Nonlinear Rheological Modeling of Asphalt Using White-Metzner Model with Structural Parameter Variation Based Asphaltene Structural Build-up and Breakage

Rohit Vijay, Abhijit P. Deshpande* and Susy Varughese

Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036, India

* Email: abhijit@iitm.ac.in
Fax: x91.44.22574152

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Abstract:
Rheological behavior of asphalt is strongly affected by loading conditions, temperature and environment. One of the main challenges in understanding the rheology of asphalt is to relate the chemical constituents and the micro-structure of asphalt on one hand to its rheological behavior on the other hand. In this work, nonlinear rheological behaviour of asphalt was investigated using a structural rheological model. A first order kinetic equation to describe structural changes in asphalt has been incorporated with the nonlinear rheological model of White- Metzner. The resulting set of governing equations was solved numerically to describe the rheology of asphalts. Different modes of rheological testing and asphalts with different compositions were considered. An analysis and comparison of model behaviour with experimental data from the literature is carried out in both stress growth at constant shear rate and oscillatory shear modes. A strategy is proposed for the estimation and tuning of the model parameters based on available experimental data and literature. Qualitatively, the model can capture the rheological behaviour of non-Newtonian fluids such as asphalt under different modes of rheological testing. Quantitative analysis from this work shows that the model describes the rheological behaviour of asphalt for the temperature range of 20 – 60°C. It is demonstrated that a single set of equations tuned with the steady shear experimental data can be used to predict the nonlinear rheological behaviour of asphalts. In addition, it is shown that the model parameters can be related to the chemical composition of asphalts.

Zusammenfassung:
Das rheologische Verhalten von Asphalt ist stark von den Beanspruchungsbedingungen, der Temperatur und der Umwelt beeinflusst. Eines der größten Herausforderungen der Asphaltrheologie ist die Verknüpfung der chemischen Zusammensetzung und der Mikro-Struktur des Asphalts auf der einen Seite und sein rheologisches Verhalten auf der anderen Seite. Eine Gleichung erster Ordnung, welche die Veränderung der Struktur in Asphalt beschreibt, kann mit dem nicht linearen rheologischen Modell von White-Metzner verbunden werden. Die Gleichungssysteme wurden numerisch gelöst, um die Rheologie von Asphalt zu beschreiben. Asphalte unterschiedlicher Zusammensetzung wurden durch verschiedene rheologische Experimente charakterisiert. Analyse und Vergleich vom Modelverhalten mit den experimentellen Daten aus der Literatur wurden bezüglich Belastungsentwicklungen bei konstanter Schergeschwindigkeit und bei oszillierenden Scherarten durchgeführt. Eine Strategie zur Beurteilung und Verbesserung der Modelparameter basierend auf vorhandenen experimentellen Daten und Literaturwerten kann somit vorgeschlagen werden. Qualitativ kann das Model das rheologische Verhalten von nicht-Newtonschen Flüssigkeiten wie Asphalt bei unterschiedlichen Versuchsbedingungen erfassen. Quantitative Analysen von dieser Arbeit zeigen, dass das Model das rheologische Verhalten von Asphalt in einem Temperaturbereich von 20 – 60°C beschreibt. Es wurde gezeigt, dass ein einzelnes Gleichungssystem, das mit den konstanten Scherexperimenten abgestimmt wurde, zur Vorhersage von nicht linearen rheologischen Verhalten von Asphalt verwendet werden kann. Zusätzlich wurde gezeigt dass die Modelparameter in Beziehung zur chemischen Zusammensetzung des Asphalts gebracht werden kann.

Résumé:
Le comportement rhéologique de l'asphalte dépend fortement des conditions de son application, de la température et de l'environnement. L'un des principaux défis associé à la compréhension de la rhéologie de l'asphalte est de relier les constituants chimiques et la microstructure de l'asphalte à son comportement rhéologique. Dans ce travail, le comportement rhéologique non linéaire de l'asphalte a été étudié en utilisant un modèle structural. Une équation cinétique du premier ordre pour décrire les changements structuraux de l'asphalte a été incorporée au modèle rhéologique non linéaire de White-Metzner. L'ensemble d'équations résultant de cette approche a été résolu numériquement afin de décrire la rhéologie des asphaltes. Différents types de tests rhéologiques ont été considérés ainsi que différentes compositions d'asphaltes. Une analyse et une comparaison du comportement du modèle avec les données expérimentales trouvées dans la littérature ont été entreprises pour la montée en contrainte à vitesse de cisaillement constant et pour le test de cisaillement dynamique oscillatoire. Une stratégie basée sur les données expérimentales disponibles et sur la littérature est proposée pour une estimation et un contrôle des paramètres du modèle. Qualitativement, le modèle est capable de capturer le comportement rhéologique de fluides non Newtoniens tels que l'asphalte soumis à différents

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types de tests rhéologiques. Une analyse quantitative de ce travail montre que le modèle décrit le comportement rhéologique de l'asphalte dans une gamme de température de 20 à 60°C. Il est démontré qu'un seul ensemble d'équations ajustées avec les données expérimentales de cisaillement constant peut être utilisé pour prédire le comportement rhéologique non linéaire des asphaltes. De plus, nous montrons que les paramètres du modèle peuvent être reliés à la composition chimique des asphaltes.

Key words: asphalt, structure, nonlinear viscoelasticity, rheology, kinetic equation

1 INTRODUCTION

Asphalts consist of hydrocarbons with greatly varying physicochemical properties and with broad molecular weight distribution. In addition, asphalts are known to have multiple phases such as crystalline waxes, polar asphaltenes and non-polar oils. Because of these constituents and their interactions, asphalts exhibit complex rheological behavior. Rheological investigations of different asphalts have shown that their behavior is different depending on the source of asphalt, temperature, loading and environmental conditions [1–9]. It is very important to understand the relationship between the chemical constituents of asphalt and the micro-structure and how these are related to its rheological behavior. Such an understanding is essential for explaining the asphalt behaviour due to variation in its source and due to aging under field conditions.

Asphalt shows significant temperature and time dependent behaviour, and this complex behaviour is one of the most important reasons for the requirements of continuing maintenance, rehabilitation and management of asphalt pavements [10]. Several modifications of asphalt have been proposed as well as implemented to enhance the performance of the pavements [10 – 21]. The polymeric modifiers include linear and branched homopolymers such as polyethylene [11, 12], crosslinked polymers such as ethylene propylene diene monomer (EPDM) [11], copolymers such as styrene butadiene styrene (SBS) and ethylene vinyl acetate (EVA) [11–18]. In these polymer modified asphalts (PMA), the knowledge of microstructure and rheology of asphalt has to be combined with that of polymeric systems to understand the overall performance.

1.1 MICROSTRUCTURE AND RHEOLOGY

Analytical and spectroscopic techniques have been used to investigate the chemical makeup of asphalt [1,2]. The effect of various constituents on the rheological behavior has also been studied. All these studies have indicated the importance of asphaltenes, resins and crystallizable fractions among the constituents for describing asphalt behaviour. Understanding of the rheological behaviour of asphalt can be said to depend on two related aspects, a physico-chemical conceptualization and a rheological model. The physico-chemical conceptualization is based on different hypotheses regarding the micro-structure of asphalt. Two different approaches have been proposed. In the Colloidal Model asphalt behavior is analyzed based on its micro-structure as a colloidal system [3]. Asphalt is said to be a colloidal dispersion of asphaltene particles in non-polar oily solvents. A solvation layer (of resin fraction) is assumed to be around the asphaltene particles. The change in rheological behavior as a function of temperature is explained based on physical changes in the solvation layer. Results from small angle X-Ray and Neutron scattering techniques [2], show that both the small and large aggregates of asphaltenes have well defined fractal structures. Hence, diffusion limited cluster and diffusion limited particle aggregate models can be used to obtain the kinetics of aggregation. Network Model is based on the hypothesis of asphalt being a network of asphaltene domains dispersed in continuous oily medium [4]. Due to changes in properties, asphalt behaviour below the glass transition and above the glass transition is characterized using different experimental methods [3, 7, 8].

