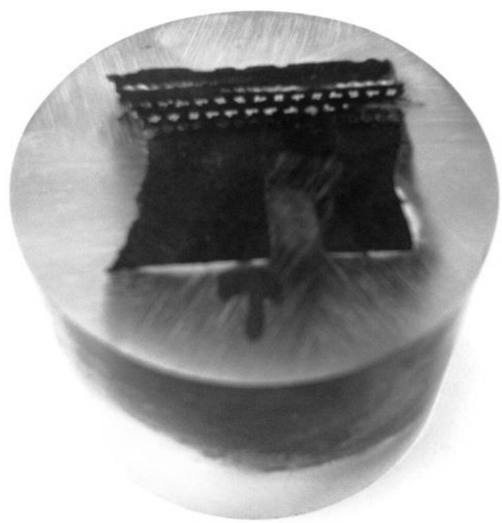
DMA FREQUENCY SWEEP ON POLYMER USING NANOINDENTATION



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INTRODUCTION

Viscoelastic materials exhibit both viscous and elastic characteristics when undergoing deformation. Long molecular chains in polymer materials contribute to their unique viscoelastic properties, i.e. a combination of the characteristics of both elastic solids and Newtonian fluids. Stress, temperature, frequency and other factors all play roles in the viscoelastic properties. Dynamic Mechanical Analysis, also known as DMA, studies the viscoelastic behavior and complex modulus of the material by applying a sinusoidal stress and measuring the change of strain.

IMPORTANCE OF DMA FREQUENCY SWEEP TEST

The changing frequency of the stress often leads to variations in the complex modulus, which is a critical mechanical property of polymers. For example, tires are subjected to cyclical high deformations when vehicles are running on the road. The frequency of the pressure and deformation changes as the car accelerates to higher speeds. Such a change can result in variation in the viscoelastic properties of the tire, which are important factors in the car performance. A reliable and repeatable test of the viscoelastic behavior of polymers at different frequency is in need. The Nano module of Nanovea Mechanical Tester generates sinusoidal load by a high-precision piezo actuator and directly measure the evolution of force and displacement using ultra-sensitive load cell and capacitor. The combination of easy setup and high accuracy makes it an ideal tool for DMA frequency sweep.

MEASUREMENT OBJECTIVE

In this application, the Nanovea Mechanical Tester, in Nanoindentation mode is used to study the viscoelastic properties of a polished tire sample at different DMA frequencies.

