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Published in:
Journal of Non-Crystalline Solids

DOI:
[10.1016/j.jnoncrysol.2017.12.029](https://doi.org/10.1016/j.jnoncrysol.2017.12.029)

Published: 01/03/2018

Document Version
Peer reviewed version

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Please cite the original version:
Laukkanen, O-V., Winter, H. H., Soenen, H., & Seppälä, J. (2018). Systematic broadening of the viscoelastic and calorimetric glass transitions in complex glass-forming liquids. *Journal of Non-Crystalline Solids*, 483, 10-17. <https://doi.org/10.1016/j.jnoncrysol.2017.12.029>

Systematic broadening of the viscoelastic and calorimetric glass transitions in complex glass-forming liquids

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Abstract In this experimental study, we explore the broadening of the glass transition in chemically and structurally complex glass-forming liquids (CGFLs) by means of thermal and rheological characterization techniques. Petroleum fluids with different levels of chemical and structural complexity are used as model materials. Thermal characterization by temperature-modulated differential scanning calorimetry (TMDSC) reveals a systematic increase in the width of the glass transition region ΔT_g with increasing chemical and structural complexity. The broadening of the glass transition is also strongly reflected in the linear viscoelastic properties that are measured by small-diameter parallel plate rheometry. Most notably, this is observed as the broadening of the relaxation time spectrum at long times. The recently proposed broadened power-law spectrum model is used to describe the constitutive behavior of the investigated petroleum fluids. In this model, the stretching parameter β serves as a quantitative measure of the spectral broadening. A strong power-law correlation is found between ΔT_g and β , manifesting a relationship between the broadness of the calorimetric and viscoelastic glass transition in CGFLs.

Keywords: Glass-forming liquids; Glass transition; Rheology; Viscoelastic properties; Relaxation time spectrum; Differential scanning calorimetry

1. INTRODUCTION

As documented by several excellent review articles [1-5], the dynamics of supercooled glass-forming liquids (GFLs) have been a subject of intense research over the past five decades or so. For example, a lot of research has been devoted to the study of non-exponential relaxation in GFLs [6,7]. Although experimental techniques such as rheology [8] and dielectric spectroscopy [9] have provided extensive information on glassy dynamics, the underlying theory remains relatively obscure [10-12]. In particular, the dynamics of chemically and structurally complex glass-forming liquids (CGFLs) are still largely unexplored and poorly understood [13].

In terms of rheological properties, the glass transition manifests itself as a rapid increase in the relaxation time τ and in the viscosity η upon cooling. Indeed, in many glass-forming systems, this increase is observed to be more than 15 orders of magnitude over a relatively narrow temperature range. It is particularly notable that the extreme temperature dependence

of GFLs poses a major challenge to their rheological characterization. At low temperatures – i.e. near and below the glass transition temperature (T_g) – GFLs are extremely stiff, in which case measurement errors due to torsional instrument compliance may become an issue [14,15]. To overcome this experimental difficulty, sophisticated measurement techniques such as small-diameter parallel plate (SDPP) rheometry have been developed. To accurately measure the high stiffness values of a glassy material, the SDPP technique relies on minimizing the instrument compliance errors by decreasing the diameter of a parallel plate measurement geometry and by applying instrument compliance corrections [16].

With the help of improved measurement techniques, the linear viscoelastic data of GFLs have become increasingly available during the past decade. This has allowed more comprehensive constitutive models to be developed for GFLs. Particularly, special attention has been recently paid to the modeling of the relaxation time spectra $H(\tau)$ of GFLs. Winter and coworkers [17,18] discovered that the $H(\tau)$ of selected colloidal and molecular glass formers can be described by a power-law function that is cut off at the longest relaxation time τ_α :

$$H(\tau, \varepsilon) = n_\alpha G_c \left(\frac{\tau}{\tau_\alpha(\varepsilon)} \right)^{n_\alpha}, \text{ for } \tau < \tau_\alpha(\varepsilon) \text{ and } n_\alpha \geq 0 \quad (1)$$

