

# Ethylene–Norbornene Copolymerization by Carbon Nanotube-Supported Metallocene Catalysis: Generation of High-Performance Polyolefinic Nanocomposites<sup>a</sup>

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Homogeneous surface coating of multi-walled carbon nanotubes is achieved for the first time by in situ copolymerization of ethylene (E) and 2-norbornene (N) as catalyzed directly from the nanotube surface previously treated by a highly active metallocene-based complex, i.e., *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>/MMAO-3A. The copolymerization reaction allows for the deconstruction of the native nanotube bundles, which upon further melt blending with an ethylene–vinyl acetate copolymer (27 wt.-% vinyl acetate) matrix, leads to high-performance polyolefinic nanocomposites. The microstructural analysis of the surface-coating copolymer was carried out by <sup>13</sup>C NMR spectroscopy and allowed determination of the actual N content incorporated along the chains. Depending on the experimental conditions used (e.g., E pressure, solvent, feed N concentration) the relative quantity of E–N copolymer can be tuned, as well as the N content in the formed copolymers and accordingly their glass transition temperature.



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<sup>a</sup> Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author.

## Introduction

Since their discovery,<sup>[1]</sup> carbon nanotubes (CNTs) have attracted unlimited attention as a result of their unique properties such as extremely high mechanical strength, and high electrical and thermal conductivity.<sup>[2,3]</sup> As a

result of these outstanding properties, many researchers expect CNTs to prove useful in a wide range of areas, including construction, mechanical, automotive, and aerospace engineering; electrochemical, biomedical, and electrical applications, etc.<sup>[4]</sup> Undoubtedly, polymer nanocomposites represent a new class of composite materials with remarkable thermo-mechanical performances when using CNTs as nanofiller precursors. Applications of CNTs, however, are hindered by their very strong aggregation tendency, and thus very poor dispersability in solutions or in polymer composites. They easily agglomerate, bundle together, and entangle, which leads to many defect sites in the composites.<sup>[5]</sup> Indeed, CNTs tend to form long bundles that are thermodynamically stabilized by numerous  $\pi$ - $\pi$  interactions between the tubes. The key challenge remains reaching a high level of nanofiller dissociation (to break down the bundles of aggregated CNTs) with an ultimately fine individual dispersion upon melt blending within the selected polymer matrix. Several techniques have been applied up to now to achieve a homogeneous and fine dispersion of CNTs in the polymer matrices. It is worth mentioning optimum physical blending, in-situ polymerization, ultrasonication, and chemical functionalization of the nanotube surface.<sup>[6–11]</sup> However, the extended delocalized electronic system responsible for the unique properties displayed by CNTs is susceptible to being broken down or at least perturbed by the above methods. This communication aims at describing the exceptional efficiency of the in-situ (co)polymerization/coating reaction as catalyzed directly from the nanofiller surface, which allows for the complete destructure of the native filler aggregates. In a preliminary communication, some of us have recently approached this original method derived from the polymerization filling technique (PFT) to coat CNTs with semi-crystalline high-density polyethylene (HDPE) chains.<sup>[12]</sup> Interestingly, and to the best of our knowledge for the first time, we have been able to apply this method to ethylene (E)–norbornene (N) copolymerization. E–N copolymers, first reported by Kaminsky et al.,<sup>[13]</sup> are materials with superior properties such as excellent transparency, high glass transition temperature ( $T_g$ ), good solvent resistance, and high thermal stability.<sup>[14]</sup> In this communication, E–N copolymerizations catalyzed in situ by a highly active metallocene complex physico-chemically anchored onto the nanotube surface have been carried out. As a result, depending on the experimental conditions used (e.g., E pressure, solvent, feed N concentration) the relative quantity of E–N copolymer can be tuned, as well as the N content in the formed copolymers, and accordingly their  $T_g$ . This work will also demonstrate that such surface-coated carbon nanotubes can be used as a ‘masterbatch’ in commercial polymers (e.g., ethylene-co-vinyl acetate (EVA) copolymer, here selected as a model matrix), which leads to polymer nanocomposites with

much higher thermo-mechanical properties even at very low nanofiller loading. The authors stress that while they were writing and submitting this communication, Funck and Kaminsky interestingly reported on the possibility to polymerize propylene from CNTs by also using a metallocene/methylaluminoxane (MAO) catalytic system. In their study, the MAO cocatalyst proved to be covalently bound onto the surface of oxidized CNTs.<sup>[15]</sup> A better CNT/matrix interfacial adhesion was observed.

