Materials Characterisation Programme

Polymers: Multiscale Properties

SECOND INDUSTRIAL ADVISORY GROUP MEETING

Module 16
National Physical Laboratory, Teddington, Middlesex

Thursday 28th June 2007

AGENDA

10.00	**Tea/Coffee**
10.30	**Welcome and Introduction**
10.45	**Materials 2007+ and Other Programmes** *Bill Nimmo/Bill Broughton*
11.00	**Use of Nanoindentation Measurements for Determining Time-Dependence Behaviour of Polymers** *Dr Ben Beake (Micro Materials Limited)*
11.30	**SE02: Improved Design and Manufacture of Polymeric Coatings Through the Provision of Dynamic Nano-Indentation Measurement Methods** *Dr Nigel Jennett*
12.00	**SM06: Knowledge Based Design of Plastics** *Dr Greg Dean*
12.30	**SM10: Characterising Micro- and Nano-scale Interfaces in Advanced Composites** *Dr Bill Broughton*
13.00	**Lunch**
14.00	**Discussion – Future Direction**
	Any Other Business
14.30	**Closure of Meeting**

Multiscale Properties

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Attendees:

Dr Chris Stevens	NGF Europe (Chair)
Dr Paul Morrell	AWE, Aldermaston
Dr John Meegan	AWE, Aldermaston
Mr Paul Abraham	DuPont (UK)
Dr Ben Beake	Micro Materials
Mr Darren Hodson	AstraZeneca
Dr Ian Robinson	Lucite International UK
Mr Andrew Hulme	RAPRA
Bill Broughton	NPL
Greg Dean	NPL
Nigel Jennett	NPL
Tony Maxwell	NPL
Tim Young	NPL
Miguel Monclus	NPL
Martin Rides	NPL

Apologies:

Hardyal Kalsi	Kohler Mira Ltd
Stuart Bates	Altair UK
Chris Price	Security Composites Ltd
David Mason	NGF Europe
Tol Purewal	Bespak
Anis Zakaria	AKZO Nobel Nippon Paint Ltd
John Hartley	Exel Composites UK Ltd
Neil McDermott-Evans	GKN Aerospace Kings Norton

Note: Presentation can be viewed on the NPL website, by clicking the title in the minutes and entering the username "multiscale" and password "iagmember".

Website address:
http://www.npl.co.uk/materials/programmes/characterisation/pw/polymers/meetings.html

Introduction
Bill Broughton

Bill Broughton welcomed everyone to the meeting and thanked attendees for coming. Bill described the aims of the current work programme and the IAG were informed that all documentation and information from current and past projects would be placed on the NPL website (web address and password are given at the top of this page).

Use of Nanoindentation Measurements for Determining Time-dependence Behaviour of Polymers
Ben Beake

Ben described a method that has been developed to determine the time-dependent properties of viscoelastic materials from nanoindentation. Ben described how Micromaterial's instrument operates and the experimental procedure that is used to determine the modulus of non-viscoelastic materials. The creep of conventional materials is obtained by loading the indenter with a known force and measuring the displacement as a function of time. Simple equations are available for the measurement of creep in elastic materials and these have now been adapted for viscoelastic materials. These equations appear to work well with PMMA but have not been as successful with other more complex polymers. Nanoindentation has also been conducted at elevated temperatures. A significant decrease in the hardness and modulus of PET was observed at 70ºC corresponding to its glass transition temperature. Viscoelastic data has also been extracted from nanoimpact tests by measuring the degree to which the indenter rebounds from the surface. Several interesting approaches are being developed to determine the viscoelastic properties; these include work that is being conducted at both Dupont and by Nigel Jennett at NPL.

Improved design and manufacture of Polymeric Coatings Through the Provision of Dynamic Nano-indentation measurement methods (SE02)
Nigel Jennett

Nigel Jennett introduced himself and explained the aims and objects of the project. The main objectives are tovalidate protocols for dynamic indentation measurements suitable for ISO standardisation and for future development of a reference material with an Elastic Modulus ~ 1 GPa, which are much in demand by users measuring polymers. Nanoindentation has been used extensively to determine the properties of non-time dependent materials such as metals and ceramics where NPL has been involved in the development of test protocols and international standards. The testing of polymers is, however, significantly more complex due to their visco-elastic behaviour. As a consequence of their time-dependent nature it is necessary to use a dynamic rather than static indentation method. The project is now reaching its midpoint with considerable amounts of data currently being produced. Sensitivity studies have been conducted which have shown that it is important to choose the correct value for dynamic parameters. E.g. using constant amplitude of force oscillation, the displacement amplitude decreases and so the

measurement uncertainty increases with indentation depth. The data is now being processed to determine the parameters that are critical in determining the reproducibility of the results. The next stage in this work will be to assess methods to measure at different frequencies. Finally, high temperature measurements are planned.

Questions

Paul Morrell: There is an oscillation in the damping dispersion vs drive amplitude, which does not appear to be a signal to noise issue. Could it be an external vibration?.

Nigel Jennett: External parasitic oscillations have been considered and the system has been insulated to reduce their effect. This external oscillations are only seen at very small oscillation amplitudes (< 1 nm).

Chris Stevens: Have you plotted E" against E' to examine whether you have a perfect ellipse for the first harmonic.

Nigel Jennett: This has not been done yet but will be considered.

Chris Stevens: If you are measuring only 1 Angstrom are you suppressing the rotational modes in the polymer?

