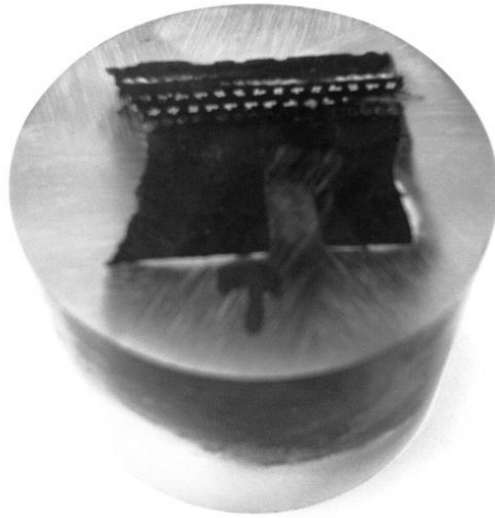


**VISCOELASTIC ANALYSIS OF RUBBER
WITH NANOINDENTATION DMA**



Prepared by
Duanjie Li, PhD & Andrea Herrmann

INTRODUCTION

Viscoelasticity is referred to as the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. A viscous material resists shear flow and strains linearly with time when a stress is applied, unlike an elastic material that strains immediately when stressed and returns to original state once the stress is removed. A viscoelastic material exhibits elements of both properties and therefore has a complex modulus.

IMPORTANCE OF NANOINDENTATION DMA FOR RUBBER

Tires are subjected to cyclical high deformations when vehicles are running on the road. When exposed to harsh road conditions, the service lifetime of the tires is jeopardized by many factors, such as the wear of the tread, the heat generated by friction, rubber aging, and others. As a result, tires usually have composite layer structures made of carbon-filled rubber, nylon cords, and steel wires, etc. In particular, the composition of rubber at different areas of the tire systems is optimized to provide different functional properties, including but not limited to wear resistant tread, cushion rubber layer and hard rubber base layer. A reliable and repeatable test of the viscoelastic behavior of rubber is critical in quality control and R&D of new tires, as well as evaluation of life span of old tires. Dynamic Mechanical Analysis (DMA) during Nanoindentation is a technique of characterizing the viscoelasticity. When controlled oscillatory stress is applied, the resulting strain is measured, allowing users to determine the complex modulus of the tested materials.

