Chapter 4.
Materials, methods and characterization techniques

This chapter describes the materials, synthesis methods and characterization techniques used to functionalize and polymer-graft carbon nanotubes, as well as the use of these tube materials to produce polymer nanocomposites.

4.1. Nanocomposite materials

The materials used in the preparation of the nanocomposites are described below in addition with some of their raw characteristics.

4.1.1. Carbon nanotubes

Multi-walled carbon nanotubes (MWNT) and nitrogen-doped multi-walled carbon nanotubes (CN\(_x\)) were produced at IPICYT [1] by pyrolysing solutions of ferrocene (Fe(C\(_5\)H\(_5\))(C\(_5\)H\(_5\))\(_2\)) and/or benzylamine (PhCH\(_2\)NH\(_2\)) at 850 °C under an Argon atmosphere.

Fig. 4.1 shows SEM images of as-produced CN\(_x\) nanotubes. The obtained material consists of bundles by a pyrolytic self-assembly process. The nanotube composition is C\(_9\)N\(_x\) (x\(\leq\)1) with a typical nitrogen concentration around 1.6%, whereas the oxygen concentration corresponded to 2.4%. Characteristic dimensions are <80 nm in diameter and 80 µm in length, in agreement with data reported elsewhere [1]. The overall morphology exhibits a carpet-like structure that sometimes shows a metal layer of iron catalyst (Fig. 4.1 (a) and (b)).
In order to get details on the structure, Fig. 4.2 depicts HRTEM images of as-produced CN\textsubscript{x} nanotubes dispersed in ethanol thanks to ultrasonic technique. It can be observed that several kinds of morphologies of CN\textsubscript{x} nanotubes are produced at the same time by the pyrolytic method, (general view in Fig. 4.2 (a)). Nevertheless, the most typical nanotube structure synthesized by this pyrolytic method is the multiwalled bamboo-type structure exhibiting diameters ranging from 20 to 80 nm, eventually covered by an amorphous carbon layer with a typical thickness of 3-5 nm (Fig. 4.2 (b)).

As illustrated in Fig. 4.2 (b), it appears from several TEM observations that the CN\textsubscript{x} nanotubes used in this study exhibit generally a good tubular perfection with several graphitic walls. Because of the low nitrogen concentration, the CN\textsubscript{x} nanotubes used in this work are expected to have a low proportion of pyridine-like N sites. It has been previously reported that the pyridine-like nitrogen sites in the predominant graphitic walls are known
to be responsible for the roughness and for interlinked morphologies observed in the doped nanostructures [2, 3]. Moreover, it was reported (using EELS and \textit{ab initio} calculations based on local density approximation of density functional theory and tight binding calculations) that nitrogen was predominantly in pyrolytic and coordinated N atoms replacing C atoms within graphene sheets. Using this information, it was concluded that the reactivity of carbon nanotubes is related to the low roughness of the nanotube layers.

Complementary studies using EELS were performed on carbon nanotubes. In the EEL spectra of the CN\textsubscript{x} nanotubes (Fig. 4.3), it can be clearly observe the ionization edge at ca. 284.5 eV, corresponding to the C K-edge. The C-K edge exhibits bands for the $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions at 285.5 eV and 293 eV, respectively. The fine structure of the C-K edge confirms that nanotubes consist in a graphitic network with the typical sp$^2$-type bonding. In addition, the almost negligible ionization edges at ca. 400 eV corresponding to the N K-edge can be detected with intensity dependent on the N concentration. Previous studies reported [2] a splitting in the $\pi^*$-type peak of the nitrogen K edge exhibits two features at ca. 398.7 eV and 400.7 eV, corresponding to highly coordinated N atoms replacing C atoms within the graphene sheets (ca. 401-403 eV) and pyridinic nitrogen (ca. 399 eV). In this work, the N edge was very little because the analysis conditions were not good enough to observe it. This substitution of N could create radical sites in the graphene sheet, which, in the case of the outer layer, might be saturated with suitable reactants [3].

![Fig. 4.3. Core-loss EEL spectra of the as prepared-CN\textsubscript{x} nanotubes, showing the C and N edges.](image)

Raman Spectra of several samples of CN\textsubscript{x} nanotubes (Fig. 4.4) were recorded in order to determine the average position of peaks D and G, and their relative intensities. The selected samples exhibited the peak D at 1358 cm$^{-1}$, the peak G at 1579 cm$^{-1}$, and an intensity ratio $I_D/I_G$ of 0.36. Due to the low intensity ratio $I_D/I_G$, these kinds of nanotubes
are considered to be highly crystalline with a little amorphous carbon layer, which is in agreement with HRTEM observations (Fig. 4.2).

![Raman spectra](image)

Fig. 4.4. D and G peak position and their relative intensities ($I_D/I_G$) of CNx nanotubes Raman Spectra from samples of different batches production.

In addition, as can be seen in Fig 4.5, MWNTs and CNx nanotubes globally present a good thermal stability up to 700°C under N₂ atmosphere. Below this temperature, it can be noticed that MWNTs start loosing weight at temperatures below 200°C, which is expected to be only due to the loss of adsorbed molecules onto the surface of the MWNTs. Contrarily, for CNx nanotubes the weight loss begins at 200°C, and could be associated to some attached molecules on the higher reactive surfaces of the CNx nanotubes. When comparing both thermograms, it is observed that the doping of MWNTs (at least at low values, i.e. ~2%) does not change significantly their global average extent of thermal degradation. Indeed, only slight differences (around 2%) in weight losses of MWNTs and CNx nanotubes were observed.

4.1.2. Polymerization monomer, initiator and controllers

Styrene was chosen as the monomer of interest in the polymer-brushes synthesis due to the commercial importance of polystyrene, and also due to the well established nitroxide mediated radical polymerization protocols. Styrene (Aldrich, >98%) was purified of the inhibitor by a sodium hydroxide aqueous solution (10%) in a vol. ratio of 3:1 and subsequently cleaned with distillated water, the water molecules were removed with anhydrous sodium sulfate before used.
In this work, the reaction conditions to functionalize the carbon nanotubes and to synthesize the polystyrene-grafted carbon nanotubes were selected using a combinatorial experimental design. The nitroxide mediated radical polymerization requires the choice of a solvent, a controller and an initiator.

TEMPO type nitroxides are considered as efficient controllers in PS polymerization. Thus, this work has considered the evaluation of several molecular configurations of nitroxide controllers to determine the more convenient reactant for the carbon nanotube system. Three different controllers/regulators for the controlled free radical polymerization have been evaluated, namely TEMPO \((2,2,6,6\text{-tetramethyl-piperidine}-1\text{-oxyl}, \text{C}_9\text{H}_{18}\text{NO})\), OH-TEMPO \((\text{C}_9\text{H}_{18}\text{NO}_2)\), and PR CGX 505 (an experimental nitroxide from Ciba Specialty Chemicals).

BPO is known as an efficient initiator in free radical polymerization reactions, especially for styrene. In this work, benzoyl peroxide (BPO) supplied by Baker was used to create the initial free radical sites used during the grafting of polystyrene chains. Several solvents, such as toluene, benzene, xylene, were also supplied by Baker. All reagents were used as received.

**4.1.3. Polymer matrices**

A second route to prepare carbon nanotube-polymer nanocomposites has been also used, based on the so-called solvent route. Several polymers have been investigated (i) an organic soluble polystyrene (PS) homopolymer which is amorphous, (ii) a water soluble polyethylene oxide (PEO) homopolymer, known to be semicrystalline, and (iii) a polymer blend of the two homopolymers.
The polymer blends were prepared using commercial polystyrene (PS HH104) from Resirene (Mw=46,000 gr/mol), and polyethylene oxide PEO14000 from Polioles and PEO1-5M from Rita Corporation (PEO14k of Mw=14,000 gr/mol and PEO210k of Mw=200,000 gr/mol, respectively) and blending them in a solution using toluene (Aldrich, >98%), as solvent.

### 4.2. Preparation methods

The functionalized CN\textsubscript{x} nanotubes, polymer-grafted CN\textsubscript{x} nanotubes and polymer-carbon nanotubes nanocomposites are prepared in two separate steps that will be described in the following sections.

#### 4.2.1. PS-grafted CN\textsubscript{x} nanotubes

PS-grafted CN\textsubscript{x} nanotubes (PS-\textit{g}-CN\textsubscript{x}) are synthesized by \textit{in situ} radical polymerization via NMRP of styrene, as described in Dehon et al [4].

The MWNT and CN\textsubscript{x} raw tubes are dispersed ultrasonically in benzene for 60 min in order to eliminate the nanoparticles and decrease the catalyst moieties. Subsequently, the nanotube suspension is precipitated, filtered (0.5\textmu m PTFE filter) and dried in vacuum at 60°C for 4 h.