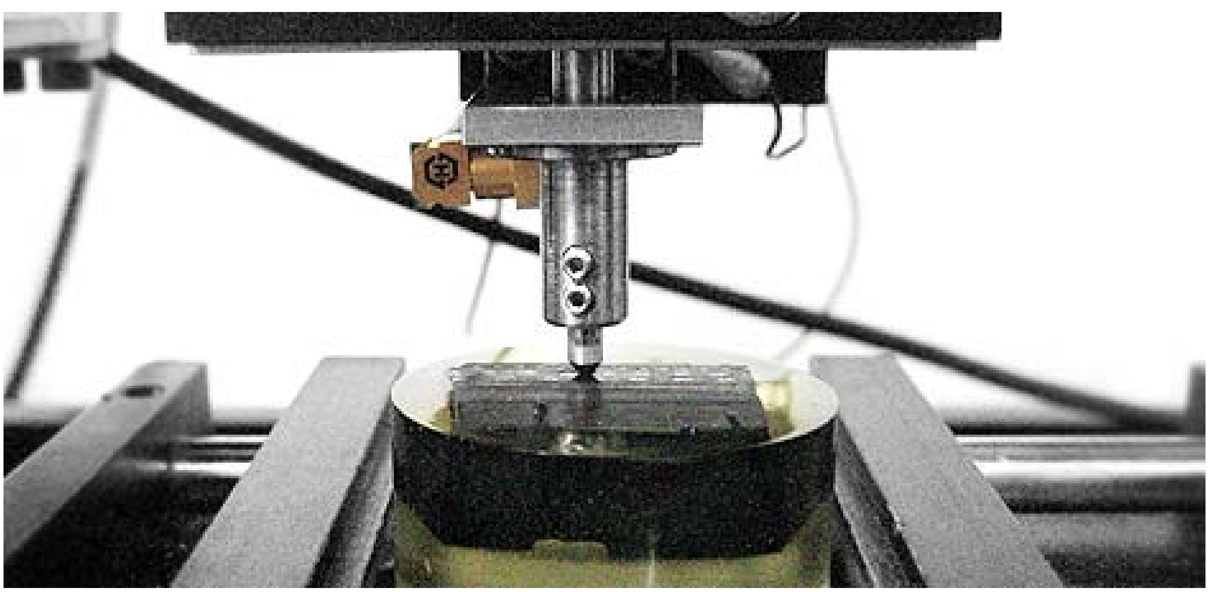

Fig. 1: Setup of the DMA frequency sweep test.

TEST CONDITIONS

DMA frequency sweep test by nanoindentation was performed on a tire sample. The test conditions are summarized in Table 1.

Loading voltage (V)	1
Oscillation voltage (V)	0.1
Frequency (Hz)	0.1, 1, 5, 10, 20
Creep time at each frequency (s)	50
Indenter type	100 µm spherical diamond

Table 1: Test conditions of the DMA frequency sweep by nanoindentation.

RESULTS AND DISCUSSION

The load & depth curve of the full frequency scan is plotted in Fig. 2 and the Load & depth vs. time at different frequencies are shown in Fig. 3. The DMA frequency sweep at the maximum load allows a fast and simple measurement on the viscoelastic characteristics of the sample at different loading frequencies in one test. The phase shift and the amplitudes of the load and displacement waves at different frequencies, i.e. 0.1, 1, 5, 10 and 20 Hz in this DMA sweep test can be used to calculate a variety of fundamental material viscoelastic properties, including Storage Modulus, Loss Modulus and Tan (δ) as summarized in Fig. 4 to Fig. 6. Frequencies of 1, 5, 10 and 20 Hz in this report, correspond to speeds of about 7, 33, 67 and 134 km per hour. As the test frequency increases from 0.1 to 20 Hz, it can be observed that both Storage Modulus and Loss Modulus progressively increase. Tan (δ) decreases from ~0.27 to 0.18 as the frequency increases from 0.1 to 1 Hz, and then it gradually increases to ~0.55 when the frequency of 20 Hz is reached. DMA frequency sweep allows measuring the trends of Storage Modulus, Loss Modulus and Tan (δ), which provide information on the movement of the monomers and cross-linking as well as the glass transition of polymers. By raising the temperature using a heating plate during the frequency sweep, a more complete picture of the nature of the molecular motion under different test conditions can be obtained.

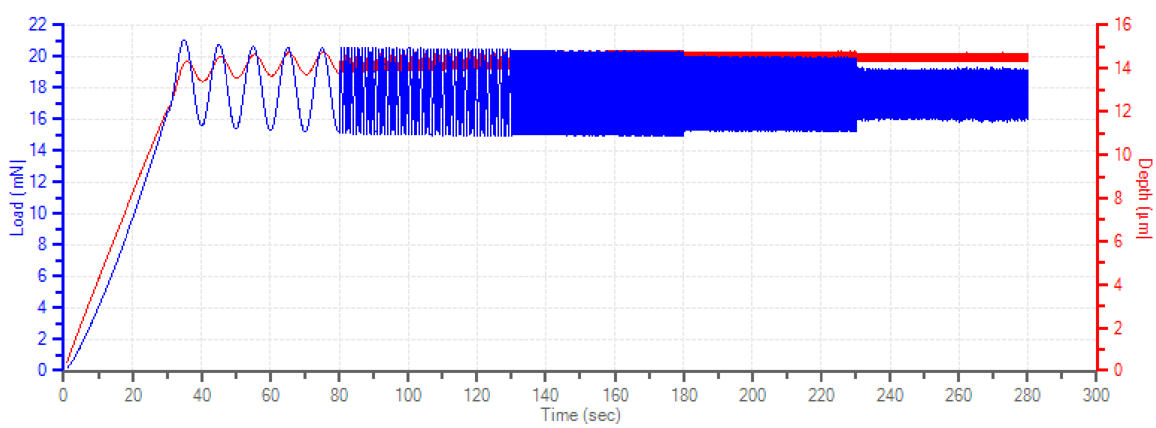

Fig. 2: Evolution of load & depth of the full DMA frequency sweep.

