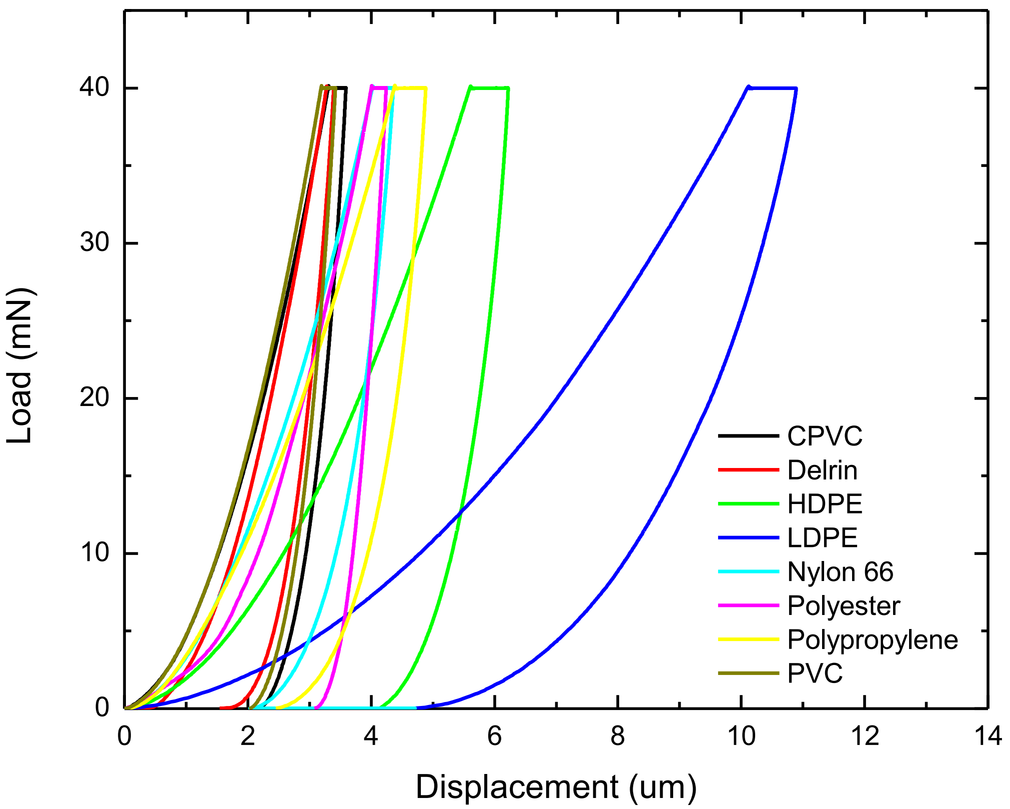
NANOVEA®
A Better Measure.

CREEP DEFORMATION OF POLYMERS BY NANOINDENTATION



Prepared by
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INTRODUCTION

As viscoelastic materials, polymers often undergo a time-dependent deformation under a certain applied load, also known as creep. Creep becomes a critical factor when the polymeric parts are designed to be exposed to continuous stress, such as structural components, joints and fittings, and hydrostatic pressure vessels.

IMPORTANCE OF CREEP MEASUREMENT FOR POLYMERS

The inherent nature of viscoelasticity plays a vital role in the performance of the polymers and directly influences their service reliability. The environmental conditions such as loading and temperature affect the creep behavior of the polymers. Creep failures often occur due to the lack of alertness of the time-dependent creep behavior of the polymer materials used under specific service conditions. As a result, it is important to develop a reliable and quantitative test of the viscoelastic mechanical behaviors of the polymers. 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 in situ. The combination of accuracy and repeatability makes it an ideal tool for creep measurement.

MEASUREMENT OBJECTIVE

In this application, we showcased that the Nanovea Mechanical Tester in Nanoindentation mode is an ideal tool for studying the viscoelastic mechanical properties including hardness, Young's modulus and creep of polymeric materials.

