



Analysis on Data Collected by the DMA 8000 Using Time Temperature Superposition

Background

Time-Temperature Superposition (TTS) analysis allows DMA data to be applied to data collected within the measuring range of the DMA 8000 (0.001 Hz to 600 Hz) to allow modelling of material behavior at much higher or lower frequencies, which may be more representative of "real world"

applications. At the low frequency end of the frequency spectrum, "creep" measurements may be carried over many months or even years, however modelled data from DMA using TTS can give an indication of long-term behavior in a very short time. Similarly, higher frequencies such as those which represent "impact", typically in the kHz range, can be investigated quickly and easily using DMA in a way which allows meaningful comparisons between different sample treatments or modifications to be assessed.

It should be stressed that TTS is a modelling technique and results may be incorrect and misleading or wildly inaccurate in the worst cases. It is up to the scientist carrying out the measurements to make an assessment of the validity of the data and this will usually involve a correlation with other forms of measurement. A full treatment of the technique and its theory is outside the scope of this paper.

Author
Phil Robinson
Consultant,
Ruston Services, LLC.

How does TTS Work?

The data required for TTS is collected using a series of frequency scans collected at isothermal temperatures in a range which passes across the glass transition of the material being tested. When correctly chosen the start temperature, end temperature and the temperature steps produce a set of data called a "frequency dispersion", and an example taken from a PET film in tension mode is shown in Figure 1.

The data shows the classical series of scans which start off at the highest modulus of the sample when the temperature is below its glass transition then, as the sample starts to enter the glass transition, the lowest frequencies show the "below Tg" modulus while the higher frequencies still show the "above Tg" modulus – this is related to the shift in glass transition due to frequency and these are seen in the PET sample below. This data was collected at 1 Hz, 2 Hz, 5 Hz, 10 Hz and 20 Hz and scanned at a rate of 3 °C/min and demonstrates the measured shifts to higher temperatures as the frequency increases.

This frequency-dependant shifting is the behavior which allows us to create the classic frequency dispersion curves shown in Figure 2.

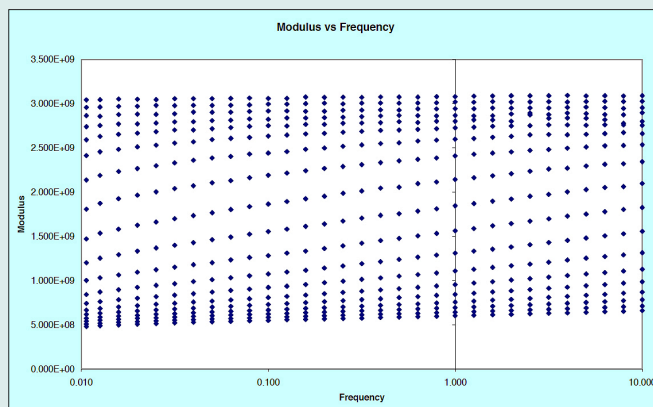


Figure 1. Frequency dispersion plot. Note that frequency is on a log scale

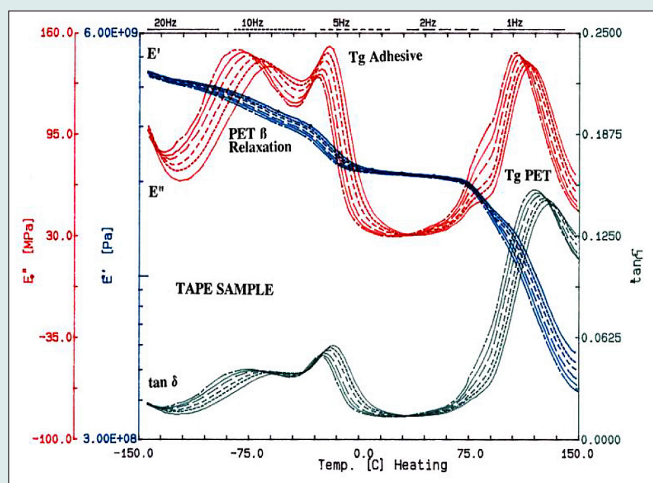


Figure 2. This plot shows the effect of frequency on measured transitions and shows the basis for the frequency dispersion plot.

Will TTS Work on my Sample?

Before TTS can be used, suitable data must be collected. The first stage is to assess whether the material itself is suitable for TTS analysis. To do this, a simple temperature scan at 1 Hz eg at 3 °C/min must be run, such as the test below.

This measurement shows several things. **Firstly**, it provides the temperature range needed to produce the frequency dispersion data. Secondly, it allows the assessment of the validity of the sample behavior for TTS by converting this data into the "wicket or Cole-Cole plot". From the curve of this PET sample, we need to start from about 50 °C and go to about 140 °C since this covers the whole of the change in modulus over the glass transition.

The second step is to produce what is called a "wicket or Cole-Cole plot", which can be conveniently produced using the Excel Chart Wizard which is included with the DMA 8000 software. Start the chart wizard and select "x = modulus" and "y = Tan Delta" from the drop-down menu's.

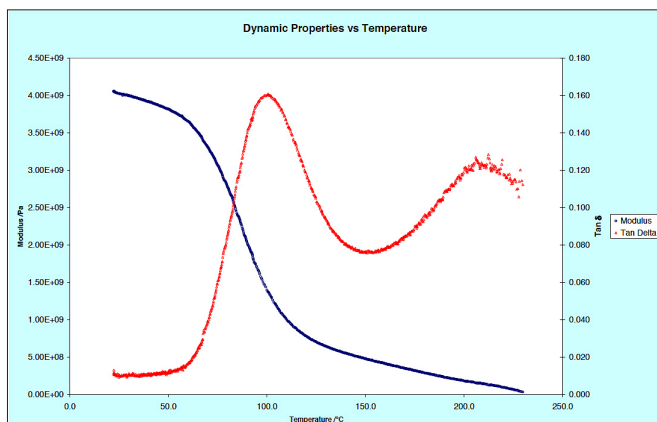


Figure 3. Data collected at 1 Hz scanning at 3 °C/min which will form the basis for the wicket plot.

