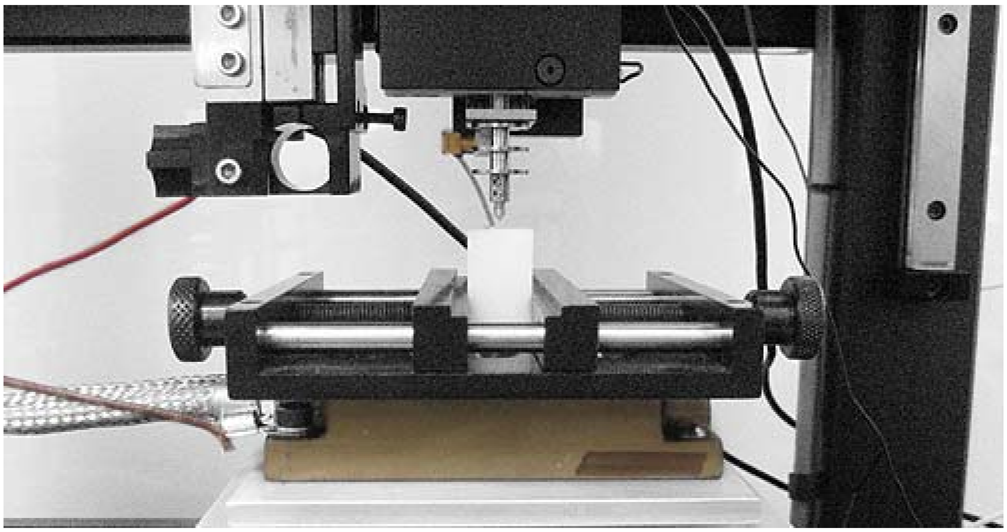
NANOINDENTATION OF POLYMER AT ELEVATED TEMPERATURE



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INTRODUCTION

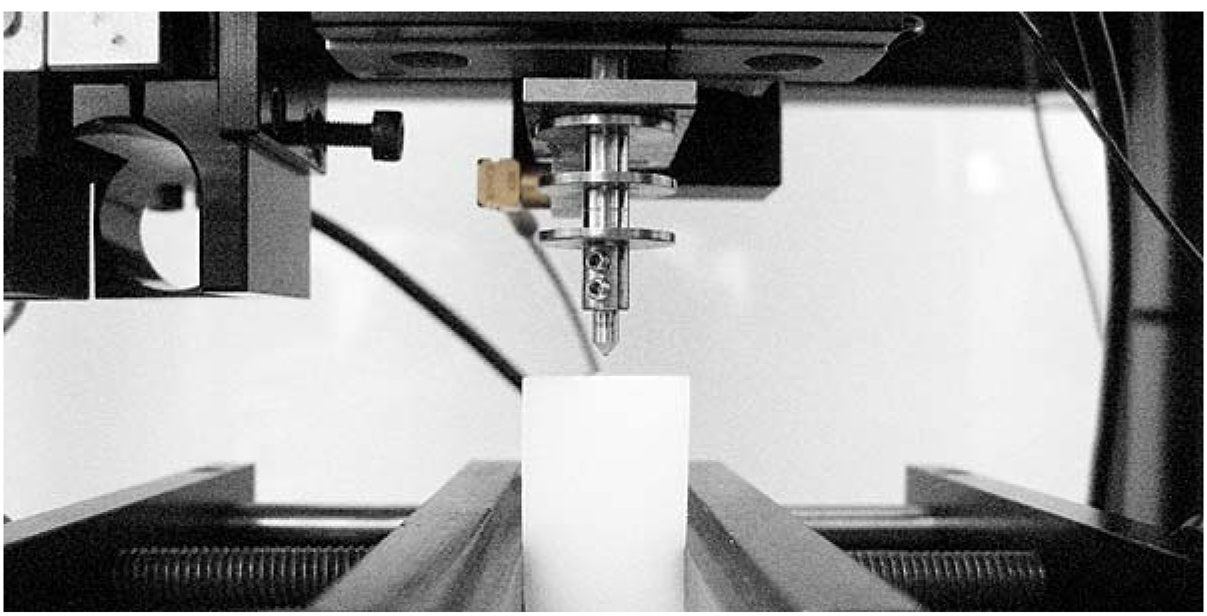
Materials such as Polymers are not often considered to be used with elevated temperature applications because it has been thought that polymers would degrade and would only be suitable in low temperature applications. In recent years, there has been an increasing importance in how polymers are engineered. Improving performances at elevated temperatures can increase what is called the "maximum service temperature". Polymers can soften at elevated temperatures but most importantly degrade. When this starts to happen polymers can only be classified for lower temperature applications.

