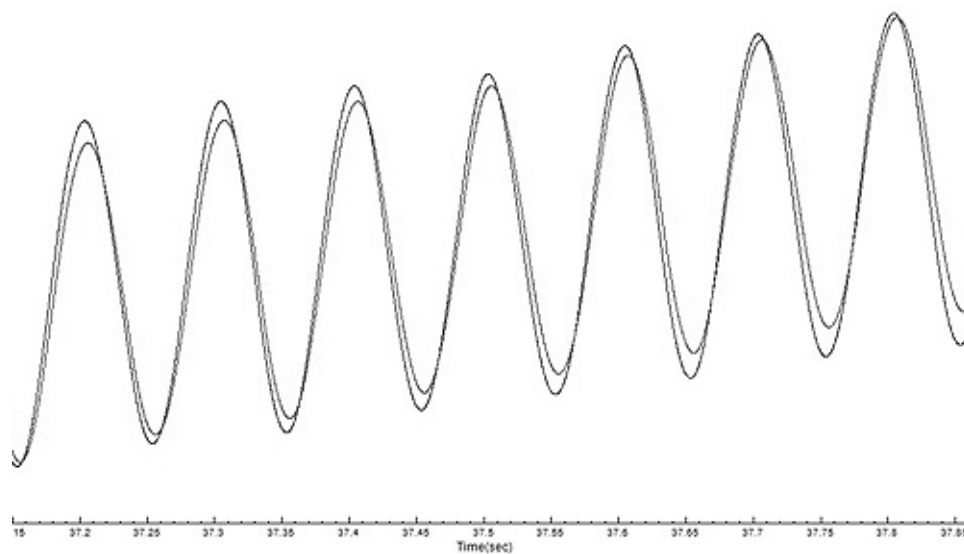


VISCOELASTIC ANALYSIS WITH NANOINDENTATION DMA



Prepared by
Jorge Ramirez

INTRO

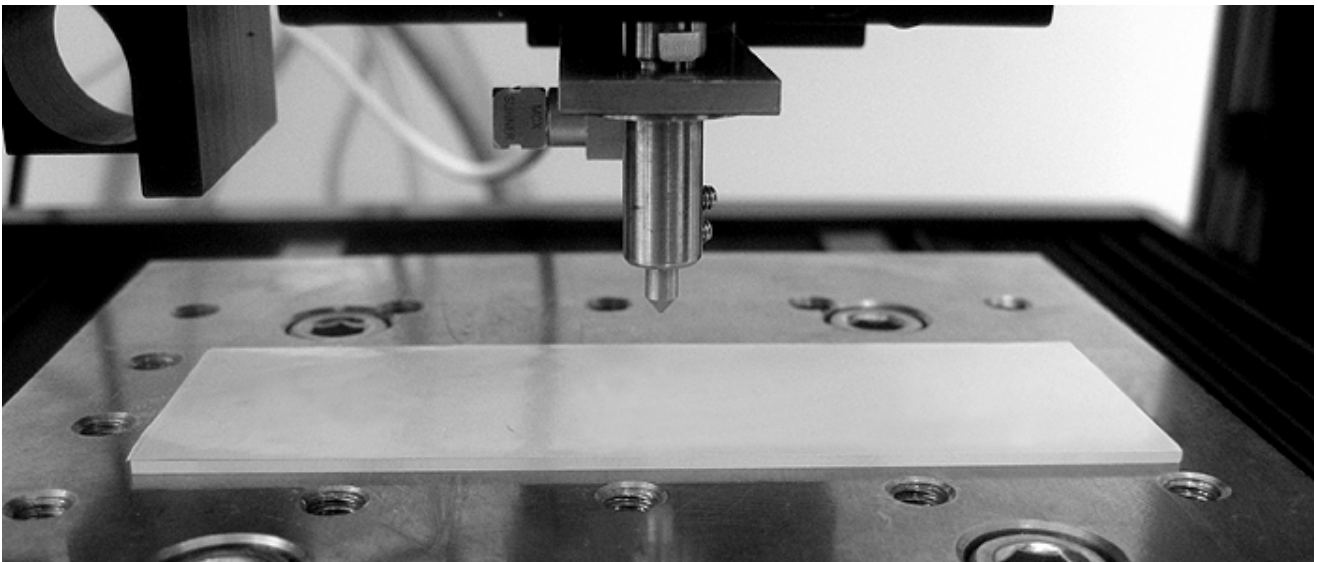
Viscoelasticity is referred to as the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation; in this note we will be focusing on polymer coatings. A viscous material resists shear flow and strains linearly with time when a stress is applied, unlike elastic materials that strains immediately when stressed and returns to original state once the stress is removed. Therefore a material that is viscoelastic combines both properties and because so exhibits time dependent strain.