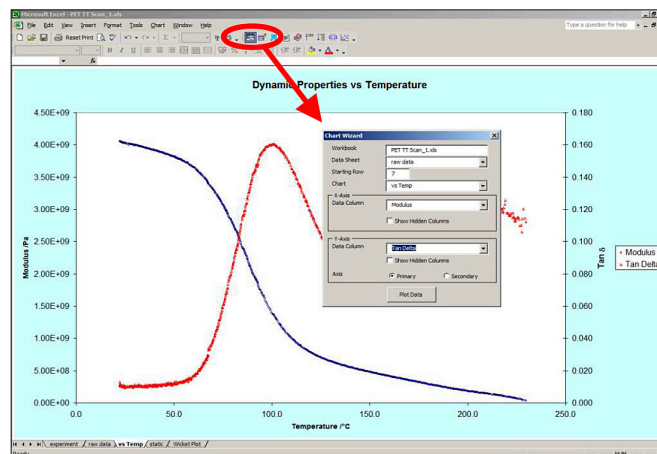


Figure 4. Using the Chart Wizard to produce the "wicket plot" data display

This will produce the “wicket plot” shown in Figure 6, which allows the assessment of whether the data is suitable for the WLF analysis. An example of suitable data in wicket plot form is shown in Figure 5, while the data shown in Figure 6 requires some correction before it can be used.

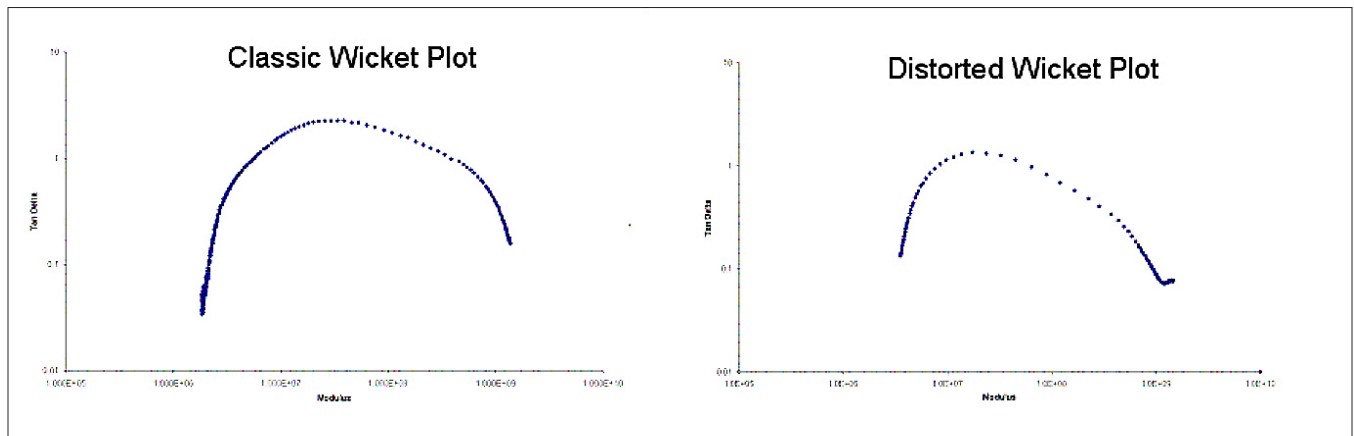


Figure 5. Left - Classical wicket plot showing sample behavior which is suitable for TTS analysis. Right - Distorted wicket plot, showing an anomaly at higher frequencies.

It will be seen in the “classic” wicket plot that an *almost* symmetrical curve is produced, while in the “distorted” plot, there is an anomaly in the higher modulus region which, in this case, is attributed to a beta transition in the material.

Reference to the wicket plot for the PET sample (Figure 6) shows that it is distorted in the lower modulus region. This may be the result of the tensile test mode used to collect the data allowing the sample to stretch slightly, it may be that too much data was collected above the glass transition, or it may mean the relaxation times of the material are such that they do not fit well with the assumptions of the WLF model used for TTS. Nevertheless, it suggests that some care must be taken in interpreting any modelled data.

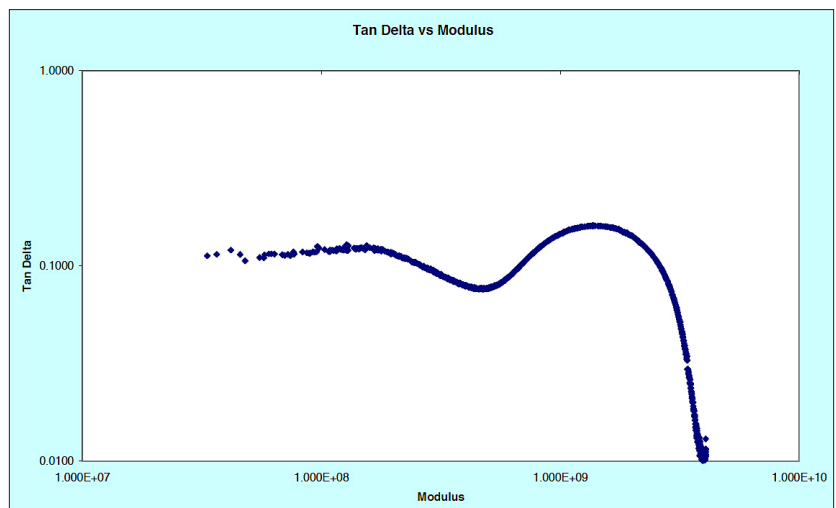


Figure 6. Wicket plot produced from PET sample data shown in Figure 3.

It may be necessary in some cases to mathematically “treat” the data to remove the effects of any distortions in order to obtain reliable data. For more information about use of the wicket plot refer to *David I. G. Jones: Handbook of Viscoelastic Vibration Damping*.

Experimental

Having determined the temperature range needed, the DMA 8000 software can now be set up to collect the data needed. Follow these steps:

Step 1: Start the Experiment Wizard

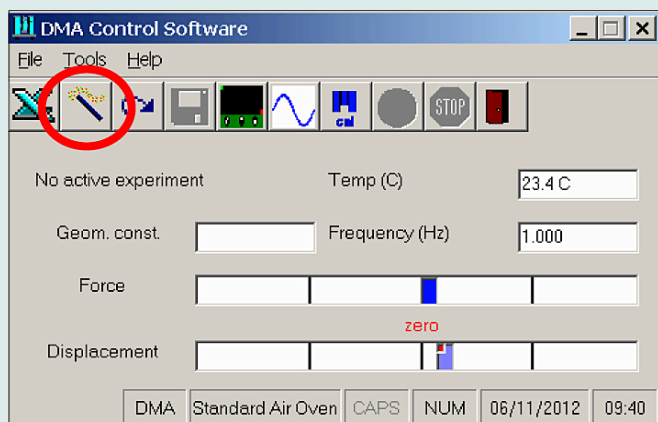


Figure 7. Starting the experiment wizard to set up TTS data collection.

