Polymeric

MICRO MATERIALS

MEASURING NANOTECHNOLOGY

The NANOTEST™

Bringing nanomechanical measurements into the real world

NANOMECHANICAL TESTING OF POLYMERIC MATERIALS

The NanoTest advantage for polymer testing

- Highest resolution measurements
- Flexibility of design and thermal stability
- Minimal thermal drift even at elevated temperatures
- Ultra-high strain rate tests
- Tests in fluid environment

NANOMECHANICAL TESTING OF POLYMERIC MATERIALS

NANOTEST CAPABILITY

- **Viscoelastic properties**
- **Nanotribology**
- **Elevated temperature nanoindentation**
- **Testing in fluid environment**
- **Ultra-high strain rate testing**
- **Ultra-low load tests**
- **Nano-scale fatigue testing**

INTRODUCTION

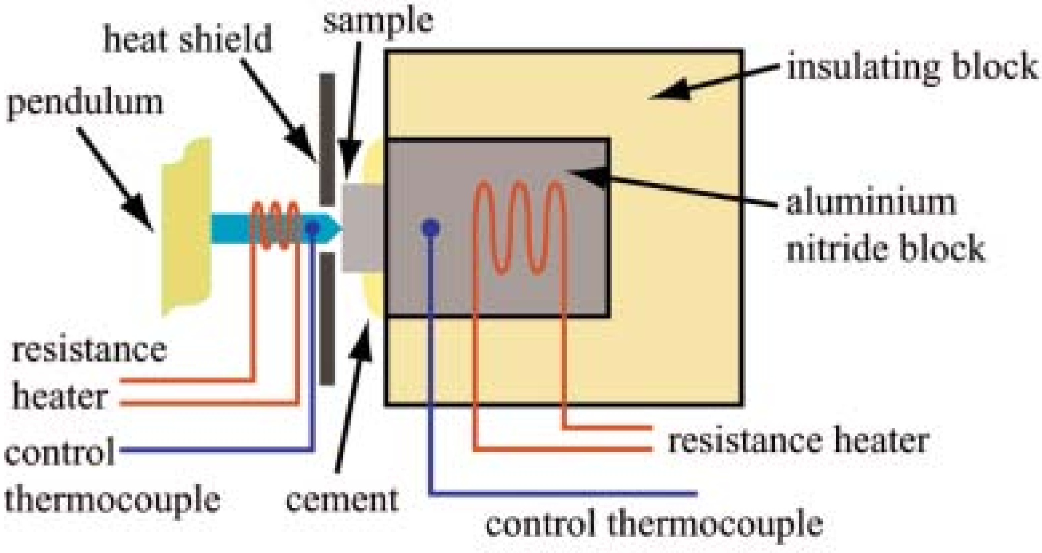
Thermal stability of the testing instrument is key to meaningful measurements of the viscoelastic properties of time-dependent materials. At room temperature the thermal drift of the NanoTest is very low, typically an order of magnitude less than some other commercial systems.

STABILITY AT HIGH TEMPERATURE:

ELEVATED TEMPERATURE NANOINDENTATION TESTING

The NanoTest advantage becomes more pronounced when testing at elevated temperatures. This is due to the unique design for elevated temperature testing that relies on separate heating (and active temperature control) of both probe and sample ensuring no heat flow occurs during the indentation process.

