Hydrogel Hardness Using Nanoindentation

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INTRO

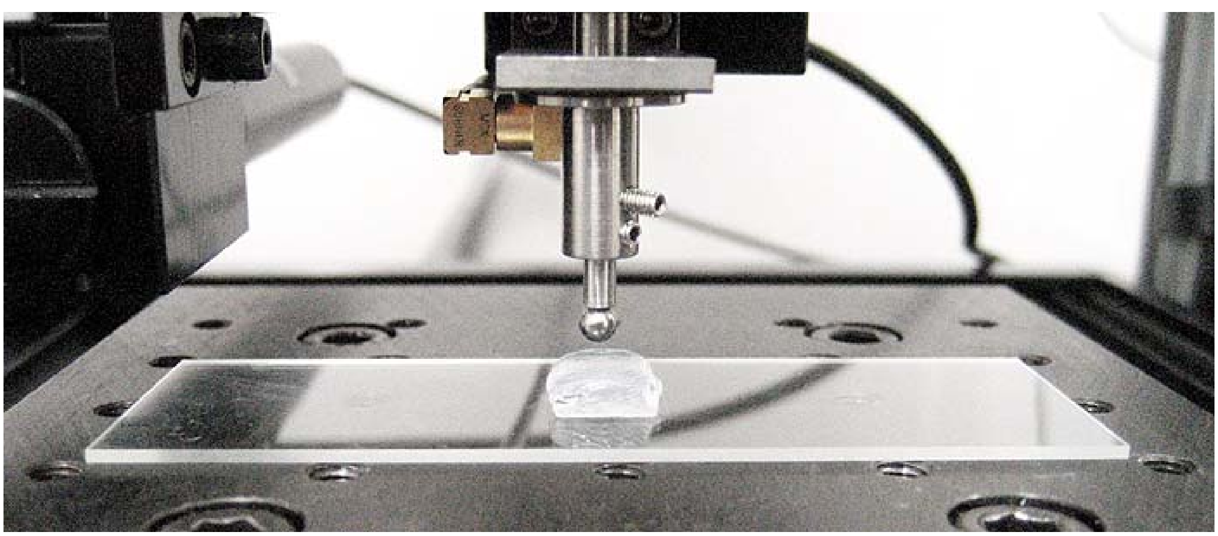
Hydrogel is known for its super absorbency of water allowing for a close resemblance in flexibility as natural tissue. This close resemblance has made Hydrogel a common choice not only in biomaterials, but also electronics, environment and consumer good application such as contact lens. The use and diversity in application have each their own unique needs and requirements. One such requirement will be known and controlled mechanical properties.

USING NANOINDENTATION FOR HYDROGELS

Hydrogels create unique challenges to Nanoindentation including test parameters and sample preparation. Additionally, many Nanoindentation systems have major limitations since they were not originally designed for such soft materials. For example, Nanoindentation systems using contact as a reference point can sink on very soft materials. Others use an electromagnet to apply force on the sample and because there is no actual force measurement, the loading is inaccurate and non-linear when testing soft materials. Therefore, determining the point of contact is extremely difficult since depth is the only parameter actually measured. Seeing a change of slope in the approach of the tip becomes almost impossible for soft materials and adds uncertainty to the accuracy of the data. These limitations are critical because the mechanical properties of soft materials depend on loading rate. Unlike the limitations of these systems, Nanovea's nano module is designed with force feedback to ensure high accuracy on all materials, extremely soft or hard. The piezo controlled displacement is extremely precise and fast providing direct measurement of load and depth. This allows unmatched measurement of viscoelastic properties by eliminating many theoretical assumptions that systems with electromagnet and no force feedback must account for to calculate the shift between load and depth measurement necessary to calculate loss and storage moduli.

