Synchrotron scattering characterization for the development of new materials
- experience to share with the ForMAX beamline

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Advanced Polymers Beamline (X27C) at National Synchrotron Light Source, Brookhaven National Lab

NSLS: 1982-2014
X27C: 1998-2014
Unique features of X27C

• The mission of the X27C beamline was to support continuing development and application of a dedicated facility for real time SAXS and WAXD experiments with emphasis on structure and dynamics studies in polymer materials.

• Major benefits of this facility are that no extensive synchrotron experience and equipment preparation are required from general users to carry out most of the experiments.
Measurable impacts of X27C for the polymer community (1997-2014)

- **Users**
  - Number of research institutes
    - > 100 national and international research institutes
  - Number of total users
    - > 1000 (students, postdocs, and scientists)

- **Publications**
  - Number of published papers
    - > 500 scientific papers
Advanced Polymers Beamline at NSLS

AP-PRT SWAXS setup at X27C

1-D PSDs  Vacuum chamber  Draw unit  Pinhole collimation system  Monochromator assembly

Optical tables  x-z Translational stages

Advanced Polymers Beamline, X27C, NSLS
Pin-Hole Collimation
Dual-Chamber Temperature Jump Apparatus

Detection System
1. Gas filled delay-line position-sensitive wire detectors
2. PC based (Mbraun PSDs) and CAMAC based (EMBL) histogram memory access

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**In-situ Fiber Processing Apparatus**

**Solution Spinning Unit**
- Diameter of barrel: 9.52 mm
- Diameter of die: 0.75 mm

**Fiber Draw Unit**

**Draw Unit with X-ray Collimator**
- Yarn Supply
- Hysteresis Brake
- Separator Roll
- Roller Guide
- Godet Rolls
- Heat Pins
- Particle Collimator
- Synchrotron X-rays
- Yarn Uptake

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On-line Fiber Melt-Spinning Apparatus

Synchrotron Fiber Spinning Apparatus
Using SAXS/WAXS Detectors

- Metering Pump
- Extruder
- Synchrotron X-Rays
- Collimator
- SWAXS Camera
- SAXS Image Plate or 2-D Detector
- WAXS Image Plate or 1-D Detector
- Beam Stop (Pin-Diode)
- Polymer Fiber
- Take Up Motor

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Rheo-X-ray Apparatus

Oscillatory Shear

Steady Shear

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X-Ray Modified Stress-Controlled Rheometer

1 - hood H-ETD400;
2 - enclosure for the bottom part P-ETD400;
3a - recess in the top hood H-ETD400;
3b - recess in the bottom enclosure P-ETD400;
4 - Kapton window;
5 - slit for incident X-ray;
6 - cylindrical insert/bottom “parallel plate”;
7 - top “parallel plate”;
8 - sample

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High pressure and temperature controlling setup

High Pressure X-ray Apparatus

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In-situ Tensile Stretching Apparatus

Stretch Unit (modified Instron 4410)

Load Capacity: 500 N
Temperature: up to 300 °
Stretch Speed: 0.2-1000 mm/min

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Polymer Research Opportunities via Scattering/Diffraction (SAXS/WAXD) at X27C

- Changes in Supramolecular Structures of Biological/Bio-Synthetic Macromolecules, Ionomers, Block Copolymers, Dendrimers, Charged Gels and Colloidal Systems, Nanocomposites in Solutions and Melts
- Kinetics of Phase Transition in Semicrystalline Polymers (Crystallization and Melting), Multicomponent Mixtures and Molecularly Segmented Systems (Phase Separation)
- High Pressure Experiments (Hydrostatic Pressure, Supercritical Solvents) for Environmental Process Development
- *In-situ* Chemical Reaction and Polymerization
- Polymer Fibers/Films during Processing (Spinning, Extrusion, Deformation)
- Polymer Melts/Solutions in Flow
Stretching of Natural Rubber

Instrumentation & Sample

- Synchrotron X-rays, X27C/NSLS at BNL & MAR-CCD
- Modified stretching machine
- Vulcanized Natural rubber with sulfur
Stress-strain and in-situ WAXD of natural rubber