where ε is the distance from the glass, n_α is a positive-valued exponent that originates from the mode coupling theory (MCT), and G_c is the plateau modulus of the G' data. Notably, Eq. (1) is identical to the Baumgaertel-Schausberger-Winter (BSW) model [19] without contributions from the β -relaxation. In a more recent study by the authors [13], it was shown that Eq. (1) is valid only for chemically and structurally simple glass-forming liquids (SGFLs). On the contrary, the relaxation time spectrum of bitumen – a material that can be considered as a model material for CGFLs [13] – exhibits a significantly different shape. Specifically, the bitumen spectrum is characterized by a broad distribution of long relaxation times. This spectrum can be described by a power-law function with a stretched exponential cut-off [13]:

$$H(\tau) = n_\alpha G_c \left(\frac{\tau}{\tau_\alpha} \right)^{n_\alpha} \exp \left[- \left(\frac{\tau}{\tau_\alpha} \right)^\beta \right], \text{ for } \beta < 1 \text{ and } 0 < n_\alpha \leq 1 \quad (2)$$

where β is a stretching parameter that describes the broadening of the relaxation time spectrum at long relaxation times.

In this broadened power-law spectrum model, the stretched exponential function, $\exp(-t^\beta)$ with $\beta < 1$, is used in a way which significantly differs from its common use in the modeling of the glass transition. The stretched exponential function is able to describe decaying processes, which occur more slowly than a regular exponential function ($\beta = 1$) would predict. Conventionally, in the context of the glass transition dynamics, the broadening of stress relaxation has been expressed by a relaxation modulus of stretched exponential format [20,21]. Here, using a different property of the stretched exponential, the stretched exponential function is multiplied into the BSW powerlaw relaxation spectrum with the purpose of broadening the cut-off at the longest relaxation time. For a large β value ($\beta = 10$, for instance), the sudden cut-off of the BSW spectrum is preserved. However, for a small β value, the cut-off is broadened as needed for expressing the glassy relaxation of CGFLs. This β parameter is solely used for the broadening of the relaxation time spectrum but is unrelated to the conventional KWW

relaxation modulus. In our previous paper [13], the broadened shape of the relaxation time spectrum was attributed to the broad distribution of glass transition temperatures. A schematic representation of the empirical constitutive models of Eqs. (1) and (2) and their associated parameters is given in Fig. 1.

Fig. 1 Schematic representation of the constitutive models described by Eqs. (1) and (2). n_α describes the slope of the relaxation time spectrum at short relaxation times, τ_α is the longest relaxation time in the power-law spectrum model of Winter [17,18], and β defines the width of the broadened power-law spectrum at long relaxation times [13]. The dashed line shows the contribution of the power-law term $H(\tau) = n_\alpha G_c (\tau/\tau_\alpha)^{n_\alpha}$.

Thermal properties of glass-forming materials are often characterized by differential scanning calorimetry (DSC) or temperature-modulated differential scanning calorimetry (TMDSC) [22]. The main advantage of TMDSC over conventional DSC is that it allows a quantitative separation between heat capacity-related (reversing) and kinetic (non-reversing) thermal events [23]. From an application point of view, TMDSC has proven to be a particularly powerful technique in the characterization of CGFLs, such as bitumen and its fractions [24,25] and naphthenic and paraffinic oils [26]. Masson et al. [25,27] showed, for example, that TMDSC can detect multiple glass transitions in bitumen and quantify time-dependent changes in its microstructure. Moreover, the reversing heat flow in TMDSC allows accurate determination of glass transition temperatures without interference from non-reversing thermal events such as enthalpy relaxation and cold crystallization; this will be demonstrated later on in Section 3.1.

