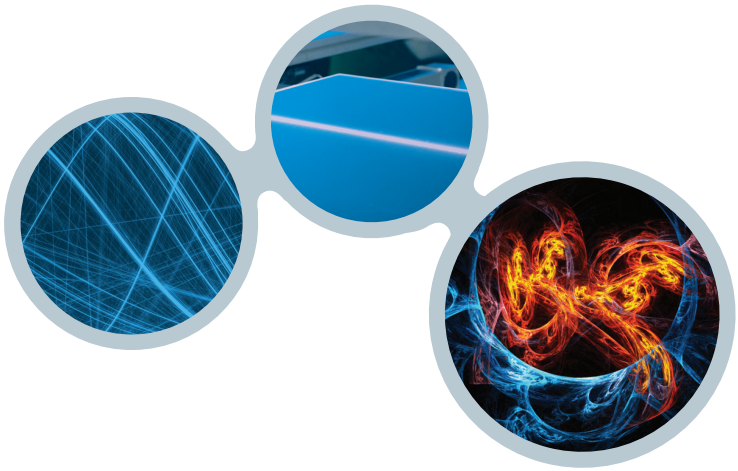

Application Note #1531

Polymer Thin Film Characterization at Cold Temperatures Using nanoDMA III and xSol Cryo

Polymer thin films are widely used for a variety of applications, ranging from artificial skin to anti-reflective coatings. Understanding of the viscoelastic properties at various temperatures is important for ensuring engineering performance. The measurement of viscoelastic properties of polymer thin films across a range of temperature can prove difficult in comparison to a bulk sample. In this application note, the viscoelastic properties of polymer thin films are investigated from -125°C to 23°C using dynamic nanoindentation.

Experiment Introduction

Many polymers are viscoelastic, where the properties of the material have a time-dependence in addition to the effect of temperature. Shorter times (high frequencies) correspond to low temperatures, and longer times (low frequencies) correspond to high temperatures. This principle can be quantitatively applied and is known as time-temperature superposition (TTS) [1]. In addition, there can be drastic changes in the response of the polymer due to glass transition or melting.

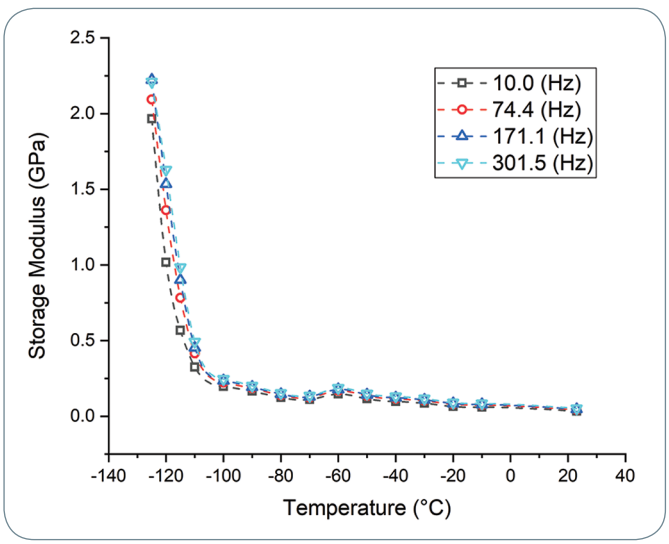

Figure 1. Storage modulus versus temperature for PDMS thin film.

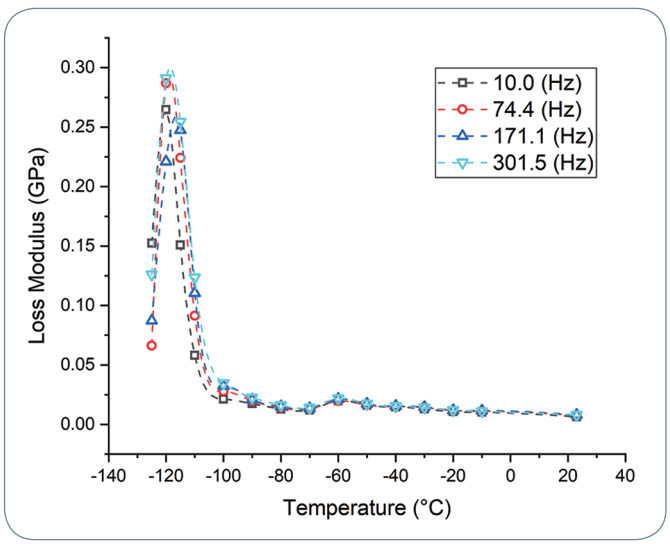

Figure 2. Loss modulus versus temperature for PDMS thin film.

