NANOVEA
A Better Measure

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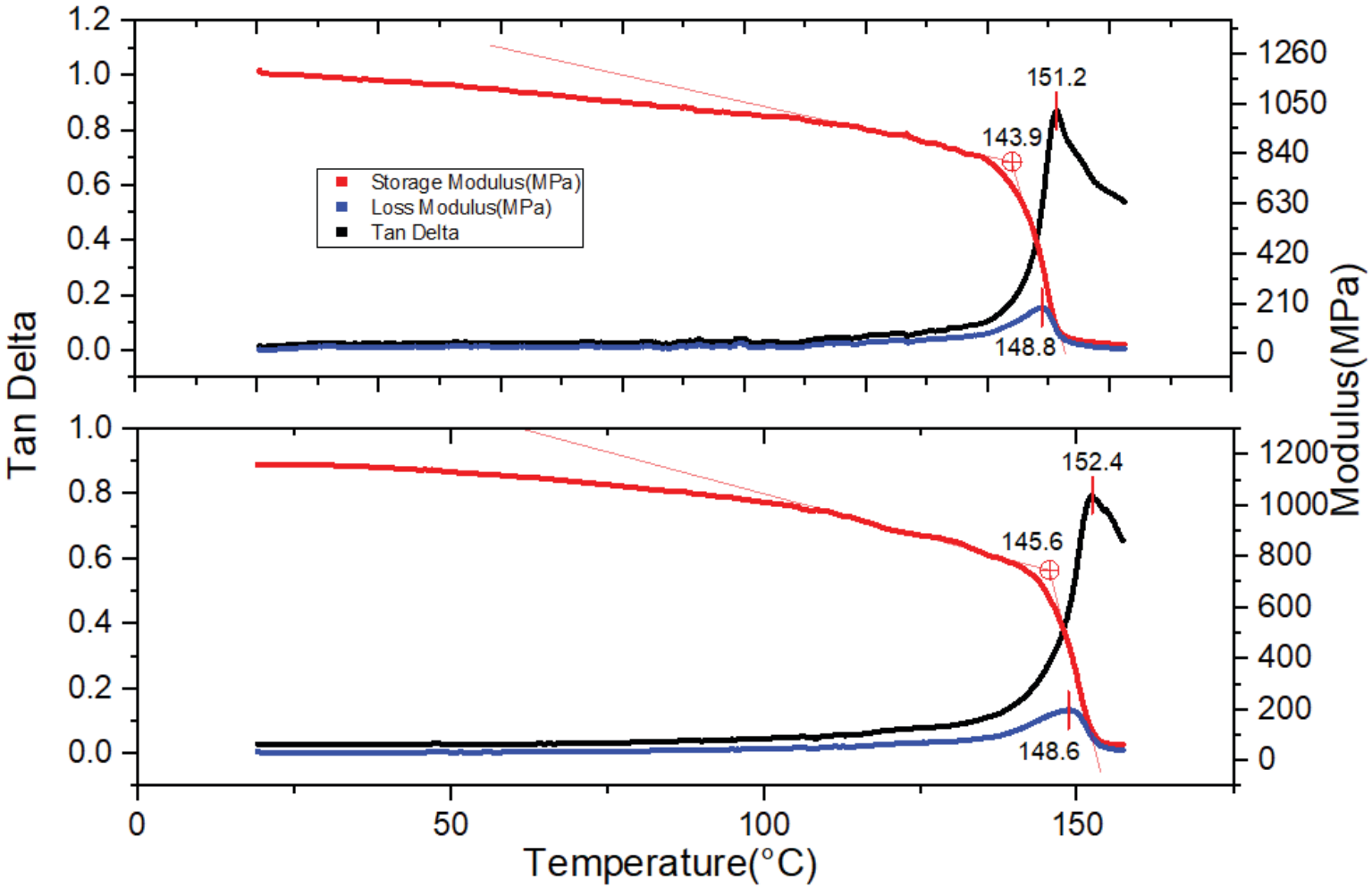
Precise Localized Glass Transition

with

Nanoindentation DMA



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Introduction

Imagine a scenario where a bulk sample is uniformly heated at a constant rate. As a bulk material heats up and approaches its melting point, it will start to lose its rigidity. If periodic indentations (hardness tests) are conducted at the same target force, the depth of each indent should be constantly increasing since the sample is becoming softer (see figure 1). This continues until the sample begins to melt. At this point, a large increase in the depth per indent will be observed. Using this concept, phase change in a material can be observed by using dynamic oscillations with a fixed force amplitude and measuring its displacement, i.e. Dynamic Mechanical Analysis (DMA).

