

Supported coordination polymerization: a unique way to potent polyolefin carbon nanotube nanocomposites†

Daniel Bonduel,^a Michaël Mainil,^a Michaël Alexandre,^a Fabien Monteverde^b and Philippe Dubois^{*a}

Received (in Cambridge, UK) 16th September 2004, Accepted 15th November 2004

First published as an Advance Article on the web 22nd December 2004

DOI: 10.1039/b414164d

Homogeneous surface coating of long carbon nanotubes is achieved by *in situ* polymerization of ethylene as catalyzed directly from the nanotube surface-treated by a highly active metallocene-based complex and allows for the break-up of the native nanotube bundles leading, upon further melt blending with HDPE, to high-performance polyolefinic nanocomposites.

Since their first observation in 1991 by Iijima,¹ carbon nanotubes have been attracting both academics and industries, owing to their exceptional properties. Offering a very high level of strength along its length and transverse flexibility while also displaying both excellent thermal and electrical conducting properties, this new allotropic variety of carbon has been tested as an advanced multifunctional filler in polymer-based nanocomposites.^{2,3} However, the homogeneous dispersion of native carbon nanotubes is relatively difficult to achieve, especially in apolar polymer matrices such as polyolefins.⁴⁻⁶ Indeed, carbon nanotubes tend to form long bundles that are thermodynamically stabilized by numerous π - π interactions between the tubes. Most of the techniques that have been used to disperse these bundles, *e.g.*, ultrasonication,⁷ chemical oxidation or reduction followed by chemical modification of the nanotube surface and subsequent polymer grafting,⁸⁻¹⁴ are susceptible to break down or at least to perturb the extended delocalized π system responsible for the unique properties displayed by carbon nanotubes.

This communication aims at describing an original and much softer method which relies upon the *in situ* polymerization of ethylene catalyzed by a highly active metallocene complex physico-chemically anchored onto the nanotube surface. As a result, carbon nanotubes are homogeneously coated by the *in situ* grown polyethylene chain, finally leading to the break-up of the nanotube bundles.

The method used is derived from the Polymerization-Filling Technique (PFT) initially investigated in Ziegler-Natta polymerization^{15,16} and more recently developed for metallocene catalysis applied to a broad range of microfillers such as kaolin, silica, wollastonite and graphite.¹⁷⁻²⁰ Due to the similarity between the chemical structures of graphite and carbon nanotubes, which may be represented as graphene sheets rolled up in a cylinder, this technique has been tentatively applied to polymerize ethylene directly onto the nanotube surface.

As schematized in Fig. 1, the PFT applied to carbon nanotubes† consists of anchoring methylaluminoxane (MAO), a

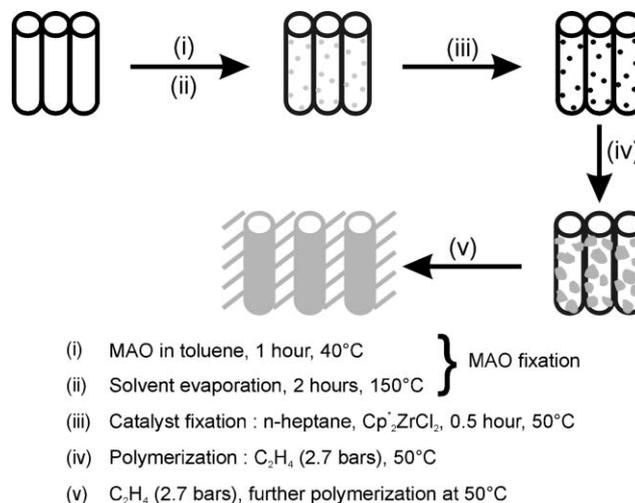


Fig. 1 Scheme of the Polymerization-Filling Technique (PFT) applied to carbon nanotubes. MAO stands for methylaluminoxane and Cp^{*}₂ZrCl₂ for bis(pentamethyl- η 5-cyclopentadienyl)zirconium(IV) dichloride.

commonly-used co-catalyst in metallocene-based olefin polymerization, onto the carbon nanotube surface firstly by a reaction in heptane at 40 °C for 1 hour (step (i) in Fig. 1), then for 2 hours at 150 °C, after solvent evacuation (step (ii)). Under these conditions, most of the MAO (<98 mol%) is immobilized onto the carbon nanotube surface and cannot be removed, even by hot toluene washings.

