

Influence of MWNT on the physical properties of polyethylene nanocomposites

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ABSTRACT

Physical properties of a series of multi-walled carbon nanotube-high density polyethylene (MWNT-HDPE) composites, prepared by melt mixing in a micro-twin screw extruder, were investigated. The effect of MWNT concentration (0.5-7 wt%) and nanotube surface treatment (oxidative treatment in a tubular furnace at 500°C for 1 - 2 hr in a 95% nitrogen, 5% oxygen atmosphere) was investigated by several experimental techniques.

Scanning electron microscopy showed good adhesion and dispersion of nanotubes in the matrix, independently of the surface treatment. TG analysis suggests that the incorporation of MWNT in the polymer results in increased oxidative stability. Electrical and rheological measurements showed that the oxidative treatment, causing some reduction of the MWNT quality (indicated by Raman Spectroscopy), decreases the efficiency of the nanotube-matrix interaction. The evaluated electrical percolation threshold is in good agreement with rheological percolation threshold.

The isothermal quiescent crystallization, studied by rheometric techniques, clearly indicates that increasing the MWNT concentration in the composite the onset of crystallization occurs earlier. Such a behavior confirms the nanotube nucleant effect previously observed by non-isothermal DSC. Finally, flow induced crystallization has been investigated.

Keywords: Carbon nanotubes, electrical properties, viscoelasticity

1 INTRODUCTION

Carbon nanotubes (CNTs) have been extensively investigated in many application fields due to the combination of unique conductivity (electrical and thermal), low density and mechanical properties [1-2]. Indeed, CNTs have potential applications in many areas such as biosensing, conducting agent, field-effect transistor, and nanocomposites. From processing and application point of view, the mechanical and rheological properties of the

CNTs nanocomposites are very important. These properties are related to the material's microstructure, particle-particle interactions, particle dispersion, shape and orientation of dispersed particles [3]. Therefore it is of great importance to understand the rheological behavior for optimizing the manufacturing process of CNT filled nanocomposites.

In this study a series of multi-walled carbon nanotube (MWNT)/high density polyethylene (HDPE) composites with the inclusion of several quantities of functionalised or not carbon nanotubes (0.5-7wt%) were prepared and analyzed. The structural characteristics and thermal properties of the nanocomposites were investigated by Raman spectroscopy and thermogravimetric analysis (TG-DTG). The good dispersion of the carbon nanotubes in the HDPE matrix was proven by scanning electron microscopy. The dynamic melt rheology was used to evaluate the percolation state of CNTs within the polymer matrix. Furthermore, the effect of the chemical modification of the nanotubes on the electrical transport and rheological properties of the nanocomposites was investigated. Finally, the isothermal crystallization of the nanofilled systems was studied through dynamic rheometry in order to clarify the nanotube role on the polymer crystallization phenomenon.

2 MATERIALS AND METHODS

2.1 Materials

The multiwalled carbon nanotubes used in this work were produced at CSIRO (Commonwealth Scientific and Industrial Research Organization, Australia). They were synthesized by a CVD method, using a continuously fed iron catalyst to encourage growth rate. Nanocomposites with different amounts (0.5-7wt%) of nanotubes were prepared by 10 min melt mixing in a micro-twin screw extruder (Haake MiniLab Rheomex CTW5) operated at 50 rpm and 235°C. A high density polyethylene (HDPE0390 - Qenos) was used as polymer matrix, with weight average molecular weight (Mw) ~ 58886 g/mol and a polydispersity of 5.8. Non-functionalized (MWNTs) or functionalized (OXIMWNTs) carbon nanotubes were used. The functionalization treatment was an oxidative treatment in a

tube furnace at 500°C for 1 - 2 hrs, in a 95% nitrogen 5 % oxygen atmosphere.

2.2 Methods

Scanning electron microscopy (SEM LEO420) was used to characterize the morphology, the interfacial adhesion and the degree of dispersion of cryo-fractured CNT/polymer composites. Extruded strands of each nanocomposite were dipped in liquid nitrogen and then snapped at the centre. This technique freezes the polymer matrix which breaks cleanly with nanotubes protruding from the fracture surface. The samples were then gold coated.