Step 2: Enter the Sample Name and Select the "Frequency Scan" Experiment Type

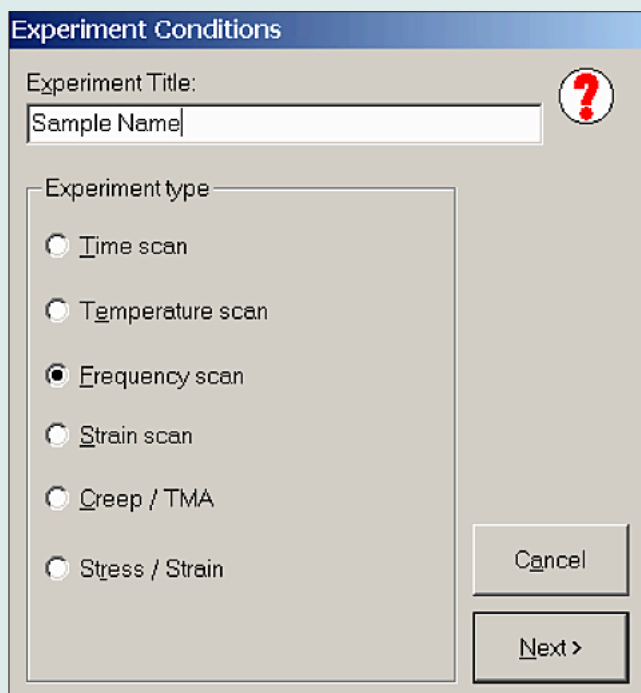


Figure 8. Select the frequency scan experiment type.

Note that the first test using this method is completed, the "Re-use Experiment" button can be used as below. This means that any scaling used, any charts set up, plus all other settings are loaded automatically, leaving only the sample dimensions and the sample name needing to be changed from test-to-test.

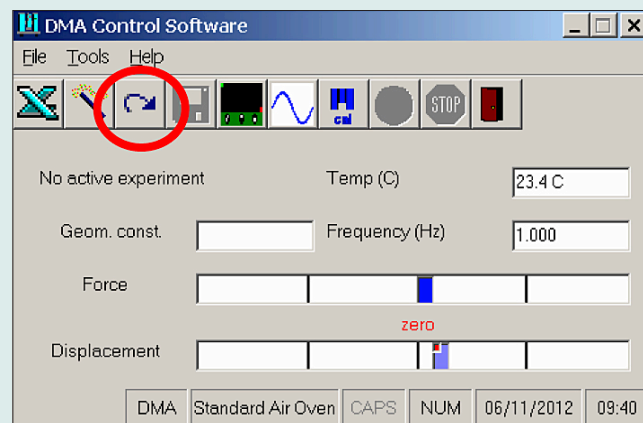


Figure 9. The "re-use experiment" option can be used to collect further data sets once the first experiment has been completed.

Step 3: Set the Frequency Range and Displacement Amplitude

Frequency Scan Conditions

Frequency

Start	Stop	Points per decade
0.01	100	10

☐ Discrete ☐ Linear ☒ Log

Displacement (mm): 0.03

Temperature conditions

Start T (C)	End T (C)	Ramp rate (C/min)	Interval T (C)
60	120	5	5

< Back Next >

Figure 10. Select the frequency analysis range.

The software must be set to run from low frequencies to high as show in Figure 10. There is a choice from either linear or logarithmic sampling and how many points per decade is needed. Since the data is normally displayed on a log-log scale, log and 10 points are chosen here to give a nice graph.

Note that using very low frequencies (eg from 0.001 Hz) takes a long time to collect data! The displacement (which is the "strain" on the sample in relation to the sample size) should not be too large as this will "over-stress" the sample. In DMA it is normal to work below a maximum of 1% strain for most materials, and conventional to work around 0.1%.

The requirement of the frequency range used for TTS is at least three decades of frequency, however four decades of frequency is usually better.

What is meant by "decades"? A decade is from eg 1 Hz to 10 Hz or from 0.001 Hz to 0.01 Hz. Using a larger number of decades allows the modelling to be more reliable, however there are practical limits. Selecting 0.001 Hz as the starting value and choosing 10 points per decade will cause the experiment for ONE frequency scan to last about 6 hours!

Similarly at the higher end of the frequency range, choosing 200 Hz or 600 Hz as the ending frequency are still both less than a full decade of data so, with 10 data points per decade, 200 Hz will produce perhaps 3 extra data points, while 6 will gain 2 more.

Considering that the x-scale (frequency) will be on a logarithmic scale for the displayed data, there is little advantage in extending the upper frequency much higher than 100 Hz since an upper frequency of 1000 Hz would need to be set to produce another full decade of data. Issues such as inertia become significant at such high frequencies and are beyond the working range of most analyzers including the DMA 8000.

The preferred frequency range, considering the practical issues would therefore be from 0.01 Hz to 100 Hz as this covers 4 decades of frequency, with each scan taking about 30 minutes if 10 points of data are taken per decade.

Step 4: Select the Temperature Range and Isothermal Step Increment

The correct temperature range was determined from the simple heating experiment at 1 Hz (Figure 3) as being from 50 °C to 140 °C, and these values are entered into the dialog box.

The ramp rate is not too critical for small temperature intervals, so the default 5 °C/min is usually OK. The problem caused by larger temperature steps and faster heating rates will be temperature “overshoot”, so time to stabilize the temperature at the new isothermal value will be needed if the data collected is to be reliable or the sample will not be properly equilibrated at the start of each of the frequency scans.

The temperature interval should be considered carefully! For a “wide” glass transition such as the PET sample, 5 °C intervals are acceptable. However, in samples where the glass transition has a smaller temperature range, the intervals should also be made smaller, allowing the frequency scans to properly examine the modulus changes over the glass transition.

The example below shows a much smaller temperature range for a glass transition, and in this example, a 3 °C interval would be used.

