



Experiment title: Processing effects on the structure of SWCNT-polymer nanocomposites: The organization of SWCNT as a clue for the nanocomposite properties.	Experiment number: MA-472
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Report:

The aim of these experiments was to perform simultaneous micro-Raman and X-ray microdiffraction experiments on SWCNT-polymer nanocomposites in order to reveal the aggregation and self-assembly of SWCNT in two sets of samples:

1. SWCNT-polymer nanocomposites with two different polymer matrices (PBT and PET) prepared by different processing methods: injection moulding, extrusion and melt pressing.
2. Thin films of SWCNT-polymer nanocomposites crystallized in order to obtain spherulitic morphology.

We had some problems when performing the simultaneous experiments:

For the first set of samples we could not focus the laser beam on the sample for Raman measurements due to an excess of surface roughness. For the second set of samples when the surface was smooth enough for Raman measurements, when the thickness of the samples is below 400 nanometres (spin coated on top of a thin glass slide) collection of X-ray diffraction pattern becomes complicate due to the small sample to substrate ratio. In Figure 1 (a) we present the AFM picture of a PBT/0.2%SWCNT nanocomposite with spherulitic morphology and some heterogeneities (bright spots). The same morphology is shown by the optical micrograph taken with the Raman microscope (Figure 1 (b)), where the rectangle represents the region of interest scanned by the laser beam with steps of 1 μm . Taking into account the intensity of the G' band, characteristic of the carbon nanotubes, we have generated the intensity map of figure 1 (c) that gives information about the distribution of SWCNT in the sample. It is clear that the maximum concentration of nanotubes corresponds to the centre of the spherulites, acting as nucleation points for spherulitic growth and no discontinuities related to the boundaries are observed. These results can help to understand the electrical behaviour of these materials [1]. Corresponding very weak X-ray patterns are currently being analyzed in order to seek for a substrate contribution subtraction aiming a complementary structural information.

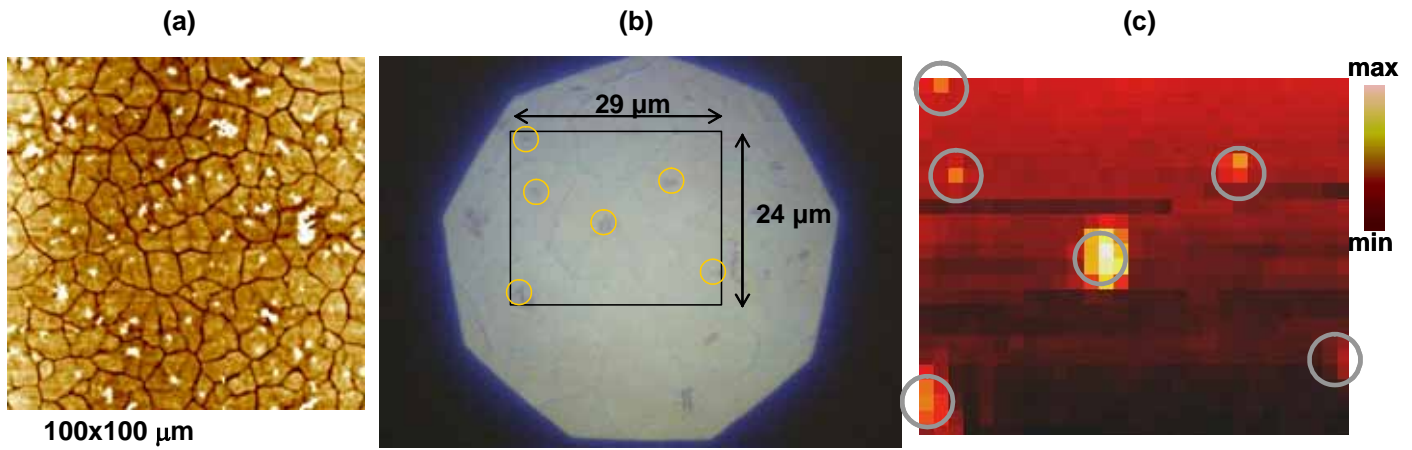


Figure 1. Thin film of PBT/0.2%SWCNT nanocomposite with 60 nm thickness: (a) AFM picture. (b) Optical micrograph taken with the Raman microscope where the rectangle represents the region of interest (ROI) scanned by the laser beam. (c) Raman intensity map of the ROI.

