Conclusions and Perspectives

The enhancement of general performances of nanotube-based polymer composites is expected when the dispersion, contact and load transfer from filler to the matrix is optimized. According to several reports, these characteristics could be facilitated when the nanotubes are functionalized [1-4] and/or polymer-grafted [5-9] with molecules compatible with the host polymer matrix.

The main goal of the work reported in this thesis is devoted to the production of polymer composites of PS-grafted CN$_x$ nanotubes. The synthesis of these materials involves:

(i) the development of a novel chemical methodology to polymer grafted nitrogen-doped carbon nanotubes using a nitroxide-mediated radical polymerization (NMRP) approach. The NMRP is used with radical functionalized CN$_x$ nanotubes to obtain macroinitiators that could overcome *in situ* solution polymerization to form polystyrene-grafted nanotubes. Some advantages of the methodology involve the preparation of materials without an extended degradation of nanotube structure (like in the acid treatment); furthermore the *in situ* polymerization could favor the grafted polymer architecture, the density grafting control as well as the polymer chain polydispersity. In summary, radical functionalization and NMRP methodology represent an interesting approach to the synthesis of polymer brushes of carbon nanotubes. It is important to highlight that at the present time, some reports support the feasibility of the use of radical functionalization [3, 8, 10] and NMRP [11-13], independently, to functionalize carbon nanotubes. Nevertheless, an approach using both combined techniques has not being used before.

(ii) the preparation by solvent-casting-pressing of polymer-carbon nanotubes composites using polymer-grafted CN$_x$ nanotubes in order to improve the dispersion and interfacial adhesion between the filler and the matrix. Some of the desired properties involve the enhancement of the thermal, electrical and/or mechanical behavior of the original materials. This work, in addition, present an effort to use different polymer matrices as PEO and PS-PEO polymer blends, in addition to the already studied PS.
The preparation of polymer composites of PS-grafted CN$_x$ nanotubes, thus, was delimited by the main objectives described in the introduction and the main results will be outlined in the following paragraphs.

First of all, the synthesis of polymer-grafted CN$_x$ nanotubes, using a two step approaches (the initiator-controller attachment (radical functionalization), and the in situ polymerization via NMRP) was carried out as confirmed by several characterization techniques.

The radical functionalization of CN$_x$ nanotubes by initiator-controller (BPO and nitroxides) radicals was achieved, proceeding by covalent attachment. It was observed that the functionalization reaction preserves the internal structure of the bamboo type nanotubes. Furthermore, an homogeneous radical reaction over the nanotube surface was evidenced. The attached radicals seem to be resonant or trapped over nanotube surface depending on the nanotube superficial group (based on nitrogen or any other). Thus, the radical attachment of initiator-controller radicals to carbon nanotube surface could determine the formation of macroinitiators, or even more controlled macroinitiators labile to initiate in situ polymer-grafted chains.

The polymer grafted-CN$_x$ nanotubes (PS-g-CN$_x$) have been successfully formed using in situ NMRP. The polymerization of PS takes place on radical functionalized carbon nanotube surfaces. The grafted polymer is covalently attached to carbon nanotubes, forming an amorphous layer surrounding the nanotubes. Some properties of the novel materials involve the enhancement of their solubility and stability in organic solvents. The comparison of PS and CN$_x$ physical blends with grafted PS-g-CN$_x$ systems determine strong differences in their behavior, due to the nature of the attachment. Also, the importance of the reactivity of CN$_x$ nanotubes in the polymer-brushes preparation was highlight in comparison with un-doped MWNTs.

Some of the main goals of this thesis in the polymer-grafting step involved: the development of a novel methodology to attached polymer chains to the nanotube surface, the exploration of the synthesis conditions using a Parallel Polymerization Reactor (PPR) system, the chemical process to functionalized carbon nanotubes that does not induce extended nanotube structural damage, and finally the innovative PS-g-CN$_x$ nanotube materials properties that could be used in the preparation of polymer nanocomposites (enhancing the dispersion of the nanotubes within the matrix and the interfacial strength).

As a second part of the work, the preparation of PS, PEO and PS/PEO nanocomposites of PS-grafted CN$_x$ nanotubes was carried out by a solution-casting-pressing method. The analysis of the materials gives interesting results about the preparation method and the inherent nanocomposite morphology. The effect of the addition of polymer-grafted CN$_x$ nanofillers was compared to the addition of MWNT and CN$_x$ nanotubes.

In terms of morphology, the homogeneity of the samples (in terms of filler dispersion) is higher for the homopolymer nanocomposites (PS-based and PEO-based) than for the polymer blend (PS-PEO based nanocomposite) using several kinds of carbon nanotubes as fillers. In addition, the adhesion of the nanotubes with the polymer matrixes can be obtained indirectly from morphological observations. This parameter seems to vary according to polymer and filler types: for example a strong adhesion and good interaction
to PS is observed with PS-g-CN$_x$ nanotubes. Conversely, MWNTs display good interactions with PEO. Finally, the tortuosity of nanotubes seems to increase according to the polymer matrix and according to the local nanotube concentration, thus higher for polymer blend composites, followed by PEO and finally PS.

In general, the processing critical issues as dispersion and interfacial adhesion strongly vary between materials. The PS-based nanocomposites exhibited better properties due to the homogeneity of the samples, but also due to the compatibility of the polymer-grafted around nanotubes and the composite matrix. In the other polymer cases, some trends were highlighted in the preparation and processing of the samples. Therefore, an optimization of the process becomes necessary to obtain better composite materials when PEO and PS-PEO blends are used.

Additional results are related to the characterization of the composite samples in relation to their physical properties. The results vary according to the type of polymer matrix and filler, as well as filler content. Some relevant results are summarized below.