Figure 1

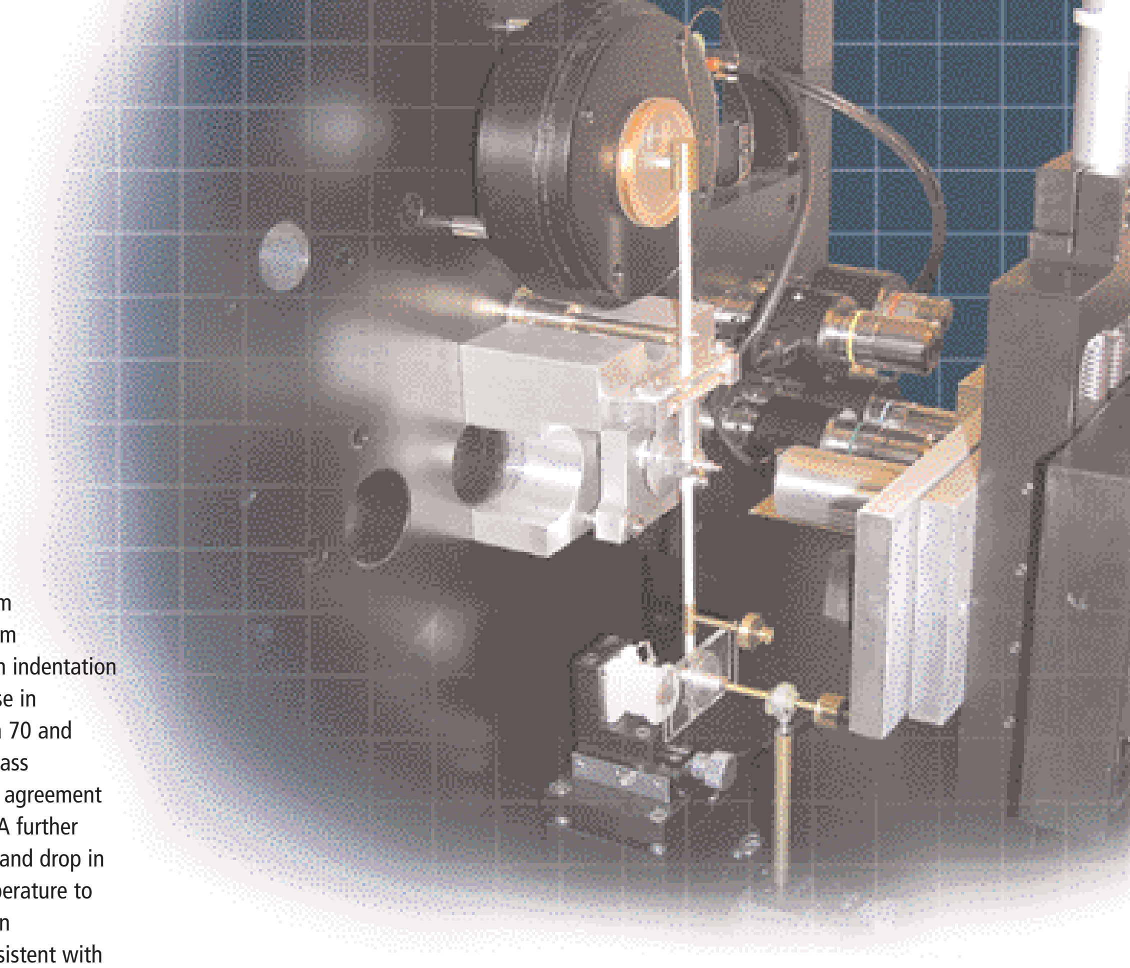


Schematic of NanoTest hot stage showing separate tip and sample heaters, figure courtesy of AJ Muir Wood, University of Cambridge

The NanoTest is unique in this isothermal contact. As no significant thermal drift occurs during elevated temperature measurements it becomes possible to perform long-duration tests – such as indentation creep tests – at elevated temperatures and observe how the properties of polymeric materials change as they go through the glass transition temperature. This can be done in a fully automated procedure at a more local scale and on thinner films than by other methods such as DMA.

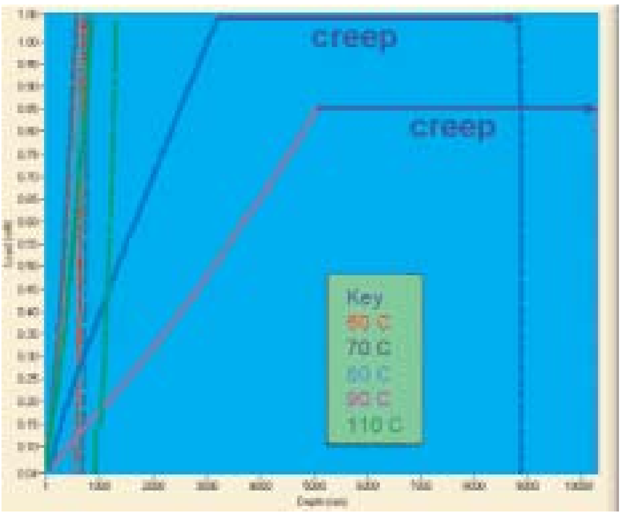
The localised approach enables more rapid heating/cooling than by heating the entire sample chamber, and so thermal history/recrystallisation processes can now be studied in detail at the nanoscale.

