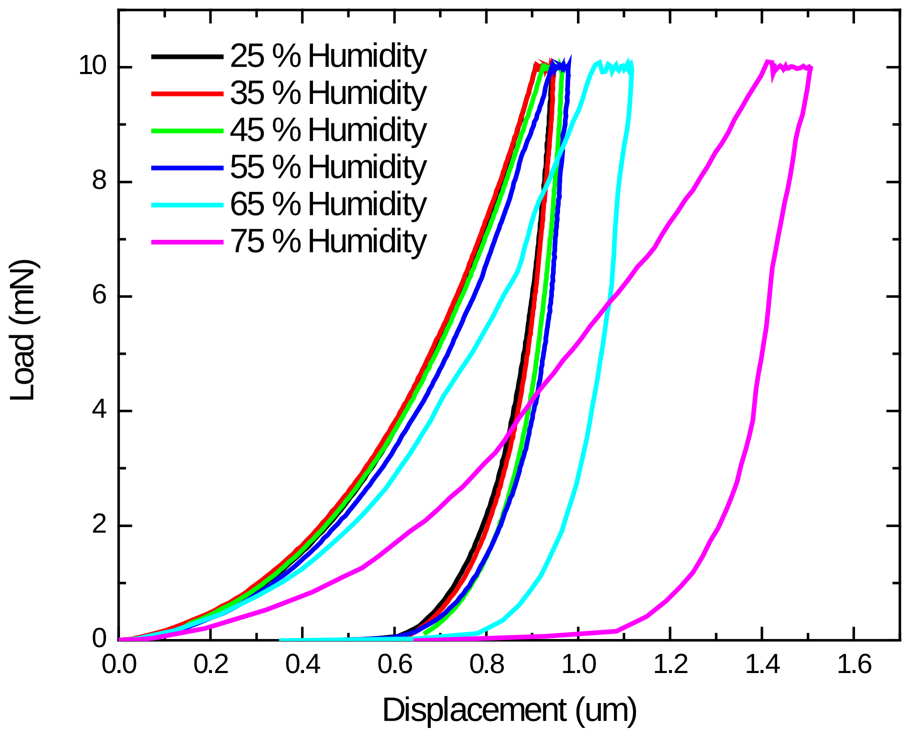
NANOVEA®
A Better Measure.

CONTROLLED HUMIDITY NANOINDENTATION OF POLYMER FILMS



Prepared by
Duanjie Li, PhD & Andrea Novitsky

6 Morgan, Ste156, Irvine CA 92618 · P: 949.461.9292 · F: 949.461.9232 · nanovea.com

INTRODUCTION

Creep takes place when a solid material deforms slowly as a result of long-term exposure to high levels of stress. Viscoelastic materials such as polymers are susceptible to creep. Depending on the material properties, exposure time, temperature and humidity, polymer materials under stress deforms at different rates.

IMPORTANCE OF NANOINDENTATION TEST OF POLYMER IN HUMIDITY

The mechanical properties of polymer is modified as the environmental humidity elevates. Transient moisture effects, a.k.a. mechano-sorptive effects arises as the polymer absorbs high moisture content and experiences accelerated creep behavior. The higher creep compliance is a result of complex combined effects such as increased molecular mobility, sorption-induced physical aging and sorption-induced stress gradients.

Therefore, a reliable and quantitative test of the sorption-induced influence on the mechanical behavior of polymeric materials at different moisture level is in need. The Nano module of the Nanovea Mechanical Tester applies the load by a high-precision piezo and directly measures the evolution of force and displacement. Uniform humidity is created surrounding the indentation tip and the sample surface by an isolation enclosure, which ensures measurement accuracy and minimizes the influence of drift caused by humidity gradient.

MEASUREMENT OBJECTIVE

In this application, we showcased that the Nanovea Mechanical Tester in Nanoindentation mode measures the mechanical properties such as hardness and creep of a polymer film in an isolated environment with uniform humidity.