MEASUREMENT OBJECTIVE

In this application, the Nanovea Mechanical Tester, in Nanoindentation mode, is used to study the hardness, elastic modulus and creep of a Hydrogel sample. In this case a sample of Hydrogel can simply be placed on a glass slide due to the softness and low load being used to test; testing could also be preformed while in liquid. For this soft material a 3mm spherical tip will be used. This is to give good information on the Hydrogel and not on surface properties that might be different. This can be studied using a shaper Berkovich tip.



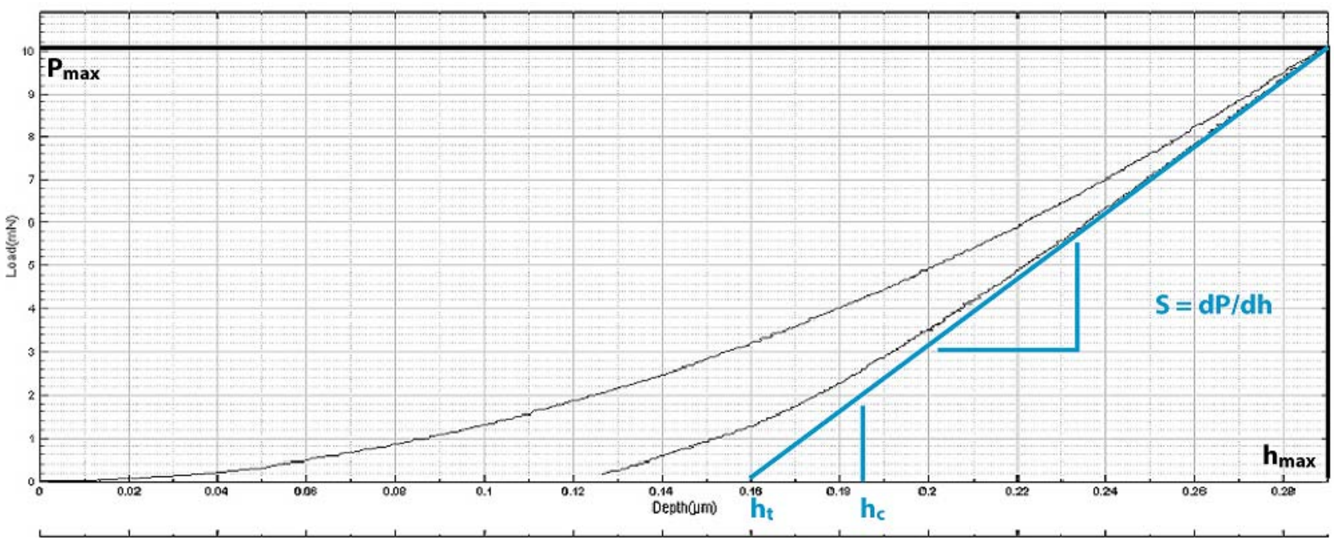
MEASUREMENT PRINCIPLE

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 250µm
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:

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

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 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:

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

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

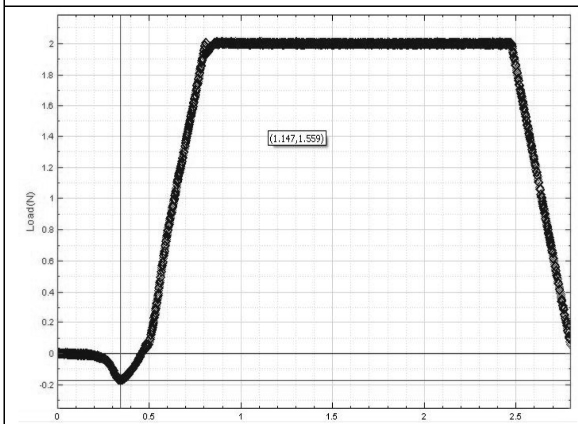
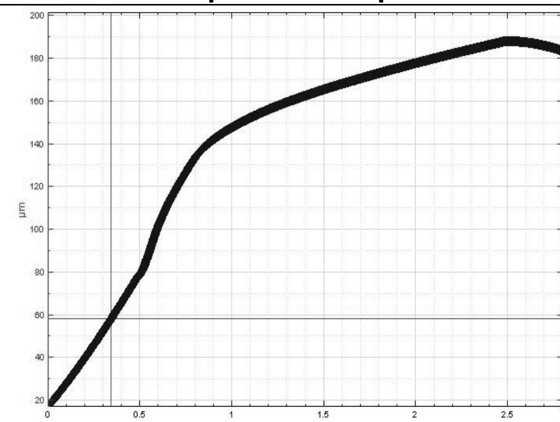
For a perfect Berkovich and Vickers indenters, the area function is $A_c=24.5h_c^2$ For Cube Corner indenter, the area function is $A_c=2.60h_c^2$ For Spherical indenter, the area function is $A_c=2\pi Rh_c$ where R is the radius of the indenter. The elastic components, as previously mentioned, can be 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 dε/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.

