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Published in:
Annual Transactions of the Nordic Rheology Society

Published: 01/01/2017

Document Version
Publisher's PDF, also known as Version of record

Please cite the original version:
Laukkanen, O.-V., Winter, H. H., Soenen, H., & Seppälä, J. (2017). From simple to complex glass-forming liquids: broadening of the glass transition as studied by shear rheology. *Annual Transactions of the Nordic Rheology Society*, *25*, 158-161.

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From simple to complex glass-forming liquids: broadening of the glass transition as studied by shear rheology

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ABSTRACT

This paper investigates the effect of chemical and structural complexity on the rheological patterns of molecular glass-forming liquids (GFLs). Rheological properties of various petroleum-based complex glass-forming liquids (CGFLs) are measured near and below their glass transition temperatures, and these properties are compared with those of simple glass-forming liquids (SGFLs). Our recently proposed broadened power-law spectrum model is used to describe the relaxation time spectra of CGFLs, and the broadness parameter of this model, β, is shown to exhibit a power-law correlation with the width of the glass transition region, ΔT_g, as measured by differential scanning calorimetry (DSC).

INTRODUCTION

The dynamics of molecular glass-forming liquids (GFLs) have been investigated intensively during the past five decades or so, mainly by means of rheology and dielectric spectroscopy. One of the most widely-used constitutive models for GFLs is the Kohlrausch-Williams-Watts (KWW) function that assumes a stretched exponential form for the shear relaxation modulus $G(t)$:[1]

$$G(t) = G_g e^{-(t/\tau)^\beta} \quad (1)$$

where G_g is the glassy modulus, τ is the characteristic relaxation time, and β is a stretching parameter related to the breadth of the relaxation time spectrum. Recently, Winter[2] proposed that the relaxation time spectra of molecular and colloidal glass formers adopt power-law format with a positive power-law exponent:

$$H(\tau,\varepsilon) = n_\alpha G_c \left(\frac{\tau}{\tau_\alpha(\varepsilon)}\right)^{n_\alpha}, \quad \text{for } \tau < \tau_\alpha(\varepsilon) \text{ and } n_\alpha \geq 0 \quad (2)$$

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 possible shortcoming of the KWW and power-law spectrum models is that their validity has been tested only on chemically and structurally simple glass-forming liquids (SGFLs). Meanwhile, rheological characterization and constitutive modelling of chemically and structurally complex glass-forming liquids (CGFLs) have received very little attention.

The scope of this paper is to investigate the rheological properties of CGFLs near and below their glass transition temperatures, especially in comparison with SGFLs. The systematic evolution in the rheological patterns of GFLs as a function of increasing chemical and structural complexity is demonstrated, emphasizing the broadening of rheological features in the vicinity of the glass transition. In addition, an analysis is performed to correlate observations of the broadening of the glass transition in rheological and differential scanning calorimetry (DSC) experiments.

EXPERIMENTAL

Materials

In total, 36 petroleum-based CGFLs were investigated in this study, including 32 bitumen samples (27 of them in the unaged state and 5 of them oxidatively aged), three naphthenic process oils, and one soft asphalt residue. Additional information on some of these materials is provided elsewhere[3].

Rheological characterization

To avoid torsional instrument compliance effects caused by high sample stiffness, small-diameter parallel plate rheometry[4] was employed in the measurement of the linear viscoelastic properties of the CGFLs near and below their glass transition temperatures. As an integral part of this technique, all measured rheological data were corrected for torsional instrument compliance using Eqs. (3)-(5):

$$G_s' = \frac{G_m'\left(1 - \frac{J_{inst}}{k_g} G_m'\right) - \frac{J_{inst}}{k_g} G_m''^2}{\left(1 - \frac{J_{inst}}{k_g} G_m'\right)^2 + \left(\frac{J_{inst}}{k_g} G_m''\right)^2} \quad (3)$$

