Using TRIOS Analysis and Transformations Functions

July 18, 2016

Abstract

This document describes how to use the analysis and transformation function in TRIOS. After a brief introduction on data handling in TRIOS, Example Data Files supplied with TRIOS software installation are used to demonstrate how to use Data Analysis Functions for Rheology. In the Analysis section, the use of basic analysis and curve fitting functions are presented and the database functionality demonstrated. The transformation section describes the determination of discrete and continuous relaxation and retardation spectra from oscillation experiments as well as the interconversions of rheological material functions. The section time temperature superposition (TTS) explains the use of the equivalence of time(frequency) and temperature in order to create mastercurves and analyse the temperature dependence of materials.

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1   Introduction

This document describes the use of analysis and transformation function in TRIOS with example data files supplied with the TRIOS^TMsoftware. The example files are automatically installed as part of the standard installation and are located in the folder
c:\ProgramData\TAInstrument\TRIOS\Data\ExampleFiles\Rheology.
The files are intended to be used with the Data Analysis functions and are supplied for illustrative purposes only. These data files have all been obtained using TA rheometers. The procedure and geometry information can be viewed by selecting the Experiment tab after the file has been opened and displayed in TRIOS.

1.1   Data Handling in TRIOS

In order to apply data analysis functions in TRIOS, experimental data must be loaded into the TRIOS workspace. Use the controls on top of the file manager form (figure 1) to load a new file, close a document file, display a file in the workspace, send a file to the active graph, send a file to a new graph display, remove a file from the active graph or send data to a new spreadsheet view (Refer to *TRIOS Getting Started Guide* if you are not familiar with TRIOS). Two types of files can be loaded, experimental files and overlay/database files. Experimental data files include raw data. These files show an *Experiment* tab with information on the test procedure and geometry as the first tab at the bottom of the workspace. Overlay and database files do not have an experiment tab at the bottom of the workspace.
Spreadsheet and plot views can be changed from the *Format* and *Edit* menus. Refer to TRIOS on-line help for more information. Click the TRIOS icon on the top left and then the save button to save results files after the analysis is completed. Alternatively, the save icon on the Quick menu can be used.

2   Analysis

Analysis functions in TRIOS are available via the Analysis ribbon menu (Figure 2). The analysis functions available in TRIOS can be split into four groups:
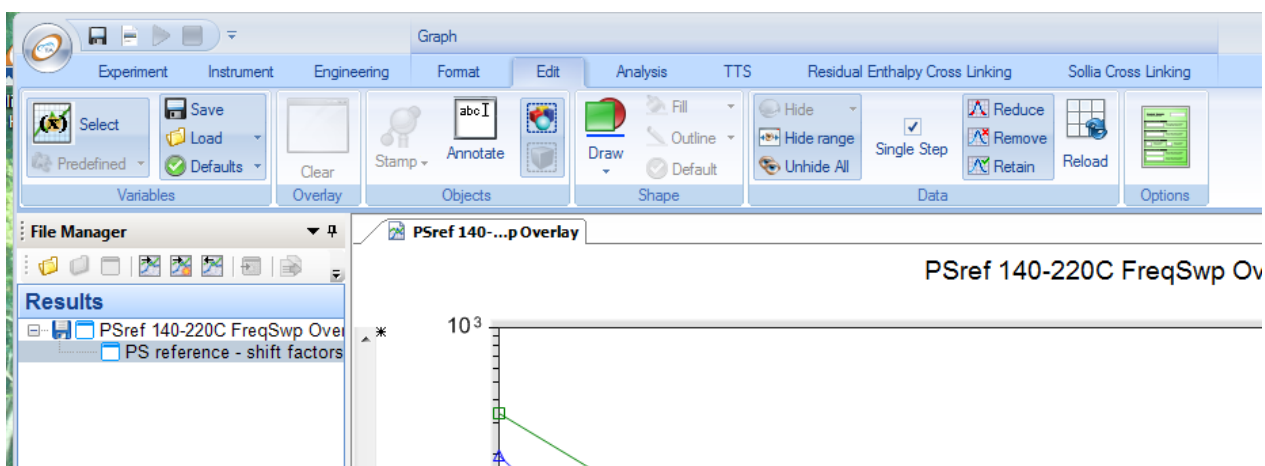

Figure 1: The File Manager provides the necessary functionality to import test data and organize various data files during analysis

- Basic Analysis Tools. These include common data handling functions such as smoothing, derivatives, etc.

- Modeling. These include mathematical and rheological models.

- Database Files. Results from modeling can be saved in data base files for trend and advanced data analysis.

- Options. Default settings for all analysis functions are set in the Options section.
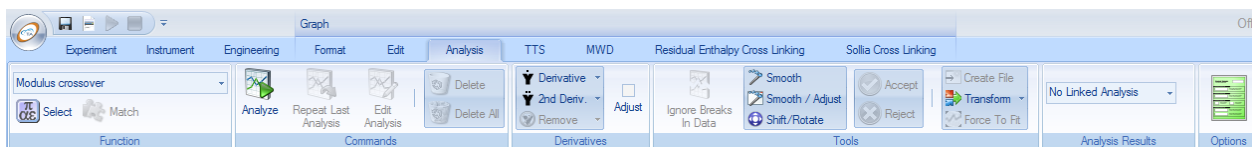
Figure 2: Layout of the Analysis ribbon with the sections Function, Commands, Derivatives, Tools, Analysis Results and Options

Transformations are special analysis functions and are discussed in section 3: *Transformations*. These functions convert the data into new datasets, which are then copied into a new Results document. Transformations can be started from the *Transform* button on the Analysis ribbon or from the drop down menu available by right clicking in the file manager workspace.

2.1 Basic Analysis Tools

Most of the experimental oscillation results are smooth and do not require any massaging before analysis. However, transient data can be quite noisy and it can be advantageous to apply curve smoothing before proceeding with the analysis. Load and display the experiment file **'5cP oil APS Couette Step shear.tri'** from the ExamoleFiles folder (refer to section 1 for details). Display the file in the workspace and plot the torque M on the right and the viscosity $\eta(t)$ on the left axis versus step time t_s. Select the torque signal; left click the first point on the graph and drag the pointer with the mouse button pressed along the complete data trace. Select the *Analysis* ribbon from the main menu on top (Figure 2). Click *Smooth* in the *Tools* section. The curve will be smoothed immediately based on the default smoothing settings (refer to the Options for Analysis in section 2.4 to set the analysis default values). If the smoothing is acceptable, hit the *Accept* button on the ribbon, otherwise hit the *Reject* button. Note that all variables dependent on the torque signal, such as the viscosity for example, will be smoothed at the same time. If the default smoothing is not acceptable, select the *Smooth/Adjust* control. A floating *Smoothing Window* opens and the smoothed data curve is displayed in black on top of the original trace. Use the mouse to move the slider to the right. The black data curve is adjusted immediately. Alternatively, type a number in the edit field on the top. Left click the slider to move it to the new position. If you are satisfied with the results, click *OK*. The new smoothing setting can also be saved as default; left click on the *Save* icon before closing the window. To make the smoothing permanent, hit the *Accept* button. When the strain rate is required and only a strain signal is available, the strain rate signal can be calculated using the derivative function. 1st and 2nd derivative of any curve can be generated by using the corresponding button on the *Analysis* ribbon.
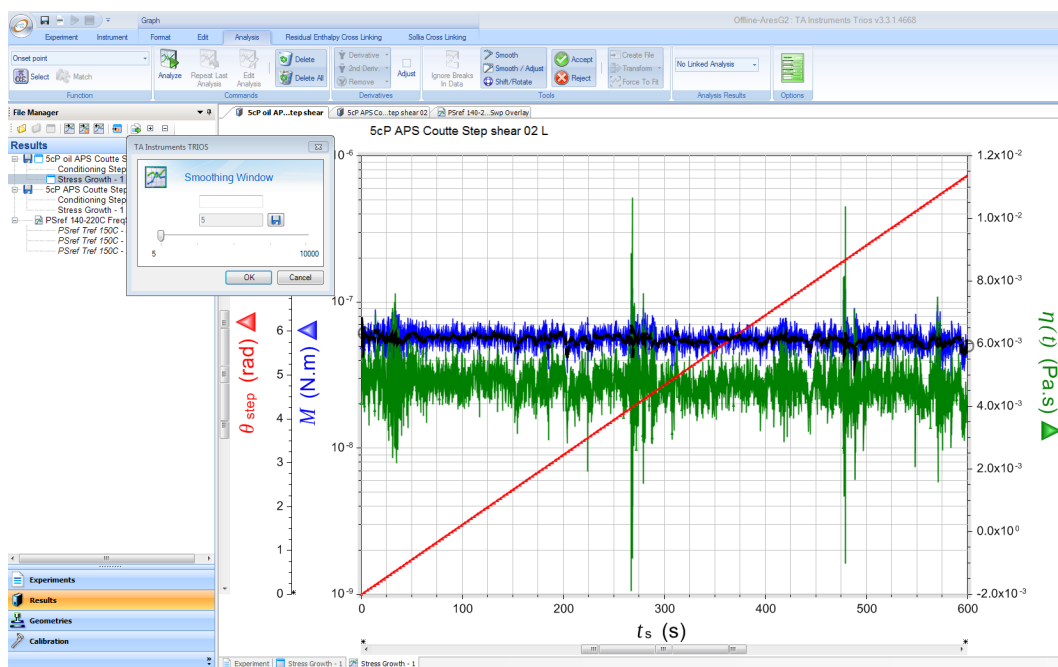
Figure 3: The slider in the smoothing window increases the degree of smoothness when dragged to the right. A new default setting can be set with the *Save* icon.

Load the oscillation data set **'A1 40mm 1° CP StrnSwp trans.tri'** from the ExampleFiles folder. Select any of the *Sine Strain* files and display the strain $\gamma()$ versus the step time t_s. Select the *stain* trace and click on the *Derivative* button on the *Analysis* ribbon. There is a choice to derive the selected curve with respect to time, temperature or the current x-axis. Select *wrt X*. The derivative is calculated and plotted on a new axis on the same graph. Change the X-axis to strain and re-plot the data (figure 4). The derivative is a noisy signal. Use the smoothing function from the Analysis menu to smooth the data if desired. Another possibility to adjust the smoothness of the derivative is to change the window size of the derivation algorithm in real time. Before activating the derivative button, check the box *Adjust* on the right side of the Derivative section on the Analysis menu (see figure 2). After the derivative algorithm has been initiated, the floating *Derivative Window* opens. By moving the slider, the smoothness of the derivative can be adjusted. The functionality of the derivative and the smoothing window is the same. The *Remove* button in the Derivative section of the Analysis menu removes the selected or all derivatives from the graph and spreadsheet.

