DOI: 10.1002/masy.200750110

Rheological and Structure Investigation of Melt Mixed Multi-Walled Carbon Nanotube/PE Composites

Maria R. Nobile,[*1] *George P. Simon,*[2] *Olga Valentino,*[1] *Melanie Morcom*[2]

Summary: In this study a series of melt mixed multi-walled carbon nanotube (MWNT)/Polyethylene composites with several carbon nanotube (CNTs) concentrations were investigated. A good dispersion of the nanotubes in the matrix was seen using scanning electron microscopy. Melt rheological measurements in dynamic mode were used to estimate the percolation state of the CNTs within the polymer and to provide information about the structure of the CNT/polymer composites. The effect of nanotubes on the non-isothermal crystallization behaviour of the nanocomposites was also studied by differential scanning calorimetry.

Keywords: carbon nanotubes; crystallization; melt rheology; nanocomposites

Introduction

In 1991, Iijima published a paper showing TEM images of needle like tubes produced by arc discharge.[1] Since this paper many studies have been undertaken to determine the properties and potential applications of these materials (now known as carbon nanotubes), particularly since nanotubes are more rigid than conventional carbon fibers, and have a Young's modulus greater than 1000 GPa (Treacy et al. (1996)[2]; Wong et al. (1997)[3]) along their long direction. Moreover, CNTs are extremely flexible when subjected to large strains and they can be twisted and distorted without damage because they deform reversibly.[4] They show either metallic or semiconducting behaviour (Wildöer et al. (1998)[5]; Odom et al. (1998)[6]) and their thermal conductivity is also much greater than most other materials.[4]

Due to these excellent properties, combined with a low density (~1.3 g/cm^3), carbon nanotubes are considered ideal filler for making polymer composites. In addition, CNTs have a very high aspect ratio (length/diameter) that can be as high as 10,000[7] making it likely that the addition of a small amount ($\leq$5 wt%) into the polymer is enough to strongly improve the electrical,[8] thermal[9] and mechanical[10] properties of the matrix. In recent times, such nanocomposites have attracted considerable attention of researchers, who recognized many possible applications of these novel materials, such as for their use in automobile, electrical and aerospace areas.[11]

Despite this, the published data are often contradictory. This could be due to different factors, such as the purity, quality, aspect ratio, degree of alignment of carbon nanotubes and the preparative methods used to make the nanocomposites. In particular, the effective use of nanotubes as fillers in polymer composites depends on the capacity to obtain a good dispersion of CNTs in the matrix, without damaging them or reducing their aspect ratio. Due to the very high aspect ratio of nanotubes, large interfacial areas are available for matrix-to-fillers stress transfer, but an adequate interfacial adhesion is necessary in order to achieve a good load transfer.[12]

Recently, studies have commenced on the melt rheological properties of different CNT/polymer composites. Oscillatory

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[1] Dipartimento di Ingegneria Chimica ed Alimentare, Università di Salerno, 84084 Fisciano (SA), Italy
E-mail: mrnobile@unisa.it

[2] Department of Materials Engineering, Monash University, Clayton, VIC 3800, Australia