IMPORTANCE OF NANOINDENTATION DMA FOR POLYMER

Viscoelasticity can be studied using Dynamic Mechanical Analysis (DMA) during Nanoindentation. By applying controlled oscillatory stress the resulting strain can easily be measured. An elastic material will have stress and strain in phase while a viscous-elastic material will have strain lagging stress. In many applications during quality control and R&D, it is important to reliably test this behavior. For example, polymer coatings, like that found on solar panels and medical devices, need to be studied by DMA Nanoindentation to understand the transition between viscous and elastic properties. The behavior of polymers is greatly affected by time and temperature which can greatly affect the long term longevity of a device if the properties are not well understood. These results will be used to better understand the life cycle of the polymer coating among others.

MEASUREMENT OBJECTIVE

In this application, the Nanovea Mechanical Tester, in Nanoindentation mode with DMA is used to study the comparative viscoelastic properties between several coating samples.



MEASUREMENT PRINCIPAL

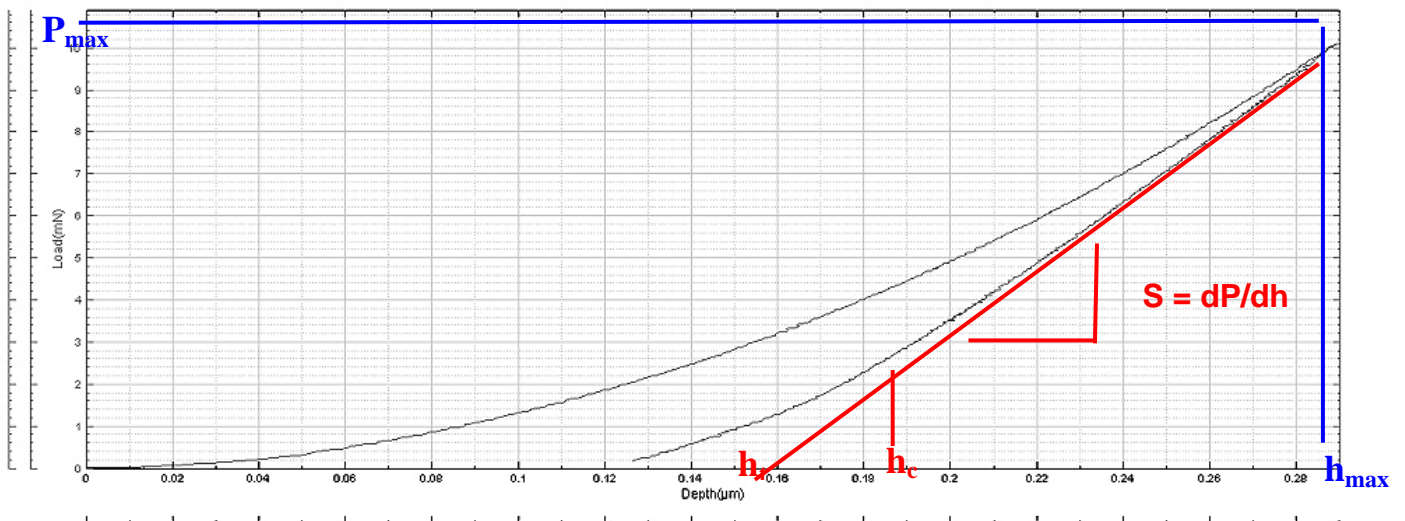
Nanoindentation is based on the standards for instrumented indentation, ASTM E2546 and ISO 14577. It uses an already established method where an indenter tip with a known geometry is driven into a specific site of the material to be tested, by applying an increasing normal load. When reaching a pre-set maximum value, the normal load is reduced until complete relaxation occurs. The load is applied by a piezo actuator and the load is measured in a controlled loop with a high sensitivity load cell. During the experiment the position of the indenter relative to the sample surface is precisely monitored with high precision capacitive sensor.