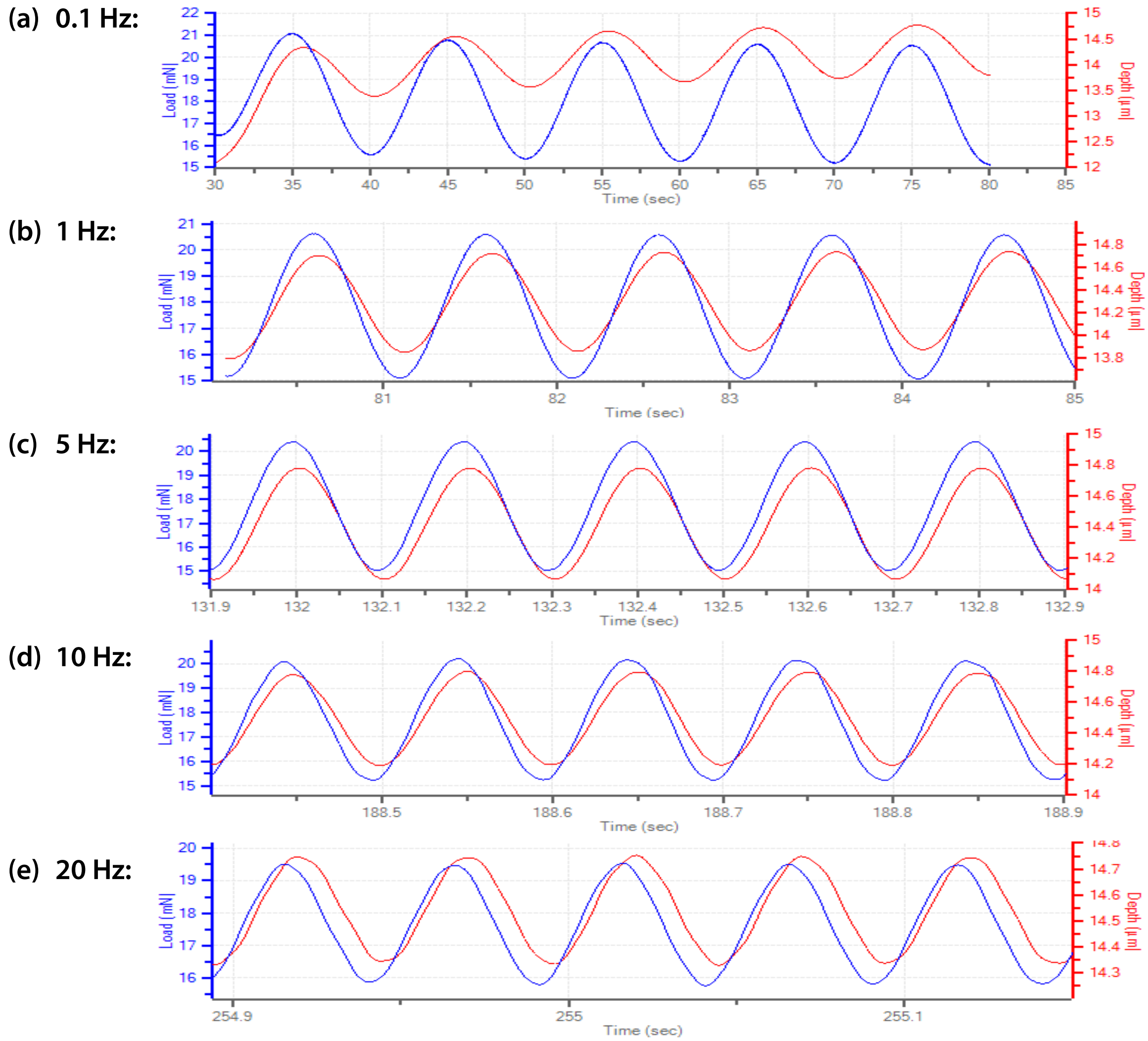

Fig. 3: Load & depth vs. time at different frequency.

