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Interlaboratory Comparison of Reduced Modulus Measurement of Polymers at the Nanoscale Using an AFM or a Nanoindenter

- Protocol For Analysis

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National Measurement System

Interlaboratory Comparison of Reduced Modulus Measurement of Polymers at the Nanoscale Using an AFM or a Nanoindenter - Protocol For Analysis

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ABSTRACT

This report describes the protocol for analysis for an interlaboratory comparison of reduced modulus measurement of polymers at the nanoscale using an AFM or a Nanoindenter. Five samples are provided for this study, along with this protocol, which contains simple instructions for the analysis.

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Approved on behalf of the Managing Director, NPL
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1 OBJECTIVES

The measurand in this study is the reduced modulus in the surface or near surface region of each of a total of 5 samples in order to (i) to evaluate the current comparability of reduced modulus measurement at the nanoscale, (ii) to evaluate the repeatability of reduced modulus measurements.

2 TIME TABLE

You should complete the analysis for this work by 31 August 2006. If you cannot do so and need extra time please inform charles.clifford@npl.co.uk.

3 THIS PACKAGE

This package, unless you have otherwise specified, contains this protocol and a set of 5 Fluoroware containers, each containing one sample. Inspect the packaging to check if it has been opened by customs and if the integrity of the samples has been compromised. Please notify us that everything is received in order.

☐ I have emailed NPL that all is OK with the samples on / / 2006

4 THE MATERIAL

The materials for analysis in the standard set comprise one piece of each of low-density polyethylene (LDPE), polypropylene (PP), polymethylpentene (PMP) polycarbonate (PC), polystyrene (PS). The 5 pieces of material are each supplied **face down** in separate containers to maintain their identity and integrity.

Your sample codes are given in the covering letter in a completed table of the form:

Serial Numbers of Your Samples

Polymer				
LDPE (0.2 GPa)	**PP (1.4 GPa)**	**PMP (1.7 GPa)**	**PC (2.5 GPa)**	**PS (3.3 GPa)**

Also included in the table are nominal values of the reduced modulus of each sample taken from the literature and given as a guide in case you need to pre-select instrumental options or parameters. Each sample, unless you have otherwise specified, is approximately 1 cm^2 in area. All measurements should take place on the smoother or shinier side of the samples.

Do not unpack these samples until you are nearly ready to analyse them. Before doing so, read the rest of this protocol so that you are clear about the next steps.

5 SAMPLE HANDLING

The following comments should prove helpful in handling samples.

If you intend to analyse the samples one by one by mounting them on the same sample holder, it is good practice to keep the samples in their containers and remove them only when you are ready to mount them. If you mount them together on one sample holder, ensure that their identities are maintained.

Inspect the samples for any scratches, blemishes or marks on the shinier surface. There may be some scratches on some of the samples. Choose as featureless an area as possible for the analysis. Note the condition of the surface.

You may have appropriate sample handling procedures as routine in your laboratory. Keep to those procedures but ensure that they are always superior to the minimum level given below.

You may need to handle the samples using uncoated clean stainless steel tweezers. If so, grip the sample at the edge only, in a region that will not be analysed. Avoid breathing or speaking over the samples. Use polythene gloves, or gloves of a higher quality, to avoid contaminating the tweezers or your cleaning equipment with finger grease. Do not use moulded gloves, for example vinyl, which may be covered with highly contaminating release agents.

6 PRACTICAL ISSUES IN MEASURING THE REDUCED MODULUS

If necessary, remove any dust or particulate matter on the surface [use, for instance, pure dry inert gases such as Argon or nitrogen to remove any particles. Do not use gas from pressurised cans that include a propellant or from compressed air lines that may contain oil vapour, do not use a method likely to contaminate the sample]. Do not use any other cleaning method as this may affect the results.

Ensure that any necessary instrument calibrations are up to date. For AFM this may include

z piezoelectric scanner calibration, tip shape, spring constant [1] and laser sensitivity. For nanoindenters this may include tip shape, force and displacement. For issues relating to calibration, please use the methods that you normally employ. If in doubt, some methods are given in reference [2-6].

To mount the samples, in order of preference the following methods are recommended: 1) use of a vacuum stage or a very secure mechanical holder, 2) epoxy glue (e.g. araldite), 3) cyanoacrylate glue (superglue). Sticky tape should be avoided if at all possible. Please note the holding mechanism in your report.

Conduct your analyses of the 5 samples. Seven measurements are required at two indentation depths for each sample and for two instrumental conditions, as described in the following sections.

Try to ensure that your analyses are in the central regions of the samples in a featureless area of the sample. Do not acquire data within 1 mm of the sample edge. Note the order of analysis of the samples. Record all of the instrumental parameters used. Record the temperature and humidity of the laboratory at the time of the experiment and whether this was similar or noticeably different to the temperature and humidity in the 2 days leading up to the experiment.