First, the functionalization reactions to create polymer brushes have been carried out by a variable screening through combinatorial chemistry, and then by batch reactions in glass reactors or vials.

The initial screening of radical functionalization and polymer-grafting conditions has been realized using combinatorial design experiments in a Parallel Polymerization Reactor (PPR equipment) [5]. The investigated variables were carbon nanotube type (CN\textsubscript{x} and MWNT), solvent type (xylene or benzene), controller type (TEMPO, OH-TEMPO, and PR-CGX505), initiator concentration (0.05 molar% or 0.1 molar %), and temperature (80 or 130°C). In all cases, BPO was used as initiator and the amount of sonicated carbon nanotubes was 10 mg. The initiator: controller molar ratio was set to 1:1.3, whereas the monomer: initiator molar ratio was chosen equal to 96:1, and finally the monomer:solvent molar ratio of 2:3 in volume. Also, the PPR equipment operated at 120 rpm in an O\textsubscript{2} atmosphere, in two steps of respectively 3 and 24 hr of reaction. At the end of this screening study, the best conditions have been retained to scale up the reaction using batch conditions with 100 mg of carbon nanotubes in glass containers.

As indicated above, the overall reaction including radical functionalization and polymer-grafting involves two steps to produce (PS-\textit{g}-CN\textsubscript{x}), as shown in Fig. 4.6.

The first step, i.e. the radical functionalization, corresponds to the upper part of Fig. 4.6. The previously purified CN\textsubscript{x} nanotubes are mixed with initiator and controller solutions to functionalized carbon nanotubes with free radical sites (hereafter called CN\textsubscript{x}-R• and CN\textsubscript{x}-RNO\textsubscript{x}). Then, the reactor is heated up to 130°C and maintained for 3 h. The functionalized nanotubes are then filtered using a 0.5\textmu m PTFE filter and repeatedly washed using toluene to eliminate remaining dissolved species of initiator and controller.
The second step concerns the polymer-grafting as illustrated in the lower part of Fig. 4.6. Either the radical functionalized or the unreacted carbon nanotubes are added to monomer-solvent (volumetric ratio 2:3) solutions to proceed to the \textit{in situ} polymerization of polystyrene at 130°C during 24 hr. After the reaction completion, the materials (PS-g-CN\textsubscript{x}), obtained in solution, are precipitated in methanol and vacuum dried during 24 h at 60°C.

The vacuum dried grafted-CNTs were redissolved in toluene and then the products are separated by solvent filtration (PTFE filters of 0.5 μm) and repeatedly washed.

![Fig. 4.6. Polymer brushes reaction scheme: functionalization of CN\textsubscript{x} nanotubes (1) with the NMRP initiator (2) and controller (3), and synthesis of polymer brushes of polystyrene (4).](image)

### 4.2.2. PS-PEO blend nanocomposites preparation

The polymer-nanocomposites are prepared with 40 ml of toluene and 2 g of the corresponding polymer matrix (PS, PEO and PS-PEO) and the different kinds of nanotubes (MWNT, CN\textsubscript{x} and PS-g-CN\textsubscript{x}) at several concentrations (0.1, 0.3, 0.5, 0.7, 1.0, 2.0 and 5.0 w%).

PS-based nanocomposites solutions are mixed in toluene at 130°C during 30 min. Then, films are prepared by solution casting over aluminum layers. After a solvent evaporation step at low temperature (20°C), the materials are dried in a vacuum oven at 60°C for 24 hrs and in an oven at 150°C for 4 hrs in order to remove all the residual toluene solvent. After these drying steps, the samples are pressed at 180-190°C and 13.79 MPa (2000 lb) for 10 min.

PEO and PS-PEO (35:65 w %) based nanocomposites are prepared in toluene at 130°C for 30 min. Films are also prepared by solution casting. After the solvent evaporation at low temperature (20°C), the materials are dried in a vacuum oven for 24 hrs at 60°C. Then, they are pressed at 150-160°C and 13.79 MPa (2000 lb) for 10 min, and then quenched in cold water at 55°C, maintained for crystallization during 2 min. The formed samples are approximately 0.5 mm thick.
The morphological and physical characterization of these materials will be presented in chapter 6.

4.3. Nanocomposite characterization

The synthesized materials, i.e. functionalized carbon nanotubes, polymer-grafted carbon nanotubes, and carbon nanotubes-polymer nanocomposites have been characterized using several techniques to determine their morphology, structure and composition, as well as their thermal, electrical and mechanical properties.

4.3.1. Morphology, structure and composition characterization

Carbon nanotubes show a strong dependence of their properties (electronic, vibrational and other physical properties) with their geometrical structure often characterized through parameters such as (n,m) or (d, θ). Consequently, the structural characterization of carbon nanotubes is very important. Several microscopic techniques have been used to characterize the morphology, structure and composition of the nanosized polymer brushes and polymer-nanocomposites. Electron microscopy and related techniques High-Resolution Transmission Electron Microscopy (HRTEM), Transmission Electron Diffraction (ED), Electron Energy Loss Spectroscopy (EELS), Energy-filtered Transmission Electron Microscopy (EFTEM), Scanning Electron Microscopy (SEM), were selected. SEM is a versatile and widely used technique for characterizing the morphology of carbon nanotubes and their architectures, but is not adapted to study the structure of SWNT.

Note that overall morphological observations can also been performed using Scanning Tunneling Microscope (STM) and Atomic Force Microscopy (AFM). Imaging by AFM could give information about exfoliation of carbon nanotubes in organic solvents after chemical functionalization. In addition, AFM along with TEM were used to study the dispersion of nanotubes in the polymer matrix for the case of nanocomposites.

4.3.1.1. Electron Microscopy and allied techniques

TEM and SEM have been extensively used to characterize carbon-nanotubes composites; nevertheless, and to the best of our knowledge other associated techniques such as EELS and EFTEM have been scarcely used by the time of the research. They can be useful to probe the chemical attachment of small molecules and to study polymer grafting via chemical bonding on the carbon nanotube surface. Thus, this work proposes the use of these techniques to investigate differences between as-produced CN\textsubscript{x} carbon nanotubes, radical functionalized CN\textsubscript{x} nanotubes, polystyrene-brushes of CN\textsubscript{x} nanotubes, and finally physical blend of CN\textsubscript{x} nanotubes and PS. The potential usefulness of these techniques to determine the structures, morphologies, chemical composition, and chemical bonding of carbon nanotubes with low molecular species and polymers will be addressed.
**Principles**

In Transmission Electron Microscopy, a high energy electron beam is directed to a material sample. The incident electrons \( (e^\prime) \) with energy \( E_0 \) can encounter three types of interaction with the sample atoms, as represented in Fig. 4.7,

(i) *Elastic scattering*, when \( e^\prime \) interact with the nucleus atom and continues with the same energy \( (E_0) \):

(ii) *Inelastic scattering*, when \( e^\prime \) interact with electrons leading to an energy loss \( (E_0-\Delta E) \). The value of the energy loss, \( \Delta E \), gives information on excitation energy for the inner-shell, valence or conduction electrons in the materials.

(iii)*Element-specific X-rays*. Collisions with material electrons are responsible for the emission of X-rays. The energies of the emitted X-rays give information about the elements present in the material sample.

![Fig. 4.7. Elastic and Inelastic Interactions between incident electron beam and atom [6].](image)

**Experimental Technique**

Fig. 4.8 shows a typical scheme of an electron ray path of a TEM equipped with an in-column EELS filter (for EFTEM experiments). In the experimental set up, imaging filter lens consists in a double magnetic prism, or \( \Omega \) omega filter (purely magnetic filter lens). Alternatively, an energy post-column imaging spectrometer, Gatan Imaging Filter (GIF) is also used and set under the fluorescent screen.

A Transmission Electron Microscope provides a two-dimensional intensity distribution of the electrons interacted with the specimen that can be recorded on a 2D detector as image, diffraction, or spectra. The imaging filter separates the electrons dispersed by the sample in elastically \( (E_0) \) and inelastically scattered electrons \( (E_0-\Delta E) \). EELS pattern are formed by inelastically scattered electrons signal, separated by the differences between their respectively bents. Energy-filtering is used to obtain electron spectroscopic images (ESI) with an energy selecting slit in the energy dispersive plane. With this information, the zero loss images can be obtained and zero-loss diffraction eliminated the inelastic component; better contrast images taken at different energy losses, and elemental distribution (mapping) using energy-lost electrons at the ionization edges. Options of high resolution and high energy images have been used to obtained better image information.
Applications to carbon nanotubes and nanocomposites

Electron Microscopy studies devoted to carbon nanotubes include:
(i) longitudinal-direction and cross-sectional observations using HR-TEM,
(ii) structural analysis by Transmission Electron Diffraction (ED), and
(iii) electronic structures evaluation by EELS

Fig. 4.8. Electron ray path of a Transmission Electron Microscope equipped with an in-column energy filter [6].

