Application of Scanning Transmission X-ray microscopy for observation of organic compounds in toner particles

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Abstract

Toners for copy machines, printers, etc. are constructed of several kinds of resin, pigment, wax and other components. Transmission electron microscopy (TEM) has been used to study the dispersion of components in toners, but TEM imaging cannot easily distinguish various kinds of materials in toners. Scanning Transmission X-ray Microscopy (STXM) is a synchrotron-based analytical microscopy that uses carbon 1s near edge X-ray absorption fine structure (NEXAFS) to identify organic compounds at sub-50 nm spatial resolution. The observation of toner particles and organic compounds was carried out by a STXM at the Advanced Light Source (ALS) in Berkeley, CA, U.S.A. Although staining methods made the TEM observation of wax possible, carbon black could not be observed simultaneously, STXM provides simultaneous observation of both species. Furthermore STXM can distinguish chemical components that have very similar NEXAFS and provide information on the dispersion of pigments by selected X-ray energy imaging. These results demonstrate the high capability of STXM to investigate the dispersion of organic compounds, thus aiding efforts for developing new, well-controlled toner.

Introduction

Toner particles have been produced by the pulverization method conventionally, but recently, synthesis methods to form toner particles have been developed and are now an established technology [1]. This brings to toner design more possibilities for controlling functions such as printing resolution, fixing temperature, color and so on. These functions are dependent on the nature and distributions of components in toner particles such as resin, wax, pigment, etc. Therefore it is very important for the design of well-controlled toner to know the distribution of components in toner particles.

Transmission electron microscopy (TEM) has been used to study the dispersion of components in toners [2,3], but, without extensive selective staining of the specimen, TEM imaging cannot easily distinguish various kinds of materials in toner particles.

Scanning transmission X-ray microscopy (STXM) [4-6] is a powerful tool for analysis of organic materials because it provides two- and three-dimensional [6] chemical component mapping based on the near edge X-ray absorption fine structure (NEXAFS) spectra of the components.

The aim of this study is to use STXM to discriminate various materials important in the rational design of toner and to show the advantages of STXM relative to TEM in this application.

Experimental

The samples 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 materials and observation of the section were performed with an interferometrically-controlled STXM [7] at bend magnet beam line 5.3.2 [8] 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 [9,10], implemented in the 'aXis2000' program [11]. TEM measurements were performed with a JEOL 2010 TEM at 100 keV.

Results and discussion

1. Simultaneus Observation of Wax, Resin and Carbon Black in Toners [12]

Fig. 1 shows TEM images of a section stained by RuO_4. White contrast can be observed on the right hand side of the toner particle and at the center in the magnified image. Because the straight chain hydrocarbons in wax are relativity inert to reaction with RuO_4 [13], the wax presents more white contrast than the resin in the toner. Therefore it is possible to observe the wax in the toner by staining. Though there are carbon black particles in this toner, they cannot be seen in Fig.1, since the resin stained by RuO_4 is darker than the carbon black particles.
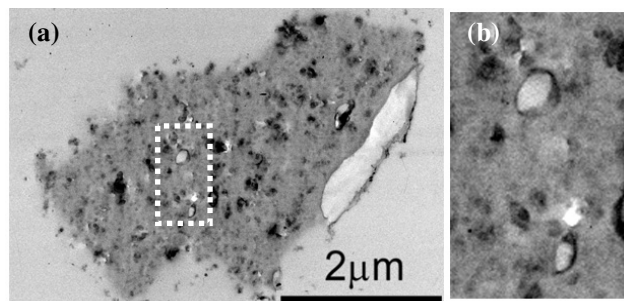

Fig.1 TEM image of pulverized toner stained with RuO_4 vapor.

The C 1s NEXAFS spectra of the wax, toner resin and carbon black are shown in Fig. 2. The spectra, originally recorded in transmission mode from pure materials, have been converted to absorbance (Beer-Lambert Law) and then placed on an absolute linear absorption scale by matching the signal below 280 eV and above 320 eV (extended range spectra are not shown) to the