IMPORTANCE OF ELEVATED TEMP NANOINDENTATION FOR POLYMER

Nanoindentation can be used during elevated temperature to study effects on Hardness, Young's Modulus and Creep by applying a controlled, increasing load that is precisely measured. Using the Nanovea Mechanical tester during elevated temperatures the mechanical properties of materials can be precisely measured as to what the effect. With this capability the properties of coatings, films and substrates intended for elevated temperatures can be identified.

MEASUREMENT OBJECTIVE

In this application, the Nanovea Mechanical Tester, in Nanoindentation mode with a temperature heating plate (up to 120°C) is used to study the comparative Hardness, Young's Modulus and Creep analysis properties between High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE). The temperature was measured directly on the surface of the polymer with a thermocouple.



MEASUREMENT PRINCIPAL

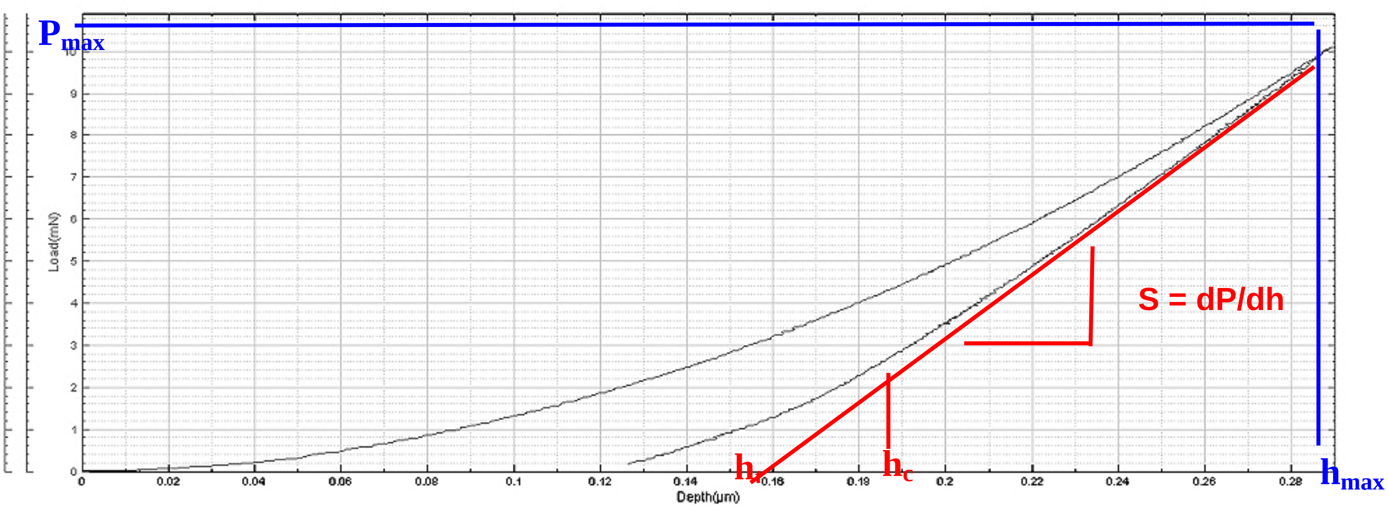
Nanoindentation is based on the standards for instrumented indentation, ASTM E2546 and ISO 14577. It uses an already established method where an indenter tip with a known geometry is driven into a specific site of the material to be tested, by applying an increasing normal load. When reaching a pre-set 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:

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

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.

