



thermo scientific

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HAAKE RheoWin

User Guide

Polymer Tools: TTS, Spectra and MWD

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Contents

Chapter 1	The Time-Temperature Superposition (TTS) Data Analysis Tool	1
	Introduction to TTS	1
	Working with the RheoWin TTS data analysis tool	3
	The data and parameters page	3
	The layout page	5
	Starting the shifting process	7
	How it works	7
	Judging the results of the shifting process	8
	Shifting is just mathematics not physics	8
	The original data	8
	The resulting shifted data	9
Chapter 2	The Spectra Calculation Data Analysis Tool	11
	Introduction to spectra	11
	Theory	11
	An example	13
	Working with the RheoWin spectrum data analysis tool	14
	The data and parameters page	15
	The Layout page	16
	The Calculation page	17
	Starting the calculation	17
	How it works	18
	Judging the results of the spectrum calculation	18
Chapter 3	The MWD Calculation Tool	19
	MWD calculation from rheological data	19
	Working with the RheoWin MWD data analysis tool	19
	The Data page	20
	The Substance page	21
	The Layout page	23
	MWD calculation	24
Appendix A	Licensed static linked external libraries	27
	OpenBLAS	27
	NNLS	27
	C/C++ Minpack	28

The Time-Temperature Superposition (TTS) Data Analysis Tool

The RheoWin TTS data analysis tool is an optional RheoWin module that allows the user to perform time-temperature superposition (TTS) of data. This chapter gives a short introduction to the TTS principles and explains in detail how to use the RheoWin TTS data analysis tool.

For a more detailed description of the TTS principles please refer to the literature (e.g. Dealy¹ and Ferry², chapter 11-C).

Please note that the TTS data analysis tool is *not* part of the standard RheoWin delivery content but a module which must be ordered and installed separately.

Introduction to TTS

The properties of viscoelastic materials vary with both time (frequency) and temperature. Taking measurements over a wide enough temperature range (-160 °C to 600 °C) is normally not a problem. Taking measurements over a frequency range, which is wide enough to adequately track the visco-elastic behaviour of a material from the high-frequency end of the plateau zone into the low-frequency terminal zone however, is normally not possible using a single rotational rheometer in oscillation mode.

For short times (high frequencies) the limit is set by technical issues like the instrument and sample inertia as well as sampling time, whereas the limit for long times (low frequencies) is mainly set by practical considerations, see [Table 1](#).

Table 1. Duration of one oscillation period as a function of the oscillation frequency (Sheet 1 of 2)

Oscillation frequency		Duration of 1 oscillation period			
f in Hz	ω in rad/s	t in s	t in min	t in hours	t in days
100	628	0.01			
10	62.8	0.1			
1	6.28	1			
10^{-1}	$6.28 \cdot 10^{-1}$	10	0.167		
10^{-2}	$6.28 \cdot 10^{-2}$	100	1.67		

¹ J. Dealy, D. Plazek, Time-Temperature Superposition – A Users Guide, Rheology Bulletin, 78(2) July 2009

² J.D. Ferry, Viscoelastic Properties of Polymers, 3rd ed., John Wiley & Sons, N.Y. 1980

Table 1. Duration of one oscillation period as a function of the oscillation frequency (Sheet 2 of 2)

Oscillation frequency		Duration of 1 oscillation period			
f in Hz	ω in rad/s	t in s	t in min	t in hours	t in days
10^{-3}	$6.28 \cdot 10^{-3}$	1000	16.7	0.278	
10^{-4}	$6.28 \cdot 10^{-4}$	10000	167	2.78	0.116
10^{-5}	$6.28 \cdot 10^{-5}$	100000	1670	27.8	1.16
10^{-6}	$6.28 \cdot 10^{-6}$	1000000	16700	278	11.6

An example: One frequency sweep measurement from 10^{-3} Hz to 100 Hz using 6 frequencies per decade, one waiting period and 3 repetitions pro data point (that is per frequency) takes 12550 seconds, that is 209 minutes or 3 hours and 29 minutes!

By measuring data with frequency sweeps, in the practically and technically usable range from approximately 10^{-3} Hz – 10^{-2} Hz to approximately 10 Hz – 100 Hz, at several temperatures, time-temperature superposition (TTS) can be used to generate a “master curve” showing the behaviour at a “reference temperature” that covers many decades of frequency (or time). A material to which this technique is applicable is said to be “thermo-rheologically simple”.

Figure 3 gives an example of what can be achieved with TTS: A polystyrene material was measured at 6 different temperatures from 140 °C to 230 °C over almost 4 decades of frequency, the resulting master curve at 150 °C covers 7 decades of frequency!

In the process of creating a “master curve”, quantities which have the unit of time (or reciprocal time, i.e. frequency) are subject to horizontal shift, while those having the unit of stress (or reciprocal stress) are subject to vertical shift. For example, in a $G'(\omega)$ “master curve”, the quantity plotted on the vertical axis is $b_T G'(\omega)$, and that plotted on the horizontal axis is $a_T \omega$, while in a compliance “master curve”, the variable plotted on the vertical axis is $J(t)/b_T$, and that plotted on the horizontal axis is t/a_T . In both cases a_T is the horizontal shift factor and b_T the vertical shift factor, which both depend on the temperature.

A material is called “thermo-rheologically simple” when all contributing retardation or relaxation mechanisms of the material have the same temperature dependence and when stress magnitudes at all times or frequencies have the same temperature dependence.

The implication of this is that when viscoelastic properties such as the moduli $G'(\omega)$, $G''(\omega)$ or the creep compliance $J(t)$ are plotted in a double logarithmic graph, data measured at different temperatures can be shifted horizontally by a constant (independent of time or frequency) distance $\log(a_T)$ and vertically by an another constant distance $\log(b_T)$ to obtain one single “master curve” containing all the data. The master curve displays data over a wide range of frequencies (or times) “reduced” to a reference temperature T_0 .

Examples of “thermo-rheologically simple” materials to which TTS can be applied are elastomers, amorphous and semi-crystalline homopolymers as well as certain filled systems.

In general materials show “thermo-rheologically simple” behavior only in a limited temperature or frequency range, as long as there is only one transition covered. Amorphous homopolymers are “thermo-rheologically simple” from the terminal region (high temperatures) to the glass transition region but not for temperatures in the low temperature transitions regions. For semi-crystalline polymers the crystallization and melting temperature range should be avoided. For polymeric blends TTS can be used as long as only one of the components has its transition in the measured temperature or frequency range.

Working with the RheoWin TTS data analysis tool

The RheoWin TTS data analysis tool is available in the RheoWin DataManager only.

❖ To open the TTS dialog

1. Select the **TTS** command from the Analysis menu.
or
2. Click on the **TTS** icon in the evaluation toolbar which is by default located on the right hand side of the DataManager program window.

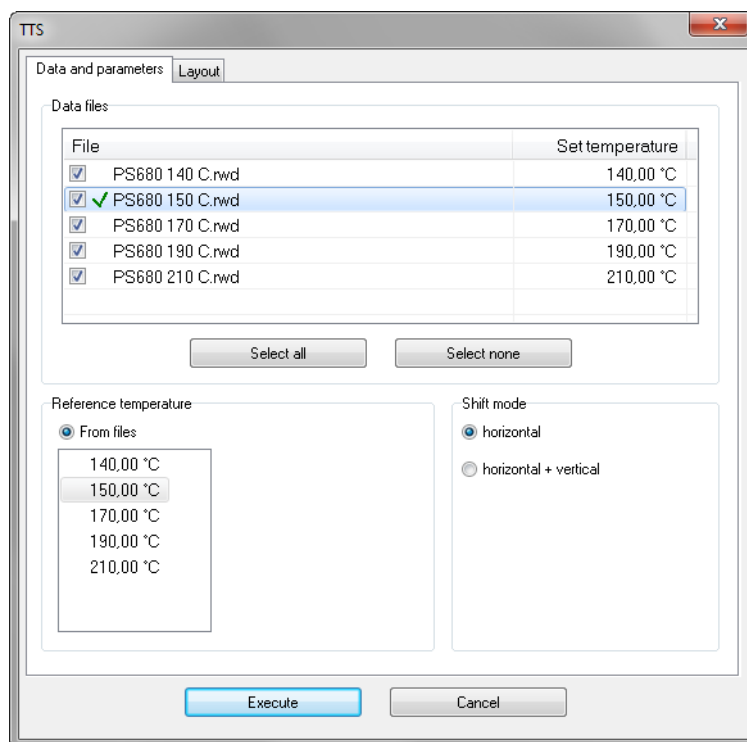
The TTS dialog can only be opened when the RheoWin DataManager contains at least one Page containing at least one RheoWin *.rwd data file. For the shifting process to work at least two data files are needed, see the ‘Data files’ chapter below.

