In situ Polymerization of Nanocomposites by $TpTiCl_2(Et)$ System: UHMWPE Filled with Carbon Nanotubes

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Summary: Nanocomposites of ultra-high molecular weight polyethylene (UHMWPE) filled with multi-walled carbon nanotubes (CNT) were obtained by in situ polymerization of ethylene by $TpTiCl_2Et$. This novel catalytic complex activated with polymethylaluminoxane (P-MAO) (Al:Ti = 200) allowed to incorporate the CNT at different compositions (0,1-1 w/w %) into the UHMWPE matrix. The filler addition produced an important enhancement of the catalytic activity when it was compared to that of homogeneous ethylene polymerization carried out under the same experimental conditions (30 min; 1bar; 25 °C). This fact was attributed to *in situ* support of $TpTiCl_2Et$ onto the CNT surface, which not only could induce the stabilization of the catalytic system but also allowed the growing of polymeric chains around the CNT structures. The characterization of these nanocomposites was carried out by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Thermal analysis showed that the incorporation of CNT (at the tested concentrations) did not produce changes in the polymer thermal stability, as revealed by the initial degradation temperature values. However, the CNT produced a nucleating effect in the crystallization of UHMWPE as observed by DSC, independently of the filler content. The crystallization temperature of the obtained nanocomposites increased and the crystallinity degree slightly increased as well.

Keywords: carbon nanotubes; DSC; *in situ* polymerization; polyethylene; TGA

Introduction

Titanium hydrotris(pyrazolyl)borate complexes have been synthesized and evaluated as catalysts in olefin polymerization.[1,2] These complexes have shown not only catalytic activity when activated with polymethylaluminoxane (P-MAO), but also significant productivity towards ethylene polymerization to yield ultra-high molecular weight polyethylene (UHMWPE). This polymer has been widely used for such biomedical applications as hip prosthesis, due to its improved mechanical performance when compared to conventional polyethylene.[3] Nevertheless, it is not suitable when higher requirements are to be met, as in other bone replacements. To overcome this limitation, its reinforcement could be an alternative.

On the other hand, several studies have demonstrated that carbon nanotubes (CNT) are an excellent option to enhance UHMWPE tensile stiffness.[4] However, most composites are commonly prepared through mechanical blending, which often lead to materials with poor filler dispersion and many aggregates, that produce decreased mechanical properties.[5,6] These disadvan-

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tages can be resolved by *in situ* polymerization, which has demonstrated to be a better way of obtaining a homogeneous dispersion of the carbon nanotubes into polymer matrices.[6–8]

The aim of this work was to obtain composites of UHMWPE reinforced with CNTs by *in situ* polymerization, using TpTiCl2OEt/P-MAO as the catalytic system, and to evaluate their thermal properties.

Experimental Part

The handling of all air and/or moisture-sensitive compounds was carried out under nitrogen, using the standard Schlenk or glovebox techniques. Toluene was dried over sodium/benzophenone and distilled under nitrogen prior to use. Ethylene was supplied by BOC Gas and used after passing it through columns packed with BASF oxygen scavenger and a 4-Å molecular sieve. The pre-catalyst $TpTiCl_2(OEt)$ (Figure 1) was synthesized according to the procedure described in the literature.[9] P-MAO, manufactured by AkzoNobel Corp, was used as co-catalyst. Multi-walled carbon nanotubes, supplied by Nanocyl S.A, Belgium, were used as reinforcement filler.

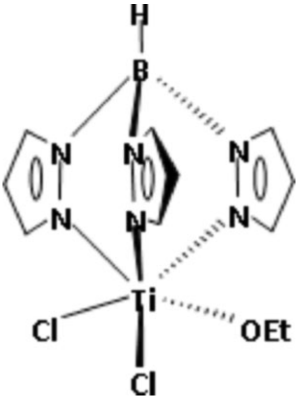

Figure 1.
Chemical structure of $TpTiCl_2$ (OEt) pre-catalyst.