The metallocene catalyst is then added to the surface-activated carbon nanotubes suspended in *n*-heptane (step (iii)). In this study, bis(pentamethyl- η 5-cyclopentadienyl)zirconium(IV) dichloride (Cp^{*}₂ZrCl₂) was used as a typical polymerization catalyst. Upon reaction with the anchored MAO, Cp^{*}₂ZrCl₂ classically forms the methylated cationic zirconocene species, Cp^{*}₂ZrMe⁺, which remains immobilized at the vicinity of the nanotube surface by electrostatic interactions with simultaneously formed MAO counteranions anchored onto the nanotube surface. Upon ethylene addition, polyethylene (PE) is exclusively formed near the carbon nanotube surface and, with increasing molecular mass, precipitates onto the nanotubes (step (iv)) to coat them and ultimately separate them (step (v)).

In an initial approach, the PFT was carried out for one hour on long multi-walled carbon nanotubes (MWNTs) obtained by chemical vapor deposition. The course of the ethylene polymerization by the PFT was followed and compared to ethylene polymerization with soluble Cp^{*}₂ZrCl₂-MAO as the catalyst, with or without the presence of pristine MWNTs. Fig. 2 shows the

† Electronic supplementary information (ESI) available: typical experimental procedure for PFT applied to carbon nanotubes. See <http://www.rsc.org/suppdata/cc/b4/b414164d/>
*philippe.dubois@umh.ac.be

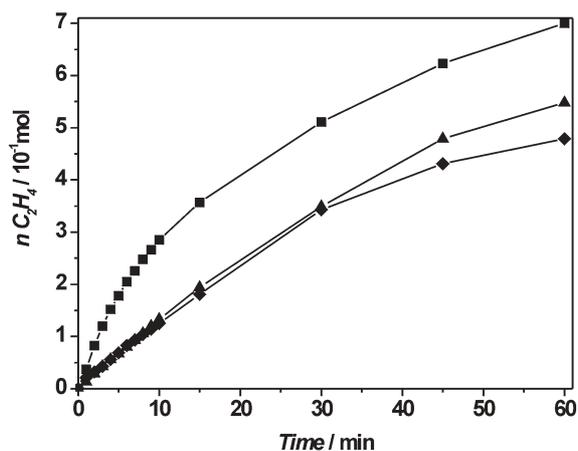


Fig. 2 Ethylene consumption *versus* time for ethylene polymerization in the absence of a filler (triangle), in the presence of pristine MWNTs (diamond) and for a polymerization catalyst supported on MWNTs (square). Polymerization conditions: solvent = heptane (total volume: 100 ml), 11.5 μmol Cp^*ZrCl_2 , polymerization at 50 °C for 1 h under constant ethylene pressure (2.7 bars).

ethylene consumption *versus* time for the three polymerization experiments.

While the presence of pristine MWNTs does not perturb the course of ethylene polymerization in solution, the PFT experiment is surprisingly characterized by a boost in ethylene consumption and subsequent polyethylene production. After one hour of polymerization, ethylene consumption for the catalyst supported on MWNTs is 28% more than for ethylene polymerization in the absence of any filler, far above the usual 10% variability observed during reproducibility studies. Clearly, supporting the catalytic system onto MWNTs significantly increases the ethylene polymerization rate.