$$G_s'' = \frac{G_m''}{\left(1 - \frac{J_{inst}}{k_g} G_m'\right)^2 + \left(\frac{J_{inst}}{k_g} G_m''\right)^2} \quad (4)$$

$$\tan \delta_s = \frac{G_m''}{G_m'\left(1 - \frac{J_{inst}}{k_g} G_m'\right) - \frac{J_{inst}}{k_g} G_m''^2} \quad (5)$$

where G'_s, G''_s, and tan δ_s denote the true (compliance corrected) values of the storage modulus, loss modulus and loss tangent of the sample, respectively, G'_m and G''_m are the measured storage modulus and loss modulus values, J_{inst} is the instrument compliance, and k_g is the geometry conversion factor (for the parallel plate geometry, $k_g = 2h / \pi R^4$ where h is the gap between the plates of radius R).

Rheological properties of the bitumen samples were measured with a stress-controlled Malvern Kinexus Pro rheometer, equipped with a Peltier plate and active hood for temperature control. In these experiments, 4-mm diameter parallel plate geometry was used with a gap of approximately 1.75 mm. Frequency sweep measurements were performed at various temperatures ranging from 10 to -40 °C with 10 K intervals. Strain amplitudes were kept low enough to ensure linear viscoelastic response (γ_0 = 0.075-0.01 % depending on the measurement temperature). Details of the measurement procedure and specimen preparation are described elsewhere[3].

Rheological characterization of the naphthenic process oils and soft asphalt residue was performed with a stress-controlled Anton Paar Physica MCR 301 rheometer, equipped with a CTD 450 convection oven for temperature control. 4-mm diameter parallel plate geometry with a gap of 1.2-1.5 mm was employed in these measurements. Frequency sweeps were carried out at various temperatures near and below the glass transition temperature of the investigated material (the exact temperature range varied depending on the material). Small strain amplitudes were applied to ensure linear viscoelastic response (γ_0 = 0.05-0.01 % depending on the measurement temperature).

Differential scanning calorimetry

Thermal properties of the investigated CGFLs were determined by conventional or temperature-modulated differential scanning calorimetry (DSC/TMDSC). DSC measurements on the bitumen samples were performed with a Mettler Toledo DSC1 instrument at a heating/cooling rate of 10 K/min. TMDSC measurements on the naphthenic process oil and soft asphalt residue samples were carried out with a TA Instruments Q2000 differential scanning calorimeter at an underlying cooling/heating rate of 3 K/min, modulation amplitude of 0.5 K, and modulation period of 60 s.

Rheological data on SGFLs from the literature

Linear viscoelastic frequency sweep data of various SGFLs were retrieved from the literature and analyzed for comparison purposes. Information on these data sets is summarized in Table 1.

RESULTS AND DISCUSSION

CGFLs investigated in this study are characterized by different amounts of chemical and structural complexity. As described in our previous papers[13,14], bitumen is an extremely complex mixture of mainly hydrocarbons whose physical properties are also strongly influenced by various types of molecular interactions, such as dispersive, polar, hydrogen bonding and π-π interactions[15]. In particular, it is the heavy fractions of bitumen that contribute the most to the complexity of this material as a glass-forming liquid. These complex heavy fractions become gradually absent when moving from very heavy to lighter crude oil distillates, which is also the case with the soft asphalt residue and naphthenic process oils investigated in this study. In these materials, the reduction in the chemical and structural complexity is manifested, for example, by decreasing molecular weight and aromaticity.

The effect of the complexity of a GFL on its rheological behavior is remarkable. This becomes evident when comparing the linear viscoelastic data of the CGFLs and SGFLs in the plot of loss angle versus $\log|G^*|$ (also known as the van Gurp-Palmen plot[16] or the Booij-Palmen plot[17]). The shape of the curve in this plot is observed to broaden systematically and significantly with increasing chemical and structural complexity. This demonstrates a more gradual transition from the liquid state to the glassy state, i.e. broadening of the glass transition, in CGFLs as compared with SGFLs.