MEASUREMENT OBJECTIVE

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

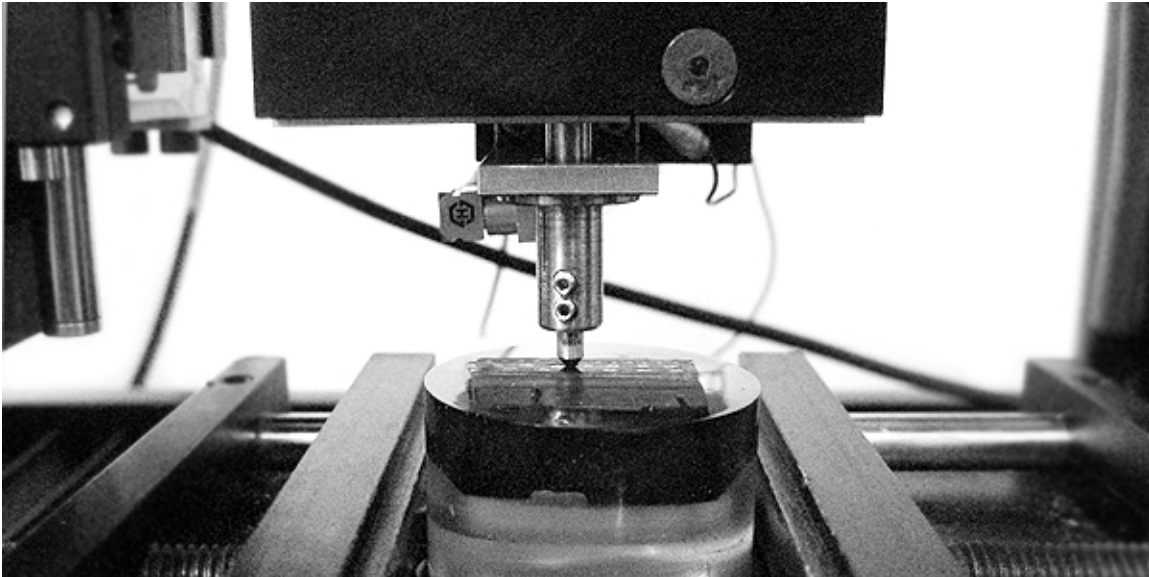


Fig. 1: DMA analysis of rubber tire using nanoindentation.

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.

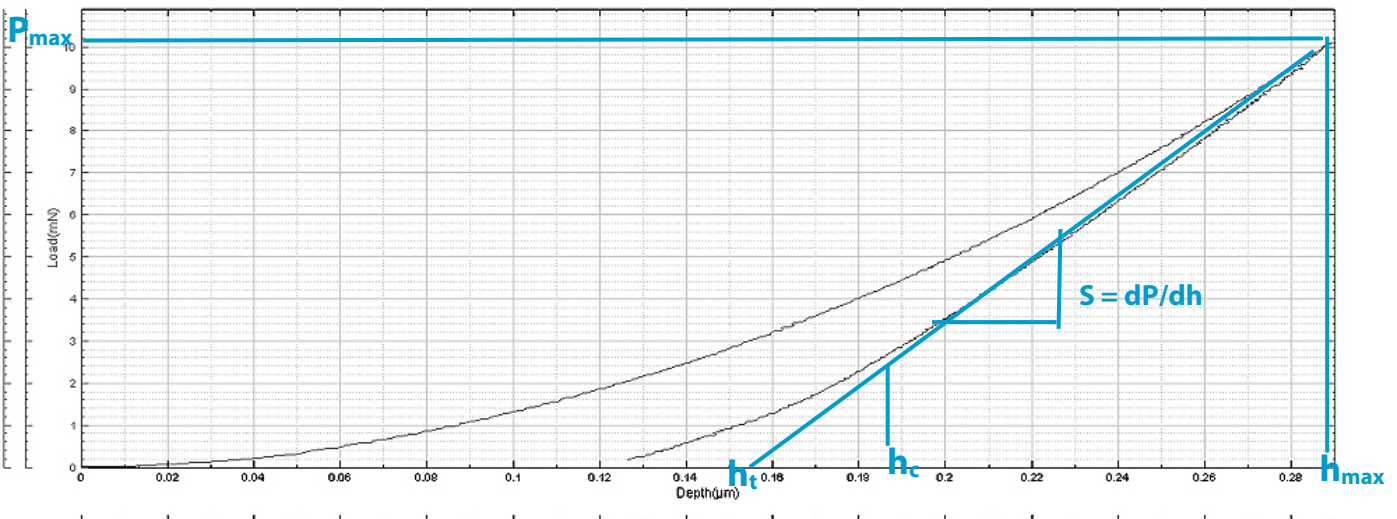


Fig. 2: Load-displacement curve of nanoindentation.

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 to 1/2 of the unloading data intersects the depth axis at h_c . 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 $A_c=2\pi R h_c$, 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 PRINCIPAL

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).

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

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

TEST CONDITIONS

A series (40 points) of nanoindentation DMA was performed along the thickness of the tire sample and the distribution of the indentations is illustrated in Fig. 3. The test conditions are summarized in Table 1.

Maximum force (mN)	75
Loading rate (mN /min)	150
Unloading rate (mN /min)	150
Creep (s)	20
Amplitude (mN)	15
Frequency (Hz)	10
Indenter type	100 μ m spherical diamond

Table 1: Test conditions of the nanoindentation DMA.

