Workshop in Analysis Techniques for Polymer Nanostructures

April 8th – 10th 2002

Department of Materials and St Anne's College
Oxford, UK

Sponsored by: US Army, European Research Office
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Organising Committee:

Dr Chris Grovenor,
Materials Department
Oxford University,
Parks Road,
Oxford, OX1 3PH, UK

Dr Robert Shaw, ARL-European Research Office
Edison House, 223 Old Marylebone Road,
London NW1 5TH, UK

Dr David Bucknall,
Materials Department,
Oxford University,
Parks Road,
Oxford, OX1 3PH,

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Introduction:

There is considerable world-wide activity in the fabrication of Polymer Nanocomposites for a variety of application areas. While some considerably enhanced properties have been reported (both mechanical and electrical), the microstructural and morphological characterisation of these materials is not easy – often requiring the development of novel analysis techniques or the radical modification of familiar ones. The objective of the workshop is to bring together representatives of the US Military community with questions on the nanostructure and chemistry of Polymer Nanocomposites with European scientists who are developing the techniques that may provide some of the critical answers. A major emphasis of the workshop will be to identify **non-destructive** probes appropriate for the study of key problems in nano-structured polymer matrix composites.

The targets for discussion had been set in part as a result of the discussions at a previous workshop in Nottingham in September 2001. This meeting identified the following as a key set of questions in the future development of Polymer Nanocomposites

- How can we probe the interfaces between the structures and the polymer matrix? We want experimental measures that can be used to understand observed bulk properties and to design improved properties.

- What experimental tools now exist that are likely to be the most useful? For instance, to measure adhesion as a predictor of toughness or to measure charge transfer as a predictor of more complex mechanical and electrical functions.

- What promising tools are currently not being applied in this area. If you could invent a better tool, what would it do?"

20 scientists from Europe and the USA met for 2 days in Oxford to discuss these questions. 3 sessions were devoted to presentations from the participants and 2 more to informal discussions. The final session was a general discussion that formulated a number of different possible actions for future development. The notes from this final discussion are included at the end of this report.

The programme for the meeting is given below.

April 8th 2002	
pm	**Introduce participants and discuss aims of workshop** Welcome: Dr Chris Grovenor Workshop goals: Dr Robert W. Shaw **Introductory presentations on materials and problem areas** Army programmes Dr Michael Sennett AF programme Dr Richard A. Vaia DSTL programme Dr Doug Imeson **Modelling polymer nanocomposites** Hans Rudolf Lusti Computer-aided design of nanocomposites for barrier applications
April 9th	
am	**Presentations on analysis techniques** Professor Frank Jones Nano-mechanical characterisation of thin soft polymeric films Dr Robert Magerle Nanotomography: 3D volume imaging of polymeric nanostructures Dr Rainer Fink Spectromicroscopy of ultrathin polymer films Professor Erik Geissler Small angle neutron and coherent X-ray scattering from nanosized filler particles in polymer melts Dr Patrick Fairclough
pm	Dr Drahosh Veseley Microstructure of Polymer Nano-Composites. Professor Daniel Wagner Recent Advances in Carbon Nanotube Mechanics Dr Graham Beamson Characterisation of Polymer Nanocomposites. Can XPS help? Professor R. K. Harris Can NMR address Nanostructured Polymers?

Evening session	Sub group meetings chaired by Sennett and Vaia. Discussion of future directions for instrumental development
April 10th	
am	Sub groups report on discussions Discussion on conclusions of Workshop

Participants

Dr Graham Beamson
CLRC Daresbury Laboratory
Research Unit for Surfaces Transforms and Interfaces
Daresbury
Warrington, Cheshire. WA4 4AD, UK
Tel +44 (0)1925 603479(office)/603514(lab), Fax +44 (0)1925 603596
g.beamson@dl.ac.uk

Dr David Bucknall
Department of Materials
Oxford University
Parks Road
Oxford OX1 3PH, UK
Tel (44) 1865 273763
david.bucknall@materials.ox.ac.uk

Dr Richard K. Everett
Head, Simulations & Imaging Section
Office of Naval Research International Field Office,
223 Old Marylebone Road, London NW1 5TH
everett@anvil.nrl.navy.mil