## Experimental Part

All air- and moisture-sensitive compounds (e.g., catalyst and cocatalyst) were manipulated using standard vacuum line, Schlenk, or cannula techniques under dry nitrogen or in a glove-box under a dry deoxygenated nitrogen atmosphere ( $O_2$  and  $H_2O < 1$  ppm). Dichloro[*rac*-ethylenebis(indenyl)]zirconium (IV) (*rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>) was purchased from Aldrich and used without further purification. Methylaluminoxane (MMAO-3A, 7.0 wt.-% solution in heptane) was purchased from AkzoNobel and used as received. 2-Norbornene (N, Aldrich) was purified by distillation over sodium/potassium and then stored at 0 °C as a feed stock solution in toluene or in heptane ( $C = 7.60$  M). Ethylene (E, Air Liquide, 99.95%) was used without further purification. The purified multi-walled carbon nanotubes (MWNTs, Nanocyl<sup>®</sup> 3100) were kindly supplied by Nanocyl S.A. and were previously dried at 105 °C under reduced pressure ( $10^{-2}$  mmHg) for 8 h and then stored under inert atmosphere. The MWNTs were characterized by an average diameter of 10 nm with a length ranging from ca. 0.1 to 10  $\mu$ m.

A typical experimental procedure for the PFT applied to carbon nanotubes is available in the electronic Supplementary Information. These reactions were performed in a glass reactor by following the E consumption with a Zipperclav Batch Reactant Gas Delivery System.

The E–N copolymer-coated MWNTs were extracted in boiling toluene in order to analyze the E–N copolymer obtained by NMR spectroscopy and size exclusion chromatography (SEC). The N content of the copolymers was determined by <sup>13</sup>C NMR analysis using samples dissolved in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> and hexamethyldisilazane (HMDS) as internal reference. The NMR spectra were performed at 103 °C using a Bruker AM-270 spectrometer operating at 67.89 MHz (<sup>13</sup>C) direct observation, in the FT mode. Composite pulse decoupling was used to remove <sup>13</sup>C–<sup>1</sup>H couplings.

The molar masses and molar mass distribution ( $\overline{M}_w/\overline{M}_n$ ) were determined on a high-temperature dual-detector SEC system in 1,2-dichlorobenzene at a column temperature of 145 °C. The SEC system was a GPCV2000 from Waters that used two on-line detectors, a differential viscometer, and a differential refractometer as concentration detector. The universal calibration was constructed from eighteen polystyrene standards, with the molar mass ranging from 162 to  $5.48 \times 10^6$  g · mol<sup>-1</sup>.

The EVA-based nanocomposites were prepared by twin-screw mini-extrusion at 160 °C, for 10 min with a rotation speed of 45 rpm. Commercial EVA copolymer from ExxonMobil (Escorene UL00328) that contained 27 wt.-% of vinyl acetate was studied.

**Table 1.** E–N copolymerization as obtained by PFT with the catalyst *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> (E pressure: 1.3 bar), mol-% of N in the copolymer, activity, molecular mass, E–N content, and thermal characteristics of the *co*-E–N-MWNT nanocomposites.

Entry	Activity <sup>a)</sup>	N <sup>b)</sup> mol-%	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$ <sup>c)</sup>	E–N content <sup>d)</sup> wt.-%	$T_g$ <sup>e)</sup> °C	
						<i>co</i> -E–N-MWNTs nanocomposites	Extracted E–N copolymers
1	120	47.5	n.d.	n.d.	47.0	140.0	135.1
2	215	n.d.	n.d.	n.d.	83.0	138.0	n.d.
3 <sup>f)</sup>	65	41.8	55 840	1.7	69.7	108.3	107.3
4 <sup>g)</sup>	44	51.5	20 700	1.8	36.8	154.0	134.3
5 <sup>g)</sup>	35	43.7	23 100	1.6	28.4	165.7	128.1

