SPECTRAL ANALYSIS AND THE INTERCONVERSION OF LINEAR VISCOELASTIC FUNCTIONS

1 INTRODUCTION

TA Instruments' Rheology Advantage spectral analysis and interconversion software was developed in collaboration with Prof. Dr. J. Hönerkamp and Dr. C. Friedrich of the University of Freiburg. For further information, users are referred to their work [1, 2].

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

There are several ways to investigate the linear viscoelastic properties of materials experimentally. The simplest is to perform a creep test, in which a small, fixed, stress, σ, is applied to a sample, and to monitor the resulting strain, $\gamma(t)$ is monitored over time, t. It is then usual to report the creep compliance, $J(t)$ defined as $\gamma(t)/\sigma$. An alternative is to apply a small, fixed strain, γ, to a sample, and to monitor the resulting stress, $\sigma(t)$ over time. The relaxation modulus, $G(t)$, defined as $\sigma(t)/\gamma$, is usually reported.

A more elegant procedure is to apply a low amplitude, sinusoidally oscillating, stress or strain. The amplitude of the response is monitored, along with the phase lag, δ, between the stress and the strain. Both these functions depend on the oscillation frequency, ω. The ratio of the stress amplitude to the strain amplitude, $|G^*(\omega)|$ is sometimes reported along with δ, but it is more usual to quote the storage modulus, $G'(\omega)$ and loss modulus $G''(\omega)$, defined by $G'(\omega) = |G^*(\omega)| \cos \delta$, and $G''(\omega) = |G^*(\omega)| \sin \delta$ respectively. The storage and loss compliances, defined by $J'(\omega) = |J^*(\omega)| \cos \delta$ and $J''(\omega) = |J^*(\omega)| \sin \delta$, respectively, where $|J^*(\omega)| = 1 /|G^*(\omega)|$, are also sometimes used.

Provided that the condition of linearity is observed, the functions $J(t)$, $G(t)$ and $G'(\omega)$, $G''(\omega)$ or $J'(\omega)$, $J''(\omega)$, can be interconverted. This operation is not performed directly, but through the intermediate functions, the relaxation spectrum, $H(\tau)$ and retardation spectrum, $L(\lambda)$; these functions themselves are not directly measurable. The relaxation spectrum can be further used in Rheology Advantage to generate the molecular weight distribution for polymer melts, $w(M)$. To calculate the spectrum from experimental data is a mathematically ill-posed problem, in that small differences in the data (below the error level associated with the measurement) can result in large differences in the spectra. Sophisticated mathematical techniques are used to counter this problem [1, 2].

2 THEORY

2.1 The creep compliance, *J(t)*

Linear viscoelastic theory allows the creep compliance to be described by a set of *m* elements, each with a characteristic compliance J_k and timescale λ_k, termed the retardation time (the symbol τ is often used for this parameter in the scientific literature, but Rheology Advantage uses λ throughout, to distinguish it from the relaxation time, given the symbol τ) [3], i.e.:

$$J(t) = J_0 + \sum_{k=1}^{m} J_k [1 - \exp(-t/\lambda_k)] + t/\eta_0 \tag{1}$$

where J_0 is the instantaneous compliance (sometimes referred to as the glassy compliance, with symbol J_g), and η_0 is the zero shear viscosity. λ_k is referred to as the retardation time of the *k* th element. Equation 1 can be recast as:

$$J(t) = J_{ss} - \sum_{k=1}^{m} J_k \exp(-t/\lambda_k) + t/\eta_0 \tag{2}$$

where J_{ss} is the steady state compliance (sometimes referred to as the equilibrium compliance, with symbol J_e, although this terminology strictly applies only to the case when $\eta_0 = 0$). The component elements in this description are termed Voigt or Kelvin elements, after the developers of the theory.

2.2 The relaxation modulus, *G(t)*

Similarly, the relaxation modulus can be described by a set of n elements, each with a characteristic modulus, G_i, and timescale, τ_i, termed the relaxation time [4], i.e.

$$G(t) = G_e + \sum_{i=1}^{n} G_i \exp(-t/\tau_i) \tag{3}$$

where G_e is the equilibrium modulus, or:

$$G(t) = G_0 - \sum_{i=1}^{n} G_i [1 - \exp(-t/\tau_i)] \tag{4}$$

The instantaneous modulus, G_0 is sometimes called the glassy modulus, with symbol G_g. the component elements in this description are referred to as Maxwell elements.

2.2 The discrete retardation spectrum, $L_d(\lambda)$ and relaxation spectrum $H_d(\tau)$..

Collectively, the *m* elements referred to in section 2.1 are termed the discrete retardation spectrum, $L_d(\lambda)$, the compliances then being viewed as spectral strengths at each retardation time. Graphically, this is usually displayed as J_k plotted against λ_k or $\log[\lambda_k]$.

