa           | 765.3 | -30.6 | 135.8 | 21.1  | -1.2  |
| 10 kPa          | 1468.3| -7.6  | -3.2  | 6.2   | 2.1   |
| 7 kPa           | 57.0  | -899.3| 0     | -2.1  | 19.0  |
| 8 kPa           | -12.9 | -276.2| -124.8| 5.6   | 3.8   |
| 9 kPa           | -84.5 | -206.8| 61.8  | 34.3  | 0.2   |
### TABLE 5. The shift factors of bitumen B at different conditions.

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<thead>
<tr>
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<th>10</th>
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<td>0.5</td>
<td>-0.2</td>
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<tr>
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#### References


[28] Rogers, S.A., M.P. Lettings, “A sequence of physical processes determined and quantified in large-amplitude oscillatory shear (LAOS): Application to theoretical