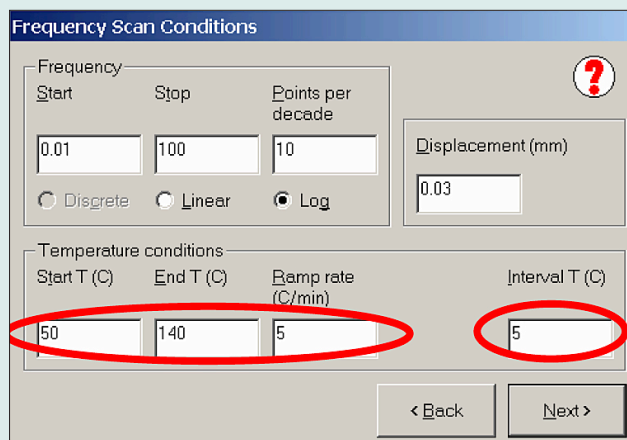


Figure 11. Set the temperature range over which data will be collected.

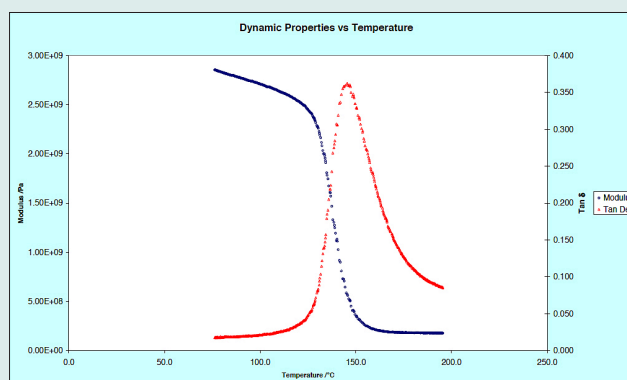


Figure 12. The PET data seen also in Figure 3.

Step 5: Enter Sample Sizes and Measuring System Information

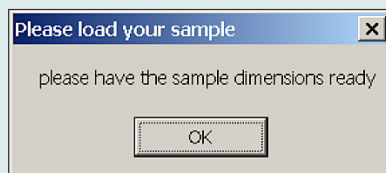


Figure 13. After pressing “next” (figure 11), press OK and then provide the sample dimensions.

Click “OK” to move on to the next dialog box

Based on the sample, select the deformation mode that will be used. This should be based on the sample properties and NOT on how the sample will be used in its final application. The modulus and other properties of the material are independent of the deformation mode being used so, in principle, all modes would give the same answer from the same material.

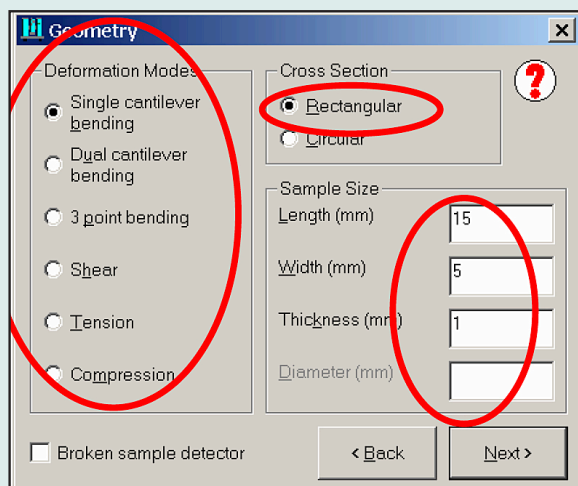


Figure 14. Select the measuring system to be used, the cross section shape of the sample and the sample dimensions.

Therefore, select the mode according to the sample stiffness below the glass transition, and also with consideration to the sizes which can be used. Eg a thin film or a fibre, is usually limited to using tension mode, but for a thicker film, one of the cantilever modes might be more appropriate. Compression or shear modes will rarely give good data below a glass transition and are usually avoided for this type of testing.

The set-up left assumes that a stiff material will be used in a single cantilever mode in the form of a “bar” of material.

Note that the “broken sample detector” is switched “off” since the experiment should not stop when the modulus drops as it passes through the glass transition.

Step 6: Enter a Filename

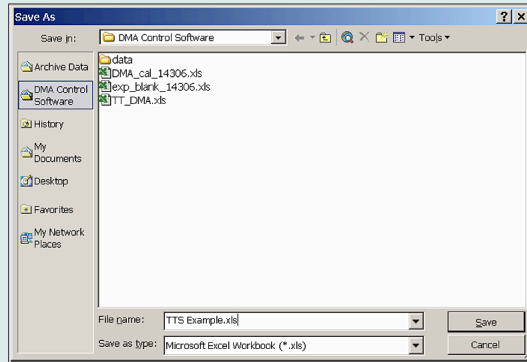


Figure 15. Sample the sample Excel data file.

Clicking next will ask for a filename under which to save the data. Select a suitable folder for your data on the PC you are using, and an Excel filename.

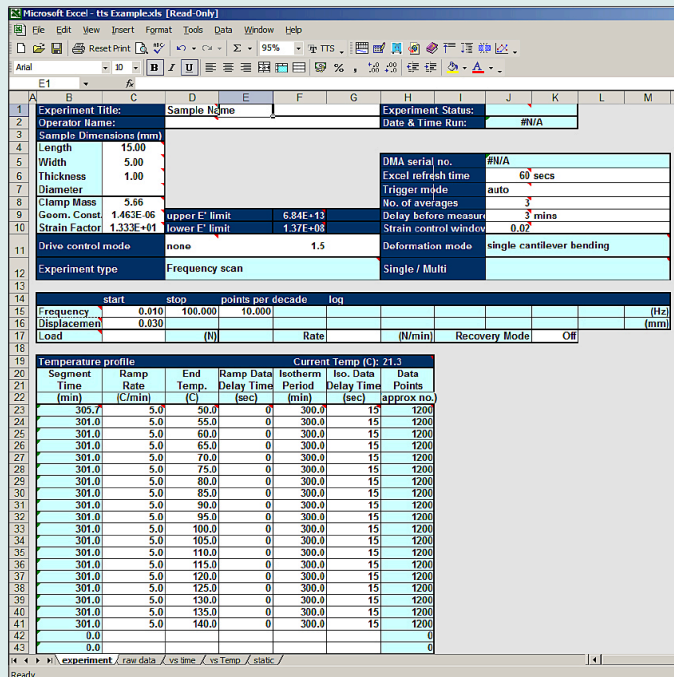


Figure 16. The resulting experiment sheet in Excel will be filled in by the DMA software to show a series of isothermal steps for each of the separate frequency scans.

