ADVANTAGES OF FREQUENCY MULTIPLEXING DMA EXPERIMENTS

Introduction

Dynamic mechanical analysis (DMA) provides an excellent means of characterizing the properties of polymeric materials, such as elastomer, fibers, composites, thermosets and thermoplastics. The technique offers the highest inherent sensitivity of any of the thermal analytical techniques for the detection of weak transitions. DMA provides useful information on the stiffness and damping or energy absorbing properties of materials as a function of both temperature and time (frequency).

With dynamic mechanical analysis, a sinusoidal force or stress is applied to a sample and the resulting sinusoidal deformation or strain is monitored. The sample strain response lags behind the input stress with respect to time and this lag is known as the phase angle, δ. The ratio of the dynamic stress to the dynamic strain yields the complex modulus, E*, which can be further broken down to yield the storage modulus, E', and the loss modulus, E". The storage modulus refers to the ability of a material to store energy and is related to the stiffness of the material. The loss modulus represents the heat dissipated by the sample as a result of the material's molecular motions and this reflects the damping characteristics of the material. Because of the time and temperature dependence of viscoelastic materials, which includes all polymers, the responses of these properties of these properties of functions of time (frequency) as well as the temperature of the measurements.

DMA measures the following:

- measurement of the glass transition temperature (Tg) where the material converts from a hard, brittle solid to a soft, flexible rubber
- the stiffness of a material as a function of temperature as well as time
- the energy absorbing or damping properties of a material
- the detection of weak, sub-Tg relaxation events which are often related to a material's impact resistance
- lifetime predictions based on master curves
- the assessment of crosslink density or crystallinity

Advantages of Frequency Multiplexing

The power of dynamic mechanical analysis is greatly increased through the use of frequency multiplexing experiments where the frequency applied to the sample is automatically varied during the experiment. This permits the direct assessment of the effects of time on the viscoelastic response of the material. Single frequency DMA measurements limit the scope of the

THASS
Thermal Analysis & Surface Solutions GmbH
Pfingstweide 21
61169 Friedberg - Germany

+49-6031-16223-1
+49-6031-16223-29
Info@thass.net
http://thass.net

characterization information obtainable from a sample since the effects of time cannot be directly observed.

The Seiko DMS6100 provides an easy means of probing the time dependency of polymeric materials using frequency multiplexing experiments. This is made possible through the use of patented fast Fourier transform technology (U.S. Patents 5287749 and 5452614). The Fourier transform approach, featured with the Seiko DMS6100, permits rapid data acquisition, which is absolutely essential when performing frequency multiplexing experiments under dynamic heating conditions. In addition, the Fourier transform approach provides a higher degree of sensitivity than non-Fourier DMA instruments for the detection of very weak loss transitions.

In addition, the Seiko DMS6100 offers a unique Synthetic Oscillation (SO) mode for the characterization of materials. With the SO mode, a complex stress wave form is applied to the sample and this stress wave contains 5 simultaneous frequencies. The resulting complex strain wave form is deconvoluted and compared to the complex stress wave form using Fourier transform technology to ascertain the quantitative viscoelastic quantities. The SO mode is different from standard frequency multiplexing in that with the latter, one single frequency is sequentially applied after another. With the SO mode, the sample is exposed to all 5 frequencies in one instant.

The rapid data acquisition featured with the Seiko DMS6100 permits samples to be dynamically heated at relatively fast heating rates (e.g., 5°C/min) in the frequency multiplexing mode of operation. With other DMA instruments, the much slower isothermal step mode of operation is required when performing frequency multiplexing experiments. The Seiko DMS6100 permits operation in either the dynamic or the isothermal step modes when performing frequency multiplexing experiments. For the analyst concerned about lab efficiency or sample throughput, the dynamic heating mode provides rapid sample analyses. For the DMA 'purist', the slower isothermal step mode of analysis is also available with the Seiko DMS6100.