In this study, we investigate the rheological and thermal properties of CGFLs near and below the glass transition. The main objective is to evaluate the effect of chemical and structural complexity on the broadening of the glass transition. To investigate this, we selected petroleum liquids as model materials for CGFLs. They are obtained from the distillation of crude oil and can be considered as highly complex mixtures of different types of hydrocarbons with small amounts of heteroatoms such as sulfur, oxygen, nitrogen and organic metals [28]. The distillation process separates the crude oil into different fractions based

on boiling point ranges. The resulting petroleum fractions exhibit a wide spectrum of chemical and physical properties [28,29]. Low-boiling point fractions of crude oils are mostly composed of paraffinic and naphthenic hydrocarbons that are of relatively low molecular weight and contain only minute traces of heteroatoms [28]. The physical properties of these liquids are mainly governed by the London dispersive interactions that are the dominating type of molecular interaction in non-polar hydrocarbons [30]. Upon increasing boiling point, petroleum fluids become more complex in terms of chemical composition and molecular structure [31,32]. This evolution is often accompanied by an increase in the molecular weight and the molecular weight distribution [33]. Furthermore, aromatic and polar interactions start to play a role with increasing heteroatom content [28]. In the asphaltene fraction, which is the highest molecular weight and most polar component of crude oil and its derivatives, polycondensed aromatic compounds are believed to form π - π stacked structures [34]. Consequently, heavy petroleum products such as vacuum residue and bitumen are best described as extremely complex mixtures of different molecular species exhibiting various forms of molecular interactions [35]. Importantly for the purposes of this study, the varying chemical and structural properties of different petroleum fluids result in vast differences in their rheological behavior [36].

2. EXPERIMENTAL

2.1. Materials

Five petroleum fluid samples were investigated in this study. A summary of the basic properties of these samples is given in Table 1. The chemical and structural complexity – of the petroleum fluids increases in the following order, as evidenced by increasing density and molecular weight: NPO1 < NPO2 < NPO3 < SVR < BIT. The average molecular weights reported in Table 1 were measured by gel permeation chromatography (GPC). It needs to be emphasized, however, that these molecular weights are only directional as the GPC of petroleum fluids is prone to experimental artifacts e.g. due to molecular associations and the tendency of asphaltenes to adsorb on the column wall [37,38]. Table 1 also shows the mean molecular polarizability α of the petroleum fluids. This parameter characterizes the magnitude of the London dispersion forces that are the most important molecular interactions for the physical properties of petroleum hydrocarbons [30]. The polarizability is defined as [39,40]:

$$\alpha = \left(\frac{3}{4\pi N_A} \right) \left(\frac{M}{\rho} \right) \left(\frac{n^2 - 1}{n^2 + 2} \right) \quad (3)$$

where N_A is Avogadro's number, M is the molecular weight, ρ is the density, and n is the refractive index. In our calculations, we employed the number-average molecular weight ($M = M_n$) in Eq. (3) to yield an average value for the polarizability (it needs to be remembered that petroleum fluids are complex mixtures of different types of hydrocarbons with different polarizability characteristics). In addition to increasing polarizability, the increase in the structural complexity is manifested by increasing aromaticity. This is demonstrated in Fig. 2 which shows ultraviolet-visible (UV-Vis) spectroscopy data for the investigated petroleum

fluids. Specifically, the observed increase in the absorption at long wavelengths can be attributed to the increasing content of large conjugated aromatic structures [41].

Table 1 Basic properties of the investigated petroleum fluid samples

	Sample code	Appearance	ρ at 15 °C [g/cm ³] ^a	API gravity [°] ^b	API classification ^c	M_n [g/mol] ^d	M_w [g/mol] ^d	M_w/M_n [-]	n at 20 °C [-] ^e	α [10 ⁻²⁴ cm ³]
Naphthenic process oils	NPO1	Clear and bright	0.90	25.5	Medium oil	228	348	1.53	1.494	29.2
	NPO2	Clear and bright	0.92	22.0	Heavy oil	469	637	1.36	1.507	60.1
	NPO3	Dark brown	0.94	19.0	Heavy oil	467	873	1.87	1.524	60.3
Soft vacuum residue	SVR	Black	0.98	12.9	Heavy oil	681	1630	2.39	1.558	88.8
Bitumen	BIT	Black	1.03	5.9	Extra-heavy oil	1053	2320	2.20	1.612	140.9