2.2   Modeling

Rheological test results are very diverse. A large variety of model functions with well defined model parameters are available to fit the experimental data. TRIOS incorporates major rheological and mathematical models that can be applied to the rheological test results. The fit/model parameter can be copied into a model parameter database for further analysis(see section 2.3). The mathematical models can be applied to any test variables, whereas the rheological models are test variable specific. To demonstrate the model fitting analysis function, the stress as a function of the shear rate $\sigma(\dot{\gamma})$ is modeled using the Herschel-Bulkley model.
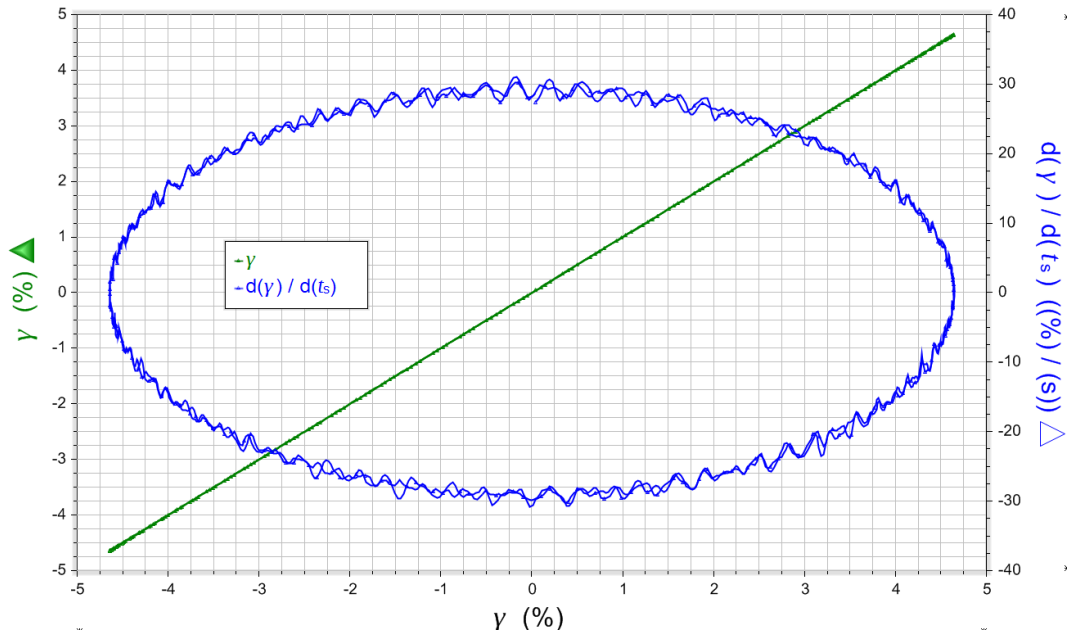
Figure 4: The derivative of the sinusoidal strain versus the strain is an ellipsoid with the main axes parallel to the x and y axes.

Select the stress curve as shown in figure 5 by clicking one data point on the curve. From the drop down menu in the *Function* section of the *Analysis* ribbon, select *Herschel-Bulkley*. Click the *Analyze* button in the *Commands* section. The model is fitted immediately (black curve) and the fit parameters displayed in the graph. If the results are not satisfactory, click the *Edit Analysis* button in the *Commands* section. A floating multi-tab evaluation window will be displayed (figure 5). The *Cursor* tab permits changes to the data points of the underlaying dataset of the fit. Grab one of the cursor markers on the plot and move it along the curve to change the data point selection. The fit parameters displayed on the graph are updated immediately. Alternatively, the end and starting points can be edited manually in the floating window. The *Appearance* tab allows changes to the fitted line color and labels. The *Label* tab has a selection list for information to display in the graph. The *Results* tab shows the values of the fitted variables. The icons on the left side can be used to edit the selected variable value. Increment the value in the selected value field with the blue up/down arrows. The fitted model curve is adjusted instantaneously. Alternatively, use the *Edit Value* button below the blue arrows to edit the selected field. In order to refit the data, click the *calculator* icon.

Non-linear curve fitting requires good starting values to find the best solution. TRIOS sets these starting values automatically when the *Analyze* button on the *Analysis* ribbon is pressed. Sometimes these starting values are inadequate and the algorithm converges to a local minimum. In this case different starting values can be entered manually in the column *Input Value*. Select the parameter (for example: yield stress in figure 6) and click the information control on the right. Change the *Input value* for the parameter as desired. The information icon in front of the parameter name means that during the next fit, the new starting values are used. The user starting value can be removed by clicking the *Unlock* icon. If it is desired to exclude a parameter during the fit, while the other parameters are determined by the non linear solver, edit the *Value* field manually and lock it using the *Lock* control button.
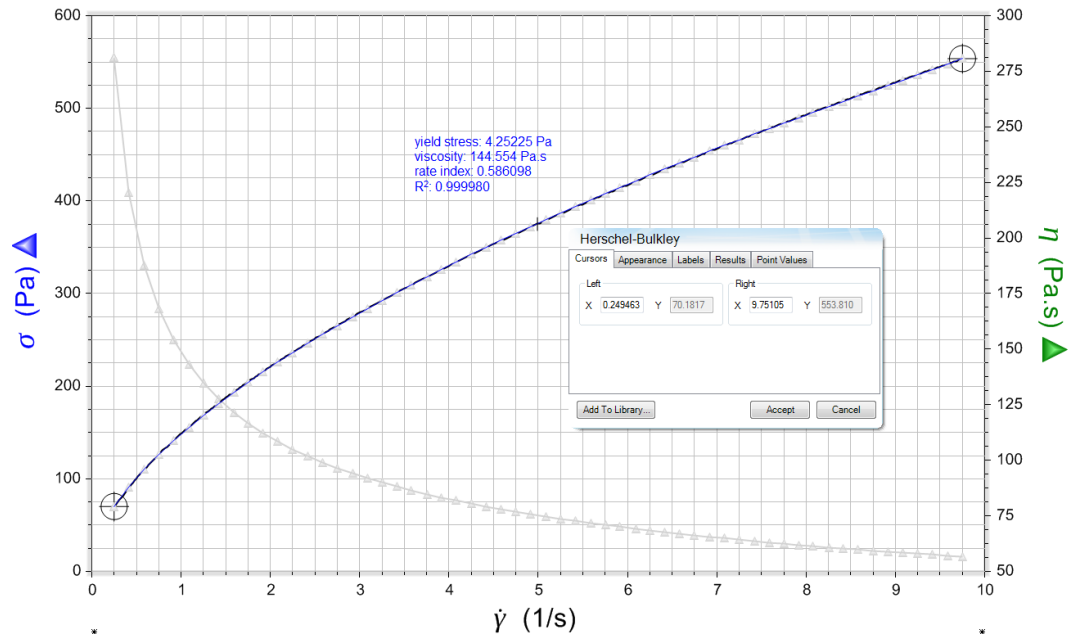
Figure 5: The Herschel-Bulkley model is fits the stress as a function of shear rate. Use the Edit Analysis feature to modify the fitting parameters of the model

In order to interpolate or extrapolate the function value of the model, select the *Point Value* tab. Click the *Add* (top icon on the left side) button to add a new point value. Double click in the corresponding field in the *At* column or click the *Edit Value* button (bottom icon on the left side). Enter the value for which the function value should be calculated. Use the *Delete* button to remove a point value.

If a specific analysis has to be repeated more often, the optimized fitting conditions can be set as default. These settings can also be added to a library for later retrieval, when conditions for other fitting tasks need to be saved. Hit the *Accept* button to finish the Analysis step and to obtain the results.
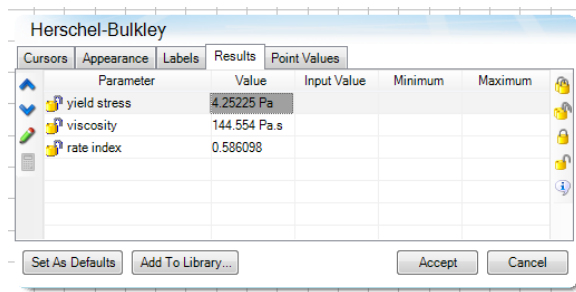
Figure 6: Use the *Results* tab in the *Edit Analysis* window to change the settings for the fit algorithm
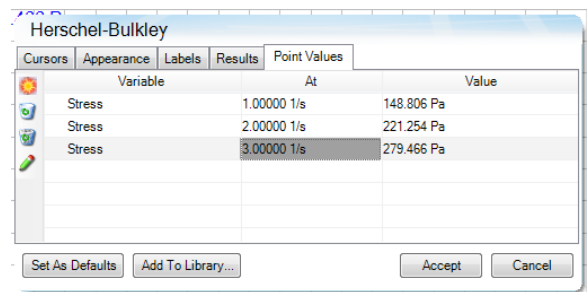
Figure 7: Use the *Point Values* tab in the *Edit Analysis* window to calculate the model values for specific input values

When function values for an experimental curve are required for other applications, the experimental data in the spreadsheet can be replaced with the function values by clicking the control *Force to Fit* in the *Tools* section of the *Analysis* ribbon menu. If the page has multiple analyses, make sure that the correct analysis is selected. It is recommended to save the results as a new Results file to avoid overwriting the experimental datafile. Note that if the original file is overwritten accidentally, it can be recovered using the *Reload* button in the *Data* section of the *Edit* ribbon menu. Be aware that this step also deletes all current analyses on the page.

2.3   Database

In addition to single file data analysis, TRIOS also has the capability to analyze data across a series of test data files. In order to do so, the relevant analysis results from each test file are copied to a database. The available analysis tools on TRIOS can than be applied to the test data base file.

2.3.1   Copying data to the database file

To create a new database file, select *Create New* from the drop down menu in the *Analysis Result* section of the *Analysis* ribbon menu. Now the current datafile is connected to the Analysis database. The *Analysis* database file is added to the file manager in the Results section. Save the file and change the name if desired. Results can only be transferred to the database when at least one Analysis has been completed on a document page.

Load the test file **'Toothpaste flow.tri'** from the default location if not loaded already. Display the stress and viscosity as a function of the shear rate (linear plot). In the graph view select the Herschel-Bulkley analysis, which has been performed previously. Create a new analysis database (see above) or select an existing analysis database from the drop down menu in the *Analysis Results* section. Click the *send control (green arrow)* to send the analysis results to the database. The data sent include all the analysis results as well as the current page scalars. Select the database tab on top of the work space and open the spreadsheet for the exported analysis results (Herschel-Bulkley in this case) as shown in figure 8.
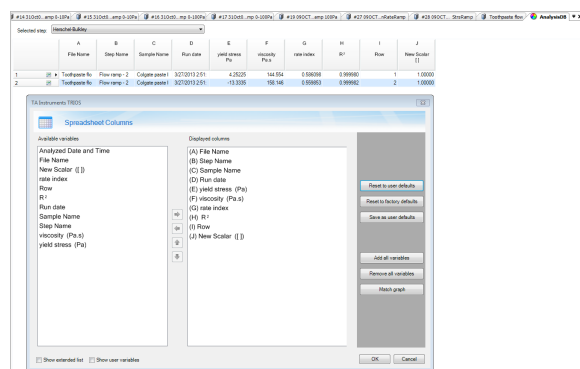
Figure 8: List of variables for display in the spreadsheet. Select the desired variable on the left side and click the green arrow to add it as a column to the spreadsheet. Use the green up and down arrows to sort the columns in the spreadsheet.
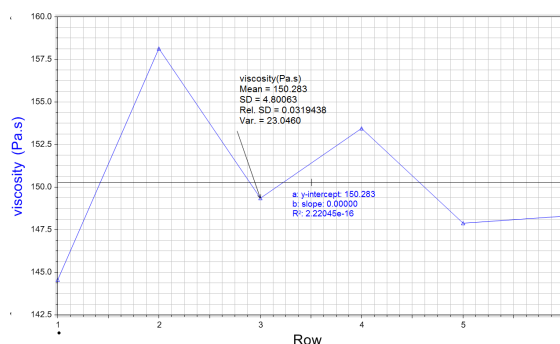
Figure 9: The graph represents the data for the viscosity extracted from the Herschel-Bulkley model in the analysis database file. The average viscosity is determined using the column averaging as well as the *straight line* model with the slope forced to zero.

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Most model parameters are in the standard list, the user defined scalars are in the extended list. User defined variables can also be set up and used in the database file. If multiple analyses exist in a page, they can all be transferred to the analysis database with the *send all* control on the *Analysis* ribbon menu. Note that in the analysis database, files are created for each analysis model. Only results from the same model type are copied into a spreadsheet list. Analysis results can be removed from the list and results of multiple instances of the analysis can be copied to the database. Once the analysis results are sent to the database file and the experiment file removed, the parameters are disconnected from the experiment file. Only a link to the original file remains. When the analysis is deleted in the original file, the results are not deleted from the database file. In the data basefile the results can be masked or deleted like data points in an experiment file.

2.3.2   Database operations

New analyses from new experiment files can be added to the database file at anytime. Before sending the results, the experiment file has to be connected to the database file by specifying the database file from the drop down menu in the *Analysis Results* section of the *Analysis* menu (see figure 2).

The database can be updated automatically using the *mirror* mode. In this mode the current analysis results are copied to the analysis database, as soon as the analysis closes without user intervention. If *append on adjust* is selected, any update of the analysis appends as a new row in the data base file, otherwise the current row in the database spreadsheet is updated.

