DMA AS PROBLEM-SOLVING TOOL: CHARACTERIZATION OF ASPHALT ROOFING SHINGLES

Problem

An chemist working for an R&D center at a facility where asphalt roofing shingles are manufactured has a need to determine the mechanical properties of the shingles. There is a need to better characterize the properties of the shingles for quality assurance purposes, to optimize the formulations of the asphalts for different roofing applications, trouble shooting purposes (shingles which crack versus those that do not), and aging studies to determine the long term performance of the shingles.

Solution

Dynamic mechanical analysis (DMA) provides an excellent means of characterizing the properties of polymeric materials, including asphalt roofing shingles. 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 frequency.

In 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 the 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 molecular motions and this reflects the damping properties of the material. Because of the time and temperature dependence of viscoelastic materials, which includes all polymers, the responses of these properties are functions of time (frequency) and the temperature of the measurements.

DMA can provide the following valuable information on polymeric materials:

- measurement of the glass transition temperature where the material converts from being hard and brittle to soft and flexible
- assessment of the effects of formulations or compounding
- the stiffness of the material as a function of temperature as well as time
- the energy absorbing or damping characteristics of the material
- detection of sub-Tg relaxation events which are oftentimes related to impact properties
- lifetime predictions based on the generation of master curves

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The Seiko EXSTAR DMS6100 provides state-of-the-art measurements of the viscoelastic characteristics of polymeric systems and asphalt roofing shingles with the following features and benefits:

- Synthetic Oscillation (SO) mode in which five different frequencies are simultaneously 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 (5°C/min).
- Dynamic and static test modes by which the DMS6100 can perform both dynamic DMA experiments as well as creep and stress relaxation measurements.
- Multiple modes of sample deformation including bending (dual and single cantilever), shear, film shear, tension and compression. The multiple modes permit the instrument to handle an unsurpassed variety of sample types and geometries.
- Fourier transform (patented) technology for the deconvolution of the complex wave form and for the highly sensitive measurements of the phase lag, δ. The use of the Fourier transform technology permits the detection of extremely weak or low energy transitions.
- Ability to handle samples over a 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 sample fixtures.

The latter feature is very useful for asphalt materials as the stiffness response of shingles can change by more than 4 decades from -80 to 150°C. The Seiko DMS6100 allows the detection of the shingle's Tg as well as the melting phase characteristics of the olefin component that occur well above the glass transition event.

In this study, the viscoelastic properties of two roofing shingles were characterized by the Seiko DMS6100. One shingle was the control and the other shingle had been placed on the roof of a house and aged for a prolonged period. The following experimental conditions were utilized to analyze the two asphalt roofing shingles:

Instrument:	Seiko DMS6100
Mode of deformation:	8 mm bending, single cantilever
Mode of operation:	frequency multiplexing
Frequencies:	0.5, 1, 2, 5 and 10 Hz
Heating rate:	5°C/min
Initial temperature:	-80°C
Sample width:	approx. 12 mm
Sample thickness:	approx. 2.7 mm
Strain amplitude:	20 μm

In order to prevent the sample from sticking to the clamps, the ends of the samples in contact with the clamping surfaces were wrapped with aluminum foil. Even though the asphalt become quite sticky when heated up to high temperatures, the use of the foil permits the sample to be easily removed from the clamps at the conclusion of the experiment.

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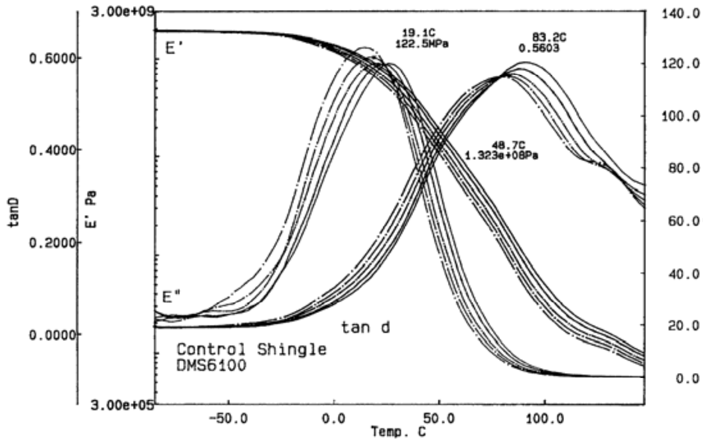

Figure 1

Displayed in Figure 1 are the DMA results generated on the control roofing shingle specimen. The plot shows the log of the flexural storage modulus, E′, the loss modulus, E″, and tan δ (E″/E′) as a function of sample temperature at the 5 different frequencies. It should be noted that all of the data shown in this graph was obtained during a single experiment. The control shingle exhibits a well-defined Tg at 19°C based on the E″ peak temperature at a frequency of 1.00 Hz. The loss peak is symmetrical which is typical of an amorphous polymer. At the glass transition event, the sample undergoes significant softening as reflected by the large decrease in the storage modulus, E′. The value of E′ at 50°C is 0.13 GPa.