response expected for a material with the known elemental composition and density of each component, based on weighted sums of tabulated X-ray absorption coefficients of the elements [14]. In the 282 – 292 eV region these spectra are very different, providing the basis for high contrast differentiation of the chemical components. The spectrum of the resin has a sharp, high intensity peak at 285 eV corresponding to the C 1s → $\pi*_{C=C}$ transition at the phenyl rings of the aromatic resin species, that of carbon black shows a much broader $\pi*$ peak stretching from 284 to 286 eV, which is associated with a broad range of graphitic environments in the 50 nm particles, while that of the aliphatic wax has very little signal at 285 eV (which may be associated with a small amount of nature ingredients in wax) but instead, shows a strong, broad peak at 287.7 eV associated with C 1s → C-H transitions. All three species have more complex spectral structure above 290 eV, which is associated with a range of transitions to the various types of $\sigma*$ orbitals in each species. While the shape at higher energy can assist in chemical identification, the range from 282 to 292 eV was found to be best for differentiating the majority species in toners by STXM image sequences.
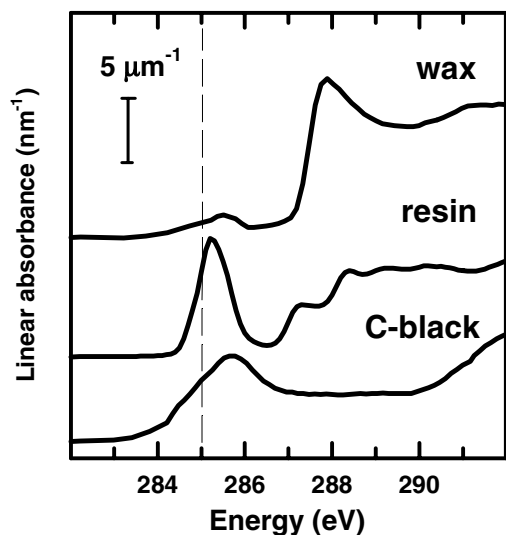

Fig. 3 (a) STXM transmission image at 285 eV. of a section of a whole toner particle.

Fig. 2 Reference C 1s spectra of wax, toner binder resin and carbon black placed on an absolute liner absorbance scale.

Fig. 3(a) shows the STXM transmission image at 285 eV of a section of a toner. At this energy the resin absorbs strongly, the carbon black particles absorb relatively weakly, and the wax has negligible absorption. Fig. 3(b) presents quantitative maps of the carbon black, wax and resin components in the area surrounded by the dotted line in Fig 3(a). These component maps were obtained by SVD analysis of a sequence of 40 images between 282 and 292 eV, using the energies specified in the experimental section. Comparing the STXM transmission image with the component maps, the round shape with white contrast in the image corresponds to the wax component. Fig. 3(b) shows that the carbon black particles are present in the resin but not in the wax. Therefore STXM provides simultaneous observation of the spatial distributions of wax, resin and carbon black in toners.
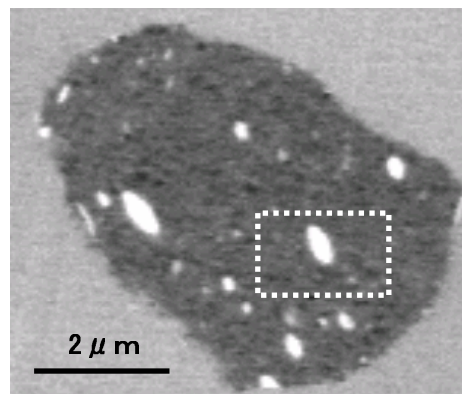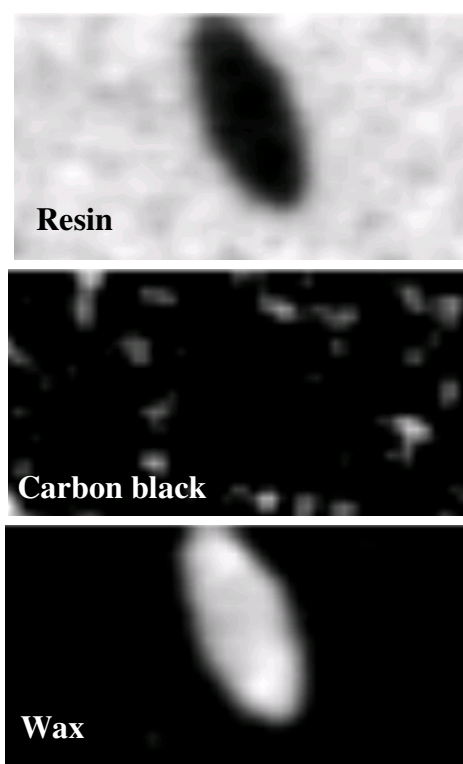

Fig. 3 (b) Chemical component maps of part of (a) indicated by dotted line, derived from SVD of a C 1s image sequence.

