TEM and SEM tomography of polymer-based nanocomposites re-inforced by carbon nanotubes

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Keywords: Polymer nanocomposites, electron tomography, carbon nanotubes

Nanofillers of different nature and aspect ratio are usually added to polymer materials in order to modify, control and improve their physical, e.g. mechanical and electrical, properties. For this purpose, such polymer nanocomposites require 3D characterization at the nanometer scale, which can be performed using electron tomography.

In the present study, electron tomography is applied to a polystyrene co-butyl acrylate matrix (P(S-BuA)) filled with multi-wall carbon nanotubes (CNTs) [1]. In a previous study [2], it was shown that similar materials elaborated under different synthesis conditions, but having identical populations of CNTs (i.e., mean size and volume fraction) exhibit different properties: as a stringent example, the electrical conductivity has been shown to strongly depend on the fraction of filler-filler contacts which may insure electrical percolation. Attempts to measure such interactions require a quantitative 3D analysis at the nanometric level. For that purpose, both TEM and SEM tomographic approaches were performed on ultramicrotomic sections of thicknesses typically ranging between 200 and 500 nm. Reconstructions were performed using the GPU SIRT algorithm from Gatan Inc (www.gatan.com).

'Low voltage' EFTEM (Energy Filtered Transmission Electron Microscopy) was performed at 80keV in a FEI TITAN C_s-corrected instrument equipped with a Gatan Imaging Filter (GIF). We intentionally choose this microscope under these conditions for several reasons: 1) polymers are very beam sensitive and easily damaged under the incident electron beam during electron microscopy work. This damage essentially consists in shrinkage [3] and is worse in tomography experiments since a large number of images are acquired on the same area. Imaging at a low voltage is expected to reduce this shrinkage damage. 2) Both the polymer matrix and the CNTs are composed of light chemical species, and preliminary HAADF experiments show that the contrast is too low to allow optimal 3D reconstruction; thus, EFTEM imaging has been preferred. 3) at 80keV the projected thickness of the sample (ultramicrotomic section of 200 nm) is by far too large at large tilt to allow reasonable imaging in conventional TEM (or STEM), and zero-loss filtered imaging is required under these conditions. Tomography acquisition was performed from -62° to +62° with a tilt step of 2°; different strategies were applied to enhance the contrast at high angles by duplicating images at different defocus and 'mixing' these series during the reconstruction process in order to generate the 'best' volume (Figure 1a).

Tomography in the SEM was performed at 30 keV in a Hitachi S-5500 cold-FEG microscope. Tilted projections between -40 and +40° were recorded in the transmission mode, using a dark field detector located below the sample, as already performed using a home-made montage [4]. Figure 1b) shows a typical reconstruction of the same material shown in Figure 1a).

The quantification of the fraction of contacts between CNTs was performed in two different sets of samples elaborated either via an evaporating or a freeze-drying route [1]. The following numerical procedure, illustrated by Figure 2, was developed: individual nanotubes were identified on segmented tomograms, and further approximated by perfect geometrical cylinders, on which contact areas have been automatically determined. The results will be shown on several reconstructed volumes from both samples and discussed in the light of the electrical measurements from the literature [2]. [5].

References

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[5] This work was supported by the French-Japanese ElyT international lab. (Engineering - Lyon - Tohoku, http://www.elyt-lab.com) through the financial aid of the ICC-IMR. The authors dedicate this work to the memory of their colleague, co-author and friend Agnès Bogner-Van de Moortèle, born in 1977, who passed away on February 28th, 2012 after an unfair battle against illness.