Electron Microscopy has also been applied to study the microstructure of polymer nanocomposites. Additional studies involve the adhesion of carbon nanotubes to a polymer matrix [7]. The nanotube adhesion to polymer matrices can be qualitatively observed by the interaction remaining between them in composite films after cutting, or even more, by pull-out experiments.

In the following, some of the main bibliographic studies concerning electron microscopy investigations are commented with a special attention to EEL results.

TEM reveals details of the internal structure of carbon nanotubes, and can provide information about the graphitic lattice such as the lattice points distance, orientation and tube chirality. Structural defects in multi-walled carbon nanotubes can be also determined using TEM, as well as their diameter distribution and packing configuration. Furthermore, the morphology and dispersion of carbon nanotubes inside the composites could also be observed.

EEL Spectra of carbon nanotubes can be taken at low and high energy loss. In the low-loss energy region, there are two peaks for graphite and carbon nanotubes: (i) the one at 5-8 eV is assigned to the $\pi$ plasmon caused by the transition between $\pi$ and $\pi^*$ electron energy states, and (ii) the other at 20-28 eV is related to the collective excitation of all the
valence electrons (\(\pi + \sigma\) plasmon). In the core-loss region, there are also two peaks for the materials: (i) \(\pi^*\) (1s) excitation peak at 285 eV, and (ii) unoccupied \(\sigma^*\) levels at 292 eV. Carbon nanotubes exhibiting \(sp^2\) bonding present \(\pi^*\)-excitation peak lower than the \(\sigma^*\)-excitation peak.

The comparison of EEL spectra of CNTs with that of graphite (Fig. 4.9) reveals that \(\pi\) peak is at lower energy loss for CNTs than for graphite. That indicates a loss of valence electrons and a change in band gap due to the curvature of graphitic sheets. The peak width follows: SWNTs>MWNTs>graphite. That is related to the energy states of excitation caused by the curvature of graphitic sheets and the effect of the bundle formation.

![Fig. 4.9](image)

**Fig. 4.9.** Comparative EEL spectra of graphite, bundle of SWNTs and MWNTs in energy ranges of (a) 0 to 45 eV (plasmon region) and (b) 280-300 eV (carbon K-edge) [6].

The signature of chemical bonding can be distinguished in the core-loss region of EELS patterns, beyond the ionization edge, i.e. the energy-loss near-edge structure (ELNES). The height and width of peaks in this region depend on the density of excited states and the width of them, respectively.

**Experimental conditions**

In this thesis, two different Scanning Electron Microscopes, Jeol 5900 LV and a FEI ESEM XL 30, have been used under vacuum at accelerating voltage of 0.8 and 20 kV. The samples have been observed without any conducting coating (such as gold coating) and images have been obtained by collecting the secondary electrons. Either the powdered materials or the fracture solid materials have been investigated in the case of polymer-grafted carbon nanotubes. In the case of nanocomposites, observations have been conducted on either the fractured solid materials or pressed films.

For HRTEM, EELS, EFTEM, and STEM, specimen preparation includes the dispersion or dissolution of solid materials (polymer-grafted carbon nanotubes) in ethanol or xylene and a ultrasonication step of 2 to 10 min. A drop of the solution is then deposited
on a copper grid covered by a lacy carbon film. The nanotubes are then observed and analyzed in the holes of the lacy carbon film.

In general, carbon nanotubes HRTEM images were obtained with a JEOL 2010F high-resolution electron microscope (Field Emission Gun, 200kV) equipped with a Gatan CCD slow-scan camera and a Gatan Digiscan EELS Spectrometer. Bright field images were acquired with a Gatan Slow Scan CCD camera. EEL Spectra at high spatial resolution were obtained with a probe size diameter of 2.4 nm. EEL spectra of larger areas were obtained with probe sizes of 50 nm. The collection angle was set to 31 mrad and the convergence angle was neglected (diffraction mode). The energy resolution was measured on the zero-loss peak and was equal to 1 eV FWHM. All spectra were corrected by the dark noise and the gain, and then deconvoluted using Fourier-log or Fourier ratio procedures to obtain the spectra of an ideally thin specimen. When it was possible, the spectra were further deconvoluted by the zero-loss peak to improve the energy resolution.

EFTEM was performed on a Leo 912 Microscope (in column Omega filter). The microscope operates in the image-spectrum mode at an accelerating voltage of 120 eV. The silt size was set to 6 eV. Image series of at least 20 images were acquired with an energy step of 2eV. The elemental maps were then calculated using a three image power-law subtraction.

STEM images were obtained in a Scanning Electron Microscope FEI XL30 SFEG. The samples were directly observed in solid.

Statistical measurements of carbon nanotubes diameters were performed on a Jeol 200 CX Electron Microscope operating at an accelerating voltage of 200 kV. Fifteen conventional bright field images were acquired all over the specimens. The diameters were then measured on at least 150 nanotubes.

Low-resolution TEM images of polymer-grafted carbon nanotubes and nanocomposites were obtained with a JEOL 200 CX (Field Emission Gun, 200kV). The samples were prepared by dispersion or dissolution of solid materials in the case of polymer-grafted materials and ultramicrotomy in the case of nanocomposites. The nanocomposite films of 50 nm were cut at -75°C and 0.3 mm/s. The cuts were collected with a drop of an aqueous solution of 4 mol % of sucrose, deposited on a copper grid and then rinsed with distilled water. The films were tinted with RuO$_4$ vapors (4 w% aqueous solution) during 5 min.

AFM measurements were obtained using a JEOL Microscope Model SPM 5200. The samples were prepared by 2-10 min of ultrasonication in toluene. After sonication, a drop of the nanotube dispersion was placed on a freshly cleaved 1 cm$^2$ mica wafer while spinning at 750 rpm. A subsequent drying step was taken place in an oven at 100°C.

4.3.1.2. Raman Spectroscopy

Raman spectroscopy is the measurement of the wavelength and intensity of inelastically scattered light from molecules. Recently, the technique was used to characterize the structure of nanotubes, and to determine chemical changes at their surfaces due to functionalization. In this work, the technique was proposed to analyze the as-produced $CN_x$ nanotubes, the products from the radical functionalization, and the polymer grafting of $CN_x$ nanotubes to conclude about the proceeding of the reaction, as well as the preservation of the overall nanotube structure.
**Introduction**

Raman spectroscopy is based on the Raman effect, which is the inelastic scattering of photons by molecules, discovered by C. V. Raman and K. S. Krishan in 1928. The Raman effect concerns a very small fraction, about 1 to $10^{-7}$ of the incident photons. Moreover, scattering events occur in around $10^{-14}$ seconds or less [8].

In Raman scattering, the energies of the incident and scattered photons are different, in opposite to the Rayleigh scattering where both incident and scattered energies are equal (nearly 99%). Raman effect is divided in two phenomena: (a) Stokes lines, where the energy of the scattered radiation is lower than that of the incident radiation, and (b) anti-Stokes lines, where the energy of the scattered radiation is higher than that of the incident radiation (Fig. 4.10). The energy increase or decrease compared to the excitation is related to the vibrational energy spacing in the ground electronic state of the molecule. Therefore, the wavenumber of the Stokes and anti-Stokes lines are a direct measure of the vibrational energies of the molecule. The anti-Stoke shift spectrum has always less intensities than that for the Stokes spectrum. The frequency shift, that is the difference between the frequencies of the Raman lines and the exciting line, are independent of the frequency of the light. Furthermore, the lines are related to rotational and vibrational molecular transitions.

![Energy level diagram for Raman scattering](image)

Fig. 4.10. Energy level diagram for Raman scattering: (a) Stokes Raman scattering, and (b) anti-Stokes Raman scattering [9].

**Principles**

The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering molecule. A Raman spectrum is a plot of intensity of scattered light versus energy difference. The energy differences between the initial and final vibrational levels, $\nu$, or Raman shift in wave numbers (cm$^{-1}$) is calculated through,

$$\nu = \frac{1}{\lambda_{\text{incident}}} - \frac{1}{\lambda_{\text{scattered}}}$$

[4.1]

in which $\lambda_{\text{incident}}$ and $\lambda_{\text{scattered}}$ are the wavelength of the incident and scattered Raman photons.

