Master Curve MATLAB Program
User Guide

by Daniel Burkat

Table of Contents

Introduction

The MCR302 rheometer is used to acquire elasticity modulus vs. frequency data of polymer samples. The range of measurements is limited by the rheometer, high and low frequencies cannot be measured due to low accuracy and inconvenience respectively. The technique of time-temperature superposition can be used to shift the modulus curves along the frequency (or time) axis to extend the measurement range and create a master curve. The master curve provides important information about the behavior of the material at fast deformation rates. In our laboratory, the master curves for polyvinyl chloride (PVC) plasticized with different plasticizers will be compared. Anton Paar provides a software that can be purchased to do the data analysis and generate the master curve. However, due to cost restrictions I was tasked to write an algorithm that can produce these master curves in MATLAB. The resulting algorithm was packaged in a user interface that also provides data management.

NOTE: This user interface was built to work on Windows operating systems. It was not tested on other operating systems.

The Algorithm

The algorithm aims to produce the time-temperature superposition by shifting adjacent curves horizontally to the position of best overlap. The best overlap is determined by a method of least squares. The algorithm is separated into 11 steps illustrated by Figure 1.

1. Import the data into program workspace and preprocess to make sure it is formatted appropriately.
2. Apply the vertical shift factor to every data series.
3. Start at the curve with the lowest temperature, call it the Upper Curve (UC). The lowest temperature curve is the one with the highest storage modulus.
4. Chose the curve at the temperature just above UC to be the Lower Curve (LC).
5. Set these curves side by side and identify the Overlap Window (OW). This is the interval on the y axis shared by both UC and LC as shown in Figure 2.
6. Separate the OW into 21 equidistance points, and use Lagrange interpolation to interpolate point on the UC and LC, see Figure 3.
7. Identify point of first overlap, this is the minimum horizontal distance between the UC and LC. Identify the point of last overlap, this is the max distance between UC and LC.
8. Set the first shift value to minimum distance, last shift value to max distance, and divide this interval into 101 points. Iterate over interval and calculate sum of square errors between the 21 points.
9. Best fit value is the one with minimum sum square error, see Figure 4.
10. Set UC = LC, if there is a curve below UC go to step 4.
11. Assemble the curve and exit.