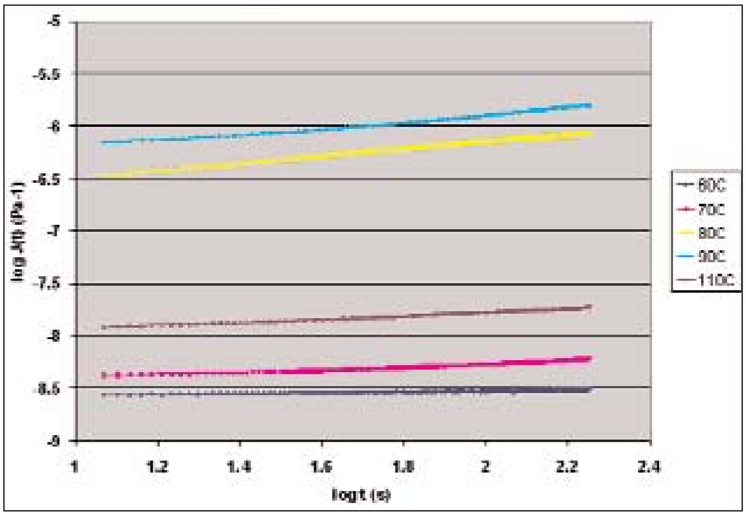
As an example, the NanoTest elevated temperature testing capability has been used to determine the variation in mechanical properties with temperature of a range of PET films with different processing history and crystallinity [1]. Figure 2 shows the behaviour of an amorphous (non-heat set) sample.



The nanomechanical properties of the film at 60˚C were virtually the same as at room temperature. Above 60˚C clear changes in indentation response were observed. A sharp decrease in mechanical properties was seen between 70 and 80˚C consistent with the presence of a glass transition over this temperature range in agreement with literature values for bulk materials. A further increase in time-dependent deformation and drop in stiffness occurred on increasing the temperature to 90˚C. At 110˚C a dramatic improvement in mechanical properties was observed consistent with cold recrystallization.

Figure 2





The variation in nanoindentation behaviour (left) and (above) creep compliance with test temperature over the range 60-110°C for an amorphous PET thin film

HIGH SPEED, HIGH ACCURACY

Combinatorial testing is fast becoming a popular new route towards producing new materials with interesting and unexpected properties. Rather than trying to engineer perfect materials, in a combinatorial approach, many hundreds or more are made at small scale.

Scientists at MIT have used the NanoTest to test the properties of polymeric materials where each material had a different combination of 2 different monomers[2-3]. Within 24 hours of automated testing (in a single continuous run) they had data on every polymer in a 576-element array and could map the effects of the % of each monomer on the properties of the material. This automated analysis of a large library of acrylate-based materials demonstrated a range of mechanical properties affected by composition in unexpected ways.

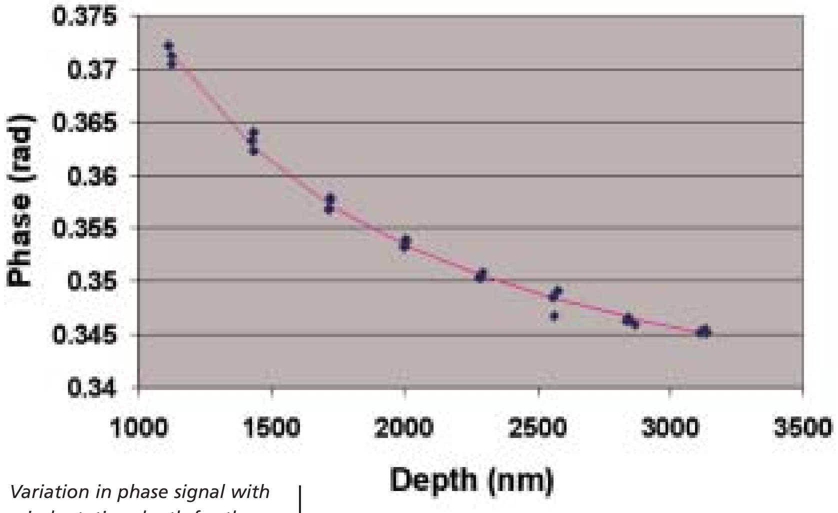
The authors noted that the absence of piezocrystal actuation in the load frame actuation (present in some other nanoindentation systems) resulted in the highly stable frame compliance and load/displacement signals necessary.