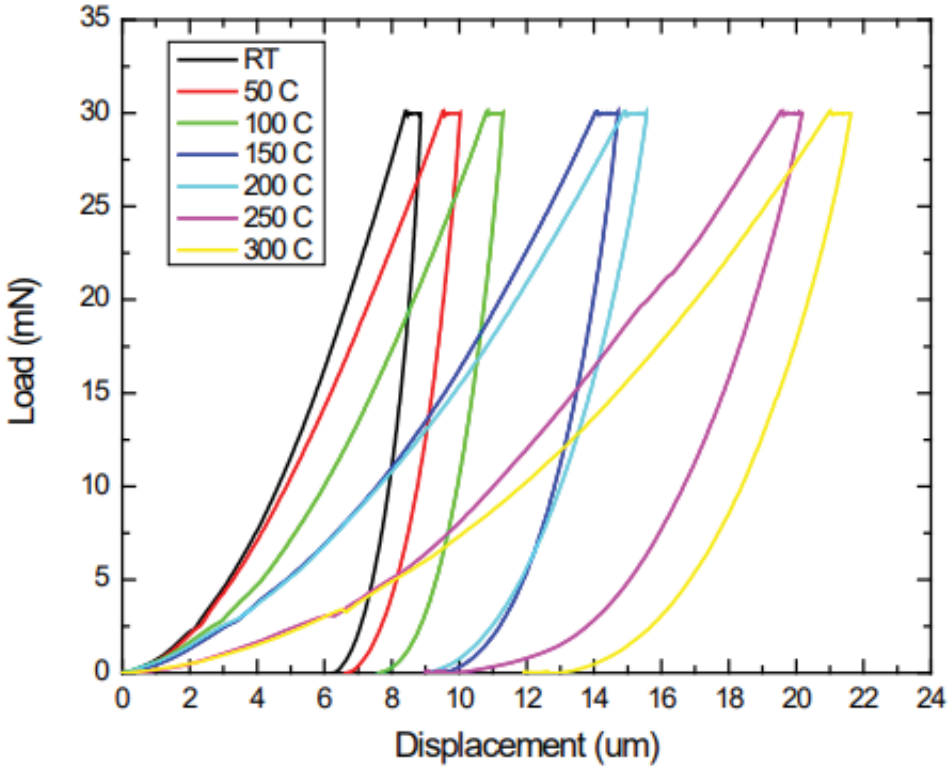

Figure 1: Indentation tests on PTFE at different temperatures
(nanovea.com/App-Notes/temperature-nanoindentation.pdf)

With polymers, this can be taken to another level. Polymers with a glass transition temperature (Tg) or a transition temperature between a glassy and amorphous (i.e. rubbery) phase can be defined very clearly using DMA. While Tg can be found with multiple methods, this case study will focus on using a nanoindentation DMA method with Nanovea's Mechanical Tester. Polycarbonate, Nylon 6/6, and PTFE will undergo a temperature-sweep DMA test to detect glass transition temperature and beta transitions.

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Importance of DMA for Polymers

The ideal operating range of the polymer can be defined using DMA. The glass phase would put the operating range below Tg, and the amorphous phase would be above Tg. DMA can is used to accurately detect this transition point. DMA has been seen to be 10 to 100 times more sensitive to detecting Tg than differential scanning calorimetry (DSC) or differential thermal analysis (DTA) [1]. Beta transitions (Tß), or secondary transitions often related to toughness of polymer, can also be detected by DMA, but not by other methods. These transitions can also be a boundary condition when defining the polymer's operating range.

Additionally, DMA can be used to better understand how additives blended into polymers affects their bulk properties. For example, fillers added to rubber will increase the storage modulus and improve their resistance to abrasion, making them more suitable as tires [1]. Copolymers and blends can also change Tg. It is also possible to observe multiple Tg from multiple copolymers or a single Tg that will shift depending on polymer concentration.

