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Optical properties of single-walled carbon nanotubes highly separated in semiconducting and metallic tubes functionalized with poly(vinylidene fluoride)

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ABSTRACT

In this paper, the interaction of poly(vinylidene fluoride) (PVDF) with single-walled carbon nanotubes (SWNTs) highly separated in metallic (M) and semiconducting (S) tubes is studied by resonant Raman scattering and FTIR spectroscopy. In this order, the PVDF/SWNTs membranes were prepared by the evaporation of dimethylformamide (DMF) from PVDF solutions containing i) the as-prepared SWNTs samples, i.e., as mixtures of metallic (33%) and semiconducting (66%) tubes (M + S-SWNTs), ii) SWNTs highly separated in metallic tubes (98%, M-SWNTs), and iii) SWNTs highly separated in semiconducting tubes (99%, S-SWNTs). An increase in the PVDF β phase weight, highlighted by the increase in the absorbance of IR band at 843 cm^{-1}, is reported to take place in the presence of M + S-SWNTs and S-SWNTs. An increase of the PVDF γ crystalline phase weight is reported for the PVDF/M + S-SWNTs, PVDF/M-SWNTs and PVDF/S-SWNTs membranes. Using Raman scattering, a donor-acceptor interaction is invoked to take place at the interface PVDF/M + S-SWNTs and PVDF/S-SWNTs. In the case of the membranes based on PVDF and M-SWNTs, the changes reported in Raman spectra of the two constituents are explained on the base induction-interaction forces between the permanent dipole of PVDF and induced dipole of M-SWNTs.

1. Introduction

Beginning in 2002, a special effort has been assigned to the composites based on poly(vinylidene fluoride) (PVDF) and carbon nanotubes (CNTs) both for fundamental and applicative research [1,2]. The main applications of these composites were reported in the field of: a) membranes based on PVDF and multi-walled carbon nanotubes (MWNTs) functionalized with poly(amine-ester) for protein filtration [3]; b) strain sensors [4,5]; c) superhydrophobic coatings [6]; d) uncooled infrared detectors [7], medicine [7] and nonvolatile memory devices [5].

Four crystalline phases were reported for PVDF: α, β, γ, and δ [8]. Generally, PVDF is in the α crystalline phase [9]; its transformation into the β phase was realized mechanically via a stretching process [9]. The synthesis methods used for the preparation of PVDF/CNTs composites were: i) the electrospinning of PVDF in the presence of CNTs dispersed in dimethylformamide (DMF) when fibers with diameter between 200 and 1200 nm were obtained [10]; ii) the solution mixture of the two constituents PVDF and CNTs [11], when depending on the used solvents (dimethylsulfoxide and N, N-dimethylacetamide), different crystalline phases of PVDF were reported to be obtained; an inconvenience of this method is the non-homogenous dispersion of CNTs in the PVDF matrix. An improvement of the dispersion of CNTs in PVDF matrix was achievement in the presence of ionic liquids [12] and by ultrasonication [13]. In the latter case, the existence of the α and β phases of PVDF on the CNTs surface was reported [13]; iii) phase-inversion technique when the PVDF/MWNTs composites with a dominant β phase of PVDF was demonstrated to be obtained by FTIR spectroscopy [14]; and iv) high-pressure crystallization of the PVDF/MWNTs mixture, when 3D nanostructures based on PVDF nanowires with β crystalline phase and CNTs were prepared [15].

Despite the fact that PVDF is known as a nonreactive compound, a donor-acceptor interaction between the PVDF and CNTs was

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reported in 2006 by Owens et al. [16]. A reconfirmation of this interaction is dated to 2014, when a particular interaction between PVDF and metallic tubes with small diameters (0.86 nm) of SWNTs – HIPCO was reported by M. Ye et al. [17]. In this last case, it was demonstrated that CNTs act as nucleating agents for the crystallization of polymer chains [17]. By comparison with these studies, in the present manuscript, the chemical interaction of PVDF with SWNTs prepared by arc discharge method, which are characterized by the higher diameters of tubes than those obtained by the conversion of CO at high pressure (HIPCO), will be studied by FTIR spectroscopy and Raman scattering. A careful inspection of the literature focused on the PVDF/CNTs composites indicates that the characterization methods often used for the highlighting of physical properties of PVDF/CNTs composites were: scanning electron microscopy (SEM) [18], transmission electron microscopy (TEM) [19,20], atomic force microscopy (AFM) [21], X-ray diffraction analysis (XRD) [22], wide-angle X-ray diffraction (WAXD) [23], electrical conductivity [22,24,25], thermogravimetric analysis (TGA) [26], Raman spectroscopy [25], and Fourier transform infrared spectroscopy (FTIR) [22]. The main conclusions reported by FTIR spectroscopy and Raman scattering were: a) CNTs are nucleation agents for the PVDF β phase formation, as demonstrated by the increase in the absorbance of the IR band peaking at 840 cm^{-1}, assigned to the β phase of PVDF, simultaneously with the decrease in the absorbance of IR band at 764 cm^{-1} assigned to the α phase of PVDF, when CNTs were added in the polymer matrix [19,27]; and b) a functionalization of CNTs with PVDF was highlighted by an up-shift of the D band accompanied by an increase of the ratio between the relative intensities of the D and G bands (I_D/I_G) [22]. In all studies reported on the PVDF/SWNTs composites, SWNTs as mixtures of 66% semiconducting tubes and 33% metallic tubes were used. Therefore, two questions arise at present: Does the formation of the β crystalline phase of PVDF occur with the same probability both in the presence of semiconducting and metallic SWNTs? Can similar defects be generated into the CNTs network by the interaction of PVDF both with semiconducting and metallic SWNTs? Some answers to these questions will be shown in this paper. The chemical interactions of PVDF with SWNTs as mixtures of 66% semiconducting tubes and 33% metallic tubes (labeled M + S-SWNTs), SWNTs highly separated in semiconducting (99%, labeled S-SWNTs) and SWNTs highly separated in metallic tubes (98%, labeled M-SWNTs), respectively, will be studied by the UV-VIS-NIR and FTIR absorption spectroscopy and by Raman scattering. New features of the interaction of the two constituents of the PVDF/M + S-SWNTs, PVDF/S-SWNTs, and PVDF/M-SWNTs composites will be shown in this article.

