Characterization of Asphalt Roofing Shingles Using the Diamond DMA

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Introduction

Asphalt is a complex mixture of different hydrocarbons, the amounts of which vary widely due to the formulation of the asphalt as well as the crude sources and production materials. The given composition of an asphalt can be varied depending upon the given application (roofing shingle, road paving) as well as the intended geographic location of the end product. The temperature response of the asphaltic product for its given localized climate can be adjusted. The viscoelastic nature of asphalt has a major role in the performance of the asphalt and dynamic mechanical analysis provides a valuable characterization tool [1,2,3].

Dynamic mechanical analysis (DMA) is a powerful technique for the characterization of the viscoelastic properties of polymers [4,5,6] and asphalts. DMA measures the modulus (stiffness) and damping (energy dissipation) properties of materials as they are deformed under dynamic stress. These measurements provide quantitative information about the performance of materials. The technique can be used to evaluate a wide variety of materials such as thermoplastics, composites, thermosets, elastomers, films, fibers, coatings and adhesives. DMA is a valuable technique because of its high inherent sensitivity and is the most sensitive thermal analysis technique for the measurement of the glass transition event, Tg. Secondary relaxation events readily observed by DMA, such as the β and γ transitions, simply cannot be detected by any other thermal technique. DMA results are relatable to important mechanical properties such as impact resistance and toughness.

Polymeric materials exhibit viscoelastic behavior, which means that they simultaneously possess both solid-like as well as liquid-like characteristics. The degree to which the polymer exhibits more solid-like or liquid-like properties is dependent upon temperature as well as time or 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 wave 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 it 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 given molecular motions and this reflects the damping characteristics of the polymer. The ratio of the loss and storage properties provides another useful quantity, tan δ, where tan δ = E"/E'. Because of the viscoelastic nature of many materials, which includes all polymers, these viscoelastic properties (E', E" and tan δ) are functions of temperature as well as time (frequency).

Diamond DMA

PerkinElmer offers the Diamond DMA for state-of-the-art dynamic mechanical measurements.

The instrument offers the following valuable features and benefits:

- Patented Fourier Transform technology for unparalleled sensitivity

- Unsurpassed frequency multiplexing operation and Synthetic Oscillation Mode for more complete characterization and faster turnaround times
- Application of a wide dynamic force range (up to 18N force) to handle a wide range of samples from single fibers and thin films to thick, stiff composites and ASTM 'dog bone' test specimens
- Simplified, user-friendly operation to allow for accurate and reproducible measurements to be easily performed with minimal operator interaction
- Wide frequency range (0.01 to 100 Hz)
- Patented controlled cooling system for unsurpassed measurements in the critical subambient regions
- Multiple modes of sample deformation (bending, shear, tension, compression) to accommodate the widest range of samples and applications
- Patented advanced auto-tension control for the easy analysis of thin films, fibers and polymer plaques
- Special sample immersion temperature controlled bath and humidity environmental accessories

Benefits of Frequency Multiplexing

One powerful means of analyzing polymers and polymer-like materials (e.g., asphalt) by DMA is with frequency multiplexing experiments. In this approach, a sample is subjected to a number of different frequencies (generally five or more) in order to clearly define the effects of frequency, or time, on the mechanical responses exhibited by the polymer. In the past, the problems associated with data collection have necessitated that most DMA instruments operate in a slow isothermal step mode when performing frequency multiplexing experiments.

The Diamond DMA features real-time, patented Fourier transform technology (U.S. patents 5287749 and 5452614). The use of this technology makes it possible to perform frequency multiplexing experiments while dynamically heating even at relatively fast rates (e.g., 5 C/min). The Diamond DMA has added a further technological advance with the introduction of Synthetic Oscillation (SO) measurements. In the SO mode, a complex stress sine wave is applied to the sample and this complex stress wave contains five (5) simultaneous frequencies. The resulting complex strain and stress sine waves are deconvoluted using Fourier transform technology and compared to compute the quantitative viscoelastic properties. The SO different is different from standard frequency multiplexing in that, with the latter, one single discrete frequency is sequentially applied to the sample at a time. With the SO mode, the sample is subjected to all five frequencies instantaneously. The advantage of performing frequency multiplexing and Synthetic Oscillation DMA experiments is that much more informative sample characterization information can be generated. properties of a polymeric material can be estimated.

The Diamond DMA system features Master Curve software for the generation of these valuable and informative master curves. The software offers an automated best-fit procedure to determine the values of the WLF constants, C1 and C2, used to generate the master curves.
The viscoelastic properties of a two asphalt roofing shingles (control and aged) were characterized using the Diamond DMA.

Experimental

The following experimental conditions were used to analyze the asphalt roofing shingles.

Experimental Conditions

Instrument	Diamond DMA
Heating rate	5 C/min
Temperature range	-100 to 150 C
Frequencies	0.5, 1, 2, 4, and 10 Hz
Deformation mode	Single cantilever bending (8 mm)
Sample width and thickness	W = 11 mm, T = 2.8 mm
Deformation amplitude	20 µm
Cooling	Liquid nitrogen with Automated Cooling Accessory

Results

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 five 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.