Equipment Featured

NANOVEA PB1000

Multi Module Platform

3 Testing Modes in 1 (Scratch/Indent/Wear)

Loading Ranges from 0.8uN to 400N

XYZ Motion with 0.20um Step Resolution

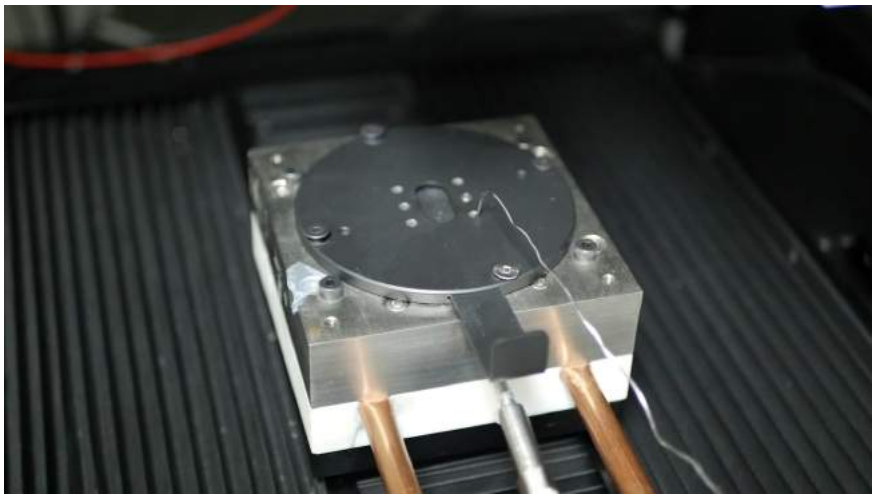
Fully Automated (Up to 100 indents in 15mins)

Integrated Imaging (AFM, Profilometer, Microscope)

Learn More About the PB1000!

Measurement Objectives

This case study uses the Nanovea Mechanical Tester's Nano Module for temperature-sweep scans with DMA. Polycarbonate, Polytetrafluoroethylene (PTFE), and Nylon 6/6 were tested to obtain their corresponding storage modulus, loss modulus, and tan delta, or tan(δ), vs temperature graphs. The scope of this study focuses on detecting the glass transition temperature and beta transitions (if applicable) with a nanoindentation DMA method.



Samples tested in oven

Mechanical Testing Results

Measurement Parameters

Table 1: Test parameters for DMA

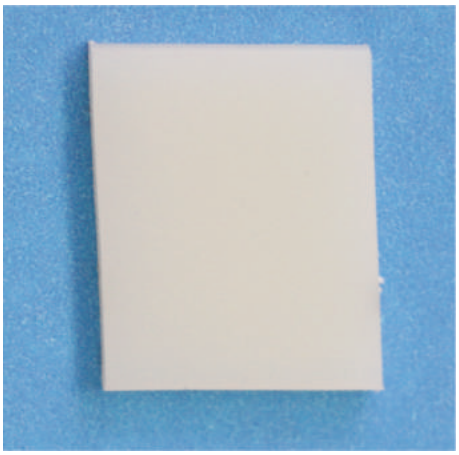
Test Parameters	
Target Force (mN)	50
Loading Rate (mN/min)	200
Unloading Rate (mN/min)	200
Oscillation Amplitude (mN)	10
Oscillation Frequency (Hz)	1
Heat rate (°C/min)	10 for PC and PTFE, 5 for Nylon 6/6
Indenter Type	Diamond Flat
Indenter Diameter (µm)	50

Note: Deviance in data from other sources may be due to the heat rate used for Polycarbonate and PTFE was higher than a typical rate of 5°C/min or lower.

Samples Tested

Sample of Nylon 66

Sample of Polycarbonate



Sample of PTFE

Results

The phase change between glassy and amorphous does not occur only at one temperature, but over a range of temperature. As a result, multiple methods can be used to find Tg. The glass transition temperature can be identified by A) a drastic decrease in storage modulus, B) a peak in loss modulus, and C) a peak in tan (delta). For more information on what each result mean, look into our isothermal DMA app note: Link A - tire http://nanovea.com/App-Notes/nanoindentation-dma.pdf and Link B – cork http://nanovea.com/App-Notes/dynamic-mechanical-analysis-nanoindentation.pdf.