In addition, we performed several microdiffraction experiments in related topics. They are the following:

1. Lamellar Crystal Orientation in Ultrathin Films of Aliphatic Polyesters.

The synthesis and characterization of new biodegradable polymers is a topic of increasing interest mainly arising from their potential applications in biology and medicine. In particular, polyesters based on 1,3-propanediol glycol and aliphatic dicarboxylic acids can be prepared with different chain length and high molecular weight [2]. The preparation of ultrathin polymer films (thickness < 100 nm) is essential for applications such as adhesion, surface wetting and liquid crystal alignment. In general, polymer ultrathin films can exhibit different structure and properties that either thick films or bulk materials. Thin films of aliphatic polyesters were prepared by spin-coating on silicon substrates covering a large range of coating thicknesses (400 down to 10 nm). The structure and morphology of these samples have been investigated by combining techniques like AFM and Grazing incidence X-ray scattering at small (GISAXS) and wide angles (GIWAXS). AFM and GISAXS measurements for films thinner than 70 nm show dewetting patterns. Thicker samples exhibit crystalline morphology as revealed by AFM and GIWAXS. The analysis of the GIWAXS patterns revealed a multiplicity of peaks and spreading in q range what makes difficult their comparison with those peaks of X-ray diffractograms of bulk polymers. In addition, the present lack of crystallographic data for these aliphatic polyesters renders difficult to determine the chain orientation in these polymer coatings. Therefore, some extra experiments were carried out at ID13, during this period of beam time, on oriented filaments of these polymers in order to determine the crystal chain packing. In addition, due to the small size of the X-ray beam (1 μm), we were able to get the diffraction pattern of a thin film of 380 nm along its cross section, what allows us to anticipate that polymer chains lie parallel to the substrate.

2. Microstructure and orientation effects in Polyethylene foams.

Scanning X-ray microdiffraction experiments were performed (Figure 2 (a)) in low density polyethylene foams with a main cell size of 420 μm and a cell wall thickness of 3.6 μm (Figure 2 (b)). From the analysis of the 2D diffraction patterns along lines red and green we can follow the spatial evolution of structural parameters like degree of crystallinity and orientation of polymer chains in the different structural elements of the foam. We can conclude from these results that the degree of crystallinity is higher in the cell edge and cell vortex than in the cell wall. Concerning the orientation of polymer chains, it is evidenced that the c axis (polymer chain) of the orthorhombic crystal unit cell is perpendicular to the cell edge direction (Figure 2 (c)) while the a axis lies on the cell wall preferently.

