Synchrotron X-ray Tomography of Flame Retardants in Polymers

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- tomography: X-ray (and e- and neutron)
- resolution: micron to nanometers
- time: minutes to hours
- chemistry: elemental and phase
- flame retardants in polymer blends
- snapshot of an inhomogeneous distribution
- radial distribution about fiber reinforcement
- diffusion as a function of annealing
- needed: instrumentation, mathematics, software
software stack (Ed)

- 10 GB per experiment (1 - 10 expts/day)
- LLNL VisIT (parallelized visualization)
- file types: HDF5 and DICOM
- huge metadata needs

- currently: FileMaker Pro and collaborators append metadata to links to HDF5 files
- collaborators in LaTech, APS, Munich, and industry

New structures in cat claws discovered with synchrotron X-ray tomography. Homberger, 2007

Real sandstone samples provides authentic geometry for flow modeling. Applications range from environmental remediation to oil & gas recovery. Thompson & Willson, 2008

flow rates
red = fast
blue = slow
Tomography and chemistry: Dispersion of flame retardants in polystyrene

- BT-93, a phthalimide dimer, and antimony(iii) oxide as synergist.
- CRT case can be up to 20 wt% Br.
- How well mixed at the micrometer scale?
- Are the chemical distributions correlated?
- As a function of time, does the system exhibit Ostwald ripening and “blooming”?
## Some 3D Methods for Chemical Imaging

<table>
<thead>
<tr>
<th>Technique</th>
<th>Resolution, Field of View, Expt. Time</th>
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<tr>
<td>synch. X-ray</td>
<td>2 µm, $1024^3$, 1-8 hrs</td>
<td>&gt; 10 beamlines in US, mature, reliable, great elemental sensitivity for $Z \geq 35$ (Br)</td>
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<tr>
<td>$^{13}C$ &amp; $^{31}P$</td>
<td>400 µm, $128^3$, 6 hrs</td>
<td>lowest S/N, poorest resolution, best chemical speciation</td>
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<td>~6 beamlines worldwide, some in renovation, elemental sensitivity. US: NIST, UC Davis</td>
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<td>electron micro. tomo</td>
<td>2 nm, $512^3$, ? hrs</td>
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<td>microtome &amp; 2D EM</td>
<td>$2 \times 2 \times 50$ nm, $&gt;1024^3$, &gt;12 hrs</td>
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Tomography with “Golden ratio” ordering

X-rays
rotate sample

acquire projections

store
projections
in “sinogram”

With GR, we can terminate experiment early, if necessary, and still have a reasonable image reconstruction.
Backprojection reconstruction

use each projection

filter and rotate projections

Back-projection reconstruction

sum all projections to reconstruct image
Tomography: Acquire transmission views as a function of sample rotation angle. Requires high-accuracy sample motion, high-resolution scintillator/CCD.

• Least squares fit of X-ray images yields two volumes of data showing BT-93 and Sb₂O₃ concentration distributions. The colorbars show volume percent composition.

• Spatial correlation is obvious. Correlated with mixing order.

By inspection, there appear to be no large, connected regions in red, that is, no regions large enough to support a flame. Thus, the mixing is judged to be good enough to make a safe material.
Sample: Fiberglass reinforced nylon with flame retardant and Sb$_2$O$_3$

Questions: What are FR and Sb$_2$O$_3$ concentrations around fibers?
Sample: Flame retardant with initial poor blend.
Question: Can dissolution of FR as a function of anneal time/temperature be measured?

IMA theme for Sept ’08 - June ’09
“Mathematics & Chemistry”

IMA Workshop:
3-D Image Acquisition and Analysis Algorithms
January 9-12, 2006
Organizers:
Les Butler
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Schedule and list of participants are not yet available.

New mathematics and algorithms are needed for 3-D image acquisition and analysis. The 3-D images come from many disciplines: biomedicine, geology, chemistry, and microfabrication. The mathematics is wide-ranging and includes at least tomography and inverse problems, wavelets, PDE, and conformal mapping. The depth of the problem and the extent of the mathematics argues for multiple, long-duration collaborations that are fostered by a workshop series.
## Instrumentation: How to image phosphorus-based flame retardants?

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Spallation Neutron Source

- Neutrons are produced at near-point source by the collision of high-energy protons with a Hg target: 695 ns pulse with 60 Hz rep. rate.
- The experimental hall is about 3/4-populated. Is there room for tomography?
Examples of Radiography in Engineering

- FRM-II (Munich): air-cooled gas engine

This work uses back projection.

