WAXS study of novel piperazine based nanocomposite membranes.

Cruz Silva Rodolfo,Morelos-Gomez Aaron,
Fajardo Juan, Takeuchi Kenji, Morinobu Endo
信州大学　先鋭材料研究所

1. Background and research purpose

Domestic water purification and wastewater treatment have become importants field of research due to increasing environmental regulations. Domestic water purification technology relies in nanofiltration membranes, sometimes also called ultra-low pressure reverse osmosis membranes. Ideally, these membranes should be able to remove heavy metals ions, divalent ions and low molecular weight organic compounds, while operating at low pressure in water that might contain free-chlorine. One of the most important membrane materials is piperazine (PIP)-based crosslinked polyamide, which is widely used in domestic water purification systems. However, piperazine based polyamide membranes are also prone to fouling. In our group, we have been exploring the preparation of nanocomposite membranes using carbon nanotubes (CNT)[1] and cellulose nanofibers (CNF)[2] with improved antifouling properties. Here, we extend this approach for the preparation of PIP based nanocomposite membranes and we report the preliminar results of their structure characterization.

2. Experiment contents

Polymers used for the membrane preparation were prepared also as bulk powders by interfacial polymerizations. We used an aqueous solution of piperazine (1%) in contact with a solution of trimesoyl chlorine in haxane (0.15 %). We added CNFs, double-walled carbon nanotubes (DWCNTs), or a mixture of both nanomaterials to the reaction mixture in order to prepare the nanocomposites. The reaction mixturewas　was polymerized by mixing under vigorous agitation. After extensive washing in methanol and water, the polymers were dried and about half of each sample was treated with chlorine (4800 ppm-h). All samples were analyzed by wide-angle (WAXS) and small angle (SAXS) X-ray scattering in dry and hydrated state at the Aichi Synchrotron facility at the BL8S3 line. The resulting patterns were analyzed using Fit2D software.[3]

3. Results and discussion

During the reaction, the effect of the addition of the nanomaterials in the reaction media was evident, mainly on the increased viscosity of the mixture. CNF/piperazine mixture was highly dispersible in water showing only one phase, while the mixture of DWCNTs/piperazine had the tendency to sediment. However, the mixture of CNF-DWCNTs showed better stability than the DWCNTs alone, suggesting the CNF fibers helped to stabilize the highly hydrophobic DWCNTs. Indeed, the surface of the Tempo-oxidized cellulose nanofibers have different degree of hydrophobicity, depending on the exposed surface. Figure 1a) and 1b) show the two-dimensional WAXS patterns of the CNF and DWCNTs, respectively. Since the material in powder form was highly anisotropic, the signals were radially integrated and shown in Figure 2a) and 2b) respectively. The prominent 002 peak of the DWCNTs sample correspond to the distance between the two concentric nanotubes. On the other hand, the CNF nanofibers show the typical signals corresponding to the cellulose I type polymorph. Figure 1c) to 1e) shows the typical 2D WAXS pattern of the polymer samples. The samples were also anisotropic, and their signals were radially integrated, and their D-spacing plot are shown in Figure 2b). We can notice the peaks corresponding to the nanomaterials does not appear and this must be due to a small mass fraction and well dispersion in the piperazine matrix. The presence of the nanomaterials has been corroborated with other techniques such as FTIR and XPS.

The main two peaks can be assigned to the presence of intrachain and interchain voids, because the polymer contains units with rings with a approximately 3 Å in diameter, while the 1.5 nm peak is relatively common in amorphous aromatic polymers such as polyimides.[4]