Similarly, the *n* elements referred to in section 2.4 are collectively termed the discrete relaxation spectrum, $H_d(\tau)$, the moduli then being viewed as spectral strengths at each relaxation time. Graphically, this is usually displayed as G_i plotted against τ_i or $\log[\tau_i]$

2.3 The continuous retardation spectrum, $L(\lambda)$ and relaxation spectrum $H(\tau)$.

To fully generalize Equations 1 and 2, the discrete retardation spectrum can be replaced by a continuous function, $L(\lambda)$, termed the continuous retardation spectrum. Since it is usually more convenient to use the logarithm of the retardation time, rather than the retardation time itself, $L(\lambda)$ is defined by the expression:

$$J(t) = J_0 + \int_{-\infty}^{\infty} L(\lambda)[1 - \exp(-t/\lambda)]d\ln\lambda + t/\eta_0 \tag{5}$$

or
$$J(t) = J_{ss} - \int_{-\infty}^{\infty} L(\lambda)\exp(-t/\lambda)d\ln\lambda + t/\eta_0 \tag{6}$$

Equations 3 and 4 can also be fully generalised, the discrete relaxation spectrum being replaced by the continuous function, $H(\tau)$, termed the continuous relaxation spectrum. Again, it is usually more convenient to use the logarithm of the relaxation time, rather than the relaxation time itself, and $H(\tau)$ is defined by the expression:

$$G(t) = G_e + \int_{-\infty}^{\infty} H(\tau)\exp(-t/\tau)d\ln\tau \tag{7}$$

or
$$G(t) = G_0 - \int_{-\infty}^{\infty} H(\tau)[1 - \exp(-t/\tau)]d\ln\tau \tag{8}$$

2.4 Relationship between the spectra and $J'(\omega)$, $J''(\omega)$ and $G'(\omega)$, $G''(\omega)$.

The storage and loss compliance, and the storage and loss modulus, are also related to the spectra, i.e.:

$$J'(\omega) = J_0 + \int_{-\infty}^{\infty} L(\lambda)\frac{1}{1+\omega^2\lambda^2}d\ln\lambda \equiv J_{ss} - \int_{-\infty}^{\infty} L(\lambda)\frac{\omega^2\lambda^2}{1+\omega^2\lambda^2}d\ln\lambda \tag{9}$$

$$\text{and} \qquad J''(\omega) = \int_{-\infty}^{\infty} L(\lambda) \frac{\omega\lambda}{1+\omega^2\lambda^2} d\ln\lambda + \frac{t}{\eta_0} \tag{10}$$

similarly:

$$G'(\omega) = G_e + \int_{-\infty}^{\infty} H(\tau) \frac{\omega^2\tau^2}{1+\omega^2\tau^2} d\ln\tau \equiv G_0 - \int_{-\infty}^{\infty} H(\tau) \frac{1}{1+\omega^2\tau^2} d\ln\tau \tag{11}$$

$$\text{and} \qquad G''(\omega) = \int_{-\infty}^{\infty} H(\tau) \frac{\omega\tau}{1+\omega^2\tau^2} d\ln\tau \tag{12}$$

2.6 Memory function, M(t)

A memory function, M(t) is also defined, as:

$$M(t) = -\frac{dG(t)}{dt} \tag{13}$$

2.7 Calculation of the spectra from experimental data

The various spectra can be calculated from the appropriate experimental data, using the relationships given above (creep data will give either the discrete or continuous retardation spectra, stress relaxation and oscillation data will give the relaxation spectra). However, the procedure is not straightforward, as the problem is mathematically ill-posed. This means that small differences in the experimental data (perhaps below the error level associated with the measurement) can lead to large differences in the spectra. Moreover, each experimental point contributes to every spectral point. So, for example, if two sets of oscillation data differ in single point, the result can be differences throughout the calculated spectrum. To counter this problem, sophisticated mathematical techniques, called non-linear regularisation procedures, have been developed. For a full description of those used in Rheology Advantage, see references [1, 2].

2.8 Interconversion between the spectra

The relationships between the spectra are given in reference [4]. Interconversion between the complementary (i.e. retardation and relaxation) discrete spectra or between the complementary continuous spectra can be made. Conversion from the discrete to the continuous form is not possible. Note that numerical techniques are used for interconversion between the continuous spectra, whereas the discrete spectral interconversion is exact. Details of the latter are given in reference [5].

2.9 Input parameters and ranges

The input parameters and ranges apply to the target function, i.e. the function to be calculated, not the source function.

Time range: the range of retardation or relaxation times over which the spectrum is to be calculated (for the discrete spectra these are only the upper and lower limits; it may be that no spectral point actually occurs at the limit). The spectral time range should show reasonable correspondence with the experimental time range (in the case of oscillation data, the time corresponds to the reciprocal of the angular frequency, measured in rad s^{-1}). It has been shown that the spectral information is trustworthy only over a range which is narrower than the experimental range by a factor of $\exp(\pi/2)$, i.e. 4.81, at each end, and is untrustworthy beyond the range broader than the experimental range by the same factor. In the intermediate region, the spectral information is doubtful [5]. For example, an oscillation experiment may be performed over the experimental range 0.1 to 100 rad s^{-1}, corresponding to a time range of 0.01 s. Then the relaxation spectrum is trustworthy over the range 0.481 to 20.8 s, is untrustworthy below 0.0208 s and above 481 s. The spectrum is doubtful in the regions 0.0208 to 0.481 s and 20.8 to 481 s. The ranges chosen will therefore depend on how secure the spectral information is required to be, but it is suggested that the default range of $\exp(\pi/2)$, denoted e^(PI/2) in Rheology Advantage, is used in normal circumstances.