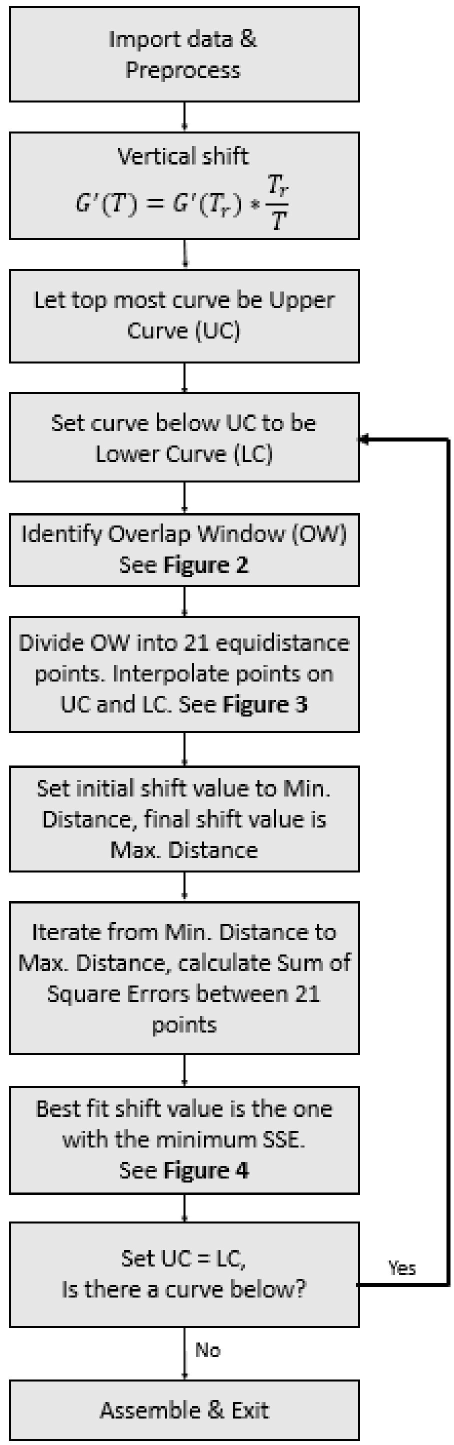


Figure 1. The time temperature superposition algorithm

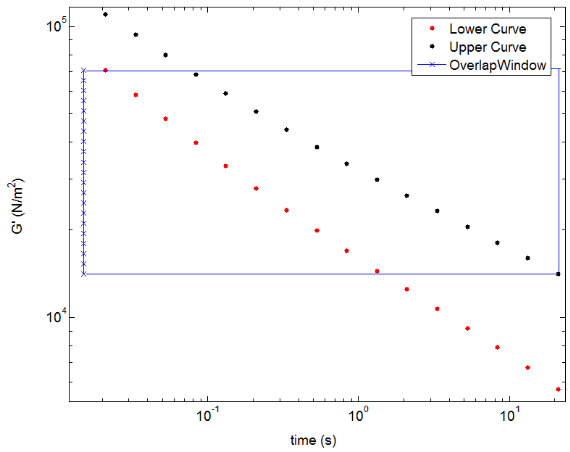


Figure 2. Identification of the overlap window

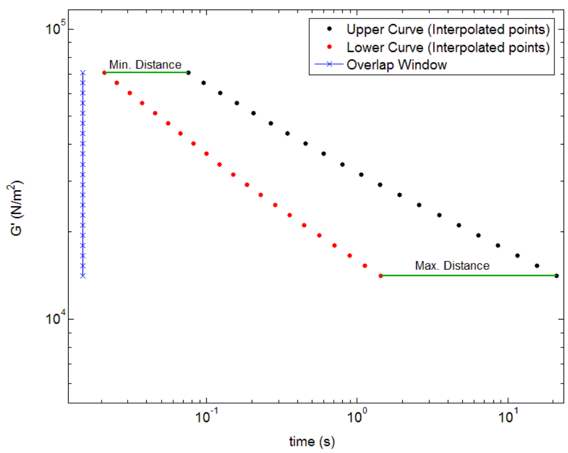


Figure 3. Interpolated points on UC and LC in overlap window

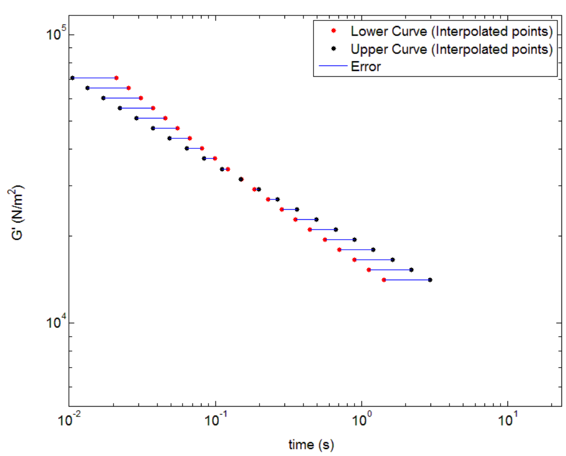


Figure 4. Best fit based on minimum error between interpolated points of UC and LC