Melt rheological measurements were performed with an ARES rheometer (TA) under nitrogen atmosphere, using a parallel plate geometry (D=25mm, gap of 1mm). The isothermal quiescent crystallization experiments were performed using a stress controlled rotational rheometer (SR5000, Rheometric Scient. Inc.) in the cone and plate configuration (D=25mm, angle=0.1rad), at 1rad/s constant oscillation frequency and 1000Pa shear stress, under nitrogen atmosphere. The tests were conducted according to the following protocol: after a thermal annealing at T=200°C for 20 min, the sample was cooled down to the crystallization temperature, T_c (128°C).

Additional information on thermal properties and structural characteristics of the nanocomposites was obtained by (TG-DTG) analysis performed with a Thermogravimetric Analyzer SDTQ 500 (TA instruments) at 10 K/min heating rate, under flowing air.

Raman spectra were obtained at room temperature with a microRaman spectrometer Renishaw inVia with 514 nm excitation wavelength.

Electrical conductivity experiments were carried out with a Keithley 2400 source measurement unit in a two-probe measurement configuration. The investigated sample films were molded in a hot press (Carver Inc.) at 250°C to form thick films, which were rapidly quenched in iced water (0°C). The films were 0.8 ± 0.1mm thick, about 2 cm wide and 2.5 cm long. On top 25 nm thick, 5 mm wide and about 1mm distant coplanar gold electrodes were deposited by sputter deposition. Electrical measurements were performed on the nanocomposites at room temperature in order to study the effect of the nanotubes on the electrical conductivity of the samples.

3 RESULTS

3.1 Dispersion and Morphology

SEM micrographs of both MWNT/HDPE and OXIMWNT/HDPE composites showed a good dispersion of nanotubes in the polymer matrix, and proved the existence of nanotube-polymer interactions in the MWNT/HDPE composites with nanotube concentrations greater than 2.5wt% [4]

3.2 Raman spectroscopy analysis

Raman spectroscopy was used to investigate the interfacial interaction between HDPE matrices and CNT (Fig. 1). The spectrum of PE exhibits typical Raman modes of polyethylene. Carbon nanotubes show two main Raman lines, one at ~ 1565 cm⁻¹ (G-line, due to the in-plane vibration of the C-C bonds), the other at ~ 1340 cm⁻¹ (D line, attributed to disorder induced by defects in the nanotube lattice and other carbon species); the overtone of the D band, 2D at about 2680 cm⁻¹, is also evident. In the CNT/HDPE Raman spectra the characteristic bands of MWNTs are shifted to higher wavenumbers when increasing the CNT content [5, 6]. The upshifts are also a consequence of strong compressive forces associated with PE chains on MWNTs [7]. Raman spectroscopy analysis of the carbon nanotubes was also performed after the oxidative treatment to evaluate its effect. The intensity ratio I_D/I_G, indicative of the disordered fraction, increased for OXIMWNTs, suggesting a decrease of the sample degree of order.

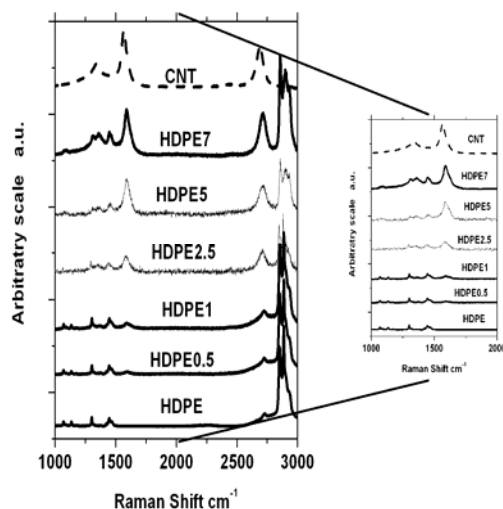


Figure 1 Raman spectra of CNTs, HDPE and CNT/HDPE composites

3.3 TG-DTG Analysis

In Fig. 2 air flow TG-DTG profiles of CNT/HDPE samples, in the range 250-700°C, are reported and compared with those of pure polyethylene. The incorporation of MWNTs in the polymer results in an increased oxidative stability of the composites.