Spectral points: entered as points per decade or total points in Rheology Advantage. This refers only to the continuous spectra; the number of elements in the discrete spectra cannot be fixed. The greater the number of points calculated, the more secure the information will be, but the longer the process will take. It is suggested that the default value of 15 points per decade is used in normal circumstances.

Calculation of G_e or J_0. These parameters are defined in Equations 1 and 5 and 3 and 7 above. G_e can be calculated with the discrete or continuous relaxation spectrum, J_0 with the corresponding retardation spectrum. They can be viewed respectively as representing the contribution to the relaxation spectrum of processes with relaxation times at $\tau = \infty$, i.e. too long to be experimentally available, or to the retardation spectrum of processes with retardation times at $\lambda = 0$, i.e. too short to be experimentally available. It is suggested that J_0 should be calculated, but G_e omitted unless other information is available.

3 OPERATION

The operation to generate a discrete or continuous spectrum from experimental data, or to convert between linear viscoelastic functions, using Rheology Advantage, is described here. It is assumed that the user is familiar with the basic operation of the Rheology Advantage Data Analysis Module. The example data were obtained on a polystyrene sample of nominal weight average molecular weight of 250 000, at 160°C.

3.1 Calculation of the spectra from experimental data

Experimental data must be either creep (files have termination –c), stress relaxation (termination –x), or oscillation (termination –o).. The example shown here uses oscillation data from the example polymer. The procedure for analysing creep or stress relaxation data is similar.

Step 1 Open the file to be operated on. Shown below are the example data, with $G'(\omega)$ and $G''(\omega)$ plotted against angular frequency.
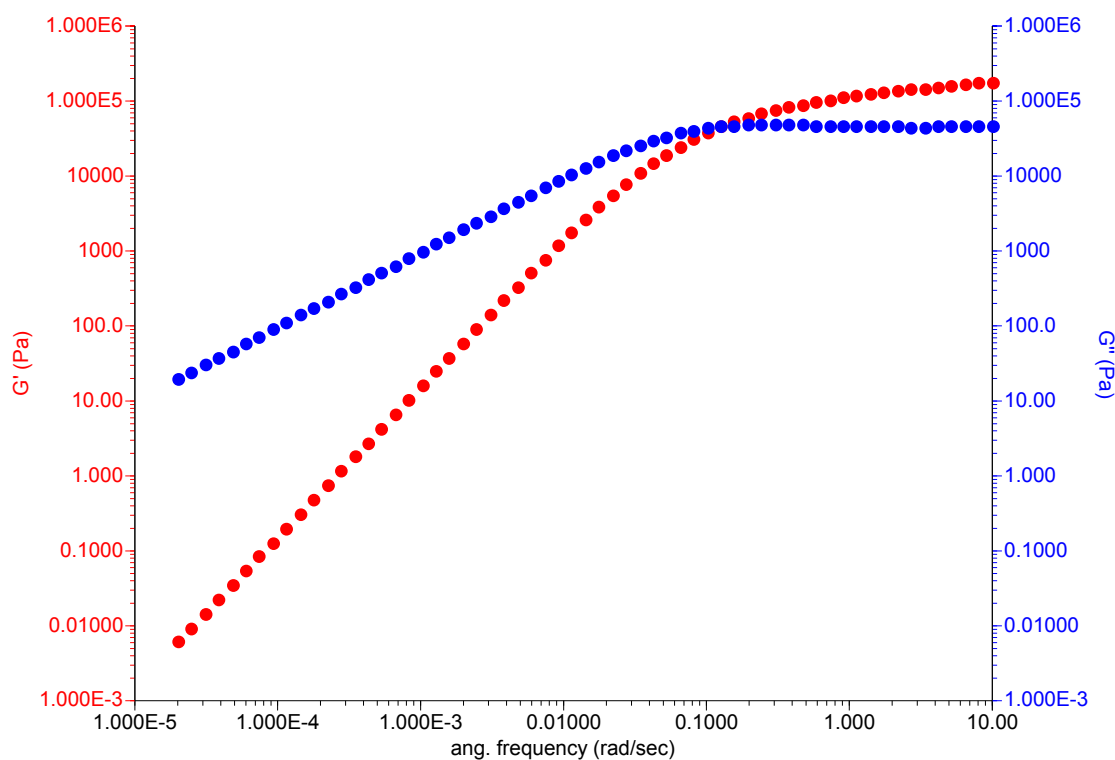

