New route to manufacture high performance carbon nanotubes nanocomposites based on pre-dispersed concentrates generated by in-situ polymerisation

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ABSTRACT

Since their first observation, carbon nanotubes (CNTs) have been attracting both academics and industries, owing to their exceptional properties. Thus, they have been tested as advanced multifunctional filler in polymer-based nanocomposites. However, when dispersed in a polymer matrix, pristine carbon nanotubes tend to maintain their aggregated state, and their poor dispersion leads to non-optimized mechanical and conductive properties of the resulting materials. We describe here an original method which relies upon the in situ polymerization of an olefin. As a result, carbon nanotubes are homogeneously coated by the in situ grown polyolefin chains, finally leading to the break-up of the nanotube bundles. A mechanism is proposed and evidences of the coating are established in this paper. The resulting polymer-coated CNTs have been used as concentrates that have been dispersed in various polymers. This dispersion improvement has allowed increasing of the mechanical and the electrical properties with comparable success in commodity, engineering and high performance plastics.

Keywords: carbon nanotube, in-situ polymerization, nanocomposite, polyolefin, dispersion.

1 INTRODUCTION

Owing to their exceptional properties, carbon nanotubes are currently investigated for a large panel of applications, including conductive materials, energy storage and energy conversion device sensors, field emission displays and radiation sources, hydrogen storage media, nanometer-sized semiconductor devices, probes, interconnects, biosensors as well as high-strength polymer nanocomposites[1-3]. The carbon nanotubes (CNTs) can be seen as a single, a couple of, or several graphite layers that have been rolled up into a tube-shape and capped at each end. Depending on the number of graphite layers, nanotubes are described as « single-walled », « double-walled » or « multi-walled » CNTs.

This peculiar structure affords very efficient properties such as, i.e., very high stiffness, strength and resilience : carbon nanotubes are about a hundred times tougher than steel or Kevlar. They also exhibit semi-conductor or conductor properties, depending on the way they are rolled up.

In the frame of polymer-based nanocomposites, one of the key-challenges lies in the successful association of the physico-chemical properties of polymer matrices with those offered by the carbon nanotubes. One of the main problems that arise with such type of composites concerns the nanotube individual dispersion, since strong Van der Waals interactions between nanotubes tend to maintain these nanofibers toughly aggregated in bundles. Therefore, when polyolefins are mixed with nanotubes, poor filler dispersion is obtained, owing to this aggregation phenomenon and relatively poor mechanical properties of the resulting composite are observed.

However production of polymer/carbon nanotube nanocomposites faces a major problem. When dispersed in a polymer matrix, pristine carbon nanotubes tend to maintain their aggregated state, and their poor dispersion leads to non-optimized mechanical and conductive properties of the resulting materials[4-6]. Indeed, carbon nanotubes form long bundles that are thermodynamically stabilized by numerous π-π interactions between the tubes and simple polymer processing is not able to break down these bundles. Moreover, most of the techniques that have been used to disaggregate these bundles, e.g., ultrasonication[7], chemical modification (oxidation, reduction,…) of the nanotubes surface and subsequent polymer grafting[8-10], often tends to disrupt or at least to modify the extended delocalized π system that is responsible for the unique properties of carbon nanotubes.

We recently develop a soft method that allows to coat carbon nanotubes with polyolefins[11]. This method is derived from the polymerization-filling technique (PFT) initially developed for Ziegler-Natta catalysts[12] and more recently for metallocene catalysis[13-15].

2 POLYMERISATION FILLING TECHNIQUE AND MECHANISM PROPOSAL

PFT applied to carbon nanotubes consists in anchoring methylaluminoxane (MAO), a well-known co-catalyst used in metallocene-based olefin polymerization process onto the surface of carbon nanotubes. After high temperature treatment, most of the MAO is anchored onto the carbon nanotubes surface. A metallocene catalyst, i.e., bis(pentamethyl-η5-cyclopentadienyl)zirconium (IV) dichloride (Cp_2*ZrCl_2) in this study, is then reacted with the surface-activated carbon nanotubes. A methylated cationic species (Cp_2*ZrMe^+) is formed upon reaction and remains immobilized at the vicinity of the nanotubes surface by electrostatic interactions with simultaneously formed MMAO counteranions fixed at the nanotubes surface. Addition of ethylene leads to the synthesis of polyethylene (PE) exclusively at the surface of the carbon nanotubes.