TEST CONDITIONS

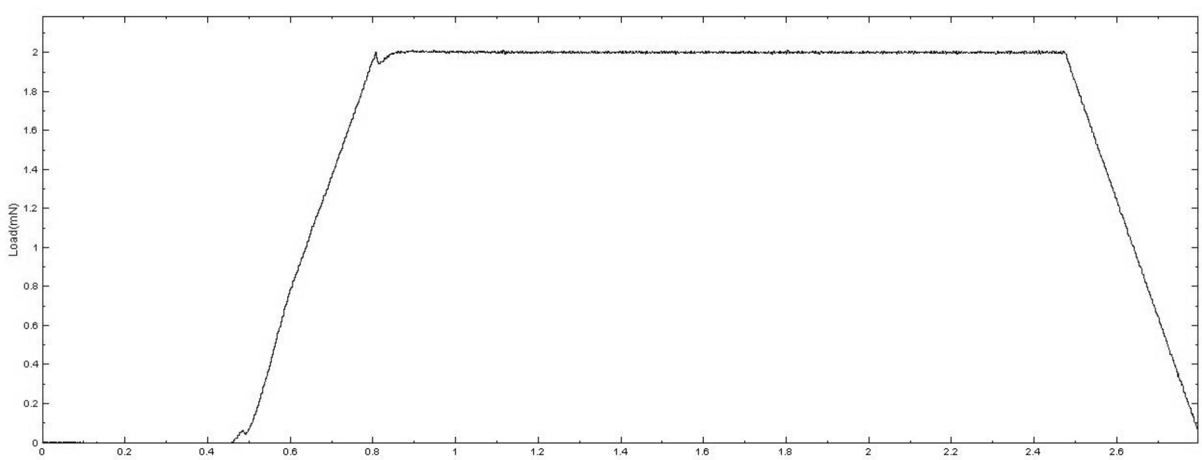
Approach Speed	100 µm/min
Contact Load	0.06 mN
Max Load	10mN
Unloading Rate	20mN
Creep (sec.)	70
Indenter Type	Spherical | 3mm | 1500 µm Radius

RESULTS

Point of Contact Selection on Load vs. time	**Point of Contact position on depth vs. time**
	