A database file can be analyzed like any experiment file. Analysis results generated can be exported to a new analysis file and analyzed. Figure 9 shows the viscosity extracted from 6 instances of the Herschel-Bulkley model involving slightly different data point selections of the **Toothpaste flow** test file.

2.4   Analysis options

Many analysis functions have default values associated with them. Some of these defaults can be preset in the *Options* from the *Analysis* ribbon menu. The smoothing techniques are based on least squares moving window, polynomial and FFT algorithms. The algorithms for derivation are least squares window, central difference and cubic spline. The windows size can be set as number of data points or as a percent of the total curve. Defaults for the database update can be set to *mirror* and *append on adjust* mode. Refer to the TRIOS software on-line help for further details.

3   Transformations

Transformations are operations which convert experimental data to a new dataset. Converted datasets usually result from corrective actions applied to the measured data such as the fluid's inertia, Weissenberg-Rabinowicz corrections or from data handling operations such as splitting or merging data files. New datasets are also obtained by converting the measured material function into another function. The typical example is the determination of the relaxation time spectrum. Transformations in TRIOS can be separated into 3 groups:

- Basic Transformations. These includes simple data handling as well as data correction operations.

- Determination of relaxation and retardation time spectra. In TRIOS these transformations are implemented in the Analysis functionality.

- Conversion of linear viscoelastic functions. These transformations are used to calculate the linear viscoelastic material properties from the relaxation and retardation time spectrum or other rheological functions.

Transformation functions can be activated either from the drop down menu (right click) in the file manager workspace or from the *Transform* button on the Analysis ribbon (see figure 2). The latter can be applied to partial datasets as well. In this case, the data point range must be preselected on the graph or spreadsheet before applying the desired transformation.

3.1 Basic Transformations

Splitting data files based on frequency and temperature to create datasets for TTS, extracting data from multi-step result files or merging multiple steps within a single result file are basic transformation functions. In figure 10 and 11 a dataset with oscillation data as a function of frequency and temperature have been split in individual frequency sweep datasets.

Load and display the experiment file **'PS Freq-Temp Sweep.tri'** from the ExampleFiles folder (refer to section 1 for details). Use the menu item *Split frequency cycles into frequency sweeps* from the drop down menu under *Transformations* to split the datafile. The drop down menu can be accessed by right-clicking on the result file in the file manager. The extracted results are saved and displayed in the file manager in a new file with individual datasets for each temperature. In the graph the data are shown as overlays of frequency sweeps. Use this file to apply the TTS (Time-Temperature Superposition) functionality. For details see chapter 4.
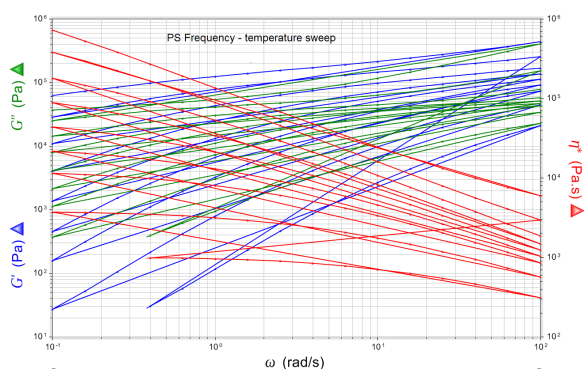
Figure 10: Test file with oscillation data as a function of frequency and temperature as obtained in a temperature step test with logarithmic frequency sweep
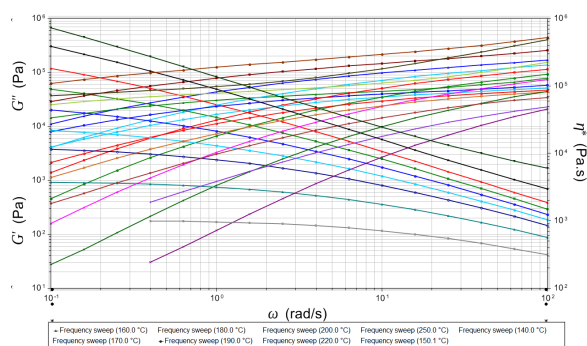
Figure 11: Frequency sweep data files at constant temperature after file splitting, in the overlay graph. The temperature of each sweep are reported in the legend below.

Commonly used rheological transfomations are the Cox-Merz and the Rabonowicz correction. Load and display the experiment file **'PIB2490 C50 p04 freqswp.tri'** and **'PIB2490 C50 p04 flowswp.tri'** from the ExampleFiles folder (refer to section 1 for details). Click on the complex viscosity curve to select the curve section from 0.1 to 628 rad/s. Start the transformation from the *Analysis* ribbon menu with *Transforma/Cox-Merz*. A new file is generated with the viscosity as a

function of shear rate. Display the second normal stress difference N_1 on the second axis. Overlay the data from the flow sweep by dragging the file with the mouse from the file manager into the graph. The viscosity curve in the overlay plot in figure 12 now covers a shear rate range from 0.01 to 628 1/s. In the section between 0.01 and 2 1/s, the viscosity curves match well. The normal stress data below 0.1 1/s obtained from the flow sweep show a plateau, the N_1 transformed from oscillation data decreases as expected. The reason for the discrepancy is the normal force sensitivity limit of the normal force transducer in the flow sweep experiment.
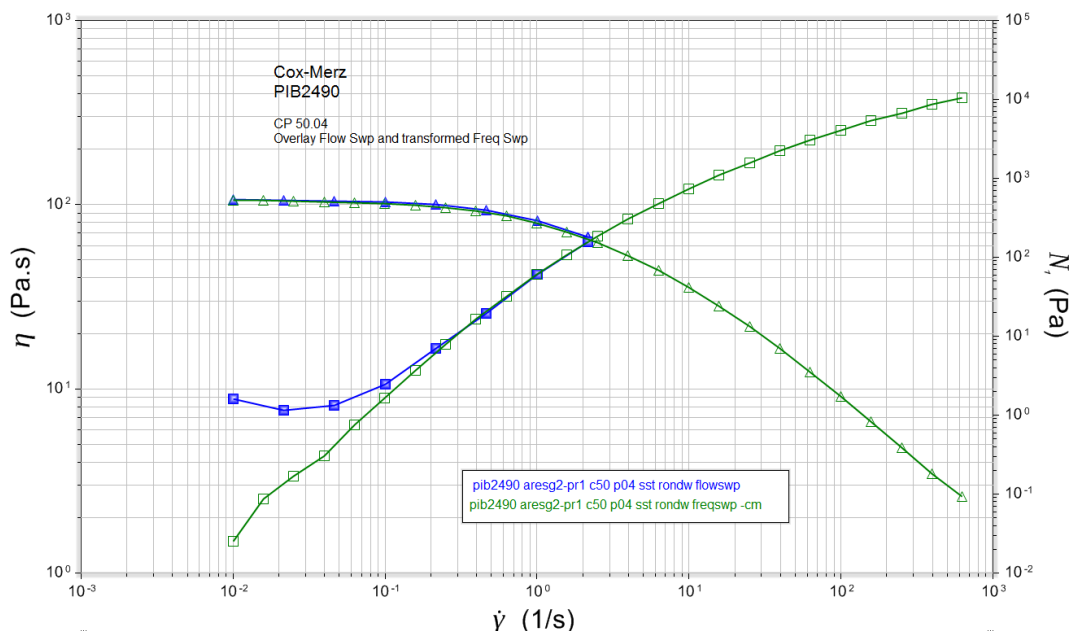
Figure 12: Viscosity and normal stress transformed from an frequency sweep test using Cox-Merz. Overlay with the measured results from a flow sweep experiment. Transient normal stress measurement is limited by the force sensitivity at low rates in an oscillation experiment

The Weissenberg-Rabinowicz correction converts the apparent viscosity and stress, measured in parallel plate geometry to the true viscosity and stress. Load the test data **'PIB2419 FlowSwp 0.001-100 s-1 (P40 HB SST Evap).tri'** and **'PIB2419 FlowSwp 0.001-100 s-1 (40C0.04 SST HB Evap).tri'** from the RheologySamples folder. Display the viscosity and stress and overlay the two test files. The linear viscoelastic region at low shear rate the viscosity measured with cone plate and parallel plates match, whereas the viscosity deviates at higher shear rate (see figure 13). Select the viscosity curve obtained from parallel plate geometry and apply the Weissenberg-Rabinowicz correction from the *Transform* menu on the *Analysis* ribbon. Alternatively, select the file in the file manager and apply the correction from the right-click drop down menu in *Transformations.../Rabinowicz correction*. Drag the transformed datafile into the current overlay. Viscosity and stress obtained with parallel plates now match with results from cone plate geometry throughout the whole shear rate range.

Fluids inertia in oscillation measurements is significant only when the fluid viscosity is below 0.1 Pa.s and the sample gap 1mm or larger. In this case, the wave propagation through the sample is slow enough to cause a delay in phase response. Load the test data **'10cP oil DIN CC freqswp**

Figure 13: Comparison of Rabinowicz corrected apparent stress and viscosity obtained in parallel plate geometry with the true stress and viscosity obtained in cone plate geometry.

density=0.0.tri' from the RheologySamples folder. Concentric cylinders with 1mm gap have been used to perform the experiment. As can be seen in figure 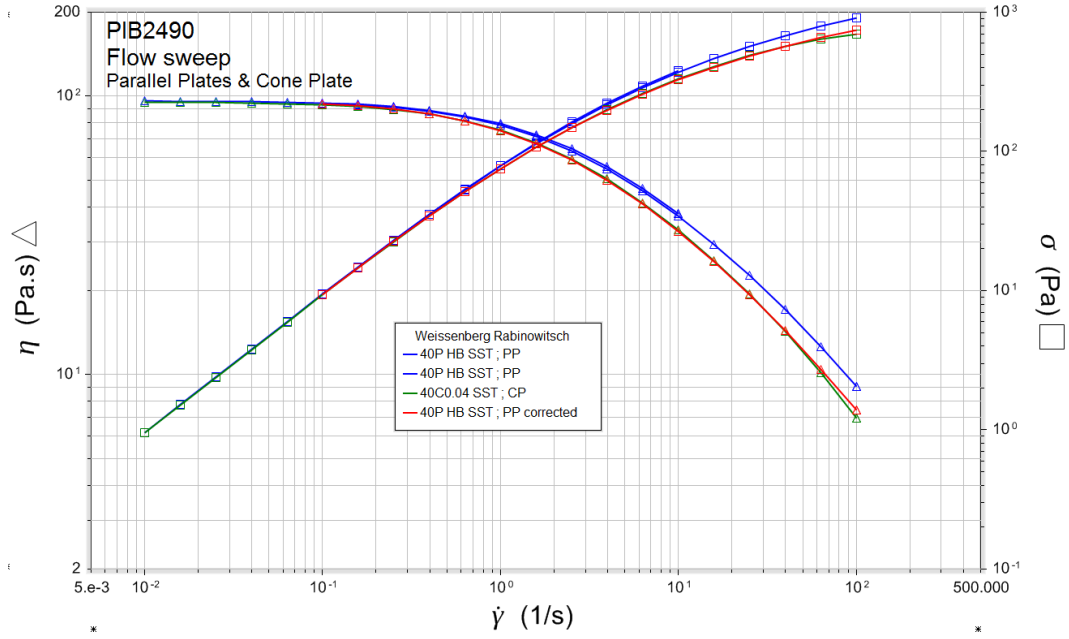14, the phase for the Newtonian oil decreases with increasing frequency and a significant G' contribution is measured. In order to apply the fluid inertia correction, in the experiment tab change the *Fluid density* in the sample section to 0.88 g/cm^3. Then select *Fluids inertia correction* from the *Transformation* menu (either File manager or Analysis ribbon). The phase has changed significantly now and stays at $\approx 90^o$ up to the maximum frequency. The storage modulus G' disappears above 100 rad/s. Since the correction is slightly over-correcting in this region, G' becomes negative and therefore undefined in the logarithmic representation.