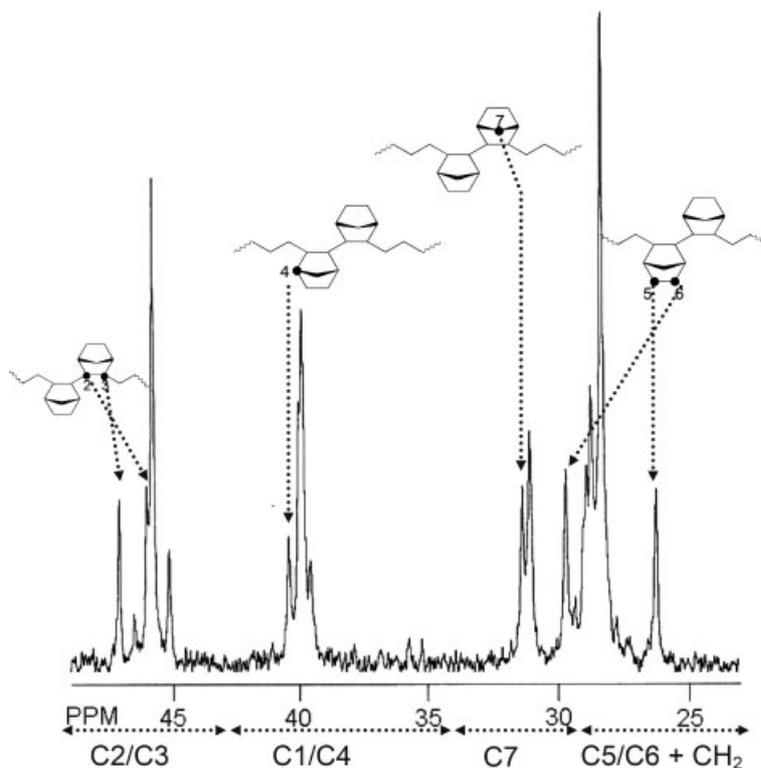
<sup>a)</sup>Activity = kg of polymer · (mol Zr · h · bar)<sup>-1</sup>; <sup>b)</sup>Calculated by analysis of <sup>13</sup>C NMR spectra; <sup>c)</sup>Measured by SEC at 145 °C in 1,2-dichlorobenzene; <sup>d)</sup>As determined by TGA (weight loss recorded under helium flow with a heating ramp of 20 K · min<sup>-1</sup>); <sup>e)</sup>Determined by DSC (2<sup>nd</sup> heating scan at 20 K · min<sup>-1</sup>); <sup>f)</sup>E pressure: 2.7 bar; <sup>g)</sup>Starting N solution in heptane.

The Young's modulus of unfilled EVA, EVA–pristine MWNT (pMWNT), and EVA–coated MWNT (cMWNT) nanocomposites was evaluated by dynamic mechanical analysis (DMTA) in tensile mode at 25 °C on thick (0.5 mm) films processed by compression moulding. The results presented in this study correspond to mean values obtained from eight experiments for each formulation. Thermogravimetric analysis (TGA) under helium or air atmosphere was used to determine the composition of the recovered *co*-E–N-MWNTs samples, using samples of typically 10 mg, submitted to a temperature ramp from 30 to 850 °C (helium) or 950 °C (air), at a heating rate of 20 K · min<sup>-1</sup>. Differential scanning calorimetry (DSC) was employed under nitrogen flow to determine the  $T_g$  of the E–N-copolymer coating. Samples of 5–10 mg were studied and the measurement cycle (two-fold) involved heating from 55 to 220 °C at 20 K · min<sup>-1</sup> and then cooling from 220 to 55 °C at 20 K · min<sup>-1</sup>. The morphology of the coated MWNTs (first deposited on a grid) and of the EVA-based nanocomposites was evaluated by transmission electron microscopy (TEM) using a Philips CM100 apparatus using an accelerator voltage of 100 kV. The nanocomposite samples were 60 nm (or less) thick and prepared with a Reichert Jung Ultracut 3E, FC4E ultracryomicrotome cutting at –130 °C.

## Results and Discussion

As the surface coating of MWNTs has been achieved by in-situ polymerization of E catalyzed directly from nanotubes that have been previously surface-treated by a highly active metallocene-based complex,<sup>[16,17]</sup> the same technique was tentatively applied to copolymerize E/N directly onto the nanotube surface.

