

Rheological analysis of bitumen as a complex glass-forming liquid and comparison with some simple glass-forming liquids

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ABSTRACT

This experimental study investigates the glassy dynamics of bitumen by means of small-diameter parallel plate rheometry. Bitumen is considered as a complex glass-forming liquid, and its rheological properties are compared with those of selected simple glass-forming liquids. The results demonstrate that the chemically and structurally complex nature of bitumen has a profound effect on its glassy dynamics, and thus a broadening effect is observed.

INTRODUCTION

The low-temperature dynamics of molecular glass-forming liquids is a highly important, yet poorly understood phenomenon in material physics¹. In particular, the glassy dynamics of compositionally and structurally complex materials are currently far from being understood. In this study, the low-temperature glassy properties of various bitumens are investigated by means of small-diameter parallel plate rheometry. Due to its chemical and structural complexity, bitumen exhibits relaxation dynamics that are significantly different from those of previously studied simple glass-forming liquids. As a result, this paper provides new insights into the dynamics and rheological behavior of complex glass-forming systems.

EXPERIMENTAL

Materials

Bitumens originating from different crude oil sources and produced with various refining processes were investigated. These bitumen samples differed significantly from each other by their chemical and physical properties; details of the samples are given in Laukkanen². In addition, for comparison purposes, literature data³ of three simple glass-forming liquids – namely, glycerol, *m*-toluidine, and sucrose benzoate – were analyzed in this study.

Rheological characterization

Low-temperature rheological properties of the bitumen samples were characterized with a stress-controlled rotational rheometer (Malvern Kinexus Pro). The rheometer was equipped with a parallel plate geometry using 4-mm diameter plates with a gap of 1.75 mm; a small plate diameter and large gap were used to minimize errors due to torsional instrument compliance^{3,4}. An actively-controlled Peltier plate and hood were used to accurately control the temperature of the test specimen, and the rheometer was connected to a refrigerated circulator (Julabo CF41) to access the lowest measurement temperatures. Frequency sweep tests ($f = 10 \dots 0.01$ Hz) were performed at various temperatures

down to -40 °C, and the strain amplitudes were kept in the linear viscoelastic region. At sub-zero temperatures an automatic normal force control was used to adjust the measurement gap in order to keep the normal force close to zero. The measured rheological data were corrected for instrument compliance using Eqs. 1-3, derived from the equations presented in Marin⁵ and further based on the work of Macosko and coworkers^{6,7}.

$$G'_s = \frac{G'_m \left(1 - \frac{J_{inst}}{k_g} G'_m\right) - \frac{J_{inst}}{k_g} G''_m{}^2}{\left(1 - \frac{J_{inst}}{k_g} G'_m\right)^2 + \left(\frac{J_{inst}}{k_g} G''_m\right)^2} \quad (1)$$

$$G''_s = \frac{G''_m}{\left(1 - \frac{J_{inst}}{k_g} G'_m\right)^2 + \left(\frac{J_{inst}}{k_g} G''_m\right)^2} \quad (2)$$

$$\tan \delta_s = \frac{G''_m}{G'_m \left(1 - \frac{J_{inst}}{k_g} G'_m\right) - \frac{J_{inst}}{k_g} G''_m{}^2} \quad (3)$$

where G'_s and G''_s are the true storage and loss modulus of the sample, $\tan \delta_s$ is the true loss tangent of the sample, G'_m and G''_m are the measured storage and loss modulus values, J_{inst} is the instrument compliance (the total torsional compliance of the rheometer system), and k_g is a geometry conversion factor. In this study, $J_{inst} = 9.64 \times 10^{-3}$ rad/Nm was determined by gluing the upper and lower plate of the rheometer together with superglue, and by measuring the angular deflection of the measurement system and the rheometer while applying different levels of torque. Details of this procedure are described in the Appendix C of Laukkanen². The geometry conversion factor k_g for the parallel plate geometry with plate radius R and measurement gap h is defined by Eq. 4.

$$k_g = \frac{2h}{\pi R^4} \quad (4)$$

In addition, complementary frequency sweep measurements were performed at higher temperatures (up to 90 °C) using a stress-controlled Paar Physica MCR 500 rheometer with 8-mm and 25-mm diameter parallel plate geometries. Also this rheometer was equipped with a Peltier plate and hood for precise temperature control. A full description of the experimental procedures is given in Laukkanen².

RESULTS AND DISCUSSION

In an earlier publication by the authors⁸, it was shown that unmodified bitumens are thermorheologically simple materials at low temperatures ($T \leq 10$ °C), irrespective of their wax content. Hence, time-temperature superposition (TTS) principle can be successfully utilized in the analysis of the glassy dynamics of these materials, and rheological master curves can be constructed. Furthermore, from the construction of master curves horizontal shift factors a_T are obtained, and the temperature dependence of these shift factors over a wide temperature range (both below and above T_g) can be accurately modeled by the modified Kaelble equation⁹, Eq. 5.

$$\log a_T = -c_1 \left(\frac{T - T_d}{c_2 + |T - T_d|} - \frac{T_r - T_d}{c_2 + |T_r - T_d|} \right) \quad (5)$$

where c_1 and c_2 are fitting parameters, T_d is the defining temperature at which the curvature of the shift factor curve changes, and T_r is the reference temperature. A feature peculiar to the rheological behavior of bitumen is that it undergoes a transition directly from the liquid to the glassy state upon cooling, without an intermediate elastic regime. The non-existence of rubbery elastic behavior in bitumen is due to its low molecular weight and lack of entanglements.