For the analysis, do 2 experiments under the following conditions

i) FIXED CONDITIONS FOR ALL 5 SAMPLES

Allow the instrument to warm up for at least one hour. For AFM do this with the laser aligned on the cantilever. Please choose a suitable tip shape and radius to use. For AFM, a stiff cantilever is required, some of the samples may be too stiff for indentation with lower spring constants and larger radius tips.

Undertake any necessary calibrations, e.g tip shape, laser sensitivity, etc.

For each sample, land on the sample with the lowest set-force needed to keep the tip in contact. Choose an area with minimal surface features. Undertake the indentation experiments with:

1) A constant load and unload rate with no hold time, so that the total load/unload cycle lasts 20 seconds (0.05 Hz).

2) Conduct measurements at two indentation depths of nominally 50 and 150 nm with 7 indents at each depth.

3) Keep the indents well spaced from each other. A pattern you may choose, depending on the radius of your tip is to: land at (0,0), and indent at the following positions in micrometres from the landing point, for the first indentation depth: (0, 4), (4, 4), (4, 0), (4, -4), (0, -4), (-4,-4), (-4, 0), and for the second indentation depth: (-4, 4), (-4, 8), (0, 8), (4, 8), (8, 8), (8, 4), (8, 0). If you wish to conduct more analyses continue with (8,-4), (8,-8), etc as shown in figure 1.

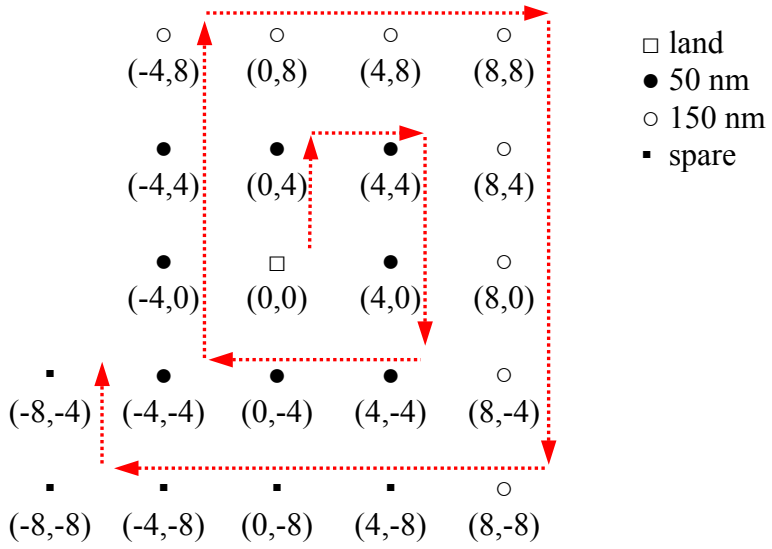

Figure 1. Possible arrangement of indents for each sample

4) When all the polymers have been analysed undertake and/or repeat any calibrations. You may also find it useful to check some calibrations throughout the experiment.

You may measure machine compliance and the drift rate, however, unless they are significant please ignore them when analysing the data.

ii) NORMAL USER CONDITIONS FOR ALL 5 SAMPLES

The conditions in the above section i) are not necessarily the best. They are, however, the conditions that everyone should be able to use.

In this second section, therefore, repeat the above sequence of measurements for the 14 measurements on each of the five samples and use the conditions that you think would give the best results, i.e the conditions you would normally use to analyse these types of materials. For instance, you may wish to use a hold time of 10 seconds before unloading.

When all analyses are complete, return the samples to their containers. Please retain the samples in case we find any anomalies in your data.

7 REPORTING AND CALCULATING THE RESULTS

Calculate, using a suitable method, and report the reduced modulus of each measurement and also the average reduced modulus for each set of 7 indents at one depth on each sample for each method. Also, supply Charles Clifford with an electronic copy of the original force versus indentation depth data, calibration data, temperature and humidity and the calculations that you have made.

8 DATA REPORTING FORMAT

In decreasing order of preference, the preferred digital data formats are:

(1) Three column ASCII format as shown in Table 1.
(2) Manufacturer's text data format.
(3) A simple binary format – with details of structure supplied.

Table 1 - Format for ASCII data

Column 1	Column 2	Column 2
Indentation depth (nm)	Force (nN)	Time (s)
0.113	0.000	0.000
0.325	14.881	0.014
0.654	29.763	0.029

Send your report and data preferably electronically or if not hardcopy to:
C A Clifford, National Physical Laboratory, Hampton Road, Teddington, Middlesex TW11 0LW, UK, email: charles.clifford@npl.co.uk
(Tel: +44 20 8943 6620; Fax: +44 20 8943 6453)

9 ANY DOUBTS

If you are unsure of anything or need advice please contact Charles Clifford, email: charles.clifford@npl.co.uk.

ACKNOWLEDGEMENTS

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