In order to get more insight into the course of ethylene polymerization and to characterize MWNTs coated by different amounts of PE, another ethylene polymerization supported on MWNTs was carried out during which samples were taken and analysed every two minutes. Composition and thermal characteristics of the recovered MWNT–PE samples are given in Table 1.

Table 1 PE content and thermal characteristics of PE–MWNT nanocomposites taken successively (polymerization conditions: 1 g MWNTs dispersed in 200 ml *n*-heptane, 23 μmol Zr per g MWNTs, Al–Zr = 1340, pressure (ethylene) = 1.1 bar, temperature = 50 °C)

Entry ^a	Recovered mass/g	PE content ^b (wt%)	T_m ^c /°C	W_c PE ^d (%)
1	0.809	51	130.6	33
2	1.346	64	132.6	44
3	1.476	72	132.8	52
4	1.518	77	133.5	55
5	2.590	83	133.6	59

^a The time interval between each sample is *ca.* 2 minutes. ^b As determined by thermogravimetric analysis (weight loss recorded under He flow with a heating ramp of 10 K min⁻¹). ^c T_m = melting temperature as determined by differential scanning calorimetry (2nd heating scan at 10 K min⁻¹). ^d W_c PE = polyethylene crystallinity obtained from differential scanning calorimetry (2nd heating scan at 10 K min⁻¹).

As expected, the successively recovered samples are characterized by an increased relative content in PE as determined by thermogravimetric analysis. These samples are also characterized by an increase of melting temperature and crystallinity with an increase in the amount of PE formed. This might be due to the interaction between the MWNT surface and the *in situ* grown PE chains, which limits their ability to crystallize readily, as already observed for PFT on graphite.²⁰ When the amount of PE increases, a lower relative amount of polyolefinic chains stays in close contact with the nanotube surface and their overall crystallization is therefore favoured.

In order to characterize the extent of PE coating around the nanotubes, the TEM observation of a MWNT-based composite containing 72 wt% of polyethylene (entry 3, Table 1) was carried out and compared to pristine MWNTs (Fig. 3).

Fig. 3 shows a typical single long MWNT completely separated from the starting bundle and homogeneously covered by a polyethylene layer, leading to the conclusion that the PFT is an efficient technique to destroy MWNT bundles and to coat these nanoparticles with a thin layer of PE. It is worth pointing out that such efficient and homogeneous coating has been observed for the PFT carried out on other types of carbon nanotubes, *i.e.*, single-walled nanotubes (SWNTs) and double-walled nanotubes (DWNTs). Again, higher catalyst activities were detected for the surface-treated nanotubes, with large increases (by 36% for SWNTs and by 94% for DWNTs) when compared to homogeneous ethylene polymerization carried out under the same experimental conditions.

Interestingly enough, preliminary experiments have shown that PE-coated MWNTs, as obtained by the PFT, could be homogeneously dispersed when melt blended in a HDPE matrix, *e.g.*, by twin-screw extrusion. As a result of the pre-break-up of the MWNT bundles by the PFT, it transpires that the resulting HDPE–MWNT nanocomposites display higher tensile properties even with a nanofiller loading as tiny as 1 wt%. These results will be reported in a forthcoming paper.

The authors wish to thank Nanocyl S. A. (Namur, Belgium) for kindly providing the carbon nanotubes. Authors are very grateful for the financial support from “Région Wallonne” and European Community (FEDER, FSE) within the framework of “Pôle d’Excellence Materia Nova”. LPMC thanks the Belgian Federal Government Office of Science Policy (SSTC-PAI 5/3).

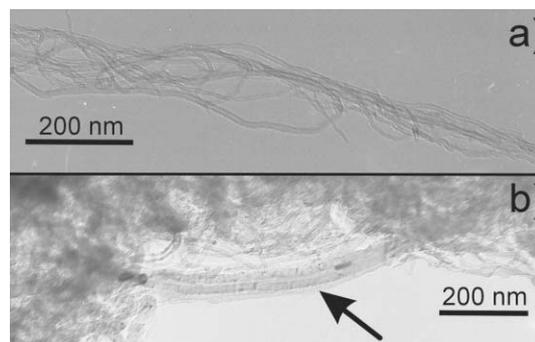


Fig. 3 TEM micrographs: (a) pristine MWNTs; (b) MWNTs coated with *in situ* grown polyethylene (shown by the arrow) as obtained by the Polymerization-Filling Technique (72 wt% PE).

