

Experiment Brief

eaSI multipass *in-situ* spectrum imaging

Title

Phase mapping of dose-sensitive polymers using direct detection and multipass *in-situ* spectrum imaging

Gatan instruments used

GIF Continuum® K3®, eaSI technology, and model 626 Single-Tilt Liquid Nitrogen Cryo-Transfer Holder

Background

Extracting chemical and phase information at the nanometer scale is critical to understanding and enhancing the functional properties of polymer blends. However, organic materials, such as polycarbonate polymer blends, are susceptible to radiolysis, making them challenging to study using EELS spectrum imaging [1]. Due to the high sensitivity of direct detection sensors, the total dose needed to detect the features in the C K-edge ELNES is reduced, allowing scientists to extract information from organic materials at a higher resolution. Multipass *in-situ* spectrum imaging in DigitalMicrograph® fractionates the total dose over several individually saved passes, allowing the user to remove passes compromised by radiolysis. We demonstrate that phase information can be extracted at higher spatial resolutions from dose-sensitive polymer blends by combining direct detection and eaSI multipass *in-situ* spectrum imaging.

Materials and methods

A polymer blend of polycarbonate (PC) and 75:25% poly(styrene-acrylonitrile) (SAN) was used as a model system to study the increased sensitivity afforded by direct detection. The shape of the C K-edge near-edge fine structure is a projection of the local unoccupied density of states. It is used to study local changes in the carbon's bonding characteristics. To study the changes in near-edge fine structure with accumulated dose, multipass *in-situ* spectrum imaging was used. This allows researchers to monitor changes in the shape of the C K-edge ELNES with total dose. Figure 1a and b shows the changes in the C K-edge ELNES acquired from the SAN and PC phases, respectively, as a function of the total dose. Changes in the C K-edge ELNES extracted from the SAN phase are subtle as the dose increases. The largest change is observed in peak a, where the intensity decreases with increasing dose (Figure 1a). Several noticeable changes are observed in the C K-edge ELNES acquired from the PC phase. ELNES peaks a and c are observed to decrease in intensity with increasing dose, while peak b increases in intensity (Figure 1b). Due to changes observed in the C K-edge fine structure, only the first two passes were kept. Using internal references for the C K-edge ELNES extracted from the PC and SAN phases, the DigitalMicrograph software quantification tool pallet was used to map the spatial distribution of PC and SAN phases within the selected region (Figure 1c). Since we observe changes in the C K ELNES above 1000 e⁻/nm², a larger area map was acquired at a total dose of 828 e⁻/nm² (Figure 2b). Several smaller PC inclusions are observed in the SAN matrix, and the morphology of the larger inclusions is observable.

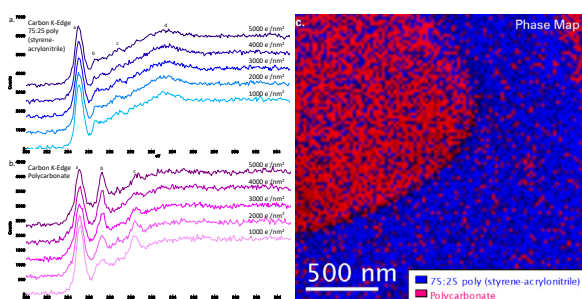


Figure 1. Carbon K-edges from the (a) SAN and (b) Polycarbonate in the mixed polymer blend acquired at different total doses. (c) Phase map generated using internal ELNES standards extracted at a total dose of 1000 e⁻/nm².

Summary

The distribution of the PC and SAN phases is observed in Figures 1c and 2b. A significant improvement in spatial resolution, from 25 nm/pix to 20 nm/pix, is achieved in the phase maps while requiring ~1/10th of the dose compared to a previous study that used an optically coupled CCD camera [1]. eaSI multipass *in-situ* spectrum imaging enables dose fractionation during data acquisition on beam-sensitive materials. Integrating the high-performance optics of the Continuum with the high DQE of the K3 camera gives the ability to generate elemental maps at a sufficiently low dose to preserve the spectral features in the C K-edge ELNES. This, combined with Gatan cryo-holders, will allow researchers to push the acquisition of EELS to other dose-sensitive materials previously thought impossible to analyze.

Credit(s)

Thanks to Robert Colby at ExxonMobil Technology and Engineering Company for sharing the samples, data, and feedback.

[1] Colby R. et al., Ultramicroscopy 246 (2023) 113688

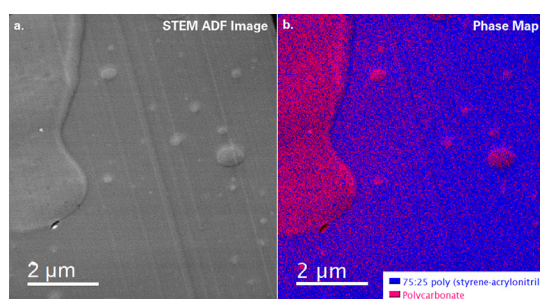


Figure 2. (a) ADF STEM image of the polymer blend. (b) Phase map generated by using ELNES standards from the C K-edge.