Time Temperature Superposition using Creep Recovery to moduli conversion for Master curve generation

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ABSTRACT

Frequency sweeps are commonly used for determination of master curves using Time Temperature Superposition or TTS. Here we propose to use the approach based on creep testing and the subsequent transformation of creep compliance J(t) to viscoelastic moduli, G'(ω) and G'' (ω) proposed by Duffy et al. The creep compliance J(t) contain information about all frequencies not just the individual frequencies selected in the frequency sweep Furthermore, a frequency spectrum can be acquired in a fraction of the time required for standard frequency sweep so for systems that are changing with time, temperature or other physical or chemical reactions taking place time saving can be important.

Using creep testing, applying a Burgers model to the creep data and the following conversion to moduli and create master curves can generate time savings and higher accuracy since data are less affected by physical or chemical reaction like solvent evaporation and drying.

Master curves will be created from both frequency sweeps and moduli from creep converted data.

In this paper we propose an alternative to Small Amplitude Oscillatory Shear (SAOS) to generate fast informative information at low frequencies by using creep testing and the subsequent transformation of J(t) to G'(ω) and G"(ω) using the method proposed by Duffy et al[4], since J(t) contains information about all oscillation frequencies it is possible
to determine a frequency spectrum in a fraction of the time required for generating a frequency sweep to low frequencies.

INTRODUCTION

Standard Small Amplitude Oscillatory shear measurements to low frequencies can be time consuming and measurement times exceeding 600s is not uncommon. Creep measurements and the subsequent creep to modulus conversion method has the advantage of shortening the time scale of experiment and measure on different time scales/ frequency scale compared to a frequency sweep from high too low frequency. Each creep test contains discrete information about each frequency and strain.

METHOD

The method for the Creep to Modulus conversion is based on microrheology testing using tracer particles, where the mean square displacement of the tracer particle as function of time is monitored using a dynamic light scattering technique.

A relationship between the MSD of a tracer embedded in a viscoelastic fluid and the creep compliance of that fluid J(t) can be established since in the Laplace frequency domain $\tilde{J}(s) = 1/s\tilde{G}(s)$, can be shown that J(t) and $\Delta r^2(t)$ are linearly related according to Eq. 1. A microrheology experiment can therefore be considered analogous to a mechanical creep test performed in the linear viscoelastic regime and data can be presented in a common rheological format using J(t)

without the need for transformation to the frequency domain

$$J(t) = \frac{\pi a}{k_B T} \left\langle \Delta r^2(t) \right\rangle \quad (1)$$

Furthermore, the mean square displacement in Eq. 1 can be substituted with the creep compliance to give the following relation,

$$\left| G^*(\omega) \right| \approx \frac{1}{J(1/\omega)\Gamma\left[1+\alpha(\omega)\right]} \quad (2)$$

with $\alpha(\omega)$ defined according to Eq. 3

$$\alpha(\omega) = \frac{d\ln J(t)}{d\ln t}\bigg|_{t=1/\omega} \quad (3)$$

Therefore, the methods developed for obtaining viscoelastic properties from the MSD in a microrheology measurement can be equally applied to the creep compliance, thus facilitating an approach for converting the time dependent creep compliance to frequency dependent moduli for measurements made on a rotational rheometer.

The subsequent transformation of J(t) to G'(ω) and G"(ω), using the method proposed by Duffy et al[4], contains information about all oscillation frequencies, not just the discrete harmonics used in a multiwave test.

Creep data can be converted to modulus data either without model fitting or fitted to a Burgers model given by Eq. 4 below and then converted to modulus data.

$$J(t) = J_g + \sum J_t \left(1 - e^{\frac{t}{\tau}}\right) + \frac{t}{\eta_0} \quad (4)$$