Other tests possible includes the following:

DMA Sinus Mode, Storage modulus E', Loss Modulus

PARAMETERS USED:

	HDPE & LDPE	HDPE & LDPE
Maximum force (mN)	50	50
Loading rate (mN/min)	100	100
Unloading rate (mN/min)	100	100
Temperature (°C)	24	45
Creep (s)	30	30
Computation Method	ASTM E-2546	ASTM E-2546
Indenter type	Berkovich Diamond	Berkovich Diamond

RESULTS:

This section includes a table of measurements for High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE). Both types of polymers were subjected to room temperature hardness analysis as well as elevated temperature hardness analysis. Other types of analysis studied were: Young's Modulus and Creep

Table of main numerical results:

TESTING PERFORMED @ 24.3°C

		Hardness(MPa)	Hardness(HV)	Modulus (Mpa)
HDPE	Test 1	71.99	6.802	1324
	Test 2	76.53	7.232	1400
	Test 3	73.46	6.942	1398
	Test 4	76.05	7.186	1417
	Test 5	76.47	7.226	1479
	AVG	**74.90**	**7.078**	**1404**
	STDEV	**1.843**	**0.174**	**49.49**

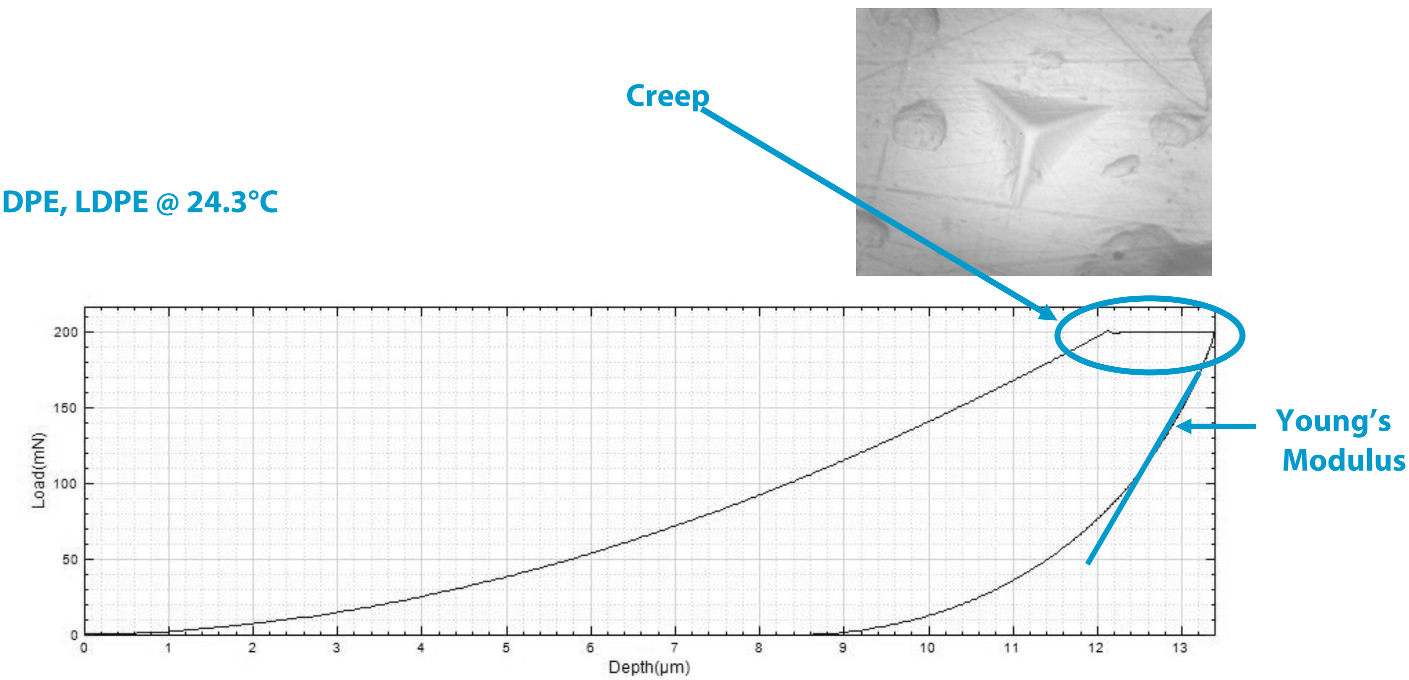
		Hardness(MPa)	Hardness(HV)	Modulus (Mpa)
LDPE	Test 1	73.18	6.916	1410
	Test 2	71.51	6.758	1340
	Test 3	71.84	6.789	1364
	Test 4	70.33	6.647	1349
	Test 5	71.45	6.752	1354
	AVG	**71.66**	**6.772**	**1363**
	STDEV	**0.914**	**0.086**	**24.56**