PFT applied to CNTs consists of anchoring modified MMAO-3A, a commonly-used cocatalyst in metallocene-based olefin polymerization processes, onto the surface of CNTs first by a reaction in heptane at 50 °C for 1 h. After solvent evaporation and high temperature treatment (1.5 h at 150 °C), most of the MMAO remains immobilized



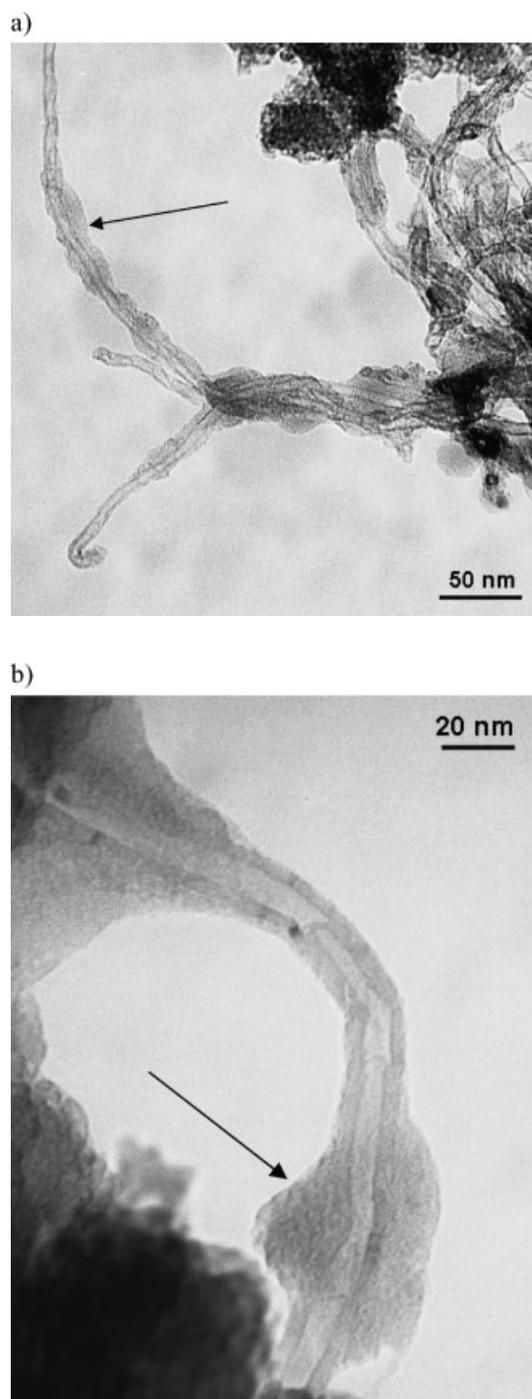
**Figure 1.** <sup>13</sup>C NMR spectrum of an E–N copolymer sample, prepared with *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, entry 1, with an N content of 47.5 mol-%.

on the CNT surface and cannot be extracted in solution. The treated MWNTs are then dispersed in heptane followed by the addition of N solution (50 mmol in either toluene or heptane). The reaction mixture is then saturated with ethylene ([N]/[E] feed ratio ranging from 4.6 to 6.5). After complete temperature and pressure equilibration, the metallocene catalyst, *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, is then reacted with the surface-activated CNTs. Upon reaction with the anchored MMAO, an alkylated cationic species (*rac*-Et(Ind)<sub>2</sub>ZrR<sup>+</sup>) is formed and is immobilized at the vicinity of the nanotube's surface by electrostatic interactions with simultaneously formed 'MMAO counter-anions'. According to PFT, poly (E-co-N) will be formed around the nanotubes, coat them, and ultimately disrupt the native bundles.

E–N copolymerizations have been carried out by varying several parameters (i.e., time reaction, E pressure, solvent type). The N content in the copolymer was assessed by <sup>13</sup>C NMR spectroscopy after their extraction by the Soxhlet method with boiling toluene. Molecular masses were estimated by SEC measurements. The *T*<sub>g</sub> was estimated by DSC analysis. The results concerning the synthesis and the characterization of some selected and most representative copolymers are summarized in Table 1. The obtained results show that increasing the reaction time by a factor 2 (Table 1, entries 1 and 2) result in an increase in the E–N copolymer content in the so-produced nanocomposite with a *T*<sub>g</sub> that remains almost constant. An increase of the E pressure from 1.3 to 2.7 bar (Table 1, entry 3) strongly modifies the amount of incorporated N, as evidenced by DSC (*T*<sub>g</sub> at 108 °C compared to 138 °C).<sup>[18]</sup> Such a large decrease of the amount of incorporated N with an increase of the E pressure depends on the lower [N]/[E] feed ratio. This tendency was confirmed by <sup>13</sup>C NMR analysis of the extracted copolymers. Figure 1 shows the <sup>13</sup>C NMR spectrum of an E–N copolymer that contains 47.5 mol-% of N (Table 1, entry 1). This spectrum is similar to those of E–N copolymers prepared with the same catalytic system 'not supported on CNTs' under similar conditions.<sup>[14]</sup> Signals typical of meso NN diads, obtained with this catalytic system, are clearly visible. A more detailed NMR analysis is being carried out to verify if the PFT has an influence on the copolymerization parameters and will be published in a forthcoming paper.