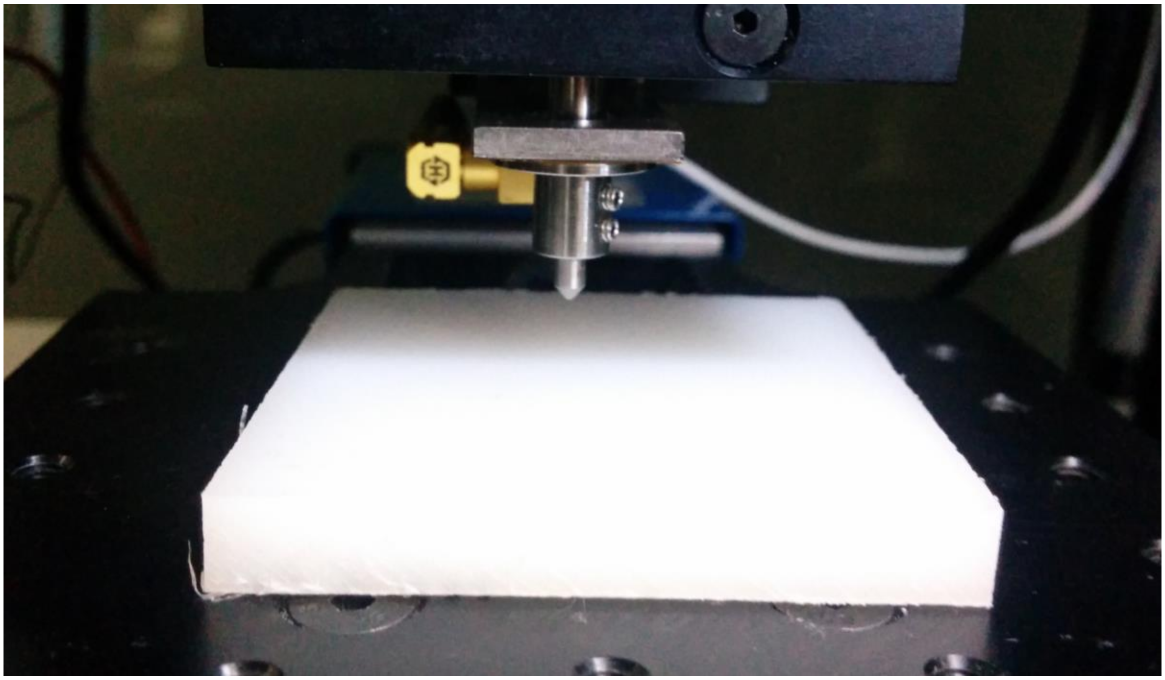

Fig. 1: Setup of the nanoindentation test.

TEST CONDITIONS

Eight different polymer samples were tested by nanoindentation technique using Nanovea Mechanical Tester. As the load linearly increased from 0 to 40 mN, the depth progressively increased during the loading stage. The creep was then measured by the change of indentation depth at the maximum load of 40 mN for 30 s. The test conditions are summarized in Table 1.

Maximum load (mN)	40
Loading rate (mN/min)	80
Unloading rate (mN/min)	80
Creep time (s)	30
Indenter type	Berkovich Diamond

Table 1: Test conditions of the nanoindentation.

RESULTS AND DISCUSSION

The load vs. displacement plot of the nanoindenation tests on different polymer samples is shown in Fig. 2 and the creep curves are compared in Fig. 3. The hardness and Young's modulus are summarized in Fig. 4, and the creep depth is shown in Fig. 5. As an example in Fig. 2, the AB, BC and CD portions of the load-displacement curve for the nanoindentation measurement represent the loading, creep and unloading processes, respectively.

Delrin and PVC exhibit the highest hardness of 0.23 and 0.22 GPa, respectively, while LDPE possesses the lowest hardness of 0.026 GPa among the tested polymers. In general, the harder polymers show lower creep rates. The softest LDPE has the highest creep depth of 798 nm, compared to ~120 nm for Delrin.

The creep properties of the polymers are critical when they are used in structural parts. By precisely measuring the hardness and creep of the polymers, a better understanding of the time-dependent reliability of the polymers can be obtained. The creep, change of the displacement at a given load, can also be measured at different elevated temperatures and humidity using the Nanovea Mechanical Tester, providing an ideal tool to quantitatively and reliably measure the viscoelastic mechanical behaviors of polymers in the simulated realistic application environment.