The TTS dialog contains two pages: The **Data and Parameters** page (see [Figure 1](#)) and the **Layout** page (see [Figure 2](#)), the contents of which are described below.

The data and parameters page

On this page the data files to be shifted, the reference temperature and the shift mode can be selected.

Figure 1. The Data and Parameter page of the TTS dialog



Data files

The RheoWin *.rwd data files to be shifted must be loaded into one DataManager page *before* the TTS dialog is opened using the **Open** command from the **File** menu or one of the many other methods RheoWin offers for this.

The list in the **Data files** box shows all the RheoWin *.rwd data files that are contained in the active DataManager page, behind the file name the **Set temperature** of each data file is displayed.

The list in the **Data files** box must contain at least two *.rwd data files for the shifting process to work.

Removing a file from the list can only be performed by removing the file from the DataManager page, using the **Remove** command from the **File** menu or the toolbar, after closing the TTS dialog.

However a *.rwd data file included in the list can easily be excluded from the shifting process by unchecking the checkbox in front of the file name. The data from an unchecked file will not appear in the “Master curve” data.

The *.rwd data files used for the shifting process must fulfil the following requirements:

- Each *.rwd data file must contain frequency sweep data measured at one constant temperature.

The TTS data analysis tool uses the set temperature value from the measurement (job) definition contained in the *.rwd file, it does NOT check whether the measured temperature values are constant and/or correspond to the set value.

- The frequency sweep data in each *.rwd data file can consist of multiple segments, i.e. the Job with which the data was measured can contain multiple frequency sweep elements.

- The *.rwd data file must NOT contain data from other kind of oscillation elements, since the TTS module does not check the data segment types contained in the *.rwd files, it just uses all the $G'(\omega)$, $G''(\omega)$ data points that are found in the data and ignores all other data.
- The temperatures at which the data contained in the different *.rwd data files were measured must all be different from each other. When two or more files contain the same set temperature values, these files will be marked in the list with a red exclamation mark in front of the file name. In this case the concerned *.rwd data files except for one must be excluded from the shifting process. The Execute button is disabled as long as the list displays one or more red exclamation marks.

The TTS tool will NOT work with one (or more) data file(s) which contains multiple frequency sweeps measured at different temperatures (in one Job). Such data files must first be split-up in separate data files each containing a frequency sweep measured at one temperature using the Save segments separately command from the Save submenu in the File menu.

Reference temperature

The reference temperature to which all the data will be shifted can be selected by using either one of the following methods:

- Click on the temperature value in the list of temperatures in the **Reference temperature box**. The corresponding *.rwd data file will be marked with a ✓ in front of the file name.
- Double click on the file name in list in the **Data files box**.

In both case the corresponding *.rwd data file, in the list in the Data files box, will be marked with a ✓ in front of the file name.

The settings made in the Reference temperature box are automatically saved by RheoWin and restored the next time the dialog is opened.

Shift mode

During the shifting process, the data can either be shifted in the Horizontal direction only or in both the Horizontal and vertical direction.

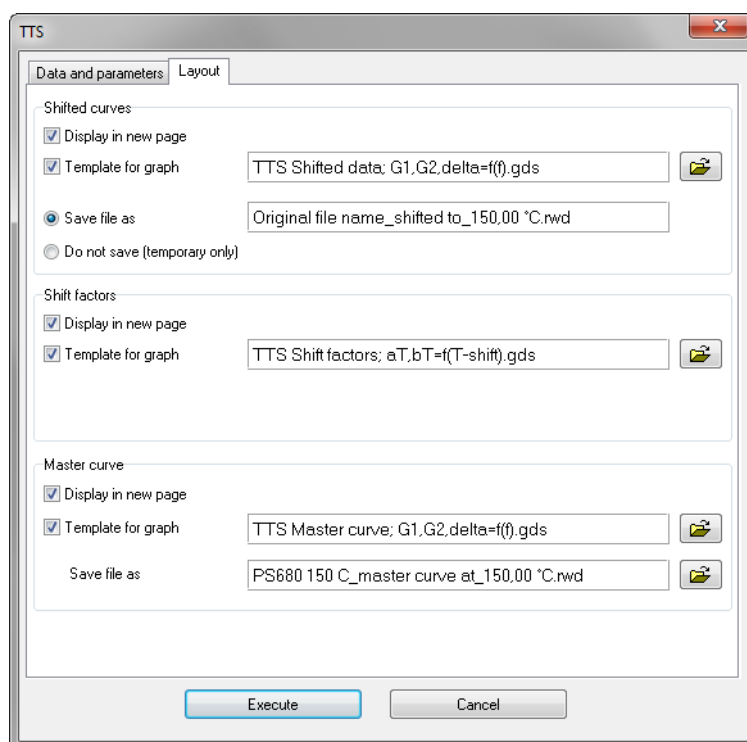
When the default shifting in the horizontal direction only does not give the expected result, shifting in the horizontal and vertical direction can be used. In this case the vertical shift factors b_T should be checked for plausibility, see the chapter 'Judging the result of the shifting process' below.

The settings made in the Shift mode box are automatically saved by RheoWin and restored the next time the dialog is opened.

The layout page

This page contains several settings which define what data are displayed in which format and what data are saved in new *.rwd data files as a result of the shifting process.

Figure 2. The Layout page of the TTS dialog



The settings made on this page of the dialog are automatically saved by RheoWin and restored the next time the dialog is opened.

Shifted curves

When the Display in new page option is active, RheoWin will display the resulting shifted data of all the *.rwd data files individually in one new DataManager page. Although the graph showing this shifted data individually will contain exactly the same data points as the “Master curve” graph, this graph is very useful because it gives a good graphical overview of how good the superposition worked out for this data (when the colours for the different data files were defined accordingly).

When the Display in new page option is not active, the shifted data will not be shown separately.

When the Template for graph option is not active, the new page will use the graph settings from the page which contains the original *.rwd data files.

When the Template for graph option is active, the new page will use the graph settings from the selected graph template. A proper template is selected by default, however another template can be selected, by clicking on the file open button behind the template file name, if desired.

When the Save file as option is selected, the shifted data for each of the original *.rwd data files will be saved in new *.rwd data files with the text _shifted to_xxx,xx °C (where xxx,xx stands for the selected reference temperature) added to the original file name.

When the Do not save (temporary only) option is selected, the shifted data will only be saved in temporary files (needed for displaying the data) which are deleted as soon as the page in which the data are shown is closed.

Shift factors

When the Display in new page option is active, RheoWin will display the resulting shift factors a_T and b_T in one new DataManager page. For this to work as intended the Template for graph option (see below) must be active and a proper template must be selected.

When the Display in new page option is not active the shifted data will not be shown separately.

When the Template for graph option is active, the new page will use the graph settings from the selected graph template. A proper template is selected by default, however another template can be selected, by clicking on the file open button behind the template file name, if desired. This option must be active for the shift factors a_T and b_T to be displayed as a function of the temperature.