3.2 Determination of Relaxation and Retardation Time Spectra

Most, if not all materials of interest are viscoelastic, meaning their response to a mechanical stimulus lies somewhere between that of a true liquid and a true solid. A complete mathematical description of viscoelastic behavior is difficult, but can be greatly simplified by assuming linear behavior, where the response is directly proportional to the stimulus [3]. This assumption is usually justified when the applied stimulus is small. Full definitions of the linear viscoelastic functions and their interrelationships are given in standard rheological texts [3, 4].

There are several ways to experimentally investigate the linear viscoelastic properties of materials. The simplest is to perform a creep test, in which a small stress, σ, is applied to a sample, and the resulting strain, $\gamma(t)$ is monitored over time, t. It is then usual to report the creep compliance, $J(t)$ defined as $\gamma(t)/\sigma$. An alternative is to apply a small, fixed strain, γ, to a sample and monitor the resulting stress, $\sigma(t)$, over time. The relaxation modulus, $G(t)$, defined as $\sigma(t)/\gamma$, is usually reported.
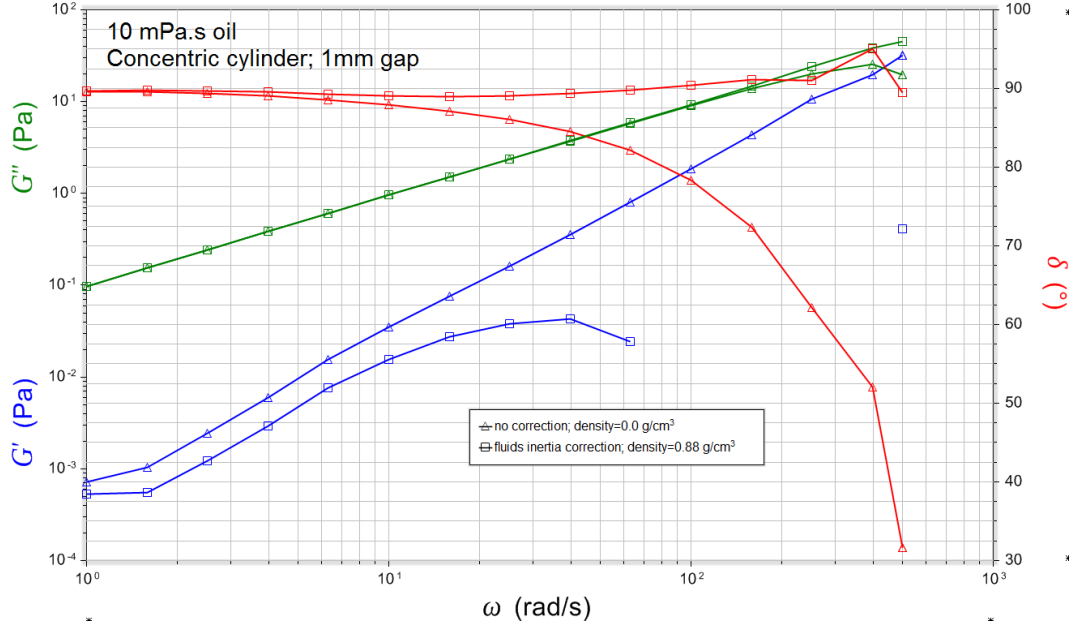
Figure 14: Fluids inertia correction applied to standard frequency sweep data of a 10cP oil. The test geometry is concentric cylinders with a gap of 1mm.

A more elegant procedure is to apply a low amplitude, sinusoidally oscillating, stress or strain. The amplitude of the response is monitored, along with the phase lag, δ, between the stress and the strain. Both these functions depend on the oscillation frequency, ω. The ratio of the stress amplitude to the strain amplitude, $|G*(\omega)|$ is sometimes reported along with δ, but it is more usual to quote the storage modulus, $G'(\omega)$ and loss modulus $G"(\omega)$, defined by $G'(\omega) = |G*(\omega)|cos\delta$, and $G"(\omega) = |G*(\omega)|sin\delta$, respectively. The storage and loss compliances, defined by $J'(\omega) = |J*(\omega)|cos\delta$ and $J"(\omega) = |J*(\omega)|sin\delta$, respectively, where $|J*(\omega)| = 1/|G*(\omega)|$, are also sometimes used. Provided that the conditions of linearity are observed, the functions $J(t)$, $G(t)$ and $G'(\omega)$, $G"(\omega)$ or $J'(\omega)$, $J"(\omega)$, can be inter-converted. This operation is not performed directly, but through intermediate functions, the relaxation time spectrum $H(\tau)$ and the retardation spectrum $L(\lambda)$; these functions themselves are not directly measurable. To calculate the spectrum from experimental data is a mathematically ill-posed problem, in that small differences in the data (below the error associated with the measurement) can result in large differences in the spectrum. Sophisticated mathematical techniques are used to counter this problem.

Using the analysis module, TRIOS is able to convert the oscillation frequency sweeps, relaxation and creep results into a discrete or continuous relaxation and retardation spectra, based on the algorithms developed by Honerkamp and Weese ([8],[1]).

The continuous relaxation spectrum $H(\ln \tau)$ and retardation spectrum $L(\ln \lambda)$ are related to the moduli and compliance as follows([6],[5]):

$$G'(\omega) = G_e + \int_{-\infty}^{+\infty} H(\ln \tau)\frac{\omega^2\tau^{2^{\,2}}}{1+\omega}\,\tau^2 d\ln \tau$$

$$G"(\omega) = \int_{-\infty}^{+\infty} H(\ln \tau)\frac{\omega\tau^{\,2}}{1+\omega}\,\tau^2 d\ln \tau$$

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$$G(t) = G_e + \int_{-\infty}^{+\infty} H(\ln \tau) exp(\frac{-t}{\tau}) d \ln \tau$$

$$J(t) = J_o + \int_{-\infty}^{+\infty} L(\ln \lambda)[1 - exp(\frac{-t}{\lambda}] d \ln \lambda$$

The discrete spectra $\{G_i, \tau_i\}$, $\{J_i, \lambda_i\}$ are given by:

$$G'(\omega) = \sum_i G_i \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}$$

$$G''(\omega) = \sum_i G_i \frac{\omega \tau}{1 + \omega^2 \tau^2}$$

$$G(t) = G_e + \sum_i G_i exp \frac{-t}{\tau_i}$$

$$J(t) = J_o + \sum_i J_i[1 - exp \frac{-t}{\lambda_i}] + \frac{t}{\eta_o}$$
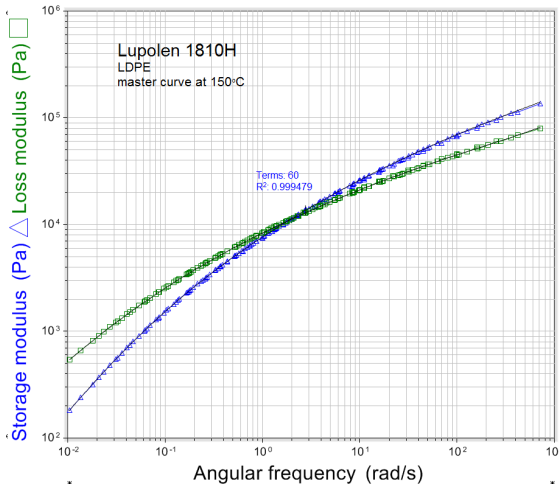
Figure 15: Experimental test results $G'(\omega), G''(\omega)$ fitted with model data after the determination of the continuous relaxation spectrum
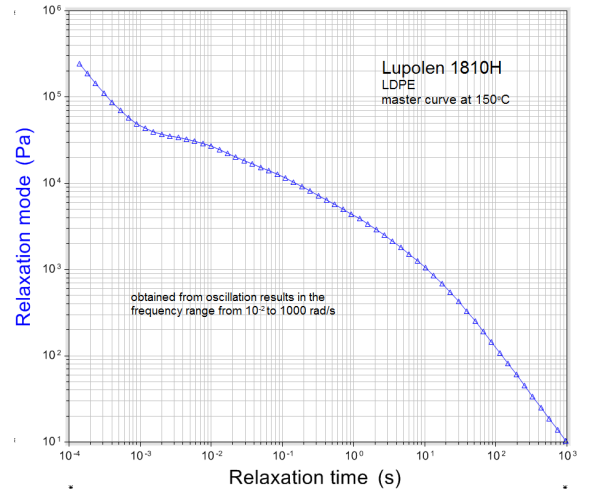
Figure 16: Continuous relaxation spectrum extracted from oscillation data of LDPE (Lupolen 1810H) in the frequency sweep range from 10^{-2} to 1000 rad/s

The various spectra are calculated from appropriate experimental data, using the relationships given above (creep will give either the discrete or continuous retardation spectrum, stress relaxation and oscillation data will give the relaxation spectrum). Load the test data **'Lupolen 1810H Freq Swp -split Mastercurve.tri'** from the RheologExamples folder. Display G' and G'' as a function of ω in double logarithmic scale. From the *Function* section in the *Analysis* ribbon, select *Continuous relaxation spectrum* from the drop down. Click the *Analyze* button to start the calculation of the spectrum with the current default settings. When completed, an information box with the number of terms and the correlation coefficient is stamped on the plot. In order to obtain the Relaxation spectrum, click the control *Create File* on the *Tool* section of the *Analysis* ribbon. The relaxation and retardation spectra are copied into new results files with the extension -H(ln tau) and -L(ln tau) respectively, and added to the file manager (figure 16).

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The algorithm to extract the continuous spectra uses a non-linear solver with regularization [1]. The solver conditions can be set with the *Edit Analysis* control. Select the *Parameter* tab on the floating window *Continuous relaxation spectrum* (figure 17). Note that the input parameter in this form applies to the spectrum analysis, not the experimental data file. The time range corresponds to the range of the retardation or relaxation times over which the spectrum is to be calculated (for discrete spectra these are only limits; it may be that no spectral point occurs at this limit). The spectral time range should show reasonable correspondence with the experimental time range ($t \approx 1/\omega$), the angular frequency given in rad/s. It can be shown that the spectral information is only trustworthy over a range, narrower than the experimental range by a factor of $exp\pi/2$ i.e. 4.81 at each end and untrustworthy beyond the range broader than the experimental range by the same factor. In the intermediate range, the spectral information is doubtful [6]. For an oscillation experiment over the experimental range of 0.1 to 100 rad/s, corresponding to a time range of 10 to 0.01s, the relaxation spectrum is trustworthy over a range from 0.481 to 20.8 s, untrustworthy below 0.0208 and above 481 s. The ranges (Reciprocal +/- one decade, Reciprocal $+/-exp PI/2$, Reciprocal) should be chosen based on how secure the spectral information is required to be. The spectral points entered as *points per decade* or *total points* refer to the continuous spectrum. The higher the number of calculated points, the more secure the information will be, but the computation process will be longer. The default is 10 points per decade. The parameter G_e (elastic modulus) and J_o (instantaneous compliance) are usually very small. They can be viewed respectively as representing the contributions to the relaxation spectrum of processes with infinite relaxation time (i.e. too long to be experimentally available), or to the retardation spectrum of processes with zero retardation time (i.e. too short to be experimentally available). The software offers to calculate the retardation spectrum at the same time, when the corresponding box is checked on the form, based on the interconversion formulas between spectra [6].

The calculation of the discrete spectrum is very similar. Instead of selecting the *continuous relaxation spectrum*, select the *discrete relaxation spectrum* from the *Function* drop down on the *Analysis* ribbon. In the parameter settings, the number of terms can be set to Auto or manual. In manual mode, use 2 or 3 terms per decade of experimental data. Selecting more terms does not improve the predictions of the discrete spectrum.

The *Results* tab on the floating window *Continuous relaxation spectrum* or *Discrete relaxation spectrum* (figure 18) displays a list of all the relaxation modes that are calculated. For the continuous spectra with up to 100 modes, it is more convenient to work with the spectrum after it has been extracted to a new file.