2. Discriminating Resins with Very Similar Chemical Structure

It is very interesting to test the capability of STXM to distinguish very similar organic components since a lot of kinds of resin are used to control toner properties. In this section we describe a STXM study of a sample composed of only polyester A and polyester B which have very similar chemical structure.

The C 1s NEXAFS spectra of pure polyester A and B are shown in Fig. 4. 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 → $\pi*_{C=O}$ transitions occur. By acquiring image sequences with a fine energy step in this energy region it

should be possible to differentiate and thus map these two species in the sample. 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.
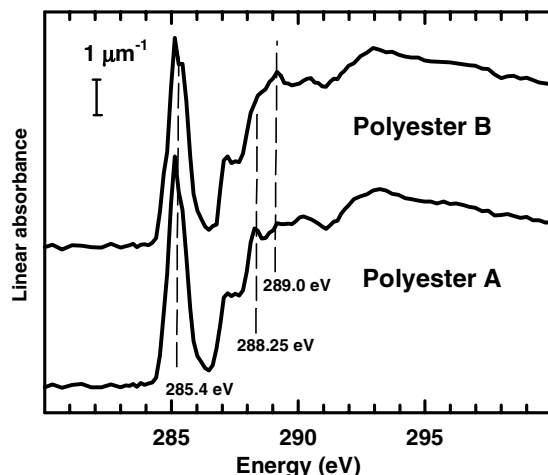

Fig.4 Reference C 1s spectra of polyester A and B

Fig. 5 shows the chemical component maps of the two resin materials derived from SVD analysis of the C 1s image sequence of this sample. The maps of polyester A and B show a fine dispersion. Polyester A is segregated in regions of a few hundred nm sizes (Fig. 5). The information about the domain size of polyester is very important with regard to optimization of the design.
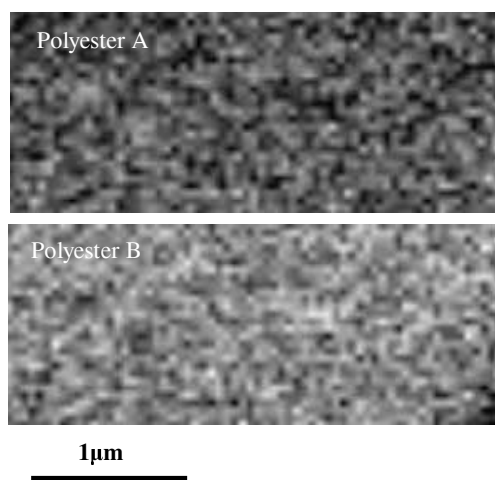

Fig.5 Chemical component maps of polyester A (up), B (down).

Fig. 6 identifies pixels with high values of polyester A and B as determined by threshold masking the component maps. Fig. 7 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. 4) confirms these features correspond to the expected differences in the spectra of polyester A and B. Therefore we conclude that chemical mapping by STXM C 1s image sequence distinguishes polyester A and B.
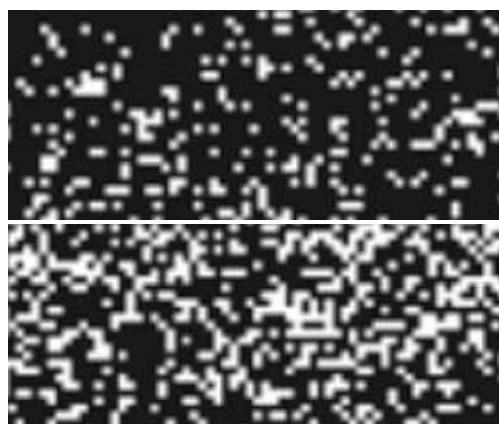