For a vibration to be active in Raman, the polarizability of the molecule must change with the vibrational motion. The induced dipole can be calculated as, $p = \alpha E_i$, where
where \( p \) is the induced dipole, \( E \) is the electromagnetic field of the incident radiation, and \( \alpha \) is referred to as the polarizability of the molecule. This induced dipole moment then emits a photon, leading to either Raman or Rayleigh scattering. The energy of this interaction is also dependent on the polarizability, \( E_{\text{interaction}} = -\frac{1}{2} \alpha E^2 \). The change in polarizability during the vibration is \( \frac{\partial \alpha}{\partial Q} \neq 0 \), where \( Q \) is the normal coordinate of the vibration. Scattering intensity is proportional to the square of the induced dipole moment, that is to say the square of the polarizability derivative.

The differences between the incident and inelastically scattered radiation are determined by the material molecule structure and environment, i.e. atomic mass, bond order, molecular substituents, molecular geometry and hydrogen bonding. Typical strong Raman scatterers are moieties with distributed electron clouds, such as carbon-carbon double bonds. The \( \pi \) electron cloud of the double bond is easily distorted in an external electric field. Bending or stretching the bond substantially changes the distribution of electron density, and strongly modifies the induced dipole moment.

Vibrational Raman spectroscopy is not limited to intramolecular vibrations. Crystal lattice vibrations and other motions of extended solids can be Raman-active. In crystalline solids, the Raman effect deals with phonons, instead of molecular vibration. Raman scattering by a crystal provides information on the crystal orientation.

**Experimental Technique**

Experimentally, only the Stokes shifts are observed in the Raman spectrum. Thus, the Stokes lines will be observed at higher wavelengths than the exciting light. High power excitation, monochromatic and polarized source are needed because Raman scattering is not very efficient and the measurement of the differences between the excitation and Stokes lines are searched. In addition, Raman spectroscopy is conventionally performed with green, red or near-infrared lasers with wavelengths below the first electronic transitions of most molecules (e.g. \( \text{Ar}^+ \), \( \text{Kr}^+ \), Nd:YAG, He-Ne, etc).

In Raman Spectroscopy, a laser beam is used to irradiate a sample. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line (due to elastic Rayleigh scattering) are filtered out and those in a certain spectral window away from the laser line are dispersed onto a detector.

The advantages of Raman spectroscopy are that the pretreatment of samples is not necessary, samples are not destroyed, and the interference with water is weak.

**Applications to carbon nanotubes**

Carbon nanotubes present active vibrational modes to infrared and Raman Spectroscopy. For all kinds of nanotube chirality and symmetry, 7 to 8 FTIR active modes (\( A_{2u}, E_{1u} \)) and 15 to 16 Raman active modes (e.g. \( A_{1g}, E_{1g}, E_{2g} \)) have been identified. An extended review of the nomenclature could be retrieved from the technical literature. The number of IR and Raman active modes is independent of the nanotube diameter for both SWNT and MWNT. However, the frequencies of these modes do vary with diameter [10].

In particular, many groups have reported Raman spectra for SWNTs in which they assigned observed Raman modes with specific (n,m) CNTs. They showed that the Raman
signal from the rope consists in the graphite related $E_{2g}$ (or $E_g$) modes and $E_{1g}$, $E_{2g}$ and $A_{1g}$ modes of carbon nanotubes with different diameters, these modes occur in the high frequency around 1550 and 1600 cm$^{-1}$. Moreover Raman spectra for SWNT also contain a low frequency (50-300 cm) $A_{1g}$-active mode that is not observed in graphite. This mode is known as the CNT radial breathing mode. In the intermediate frequency region (400-1350 cm$^{-1}$) weak signals are also observed [6]. Raman intensity for graphite in the 1300-1600 cm$^{-1}$ range is sensitive to sample quality, through the relative intensity of the D- and the G-band. This signal may come from a symmetry-lowering effect due to defects or nanotube caps, bending of the nanotube, and to the presence of carbon nanoparticles and/or amorphous carbon [11].

The Raman spectra of functionalized SWNT present additional peaks, and broadening or shift in characteristic radial breathing modes of raw carbon nanotubes. For instance, the characteristic radial breathing mode, observed at 250 cm$^{-1}$ for SWNT, is no longer present in the case of highly functionalized single-walled nanotubes. In addition, the disorder mode at 1290 cm$^{-1}$ is increased when carbon nanotubes are functionalized. Actually, disorder mode does not increase in non covalent functionalization unless aggressive processing methods alter the structure, causing defects [12].

Although the SWNT structure is extensively reported in literature, MWNTs, as well as doped-nanotubes have been less studied. In this context, Raman spectroscopy has proved to effectively determine vibrational modes attributed to the nanotube structure. As a consequence, we have used Raman spectroscopy in this work to analyze functional carbon nanotubes and to assess that the nanotube structure modification through chemisorption (bond formation) and the degree of roping left in the nanotubes. In fact, if chemical addition to the tube wall occurs in an ordered fashion, narrow, weak lines are expected in the Raman and IR spectra, depending on the symmetry and the fraction of tubes that have been functionalized.

Furthermore, Raman spectroscopy could be used to monitor the deformation of nanotubes in a polymer, to investigate individual nanotube fragmentation under composite loading, and mechanical characterization of bulk nanotube-polymer composite systems [13].

**Experimental conditions**

In this work, Raman Shift values were obtained using a Renishaw Raman Spectrometer with a Laser lamp of Ar (514 nm, 100 mW and resolution 1 cm$^{-1}$) in solid samples at room temperature. The integration time was 100s. The incident laser beam was focused onto the specimen surface through a 100x objective lens forming a laser spot of approximately 2 mm in diameter. The Raman spectra were obtained in the range of 100 to 2000 cm$^{-1}$. Charge coupled detector CCD was used as detector and data were processed with the substraction of laser-induced background luminescence using a personal computer.

**4.3.1.3. Infrared Spectroscopy (FTIR)**

Infrared Spectroscopy is the measurement of the wavelength and intensity of the absorption of infrared light by a sample. FTIR technique is useful to characterize the chemical structure of materials (chemical bonds and functional groups). Specially, the
nature of functional moieties introduced into the nanotube backbone as a consequence of the purification procedures, or chemical functionalization has been analyzed using FTIR.

The technique was used in this work to identify attached molecules and chemical bond differences between as produced CN\textsubscript{x} nanotubes, radically functionalized and polymer-grafted CN\textsubscript{x} nanotubes. Hence, it is expected to obtain information about the several chemical reaction carried out.

Introduction

At temperatures above absolute zero, all the atoms in molecules are in continuous vibration with respect to each other. When the frequency of a specific vibration is equal to the frequency of the incident IR radiation directed on the molecule, the molecule absorbs the radiation. Among the normal modes of vibration of the molecule, those that produce a net change in the dipole moment may result in an IR activity and those that give polarizability changes, may give rise to Raman activity. Some vibrations can be both IR and Raman active.

Principles

Molecules can exhibit translational, rotational and vibrational motion. Each molecular vibrational motion occurs with a frequency characteristic of the molecule and of the particular vibration (Fig. 4.11). The energy of a vibration is measured by its amplitude (the distance moved by the atoms during the vibration), so the higher the vibrational energy, the larger the amplitude of the motion. According to quantum mechanics, only certain vibrational energies are allowed to the molecule (this is also true for rotational and translational energies), so only certain amplitudes are allowed. Associated with each vibrational motion of the molecule is a series of energy levels (or vibrational energy states). The molecule may go from one energy level to a higher one by absorption of a quantum of electromagnetic radiation, such that $E_{\text{final}} - E_{\text{initial}} = h\nu$. Undergoing the transition, the molecule gains vibrational energy, and the amplitude of the vibration increases. The frequency of light required to cause a transition for a particular vibration is equal to the frequency of the vibration, so we may detect the vibrational frequencies by measuring the frequencies of light absorbed by the molecule. Since most vibrational motions in molecules occur at frequencies of about $10^{14}\text{sec}^{-1}$, light of wavelength $\lambda = c/\nu = 3 \times 10^{10}\text{cm/sec}/10^{14}\text{sec}^{-1}$ is required to cause transitions. Light of this wavelength lies in the infrared region of the spectrum. IR spectroscopy, then, deals with transitions between vibrational energy levels in molecules.

Fig. 4.11. Schematics of molecular vibration of polyatomic molecules.
An IR spectrum is displayed as a plot of the energy of the infrared radiation (usually expressed in wave numbers) versus the percentage of light transmitted by the compound.