The frequency multiplexing DMA results are extremely useful for complete and information sample characterization. The following information can be obtained from frequency multiplexing data which is not possible with single frequency data:

- assessment of apparent activation energies, Ea
- prediction of crosslink densities of elastomers and thermosets based on the values of Ea at the glass transition temperature. (Higher values of Ea for a given resin system are indicative of higher crosslink densities.)
- assignment of relaxation events (α, β, or γ) based on the value of the apparent activation energy associated with the given transition
- generation of master curves using the time - temperature superposition principle as applied to frequency multiplexing data
- prediction of long term properties of materials from master curves
- evaluation of acoustical damping characteristics from master curves

Thermal Analysis & Surface Solutions GmbH
Pfingstweide 21
61169 Friedberg - Germany

+49-6031-16223-1
+49-6031-16223-29
Info@thass.net
http://thass.net

Results from PET Injection Molded Bottle Resin

In order to demonstrate the power of the frequency multiplexing DMA mode of operation, a sample of PET injection molded bottle resin was analyzed. The sample was analyzed using the 8 mm single cantilever bending mode with the DMS6100. The sample was dynamically heated at a rate of 5°C/min at frequencies of 0.5, 1, 2, 5, and 10 Hz. Displayed in Figure 1 are the DMA results generated at a single frequency of 1.00 Hz. The log of the flexural storage modulus, E', and the loss modulus, E", and displayed as a function of temperature at a frequency of 1.00 Hz. The plot shows the major transitions associated with the PET bottle resin and this represents the general type of data obtained from most DMA instruments in the dynamic heating mode.

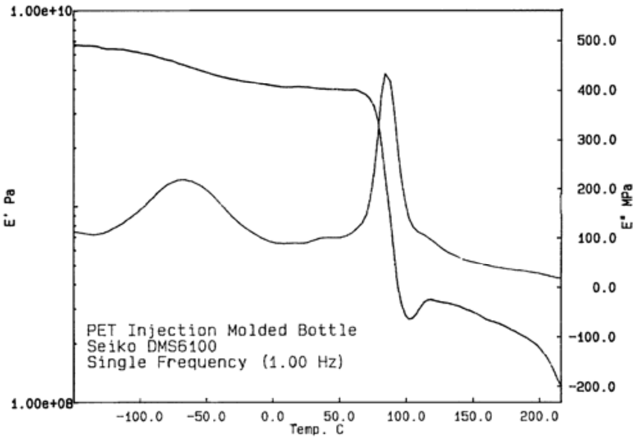

Figure 1

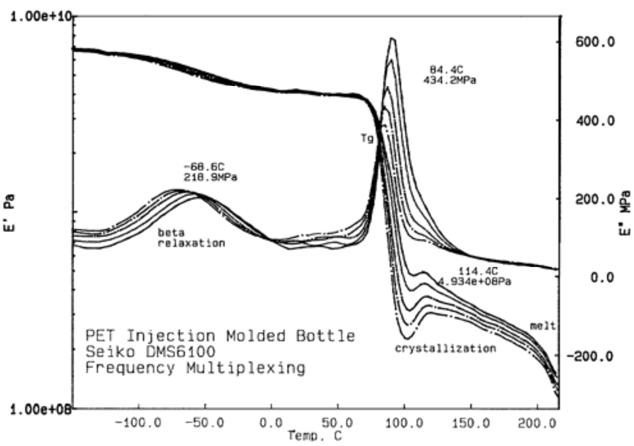

Figure 2

Thermal Analysis & Surface Solutions GmbH
Pfingstweide 21
61169 Friedberg - Germany

+49-6031-16223-1
+49-6031-16223-29
Info@thass.net
http://thass.net

With the patented Fourier transform technology associated with the Seiko DMS6100, frequency multiplexing results can also be generated at a dynamic heating rate of 5°C/min and these results are displayed in Figure 2. With the frequency multiplexing data, the effects of time via frequency are now directly observable. The relative shift in transition temperature is now apparent with respect to the applied frequency (time) and the link between temperature and time for polymeric materials is established. The Seiko DMS6100 provides five times more data as compared to single frequency DMA instruments in a single, dynamic heating experiment.