The polymerization runs were carried out in a reactor (Buchi-Glauster) fitted with a 500 mL glass vessel, using toluene as solvent. The polymerization conditions were adjusted as required (T: 25 °C, Al/Ti: 200, t: 30 min., 600 rpm). The reactor was filled with the pre-set concentrations of CNT (0.1, 0.5 and 1 w/w%), previously dispersed in toluene (30 mL) by ultrasound, and P-MAO (Al/Ti: 200) in a toluene solution (50 mL). After 10 minutes, a solution of the precatalyst (1 mg) in toluene (20 mL) was added. The polymerization was started by injection of ethylene into the reactor under stirring for the required time (30 min.). The ethylene pressure was kept constant (1 bar) during the polymerization by its continuous supply. The reaction was stopped by adding a solution of HCl (1 v/v%) in methanol. The polymer was stirred in distilled water overnight and filtered. Afterwards, the polymer was vacuum dried, until constant weight. All experiments were conducted at each condition three different times, to ascertain the reproducibility of the results.

The average molecular weight of the obtained polyethylene was determined with a Capillary Ubbelhode Viscometer.

The polymers were characterized by Differential Scanning Calorimetry (DSC) to determine the crystallization and melting behavior of the composites, by means of a Mettler Toledo DSC 822^e, under a nitrogen atmosphere. Samples of approximately 10 mg were sealed in aluminum pans and heated from 25 °C to 170 °C at 10 °C/min, kept isothermally for 3 minutes at 170 °C in order to erase any previous thermal history, and then cooled at 10 °C/min to 25 °C. A second heating cycle followed, from 25 °C to 170 °C at 10 °C/min. The first cooling and second heating thermograms allowed obtaining the crystallization and melting peak temperatures (T_c and T_m, respectively) and the experimental melting enthalpies (ΔH_{Sample}). The crystallinity degree (X_c) of the samples was estimated using the enthalpy of a perfect polyethylene crystal (293 J/g) as standard of comparison.[10]

The same DSC calorimeter was used to carry out the Successive Self-Nucleation and Annealing Technique (SSA).[11] Once the thermal history of the sample was erased, it was heated at 10 °C/ min up to a selected self-seeding and annealing temperature (Ts), where it was isothermally kept for 5 min and then cooled down to 25 °C. Then, the sample was heated again to a new self-seeding and annealing temperature, which was 3 °C lower than the previous Ts and held there for 5 min before cooling it to 25 °C at 10 °C/min. This thermal treatment was repeated, being each Ts 3 °C lower than the previous one, until the minimum temperature selected was reached. Finally, the sample was heated at 10 °C/min up to 170 °C and its thermogram recorded.

Thermogravimetric Analyses were carried out up to 700 °C in a Mettler Toledo TGA851, using a heating rate of 20 °C/min, under nitrogen atmosphere. The initial decomposition temperatures (Tid) were calculated from the first derivate of the thermograms. The reaction order *n* was estimated using the Coats-Redfern equations.[12] Once the reaction order was known, the activation energy (Ea) was calculated through the E2-Function method,[13] selecting three conversions ($\alpha1$, $\alpha2$ and $\alpha3$), and three corresponding decomposition temperatures (T1, T2 and T3).

Results and Discussion

Ethylene polymerization using P-MAO was carried out varying the CNT concentration at the same polymerization conditions in order to evaluate the influence of the amount of filler on the reaction yield and on the polymer's thermal characteristics.

The catalytic system produced a highly linear, ultra-high molecular weight polyethylene with an average molecular weight of 23×10^5 gr/mol. The same polymerization conditions were used to obtain, *in situ*, the composites of UHMWPE with CNT.

Figure 2 shows the average results of the catalytic activity as a function of the CNT content, obtained from three polymerization runs for each sample. The inclusion of the filler into the polymerization system induced an increase in the catalytic activity, achieving a maximum at 1 w/w % of CNT content. A good reproducibility of the results was ascertained, through small values of the standard deviations.