shear mode tests in particular have been found to be extremely sensitive to CNT/polymer composites structure and are used to obtain information about the dispersion and percolation state of CNTs within the matrix. Recent works[13–18] showed that the addition of small amounts of CNTs in a polymer matrix can produce significant changes in the trend of viscoelastic parameters (storage modulus, G′, loss modulus, G″, and complex viscosity, η^*). Pötschke et al.[14] assumed that the addition of nanotubes in the matrix can generate interconnected structures CNT-polymer. As the content of carbon nanotubes increases, such interactions begin to dominate and eventually lead to percolation, i.e. to the formation of a CNT-polymer network, corresponding to a liquid-like – solid-like transition. This interconnected structure influences the relaxation phenomena of the polymer chains and subsequently the rheological response of the sample. Once a critical content of CNTs is reached, marked alterations in the viscoelastic behaviour can be observed especially at low frequencies: the complex viscosity curves exhibit a non-Newtonian behaviour and the storage modulus curves exhibit a plateau, indicating the liquid-like – solid-like transition. Such a critical composition is denoted the rheological percolation threshold. Based on the data reported by Pötschke et al.,[13] Liu et al. (2003)[19] have used the Winter–Chambon method[20] to demonstrate that a physical gelation process in CNT/polycarbonate composites occurs. It was observed that tanδ becomes frequency independent at a particular gelation concentration, c_g, defined as the gel point. According to the Winter–Chambon method, the authors calculated relaxation exponent n and gel strength S_g values comparable with those characteristics for polymer gels.[21,22] Therefore, the results revealed a new kind of physical gel phenomenon originated from a combination of entanglement of CNTs and interactions between CNTs and polymer chains.

In this study a series of melt mixed CNT/Polyethylene nanocomposites has been studied. The High Density Polyethylene (HDPE), chosen as matrix, has excellent chemical and impact resistance, high density, hardness and toughness. HDPE is used for film, injection moulding and extrusion processes and has a very wide range of application including orthopedic implants, distribution pipes and auto parts. To improve stiffness, rigidity and electrical conductivity of HDPE carbon nanotubes can be added.

In the present work, the degree of dispersion of the nanotubes in CNT/HDPE nanocomposites has been firstly verified. Following this, the effect of the different CNTs concentrations (wt%) on the rheological and thermal behaviour of the nanocomposites has been investigated. The role of the CNTs on the crystallization process of the HDPE has been studied and discussed. The study of mechanical and electrical properties of these CNT/HDPE nanocomposites will be object of a future work.

Experimental Part

Materials

Multi-walled carbon nanotube (MWNT)/Polyethylene composites with several CNTs concentrations were studied.

MWNTs, with diameter ~60 nm and length >20 μm, were synthesized by CVD (Chemical Vapour Deposition) and made at CSIRO (Commonwealth Scientific and Industrial Research Organization, Australia).

Two High Density Polyethylene, HDPE0790 and HDPE0390 (Qenos), with average molecular weigh of $M_w \sim 52{,}570$ g/mol and $M_w \sim 58{,}886$ g/mol and polydispersity of 5.3 and 5.8, respectively, were chosen as matrices.

Preparation

Nanocomposites with three different nanotube concentrations (0.5, 1, 2.5 wt %) were prepared by melt mixing in a micro-twin screw extruder (Haake MiniLab Rheomex CTW5). Thanks to a recirculating channel, this extruder is capable of cycling the melt, ensuring good mixing and making good quality samples from limited amounts of material.

Each nanocomposite was mixed for 10 min, with a screw speed of 50 rpm. Two different mixing temperatures, $T = 225\,^\circ C$ and $T = 235\,^\circ C$ for the MWNT/HDPE0790 and MWNT/HDPE0390 composites, respectively, were chosen in order to blend the nanocomposites at approximately the same shear stress value. The addition of a larger amount (2.5 wt%) of CNTs increased the viscosity of the system, resulting in the need to increase the processing temperature slightly by about 5 °C.

Measurements

The morphological properties and the degree of dispersion of cryo-fractured CNT/polymer composites were analyzed by scanning electron microscopy (SEM LEO420).

Melt rheological measurements were performed in dynamic mode by an ARES-rheometer (TA) using a parallel plate geometry (diameter of 25 mm and gap of 1 mm) under a nitrogen atmosphere. Small pieces of extrudated strands were held between preheated plates at 200 °C for an adequate annealing time in order to equilibrate before tests. Preliminary strain sweep tests at 200 °C were achieved to estimate the linear viscoelastic range. Afterwards, frequency sweep tests in the linear viscoelastic regime were conducted between 0.01 and 100 rad/s at 200 °C, to study the viscoelastic behaviour of the nanocomposites and to have indication of the rheological percolation threshold.