At temperatures higher than 520°C, the residual weight of all composites is consistent with their CNT content whose oxidation starts at about this temperature.

To better understand the effect of CNT on the enhanced oxidative stability of the composites a TG-DTG analysis

was performed on a physical mixture of HDPE and 5 wt% CNT: no increased stability has been detected as shown in Fig. 2.

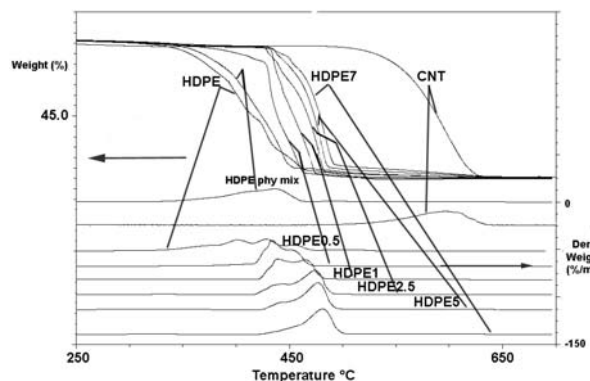


Figure 1 TG-DTG profiles of CNTs, HDPE, CNT/HDPE composites and of CNT/HDPE “physical”.

3.4 Melt Rheology

Oscillatory shear rheology is known to be very sensitive to CNT/polymer composites structure and the frequency response has been used to obtain information about the percolation state of CNTs within the matrix. The results of the frequency sweep experiments for MWNT/HDPE composites showed that the neat matrix exhibits a typical liquid-like behavior at low frequencies whereas, at CNT concentration higher than 1 wt%, a clear change in the viscoelastic behavior was found [4, 8]. It can be assumed that increasing the CNT concentration above a critical value (c_g) a significant change in the material structure occurs: the MWNTs can entangle with the polymer chains to form a CNT-polymer network structure based on physical contacts. Such a condition is denoted as the *rheological percolation threshold*. The critical concentration, c_g , was estimated to be 1.7 wt% at $T = 200^\circ\text{C}$ with the *Winter-Chambon criterion* [9]. Further details on the adopted methodology are given elsewhere [4]. This rheological analysis was also performed on the nanocomposites, with the inclusion of functionalized nanotubes (OXIMWNT/HDPE, Fig.3) and the results compared with those of the MWNT/HDPE composites. A higher value of the rheological percolation threshold, as also confirmed by electrical measurements, was found for the OXIMWNT/HDPE composites investigated.

3.5 Electrical Conductivity

Current-voltage (I-V) characteristics of MWNT/HDPE composite films were obtained by applying suitable voltages (V) and recording the corresponding electrical currents (I) (Fig. 4). The calculated electrical conductivity values for MWNT/HDPE composites are reported as a function of CNT concentration in Fig. 5. There was a 6 orders of magnitude increase in electrical conductivity from

1 to 2.5 wt% nanotubes and this can be regarded as the electrical percolation threshold. This result confirms the rheological data [8]. The oxidized MWNT/HDPE composites show lower conductivity, compared to the

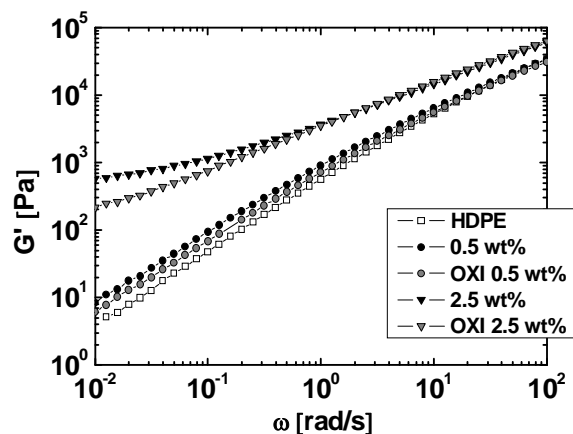


Figure 3 Storage modulus (G') vs. frequency (ω) for MWNT/HDPE composites, OXIMWNT/HDPE composites and pure HDPE. $T = 200^\circ\text{C}$.

