Electrically conductive polypropylene fibers and tapes

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ABSTRACT

We report here the development of electrically conductive polypropylene MWCNT fibers and tapes with conductivities up to 50 S/m (8% wt of MWCNT) and a percolation threshold at 0.5% wt.

Using a solution compounding method assisted by sonication we have produced composite master-batches (1Kg/batch) with improved MWCNT dispersion levels. These composites have been extruded into fibers by melt spinning which is a well implemented technique in textile industry that allows mass production of woven textiles. Different stretching rates of the tapes and fibers are obtained depending on the wt% of MWCNT in the composites. In good agreement with previous studies, alignment of the MWCNT along the fiber axial direction has been observed. An extensive characterization of the fiber and materials has been carried out (including SEM, XRD) to describe their internal structure and morphology. Macroscopic properties (MFI, DC, AC conductivities) have been also studied.

Keywords: fiber, tape, MWCNT, CNT, thermoplastic, conductivity.

1 INTRODUCTION

Electrical conductor fibers and yarns are very desirable kind of materials in nanotechnology. With the rapid development of electrical, and particularly electronics industry, flexible electrically conducting and semi-conducting materials are receiving a widespread attention. These materials are playing an important role in the development of lightweight, wireless and wearable interactive electronic textiles used in Smart Materials. [1]

Fibers composed of pure carbon nanotubes (CNTs) or CNTs embedded in a polymeric matrix have been produced by various techniques. [2] In the case of pure CNT fibers (100% wt CNT) outstanding properties are being achieved (Young´s modulus: 120±10 GPa) and electrical conductivity ($5x10^5$ S/m). [3] For CNT/polymer composites fibers, lower mechanical and electrical properties are expected due to the much lower amounts of filler introduced. Many CNT/polymer fibers are prepared by electrospinning. Nevertheless, woven fibers prepared by melt spinning can be obtained from CNT/polymer masterbatches and compounds. These CNT/polymer blends are prepared by melt blending techniques which impair poor dispersion degree to the filler. [4] As a result only composites with low filler loadings (up to 2% wt) can be extruded into low electrical conductivity fibers (antistatic fibers).

A critical issue in taking advance of the superior properties of the CNTs is the ability to disaggregate and control their dispersion in the polymer. Many authors report improved mechanical and electrical properties for the materials prepared using solution techniques assisted by sonication compared with the same materials prepared by more traditional methods such as melt blending. [5] We have implemented an scaled up (Kg/batch) a solution processing of composites assisted by ultrasonication for thermoplastics. Basically this method combines the good dispersions produced by a ultrasonication with a fast quenching of the composite by precipitation, see experimental.

In this work, the dispersion of the MWCNTs was improved sustantially using a solution compounding method assisted by sonication. This method has allowed the extrusion of fibers with high CNT loadings (up to 8% wt) and, therefore, high electrical conductivity (50 S/m).

2 MATERIALS AND METHODS

For this study, isotactic polypropylene Boraelis HG245 FB was used without further treatment. As CNT material, Nanocyl NC7000 was used in powder shape and used without further purifications. These are MWCNTs with an average diameter of 9.5 nm and a length of 1.5µm. Their BET is between 250-300 m^2/g and have a carbon purity of 90%. Polypropylene was disolved at 150 ºC. MWCNT were previuosly dispersed in the same solvent at 150 ºC using Hieslcher UIP 1000hd ultrasonic device. Once the polymer was dissolved the resulting suspension was sonicated to

ensure a good dispersion within the polymer matrix. Precipitation of the composite was accomplished by the addition of the polymer mixture to a suitable precipitating agent. The black composites were filtered off and dried in vacuum oven overnight.