Step 2 From the **Analysis** menu click **Enhanced Analysis Options…** The box below will appear. For information on entries to this box, see section 2.9 above.
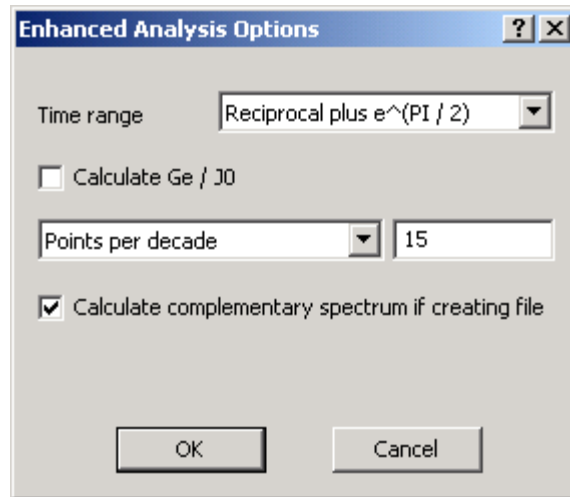
Scroll through the **Time range** options and select the required range. Alternatively select **Manual entry**, and enter the required minimum and maximum values in the boxes that appear. Note that the word reciprocal applies only to oscillation data. For creep data the time range conversion is direct. Check the **Calculate Ge/J0** box if calculation of *Ge* or J_0 with the spectrum is required. Enter the required number of points in the **Points per decade** box or scroll to **Total points** before entering. Note that the **Calculate complementary spectrum if creating file** applies only to the continuous spectra.

Step 3 From the **File** menu click **Model…** The box shown below will appear:
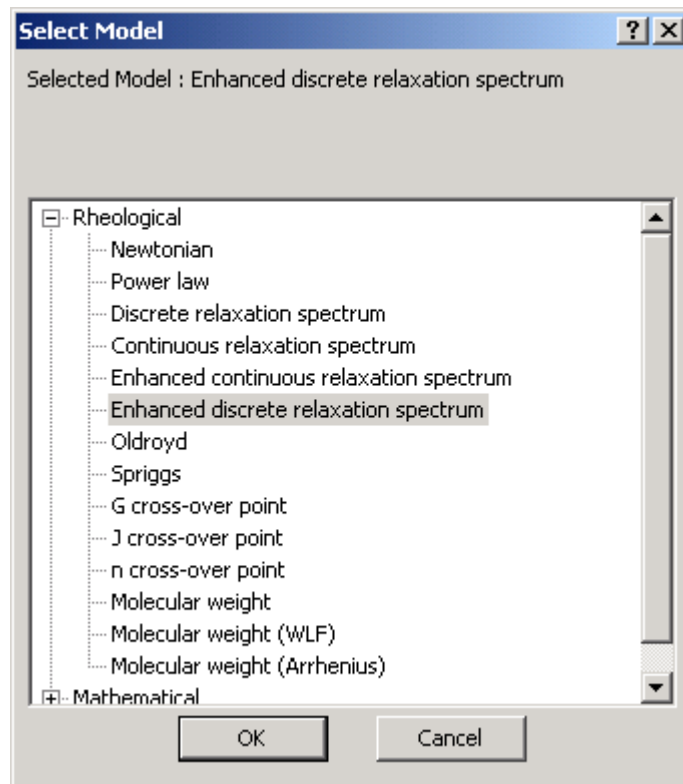
Highlight **Enhanced continuous relaxation spectrum** or **Enhanced discrete relaxation spectrum** as required, and click **OK**.

Step 4 To create a spectrum file immediately on fitting the oscillation data, from the **Options** menu point to **Settings…** and click the **Analysis** tab. Check the **Automatically create spectrum file following analysis** box and click **OK**.