Thermal analysis was carried out with a differential scanning calorimeter (DSC 822 Mettler-Toledo) under a nitrogen atmosphere, so as to observe the effect of nanotubes on the non-isothermal crystallization process of the polymer matrix. The samples were heated from room temperature to 250 °C at a heating rate of 10 °C/min and held for 20 minutes to destroy any thermal history. Afterwards, they were cooled to 25 °C using a cooling rate of 10 °C/min. To observe the melting peak after crystallization, a second heating scan was recorded from 25 °C to 250 °C at 10 °C/min. The crystallinity was determined, using the enthalpy of fusion of PE with 100% crystallinity, $\Delta H_{100\%} = 293.6$ J/g.[23]

Results and Discussion

Dispersion and Morphology

Nowadays SEM micrographs on their own are adequate to give a qualitative idea about dispersion and, above all, to show the existence of a CNT-polymer network, as recent published works have shown.[13,24] Moreover, our MWNTs are characterized by a diameter of 60 nm that can be clearly seen by SEM. Scanning electron microscopy of our MWNT/HDPE samples indicates that a good degree of dispersion was obtained in the nanocomposites and confirmed that an adequate preparation technique was achieved. A SEM micrograph of the 2.5wt%MWNT/HDPE0790 composite made by melt extrusion in the Haake MiniLab (50 rpm for 10 min, at $Tmix = 230\,^\circ C$) is reported in Figure 1, clearly showing the appreciable good dispersion of the nanotubes.

A second image of the 2.5wt%MWNT/HDPE0790 composite (Figure 2) was taken at higher magnification to prove the existence of a CNT-polymer network.

Scanning electron micrographs also showed that such a network is not present in the composites with smaller amounts of CNTs (1 and 0.5 wt%). These results are confirmed by melt rheological measurements, that will be discussed in the next section.

Melt Rheology

Preliminary strain sweep tests were performed to estimate the linear viscoelastic range of the nanocomposites. In order to study if a frequency (ω) effect on the linear viscoelastic limit is present, the strain sweep measurements were carried out at different ω (0.05, 0.1, 1, 10 rad/s) on the

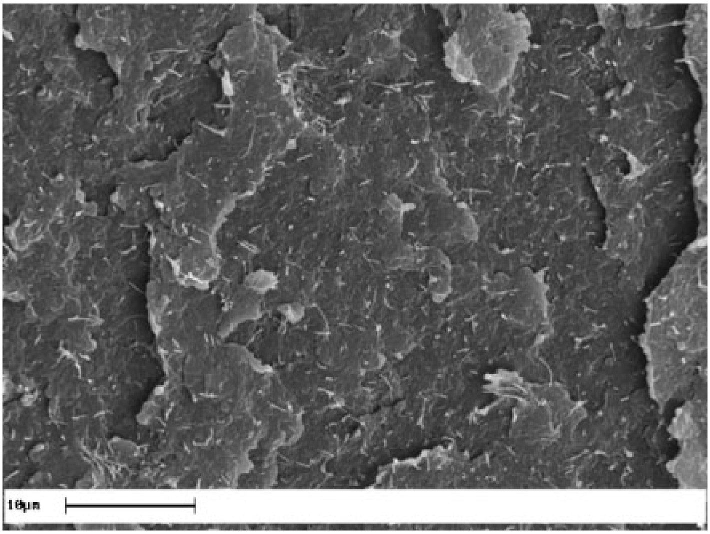

Figure 1.
SEM image of cryo-fractured 2.5wt%MWNT/HDPE0790 composite. Dispersion analysis.

1wt%MWNT/HDPE0790 sample. Figure 3 demonstrates that no frequency effect has been recorded since the storage modulus (G') shows a critical strain (γ_c) of about 5% for all the frequencies tested.