^a Data provided by the material supplier

^b API gravity = $141.5 / \rho - 131.5$

^c light oil: API > 31.1°; medium oil: 22.3° < API < 31.1°; heavy oil: 10.0° < API < 22.3°; extra-heavy oil: API < 10.0°

^d measured by GPC; see Soenen and Redelius [42] for experimental details

^e measured by refractometer; see Soenen and Redelius [42] for experimental details

Fig. 2 UV-Vis absorbance spectra of the investigated petroleum fluid samples. A detailed description of the test procedure is given in Soenen and Redelius [42].

2.2. Methods

2.2.1. Temperature-modulated differential scanning calorimetry (TMDSC)

Temperature-modulated differential scanning calorimetry (TMDSC) is an extension of the conventional DSC technique that was originally developed by Reading and coworkers [23,43]. It allows a separation of the heat capacity-related (reversing) and kinetic (non-reversing) characteristics of thermal events by superimposing a sinusoidal modulation on the linear heating or cooling ramp. In this study, TMDSC experiments were performed on a TA Instruments Q2000 differential scanning calorimeter equipped with a Refrigerated Cooling System (RCS). The instrument was calibrated with high-purity sapphire and indium standards. Approximately 15 mg of sample was weighed into an aluminum pan that was hermetically sealed and transferred to the DSC instrument. The samples were annealed for 5 min at 100 °C to remove any effects of thermal history, after which modulated cooling and heating scans were carried out in the temperature range between -90 and 140 °C. The following modulation parameters were chosen based on previous TMDSC studies on similar petroleum fluids [24,26]: underlying cooling/heating rate = 3 K/min, modulation amplitude = 0.5 K, and modulation period = 60 s. The DSC cell was purged with pure dry nitrogen at a flow rate of 50 ml/min. The data from the TMDSC experiments were analyzed with a commercial Universal Analysis 2000 software (version 4.5A, TA Instruments). Unless otherwise stated, the analysis was performed on the data collected during the modulated heating scan.

2.2.2. *Small-diameter parallel plate (SDPP) rheometry*

Small-diameter parallel plate (SDPP) rheometry [16] was employed to measure the linear viscoelastic properties of the petroleum fluids in shear. Frequency sweep experiments were performed using a stress-controlled Anton Paar Physica MCR 301 rheometer equipped with a 4-mm diameter parallel plate geometry. The frequency was varied from 10 to 0.01 Hz, while the strain amplitude was decreased incrementally from 0.05 to 0.01 % upon lowering the measurement temperature. The measurement gap was set at 1.2-1.5 mm in the beginning of the test sequence. The frequency sweep experiments were conducted at various temperatures near and below T_g , from the highest to the lowest temperature with 5 or 10 K steps (see Table 2 for details). The temperature of the test specimen was controlled with the accuracy of better than ± 0.5 K using a CTD 450 convection oven (Anton Paar). The rheometer was also equipped with an EVU 10 liquid nitrogen evaporation unit (Anton Paar), which allows the cooling of the CTD 450 oven down to -130 °C. The flooding of the oven with nitrogen vapor also prevents moisture uptake and ice formation in the test specimen. Due to the thermal contraction of the test specimens upon cooling, it was necessary to employ the normal force control of the rheometer at temperatures near and below T_g . This setting automatically adjusts the measurement gap in order to avoid the build-up of normal forces in the test specimen while maintaining good adhesion between the plates and the specimen.

