

## Mapping Very Similar Chemical Components in Micron-Scale Organic Rods by Scanning Transmission X-ray Microscopy

Noriyuki Iwata<sup>1,2,\*</sup>, Katsuhiko Tani<sup>1</sup>, Atsuyuki Watada<sup>1</sup>, Hiromi Ikeura-Sekiguchi<sup>3</sup>, Tohru Araki<sup>4</sup>, Adam P. Hitchcock<sup>4</sup>

<sup>1</sup>Ricoh Co. Ltd., 16-1 Shinnei-cho, Tsuzuki-ku, Yokohama, 224-0035, Japan

<sup>2</sup>Graduate School for Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

<sup>3</sup>Reserch Institute of Instrumentation Frontier, AIST, 1-1-1, Umezono, Tsukuba, Ibaraki, 305-8568, Japan

<sup>4</sup>Department of Chemistry, BIMR, McMaster University, Hamilton, Ontario L8S 4M1, Canada

We have used chemical component mapping with scanning transmission X-ray microscopy to distinguish two kinds of polyester with very similar NEXAFS spectra. NEXAFS spectra extracted from specific sub-micron regions of a micron-scale organic rod were examined to confirm the mapping by comparison to the NEXAFS spectra of the pure polyester materials. These results demonstrate the high capability of STXM to distinguish very similar chemical components at high spatial resolution.

**KEYWORDS:** scanning transmission X-ray microscopy, chemical component mapping, organic rod, polyester

### 1. Introduction

Micron-scale organic rods have attracted attention for use in optical devices, functional fiber, micro spacers and so on. The dispersion of component materials in the rod is closely related to the quality of a rod for a given application. Transmission electron microscopy (TEM) has been used to assist optimization of component dispersion<sup>1,2</sup>, but in many cases TEM images cannot distinguish the constituent polymer materials.

Scanning transmission X-ray microscopy (STXM)<sup>3-5</sup> is a powerful tool for analysis of organic materials because it provides two- and three-dimensional<sup>6</sup> chemical component mapping based on the near edge X-ray absorption fine structure (NEXAFS) spectra of the components. It is very interesting to test the capability of STXM to distinguish very similar organic components since subtle differences are often used to control material properties. This work reports a C 1s STXM study of micro organic rods constructed from two kinds of polyester, called polyester A and B. Their chemical structure is very similar, but the function of polyester A is to form the overall shape of the rod whereas rod B has a different role. Quantitative information about the overall composition and internal spatial distributions of components is very helpful in process development.

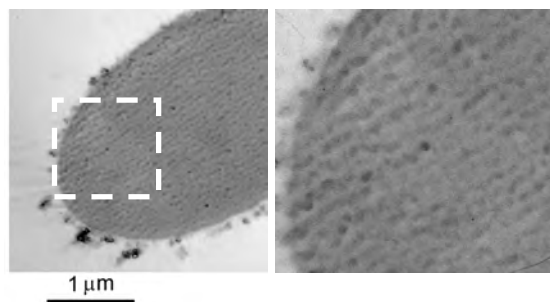
### 2. Experimental

The sample was an organic rod composed of only polyester A and B. To observe by TEM and STXM, the organic rod, pure polyester A and B were embedded in an epoxy resin and were sliced into sections by ultra-microtomy. The thickness of the section is 100 ~ 150 nm as estimated from the interference color of the sections. The sections were placed on 3 mm TEM Cu mesh grids. STXM measurements of the reference spectra of pure polyester A and B and observation of the section were performed with an

interferometrically-controlled STXM<sup>7</sup> at bend magnet beam line 5.3.2<sup>8</sup> at the Advanced Light Source in Berkeley. Measurements were performed with the sample in a helium atmosphere. Chemical component maps were derived from image sequences by using singular value decomposition analysis<sup>9,10</sup>, implemented in the 'aXis2000' program<sup>11</sup>. TEM measurements were performed with a JEOL 2010 TEM at 100 keV.