PS/CNTs composites revealed interesting results in the modification of the properties as the nanotubes were added: enhancement in the conductivity at low electrical percolation thresholds, a moderated increase in the storage modulus above T$_g$, and a small improvement in the thermo-mechanical stability. Thus, the materials form percolating networks at different dispersion quality and where nanotubes present entanglements. In general, the synthesized composites at the studied conditions exhibit better performance when MWNT are used in comparison to CN$_x$ and PS-g-CN$_x$ nanotubes.

PEO/CNTs composites exhibit dispersion trends mainly due to the processing conditions. This fact determines inhomogeneity in samples that consequently produces precision and reproductibility problems. In these conditions, no clear enhancement was obtained. In fact, a geometrical percolation network was formed that increases the conductivity level of the insulating polymer matrix, but did not efficiently enhance the mechanical properties.

PS-PEO/CNTs composites presented even stronger problems in their physical performance due to inherent immiscibility of the homopolymers and the processing conditions. Thus, the experimental results of their characterization were not reported.

Finally, a close relation between morphology and physical properties were found. Thus, all the nanocomposite materials exhibited differentiated thermal, electrical and mechanical properties. In general, the properties enhancements due to the addition of carbon nanotubes to polymer matrices are good in the case of electrical properties, but moderate in the case of mechanical properties. The most promising at the moment are those related with the PS/CNTs composites.

In addition, very different properties modifications were induced by the use of PS-grafted CN$_x$ nanotubes compared to MWNT and CN$_x$ nanotubes in terms of interaction with polymer matrixes. These modifications can be with no doubt attributed to the grafted polymer and could be indicative of the successful synthesis of the polymer brushes.

At this point the main goals of the work concerning the polymer nanocomposite preparations are: the synthesis and systematical study of several kinds of polymer-nanotube materials, particularly using PEO and PS-PEO polymer blends as matrices, and several
types of nanotubes including PS-g-CN₃ nanotubes and the preparation of novel composite materials with interestingly conductor properties and moderated mechanical properties.

After all these commentaries, it can be possible to state that most of the thesis objectives were satisfied. At this point it has to be remarked the enormous utility from the basic and technological point of view of the developed nanomaterials.

The polymer-grafting of carbon nanotubes and the composite synthesis methodology presented hold immense promise for future work encompassing different areas. Some ideas regarding possible directions are described below.

**Polymer-grafting of carbon nanotubes**

1. As discussed in previous sections, the current NMRP grafting technique can be significantly improved, i.e. optimization of the synthesis processing variables of PS-g-CN₃ polymer brushes for highly specific applications. Among them, the evaluation of the control polymerization process in order to produce monodispersed and copolymer chains grafted from the nanotube surface; and the evaluation of several initiator-controller systems (like AIBN and alcoxiamines) and solvents. In addition, a theoretical study in terms of kinetics and modeling of the NMRP systems can be also performed.

2. The knowledge about the polymer-grafting of PS over nanotube surfaces could be extended to other polymers to enhance other polymer-composite systems. Thus a variety of thermoplastics can be synthesized and grafted to carbon nanotubes.

3. Additional studies in the use of several kinds of carbon nanotubes (i.e. MWNT, CN₃) according to the polymer grafted and the specific applications could be carried out. Particularly, an optimization of the behavior of each nanotube system can be done.

**Polymer-carbon nanotubes composite preparation**

4. In relation to the nanocomposite preparation, the optimization of the production method can be done using several solvent systems and conditions for the solvent-casting-pressing method, or even more using alternative methods, as melt blending.

5. Studies of composites prepared by *in situ* polymerization using PS-g-CN₃ nanotubes or even non functionalized type can be suggested due to the apparently good dispersion properties.

6. Evaluation of several kinds of polymer matrices in the production of polymer/CNTs composites, like using different polymer blends with controlled morphology and/or specific physico-chemical properties (miscibility, amphiphilic, etc)

7. Several studies of the electrical behavior of polymer/CNTs composites, as:
   (i) The enhancement of the electrical properties of the composites by the addition of inorganic salts in the case of PEO/CNTs systems.
   (ii) the electrical evolution of nanocomposite materials, i.e. AC electrical conductivity, during tensile tests to understand microstructure, obtaining graphs of conductivity vs. strain;
(iii) the evaluation of the current as a function of voltage to determine the Ohmic (linear) and non Ohmic (quadratic) behavior and thus the type of conductivity. In the linear region the current is dominated by carriers injected by the electrodes and known as space-charge limited current (SCLC). The quadratic behavior holds in the presence of shallow traps, or in the theoretical limit of no traps. This behavior could be described by the Child-Langmuir equation: \[ J = \frac{9\mu e V^2}{8l^3} \], where \( \mu \) is an effective mobility, \( \varepsilon \) the permittivity, and \( l \) the electrode spacing. The effective mobility is the product of the free carrier mobility and the fraction of free charge \( \theta \). Hence the effective mobility of carriers from the current-voltage characteristics could be calculated;

(iv) the temperature dependence of the conductivity using \[ \ln \left[ \frac{\sigma(T)}{\sigma_0} \right] = \gamma \left( \frac{T}{T_0} \right) \] where \( \gamma \) is the temperature exponent, \( T_0 \) is the reduction temperature.

7. Several studies respect to the mechanical properties of the materials, such as the evaluation of other mechanical properties of the materials.

8. The proposition of a specific model adapted to the polymer/CNT composite produced.

As can be seen the future directions of the work presented in this thesis are enormous and diverse. In all cases it has to be highlighting the actual importance of nanocomposite materials that could also forward autoensambling and that present specifically design properties, like in the polymer/CNTs composites using high developed fillers.
References