Figure 4 shows the results obtained by strain sweep experiments at $\omega = 1$ rad/s for all the samples with different concentration of nanotubes. As the nanotube content increases, the upper limit of the viscoelastic range decreases because of the CNTs influence on the relaxation processes of the polymer chains. Indeed, the critical strain (γ_c) is 40% for the neat matrix, 25% for the 0.5wt%MWNT/HDPE0790 composite, 5% for the 1wt%MWNT/HDPE0790 composite and 1% for the 2.5wt%MWNT/HDPE0790 composite. Thus, lower strains

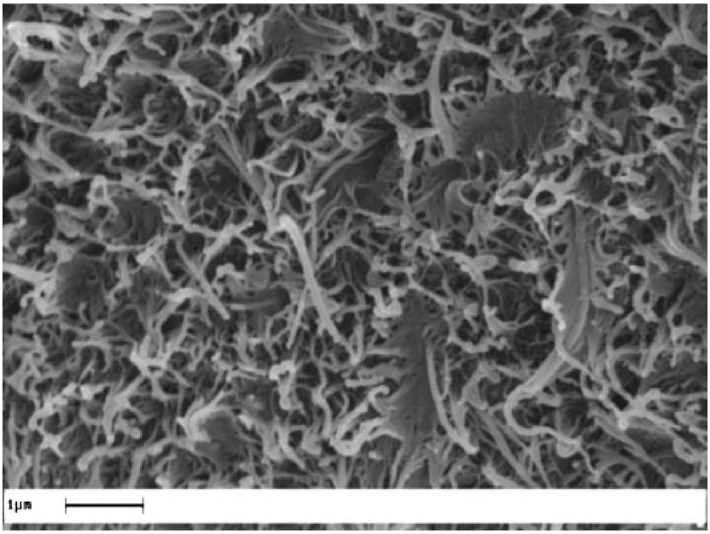

Figure 2.
SEM image of cryo-fractured 2.5wt%MWNT/HDPE0790 composite. CNT-polymer network evidence.

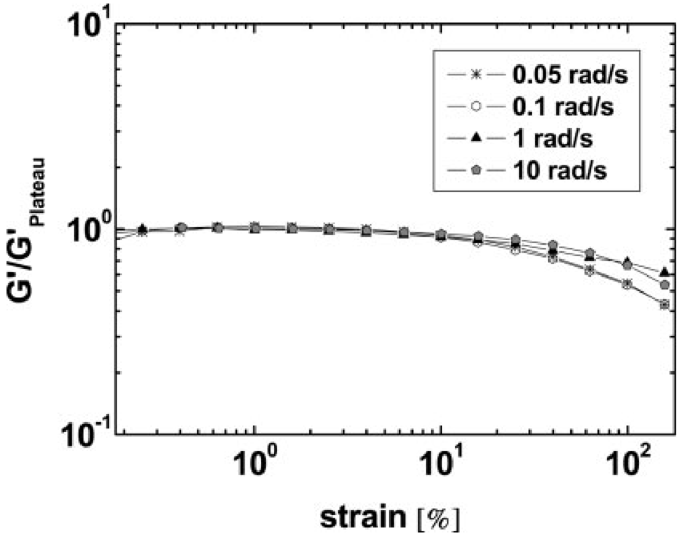

Figure 3.
Storage modulus (G′) normalized to the plateau value vs. strain (γ) at different frequencies for the 1wt%MWNT/HDPE0790 composite. T = 200 °C.

of 0.2% for the 2.5wt%MWNT/HDPE0790 composite and 1% for the other nanocomposites and neat matrix were chosen to guarantee that the frequency sweep tests were within the linear viscoelastic region.

The results of the frequency sweep experiments for the MWNT/HDPE0790 composites are shown in Figure 5 and Figure 6.