Highlight the data to be fitted by placing the cursor arrow over one of the points on the curve and clicking. Then from the **Analysis** menu click **Go**. A spectrum file will be created with termination –spx or –cspx for the discrete or continuous relaxation spectrum resectively –spr and –cspr for the corresponding retardation spectra. To display the data graphically, from the **View** menu click **Send data to graph**. The discrete and continuous spectra for the example data are shown below.
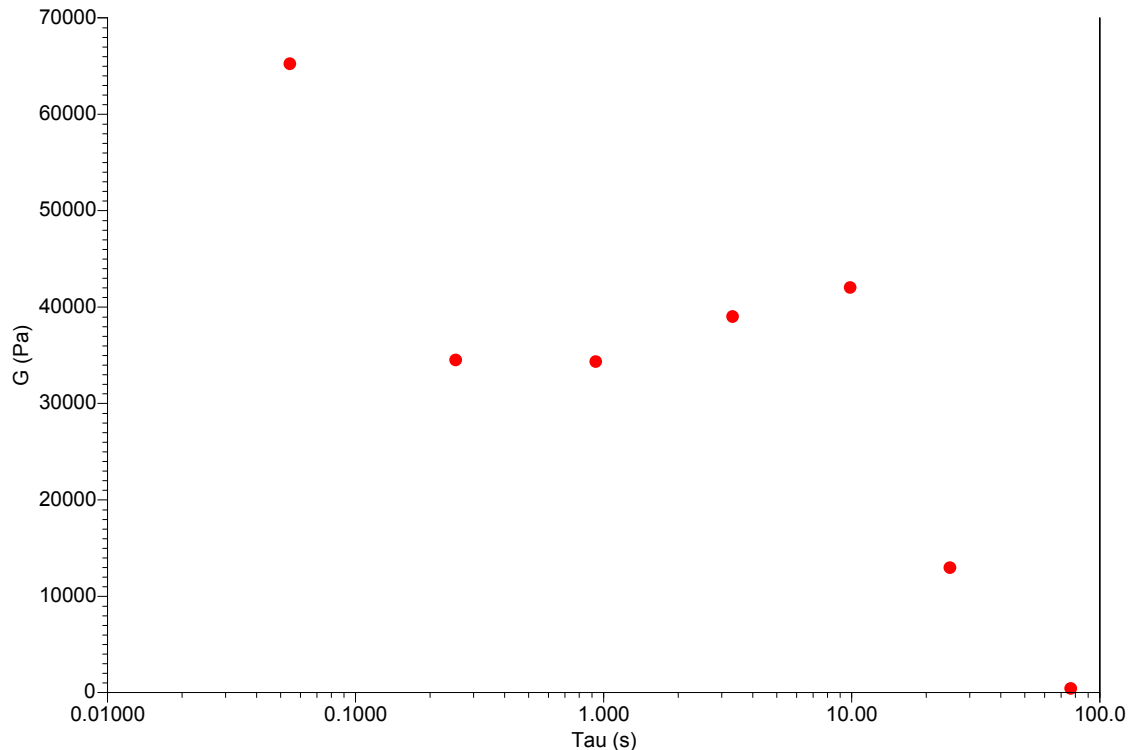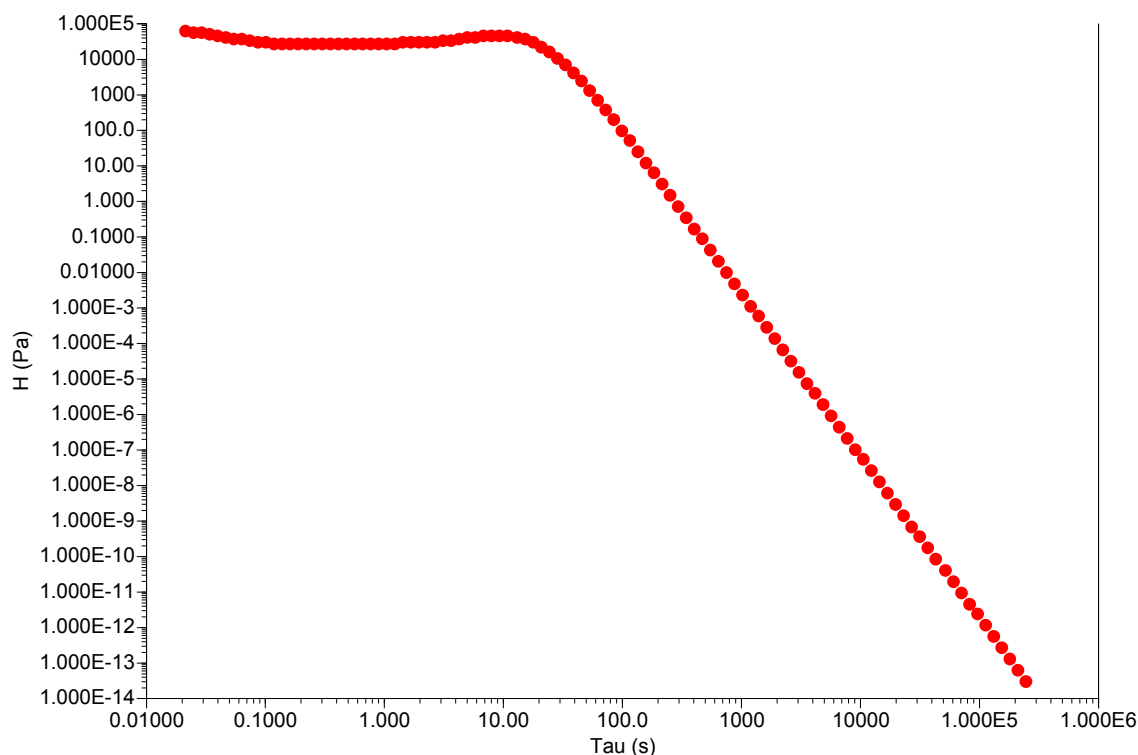
The parameters used in the calculation of the spectrum are stored with the file. To view these, from the **View** menu click **Notes**. Parameters are shown in the **Experiment notes** box. The list for the continuous spectrum for above example is shown below.