The resulting load/displacement curves provide data specific to the mechanical nature of the material under examination. Established models are used to calculate quantitative hardness and modulus values for such data. Nanoindentation is especially suited to load and penetration depth measurements at nanometer scales and has the following specifications:

Maximum displacement (Dual Range)	: 50 μm or 250 μm
Depth Resolution (Theoretical)	: 0.003 nm
Depth Resolution (Noise Level)	: 0.05 nm
Maximum force	: 400 mN
Load Resolution (Theoretical)	: 0.03 μN
Load Resolution (Noise Floor)	: 1.5 μN

Analysis of Indentation Curve

Following the ASTM E2546 (ISO 14577), hardness and elastic modulus are determined through load/displacement curve as for the example below.



Hardness

The hardness is determined from the maximum load, P_{max} , divided by the projected contact area, A_c :

$$H = \frac{P_{\text{max}}}{A_c}$$

Young's Modulus

The reduced modulus, E_r , is given by:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_c}}$$

Which can be calculated having derived S and A_c from the indentation curve using the area function, A_c being the projected contact area. The Young's modulus, E , can then be obtained from:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}$$

Where E_i and ν_i are the Young's modulus and Poisson coefficient of the indenter and ν the Poisson coefficient of the tested sample.

How are these calculated?

A power-law fit through the upper 1/3 to 1/2 of the unloading data intersects the depth axis at h_i . The stiffness, S , is given by the slope of this line. The contact depth, h_c , is then calculated as:

$$h_c = h_{\max} - \frac{3P_{\max}}{4S}$$

The contact Area A_c is calculated by evaluating the indenter area function. This function will depend on the diamond geometry and at low loads by an area correction.

For a perfect Berkovich and Vickers indenters, the area function is $A_c=24.5h_c^2$ For Cube Corner indenter, the area function is $A_c=2.60h_c^2$ For Spherical indenter, the area function is $A_c=2\pi Rh_c$ where R is the radius of the indenter. The elastic components, as previously mentioned, can be modeled as springs of elastic constant E , given the formula: $\sigma = E\epsilon$ where σ is the stress, E is the elastic modulus of the material, and ϵ is the strain that occurs under the given stress, similar to Hooke's Law. The viscous components can be modeled as dashpots such that the stress-strain rate

relationship can be given as,
$$\sigma = \eta \frac{d\epsilon}{dt}$$
 where σ is the stress, η is the viscosity of the material, and $d\epsilon/dt$ is the time derivative of strain.

Since the analysis is very dependent on the model that is chosen. Nanovea provides the tool to gather the data of displacement versus depth during the creep time. The maximum creep displacement versus the maximum depth of indent and the average speed of creep in nm/s is given by the software. Creep may be best studied when loading is quicker. Spherical tip might be a better choice.

Other tests possible includes the following:

Stress-Strain & Yield Stress, Fracture Toughness, Compression strength, Fatigue testing and many others.