For the PET bottle resin sample, the following transition are clearly observed with the Seiko DMS6100:

- the beta relaxation event at -69°C (1.00 Hz), which is related to the good impact properties associated with PET resin
- the alpha or glass transition event at 84°C (1.00 Hz), where the polymer undergoes significant softening
- the cold crystallization at 114°C, where a portion of the amorphous polymer undergoes crystallization
- and softening due to pre-melting effects at 200°C

In the frequency multiplexing mode, the shift in the given transition peak temperature with respect to frequency or time is now clearly evident. Due to the particular rotational molecular motions, the shift in temperature at the subambient β transition is much greater with respect to the applied frequency than at Tg.

<u>Activation Energies from Frequency Multiplexing Data</u>

The amount of shifting in the peak temperature with respect to the applied frequency can be easily assessed using the Arrhenius approach by which the log of the DMA frequency is plotted versus the inverse of the loss peak temperature. Over a limited frequency interval, a linear relationship is obtained and the best fit line through the resulting data points yields a slope from which the apparent activation energy, Ea in units of kJ/mole, is calculated. The Seiko DMS6100 offers RheoDeltaE software which automatically determines the value of the apparent activation energy based on the Arrhenius approach.

THASS
Thermal Analysis & Surface Solutions GmbH
Pfingstweide 21
61169 Friedberg - Germany
+49-6031-16223-1
+49-6031-16223-29
Info@thass.net
http://thass.net

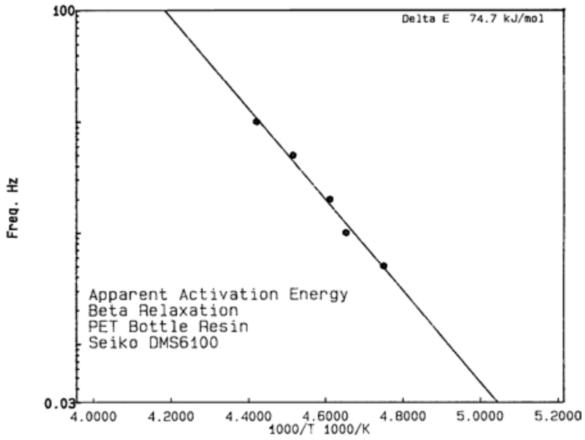

Figure 3

Displayed in Figure 3 is the Arrhenius plot for the subambient β relaxation event associated with the PET bottle resin. The plot shows the log of the DMA frequency (0.5, 1, 2, 5, and 10 Hz) versus the inverse of the loss peak temperature, 1/T (K). The value of the activation energy, assessed from the slope of the best-fit line, is found to be 74.7 kJ/mole for the β relaxation event. The value of Ea is useful in assigning a particular designation to a loss transition. Higher values of Ea are generally associated with α transitions, while medium values are associated with β relaxation events, and the lowest values are reflective of γ dispersions.