The neat matrix exhibits a typical liquid-like behaviour at low frequencies whereas, as expected, the viscoelastic parameters increase with the CNTs content. At 2.5wt% nanotube content, a clear change in the

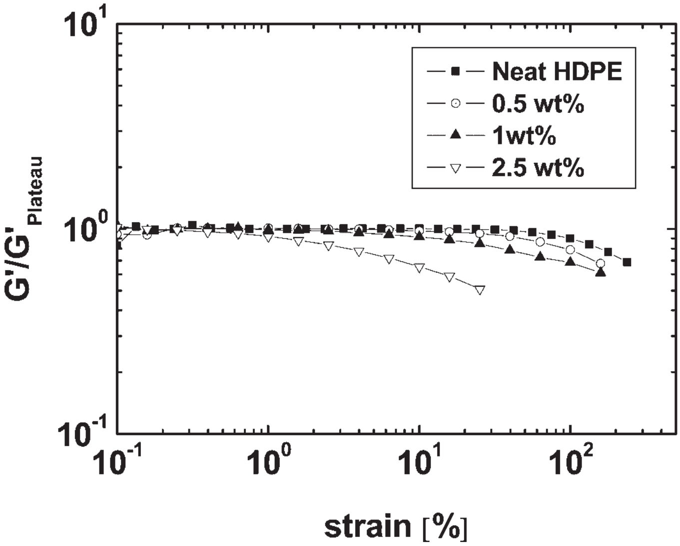

Figure 4.
Storage modulus (G′) normalized to the plateau value vs. strain (γ) at ω = 1 rad/s for the MWNT/HDPE0790 composites and the pure HDPE0790. T = 200 °C.

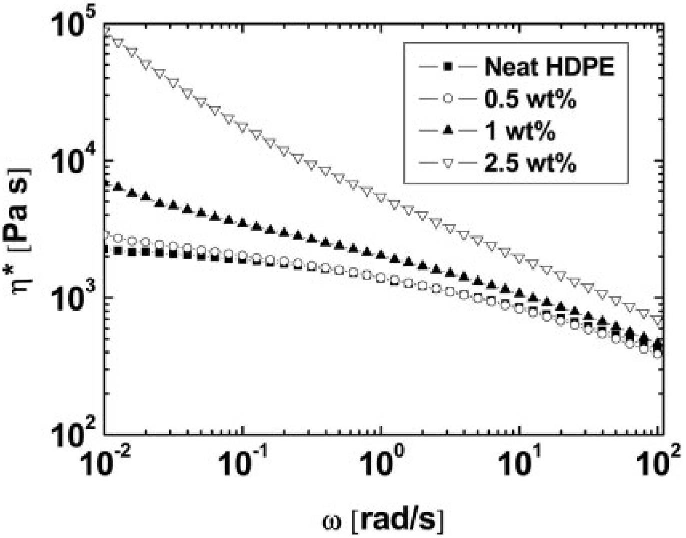

Figure 5.
Complex viscosity (η*) vs. frequency (ω) for the MWNT/HDPE0790 composites and the pure HDPE0790. T = 200 °C.

viscoelastic behaviour is recorded, particularly at low frequencies: the complex viscosity shows a non-Newtonian behaviour (Figure 5) and the storage modulus shows a plateau (Figure 6), indicating a change in structure, i.e. the formation of a CNT-polymer network, and confirming what was established by the scanning electron microscopy. As suggested in literature,[14,25] to better identify the rheological percolation threshold, the phase angle (δ) has been plotted against the complex modulus |G*| (van Gurp-Palmen plot, Figure 7). This plot indicates that the rheological percolation threshold is between 1wt% and 2.5wt% nanotubes at 200 °C.