Some of the most important factors that influence rheology of suspensions, are the nature and size of particles, nature of suspending medium, and physico-chemical interactions in the material system [22]. It is well known that the application of steady-shear flow to suspensions induces a rich variety of structural ordering, orientation and phase separation [23]. Oscillatory-shear flow can also generate similar structural features [23]. Inter-particle interactions are mainly responsible for the behaviour of suspensions at rest and during flow. The inter-particle interactions can also lead to network of particles and to gel formation and can be used to predict the rheological behaviour of the suspensions [22 – 24]. Rheological modeling along with an evolution equation for structure, or a kinetic equation for structural evolution, has been used to model different colloidal solutions and suspensions [25 – 31]. Due to complexity of asphalt, the interaction forces are not known as quantitatively as in case of ceramic pastes and clay-water suspensions [25]. Therefore, the structural features of asphalt are arrived at by limited observations on structure supported by phenomenological rheological information.

Rheological behaviour and the influence of microstructure on rheology is considered very crucial [13, 14, 16, 21, 32] for PMA as well. Morphology of the PMAs is very different when compared to that of asphalt. For example, SBS modified asphalt can be considered to be a multiphase system comprising of an asphalt phase, whose composition is different from that of asphalt alone [16]. Additionally, polymer phase itself can consist of a butadiene rich phase and a styrene rich phase [16]. The polymer phases are expected to be swollen with compatible constituents of the asphalt [14, 16, 21]. It is also possible to evaluate these different phase compositions based on phase equilibria considerations [16, 32]. The sizes of different phases and their interactions depend on the concentrations as well as their compatibility and reactivity [20, 21].

1.2 PERFORMANCE EVALUATION USING OSCILLATORY RHEOLOGY

Extensive literature results are available on the characterization of asphalts using linear viscoelastic material functions [3, 33, 34]. Asphalt is usually assumed to be a thermorheolgocially simple material, and its performance is analyzed with construction of master curves. Parameters based on complex modulus, storage modulus and phase difference have been used extensively as specification parameters for pavement performance [10, 34]. The role of different geometries in performance evaluation has been demonstrated and exploited to extend the range of master curves [5, 9, 19, 33, 34]. It is possible to relate the oscillatory material functions to limiting steady rheological material functions or vice versa. The usefulness of such approach has been demonstrated by relating zero shear viscosity and first normal stress difference to oscillatory material functions with the assumptions of linear viscoelasticity [34]. PMAs as well are assumed to be thermorheologically simple materials and have been characterized extensively using linear oscillatory viscoelastic material functions [20]. However, material functions from nonlinear rheological modes such as stress growth, which cannot be related to linear rheological material functions, are also interesting characterization tools to understand rheology of asphalt and PMA [6, 12, 13, 21, 35, 36].

Non-oscillatory linear viscoelastic characterization such as creep and stress relaxation tests are also used to evaluate the creep compliance and relaxation modulus, which is considered to be an indication of susceptibility to low temperature cracking [10].

Based on the prevalent experimental data, rheological characteristics of asphalt have been modeled mostly using linear viscoelastic models [3, 7, 33]. An important aspect of the rheological modeling of asphalt is to relate material functions to the microstructure. Several structure-related rheological models have been proposed to describe linear viscoelastic material functions [3]. In models such as these, asphaltene volume fraction, solvation layer thickness and volume of crystallizable fractions etc. are the microstructural parameters to be incorporated [3, 8].

1.3 NONLINEAR RHEOLOGY OF ASPHALT AND PMA

Steady shear viscosity has been characterized for great many varieties of asphalt [3, 5, 7]. Variation of viscosity in different asphalts has been modeled mostly using Generalized Newtonian fluid models [3, 7]. Several structure-related rheological models have also been proposed to describe viscosity [3]. Viscosity of several PMAs was described using Generalized Newtonian models such as Cross and Power law models [11]. The effect of inter-particle interaction forces on the functional form of viscosity variation has been studied for many suspensions [22, 24].

Fewer investigations have been carried out to experimentally probe asphalt and PMA in the nonlinear regime, e.g. using stress growth, normal stress differences, creep or stress relaxation in non-linear regime [3 – 6, 12, 13, 21, 34]. In an experimental investigation of the nonlinear rheology, stress overshoots were observed at the start-up of steady shear for PMAs while such phenomenon was not seen in unmodified asphalt [13]. The magnitude of the stress overshoots and the time scales of recovery of stress overshoots were found to be functions of the polymer type and concentration [13].

Modeling of the nonlinear rheological behaviour of asphalt and PMA has been attempted in recent times [8, 12, 21]. A constitutive nonlinear viscoelastic model was developed based on multiple configurations of asphalt [8] and was shown to describe experimental observations of creep and recovery in the nonlinear regime. Lodge rubberlike liquid model was used to describe different types of variations of the steady viscosity with shear rates, for PMAs [21]. From such generalized models, it is possible to obtain the memory functions and damping functions for a material system [12, 21]. Construction of these functions will be very helpful in understanding the nonlinear rheological behaviour of asphalt and PMA.

In this work, we have examined the nonlinear rheological modeling of asphalt as a structure dependent material. Nonlinear convected White-Metzner model has been used, with its parameters assumed to be dependent on a structural parameter. A first order kinetic equation is proposed for the structural parameter. The governing equations are solved numerically and the rheological behaviour is compared with experimental data from stress growth and oscillatory testing of several asphalts. An attempt is made to relate the parameters of the model with the composition of asphalts, mainly in terms of asphaltene fraction.

2 MODEL FORMULATION

Although phenomenological models are useful for describing the macroscopic behaviour, a connection of the rheological behavior to the structural changes can provide additional insights. Such a connection has been justified for the White-Metzner model based on very general arguments [37]. In this work, we make a hypothesis of such a connection for asphalt as a structural material. Generally, the variation of structure is captured with an equation governing the time derivative of a structure parameter, λ [25]:

$$\frac{d\lambda}{dt} = a(1-\lambda)^b - c\lambda(\dot{\gamma})^d \qquad (1)$$

The structure parameter λ can be interpreted as representing the fraction of inter particle bonds still unbroken with respect to their non-deformed conditions. In Eq. 1, $\dot{\gamma}$ is the shear rate in case of viscometric flow or can be estimated from the second invariant of the rate of strain tensor (symmetric part of the velocity gradient tensor). The rate constants for the structural break-up and building are c and a, respectively. The concept of a scalar structure parameter has been used to explain flow behavior of materials such as ceramic pastes and clay-water suspensions [25]. Cheng and Evans generalized the Moore model and developed conditions for thixotropic and anti-thixotropic behaviour [25, 26]. A similar approach was employed by Alessandrini et al. to analyze the rheology of gypsum plaster pastes, and also by Baravian et al. to explain the flow behavior of non-elastic, non-yielding food products [25 – 27]. The structural break-up and building in PMA, as described by Eq. 1, was used to explain the rheological behaviour of PMAs in stress growth experiments [13].