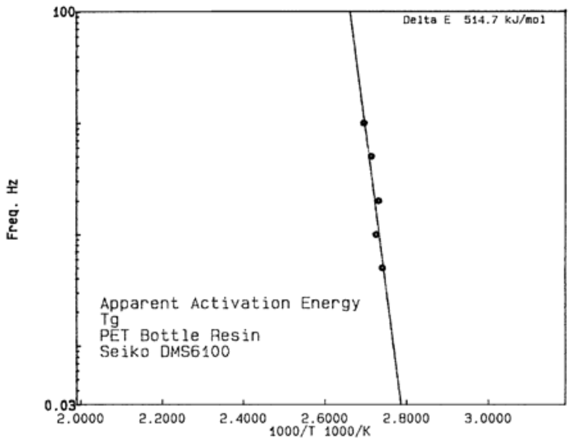

Figure 4

Shown in Figure 4 is the Arrhenius plot generated using the Seiko RheoDeltaE software for the Tg or α transition of the PET bottle resin. It may be seen that the Tg frequency - temperature results have a much greater slope than that associated with the subambient β event. The apparent activation energy associated with the glass transition event of the PET bottle resin is 515 kJ/mole. This value is very high (even for an α transition) and is reflective of the hindrance

Thermal Analysis & Surface Solutions GmbH
Pfingstweide 21
61169 Friedberg - Germany

+49-6031-16223-1
+49-6031-16223-29
Info@thass.net
http://thass.net

of the rotation of the main chain molecules for this PET bottle resin. During the injection molding process, the bottle resin apparently develops a unique morphology resulting in a highly 'pinned' amorphous component. This detailed information about the polymer is only possible through the use of frequency multiplexing DMA experiments. A single frequency experiment would not provide direct information relative to the unique structural aspects of the bottle resin.

Generation of Master Curves from Frequency Multiplexing Data

One additional benefit of performing frequency multiplexing experiments is that master curves can be generated using the well known time - temperature superposition principle. The curves permit the estimation of mechanical properties of a polymeric material at frequencies or times which are well outside the range of normal DMA experiments. Master curves are frequently used for lifetime prediction based on the time that it takes to achieve a 'critical' modulus value at the given isothermal reference temperature. The Seiko Rheo Master Curve software uses an automated best fit procedure to determine the values of the WLF constants C1 and C2.

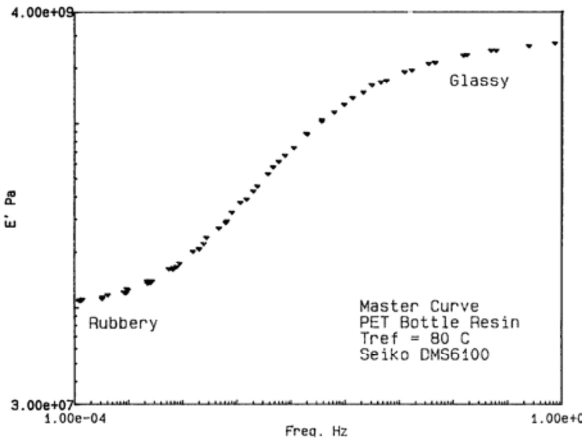

Figure 5

Shown in Figure 5 is the E' modulus master curve associated with the glass transition event of the PET resin at a reference temperature of 80°C. This plot shows the stiffness response of the polymer under isothermal conditions and demonstrates, that at longer times or lower frequencies, the polymer exhibits a more liquid like response. At shorter times or higher frequencies, the resin behaves more like a rigid, glassy solid. The generation of the master curves is possible using frequency multiplexing results and cannot be generated from single frequency DMA data.

Summary

The patented real time Fourier transform technology associated with the Seiko DMS6100 permits valuable frequency multiplexing data to be acquired at either relatively fast dynamic heating conditions or using isothermal steps. Compared to the limited single frequency DMA experiments,

Thermal Analysis & Surface Solutions GmbH
Pfingstweide 21
61169 Friedberg - Germany

+49-6031-16223-1
+49-6031-16223-29
Info@thass.net
http://thass.net

frequency multiplexing results provide more characterization information, permit assessments of activation energies and allow for the generation of master curves. With the Seiko DMS6100, each and every sample can be analyzed using frequency multiplexing conditions providing 5 times more data than with standard single frequency measurements.

Thermal Analysis & Surface Solutions GmbH
Pfingstweide 21
61169 Friedberg - Germany

+49-6031-16223-1
+49-6031-16223-29
Info@thass.net
http://thass.net