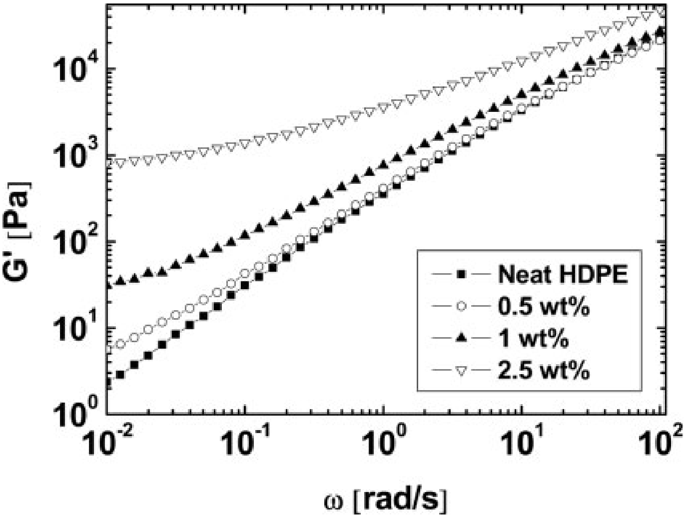

Figure 6.
Storage modulus (G′) vs. frequency (ω) for the MWNT/HDPE0790 composites and the pure HDPE0790. T = 200 °C.

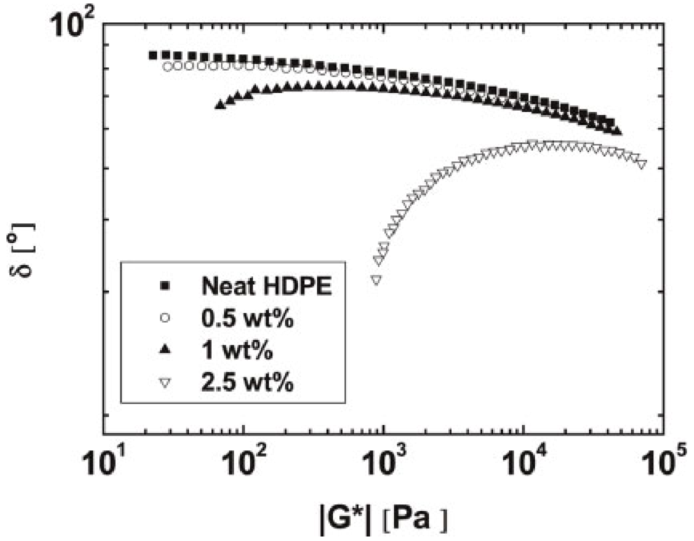

Figure 7.
Phase angle (δ) vs. the absolute value of the complex modulus $|G^*|$ (van Gurp-Palmen plot) for the MWNT/HDPE0790 composites and the pure HDPE0790. T = 200 °C.

These results agree with literature data.[13–18] Pötschke et al.[13] observed similar behaviour in melt mixed MWNT/Polycarbonate composites and the rheological percolation threshold was found to be about 2 wt% CNTs. Zhang et al.[17] published analogous data for single-walled nanotube (SWNT)/HDPE composites; the authors estimated the rheological percolation threshold around 1.5wt% nanotubes.

Frequency sweep measurements were also undertaken for the MWNT/HDPE0390 composites. As observed in Figure 8, these composites show a viscoelastic behaviour similar to the nanocomposites made with the lower molecular weight matrix (HDPE0790).

In order to make clear the slight molecular weight effect due to the difference between the two HDPE samples, a comparison between the two types of nanocomposites (MWNT/HDPE0790 and MWNT/HDPE0390) is reported in Figure 9. As expected, the pure matrix with higher molecular weight, named HDPE0390, exhibits higher G′ values respect to those measured for the lower molecular weight HDPE0790. Both of the composites containing 2.5wt% nanotubes show a solid-like behaviour at low frequencies, with only small differences in G′ values. Du et al.[15] studied SWNT/poly(methyl methacrylate) (PMMA) composites with two PMMA characterized by significant different average molecular weights ($M_{w1} \sim 25{,}000$ g/mol and $M_{w2} \sim 100{,}000$ g/mol) in order to investigate the molecular weight effect on the melt rheology of the nanocomposites. Frequency sweep measurements indicated smaller slope of G′ vs ω and larger G′ values at low frequencies for the nanocomposites made with the higher molecular weight PMMA. Du et al. suggested that longer polymer chains (i.e. higher M_w) easily link closely-spaced nanotubes and consequently enhance the CNT-matrix interconnection. Therefore, in our case it can be concluded that the two HDPE matrices used to obtain the nanocomposites have molecular weights not sufficiently different to achieve such an enhancement in the CNT-matrix interconnections.