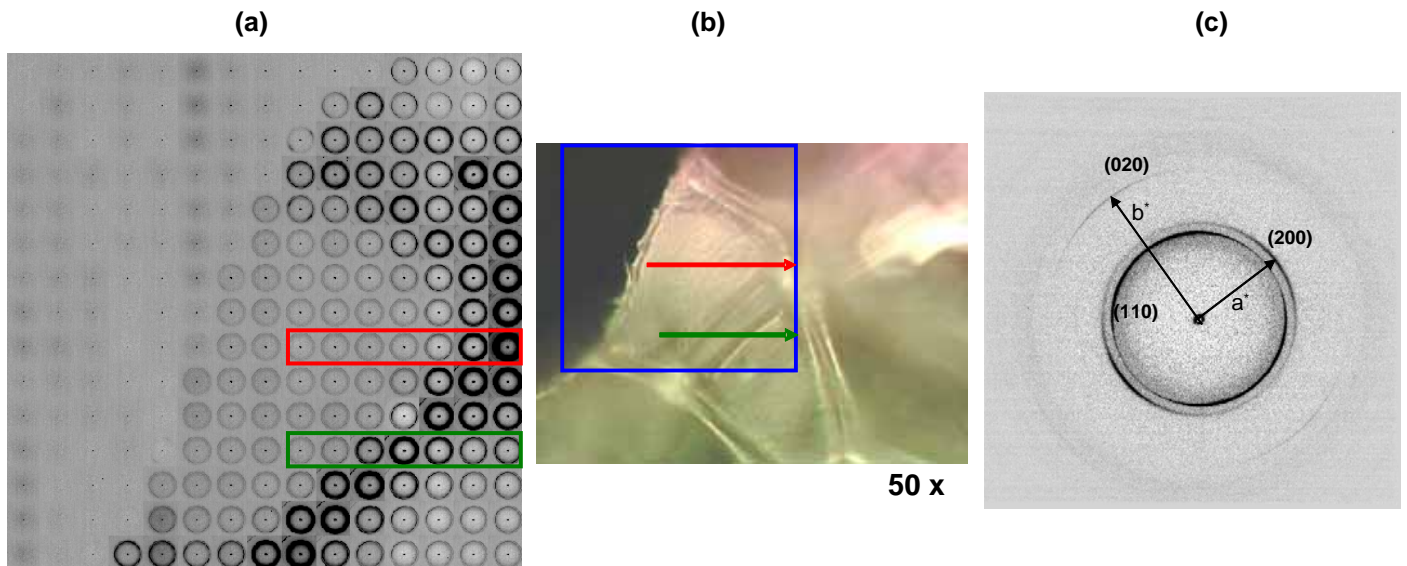


Figure 2. (a) Composite XRD image obtained by scanning the sample with 1 μm beam. (b) Optical micrograph of the polymer foam showing the region of interest. (c) 2D diffraction pattern from the cell edge position.

3. Confinement effects in one-dimensional polymer arrays.

Wetting of porous anodic aluminium oxide (AAO) templates has been used for the preparation of 1D poly(vinylidene fluoride) (PVDF) nanostructures. This technique is based on the fact that polymer melts and solutions tend to wet the walls of nanoporous templates avidly if the walls exhibit a high surface energy [3]. Scanning $\mu\text{-XRD}$ with 1 μm beam diameter was performed along the cross section of the sample (Figure 3), from the residual PVDF film (bulk) to the nanorod array. The synchrotron beam was carefully aligned perpendicular to the nanorod axis and the 2D-diffraction patterns were recorded in transmission geometry. Analysis of the 2D-patterns has allowed us to investigate the spatial evolution of degree of crystallinity, crystal orientation and what is even more interesting the solid-solid phase transition from the α non polar crystal form (bulk) to the γ polar ferroelectric form (nanorod array).

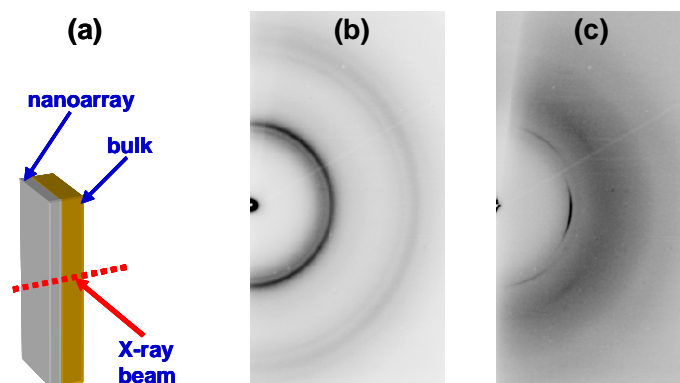


Figure 3. (a) Schematic view of the scanning $\mu\text{-XRD}$ geometry. (b) Diffraction pattern of the residual PVDF film. (c) Diffraction pattern of the nanorod array.

References

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