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Multiwalled Carbon Nanotubes Produced by a Continuous CVD Method and Their Use in Melt Mixed Composites with Polycarbonate

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Summary: In this study, two samples of multiwalled carbon nanotubes (MWNT) were synthesized by CVD of acetylene over Fe_2Co catalysts supported by $CaCO_3$ using different temperatures. The material produced at 660 °C (MWNT600) shows slightly better performance as evidenced by lower mean tube diameter and better conductivity as compared to the sample produced at 700 °C (MWNT700). In addition, it has a higher [O]:[C] ratio. Both materials were incorporated into polycarbonate using melt mixing using a small scale compounder. The results prove that these materials are very suitable for polymer composite applications as they show low electrical percolation concentration and good mechanical enhancement. The percolation threshold is as low as <0.875 wt% for MWNT660 and <1 wt% for MWNT700. MWNT700 showed slightly better dispersability as evidenced from light microscopy, SEM, and TEM. The effects in the stress-strain curves are similar in both composites, indicating a stress increase with MWNT incorporation.

Keywords: electrical percolation; mechanical behaviour; melt mixing; multiwalled carbon nanotubes

Introduction

Beside of many efforts it is still a challenge to synthesize multiwalled carbon nanotubes (MWNT) on a large scale at high quality and low cost. Currently, chemical vapour deposition (CVD) over supported catalysts has become the most popular technique to scale up the MWNT synthesis. At the EPFL it was shown recently that by using a rotary tube furnace an upscaling of the production is possible.[1–3] Carbon nanotubes are produced by the recently evidenced equimolar reaction between acetylene (C_2H_2) and CO_2.[2] CO_2 is provided to the reactor by the thermal decomposition of $CaCO_3$ used as support. This is the first growth conditions were carbon atoms, to build the nanotube structure, is not produced by the classical decomposition of the carbon source used (classical decomposition reactions are: $C_xH_y \rightarrow \times C + y/2\ H_2$ or $2\ CO \rightarrow C + CO_2$). The kinetics characteristics of the C_2H_2–CO_2 equimolar reaction are outstanding. Catalyst lifetime reaches about 15 minutes while the growth rate is up to 15 mg/min of CNTs from 100 mg of $Fe_2Co/CaCO_3$ supported catalyst. In such growth conditions, more than 50% of acetylene is converted into carbon nanotubes. This very high reaction yield allows the mass production of carbon nanotubes. Furthermore, the diameter of the CNTs can be controlled by the growth temperature. Actually, Fe_2Co metallic particles are coarsening by raising growth temperature leading to CNTs with higher diameter.

In this contribution, two different samples synthesized at different temperatures

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were incorporated into polycarbonate (PC) by melt mixing in order to detect their percolation behaviour in an insulating matrix.

MWNT Synthesis and Characterization

MWNTs were synthesized by CVD of acetylene over Fe_2Co catalysts supported by $CaCO_3$.[1–3] Sample MWNT700 was produced at 700 °C whereas sample MWNT660 was produced at 660 °C. The obtained samples were purified in diluted hydrochloric acid in order to remove metallic catalyst and support.

Raman spectra of both MWNT (Figure 1) show the disorder induced D band at 1317 cm^{-1}, the graphite mode G-band at 1614 cm^{-1}, and the D* band (overtone of D band) at 2625 cm^{-1}.

The Raman spectra were taken using a laser excitation wavelength of 785 nm. The D/G ratios calculated from the height of the bands as well as from the areas of the bands are comparable for both samples indicating no significant differences in the perfectness (crystallinity) of the graphite layers.

Transmission electron miscroscopy (TEM) and scanning electron miscroscopy (SEM) are shown in Figure 2 and 3, respectively.

The micrographs indicate that the MWNT diameter range is somewhat larger in the sample prepared at 700 °C (15–50 nm) compared to the sample synthesized at 660 °C (10–50 nm). This is connected with the coarsening of the Fe_2Co metallic catalysator particles by raising the growth temperature. The MWNT diameter distributions were determined from SEM images using 200 tubes per sample and are shown in Figure 4. For MWNT660 a mean diameter of 22 nm was found, whereas for MWNT700 the mean diameter was 28 nm. The length were up to 10 μm in both materials. For SEM a Philips XL 30 FEG operated at 30 kV was used, for TEM a Philips CM200 system equipped with an EDAX system.