The nonlinear White-Metzner model is used extensively to describe non Newtonian fluid behaviour including that of polymer melts [35] and is given by

$$\sigma + \tau \overset{\nabla}{\sigma} = -\eta\dot{\gamma} \qquad (2)$$

Where, σ is the stress tensor, $\dot{\gamma}$ is the rate of strain tensor (symmetric part of velocity gradient tensor or the stretching tensor) and $\overset{\nabla}{\sigma}$ is the upper convected derivative of the stress. The model parameters, the relaxation time τ and the viscosity η are both functions of temperature and second invariant of $\dot{\gamma}$. This model is used extensively engineering applications as it can exhibit both the shear thinning behaviour and the elastic effects. However, one of the shortcomings of this model is that it does not have a linear viscoelastic limit for infinitesimal deformations. In this work, the White-Metzner model is chosen as it is one of the simplest models and it can be used to examine nonlinear rheology with less numbers of parameters.

We simplify Eq. 2 for viscometric flow in spherical coordinates. Based on the solution to these simplified equations, material functions such as viscosity under steady shear, stress growth, storage and loss moduli can be evaluated. The above model reduces to the following set of equations for simple shear flow:

$$\sigma_{rr} + \tau \frac{d\sigma_{rr}}{dt} = 0 \tag{3a}$$

$$\sigma_{\theta\theta} + \tau[\frac{d\sigma_{\theta\theta}}{dt} - 2\sigma_{\theta\varphi}\dot{\gamma}] = 0 \tag{3b}$$

$$\sigma_{\theta\varphi} + \tau[\frac{d\sigma_{\theta\varphi}}{dt} - \sigma_{\varphi\varphi}\dot{\gamma}] = -\eta\dot{\gamma} \tag{3c}$$

$$\sigma_{\varphi\varphi} + \tau \frac{d\sigma_{\varphi\varphi}}{dt} = 0 \tag{3d}$$

Microstructural effects must be incorporated in these equations by assuming that relaxation time and viscosity are functions of shear rate, temperature and structural parameter, as follows:

$$\tau = \tau_0 \exp\left(\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)(\lambda)^n \tag{4}$$

Where τ_o is the proportionality constant, T_{ref} is the reference temperature, E_a is the activation energy in and R is the universal gas constant. Similarly, the viscosity is defined as

$$\eta = L\exp\left(\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)\left(\frac{1}{1-\lambda K}\right)\left(\eta_\infty + \frac{\eta_0 - \eta_\infty}{1+(t_\gamma\dot{\gamma})^p}\right) \tag{5a}$$

$$K = 1 - \left(\frac{\eta_\infty}{\eta_0}\right)^{\frac{1}{2}} \tag{5b}$$

Where, L is proportionality constant and η_o, τ_∞, t_γ, and p are the parameters of Cross model [7] for describing shear thinning fluids. Based on Eq. 4, relaxation time has been assumed to be a function of strain rate through the structural parameter. On the other hand, viscosity has been assumed to be directly related to both the structural parameter and strain rate. In the absence of the structural changes, the model equations will reduce to the nonlinear White-Metzner model. We refer to the model with and without structural parameter as White-Metzner model with structural parameter and White-Metzner model with no structural parameter. Recently, similar models have been used to describe the rheological behaviour of colloidal dispersions and micellar solutions [28 – 30]. It should be noted that it is possible to express White Metzner model as an integral equation of the Lodge type model considered for modeling PMAs [21]. In the modeling strategy of the present work, based on the structural parameter, the governing equation for stress is coupled with the kinetic structural equation.

Arrhenius equation or Williams Landel Ferry (WLF) equation can be used to describe the dependence of various properties such as viscosity. The choice of which equation is to be used depends on how far away one is from the glass transition temperature [22]. Free volume and its changes with temperature play a dominant role at temperatures relatively near the glass transition temperature [22]. The temperature dependence of properties such as viscosity can be expressed in terms of Arrhenius equation, if barriers in terms of molecular interactions are dominant [22, 38]. This is usually the case at higher temperatures. On the other hand, at lower temperatures (near glass transition temperature), associative processes of molecules dominate and temperature dependence is described using Williams Landel Ferry (WLF) equation or Vogel Fulcher equation [22, 38]. In Eqs. 4 and 5a, Arrhenius temperature dependence has been assumed. However, depending of the asphalt and temperature range of interest, the WLF equation can also be used. The second term in Eqs. 4 and 5 describes the effect of structural parameters on relaxation time and viscosity, respectively.

These model equations are combined with the structure variation kinetic model given in Eq. 1. However, we assume the structural kinetics of first order, implying $b = d = 1$. Similar assumptions were made in previous studies [25, 26]. Additionally, for parameters a and c, we can state that [2]:

$$a \propto \text{Diffusivity} \propto \frac{1}{M_{avg}}$$

$$c,\ a \propto \text{composition of asphalt}$$

where M_{avg} is the average molecular weight of asphalt. Hence, both c and a depend on the composition of asphalt. The composition could be defined based on fractionation or nature of phases such as crystalline and amorphous. For example, if the fraction of asphaltenes (x) is different for two asphalts, a different time constant will describe the characteristics of the building and break-up of the structure. The kinetic structural equation (Eq. 1) therefore reduces to:

$$\frac{d\lambda}{dt} = a(1-\lambda) - c\lambda(\dot{\gamma}) \tag{6}$$

Evolution of asphaltene floc size distribution in organic solvents under shear has been studied and it has been found that agglomeration/breakage is dependent on both the shear rate and asphaltene concentration [39]. Parameters *a* and *c* of Eq. 6 signify the time scales of the agglomeration and breakage. It is possible to arrive at these time scales through knowledge of interaction forces in the system [24]. However, details of interaction forces are not as well understood in complex materials such as asphalt and PMA.

Equations 3 – 6 have to be solved to obtain the rheological response of the material. Since there are a number of parameters, appropriate strategy is proposed to estimate them. It should be highlighted that one of the objectives of this work was to describe the nonlinear rheological behaviour of different asphalts. The nonlinear rheological behaviour is examined with the following material functions [35] for viscosity, stress growth, normal stress difference, normal stress coefficient, normal stress growth, and storage and loss moduli, respectively:

$$\eta = -\frac{\sigma_{\theta\varphi}}{\dot{\gamma}} \tag{7a}$$

$$\eta^{+}(t,\dot{\gamma}) = -\frac{\sigma_{\theta\varphi}(t)}{\dot{\gamma}} \text{ or } \sigma_{\theta\varphi}^{+}(t,\dot{\gamma}) = \sigma_{\theta\varphi}(t) \tag{7b}$$

$$N_1 = -\left(\sigma_{\theta\theta} - \sigma_{\varphi\varphi}\right) \tag{7c}$$

$$\Psi_1 = \frac{N_1}{\dot{\gamma}^2} \tag{7d}$$

$$\sigma_{\theta\theta}^{+}\left(t,\dot{\gamma}\right) = \sigma_{\theta\theta}\left(t\right) \tag{7e}$$

$$\sigma_{\theta\varphi}(t) = \gamma_o\left(-G'\sin\omega t - G''\cos\omega t\right) \tag{7f}$$

2.1 PARAMETER ESTIMATION

The following procedure is proposed to estimate the parameters of the model. Experimental data used for demonstration and comparison are taken from Vinogradov et al. [36] and Attano et al. [6]. Parameters of the model τ_o, E_a, n, $L\eta_\infty$, $L\eta_o$, t_γ, p, a, and c can be estimated based on, theoretical considerations or generic behaviour, by using measurement of the independent physical and chemical properties, and by fitting with the experimental data. In the procedure described below, it is assumed that steady shear experimental data on viscosity as functions of shear rate and temperature are known for given asphalt. Parameters thus estimated are used to examine the asphalt behaviour for different modes of testing such as stress growth and oscillatory shear.

