A Brief Introduction to Time-Temperature Superposition Principle

The linear viscoelastic properties of polymers are dependent on both time and temperature. A thorough description of the theories behind the inter-relationship of time and temperature is beyond the scope of this tutorial. In general, however, the relaxation process of a polymer at a particular temperature will be enhanced at elevated temperatures, i.e. the relaxation times will be shorter at any higher temperature. In essence, the time-temperature superposition principle assumes that by changing the temperature, the complete relaxation spectrum is affected by the same degree. Hence, increasing the temperature shortens all relaxation times by the same factor. There are some empirical relationships that deal with the dependence of the enhancement or slowing down of the relaxation processes on the change in temperature. One should note that not all materials obey the time-temperature superposition principle. The polymers that do obey are referred to as thermo-rheologically simple materials.

Usually, rheological measurements are made such that either the temperature or the frequency/time is held constant while the other parameter is varied. In the case of oscillation experiments in which the temperature is held constant and the frequency or time is varied, the data spans over a two to four decade range in frequency/time. By repeating such tests over a number of temperatures, one obtains a set of isothermal dependencies of, say, storage modulus ($E'$) or loss modulus ($E''$) in shear versus frequency, $\omega$. If the material is thermo-rheologically simple, then one can shift any of the linear viscoelastic parameters, e.g. $E'$, $E''$, $\eta'$, $\eta''$, or $G(t)$, $J(t)$, etc., along the time/frequency axis such that they are superimposed on one another to generate a master curve at a particular temperature.
So, time-temperature superposition (TTS) makes it possible to characterize the viscoelastic properties of materials at various temperatures over an experimentally convenient time or frequency range. The curve shifting procedure creates a master curve that represents the time response of a material over a wide range of times/frequencies at a particular reference temperature. TTS can be used to obtain master curves from creep, stress relaxation and oscillations experiments. This tutorial highlights the use of TTS for data obtained from oscillatory experiments in tension.

Programming a TTS Experiment on the DMA 2980

It is necessary to ascertain what one would like to accomplish using TTS. Usually, the material under consideration will have a use temperature (or a range thereof), and an understanding of its properties at different time scales at this temperature is desired. A reference temperature, $T_r$, is selected based on the use temperature and the data at other temperatures is shifted to this reference temperature. To obtain information at higher frequencies or shorter times, frequency scans (stress relaxation or creep) should be performed at temperatures lower than $T_r$. To obtain information at lower frequencies or longer times, frequency scans have to be performed at temperatures higher than $T_r$. For example, to get a description of PET for room temperature application over very long time scales, one should perform frequency sweeps within the temperature range of, say, 25°C to 200°C, and then pick 25°C as the reference temperature.

A good starting point is to perform a temperature scan of the material at a single frequency to get an idea of the modulus–temperature and transition behavior. This provides a basis for the temperature range to be covered on the DMA 2980 relative to the reference temperature.

Test Parameters

To run any TTS experiment with the Thermal Advantage NT software, first the clamp type and the program mode must be selected. This is done by either clicking on Experimental Mode... or going to

One may select any one of the following modes for experimentation for TTS and then click OK:

- DMA Multi-Frequency
- DMA Creep
- DMA Stress Relaxation

The film tension clamp has been selected in this example.
There are procedure templates for TTS experiments in the Thermal Advantage software. Based on the mode selected, one should select the appropriate procedure on the Summary page, as shown below:

After selecting the procedure, click on...
Now, the user has to enter the test parameters in the Procedure page, which is shown below in Fig. 3. Since TTS relies on linear viscoelastic information, it is important to select an amplitude such that the deformation is in the linear regime. A good rule of thumb is that polymeric solids are linear up to 0.1% strain (or 0.001 strain units). A strain lower than 0.1% is preferable. To calculate the amplitude that translates to the required strain, please refer to Chapter 6 of the DMA 2980 Operators Manual.

Next, enter values in the fields for Start temperature, which is usually the lowest temperature, and the Final temperature, i.e., the highest temperature to run the frequency sweeps/creep/stress relaxation. A Temperature increment of 5°C is usually a well-sized step to get good overlapping in the various frequency scans. Refer to the “DMA 2980 Getting Started Guide” for preload force and force track information, if needed. For most materials and sample dimensions, an Isothermal soak time of 5 minutes is usually enough for homogeneous temperature distribution within the sample. When all the parameters have been entered, click on Apply.

Clicking on Advanced in the procedure page brings up the following window:

The data sampling interval should be set to 2 sec/pt for TTS experiments.

† For a detailed discussion of the linear viscoelastic region, see DMA 2980 Getting Started Guide.

Fig. 3. Screen capture of the Procedure page in Thermal Advantage NT.

Fig. 4. Screen capture of the Advanced setting window. The data sampling interval should be set to 2.0 sec/pt.
Again, on the procedure page, the post-test conditions can be set by clicking on the Post Test button which brings up the following window:

![Post Test settings window](image)

Fig. 5. Screen capture of the Post Test settings window. The data sampling interval should be set to 2.0 sec/pt.