This behavior could be a consequence of the *in situ* supporting of $TpTiCl_2(OEt)$/P-MAO onto CNTs, which might induce a stronger and more stable catalytic system.[1–8] This can be explained by the possible sp3 carbon hybridization of the

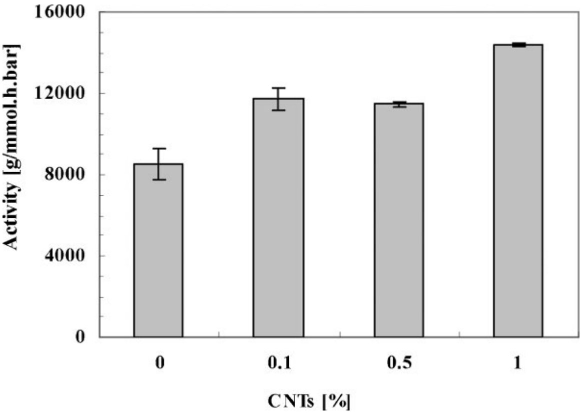

Figure 2.
Effect of CNT concentration on the catalytic activity in the polymerization of UHMWPE. Polymerization Conditions: Toluene (100 ml), $TpTiCl_2OEt = 1$ mg, Al/Ti = 200,P = 1 bar, T = 25 °C, t = 0.5 h., rpm = 600.

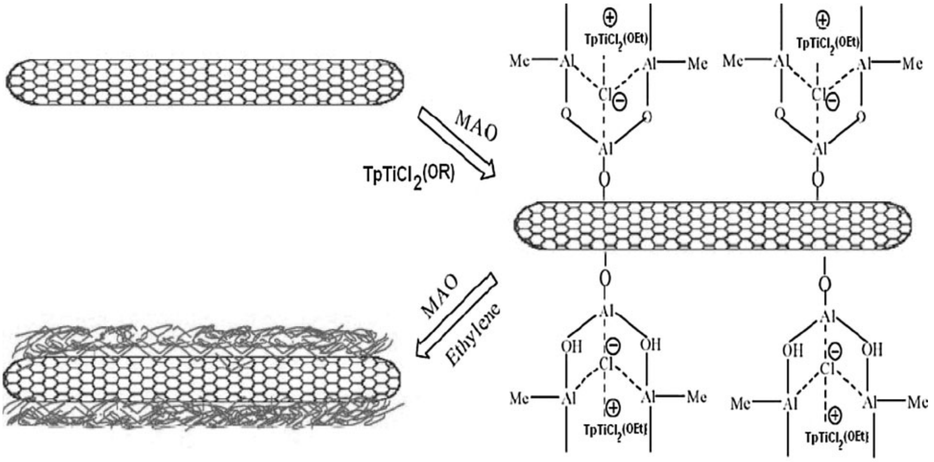

Figure 3.
Probable supported catalytic system of CNT-PMAO-$TpTiCl_2(OR)$.[8]

CNT when P-MAO is attached to their surface, which could induce the stabilization of the catalyst due to the delocalization of the electronegative charge (Cl^-) towards the covalent bond.

In this sense, the mechanism suggested by Dong et al.[8] can be used to show the probable supported catalytic system when $TpTiCl_2(OEt)$ is employed to induce the *in situ* polymerization of UHMWPE with CNT (Figure 3). The catalytic system remains immobilized at the vicinity of the CNT by electrostatic interactions with simultaneously MAO counteranions anchored onto the CNT's surface. When ethylene polymerization occurs, polyethylene is formed around the filler, covering the CNTs and increasing its molar mass.