The conductivity of the powdery MWNT materials was measured using a special cell (IPF construction) consisting of a sample channel with a diameter of 5 mm connected with two gold electrodes, whereas the upper electrodes acts as indenter realising pressures up to 30 MPa. Small sample amounts leading to about 2 mm sample thickness (at 30 MPa pressure) were filled in the channel and the conductivity was measured as function of pressure. The sample MWNT660 showed a conductivity of 24 S/cm, whereas MWNT700 showed 18 S/cm at 30 MPa, indicating slightly better

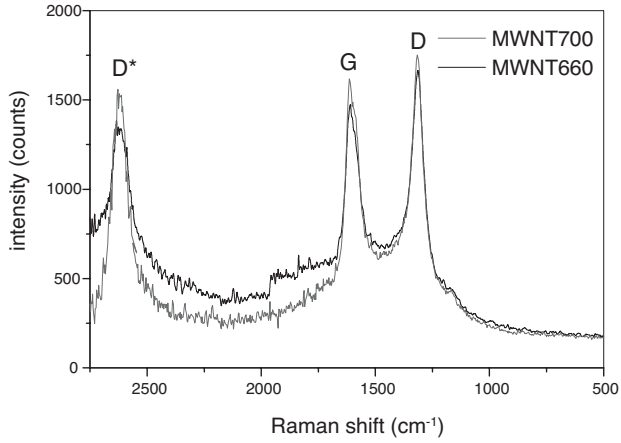


Figure 1.
Raman spectra of both MWNT.

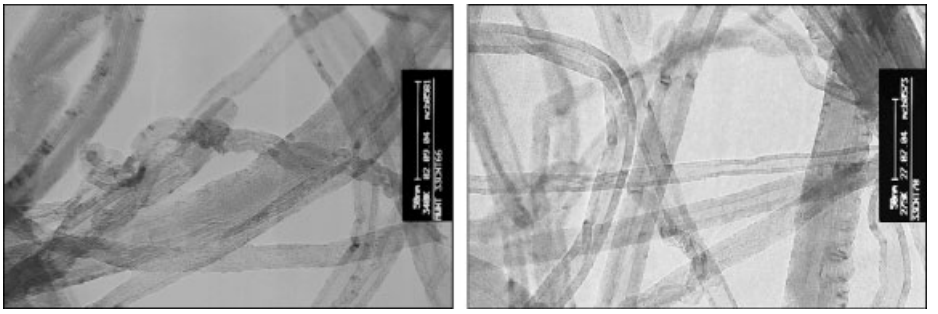


Figure 2.
TEM of MWNT660 (left) and MWNT700 (right) after purification.

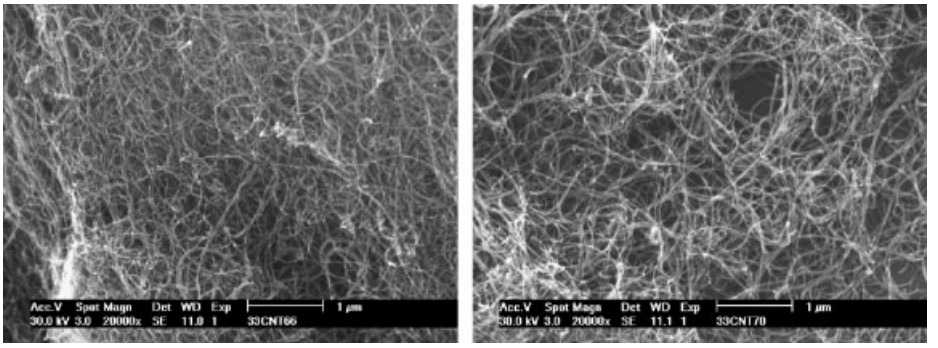


Figure 3.
SEM of MWNT660 (left) and MWNT700 (right).

conductivity for the sample produced at lower temperature having thinner tube diameter.

XPS studies revealed a higher atom ratio [O]:[C] in the MWNT material prepared at 660 °C which was 0.019 as compared to 0.004 for the material produced at 700 °C. Here, an AXIS ULTRA system (Kratos Analytical, England) combined with a Mono-Al $K\alpha_{1,2}$, X-ray-Source (300 W at 20 mA) and an analysator having a pass energy of 160 eV or 20 eV was used. The XPS wide-scan spectra did not analyse traces of iron or cobalt in the MWNT surfaces. Hence, the higher [O]:[C] ratio in sample MWNT660 can be considered as a higher functionalisation degree of the outer carbon-nanotube surface.