Differential Scanning Calorimetry

Peak temperatures (T_{peak}) and crystallization enthalpies (ΔH_c) obtained for the MWNT/HDPE0790 composites and the

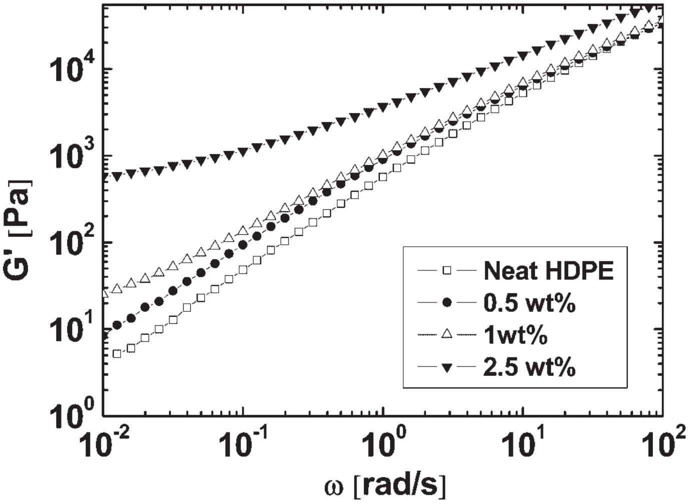

Figure 8.
Storage modulus (G′) vs. frequency (ω) for the MWNT/HDPE0390 composites and the pure HDPE0390. T = 200 °C.

neat HDPE0790 by thermal analysis are listed in Table 1.

In addition, Figure 10 shows the cooling curves of the MWNT/HDPE0790 composites and the neat HDPE0790.

DSC data indicate no significant changes in the second melting temperatures (T_{peak}, Table 1) but, as clearly shown in Figure 10, the addition of the MWNTs in the polymer matrix produces an increase in the crystallization temperature of about 3 °C, i.e. an enhancement in the heterogeneous nucleation process of the HDPE. This effect is already evident at the lowest filler content analyzed (0.5 wt%).

Similar behaviour has been observed in the literature.[26–28] In particular, Anand et al.[26] investigated the non-isothermal

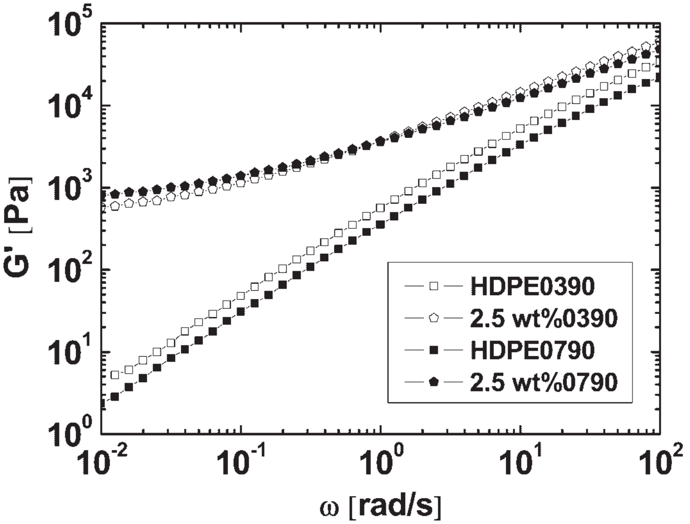

Figure 9.
Storage modulus (G′) vs. frequency (ω). Comparison between MWNT/HDPE0790 and MWNT/HDPE0390 composites and the pure matrices. T = 200 °C.

