ADVANCED FUNCTIONAL MATERIALS

DOI: 10.1002/adfm.200600936

Mechanical Properties and Flame-Retardant Behavior of Ethylene Vinyl Acetate/High-Density Polyethylene Coated Carbon Nanotube Nanocomposites**

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High-density polyethylene coated multiwalled carbon nanotubes (c-MWNTs) and multiwalled carbon nanotubes (MWNTs) have been dispersed into an ethylene vinyl acetate (EVA) copolymer by mechanical kneading. The effect of c-MWNTs on tensile properties, thermo-oxidative degradation, and fire behavior has been studied in comparison with virgin EVA and EVA/MWNTs nanocomposites. Due to the better dispersion of the coated nanotubes, the incorporation of 3 wt % of c-MWNTs leads to an increase of the Young's modulus, the cohesion of the combustion residues, and a decrease of the peak heat-release rate.

1. Introduction

Carbon nanotubes have been a major of interest since 1991.[1] A panel of properties and phenomena associated with carbon nanotubes caused by their special combination of dimension, structure, and topology have been investigated over the past number of years.[2,3] Recently, it appears interesting to use carbon nanotubes at low-loading content to obtain materials with enhanced mechanical properties and reduced flammability.[4,5] One of the major challenges is actually to easily and individually disperse these nanotubes in polymer matrices to obtain materials with improved properties for different applications.

Ethylene vinyl acetate (EVA) copolymer is commonly used in the cable industry. It is required to introduce fire retardants alumina trihydrate (ATH) or magnesium dihydroxide (MDH) in high content to avoid fire hazards and reduce flammability. But this high mineral loading results in a worsening of the mechanical performance of the materials.[6] Recently, great interest has been shown in the use of tiny amounts of carbon nanotubes as flame retardant systems using the EVA matrix.[7]

This work aims to study the influence of the incorporation of multiwalled carbon nanotubes (MWNTs) and especially high-density polyethylene (HDPE)-coated multiwalled carbon nanotubes (c-MWNTs), obtained by the polymerization-filling technique (PFT),[8,9] on the tensile properties and the fire retardation behavior of EVA nanocomposites. The mechanical properties have been determined by tensile testing and the fire retardation properties have been evaluated by cone calorimeter testing. Only limited studies on the fire retardation behavior of polymer/carbon nanotube nanocomposites have been published,[4,5,10,11] and the mechanism of the MWNTs therein is not well-known. This work demonstrates, on the one hand, the significant effect of the HDPE coating on the mechanical behavior of the thus obtained nanocomposites and explains, on the other hand, the flame-retardant efficiency of MWNTs in EVA nanocomposites. An original mechanism related to the action of the MWNTs during the combustion process is proposed, and the effect of the coating on the cohesion of the residues is discussed.

2. Results and Discussion

An EVA/c-MWNT nanocomposite (3 wt % of pure MWNTs as measured by thermogravimetric analysis) has been prepared by melt-blending the coated nanotube filler (c-MWNTs) with EVA in an internal mixer at 140 °C; this composite was then compared with an EVA/MWNT nanocomposite (3 wt % of

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[**] This work was supported by the Région Wallonne within the framework of the Nanotechnology project: BINANOCO. L.P.C.M. thanks the Belgian Federal Government Office Policy of Science (SSTC) for general support in the framework of the PAI-5/03. Materia Nova ASBL is grateful to the Région Wallonne and the European Union (FEDER, FSE) for financial support through the Phasing-Out of Objectif-1 Hainaut: Materia Nova.

pure MWNTs) prepared under the same processing conditions but starting from non-surface-treated nanotubes. Both materials contained 3 wt % of carbon nanotubes and have been compared in terms of morphology at the sub-micrometer scale, tensile properties, thermal degradation, and fire resistance.

Figure 1 shows the transmission electron microscopy (TEM) images of EVA/c-MWNT and EVA/MWNT nanocomposites. One can observe that the HDPE-coated MWNTs have been individually and homogeneously dispersed throughout the EVA matrix (Fig. 1a) contrary to the nonmodified MWNTs (Fig. 1b), for which very large MWNTs aggregates are still visible. This drastic change in the quality of MWNT dispersion originates from the destruction of the native MWNT aggregates, which are thermodynamically stabilized by numerous π–π electronic interactions between the carbon nanotubes; these electronic interactions are still present in the EVA matrix. Indeed, PFT, as applied to MWNTs, allows the nanotubes' surface to be covered with a thin layer of HDPE, which impedes the formation of π–π interactions and promotes the formation of individual MWNTs that easily disperse in EVA.