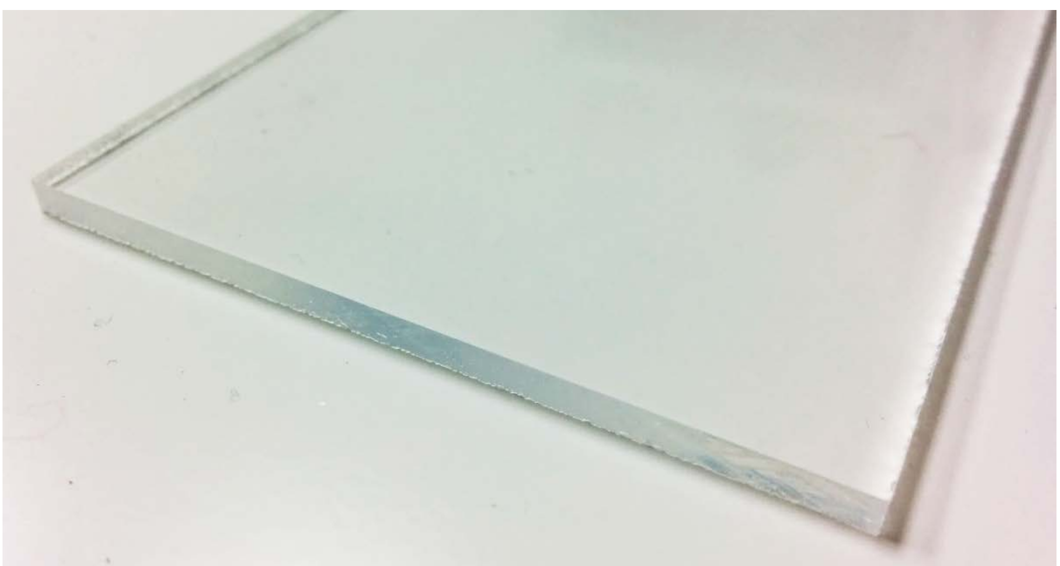


Fig. 1: The polymer film for this study.

TEST CONDITIONS

In this study, a polymer film sample is tested by nanoindentation in an isolated environment of different humidity ranging from the 25 to 75%. Both the sample and indenter are kept in an isolated enclosure with uniform humidity controlled by a humidity controller. The contact of the sample surface and the indenter maintains the desired humidity during the indentation test to guarantee measurement accuracy. The creep is measured by the change of indentation depth at the maximum load of 10 mN for 10 s. The test conditions are summarized in Table 1.

Humidity (%)	25, 35, 45, 55, 65 and 75
Maximum load (mN)	10
Loading rate (mN/min)	20
Unloading rate (mN/min)	20
Creep time (s)	10
Computation Method	ASTM E-2546 & Oliver & Pharr
Indenter type	Berkovich Diamond

Table 1: Test conditions of the nanoindentation at different humidity.

RESULTS AND DISCUSSION

The load vs. displacement plot of the nanoindenation tests at different humidity is shown in Fig. 2. The evolution of hardness and creep as a function of the humidity is plotted in Fig. 3. As the humidity increases from 25 to 55 %, the load-displacement curve shifts slightly towards higher penetration depth, leading to progressively decreased hardness from ~0.60 to ~0.54 GPa. When the humidity continues to rise to 75 %, the hardness value drops at a higher rate, resulting in hardness of 0.46 and 0.31 GPa, respectively, in humidity of 65 % and 75 %. Meanwhile, as the humidity increases from 25 to 55 %, the creep depth slowly increases from 36 to 48 nm. This is followed by a substantial increase to values of 80 and 105 nm, respectively, as the humidity continues to increase to 65 and 75 %.

Analogous to the influence of temperature, the time-dependent visco-elastic deformation of the polymer film in this study is affected by the humidity level. Hydrophilic materials usually exhibits significantly higher creep rate with moisture content. The polymer film starts to swell upon exposure to the high ambient level of solvent (e.g. the relative humidity of water vapor). The water vapor induces swelling only upon reaching certain threshold value. When the humidity increases from 55 to 65 %, swelling of the polymer film takes place, leading to significant creep when the film is subjected to high concentrated external load.

