SII NanoTechnology Inc. SII

DMA AS PROBLEM-SOLVING TOOL: CHARACTERIZATION OF PROPERTIES OF ELASTOMERS USING MASTER CURVES

Problem

A chemist working for a tire research and development center has a need to optimize the properties of the elastomers to be used for the manufacture of automotive and truck tires. The chemist wishes to have a technique which provides information on crosslink density and the effects of formulations on the properties of the tires. DSC (differential scanning calorimetry) has not proven to be satisfactory since the various elastomers yield essentially equivalent glass transition temperatures (Tg) and cannot discriminate between the various crosslink densities and formulations.

Solution

- Dynamic mechanical analysis (DMA) provides a highly sensitive means for testing the properties of elastomers used for automotive applications. The technique measures the storage modulus, E' or stiffness, the loss modulus, E" or damping, and tan δ (E"/E') as a function of both temperature and frequency. DMA can be used to provide the following information Relative degree of cross-linking of cured elastomer systems
- Examination of the curing characteristics of uncured or green elastomers
- Assessment of the effects of formulations or compounding
- Determination of carbon black loading
- Lifetime predictions based on the generation of master curves
- Prediction of tire performance based on the values of tan δ over a temperature range
- Measurement of the damping or energy absorbing properties
- Assessment of the glass transition temperature (Tg)
- Detection of relaxation transitions below Tg
- Creep and stress relaxation and recovery characteristics of elastomers

The Seiko EXSTAR DMS6100 provides state-of-the-art measurement of the viscoelastic characteristics of elastomeric materials with the following features and benefits:

- Synthetic oscillation mode in which five different frequencies are applied to the sample using a complex wave form. This permits the DMS6100 to be operated in the frequency multiplexing mode and yet still collect data at a relatively fast heating rate (4°C/min)

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- Dynamic and static test modes in which the DMS6100 can perform both dynamic DMA experiments as well as creep and stress relaxation measurements.
- Multiple modes of deformation including bending, shear, tension and compression
- Fourier transform technology for the deconvolution of the complex wave form and for highly sensitive measurement of the phase angle, δ. This permits the detection of extremely weak or low energy transitions.
- Ability to handle samples over very wide modulus range (5 decades). This feature permits the DMS6100 to continuously measure the properties of materials from below, through and above the glass transition event without the need for changing transducers.

The best means of characterizing the properties of elastomers is with the dual cantilever or bending mode of deformation. This permits the continuous assessment of the elastomer's mechanical properties from well below Tg into the rubbery plateau region. The measurement of properties in the rubbery plateau region is especially important for elastomers since the effects of crosslinking become most pronounced. A higher crosslink density, for a given elastomeric system, results in a higher value of E′ at a given temperature in the rubbery region. The effects of compounding can oftentimes be observed in the tan δ response at Tg. The intensity and shape of the DMA tan δ peaks at the glass transition event, especially on the higher temperature portion, can provide valuable characterization information on the compounding of elastomers.

Shown in Figure 1 are the DMA results obtained on elastomer sample A using the Seiko DMS in the bending mode of operation.

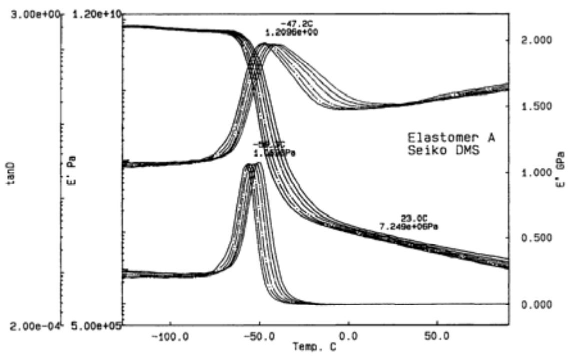

Figure 1

The plot shows the log of the flexural storage modulus, E′, the loss modulus, E″, and tan δ as a function of both temperature and frequency. All of the data displayed in this plot was generated during a single frequency multiplexing experiment and the sample

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was analyzed at frequencies of 0.5, 1, 2, 5, 10, and 20 Hz. The glass transition event of the elastomer is observed as a large drop in the modulus beginning at –55°C. The time or frequency dependent nature of Tg is clearly seen in the E″ and tan δ signals where the peak temperatures increase as a function of the applied frequency. The Tg for elastomer A may be defined as the E″ peak temperature at a frequency of 1.00 Hz which would yield -56.3°C. The value of the storage modulus at room temperature is 7.2 MPa at 1.00 Hz.

