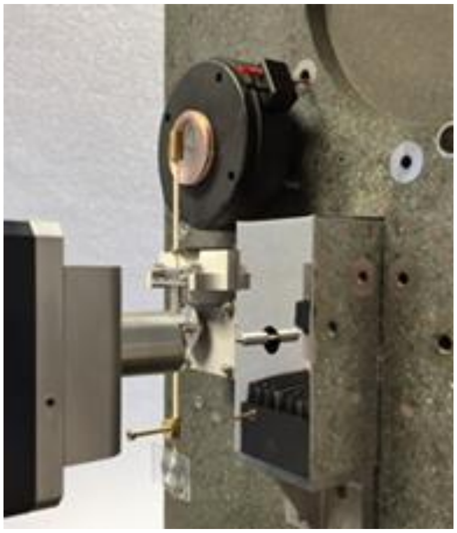
Micro Materials

Excellence in Nanomechanics

Dynamic Mechanical Compliance Testing for depth profiling and viscoelastic properties

Introduction

In conventional indentation, the load on the indenter is increased continuously to a maximum value before being reduced to produce an unloading Depth vs. Load curve. A single value of contact stiffness is derived from this curve. In DMCT, on the other hand, a sinusoidal signal is superimposed on the load ramp such that, in effect, multiple nano-unloading steps may be observed during the loading phase. The final unloading curve is not utilised. The behaviour of the oscillating indenter is described by a forced harmonic motion model that, during a calibration procedure, provides information on system damping, spring stiffness, and the mass of the loading head. These system characteristics, together with measured values of oscillation amplitude for a given oscillatory force or displacement allow contact stiffness values to be determined along the loading curve. By monitoring the phase difference between the applied oscillatory force and the resulting indenter displacement, in a similar way to normal large-scale DMA, it is also possible to measure the storage and loss moduli of polymers.



A NanoTest Vantage system showing permanently mounted standard (left) and DMCT (right) 500 mN load heads

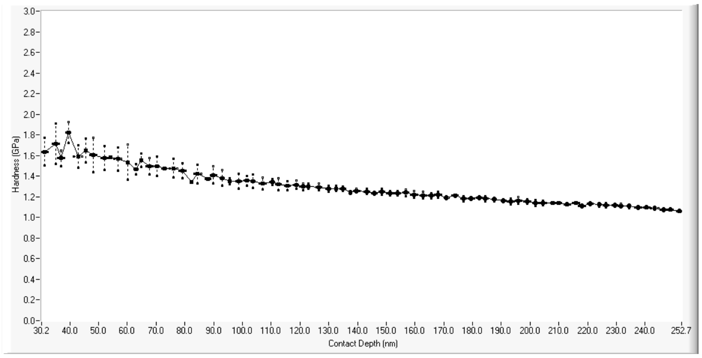
In the DMCT module Micro Materials have developed an improved approach using an additional 0-500 mN dynamic loading head with software and hardware features enabling a greater control of oscillation parameters, producing more reliable data.

The DMCT module is used for (i) depth profiling of mechanical properties (hardness, elastic modulus, *H*/*E*, contact stiffness) using the continuous stiffness approach, and (ii) viscoelastic property measurements (storage modulus, loss modulus, tan delta) at chosen frequencies and test temperatures.

The new developments include (i) a novel procedure (patent pending) for optimising indenter oscillation control at low loads, (ii) an option for non-constant oscillation amplitude, where the oscillation force varies with load to achieve a fixed oscillation depth and therefore elastic modulus measurements on metallic materials that are constant vs. depth, and (iii) a new loading head design with the option of variable damping for optimised polymer analysis. The new loading head is again horizontal, thus maintaining a significant advantage for high temperature testing. The capabilities of the DMCT module are illustrated by Case Studies on (i) metallic materials, (ii) thin films, and (iii) viscoelastic nanocomposites as described below.

Case studies

Single crystal copper

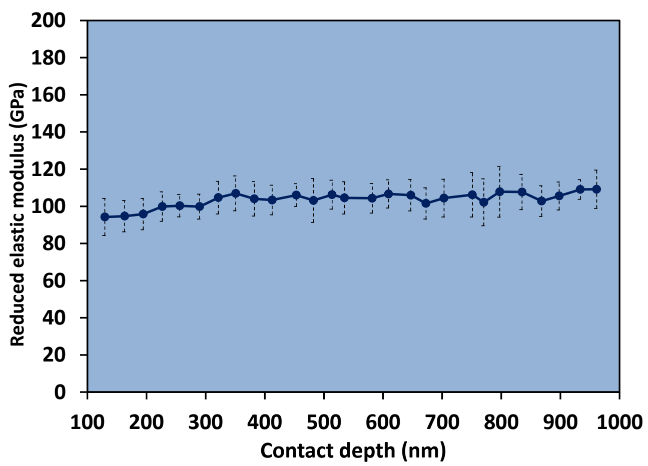


Depth dependence of hardness for Cu(100) single crystal from DMCT – note the absence of any anomalous results or data variability at low depths. The data show mean values from 3 repeat tests.

