



# Microstructure study of carbon nanotubes nanocomposites with aromatic polyamides

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## 1. Background and research purpose

In the last 10 years, there has been great interest in nanocomposite reverse osmosis (RO) membranes. These membranes have great potential to replace the traditional polymeric RO membranes because of their higher chlorine resistance and better antifouling behavior.<sup>[1]</sup> In addition, these membranes often show higher permeability compared to the polymeric membranes without decreasing the salt rejection. However, the influence of these nanomaterials on the microstructure of these membranes is still poorly understood. We have found that carbon nanotubes (CNTs)<sup>[2]</sup> and cellulose nanofibers (CNFs)<sup>[3]</sup> modify the topology of the fully aromatic polyamide. These changes in the polymer microstructure might have important effect on pore size distribution and water diffusion. In addition, the presence of nanomaterials within the polyamide active layer has increased their chlorine resistance compared to the plain membranes.<sup>[4]</sup> While the resistance has been attributed to electronic withdrawing effect in the case of CNTs it is less clear how the CNF can provide such chlorine protection to polyamide. It is possible that changes in polyamide topology might be in part responsible of the different chemical reactivity. In this work we analyze several nanocomposite membranes by using wide angle and small angle X-ray scatter in order to understand their microstructure, focusing mainly on the CNT-MPD structure which is the best well-known among them. We aim to develop a general model of how the nanomaterials can modify the polyamide structure.

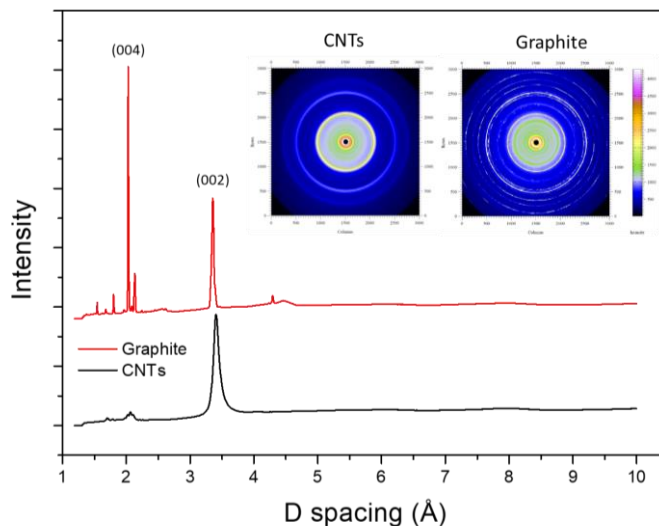
## 2. Experiment contents

Four different polymeric nanocomposites used to prepare RO membranes were synthesized in bulk quantity using the typical interfacial condensation reaction. The studied nanomaterials were CNTs, CNFs and graphene oxide (GO). The membrane polymers were prepared as previously reported<sup>[4]</sup> by reaction of trimesoylchloride dissolved in organic solvent and either m-phenylenediamine or piperazine dissolved in the aqueous phase. Both phases were mixed vigorously in a shaker where the crosslinking polymerization rapidly took place. For the nanocomposite materials, a certain amount of the nanomaterial was dispersed in the aqueous phase prior to the polymerization reaction. The resulting polymer powders were washed with methanol three times and finally with water, before drying at 80 °C for 2h. These materials were analyzed with Fourier transformed infrared spectroscopy, X-ray photoelectron spectroscopy, and wide angle and small angle X-ray scattering. For the wide (WAXS) and small (SAXS) angle X-ray scattering studies, the nanocomposite polyamide powders were loaded in aluminum sample holders and analyzed in the BL8S3 line (0.92 Å) at the Aichi synchrotron radiation center using two sample to detector distance configurations: 208 mm and 2134 mm for the WAXS and SAXS measurements.

## 3. Results and discussion

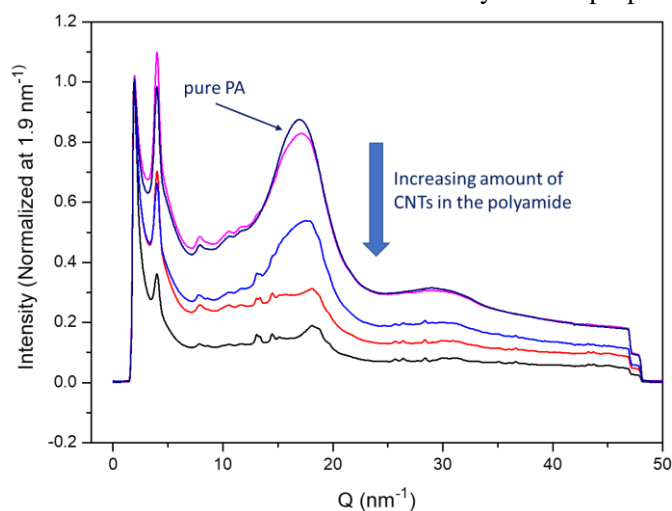
In figure 1 the D-spacing of the radially integrated WAXS pattern of CNTs is shown compared to a graphite

standard. The most prominent peak of the CNTs corresponds to the 002 peak of the concentric graphitic layers. Compared to the standard is slightly shifted to a higher D-spacing value and is broader due to the crystalline defects and stress induced by the concentric arrangement. The 004 peak is very weak in comparison to that shown by the graphite and it is the result of the reduced order in the z direction of the concentric graphitic layers. There are very weak peaks in the areas corresponding to the d-spacings of iron oxide that suggest the catalyst was removed after synthesis by the heat treatment. These CNTs were used as the main material to prepare a series of crosslinked aromatic polyamide powders containing increasing amount of CNTs by interfacial polymerization.



**Figure 1.** D-spacings plot from the radially integrated WAXS pattern of CNTs.

Figure 2 shows the Wide-angle X-ray scattering patterns of these nanocomposite polymers. These patterns are characterized by a sharp peak at  $3.97 \text{ nm}^{-1}$  and a broad peak at  $16.9 \text{ nm}^{-1}$ , which correspond to d spacings of 1.6 nm and 0.37 nm, respectively. The first one can be assigned to intermolecular spacing of the aromatic rings of the polymer, while the second one might correspond to the intramolecular packing of the chains. When the concentration of the nanotubes increases, the peak at  $16.9 \text{ nm}^{-1}$  decreases its intensity and a shoulder at  $18.7 \text{ nm}^{-1}$  appears, probably due to the graphitic d-spacing of the nanotubes at 0.336 nm. The lower scattering of the samples also suggests the densification of the nanocomposite structure. Additional analysis by FTIR would help to confirm the packing by correlation between the molecular vibrational intensity and the proposed polymer packing.



**Figure 2.** WAXS pattern from a series of aromatic polyamide samples with increasing amount of CNTs.

#### 4. References

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