Thermal analysis measurements were performed utilizing a differential scanning calorimeter (TA-instruments 2920 DSC). Ten milligrams sample was heated from 30-200ºC at a scan rate of 10 ºC/min and maintained at that temperature for 1 min to eliminate any previous thermal history of the material. Subsequently, the sample was cooled to 30 ºC at the same scan rate, and then heated up to 200ºC at a scan rate of 10ºC/min. The microstructure of MWCNTs/PP nanocomposites was studied using a Scanning Electron microscope (FE-SEM HITACHI S4800). The electrical resistivity of composite the composites have been determined using the four-point probe method (Keithley 2182A nanovoltmeter; 6221 Keithley current source). X-ray diffraction measurements were obtained using a Bruker D8 Discover type XRD system. Each sample was scanned with Cr Ka targets (30 kV, 20 mA) at a continuous scan rate of 5º min^{-1}. The melt spinning behavior of the compounds (200 g-1 Kg) was evaluated on a low speed lab spinning line, working at a maximum velocity is 50 m/min. The spinning line comprises with a extruder (no meltpump), spinneret, cooling fan, first series of 4 godets, drawing godet, relaxation godet, V&V and winder.

3 RESULTS AND DISCUSSION

After the process (see experimental) the PP-MWCNT composite in pellet form will suffer further processing that can alter their microscopic structure and subsequently their macroscopic properties. So, the pelletized composite is reprocessed in two independent ways. In one hand, a composite is reprocessed into hot-pressed disks that will be used to determine the electrical conductivity and their structure by SEM. On the other hand, the pelletized composite is extruded into tapes in Centexbel that will be also studied.

3.1 Melting and crystallization behaviour of CNTs/PP composites

Thermal behavior of PP/MWCNT composites has been evaluated by differential scanning calorimetry (DSC). Neither the processing by ultrasonication of PP nor the presence of MWCNTs showed significant effect on the melting temperature of the composite in comparison to pure PP (non-processed). The average melting temperature is 163.9 ± 0.7 ºC.

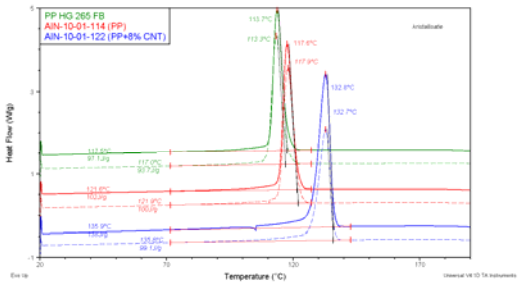

Figure 1. Crystallization curves of PP, PP processed by ultrasonication solution method and PP/MWCNT 8% wt in green, red and blue, respectively

However, differences on the crystallization temperature are found upon processing the composites, as can be observed in Figure 1. Pure iPP has a T_c around 113.7ºC. Processing the polymer with the ultrasonication process leads to an increased T_c of 117.6 ºC. Due to the nucleating effect of MWCNTs on the crystallization of PP, the addition of CNTs increases even more the crystallization temperature, which is of 132.8ºC in the composites with 8% wt MWCNTs.

The addition of fillers into the polypropylene matrix can cause changes in the crystallization rate of the polymer, and even induce changes on its crystal conformation. X-ray diffraction measurements have been carried out in order to study the crystalline structure of the composites.

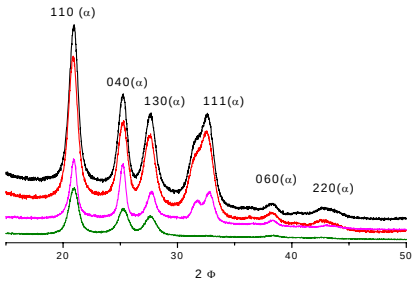

Figure 2. X-Ray diffractograms of pure PP (black) and PP-MWCNT (5% wt) composites in powder (red), tape 4 times stretched (pink) and tape six times stretched (green), respectively.

As can be observed in Figure 2, both pure PP and PP-MWCNT nanocomposites display characteristic diffracting peaks correspondent to the α-phase of polypropylene and exhibit complete absence of the β-crystal form (hexagonal).[6] β-phase can be promoted by using high orientation or deformation in the melt, high crystallization temperatures or by the incorporation of some nucleating agents.[7] No presence of β-phase is observed upon the addition of MWCNTs, or upon the application of high deformation stretching forces on the tapes. However the increasing stretching rate of the material induce a preferential orientation of the crystalline planes of

polypropylene: (110) becomes the preferential orientation, while the plane (111) is completely lost when stretching the tapes for six times.