The converted data using the Burgers model can be compared with a frequency sweep for the same sample. The data are shown in Fig. 1. Representing a polymer melt, polypropylene, at 200°C.
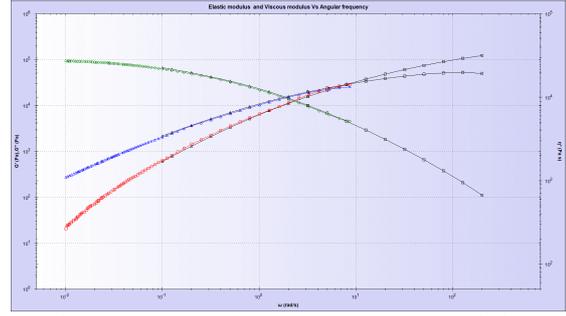

Figure 1. Data from a Creep to modulus conversion compared with data from a frequency sweep (black)

The data in Fig. 1. shows a very good agreement between creep converted data and frequency sweep data. The results show that creep recovery experiments can be converted to dynamic data over a wide frequency range.

For most applications frequency sweep data should be selected for high frequencies since data are of better quality. Creep data will generate faster data at low frequencies.

The master curve generation is done by shifting data either from complex viscosity or complex modulus in a horizontal shift to a reference temperature. In this paper all reference temperature is the lowest measured temperature for each example.

The use of Time Temperature Superposition is common for polymer melts and polymer solutions but it is also possible to use with care for other types of viscoelastic liquids and solids.

The Superposition is based on the temperature dependence of materials and this is expressed by the Williams-Landel-Ferry relation, Eq. 5 below.

$$\log a_T = -C_1(T-T_{ref})/C_2+(T-T_{ref}) \quad (5)$$

By plotting the $\log a_T$ vs. temperature a characteristic graph of the temperature dependency of the shifted parameter is obtained. For multiple parameters within the same data set similar shift factors should be obtained.

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The vertical shift factor, which is not used in this paper, is to correct for the density change of the sample with temperature given by Eq. 6.

$$b_T = \rho_{ref}T_{ref}/(\rho T) \qquad (6)$$

The shift factors have different temperature dependence and a_T has a larger temperature dependence compared to b_T. Over a limited temperature range therefore b_T shift factors can be ignored.

For temperature above the glass transition temperature the horizontal shift factors can be used to predict the activation energy of the tested material, according to Eq. 7.

$$ln a_T = (\frac{1}{T} - \frac{1}{T_{ref}})\frac{E_a}{R} \qquad (7)$$

RESULTS

The results presented are for three types of systems, a yield stress food pure sample, a low viscosity shower gel and a high viscosity polymer solution.

The experimental data are gathered using a set of fixed temperatures. For the food pure the test temperature was set to 10, 20 and 40°C using a splined bob and cup geometry. Each temperature step contains an equilibrium time of 5 min, followed by and amplitude sweep to determine the linear viscoelastic region. The results from the amplitude sweep (0.0001-0.005) are used to deduce the stress/strain condition to be used in frequency sweep (10-0.01Hz) and creep recovery respectively. For the food pure a rest period of 30s between frequency sweep and creep testing is introduced to allow for rest stresses from oscillation to dissipate. The test is set in a loop form that allows for the instrument to control the complete measurement without user interference.

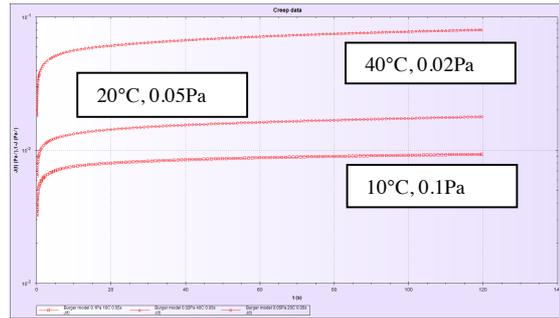Fig. 2. show the creep tests over 120s at three test temperatures and shear stress used.

Figure 2. Creep curves for 10, 20 and 40°C for an apricot food pure.