NANOMECHANICAL TESTING OF POLYMERIC MATERIALS

DYNAMIC MECHANICAL COMPLIANCE TESTING

The NanoTest dynamic compliance testing module includes a lock-in amplifier and sample oscillation system to vibrate a sample and allow the compliance to be measured on a continuous basis. It can be thought as a nanoscale analogue of dynamic mechanical analysis (DMA) [4]. After collecting the raw phase angle data with spherical or pyramidal indenters, it is analysed with a 4-element linear viscoelastic model to determine loss and storage modulus, indentation complex modulus and tan delta which are indicative of energy damping in the surface/near surface of the material. The example below shows an excellent fit of the model to experimental data on an epoxy sample. A value for tan delta of 0.017 was determined in good agreement with bulk DMA values.

Figure 3



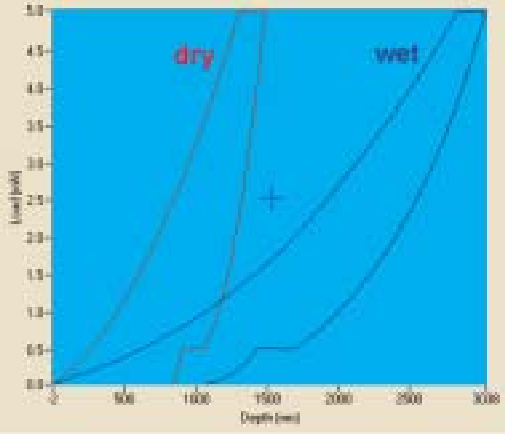
Variation in phase signal with indentation depth for three repeat tests on an epoxy sample. The reproducibility of the data and its fit to the 4-element linear viscoelastic model used in the analysis is good and produces a value of tan delta of 0.017.

FLUID CELL

The mechanical properties of biological and polymeric samples often vary considerably when in a fluid environment compared to the usual dry testing conditions. If we wish to understand their properties and behaviour in fluid media it is therefore highly desirable to test under these conditions rather than to attempt to infer from measurements on dry (or 50% relative humidity) samples. To meet this need, the testing capability of the NanoTest has been extended by the development of a fluid cell allowing nanoindentation, nano-scratch and nanowear testing of samples fully immersed in fluids.

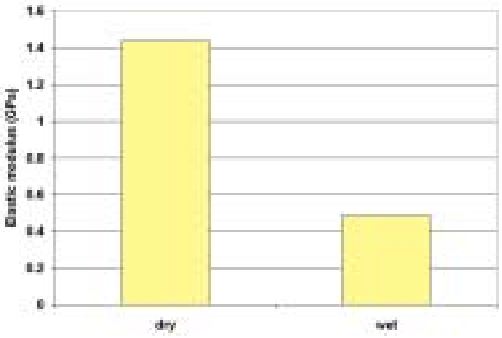
For example, nylon (PA6) can swell by 7-9% at saturation. The NanoTest fluid cell has been used to investigate how its nanomechanical properties (primarily elastic modulus and creep compliance) are affected by the test medium. Typical indentation curves for a low molecular weight PA6 sample are shown for dry (~50% relative humidity) and after immersion in deionised water for several hours are shown in figure 4. There is a decrease in elastic modulus of about 67% after 24 hours immersion (figure 5) [5].