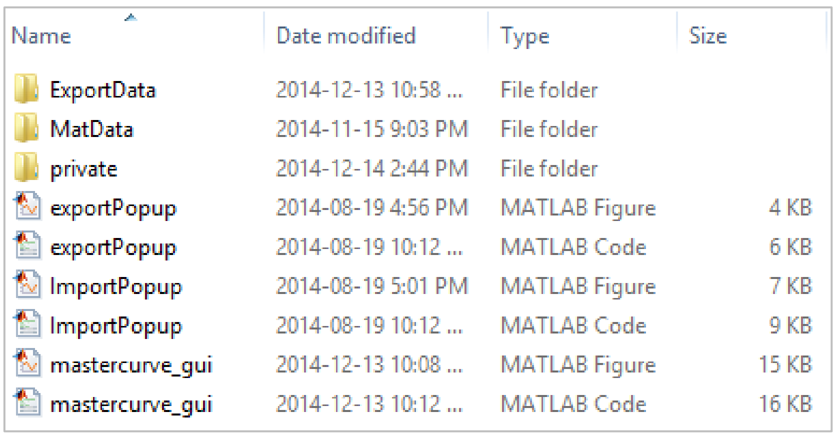
Install

Decompress the zipped folder 'MasterCurveProject' and move the unzipped folder into your 'MATLAB' folder, usually located in your 'Documents' folder. An example of the file path would be **This_PC/Documents/MATLAB/MasterCurveProject**.

Folders and Files

Folder structure

Open the folder and note the arrangement of the files and folders. The file structure is very important in the MasterCurveProject. **DO NOT CHANGE IT**. The structure of the folder is shown in Figure 5 .



Name	Date modified	Type	Size
ExportData	2014-12-13 10:58 ...	File folder	
MatData	2014-11-15 9:03 PM	File folder	
private	2014-12-14 2:44 PM	File folder	
exportPopup	2014-08-19 4:56 PM	MATLAB Figure	4 KB
exportPopup	2014-08-19 10:12 ...	MATLAB Code	6 KB
ImportPopup	2014-08-19 5:01 PM	MATLAB Figure	7 KB
ImportPopup	2014-08-19 10:12 ...	MATLAB Code	9 KB
mastercurve_gui	2014-12-13 10:08 ...	MATLAB Figure	15 KB
mastercurve_gui	2014-12-13 10:12 ...	MATLAB Code	16 KB

Figure 5. Files in MasterCurveProject folder

ExportData

The data export function creates excel files and writes to them when the user requests it from the program. The program will place the excel files into the 'ExportData' folder.

MatData

The program makes it possible to save processed data in a convenient way. The MATLAB workspace saving function is used to create dot-mat files that contain the data that was in the program. When the user saves a file, it is recommended to choose the 'MatData' folder to contain the dot-mat files. This will make it easier to locate and open saved sessions.

private

The files in a private folder are only visible to the folder above in the MATLAB file structure. This means that the code contained within the private folder can only be accessed by the MATLAB dot-m files in the folder right above (in this case the 'MasterCurveProject' folder), or dot-m files in the same private folder. The private folder contains all code that is not a part of the **User Interface (UI)**. It is recommended to not change the code in the private folder unless you really know what you are doing.

exportPopup

There are two files with the name exportPopup. The dot-fig file is the figure that appears on screen when the user wants to export the data to excel. The dot-m file contains the code that controls the response of the figure to the user's requests.

ImportPopup

There are two files with the name ImportPopup. The dot-fig file is the figure that appears on screen when the user wants to import rheometer data into the UI. The dot-m file contains the code that controls the response of the figure to the user's requests.

mastercurve_gui

There are two files with the name mastercurve_gui. The dot-fig file is the figure that appears on the screen when the master curve program is run. The dot-m files contain the control of the program. Meaning from this code all other pieces of code are called when needed.

Preparing Rheometer Data

Raw data example

Raw data that is outputted from the MCR302 for the frequency sweep experiment at one temperature in an excel table as seen on Figure 6. The frequency sweep is ran at several temperatures so it results in a lot of information. For this program there are only two columns of each temperature value that are of importance, the angular frequency and the storage modulus.