Composite Preparation and Characterization

Composites were prepared from dry powder premixtures using a DACA Micro Compounder (small scale conical twin screw compounder, capacity 4.5 cm^3) operated at 280 °C melt temperature, 50 rpm screw speed, and 15 min mixing time. As polymeric matrix polycarbonate Iupilon E 2000 (powder, Mitsubishi, Japan) was used. Plates (thickness 0.35 mm, diameter ~70 mm) were compression moulded at 280 °C in order to test electrical, thermal, and mechanical properties of the nanocomposites.

The electrical volume resistivity was measured on the pressed plates using a Keithley 8009 test chamber combined with a 6517A electrometer (full symbols). Below resistance values of 10^7 Ohm a 4-point fixture combined with a Keithley DMM 2000 electrometer was used and the measurements were performed on strips ($3 \times 20 \times 0.35$ mm^3) cut from the plates (open symbols).

The percolation curves of the MWNT in PC are shown in Figure 5. Electrical

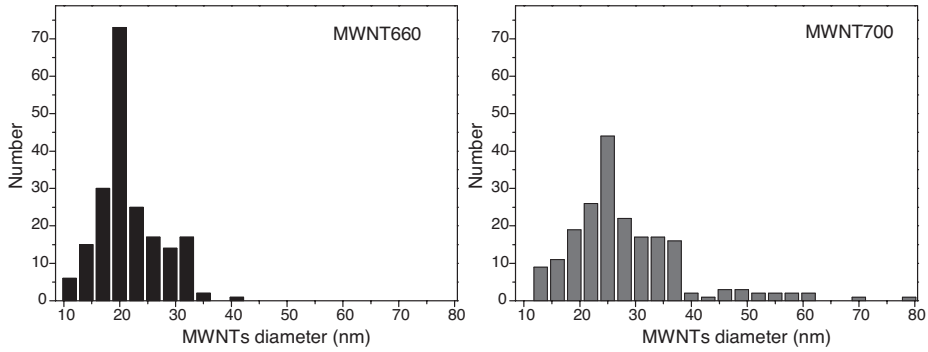


Figure 4.
MWNT diameter distribution as determined from SEM investigations.

percolation is reached between 0.75 and 0.875 wt% for MWNT660 and between 0.875 wt% and 1.00 wt% for MWNT700. The resistivity values at a given content of MWNT are lower for all the composites with MWNT660 as compared to MWNT700. At higher contents the difference is less significant. These percolation thresholds are quite low when comparing with previous results on industrially available MWNT[4] which confirms the suitability of these MWNT for composite applications. The higher percolation concentration for MWNT700 can be explained by the higher tube diameters leading to a lower CNT aspect ratio. The higher resistivity values in all samples with MWNT700 may be explained by the lower conductivity of the nanotube materials itself as determined from the powder conductivity measurements.

Transmission light microscopy on thin sections sliced from the pressed plates was used to get information about microscaled MWNT agglomerates within the samples. The images shown in Figure 6 for PC +0.875 wt% MWNT illustrate that there are nearly no remaining agglomerates within the samples. The sample with MWNT700 appears somehow more homogeneous as compared to that containing MWNT660.

SEM images (Figure 7) obtained on cryofractured surfaces of the plates indicate relatively good distribution and dispersion of the MWNT in the PC. However, some small agglomerates can be seen at 0.875 wt%

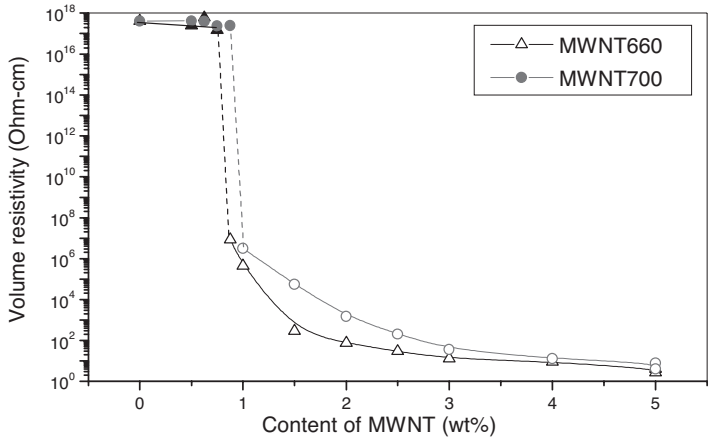


Figure 5.
Electrical volume resistivity versus content of MWNT.