Daniel Bonduel,^a Michaël Mainil,^a Michaël Alexandre,^a
Fabien Monteverde^b and Philippe Dubois*^a

^aLaboratory of Polymeric and Composite Materials, University of
Mons-Hainaut, place du Parc 20, Mons, Belgium.

E-mail: philippe.dubois@umh.ac.be; Fax: +32 65 373484;

Tel: +32 65 373480

^bUnit of Electronic Microscopy, Materia Nova Research Center, avenue
N. Copernic 1, Mons, Belgium

Notes and references

- 1 S. Iijima, *Nature*, 1991, **354**, 56–58.
- 2 P. M. Ajayan, *Chem. Rev.*, 1999, **99**, 1787–1799.
- 3 P. F. J. Harris, *Int. Mater. Rev.*, 2004, **49**, 31–43.
- 4 W. Z. Tang, M. H. Santare and S. G. Advani, *Carbon*, 2003, **41**, 2779–2785.
- 5 L. Valentini, J. Biagiotti, J. M. Kenny and S. Santucci, *Compos. Sci. Technol.*, 2003, **63**, 1149–1153.
- 6 E. Assouline, A. Lustiger, A. H. Barber, C. A. Cooper, E. Klein, E. Wachtel and H. D. Wagner, *J. Polym. Sci., Part B: Polym. Phys.*, 2003, **41**, 520–527.
- 7 Y. B. Zou, Y. C. Feng, L. Wang and X. B. Liu, *Carbon*, 2004, **42**, 271–277.
- 8 S. Niyogi, M. A. Hamon, H. Hu, B. Zhao, P. Bhowmik, R. Sen, M. E. Itkis and R. C. Haddon, *Acc. Chem. Res.*, 2002, **35**, 1105–1113.
- 9 D. Baskaran, J. W. Mays and M. S. Bratcher, *Angew. Chem., Int. Ed.*, 2004, **43**, 2138.
- 10 Y. Lin, B. Zhou, K. A. S. Fernando, P. Liu, L. F. Allard and Y. P. Sun, *Macromolecules*, 2003, **36**, 7199.
- 11 S. J. Park, M. S. Cho, S. T. Lim, H. J. Cho and M. S. Jhon, *Macromol. Rapid Commun.*, 2003, **24**, 1070.
- 12 M. S. P. Shaffer and K. Koziol, *Chem. Commun.*, 2002, 2074.
- 13 H. Kong, C. Gao and D. Y. Yan, *Macromolecules*, 2004, **37**, 4022–4030.
- 14 G. L. Hwang, Y. T. Shieh and K. C. Hwang, *Adv. Funct. Mater.*, 2004, **14**, 487–491.
- 15 N. S. Enikolopian, *USSR Pat. 763 379*, 1976.
- 16 E. G. Howard, *US Pat. 4 097 447*, 1978.
- 17 W. Kaminsky and H. Zielonka, *Polym. Adv. Technol.*, 1993, **4**, 415.
- 18 M. Alexandre, E. Martin, P. Dubois, M. Garcia-Marti and R. Jérôme, *Macromol. Rapid Commun.*, 2000, **21**, 931–936.
- 19 M. Alexandre, E. Martin, P. Dubois, M. Garcia-Marti and R. Jérôme, *Chem. Mater.*, 2001, **13**, 236–237.
- 20 M. Alexandre, M. Pluta, P. Dubois and R. Jérôme, *Macromol. Chem. Phys.*, 2001, **202**, 2239–2246.