Data Series Information								
Name:			DEHP_40phr_Roya_120 °C 1					
Sample:			DEHP_40phr					
Operator:			Roya					
Remarks:			TTS freq sweep					
Number of Intervals:			1					
Application:			RHEOPLUS/32 V3.61 21006127-33056					
Device:			MCR302 SN81122530; FW3.65; Slot(1,-1)					
Measuring Date/Time:			17/06/2013; 3:46 PM					
Measuring System:			PP25-SN27491; [d=1 mm]					
Accessories:			TU1=CTD450L+R+L-PP-SN81082407-0-17713641					
Calculating Constants:								
- Norm. Csr [min/s]:			1.3076251					
- Norm. Css [Pa/mNm]:			326.97626					
- Start Delay Time [s]:			453.743					
- Substance Density [rho]:			1,000					
- Measurement Type:			1					
- Axial Compliance [m/N]:			1.00E-06					
- Position [m]:			1.00E-06					
Interval:			1					
Number of Data Points:			16					
Time Setting:			16 Meas. Pts.					
Measuring Profile:								
#NAME?			Amplitude gamma = 10 %					
			Angular Frequency omega = 300 ... 0.3 rad/s log					
Meas. Pts.	Angular Freque	Storage Modulu	Loss Modulu	Damping Fact	Complex Viscos	Deflection Angle	Torque	Status
	[1/s]	[Pa]	[Pa]	[1]	[Pa·s]	[mrad]	[µNm]	[]
1	300	2.00E+05	8.28E+04	0.413	7.23E+02	7.99E+00	6.62E+04	DSO
2	189	1.79E+05	7.33E+04	0.41	1.02E+03	7.98E+00	5.89E+04	DSO
3	119	1.60E+05	6.47E+04	0.405	1.44E+03	7.97E+00	5.24E+04	DSO
4	75.4	1.43E+05	5.74E+04	0.402	2.04E+03	8.01E+00	4.70E+04	DSO
5	47.5	1.29E+05	4.94E+04	0.383	2.91E+03	8.02E+00	4.23E+04	DSO
6	30	1.17E+05	4.30E+04	0.368	4.15E+03	8.01E+00	3.81E+04	DSO
7	18.9	1.06E+05	3.75E+04	0.353	5.95E+03	8.01E+00	3.45E+04	DSO
8	11.9	9.73E+04	3.28E+04	0.337	8.60E+03	8.01E+00	3.14E+04	DSO
9	7.54	8.95E+04	2.88E+04	0.322	1.25E+04	8.01E+00	2.88E+04	DSO
10	4.75	8.28E+04	2.56E+04	0.309	1.82E+04	8.01E+00	2.65E+04	DSO
11	3	7.69E+04	2.31E+04	0.301	2.68E+04	8.01E+00	2.46E+04	DSO
12	1.89	7.17E+04	2.13E+04	0.297	3.95E+04	8.01E+00	2.29E+04	DSO
13	1.19	6.70E+04	2.01E+04	0.3	5.85E+04	8.01E+00	2.14E+04	DSO
14	0.754	6.25E+04	1.95E+04	0.311	8.69E+04	8.01E+00	2.00E+04	DSO
15	0.475	5.83E+04	1.93E+04	0.332	1.29E+05	8.01E+00	1.88E+04	DSO
16	0.3	5.40E+04	1.96E+04	0.363	1.92E+05	8.01E+00	1.76E+04	DSO

Figure 6. The data outputted by the MCR302. In the red rectangles there is the data of interest for this program, the angular frequency and the storage modulus

Formatting Raw Data for the Program

To successfully import the data into the program there is need to arrange it in a specific way. I suggest doing it in 3 steps.

1. Place the important data into an excel sheet in the format show in Figure 8. The order is easy to follow, the column header should start at the lowest temperature value and increasing to the right, and then the last row is the common frequency x-axis. For example, if the data is in an excel spreadsheet and the lowest temperature is 110^{o}C and the max is 200^{o}C.