The creep curves are converted to modulus and the converted data together with frequency sweep data show a good agreement in Fig. 3. A small deviation is observed at high angular frequencies that could be an effect of creep ringing at short times and/or that the model is overpredicting elastic properties at short time scales.
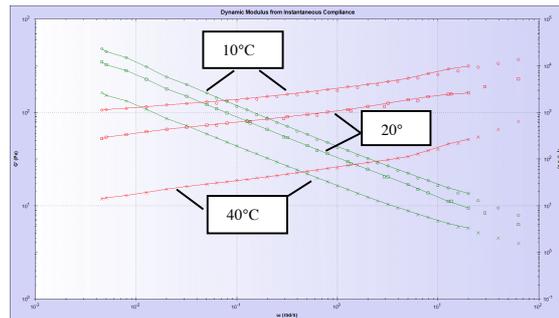

Figure 3. Creep to modulus converted data (symbols and lines) compared with frequency sweep data (symbols only) for 10°C (circles), 20°C (squares) and 40°C (crosses)

The creep converted moduli can be used for generating a master curve using the Time Temperature Superposition method. In Fig. 4 the master curve from the creep converted moduli is compared with a master curve created from the frequency sweep data with 10°C as the reference temperature utilizing η^* as the shift parameter.
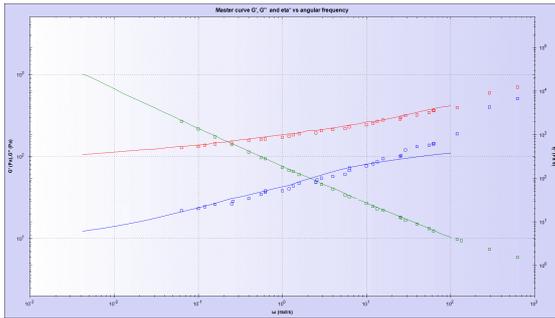
Figure 4. Master curves for both creep converted moduli (lines) and frequency sweep (symbols)

A good agrement is observed and the only difference is that the frequency sweep data show a slightly lower modulus that can be explained by a thermal equilibrium and build up time during measurement for a structured sample.

The shift factors for the Time Temperature Superposition from creep converted data and frequency sweep are shown in Table 1.

Action Name	Temperature(°C)	Log (Shift factor)
Superposition creep	10.00	0.000
Superposition creep	20.00	0.6547
Superposition creep	40.00	2.311
Superposition freq sweep	10.00	-6.867E-005
Superposition freq sweep	20.00	0.6387
Superposition freq sweep	40.00	2.253

Table 1. Shift factors with reference temperature 10°C from master curves generated with creep and frequency sweep data

For a high viscous polymer solution, the test was performed, using parallel plates of 20mm diameter, as an automatic sequence from 5-80°C in steps of 15°C. The sequence performs at each temperature a thermal equilibrium for 15 min followed by a frequency sweep from 10 to 0.01Hz at a fixed strain of 0.005. This is followed by a creep test at 50Pa for 120s, a rest period of 5 min followed by another creep test at 100Pa for 120s. The resulting master curves from both creep converted moduli from creep data (100Pa) and frequency sweep are shown in

Fig. 5 with 5°C as reference temperature and G* as the shift parameter.
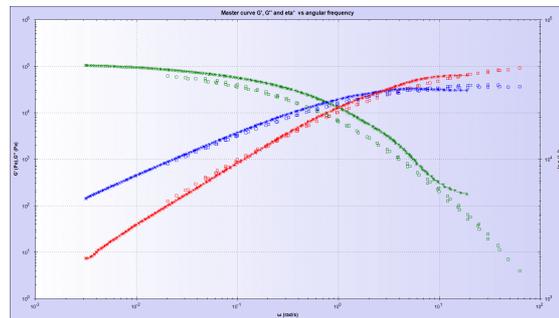

Figure 5. Master curves for creep converted moduli data (symbols and lines) and frequency sweep data (symbols) at a reference temperature of 5°C.

