SII NanoTechnology Inc.

DMA AS PROBLEM SOLVING TOOL: CREEP OF UNCURED ELASTOMERS

Problem

A production facility, where uncured elastomeric materials are made, is experiencing difficulties with the creep or flow characteristics of the elastomers during shipments to customers. Sheets of the elastomeric materials are stacked for shipment and, it is observed with some formulations, that the resins exhibit excessive flow or creep during shipment rendering the materials unsatisfactory to the customer. The manufacturing site desires to have a means of characterizing the creep or flow properties of the uncured elastomeric materials for problem solving purposes.

Solution

Dynamic mechanical analysis (DMA) affords a excellent means of characterizing not only the creep or flow characteristics of a material, but the viscoelastic properties as well, including storage modulus, E', loss modulus, E", and tan delta (E"/E'). With DMA, measurements can be performed in the static modes (creep and stress relaxation) as well as the dynamic modes, where a sinusoidal force or stress is applied to the sample.

Because of the viscoelastic nature exhibited by elastomers and other polymeric materials, the material will exhibit some amount of flow or creep when a force or loading is applied to the sample. Creep can even occur at temperatures below the glass transition event (Tg) and the deformation of the sample is known as 'cold flow'.

In the creep mode of analysis, the sample is subjected to a constant force or stress over a period of time under isothermal conditions. The resulting sample deformation, or flow, under the application of a load is monitored as a function of time. A higher level of deformation corresponds to a higher degree of creep exhibited by the material. In the stress relaxation mode, the sample is subjected to a constant displacement or deformation and the resulting decay in the force is monitored as a function of time.

The following are practical applications of creep and stress relaxation measurements:

- ability of a thermoplastic to maintain its shape over a long period of time
- effectiveness of adhesives or sealants in maintaining the integrity of the seal
- estimation of the deflection of thermoplastic beams or composite laminates under a load
- prediction of the ability of a composite to resist the onset of micro-cracking
- estimation of bolt retention, especially in the cases where metal screws or bolts are used to maintain plastic boards or thermoset laminates
- the ability of a gasket to maintain an effective seal over time

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- effectiveness of force-fits or snap-fits of plastic components in maintaining joint integrity
- ability of a lid to retain a good seal on a plastic bottle over time

In this application, the customer was concerned about the propensity of the uncured elastomer to undergo creep or flow because of the load caused by stacking sheets of the material during shipment. It is desired to reduce the level of creep by modifying the formulation of the elastomer.

The Seiko DMS6100 is an excellent instrument for characterizing the complete viscoelastic properties of polymers, including the following means of analyses:

- creep
- stress relaxation
- single frequency DMA
- frequency multiplexing DMA
- Synthetic Oscillation DMA

The capabilities of the Seiko DMS6100 are unparalleled because of the use of real time Fourier transform technology (U.S. patents 5287749 and 5452614). The state-of-the-art Fourier transform approach permits the DMS6100 to collect data at an extremely rapid rate. This permits the DMS6100 to routinely perform frequency multiplexing experiments at a relatively fast dynamic heating rate (e.g., 5°C/min) for rapid sample turnaround. In addition, the Fourier transform technology provides the highest degree of sensitivity for the detection of very weak transitions. The Seiko DMS6100 permits operation in a large variety of sample deformations, including:

- dual cantilever bending (32, 20, 8 mm)
- single cantilever bending (32, 20, 8 mm)
- tension (auto-tension)
- compression
- shear
- film shear

In this characterization study, the creep properties of two elastomeric samples were measured to determine the propensity of the materials to undergo flow at room temperature. The two elastomers ('A' and 'B') were analyzed using the compression clamps. The compression mode provides excellent results on the properties of soft materials, such as uncured elastomers or adhesives at temperatures above the glass transition temperature. The samples were cut to yield disks with a diameter of 10 mm, which then exactly matches the diameter of the compression clamps. The DMS6100 was programmed to provide a constant load of 100 g to the samples for a period of 60 minutes at room temperature. The resulting sample displacement was then monitored as a function of time.

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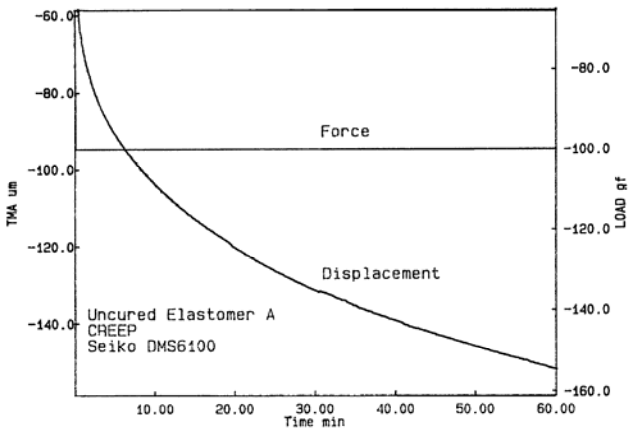

Figure 1

Displayed in Figure 1 are the DMA creep results generated for elastomer A. The plot shows the displacement (TMA, μm) and load (grams force) versus time under isothermal conditions at room temperature. Under the application of the compressive loading, the sample shows an initial rapid decrease in its deformation. After about 25 minutes, the response of the sample to the loading becomes essentially linear, indicating that the rate of change in the creep of the sample is constant and is no longer accelerating.