Table 1.
DSC parameters of the MWNT/HDPE0790 composites and the pure HDPE0790.

Sample	ΔH_c (J/g)	Crystallization T_{peak} (°C)	2° melting T_{peak} (°C)
HDPE	197.6	117.1	129.9
0.5wt%MWNT/HDPE	192.2	120.7	130.5
1wt%MWNT/HDPE	188.9	120.7	131.2
2.5wt%MWNT/HDPE	185.1	120.8	131.0

crystallization of melt compounded SWNT/Poly(ethylene terephthalate) (PET) composites. It was reported that at 0.03 wt% nanotubes the sample crystallizes some 10 °C higher temperature than neat PET; further increasing the SWNT concentration causes the crystallization temperature to continue to rise, but at a slower rate. The authors hypothesised a saturation of the nucleant effect at low nanotubes concentrations, probably due to the good dispersion of the SWNTs in the matrix.

Data in Table 1 gives evidence that the crystallization enthalpy decreases more than expected from the simple reduction of the HDPE content, as nanotube concentration increases. Specifically, the pure HDPE has higher crystallinity ($Xc \sim 67\%$) than the MWNT/HDPE composites (i.e. the 2.5wt%MWNT/HDPE0790 composite has $Xc \sim 65\%$, evaluated with $\Delta H_c = 192.7$ J/g that is the ΔH_c reported in Table 1 and subsequently normalized with respect to the amount of the neat HDPE content). Indeed, due to the filler presence, the cristallinity in the nanocomposites could be affected by the restricted mobility of the chains, which does not allow the growth of well developed crystals.

Conclusions

In this work, novel melt mixed MWNT/Polyethylene composites have been studied. SEM images have proved that a good dispersion of the nanotubes in the polymer matrix has been obtained and have shown a CNT-polymer network in the 2.5wt%MWNT/HDPE0790 composite.

Melt rheological analysis in dynamic mode has indicated a rheological percolation threshold between 1wt% and 2.5wt% nanotubes, proving that rheology is a very

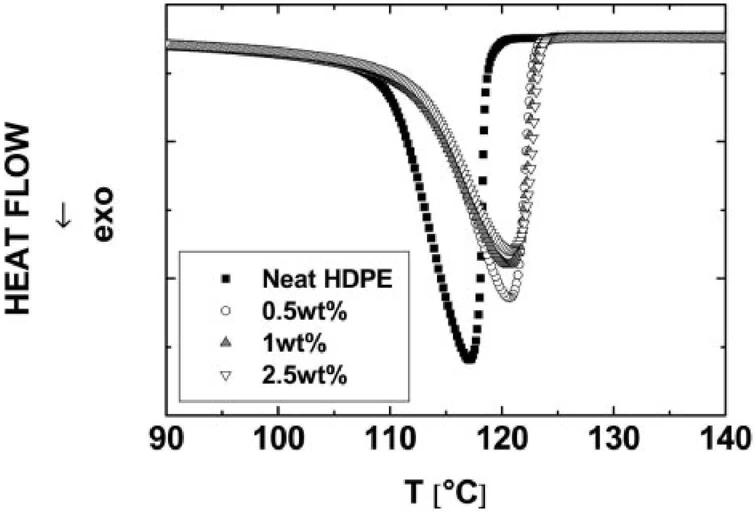

Figure 10.
Non-isothermal crystallization curves of the MWNT/HDPE0790 composites and the pure HDPE0790.

good method to have information about the structure of the samples. Finally, thermal analysis has revealed that nanotubes, acting as nucleating agents, influence polymer crystallization, giving further confirmation of their good dispersion.

Acknowledgements: We thank Stephen Hawkins and Ken Atkinson of CSIRO Textile and Fiber Technology for providing the MWNTs used in this work.

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