The spectrum of the molecule appears as a series of broad absorption bands of variable intensity, each of them providing structural information. Each absorption band in the spectrum corresponds to a vibrational transition within the molecule, and gives a measure of the frequency at which the vibration occurs. The frequencies which are absorbed are dependent upon the functional groups within the molecule and the symmetry of the molecule. The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms. Furthermore, the number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules. The infrared spectrum can be divided into two regions, one called the functional group region and the other the fingerprint region. The functional group region is generally considered to range from 4000 to approximately 1500 cm\(^{-1}\) and all frequencies below 1500 cm\(^{-1}\) are considered characteristic of the fingerprint region. The fingerprint region involves molecular vibrations, usually bending motions that are characteristic of the entire molecule or large fragments of the molecule: hence the origin of the term. Used together, both regions are very useful for confirming the identity of a chemical substance. The functional group region tends to include motions, generally stretching vibrations, that are more localized and characteristic of the typical functional groups found in organic molecules. In fact a great number of functional groups are displayed in tables to analyze the spectra [14].

**Experimental Technique**

An IR spectrometer consists of a continuum radiation source of light, interferometer, and detector (Fig. 4.12). The common radiation source is an inert solid heated electrically to 1000 to 1800°C. The considered frequency range is \(10^{12}-10^{14}\) with their corresponding wavenumber of 13000 to 10 cm\(^{-1}\). The most frequently used is the mid-IR region, between 4000 and 400 cm\(^{-1}\). Infrared is energetic enough to excite molecular vibrations to higher energy levels.

![Michelson Interferometer](image)

**Fig. 4.12. FTIR experimental set up. [15]**

In a typical dispersive IR spectrometer, radiation from a broad-band source passes through the sample and is divided and recombined after the split beams travel different optical paths to generate constructive and destructive interference by an interferometer.
The most used interferometer is the Michelson Interferometer. Then the beams fall on the detector, which generates an electrical signal and results in a recorded response. In a Fourier Transform IR all frequencies are examined simultaneously. The standard infrared spectrum is calculated from the Fourier-transformed interferogram, giving a spectrum in percent transmittance (%T) vs. light frequency (cm$^{-1}$). Samples could be analyzed in solid, liquid or gas state. It is considered as a non destructive method.

Attenuated Total Reflectance (ATR) is useful for obtaining IR spectra of difficult samples that cannot be examined by normal transmission method. They are suitable for studying thick or highly absorbing solid and liquid materials.

**Applications to carbon nanotubes and nanocomposites**

The typical applications of the technique are in structure determination, multicomponent qualitative analysis, and quantitative analysis.

FTIR can be used to compare pristine carbon nanotubes and nanotubes with functionalized open ends and/or functionalized sidewalls. The technique is more difficult to carry out in the case of functionalization restricted to nanotube ends.

Some of the absorption characteristic bands associated to functionalized CNTs are presented in summary [16] in Table 4.1.

<table>
<thead>
<tr>
<th>Wavelength cm$^{-1}$</th>
<th>Vibrational mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>2843-2922</td>
<td>C-H stretch modes</td>
</tr>
<tr>
<td>1646</td>
<td>Amide C=O stretch</td>
</tr>
<tr>
<td>1590</td>
<td>amide N-H motion</td>
</tr>
<tr>
<td>1540</td>
<td>amide C-N stretch</td>
</tr>
<tr>
<td>1427-1454</td>
<td>amide N-H bend</td>
</tr>
<tr>
<td>1332</td>
<td>amide C-N stretch</td>
</tr>
<tr>
<td>1187-1257</td>
<td>out-of-plane N-H motion</td>
</tr>
</tbody>
</table>

Traditional FTIR is used until the limit imposed by the high molar absorptivity of carbon nanotubes. Some specialized techniques, as Attenuated-Total-Reflectance (ATR) and reflection, have been applied to avoid spectra acquisition problems.

**Experimental conditions**

In this thesis, FTIR spectra were recorded on a Nicolet 20SXB Fourier-transform infrared spectrophotometer at room temperature. Thin films suitable for FTIR were prepared by casting 2% (w/v) solution in toluene directly on a ZnSe plate. Film thickness was adjusted so that the maximum adsorbance was about 1.0. The films were dried until most of the solvent was evaporated. Using this technique, 32 scans were made for each sample at a resolution of 2 and 4 cm$^{-1}$. The spectra were taken over the range of 4000 to 700 cm$^{-1}$. 

4.3.2. Thermal properties characterization

The thermal analysis comprises a series of methods, which detect the changes in the physical and mechanical properties of a substance and/or its reaction products by the application of heat or thermal energy. The physical properties include mass, temperature, enthalpy, dimension, dynamic characteristics and others.

Thermal properties characterization are used to determine the purity, integrity, crystallinity and thermal stability of the chemical substances under study. Sometimes it is used in the determination of the composition of complex mixtures and/or material inspection [8].

In this thesis, the selected techniques to the study of nanotube polymer-brushes and polymer-nanocomposites were Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

4.3.2.1. Thermogravimetric Analysis (TGA)

TGA is an analytical technique used to measure any reaction involving mass change. Some applications are to determine the material stability, its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated.

The TGA technique has been extensively used to investigate the chemical modification of carbon nanotubes, as well as the thermal stability of polymer nanocomposites made off them. In this thesis, the technique was selected (i) to determine the effect of the purification and disentanglement steps on the as-produced carbon nanotubes, (ii) to verify that the proposed functionalization and polymer grafting of carbon nanotubes took place, (ii) to select the process variables and conditions and to measure the reaction efficiencies in the polymer brushes synthesis, and finally (iii) to determine the composition and thermal stability of the polymer-nanotube composites prepared with polymer brushes.

Experimental Technique

In TGA the change in sample weight is measured while the sample is heated or cooled at a constant rate. The Fig. 4.13 presents a simplified diagram for the thermogravimeter instrumentation.

A sample of the tested material is placed into a high alumina cup that is supported on, or suspended from an analytical balance located outside the furnace chamber. The balance is zeroed, and the sample cup is heated according to a predetermined thermal cycle. The balance sends the weight signal to the computer for storage, along with the sample temperature and the elapsed time. The TGA curve plots the TGA signal, converted to percent weight change on the Y-axis against the reference material temperature on the X-axis [17].

The measurement is normally carried out in air or in an inert atmosphere, such as helium or argon, and the weight is recorded as a function of increasing temperature (usually linear temperature ramp). The maximum temperature is selected so that the specimen weight is stable at the end of the experiment, implying that all chemical reactions are
completed. This approach provides information of the ash content (residual mass, $M_{\text{res}}$) and oxidation temperature ($T_0=\frac{\text{d}m}{\text{d}T_{\text{max}}}$).

![Fig. 4.13. Experimental set up of a Thermogravimeter.](image1)

The furnaces of commercial thermo balances cover the temperature range of 25 to 1700°C.

![Fig. 4.14. TGA of purified SWNTs.](image2)

**Applications to carbon nanotubes and nanocomposites**

The TGA were used to determine the level of purification of raw carbon nanotubes [18] (Fig. 4.14). Thermograms present material weight losses after heat treatment. Organic moieties are first removed, just remaining carbon nanotubes. At higher temperatures, the weight change in an air atmosphere is typically a superposition of the weight loss due to
Materials, methods and characterization techniques

Oxidation of carbon into gaseous carbon dioxide and the weight gain due to oxidation of residual metal catalyst into solid oxides. Oxidation temperature, To, is basically a measure of the thermal stability of nanotubes in air and depends on a number of parameters (diameter, defects and derivatization moiety, active metal particles, etc.) It is impossible to distinguish these contributions, but, nevertheless, thermal stability is a good measure of the overall quality of a given nanotube sample. Higher oxidation temperature is always associated with purer, less defective samples.

In addition, the modified nanotubes were analyzed using TGA to quantitatively determine the amount of attached molecules. For this application, TGA appears as a complementary technique to FTIR (that also detects the presence of these attached molecules and can be used to characterize the changes that occurred chemically) and DSC (sometimes reported to detect changes that occurred between reactive functional groups and the nanotube surface) [19]. The characterization by TGA, once covalent functionalization is confirmed, provides accurately results related to the degree of functionalization if the material is free of impurities [12, 20-22].

In order to obtain additional confirmation of both nanotube content and of the structure of the material, as well as to investigate the effects of the nanotubes on the thermal stability of the matrix, TGA was performed on composites [23]. In nanocomposites, the remaining polymer amount was determined by TGA [24].

Experimental conditions
In this thesis, TGA was carried out in a TA Q500 from 20°C to 900°C at 10°C/min in a N2 atmosphere.

4.3.2.2. Differential Scanning Calorimetry (DSC)

Introduction
DSC measures the amount of energy absorbed or released by a sample when it is heated, cooled (or hold at a constant temperature) as a function of temperature (or time). Practically all physical and chemical processes involve changes in enthalpy or specific heat, and the applicability of DSC to condensed-phase systems is almost universal. A DSC measurement gives the rate of change of enthalpy, so that the area between a DSC curve and its extrapolated baseline indicates the total heat of the reaction.