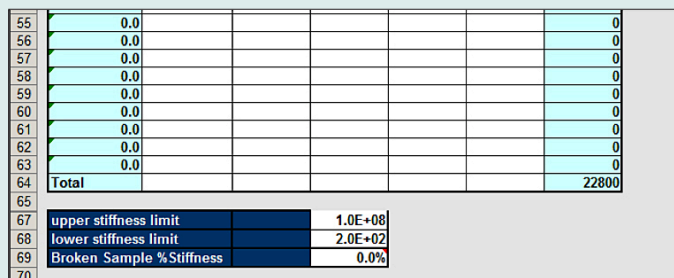


Figure 17. Cell 69C should be set to be "0" to prevent the broken sample detection system from stopping the test.

The experiment set up in the steps above will produce a series of isothermal temperature steps, and each individual isothermal temperature will be used for a frequency sweep at that temperature. The appearance of the Excel sheet is shown to the left.

Note that the "broken sample detector" can be manually set to "off" by setting the value in cell D69 to be zero percent as shown to the left.

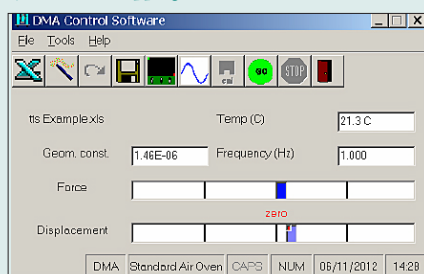
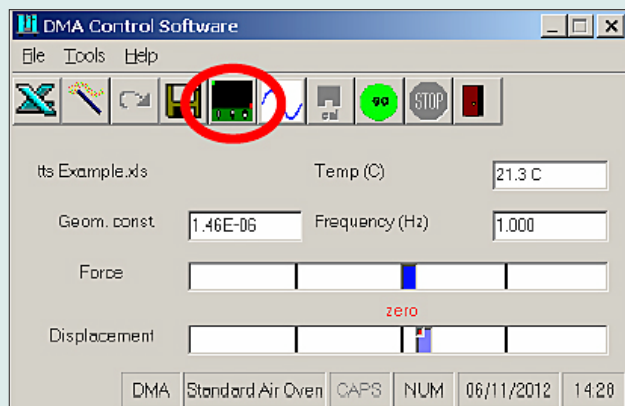


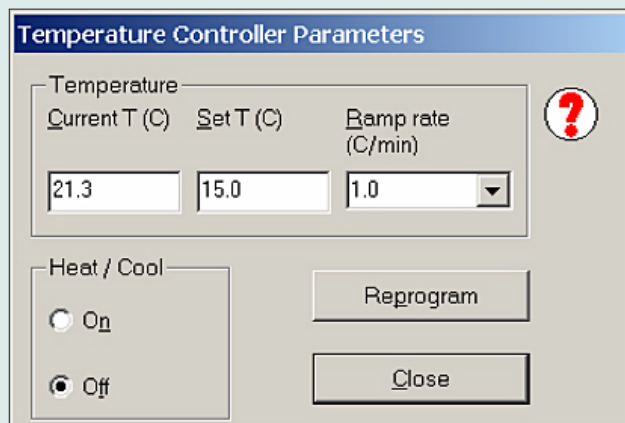
Figure 18. The green "go" button is now available.

Next, return to the DMA control software panel which will now show the "Go" button as being available. (see left).

Step 7: Go to the Start Temperature

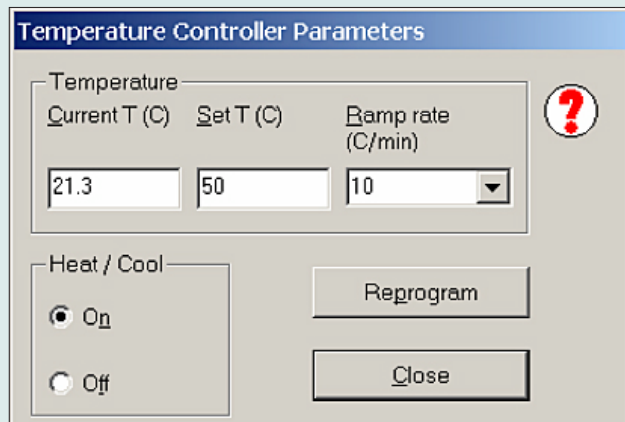


Unless the tests start from room temperature, it is useful to set the temperature program to the start temperature before starting the test. To do that, select the "Temperature programmer" button from the DMA Control Software window.



This opens a new window.

Type in the starting temperature in the "Set T (C)" box and change the ramp rate either using the drop-down menu or simply type in a heating/cooling rate.



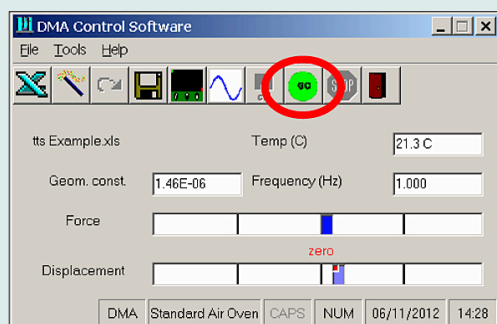
In the example, the starting temperature is set at 50 °C so the program was set at 10 °C/min as shown to the left.

Press the "Reprogram" button, then click the "Heat/Cool" control to "on".

The "Temperature Controller Parameters" window can be left open or can be closed. The sample temperature will change to the start temperature selected and, when it has stabilized at the start temperature, the temperature controller on the DMA will display "SoAK" and will alternate the display with the temperature display.

Figure 19. Activating the temperature programmer control.

Step 8: Start the Experiment



When the temperature has stabilized, press the "Go" button.

Figure 20. Starting the test.

Data Display and Analysis

Once the data has been collected, it is useful to produce a plot of frequency versus modulus in Excel using the chart wizard.

