CARBON NANOTUBES DISPERSION TOWARDS POLYMER INTEGRATION

J.M. González-Domínguez , W. Maser, A. Benito, P. Castell, A. Ansón, M.T. Martinez*.
Instituto de Carboquímica (CSIC), C/ Miguel Luesma Castán nº4 50018, Zaragoza, Spain
* Corresponding author's e-mail : mtmartinez@icb.csic.es

INTRODUCTION

Single wall carbon nanotubes, SWNTs, are born in their synthesis as bundles of tubes well aligned and packed in a triangular compact lattice entangled in nets due to Van Der Waals interactions. Their applications and excellent performance usually make reference to the individual tube, and the fact of appearing entangled-synthesized, provokes their complete insolubility in both aqueous and organic media, making SWNTs practically unprocessable. Thus, bundles represent the main obstacle in developing SWNTs technological potential, being necessary debundling in individual tubes. Some of the strategies used cause modification of physical properties and electronic structure of nanotubes [1], which could not be desirable for their applications, specially in fabricating composites. The debundling of SWNTs and the possibility of influencing SWNTs' alignment are major goals, specially in the field of nanocomposite materials [2,3].

Polymers could offer a suitable alternative in carbon nanotubes' interfacial union engineering [4]. It is possible to achieve this goal, by making them interact via weak bonding Van der Waals type, resulting in a "polymer–decorated", adsorbed or extreme–connected nanotube. This causes steric repulsions among polymer layers which, because of the system's entropy alteration, leading to a separation of tubes. Typical examples can be observed in block copolymers. They are excellent promoters of wetting and adhesion. Choosing a chemically compatible block copolymer with the target matrix of SWNTs, and codispersing them in the target polymer, it is possible to prepare SWNTs–Polymer nanocomposites.

EXPERIMENTAL AND RESULTS

Attending to what's been said before, and having a future look on integrating SWNTs in epoxy resins, a block copolymer was chosen containing the polyethylenoxide (PEO) block. A suitable homopolymer to the other block is polypropylenoxide (PPO). PEO was used as one of the monomers because of its good affinity to water. The second monomer, PPO, was chosen for being more hydrophobic than PEO in order to reach good interactions with SWNTs surface in aqueous media. A commercial block copolymer containing those blocks has been the one used in the present work, F68 PLURONIC ® with average molecular weight of 6800 g/mol. It is registered by BASF and consists in a triblock copolymer having the sequence PEO-PPO-PEO. At room temperature is a white solid with grain aspect and water soluble (maximum solubility above 20% wt).

Dispersions of Single Walled Carbon Nanotubes (SWNTs) were prepared using PEO-PPO-PEO triblock copolymer as dispersing agent. Thus, several series of polymer's aqueous solutions were made varying both polymer and SWNTs' concentration. They were prepared in the range of 0.4 – 10% wt of PLURONIC ® in water. SWNTs concentrations were also varying from 0.4 to 1% wt. It implies that total load in the solvent moved in the range 0.9 – 11% wt. Optimum ratio (polymer:SWNT) was found to be 5:1. Applying sonication by ultrasonic horn in different conditions of time and oscillation amplitude and controlling experimental conditions, fine and stable dispersions were eventually obtained. The experimental protocol includes optical microscopy and density measurements as a first step to control the SWNTs dispersion. Optical microscopy (50X) showed whether the initial mixture of components was homogeneous. Density measurements were used to check changes in mass/volume ratio of mixtures during sonication which could be attributed to bundle exfoliation.

The dispersed SWNTs were characterized by TEM, Raman Spectroscopy and X-Ray Diffraction. XRD (figure 1) indicated disgregation because of bundle's lattice peaks disappearance [5]. Raman Spectroscopy supported the debundling of SWNTs (figure2) due to the Radial Breathing Mode shift displacement, since the radial character of RBM band is likely to be much influenced by the nanotube packing [6]. It also observed the effect of the polymer presence because the G/D band ratio alteration. TEM micrographies were the ultimate proof as they were clearly showing individual polymer-decorated nanotubes and small bundles (3-4 tubes) probably also wrapped by the polymer (figure 3). From the characterization data, optimum time of sonication was established at two hours.