- $\eta_\infty, \eta_o, t_\gamma$: The values of the product of *L* and the limiting viscosities $L\eta_\infty$ and $L\eta_o$ were evaluated by regression analysis of the available experimental results for the steady viscosity as a function of strain rate.
- *p* index in the Cross model: For most polymeric systems, the power law index has been observed to vary from 0.3 – 0.7. A value of 0.5 was chosen to describe the behaviour of asphalts [6 ,36]. It should be highlighted that this index will be different for different asphalts as well as for PMAs. Its choice will also depend on the temperature range of interest.
- E_a activation energy for temperature dependence of viscosity: The activation energy is mainly determined by most active structure forming components of asphalt i.e. asphaltenes. Asphalts obtained by oxidation of the same starting material with a more developed structural skeleton always have higher activation energies. At the same time, the activation energy depends on the type of resins, their amount and the composition of the hydrocarbon medium. An increase in the content of aromatic hydrocarbons reduces the activation energies whereas a higher content of resins in the medium increases it. Similarly, crystallization and melting behaviour of crystallizable fractions will significantly affect variation of the viscosity as a function of temperature.

Asphalt sample	Parameters estimated from experimental data [36]			
	$L\eta_o$	$L\eta_{inf}$	E_a/R	t_γ
Asphalt 1 [36]	2.31×10^{15}	7.70×10^{12}	17.0×10^{3}	1000
Asphalt 2 [36]	3.85×10^{13}	1.16×10^{12}	14.4×10^{3}	10000
Asphalt 7 [36]	3.08×10^{10}	7.70×10^{7}	1.03×10^{4}	10000
	Parameters estimated from model results of stress growth			
	a	c	τ_0	
Asphalt 1 [36]	2×10^{-1}	10a	5×10^{9}	
Asphalt 2 [36]	1×10^{-1}	2a	5×10^{8}	
Asphalt 7 [36]	5×10^{-2}	0.01a	1×10^{6}	
	Parameters estimated from experimental data [6]			
	η_o	η_{inf}	t_γ	
B80/100 [6]	3	0.05	10000	
	Parameters estimated from model results of stress growth			
B80/100 [6]	a	c	τ_0	
	1	0.045a	0.06	
	Parameters chosen *a priori*			
	n	p		
	1.4	0.5		

Table 1: Parameters used with the model [6, 36].

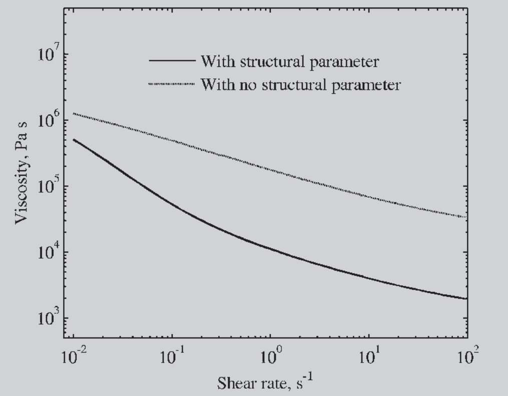


Figure 1: Shear rate dependence of the viscosity (parameters listed in Table 1, for Asphalt 1).

E_a/R can be determined from the slope of log (viscosity) versus $1/T$ plot for different asphalts [36]. For the experimental data from Attano et al. [6] the WLF equation was used based on the reported constants.

- *n* index describing the dependence of relaxation time τ on the structural parameter λ: has been assumed to be 1.4 in prior research work by Acierno et al. [31] who developed a structural model. Hence, we have chosen $n = 1.4$ for our model. These parameters have been used extensively for the modeling of suspensions and colloidal dispersions. They will be different for different material systems, due to variation in microstructural features. Therefore, they are likely to be different for asphalts and PMAs.

Parameters described so far are estimated from the experimental data or chosen a priori based on literature results. The remaining parameters, *a* and *c* (from Eq. 6) and the relaxation time (from Eq. 3) are estimated as follows:

- *a, c* parameters in the kinetic structural equation: we have assumed a direct dependence on the most active structure forming component i.e. the asphaltenes. Using steady shear data provided by Vinogradov et al. [36], for three different asphalts with asphaltene contents of 20%, 15% and 7.4% (asphalt 1, asphalt 2 and asphalt 7, respectively in [36]). The values of *a* and *c* estimated for these asphalts can be interpolated to obtain the values for other asphalts with different asphaltene contents. The parameters *a, c,* and τ_o (in the definition of relaxation time) can be obtained by fitting of experimental data on stress growth. In the following discussion of results, we have reported example values of *a* and values of *c* have been reported in terms of multiples of *a*. The ratio *c/a* indicates the relative importance of the structural breakdown and buildup processes for given asphalt.

The governing set of ordinary differential equations was solved using MATLAB 7.0 to obtain the results for different material functions.

3 RESULTS AND DISCUSSION

3.1 QUALITATIVE ANALYSIS OF THE MODEL RESULTS

Initially, the qualitative results obtained from the model are discussed. Figure 1a shows the shear thinning behaviour of asphalt under steady shear flow. If no structural parameter is included in the estimation (implying $\lambda = 1$ in Eq. 6), the viscosity is higher for a given shear rate. Additionally, the extent of shear thinning is greater with the inclusion of the structural parameter in the model. The corresponding values of structural parameters in steady shear decreases from 1 at very low shear rates to nearly 0 for large shear rates such as 100 s^{-1} (data not shown). This variation is observed over 3 decades of shear rates. The extent of decrease will be different based on the values of the parameters chosen (in Eq. 6). The set of parameters chosen for the discussion of the qualitative rheological behaviour of asphalt is given in Table 1, for Asphalt 1.

The variation of stress growth viscosity is shown in Figure 2a. The normalized viscosity is defined as the ratio of stress growth viscosity and the steady viscosity (η^+/η)at the same shear rate. At low shear rate (0.001 s^{-1}), we observe a response similar to the linear viscoelastic response of an exponential and monotonic increase in viscosity as a function of time. At steady state, the model exhibits a constant value of viscosity. At a higher shear rate (1 s^{-1}), nonlinear viscoelastic behaviour, in the form of an overshoot in viscosity as a function of time followed by a decrease, can be observed. Such overshoots have been reported

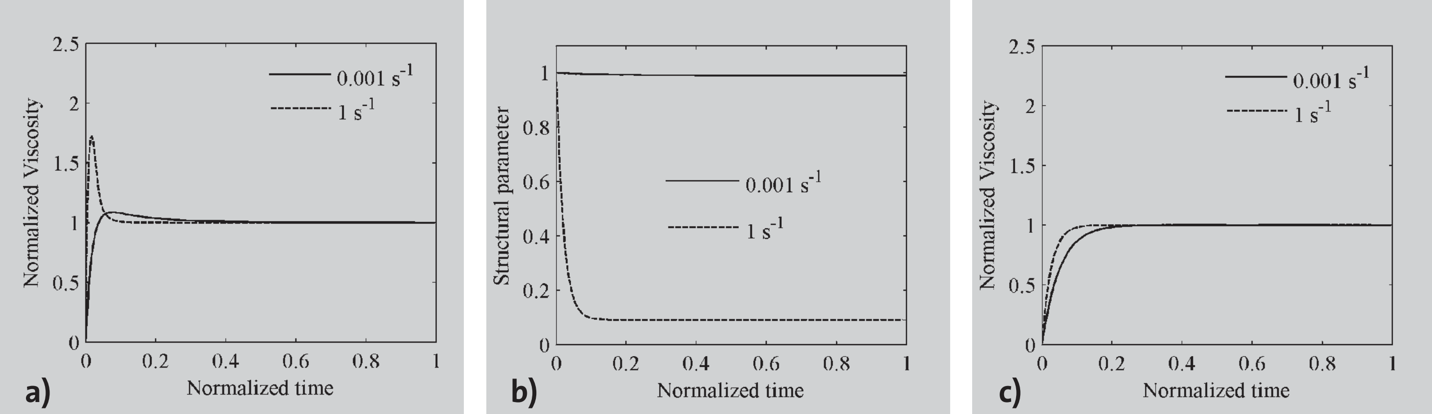


Figure 2 (above):
(a) Stress growth during steady shear at different shear rates (parameters for Asphalt 1; Table 1).
(b) Variation of structural parameter during stress growth experiment.
(c) Stress growth during steady shear, with no variation in structural parameter (λ = 1) at different shear rates.