Figure 4

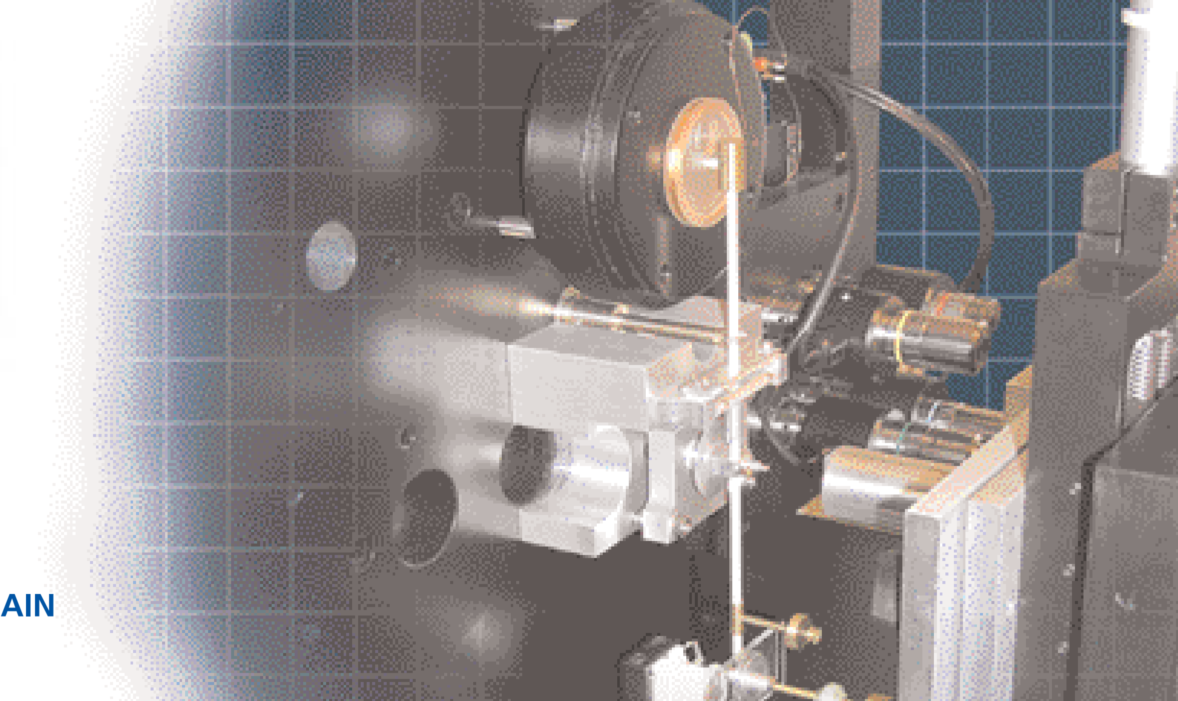


Typical nanoindentation curves dry and wet for low MW PA6 using a Berkovich indenter loading at 0.2 mN/s to a peak load of 5 mN. Holding periods at peak load and 90% unloading allow investigation of viscoelastic response.

Figure 5



Effect of test environment on elastic modulus of PA6 after >24 hr immersion



TESTING AT HIGH STRAIN RATE

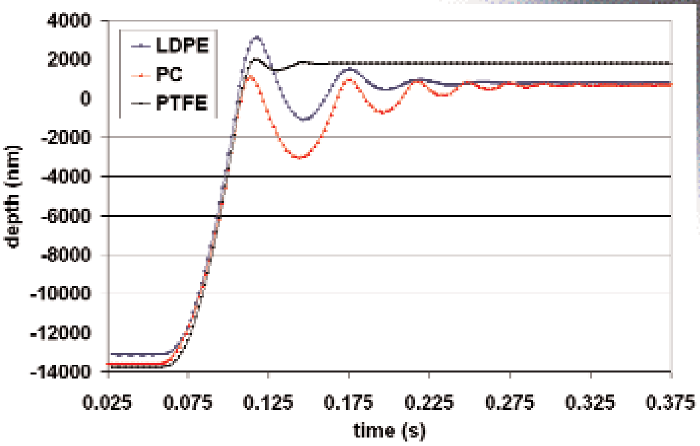


Figure 6

The damping ability of the PTFE material is shown by the lack of recoil (energy absorption).

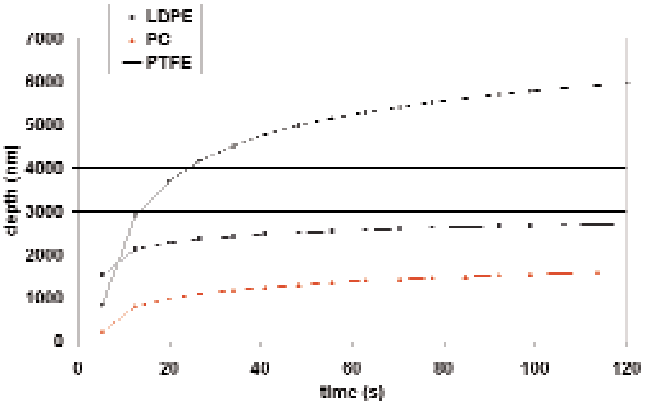
Materials show differences in mechanical behaviour at high and low strain rates[6]. The NanoTest is unique amongst indentation systems in having the (patent protected) ability to produce ultra-fast, high strain rate indentations and can be used to study material behaviour at strain rates far in excess of those on any other instrument.