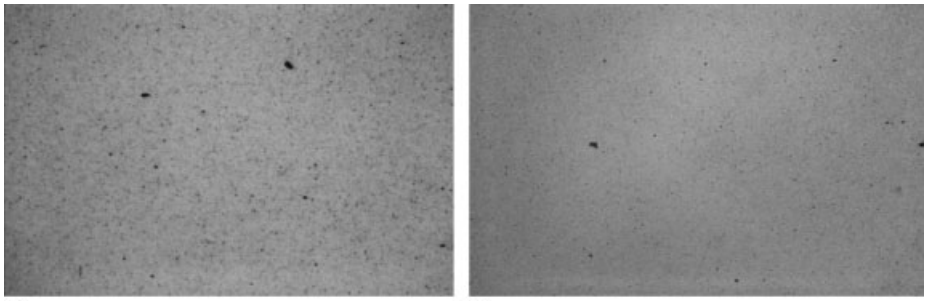


Figure 6.
Transmission light microscopy (Zeiss Axioplan 2) on thin sections (thickness 3 μm) of samples with 0.875 wt% MWNT, a) MWNT 660; b) MWNT700; the size of the frame is 75 μm x 48 μm.

MWNT in the sample containing MWNT660 indicating a lower dispersability under the same mixing conditions (Figure 8). Interestingly, even within such agglomerates the MWNT are wetted by the polymer. Within the agglomerates the tubes can be seen to be still quite long (up to >2 μm).

TEM investigations (LEO 912) on thin section with about 70 nm thickness cut from the plates also confirm the good dispersion and the dominance of well separated single tubes (Figure 9). Some small agglomerations are seen which seem to be more pronounced in the sample with MWNT660. In addition, again the existence of tubes with higher diameters is evident in the sample with MWNT700.

Mechanical tensile tests were performed on miniature dogbones punched from the pressed plates. Seven samples were tested for each composition at 5 mm/min testing speed, which showed good reproducibility. Typical stress-strain curves are shown in Figure 10. With the MWNT incorporation tensile modulus, stress at yield, and stress beyond yield point are increased. The stress values are enhanced up to 10 MPa. High elongation at break is retained up to 1 wt% MWNT addition, but decreases significantly at 3 wt% and 5 wt%. These trends are similar for both MWNT samples, whereas a slightly higher stress enhancement was observed in MWNT660 composite samples.

In addition, differential scanning calorimetry (DSC Q 1000 TA Instruments, first heating, cooling, second heating with 10 K/min) was performed in order to see effects

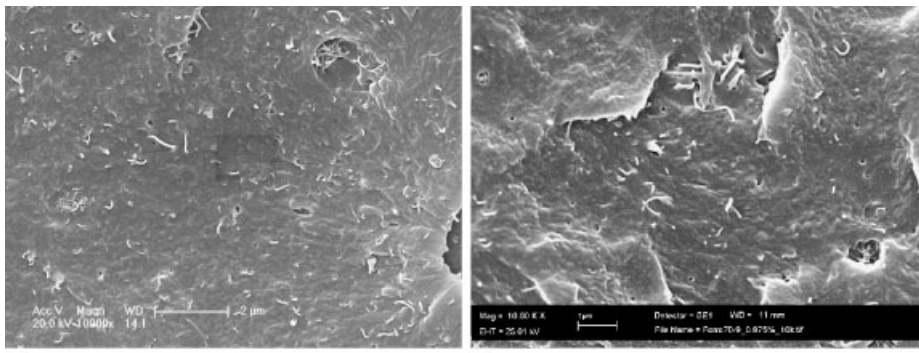


Figure 7.
SEM micrographs (LEO VP 435 or Philips XL3) of cryofractured surfaces of plates of samples with 0.875 wt% MWNT, a) MWNT660; b) MWNT700.