Tg is time and temperature dependent [1]. As a result, Tg can change depending on the oscillation frequency. This can be used to create a time-temperature superposition (TTS) curve. TTS can be used to test higher or lower frequencies by changing the temperature and vice-versa. Target load, oscillation amplitude, and indenter type will influence the moduli and tan(delta) values obtained.

Table 2: Tg detected from DMA on Polymers

	Storage Modulus	Loss Modulus	Tan (delta)
Polycarbonate	**143.9/145.6**	**148.8/148.6**	**151.2/152.4**
Nylon 6/6	**N/A**	**N/A**	**54.34**
PTFE	**N/A**	**30.72***	**37.11***

*: Detected results for PTFE were Tß, not Tg.

From the data collected, variation will be seen from difference in temperature between the thermocouple probing location and testing location. This was corrected by measuring the difference in temperature between the two locations when heating the sample at the same rate. The resulting difference was used correct the dataset obtained.

Mechanical Testing Results

POLYCARBONATE

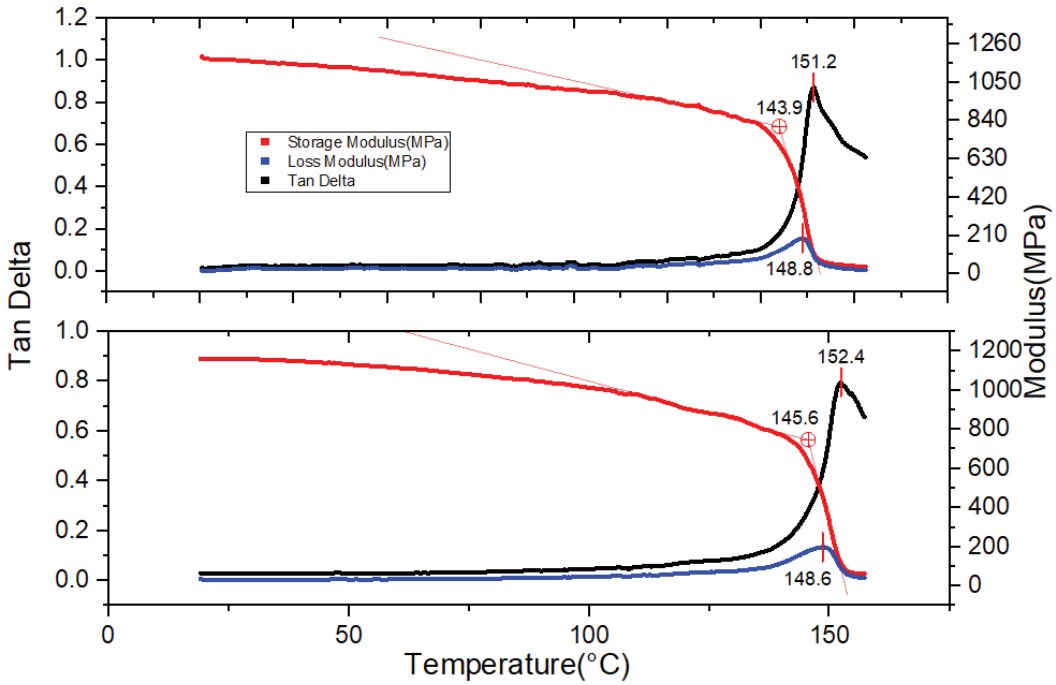


Figure 2: DMA graph on Polycarbonate.
Top: Multiple reheating of sample. Bottom: Unheated new sample.

Polycarbonate is an ideal sample to showcase DMA due to its prominent trends at its glass transition temperature. Two samples of polycarbonate were tested. One has been heated above its Tg and cooled to room temperature multiple times. The other is a new, unheated sample. While the properties of polymers can change through thermal cycles, polycarbonate does not show this. The two samples tested shows results that are very similar to each other. Polycarbonate shows a Tg averaged to 144.8, 148.7, and 151.3 for storage modulus, loss modulus, and tan delta respectively. Literature states Tg at approximately 153°C for polycarbonate. [1].