Analysed file: mwdexample-o
Time range: Reciprocal plus e^(PI / 2)
Minimum time: 0.02079
Maximum time: 2.405E5
Spectrum points per decade: 15
Calculate Ge: no

3.2 Interconversion between the spectra

If conversion is required from either continuous spectrum to the complementary spectrum, then the operation must be performed when the original spectrum is calculated. In the **Enhanced Analysis Options** box shown in Section 3.1 step 2, above, check the **Calculate complementary spectrum if creating file** box. The continuous retardation spectrum for the example data, generated from the continuous relaxation spectrum shown above, is shown below.
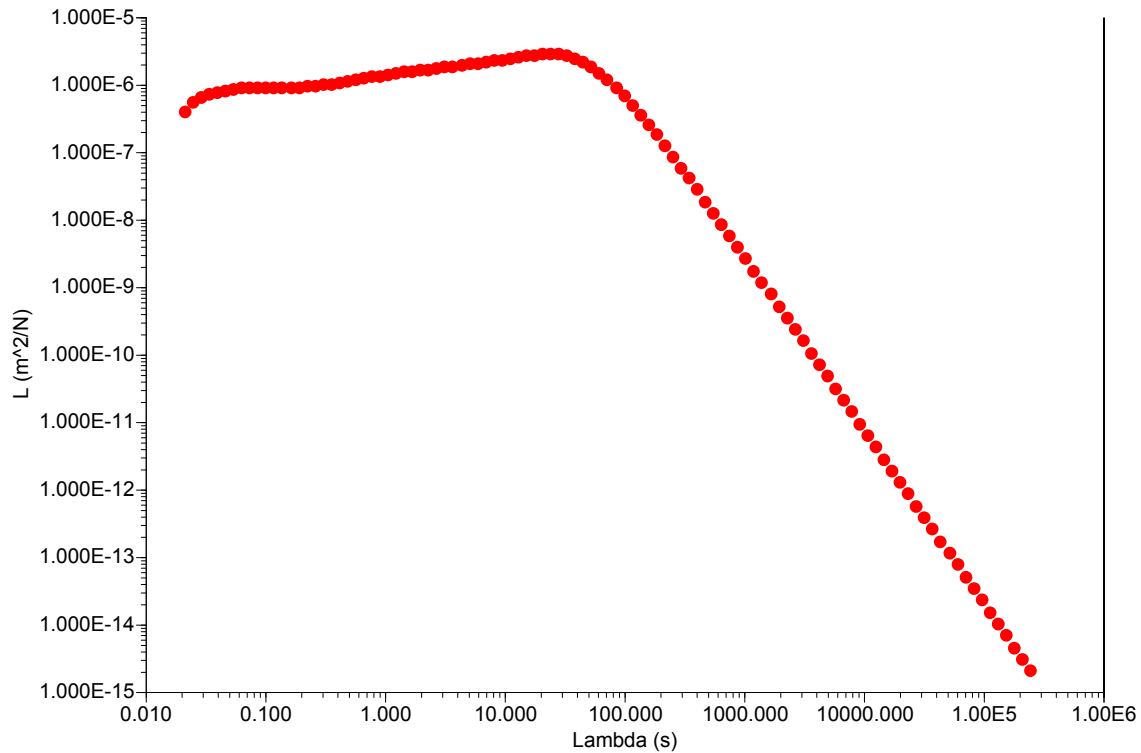
Conversion form either discrete spectrum to the complementary spectrum can be made at any time. Highlight the spectrum filename, and from the **File** menu point to **Transformations** and click **To Retardation Spectrum** or **To Relaxation Spectrum**. The discrete retardation spectrum for the example data, generated from the discrete relaxation spectrum shown above, is shown below.

3.3 Calculation of creep, stress relaxation and oscillation data from spectra.

The retardation spectrum, whether discrete or continuous, can be transformed to creep data. Highlight the spectrum filename, and from the **File** menu, point to **Transformations** and click **Creep…** The box shown below will appear.