Literature reports have highlighted difficulties in using the conventional continuous stiffness technique to make meaningful measurements at low depths, especially on soft metals with high *E*/*H* ratios such as copper or aluminium which are subject to probe bouncing and plasticity errors (e.g. see [1-3]). Copper is a challenging material with the literature reports (e.g. [2]) showing anomalous results, especially for low depths and higher oscillation amplitudes.

In comparison, the new approach taken in the NanoTest DMCT module has produced significantly improved results, with the problem of the probe bouncing on the surface at low depth effectively suppressed thus avoiding the anomalous low-depth data. As an example, a NanoTest DMCT result for a copper single crystal is shown on p1. This sample was chosen to provide a direct comparison to the data reported by Pharr et al [2].

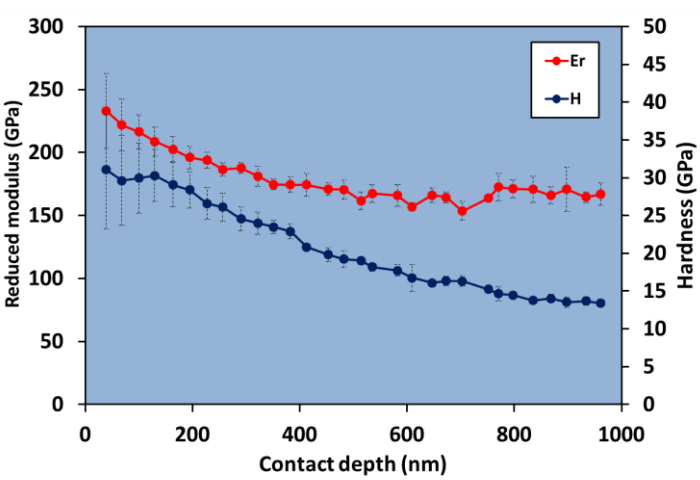
With this improved low depth performance and the absence of anomalous near-surface data even on soft samples it is now possible to more reliably study indentation size effects on soft metals as well as their strain rate sensitivity.



Depth dependence of elastic modulus for a copper sample. The mean values from 10 measurements are shown.

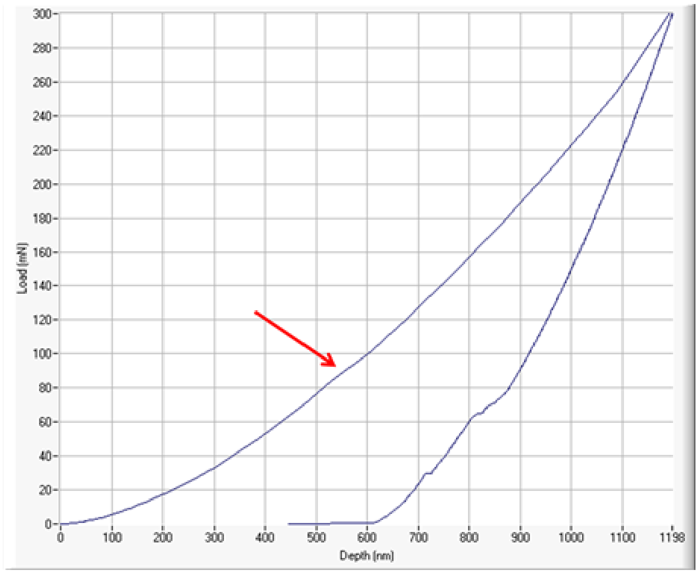
Thin films

Using continuous stiffness measurements, the DMCT module enables faster mechanical property depth profiling. A typical example for a hard coating on a softer silicon substrate is shown in the figure below. Variations in hardness and elastic modulus have been clearly revealed by means of a relatively fast continuous stiffness test.



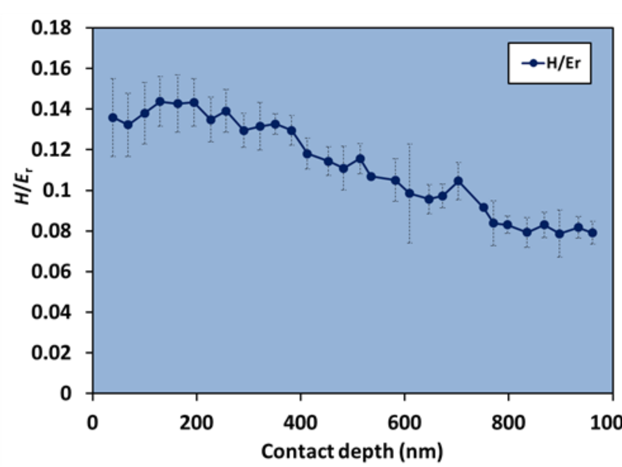
Variation in hardness and reduced modulus with contact depth from continuous stiffness measurements to 300 mN on a 750 nm thick DLC coating on a silicon wafer. The mean values were from 10 experiments.