These parameters control the state of the DMA 2980 after the experiment has concluded. To bring the system back to room temperature after the test is completed, enter the appropriate values in Return to temperature range fields as shown above. One may choose to keep the furnace open or closed after the experiment by selecting the appropriate radio button, as shown above. It should be noted that while the oven is closed, the instrument tries to maintain the range of temperatures. This could lead to unnecessary loss of cooling liquid. To allow the relaxation of any stresses that may be built up in the sample during the rapid cool-down, the clamp may be left in Float mode. When repeating a number of tests one after another, check the GCA Autofill box for convenience.

**Creating the Frequency Table**

The set of frequency values at which the material will be tested must be evenly spaced over a log scale because viscoelastic data is interpreted on a log-log scale. Also, individual sweeps have to be performed with a wide enough range in frequencies so that there is ample overlap between the sweep data at different temperatures. Usually, a 3 decade span between the lowest and the highest frequencies and a temperature increment of 5°C will lead to sufficient overlap in the data. Press the “Frequency Table” tab on the procedure screen to get to the following screen:
Select the Log radio button and enter the frequency range. A frequency range of 100 to 0.1 Hz is adequate for any TTS experiment. Gathering data at frequencies below 0.1 Hz will greatly lengthen the time of the experiment. For the field for Points Per Decade field, a value of 5 is standard for most applications. In this example, three decades of frequencies are programmed (100 to 10, 10 to 1 and 1 to 0.1 Hz) at 5 points per decade. These parameters will yield 15 points in each frequency sweep. When selecting the frequency range and points per decade parameters, values must be chosen such that the total number of frequencies to be scanned does not exceed 28. One can also enter a discrete set of frequencies.

The lower the frequency, the longer are the times required for measurement. Hence, the total duration of the test will be dominated by the time taken to measure low frequency values. For this reason, it is recommended that the range of frequencies be programmed starting with the highest frequency and decreased to end with the lowest one.

Viewing and Shifting Data

This section deals with viewing multiplexed data generated by the DMA 2980 using Universal Analysis NT and shifting the data using the TTS Data Package. The example that follows uses a demonstration file that comes with Universal Analysis NT, called Dma-pet.001 in the C:\TA\data\DMA directory.

Viewing Data in Universal Analysis NT

The raw data are typically viewed as frequency scans at different temperatures or as temperature scans at different frequencies using Universal Analysis NT. Examples of both scenarios are shown here. Once the file C:\TA\Data\DMA\Dma-pet.001 has been selected, the following window enables one to select the signals
and their axes.

Fig. 7. Screen capture of the opening of a data file in Universal Analysis NT.

Click on **Signals** to bring up the following window and select the signals that need to be assigned to the different axes.

Fig. 8. Assigning signals to different axes in Universal Advantage NT.

Selecting Frequency as the X signal brings up the following screen (Fig. 8). Figure 9 shows the scenario in which temperature is plotted on the X axis.
Convert the DMA 2980 Data File to TTS Format

Once the data are plotted as shown above, the file has to be exported in text format prior to shifting. To convert the file to the required text format, select the following from the file menu:

File _ Export Data File _ TTS Signals
This is shown in the illustration below:

**Fig. 11.** Screen capture of exporting the TTS Signals from Universal Analysis NT.

This will bring up the the window shown below in Fig. 8. All the signals are selected by default. Upon selecting the output signals to be exported, click on

**Fig. 12.** Screen capture of the selection window for the signals to be exported.

This brings up the following window, in which, a new filename may be entered. The program automatically assigns a ‘.txt’ extension to the filename.
When the desired name has been entered in the File name field, click on Save.

**Shifting the TTS Data**

Start the *TTS Data Analysis* package. This is found in the Windows® Start menu as shown below:

Once *TTS Data Analysis* is running, open the text file that was created using Universal Analysis using

File _ Open
Fig. 15. Opening the TTS signals text file.

Plot the graph by clicking on the “To New Graph” button, or by the following:

Right Click on the file _ To New Graph

This is shown below:

Fig. 16. Right-click on the file Dma-pet.txt and select "To New Graph" to plot the graph.

If the data are generated by the DMA 2980 using tension, compression, or bending clamps, then the moduli will be denoted by the letter “E”. If the data are generated using the shear sandwich clamp, then the moduli are denoted by the letter “G”. Data Analysis must be set up for the correct type of modulus to be shifted. This is done by the following steps:

Graph _ Miscellaneous
Fig. 17. Changing the modulus type in TTS Data Analysis. Change the modulus type (Oscillation labels) using the pull-down selector at the bottom of the Graph Miscellaneous window.

The x-axis variable must be set to Frequency or Angular Frequency. To select the graph variables, use the following sequence:

Graph _ Change Variables

This brings up the following window, in which the desired x- and y-axes variables can be selected:

With Frequency on the x-axis and $E'$, storage modulus, as the y-axis variable, the graph should look like the following:
Fig. 19. Graph of TTS Data before shifting.