Performing nanoDMA® III frequency sweep tests at varying temperatures makes measuring the glass transition (Tg) temperature of a polymer thin film possible, where such tests would not be possible on a traditional dynamic mechanical analysis (DMA) instrument due to sample geometry. This data can then be used in conjunction with TTS to create a master curve at a specified reference temperature. This provides frequency dependent information beyond that of which the instrumentation is capable. The xSol® temperature control stage with the cryo option has a broad temperature range of -120°C up to 800°C, suitable for most applications.

Polydimethylsioxane (PDMS) is a conventional polymer used in many everyday items, including contact lenses, lubricants, and shampoos. At room temperature and long time scales, PDMS behaves like a liquid and will conform to surface imperfections. Over short time scales, it behaves like elastic solids, such as rubber [2].

A 500µm PDMS film was tested using a Hysitron® TI 980 TriboIndenter® equipped with nanoDMA III and an xSol Cryo temperature stage with a 10µm radius conical indenter probe. Reference frequency sweep tests from 10 Hz to 301 Hz were performed from -125°C to 23°C (room temperature) [3]. Due to the time dependence of most polymers, the strain rate of an indentation test can have a large effect on the measured properties. Here, the material was allowed to relax prior to the dynamic test. Additionally, the effective strain was held constant by indenting to 1600nm at each temperature.

Time-Temperature Results

There is a clear change in both the storage and loss modulus at cooler temperatures (see Figures 1 and 2). A peak in the ratio of storage to modulus (tangent delta) occurred around the Tg of PDMS. A closer look at this peak demonstrates the frequency dependence of the modulus as seen in a shift of the tangent delta peak as the frequency is increased (see Figure 3). The tangent delta measurements using nanoDMA III are consistent with measurements taken on a traditional DMA instrument, performed on the same sample by a professional contract testing lab. (see Figure 4).

A master curve with a reference temperature of -115°C was created using TTS and the Williams-Landel-Ferry (WLF) equation [4]. This analysis shows the frequency dependence of PDMS from 10^{-11} Hz to 10^{3} Hz. These frequencies are well beyond the testing capabilities of both nanoDMA III and traditional macro DMA instruments. A comparison of master curves generated by nanoDMA III and a traditional DMA instrument show a similar trend in storage modulus (see Figure 5).