About XPOLAR

- A unique software capable of:
  - 2D and 3D visualization,
  - data reduction and treatment,
  - structure analysis for both SAXS and WAXD data,
  - Structure simulation,
  - batch analysis of time-resolved data;
- Stand-alone program with user-friendly Graphic User Interface (GUI);
- Current user community > 300 users
Characterization of Nanocelluloses

- Agave
- Switchgrass
- Miscanthus
- Bamboo

Plant Cell Wall

1. Cellulose Fiber
2. Cellulose Nanofiber
3. Cellulose Microfibril (2-5 nm)
Simultaneous SAXS/WAXS on cellulose nanofiber suspensions

Beam-line: X9 (NSLS, BNL)
Beam wavelength: 0.0885 nm
Sample-to-detector distance:
SAXS: 3.2 m
WAXD: 463 mm
30 s for each measurement
3 measurements for each sample

Biofloc-96

0.6 wt%
0.3 wt%
0.1 wt%
0.05 wt%

Weight-average sizes:

\[ a_w = 3.2 \pm 2.2 \text{ nm} \]
\[ b_w = 9.5 \pm 5.0 \text{ nm} \]
\[ a_w + b_w = 12.7 \pm 5.5 \text{ nm} \]

Ribbon-like structure

The Life Science X-ray Scattering (LiX) Beamline at NSLS-II, Brookhaven National Laboratory
LiX beamline

- 2.1-18 keV energy range
- As small as 1 micron beam size at the sample
- Use a secondary source aperture to improve beam stability
- Compound refractive lenses for secondary focusing
- 3 detectors to collect scattering data simultaneously
- Interchangeable experimental modules for rapid switching between different types of experiments
The scientific areas supported by LiX

Solution scattering
- High throughput: 1 sample-buffer pair or better [beam intensity]
- Time-resolved solution scattering: down to 10 μs time resolution [beam size]

Lipid membrane structure
- Structures in multi-bilayers [energy range] Single lipid bilayer
- [beam size, energy range]

Biological tissues
- Micro-diffraction mapping [beam size] Coherent
- diffraction imaging [coherence]
High throughout solution scattering

Sample handler at X9

Sample handler built by EMBL

- Faster measurements provide more and flexible opportunities for researchers
- Enable experiments that involve large numbers of samples (e.g. ligand screening)
Turn distance into time with continuous flow mixers

mixing time \( \sim \frac{\lambda^2}{D} \)

\( \lambda \): characteristic length, \( \sim 0.1\mu m \) for turbulence mixing (Re>10^3)

D: diffusion constant, \( \sim 10^{-5} cm^2/s \) for small solutes, \( \sim 10^{-7} cm^2/s \) for macromolecules

• Not limited by detector/shutter speed or beam intensity
• Time resolution can reach a few microseconds

Kathuria et.al., Biopolymer, 2011


\( P_{inlet} = 5 \text{psi} \)

\( \alpha = 1.0 \)

\( \alpha = 0.5 \)
Flow mixer development at LiX

- Chaotic mixing. Mixing time less susceptible to flow speed.
- A gas pressure-driven pump (up to 8 bar) for sample injection
- Profiled flow channel to improve mixing uniform
• Integrating 4 flavors of solution scattering (high throughput scattering using either the 8-cell sample holder or a flow-through cell; in-line purification; time-resolved scattering using flow mixers) into a single enclosure

• 6-axis robot to be used for automated sample handling
Scanning imaging with micro-beam

Inouye et.al., PLoS One, 2014
Microbeam diffraction showing the local orientation of the myelin sheath in nerve fibers

Litchenegger et.al., J. Appl. Cryst., 1999
Orientation of the cellulose fibers in cell wall
Tomography

Jensen et.al., Neuroimage, 2011

Tomographic images of a rat brain, using the scattering from myelin as the contrast mechanism.


Distribution of collagen orientation and amount (color) in a tooth sample
Ptychography

Illustration of ptychographic imaging. Diffraction patterns are recorded on overlapping regions on the sample. The redundancy helps the phase retrieval algorithm to converge more quickly.


Tomography of a root nodule
2D resolution ~ 10nm, 3D resolution ~ 100nm
Learning to share with the ForMAX beamline

- Instrumentation
  - Best detection systems
  - Diverse sample chambers (as flexible as possible)
  - State of the art data analysis software(s)

- Users
  - Focused on the most relevant problems