As rheological experiments were performed near and below the glass transition temperature (see Table 2 below for details), physical aging effects had to be considered in the experimental design. For this reason, each frequency sweep measurement was preceded by an isothermal annealing period that was sufficiently long to bring the test specimen to the metastable thermodynamic equilibrium (fully aged state) or at least very close to it. This was feasible due to the relatively rapid physical aging of the investigated petroleum fluids that were

completely amorphous or only slightly crystalline. As an example, physical aging data measured for the bitumen sample at and below its T_g are shown in our previous paper [13]. Further physical aging data will be provided in a subsequent publication.

As described by Laukkanen [16], rheological data measured in the glassy state need to be corrected for torsional instrument compliance. The corrections for the storage modulus (G'), loss modulus (G'') and loss tangent ($\tan \delta$) can be derived analytically and expressed as follows [16,44]:

$$G'_s = \frac{G'_m \left(1 - \frac{J_i}{k_g} G'_m\right) - \frac{J_i}{k_g} G''_m{}^2}{\left(1 - \frac{J_i}{k_g} G'_m\right)^2 + \left(\frac{J_i}{k_g} G''_m\right)^2} \quad (4)$$

$$G''_s = \frac{G''_m}{\left(1 - \frac{J_i}{k_g} G'_m\right)^2 + \left(\frac{J_i}{k_g} G''_m\right)^2} \quad (5)$$

$$\tan \delta_s = \frac{G''_s}{G'_s} = \frac{G''_m}{G'_m \left(1 - \frac{J_i}{k_g} G'_m\right) - \frac{J_i}{k_g} G''_m{}^2} \quad (6)$$

where G'_s , G''_s , and $\tan \delta_s$ 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 values, and k_g is the geometry conversion factor (for the parallel plate geometry, $k_g = 2h / \pi R^d$, where h is the gap between the plates of radius R). The torsional compliance of the rheometer setup used in this study, $J_i = 0.01925$ rad/Nm, was determined experimentally as outlined in Fig. S1 of the Supplementary Material. In this study, all rheological data were corrected online for the instrument compliance using a commercial RheoPlus software (version 3.62, Anton Paar) [45].

3. RESULTS AND DISCUSSION

3.1. Broadening of the calorimetric glass transition

TMDSC is a particularly useful technique for measuring glass transition temperatures in semi-crystalline materials. This is because TMDSC can separate the glass transition (reversing thermal event) from the enthalpy relaxation and cold crystallization (non-reversing thermal events) [23]. The separation of these partially overlapping thermal transitions is demonstrated in Fig. 3 where reversing and non-reversing heat flow curves obtained from TMDSC heating scans are presented.

In the present study, particular emphasis is given to the broadening of the glass transition. The width of the glass transition region – defined here as the difference between the onset and end temperatures of the glass transition, $\Delta T_g = |T_{g,onset} - T_{g,end}|$ – increases systematically with the increasing chemical and structural complexity of a GFL (in the order

NPO1 < NPO2 < NPO3 < SVR < BIT). These CGFLs are characterized by a broad distribution of glass transition temperatures. In particular, the bitumen sample exhibits an unusually broad glass transition ($\Delta T_g = 29.1$ K), which we attribute to its extremely complex molecular composition. It is also observed that the nominal glass transition temperature increases in the same order in these materials. This is an expected trend due to increasing molecular weight [26]. The glass transition temperatures of the petroleum fluids are summarized in Table 2, together with the temperature ranges covered in the following rheological experiments.

Fig. 3 Reversing (top panel) and non-reversing (bottom panel) heat flow curves of the petroleum fluids (curves shifted vertically for clarity). The widths of the glass transition regions are indicated in the top panel; the thick vertical lines represent the onset and end temperatures of the glass transition region and the thin vertical lines show the half-height midpoint of each transition. In the bottom panel, labels (1) and (2) denote the endothermic enthalpy relaxation and exothermic cold crystallization, respectively. Note that cold crystallization is not present in samples NPO1 and BIT due to the absence of crystallizable fractions.