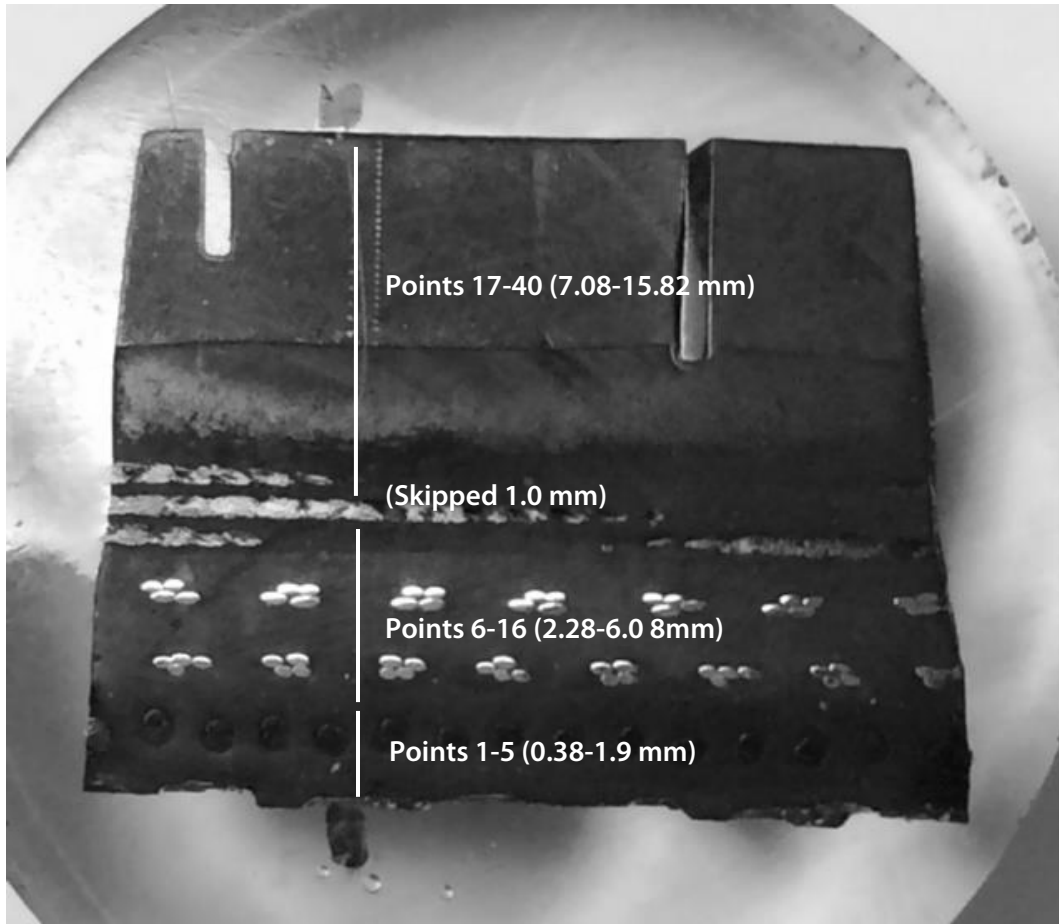


Fig. 3: Distribution of the indentation on the cross section of the tire sample.

RESULTS AND DISCUSSION

40 indentations along the tire thickness were performed spaced 0.38 mm apart for a total distance of ~15.5 mm as illustrated in Fig. 3 and the corresponding Tan (δ), Storage Modulus, Loss Modulus and Hardness measured from the DMA are summarized in Fig. 4 to Fig. 7. The distribution of the hardness and complex modulus meets the functionality requirements of the rubber at different layers of the tires. The rubber at the positions from 0.38 to 2.66 mm and from 8.22 and 11.64 mm exhibits a relatively low hardness below 2 MPa and low complex modulus. Such a relative soft feature allows the rubber in these regions to serve as a cushion layer and absorb the shocks and vibrations. In comparison, the rubber at the positions from 3.04 to 7.84 mm shows an enhanced hardness and complex modulus, due to the composite structure consisting of reinforcing fabric or high tensile-strength steel wires encased in the rubber compound. The enhanced mechanical properties of this layer provide the tire structure strength and toughness. The positions from 12.02 to 15.82 mm reside in the tire tread and exhibit higher Hardness and complex modulus compared with the “cushion region”. The high carbon black concentration at this area gives reinforced abrasion resistance, cut resistance as well as traction.