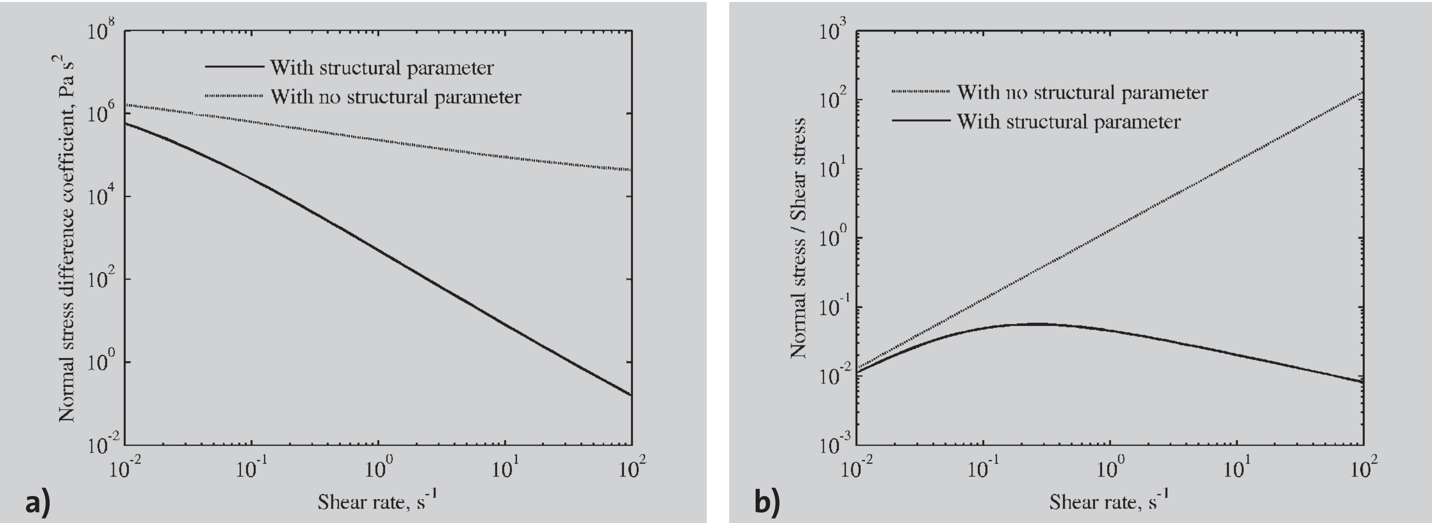


Figure 3 (below):
(a) Variation of normal stress coefficient as a function of shear rate with and without structural parameter.
(b) The ratio of normal stress to shear stress for White Metzner model with and without the variation of structural parameter (parameters for Asphalt 1, Table 1).

recently for PMA [13]. The presence and the extent of the overshoots depend on the asphalt type, as is discussed later, and on modification, as is discussed in the reported study [13].

The change in structural parameter during the stress growth is shown in Figure 2b (for the same shear rates as shown in Figure 2a). As expected, at low shear rates marginal variation in structural parameter is observed. At higher shear rates, the structural parameter decreases before reaching a steady value. The stress growth, when structural parameter is fixed at 1, is shown in Figure 2c. It should be noted that the normalized viscosity variation, even with no structural parameter, is slightly different for the two shear rates. For a linear viscoelastic material, this variation would be independent of the shear rate. Since the White-Metzner model does not have a linear viscoelastic limit, the different variation of viscosity is observed even at low shear rates, e.g. between 0.001 and 0.005 s^{-1}. Importantly, the White-Metzner model with no structural parameter does not exhibit the stress overshoot, observed in the case of various materials including asphalt.

The normal stress difference estimated from the model is shown in Figures 3a and 3b. In Figure 3a, normal stress difference coefficient Ψ_1 as a function of shear rate is shown. With no structural parameter, the coefficient is expected to decrease with increasing shear rate as the viscosity is a decreasing function of shear rate for the White-Metzner model. The coefficient (as a function of shear rate) decreases to a greater extent when the structural parameter variation is included in the model.

The ratio of normal stress to shear stress is also a function of the shear rate in nonlinear viscoelasticity. For the White-Metzner model with no structural parameter, the variation of the stresses is given by: $\sigma_{\theta\theta} \sim \dot{\gamma}^2$, $\sigma_{\theta\varphi} \sim \dot{\gamma}$. Therefore, the ratio increases linearly with the shear rate, as shown in Figure 3b. However, when structural parameter variation is included in the White-Metzner model, the ratio increases and then decreases a function of the shear rates. The magnitude of the ratio and the decrease/increase would depend on the parameters of the model, especially those defining structural breakdown and build up. In general, the variation in the normal stress to shear stress ratio is smaller when compared to the variation with no structural parameter. This is due to the decrease in the structural parameter at larger shear rates, leading to lower relaxation time. At very large shear rates, the increase in the ratio due to larger value of shear rate is offset by correspondingly smaller relaxation time.

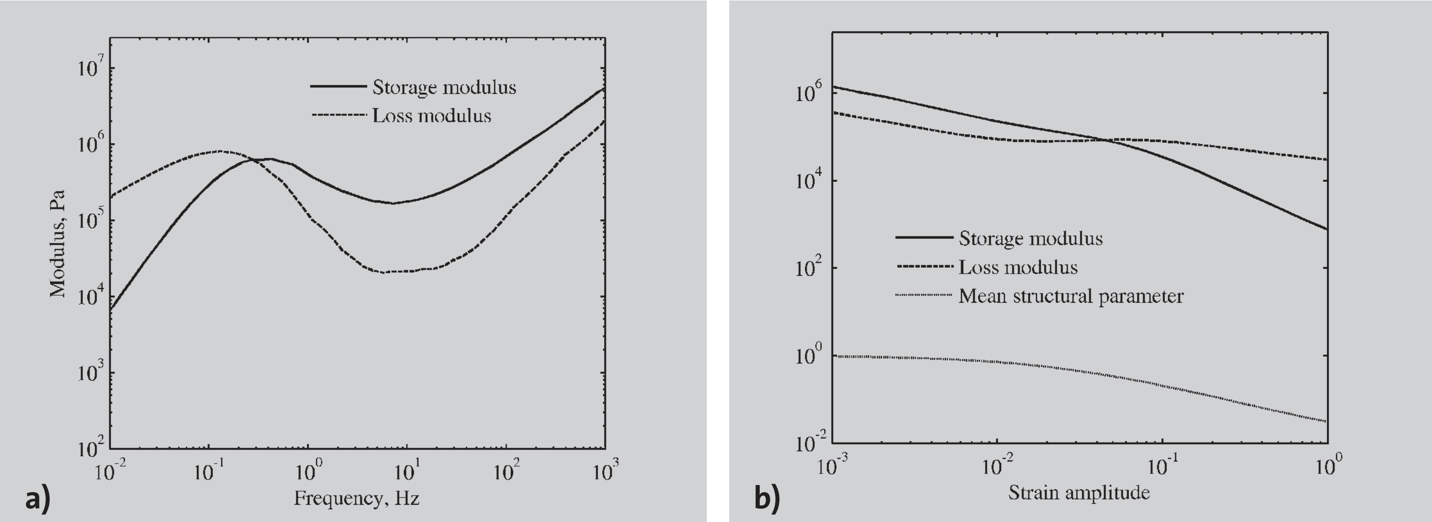


Figure 4:
(a) Frequency dependence of the storage and loss moduli.
(b) Variation of the mean structural parameter and moduli for different strain amplitudes (parameters for Asphalt 1, Table 1).