Note that the entries refer to the target file, i.e. the creep file to be generated, not the source file. Enter the required values, and click O.K. A creep file that can be handled as a standard Rheology Advantage creep file, will be generated. Creep data calculated from the discrete relaxation spectrum of the example polymer is shown below.
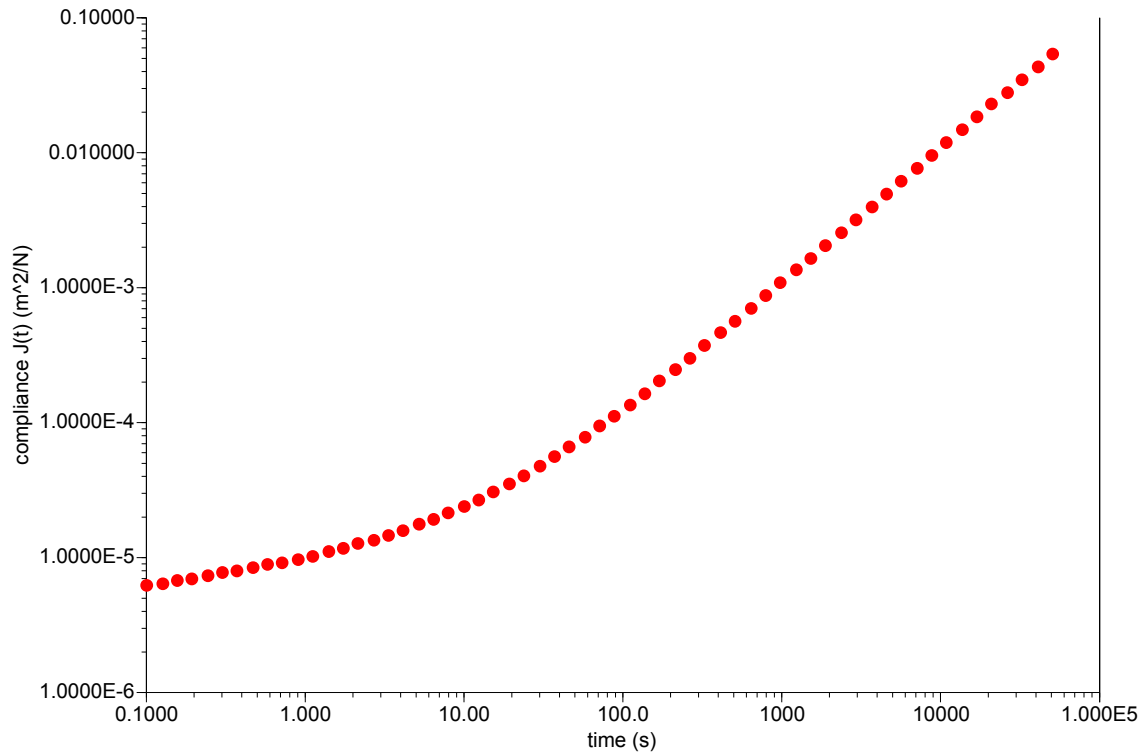

The discrete and continuous relaxation spectra can be transformed to stress relaxation or oscillation data. The procedures are similar to that used for the transformation of the retardation spectra to creep data. Shown below is the relaxation modulus generated from the discrete relaxation spectrum of the example polymer.
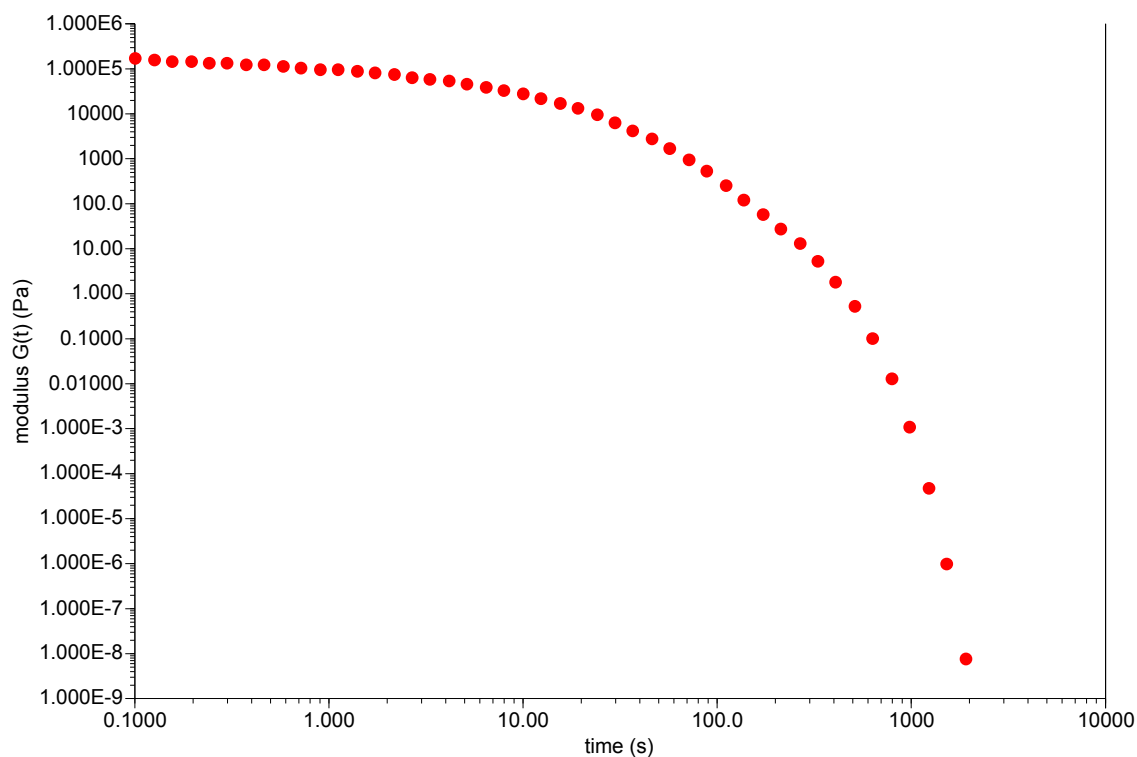
3.4 Calculation of the memory function