Bitumens experience a glass transition usually in the temperature range of -10 to -30 °C, a typical value being -20 °C². Therefore, the used experimental set-up, capable of performing rheological measurements at temperatures down to -40 °C, is ideal for studying the dynamics of bitumen in the glass transition region and glassy state using only very small amounts of material (~ 25 mg). Moreover, it is shown that physical aging proceeds particularly fast in bitumens, especially in non-waxy ones, allowing low-temperature rheological measurements to be made in a pseudo-equilibrium state where the rheological response is time independent. This makes (non-waxy) bitumen an ideal material for the investigation of glassy dynamics in viscoelastic materials.

In a wider context, bitumen can be regarded as a complex glass-forming liquid, whose chemical composition and microstructure are extremely complicated and even partially unknown¹⁰. When the rheological behavior of bitumen is compared with that of chemically and structurally simple glass-forming liquids (glycerol, *m*-toluidine and sucrose benzoate), some similarities are observed. For example, similarly to bitumen, these simple glass-forming liquids do not form entanglements due to their low molecular weight, and thus exhibit a monotonic transition from the liquid to the glassy state. This characteristic behavior can be conveniently visualized by constructing and comparing the Booij-Palmen plots $\delta(\log|G^*|)$ (also known as the van Gurp-Palmen plots) or dynamic master curves of these materials.

However, a detailed investigation of these two types of materials reveal some remarkable differences between their low-temperature dynamics. By studying the Booij-Palmen plots and master curves more carefully, it is observed that bitumen exhibits a much more gradual liquid-to-glass transition than the investigated simple glass-forming liquids. The broadness of this glass

transition can be attributed to the chemically complex nature of bitumen. In other words, it can be postulated that different chemical components in bitumen have different T_{gs} , and the observed broad glass transition results from the superposition of the glass transitions of these different bitumen fractions¹¹. It is also pointed out that the broad glass transition of bitumen is visible from differential scanning calorimetry (DSC) data as well; the width of the glass transition region of bitumen, as measured by DSC, is typically on the order of 30-40 °C.

The unusual patterns in the glassy dynamics of bitumen become apparent also when model fitting is performed. It has been reported that the dynamic mechanical response of most glass-forming materials can be well fitted with the Kohlrausch-Williams-Watts (KWW) stretched exponential function^{12,13}, Eq. 6.

$$G(t) = G_0 \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right) \quad (6)$$

where G_0 is the glassy modulus, τ is the characteristic relaxation time, and β is the stretching parameter related to the breadth of the relaxation time spectrum. The investigated simple glass-forming liquids have also been reported to approximately follow the KWW function (Eq. 6)³. However, this function does not fit properly to the bitumen data, which is once again attributable to the unusually broad glass transition of this complex glass-forming liquid.

To gain a more fundamental understanding of the rheological characteristics of the investigated materials, their relaxation time spectra $H(\tau)$ were calculated. The spectrum calculation was performed with the Interactive Rheology Information Systems (IRIS) software¹⁴, utilizing the parsimonious spectrum model developed by Baumgaertel and Winter^{15,16}. As proposed by Winter¹⁷, the relaxation

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time spectrum of the simple glass-forming liquids can be described by a power-law equation with a positive exponent, Eq. 7.

$$H(\tau, \varepsilon) = n_\alpha G_c \left(\frac{\tau}{\tau_\alpha(\varepsilon)} \right)^{n_\alpha},$$

for $\tau < \tau_\alpha(\varepsilon)$ and $n_\alpha \geq 0$ (7)

where ε is the distance from the glass, n_α is a positive-valued exponent that originate from the mode-coupling theory (MCT), G_c is the plateau modulus of the G' data, and τ_α is the longest relaxation time. However, the relaxation time spectrum of bitumen has a distinctly different shape that cannot be described by Eq. 7. Instead of exhibiting an abrupt cutoff at the longest relaxation time, the bitumen spectrum is broadly distributed at long relaxation times. Mathematically, this broadening effect can be adequately taken into account by adding a stretched exponential term to Eq. 7 as follows:

$$H(\tau) = n_\alpha G_c \left(\frac{\tau}{\tau_\alpha} \right)^{n_\alpha} \exp \left[- \left(\frac{\tau}{\tau_\alpha} \right)^\beta \right],$$

for $\beta < 1$ and $n_\alpha \geq 0$ (8)

where β is the stretching parameter that describes the broadness of the relaxation time spectrum at long relaxation times. Eq. 8 has also been found to adequately describe the dynamics of various other complex glass-forming systems^{18,19}, and therefore the universality of this equation in describing complex glassy dynamics can be postulated.

The broad glass transition of bitumen also appears to have an impact on the temperature dependence of horizontal shift factors a_T in the glassy state. While many simple molecular glass formers, including *m*-toluidine and glycerol²⁰, have been reported to follow an Arrhenius-type temperature dependence in the sub- T_g region (as evidenced by a straight line in the $\log(a_T)$ vs. T plot), bitumen clearly exhibits non-Arrhenius type of temperature dependence below T_g (that fits well to the

modified Kaelble equation, Eq. 5). The curved shape of the shift factor curve below T_g is postulated, once again, to result from the superposition of multiple glass transitions in bitumen. This claim is supported by the fact that the shift factor curve of amber – which can also be considered as a complex glass forming system – shows similar type of curvature below T_g ²¹.

CONCLUSION

The results of this study show that bitumen is an interesting “model material” for complex glass-forming material systems that exhibits significantly different glassy dynamics as simple glass-forming liquids.

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