Plans to use discrete tomography for 3D movies.

Movie recorded at ILL by G. Frei (PSI), B. Schillinger (FRM-II), and A. Hillenbach (ILL), et al.
The Spallation Neutron Source is an accelerator-based neutron source in Oak Ridge, Tennessee, USA. At full power, the SNS will provide the most intense pulsed neutron beams in the world for scientific research and industrial development.

http://sns.gov

IAN2006

Imaging and Neutrons 2006
October 23-25, 2006
Oak Ridge, TN

IAN2006 is an international action-oriented workshop to
- Identify the current needs and potential contributions of imaging with neutrons in a wide range of science and areas of applications.
- Recognize new imaging techniques that may be made possible by advanced next generation sources that go beyond established techniques of radiography and tomography.
- Produce a report identifying both potentially valuable imaging techniques and directions for additional research and investment to realize this potential worldwide.

Applications areas
- Medical/Biomedical
- Molecular and Cellular Biology
- Chemistry
- Engineering
- Physics
- Geology
- Energy/Nuclear Power
- Materials Research
- Cultural Heritage
- Homeland Security
- Contraband Detection

Techniques
- Radiography
- Tomography
- Microscopy
- Holography
- Neutron Simulated Emission
- Computed Tomography
- Magnetic imaging
- Resonant imaging
- Bragg-edge imaging by Time of Flight
- Advanced reconstruction algorithms
- Other techniques to be identified

International Organizing Committee

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L. Buffa (Louisiana State University)
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C. Hubbard (UTBattelle, LLC)

www.sns.gov/workshops/ian2006

For additional information, contact: Al Ekkabos, ekkabosae@sns.gov, (865) 241-5644

Workshop supported by Oak Ridge National Laboratory, Spallation Neutron Source
- Integrated Infrastructure Initiative for Neutron Scattering and Muon Spectroscopy (INMSI)
- Oak Ridge Associated Universities
- Joint Institute for Neutron Sciences
- in cooperation with the International Atomic Energy Agency

Sources:
[1.] (a) E. Christian et al., *Neutron News* (2003), Neutron Facility, ORNL
[2.] (b) E. Lehmann et al., *Neutron News* (2004), Neutron Facility, ORNL
[3.] (c) D. Floyd et al., *Neutron News* (2005), Neutron Facility, ORNL
[4.] (d) W. Kucharzewski et al., *Proceedings of the 9th International Conference on Neutron Scattering* (2005), Neutron Facility, ORNL
The Spallation Neutron Source is an accelerator-based neutron source in Oak Ridge, Tennessee, USA. At full power, the SNS will provide the most intense pulsed neutron beams in the world for scientific research and industrial development.

Test beamline under construction at HFIR. Will test neutron optics and detectors. Might be operational by mid-2008.
Lab tomography: the Phoenix X-ray nanoTom
nanoTomo

~210 keV, 34 µm
Tomography: future

- If DOE BESAC recommends 4-th gen. soft X-ray source (< 1 keV), then
  - Image biological cells at ~500 eV, the ‘water window’. Full 3D volumes can be imaged at ~40 nm resolution today, and potentially to 10 to 15 nm. Concerns are X-ray flux damage to cell will require better projection reconstruction methods, better attention to sampling theory. (McDermott, ALS)
  - Many applications to polymer blends, composite materials, especially with coherent diffractive imaging
  - MHI-ers: ALS nanotomography: Carolyn Larabell, Gerry McDermott, (or from their groups), Ian McNulty (APS), Franz Pfeiffer (Swiss Light Source)

Budding yeast cells at 30 nm resolution

CAMD now: absorption & phase contrast
4-th gen. X-ray
X-ray optics for ~10 nm resolution & coherent diffractive imaging

Early
Late
During division

Raw tomograms
Segmented organelles
Most dense organelles
Least dense organelles

D.Y. Parkinson et al, Journal Structural Biology in press
software stack (Ed)

• 10 GB per experiment (1 - 10 expts/day)
• LLNL VisIT (parallelized visualization)
• file types: HDF5 and DICOM
• huge metadata needs
• currently: FileMaker Pro and collaborators
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Thompson & Willson, 2008

New structures in cat claws discovered with synchrotron X-ray tomography. Homberger, 2007

flow rates
red = fast
blue = slow

Blades of cornified tissue
Cornified tissue
Soft tissue
Bony tissue

0 0.5 mm