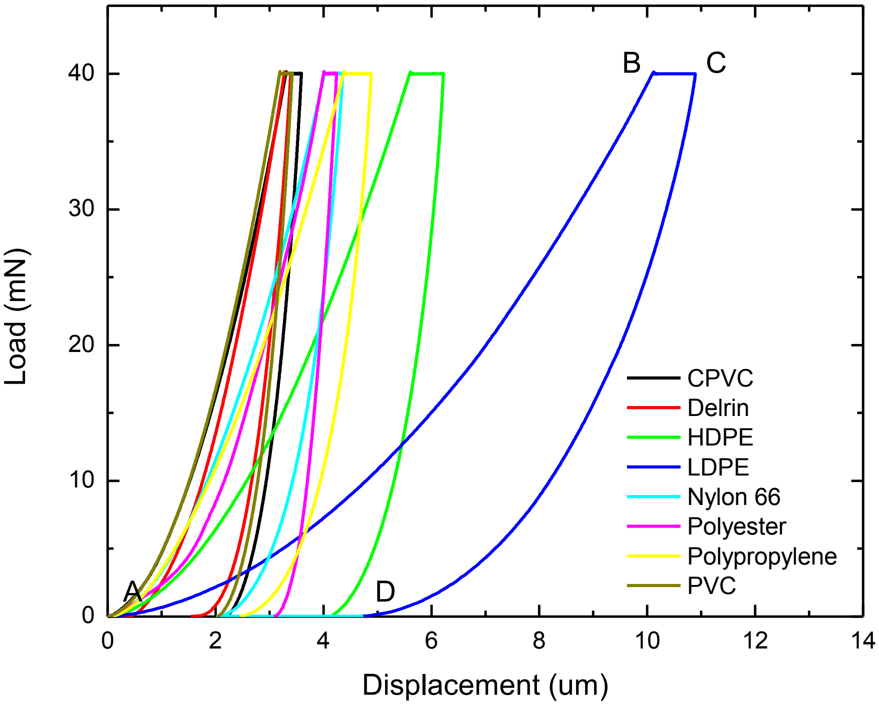

Fig. 2: The load vs. displacement plots of different polymers.

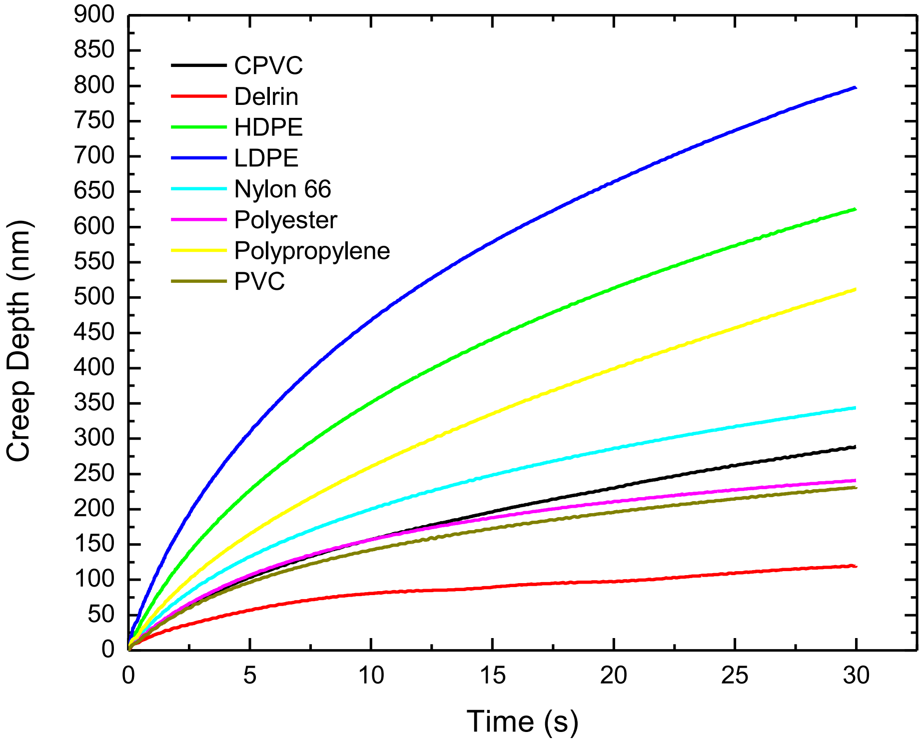

Fig. 3: Creeping at a maximum load of 40 mN for 30 s.

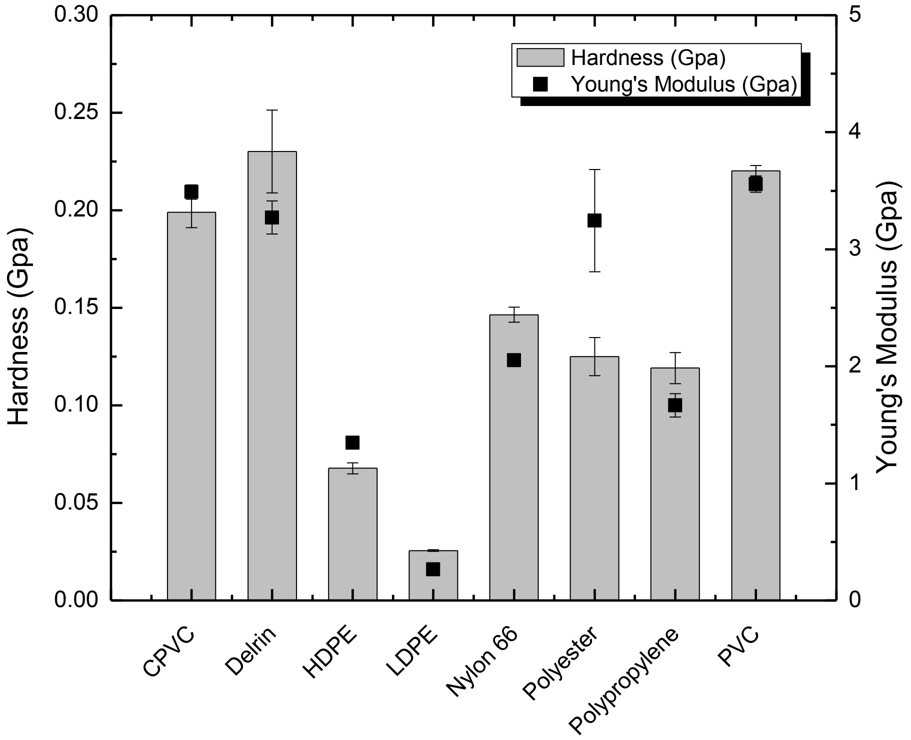

Fig. 4: Hardness and Young's modulus of the polymers.