Differential Scanning Calorimetry is the dominant technique for the thermal analysis of polymeric materials. Thus, in this work, the DSC has been used to determine differences in thermal properties of polymer matrixes used to produce carbon nanotube composites. Glass transition (Tg), melting (Tm) and crystallization temperatures (Tc) were determined at several filler concentrations. In addition, a determination of changes in the miscibility of the polymer blend PS-PEO could be deduced from Tg measurements.

Experimental Technique
When a sample undergoes a physical transformation (such as melting, crystallization and glass transition), heat will be needed to maintain both the reference and the sample at the same temperature, depending on the type of process exothermic or endothermic. By observing the difference in heat flow between the sample and reference,
DS calorimeters are able to measure the amount of energy absorbed or released during such transitions.

A typical DS calorimeter (Fig. 4.15) consists of two sealed pans (reference and sample pan). These pans are often covered by or composed of aluminum, which acts as a radiation shield. The two pans are heated, or cooled, uniformly while the heat flow is monitored. This can be done isothermally or by changing the temperature at constant rate. The result is a plot of the differential heat flow as a function of temperature: a DSC curve. Generally, the differential heat flow is calculated by subtracting the sample heat flow from the reference heat flow. Thus in this case, exothermic processes will show up as positive peaks, while peaks resulting from endothermic processes are negative.

The sample is generally placed in an aluminum sample pan in the sample cell. The reference consists of a matched empty aluminum sample pan (high thermal conductivity) placed in the reference cell. Sample sizes generally range from 0.1 to 100 mg. Experiments could be performed under variable pressures and atmospheres.

Commercial DSC instruments operate from -200°C to about 900°C. This range covers most applications for polymeric materials. Purge gases of helium, argon, nitrogen, or oxygen may be circulated through the calorimeter chamber. The temperature can be maintained isothermally or programmed at heating or cooling rates from 0.1 °C/min to about 20°C/min.

![Fig. 4.15. Experimental device of a DS Calorimeter.](image)

A DSC trace for a polymer at constant heating and cooling rates (Fig. 4.16) shows the main thermal events: glass transition temperature ($T_g$), temperature of crystallization ($T_c$) and its enthalpy and temperature of melting ($T_m$) and its enthalpy. The result of a DSC experiment is a heating or cooling curve. This curve can be used to calculate enthalpies of transitions, by integrating the peak corresponding to a given transition.
Fig. 4.16. Differential Scanning Calorimetry curve for a polymer which shows the glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), heat of crystallization (∆H_{cryst}), heat of melting (∆H_{melt}), heat of degradation (∆H_{decom}) and heat of crystallization from the melt (∆H_{melt-cryst}) [8].

Applications to nanocomposites

A DSC trace may be interpreted to obtain information about the previous thermal and mechanical history of a polymer sample. DSC is often used to study the effects of thermal pretreatment on polymer morphology. Additionally, the fraction of crystallinity can be determined by dividing the enthalpy per gram calculated from the areas under the melting or crystallization peaks by the enthalpy of fusion.

DSC is widely used to investigate the properties of polymer blends. It is especially useful for distinguishing compatible and incompatible polymers; the former have a glass transition temperature intermediate between those of the two components, whereas the latter exhibit the two individual glass transitions. Effects of varying component fraction on the melting temperatures of the blends are determined as well, so that phase diagrams can be developed showing regions of incompatibility, solution and eutectics, and interaction parameters can be calculated.

Many inert additives have a dilution effect and diminish physical transformations as measured by DSC in proportion to their concentrations. Others, such as plasticizers, decrease the glass transition temperature. DSC studies of composite materials help in the interpretation of the interactions among polymers and additives. As T_g is sensitive to quite a series of factors, it is suited to be used in microstructural and phase-behavioral studies in polymer blends and composites. In polymer blends, T_g has been used as a parameter to determine thermodynamic component miscibility. In composite materials, T_g has been proved useful in the study of the effects related to the polymer adhesion at the interface. Thus, the shift in the T_g value is commonly associated to a difference in the polymer chain mobility due to the presence of filler. In the last case, a controversy between the lower and higher shift values comparing to raw material remains. In both cases, T_g shifts towards higher or lower temperatures which allows the related effect to be inferred. In general the decrease of glass transition temperature in polymer composites is interpreted as an improvement of adhesion at the filler polymer interface in accordance with the general theory of polymer composites.
Experimental conditions

Differential Scanning Calorimetry was performed using a TA Instruments DSC 2920. The nanocomposite samples were allowed to equilibrate at 20°C before being heated at 10°C/min to 120°C for PS, PEO and PS-PEO blends materials. The temperature was held for 2 min, then cooled at 10°C/min to 20°C for the case of PS materials and to -70°C for the case of PEO and PS-PEO materials. The samples were held at this temperature for 2 min before being reheated until 20°C. This cooling and heating method was adopted to ensure complete melting of the crystalline fraction for the case of crystalline materials and to remove the thermal history of the samples. The glass transition temperature (Tg), the melting temperature (Tm) and the crystallization temperature (Tc) were measured using this non-isothermal method. The endothermic peak temperature was taken as the melting temperature and the weight percentage crystallinity was calculated using an equilibrium heat of fusion for PEO of 213.7 J/mol.

4.3.3. Electromagnetic and electrical properties characterization

4.3.3.1. Electron Spin Resonance (EPR)

Electronic Paramagnetic Resonance was used to study the chemical interaction of radical solutions with carbon nanotubes. Particularly, the EPR characterization is devoted to (i) the confirmation of the radical trapping behavior of CN$_x$ nanotubes that was observed in other carbon structures and (ii) the determination of the reaction mechanism of carbon nanotubes with radicals, i.e. radical resonance or scavenging. Furthermore, the differences in the interaction of carbon nanotubes with peroxides and nitroxides were explored, as well as the differences between MWNTs and CN$_x$ nanotubes in the radical uptake, i.e. effect of doping.

Introduction

The electronic spin and its interactions with its microscopic neighborhood provide a unique tool for the study of the structure and dynamics of paramagnetic centers. In order to exhibit paramagnetic resonance absorption a specimen must contain unpaired electrons. Paramagnetism occurs: (a) in all atoms and molecules having a net odd number of electrons, e.g. atomic hydrogen, nitrogen, molecular NO, etc.; in a few molecules with an even number of electrons but which still exhibit a resultant magnetic moment; (b) in the transition elements where unfilled inner electron shells results in unpaired electrons; (c) in conductors or semiconductors where the paramagnetism is due to the conduction electrons; and (d) in crystals or glassy materials whose normal bonds have been modified of broken [25]. Electron Paramagnetic Resonance (EPR) or Electron Spin Resonance (ESR) spectroscopy is a technique applicable only to systems with a net electron spin angular momentum, like species containing one or more unpaired electrons, like radicals. Thus, detail analysis of the EPR spectrum frequently make possible to deduce not only the gross chemical structure of a radical but also its conformation [26].
**Principles**

The electron with the corresponding spins has an associated magnetic moment. Consequently, the electron will precess in an applied magnetic field with a precise precessional frequency and will undergo transitions between spin states if energy of the correct frequency is applied (Zeeman effect). The difference in energy of these spin states is given by the equation

\[ \Delta E = \hbar \nu = g \mu_B B \]  

where \( g \) is a dimensionless proportionality constant (g-factor), \( \mu_B \) is the Bohr magneton, and \( B \) is the magnetic induction. In addition, \( \mu_B = eB/4\pi m_e \), where \( e \) and \( m_e \) are the charge and the mass of electron respectively and \( \hbar \) is Planck’s constant [26].

**Technique**

EPR concerns the resonant absorption of microwaves for a material submitted to a magnetic field. The technique involves placing a specimen in a strong magnetic field and observing resonance effects in a radar circuit surrounding the specimen. EPR spectrometers could measure absorptions at (a) fixed frequency, varying the magnetic induction, or at (b) fixed magnetic induction, varying the frequency. Particularly, organic radicals are determined at the former conditions. The measurements are carried out at microwave frequencies range of 9-10 GHz range (X-band) and variable magnetic induction. At resonance, some of the incident microwave radiations are absorbed. The value of \( B \) for resonance is typically about 330-350 mT [27]. Sufficiently high steady-state concentrations of radicals for ESR studies are achieved by the generation of radicals in a matrix at very low temperatures, or by temperature increment, ultraviolet or X-ray irradiation of a radical solution.