Master curve

When the Display in new page option is active, RheoWin will display the resulting “Master curve” data in a new DataManager page.

When the Display in new page option is not active the “Master curve” data will be shown in the existing page which contains the original *.rwd data files.

When the Template for graph option is active, the new page for the “Master curve” will use the graph settings from the selected graph template. A proper template is selected by default, however another template can be selected, by clicking on the file open button behind the template file name, if desired.

The resulting “Master curve” data is always automatically saved in a new *.rwd data file with a name which consists of the name of the file which contains the data at the reference temperature plus the text _master curve at_ xxx,xx °C (where xxx,xx stands for the selected reference temperature).

The “Master curve” *.rwd data file also contains the shift factors a_T and b_T as data columns as well as the names of the original data files in the information window.

Starting the shifting process

After all the necessary settings have been made the shifting process can be started by clicking the Execute button at the bottom of the TTS dialog. The calculation of the shift factors and master curve takes less than a second. Depending on the settings on the Layout page of the TTS dialog, RheoWin will open up to three new pages in the DataManager and display the result in those pages.

By using the Tile horizontal command from the DataManager Windows menu the four graphs are automatically displayed in a tiled layout, see the screen-shot in [Figure 3](#).

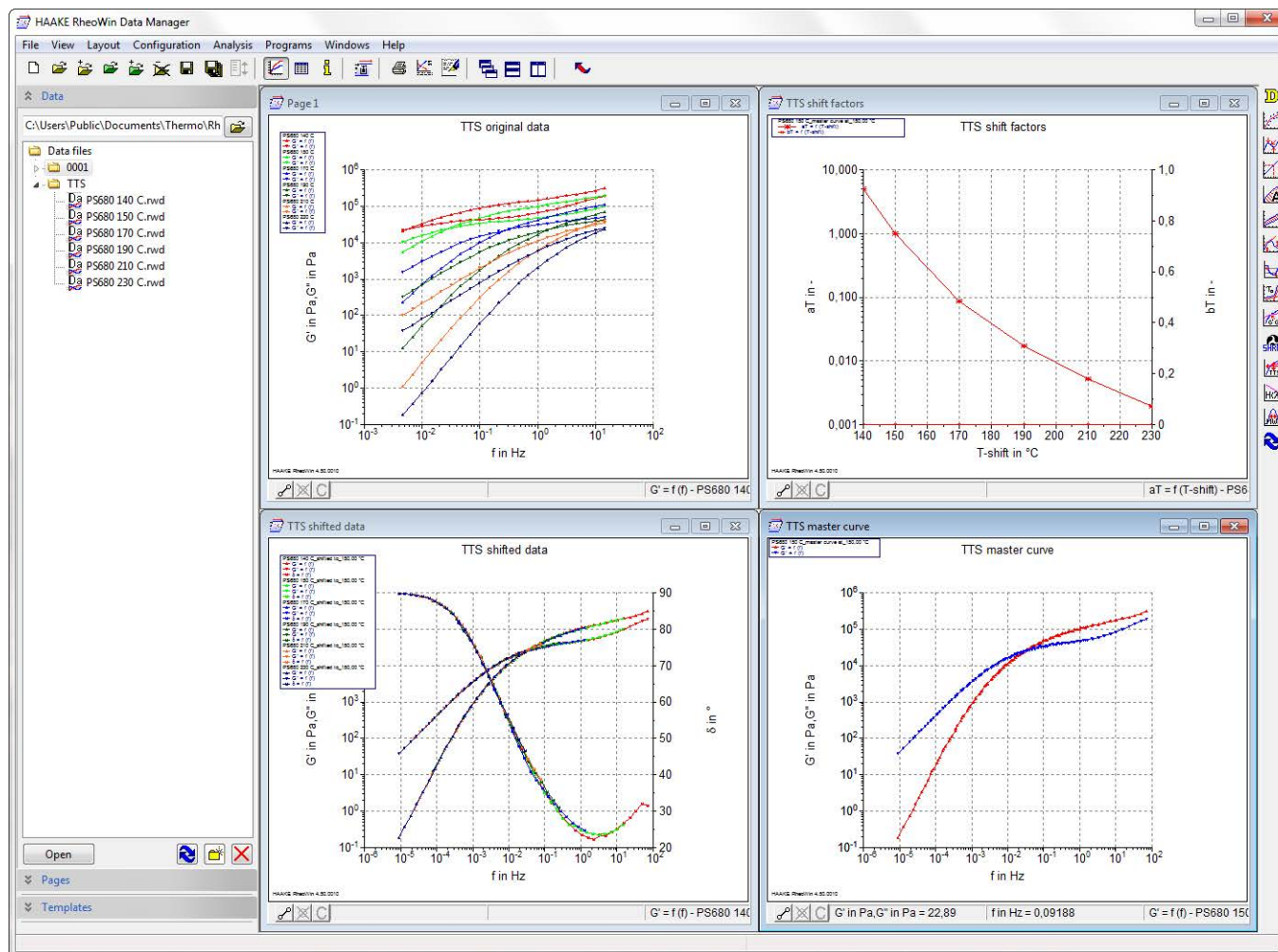
This screen layout gives a good overview of the results of the shifting process: The upper left graph shows the $G'(f)$ and $G''(f)$ of the original data, the upper right graph shows the shift factors $a_T(T)$ and $b_T(T)$, the lower left graph shows the shifted original data $G'(f)$, $G''(f)$ and $\delta(f)$ and the lower right graph shows the $G'(f)$, $G''(f)$ and $|\eta^*|(f)$ “Master curves”.

How it works

The shifting process is performed completely automatic. The shift factors are calculated by the LSSHIFT algorithm developed by Honerkamp and Weese³ at the University of Freiburg, Germany.

Judging the results of the shifting process

Figure 3. RheoWin screenshot showing the original data, the shift factors, the shifted data and the master curve



Shifting is just mathematics not physics

The results of the shifting process should always be viewed critically. A theory based on physics which would enable us to calculate the shift factors does NOT exist! Therefore the shifting is performed by “clever” and “high-tech” mathematics which doesn’t care for and doesn’t know about the physical properties of the material the rheological data is referring to, to put it bluntly. The mathematics only tries to superpose the data measured at different temperatures in the best possible way. In that it is very good, and certainly much better and quicker than any manual shifting method.

The original data

The quality of the resulting “Master curve” is mainly influenced by the quality of the data used for the shifting process. The following requirements should always be fulfilled:

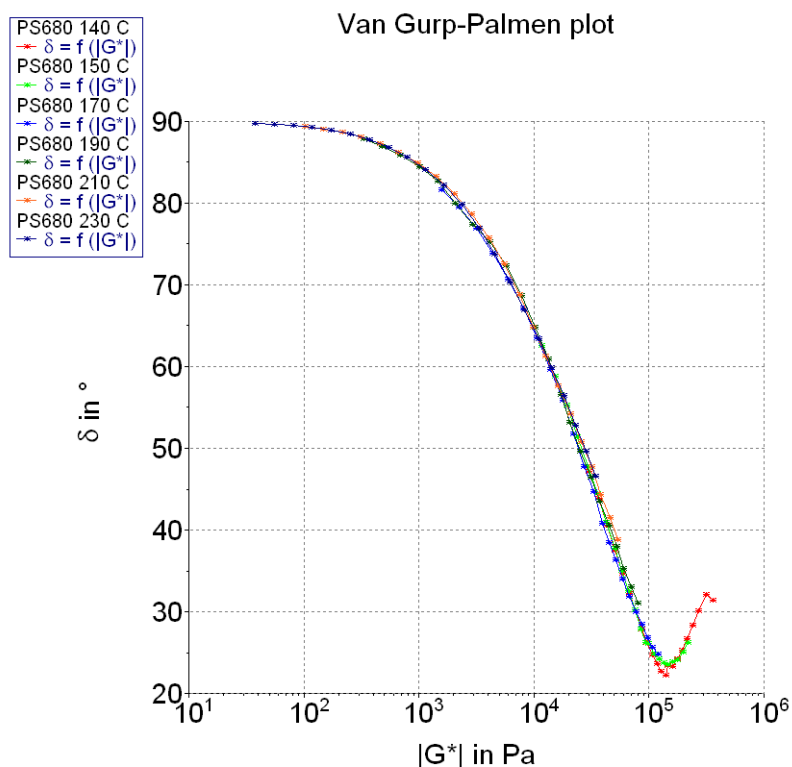
- Make sure that the sample temperature is really constant and corresponds to the set temperature during each frequency sweep measurement.