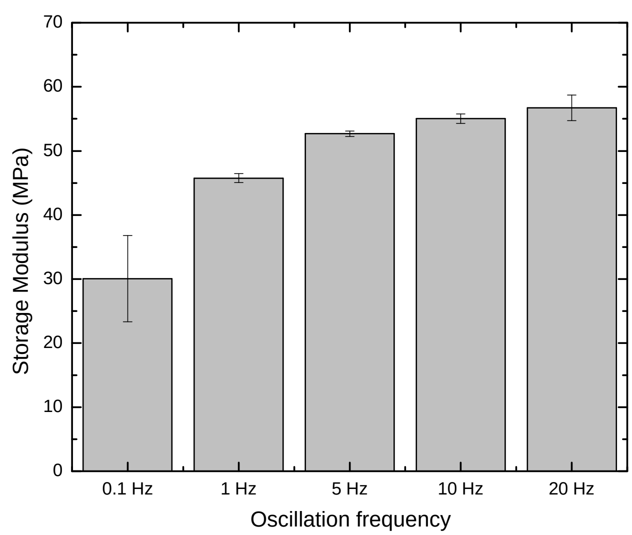

Fig. 4: Storage Modulus at different frequency.

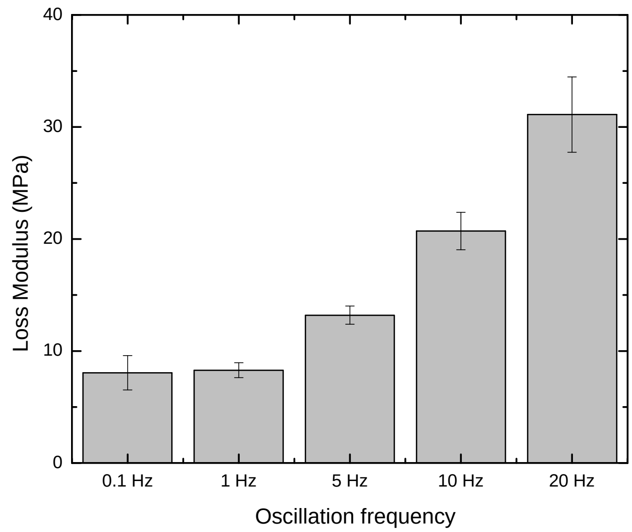

Fig. 5: Loss Modulus at different frequency.

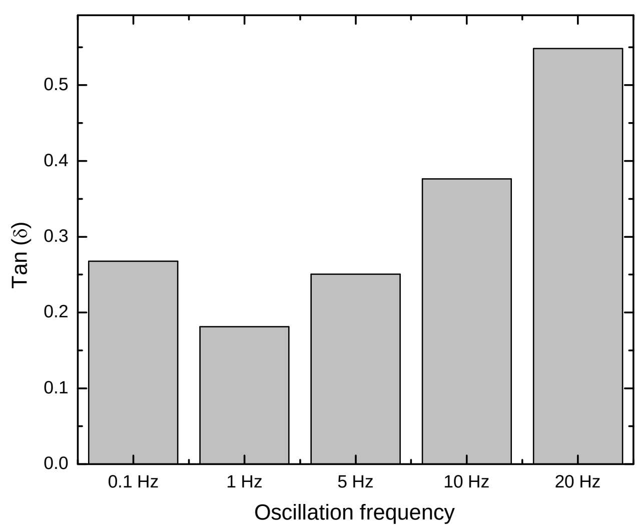

Fig. 6: Tan (δ) at different frequency.

CONCLUSION

In this study, we showcased the capacity of the Nanovea Mechanical Tester in performing the DMA frequency sweep test on a tire sample. This test measures the viscoelastic properties of the tire at different frequency of stress. The tire shows increased storage and loss modulus as the loading frequency increases from 0.1 to 20 Hz. It provides useful information on the viscoelastic behaviors of the tire running at different speeds, which is essential in improving the performance of tires for smoother and safer rides. The DMA frequency sweep test can be performed at various temperatures to mimic the realistic working environment of the tire under different weather.