This is possible due to the pendulum geometry that enables the probe to be accelerated to produce high-energy impacts in a fraction of a second. With the aid of a fast DAQ system (up to 500000 Hz possible) all the probe displacement-time data is captured and can be analysed to produce dynamic hardness and viscoelastic property information. Dynamic hardness is defined (after Tabor) as energy per unit volume and has units of pressure just as conventional hardness.

As an example the high-strain indentation behaviour of commercial low-density polyethylene [LDPE], polycarbonate [PC] and polytetrafluoroethylene [PTFE] polymers is shown in the figure above. The probe (a diamond indenter in this case) bounces on the surface of all three polymers before the energy is dissipated but there are clear differences in how this occurs. PC shows essentially elastic behaviour, LDPE shows rubber-like behaviour and PTFE damps out the impact energy very effectively.

In addition to single impacts the nano-impact module can be used to investigate differences in fatigue due to repetitive impact [7]. Differences in impact behaviour have been correlated to differences in ductility on nanocomposites. In the example below (figure 7) there are clear differences in deformation due to the repetitive impacting, with PTFE in particular showing dramatic continuing deformation.

Figure 7



Deformation due to multiple impact on PTFE, LDPE and PC at 0.14 Hz, applied load 2 mN accelerated from 14 µm in 40 ms, with 3 µm impact probe.

NANOMECHANICAL TESTING OF POLYMERIC MATERIALS

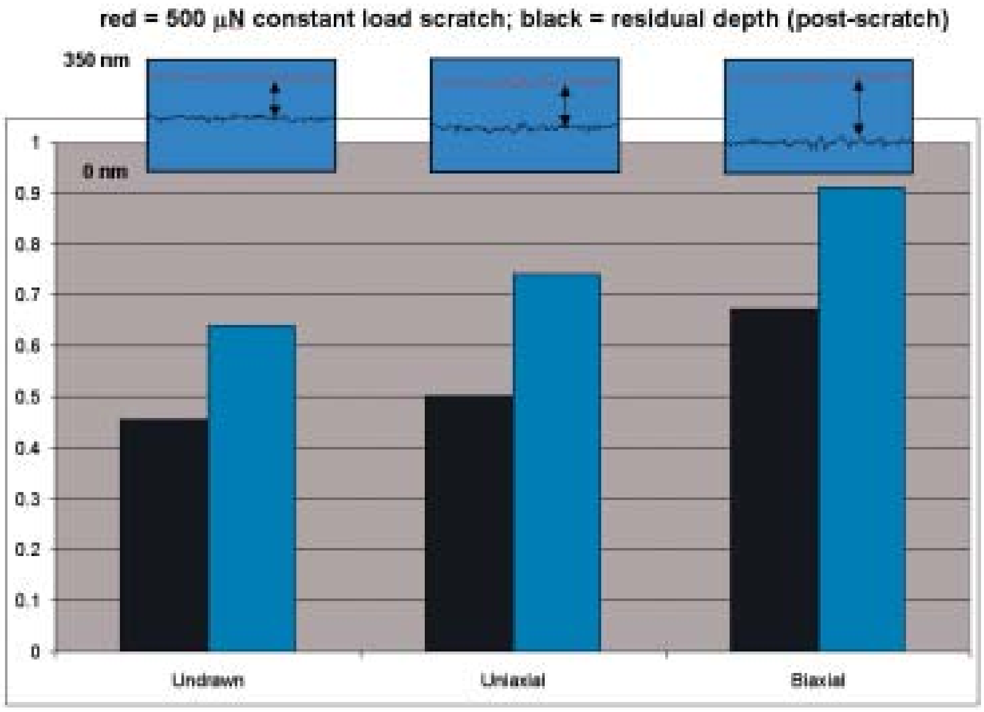
NANO-SCRATCH AND NANOWEAR TESTING

Nanotribological testing of polymeric materials is performed using the nano-scratch and nanowear module of the NanoTest system. In addition to measuring the critical load to failure of polymer coatings the technique has found application in fundamental studies of scratch resistance at small scale.