The shift factors for the TTS are shown in Table 2 with 5° as reference temperature

Action Name	Temperature(°C)	Log (Shift factor)
Superposition creep to modulus	5.00	0.000
Superposition creep to modulus	20.00	-0.2414
Superposition creep to modulus	35.00	-0.5185
Superposition creep to modulus	50.00	-0.7487
Superposition creep to modulus	65.00	-0.9681
Superposition creep to modulus	80.00	-1.174
Superposition freq sweep	5.00	1.510E-005
Superposition freq sweep	20.01	-0.2639
Superposition freq sweep	35.00	-0.4927
Superposition freq sweep	50.01	-0.7248
Superposition freq sweep	65.01	-0.9304
Superposition freq sweep	80.02	-1.128

Table 2. Shift factors for the Time Temperature superposition of creep converted data and frequency sweep data

The Arrhenius model fit to the data from the superposition for both frequency sweep and creep converted data are presented in Table 3 where K1 represents E_a/R

Action Name	K1
Superposition creep to modulus	1.499E+003
Superposition freq sweep	1.453E+003

Table 3. Arrhenius model data from the Time temperature superposition of creep converted data and frequency sweep data

Action Name	K1	K2
Superposition creep	9.263	515.1
Superposition freq sweep	7.099	397.5

Table 4 The C1 (K1) and C2 (K2) constants from the WLF (Williams-Landel-Ferry) model

From Table 4 the model fit is quite different as can be seen from the data of log (shift factor) plotted vs temperature in Fig. 6.
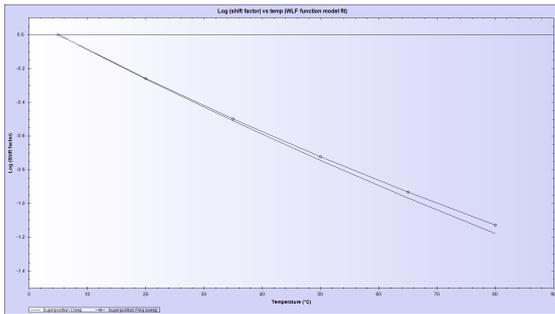

Figure 6. Log shift factor vs temperature for the Williams-Landel-Ferry model fit with creep data (line) and frequency sweep data (line and symbol)

These differences can be expected when the fit data are in different frequency regions.

As seen from Fig. 5 the data are not overlapping. A hypothesis can be that the sample is expanding with temperature. This is compensated in two ways:

• Thermal expansion of sample
• Thermal expansion of geometries

The geometry expansion due to expansion of metal with temperature are utilized so gap change due to the thermal expansion is compensated by a small gap increase with temperature. The thermal expansion of the of sample has not been controlled in the same way and this leads to a slight increase in sample diameter at elevated temperatures that can give rise to a shift in data with temperature.

The result in a creep experiment is that for a fixed stress the strain will be lower than expected and therefore the creep to modulus

conversion will generate higher moduli data. The frequency sweep will give lower data since the strain is transmitted to the sample with a larger area, thus measuring a lower complex shear stress.

The last practical example is a body shampoo that can be treated as a low viscosity polymer solution. The test was performed using a parallel plate of 40 mm diameter. At each temperature the following test order was performed.

• Sample loading
• Thermal equilibrium for 5 min
• Amplitude sweep (0.0001-0.5 strain)
• Frequency sweep (10-0.1Hz)
• Creep recovery (5 Pa)
• Set new test temperature and change sample

The creep curves results from the temperatures 5, 25 and 45°C with models are shown in Fig. 7.
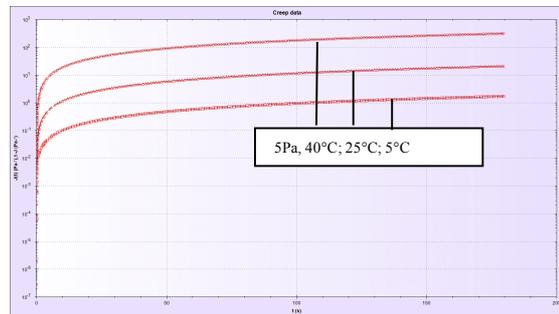

Figure 7. Creep curves (red symbols) and creep model fit (black lines)

The main concern using modelling is that at short time scale the model will never fit the creep curve (creep ringing). To use a time limit, here 0.05s, as the minimum time can partly overcome this fact.

One of the main criteria to use creep measurements and using a model to get faster access to low angular frequencies is to model data for zero shear viscosity or predict at viscosity increase at lower frequencies for gels or yield stress viscoelastic solids.