DMA SINUS MODE PRINCIPAL

Sinus Mode (lower than 0.2Hz to 20Hz) This is applying a sin wave to the measurement. This allows plotting hardness and elastic modulus versus depth. The technique also allows studying of viscoelastic materials such as polymers, varnishes, plastics.

Storage modulus E' characterizes elastic behavior (corresponds to standard Elastic modulus)

Loss Modulus E'' characterizes the viscous behavior (loss of energy due to internal friction)

$$E^* = E' + iE'' \quad E' = \frac{\sqrt{\pi}}{2\sqrt{A_{co}}} \frac{\Delta P}{\Delta h} \cos\phi (1-\nu^2) \quad E'' = \frac{\sqrt{\pi}}{2\sqrt{A_{co}}} \frac{\Delta P_o}{\Delta h_o} \sin\phi (1-\nu^2)$$

Where ϕ , the phase shift between depth and load curves, $\frac{\Delta P_o}{\Delta h_o}$, the variation of load and depth respectively for one oscillation. A_{co} , the projected contact area for the oscillation. The viscosity factor λ can be calculated from

$$\lambda = \frac{1}{2\pi f} \frac{\Delta P_o}{\Delta h_o} \sin\phi \quad \text{where } f \text{ is the frequency at which the test was performed.}$$

Results

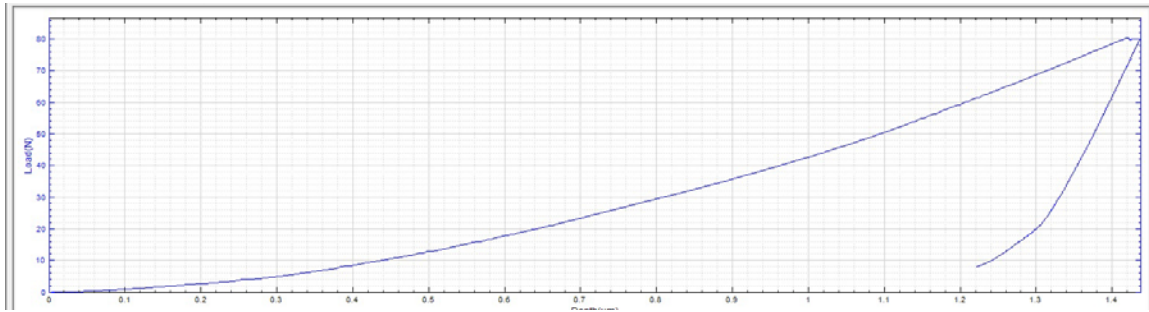
This section includes a summary table with measurements on Aluminium and a polymer and a plastic. Aluminium was used to show the correspondence between DMA data and standard Nanoindentation. EVA and a Thermoplastic were used to show two materials that behave very differently in DMA application.

Summary table of main numerical results

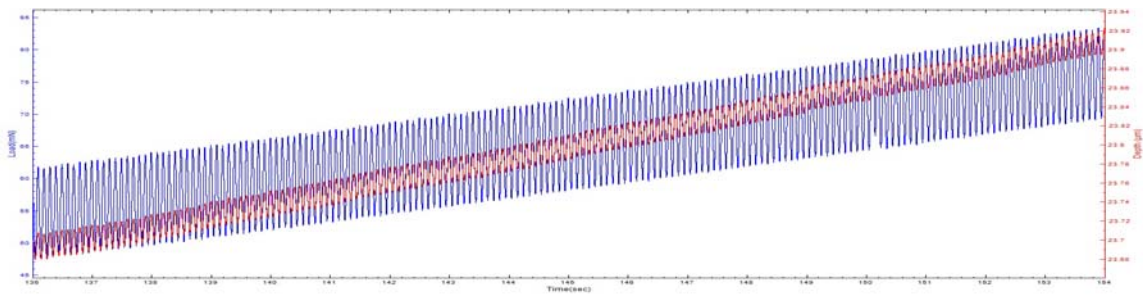
Sample	Hardness [Vickers]	Hardness [GPa]	Storage Modulus [GPa]	Loss Modulus [GPa]	Depth [μm]	Phase Shift
Al Without DMA	178.5	1.75	66.5		1.43	
Al With DMA	181.5	1.77	66.0	1.45	1.37	1.16
Ethylene Vinyl Acetate Without DMA	0.423	0.0045	0.021		32.74	
Ethylene Vinyl Acetate With DMA	0.247	0.0024	0.021	0.0016	23.44	4.33
Thermoplastic Without DMA	2.81	0.0297	0.374		11.73	
Thermoplastic With DMA	3.38	0.0331	0.560	0.086	9.78	8.82

