

# Supported Coordination Polymerization : a Unique Way to Potent Polyolefin Carbon Nanotube Nanocomposites

By Daniel Bonduel et al

## Electronic supplementary information

### Polymerization - Filling Technique :

#### *i) Carbon nanotubes activation*

0.25g of carbon nanotubes (CNTs), previously dried overnight at 105°C under reduced pressure ( $10^{-2}$  mm Hg) were added, under nitrogen, with 100 ml of dried and deoxygenated n-heptane and 8.5 ml of MAO (1.33 M) deprived from its trimethylaluminum (TMA) by distillation. TMA is recovered and kept for titration (fraction 1). The CNTs in contact with MAO were stirred for 1 h at 40°C. Solvents were then distilled off at 40°C under reduced pressure. The solvents together with any volatile organoaluminum compounds were trapped in a flask cooled down by liquid nitrogen (fraction 2). Treated CNTs were heated up at 150°C under reduced pressure for 90 minutes. The MAO excess was removed by washing thrice with dried toluene (3x70 ml) at 60°C (fraction 3). Fractions 1, 2 and 3 were hydrolyzed by addition of 150 ml aqueous HCl (ca. 2M) and extracted. Aluminum was back-titrated by EDTA, for assessing the amount of MAO fixed on the CNTs. Al concentration was thus evaluated by titration with EDTA as the mean of three aliquots. The organics solvents were evaporated by heating the solution to ebullition under magnetic agitation. 5 ml of the acidic solution was 20-fold diluted and 20 ml of a solution 0.025 M of EDTA was added. The solution was heated to ebullition and then cooled to room temperature. The solution was then buffered at pH=4.76 with sodium acetate. The excess of EDTA was determined by titration with a solution of ZnSO<sub>4</sub> 0.05 M with xylenol orange as indicator. The as-determined concentration of the Al complex was used to calculate the amount of Al evacuated during the solvent evaporation and the CNTs washing steps.

#### *ii) Polymerization step*

The treated CNTs, approximately 0.25g, were dispersed in 100 ml dried n-heptane and the all was transferred into 250 ml glass-reactor in a glove-box. Then, 2.2 ml of Cp\*<sub>2</sub>ZrCl<sub>2</sub> ( $5.2 \cdot 10^{-3}$  M) was added to the suspension. The stirred mixture was then heated up to 50°C for 15 min. The reactor was purged by ethylene (0.5 min) in order to remove nitrogen. The synthesis was carried out under a constant pressure of 2.7 bars of ethylene at 50°C and vigorous stirring for 1 h. The final material was precipitated in 600 ml methanol acidified with hydrochloric acid and was dried at 70°C for ca. 7 h under reduced pressure.

### **In-situ polymerization in the presence of untreated MWNTs :**

0.25 g of carbon nanotubes (CNTs) was placed in the 250 ml polymerization flask and dried overnight at 105°C under reduced pressure ( $10^{-2}$  mm Hg). The CNTs were then dispersed in 100 ml dried n-heptane under nitrogen followed by the addition of 8.1 ml MAO (1.5 M) and 2.3 ml Cp\*<sub>2</sub>Zr Cl<sub>2</sub> ( $4.9 \cdot 10^{-3}$  M). The stirred mixture was then heated up to 50°C for

15 min. The reactor was purged by ethylene (0.5 min) in order to remove nitrogen. The polymerization then proceeded under a constant pressure of 2.7 bars at 50°C and vigorous stirring for 1 h. The final material was precipitated in 600 ml methanol acidified with hydrochloric acid and was dried at 70°C for ca. 7 h under reduced pressure.