

Parallel Electron Energy Loss Spectroscopy of Highly Irradiated PVC

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Abstract

Highly irradiated PVC samples were analyzed by EELS in transmission mode using in a Philips CM-200 Transmission Electron Microscope equipped with a Gatan - 766 PEELS spectrometer. A primary energy of 200 KeV was used and the average time for a single run was about 15 minutes. The analysis was focused to the carbon K-edge by measuring the chemical shift of the π^* and σ^* in the energy loss spectrum. Also the identification of the π and $\pi+\sigma$ plasmons were done. The results were compared with those known for clean HOPG surface (0001), amorphous carbon surface and a diamond thin film grown by Hot Filament Chemical Vapor Deposition (HFCVD)..

Keywords: Electron Energy Loss Spectroscopy, HR-TEM

Introduction

With the availability of synchrotron radiation sources for materials science application, a powerful technique evolved for the study of the local structure of a wide variety of materials. This technique focuses on the fine structure found in the vicinity of sharp x-ray absorption edges and is known as EXAFS (Extended X-ray Absorption Fine Structure). (1) A similar process occurs when electrons interact with the surface of a given material. The incident particle may loose a discrete amount of energy by the ionization of a core level corresponding to atoms near the surface. In the vicinity of the ionization threshold, a fine structure has been found to have the same physical significance as that found in EXAFS. In this case, the techniques is called Extended Electron Energy Loss Fine Structure Spectroscopy (EXEELFS) in both transmission and reflection modes. This technique has been applied to the study of local structure of crystalline surfaces, (2-5) polycrystalline systems (6) and due to the strong electron solid interaction, EXEELFS has been used to study adsorbates, (7-10) clusters (11) and thin films. (12) In the reflection mode, these experiments have been performed in commercial surface spectroscopy systems equipped with an electron spectrometer, typically a CMA (cylindrical mirror analyzer). In most of these experiments, the incident electron energy used is between 500 and 3000 eV.

The main objective of this paper is to show the possibility to identify structural changes in the HI-PVC samples by analyzing the energy loss spectrum.

Experimental

The PEELS experiments were performed in a Philips CM-200 Transmission Electron Microscope equipped with a Gatan - 766 PEELS spectrometer. The samples were electron highly irradiated poly(vinyl chloride), HI-PVC, (5,000, 10,000 and 15, 000 Mrads). The raw data was collected in the standard electron energy loss spectroscopy mode, in a range of 0 to 100 eV for the low loss region and 100 eV beyond the carbon K-edge ionization energy for the near edge analysis, which corresponds to an energy loss of 283.8 eV with respect to the elastic peak. A primary energy of 200 KeV was used and a typical run for a single spectrum took 15 minutes. Detailed sample preparation were published elsewhere for the authors in reference (10) for diamond sample and reference (26) for HI-PVC

Results and discussion

Figure 1 shows the PEELS spectra in the low loss region for the HI-PVC at different doses. As we can see, the most prominent plasmon loss peaks, $(\pi + \sigma)$ are located at an energy loss of 21.9 ± 0.1 eV, 22.1 ± 0.1 eV and 22.1 ± 0.1 eV for 5,000, 10, 000 and 15, 000 Mrads respectively. These numbers differs slightly with the respective values for the $(\pi + \sigma)$ of amorphous carbon, $E_p = 23$ eV, HOPG, $E_p = 26$ eV and diamond, $E_p = 36$ eV (table 1) characterizing the diamond film are located at the same energy loss for natural diamond (33 eV),