Aluminium

Without DMA



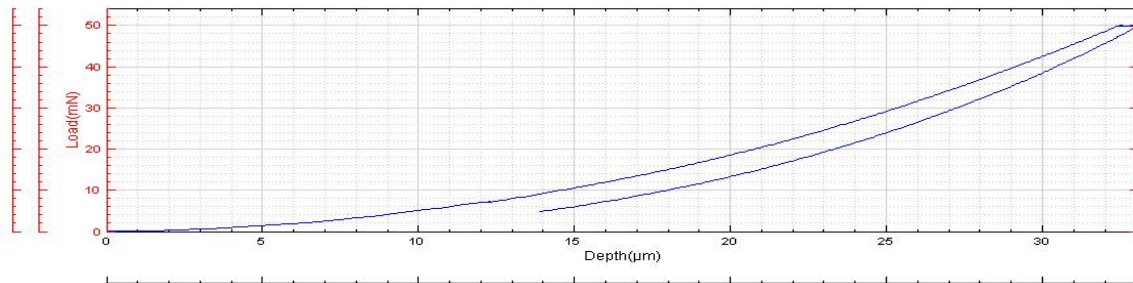
With DMA, 10Hz.



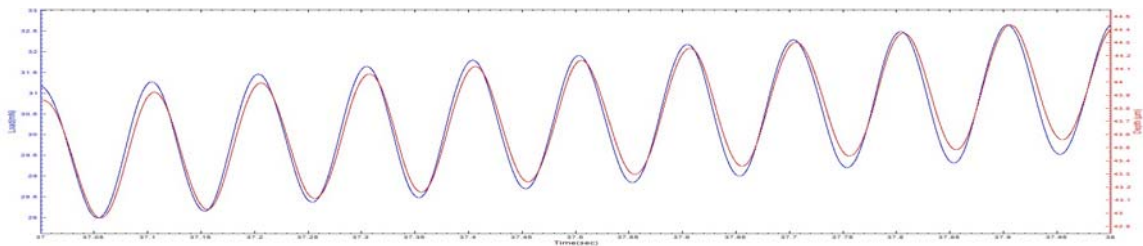
The phase shift measured for Aluminium of 1.16 degree is in the range of accepted value for the material which shows the sensitivity of the instrument used. Averaging gives values with variation less than 1%.