In the Nano Module of the Nanovea Mechanical Tester, the load application with the fast piezo is independent from the load measurement done by a separate high sensitivity strain gage. This gives a distinct advantage during DMA since the phase between depth and load is measured directly from the data collected from the sensor. The calculation of phase is direct and does not need mathematical modeling that adds inaccuracy to the resulting loss and storage modulus. This is not the case for coil systems.

In conclusion, DMA measures loss and storage modulus, complex modulus and Tan (δ) as a function of contact depth, time and frequency. Optional heating stage allows determination of materials phase transition temperature during DMA. 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 Mechanical Tester or Lab Services.

MEASUREMENT PRINCIPLE

Nanoindentation is based on the standards for instrumented indentation, ASTM E2546 and ISO 14577. It uses an 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)	: 0.15 nm
Maximum force	: 400 mN
Load Resolution (Theoretical)	: 0.03 μN
Load Resolution (Noise Floor)	: 0.3 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.

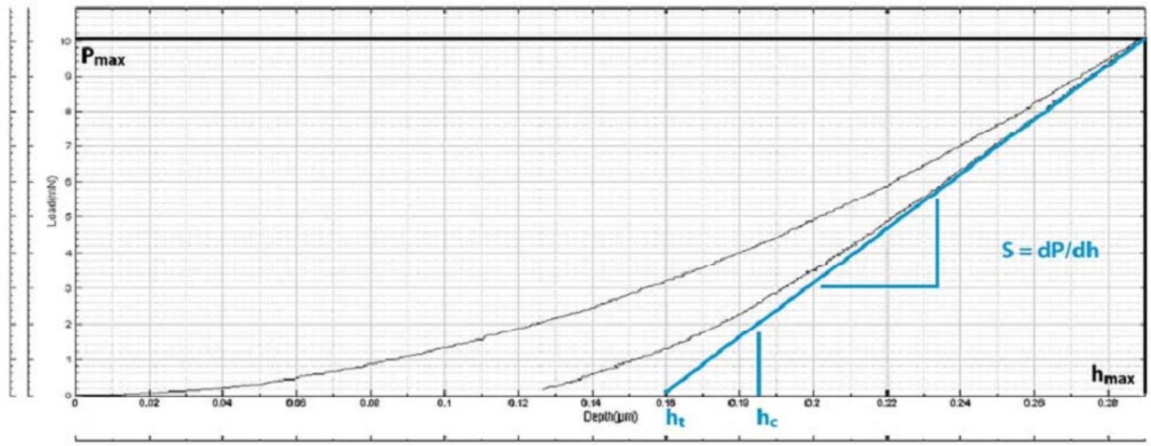

Fig. 7: Load-displacement curve of nanoindentation.

Hardness

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

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

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's ratio of the indenter and ν the Poisson's ratio of the tested sample.

How are these calculated?

A power-law fit through the upper 1/3 to1/2 of the unloading data intersects the depth axis at h_t. The stiffness, S, is given by the slope of this line. The contact depth, h_c, is then calculated as:

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

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: $\sigma = E\varepsilon$ 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 $\sigma = \eta \frac{d\varepsilon}{dt}$, where σ is the stress, η is the viscosity of the material, and $d\varepsilon/dt$ 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 is a better choice.

Other possible measurements by Nanovea Mechanical Tester:
Stress-Strain & Yield Stress, Fracture Toughness, Compression strength, Fatigue testing and many others.

DMA SINUS MODE PRINCIPLE

Sinus Mode (Ranging from 0.1 Hz to 100 Hz): A sinusoidal stress is applied and the strain in the material is measured. This allows plotting hardness and elastic modulus versus depth and can be used to study viscoelastic materials such as polymers, varnishes, plastics.

Storage modulus *E'* characterizes the elastic behavior.
Loss Modulus *E''* characterizes the viscous behavior (loss of energy due to internal friction).

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

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