3.2 Yarn and tape extrusion and rheology

Yarn extrusion has very demanding requirements for nanocomposite materials (take-up speed of 1000-2000 m/min plus drawing process). The small diameter of the fibers (few microns) sets strict requirements for dispersion and small particle size. Addition of CNTs has a huge influence on the viscosity of the polymer matrix. In fact, melt flow index (MFI) measurements dramatically decreases upon increasing the concentration of the CNTs, being 8% wt composites the maximum compound of which MFI could be measured.

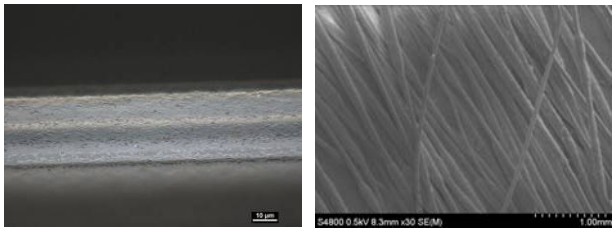

Figure 3. Left: optical microscope analyses of a hard filament 2 % CNTs; right: SEM picture of these fibers.

The different formulations (up to 8% wt) could be extruded into fibers or tapes (Figure 3). Optical microscopy of the tapes and fibers shows better finishing compared with the composites obtained by traditional melt-mixing (twin screw extruder) methods.

The size and agglomeration degree of clusters have been throughout studied by SEM (scanning electron microscopy), see following section.

3.3 SEM study and DC electrical conductivity of the composites and tapes

We have used SEM to study the evolution of the conductive network and their relationship with the macroscopic properties (electrical conductivity and procesability). In order to assess the agreement between the different properties in a composite we have studied a 5 % wt MWCNT composite through the different stages of the process. This composite was sonicated for 2h in solution and then precipitated and overnight dried. The resulting material was reprocessed into hot pressed disks or extruded into tapes (x4 and x6 times stretched). This composite have been characterized by SEM (as powder, hot pressed disk and tapes), and their electrical conductivity in the different forms have been determined. In Figure 4 (left) we observed a **pristine sample** of Nanocyl NC 7000 powder suspended in solvent prior to sonication (with no PP). We can observe large clusters (larger than 15-20 μ) of highly entangled MWCNT. In Figure 4 (right) we observe SEM picture of a 5% wt PP-MWCNT **as powder** or pellet forms after overnight drying. Although there are still highly entangled clusters entrapped within the polymer matrix the sonication has considerably reduced the size of the clusters.

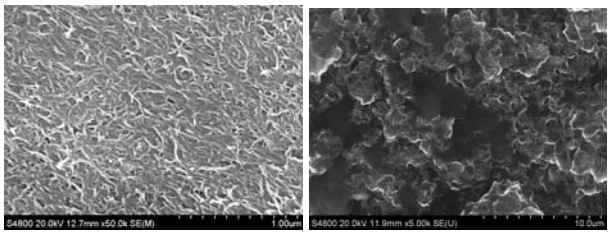

Figure 4: left: SEM pictures of Nanocyl NC 7000 powder as received (Prior to sonication and addition of PP); right: SEM pictures of 5% wt PP-MWCNT composite after vacuum drying.

SEM pictures of powders are useful to have a general idea of the grain size and the dispersion degree of MWCNT in our composites. However, in powder form is difficult to have a good estimation of the dispersion degree and size of the clusters to establish a good comparative among the different composites synthesized in this study. Besides it is not possible to determine the electrical conductivity of the composites using powders due to their discontinuous nature. For these reasons we reprocess part of the composites into hot pressed disks. These are good specimens to determine the electrical conductivity using a four probe method, which can be also used to determine the electrical conductivity of the tapes. For these composites we have observed a percolation threshold at 0.5% with a maximum conductivity of 70 S/m at 8% wt (Figure 5).

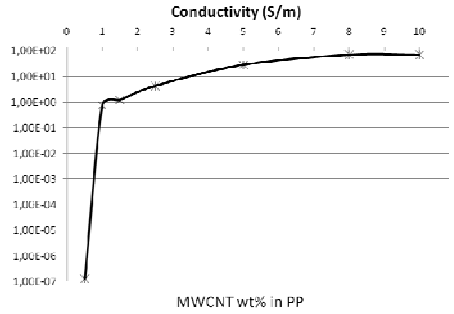

Figure 5. Electrical conductivity in hot pressed disks.