³ J. Honerkamp, J. Weese, A note on estimating mastercurves, Rheology Acta 32:57-64 (1993)

- Make sure that the material is “thermo-rheologically simple”. A simple and direct technique for detecting complexity in the material (as opposed to “simple”) is the use of a ‘van Gurrp-Palmen’ plot. In this type of plot the phase angle δ is plotted as a function of the complex modulus $|G^*|$. If the effect of the horizontal shift factor b_T on the magnitude of the complex modulus is negligible, the originally measured (not yet shifted) data will superpose without shifting if the material is “thermo-rheologically simple”.

The graph in [Figure 4](#) shows a ‘van Gurrp-Palmen’ plot of the data used above. The data superposes well.

Figure 4. A ‘van Gurrp-Palmen plot’ of the data showed in [Figure 3](#)



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In RheoWin DataManager this plot is conveniently created by selecting the page which shows the original data files and then performing a double click on the van Gurrp-Palmen plot; $\delta = f(GC)$.gds graph layout template (file) in the Templates explorer tree on the right hand side of the DataManager main window (see above).

The resulting shifted data

The quality of the resulting “Master curve” can of course also be judged from the resulting data itself. The following simple checks can be made:

- The horizontal shift factors $a_T(T)$ data should always form a monotonously decreasing curve, see the screen-shot above.
- When using horizontal *and* vertical shifting (for shifting G' and G'') the vertical shift factors b_T should be close to unity, as a rule of thumb $0.9 < b_T < 1.1$, values outside this range should be viewed very critically. Causes for b_T being non-zero are gap errors and sample loading errors as well as (strong) changes in the density of the sample material as function of the temperature.

1 The Time-Temperature Superposition (TTS) Data Analysis Tool

Judging the results of the shifting process

- From the phase angle “master curve” $\delta(f)$ a less than perfected superposition is (much) easier visible than from the $G'(f)$, $G''(f)$ or $|\eta^*|(f)$ “master curves”. See the two lower graphs in the screen-shot above. Although $G'(f)$, $G''(f)$ and $|\eta^*|(f)$ “master curves” seem to be almost perfect, it is clearly visible from the $\delta(f)$ “master curve” that at higher frequencies the superposition is good but not perfect.

The Spectra Calculation Data Analysis Tool

The RheoWin spectrum data analysis tool is an optional RheoWin module that allows the user to calculate relaxation and retardation spectra from oscillation frequency sweep data or from master curve data. This chapter gives a short introduction to the theory of spectra in rheology and how they are calculated and explains in detail how to use the RheoWin data analysis tool.

For a more detailed description of theory of spectra in rheology please refer to the literature (e.g. Dealy¹, Ferry², Dealy³).

Please note that the spectrum data analysis tool is *not* part of the standard RheoWin delivery content but a module which must be ordered and installed separately.

Introduction to spectra

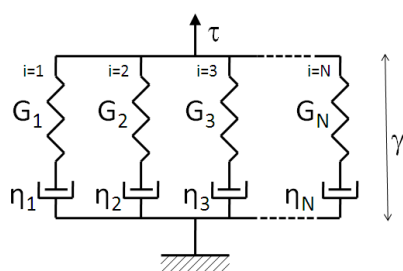
Theory

According to the theory of linear viscoelasticity the form of the time dependence of the relaxation modulus $G(t)$ or the frequency dependence of the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ can be described by the behaviour of a mechanical model with a sufficient number of elastic elements (springs) and viscous elements (dampers).

The springs are defined by a spring stiffness or shear modulus G_i , $G = \tau / \gamma$, and the dampers are defined by a friction or viscosity η_i , $\eta = \tau / \dot{\gamma}$. The relaxation time of one Maxwell element, consisting of one spring and one damper in series, is given by $\lambda = \eta / G$.

The specific combination of springs and dampers as shown in Figure 5 is known as the generalized Maxwell model of a viscoelastic material.

Figure 5. Generalized Maxwell model



¹ J. Dealy, Questions About Relaxation Spectra Submitted by a Reader, Rheology Bulletin, 76(1) January 2007.

² J.D. Ferry, Viscoelastic Properties of Polymers, 3rd ed., John Wiley & Sons, N.Y. 1980.

³ J. Dealy, K. Wissbrun, Melt Rheology and Its Role in Plastics Processing: Theory and Applications, Springer, 1999.

The relaxation modulus $G(t)$ of the generalized Maxwell model is given by equation (1),

$$G(t) = \sum_{i=1}^N G_i e^{(-t/\lambda_i)} \quad (1)$$

and the storage and loss moduli G' and G'' are given by the equations (2) and (3)

$$G'(\omega) = \sum_{i=1}^N \frac{G_i (\omega \lambda_i)^2}{1 + (\omega \lambda_i)^2} \quad (2)$$

$$G''(\omega) = \sum_{i=1}^N \frac{G_i (\omega \lambda_i)}{1 + (\omega \lambda_i)^2} \quad (3)$$

Here G_i and λ_i are the moduli and relaxation times of the individual Maxwell elements. The set of parameters $\{G_i, \lambda_i\}$ are said to constitute a *discrete relaxation spectrum*, discrete because of the finite number of N .

The *continuous relaxation spectrum* is defined by letting the numbers of elements in the generalized Maxwell model increase to infinity so that $G(t)$ can be represented in terms of a continuous functions, $F(\lambda)$, such that $F \cdot d\lambda$ is the contribution to the modulus from relaxation times between λ and $d\lambda$. The relation between the relaxation modulus $G(t)$ and the spectrum is given by equation (4)

$$G(t) = \int_0^{\infty} F(\lambda) e^{(-t/\lambda)} d\lambda \quad (4)$$

Normally the natural logarithm of the relaxation time λ , i.e. $d \ln(\lambda)$, is used for the spectrum and the continuous spectrum $H(\lambda)$ is used in place of $F(\lambda)$, where $H = F \cdot \lambda$ and $H \cdot d \ln(\lambda) = F \cdot d\lambda$. The relation between the relaxation modulus and $H(\lambda)$ is given by equation (5)

$$G(t) = \int_0^{\infty} H(\lambda) e^{(-t/\lambda)} d(\ln \lambda) \quad (5)$$

and the storage and loss moduli G' and G'' are related to $H(\lambda)$ as follows

$$G'(\omega) = \int_0^{\infty} \frac{H(\omega \lambda)^2}{1 + (\omega \lambda)^2} d(\ln \lambda) \quad (6)$$

$$G''(\omega) = \int_0^{\infty} \frac{H(\omega \lambda)}{1 + (\omega \lambda)^2} d(\ln \lambda) \quad (7)$$