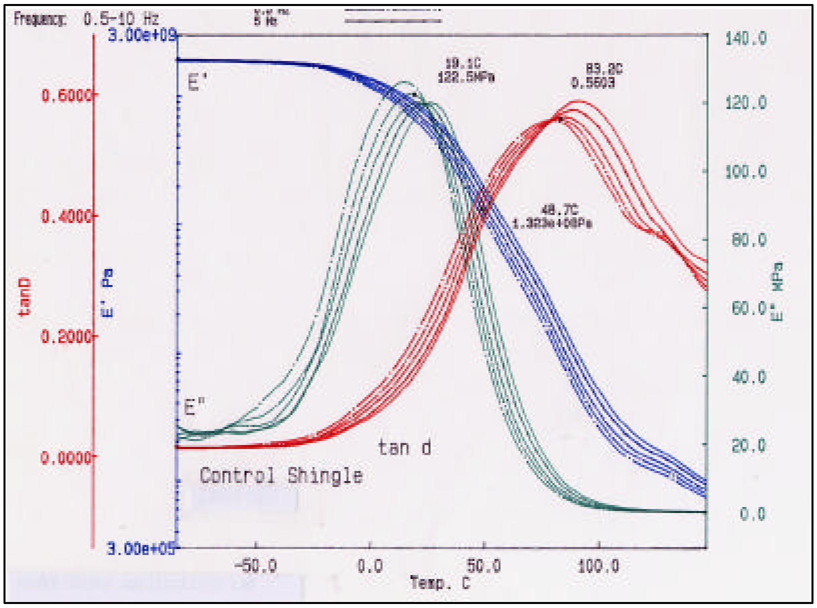

Figure 1. DMA results (log E’, E” and tan delta) for the control asphalt roofing shingle

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

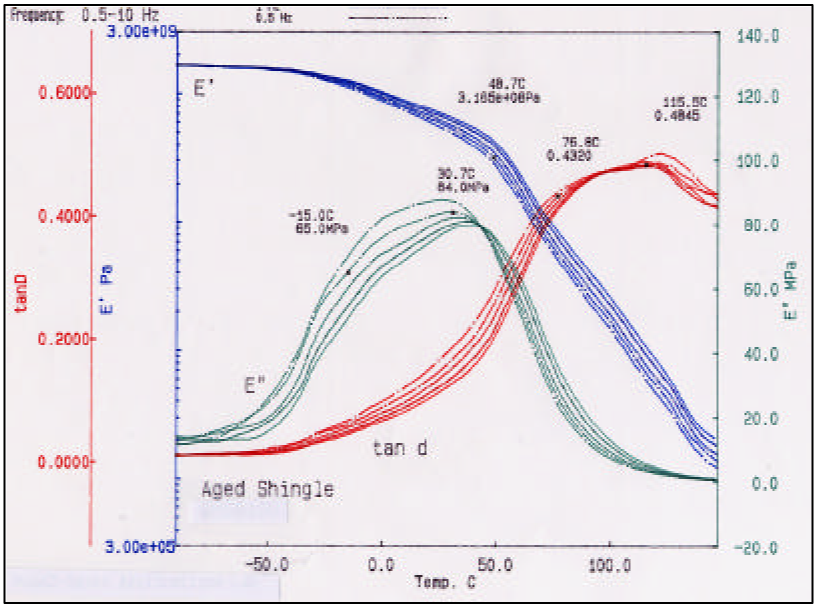

Figure 2. DMA results for aged asphalt roofing shingle

the control in the regions at the glass transition event.

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 Pyris Diamond Master Curve software and the software features an automated best-fit determination of the WLF constants (C1 and C2).

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 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

Dynamic mechanical analysis (DMA) provides a highly sensitive means of characterizing the properties of all polymeric materials, including asphalts. The technique yields very useful information on the softening or glass transition temperature, stiffness or modulus, and damping or loss properties. The Diamond DMA provides state-of-the-art results on polymeric and asphaltic materials. In this study, the viscoelastic properties of two asphalt-based roofing shingles (control and aged) were measured using the Diamond DMA. It was found that the aged shingle was stiffer and that the loss peak at Tg split into two distinct events due to the effects of aging.

The outstanding frequency multiplexing data obtained from the Diamond DMA permitted the generation of information master curves, which are useful for predictive purposes and lifetime assessments.

References

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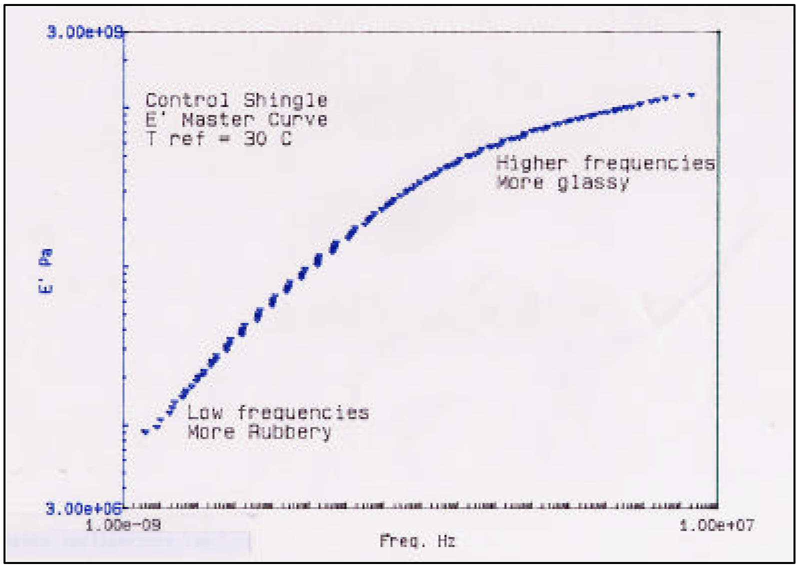

Figure 3. Modulus (E') master curve generated for control roofing shingle at a reference temperature of 30 C