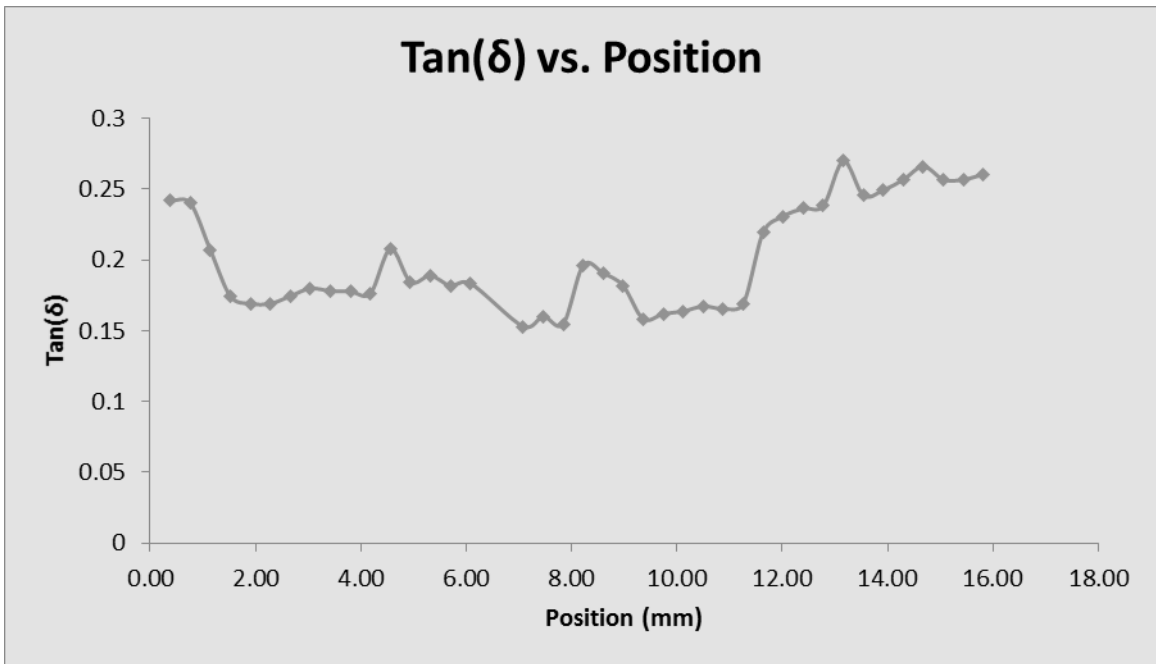


Fig. 4: Distribution of Tan(δ) at different locations of the tire.