A second elastomer material, sample B, was analyzed using identical experimental conditions and the results are displayed in Figure 2. This sample yields similar, but significantly different, viscoelastic responses.

The Tg is observed at -54.5 C based on the E″ peak temperature at 1.00 Hz. The value of E′ at room temperature is 3.3 MPa which is significantly less than that for sample A. This indicates that sample B has a lower crosslink density has compared to A.

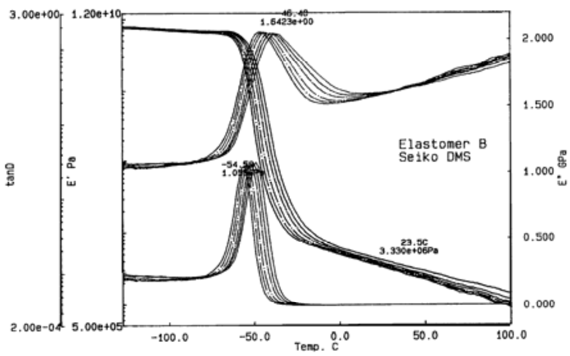

Figure 2

A very sensitive means of further analyzing the DMA results can be performed through the generation of master curves. This is done using the Seiko Rheo Master Curve software which utilizes the well known time - temperature superposition principle to generate the E′, E″ and tan δ master curves at a user-selected reference temperature. The master curves are easily generated from the DMA frequency multiplexing data and the curves permit the estimation of mechanical properties at frequencies or times which are well outside the range of a normal experiment. Master curves are frequently used for lifetime predictions based on the time that it takes to achieve a 'critical' modulus value at the given reference temperature.

The generation of the master curves is performed using the following steps:

- A DMA frequency multiplexing experiment is performed

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- The viscoelastic data in the transition region is isolated
- The data is analyzed using the Seiko Rheo Master Curve software which provides automated determination of the best-fit WLF constants (C1 and C2)
- The Seiko Master Curve software automatically generates the E', E" and tan δ master curves based on the best-fit values of the two WLF constants

Shown in Figure 3 is the E' data for sample A plotted as a function of frequency rather than temperature. The upper curves represent the

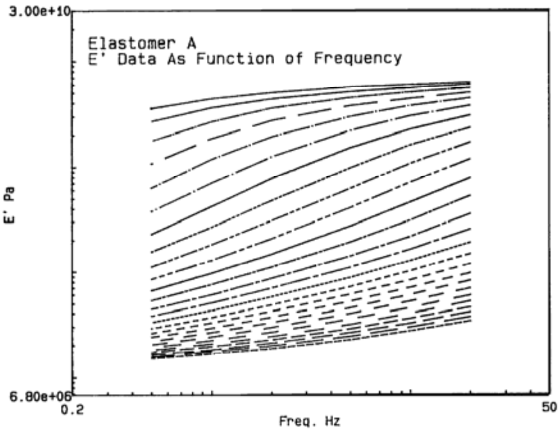

Figure 3

data points obtained at lower temperatures, in the glassy regions, while the lower curves are the data points generated at the higher temperatures, in the rubbery regions. The data curves are shifted along the X-axis (frequency) to generate a smooth, continuous master curve. The upper curves are shifted to higher frequencies, while the lower curves are shifted to lower frequency regions. The shifting follows the mathematical expression known as the Williams-Landel-Ferry (WLF) equation, which implies an equivalency between frequency and temperature.