Table 2 Glass transition temperatures of the petroleum fluids and temperature ranges employed in the rheological characterization

	$T_{g,onset}$ [°C]	$T_{g,midpoint}$ [°C] ^a	$T_{g,end}$ [°C]	ΔT_g [K]	Temperature range for the rheological characterization
NPO1	-76.7	-74.4	-72.1	4.6	$T = -60 \dots -95$ °C with 5 K steps
NPO2	-57.7	-54.1	-50.6	7.1	$T = -40 \dots -75$ °C with 5 K steps
NPO3	-57.9	-52.8	-47.6	10.3	$T = -40 \dots -75$ °C with 5 K steps
SVR	-38.6	-27.7	-17.2	21.4	$T = 0 \dots -60$ °C with 10 K steps
BIT	-26.6	-12.2	2.4	29.0	$T = 10 \dots -40$ °C with 10 K steps

^a determined with the half-height method

3.2. Broadening of the viscoelastic glass transition

A simple way to present linear viscoelastic data is the Booij-Palmen plot [46], sometimes also known as the van Gorp-Palmen plot [47], which is plot of loss angle versus $\log|G^*|$. This data representation can be used to assess the thermorheological simplicity of the investigated material while the construction of this plot does not require any data manipulation by means of time-temperature superposition (TTS) [48]. Fig. 4 shows the reduced Booij-Palmen plot of the petroleum fluids, together with data for selected SGFLs. In this plot, the modulus axis (x-axis) is normalized with respect to the glassy modulus G_g (i.e. the modulus at infinite frequency) for easier comparison of the shapes of the curves. A significant and systematic broadening of the curves is observed with increasing chemical and structural complexity. In other words, this signifies a broadening of the viscoelastic glass transition, i.e. the transition from the liquid ($\delta = 90^\circ$) to the glassy ($\delta = 0^\circ$) state.

Fig. 4 Comparison of the linear viscoelastic properties of the petroleum fluids in the reduced Booi-Palmen plot (symbols). Data for selected SGFLs are shown for comparison purposes (lines). The following symbols are used to indicate SGFL data sources: ($\dagger$) for Hutcheson and McKenna [14], ($\S$) for Schröter and Donth [49], ($\S$) for Hecksher et al. [50], and ($\circ$) for Maggi et al. [51]. Modulus shifts b_T originating from the density changes of the sample material [52] are used to generate smooth curves, and the modulus data are normalized with respect to the glassy modulus G_g to allow easier comparison of the shapes of the curves. The b_T and G_g values of the petroleum fluids and SGFLs are listed in Table S1 of the Supplementary Material.

The glass transition dynamics of different GFLs can also be compared by investigating the shapes of their dynamic moduli master curves. This is done in Fig. 5 where reduced master curves for the storage (G') and loss (G'') modulus are shown. Similarly to the analysis above, a pronounced broadening of viscoelastic features is observed in the vicinity of the glass transition towards increasingly complex GFLs. The frequency and modulus shift factors, a_T and b_T , used in the construction of the master curves are reported in Table S1 of the Supplementary Material.

Fig. 5 Reduced storage modulus (left panel) and loss modulus (right panel) master curves for the petroleum fluids (symbols). Data for selected SGFLs are shown for comparison purposes (lines). See Fig. 4 for the explanation of the symbols in the legend. The frequency axis is normalized with respect to the reduced angular frequency corresponding to the maximum in G'' . The G' values are normalized with respect to the glassy modulus G_g and the G'' values are normalized with respect to the maximum in G'' to allow easier comparison of the shapes of the curves.