An example

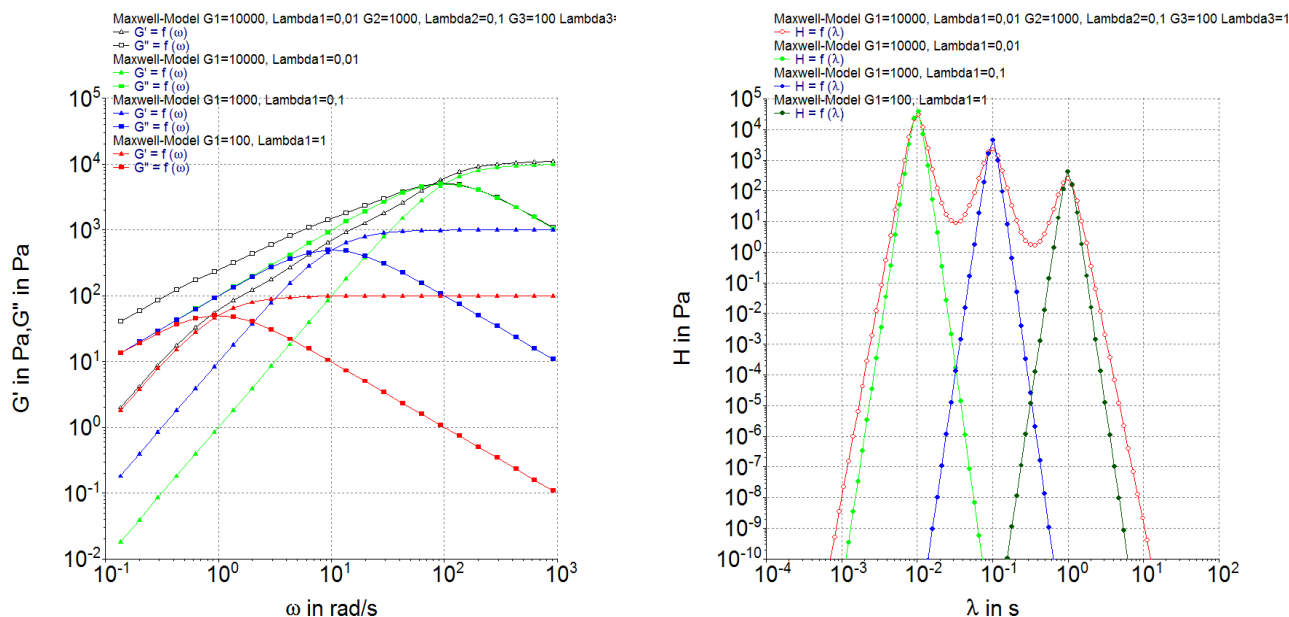
The graphs in Figure 6 show the (calculated, i.e. not measured) $G'(\omega)$ and $G''(\omega)$ data of a Maxwell model “material” consisting of three Maxwell elements ($N = 3$) as well as the corresponding spectrum of this model “material”. The spectrum data were calculated from the $G'(\omega)$ and $G''(\omega)$ data by the RheoWin spectrum data analysis tool, the regularization factor was set to 10^{-6} for this calculation.

The $G'(\omega)$ and $G''(\omega)$ data were calculated using the “Simulator device” in the RheoWin JobManager with the Maxwell model parameters as shown in Table 2.

Table 2. Parameters for a 3 element Maxwell model

Index i	G in Pa	λ in s
1	10000	0.01
2	1000	0.1
3	100	1

Figure 6. $G'(\omega)$ and $G''(\omega)$ data (left) and the spectrum $H(\lambda)$ (right) of a 3 element Maxwell model “material”



Both graphs in Figure 6 show the data of the 3 elements Maxwell model “material” (see Table 2) plus the data of the three single Maxwell elements which make up the 3 element “material”. It is easily seen that the data of the 3 elements Maxwell model “material” (the larger black symbols and black solid lines) is the sum of three single Maxwell element data (the smaller green, blue and red symbols and dashed lines) according to equations (2) and (3).

In the spectrum data the three relaxation times (of the three elements Maxwell model) at 0.01 s, 0.1 s and 1.0 s are clearly visible, proofing, that the RheoWin spectrum module works correctly. Due the fact that the peaks in the spectra are very narrow there are not enough data points calculated to show the real peak of the spectra, but although it is not easily seen from the data the actual peak values are in fact equal to $G_i \cdot \lambda_i$ as it should.

It should be noted that both graphs in [Figure 6](#) supply different views on exactly the same information, a spectrum (calculated from oscillation data) does *not* give new information, it just presents the same information in a different way.

Working with the RheoWin spectrum data analysis tool

The RheoWin spectrum data analysis tool is available in the RheoWin DataManager only.

❖ To open the spectrum dialog

1. Select the Spectrum command from the Analysis menu.
- or
2. Click on the Spectrum icon in the evaluation toolbar which is by default located on the right hand side of the RheoWin DataManager program window.

The Spectrum dialog can only be opened when the RheoWin DataManager contains at least one Page containing at least one RheoWin *.rwd data file. For the spectrum calculation to work properly, the data file must contain frequency sweep data over a wide enough frequency range, see the 'Data files' chapter below.

The Spectrum dialog contains three pages: The Data and parameters page (see [Figure 7](#)), the Layout page (see [Figure 8](#)) and the Calculation page (see [Figure 9](#)), the contents of which are described below.

Figure 7. The Data and parameters page of the spectrum dialog

The screenshot shows the 'Spectrum (Dynamo)' dialog box with the 'Data and parameters' tab selected. The dialog has three tabs: 'Data and parameters', 'Layout', and 'Calculation'. The 'Data files' section contains a table with one row: 'PS680 150 C_master curve at_150,00 °C.rwd' and '150,00 °C'. The 'Spectrum type' section has a checked box for 'Calculate relaxation spectrum'. The 'Range' section has input fields for 'From' (λ 0,0101466 s <==> 0,0001404 rad/s <==> f 2,235e-05 Hz) and 'To' (λ 1424,08 s <==> 473,1 rad/s <==> f 75,29 Hz). The 'Data / Decade (3-15)' field is set to 5. There is a checkbox for 'Show confidential result only' which is unchecked. At the bottom are 'Execute' and 'Cancel' buttons.

File	
PS680 150 C_master curve at_150,00 °C.rwd	150,00 °C

Spectrum type
☒ Calculate relaxation spectrum

Range
From λ 0,0101466 s <==> 0,0001404 rad/s <==> f 2,235e-05 Hz
To λ 1424,08 s <==> 473,1 rad/s <==> f 75,29 Hz
Data / Decade (3-15) 5
☐ Show confidential result only

Execute Cancel

The data and parameters page

Data files

The RheoWin *.rwd data file from which a spectrum is to be calculated must be loaded into a DataManager page before the Spectrum dialog is opened, using the Open command from the File menu, or one of the many other methods RheoWin offers for this.

The list in the Data files box shows all the RheoWin *.rwd data files that are contained in the active DataManager page (behind the file name the Set temperature used for the data in that *.rwd data file is displayed).

Since the spectrum calculation uses the data of one RheoWin *.rwd data file (for each calculation) only, the list in the Data files box only needs to contain one *.rwd data files for the spectrum calculation to work. When the active page and therefore the list in the Data files box contains more than one RheoWin *.rwd data file, the spectrum will be calculated from the file which is selected (highlighted) in the list.

Removing a file from the list can only be performed by removing the file from the DataManager page, using the Remove command from the File menu or the toolbar, after closing the spectrum dialog.

The *.rwd data file used as input for the spectrum calculation must fulfill the following requirements:

- The *.rwd data file must contain frequency sweep data measured at one constant temperature.
- The frequency sweep data in the *.rwd data file can consist of multiple segments, i.e. the Job with which the data were measured can contain multiple frequency sweep elements.
- The *.rwd data file must NOT contain data from other kind of oscillation elements, since the spectrum calculation tool does not check the data segment types contained in the *.rwd files, it just uses all the $G'(\omega)$, $G''(\omega)$ data points that are found in the data and ignores all other data.

Spectrum type

Currently the RheoWin spectrum data analysis tool can only calculate a relaxation spectrum.

