Silicon distribution in biocompatible and cross-linked organic-inorganic hybrid nanocomposites.

da Silva, L.[1], Plivelic, T.S.[2] and Gonçalves, M.C.[1]

[1] Institute of Chemistry, University of Campinas (UNICAMP), P. O. Box 6154, Campinas, SP 13083-970, Brazil, [2] MAX IV Laboratory - Lund University, Sweden

Organic-inorganic (O-I) hybrids emerged in the flexible electronic industry. With the recent findings that Si atom is beneficial to a number of biological processes, a new emerging market for the O-I hybrids arose. However, for biomedical applications a thorough knowledge of the material nanostructure is key. In this context, ternary O-I hybrid materials having the organic moiety composed of both poly(ε-caprolactone) (PCL) and poly(ethylene glycol) (PEG) and the cross-linking inorganic moiety composed of silsesquioxane (SS) were chosen as subject of study due to their well-known properties which are of interest to the biomedical field: PEG contributes to the hydrophilicity of the device, while PCL, that is hydrophobic, contributes not only to device flexibility and cell adhesion but may also provide biodegradation ability. The O-I hybrid nanocomposites investigated herein were synthesised using a solvent-free and atoxic pathway. Transmission electron microscopy (TEM), energy-loss spectroscopy (EELS) and X-ray scattering correlation were used to investigate the morphology and nanostructure of these ternary hybrid nanocomposites.

Figure 1 shows the TEM micrographs of ultrathin sections of an amorphous and a crystalline ternary O-I hybrid with a 1 PCL/PEG weight ratio. Amorphous PCL_{24}-PEG_{24}/SS_{52} and Crystalline PCL_{39}-PEG_{39}/SS_{22} differ only on the organic precursors molecular weight. PCL_{24}-PEG_{24}/SS_{52} (A) shows a homogeneous matrix in which dark spherical domains are uniformly dispersed. PCL_{39}-PEG_{39}/SS_{22} (B) shows phase separation. Phases might be assigned to PCL/SS (D) and PEG/SS (C) due to the morphology of the binary O-I hybrids. Silsesquioxane occurrence on both phases of the PCL_{39}-PEG_{39}/SS_{22} O-I hybrid confirms that phase separation is due to the organic precursors immiscibility.

Figure 2 shows the EELS spectra taken at the region from which the ESI-TEM images (G,H), shown in Figure 1, were obtained. Both the amorphous (left) and the crystalline (right) O-I hybrid EELS spectra have clear and well-defined Si and C edges, indicating that both organic and inorganic moieties occur within the imaged area. An interesting aspect of the PCL_{24}-PEG_{24}/SS_{52} sample is the occurrence of a sharp Si L_1-edge at 155 eV, which shows that within the investigated region, at least a fraction of the Si atoms is bonded to an oxygen atom in a silica-like environment. In the PCL_{24}-PEG_{24}/SS_{52} spectra the Si L_1-edge is not resolved. Further EELS spectra were taken from PCL_{39}-PEG_{39}/SS_{22}. EELS spectra are colour coded to aid correspondence. The red spectrum was taken from the bright matrix, while the orange spectrum was taken from the dark domains. Si $L_{2,3}$-edge is clearly observed in both regions. C, N and O K-edges are also observed in both regions, while the S K-edge is only verified in the dark domains. Moreover, the Si L_1-edge is only observed in the brighter matrix, indicating that $(SiO_{1.5})_n$ rings and cages are present at the continuous bright matrix. These results point out to the conclusion that, on the contrary of what is commonly reported based on X-ray scattering results, both amorphous and crystalline O-I hybrids show two distinct silsesquioxane structures, one located in the matrix and another located in the dark domains.