Sample of Polycarbonate

Mechanical Testing Results

PTFE

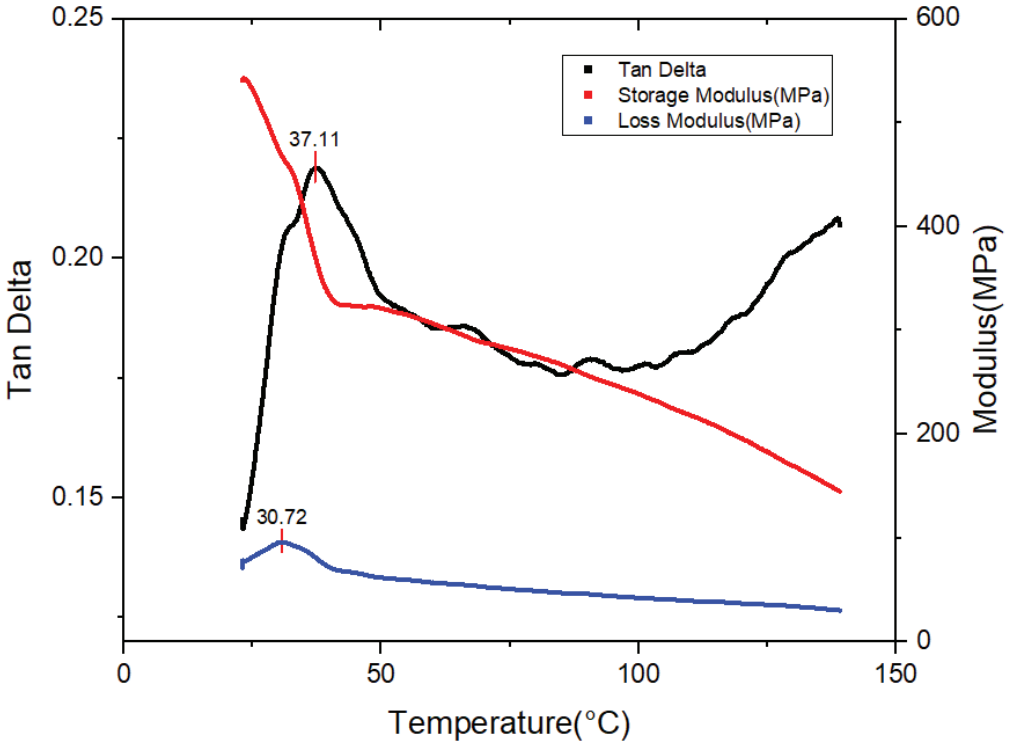
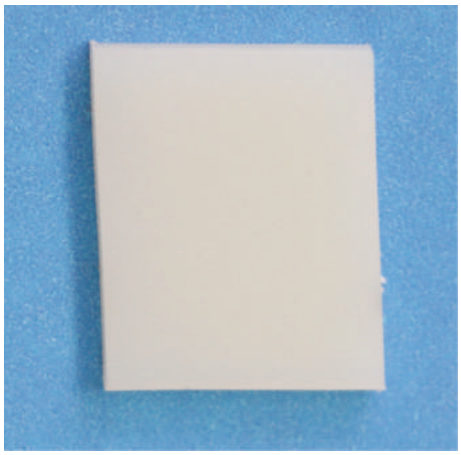


Figure 3: DMA graph for PTFE.

From literature, PTFE has two beta transition at approximately 19°C and 31°C and a glass transition at approximately 126°C [Nasa]. Nanoindentation DMA has found a beta transition at 30.72 and 37.11 with the loss modulus and tan delta respectively. Beta transitions, which are difficult to detectable with other thermal analysis methods, have been successfully detected with this nanoindentation DMA method. Signs of the glass transition can be seen from the steady increase in tan delta as temperatures approaches 150°C. Unfortunately, due to other constraints, further testing of PTFE cannot be conducted at the moment of writing.