This mechanism supports the fact that the obtained polymer lost its powder appearance to show a fibrous morphology, which could be expected if the catalytic system is supported onto the CNT's surface.[14] It is well known that the polymer duplicates the morphology of the catalytic support used for its polymerization.[8,14] Additionally, some studies have demonstrated that the *in situ* polymerization allows obtaining more homogeneous systems than those resulting from conventional melt blending.[6–8] This is a consequence of a better dispersion of the filler into the matrix, due to the isolation of the CNTs by the catalytic system and to the formation of a polymer matrix around the filler, which hinders the Van der Waals interactions among the filler particles, thus reducing their agglomeration. On the other hand, works by Bonduel et al.[7] and Dong et al.[8] demonstrated, using Transmission Electron Microscopy, that the anchoring of the catalytic system onto the CNT's surface allows the growth of the polymer chains surrounding them, giving a fibrillar appearance (observed in the present study).

The supporting done in one step allows reducing the polymerization times, because the pre-treatment of the CNTs with P-MAO requires longer times and higher amounts of reactive. In this sense, even though the time of contact between the co-catalyst and the CNTs was shorter in the present study, some anchoring coul be expected (partial anchoring). Hence, one part of the reaction could be heterogeneous, giving rise to the growing of the polymer chains around the nanotube, and the other part could be homogeneous, where the catalytic system produces the major part of the matrix. The first case wiould be responsible for the filler dispersion, whereas the second one would be

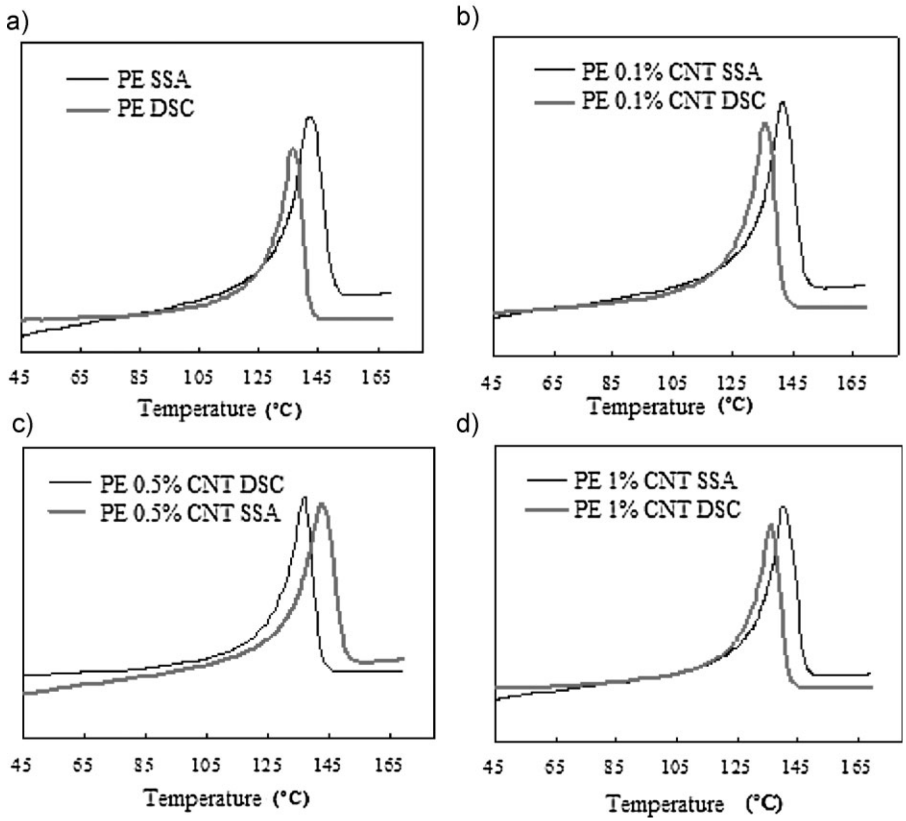

Figure 4.
DSC scans of composites of UHMWPE-CNT before and after SSA treatment: a) neat UHMWPE, b) 0.1 w/w % CNT, c) 0.5 w/w % CNT, d) 1 w/w % CNT.

responsible of the filler distribution into the matrix.