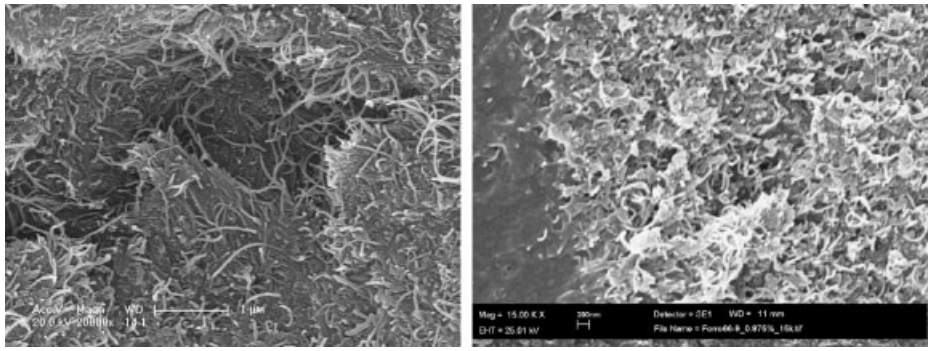
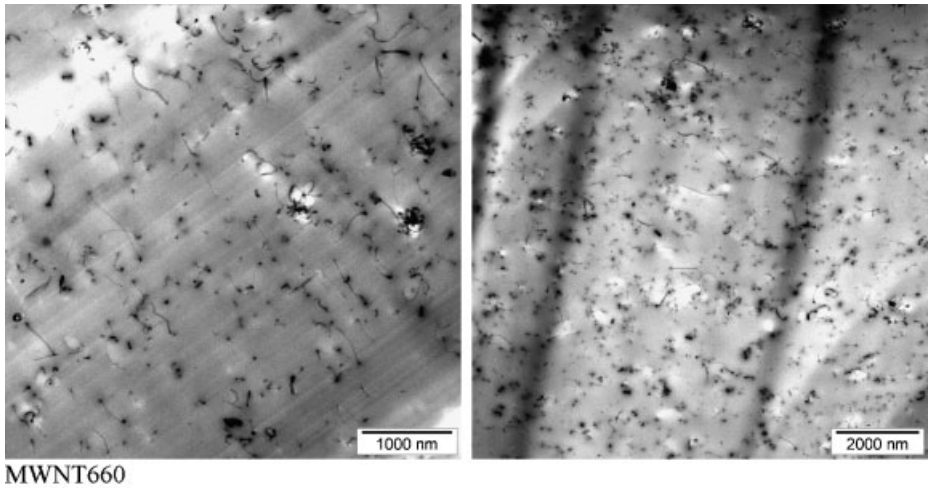
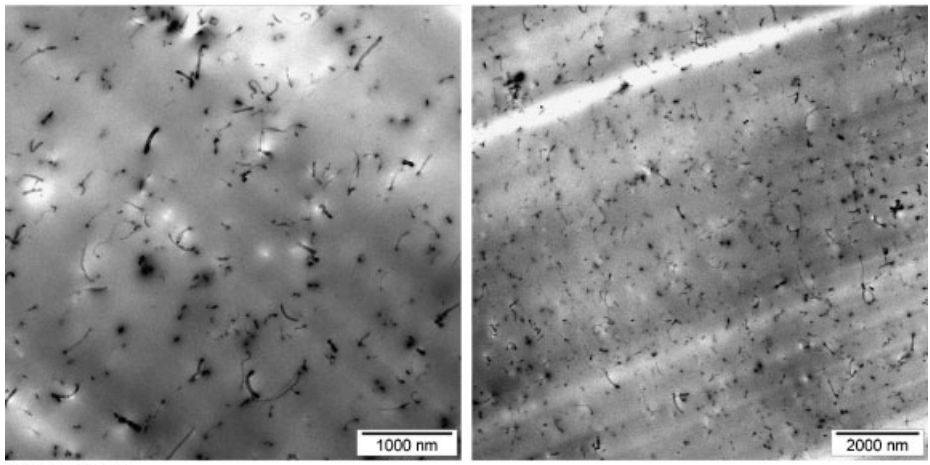


Figure 8.
SEM micrographs of agglomerate areas (from 0.875 wt% MWNT660).



MWNT660



MWNT700

Figure 9.
TEM micrographs of samples with 0.875 wt% MWNT.