Dr. Patrick Fairclough
Department of Chemistry
University of Sheffield
Sheffield, S3 7HF, UK
p.fairclough@sheffield.ac.uk

Dr. Rainer Fink
Universität Würzburg, Experimentelle Physik II
Am Hubland, 97074
Würzburg, Germany
Tel. 0931-8885163 Fax: 0931-8885158
Mobiltel.: 0170-6845165 or 0163-6452250
e-mail: raifi@physik.uni-wuerzburg.de or raifi@raifi.de

Professor Erik Geissler
Laboratoire de Spectrométrie Physique,
Université Joseph Fourier de Grenoble,
B.P.87,
38402 St Martin d'Hères,
France
tel (33) 476 63 58 23
fax (33) 476 63 54 95 geissler@spectro.ujf-grenoble.fr

Dr Chris Grovenor
Department of Materials
Oxford University
Parks Road
Oxford OX1 3PH, UK
Tel (44) 1865 273761
Chris.grovenor@materials.ox.ac.uk

Professor R. K. Harris,
Department of Chemistry,
University of Durham,
South Road,
Durham DH1 3LE, U.K.
R.K.Harris@durham.ac.uk
Phone +44-191-374-3121, FAX +44-191-384-4737

Dr. Simon Hayes
Lecturer in Aerospace Materials
Dept. Engineering Materials
Sheffield University
Sir Robert Hadfield Building
Mappin Street
Sheffield, S1 3JD, UK
S.A.Hayes@sheffield.ac.uk

Dr. Doug Imeson
Platform Systems & Technology Department
Defence Science and Technology Laboratory
Farnborough
Tel. +44 (0) 1252 455014
DIMESON@dstl.gov.uk

Dr S A Impey
Advanced Materials
Cranfield University
Cranfield
Bedfordshire MK43 OAL, UK
Tel: 01234 750111 ext 2550, Fax: 01234 752473
S.A.IMPEY@cranfield.ac.uk

Professor Frank Jones
University of Sheffield
Department of Engineering Materials
Sir Robert Hadfield Building
Mappin Street, Sheffield S1 3JD
f.r.jones@sheffield.ac.uk

Mr. Hans Rudolf Lusti
Department of Materials
Institute of Polymers
ETH, CH-8092 Zurich
Switzerland
gusev@ifp.mat.ethz.ch

Dr. Robert Magerle
Universität Bayreuth
Physikalische Chemie II Tel: +49-921-55-2641
D-95440 Bayreuth Fax: +49-921-55-2059
Germany E-mail: robert.magerle@uni-bayreuth.de

Dr. Michael Sennett
Natick Soldier Center,
Natick, MA 01760-5018, USA
(1) 508-233-5516 michael.sennett@natick.army.mil

Dr. Robert W. Shaw
European Research Office, 223 Old Marylebone Road,
London NW1 5TH
(44) 207 514 4909
rshaw@usardsguk.army.mil

Dr Richard A. Vaia
Air Force Research Laboratory
Materials and Manufacturing Directorate
AFRL/MLBP, Bldg 654, 2941 P St.
Wright-Patterson AFB, OH 45433-7750
phone 937-255-9184, fax 937-255-9157
richard.vaia@afrl.af.mil

Dr Drahosh Vesely
Department of Materials
Oxford University
Parks Road
Oxford OX1 3PH, UK
Tel (44) 1865 273790
Drahosh.Vesely@materials.ox.ac.uk

H Daniel Wagner
The Livio Norzi Professorial Chair
Weizmann Institute of Science
Rehovot, Israel
Tel: +(972) 8 934 2594, Fax: +(972) 8 934 4137
E-mail: daniel.wagner@weizmann.ac.il

Outcome of Discussion Groups

The participants split into 2 discussion groups chaired by Drs. Richard Sennett and Richard Vaia to explore different aspects of the analysis of Polymer Nanocomposites. The following morning these two groups recombined to discuss suggestions and possible ways of moving forward to collaborative activities.

Points arising from discussions

[1] How special are nanocomposites?

What makes them special? Particles size is comparable to the distance between them which is comparable to the 'interphase' size if we believe that an interface region with 'special' or different properties exists between the particles and the bulk polymer.