Figure 4 displays the DSC scans of the samples. All of them exhibit a single melting endotherm. The main differences between the neat polymer and the composites are in the characteristic peak crystallization temperatures and in the values of the associated melting enthalpies (see Table 1). The crystallization temperature increases and the crystallinity degree slightly increase with CNT content as a result of a nucleating action of the CNT. This is an expected behavior when compared to the usual action of nucleating agents, since they normally do not affect the crystallinity degree or tend to increase it. Trujillo et al.[15] found that CNT are more efficient in nucleating HDPE than its own crystals, possible because of the way the chains were grown onto the surface of the CNT, creating a remarkable nucleation enhancement.

SSA is based on the sequential application of self-nucleation and annealing steps

Table 1.
Crystallization temperature (Tc), melting temperature (T*m*) and crystallinity degree (Xc) values of composites of UHMWPE with CNT by standard DSC analyses, and after SSA treatment.

	DSC			SSA	
[CNT] w/w %	Tc (°C)	Tm (°C)	Xc (%)	Tm (°C)	Xc (%)
0	115	139	40	142	49
0.1	116	134	47	142	52
0.5	117	137	43	143	45
1	118	136	42	140	47

to a polymer sample. After thermal conditioning, a final DSC heating run reveals the distribution of melting points induced by the SSA treatment as a result of the heterogeneous nature of the chain structure of the polymer under analysis. The final heating scans after performing the SSA fractionation of the HDPE composites are shown also in figure 4. All the curves exhibit only one endotherm, with higher peak temperatures than those displayed in dynamic DSCs. Furthermore, the crystallinity degrees of the SSA samples are higher than those of the materials without any treatment (Table 1). These results are consistent with the annealing of the polymer. The highly-regular polyethylene produced with the catalyst used in this work almost does not have any short chain branching. Hence, it could not be fractionated, unless it contained at least some amount of comonomer. Trujillo et al.[15], using the SSA technique, found that CNTs induced the formation of a population of thicker lamellar crystals in high-density polyethylene (HDPE) that melt at higher temperatures as compared to crystals formed in neat HDPE prepared under the same conditions. In other words, CNT were able to produce thicker and more stable crystals. However, results of the present research demonstrated that more stable crystals were not produced by the incorporation of the CNT in the polymerization process.

On the other hand, lower CNT contents (0.1 w/w%) produced an increase in the thermal stability (Table 2), which is evidenced by the increases of the initial decomposition temperature (Tid) and in the activation energy values for degradation (Ea). This behavior can be explained if the transference of the thermal stability properties from CNT to the polymer matrix is considered. However, this tendency does not hold when CNT content increases. As it can be noted, higher filler contents produce a decrease in the thermal stability. This behavior could also be attributed to CNT agglomeration, which increases the interfacial space between filler and matrix, so that oxygen diffusion into the matrix is higher, promoting a faster degradation.

Table 2.
Initial decomposition temperatures (Tid) and activation energy (Ea) values of composites of UHMWPE with CNT.

[CNT] w/w%	Tid	Ea
0	449	151
0.1	458	193
0.5	444	141
1	450	150

Conclusion

The $TpTiCl_2OEt$ complex was able to produce ultra-high molecular weight polyethylene and promote the *in situ* preparation of UHMWPE reinforced with carbon nanotubes. Results showed that the catalytic activity increased with the inclusion of CNTs. This was attributed to the *in situ* supporting of $TpTiCl_2(OEt)$/P-MAO onto the CNT's surface, which might induce a stronger and more stable catalytic system.

A slight increase in the crystallization temperature with the inclusion of CNTs was obtained, which was attributed to the nucleating effect of the CNT nanoparticles on the polyethylene matrix.

The thermal stability was enhanced at the lowest CNT incorporation (0.1 w/w%), while at higher CNT contents, the likely formation of agglomerates produced a decrease in the initial decomposition temperatures and/or activation energies.

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