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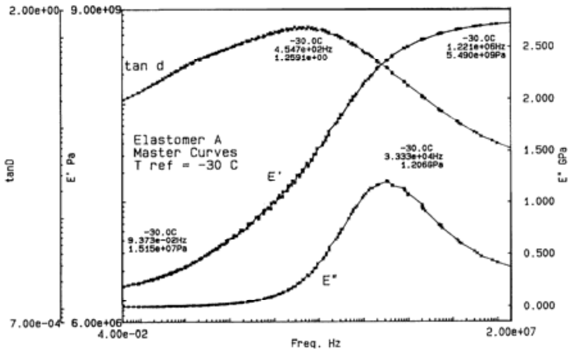

Figure 4

Displayed in Figure 4 are the master curves generated for elastomer sample A at a reference temperature of –30°C. The best fit values of the WLF constants are: C1 = 17 and C2 = 52. The effects of frequency or time on the viscoelastic properties of the elastomer are clearly evident from the master curves. At higher frequencies (shorter times), the modulus represents that of the stiff, glassy material, while at lower frequencies (longer times), the modulus reflects more rubbery or liquid-like characteristics. The frequency range covered by the master curves covers nearly 9 decades, from 20 MHz down to 0.04 Hz.

The E” and tan δ master curves show a well-defined peak maxima at a particular frequency at the given reference temperature. This represents the frequency at which the maximum energy absorption occurs. This is useful for acoustical damping or other energy absorption purposes. Elastomers or acoustical damping materials can be formulated or ‘tuned’ so that the peak maximum occurs at a specific frequency range at a given operating temperature.

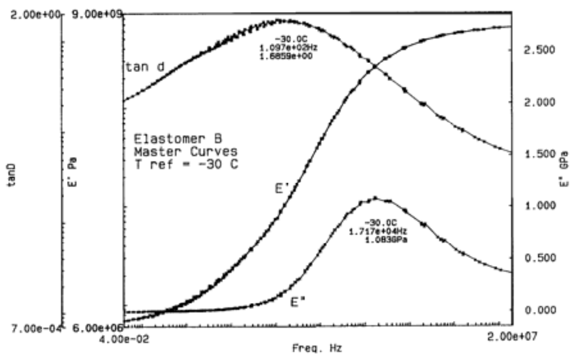

Figure 5

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The master curves generated for elastomer sample B at a reference temperature of –30°C are shown in Figure 5.

The Seiko software permits a direct overlay of the DMA master curves for comparative purposes. Displayed in Figure 6 is an overlay of the E′ and tan δ master curves for elastomers A and B. The lower crosslink density of elastomer B is clearly evident in the rubbery regions (low frequencies) in the E′

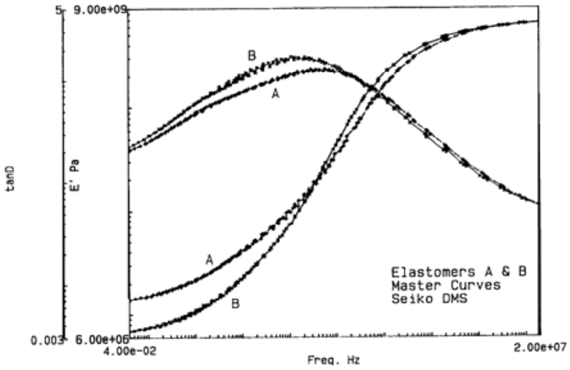

Figure 6

master curves. In the glassy domains (higher frequencies), both elastomers yield essentially equivalent responses. The tan δ responses are also distinctly different where elastomer B is more Guassian shaped.

Summary

Dynamic mechanical analysis (DMA) is useful technique for the characterization of elastomeric materials. The high inherent sensitivity of DMA provides information on: relative crosslink densities, compounding, effects of carbon black, Tg, damping or energy absorbing properties, and lifetime predictions. Further valuable information can be obtained by the generation of DMA master curves. The Seiko Rheo Master Curve software provides an automatic best fit assessment of the WLF constants as well as the automatic generation of the E′, E″ and tan δ master curves.

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