For further analysis, master curves of dynamic material functions (G', G'' and tan δ) were constructed. As expected, the master curves of all SGFLs can be described by the KWW function (Eq. 1). However, the KWW function is not able to describe the broadly shaped master curves of CGFLs. This observation clearly demonstrates the inability of the KWW function to model the dynamics of a broad glass transition.

The relaxation time spectra of the GFLs were calculated using the method of Baumgaertel and Winter[18,19]. All SGFLs

Table 1. Rheological data sets of SGFLs analyzed in this study.

Source of data	Material	Measurement method
McKenna Group (Texas Tech)[5]	sucrose benzoate	8-mm diameter parallel plates with torsional instrument compliance corrections[6]
	m-toluidine	
	glycerol	
Schröter & Donth (Univ. Halle)[7]	glycerol	hyperbolically shaped sample between 8-mm diameter parallel plates[8]
Glass & Time group (Roskilde Univ.)[9,10]	tetraphenyl-tetramethyl-trisiloxane (DC704)	self-built piezoelectric shear-modulus gauge (PSG)[11] + self-built cryostat and temperature control system[12]
	1,2-propanediol	
	pentaphenyl-trimethyl-trisiloxane (DC705)	

are found to exhibit a power-law spectrum with a sharp cutoff at the longest relaxation time (Eq. 2). On the contrary, the power-law spectra of CGFLs are accompanied by a broad distribution of long relaxation time modes. The CGFL spectra can be described by our newly proposed broadened power-law spectrum model[13]:

$$H(\tau) = n_\alpha G_c \left(\frac{\tau}{\tau_\alpha}\right)^{n_\alpha} \exp\left[-\left(\frac{\tau}{\tau_\alpha}\right)^{\beta}\right], \quad \text{for } \beta < 1 \text{ and } n_\alpha \geq 0 \qquad (6)$$

where β is a stretching parameter that describes the broadness of the relaxation time spectrum at long relaxation times. The β parameter is observed to decrease systematically with the increasing chemical and structural complexity of a GFL, and it is suggested that this parameter can be used as a rheological measure of the breadth of the glass transition in CGFLs.

Similarly to the rheological experiments, DSC and TMDSC experiments reveal a broadening of the glass transition with the increasing complexity of a GFL. In the case of bitumen, the width of the glass transition region, ΔT_g, is typically several tens of Kelvin, and can be even as high as ~60 K.

As rheological and DSC/TMDSC experiments provided similar information of the broadening of the glass transition in CGFLs, an effort was made to correlate the rheological and thermal characteristics of the broad glass transition. Interestingly, a strong power-law correlation is found between the rheological and thermal measures of the broadness of the glass transition, i.e. between the β parameter from the broadened power-law spectrum model (Eq. 6) and ΔT_g as measured by DSC/TMDSC. This finding provides important insight into the origin and nature of the broad glass transition in CGFLs. However, further studies on well-defined model materials are needed to develop a comprehensive understanding of this phenomenon.

CONCLUSION

This study examined the effect of chemical and structural complexity on the rheological characteristics of GFLs in the vicinity of the glass transition. The broadening of the glass transition dynamics in petroleum-based CGFLs is demonstrated. The newly proposed broadened power-law spectrum model is found to be suitable for describing the glassy dynamics of CGFLs, and the parameter β of this model is suggested as a quantitative rheological measure of the breadth of the glass transition. The observed correlation between β and ΔT_g provides an interesting starting point for the future work to better understand the physical fundamentals of the broad glass transition in CGFLs.

ACKNOWLEDGMENTS

The authors wish to thank Anton Paar GmbH and Malvern Instruments Ltd for technical support and equipment loans. O.V.L. gratefully acknowledges funding from the Vilho, Yrjö, and Kalle Väisälä Foundation and Nynas AB.

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