In order to understand the mechanism of carbon nanotubes coating by PFT, two syntheses have been performed, by varying the amount of PE produced at the surface of multi-walled carbon nanotubes (MWNTs). The quantity of PE coating has been determined by thermogravimetric analysis. Sample A consists of MWNTs coated by 43 wt% of polyethylene while MWNTs in Sample B are coated by 75 wt% of PE. The morphology of both samples has been characterized by transmission electron microscopy (TEM). **Fig. 1a** shows a TEM micrograph of the pristine MWNTs, characterized by the presence of long nanotubes bundles. When coated by 43 wt% of PE (Sample A), MWNTs appear much less densely packed (**Fig. 1b**). At this PE content, each nanotube is covered by numerous PE patches most probably indicating the localization of anchored active catalyst species from which PE chains are produced and precipitate at the nanotube surface. A closer observation of **Fig. 1b** (inset) shows that besides the PE patches, one can observe PE sleeves that originates from the growth and possible junctions of PE patches.

Sample B, characterized by a much higher PE content (75 wt%), shows MWNTs totally covered by an homogeneous coating of PE (**Fig. 2c**). In this case, all the polyolefinic sleeves have joined together in order to produce this regular PE coating. A closer observation of the tip of a nanotube (see inset) allows evaluating the size of the coating: the observed MWNT has a diameter of ca.10 nm and the coated nanotube is ca. 35 nm in diameter. The thickness of the PE coating is therefore ca. 12 nm. One can remark on this inset that the tip of the MWNT is also homogeneously coated (as all the tips that can be observed on **Fig. 1c**). Such observation seems to indicate that the PE coating might tend to slide all along the MWNTs surface until it reaches their ends.

Fig. 2 presents the idealized sketch for PE growth onto MWNT surface ultimately leading to complete and homogeneous coating of the carbon nanotubes. Upon treatment with MMAO and Cp_2*ZrCl_2, catalyst spots are created at the carbon nanotube surface. Upon ethylene addition, these spots start to produce PE chains that precipitate in the medium as soon as their molecular masses reach their solubility limit, forming PE patches. Upon continuous feeding of ethylene, the PE patches grow and slide along the nanotube to form PE sleeves. Eventually, the PE sleeves join together to form a continuous and homogeneous PE coating around the carbon nanotubes.

Such a mechanism is supported by the kinetics of ethylene consumption, reported elsewhere[13] and which does not show any rate reduction with time, attesting for a continuous production of PE at a constant pace that is coherent with the PE sliding process. The macroscopic morphology of the recovered powder of PE-coated MWNTs is much more compact and dense than pristine MWNTs. Such an increase in bulk density can be explained by the fact that the individually coated MWNTs tend to slightly stick to the others through the PE coating. There is therefore a much less production of airborne particles, which eases MWNTs handling during melt-blending processes.