The mechanical properties of the polymeric materials in the environment of elevated humidity are critical for high moisture industrial applications, such as in the oil and marine industries. By quantitatively measuring the hardness and creep of the polymers in different humidity, a more complete picture of the mechanical reliability of the polymer can be obtained.

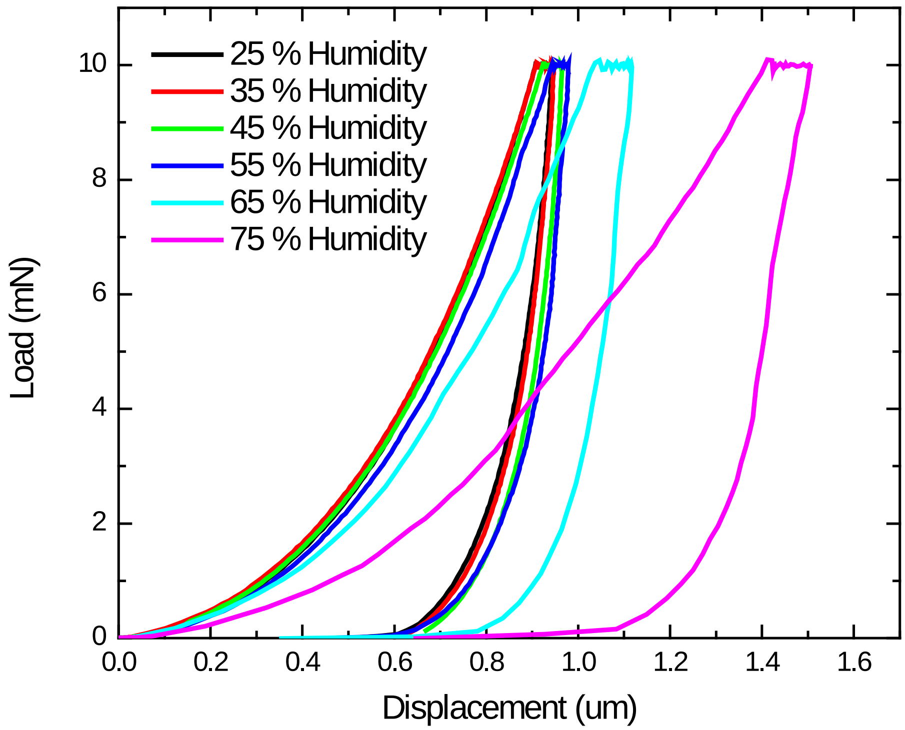


Fig. 2: The load vs. displacement plots in various humidity.