100	110	120	130	140	150	160	170	180	190	200	Freq
3.61E+05	2.69E+05	2.00E+05	1.52E+05	1.17E+05	8.26E+04	5.12E+04	3.03E+04	1.80E+04	1.06E+04	6.51E+03	3.00E+02
3.33E+05	2.45E+05	1.79E+05	1.33E+05	1.01E+05	6.14E+04	4.09E+04	2.30E+04	1.30E+04	7.46E+03	4.57E+03	1.89E+02
3.09E+05	2.23E+05	1.60E+05	1.17E+05	8.69E+04	5.84E+04	3.30E+04	1.69E+04	9.41E+03	5.22E+03	3.18E+03	1.19E+02
2.88E+05	2.04E+05	1.43E+05	1.02E+05	7.39E+04	4.92E+04	2.66E+04	1.33E+04	6.79E+03	3.64E+03	2.22E+03	7.54E+01
2.69E+05	1.88E+05	1.29E+05	9.09E+04	6.58E+04	4.20E+04	2.17E+04	1.02E+04	4.98E+03	2.58E+03	1.55E+03	4.75E+01
2.52E+05	1.73E+05	1.17E+05	8.09E+04	5.78E+04	3.61E+04	1.79E+04	7.95E+03	3.68E+03	1.84E+03	1.11E+03	3.00E+01
2.37E+05	1.61E+05	1.06E+05	7.25E+04	5.12E+04	3.13E+04	1.49E+04	6.28E+03	2.75E+03	1.33E+03	8.02E+02	1.89E+01
2.24E+05	1.50E+05	9.73E+04	6.54E+04	4.57E+04	2.74E+04	1.26E+04	5.04E+03	2.08E+03	9.66E+02	5.84E+02	1.19E+01
2.12E+05	1.40E+05	8.95E+04	5.93E+04	4.11E+04	2.42E+04	1.08E+04	4.10E+03	1.59E+03	7.09E+02	4.29E+02	7.54E+00
2.01E+05	1.31E+05	8.28E+04	5.42E+04	3.72E+04	2.17E+04	9.41E+03	3.38E+03	1.23E+03	5.24E+02	3.18E+02	4.75E+00
1.92E+05	1.24E+05	7.69E+04	4.99E+04	3.40E+04	1.95E+04	8.28E+03	2.83E+03	9.57E+02	3.89E+02	2.37E+02	3.00E+00
1.82E+05	1.16E+05	7.17E+04	4.61E+04	3.12E+04	1.77E+04	7.35E+03	2.39E+03	7.50E+02	2.89E+02	1.78E+02	1.89E+00
1.73E+05	1.10E+05	6.70E+04	4.28E+04	2.87E+04	1.62E+04	6.59E+03	2.03E+03	5.89E+02	2.16E+02	1.35E+02	1.19E+00
1.64E+05	1.03E+05	6.25E+04	3.97E+04	2.64E+04	1.48E+04	5.93E+03	1.74E+03	4.65E+02	1.63E+02	1.04E+02	7.54E-01
1.54E+05	9.64E+04	5.83E+04	3.68E+04	2.44E+04	1.35E+04	5.36E+03	1.50E+03	3.69E+02	1.23E+02	8.26E+01	4.75E-01
1.43E+05	8.91E+04	5.40E+04	3.41E+04	2.24E+04	1.24E+04	4.86E+03	1.31E+03	2.95E+02	9.51E+01	7.11E+01	3.00E-01

Figure 8. Relevant rheometer data collected into one matrix

2. Take the base ten logarithm of the matrix excluding the column heading. The data should now look like Figure 7. **The column header needs to be in the format shown**. Note that any temperatures values can be used, as long as they are in increasing order, and the last column is Freq.