Range

The From and To parameters define over which range of relaxation times λ the spectrum is calculated. The default values are automatically calculated from the angular frequency ω range of the original frequency sweep data and normally do not need to be modified. The fields behind the λ edit-fields shows the corresponding angular frequency ω and frequency f values which are calculated using the following equations:

$$\lambda = 1/\omega \quad (8)$$

$$\omega = 2\pi f \quad (9)$$

The value in the Data/Decade edit-field defines with how many data points per decade the spectrum is calculated. The default value is 5 which is normally good enough. Sometimes it is useful to increase the value of this parameter, for example in order to get a finer description of a narrow peak in a spectrum.

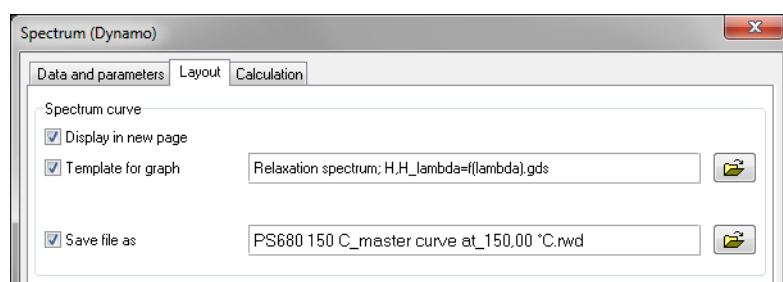
When this value is increased the time needed to calculate the spectrum will also increase: Whereas on a PC with a 3 GHz processor the calculation of a spectrum with 5 data points/decade takes approximately 1,5 seconds, the calculation of the same spectrum with 10 and 15 data point/decade, from the same data, will take around 4,5 seconds and 12 seconds, respectively. Please note that on a slower PC these calculation times can be much longer!

The Layout page

This page contains several settings which define how the calculated spectrum is displayed and in which *.rwd data file the spectrum is saved.

The settings made on this page of the dialog are automatically saved by RheoWin and restored the next time the dialog is opened.

Figure 8. The Layout page of the spectrum dialog



Spectrum curve

When the Display in new page option is active, RheoWin will display the resulting spectrum in a new DataManager page with the name Spectrum.

When the Display in new page option is not active, the relaxation spectrum data will not be shown in a separate page.

When the Template for graph option is *not* active, the new page will use the graph settings from the page which contains the original *.rwd data files. Normally this is not very useful since that page normally is not defined to show the relaxation spectrum $H(\lambda)$ and/or the weighed relaxation spectrum $\lambda \cdot H(\lambda)$.

When the Template for graph option is active, the new page will use the graph settings from the selected graph template. A proper template (for showing $H(\lambda)$ and $\lambda \cdot H(\lambda)$) is selected by default, however another template can be selected, by clicking on the file open button behind the template file name, if desired.

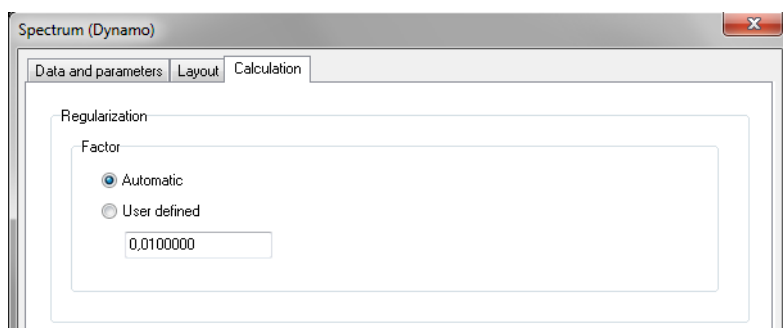
When the Save file as option is selected, the calculated relaxation spectrum data will be saved in the selected *.rwd data file. Per default the *.rwd file which contains the original frequency sweep data is selected.

When the option Save file as is not selected, the relaxation spectrum data will only be saved in a temporary file (needed for displaying the data) which is deleted as soon as the page is closed in which the data are shown.

The Calculation page

On this page contains settings which define how the spectrum is calculated.

Figure 9. The Calculation page of the spectrum dialog



Regularization

The regularization parameter controls how much the calculated spectrum will be “smoothed” (larger value) or how much detail (smaller value) will be shown.

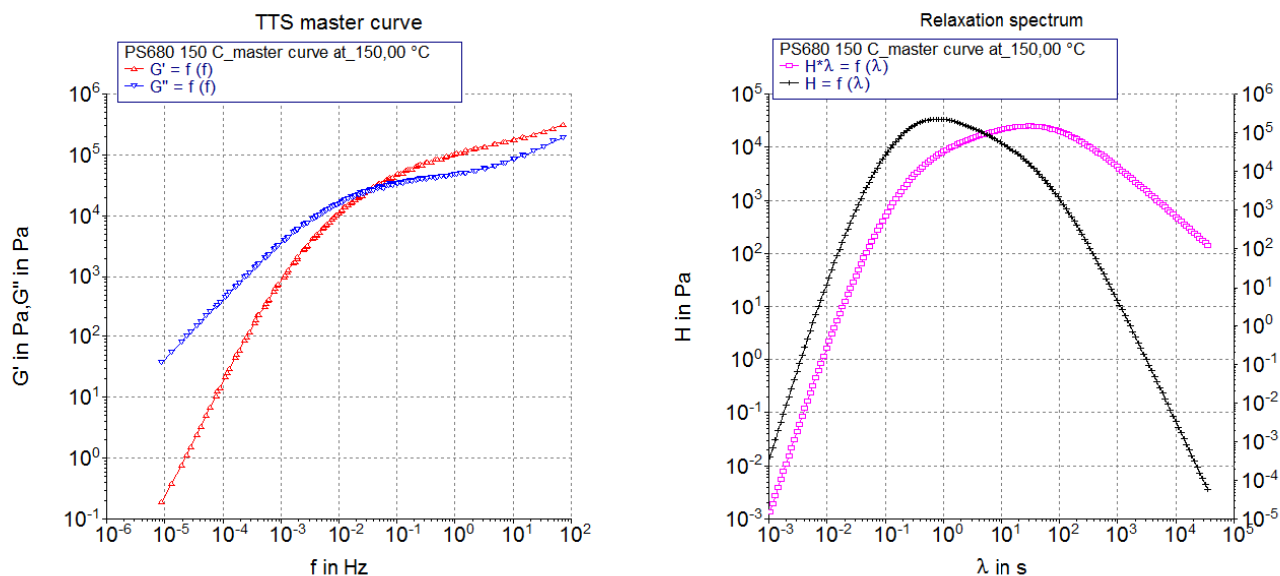
For real data, that is measured sample data, it is recommended to set the regularization factor to **Automatic** and have the algorithm decide which degree of smoothing (versus detail) is needed in order to get a spectrum that is optimally usable for a subsequent MWD calculation. Manually setting a low value for the regularization factor may result in “oscillations” in the spectrum which have nothing to do with the real data.

For simulated data, like the Maxwell model data a very small value for the regularization factor may be needed in order to see the individual modes in the spectrum, see the example in [Figure 6](#) on [page 13](#).

Starting the calculation

After all the necessary settings have been made the spectrum calculation can be started by clicking the Execute button at the bottom of the Spectrum dialog. The duration of the calculation of the spectrum depends on how many data points per decade are calculated, see above. Depending on the settings on the Layout page of the Spectrum dialog, RheoWin will open up a new page in the DataManager and display the result in that page, see above. [Figure 10](#) shows the master curve data and the spectra calculated from that master curve of a polystyrene (PS680) at 150 °C.

Figure 10. G' and G'' data (master curve) and (weighted) relaxations spectrum of a polystyrene



How it works

The spectrum calculation is performed completely automatic by the NLREG Tikhonov regularization algorithm implemented by Honerkamp and Weese⁴ at the University of Freiburg, Germany.