Figure 17: Parameters for the Continuous relaxation spectrum determination algorithm

Figure 18: List of the relaxation mode values of the continuous relaxation spectrum

3.3   Conversion of viscoelastic functions

When a discrete or continuous relaxation/retardation spectrum is available, other linear viscoelastic functions such as Relaxation and Stress Growth can be calculated using the equations from previous section. TRIOS software also includes a direct conversion (without spectrum evaluation) of creep to oscillation moduli. Refer to TRIOS online help in *Evaluating Data > Analysis > Rheological Transformations* for details on the conversion transformation equations of the linear viscoelastic transformations. Following the list of transformations (conversions), available in TRIOS:)

- Relaxation spectrum $\Rightarrow$ Relaxation ($G(t)$)

- Relaxation spectrum $\Rightarrow$ Stress Growth ($\psi(t)$)

- Relaxation spectrum $\Rightarrow$ Memory function ($m(t - t_1)$)

- Relaxation spectrum $\Rightarrow$ Retardation spectrum

- Retardation spectrum $\Rightarrow$ Creep ($J(t)$)

Other transformations:

- Direct Creep - Oscillation conversion ($J(t) \Rightarrow (G', G")$)

- Discrete Fourier Transformation (DFT) for general temporal strain and stress data sets

- Window Correlation

3.3.1   Reconstructing linear viscoelastic functions from the Relaxation spectrum

Typically the relaxation spectrum is determined from oscillation results $G'(\omega), G"(\omega)$. From the spectrum the linear viscoslastic transient material functions $G(t), J(t)$ and $\eta(t)$ can be calculated (refer to section 3.2). Load the file with the Relaxation spectrum extracted from oscillation experiments **'PIB2490 C50 p04 SST FreqSwp -1-H(ln tau).tri'** as well as the overlay file with transient viscosity data **'Overlay PIB2490 Stress growth - viscosity T=25°C).tri'**, from the ExampleFiles folder. In the **'PIB2490 C50 p04 SST FreqSwp -1-H(ln tau).tri'** file display the Relaxation modes as a function of the relaxation times. Select the curve and then choose *Stress Growth* from *Transform* on the *Analysis* ribbon. A floating *Transform To Stress Growth* window appears. In this window set the time range and the shear rate for which the viscoelastic start-up curve should be calculated. The default values are based on the limiting relaxation times of the spectrum. Select the number of points and the representation (usually logarithmic) and hit the OK control. A new file is created with time, transient stress and viscosity. Drag the the converted file Frequency - 1 H(ln tau) -g onto the viscosity overlay plot of the PIB2490 Stress growth experiments. As you can see in figure 19, the converted file is the linear viscoelastic envelope of the experimental transient viscosities obtained in a Stress growth experiment.

From the relaxation spectrum, other linear viscoelastic properties such as the Relaxation modulus, the Retardation spectrum and creep compliance can be calculated or the spectrum can be converted back to the frequency dependent storage and loss modulus.
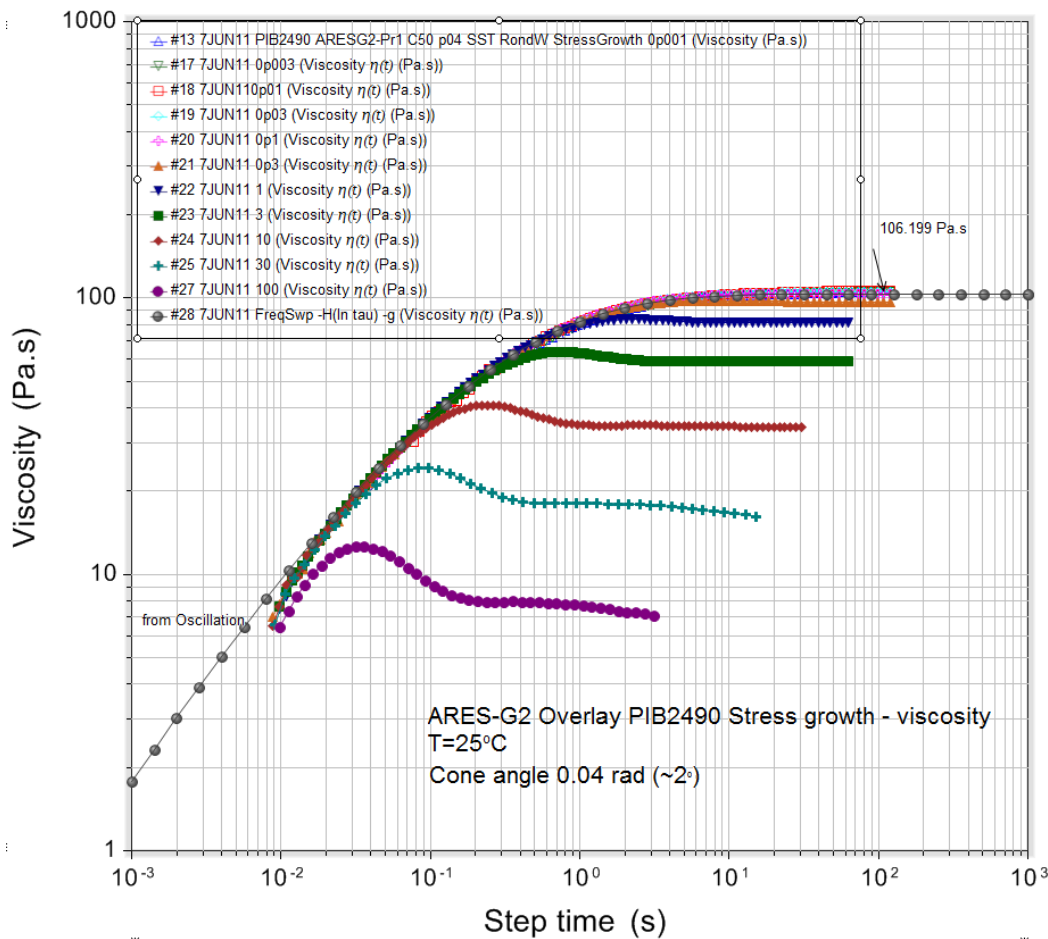
Figure 19: Linear viscoelastic transient viscosity converted from the Relaxation spectrum, superposed on experimental data obtained at shear rates from 0.005 to 100 1/s

3.3.2 Direct conversion of Creep to Storage and Loss modulus

In order to obtain the viscoelastic spectrum of materials with long relaxation times in a reasonable time frame, it is advantageous to measure the long time response in creep and then convert the compliance to oscillation frequency sweep variables. Although it would be possible to use the conversion path *creep $\mapsto$ retardation spectrum $\mapsto$ relaxation spectrum $\mapsto$ oscillation frequency sweep variables*, it is much more convenient to do the conversion in one step; this is the *direct creep-oscillation conversion* [3]. Load the files **'PIB2490 C50 p04 SST RondW FreqSwp 10%.tri'** and **'PIB2490 C50 p04 SST Creep-Recovery 10p0Pa.tri'** into the TRIOS file manager. Display the compliance of the creep step (1) on a log-log graph. Select the data points from 20ms on up. From the *Transform* drop down on the *Analysis* ribbon, click *To Oscillation*. On the *Transform to Oscillation* floating window, accept the default *Start frequency* and change the *End frequency* to 1 rad/s. A new file opens and the plot displays the variables G', G'' and η^* as a function of ω (figure 20). Overlay these results with the experimental frequency sweep data (figure 21). The converted creep results extend the experimental frequency sweep data by one decade from 0.1 to 0.01 rad/s.
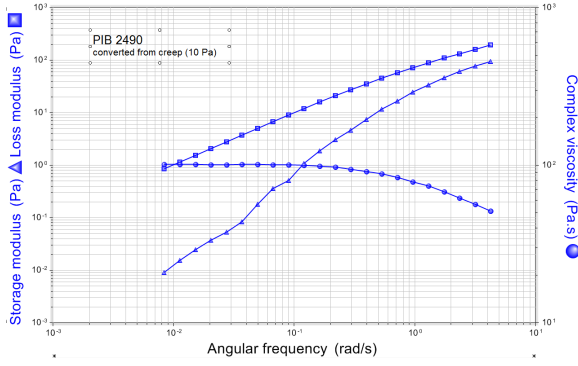
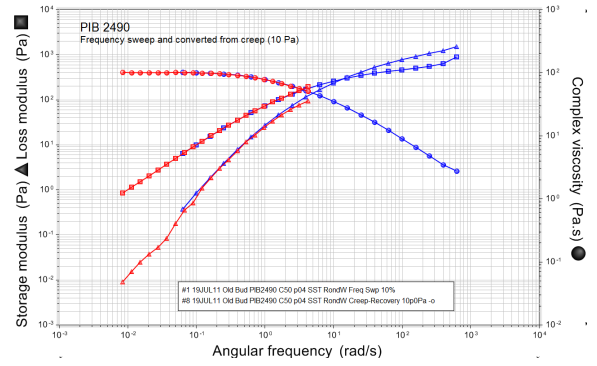Figure 20: Frequency sweep converted from creep data for PIB2490 using the direct conversion algorithm

Figure 21: Overlay of experimental frequency sweep data and frequency dependent data converted from creep

3.3.3 Fourier transformations of transient functions

The Fourier transformation converts transient data from the time into the frequency domain. TRIOS uses a discrete Fourier transformation (DFT) to convert the measured sinusoidal signals into the complex oscillation variables such as G^*, η^* at the applied frequency. The Fourier transformation can also be applied to any (non-sinusoidal) periodic time signal to extract a frequency spectrum. For example, a pulse, when converted into the frequency domain represents all of the frequencies. The frequency range that is experimentally accessible depends on the sampling rate of the time series as well as the response time of the system. TRIOS includes two types of Fourier transformations, the DFT i.e. discrete Fourier transformation of stress and strain and the window correlation. The DFT converts any time series and extracts the complete frequency spectrum while the window correlation only extracts the fundamental frequency of a section (window) of the time series as the window moves along the time series. By using a DFT instead of a continuous Fourier transformation [4], interpolation and data smoothing is unavoidable and some care is necessary to ensure trustful conversion of the experimental data.

The opera-house or 'Chirp' function is an oscillating function with a continuously changing frequency. This function provides the fastest measurement of a material's response over a defined frequency range and is ideal for testing structural changes in evolving materials [2]. The chirp function in strain is mathematically represented by:

$$\gamma(t) = \gamma_0 * \sin(K(e^{\frac{1}{L}}))$$

with the parameters: $K = \dfrac{T\omega_1}{\ln(\dfrac{\omega_2}{\omega_1})}$ and $L = \dfrac{T}{\ln(\dfrac{\omega_2}{\omega_1})}$. T is the duration of the sweep, at minimum the period of the lowest frequency, and ω_1 and ω_2 the lowest and highest angular frequency.

Load the files **'PDMS - Operahouse function - strn0p5% - 4 decades (ARESG2) .tri'** and **'standard Freq Swp 10%.tri'** into the TRIOS file manager. Display the strain and stress response for the opera-house function as shown in figure 22. Select the *Chirp* data file in the file manager, right click with the mouse and choose *Oscillation(DFT)* from the *Transform* drop down menu. A floating window titled *Transform to Oscillation (DFT)* is displayed. Set the number of
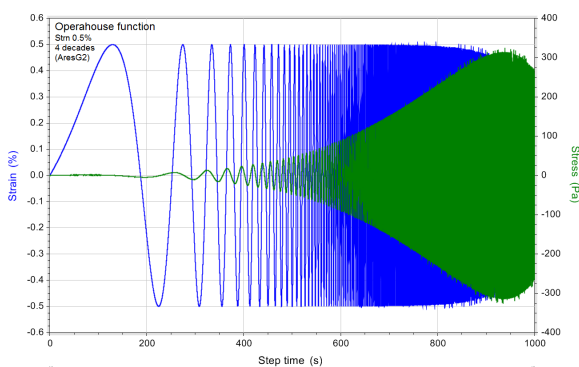
Figure 22: Stress response to a Chirp (opera house) function in strain applied in an arbitrary wave experiment
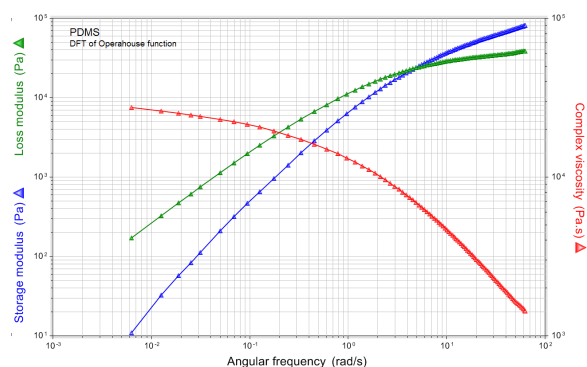

Figure 23: Frequency spectrum extracted from an arbitrary wave experiment with 'Chirp' function strain input

harmonic frequencies to extract. The default value is the maximum number of frequencies that can be extracted (defined by the Nyquist criterion, which depends on the sampling rate of the transient data). Click OK, a new file is generated and the associated graph shows the dynamic moduli G' and G" as well as the complex viscosity η^* (figure 23). Depending on the selection of the number of frequencies, the extracted signal will be more or less noisy. Remove the high frequency noise and use the smooth function (refer to chapter 2.1 for more information) from the *Analysis* ribbon to streamline the results. The overlay of the extracted frequency spectrum with the experimental frequency sweep test results in figure 24 shows excellent agreement. The results extracted from the stress response to a 'Chirp' function strain input cover a frequency sweep of 4 decades

The window correlation feature has been designed to follow the change of a fast evolving system in oscillation at a fixed frequency. The method is ideal for studying the behavior of UV curing materials. Note, that in order to obtain meaningful test results, the test frequency must be shorter than the total evolution time. This is described by the mutation number, which scales the relative change of the modulus to the duration of the measurement. The mutation number must always be less than one [9].