The response of the White-Metzner model with structural parameter was also evaluated for cyclic shear rate experiment (where a given set of shear rates are applied in a cyclic manner, each for a fixed period). It was observed that different material behaviour (in terms of viscosity as a function of time) is exhibited in the first and the second cycles. However, after a few cycles, the material behaviour remains the same for subsequent cycles. The effect of rest periods and subsequent cycling has been recently evaluated for PMA [13]. It will be interesting to describe the dependence of stress overshoots on the type of asphalt/modification and stress history based on a structure dependent rheological model.

Using the same set of parameters (Table 1; Asphalt 1), the response of the model in oscillatory mode was evaluated. Since the material is subjected to sinusoidal strain or strain rate during the oscillatory measurements, the structural parameter also exhibits oscillatory variation with time. From the numerical solution, it was observed that the mean structural parameter decreases initially and then becomes constant after certain number of cycles. The mean structural parameter decreased to a greater extent for higher frequencies and for larger strain amplitudes. Similarly, the oscillatory variation around the mean was greater for higher frequencies and larger strain amplitudes. Because of this variation of structural parameter in the oscillatory mode, variety of nonlinear viscoelastic behaviour can be observed by appropriate choice of parameters.

Figure 4a shows that both the storage and loss moduli exhibit non-monotonic variation with frequency (γ_o = 0.005). The response at low frequencies is similar to the Maxwell model response with a single relaxation time. In this regime, structural parameter variation is marginal and therefore relaxation time remains relatively constant. It should be noted that if no structural parameter is included, the White-Metzner model exhibits classical Maxwell-like behaviour (increase in *G'* at lower frequencies, constant *G'* at higher frequencies; increase and decrease in *G''*). The behaviour is termed Maxwell-like, since *G'* and *G''* are always functions of γ_o for the White-Metzner model. The absence of linear viscoelastic behaviour arises from the dependence of η and λ on $\dot{\gamma}$. Based on the trends in Figure 4a, the behaviour of asphalt appears to reach a relative plateau in the middle range of frequencies. At higher frequencies, both *G'* and *G''* increase with frequency. This qualitative behaviour is similar to that of polymer solutions, where a plateau at intermediate frequencies is observed due to entanglement effects [35]. The use of structural parameter with the White-Metzner model leads to variation of relaxation time with respect to frequency. At lower frequencies, Maxwell-like behaviour is observed since $\omega\tau$ at these frequencies is small. Hence, increasing ω still leads to dominating viscous response. At intermediate frequencies, the plateau is observed because $\omega\tau$ variation is less significant. In other words, the increase in is accompanied with a corresponding decrease in τ. Therefore, only a slight decrease is observed in *G'*. At higher frequencies, low values of τ (as λ approaches 0), lead to an increase in *G* . The variation of the moduli and mean structural parameter with different strain amplitudes is shown in Figure 4b. As was emphasized earlier, no linear viscoelastic regime is observed at low strain amplitudes. Therefore, only the qualitative trends for the oscillatory material functions have been reported in the next section. It is to be noted that the mean structural parameter is found to decrease with increasing strain amplitude of oscillation.

In the following section, the response of the White-Metzner model with structural parameter is compared with the experimental data from

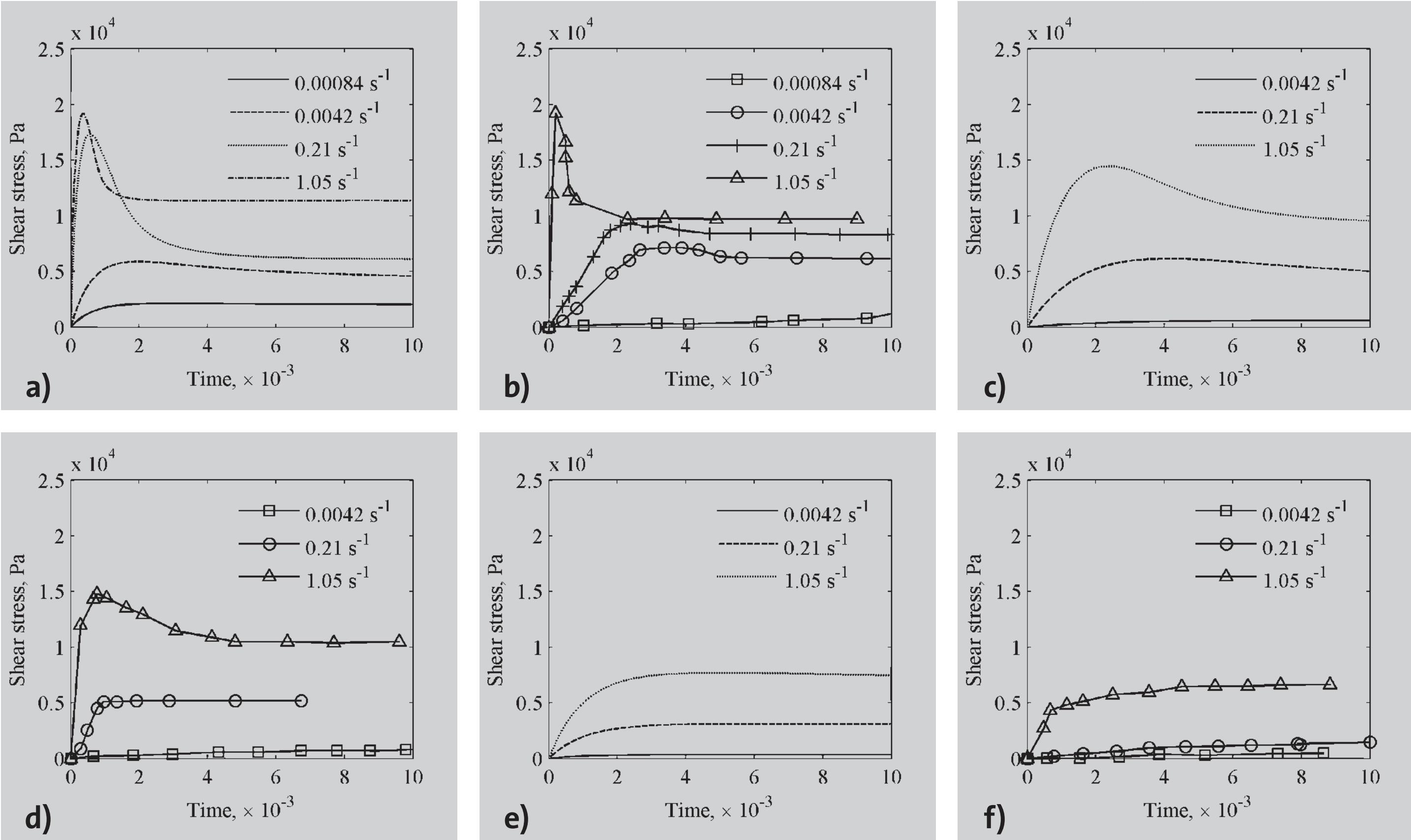


Figure 5: Comparison of the time dependence of the shear stress for different shear rates: (a) Asphalt 1, model results, (b) Asphalt 1, experimental data trends [36], (c) Asphalt 2, model results, (d) Asphalt 2, experimental data trends [36], (e) Asphalt 7, model results, (f) Asphalt 7, experimental data trends [36].

Vinogradov et al. [36] and Attano et al. [6]. The parameters used for the numerical solutions have been summarized in Table 1.