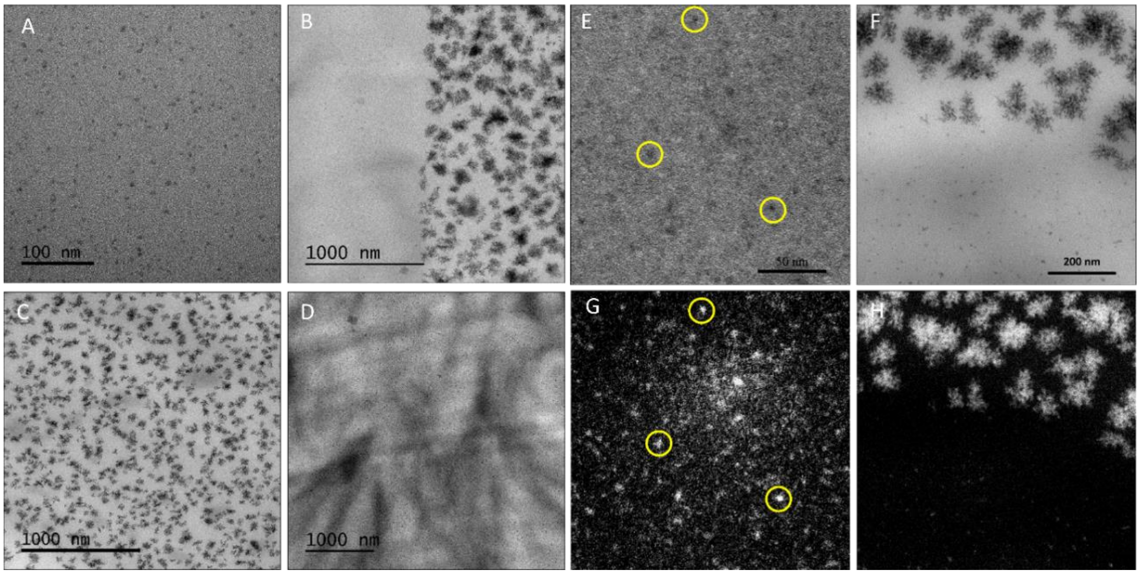

Figure 1 - TEM micrographs of the PCL24 - PEG24/SS52 (A), PCL39 - PEG39/SS22 (B) PEG75/SS25 (C) and the PCL80/SS20 (D) samples. Bright field TEM micrographs (E,F) and the corresponding silicon atom distribution (G,H) of the PCL24 - PEG24/SS52 (E,G) and the PCL39 - PEG39/SS22 (F,H) O-I hybrid nanocomposites.

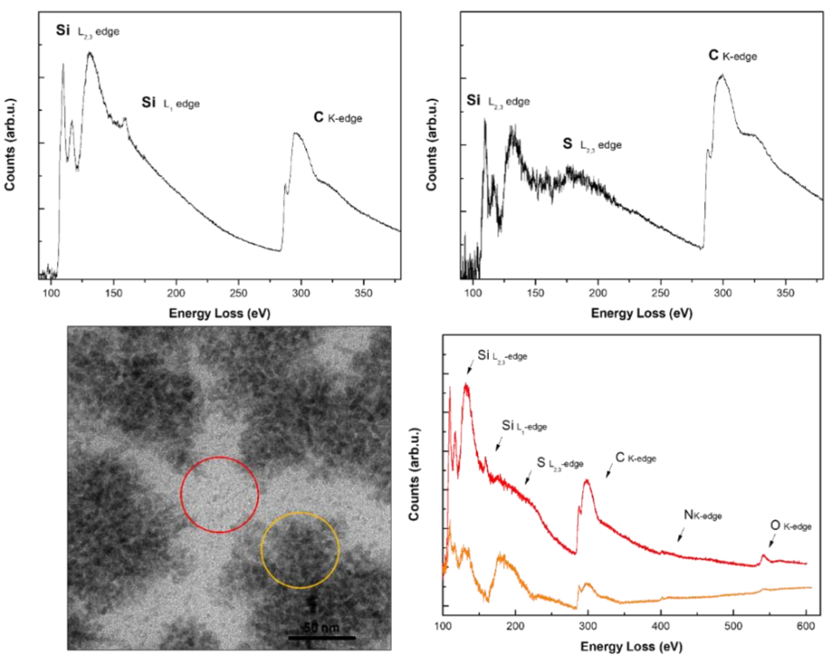

Figure 2 - Electron energy-loss spectra of the PCL24 - PEG24/SS52 (top left) and the PCL39 - PEG39/SS22 (top right) samples. Bright field TEM micrograph of the PCL39-PEG39/SS22 at the PEG/SS domain and its respective electron energy-loss spectra. Colour coded spectra correspond to the highlighted areas in the TEM.