The mechanical properties of EVA nanocomposites depend on the MWNTs dispersion state. Table 1 shows the mechanical test data for the different materials. The stress–strain curves of the nanocomposites are similar in shape to those of the unfilled EVA matrix, indicating that the presence of the two types of nanotubes does not modify the overall mechanical behavior of the EVA matrix. One can observe that the incorporation of the two types of carbon nanotubes leads to an increase of Young's modulus, as calculated from the first portion of the curve, which, interestingly, almost reaches a threefold increase in the presence of the HDPE-coated MWNTs (Table 1). The stress and strain at break decrease after addition of 3 wt % MWNTs (with or without coating) to EVA (Table 1) but the materials still maintain excellent ductile properties. Compared to the value of the neat EVA matrix, the strain at break of the composite based on noncoated MWNTs decreases by 33 % while the decrease recorded for the composite filled with coated MWNTs is limited to 27 %. This is typically what is observed for composites filled with nanofillers characterized by variable dispersion quality: a larger reduction of the elongation at break is obtained for composites with a poor quality of carbon nanotube dispersion.[12,13]

Table 1. Mechanical properties of both kinds of nanocomposite based on an EVA matrix and 3 wt % MWNTs or HDPE-coated MWNTs (c-MWNTs). The properties of the neat EVA matrix are also shown.

Formulation	Stress at break [MPa]	Strain at break [%]	Young's modulus [MPa]
EVA	28.4±0.7	1406±28	12.2±1.2
EVA + 3wt% MWNTs	21.7±0.7	949±37	19.9±1.2
EVA + 3wt% c-MWNTs	23.1±0.9	1018±21	32.3±1.5

The thermal degradation of the two nanocomposites has been evaluated by thermogravimetric analysis (TGA) under air atmosphere. The thermodegradation of ethylene vinyl acetate copolymer takes place in two steps.[14] First, de-acetylation is observed between 300 and 400 °C with the production of gaseous acetic acid and the formation of carbon–carbon double bonds along the polymer backbone. In the second degradation step (between 400 and 500 °C), the unsaturated chains are volatilized through statistic chain cleavage. The presence of the carbon nanotubes modifies the thermal degradation of the polymer matrix, as shown in Figure 2, which presents the evolution of the mass loss with temperature of the two nanocomposites. Both degradation steps are shifted towards higher temperature. The significant delay in weight loss for the first degradation step is probably due to a limited volatilization rate of acetic acid and to the production of a more thermally stable char, arising from numerous crosslinking[15] reactions, which leads to unsaturated structures. On a first approach, this phenomenon can be attributed to the higher viscosity of the composites in the melt state or by the labyrinth effect of the interconnected fillers limiting the volatilization rate of acetic acid (see hereafter). The second step of the thermo-oxidative degradation also takes place at a higher temperature in the presence of MWNTs. This behavior could be explained by the presence of the char formed during the first degradation step, which is further stabilized through π–π electronic interactions with the nanotubes.

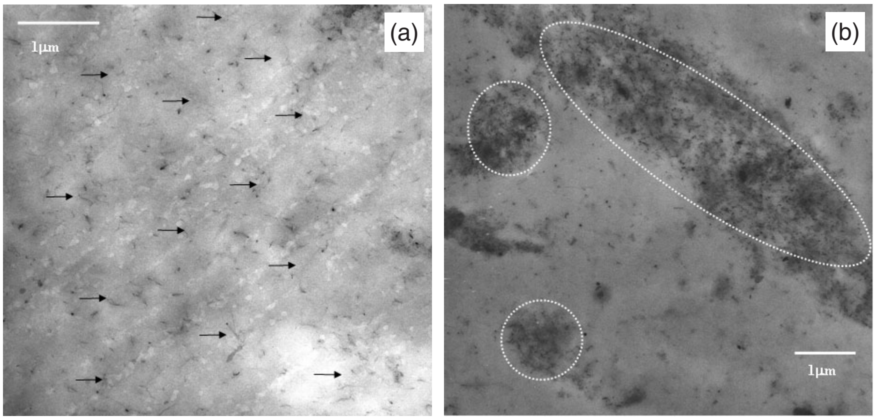

Figure 1. Transmission electron microscopy (TEM) images of the two nanocomposites at low magnification. The samples are: a) EVA + 3 wt % c-MWNTs, b) EVA + 3 wt % MWNTs (arrows in (a) indicate the location of individually spread nanotubes, while dotted curves in (b) highlight aggregates).