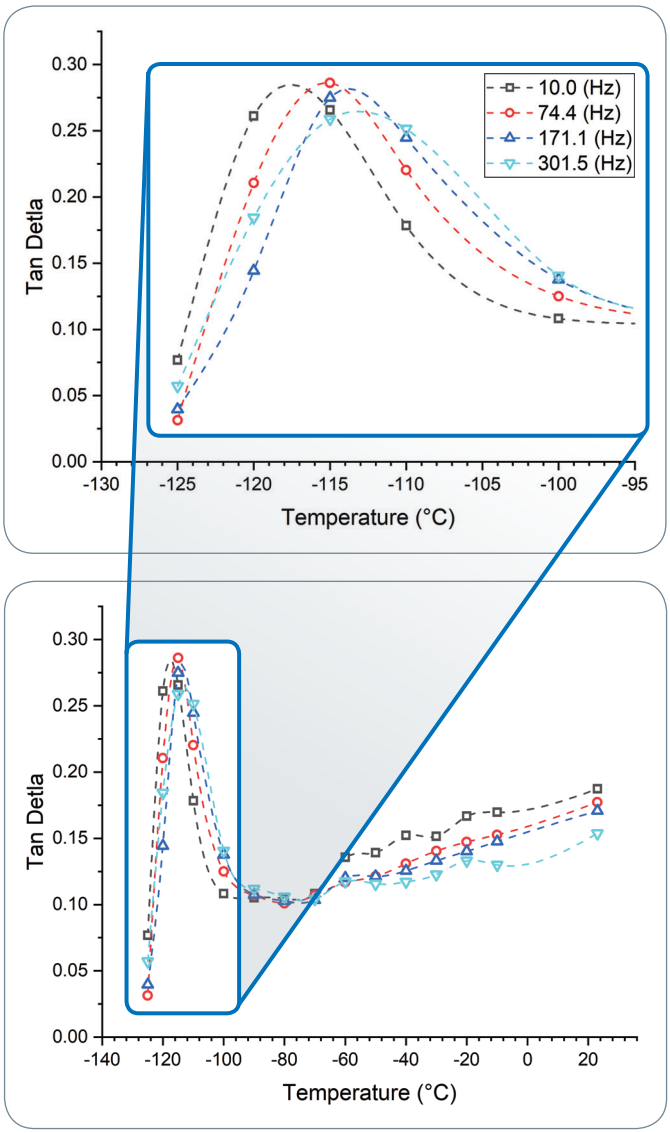

Figure 3. Tangent delta versus temperature for PDMS thin film. The upper graph shows a zoomed view of the data around the Tg temperature.

Conclusions

nanoDMA III in conjunction with the xSol Cryo temperature stage are a powerful combination. Together, they make it possible to investigate viscoelastic properties of polymer thin films where macro DMA instruments fail. This is important for understanding the Tg of polymer thin films compared to their bulk counterparts and exploring frequency dependence at very low and high frequencies.

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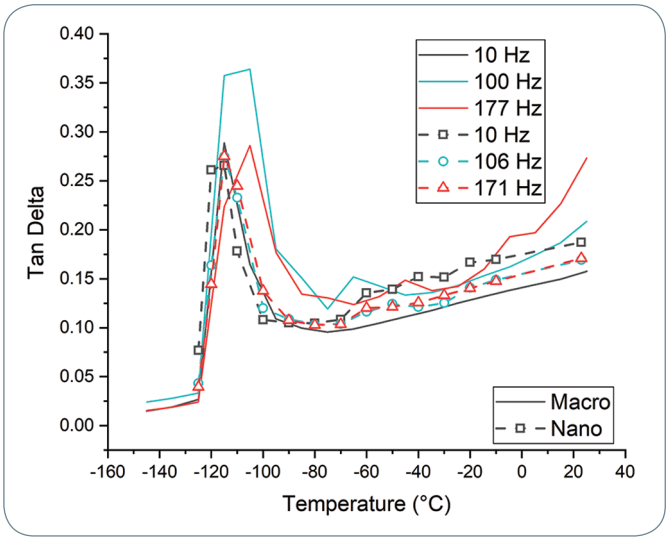

Figure 4. Tangent delta comparison between nanoDMA III and macro DMA test.

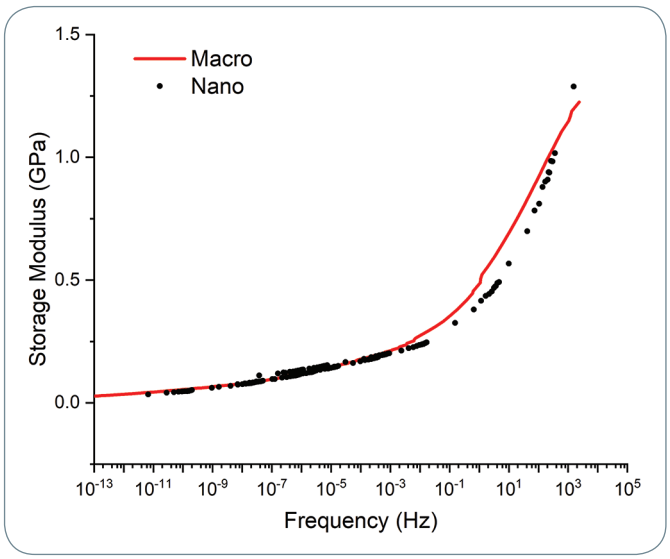

Figure 5. Storage modulus master curve at -115°C.

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