TESTING PERFORMED @ 45°C

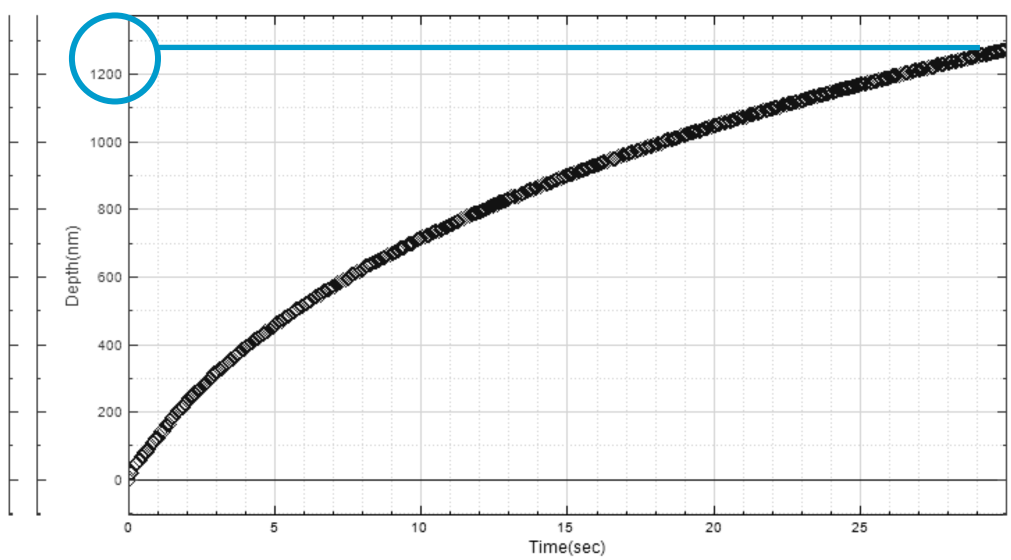
		Hardness(MPa)	Hardness(HV)	Modulus (Mpa)
HDPE	Test 1	61.09	5.772	1006
	Test 2	65.57	6.196	1127
	Test 3	62.42	5.898	1024
	Test 4	65.40	6.180	1169
	Test 5	65.68	6.206	1015
	AVG	**64.03**	**6.051**	**1068**
	STDEV	**1.908**	**0.180**	**66.74**

		Hardness(MPa)	Hardness(HV)	Modulus (Mpa)
LDPE	Test 1	53.62	5.067	844.4
	Test 2	55.77	5.270	890.1
	Test 3	58.30	5.510	872.3
	Test 4	50.68	4.789	773.7
	Test 5	52.29	4.941	817.0
	AVG	**54.13**	**5.115**	**839.5**
	STDEV	**2.669**	**0.253**	**41.22**

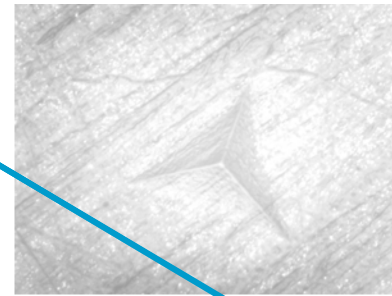
HDPE, LDPE @ 24.3°C



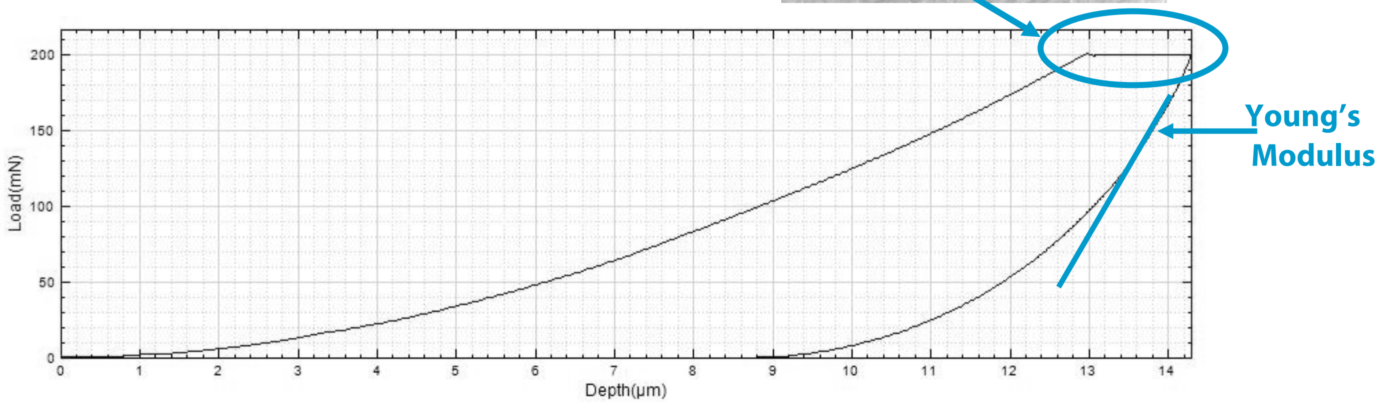
Note: Two types of polymers were tested at room temperature and in both cases the graphs behaved similar to each other.