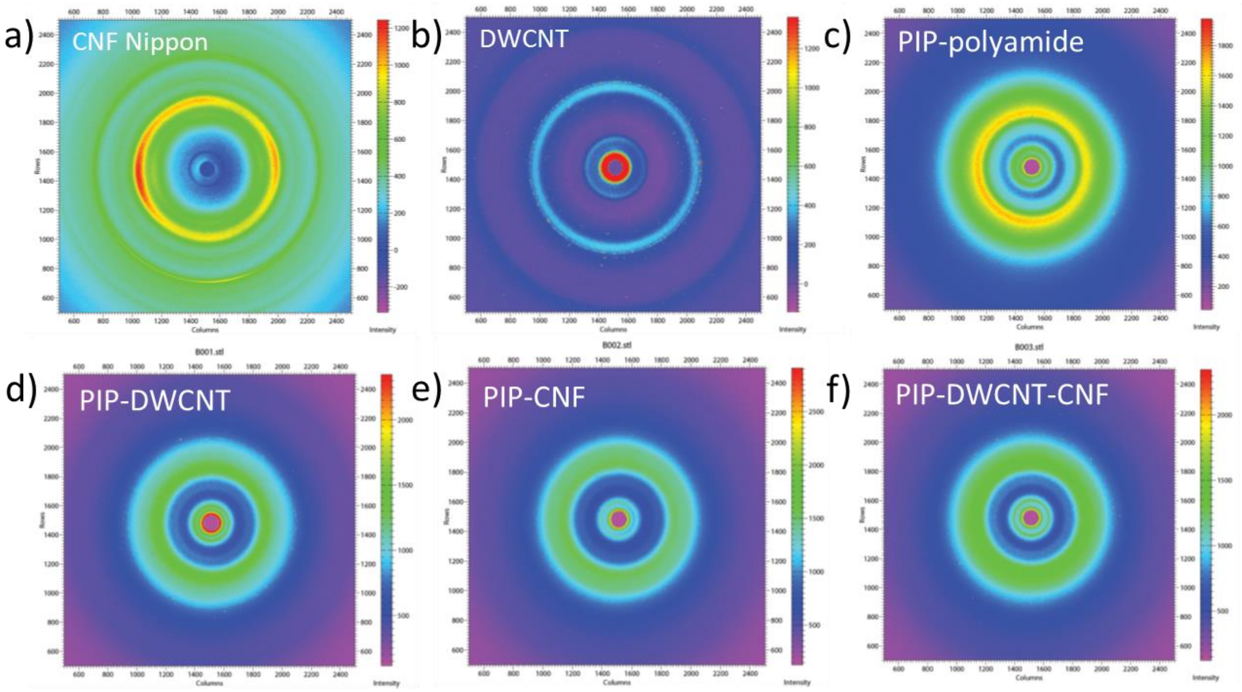

Figure 1. Two-dimensional (2D) WAXS patterns for the two raw nanomaterials (CNF and DWCNTs) and the 4 types of membranes. The raw materials: a) cellulose nanofibers (CNF), b) double-walled CNTs (DWCNTs); and the membranes: c) PIP-based polyamide, d) double-walled CNTs-piperazine, e) cellulose nanofibers-piperazine and f) mixture of CNF/DWCNTs and PIP polymer.

4.Conclusions

New nanocomposite materials of piperazine-based crosslinked polyamide containing nanomaterials such as CNFs, double-walled CNTs or both were prepared. The WAXS characterization suggest good dispersion within the matrix without disrupting the native PIP-polyamide structure necessary for water purification applications.

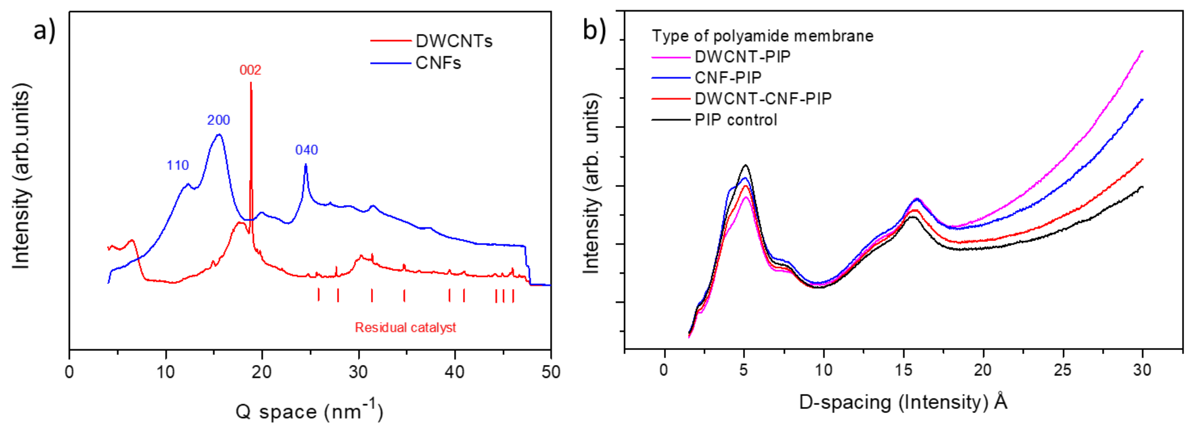

Figure 2. a) Q-space plot for the raw nanomaterials used as membranes fillers (CNFs and DWCNTs) and b) D-spacing plot from the integrated diffraction patterns for the 4 types of membranes studied.

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