Judging the results of the spectrum calculation

It is often assumed that the spectrum calculated from frequency sweep or master curve data is valid between the values of the relaxation times λ that equal the reciprocal of the minimum and maximum angular frequencies of the original data. Davies and Anderson⁵ have shown in their analysis that the range of λ over which the relaxation spectrum can be reliably calculated is around 2 decades less than the frequency range of the original data. This means that the two “ends” of a relaxation spectrum should always be considered critically.

⁴ J. Honerkamp, J. Weese, A nonlinear regularization method for the calculation of relaxation spectra, *Rheology Acta* (1993), 32, 65-73.

⁵ A. Davies, R. Andersen, Sampling localization in determining the relaxation spectrum, *J. Rheol.* (1991) 35, 1035-1049.

The MWD Calculation Tool

The RheoWin MWD data analysis tool is an optional RheoWin module that allows the user to calculate a Molecular Weight Distribution (MWD) from an relaxation spectrum which was calculated from oscillation frequency sweep data or from master curve data. This chapter explains in detail how to use the RheoWin data analysis tool.

Please note that the MWD data analysis tool is *not* part of the standard RheoWin delivery content but a module which must be ordered and installed separately.

MWD calculation from rheological data

The conventional method to determine the molecular weight distribution of a polymer is Gel Permeation Chromatography (GPC), also called Size Exclusion Chromatography (SEC). This method however has some disadvantages: The polymer to be measured must be dissolved in a solvent first, the needed instrumentation is expensive, the measurement is a time-consuming procedure and the method is less sensitive for high molecular components. Accordingly determining the molecular weight distribution from rheological data can be an interesting alternative to GPC or SEC. The relationships between the molecular weight distribution and material functions that can be determined through rheology are well investigated. Powerful numerical methods have been developed, which provide a means to determine MWD from rheological measurements.

Working with the RheoWin MWD data analysis tool

The RheoWin MWD data analysis tool is available in the RheoWin DataManager only.

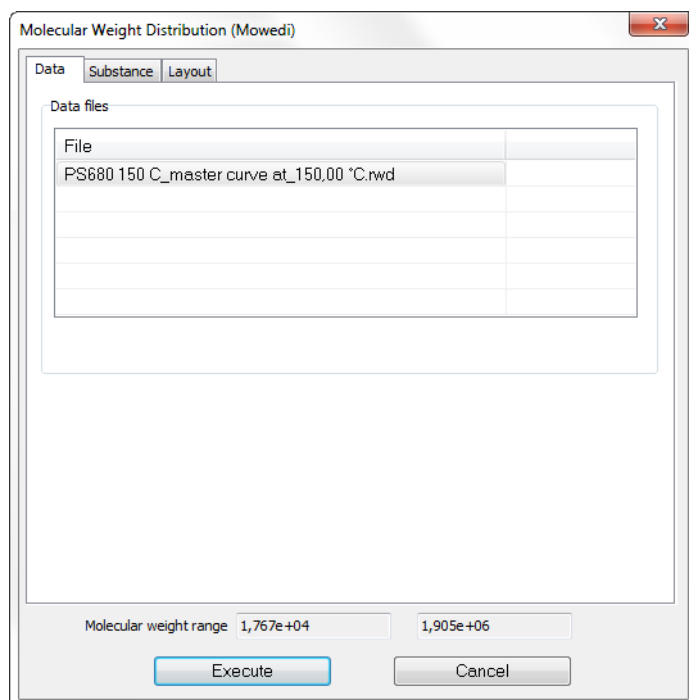
❖ To open the Molecular Weight Distribution (MWD) dialog

1. Select the **MWD** command from the Analysis menu.
- or
2. Click on the **MWD** icon in the evaluation toolbar which is by default located on the right hand side of the RheoWin DataManager program window.

The MWD dialog can only be opened when the RheoWin DataManager contains at least one Page containing at least one RheoWin *.rwd data file. For the spectrum calculation to work properly, the data file must contain spectrum data over a wide enough relaxation time range, see [“Data files.”](#)

The MWD dialog contains three pages: The Data page (see [Figure 11](#)), the Substance page (see [Figure 12](#)) and the Layout page (see [Figure 14](#)), the contents of which are described below.

Figure 11. The Data page of the MWD dialog



The Data page

From this page the operator can select from which RheoWin *.rwd data file the MWD is to be calculated.

Data files

The RheoWin *.rwd data file from which a MWD is to be calculated must be loaded into a DataManager page before the MWD dialog is opened, using the Open command from the File menu, or one of the many other methods RheoWin offers for this.

The list in the Data files box shows all the RheoWin *.rwd data files that are contained in the active DataManager page.

Since the MWD calculation uses the data of one RheoWin *.rwd data file (for each calculation) only, the list in the Data files box only needs to contain one *.rwd data files for the MWD calculation to work. When the active page and therefore the list in the Data files box contains more than one RheoWin *.rwd data file, the MWD will be calculated from the file which is selected (highlighted) in the list.

Removing a file from the list can only be performed by removing the file from the DataManager page, using the Remove command from the File menu or the toolbar, after closing the MWD dialog.

The *.rwd data file used as input for the MWD calculation must fulfill the following requirements:

- The *.rwd data file must contain spectrum data (calculated by the RheoWin Spectrum tool).

Molecular weight range

The Molecular weight range values at the bottom of the page give a rough estimation of the range of molecular weight values that will be covered by the result of the calculation, based on the currently selected material parameters.

The Substance page

The MWD calculation from rheological data needs certain input parameters for the resulting MWD data to be correct. The RheoWin MWD module contains a database for the most common polymers which lists these parameters.

Current material

In the Current material area the parameters of the material, which was last selected from the database table, are displayed. If necessary these parameters can be edited in the corresponding edit fields (in the Current materials area) and then be used for a subsequent MWD calculation. To restore the original parameter values select the material from the database list again.

Figure 12. The Substance page of the MWD dialog

Molecular Weight Distribution (Mowdi)

Substance tab

Current material

Material: PS Front factor: 7,940e-18

Density: 1000, kg/m³ Relax. time exponent: 3,400

Temperature: 159,9 °C

Database

Material	Density[kg/m³]	Temperature[°C]	Front factor	Relax. time exponent
PETFE	1000,	279,9	1,080e-21	3,400
PIB	1000,	149,9	2,200e-20	3,430
PMMA	1000,	219,9	1,000e-19	3,400
PP	1000,	184,9	5,120e-23	3,770
PS	1000,	159,9	7,940e-18	3,400
PS	1000,	149,9	1,400e-17	3,380
PTFE	1000,	379,9	3,160e-20	3,400
PTFE	1000,	369,9	2,140e-19	2,940
PVDF	1000,	100,0	4,630e-19	3,400

Sort & Save

Molecular weight range: 1,767e+04 1,905e+06

Execute Cancel

Database

In the table in the Database area the parameters of 16 different polymers are listed, see [Figure 13](#).

Figure 13. List of polymer materials with parameter values

Material	Density[kg/m³]	Temperature[°C]	Front factor	Relax. time exp
EP	1000,	99,85	5,500e-20	3,480
FEP	1000,	339,9	2,770e-19	2,940
HDPE	1000,	159,9	3,580e-20	3,420
HDPE	1000,	189,9	3,520e-21	3,600
LLDPE	1000,	219,9	6,750e-22	3,670
PA12	1000,	199,9	1,250e-18	3,550
PDMS	1000,	20,00	4,280e-21	3,400
PETFE	1000,	279,9	1,080e-21	3,400
PIB	1000,	149,9	2,200e-20	3,430
PMMA	1000,	219,9	1,000e-19	3,400
PP	1000,	184,9	5,120e-23	3,770
PS	1000,	149,9	1,400e-17	3,380
PS	1000,	159,9	7,940e-18	3,400
PTFE	1000,	369,9	2,140e-19	2,940
PTFE	1000,	379,9	3,160e-20	3,400
PVDF	1000,	199,9	4,630e-19	3,400

❖ **To select a material from the database**

1. Click in anywhere in a row in the table to select the material in that row and display the name and parameters of that material in the **Current material** area above the table.