100	110	120	130	140	150	160	170	180	190	200	Freq
5.557507	5.429752	5.30103	5.181844	5.068186	4.91698	4.70927	4.481443	4.255273	4.025306	3.813581	2.477121
5.522444	5.389166	5.252853	5.123852	5.004321	4.788168	4.611723	4.361728	4.113943	3.872739	3.659916	2.276462
5.489958	5.348305	5.20412	5.068186	4.93902	4.766413	4.518514	4.227887	3.97359	3.717671	3.502427	2.075547
5.459392	5.30963	5.155336	5.0086	4.868644	4.691965	4.424882	4.123852	3.83187	3.561101	3.346353	1.877371
5.429752	5.274158	5.11059	4.958564	4.818226	4.623249	4.33646	4.0086	3.697229	3.41162	3.190332	1.676694
5.401401	5.238046	5.068186	4.907949	4.761928	4.557507	4.252853	3.900367	3.565848	3.264818	3.045323	1.477121
5.374748	5.206826	5.025306	4.860338	4.70927	4.495544	4.173186	3.79796	3.439333	3.123852	2.904174	1.276462
5.350248	5.176091	4.988113	4.815578	4.659916	4.437751	4.100371	3.702431	3.318063	2.984977	2.766413	1.075547
5.326336	5.146128	4.951823	4.773055	4.613842	4.383815	4.033424	3.612784	3.201397	2.850646	2.632457	0.877371
5.303196	5.117271	4.91803	4.733999	4.570543	4.33646	3.97359	3.528917	3.089905	2.719331	2.502427	0.676694
5.283301	5.093422	4.885926	4.698101	4.531479	4.290035	3.91803	3.451786	2.980912	2.58995	2.374748	0.477121
5.260071	5.064458	4.855519	4.663701	4.494155	4.247973	3.866287	3.378398	2.875061	2.460898	2.25042	0.276462
5.238046	5.041393	4.826075	4.631444	4.457882	4.209515	3.818885	3.307496	2.770115	2.334454	2.130334	0.075547
5.214844	5.012837	4.79588	4.598791	4.421604	4.170262	3.773055	3.240549	2.667453	2.212188	2.017033	-0.12263
5.187521	4.984077	4.765669	4.565848	4.38739	4.130334	3.729165	3.176091	2.567026	2.089905	1.91698	-0.32331
5.155336	4.949878	4.732394	4.532754	4.350248	4.093422	3.686636	3.117271	2.469822	1.978181	1.85187	-0.52288

Figure 7. Base ten logarithm of relevant rheometer data

3. Save the data into a text document. The easiest way to do this is to open Notepad and copy the block of excel data and paste into Notepad, it will appear as tab delimited in Notepad. Now save with the desired name and place the text file in a desired folder. Another way to save to a text document is to copy and paste the data into a separate sheet in excel. Then click on 'Save As' and change the 'save as type' combo box to 'Text (tab delimited)'. Click 'Ok' and then 'Yes' when excel prompts you about converting a excel file to a text file.

The UI

Opening the UI

First open MATLAB and make the current folder 'MasterCurveProject'. There are two ways to open the UI. The first is to open the file called mastercurve_gui.m and then press the run button on the script editor. **Please do not modify this file unless you are absolutely sure of what you are doing.** The second way (better, since the file does not open in the script editor) is to type mastercurve_gui in the command window. A non-resizable window will pop up looking like Figure 9.

The UI is separated into 5 parts: menu bar, toolbar, axes, data, and plot type. Each part is expanded upon in the following sections.