When the starting N–toluene solution is replaced by an N–heptane solution (Table 1, entries 1 and 5), there is a threefold decrease of the activity and of the E–N copolymer formed (28.4 wt.-%). Furthermore, a huge increase of the *T*<sub>g</sub> is observed (*T*<sub>g</sub> = 165.7 °C) and appears to be very high for a copolymer that contains 43.7 mol-% of N (as determined by <sup>13</sup>C NMR analysis on an extracted copolymer sample). Interestingly, the *T*<sub>g</sub> values determined for the extracted E–N copolymer samples (Table 1, entries 4 and 5) are considerably lower than those of co-E–N-MWCNT compo-

sites, and are in line with the literature data. Taking into account these observations, one may assume an effect of CNTs on the copolymer chain mobility at lower copolymer content. Such observations more likely attest for a good interaction between the in-situ grown copolymers and the nanotube surface (see TEM observations later). Molar



**Figure 2.** TEM micrographs of MWNTs coated by in-situ grown E–N copolymers (highlighted by the arrow) as obtained by the PFT (45 wt.-% E–N).

**Table 2.** DMTA analyses (in tensile mode) performed on compression moulded (0.5 mm thick and 5 mm wide) sheets for neat EVA and various EVA-based compositions filled with MWNT (co-E-N-coated or not). Young's modulus was determined as the slope of the stress-strain curve obtained.

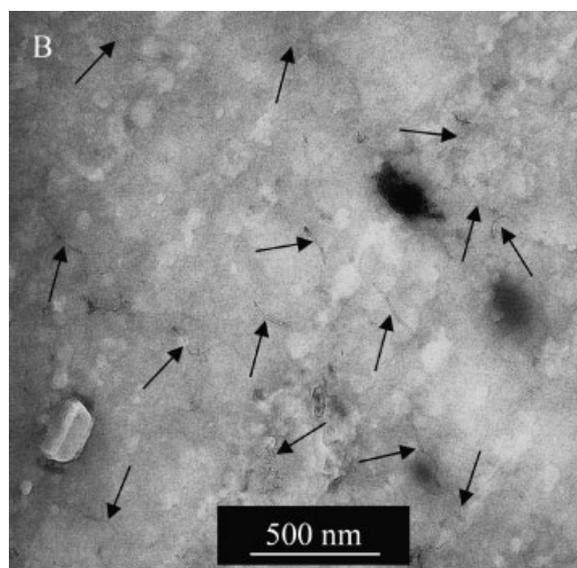
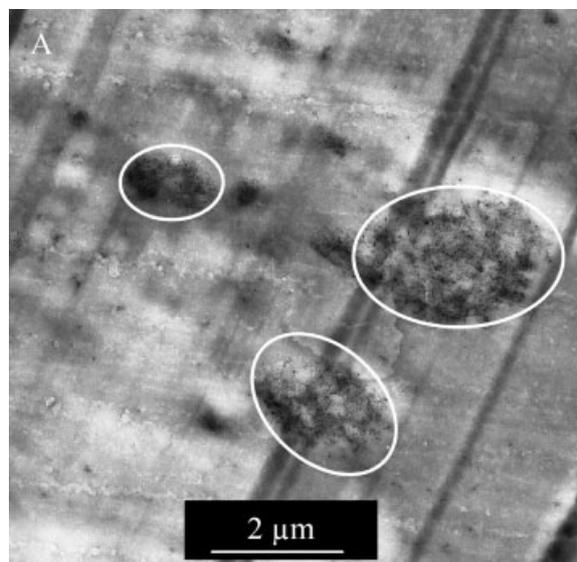
Formulation	Young's modulus
	MPa
EVA	13.4 ± 0.5
EVA + 1 wt.-% pMWNTs	14.9 ± 0.6
EVA + 3 wt.-% pMWNTs	19.2 ± 0.9
EVA + 1 wt.-% E/N cMWNTs (47 wt.-%)	17.4 ± 0.4
EVA + 3 wt.-% E/N cMWNTs (47 wt.-%)	22.5 ± 1.2
EVA + 1 wt.-% E/N cMWNTs (83 wt.-%)	19.8 ± 0.7
EVA + 3 wt.-% E/N cMWNTs (83 wt.-%)	35.6 ± 1.3

masses and molar mass distributions of the extracted E-N copolymers measured are in line with those of the E-N copolymers prepared with catalyst not supported on MWNTs (see Supporting Information).