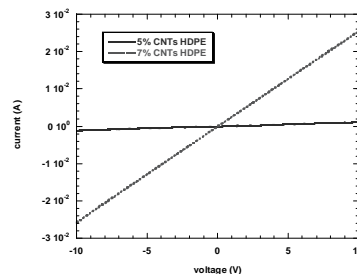


Figure 4 Current-voltage characteristics of 7 wt% and 5 wt% MWNT/HDPE composites

HDPE nanocomposite made with untreated nanotubes (Fig. 5). Indeed, according to the rheological results we can conclude that the surface treatment of the nanotubes reduces the efficiency of the CNT-matrix interaction.

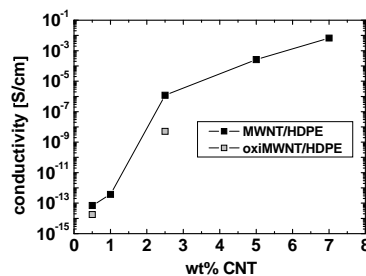


Figure 5 Electrical conductivity of MWNT/HDPE and OXIMWNT/HDPE as a function of MWNT content.

3.6 Crystallization

The isothermal crystallization ($T_c = 128^\circ\text{C}$) of the MWNT/HDPE composites was analyzed by rotational rheometry, to explore in depth the nanotube effect on the overall crystallization kinetics of HDPE. In particular, the storage modulus has been used as in situ probe to investigate the kinetics of the crystallization process [10]: in fact its increase is representative of the crystallization development. The results clearly indicate that increasing the MWNT concentration in the composite the onset of crystallization occurs significantly earlier. After 15,000s the crystallization process is already completed for the MWNT/HDPE composite with the inclusion of 0.5 wt% of nanotubes, whereas for the neat matrix the crystallization process is still slowly beginning. Such a behavior confirms that nanotubes act as nucleating agents in promoting the crystallization process of the nanocomposite compared to the neat matrix [8, 11-13]. Finally, increasing the CNT amount a sort of saturation of crystallization kinetics is observed [11].

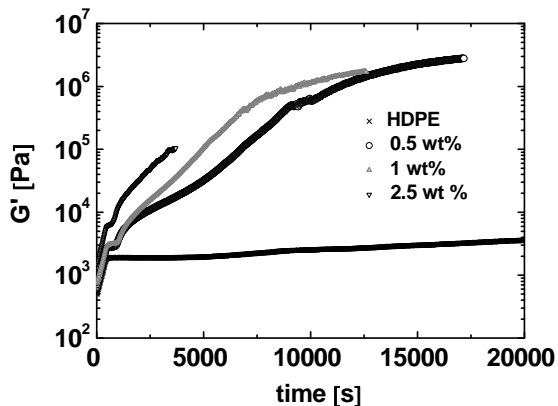


Figure 6 G' vs. time during the cooling step and the quiescent isothermal crystallization of MWNT/HDPE composites and pure HDPE. $T_c = 128^\circ\text{C}$.

4 CONCLUSIONS

Multi-walled carbon nanotube/polyethylene composites with several carbon nanotubes concentrations (ranging between 0.5 and 5 wt%) were analysed. The nanocomposites morphology was investigated by scanning electron microscopy and a good dispersion of the nanotubes in the matrix was detected, independently of the functionalisation of the MWNT. TG analysis permitted to observe that the incorporation of MWNTs in the polymer results in increased oxidative stability of the composites. The rheological investigation showed that the linear

viscoelastic behaviour strongly depends on the CNT inclusion. In particular, a significant change of the Storage Modulus profile in the low frequency region was observed (*liquid-like-solid-like transition*) above a critical concentration value, denoted as the rheological percolation threshold, indicating the presence of a CNT-polymer network. The critical concentration (c_g) to achieve the rheological percolation threshold was evaluated with the Winter and Chambon method ($c_g = 1.7\text{wt}\%$). Electrical and rheological measurements showed that the oxidative treatment, resulting in a reduction of the CNT quality, as indicated by Raman Spectroscopy analysis, decreased the efficiency of the nanotube-matrix interaction. Finally, the crystallization experiments clearly evidenced the role of carbon nanotubes as nucleating agents in promoting the crystallization kinetics of the nanocomposites with respect to the neat matrix.

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