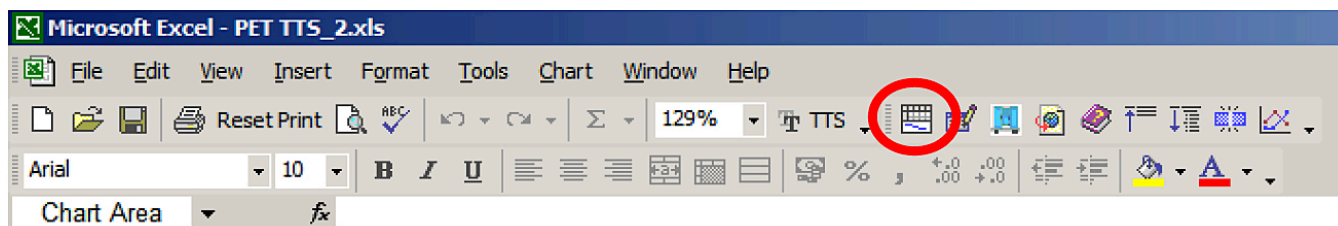


Figure 21. Starting the chart wizard (Excel 2002 and 2003).

This will create a new chart since none of the existing charts contain the correct axes.

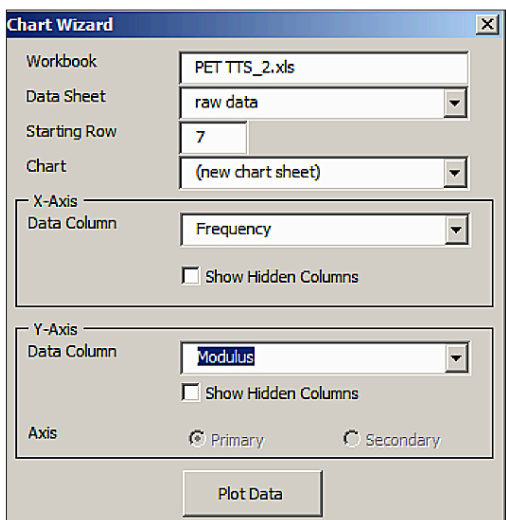


Figure 22. Settings in the chart wizard to produce a new plot for the frequency dispersion data.

The new chart will look something like this

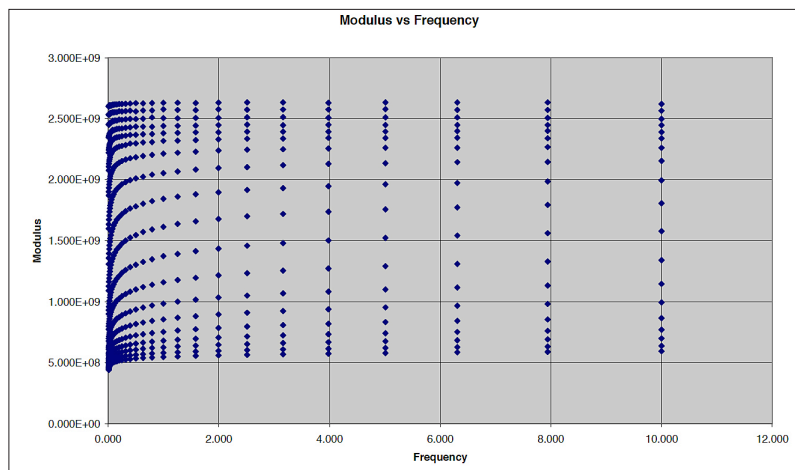


Figure 23. The initial display of the frequency dispersion data.

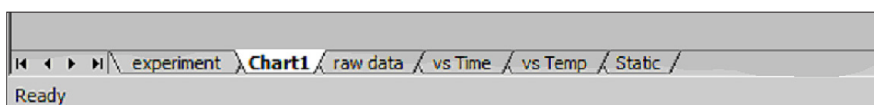
To see the frequency dispersion, edit the axis settings using the "right mouse" button – set the X scale to be logarithmic.

Grid lines can obscure the data and thus, can be deleted – point at them with the left mouse button and then hit the "Del" key.

It is also worth deleting the other worksheets in the spreadsheet since this will reduce the Excel file size because these worksheets "vs Time" and "vs temp" are generally not useful for data display from this type of experiment. Use the right mouse button to display the delete option for the unwanted tabs.

Double-click on the tab "name" to rename the data and type in the new name, so 'Chart 1' can be renamed to something more appropriate eg "vs Frequency".

The properties of the display area and external chart area can be edited to look more like the other displays – this is shown in the display below in this note. Use the right mouse button to display the colour menu for these areas of the chart. Remember that, once the tabs and appearance are changed once, the experiment can be "re-used" and do not need to be changed again until a different type of experiment is conducted.



Becomes

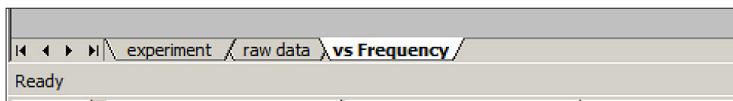


Figure 24. The frequency dispersion chart is renamed to "vs Frequency" and other chart sheets are deleted to minimize the data file size.

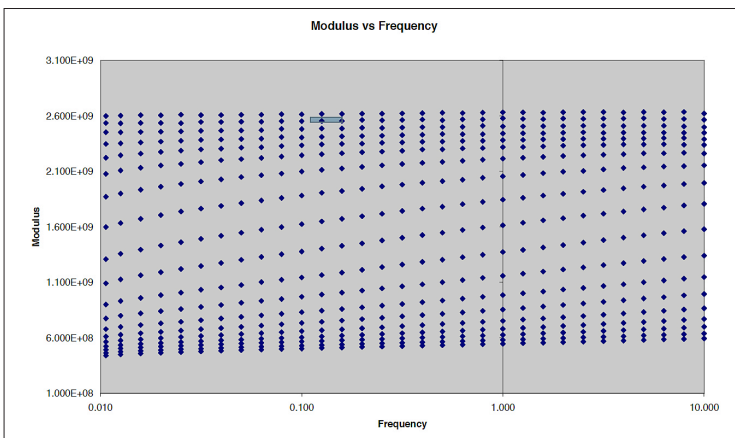


Figure 25. Frequency Dispersion plot after removal of gridlines and display the x-axis on a log scale.