Note that the frequency range is 0.1 to 20 Hz. It is not recommended that the graph key be displayed because in most cases, it obstructs the view of the graph. The graph key can be hidden by going into:

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Graph _ Key
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or by pressing lower, and then, unchecking the “Displayed” option in the following window:

![Graph Properties window](image)

Uncheck this
Now, the TTS session has to be started by

TTS _ Begin Session

Once this is done, the greyed-out items under the TTS menu will become activated. The next step is to select a reference temperature. By selecting a reference curve, one essentially chooses a frequency scan at the temperature of interest. The curve that is selected will remain unchanged, while all the other curves will be shifted relative to the reference curve. The frequency scan curves at temperatures higher than the reference temperature will shift to the left along the frequency axis, i.e., they will shift to lower frequencies or longer times. The lower temperature data will shift to the right of the reference curve (higher frequencies or shorter times). To select the reference curve, press button, or go to

TTS _ Set Reference Curve

This will bring up the following window in which, one can simply select the reference temperature (75°C in this example) and click the button.

Now that the reference temperature is selected, the curves can be shifted. To do this, click on , or go to

TTS _ Shift Curves

The software will automatically move the curves relative to the reference curve, as shown below in Fig 21. The extended frequency range obtained by the TTS method is $10^{-11}$ to $10^{18}$ Hz, an astounding 33 decade range! Hence, at 75°C, one is able to ascertain the behavior of the PET sample at very short times (or high frequencies) and very long times (or low frequencies). This clearly demonstrates the power of the TTS method.
Note that we have not generated a master curve or saved any shifting information so far. In order to save the results so that it can be used later, one must create a master curve. The procedure for doing this is described in a later section.

The individual frequency scans can be manually dragged and shifted to fine-tune the master curve as per one's liking. To do this, left-click on the frequency scan of choice in the graph, and keeping the mouse button pressed, drag the single scan to the left or right and release. In fact, for this example, the lowest temperature scan was shifted manually.

**Analysis using WLF/Arrhenius Models**

The amount of shift of a frequency scan that is associated with a particular temperature will be different from that of a frequency scan associated with any other temperature\(^{1}\). Therefore, for every temperature, there is a certain characteristic shift-factor. There are some mathematical models that relate the temperatures to the respective shift-factors. The William-Landel-Ferry (WLF) equation is usually valid for materials from temperatures below \(T_g\) up to about \(T_g+100^\circ\text{C}\) [3]. Beyond this, an Arrhenius model is better suited.

When the TTS session is first begun, the software adds a file to the results file frame on the left. This file is usually called **Graph** and it contains the shift factor versus temperature information. After performing the curve-shifting, one can click on the **Graph** file and, using the \(\text{[LT+]}\) key, make a new graph of this data. It is a good idea to assess how well the data shifted by looking at the shift-factor versus temperature data and how well a model was able to fit it. For our example, the shift factor versus temperature curve looks like the following:

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\(^{1}\) See references if unfamiliar with shift-factor concepts.
The WLF model will be used for fitting the above data because the test temperatures are within the sub-$T_g$ to $T_g + 100^\circ$C range. To select the model on the software, go to

**Analysis _ Model…**

This will bring up the following window, in which one can select the WLF model from the list, and click **OK**.

The next step is to select the range of data points to analyze. This can be done by

**Analysis _ Limits**

which will bring up the window shown below. In this example, we have opted to include all the data points, and hence, the “Whole Curve” option has been selected. One can select a limited range over which to fit any model by unchecking the “Whole Curve” option and entering the data limits on the temperature scale.
All that remains is to start the fitting session by going to

Analysis → Go

This begins the fitting procedure using the WLF model and, when done, adds the fit to the graph, as shown below. The graph is also annotated with the fit parameters characteristic to the WLF equation, namely, \( C_1 \) and \( C_2 \), and the standard error. The standard error of the fit is a good measure of the validity of the fit. Determination of acceptable values of standard error is up to the user’s discretion. It is recommended that the standard error be less than 20 for a good fit. One should note that in some cases, the Arrhenius model may be more applicable in fitting the data, in which case, the standard error will be high if one tries to fit the WLF model. If the material is not thermorheologically simple at all temperatures, one may observe a high standard error.
Generating the Master Curve

The purpose of generating a master curve is to put the data in a usable format. Once the master curve has been generated, all the data that existed as a fragmented composite of individual frequency scans will be merged into a single file. To create a master curve, one should first display the graph with the shifted frequency sweeps from the Window menu. Then, by following the steps below, the master curve is generated:

TTS _ Generate Master Curve

The software adds this master curve as a new file in the list of opened files. This filename of the master curve will be the same as the original text file, but with a “tts” suffix added. In our example, the filename is \textit{Dma-pet-txt tts}. To save the master curve, one should select the file using the mouse and perform

File _ Save (or Save As…)

The file will be saved with the extension \texttt{.rsl}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figures/figure27.jpg}
\caption{The final $E'$ master curve at $T_r = 75\, ^\circ\text{C}$.}
\end{figure}
References

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