Soft X-ray spectromicroscopy of polymers and biomaterials: from analysis to synthesis

Adam P. Hitchcock,[1] Jian Wang,[1] Daniel Hernández-Cruz, [1] Harald Stöver, [1] Marie-Eve Rousseau, [2] Michel Pézolet[2]

[1] *BIMR McMaster University, Hamilton, ON, Canada L8S 4M1;* [2] *Université Laval, Québec, QC, Canada G1K 7P4*

Introduction

Soft X-ray spectromicroscopy using scanning transmission X-ray microscopy (STXM) at the Advanced Light Source (ALS) is being applied to quantitative chemical mapping of natural and synthetic polymers at high spatial resolution (<50 nm). Current materials analysis applications include nanostructured polymer microspheres with potential applications as photonic crystals [1,2], tectocapsules [3], and orientation mapping in silk fibers [4]. In addtion, the fine focused bright STXM beam is being used "synthetically", for chemically specific pattern generation.

Methods and Materials

STXM is performed at dedicated bending magnet BL 5.3.2 at the ALS. Spatial resolution is 40 nm, determined by the zone plate. Spectral resolving power can be >5000, depending on slits. Samples are embedded in epoxy, ultramicrotomed, to a thickness of 50-150 nm and mounted on 3 mm TEM grids. Measurements are made with the STXM tank at 1/3rd atm He.

Results

Structured microspheres – towards photonic crystals: Fig. 1 shows results from C 1s STXM of a chemically structured microsphere with internal annuli on the scale of the wavenlength of light, formed by timed addition of a second reagent (PMI) during emulsion polymerization of a cross-linked divinyl benzene microsphere [1]. STXM provides important feedback for improving synthetic procedures to synthesize microspheres with a number of 100-300 nm wide internal bands of alternating refractive index with sharp interfaces. Such structures may exhibit photonic band gaps and be useful as optically active coatings, opto-electronics, etc. In addition, we have studied PS-PMMA 'onions' formed by solvation-phase segregation [2] and assembled microsphere-capsules [3].

Orientation mapping of biological fibers: Silk from silkworms and spiders has outstanding mechanical properties (strength, extensibility). Silk proteins have a high content of repetitive residues which form β-sheet regions. Alignment of β-sheets in adjacent proteins form 'crystallites' which are believed to be important for the mechanical properties (reinforcing a soft material with hard segments). We have used STXM to measure the linear dichroism of the C 1s → π^*_{amide} transition and thus map the spatial distribution of orientation in *B. mori* cocoon silk [4] and *N. clavipes* dragline spider silk. The linear dichroism maps can be converted to P_2 orientation maps [4]. Comparison among samples produced with controlled spinning speeds, and with Raman measurements of the same samples are being used to better understand the origins of the mechanical properties of these fascinating and potentially very useful materials.

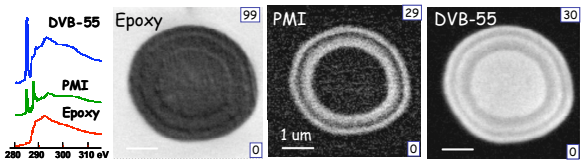

Fig. 1 (left) C 1s reference spectra. (right) component maps of a DVB microsphere with internal PMI band, derived from a C 1s STXM image sequence

Chemically specific lithography: While radiation damage is generally avoided in making analytical measurements with STXM by carefully controlling sample exposure, the high brightness of the STXM beam provides a means to explore radiation damage physics and chemistry, and to use the large differences in the absorption coefficients of different materials to perform chemically selective patterning (lithography). For that purpose we have developed a pattern generation routine for STXM, and have explored methods to create chemically specific patterns in mixed materials. Because most of the chemical damage (bond rearrangements, mass loss) are associated with secondary mechanisms, which are generally not chemically specific, it is not evident how one can retain the selectivity of the primary absorption to make chemically specific patterns. When the LBNL logo is color separated and the components written into polyethylcyanoacrylate (PECA) at 286.8 eV ($\pi^*_{C\equiv N}$) and 288.5 eV ($\pi^*_{C=O}$), there is no chemical selectivity. However, if the same exposure is made in a PAN/PMMA bilayer with each layer 30 nm thick (same functional groups and similar C 1s spectrum to PECA), the identical exposure shows exquisite chemically selective patterning (Fig. 2). We are making systematic studies to understand why the interlayer interface is so effective in controlling the range of the secondary damage processes. That informtaion could have important implications in radiation protection.

Research supported by NSERC, Canada Research Chair, CFI, and AFMnet. Measurements at ALS STXM532, funded by DoE under contract DE-AC03-76SF00098

[1] R. Takekoh, M. Okubo, T. Araki, H.D.H. Stover and A.P. Hitchcock, Macromolecules 38, 542 (2005).
[2] A.P. Hitchcock, Grace Gao and H.D.H. Stöver, Microscopy and Microanalysis 11 (Suppl 2), 1400 (2005).
[3] L.M. Croll, H.D.H. Stöver and A. P. Hitchcock, Macromolecules 38, 2903 (2005).
[4] D. Hernández Cruz, A.P. Hitchcock, M.M. West, M.-E. Rousseau, M. Pézolet, Biomacromolecules 7, 836 (2006).

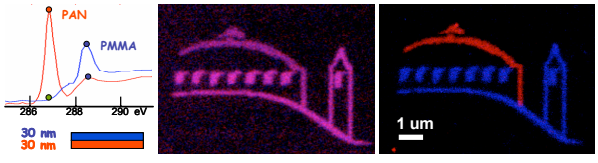

Fig. 2.(left) C 1s spectra of PAN & PMMA. (centre) non-specific patterning in PECA. (right) successful chemically selective pattern in a PAN/PMMA bilayer, written and read at the respective π energies - 286.8 (red) and 288.4 eV (blue).*