Fig. 8 shows the master curves at a reference temperature of 5°C for data from the creep conversion using Burgers model and directly measured small amplitude oscillatory shear data.
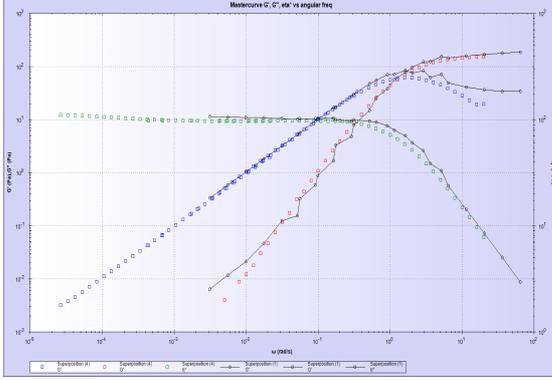

Figure 8. Master curves for creep model converted data (symbols) and frequency sweep data (black symbols and lines)

Action Name	Temperature(°C)	Log (Shift factor)
Superposition Freq sweep	4.82	0.02366
Superposition Freq sweep	24.94	-2.501
Superposition Freq sweep	45.06	-5.303
Superposition Creep	5.00	0.000
Superposition Creep	25.00	-2.445
Superposition Creep	45.00	-5.244

Table 5. Shift factors for the creep data TTS conversion compared with the frequency sweep TTS

The data from the master curves are used to model the complex viscosity using a Carreau model. The Carreau model is shown in Eq. 8.

$$\eta^* = \eta_\infty + \frac{\eta_0 - \eta_\infty}{(1+(k\omega)^2)^n} \qquad (8)$$

where
η^* is complex viscosity
η_∞ is infinite shear viscosity
η_0 is zero shear viscosity
ω is angular frequency
k inversely prop. to shear thinning onset
n is shear thinning index

In Fig. 9 and Table 6 the Carreau model for two master curves are compared.

Sample Description	Zero shear viscosity(Pa s)	K3	n
Superposition Freq sweep	102.8	0.7439	0.4288
Superposition Creep	100.8	1.561	0.2311

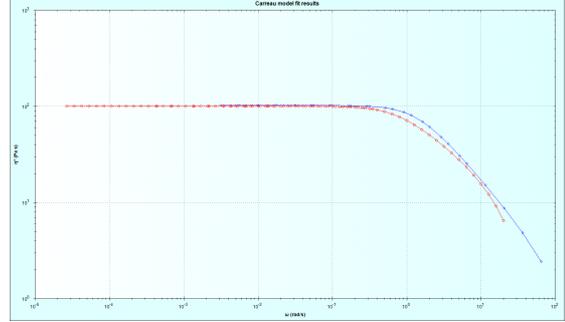Table 6. Carreau model for master curves from creep converted data and from frequency sweep data.

Figure 9. Carreau model on complex viscosity vs. ang frequency for creep converted data (red) and frequency sweep data (blue)

Shown in Table 6 and Fig. 9 the data for zero shear viscosity is very similar and the discrepancy in data are from data generated at higher angular frequencies which is evident in the K3 (k value in Eq. 8) value which is lower for the frequency sweep giving a higher shear rate for onset of non-Newtonian flow. The n value, or shear thinning index, is affected by the model fit to both the low and high frequency data and having more data in the lower shear region affect modelling at high shear rates.

CONCLUSION
Master curves from creep curves is a useful tool to expand the frequency range towards lower frequencies on measurable time scales. Coupled with high frequency sweep data to generate high frequency data this becomes an interesting combination even for single temperatures.

REFERENCES
1. Duffy, J.J., Rega, C.A., Jack, R., and Amin, S. (2016), "An algebraic approach for determining viscoelastic moduli from creep compliance through application of the

Generalised Stokes-Einstein relation and Burgers model", *Appl. Rheol.* **26(1)**

2. Ferry, J.D, "Viscoelastic Properties of Polymers", John Wiley and Sons, New York, pp 266-280

3. Collyer, A.A (editor), "Techniques in Rheological Measurement", pp 132-133, 140-145