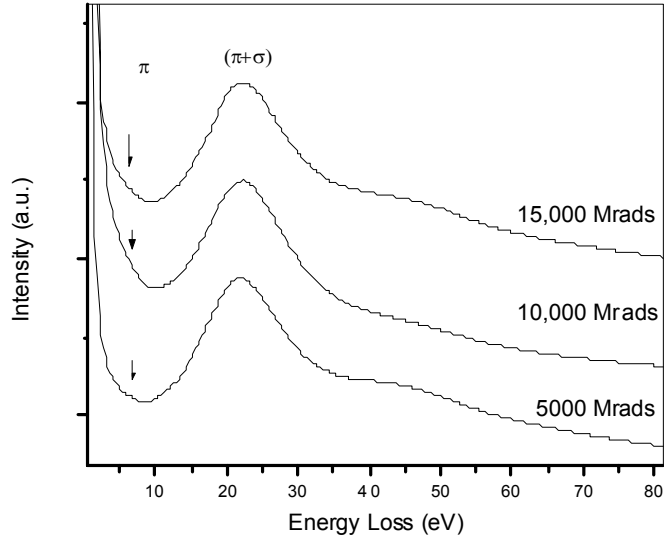


Figure 1. Plasmon window of HI-PVC samples

Figure 2 shows the main features of the electron energy loss spectra near the carbon K-edge for the same HI-PVC samples. These spectra are shown after background subtraction. It is well known that amorphous carbon and HOPG have basically the same edge shapes which may be explained in terms of similarities in their bonding, particularly the σ^* and π^* transition are clearly present as expected. In the diamond case, the lack of the π^* transition indicates the no presence of carbon layers in the sample. Thus, through these spectra one may distinguish among different structures formed by carbon atoms. Similar results have been reported for graphite and natural diamond. (17,18) The near edge structure is so different among these three forms of carbon that EELS spectra should suffice as a fingerprint for the identification of these structures. At first glance the PEELS spectra of these materials show a resemblance to amorphous carbon even though at a microscopic level, the irradiated polymer shows a very well defined crystallographic structure and a chemical composition just of carbon.

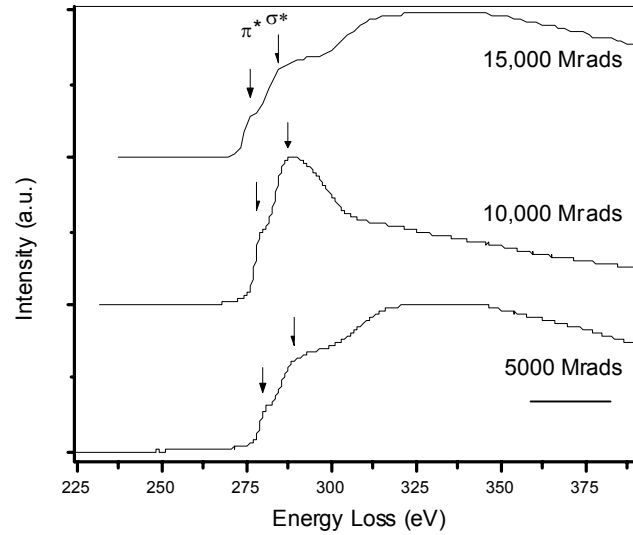


Figure 2. Energy Loss Near Edge window of HI-PVC samples

We clearly note the similarities at the near edge structure among the HI-PVC spectra. around the π^* and σ^* transitions. In these spectra we appreciate an energy shift in the antibonding shapes which indicate chemical shift and different density of states among the HI-PVC structures. Table 2 shows the values for the π^* and σ^* transitions for holey carbon and HI-PVC samples.

Figure 3 displays a TEM micrographs from each HI-PVC sample taken at different magnifications. As we can see the particles have sizes around 150 nm indicating that the degradation process also involve a reduction of the particle size.

Table 1. Numerical values of the π and $\pi+\sigma$ plasmon energies

SAMPLE	π	$\pi+\sigma$
Amorphous carbon	6.4	23
HOPG	6.7	26
Diamond		36
HI-PVC 5000 Mrads	6.6 ± 0.1	21.9 ± 0.1
HI-PVC 10000 Mrads	6.4 ± 0.1	22.1 ± 0.1
HI-PVC 15000 Mradds	6.2 ± 0.1	22.1 ± 0.1

Tables 2. Numerical values for the π^* and σ^*

SAMPLE	π^*	σ^*
Amorphous carbon	284	291
HOPG	284	291
Diamond		290
HI-PVC 5000 Mrads	280 ± 0.1	286 ± 0.1
HI-PVC 10000 Mrads	279 ± 0.1	289 ± 0.1
HI-PVC 15000 Mradds	277 ± 0.1	292 ± 0.1