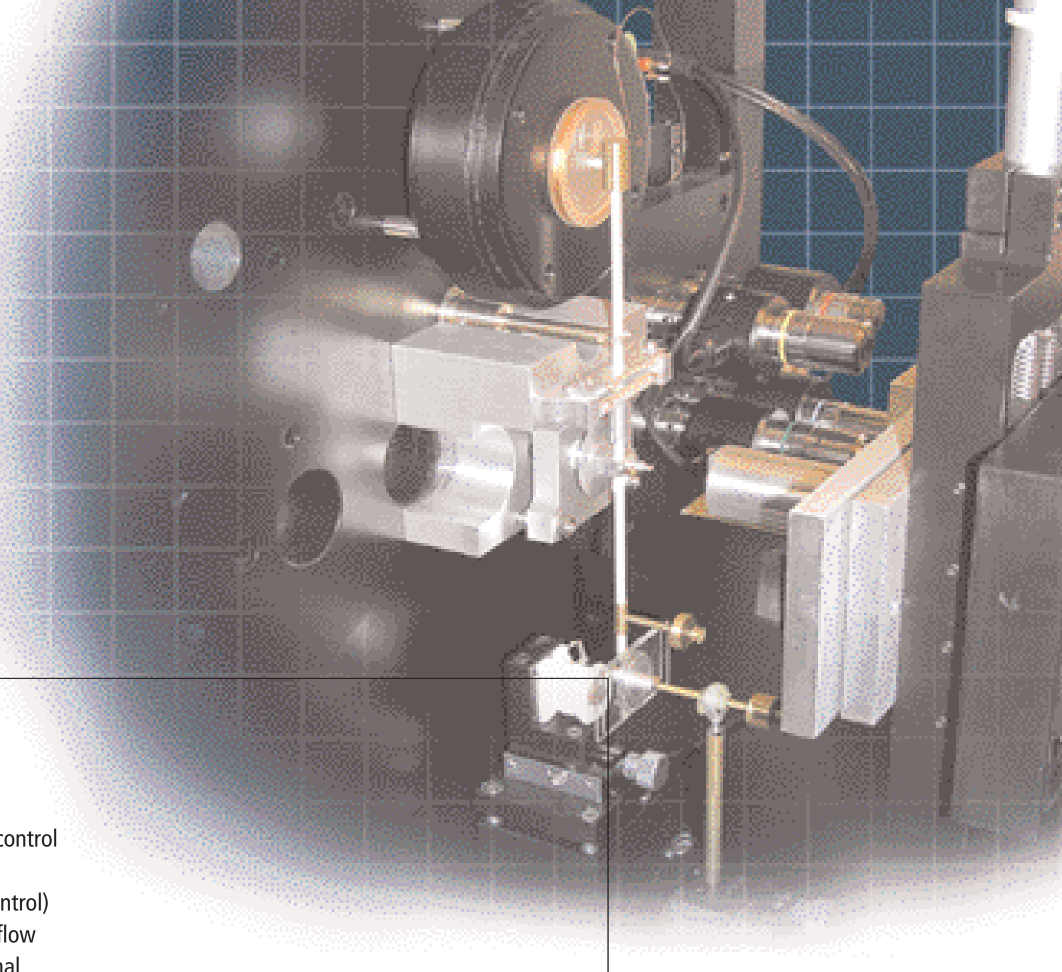
It has been found that the scratch resistance is a strong function of processing history [8]. As an example, Figure 8 shows typical scratch and post-scratch traces on three different heat set PET thin films. These were 1) undrawn (0% crystallinity), 2) uniaxially drawn (33 % crystallinity) and 3) biaxially drawn (50% crystallinity). The draw process induces crystallinity and orientational changes which alter the mechanical properties.

Ultra-low load (20μN) nanoindentation was used to determine the mechanical properties of the films. As figure 8 shows there is a 1:1 correspondance between the H/E ratio and the degree of recovery during scratching. The on-load scratch depths are rather similar but the recovery ratio differs dramatically with crystallinity in the thin films.