Load data file **'Epoxy cure Continuous Sine Strain 0.1%'** with the curing results of a commercial epoxy resin obtained in parallel plate geometry at 35°C . The sampling rate was 100 points per second (i.e. 100 pts/cycle) at a test frequency of 1 Hz. Figure 25 shows the transient stress and strain signals, measured during the curing process of an epoxy resin applying a SineStrain test mode. The strain was fixed at 0.1%. As the sample cures, the stress increases with time. In order to convert the transient oscillatory signal into the complex moduli G' and G", select the *Window correlation* from the *Transform* menu on the *Analysis* ribbon. The window correlation algorithm takes a user defined number of points, starting from the first data point and correlates the two signals to extract magnitude and phase. This is repeated while moving the window, point by point along the dataset until the end of the dataset is reached. On the floating window *DFT Transform*, set the strain as signal 1 and stress as signal 2. The number of points in a cycle is 100. Note that the number of points must represent the exact number of datapoints per cycle. If more than one cycle are to be correlated, an integer multiple of the number of data points in one cycle has to be used. Check to calculate the vectors and the magnitude and phase.
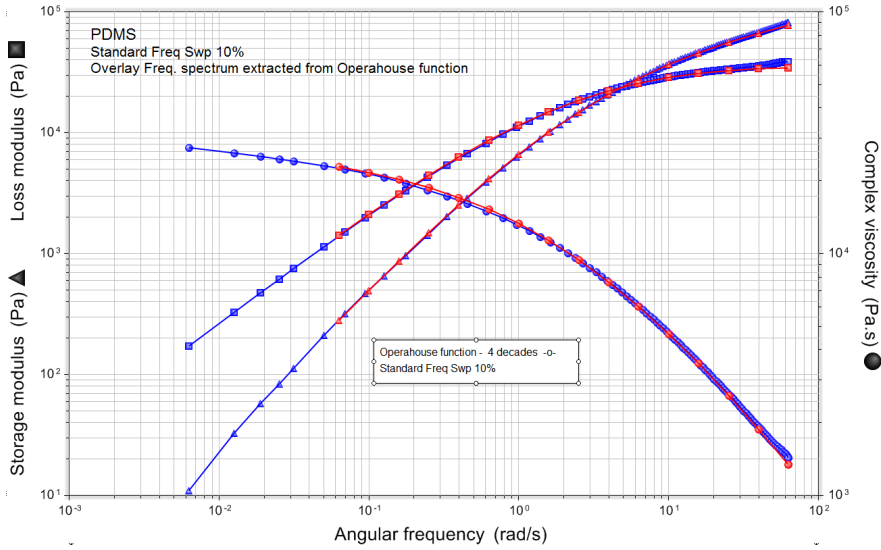
Figure 24: Overlay of oscillation variables extracted from *Chirp* function stress response with experimental frequency sweep results

The results of the transformation are given in figure 26, showing the storage and loss modulus as well as the phase as the cure proceeds. Be aware, that the period of the correlation cycle must be small in comparison to the evolution time of the sample in order to obtain a representative cure profile. On figure 26, the first 100 data points are noisy because of the low torque signal and are not shown. The cross over point, an indicator of the gel point, occurs 178s after mixing the components and starting the experiment. Note that TRIOS uses the window correlation algorithm in the *Fast data acquisition test mode* to determine the dynamic moduli in real time. In this mode the transient strain and stress results are not saved.
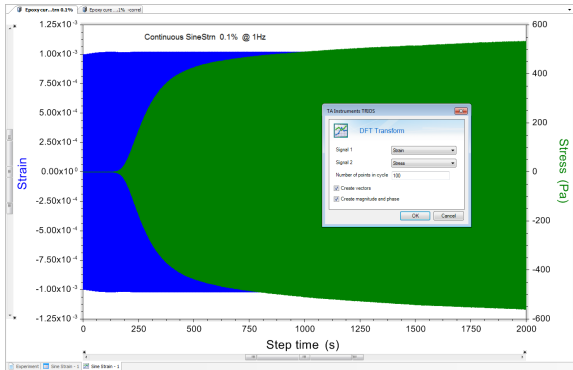

Figure 25: Transient Strain and Stress signals collected during a cure experiment at 35°C. Frequency 1 Hz; Applied strain 0.1%
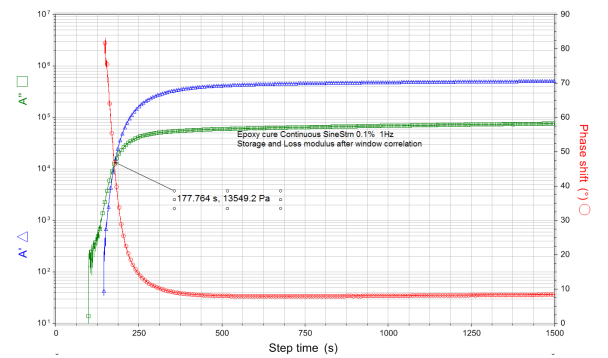

Figure 26: Storage and Loss modulus for the cure of an epoxy resin, obtained by window correlation technique from the transient data

4   Time Temperature Superposition TTS

4.1   Introduction

Interest in time frequency dependent behavior for materials such as polymers, extends over several decades of time/frequency in typical application temperature ranges. Because of experimental time/frequency window limitations, the viscoelastic properties are determined at different temperatures and then superposed in a single master curve at one reference temperature over an extended time/frequency range. In order for this superposition to work, the material must behave as a thermo-rheological simple material over the given temperature and frequency/time range. Thermo-rheological simple means that all relaxations in the material must have the same temperature dependence. This is often not the case for heterogeneous and complex polymer systems. In this section, the TTS functionality in TRIOS is explained using results of the reference material PSref, available from the ExampleFiles folder (see also section1).

4.2   Shifting frequency sweep data

Load the demo data set **'PSref 140-220C FreqSwp Overlay.tri'** into the TRIOS file manger (refer to section 1.1 for details). This file is an overlay file compiling the results of a series of individual experiments. Experiment and geometry information is not copied to an overlay file. The graph is displayed automatically in the workspace with G' and G" on the left, $\tan \delta$ on the right and the frequency ω on the bottom axis. Note that all the axes are logarithmically scaled. Since the experimental data curves are shifted on a logarithmic frequency axis, the actual shift is the logarithm of the shift factor, $\log a_T$. In TRIOS, only the shift factor a_T is reported. For the reference curve the shift factor is 1 ($\log a_T = 0$).

> NOTE: A new overlay plot can be created by right clicking in the File manger area and selecting *New overlay document*. Drag the desired data files from the file manager into the graph on the workspace. Format the axes, if necessary, and load the desired shift variables.

To access the TTS functionality, click *TTS* on the main menu at the top which appears when TTS appropriate data are displayed in the graph. The TTS ribbon is divided into 5 sections: Wizard, Session, Curves, Shift Factors and Options. Start the TTS session by either hitting *Wizard Start* or the *Session Start* buttons. Use the wizard for guidance if you are not familiar with the TTS shift procedure, otherwise select *Session Start*. The latter is used in the following instructions to demonstrate the TTS capabilities of TRIOS. After clicking the *Session Start* button, a window opens for the session name. The session name is used as a reference; this is important when more than one session exists in the same overlay file. Enter *Session 1* and hit *OK*. Two new tabs; *Session 1 - shiftfactor table* and *Session 1 - shiftfactor graph* are added at the bottom of the workspace and can be displayed by clicking the corresponding tab. The legend of the graph changes to show the test temperature associated with each curve. When a specific curve on the graph is selected, the corresponding legend entry is highlighted. This allows easy identification of the individual curves on a graph, which can be quite busy when many datasets are loaded.

> NOTE: If the legend does not display on the graph, select the *Format* menu item and check the *Legend* box in the *Show* section
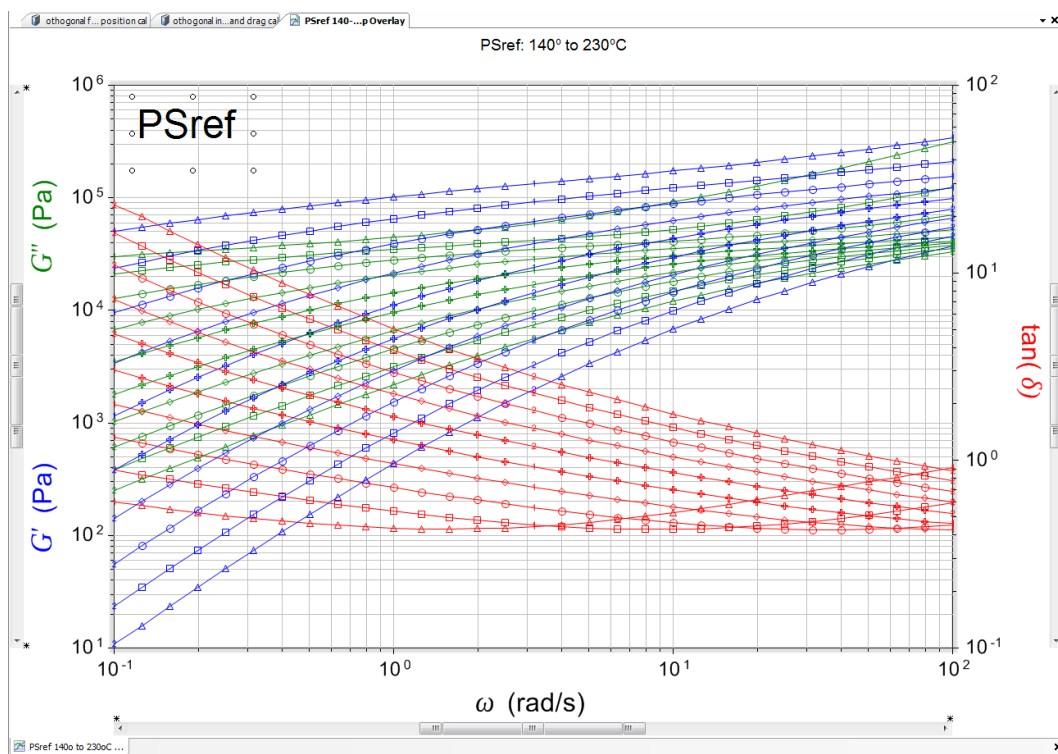
Figure 27: Unshifted frequency sweep data. All frequency sweep datasets have to be overlaid in one single overlay graph
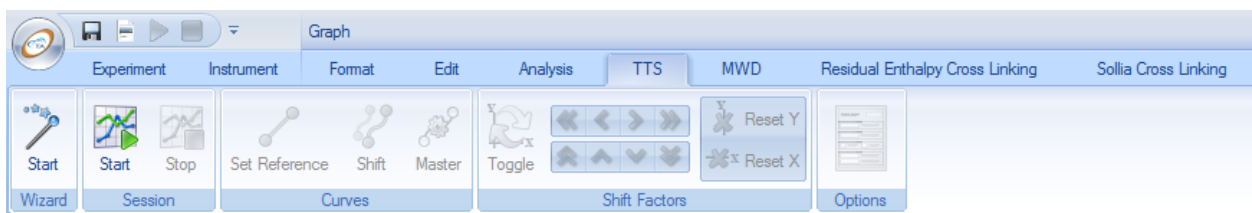

Figure 28: Layout of the TTS menu with 5 sections: Wizard, Session, Curves, Shift Factors and Options

In the next, step the reference temperature must be selected. Click the *Set reference* icon and the *TTS Set Reference Curve* form opens. Select the desired reference temperature and close the form. The reference temperature on the legend is now preceded by 3 asterisk symbols. Before proceeding with the shifting, it is good practice to check the default setting. Click the *Options* icon on the ribbon to open the *TTS Options* form. Four different settings are available.