3.2 COMPARISON WITH EXPERIMENTAL DATA

The results obtained from the modeling strategy as outlined in previous section with the experimental data of Vinogradov et al. [36] and Attano et al. [6] are compared in this section. In the former case, the experimental findings were reported for linear and nonlinear rheology of different grades of asphalt. Compositions of these asphalts were also reported in terms of the asphaltene content [36]. We show the comparison between the model and experimental data for 3 asphalts, Asphalt 1, Asphalt 2 and Asphalt 7 [36]. Parameters in the governing equation for the structural parameter that depend on the composition of asphalt, can then be estimated for the remaining asphalt by interpolation of the evaluated parameters from the picked 3 asphalts. Attano et al. have reported stress growth, stress decay and normal stress differences for different grades of asphalts [6].

Experimental data [36] and the model results from White-Metzner model with structural parameter are shown in Figure 5 for three asphalts. Figures 5a, 5c and 5e show the model results for Asphalt 1, Asphalt 2 and Asphalt 7 [36], respectively. Corresponding experimental data trends are included in Figures 5b, 5d and 5f. For all the three asphalts, there is good agreement between the experimental data and model results. It should be noted that a single set of parameters was used for estimation of asphalt response at different shear rates. The parameters and their values are given in Table 1. As mentioned earlier, steady viscosity data is used in obtaining parameters of the model governing the viscosity variation. The strength of the present modeling strategy for asphalt is indicated by the good agreement as a function of time for different shear rates with a given set of parameters.

The stress (or viscosity) overshoot at large shear rates is observed in the case of Asphalts 1 and 2, while it is absent in the case of Asphalt 7. The asphaltene contents (Vinogradov et al. [36]) of these asphalts were reported to be 20%, 15% and 7.4%, respectively. Asphalts 1 and 2 have higher asphaltene contents compared to that of Asphalt 7. As mentioned earlier, the asphaltene domains have been hypothesized as part of both the colloidal agglomerates and the network structure of asphalt. Larger asphaltene content would lead to more structuring and thereby, allowing stronger case of structure disruption due to shearing. It is noteworthy that the quantitative comparison of stress overshoot cannot be observed with the White-Metzner model with no structural parameter. Therefore, the response of asphalts can be explained better if we incorporate the kinetic structural equation. It is observed from the model results that as we con-

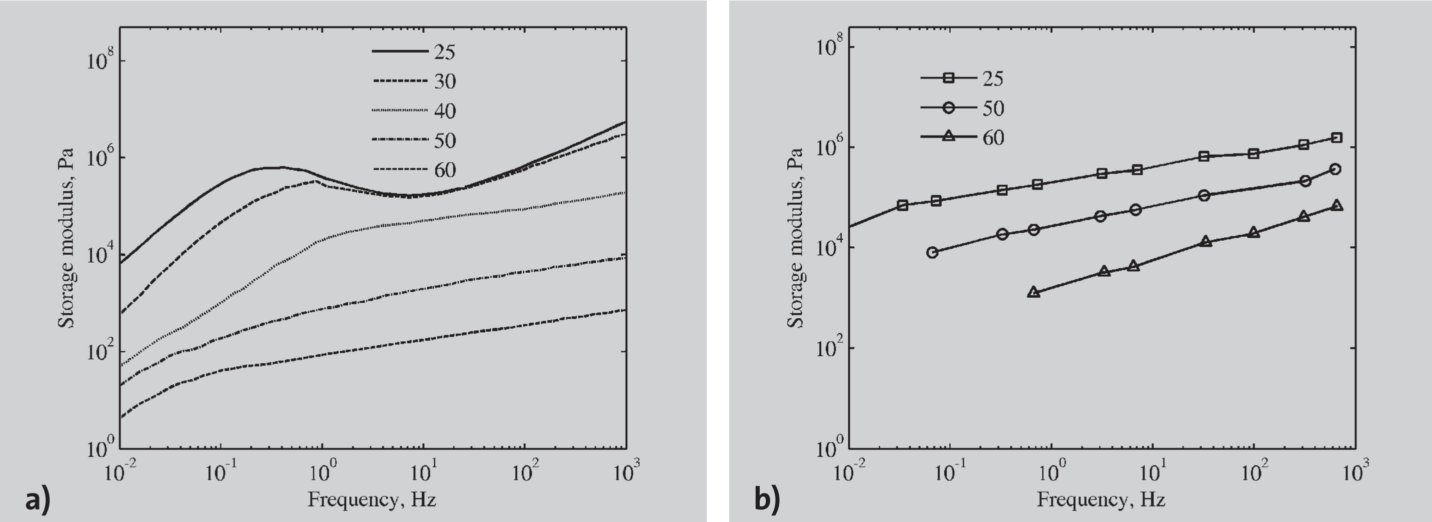


Figure 6: Comparison of the frequency dependence of the moduli at different temperatures (parameters as given in Table 1, Asphalt 1): (a) Model results, (b) Experimental data trends.

sider asphalts from Asphalt 1 to Asphalt 7, the stress overshoot (at the same shear rate) decreases. The sharpness of stress overshoot peak indicates the nonlinear viscoelastic nature of the fluid. Based on the present model, we can conclude that the nonlinear elastic nature is closely governed by the asphaltene content. Similar observations about the PMA microstructure and history of shearing have been made recently [13].

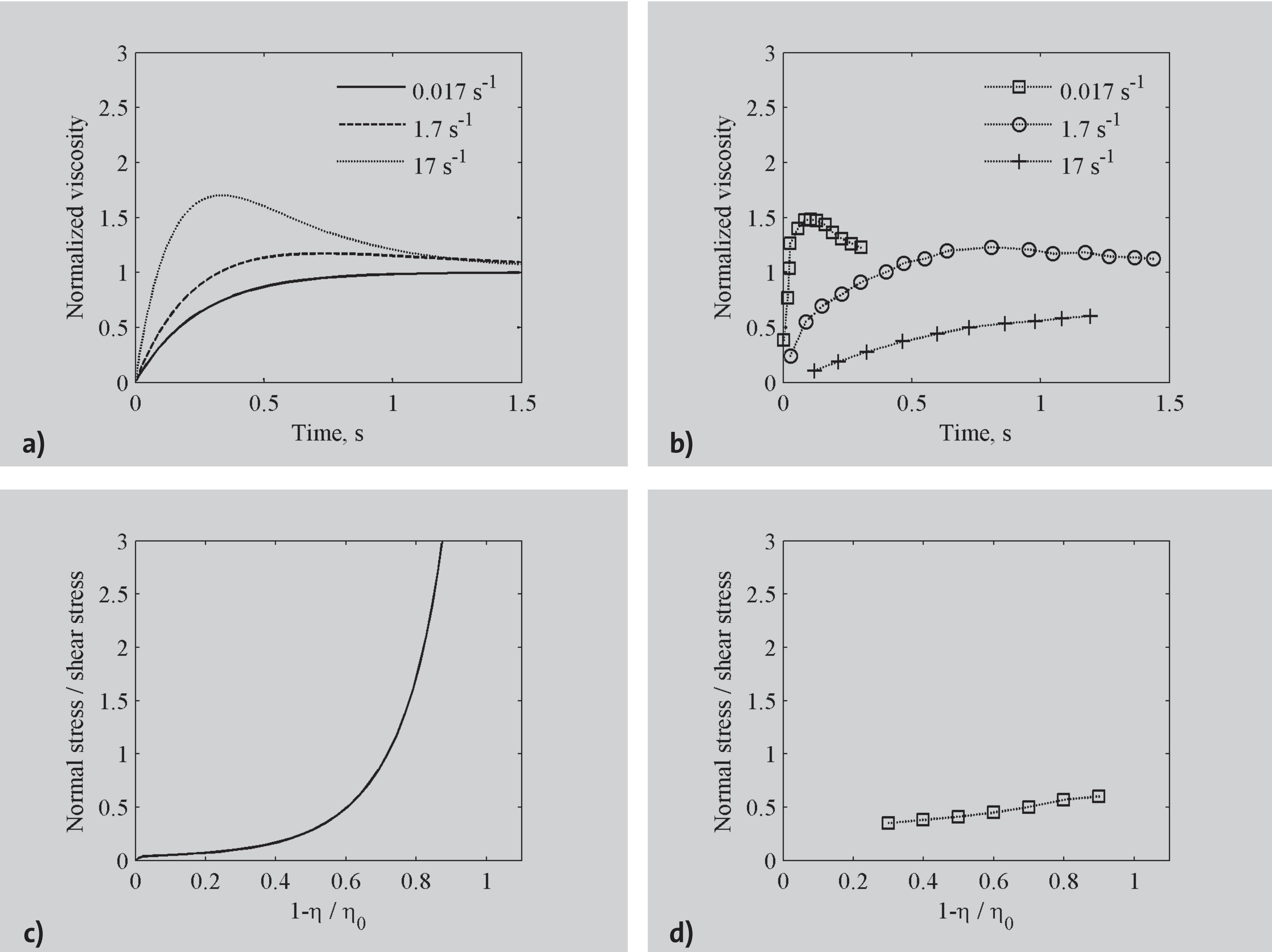
The parameters given in Table 1 were also used to calculate the model response for oscillatory shear flow experiments. The storage and loss moduli for Asphalt 1 are shown in Figure 6a. Similar results were obtained for Asphalts 2 and 7 as well. The present model does not consider a direct dependence of the structural parameter on the temperature. In the temperature range from 25 to 60°C, significant transitions take place due to crystal melting and/or solvation layer dissolution. These would have a direct effect on structural parameter, which in the present work is not a function of temperature but only a function of the shear rate. Therefore, the trends observed in Figure 6a (γ_o = 0.005), in comparison with the experimental data trends shown in Figure 6b, are only qualitatively similar. Another limitation of the present model, as mentioned earlier, is in terms of the absence of a linear viscoelastic limit. A detailed constitutive modeling with hypotheses and incorporations of the various transitions would definitely lead to better description of asphalt rheological behaviour at different temperatures, and thereby lead to more physical insights.