The memory function, the file for which will have termination -mf can also be generated form the relaxation spectra. The procedure is similar to that used for the other transformations, but note that the **Create memory function file** box contains an entry for **Integration steps**. This refers to the number of iterations used in the calculation, and it is suggested that the default value of 200 is used if no other information is available. The meory function calculated from the discrete relaxation spectrum for the example polymer is shown below.
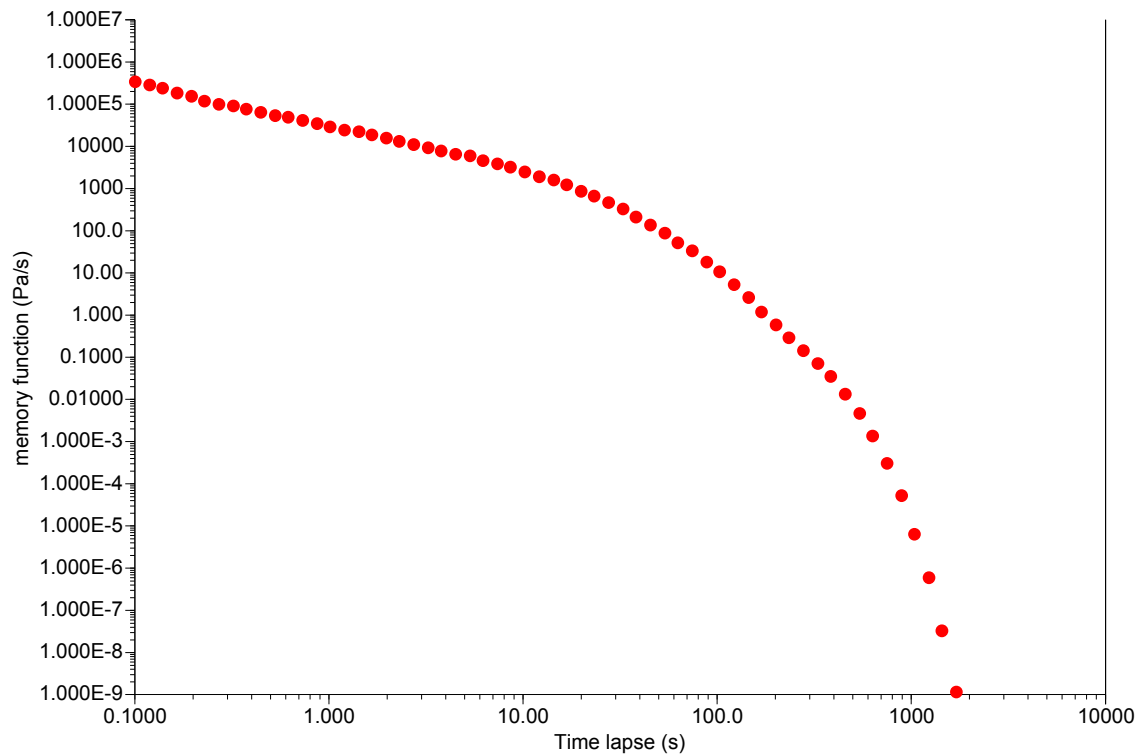
3.5 Data presentation and model fitting

Although only a finite number of points can be calculated for the continuous spectra, a curve through these points can meaningfully be drawn, or the set of points can simply be replaced by a curve (an approximation to a curve, consisting of short straight lines connecting the points, is used by Rheology Advantage). The spectra can be integrated or differentiated in the usual way, or can be fitted by a polynomial or other continuous function. However the points of the discrete spectra represent all the spectral information, and they cannot meaningfully be joined, nor can the spectra be meaningfully integrated or differentiated, or fitted by a continuous function.

4 LIMITATIONS

4.1 Samples

Although the relaxation and retardation spectra are usually discussed in the context of polymer rheology, their use need not be confined to that type of material. In principle, the operations described above can be performed on data from any type of sample, provided that the condition of linearity is obeyed.

4.2 Time and frequency ranges

The relationship between the experimental data ranges and those of the spectra is discussed in Section 2.9 above. In general, for interconversion between linear viscoelastic functions, the time ranges of the source and target data should reasonably correspond (the time scale for oscillation data should be taken as the reciprocal of the angular frequency scale, so a time of 10 s corresponds to an angular frequency of 0.1 rad s^{-1}, and vice versa). So if oscillatory data is available over the range 0.1 to 100 rad s^{-1}, it cannot be expected that meaningful creep data can be generated outside the range 0.01 to 10 s.

4.3 Data quality

Although the procedures used for the calculation of the relaxation and retardation spectra effectively contain inherent smoothing routines, the quality of the spectra generated will inevitably depend on the quality of the source data. Spurious data points, or excessively noisy data, can cause inaccuracies in the spectra, including spurious peaks. A visual inspection of the data should always be made, and any obviously incorrect data points or regions should be eliminated. Data quality can sometimes be improved through the use of the Rheology Advantage smoothing function, but care should be taken when applying this function.

REFERENCES

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