Nigel Jennett: There is an issue as to which transitions can be detected using this technique and this will need to be considered in more detail.

Knowledge Based Design of Plastics (SM06)

Greg Dean

Dupont and Ticona have supplied the materials for the project. It was agreed that Polyacetal (POM) and polybutylene terephthalate (PBT) would be studied in the project. Specimens have been produced using both compression and injection moulding. Step loading creep tests have been used to validate the model. The model appears to be more accurate for the compression moulded material than it was for the injection moulded specimens. The injection moulded material being more compliant probably due to the rapid cooling that occurs in production reducing the crystallinity of the polymer. Modifications to the creep model have also had to be made to take account of a secondary relaxation peak that occurs in the PBT specimens. The next stage in this project is to apply the creep model in FE analysis using ABAQUS. Initial work has involved correcting the superposition principle that is used in ABAQUS to take into account the non-linear nature of the material, which has significantly improved the results that have been obtained.

Questions

Ian Robinson: Were the mouldings annealed to remove the residual stresses.

Greg Dean: The material was not annealed but was left to relax for 3 months before testing.

Steven Breen: Did you consider cast material to reduce residual stresses and anisotropy. PMMA is cast and polymerised in the mould.

Materials 2008+ and Other Programmes

Bill Nimmo

Bill Nimmo introduced himself as the new formulation leader and then gave a short presentation outlining the changes that have been made to the project formulation process. One of the main changes is that we now have a rolling formulation process with one third of the projects to be developed every year. It is therefore essential to have a strategy for developing new projects within the IAG. Projects can be developed throughout the year and placed in a hopper ready for the start of the formulation process. The key requirements of such projects are that they should be both innovative and contribute to the UK's knowledge base. The current formulation process is due to start in August with the projects starting in April 2008.

Ian Robinson: Would it be possible to have a concise definition of how industry could suggest an idea for a project.

Bill Nimmo: We will be producing a document that can go on the NPL website that includes an application form to suggest ideas for new projects.

Chris Stevens: What size of project will be considered.

Bill Nimmo: Bill Martin (DTI) wants the size of the project to fit what is needed by industry. However, it is hoped that the projects will be larger than they have been in the past.

Jon Meegan: Would it be better to have a series of small projects that are linked together or one large project.

Bill Nimmo: The idea is to have grand challenges that contain smaller projects. A series of smaller projects linked together into a grand challenge would therefore be ideal.

Characterising Micro- and Nano-scale Interfaces in Advanced Composites (SM10)

Bill Broughton and Tim Young

Bill Broughton explained the aim of the project was to develop quantitative techniques for the characterisation of interfacial properties in dispersed and continuously filled polymeric materials, such as fibre-reinforced polymers, nano-composites and toughened adhesives. The first stage of the project to produce a review of measurement and modelling techniques has been completed and is now available on the NPL website. The next stage is to conduct case studies to examine adhesion in a range of three different composite systems. The first case study examined the interfacial adhesion in GPR pultruded rods, which have been supplied by Fibreforce and Vectrotex. One good and one poorly bonded composite have been produced. The modulus and the strength of the poorly bonded composite are both significantly lower than the well-bonded system. In addition, moisture adsorption is also higher for the poorly bonded composite. Tim Young described the work that has been conducted using modulation AFM. A clear difference could be seen between the well bond and poorly bonded composites, with a band approximately

200nm thick present at the interface of the poorly bonded fibres. The second case study to be conducted in this project involves examining the adhesion of glass flakes that have been embedded in a polypropylene matrix. The glass flake composite samples, supplied by NGF Europe, contained chemically treated glass flakes in order to alter the adhesion properties. No difference could be detected between the well and poorly bonded flakes in terms of hardness or density. However, all of the mechanical properties of the poorly bonded flakes were lower except for the impact resistance were the poorly bonded flakes absorbed considerably more energy than the well-bonded flakes. Problems were encountered trying to determine the average thickness of the reinforcement, as the flakes were difficult to resolve. Jon Meegan suggested that using chlorosiloxane to colour the flakes might solve this. Lucite provided PMMA nanocomposites for the third case study. This has proved to be the most technically difficult of the three case studies.

Discussion – Future Direction

Chris Stevens asked whether any of the projects should be terminated early? Everyone agreed that the projects were all extremely interesting and should continue.

Chris Stevens then asked for comments on each of the projects

Composite interface project
Ian Robinson said that the case study on nanocomposites was particular relevant to the work that they were conducting at Lucite. Ben Beake asked whether he could have off-cuts from the nanocomposite specimens.

Creep project
Darren Hodson and Ian Robinson both said that it was extremely important to have this type of model for the rapid development of new products and Darren asked whether it would be possible to develop this work further in a follow on project.

Indentation project
It was generally felt that this project was also extremely useful in that in provides a unique tool for investigating the mechanical properties of polymers on a localised scale.

Chris Stevens then asked if there were any ideas for new projects. Darren Hodson and Ian Robinson both expressed an interested in projects that link the processing conditions to the final properties. In particular there is nearly always a trade off between the speed of production and the quality. The faster products are produced that more residual stresses are prosent in the product. Another fundamental question is to understand how nanocomposite materials work.

Chris Stevens suggested that we could have a presentation at the next IAG to identify the people at NPL responsible for developing projects that we should put project formulation on the agenda. He also asked IAG members to provide project ideas before the next meeting so that they can be discussed at the meeting.

Any other business

Date for the next IAG will be the 8th November 2008.