2. Experimental

PVDF and M + S-SWNTs were purchased from Sigma-Aldrich. S-SWNTs (Iso-Nanotubes-S, 99%) and M-SWNTs (Iso-Metallic-M, 98%) were purchased from NanoIntegris USA.

The synthesis method used for preparing PVDF/CNTs composites is similar to that reported in the case of the PVDF/reduced graphene oxide/zinc oxide (PVDF/RGO/ZnO) composite [28]. Briefly, the PVDF film was prepared by dissolving 1 g of PVDF powder in 9.5 ml DMF which was then stirred for 3 h and finally, ultrasonicated for 3 min. Two ml of the PVDF in DMF solution was transferred to a Petri dish and subjected to a thermal treatment at 120 °C in order to evaporate the DMF. In the case of the PVDF/M + S-SWNTs, PVDF/S-SWNTs, and PVDF/M-SWNTs composites, the protocol was changed by the ultrasonication of 0.001 g CNTs in 2 ml of DMF for 20 min and their adding at the solution of PVDF in DMF (2 ml), followed by all steps described above. In all cases, membranes with a thickness of 1 μm were obtained.

UV-VIS-NIR and FTIR absorption spectra were recorded using an UV-VIS-NIR spectrophotometer (Lambda 950 model, Perkin Elmer) and a FTIR spectrophotometer (Vertex 70 model, Bruker), respectively. The FTIR spectrophotometer was endowed with DLaTGS detectors. The FTIR spectra of the membranes of PVDF and the PVDF/SWNTs composites were recorded in the attenuated total reflectance geometry with a resolution of 2 cm^{-1}, the scan's number in the spectral range 600–1500 cm^{-1} being equal with 64.

Raman spectra of PVDF and PVDF/SWNTs composites were recorded in a backscattering geometry under excitation wavelengths of 514 and 676 nm with an Horiba Jobin Yvon T64000 Raman spectrophotometer endowed with a multi-channel Charge Coupled Device (CCD) detector (1024 × 256 pixels), which was cooled at - 135 °C. Raman spectra of the membranes of PVDF, PVDF/M + S-SWNTs, PVDF/M-SWNTs and PVDF/S-SWNTs were recorded using two acquisitions in each window of the spectral range 100–3400 cm^{-1}, with a resolution of 2 cm^{-1}.

3. Results and discussion

To better understanding of the Raman scattering studies reported in this paper, Fig. 1 shows the Raman spectra of M + S-SWNTs, M-SWNTs, and S-SWNTs at the two excitation wavelengths, 514 nm and 676 nm. A brief review of the main vibrational features of the CNTs takes into account the following spectral ranges: 100–350, 1100–1600 and 2600–3300 cm^{-1}. The Raman lines

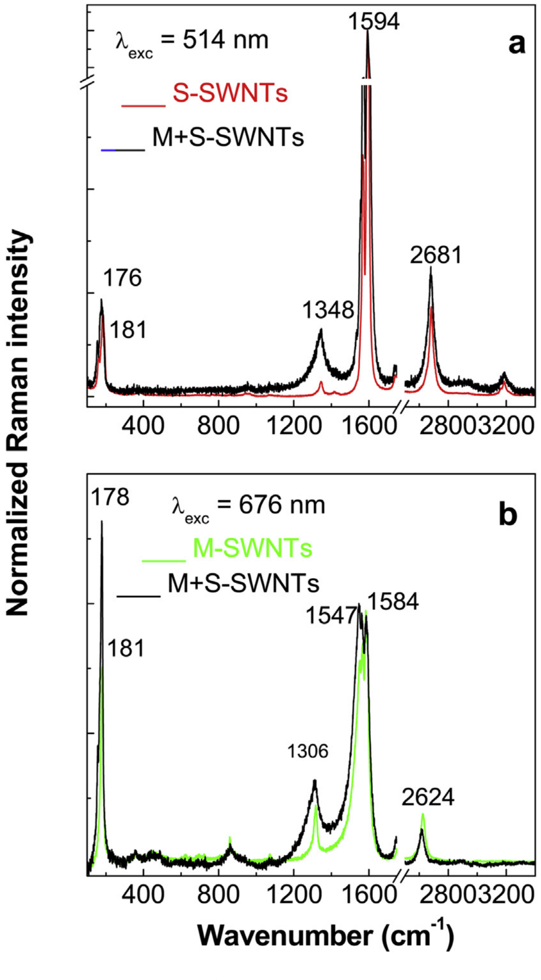

Fig. 1. Raman spectra recorded at $\lambda_{exc} = 514$ nm (**a**) and 676 nm (**b**) of the M + S-SWNTs, S-SWNTs, and M-SWNTs samples.