### 3. Results and Discussion

Fig. 1 shows a bright field TEM image of a section of the organic rod. The dark shape is a section of a part of this rod. Though the section was stained by the vapor of 5% RuO<sub>4</sub> solution, there is no contrast inside the dark shape associated with the two kinds of polyester A and B. The many parallel wavy lines in the TEM image are a sectioning artifact. Because polyester A and B have very similar chemical structures and electron densities, they cannot be distinguished by TEM, even by using chemically-modified sections.



**Fig. 1** TEM image of rod sample stained with RuO<sub>4</sub> vapor. The right image is magnified in the white frame in the left image.

The C 1s NEXAFS reference spectra of pure polyester A and B are shown in Fig. 2. Pure polyester A and B have very similar spectra but there is some difference in the energy region between 288 and 291 eV, where C 1s → π\*<sub>C-O</sub> transitions occur. By acquiring image sequences with a fine energy step in this energy region it should be possible

\*Corresponding author, N. Iwata  
E-mail address: iwata@rdc.ricoh.co.jp

to differentiate and thus map these two species in the organic rod. For the image sequence, the energy regions from 283.4 to 286.3 eV ( $C\ 1s \rightarrow \pi^*_{C=C}$  transitions) and from 288.6 to 291.4 eV ( $C\ 1s \rightarrow \pi^*_{C=O}$  transitions) were acquired with 0.15 eV energy steps, while the other regions in the overall range of 282.0 to 300 eV were acquired at 0.3 eV step spacing. In order to minimize X-ray damage, the dwell time at each energy step was 0.8 msec per 50 nm pixel. It took one hour to measure the C 1s image sequence of a  $5.1 \times 4\ \mu\text{m}$  area with these parameters.

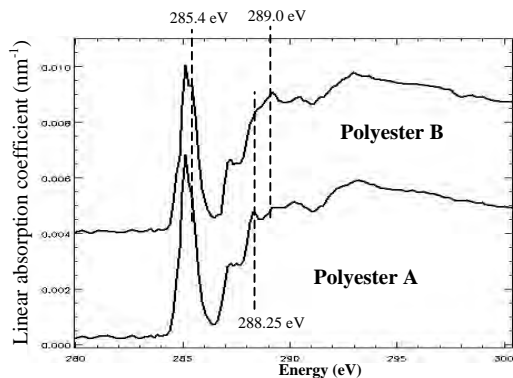


Fig. 2 Reference C 1s spectra of polyester A and B

The presence of two different polyester resin species in this rod is not evident just from examination of individual optical density images. Fig. 3 shows optical density images at 285.39 and 288.25 eV. Though there are slight differences in the NEXAFS spectra of the two species at these energies (see Fig.2), a difference of contrast can not be found in these images.

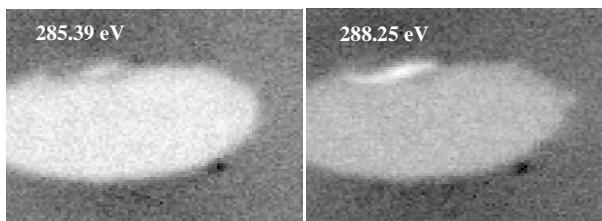


Fig. 3 Optical density images at 285.39 and 288.25 eV.

Fig. 4 shows the chemical component maps of the two resin materials derived from SVD analysis of the C 1s image sequence of this sample. The bullet shape in the maps is the rod section and the epoxy resin is outside this shape. The bright structure at the up side of the bullet shape in the maps of polyester A and epoxy is an artifact. The maps of polyester A and B show a fine dispersion inside the rod and nothing outside the rod. Polyester A is segregated in regions of a few hundred nm size (Fig. 4). The information about the domain size of polyester A is very important information with regard to optimization of the organic rod.