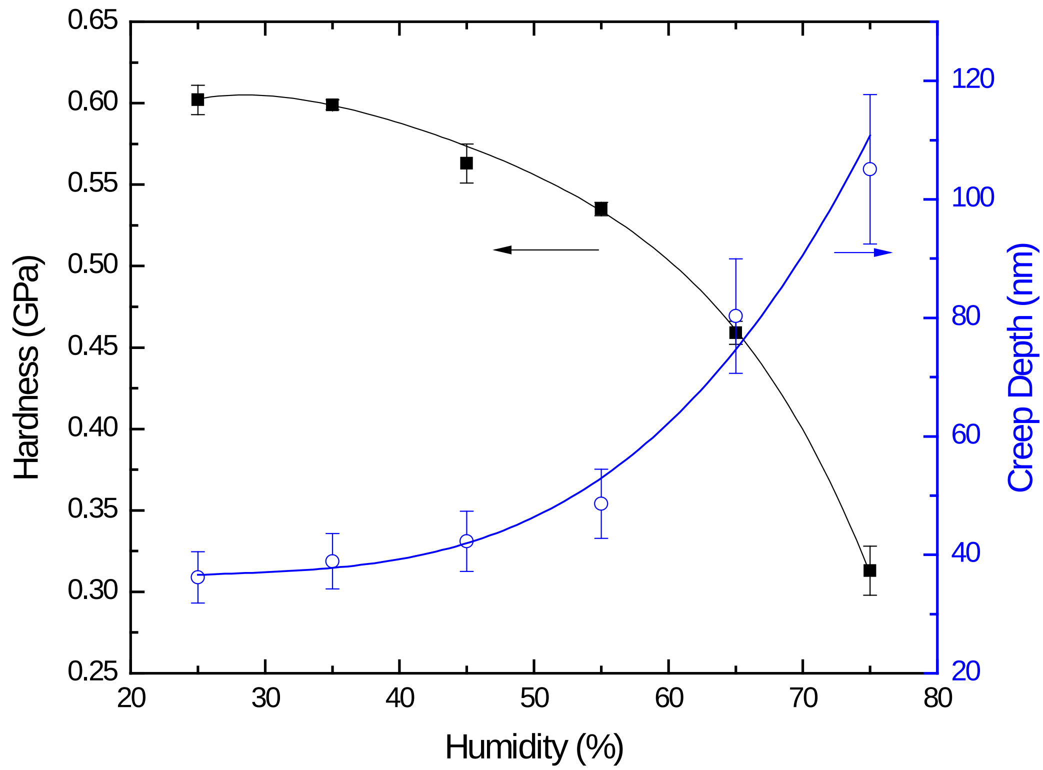


Fig. 3: The hardness and creep depth as a function of the humidity.

CONCLUSION

The Nanovea Mechanical Tester performs the nanoindentation test on a polymer film at different humidity. Both the sample and indenter are enclosed in an isolated environment with uniform humidity to minimize the effect of humidity gradient drift. The mechanical properties, such as hardness and creep, of the polymer film varies in the environment of different humidity. The creep at the maximum load under humidity between 25 and 75 % provides a quantitative and reliable measurement on the mechanical behavior of the polymer materials in humid environments. The polymer film sample in this study shows progressively decreased hardness and increased creep behavior as the humidity elevates. Creep contributes to significant plastic deformation during the indentation at elevated humidity above 65 %.

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.

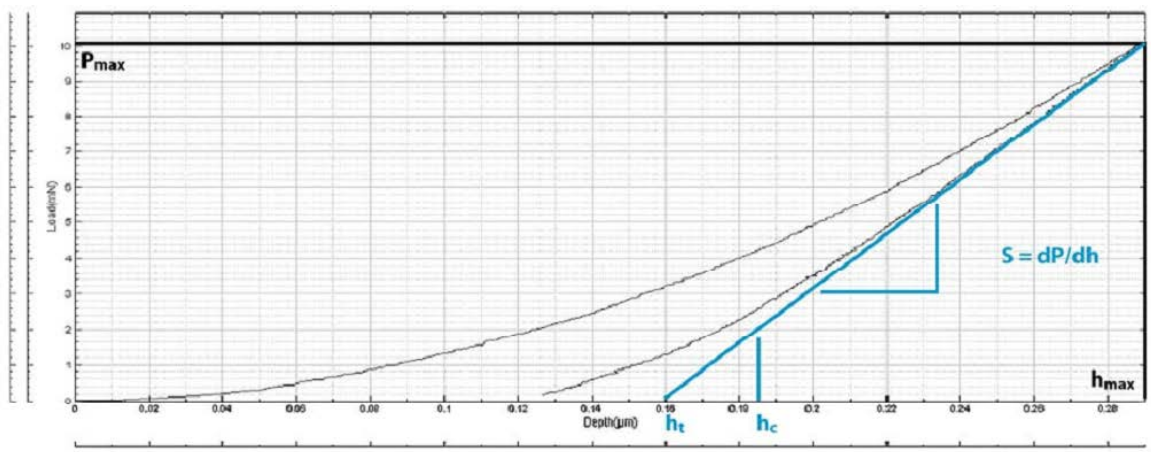


Fig. 4: Load-displacement curve of nanoindentation.

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).

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

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.