This technique has thus allowed to prepare never obtained high loading and pre-dispersed concentrates.
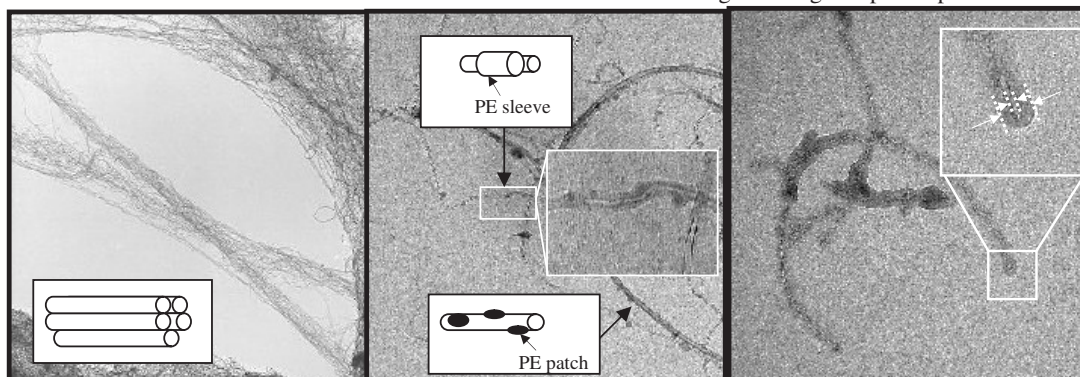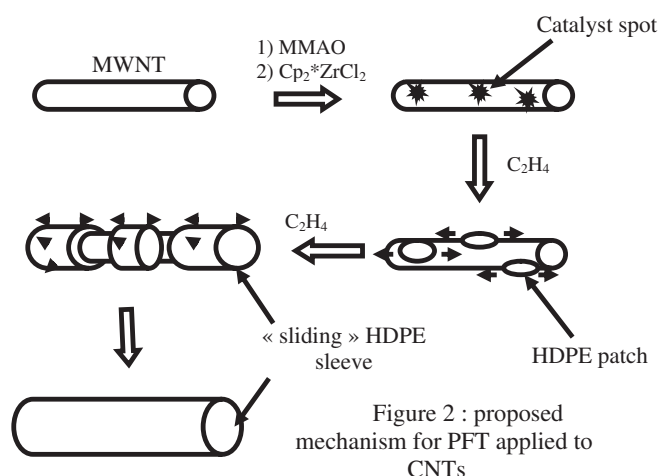

Figure 1 : MWNTs with various amounts of polyethylene coating: A. bundles of MWNTs ; B. MWNTs coated by 43wt% PE (patches and sleeves (inset)); C. MWNTs coated by 75wt% PE (homogeneous coating (inset : determination of coating diameter d_{cMWNT} in comparison with MWNT diameter d_{MWNT}))

Figure 2 : proposed mechanism for PFT applied to CNTs

3. COMPOSITES PERFORMANCES

PE-coated MWCNTs (N9000) have been used as a concentrate for the preparation of highly dispersed CNTs/polymer nanocomposites. Following the same experimental procedure, concentrates of various compositions has been prepared by PFT and dispersed in polymer matrices, using a co-rotating twin-screw extruder. These nanocomposites were then analysed and evaluated in term of dispersion level, mechanical, electrical and thermal properties with respect to the non-coated MWCNTs (N7000).

3.1 Dispersion level

Fig. 3 and **4** show TEM micrographs of respectively HDPE and EVA based composites. It is clearly evidenced that, for both case, the use of non-coated MWCNTs results in the presence of agglomerates. On the other hand, nanocomposites prepared with PE-coated MWCNTs exhibit a very high level of dispersion. Indeed, isolated nanotubes (see white arrows) are clearly observed in all the samples (B). This very good dispersion is obviously the result of the pre-dispersed state of the MWCNT in the concentrate.
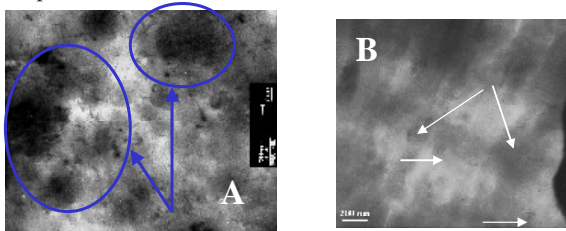

Figure 3 : TEM micrographs of HDPE-based nanocomposites filled with 1wt% of MWNTs : A. with neat MWNTs, showing large aggregates; B. with coated MWNTs showing very high level of MWNTs dispersion
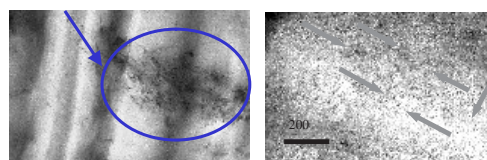

Figure 4 : TEM micrographs of EVA-based nanocomposites filled with 3wt% of MWNTs : A. with neat MWNTs, showing large aggregates; B. with coated MWNTs showing very high level of MWNTs dispersion

3.2 Impact on mechanical properties and melt viscosity

This improved dispersion provided by the use of the concentrate (N9000) instead of pristine carbon nanotubes has obviously some major repercussions on mechanical properties and also on melt viscosity. It is well demonstrated in Table 1. Where non-coated MWCNTs (N7000) have some detrimental effects on the ultimate properties and on the melt viscosity index (MFI) of PP, PC and PA66, a major improvement of the mechanical properties is observed even at low loading of HDPE-coated MWCNTs. It is important to notice that no detrimental effect is observed due to the presence of HDPE in the blend even though the extrusion is performed at temperature close to the decomposition one of HDPE. No phase segregation is either observed.

