SII NanoTechnology Inc.

DMA AS PROBLEM-SOLVING TOOL: CHARACTERIZATION OF TG OF HIGHLY FILLED COMPOSITES

Problem

A customer working for a company manufacturing injection molded parts has a need to assess the glass transition temperature (Tg) of the polymer utilized in the components. Because the materials are highly filled (80% fillers and 20% polymer), differential scanning calorimetry (DSC) does not have enough sensitivity to detect the weak Tg of the composites. The customer desires a means of assessing the glass transition temperatures of the filled polymers for quality assurance purposes.

Solution

Dynamic mechanical analysis (DMA) provides a very high degree of inherent sensitivity for the detection of weak transitions. The overall sensitivity of DMA is on the order of 100 to 1000X greater than DSC. With DMA, the clear identification of the glass transition event of a polymeric material can always be easily performed. In addition, DMA has the necessary sensitivity to detect weak sub-Tg relaxation events, such as the β and γ transitions, which DSC cannot possibly detect. These transitions are especially important for engineering purposes as the occurrence of them can be related to a polymer's impact resistance or toughness properties.

The state-of-the-art Seiko DMS6100 provides an instrument with the following desirable characteristics:

- high sensitivity
- ease of use
- frequency multiplexing
- synthetic oscillation (SO) mode
- Fourier transform technology
- wide frequency range
- wide temperature range
- wide dynamic range
- large number of modes of sample deformation
- ability to handle wide sample geometries ranging from thick polymer test bars to thin films and single fibers
- master curve software with automated best-fit selection of shift factors
- apparent activation energy software for better identification of transitions and for research purposes
- special DMA coating software for the mathematical isolation of the mechanical properties of a coating on a film sample
- Windows operation system

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With the synthetic oscillation (SO) mode, the sample is subjected to five different frequencies simultaneously. This is somewhat different from traditional frequency multiplexing where the sample is exposed to one sequential frequency after another. With standard frequency multiplexing, the sample is subjected to one frequency at a given instant. With the SO mode, the sample is exposed to all 5 frequencies at a given instant. The SO mode permits the data to be acquired at a more rapid rate, allowing the sample to be heated at faster rates (e.g., 5°C/min) thus providing significantly shorter experimental times.

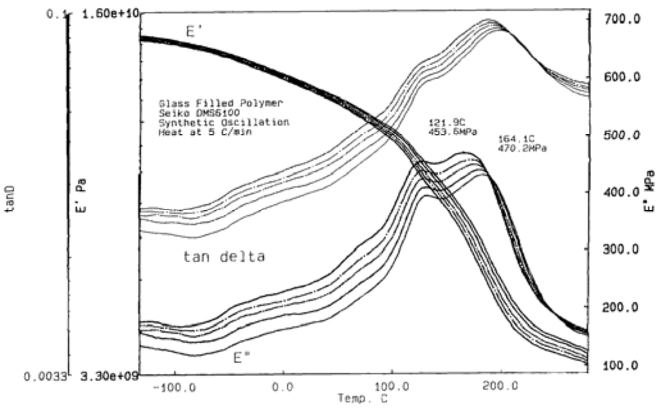

Figure 1

Displayed in Figure 1 are the DMA results obtained on a thick (2.5 mm) highly filled polymeric material (80% glass and fillers and 20% polymer) used for injection molding purposes. The sample was analyzed on the Seiko DMS6100 using the synthetic oscillation approach at simultaneous frequencies of 0.5, 1, 2, 5, and 10 Hz. The composite material was heated at a rate of 5°C/min. The plot shows the log of the flexural storage modulus or stiffness, E′, the loss modulus or damping, E″, and tan δ (E″/E′) as a function of temperature at the five different frequencies. The data generated by the Seiko DMS6100 is very noise free which is remarkable considering that the sample is relatively thick and has a high stiffness, due to the high level of glass and fillers.

The DMA results show that the sample actually exhibits two glass transition events at 121 and 164°C, based on the E″ peak temperatures. Even though the sample is comprised of 80% glass and fillers, the DMA has the very high sensitivity to detect the glass transition events of the semi-crystalline polymer component. The SO data generated by the DMS6100 shows the effects of frequency (or time) on the glass transition events of the polymer phase. As the frequency increases, the E″ and tan δ peak temperatures also increase, which is reflective of the viscoelastic nature of the polymeric component.

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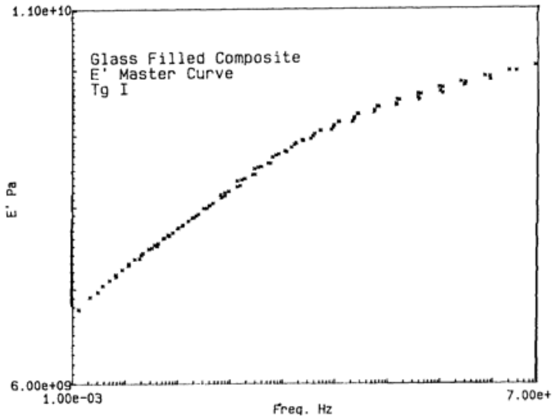

Figure 2

The acquisition of frequency multiplexing data permits the generation of master curves using the well known time–temperature superposition principle. The Seiko software provides the automatic best fit values of the two WLF constants, C1 and C2. Displayed in Figure 2 is the E' master curve generated for the lower temperature glass transition event at 122°C at a reference temperature of 100°C. The composite sample exhibits a small decrease in stiffness with decreasing frequency (or increasing time). The master curves are useful for predictive purposes.

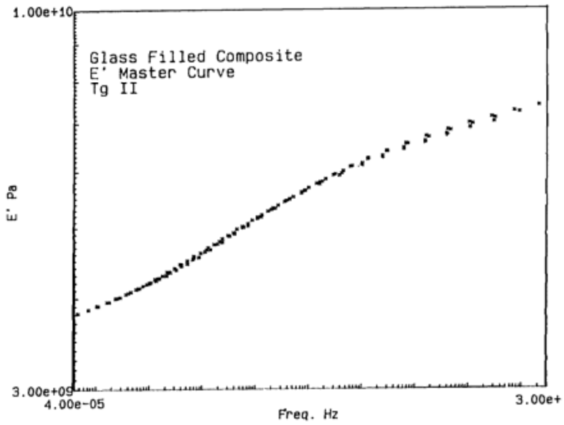

Figure 3

Displayed in Figure 3 is the E' master curve generated for the higher temperature glass transition event at 164°C. The master curves help to establish the long term mechanical response of the composite sample which greatly aids in reducing the product development time of such materials.

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Summary

DMA provides the highest sensitivity of all the thermal analytical techniques which is especially useful for the detection of weak glass transition events or for the identification of sub-Tg β and γ transitions. The limited sensitivity of DSC oftentimes makes it difficult to clearly and unambiguously identify the glass transition event, especially of highly filled or highly crystalline materials. DMA can always detect the clear glass transition of polymeric materials. The Seiko DMS6100 provides a highly sensitive technology with the unique synthetic oscillation DMS instrument incorporating Fourier transform mode (SO) for the rapid and efficient acquisition of frequency multiplexing data. The DMS6100 was utilized to study thick, highly filled composite materials containing only 20% polymer and 80% fillers.

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