Start the Time Temperature Superposition Analysis

If the TTS Software has been installed, then the TTS button will appear in Excel

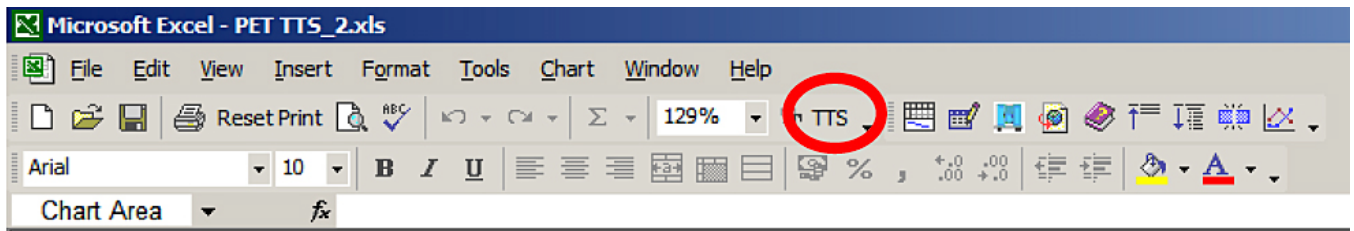


Figure 26. Activating the TTS software.

This will open a new dialog box over the Excel sheet. Press the "Load Data" button. Note that only the correct Excel file needs to be open- the view does not matter!

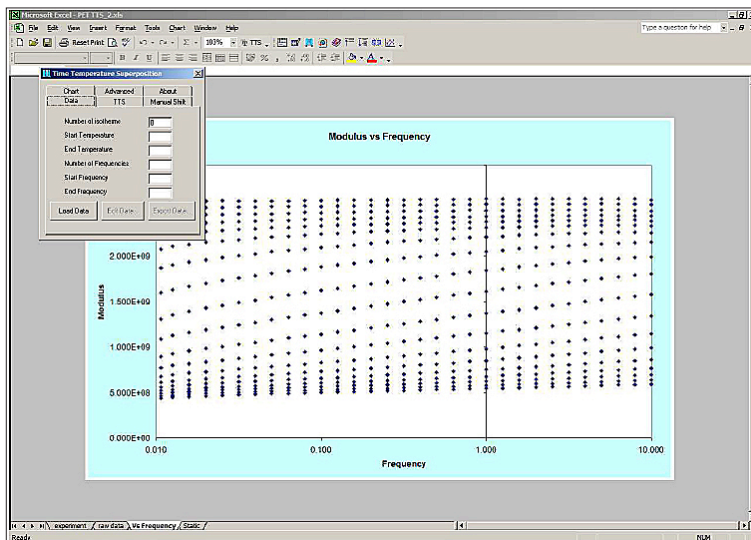


Figure 27. The TTS window displayed over the frequency dispersion plot.

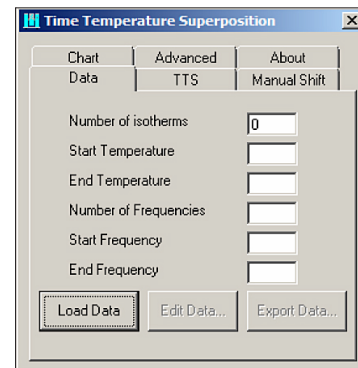


Figure 28. The TTS window.

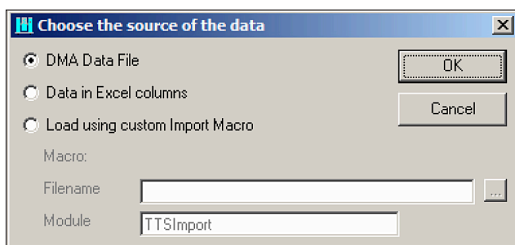


Figure 29. Selecting the TTS source data.

Since Excel is being used as the data source, click the "OK" button.

The data is automatically displayed in a new chart under the tab called "TTS" as shown left. The x- and y-scales are automatically formatted to be logarithm scales.

In the Time Temperature Superposition dialog box, select "Load Data".

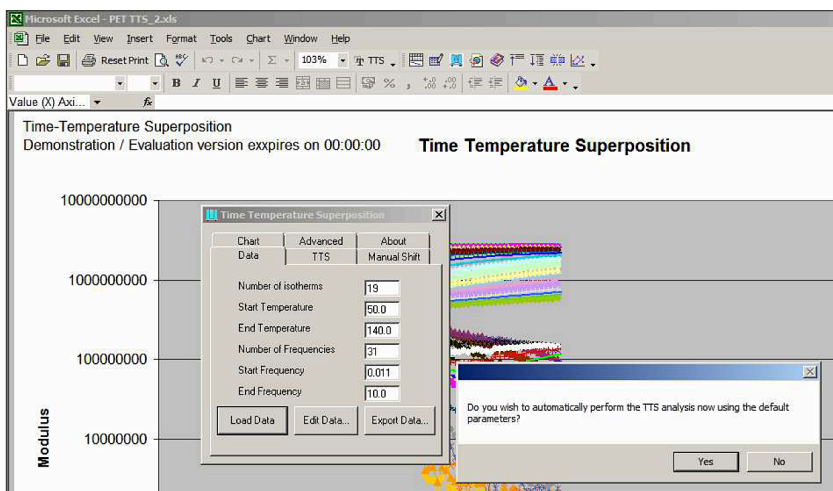


Figure 30. The TTS data before being shifted.

You are then asked if you want to perform TTS using the default values – click the "OK" button (you can adjust these settings later)

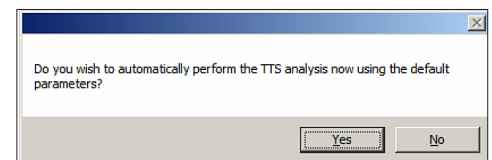


Figure 31. Perform TTS using the automatic shift factors.

At this stage, click on the TTS tab in the 'Time Temperature Superposition' dialog box so you can select to change the shift factors manually or use the "Auto Shift" function.

In this case, the "fit to WLF" option was selected on the TTS tab of the new dialog box. Note that WLF stands for "Williams Landel Ferry" after the people who developed the TTS theory. (See page 12)

The TTS software has calculated shift factors to convert the modulus curves to produce a new continuous modulus curve versus frequency. In the example above, the Tan Delta data does not make a continuous curve, suggesting that the data fit might not be good enough for the modelling, however it is useful to see that the frequency dependency of this PET material shows little increase in modulus at the higher frequencies, suggesting that the material *might* have "reasonable" impact properties over a wide range of frequencies if the impact properties are "reasonable" at frequency levels which can be easily measured in the laboratory eg using an impact tester.