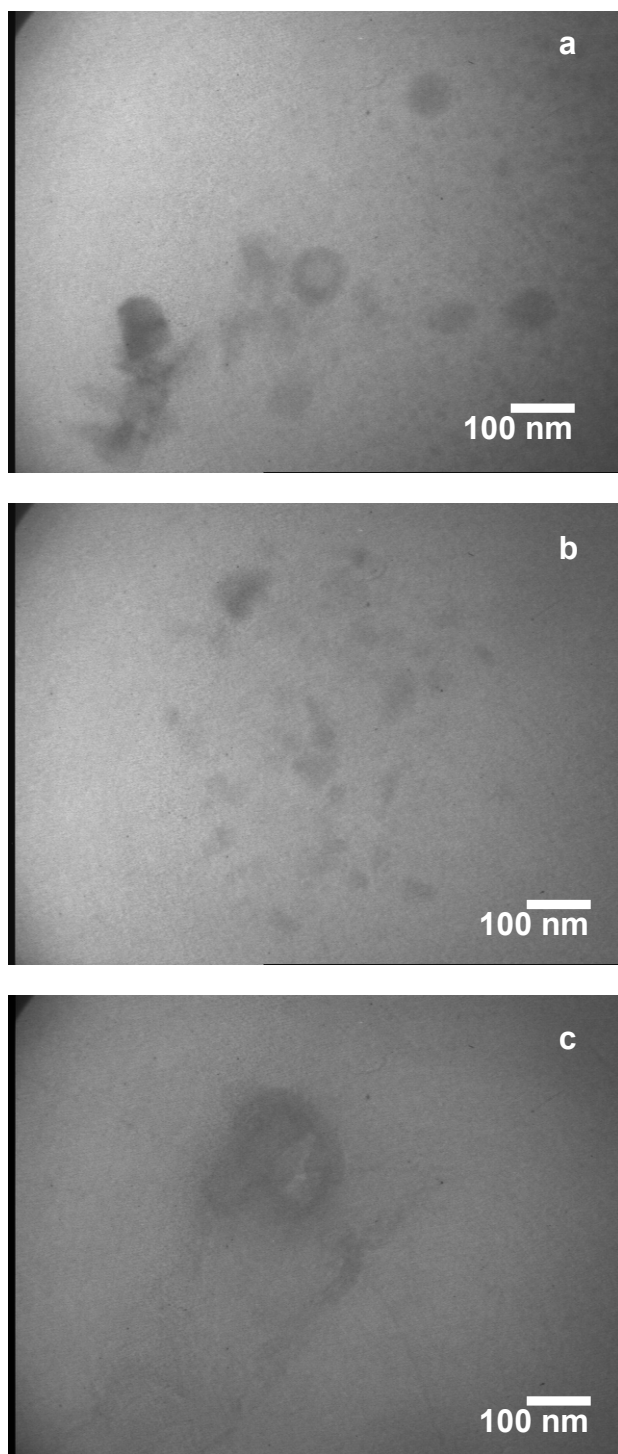


Figure 3. TEM micrographs of a) HI-PVC 5, 000 Mrads, (b) HI-PVC 10, 000 Mrads and (c) HI-PVC 15, 000 Mrads.

Conclusions

Through a careful analysis of energy loss spectra in Figures 1 and 2, and analyzing the values obtained for the antibonding transitions for carbon element, we have demonstrated the structural changes occurred in the PVC after the radiation process.

Furthermore, the presence of chemical shifts in HI-PVC, help to ensure the strong structural changes and the lack of any more elements in its compound. The surface sensitivity of the electrons render EELS a competitive technique, specially in systems where the size of the particles is very small (local order), even complex systems like quasicrystalline alloys.

Finally with a systematic study of HI-PVC at different electron radiation doses, we have obtained a finger print of each ones allowing the possibility to distinguish different structures formed by carbon atoms in samples with a spatial resolution much less than 1 μm (transmission mode).

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