The variation of model parameters *a*, *c*, and τ_o is monotonic with respect to the asphaltene contents of the corresponding asphalts. The constant used in estimation of relaxation time (τ_o) decreases with decreasing asphaltene content, implying a decrease in the relaxation time. With increasing asphaltene content, parameter a decreases, and the ratio *c*/*a* decreases as well. Therefore, variation observed in parameter *c* is more significant compared to that in parameter *a*. From Eq. 6, it can be stated that contribution of structural build-up is less for asphalts with lower asphaltene content and the contribution due to structural breakdown is even lower for the asphalts with lower asphaltene content. The variation of parameters *a* and *c* is consistent with that observed for asphaltene flocculation in organic solvents [39]. It was observed that both the agglomeration as well as breakage is higher with higher asphaltene concentrations [39].

Stress growth data reported by Attano et al. [6] was also used to compare with the model results. For the description of temperature dependence of viscosity and relaxation times, parameters from the following equation were used [6]:

$$\log\frac{\eta}{1.66\cdot10^4}=\left(\frac{-8.86(T-309.6)}{101.6+T-309.6}\right)\left(\frac{1}{1-\lambda K}\right)\left(\eta_\infty+\frac{\eta_o-\eta_\infty}{1+(t_\gamma\dot{\gamma})^p}\right) \tag{8}$$

Figure 7a and 7b show the comparison of model results and the experimental data trends for asphalt B80/100 from Attano et al. [6]. The parameters used for the model results are also listed in Table 1. As observed in earlier results, good agreement at different shear rates is observed with a single set of parameters. The variation of the ratio of normal stress to shear stress, as estimated by the model and that measured experimentally is shown in Figures 7c and 7d [6], respectively. These model results were arrived at by evaluating the response of asphalt for a wide range of shear rates, so that (1 - η/η_o) was varied between 0 and 1. The stress ratio increases up to (1 - η/η_o) ~ 0.95. This corresponds to very high shear rates. Therefore the stress ratio maximum shown by the model in Figure 3b is not apparent in Figure 7c. With the White-Metzner model with no structural parameter, the stress ratio would be under-predicted for values of (1 - η/η_o) less than 0.5 and over-predicted for larger values. There-



fore, agreement between results of White-Metzner model with structural parameter and experimental data is much better when compared to the agreement between White-Metzner model with no structural parameter. If analysis of the variation of parameters *a* and *c*, carried out for the asphalts of Vinogradov et al., is extended in this case, the contribution of structural build up is larger compared to the asphalts of Vinogradov et al. [36]. However, the contribution due to structural break down is only moderate.

Recently, it has bee shown that an important tool to investigate microstructure and rheology is to carry out cyclic shear tests with and without rest periods [13]. The stress overshoot and its variation with repeated cycles can be used to deduce aspects of microstructural evaluation [13]. The present model can also be used to carry out such cyclic calculations. Evolution of the rheological material functions and microstructural parameters can be tracked for a complex deformation history. The results from the present modeling strategy demonstrate that good agreement can be observed between nonlinear rheology of asphalt and White-Metzner model with a structural parameter. However, more extensive experimental characterization of nonlinear rheology of asphalt, with detailed micro-structural evaluation can be used to arrive at better constitutive models. For example, it has been shown that asphaltenic aggregates are polydisperse oblate cylinders [40], and therefore a rheological model incorporating asphaltene aggregation and orientation behaviour can be developed. Similarly, the change in morphology of polymer modified asphalt and the rheology can also be modeled through kinetic structural equations.

5 CONCLUSION

Linear and nonlinear rheology of asphalt is very important not only for the fundamental understanding but also for applications. In recent times, nonlinear rheology of asphalt and polymer modified asphalts has been shown to be very crucial in understanding their performance. The steady shear viscosity and linear viscoelasticity of asphalts have been analyzed in great detail in the literature. However, correspondingly less data is available for nonlinear rheological behaviour of asphalts, especially for stress growth, normal stress differences etc. In the present work, a

Figure 7:
(a) Comparison of stress growth (normalized viscosity defined as the ratio of viscosity at any time and steady viscosity at a given shear rate), the model results.
(b) Experimental data trends corresponding to Figure 7a [6].
(c) Variation of the normal stress to shear stress ratio for the same asphalt as Figures 7a and 7b, the model result,
(d) Experimental data trends corresponding to Figure 7c [6].

model incorporating structural parameter in the nonlinear White-Metzner model was considered. The model accounts for the effect of composition of asphalt on its rheological properties by considering the structural changes that occur with flow. From the qualitative analysis, it was observed that the model exhibits many important characteristics of a general non-Newtonian fluid, and hence the results obtained can be extended to other complex fluids with suitable modifications. The White-Metzner model, with structure dependent relaxation time and viscosity, does not have a linear viscoelastic limit. Hence, the results of the present model were only compared for qualitative trends in oscillatory testing. The experimental data from the literature on stress growth and normal stress difference in different grades of asphalt were compared with the model results. The variation of the parameters was observed to be consistent with the asphaltene contents of the asphalts. Cyclic shear tests with rest periods can also be modelled using the present model.

Overall, the model incorporates the effects of composition (structure), shear rate and temperature for explaining the complex rheological properties of asphalt, giving a qualitative approach of modelling rheology using microstructural methods. The results of the present model demonstrate that detailed nonlinear rheological experimental data on several asphalts and physico-chemical characterization of the same asphalts will lead to better quantitative predictive models and understanding of the nonlinear rheology of asphalt.

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