Ethylene Vinyl Acetate

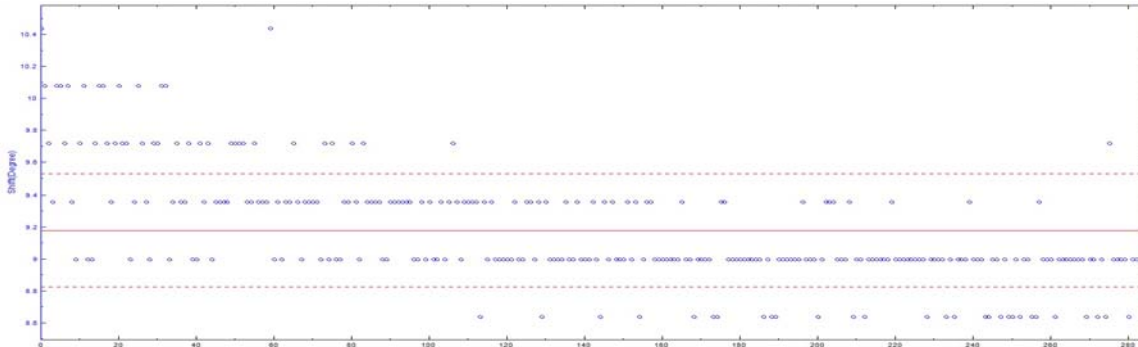
Without DMA



With DMA, 10Hz

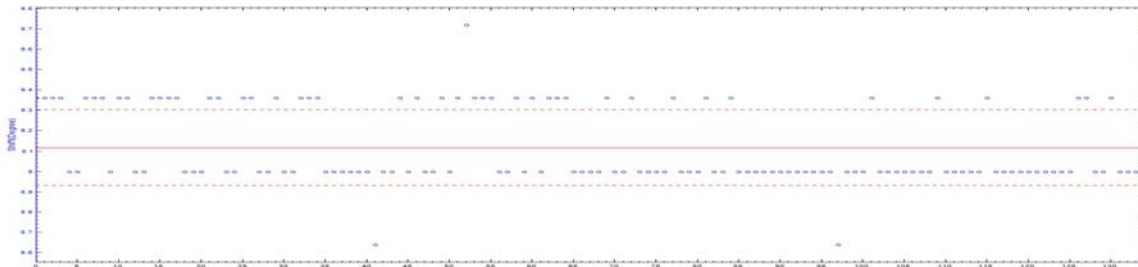


Slight decrease at shallow depth but not as big as what is seen for the Thermoplastic



Phase decrease close to the surface to become very stable.

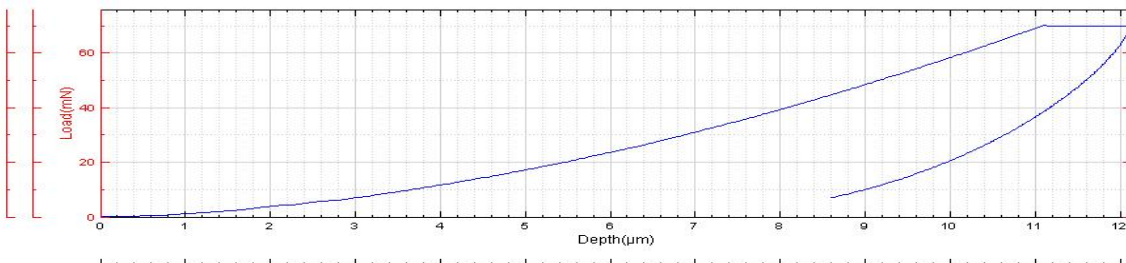
Selection of the more stable zone where modulus and phase were calculated.



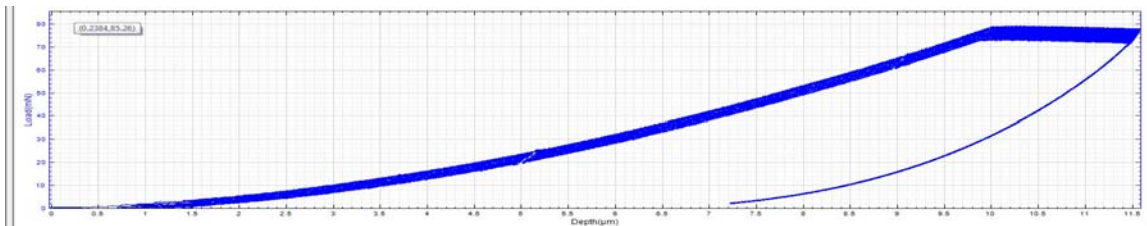
Each point is the phase for one cycle which shows the repeatability of the measurement.

