3d chemical mapping of toners by serial section scanning transmission X-ray microscopy

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Abstract We describe three dimensional chemical mapping of a 2x10x10 micron volume of a toner particle by scanning transmission X-ray microscopy using serial section sampling and computer reconstruction. To our knowledge this is the first example of serial section 3d imaging by soft X-ray microscopy. This is an attractive alternative to tomography when sample density is large and detailed 3-d chemical information requires image acquisition at a number of X-ray energies.

1. INTRODUCTION

Toners for black and white copiers, fax machines, laser printers etc, are high value added polymer-based materials. The toner studied consists of 5-20 micron irregular shaped particles which contain more than 5 different chemical components, ranging from nm-thin surface coatings, to 50 nm diameter carbon black particles, to various wax and resin components with sizes in the 0.1 to 2 micron range. The properties of toner particles depend on the three dimensional spatial organization of the chemical constituents. 3-d chemical mapping at high spatial resolution would help optimize toner fabrication.

Scanning transmission x-ray microscopy (STXM) provides imaging and, through measurements at multiple X-ray energies, quantitative chemical mapping at ~ 50 nm spatial resolution [1]. It is well suited to polymers since the chemical sensitivity, especially at the C 1s edge, is very good. It provides more information per unit sample damage than competing techniques (full field transmission X-ray microscopy (TXM) or energy loss spectroscopy in an electron microscope). STXM provides a 2-d projection through a finite sample thickness. At typical polymer densities of 0.8 - 1.5 g/cm³ the maximum sample thickness for practical carbon 1s STXM is 0.5 microns but the thickness should be less than 0.2 microns for quantitative results. This is too thin for useful 3-d chemical mapping using angle scan tomography, which has been demonstrated recently in 3-d STXM imaging of biological samples [2] and TXM imaging of various systems [3]. An alternative to tomography is serial sectioning combined with 3-d image reconstruction techniques. This is currently well developed in optical and transmission electron microscopy [4]. This paper reports our first explorations to develop the sample preparation, data acquisition and data analysis procedures for practical application of serial section STXM for 3-d chemical mapping of natural and synthetic polymers.

2. EXPERIMENTAL

Initial serial section experiments and reference spectra were acquired using the 7.0.1 STXM [5] at the Advanced Light Source (ALS). The serial section data presented here was acquired with the new ALS 5.3.2 STXM [6], which provides high spatial resolution, no drift of the field of view with photon energy, and rectilinear scanning on accurate spatial scales.



A set of 25 serial sections of a single toner particle covering a 10x10x2 micron volume were prepared by ultramicrotomy, taking care to minimize section distortion by use of an epoxy of similar hardness to the sample. We were able to record image sequences of 21 of these sections; the others were completely or partly blocked by grid bars. Thirteen carefully chosen energies were used, selected for optimum differentiation of the components of interest. The voxel size is 100 nm x 100 nm (from the image sampling) by the section thickness, nominally 100 nm. Thus we have assumed cubic voxels in the image processing. Quantitative 2d component maps derived from multiple energy images (stacks) of each section are aligned by rotation / translation and then combined to provide detailed 3-d maps of the chemical constituents.

3. RESULTS

3.1 Two dimensional chemical maps

Figure 1 presents the C 1s NEXAFS spectra of the main components. These spectra were obtained either from the same toner sample (epoxy, wax, encapsulant) or from samples of the pure materials (C-black, resin). The spectra are placed on linear absorption scales (nm⁻¹) by matching the spectral intensity below 282 eV and above 310 eV to the elemental response predicted from the tabulated mass absorption coefficients [7] and an estimate of the density of the pure material. These spectra were used as the references for deriving the component maps using singular value decomposition [8] applied to the 13 images for which data was acquired. Figure 2 is an example of the quantitative 2-d component maps derived for one section.

3.2 Alignment and three dimensional combination

Since each section was oriented in a different manner relative to the STXM scan it is necessary to translate and rotate component maps for each section to align onto a common x,y scale. Ideally it is



Figure 3 Composite of the aligned images at 285 eV, with a cut-out. The irregular exterior shape meant that alignment had to be performed using interior structure.



Figure 4 Montage of the wax component maps.

helpful to add high contrast fiducial markers to assist alignment - this can help identify and correct section distortion in microtomy as well. Since external fiducial markers were not used, it was necessary to use the internal structure of the toner to align successive images. This was carried out using the program, sEMalign [4] which is a convenient tool for applying rotations, translations (and also image distortions, although none were applied in this work) to one of a pair of images and then using several techniques to optimize successive pair wise alignment. The procedure writes a set of translation and rotation parameters which, once established on a high contrast component such as the wax, can be readily applied to the set of images at any single energy, or the other component maps. A cutaway view of the aligned images (in optical density) at 285 eV is shown in figure 3. Note that where a slice could not be recorded due to interference from a grid (3 cases) or a poor section (1 case) adjacent images were repeated in order to preserve the correct spatial registry. Figure 4 is a montage of the aligned component maps for the wax species.

3.3 Three dimensional visualization

Three dimensional (3d) visualization of the spatial distribution of the wax and encapsulant components are presented in figure 5. In addition to allowing investigations of the 3-d distribution of individual components, it is possible to combine 2 or more component maps into various 3-d color coded combination maps. These are difficult to present on paper, but when one uses a variety of computer-based presentation techniques (we currently use features of the ImageJ [9] and MRIcro [10] routines) to examine the spatial distributions of multiple components, they are a powerful way of determining the correlations in spatial location of components. The chemical organization revealed by the 3d STXM study can then be compared to that envisaged in the toner development process, or measured by other techniques. In this case, in some regions of the toner particle sampled, there is good coverage of wax component by encapsulant, while in others, there appear to be wax regions where the boundary has little or no encapsulant. This differs from that expected, indicating there is some redistribution of components in the mechanical processing of the toner. The latter adds texture and anisotropy to the internal structure, in addition to the observed component redistribution. All of these details are best revealed by 3-d chemical mapping. Such information is of considerable value to toner development specialists.



Figure 5 3-d maps of the wax (left) and encapsulant (right) components, at same viewing angles and scaling.

4. SUMMARY AND OUTLOOK

STXM of serial sections has been used to perform 3d chemical mapping at sub-micron spatial resolution. Relative to angle-scan tomography by TXM or STXM, this allows detailed analysis of samples whose density restrict the sample thickness to a small multiple of the spatial resolution. This demonstration measurement was relatively time consuming - about 10 hours of measurement and more than 100 hours of data analysis. However, an indexed optical microscope now allows rapid definition of the image region for each section which would reduce measurement time by 50%. Fiducial markers such as Au particles or wires in the epoxy would improve accuracy of image alignment which is the most tedious and time consuming part of the analysis. While much analytical information can be obtained from analysis of a single section, where 3-d information is needed, the serial section STXM technique is now available as a practical tool.

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