Summary

In this PhD thesis polymer nanocomposites containing multi-walled carbon nanotubes (MWCNT) were studied. As polymer matrices were used thermoplastic polymers, semicrystalline (polyamide 6 (PA6), polypropylene (PP), polyethylene terephthalate (PET)) or amorphous (polymethyl methacrylate (PMMA)), as well as thermosets (epoxy resins). The main objective was the preparation of conductive nanocomposites and the investigation of their structure – property relations scheme. Such type of nanocomposites can be used for electromagnetic interference shielding, electrostatic dissipation and antistatic materials.

Special attention was paid to the study of the electrical percolation threshold, where the transition from the insulating to the conducting phase is occurred, by the formation of the first conducting pathway. Additionally, the influence of the choice of the polymer matrix, the preparation method and conditions, the modification of the matrix and the addition of a third component (surfactants) are investigated, by dielectric relaxation spectroscopy (DRS) measurements. Criteria constitute both the percolation threshold values (p_c) and the levels of conductivity (σ_{dc}). Furthermore, the influence of the addition of MWCNT on the dielectric relaxation mechanisms, for the samples below p_c, and the temperature dependence of conductivity, for the samples above p_c, is also studied. For the latter direct current measurements, based on four probes configuration, were employed, from very low temperatures (~ 15 K). Additional information regarding the thermal and mechanical properties of the prepared composites was provided by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA).

The addition of carbon nanotubes induced significant changes, especially in the crystallization of the semicrystalline systems. In particular, it was shown the action of MWCNT as nuclei agents, the increase of the degree of crystallinity and the appearance of a new crystallization peak, which was attributed to trans-crystallinity. The existence of this structure is of a great interest, as concerns the mechanical properties of the nanocomposites. This crystalline layer around the carbon nanotubes walls seems to intervene between the matrix and the inclusions, transferring effectively the loads from the polymer to the stiff nanotubes.

As concerns the electrical properties, it was shown that all the systems exhibit low p_c (0.03 – 3.8 wt %). The observed low p_c, in combination with the high range of *dc* conductivity values (10^{-12} – 10^{0} S/cm), make these nanocomposites suitable to cover the whole range of possible applications. The lowest p_c values were reported in the systems which were prepared by in situ polymerization (PET/MWCNT, Epoxy/MWCNT), due to the low viscosity during the dispersion of the nanoparticles. The crucial role of viscosity was also proved in PP/MWCNT systems, obtained by the dilution of a starting masterbach. It was found that as the melt flow index of the PP used for the dilution increases, the p_c values decreases. Another parameter of a great interest is the influence of crystallinity. Comparison between the systems obtained by melt mixing indicate that the existence of crystallinity prohibits the development of the conductive network, decreasing in that way σ_{dc} values and increasing p_c. The last key parameter which was examined is preparation conditions. It was shown that DRS and DSC can be very useful techniques in optimization of the preparation conditions. The optimization of mixing conditions, as well as the appropriate choice of the dilution polymer of the masterbatch PP/MWCNT, induced a decrease in p_c from 3.8 to 1.2 wt %.

The investigation of the temperature dependence of conductivity revealed that the conductivity mechanism, which controls the movement of the charge carriers in the nanocomposites, is strongly related on the morphology of the system under examination. In particular, it was shown that the existence of a crystalline polymer layer around MWCNT walls, make the charge carriers to «travel» though tunneling between the conductive inclusions (Fluctuation Induced Tunneling, FIT). In contrast, absence of crystallinity in the system allows further approach between the inclusions, making the variable range hopping model the most precise description in the system.

Finally, findings mainly obtained by DRS, and by DSC and DMA, showed that the addition of carbon nanotubes does not affect the molecular mobility of the polymer used as a matrix. The absence of strong interactions between the matrix and the inclusions rationalized that.