The DLC coating has 30 GPa hardness and Elastic modulus of 285 GPa (ISO14577 extrapolation method). As the load increases the mechanical response is progressively influenced by the underlying softer and more compliant silicon substrate. There is an inflexion in the hardness when the contact depth reaches about 1/2 of the film thickness suggestive of reduced load support due to cracking. A typical indentation curve is shown below, with an inflexion at an indentation depth corresponding to the same contact depth, and a clear pop-out event in the final unloading due to phase transformation in the silicon substrate.



A typical indentation curve showing inflexion during loading (marked with red arrow) and phase transformation during unloading.

The ratio between the coating hardness and its elastic modulus (H/E) can be a useful index for predicting wear resistance [4-6] For coating design it can be useful to understand how this parameter changes with increasing depth, as shown below.



Variation in (hardness/reduced modulus) with increasing contact depth from continuous stiffness measurement.

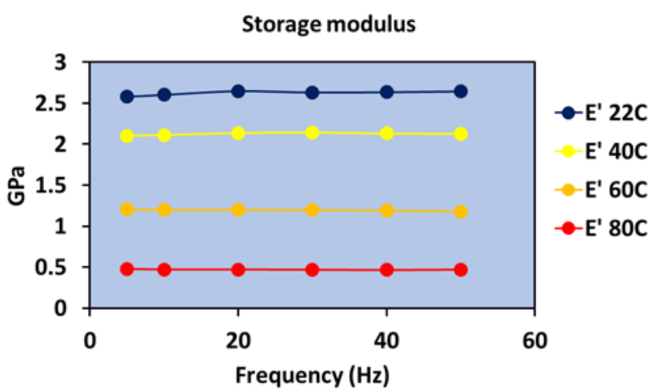
Viscoelastic materials

The DMCT module allows measurements of the viscoelastic properties (loss and storage moduli, tan delta) of viscoelastic materials and their dependence on test temperature.

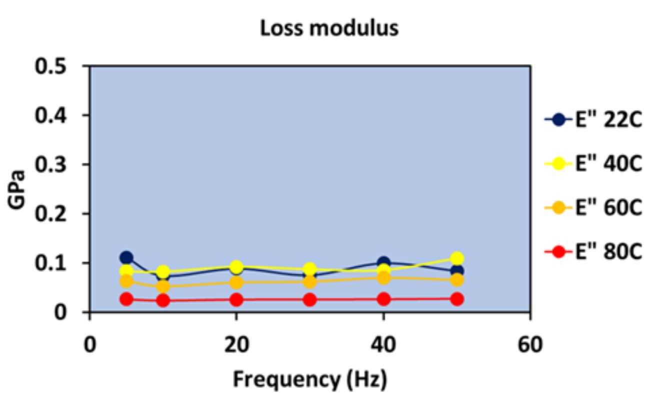
The practical test frequency has been extended to over 300 Hz and the experiments can be run as frequency sweeps at each temperature.

When developing new materials it can be necessary to test at small scale and bulk measurements may be impracticable due to the small volumes of developed material and/or small sized components. Typical examples of frequency and temperature dependent viscoelastic properties of nanocomposite materials are shown below.

Viscoelastic fluoropolymer nanocomposite material with 33% loading of thermochromic particles in a poly(vinylidene-fluoride-trifluoroethylene) matrix