	Tensile Modulus (MPa)	Stress at break (MPa)	Strain at break (%)	MFI (g/10min)	Impact (notched sharpy) (Kj/m²)
PP	1670	20.7	114.1	2.8	5.25
PP (2wt% N7000)	1900	31.4	15.3	**1.4**	5.4
PP (2wt% N9000)	2100	36.0	**16.1**	**2.8**	5.1
PC	2410	49.1	22	31.4	68.0
PC (1wt% N7000)	2510	54.1	**3.1**	**9.1**	**10.7**
PC (1wt% N9000)	2550	66.6	**10.3**	**28.0**	**40.0**
PA6,6	3000	62.5	17.0	60.2	5.8
PA6,6 (2wt% N7000)	3100	70.0	**2.1**	**29.1**	6.4
PA6,6 (2wt% N9000)	3300	79.5	**12.5**	**35.1**	**9.2**

Table 1

Some similar results were obtained in high variety of polymer matrices including high performance polymer. As an example of those, improvement of tensile modulus of 80 % was obtained in PEEK by 1.5 wt % of HDPE-coated MWCNTs instead of the 5wt% usually needed for common grade of MWCNTs.

3.3 Electrical conductivity

Better dispersion is also a key parameter to enhance electrical conductivity of a CNTs nanocomposite. In **Fig. 5**, a simple melt blending of HDPE with both pristine MWCNTs (N7000) and MWCNTs coated by PFT. The percolation occurs at lower loading with coated MWCNTs than with N7000 (3wt% instead of 5 wt%) and lower resistivity is observed.
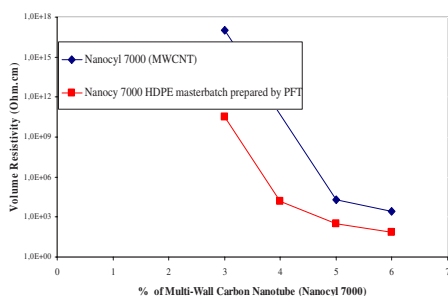

Figure 5 : percolation curves of HDPE/CNTs nanocomposites prepared by simple melt blending

A more significant modification is demonstrated in **Fig. 6**. Indeed, it shows the percolation curves in polycarbonate (twin screw extrusion + compression molding) for both products (coated and non coated) in comparison of other well-known conductive additives. Where the best carbon black exhibit a percolation threshold at ca. 5%, non-coated MWCNTs (N7000) percolate below 1 wt%. The N9000 is even below at ca. 0.5 wt%. Similar results can be observed in PA66, PA6, PP and others.
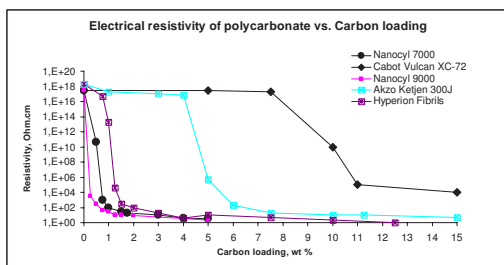

Figure 6 : percolation curves of PC nanocomposites with several additives

3.4 Thermal behavior

As a last example of property improvement, CNTs nanocomposite exhibit significant increase of their thermal stability and, interestingly enough, a flame retardant behavior is observed : presence of a charring effect and elimination of the flaming droplets (**Fig. 7**).

Figure 7 : Flame test on a HDPE/N9000 composites

4   CONCLUSIONS

This brand new system, now commercially available, marks an evolution in the field of the carbon nanotube nanocomposites since it improves drastically the dispersion and the properties (same or better properties at lower loading) and generates concentrates of never obtained high loading (till 60 % of CNTs) totally compatible with the usual processing methods and much easier to handle (it is not a fluffy carbon powder anymore).

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