References:

[1] M.T. Martínez, M.A. Callejas, A.M. Benito, A. Ansón, W. Maser. “*Sensitivity of SWNTs to oxidative processing: sturctural modification, intercalation and functionalization*”, Carbon, 41 (2003), 2247-2256.
[2] Erik T. Thostenson, Chunyu Li, Tsu-Wei Chou, “*Nanocomposites in Context*”, Composites Science and Technology 65 (2005) 491-516.
[3] R. Andrews, M.C. Weisenberger, “*Carbon nanotube polymer composites*”, Current opinion in Solid State & Material Science, 8 (2004) 31-37.
[4] Pratap Bahadur, “*Block Copolymers, their microdomain formation (in solid state) and surfactant behaviour(in solution)*”, Current Science-Soft condensed matter, Vol 80, nº8 (2001), 1002-1007.
[5] Rina Schvartzman-Cohen, Yael Levi-Kalisman, Einat Nativ-Roth, Rachel Yerushalmi-Rozen, “*Generic Approach for dispersing SWNTs: the strength of a weak interaction*”, Langmuir 2004, 20, 6085-6088.
[6] L. Alvarez, A. Righi, S. Rols, E. Anglaret, J.L. Sauvajol, “*On the Raman Spectrum of nanobundles of SWNTs*”, http://www.geocities.com/CollegePark/3972/MRS_99.pdf

Figures:

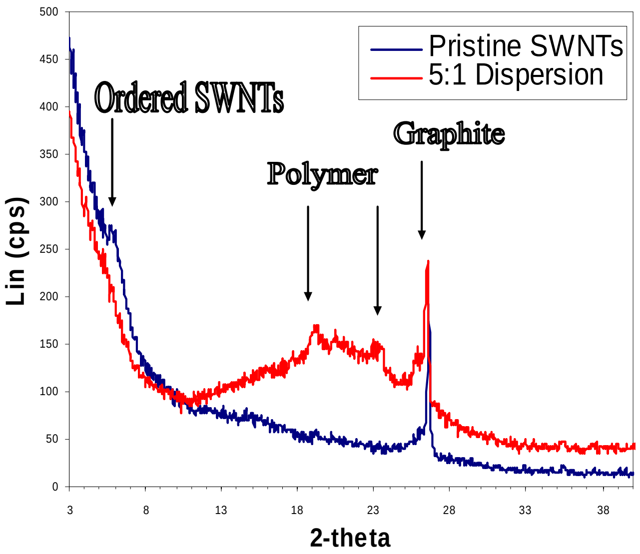

Figure 1: XRD Difractogram

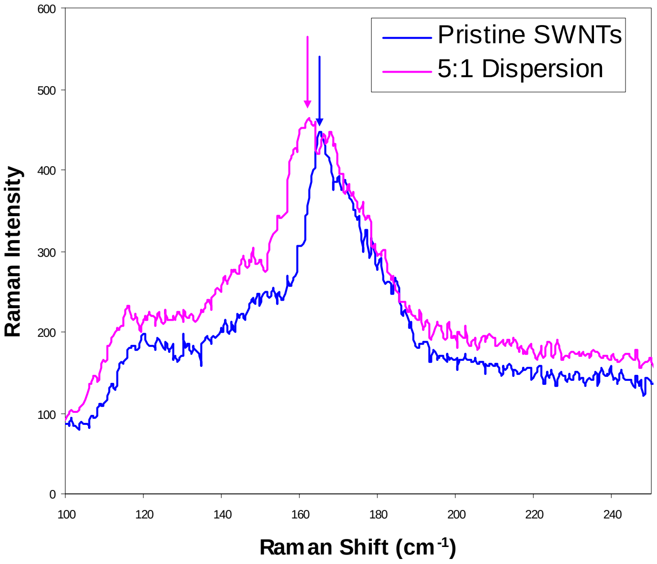

Figure 2: Radial Breathing Mode part of Raman Specter

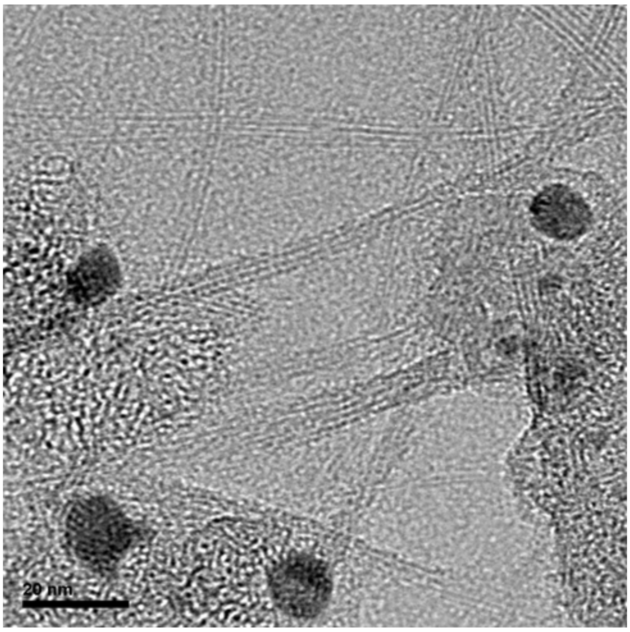

Figure 3: TEM Micrography