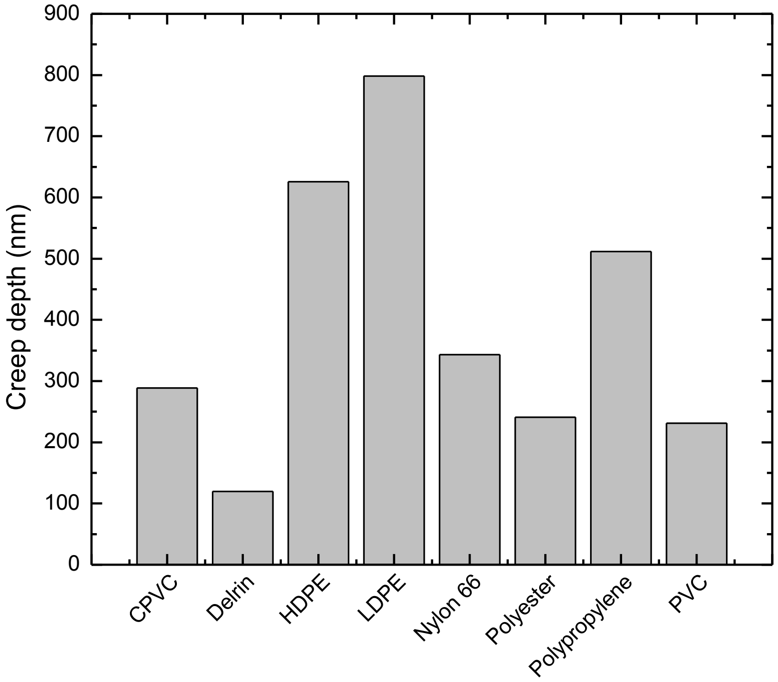

Fig. 5: Creep depth of the polymers.

CONCLUSION

In this study, we showcased that the Nanovea Mechanical Tester measures the mechanical properties of different polymers, including Hardness, Young's Modulus and Creep. Such mechanical properties is essential in selecting the proper polymer material for intended applications. Delrin and PVC exhibit the highest hardness of 0.23 and 0.22 GPa, respectively, while LDPE possesses the lowest hardness of 0.026 GPa among the tested polymers. In general, the harder polymers exhibit lower creep rates. The softest LDPE shows the highest creep depth of 798 nm, compared to ~120 nm for Delrin.

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.

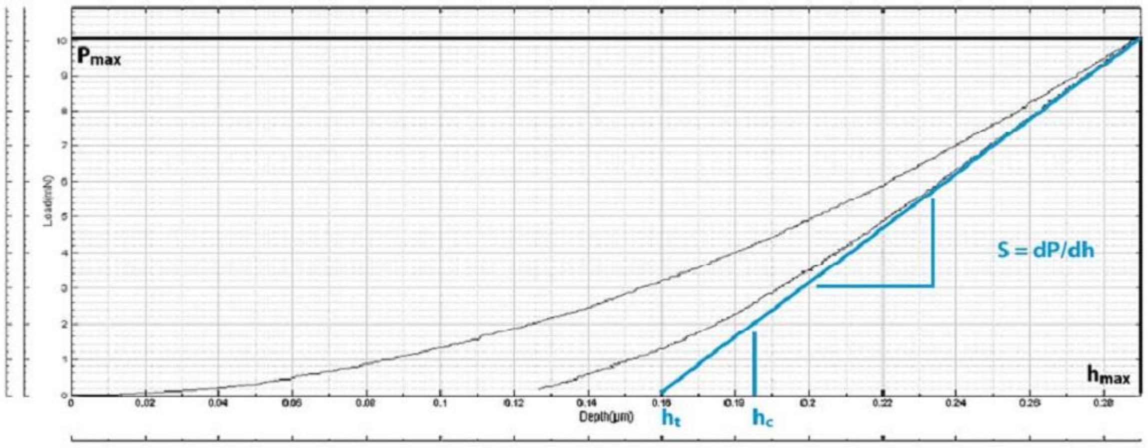

Fig. 6: Load-displacement curve of nanoindentation.

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).

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

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.