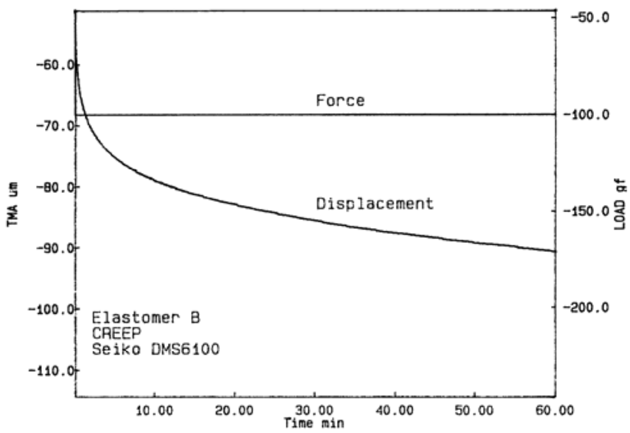

Figure 2

Shown in Figure 2 are the DMA creep results obtained for elastomer sample B. This material too exhibits a similar response as compared to sample B. However, the absolute change in the resulting deformation is significantly less for B as compared to A and this may be seen in a direct overlay of the two sets of data, shown in Figure 3. This plot demonstrates that elastomer B has a much lower propensity to undergo creep or flow under the given loading conditions as compared

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to A and that B should be a better candidate to retain its overall shape during stacking and shipment.

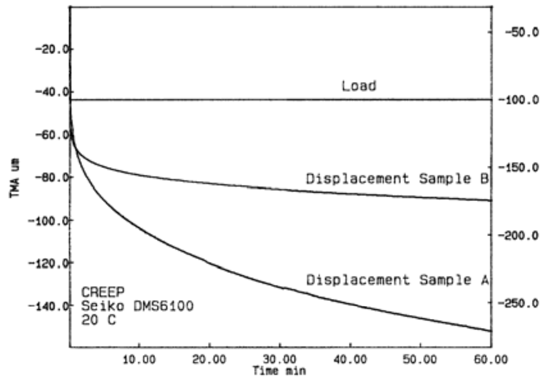

Figure 3

For additional characterization purposes, uncured elastomer A was analyzed using the frequency multiplexing DMA mode of analysis. With the Seiko DMS6100, the sample is simultaneously dynamically heated and scanned at various frequencies to determine the effects of temperature as well as time (frequency) on the viscoelastic properties of the polymeric material. Sample A was heated at a rate of 5°C/min from room temperature to 250°C and analyzed at frequencies of 0.5, 1, 2, 5, and 10 Hz. The sample was characterized using the 8 mm dual cantilever bending clamping assembly and the results are presented in Figure 4. The plot shows the log of the flexural storage modulus, E′ or stiffness and tan delta (E″/E′) as a function of temperature at the 5 different frequencies. It should be noted that all of the data presented in this plot was generated during a single DMA experiment. The results show that the sample undergoes softening beginning at 39°C as reflected by the drop in the storage modulus. The tan delta response shows a series of frequency dependent peaks corresponding to the softening of the elastomer between 50 and 130°C. The uncured elastomer undergoes curing at

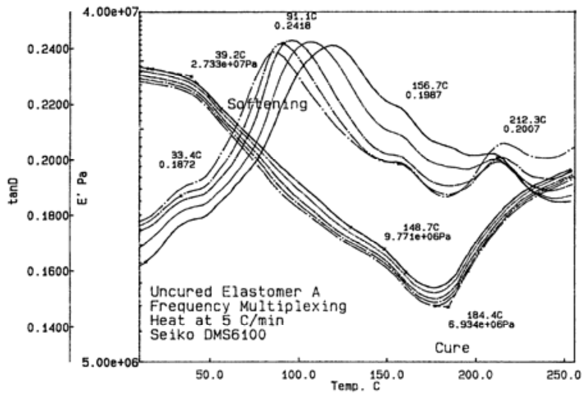

Figure 4

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184°C as shown by the increase in E′. An increase in the storage modulus corresponds to the curing or crosslinking of thermosetting or elastomeric materials or the crystallization of thermoplastics. The softening and curing characteristics along with the creep properties of the elastomeric material are critical in improving the formulation of the final product.

Summary

The Seiko DMS6100 permits operation in the dynamic (sinusoidal) mode, as well as in creep and stress relaxation. The latter two modes of analyses are useful for predicting the long term flow or force decay characteristics of polymers. This is especially useful for determining the ability of a polymer to retain its shape or to maintain its ability to hold a seal. The Seiko DMS6100 features state-of-the-art operation and technology (including real time Fourier transform methodology) for the successful characterization of a wide variety of material and for the noise-free detection of very weak transitions.

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