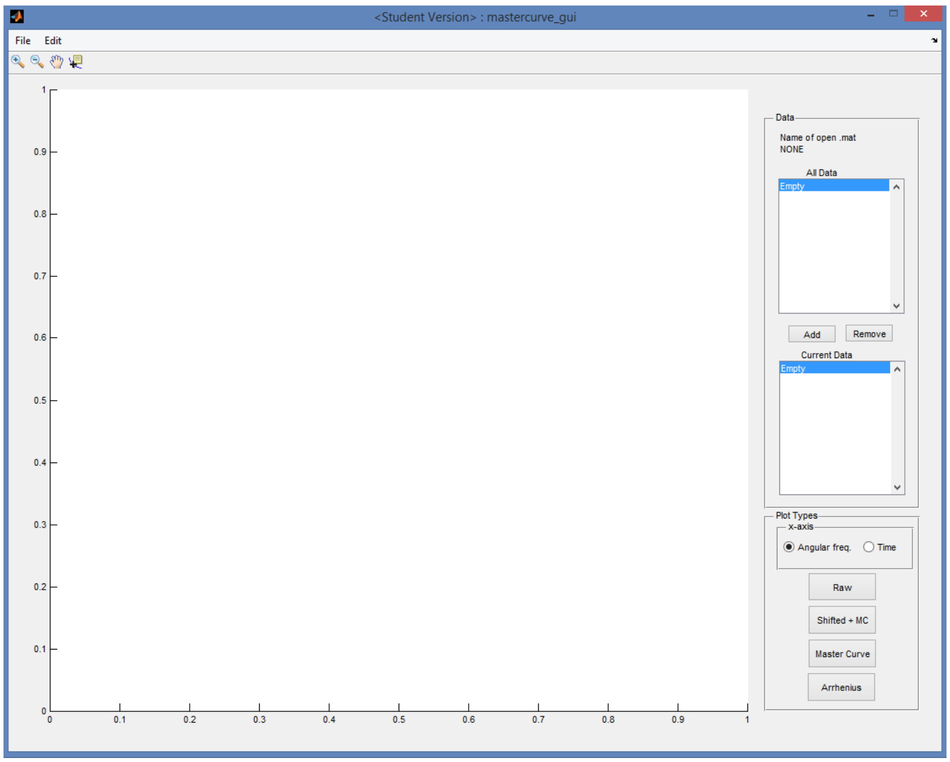


Figure 9. The user interface. The five sections are menu bar, toolbar, axes, data, plot type.

Menu bar

The menu bar has 2 menu items, **File** and **Edit**. Each has its own submenu items. The submenu items of **File** are the standard: **Open**; **Save**; **Import**; **Export**. The menu item **Edit** is left as a place holder for future implementation.

Import

File -> Import. To import the raw rheometer data there is need to first place it in a .txt file in the proper order, follow the steps outlined in section above called Formatting Raw Data for the Program. The file needs to have the values delimited by a tab, but a space or a comma is also acceptable. Find the spot on the spreadsheet where the ordered data will be placed.

1. The data is in proper order and ready to import.
2. Click the **Import** menu item to lunch the import UI, then select the text file.
3. The import wizard will appear on the screen, the column separator should be tab. Click **Next**.
4. Click **Finish**.
5. The ImportPopup will appear on the screen, read the status message.
6. Chose a name for the series.
7. Select a reference temperature from the drop down box.
8. Click **Analyze**.

If you cancel at any step before the data will not be analyzed and brought into the program.

Save

File -> Save. There are two options when saving. First is to save to a new .mat file, second is to save and replace an existing .mat file.

1. Click the **Save** menu item to lunch the UI.
2. Go to the folder /MasterCurveProject/MatData
3. To save new: write a file name. Click **Save.**
4. To overwrite: select a .mat file. Click **Save**. The UI will ask you if it is ok to replace the existing file. Click **Replace**.

Open

File -> Open. This will clear all data in the GUI workspace and open the desired .mat file. To open previously saved workspaces do the following steps.

1. Click the **Open** menu item to lunch the UI.
2. Go to the folder /MasterCurveProject/MatData.
3. Select the desired folder and click **Open**.

Export

File -> Export. This will export the data to an Excel file (.xlsx).

1. Enter the desired filename for the exported data in the text area instead of noname.
2. Then chose the data to export, the two options are the 'Master Curve' data only, and 'All data'.
3. Click **Export**

Master curve will export the data to plot the final master curve produced by the program. All data will export: the raw data; the shifted data; the check matrix; the Arrhenius model; the master curve. **Note:** The export to Excel files only works on machines running Windows OS.

Toolbar

Matlab toolbar elements are used to zoom in and out, pan the image and tag the point on the axes.

Axes

The plot area helps with comparing the different data series in the workspace. The pre-formatted plots that can be displayed in the program will appear here.

Data

The 'Data' panel is composed of 4 different parts: **Name**; **All Data**; **Add/Remove**; **Current Data**.

Name

The name of the currently opened .mat file is displayed in this text area. In the case no file is open the text area displays 'NONE'. After a save the text area is updated to the name given to the file.

All Data

'All data' displays the data series that were imported and analyzed by the program in the current open .mat file.

Add/Remove

The add button is used to add the highlighted data series in 'All data' to the 'Current data' list box. The remove button is used to remove the highlighted data series in the 'Current data' list box.

Current Data

The data series in current data are the ones that will be plotted in the axes when one of the plot push button is pressed.

Plot

X-axis

There are two choices for the x-axis, log(omega) and log(time). Select the desired x-axis for plotting in the axes here.

Raw, Shifted + MC, Master Curve push buttons

Press these push buttons to plot the data that is in 'Current Data'.