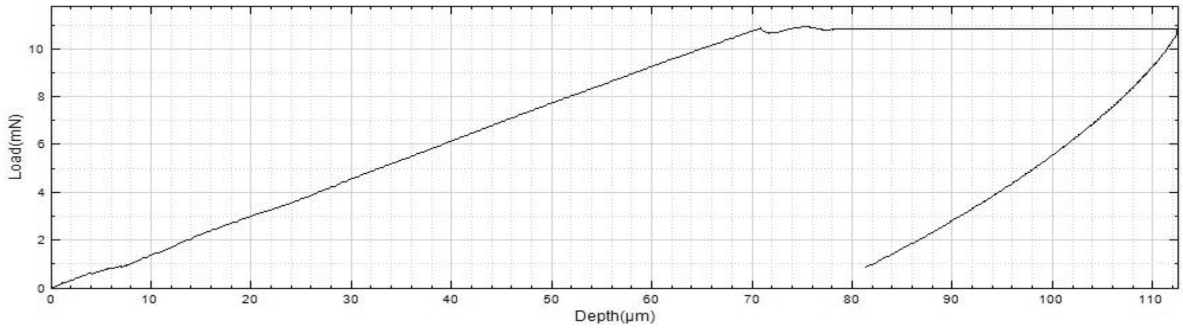
The advantage of directly measuring load during the test is seen above. The point of increased load is easily identified. While on the depth versus load, it is very difficult to determine the point of change of slope between movement in air and movement in the soft material. Below is the full loading versus time with force feedback control ensuring accurate loading. We can see how the loading and unloading follow the requested loading rate.

Load vs. Time Curve

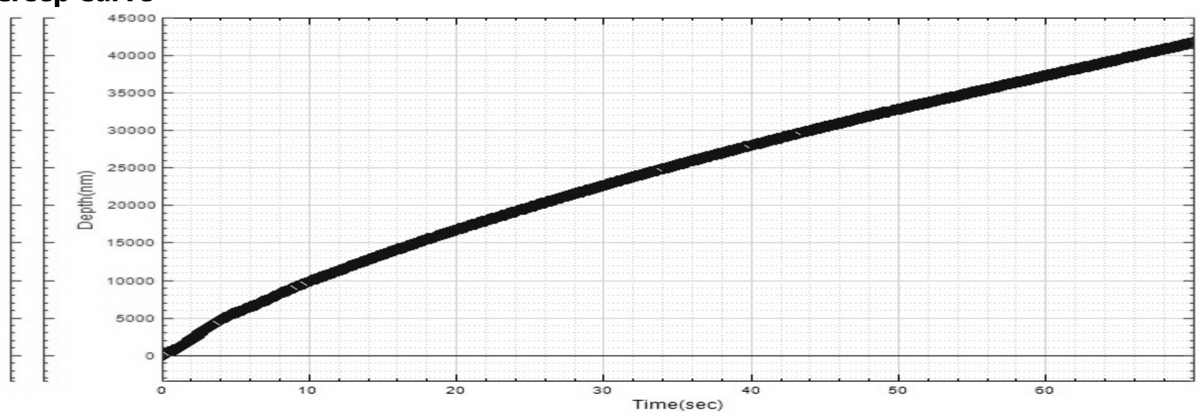


RESULTS CONTINUED

Indentation Curve



Creep Curve



Test	Hardness (KPa)	Modulus (KPa)	Martens (KPa)
Test 1	15.62	128.3	9.41
Test 2	17.39	147.6	10.4
Test 3	17.70	204.8	13.2
AVG	**16.90**	**160.2**	**11.0**
stdev	**1.12**	**28.1**	**1.4**

CONCLUSION

In conclusion, we have shown how the Nanovea Mechanical Tester, in Nanoindentation mode, provides precise measurement of the mechanical properties of Hydrogel. From the load versus time curve we show that it is very easy to select the accurate point of contact compared with depth versus time curve which is a big challenge. Using the larger 3mm ball and depth over 100micron provided repeatability. Exact positioning is still important since the sample had some waviness on the surface. Further improvement in the flatness of the sample will automatically increase the repeatability of the results. Creep is a very important factor for these samples and as we can see in creep versus time that in one minute this is equivalent to over 35micron extra on a depth that was at 70micron when the creep measurement started. This creep study with the Nanovea Nano module is extremely accurate as feedback control between piezo and ultra sensitive load cell ensure true constant loading during creep time. DMA "Dynamic Mechanical Analysis" could have also been used here to measure viscoelastic properties. To learn more about Nanovea Nanoindentation