Sample of PTFE

Mechanical Testing Results

NYLON 6/6:

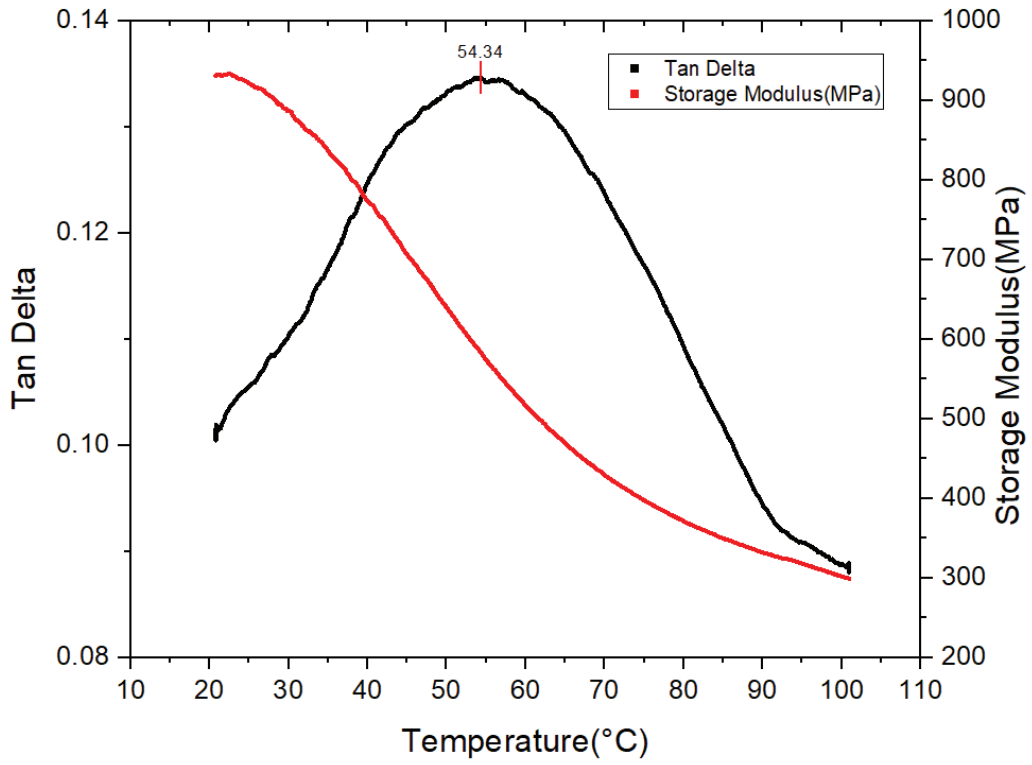


Figure 4: DMA graph for Nylon 6/6.

Nylon 6/6 is a polymer with a glass transition temperature of approximately 50°C [1]. Here, we are able to detect the glass transition temperature with the tan delta data. Loss modulus did not display any significance and was omitted as a result. The trend of a decrease in storage modulus as the sample undergoes the phase change is also observed.

Sample of Nylon 6/6

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Conclusion

Using Nanovea's Mechanical Tester's Nano Module, temperature-sweep DMA tests were conducted on Polycarbonate, PTFE, and Nylon 6/6. The Tg for Polycarbonate and Nylon 6/6 were successfully identified. Beta transitions were seen for PTFE and the onset of Tg was observed. This method of detecting the glass transition temperature and beta transitions was shown to be successful and repeatable.

Future works includes conducting DMA on analyzing more samples, creating TTS curves, and testing on thermoset samples.

Benefits of conducting nanoindentation DMA tests includes smaller samples, and localized testing. Use of smaller ovens also allows higher control of temperature. In addition to DMA, other nanoindentation techniques can still be used with the same instrument. This includes hardness, creep, relaxation, stress-strain analysis, and yield strength. Scratch testing can also be done with the addition of a friction table.

https://nanovea.com/app-notes/mechanicaltesting

Refferences

[1] Menard, Kevin. Dynamic Mechanical Analysis: A Practical Introduction. 1st ed., CRC Press LLC, 1999.

[2] Wingard, Doug. "Use of DSC and DMA Techniques to Help Investigate a Material Anomaly for PTFE Used in Processing a Piston Cup for the Urine Processor Assembly (UPA) on International Space Station (ISS)." (2010).

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Recommended Reading

Check out our other application note where we conduct a Viscoelastic Analysis on Rubber with Nanoindentation

https://nanovea.com/viscoelastic-analysis-of-rubber/