Fig. 5 identifies pixels with high values of polyester A and B as determined by threshold masking the component maps. Fig. 6 displays the C 1s spectra extracted from each set of pixels. The pixels where each polyester component map indicates high content have different C 1s spectra. In particular there is a little stronger intensity of the 285.4 and

289.0 eV peaks in the spectrum of the polyester B rich than for the polyester A rich regions, while there is a shoulder at 288.25 eV for the polyester A rich region that is not seen in the polyester B rich region. Comparison to the reference spectra of the pure materials (Fig. 2) confirms these features correspond to the expected differences in the spectra of polyester A and B. Therefore we conclude that chemical mapping based on a STXM C 1s image sequence distinguishes polyester A and B. Two important factors in achieving this result are careful selection of step spacing in the energy regions where the species have different spectra, and use of laser interferometry<sup>7)</sup> to control the area imaged and thus ensure the drift in spatial scale through the image sequence is less than the spatial resolution.

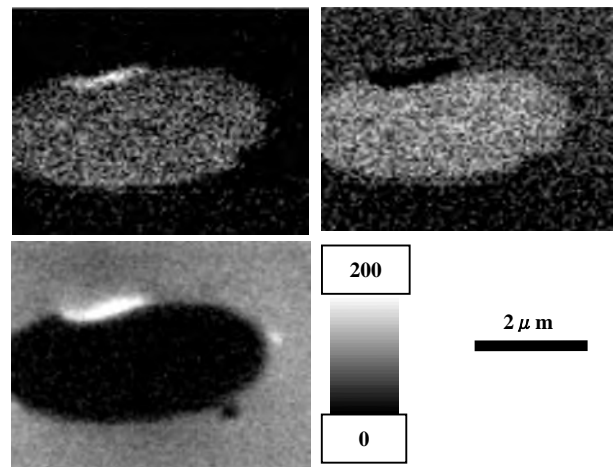


Fig. 4 Component maps of polyester A (upper left), B (upper right) and epoxy (lower left). The grayscale of each map indicates thickness in nm.

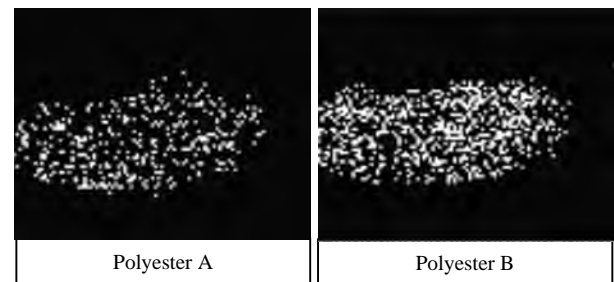


Fig. 5 Selected high-value pixels of polyester A (left) and B (right) derived by threshold masking the maps in Fig.4.

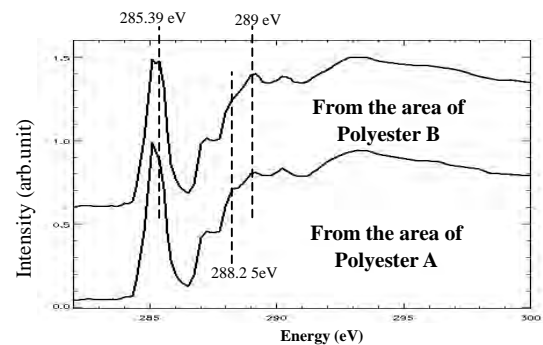


Fig. 6 Spectra extracted from the image sequence at high-value pixels of the chemical component map of polyester A and B.

#### 4. Conclusion

Chemical component mapping of an organic rod that consists of two kinds of polyester with only subtle chemical differences was successfully achieved using STXM image sequence measurements in the C 1s region. By selecting suitable measurement conditions based on differences of accurately measured reference spectra, it is possible to map very similar chemical components. Observation with STXM is a very useful tool for visualizing, and thus helping to optimize, the dispersion of resins in organic rods developed for specific applications.

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