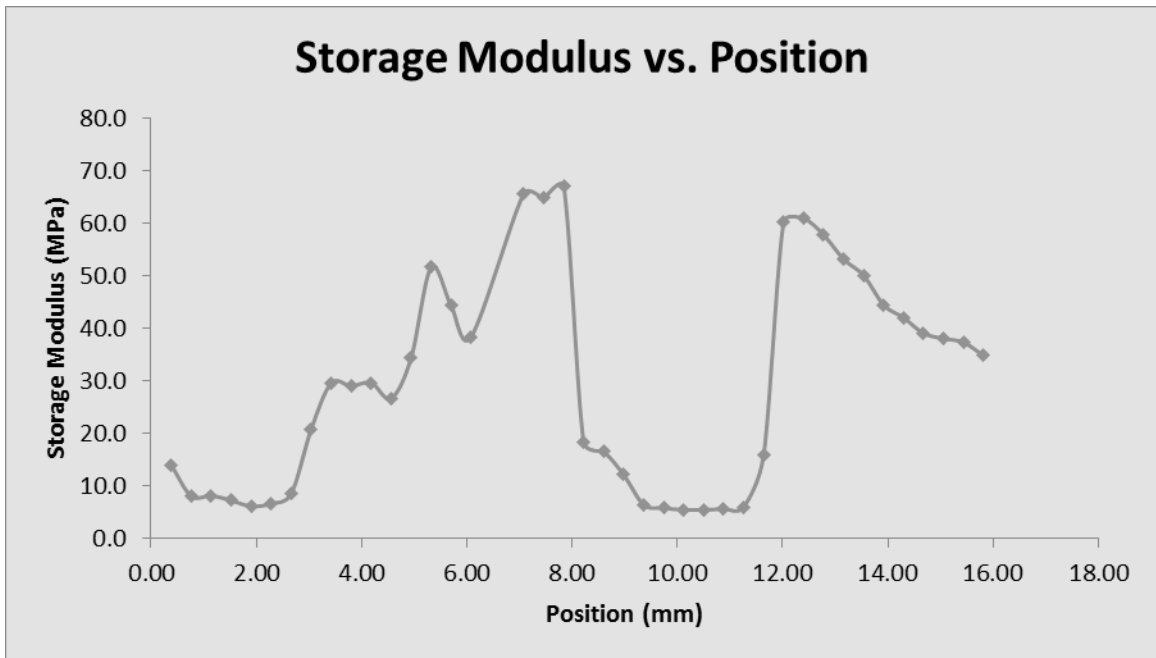


Fig. 5: Distribution of Storage Modulus at different locations of the tire.

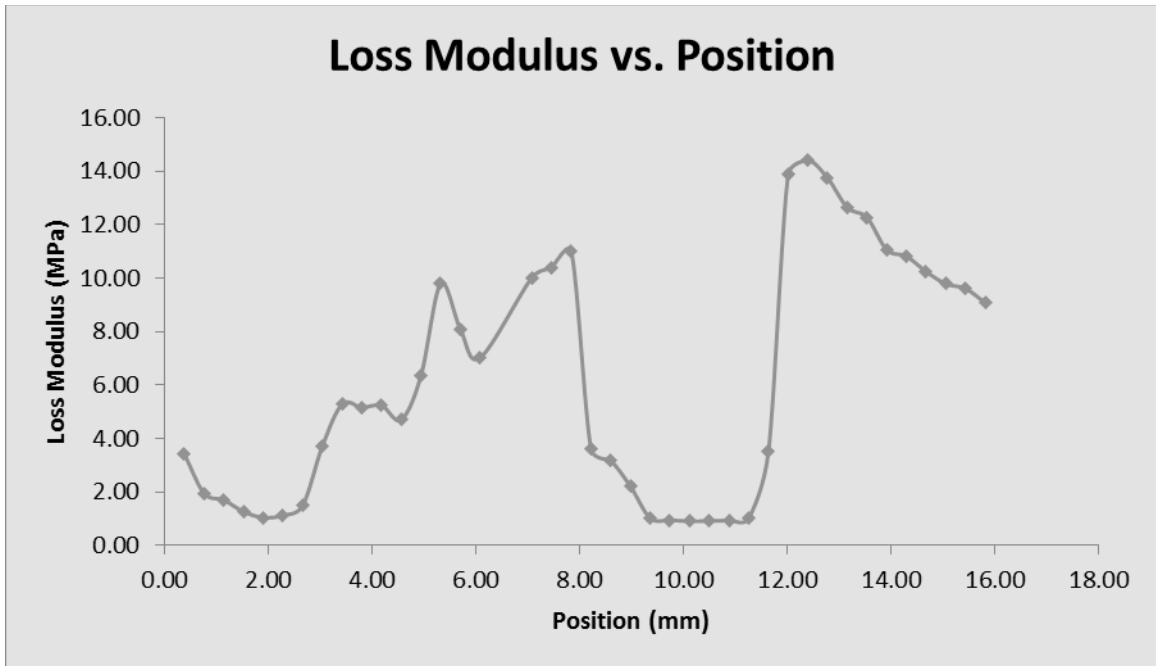


Fig. 6: Distribution of Loss Modulus at different locations of the tire.