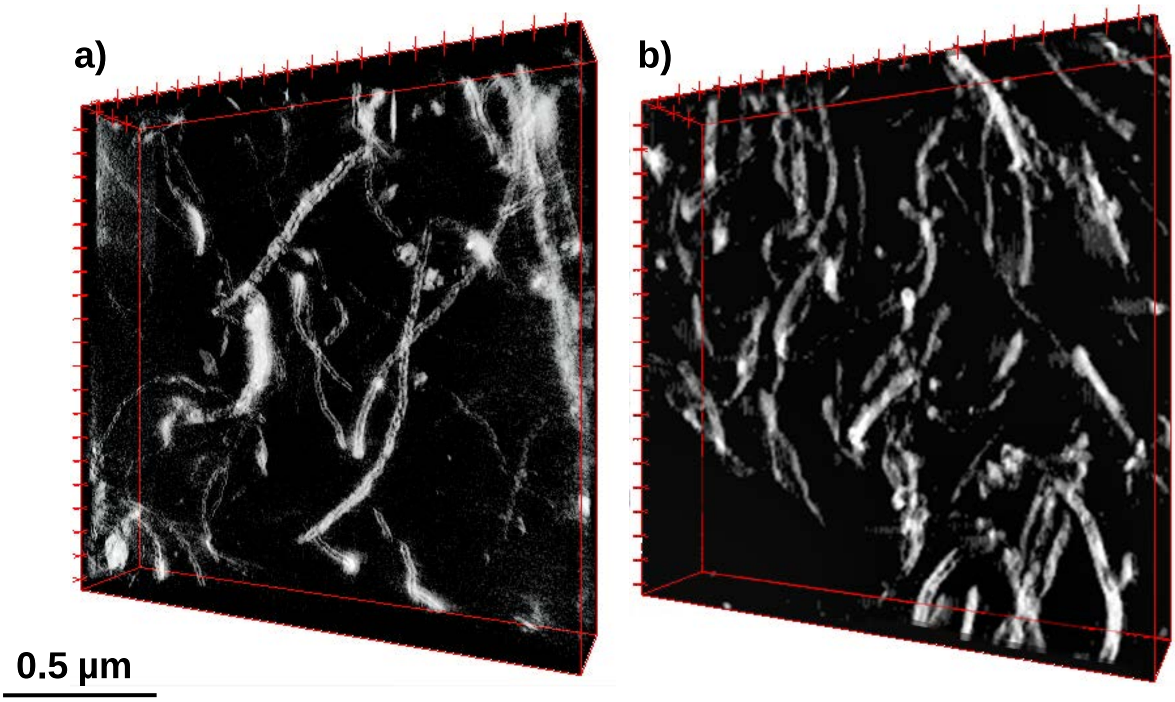

Figure 1. *Examples of 3D rendering of typical tomograms of a CNTs@co-polymer nanocomposite obtained by a) zero-loss filtered TEM, and b): low voltage STEM in a SEM.*

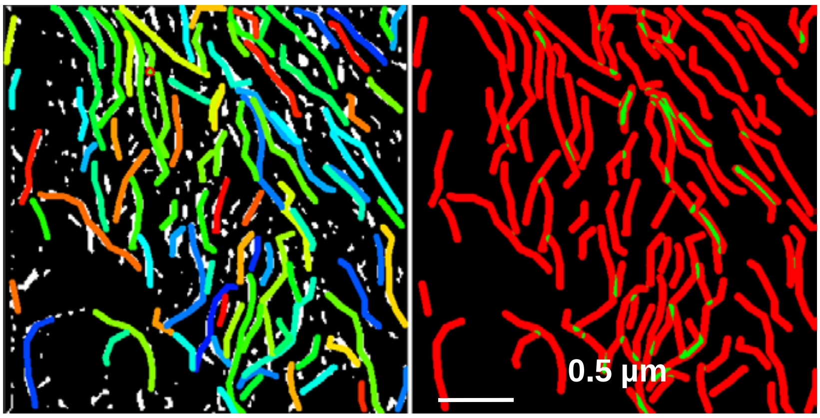

Figure 2. *Automatic computer analysis of the contacts between CNTs within one typical slice of a tomogram from the evaporated sample. Left: identified individual nanotubes are shown in wrong colors; right: detected contact areas are highlighted in green.*