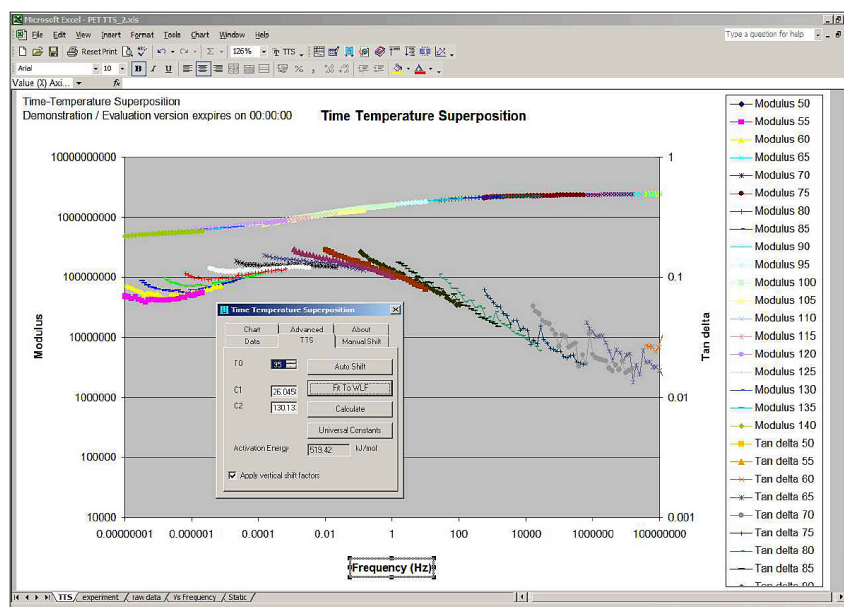


Figure 32. Data after the shift factors have been applied.

Note refer to the DMA 8000 TTS manual and other literature to understand how these factors are calculated and how they should be used.

The Master Curve

On the right is the Master Curve generated from the data showing the modulus data and the Tan Delta data. The reference temperature chosen was 85 °C since this was approximately in the centre of the glass transition, but note this is not an absolute choice.

The storage modulus data (starting in the upper right corner) shows a relatively "flat" response to frequency in the range 100 Hz to 10,000,000 Hz in the sense that the modulus does not appear to change significantly (on this logarithm Y scale) within this frequency range. The modulus appears to lie in the range 2.3×10^9 Pa to 2.9×10^9 Pa at these frequencies, suggesting that the material does not significantly risk fracturing at higher frequencies.

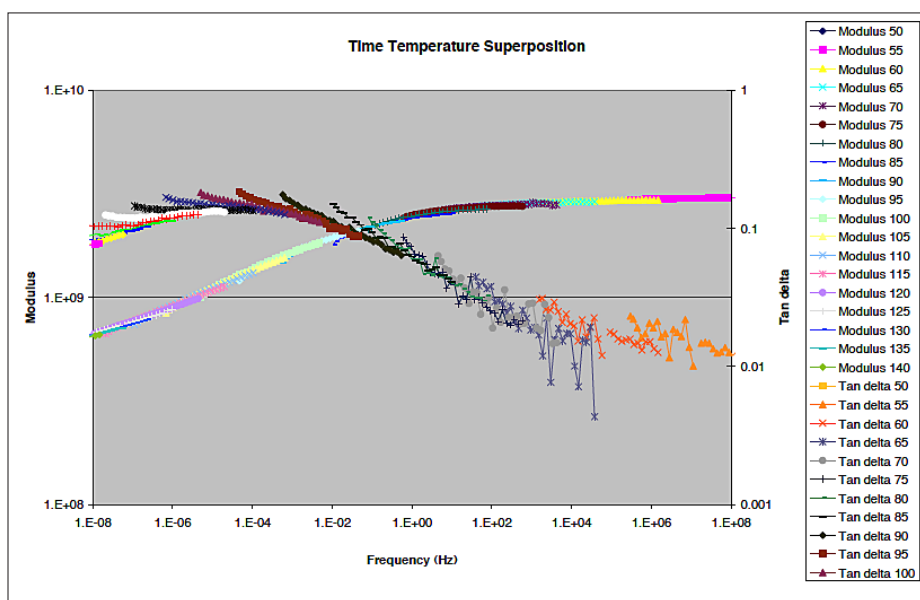


Figure 33. The final display of the TTS data.

However, it will also be seen that the Tan Delta data does not fit well into a smooth curve, and this might imply that some aspects of the modulus data prediction may be suspect.

Viscoelastic Properties of Polymers, by John D. Ferry

Dynamic Mechanical Analysis: A Practical Introduction, by Kevin P. Menard

Disclaimer

This guide is intended for individuals starting to use TTS with the DMA 8000 and the information is believed to be accurate. However, you are encouraged to look into the theory and confirm the application of TTS to your materials using other techniques before making any judgements based solely on data produced by DMA. One should at least read Plazek and Menard below before attempting to model from the results.

References

J. Aklonis and W. McKnight, Introduction to Polymer Viscoelasticity, Wiley: New York, 1983.

E. J. Barbero, Time–temperature–age superposition principle for predicting long-term response of linear viscoelastic materials, chapter 2 in Creep and fatigue in polymer matrix composites, R. M. Guedes, editor, Woodhead Pub. Co., UK, 2010.

J. Dealy and K. Wissbrum, Melt Rheology and its role in Polymer Processing, Nostrand Reinhold:Toronto, 1990.

J. Ferry, Viscoelastic Properties of Polymers, Wiley: New York. 1980.

N. McCrum, G. Williams and B. Read, Anelastic and Dielectric Effects in Polymeric Solids, Dover Reprint of the 1960 edition, New York. 1990.

K. Menard, Dynamic Mechanical Analysis: A Practical Introduction, CRC Press: Boca Raton, 2008.

D. Plazek J. Rheology 40(6) p. 987, 1996.

L. C. E. Struik, Physical aging in amorphous polymers and other materials, Elsevier Scientific Pub. Co. ; New York, 1978.

J. Sullivan, Creep and physical aging of composites, Composites Science and Technology 39(3) (1990) 207-32.

M.L. Williams, R.F. Landel, J.D. Ferry, J. Amer. Chem. Soc., 77:3701, 1955.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com



For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

Copyright ©2013, PerkinElmer, Inc. All rights reserved. PerkinElmer® is a registered trademark of PerkinElmer, Inc. All other trademarks are the property of their respective owners.

011013_01