In order to characterize the extent of E-N copolymer coating around the CNTs, TEM observations of so-coated MWNTs that contained 47 wt.-% of copolymer have been carried out (Figure 2). One can observe MWNTs relatively well separated from the starting highly entangled bundle-like associations, and they are covered by a rather homogeneous E-N copolymer layer (determination of the coating average diameter is ca. 15 nm). Such an observation allows the conclusion that PFT is an efficient method for the disruption of the native nanotube bundles through the coating of these nanoparticles with a thin layer of poly(E-co-N) chains. Even more interesting is the possibility to tune the N content of this copolymer coating and, accordingly, its thermal behaviour, i.e., a higher  $T_g$  with an increased N content.

E-N copolymer-coated CNTs (cMWNTs) have been used as a pre-dispersed 'masterbatch' for the preparation of highly dispersed MWNTs/polymer nanocomposites. Following the experimental procedure aforementioned, two masterbatches (cMWNTs coated by 47 and 83 wt.-% of co-E-N, respectively) have been prepared by PFT and dispersed in a commercially available model polymer matrix, e.g., EVA with 27 wt.-% of vinyl acetate comonomer, using a co-rotating twin-screw mini-extruder (see Experimental Part). The amount of the nanofiller in the final materials has been fixed to 1 and 3 wt.-%. For the sake of comparison, unfilled EVA and EVA filled with 1 and 3 wt.-% of pristine CNTs (pMWNTs) have been processed under the same conditions. To assess the effect of the MWNT dispersion on the final properties of the resulting

materials, their mechanical properties have been evaluated using DMTA in the tensile mode, by measuring the tensile stress for increasing tensile strain applied on thick (0.5 mm) films processed by compression moulding (Table 2). The addition of 1 wt.-% of pristine MWNTs in the EVA matrix does not significantly modify the mechanical properties of the materials. At such a low filler content and under conditions where CNT bundles are not disaggregated, 1 wt.-% of pMWNTs just acts as a microfiller when added in a rather small amount. The addition of 3 wt.-% of pMWNTs allows an increase in the Young's modulus from



**Figure 3.** TEM micrographs of EVA-based nanocomposites filled with 3 wt.-% of MWNTs: A) with neat MWNTs, showing large aggregates; B) with coated MWNTs (83 wt.-% E-N) showing a very high level of MWNT dispersion (see arrows).

13.4 to 19.2 MPa. However, the dispersion of the coated nanotubes (cMWNTs masterbatch) in the same EVA matrix allows a substantially higher Young's modulus of 22.5 and 35.6 MPa to be reached, thus a two- to threefold increase in stiffness as the co-E–N content increases from 47 to 83 wt.-%, respectively. Such behaviour is expected for a much finer dispersion of the cMWNTs in EVA. To assess the dispersion state, a TEM analysis has been performed on thin slices (<60 nm) of the nanocomposite prepared from the masterbatch (EVA/cMWNTs, 83 wt.-% E/N) and on the composite prepared from pristine MWNTs (EVA/pMWNTs). Comparison of these two materials is shown in Figure 3. While for EVA/pMWNTs composition (Figure 3A), large MWNT aggregates can be observed, the aggregation is very limited and the carbon nanotubes appear individually and finely dispersed in the EVA/cMWNT sample (Figure 3B). Since DSC analysis of the various materials does not show any difference in the nature of crystallinity (melting point at ca. 72 °C, typical for EVA), the improvement in the mechanical properties for the EVA/cMWNT nanocomposites is more likely a direct consequence of the finer nanofiller dispersion as a result of the use of the coated-MWNT masterbatch.

## Conclusion

Homogeneous surface coating of MWNTs is achieved by in-situ copolymerization of E–N as catalyzed directly from the nanotubes previously surface-treated by a highly active metallocene-based complex, which allowed for their subsequent de-aggregation. Depending on the experimental conditions, a fine tuning of the quantity of E–N copolymer formed could be considered. Copolymer composition and molar mass were also investigated and have shown tuneable N incorporation into the copolymer as well. As a result of the fine and homogeneous dispersion of a small amount of such coated CNTs (a few percent) in an EVA copolymer model matrix by rather conventional melt blending, the mechanical properties of the material proved to be significantly enhanced. Other properties such as flame-retardant behavior and electric conductivity are under current investigation.

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