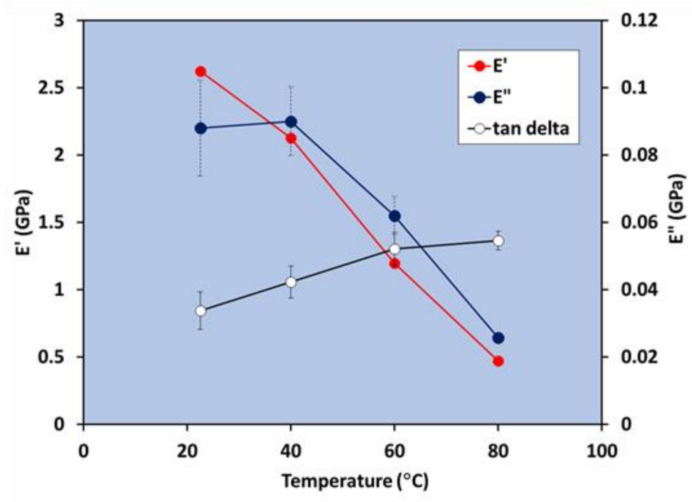


Temperature dependence of storage modulus



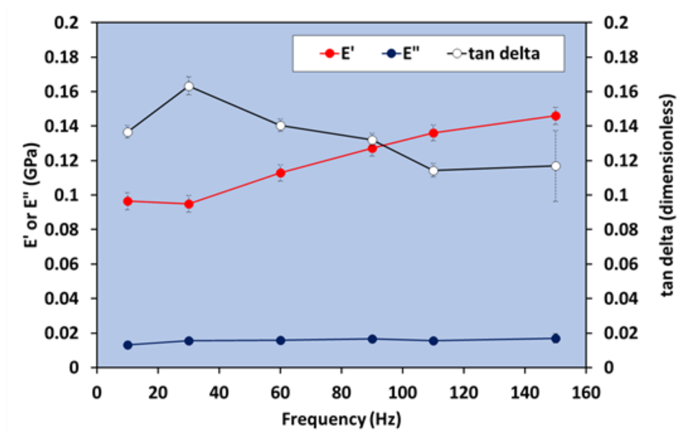
Temperature dependence of loss modulus

The graphs above show that for this system there was relatively little variation in properties with frequency. The graph shown in the next column shows results averaged over all frequencies vs. temperature.



Variation in loss modulus, storage modulus and tan delta with temperature over 22-80 ℃

Composite coating system of heterogeneously dispersed vertically aligned stiff nano-wires in a compliant elastomer (PDMS) matrix on ITO



Variation in viscoelastic properties over 10-150 Hz.

In this example the multi-frequency measurements revealed a general trend to increasing storage modulus at higher frequencies and a marked peak in tan delta at 30 Hz.

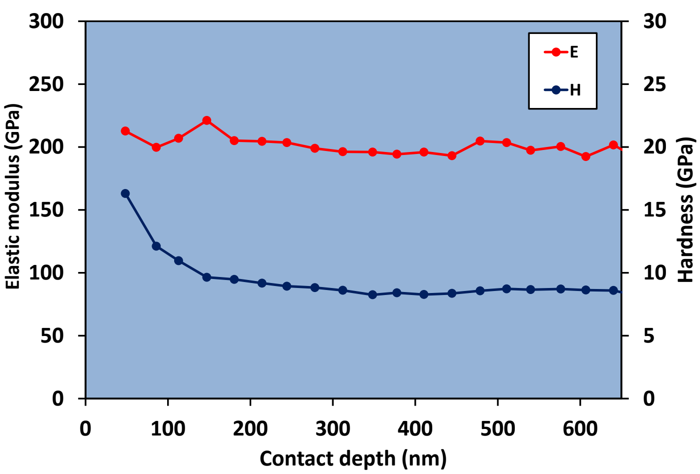
Specifications of the Dynamic Mechanical Compliance Testing (DMCT) module

- Additional 0-500 mN loading head for enhanced dynamic performance - permanently mounted alongside the other NanoTest loading heads
- Faster mechanical property depth profiling using continuous stiffness measurements
- Variable oscillation load amplitude with fixed depth option
- Excellent low depth performance – no anomalous near-surface data even on soft samples
- Compatible with hot stage for high temperature measurements
- Variable damping option for optimised measurements on viscoelastic materials
- Temperature and frequency (0.1-300 Hz) dependence of viscoelastic properties (E', E", tan delta)
- Strain rate jump tests
- Patent pending

High temperature depth profiling

The DMCT module can be used at elevated temperature to study the influence of temperature on mechanical properties of coated surfaces.

It can also be used to study the temperature-dependence of indentation size effects in metallic materials. An example is shown below.



Hardness and elastic modulus vs. depth at 200 °C in a high carbon martensitic steel from a DMCT experiment to 100 mN with a cBN Berkovich indenter

At 200 °C this sample still shows a size effect in hardness but not in elastic modulus which remains constant throughout the depth range.

References

[1] M. Cordill et al, The nano-jackhammer effect in probing near-surface properties, Int. J. Plasticity 25 (2009) 2045.
[2] G.M. Pharr et al, Critical issues in making small-depth mechanical property measurements by nanoindentation with continuous stiffness measurement, J. Mater. Res. 24 (2009) 652.
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[4] A. Leyland and A. Matthews, On the significance of the H/E ratio in wear control: a nanocomposite coating approach to optimised tribological behaviour, Wear 246 (2000) 1-11.
[5] A. Leyland and A. Matthews, Design criteria for wear-resistant nanostructured glassy-metal coatings, Surf. Coat. Technol. 177-178 (2004) 317-324.
[6] B.D. Beake, The influence of the H/E ratio on wear resistance of coating systems – insights from small-scale testing, Surf. Coat. Technol. (2022) in press.

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