❖ **To edit a materials parameter value in the database**

1. Click in the corresponding table cell to highlight the parameter value.
2. Enter the new value directly in the selected table cell.
3. Save the changed value(s) by clicking the **Sort & Save** button below the table.

❖ **To add a material to the database**

1. In the table scroll down until the last empty row is visible.
2. Enter the name and the four material parameter values in the corresponding table cells.
3. Save the new materials parameter values by clicking the **Sort & Save** button below the table.

The new material will be inserted in the table such that the table is sorted alphabetically.

❖ **To remove a material from the database**

1. Click in the corresponding table row and delete the contents of *all five* table cells.
2. Save the changes by clicking the **Sort & Save** button below the table.

Density

The density of the material at the measured (or master curve temperature). For correct results this value must be edited.

Temperature

The temperature for which the listed Front factor value was defined.

Front factor

The Front factor is a calibration factor for the MWD calculation.

When the MWD calculation is performed using the spectrum data calculated from a master curve which was created using the RheoWin TTS tool, the temperature value listed for the material in the table must not be equal to the temperature the spectrum data (that is the master curve data) was calculated for. In this case the MWD tool will automatically adapt the Front factor value to the correct value as long as the listed temperature is inside the temperature range at which the original $G'(\omega)$, $G''(\omega)$ data (used create the master curve data) were measured.

Relaxation time exponent

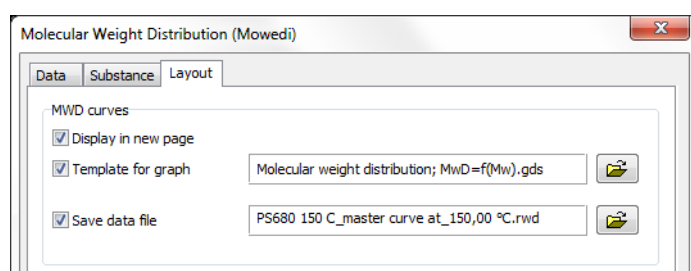
The Relaxation time exponent value, as found in the literature, for the polymer material in question. This value is temperature independent.

The Layout page

This page contains several settings which define how the calculated MWD data is displayed and in which *.rwd data file the MWD data is saved.

The settings made on this page of the dialog are automatically saved by RheoWin and restored the next time the dialog is opened.

Figure 14. The Layout page of the MWD dialog



Display in new page

When the Display in new page option is active, RheoWin will display the resulting MWD in a new DataManager page with the name MWD.

When the Display in new page option is not active, the MWD data will not be shown in a separate page.

Template for graph

When the Template for graph option is *not* active, the new page will use the graph settings from the page which contains the original *.rwd data files. Normally this is not very useful since that page normally is not defined to show the MWD(Mw) data.

When the Template for graph option is active, the new page will use the graph settings from the selected graph template. A proper template (for showing MWD(Mw)) is selected by default, however another template can be selected, by clicking on the file open button behind the template file name, if desired.

Save data file

When the Save data file option is selected, the calculated MWD data will be saved in the selected *.rwd data file. Per default the *.rwd file which contains the original spectrum data is selected.

When the option Save data file is not selected, the MWD data will only be saved in a temporary file (needed for displaying the data) which is deleted as soon as the page is closed in which the data are shown.

MWD calculation

❖ To calculate a Molecular Weight Distribution (MWD)

1. Open a RheoWin *.rwd data file, which contains Spectrum data, in a DataManager page.

Any spectrum data can be used, however the preferred method is to use spectrum data calculated using the RheoWin Spectrum tool from a master curve which was calculated using the RheoWin TTS tool.

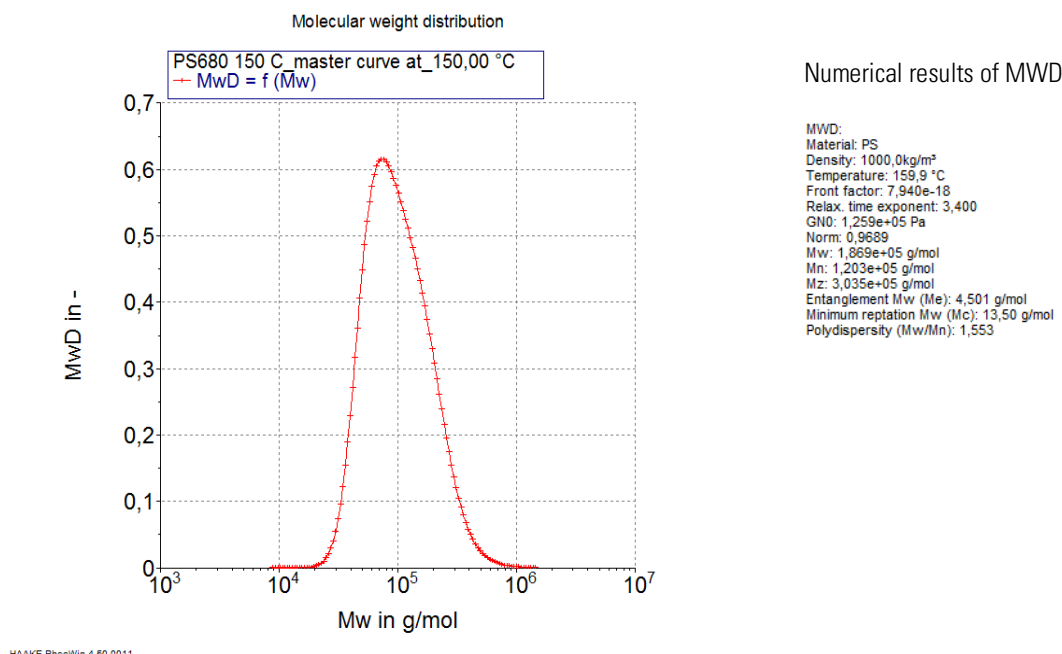
2. Open the **MWD** dialog.
3. Select the correct, matching, polymer material from the **Database** table.
4. Click the **Execute** button.

The MWD data, see [Figure 15](#), will now be calculated and the results displayed as defined on the Layout page of the MWD dialog.

MWD calculation results

The result of the MWD calculation consists of the MWD graph and the numerical results (see [Figure 15](#)), which are displayed in the information area at the right hand side of the graph and/or table.

Figure 15. MWD curve of a polystyrene plus numerical results



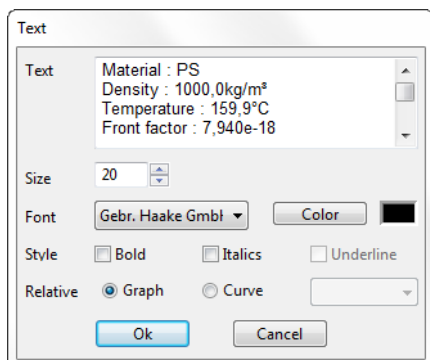
The numerical results can conveniently be added to the graph, see the following procedure.

❖ To add the numerical results to the graph

1. Right click on the graph and select the **Add clipboard text** command from the pop-up menu.

The numerical results are then displayed in the **Text** pop-up dialog, see [Figure 16](#).

Figure 16. Text popup-dialog with MWD results



2. In the Text dialog select the settings (color, font, style, etc.) for the text, and click **Ok**.
3. Position the numerical text on the graph by moving it, using the mouse.

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The RheoWin spectrum and MWD data analysis tools use routines from the open source libraries OpenBLAS, NNLS and Minpack. See below for the license agreements for these open source software libraries.

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