Thermoplastic

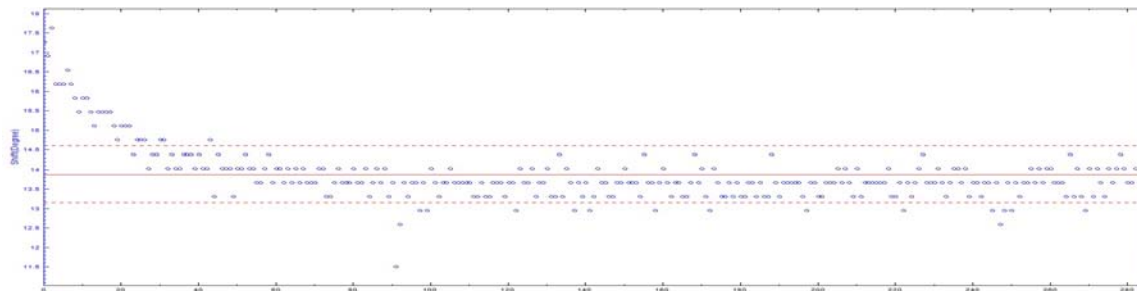
Without DMA



With DMA, 10Hz

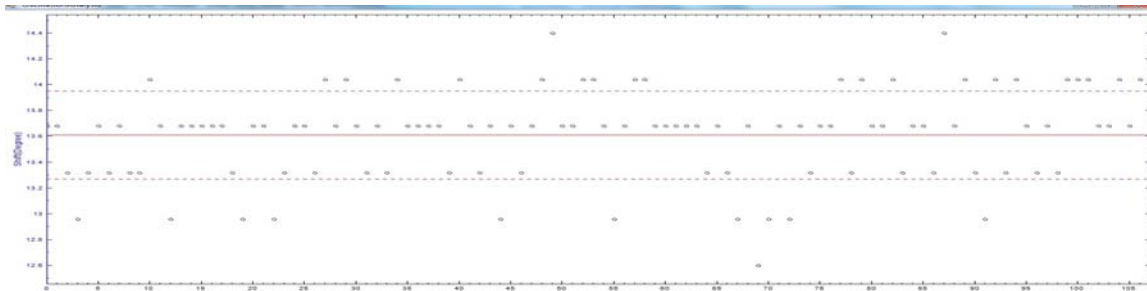


Phase decreases from 13 to below 9 degrees at the shallow depth



The thermoplastic shows more variation from the top surface to deeper.

Selection of the more stable zone where modulus and phase were calculated



Each point is the phase for one cycle which shows the repeatability of the measurement. Averaging gives values with variation less than 1% for the phase measured.

CONCLUSION

In conclusion, we have shown how the Nanovea Mechanical Tester, in Nanoindentation DMA mode provides reproducible measurement of phase shift and has a superior advantage compared to other instruments, measuring load at the same point as depth. Other systems apply a sinus wave to the current that feeds to a coil and increases the applied load without actually measuring this applied load. This makes calculating the phase shift results questionable and requires using mathematical assumptions to derive the phase shift between the measured depth and the unmeasured load. The Nanovea Mechanical Tester equipped with the nano module has a fast piezo which provides quick movement while also using a separate ultra sensitive load cell which measures directly the load created by the movement of the piezo. The depth is measured at the same time which makes the determination of the phase shift as direct as possible for superior results compared to competing instruments. This simplifies the analysis and ensures the accuracy of the final data on any materials including soft polymers. DMA also allows hardness, loss and storage modulus to be plotted versus depth. It is also possible to plot loss and storage modulus versus frequency. All of these properties can be plotted as the temperature of a sample is increased to look for materials phase transitions. The Nanovea Mechanical Testers provide unmatched multi-function Nano and Micro/Macro modules on a single platform. Both the Nano and Micro/Macro modules include scratch tester, hardness tester and wear tester modes providing the widest and most user friendly range of testing available on a single module. To Learn more about Nanovea [Nanoindentation](#).