The EPR spectrometers record the first derivative of the absorption rather than the absorption curve itself. This gives greater sensitivity and better resolution. The sensitivity of the method enables radical concentration of \( 10^{-8} \) M to be detected [26]. The intensities of the absorption spectra are a measure of the number of electrons participating in the resonance absorption, whereas their shapes provide information about the local chemical environment of the electron. Thus, the area under the absorption curve is proportional to the number of the spins in the sample, i.e. the radical concentration. The radical concentration is determined by comparison with a sample with a known radical concentration.

EPR spectra are characterized by three parameters: g-factors, hyperfine splitting constants, and line widths [26].

For a given frequency, radicals have different g-factors, and consequently resonate at different field strengths. The differences in the g-factors of a radical and a free electron give information about the radical structure. The spin-orbit coupling of the electron in a radical depends on the orientation of the radical with respect to the applied magnetic induction. Nevertheless in solution, the calculated g-factor value of the radicals is time-averaged because of their rapid tumbling. The measured g-factor of a free electron spin yields \( g = 2.002319 \). In real materials, \( g \) may differ from this value, depending on variations in coupling, between spin and orbital angular momentum. The \( g \) values of organic free radicals are usually close to the free-electron value [8].

The hyperfine splitting characteristic of EPR spectra elucidates the structure and the shape of the studied radical. It arises from the interaction between the unpaired electron and neighboring magnetic nuclei. The hyperfine coupling constant or splitting constant is the
separation between two spectra absorption lines and it is measured in milliTesla (mT) or in Gauss (1 mT=10 Gauss). In general, interaction with \( n \) equivalent protons gives \( n+1 \) lines which relative intensities are given by the coefficients of the binomial expansion. Interaction of the unpaired electron with a nucleus of spin \( I \) gives \((2I+1)\) lines. In particular, the ESR spectrum of a radical centered on nitrogen \((I=1)\), like nitrooxides, consists of a 1:1:1 triplet. The magnitude of the nitrogen coupling constant is also sensitive to the type of radical trapped. Thus, some nitrogen compounds were used as spin trapping to form nitrooxides (stable radical). Spin traps have also been used quantitatively to determine rate constants for radical processes.

Theoretical EPR spectra are often constructed using either Gaussian or Lorentzian line shapes. The derivatives of the Gaussian and Lorentzian line shapes are expressed by

\[
I_G = \frac{4I_0(H-H_0)}{(\Delta H)^2} \exp \left[ -2 \left( \frac{(H-H_0)}{\Delta H} \right)^2 \right] \\
I_L = \frac{I_0^2(\Delta H)^2(H-H_0)}{[\Delta H)^2 + (H-H_0)^2]^2}
\]

where \( I_0 \) is the peak amplitude of the absorption line, \( H_0 \) is the magnetic field, and \( \Delta H \) is the linewidth [25].

**Applications to carbon nanotubes and nanocomposites**

It was observed that EPR is sensitive to both itinerant (conduction electrons) and localized spins (defective sites). Thus, EPR experiments could determine the metallic transport properties in order to clarify the electronic structure and defective sites in carbon nanotubes. Additional information indicative of the preparation methods and the purification procedures could be also obtained.

In addition, EPR is a tool to probe experimentally the molecular occurrences associated with mechanical damage and failure of polymers [8].

**Experimental conditions**

In this work, EPR solution measurements were performed on a JEOL TE300 spectrometer, using a cylindrical cavity (TE011 mode) operating at X-band frequencies (near 9.17 GHz) with 100 kHz field modulation and using a microwave power around 1 mW. All spectra, recorded at different temperatures, were obtained using the JEOL DVT variable temperature system. Quartz tubes (2.5 mm ID, 13 mm height) were used for the ESR measurements. To avoid the distortion of the spectrum, the modulation amplitude was kept at less than or equal to one-third of the peak-to-peak linewidth. The number of spins (radicals) in each sample was obtained by double numerical integration of the first derivative of the resonance signal, according with the equation:

\[
A = \int_{HA}^{HB} dH \int dH' S(H')
\]

where \( HA \) and \( HB \) are the initial and final magnetic fields of the resonance curve, respectively, and \( S(H') \) is the absorption at magnetic field \( H \). The spin (free radical) concentrations were measured by comparison with a standard solution of TEMPO and of known concentration. The software for the data processing was Sprit-382. All spectra were recorded under identical conditions.

Sample observations were performed in organic solution/ dispersion. Initiator and controller solutions at known concentrations were prepared prior addition to solid materials.
Nanotubes samples were dispersed by 10 min of ultrasonication using benzene, toluene or xylene, and then an amount of initiator/controller solution was added. For the measurements, liquid dispersions were placed into EPR quartz tubes centered into the regular cavity.

Additional, EPR spectra of solid materials were obtained in a spectrometer at 9.42 GHz with 20 DB of microwave power. Spectra of all samples were recorded applying both a wide scan covering a range of 1000G centered at 3500G.

4.3.3.2. Dielectrical measurements

The dielectric spectroscopy (sometimes called impedance spectroscopy) consists of studying the frequency dependent complex dielectric permittivity of insulator materials. It is based on the interaction of an external electrical field with the dipole moment of the sample. In this thesis, the dielectric spectroscopy has been used to determine the dependence of the electrical behavior of carbon nanotube-polymer composites with the nanotube type and concentration.

*Introduction*

There are a number of different dielectric mechanisms, related to the reaction of the material to the applied alternating field. In general dielectric mechanisms can be divided into relaxation and resonance processes. The dielectric spectroscopy is used for physical and chemical analysis of material, because it enables investigation of dielectric relaxation processes in an extremely wide range of characteristic times ($10^6$ - $10^{12}$ s). As the frequency decreases from $10^{17}$ Hz the phenomena involved are: electronic polarization, atomic polarization, dipole relaxation and ionic relaxation, as shown in Fig. 4.17.

![Fig. 4.17. Dielectric relaxation processes as a function of the frequency [28].](image)

The application of an electric field to a material produces the polarization and eventually the apparition of an electrical charge flux. This behavior could be approached by a perfect conductor (Ohm Law).
where \( j \) is the electrical flux, \( E \) the applied electrical field and \( \sigma \) the conductivity. In addition for a perfect dielectric material,

\[ P = \varepsilon_0 \chi E \quad [4.6] \]

where \( P \) is the polarizability, and \( \chi \) is the susceptibility.

For an isotropic and homogeneous material at low frequency the polarization of the material is proportional to the electrical field applied. The polarization could be expressed as the impedance spectrum or the frequency-dependent complex permittivity and conductivity that characterizes the charge-density fluctuations within the sample. Such fluctuations generally arise from the reorientation of the permanent dipole moments of individual molecules or from the rotation of dipolar moieties in flexible molecules, like polymers. The timescale of these fluctuations depends on the sample and on the relevant relaxation mechanism. Dielectric spectroscopy is able to monitor cooperative processes and thus provides a link between molecular spectroscopy and bulk properties of the sample, especially viscoelastic and rheological behavior. Materials dielectric properties are determined by its molecular structure, if the molecular structure changes, its dielectric properties changes.

**Principles**

The conductivity of a material is measured by the application of a sinusoidal tension of the form:

\[ U = U_0 \sin(\omega t) \quad [4.7] \]

resulting in a sinusoidal current with a dephased angle \( \phi \),

\[ I = I_0 \sin(\omega t + \phi) \quad [4.8] \]

Using low electrical fields (in the order of Volt/cm), the polarization and conductivities are proportional to the electrical field. The conductivity \( \sigma^* \) could be defined as the ratio among the current and the tension in the sample and is a complex number,

\[ \sigma^* = \frac{I}{U} \quad [4.9] \]

Thus, the real and imaginary parts of the conductivity are \( \sigma' = |\sigma^*| \cos \phi \) and \( \sigma'' = |\sigma^*| \sin \phi \). The ratio between the real and the imaginary conductivity, \( \tan \phi = \sigma''/\sigma' \) represents a dissipative energy by Joule effect.

The dielectric spectroscopy in an homogeneous medium could permit the study of the relaxations in the polymer. Furthermore, the evolution of the real and imaginary parts of the conductivity a low frequency in a blend insulant-conductor could be followed [29].

Figure 4.18 shows the conductivity zones of a material:

1. **Dielectric zone.** The composite behavior corresponds to an insulating material. The measured phase is near from 90° and the conductivity is almost the same as the matrix.

2. **Transition zone.** The conductivity suffers considerable variations due to the formation of a percolating network.
3. **Conductive zone.** This zone corresponds to the increment of the density of the conductor network.

**Experimental Technique**

In dielectric spectroscopy or AC impedance spectroscopy, the sample is disposed between two parallel electrodes, constituting, hence, a capacitor during AC measurement. The sample is subjected to a sinusoidal perturbation of intensity in V with variable frequency. The analyzer detects the current (intensity and phase) through the sample at each frequency. Complex impedance is calculated as a function of frequency. The impedance can then be separated into the frequency dependent conductivity and relative permittivity [30].