Figure 8



Correlation between the variation in elastic recovery during scratching (dark blue) and the polymer's H/E ratio (light blue = 10 x H/Er). The insets show typical scratch and post-scratch traces for 500 μN scratch load with a 3 μm diamond indenter at 1 μm/s.



SPECIFICATIONS

HIGH TEMPERATURE TESTING

The hot stage, heated indenter and thermal control system operates to 500˚C (option to 750˚C). Separate heating (and active temperature control) of both probe and sample ensuring no heat flow occurs during the indentation process. Minimal instrumental thermal drift at elevated temperatures allows indentation creep tests at elevated temperatures and determination of properties through the glass transition temperature.

DYNAMIC COMPLIANCE TESTING MODULE

For the investigation of storage and loss moduli, and tan delta.
Oscillation frequency range 0.1Hz to 250Hz (larger ranges optional).
Frequency sweep capability.
Amplitude of oscillation typically sub-nm to 50 nm (larger ranges optional).
Optimised computer control of the lock in amplifier for setting the gain, time constant, frequency and amplitude.

FLUID CELL

The fluid cell package includes an indenter adapter, liquid cell software and the liquid cell itself.
In comparison to other methods (such as DMA) it enables more highly localised measurements of mechanical properties and testing of thinner and more heterogeneous samples.
Flow cell option required for controlled fluid exchange during experiments.

HIGH STRAIN RATE: NANO-IMPACT TESTING

The nano-impact module includes two distinct impact testing modes as standard.

Sample oscillation mode:
Piezoelectric oscillation system, signal generator, amplifier and software for control and data analysis allowing both impact and contact fatigue tests to be performed depending on the magnitude of the static load. Frequency range 1-500 Hz.

Pendulum impulse impact mode:
Pendulum impulse using an A/C solenoid to produce very high strain rate indentations (nano-impacts). Single and repetitive impacts. Dynamic hardness is determined from analysis of single impacts and fatigue behaviour from multiple impacts.

NANO-SCRATCH/NANOWEAR TESTING

For progressive load scratches, 3-pass multi-pass (where second scan is ramp) and longer multi-pass friction and wear tests.
Wide range of robust friction probes with different force constant available.
Choice of spheroconical diamond scratch probes with end radii 0.7-200 μm. Easy and quick probe exchange (~ 1 min) – fully modular with nanoindentation and nano-impact modules. No recalibration necessary on switching between nanoindentation and nanoscratch modules.
Robust - no danger of damage to loading head springs during scratching.

NANOMECHANICAL TESTING OF POLYMERIC MATERIALS

ACKNOWLEDGEMENTS

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REFERENCES

1. *Elevated temperature nanoindentation testing as a tool for investigating viscoelastic behaviour of thin poly(ethylene terephthalate) films,* BD Beake and A Gray, submitted.
2. *Combinatorial Material Mechanics: High throughput polymer synthesis and nanomechanical screening* CA Tweedie, DG Anderson, R Langer and KJ Van Vliet, Adv. Mater. 17 (2005) 2599.
3. *A combinatorial library of photocrosslinkable and degradable materials* DG Anderson, CA Tweedie, N Hossain, SM Navarro, DM Brey, KJ Van Vliet, R Langer and JA Burdick, Adv. Mater. DOI 10.1002/adma.200600529.
4. *Displacement modulation based dynamic nanoindentation for viscoelastic material characterisation* SP Singh, RP Singh and JF Smith, Mat Res Soc Symp Proc 841 (2005) R4.6
5. *The influence of fluid environment on the nanoindentation creep behaviour of nylon 6,* BD Beake, G Bell and D Bielinski, in preparation.
6. *Nanomechanical quantification of polymer energy absorption* CA Tweedie, JF Smith and KJ Van Vliet, Mat Res Soc Symp Proc 841 (2005) R5.6
7. *Nanoscale repetitive impact testing of polymer films* BD Beake, SR Goodes, JF Smith and F Gao, J Mater Res 19 (2004) 237.
8. *Nanoindentation and nanoscratch testing of oriented poly(ethylene terephthalate) films* BD Beake and GJ Leggett, Polymer 43 (2002) 319.
9. *Modelling indentation creep of polymers: a phenomenological approach* BD Beake, J Phys D: Appl Phys 39 (2006) 4478-4485.

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