Furthermore, these master curves were used to calculate the relaxation time spectra $H(\tau)$ of the investigated GFLs. In this study, the method of Baumgärtel and Winter [53,54] was used in the spectrum calculation. The relaxation time spectra are shown in Fig. 6, normalized with respect to the parameter τ_α (see Eqs. (1) and (2) for the definitions of this parameter). As reported previously by the authors [13], the SGFL spectra are characterized by a sharp cut-off at the longest relaxation time and can be fairly well described by the power-law spectrum model

of Eq. (1). In complex petroleum fluids the power-law form of the spectrum appears to be retained at short relaxation times, but at long times significant broadening is again observed. This observation concurs with our earlier findings [13] and suggests the validity of the broadened power-law spectrum model, Eq. (2). Indeed, this model provides excellent fits to the relaxation time spectra of the petroleum fluids as shown in Fig. 6. Of particular importance is the stretching parameter β that conveniently describes the broadness of the spectrum at long relaxation times. In the investigated petroleum fluids, the value of this parameter decreases systematically with increasing chemical and structural complexity, signifying the broadening of the viscoelastic glass transition. Thus, we propose that β can be used as a quantitative measure of the complexity of a GFL.

Fig. 6 Relaxation time spectra of the petroleum fluids calculated from the dynamic moduli master curves of Fig. 5. The lines represent fits of the broadened power-law spectrum model, Eq. (2). The relaxation times are normalized with respect to τ_α to overlap the spectra in the power-law region (at short relaxation times). Note that the endpoints of the calculated relaxation time spectra are prone to experimental uncertainties and computational errors, and therefore may show slight deviations from the model fits. The legend includes values of the β parameter obtained from the fits of the broadened power-law spectrum model. The relaxation time spectra of the selected SGFLs of Figs. 4 and 5 are not shown here for clarity, but are reported in our previous publication [13].

It is notable that the stretching parameter β of the broadened power-law spectrum model describes the liquid (long relaxation time) side of the relaxation spectrum. It therefore appears that it is really the approach of the glass transition from the liquid side that is mostly influenced by the chemical and structural complexity. In other words, CGFLs are characterized by a wide spectrum of intermediate viscoelastic states between the liquid and glass, as compared to SGFLs.

We also note that the stretching parameter β of the broadened power-law spectrum model is in no way correlated with the stretching parameter β_{KWW} of the Kohlrausch-Williams-Watts (KWW) stretched exponential function. This is obvious from the fact that the KWW

stretched exponential function is only applicable to SGFLs, whereas the broadened power-law spectrum model is more suitable for describing CGFLs.

3.3. Correlation between the broadness of the calorimetric and viscoelastic glass transition

In Sections 3.1. and 3.2., we have used TMDSC and rheological techniques to describe the systematic broadening of the glass transition as the chemical and structural complexity of a GFL increases. This is clearly manifested in the values of ΔT_g and β parameters that describe the broadness of the calorimetric and viscoelastic glass transition, respectively. For a more quantitative analysis, these parameter values are plotted against each other on a log-log scale in Fig. 7. This plot also includes data points for various bitumen samples; these samples have been previously investigated by Laukkanen [55] and by Soenen and Redelius [42], and additional information on them is provided in Table S2 of the Supplementary Material. A strong power-law relationship is found between the two broadness parameters ($R^2 = 0.966$), providing an interesting connection between the calorimetric and viscoelastic glass transition. As described previously in this article, GFLs with low chemical and structural complexity are characterized by small ΔT_g and large (close to unity) β values, while GFLs with high chemical and structural complexity are characterized by large ΔT_g and small β values. The observed correlation indicates that the same compositional and/or microstructural features are responsible for the broadened distribution of glass transition temperatures and of mechanical relaxation times in CGFLs.

Fig. 7 Correlation between the stretching parameter β of the broadened power-law spectrum model and the width of the glass transition region ΔT_g as measured by TMDSC. See Table S2 of the Supplementary Material and Laukkanen [55] and Soenen and Redelius [42] for additional information on the various bitumen samples included in the plot. Note that the ΔT_g values, and therefore the resulting correlation are dependent on the measurement parameters used in the TMDSC experiments; see Section 2.2.1. for the parameters used in this study.