The DMA results obtained on the aged roofing shingle specimen are shown in Figure 2. The data was plotted on an equivalent scaling as for the control shingle. The results demonstrate that the aged shingle has a substantially different response as compared to the control shingle. The loss peak for the aged asphalt shingle is no longer symmetrical; and has actually split into two apparent peaks at -15 and 31°C due to the effects of aging. The intensity of the loss peak is significantly lower for the aged shingle as compared to the control specimen. The data reveals that the structure of the aged asphalt has changed significantly over time with the generation of two distinct phases each having its own characteristic loss peak temperature. The value of E′ at 50°C is 0.33 GPa for the aged sample demonstrating that the aged shingle is significantly stiffer than the control in the regions at the glass transition event.

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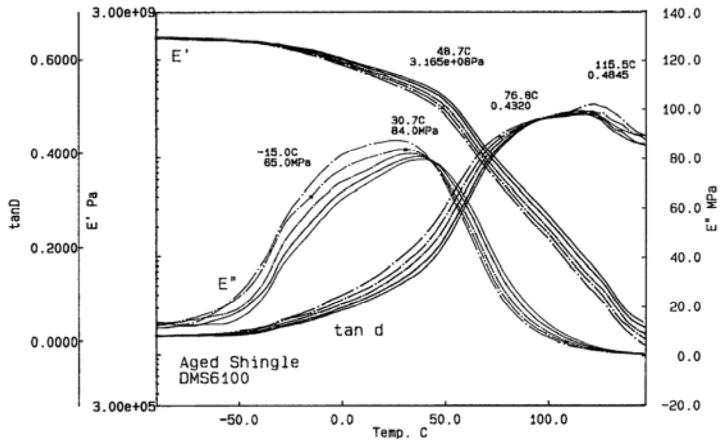

Figure 2

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

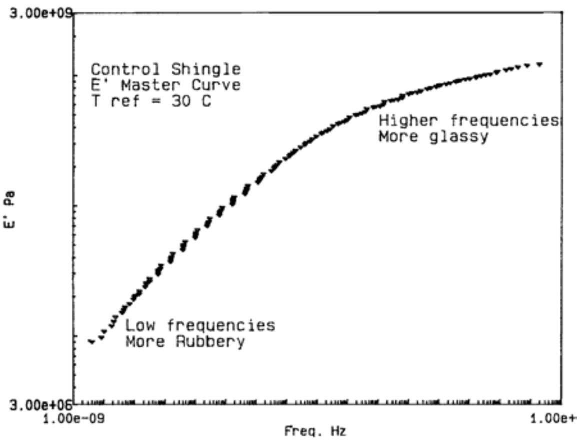

Figure 3

Displayed in Figure 3 is the E' master curve generated for the control shingle at a reference temperature of 30°C. The plot shows the stiffness response of the shingle under isothermal

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conditions and shows, that at longer times or lower frequencies, the shingle exhibits a more liquid like response. At shorter times or higher frequencies, the shingle behaves more like a glassy solid.

The master curves help explain why shingles can only be installed at certain temperatures. As the outdoor temperature becomes lower, the modulus tends towards the glassy, more brittle state. Nailing the shingle subjects the asphalt to a high impact frequency, which pushes the modulus response even more into the glassy regions. Thus cracking of the shingle around the nail can occur if a nail is driven into the asphalt at relatively cold outdoor temperatures.

Summary

DMA provides a highly sensitive means of examining the properties of polymeric materials, including asphalt roofing shingles. The technique yields useful informatio n on the softening or glass transition temperature, stiffness or modulus, and damping or loss properties. In this study, the viscoelastic properties of two roofing shingles (control and aged) were measured using the Seiko DMS6100. It was found that the aged shingle became stiffer and the loss peak at Tg split into two distinct transitions due to the effects of aging. The frequency multiplexing data obtained from DMA experiments permit the generation of master curves and these curves are useful for lifetime predictive purposes.

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