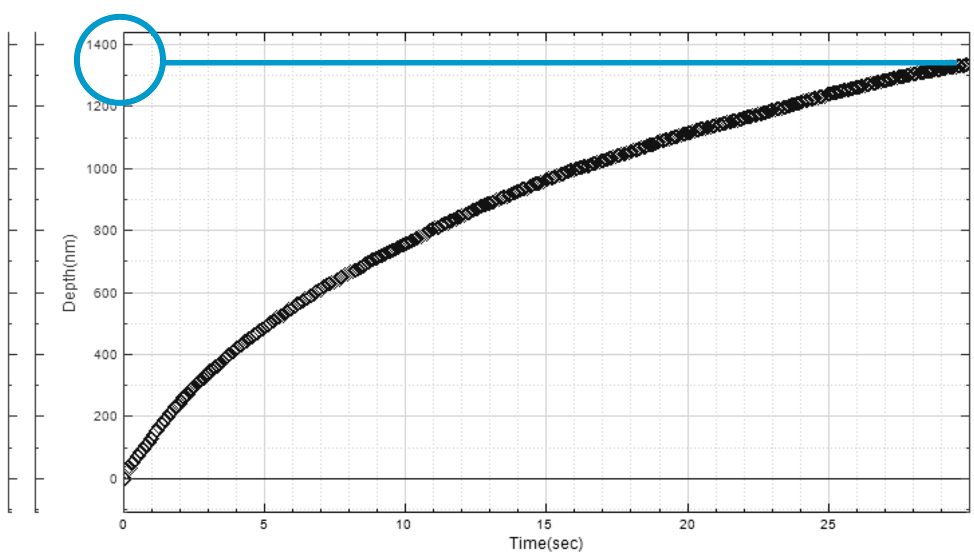
Creep is the results of material moving slowly or permanently deforming under the influences of stresses. In this case, we can determine the amount of displacement over time outputs 1.29micron over a period of 30seconds. Longer creep times would be necessary to determine when the polymer stabilizes in terms of displacement. The accuracy of this measurement using the Nanovea Mechanical Tester is excellent due to the close loop control of the load with the separate ultra sensitive load cell of the Nano Module which ensures accuracy and stability of the load control during creep time.



HDPE, LDPE @ 45°C



Here, the graphs at elevated temperature testing looked similar to that of the room temperature but with a difference in depth. Larger depths are achieved during heating of the polymer due to the softening material.



In this case, we can determine the displacement during a creep time of 30 seconds is 1.37microns. Again, because the polymer is at higher temp larger displacements are also observed during creep time.

CONCLUSION

In conclusion, we have shown that when using the Nanovea Mechanical Tester for elevated temperature applications, the system provides reproducible results with stability of measurements with the superior advantage, compared to other instruments, of measuring load directly at the same point as depth. Results at room temperature determined that the high density polyethylene is indeed harder than the low density polyethylene but not by a large degree. Results may vary depending on the types of polymers tested such as cross-linked, injection type or other. Results of the elevated temperature indentation for low density polymer indicated as we expected that it would become softer but not necessarily degrade. The high density material at elevated temperature also became softer. Both materials yielded 15-24% change in hardness after elevated temperature testing. The elastic modulus which refers to how well the material recovers under load, yielded lower at high temperatures due to flexibility of the material at said conditions.

The Nanovea Mechanical Tester equipped with the nano module has a fast piezo which provides quick movement while also using a separate ultra sensitive load cell which measures directly the load created by the movement of the piezo. To protect the load cell from the heating element, a heat sink shaft was designed to dissipated heat. 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. Nanovea Nanoindentation.