- <u>AutoShift y-variable</u>. 2 selections are possible: - *all y- variables* or - *selected y-variable only*. *All y variables* means that all variables are included in the shifting. *Selected y-variables* means that only a specific variable is used by the shift algorithm. The user is prompted to select the variable prior to the automatic shifting. Only y-variables displayed in the graph can be selected.

- <u>Y shift base</u>. This selection tells the shift algorithm how to handle the vertical shift. 3 selections are possible: - *none*, - *temperature*, - *temperature*density*. *None* refers to no vertical

shift. *Temperature* refers to correcting the y-values based on stress by multiplying the y-variable with $\frac{T_0}{T}$. *Temperature*density* refers to correct y-variables based on the stress by multiplying with $\frac{T_0 \rho_0}{T \rho}$.

NOTE: The default density is 1. The density values can be changed in the shift factor table only. Click the *Session 1 Shift factor table* tab at the bottom of the workspace to open the table (figure 29). a_T is the horizontal shift factor and is 1 because no shift has been applied, $b_T base$ is the vertical shift calculated from the temperature and density correction and is calculated before the horizontal shift is applied. If the sample density is not readily displayed, the variable may be added to the spreadsheet by choosing *select* under the *Format* ribbon.

		A	B	C	D	E
Selected step:	Session 1 - shift factors	T °C	aT (x variable)	bT base	bT delta	bT (y variables)
1	▶	140.002	1.00000	1.02421	1.00000	1.02421
2		150.003	1.00000	1.00000	1.00000	1.00000
3		160.002	1.00000	0.97691	1.00000	0.976914
4		170.003	1.00000	0.95486	1.00000	0.954868
5		180.008	1.00000	0.93378	1.00000	0.933785
6		189.995	1.00000	0.91365	1.00000	0.913650
7		199.997	1.00000	0.89433	1.00000	0.894337
8		209.998	1.00000	0.87582	1.00000	0.875825
9		219.997	1.00000	0.85806	1.00000	0.858065
10		229.996	1.00000	0.84101	1.00000	0.841013

Figure 29: Shift Factor table with temperature, shift factor a_T shift factor b_{Tbase}, b_{Tdelta} and b_T

- Auto-shift type. 2 selections - *X only* and - *X and Y*. When *X only* is selected, only a horizontal shift is applied to determine the best a_T factor. *X and Y* allows vertical and horizontal shift to determine the optimum overlay. Both shift types operate independently of the b_T base shift. In the case of the *X and Y* type, b_{Tdelta} is the additional vertical shift, applied to optimize the overlay of the adjacent curve segments. b_{Tdelta} is the experimental vertical shift and is due to experimental errors resulting from sample loading and gap changes. Refer to section shift strategies for more information on vertical shifting.

- Remove shift zone on end session. This selection sets the condition at session closure. Either - *No*, keep the session results, - *Yes*, remove the session results or - *Prompt* the user for action. It is recommended to use the *Prompt* selection.

The next step is the shifting operation. On the TTS ribbon, click the *Shift* icon. The frequency curves are now shifted to form a mastercurve based on the TTS options selected (figure 30). The graph represents the viscoelastic properties G', G'' and $\tan \delta$ over an extended frequency range at the reference temperature of 150°C. The shift algorithm was applied to all active y-variables in the graph; after applying the temperature/density correction the variables were shifted in the horizontal and vertical direction to optimize the curve overlay. The additional vertical shift is shown in the shift table (Figure 29) as b_{Tdelta} and corrects for experimental errors due to sample loading, gap changes, etc. The temperature dependence of the shift factor, a_T, can be displayed by clicking the tab *Session 1 shift factors graph* at the bottom of the workspace. The graph only shows the shift

factor, a_T, versus temperature. The b_{Tbase} and b_{Tdelta} shift factors can be easily displayed by double clicking one of the axis labels (refer to TRIOS on-line help for details on how to set up a graph) to select the desired variables to plot.
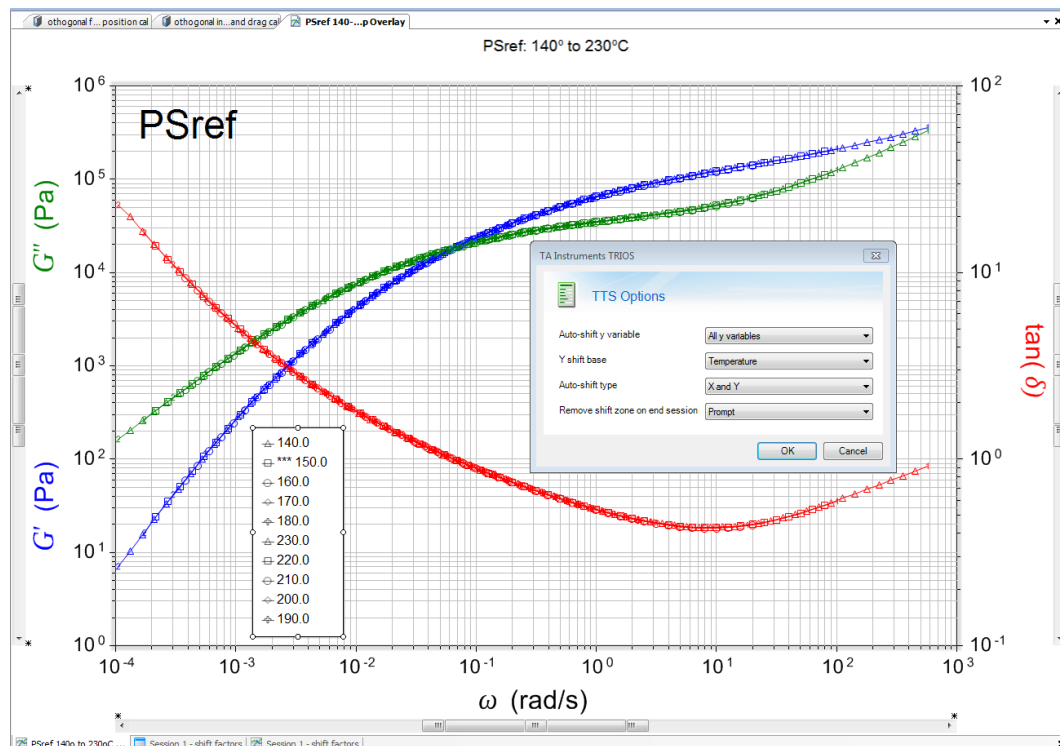

Figure 30: Once the shifting operation is completed, the viscoelastic functions G', G'' and $\tan\delta$ overlay to form a mastercurve at the selected reference temperature. The shift algorithm used all active variables, corrected the stress for temperature and applied a 2D shift to compensate for experimental errors in the modulus.

4.3   Shift strategies

In the previous shift operation, the shift algorithm has been using all of the active variables to determine a good overlay of the frequency sweep curves. What happens when only one active y-variable is used during shifting? What does the shift algorithm do exactly? Let's have a look at what the shift algorithm does.

The shift algorithm is based on piecewise fitting the overlapping curve segments by linear interpolation and minimizing the square of the errors of the reference and shift curve. The algorithm starts at the reference curve and adds the adjacent shift curves, one by one until all the curves overlay. In the *X-only* shift mode, only horizontal shifting is allowed. In the *X and Y* shift mode, the shift curve can be shifted horizontally and vertically until the curves overlay (2D shift). The shifting algorithm can operate on a single y-variable or multiple y-variables simultaneously. This approach allows the algorithm to pursue various shifting strategies quite easily. The most common strategy is to shift the $\tan\delta$ curves horizontally only. The advantage is that no vertical shift is required and most experimental errors cancel out. The vertical shift can be performed in a second shifting step for G' or/and G''. The main draw back of this approach is that $\tan\delta$ does not shift very well when
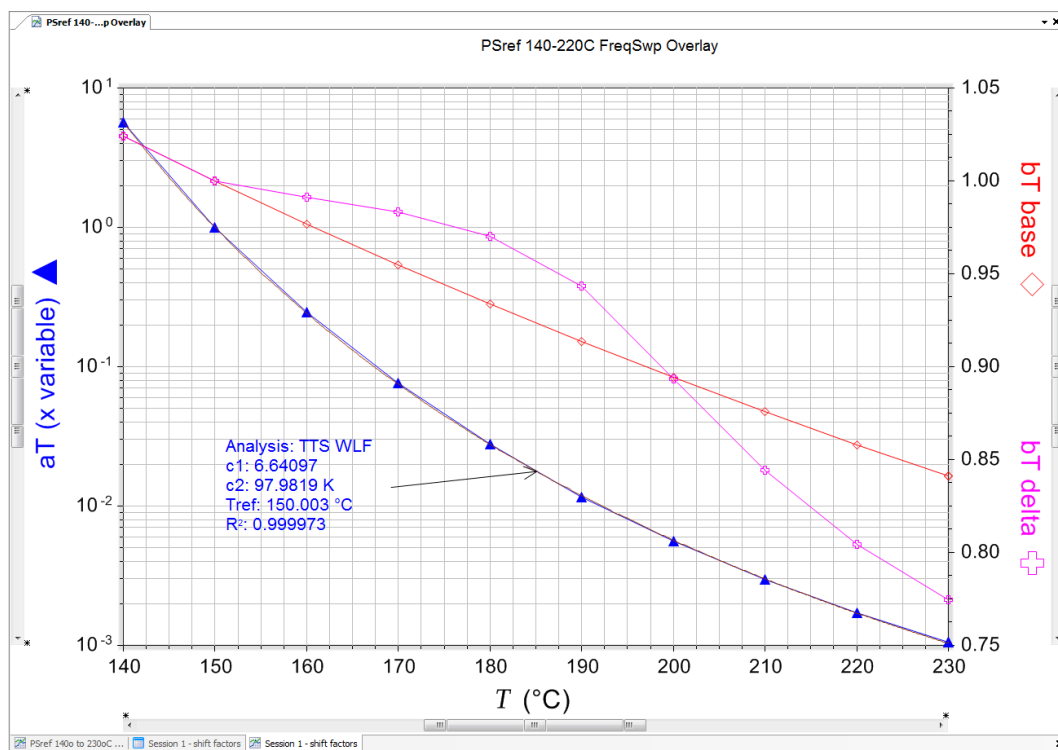
24

Figure 31: The a_T, $b_T base$ and $b_T delta$ shift factors are shown as a function of temperature. The a_T shift factor is fitted with the WLF model

the curve has a minimum or maximum. In this case it is necessary to run the minimization on multiple y-variables such as $\tan\delta$ and G'.

> NOTE: Several shifting steps can be performed consecutively with modified shift settings. It is furthermore possible to combine automatic with manual (section 4.4 below) shift operations. Shift factors can be reset anytime with the *Reset Y* and *Reset X* buttons on the *TTS* ribbon to start fresh.

The shift session can be closed with the *Session Stop* button on the ribbon. The shift factors are saved or discarded at the end of a session, based on the Options settings.