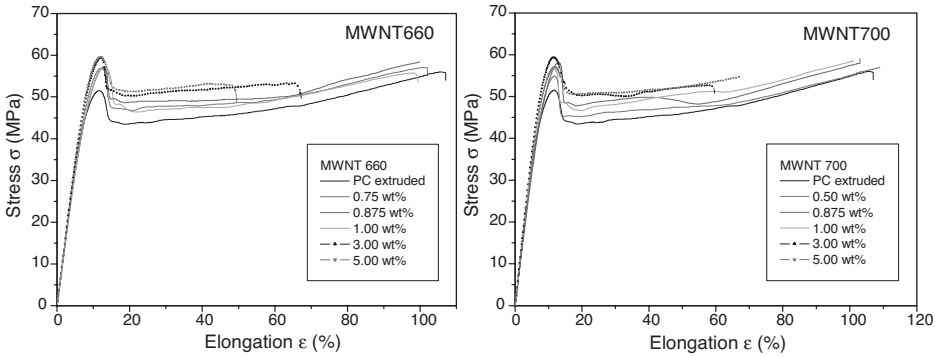


Figure 10.
Stress-strain curves of the nanocomposites (left: MWNT660, right: MWNT700).

of the MWNT addition on the glass transition temperature of the polycarbonate T_{gPC}. Interestingly, the addition of both MWNT leads to a decrease in T_{gPC} by about 1.6 K in nanocomposites with MWNT660 and by about 2.5 K in those with MWNT700 as shown in Figure 11. This decrease indicates a polycarbonate degradation as it was also found in other investigations on PC-MWNT composites.[5] Even if XPS did not show traces of iron or cobalt on the MWNT surfaces it may be likely that during the melt mixing at 280 °C very small amounts of remaining catalyst particles inside the nanotube material (possibly not detectable by XPS surface method) lead to this small degradation effect. On the other hand, the enhanced shear forces during mixing of the CNT filled materials may also lead to molecular weight reduction. Polycarbonate is known to be very sensitive to remaining metal particles in trace amounts but also to thermo-mechanical degradation effects which may by enhanced after filler addition.[6]

Conclusion

Two samples of multiwalled carbon nanotubes (MWNT) synthesized by CVD of acetylene over Fe_2Co catalysts supported by $CaCO_3$ at temperatures of 660 °C and 700 °C were incorporated into a polycarbonate matrix by melt mixing. The nanotube materials were characterized indicating

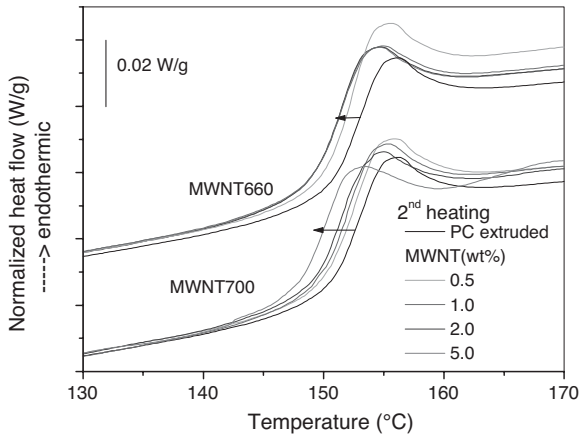


Figure 11.
DSC second heating run of polycarbonate and the nanocomposites.

that he material produced at 660 °C shows slightly better performance as evidenced by lower mean tube diameter and better conductivity as compared to the sample produced at 700 °C. In addition it has a higher [O]:[C] ratio as evidenced by XPS.

In the composites, the electrical percolation threshold was found to be between 0.75 wt% and 0.875 wt% for MWNT produced at 660 °C and between 0.875 wt% and 1 wt% for MWNT produced at 700 °C. These percolation thresholds are quite low as compared to other nanotube materials in the same polycarbonate. The material produced at 700 °C having slightly higher diameter also showed a slightly better dispersability as evidenced from light microscopy, SEM, and TEM. The effects in the stress-strain curves are similar in both composites, indicating a stress increase with MWNT incorporation. The decrease in the glass transition temperature of polycarbonate after MWNT incorporation indicates a polymer degradation possibly due to remaining catalyst particles or enhanced shear forces in the composites as compared to pure PC. It is more pronounced in the sample with the nanotube materials produced at 700 °C.

The results obtained on the nanocomposites proved that these nanotube materials are very suitable for polymer composite applications as they show low electrical percolation concentration and good mechanical enhancement.

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