

Chemical Bonding State Analysis with High Energy-resolution Carbon K-Emission Spectrum of Soft Materials Obtained by Soft X-ray Emission Spectrometer

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A soft X-ray emission spectrometer (SXES) is an analysis instrument that can be attached to a commercially scanning electron microscope (SEM) or electron probe microanalyzer (EPMA) to measure the lower energy X-ray emission spectrum from the micrometer region of a sample with high energy-resolution [1]. This emission spectrum in the soft X-ray region of about 1 keV or less is a signal mainly based on the electron transition from the valence band and the vicinity of the valence band to the core-level of the sample, and is available to measure the chemical bonding state in the sample. As for soft materials such as polymers, there are many requests to analyze the chemical bonding state of small regions, whereas in such specimens, the sample damage due to electron beam irradiation is severely large, the obtained spectrum may have been deformed, and the original chemical bonding state of the sample may not have been obtained.

In this study, we investigated the measurement conditions for obtaining a reliable, and low-damaged emission spectrum using a hydrocarbon-based polymer sample [2]. It was found that the C K-emission spectrum of the polymer obtained under appropriate analytical conditions shows a spectral shape enough to distinguish between different polymer samples. These measured spectra were also compared with the density of states (DOS) obtained by quantum chemistry calculations.

Figure 1 shows a schematic view of a soft X-ray emission spectrometer. Using a varied line-spacing (VLS) grating, it is possible to detect an emission spectrum from 50 eV to several hundred eV at a fixed position without scanning the grating and perform parallel detection with a CCD detector. Next, the optimum conditions of polymer analysis were examined. As the sample, polystyrene, which has lower thermal conductivity among hydrocarbon polymers was used. Accelerating voltage was 5 kV, probe current was 10 nA, and the probe diameter was changed from 5 to 50 μm , and 2nd order C K-emission spectrum obtained by the JS200N grating was measured (Fig. 2). The spectral shape obtained with a probe diameter of 50 μm , which might be considered to be a low-damage analysis, shows the characteristic peak due to sp^2 - π bonding [3], which is characteristic of polymers containing a benzene ring, is found. It can be seen that the signal decreases relatively as the probe diameter is reduced. This seems to indicate that the sample damage caused by the electron beam irradiation. From this experiment, it is necessary to enlarge the probe diameter to at least 50 μm or more for samples as polymers.

Figure 3 shows the comparison between measured C K spectra of polyethylene, polypropylene, and polystyrene obtained under low-damage measurement conditions, and calculated LDOS (local DOS) obtained by quantum chemistry calculations [4] of carbon part of ethylene, propylene, and styrene. When the 2nd order C K measured spectrum is converted to the 1st order energy and the peak top of measured polyethylene is aligned with the calculated LDOS peak top of ethylene, the peak on the high energy side of polystyrene with a benzene ring matches well with LDOS of styrene. In addition, the peak top of polyethylene (sp^3 - σ) is located on the higher energy side than the peak top of polystyrene (dominated sp^2 - σ). The measured spectra and the calculated LDOS matched relatively well.

In summary, it was shown that the C K-emission spectrum of the polymer sample measured by carefully reducing the sample damage with SXES has a high energy resolution capable of distinguishing the difference between the polymer materials.

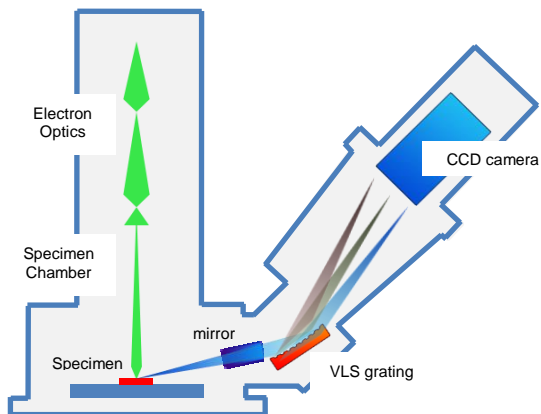


Figure 1. Schematic view of soft X-ray analysis.

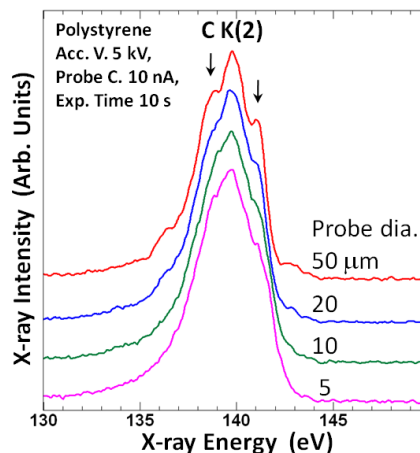


Figure 2. Changes in C K(2) spectrum of polystyrene when the probe diameter is varied.

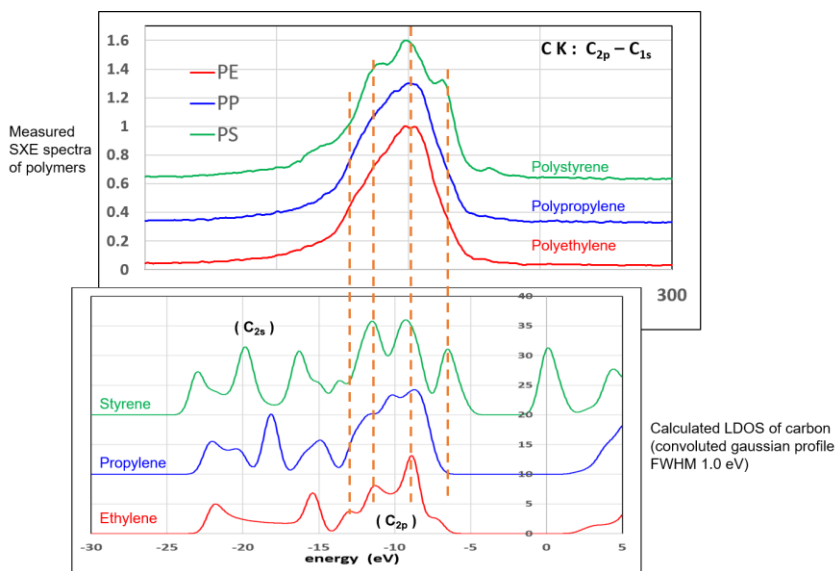


Figure 3. Spectral comparison among hydro-carbon polymers.

References:

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