For polymers the critical scales are known, however they are system specific – thermoplastic, thermoset, gels, blocks, etc. Need to establish at what length scales the particles influence the properties of the polymer – nanoindentation may help here at least for mechanical properties.

Need to define key systems to study or the field is too diverse. How can this be done - need to identify the payoff or key drivers? Even within the US Defence research community the possible application areas are quite different and various. The obvious areas are:

- Lightweight structural – auto/aero,
- Barrier
- Functionalised, electrical or electronic
- something revolutionary that we have not thought of yet?

Only a few organizations in the world have a sufficient budget, application and need to lead a programme in developing a new material. Industry will only do this if a critical need can *only* be satisfied by a polymer nanocomposite.

[2] Controlled manfacturability:

The community must be able to fabricate materials that behave in a desired way and can be produced reproducibly! Study of the processes involved in manufacturability by in-line sensors or by in-situ experiments?

Need for modelling/theory to guide experiments and interpretation.

Selection of materials combinations taking into account compatibility, functionality, cost and availability. In a discussion of the future availability of C-nanotubes there was considerable difference of opinion as to the likely cost of this critical raw material.

[3] Techniques for studying nanocomposites

Breadth of possible nanocomposites implies one technique does not apply to all materials: e.g. different techniques necessary to measure viscous/viscoelastic/elastic response, depending on properties of particles and matrix. Especially true of nanoindentation techniques where load cells are operating near limits for polymers.

Extensive discussion on whether we need to start with a model system to determine interface properties (may need a different one for each type of system): It was generally felt that existing techniques are sufficiently useful to allow us to make substantial progress if the system is simplified as much as possible. However, there was no agreement on whether a model planar system – polymer on graphite for example – was a reasonable analogue to highly curved C-nanotubes. Techniques like NMR do not require simplified geometries, while many others (TEM, Nanoindentation, XPS and to some extent X-ray and neutron techniques) would give much clearer data on the interface regions if planar samples were used.

Several participants said that if presented with samples that they would be able to study them now with their particular techniques out of interest. (See comments on Virtual Laboratory below)

Both model and real systems can only be studied in detail if the *topology* of the structure is known. This highlights the importance of developing SPM or TEM tomography for these materials.

New Techniques – very speculative discussion on techniques that need developing

General points:

- Nanoscale analysis implies you can examine micro composites, but Picoscale techniques are needed for nanocomposites

- temporal axis needs exploring – both the stability of nanocomposites and what is happening during fabrication

Phase contrast imaging – coherent X-rays with divergent beam

X-ray holography – single macromolecule analysis in the interfacial region?

NSOM techniques and evanescent fields: comparable approach with soft x-rays. Need higher diffraction orders to improve resolution, which requires an improvement in zone plate manufacturing

X-rays offer a powerful way to measure interfacial areas, but how to define interface? Is there a practical control over interface areas that can be established by in-situ studies during fabrication?

Spectroscopy techniques with soft x-rays will need an improvement in spatial resolution to be useful

THZ spectroscopy?

Ultrasonics? Holography of pressure waves to develop controlled deformation – couple to other spatially-specific probe techniques

Neutron scattering and reflectivity – need the development of contrast techniques, Neutron spin polarization contrast?

Anomalous scattering techniques for low Z materials?

AFM offers sensitivity to local mechanical properties, but the reproducible manufacturing of appropriate tips will have to be improved.

[4] Strategy for maximising information yield by collaborating

A substantial discussion in Group A centered around a possible approach for a multidisciplinary research team – a *'virtual laboratory'*

There are existing programmes, especially in the nuclear industry, where a complex set of interdisciplinary experiments are undertaken by a very large international team. This team has a built in redundancy, i.e. there are several partners representing each technique, and samples are fabricated by selected 'manufacturing' groups for analysis by <u>all</u> the technique groups. Regular meetings compare the data and address the identification of key future experiments. This kind of consortium research can offer a much greater range of techniques and expertise than any one organisation, but requires:

(a) some funding (at the very least for travel, but not every partner can undertake work pro bono - especially University partners)
(b) a whole lot of coordination!

Nanocomposites is probably a field with enough potential to justify this kind of collaborative effort, and there was some discussion at the end of the meeting about exploring the establishment of a European consortium in the area.