Fig.6 Selected high-value pixels of polyester A (up) and B (down) derived by threshold masking the maps in Fig.5.
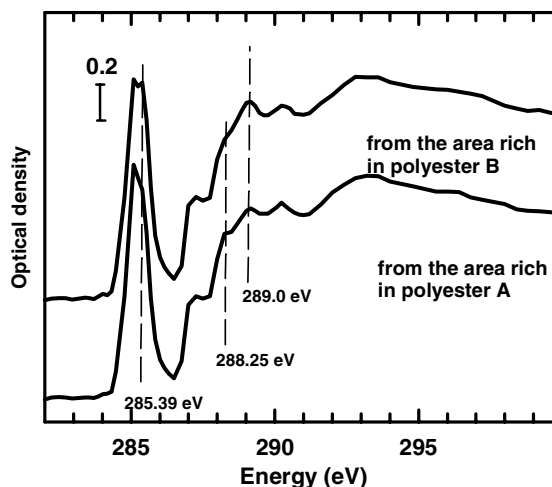

Fig.7 Spectra extracted from the image sequence at high-value pixels of the chemical component map of polyester A and B.

3.Optical Density Image of Pigment

The above examples show that, if there is a difference in the NEXAFS spectra of components, STXM can easily distinguish and quantitatively map them by obtaining optical density images in the energy region the spectra differ.

Pigments are necessary for color printing as components in toner particles. The observation of yellow pigments by TEM is more difficult than that of other pigments (cyan and magenta) because electron radiation damage easily modifies the chemical structure of yellow pigments which have special functional groups connected to phenyl rings to produce the yellow color. C 1s

NEXAFS spectra of a yellow pigment and polyester B are shown in Fig. 8. This yellow pigment has a characteristic absorption peak at 286.2 eV near the phenyl ring transition at 285 eV.
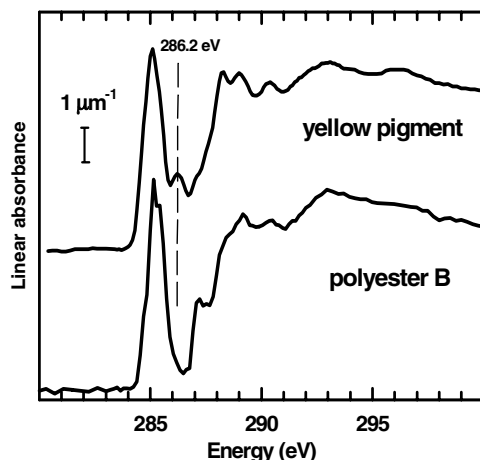

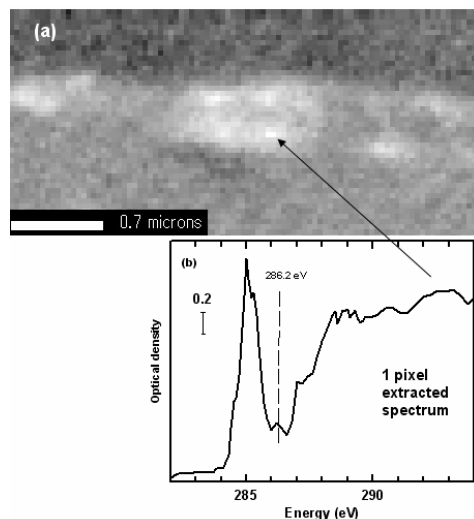Fig.8 Reference C 1s spectra of yellow pigment and Polyester B.

Fig.9 (a) Optical Density Image of the sample at 286.2eV, (b) Spectra extracted from the highest-value one pixel in the white contrast.

The sample was composed of only the yellow pigment and polyester B. Fig. 9(a) shows the optical density image of the sample at 286.2 eV. White contrast can be seen along the horizontal line in Fig. 9(a). The NEXAFS spectrum extracted from 1 pixel (shown with the arrow) in the white contrast is shown in Fig. 9(b). Although the NEXAFS spectrum of this pixel has features from both the yellow pigment and polyester B, it has a clear absorption peak at 286.2 eV. Curve fits to the spectra at each pixel then provide a means to map the pigment. For even lower radiation damage, selected energy images in the X-ray energy region near characteristic absorption peaks (e.g. 284-287 eV in this case) can be used to derive the dispersion of a pigment against a background of other components with rather similar spectra.

Summary

Although a lower spatial resolution microscopy (~50 nm in this work (20 nm is best achieved to date), versus <1 nm for

TEM), STXM not only provides simultaneous observation of the spatial distributions of wax, resin and carbon black in toners, but it also provides chemical component mapping of two kinds of polyester with only subtle chemical differences, and provides the dispersion of pigments by selected X-ray energy imaging. STXM is a very useful tool for toner development since it provides information about the spatial distribution of all components in toners.

Acknowledgements

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