1 In SGFLs, the width of the dynamic glass transition can be described by the KWW
2 stretching parameter β_{KWW} [56]. The inverse of this parameter has been found to correlate
3 linearly with the width of the calorimetric glass transition ΔT_g in experiments [57] and in
4 simulations [58]. As far as we know, however, this study is the first time that a relation between
5 the width of the calorimetric and viscoelastic glass transition has been observed in CGFLs.
6 Future studies are expected to use the presented methodology in the analysis of a greater variety
7 of CGFLs and thus prove or disprove the universality of this correlation.

8 As indicated earlier in the text, CGFLs can be considered as mixtures of different
9 chemical components that exhibit different glass transition temperatures. Consequently, the
10 macroscopically observable broad glass transition may be interpreted to result from the
11 superposition of the local glass transitions. The detected correlation between ΔT_g and β
12 indicates that the broadening of the distribution of local glass transition temperatures has
13 similar effect on the width of both the calorimetric and the viscoelastic glass transition. A
14 similar conclusion has been made by Shi et al. [59] who further suggested that it is possible to
15 predict the viscoelastic spectrum of polymer blends from the glass transition distribution
16 obtained by calorimetry. However, the application of this type of data conversion to CGFLs is
17 beyond the scope of this paper and will remain an important task for future research.

18 Finally, it should be emphasized that both chemical and structural complexity are
19 expected to contribute to the broadening of the glass transition in petroleum fluids. Although
20 it would be desirable to separate chemical and structural effects on this broadening, this cannot
21 be done in practice due to the fact that the fundamental features of bitumen chemistry and
22 microstructure are largely unknown. Similarly, it has to be acknowledged that (at least with the
23 current state of knowledge) the effect of microphase segregation in the glass transition regime
24 [60] cannot be quantitatively assessed in petroleum fluids. Future studies with more well-
25 defined model systems are needed to study the aforementioned effects more in detail.

26 27 **4. CONCLUSION**

28 In this experimental study, we have investigated the broadening of the glass transition
29 in CGFLs using petroleum fluids as model materials. The broadening of the calorimetric glass
30 transition is evidenced by increasing ΔT_g as measured by TMDSC. The increase in chemical
31 and structural complexity has also a profound impact on the rheological properties near the
32 glass transition. The broadening of the viscoelastic glass transition is clearly reflected in the
33 shapes of the Booij-Palmen plot and the dynamic moduli master curves. Most significantly, a
34 systematic broadening of the relaxation time spectrum $H(\tau)$ at long times is observed. The
35 CGFL spectra can be conveniently described by the empirical broadened power-law spectrum
36 model [13]. This model includes a stretching parameter β that serves as a quantitative measure
37 of the broadening of the viscoelastic glass transition. Interestingly, a strong power-law
38 correlation is found between the ΔT_g and β parameters. This observation provides an intriguing
39 connection between the broadness of the calorimetric and viscoelastic glass transition in
40 CGFLs. However, it must be stressed that in this study only small-molecule organic GFLs are
41 considered. Additional studies on different types of CGFLs are therefore necessary to confirm
42 the universality of the observed relation.

SUPPLEMENTARY MATERIAL

See supplementary material for the detailed description of the determination of the torsional instrument compliance, for the a_T , b_T and G_g values used in the analysis of the petroleum fluids and SGFLs in Figs. 4 and 5, and for the additional information regarding the samples whose data are shown in Fig. 7.

ACKNOWLEDGMENTS

O.V.L. gratefully acknowledges the financial support from the Osk. Huttunen Foundation, the Vilho, Yrjö, and Kalle Väisälä Foundation and Nynas AB. Anton Paar GmbH is thanked for the loan of the 4-mm diameter parallel plate measurement geometry. The rheological data of sucrose benzoate, *m*-toluidine and glycerol were kindly provided by Prof. Gregory McKenna (Texas Tech), and the rheological data of tetraphenyl-tetramethyl-trisiloxane (DC704), 1,2-propanediol and pentaphenyl-trimethyl-trisiloxane (DC705) were retrieved from the data repository of the Glass and Time group at Roskilde University (<http://glass.ruc.dk/data/>).

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