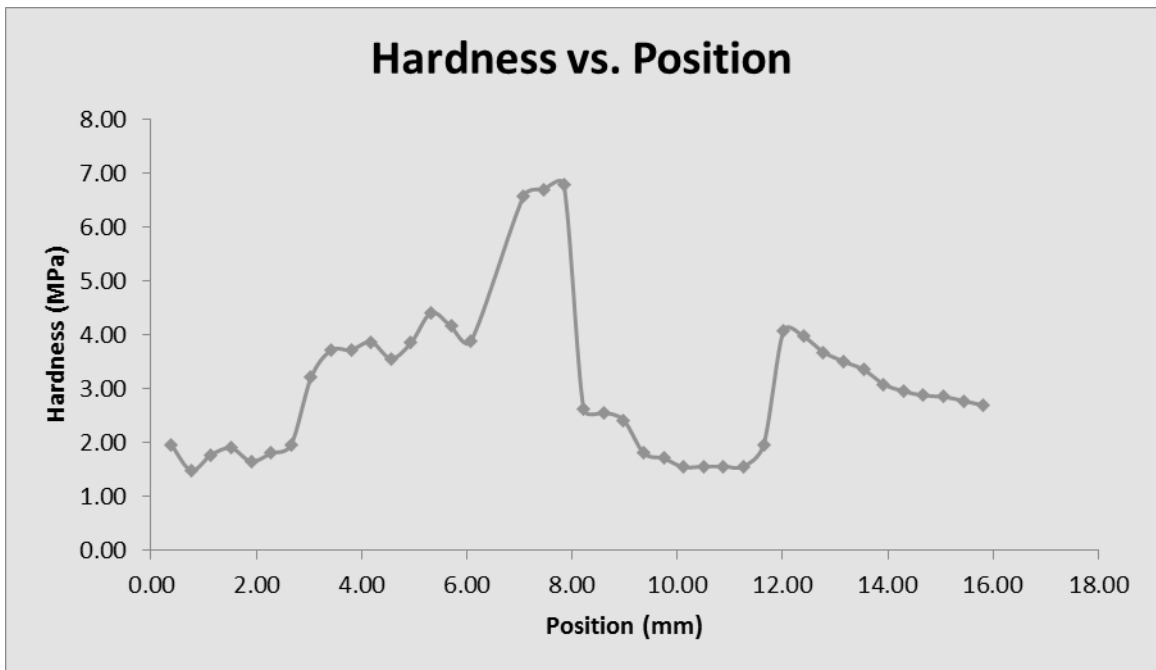


Fig. 7: Distribution of Hardness at different locations of the tire.

CONCLUSION

In this study, we demonstrate how the Nanovea Mechanical Tester in Nanoindentation DMA mode measures the viscoelastic properties of a rubber sample (used tire in this study). The profile seen across the depth of the tire shows how the different layers are used to create zones with very different behaviors. This is essential in tire design to decrease the vibration. Zones of high loss modulus will absorb differently than zones of low loss modulus. These types of studies are now essential to improve tires for smoother, safer rides that last as long as possible in different weather conditions. These tests can be performed at various temperatures and even under liquids. The test can also be conducted at various frequencies to mimic the behavior of tires as speed increases. Frequencies of 10Hz, used in this report, correspond to speed of about 67Km per hour. The Nanovea DMA can go up to 100Hz and is also possible to scan across various frequencies to obtain a sweep.

The Nanovea Mechanical Tester has true close feedback control on load applied. 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 hardness, 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](#).