It is interesting the good agreement found between the conductivity measured in the tape (four times stretched) and in the hot pressed disks. In principle, this is something not trivial since both processes could significantly alter the dispersion degree of the nanocomposites.

Table 1

MWCNT (% wt)	Conductivity (S/m) (disk)	Conductivity (S/m) (tape x4 streched)	Conductivity (S/m) (tape x6 streched)
5	20	10	-
8	70	50	-

Analyzing SEM pictures of hot pressed disks shows beautiful tree-like clusters (Figure 6). Despite of the fact that in some areas we still observed high compacted MWCNT clusters, most of the clusters observed showed a less entangled appearance than the pristine NC7000 nanotubes prior to the sonication. Due to the still high concentration of MWCNT in the cluster it is difficult to conclude if the MWCNT have been shorten by the action of sonication. It is clear is that a 3D conductive network is produced within the polymer matrix which explains the electrical conductivity of the hot pressed disks (20S/m).

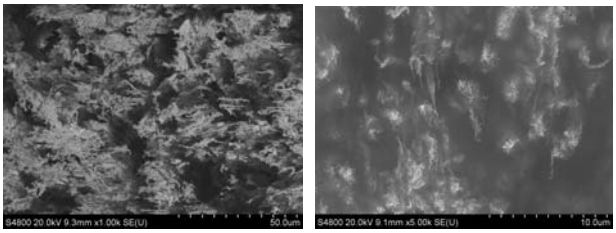

Figure 6: left: SEM pictures of 5% wt PP-MWCNT in hot pressed disks; right: SEM pictures tapes 4 times stretched.

SEM pictures of the composite **tapes 4 times stretched** clearly resemble the structure observed in the hot pressed disks with an extended network of MWCNT clusters interconnected. This is in good agreement with the similar electrical conductivities observed in both (hot pressed disks and 4 times stretched tapes). However, it is also clear that the network of clusters has been partially aligned due to the stretching forces applied in the tape.

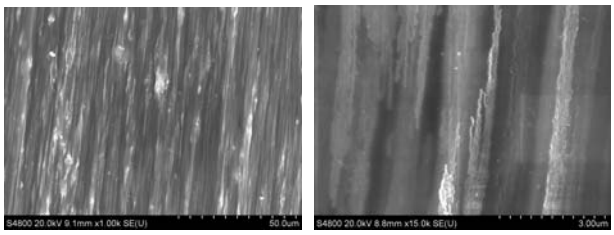

Figure 7: SEM pictures tapes 6 times stretched.

The parallel alignment and deformation (elongation) of the clusters due to the stretching forces applied in the tape extrusion is clearly observable when we analyzed the **6 times stretched tapes**. See Figure 7, Due to this alignment we also could have a good understanding of the actual sizes of the clusters produced in the composite. After stretching the composite six times, the clusters could be described as tapering or laminar shaped areas of MWCNT with a minimum dimension ranging within 500 nm to 2μ and maximum lengths within the range of 25μ to several hundred microns. This phenomenon of cluster elongation is clearly observed in the 15k augmented picture (Figure 7 right) showing the almost parallel alignment of individual MWCNT at the edges of the clusters.

The stretching of the clusters observed by SEM are in good agreement with the XRD analysis of the materials previously shown. The lack of a 3D interconnected conductive network can also explains the decrease in the electrical conductivity of these composites in tapes 6 times stretched compared to the 4 times stretched tapes or disks.

4 CONCLUSIONS

Using a solution compounding method assisted by sonication we have produced PP/CNT composite master-batches (up to 1Kg/batch) with improved dispersion levels. Composite fibers and tapes based on these composites were prepared by melt spinning (with conductivities of 50 S/m at 8% wt of MWCNT). Different stretching rates of the tapes and fibers are obtained depending on the wt % of MWCNT in the composites. In good agreement with previous studies, alignment of the MWCNT along the fiber axial direction has been observed.

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