![Conductivity zones of a material](image)

Fig. 4.18. Conductivity zones of a material.

From the AC impedance spectroscopy [31] performed at room temperature, the real and imaginary parts of the impedance (Z*) can be obtained as a function of the frequency. The complex admittance (Y* = 1/Z*) of the nanocomposites can be modeled as a parallel resistor (R) and capacitor (C) and written as a function of angular frequency (w)

$$Y^*(w) = Y' + jY'' = \frac{1}{R} + jwC$$  \[4.10\]

The specific AC conductivity of the nanocomposites as a function of frequency $\sigma(w)$ is calculated from the modulus of the complex admittance, and was used as a means of comparing the frequency behavior

$$y(w) = |Y^*| \frac{d}{A}$$  \[4.11\]

where $d$ is the sample length or distance between the electrodes, and $A$ is the contact area. Values of AC conductivity were determined from the real part of the complex admittance...
The pure insulating behavior as indicated by the frequency-dependent increase in conductivity with a slope of unity on the log-log plot of specific conductivity against frequency. This behavior is typical of a dielectric material, which for frequencies
\[ f > \frac{\sigma_0}{2\pi\varepsilon_0\varepsilon'} \]
gives a conductivity of
\[ \sigma = 2\pi\varepsilon'\varepsilon_0 \]
where \( \varepsilon_0 \) is the permittivity of the vacuum and \( \varepsilon' \) is the real part of the dielectric constant [32].

A material permittivity is usually normalized to the permittivity of vacuum. The real part of permittivity, \( \varepsilon' \), is a measure of the energy stored and is called the dielectric constant. The imaginary part of permittivity, \( \varepsilon'' \), is a measure of the energy loss and called the loss factor. In addition, loss tangent is the imaginary part divided by the real part vs. frequency.

Many materials are a mixture of different sized molecules. The permittivity of these mixtures of materials will depend on the interaction of these molecules, their mass, charge and charge distributions.

*Applications to carbon nanotubes and nanocomposites*

The relaxational dynamics of soft matter in polymers is characterized by a large frequency range. Dielectric spectroscopy can provide information about the segmental mobility of a polymer by probing its dielectric properties.

Studied materials are among others: polymers, polymer blends, polyelectrolytes, normal and supercooled liquids, and solid state materials.

*Experimental conditions*

The AC conductivity measurements were performed at room temperature in the range of frequencies of 1mHz to 1MHz with a voltage of 0.1 and 1 V using a Solartron 1226 bridge system composed by an analyzer of frequencies and a dielectric interphase with a reference module controlled by a computer. The complex admittance \( Y^* \) was recorded versus time. From this admittance, the conductivity can be deduced with the equation 4.11.

4.3.4. Dynamical Mechanical Analysis (DMA)

*Introduction*

The mechanical dynamical analysis or mechanical spectroscopy permits the study of the viscoelastic properties of a material by a measurement of the dynamic module as a function of the temperature (isochrones measurements) or the solicitation frequency (isotherm measurements).
**Principles**

Polymer are described as viscoelastic materials, which behavior is intermediate between a perfect elastic solid material (Hooke Law), where the deformation \( \varepsilon \) is proportional to the stress \( \sigma \):

\[
\varepsilon = \sigma / E
\]

\( E \) is the Young modulus, and the ideal viscous liquid (Newton Law), where the deformation speed \( \dot{\varepsilon} \) is proportional to the stress \( \sigma \):

\[
\dot{\varepsilon} = \sigma / \eta
\]

\( \eta \) is the Newtonian viscosity.

The relative importance of these parts is dependent of the stress time application (or frequency) and of the temperature. The Fig. 4.19 describes the typical evolution of the viscoelastic modulus of a polymer with the temperature:

![Fig. 4.19. Polymer modulus evolution as a function of the temperature [29].](image)

The four zones corresponds with:

1. **Glassy state.** The polymer is in the vitreous state. Its elastic behavior is from enthalpic origin.
2. **Principal relaxation.** The behavior becomes viscoelastic. The module changes rapidly with the temperature.
3. **Rubery state.** The polymer could perform considerable elongations. Its elastic behavior is entropic in nature.
4. **Flux.** The polymer behaves like a viscous fluid.

**Technique**

The mechanical spectroscopy (or Dynamical Mechanical Analysis (DMA)) permits the characterization of the viscoelastic properties of a polymer by the measurement of its Dynamic Module in function of the temperature (isochrones measurements) or the
solicitation frequency (isotherm measurements). The sample is solicited by the application of a stress, which varies periodically,

$$\sigma = \sigma_0 \sin(\omega t)$$  \[4.17\]

resulting in a sinusoidal deformation of the sample,

$$\varepsilon = \varepsilon_0 \sin(\omega t + \phi)$$  \[4.18\]

The deformation amplitude is from the order of $10^{-6}$ and $10^{-4}$ to coincide with the linear domain, where the Hooke and Newton laws are verified.

The dynamic module $E^*$ considers the ratio between the stress applied and the deformation of the sample measured,

$$E^* = \frac{\sigma^*}{\varepsilon^*} = E' + iE''$$  \[4.19\]

Additionally,

$$E' = |E^*| \cos \phi$$

and

$$E'' = |E^*| \sin \phi$$

Thus,

$$E' = (\sigma_0 / \varepsilon_0) \cos \phi$$

and

$$E'' = (\sigma_0 / \varepsilon_0) \sin \phi$$.

Furthermore, the desphase between the stress and the deformation could be measured as

$$\tan \phi = \frac{E''}{E'}$$.

This coefficient is also named frictional interior coefficient and represents the proportion of the dissipated energy in the form of heat in the sample in relation with the elastic energy involved in a deformation cycle. The variations of the complex module $G^*$ and the $\tan (\delta)$ in temperature function or the frequency permit the identification of the associated relaxations to the several freedom degrees of the polymer chains.

In homogeneous systems, the variations in the dynamic module as function of the temperature (or the frequency) corresponds with the relaxation phenomena characteristics of a polymer. These relaxations have their origin in the mobility of the polymer chains at the molecular scale and their molecular motions depending on the temperature and the characteristics of the polymer (as the molecular weight). In the case of polyphase systems, the mechanical behavior depends additionally of the domain sizes and the morphology.

**Experimental conditions**

DMA tension mode experiments were performed over polymer nanocomposite films at 1 Hz of frequency and 20 to 120°C in a TA Instrument equipment.

### 4.3.5. Other characterization techniques

**Solubility**

Differences in solubility could be used in the separation of bounded and non-bounded functional groups to carbon nanotubes. In this thesis, the use of organic solvents was selected to determine differences among functionalized and non-functionalized carbon nanotubes.

**Size exclusion Chromatography (SEC, or Gel Permeation Chromatography)**

SEC operates on the hydrodynamic volume difference between polymer chains of various sizes. When a polymer solution (mobile phase) is forced through a column containing a nanoporous material (stationary phase), smaller polymer molecules tend to pass through the pores, whereas larger chain elute from the column faster due to entropic
exclusion effects. Thus, analyzing the column outlet using a UV-visible or refractive index detector as a function of time, the molecular weight (MW), the molecular weight distribution and the polydispersity of the polymer sample can be obtained.

In this thesis, polymer molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography, using a Waters GPC equipment with a 717 plus Autosampler, a 996 RI detector, a 600 controller, a 600 pump, and equipped with two Styragel columns (HR3 and HR4). Polystyrene was used as calibration standard. THF was used as eluent at a flow of 1.0 ml/min at room temperature.

4.4. Conclusions

The materials and the methods used to prepare polymer-CNTs composites have been described. In addition, the principles of characterization techniques used in the research were considered. Some of the already known applications in the area of nanotubes and their composites were also depicted.

To sum up, some of the main techniques used in this study were: (a) Raman spectroscopy that is performed to ensure that the nanotube sidewalls are modified through chemisorption (bond formation). (b) TGA is made to provide an indication of the degree of functionalization. (c) TEM, SEM and AFM also show sidewall modifications and roping interactions. IR spectroscopy could be useful in the identification of the organic groups appended to the sidewalls of the nanotubes in combination with Raman spectroscopy. However in this case, NMR spectroscopy is usually not very informative, because traces of iron impurities, local field effects due to the nanotubes themselves, and the slow tumbling rates of the nanotubes that cause signal broadening [12].

Finally microscopy techniques were used to determine dispersion and morphological properties of the polymer-CNTs composites. Thermal, electric and mechanical behavior was also important to determine.
References


15. www.imb-jena.de/ImgLibDoc/ftir/IMAGE_FTIR.html.


Materials, methods and characterization techniques