4.4 Manual shifting

Instead of using the automatic shifting functionality, the shift curves can be moved manually along the x or y axis. Manual and automatic shifting can be used together in an active shift session.

> NOTE: Only shift curves can be shifted manually, the reference curve is always locked. When a variable curve is shifted manually, all associated variables are shifted at the same time.

The shift direction is set with the toggle button on the *TTS* ribbon in the *Shift Factor* section (figure 28). The focus changes from the row of four horizontal to vertical shift buttons and vice versa. Select the desired shift curve with the mouse and drag the curve in horizontal or vertical direction, depending on the state of the toggle button. Alternatively, the four shift buttons (slow,

fast, left, right or up, down) can be used to shift the curve. The *shift* button (on the Curves section of the ribbon) can be used at any time to automatically optimize the shift based on the current shift setting in the *Options*.

4.5 Quantifying the temperature dependence of the shift factor and building the master curve

The shift procedure continuously updates the *Session shift table and graph*.(Figure 29 & 31). The a_T shift factor represents the horizontal shift along the frequency axis and describes the temperature dependence of the material. Early observations[7] of the temperature dependence of liquids viscosity led to the empirical Arrhenius relationship.

$$a_T\left(T\right)=\exp\left[\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$$

Polymer liquids in the plateau and terminal zone, at temperatures well above the T_g show this type of dependence. The constant E_a is the flow activation energy. When test temperatures are less than $T_g + 100$, the WLF[5] (Williams, Ferry, Landel) equation, based on the relative free volume concept provides much better predictions.

$$\log a_T \equiv \frac{-c_1\left(T-T_0\right)}{\left(c_2+\left(T-T_0\right)\right)}$$
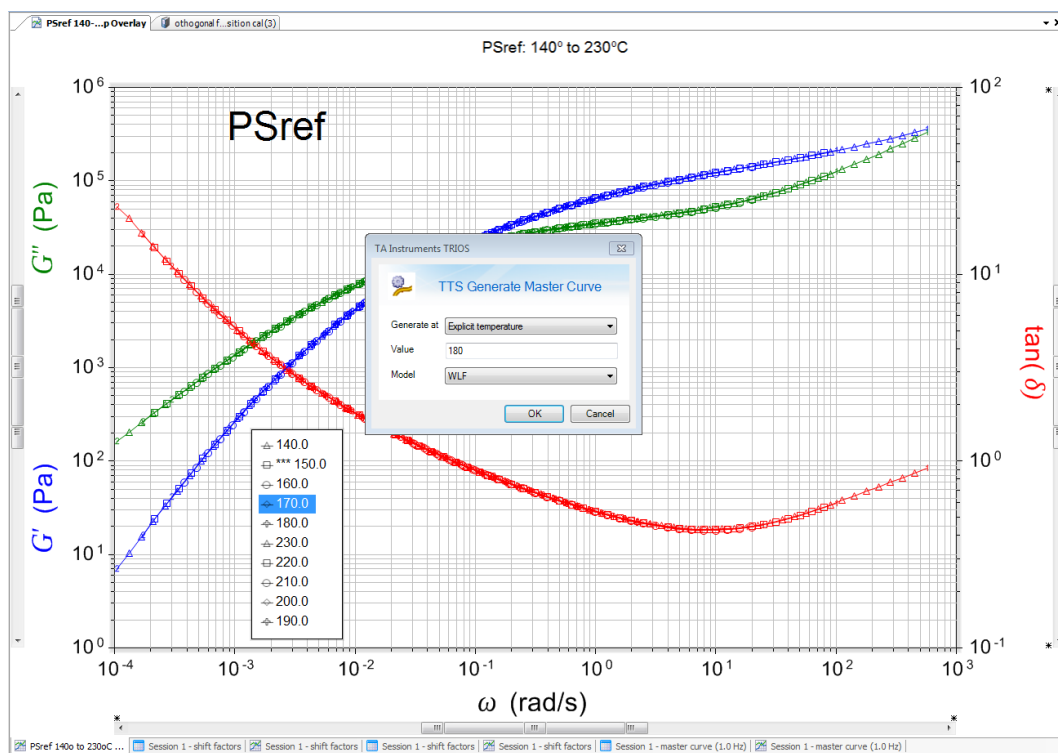

Figure 32: Master curves can be generated based on the selected reference temperature or on any other specific temperature. The master curve can also be displayed as a function of temperature at a specific frequency.

c_1 and c_2 are empirical constants. The universal values $c_1 = 17.44$ and $c_2 = 51.6$ with $T_0 = T_g$ are quite successful at predicting the temperature dependence of amorphous polymers[10]. In order to fit the a_T shift factors, select either the WLF or Arrhenius model from the analysis menu ribbon. (see analysis section 2.2).

When the shifting operation is closed, independent of the shift factor table having been saved or not, the overlay plot is reset and all curves are replotted as a function of the experimental frequency. In order to retain the reduced plot, a master curve datafile must be created. Click the *Master* icon on the *Curves* section of the *TTS* ribbon (figure 1). The *TTS Generate Master Curve* form displays. There are several choices for generating a master curve.

- **Generate at Reference temperature.** The plot with the shifted curves is saved as is over the extended frequency range with $\omega_r = \omega a_T$. (figure 33)

- **Generate at Explicit temperature.** Enter the desired temperature and the model equation for the shift factors. The choices are *WLF* and *Arrhenius*. There is no need to fit these models previously. If the model constants are not available, TRIOS will perform the fitting before completing the master curve computations. It is possible to extrapolate (choose a temperature outside of the test range), just be aware that the model equation may not be valid outside the experimental temperature range.

- **Generate at Explicit (angular) frequency.** Enter the desired frequency and choose the model equation for the shift factors.(figure 34)
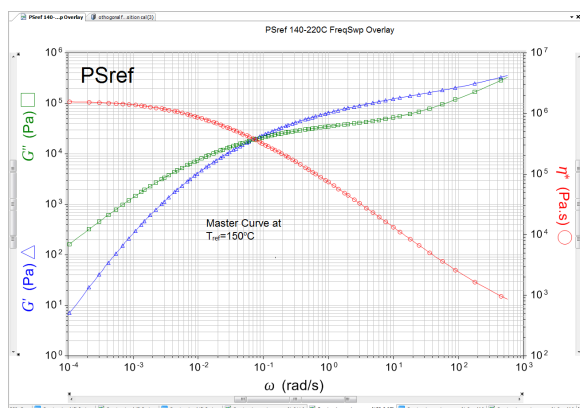

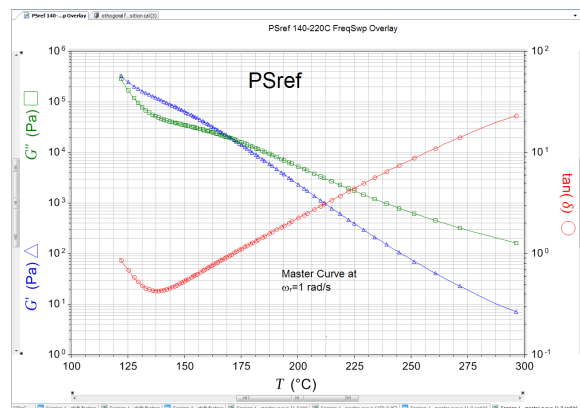
Figure 33: Master curve at the reference temperature T=150°C

Figure 34: Mastercurve at the reference frequency $\omega = 1 rad/s$

Close the TTS session by clicking the *Session Stop* button on the *TTS* ribbon.

NOTE: If the TTS session is not closed before saving and closing the document, next time the document file is reloaded and displayed, it will open with the last TTS session open. The experimental curves on the overlay page are not reset and the data analysis can be resumed from where it had been at the time the file was saved and closed.

4.6 Other shifts - time dependent functions

Although TTS is mostly applied to Oscillation Frequency Sweep data, the technique can also be used for time dependent data sets such as relaxation and creep. The approach is exactly the same.

However be aware, since the time is inversely proportional to the frequency, the reduced time is defined as $t_r = t/a_T$. In figure 35 the master curve for the compliance of the reference material PSref in a creep experiment is given. Load the demo data set **PSref-Creep** into the TRIOS file manager (refer to section 1.1 for details). For the data to be shifted automatically, the noisy short time response has to be removed. In this example, the time response below 0.2s has been removed prior to the TTS session using the *Remove* functionality from the *Data* section on the *Edit* ribbon. Note that it is not sufficient to hide the data. Removed data points can be restored using the *Reload* icon on the same menu section. If shifting fails because of experimental noise, manual shifting is always an option (section 4.4 below).
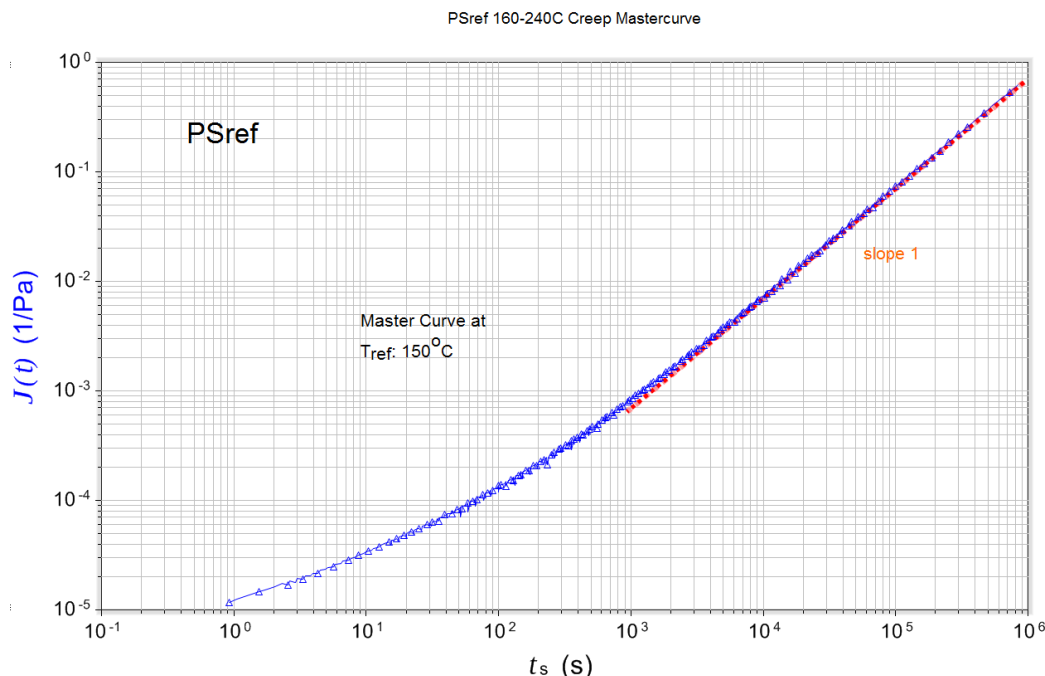

Figure 35: Mastercurve of $J(t)$ at the reference temperature of 150°C. The time is the reduced time $t_r = t/a_T$

> NOTE: Transient data files such as the compliance can be noisy. Slight smoothing (refer to section 2 for details on smoothing experimental data) of the experimental data can improve the performance of the shift procedure and the quality of the fit

4.7 Judging the quality of the superposition

It is difficult to judge the success of a superposition and very often the goodness of the superposition is not qualified at all. Using more than one rheological variable is preferred, especially when horizontal and vertical shifting are combined. Poor superposition can be a result of bad experimental data such as noise at low frequency or systematic errors at high frequency due to improper correction of instrument effects. Non-linear material response alters the temperature dependence of the relaxation times and as such affects the superposition - these deviations have to be recognized since they provide useful material information. It is important to understand whether the superposition fails because of experimental errors or because of the material itself. Vertical shifting,

when not performed properly can mask these non-linear effects, this can happen easily when the frequency range is too small. 2D shifting should never be performed without additional checks. The Van Gurp-Palmen plot is very helpful to evaluate the magnitude of the vertical shift.

Thermo-rheological simplicity is found mostly for linear homopolymers with temperatures significantly above the glass transition.

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