In order to confirm this hypothesis, the flammability properties of the materials have been studied by cone calorimeter testing. The evolution of the heat-release rate (HRR), in particular its maximum peak (PHRR), and the nature of the combustion residues are discussed. The cone calorimeter experimental results for EVA and the two corresponding nanocomposites filled with either 3 wt % MWNTs or c-MWNTs are presented in Figure 3 and Table 2. For the virgin EVA, the PHRR reaches a value of around $700\ \mathrm{kW\,m^{-2}}$,

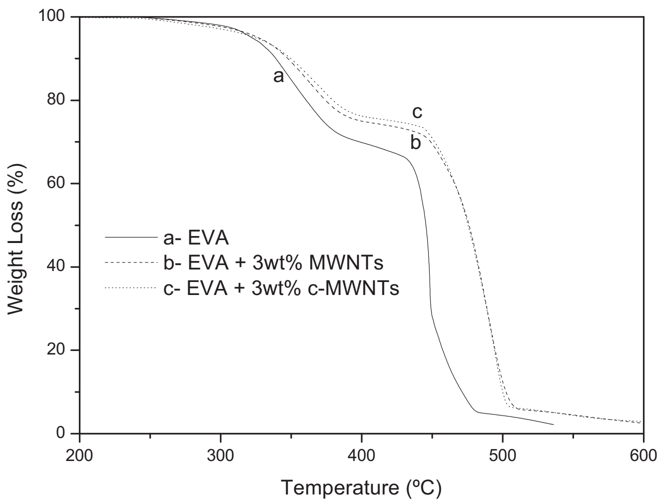

Figure 2. Thermogravimetric analysis curves of unfilled EVA and EVA-based nanocomposites under an air flow (heating ramp: 20 K min^{-1}).

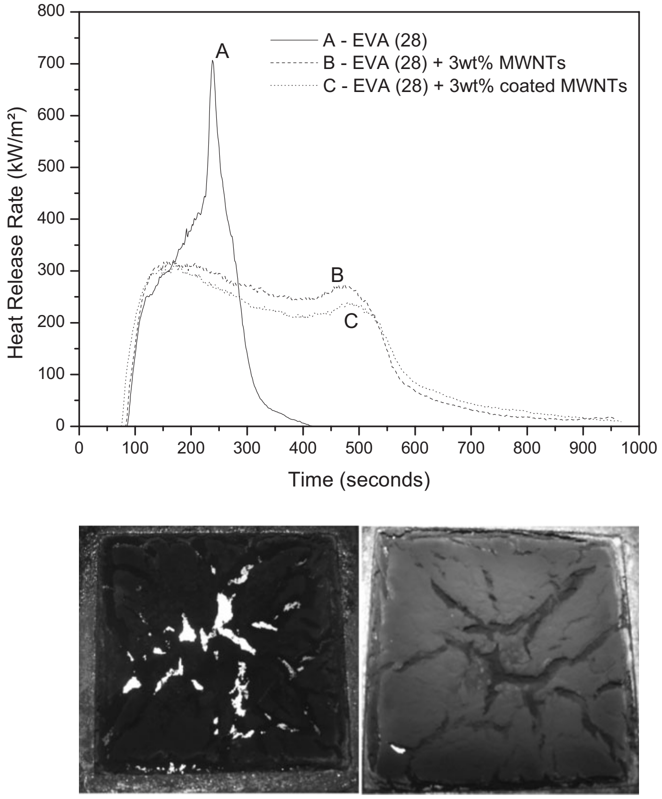

Figure 3. Cone calorimeter heat-release rate versus time of unfilled EVA and EVA-based nanocomposites. A comparison of the effect of the HDPE-coated MWNTs is shown in the photographs of the two nanocomposite residues, as recovered after the cone calorimeter test. Sample dimensions: 100 × 100 mm^2.

Table 2. Maximum peak of heat-release rate, as measured by the cone calorimeter test (35 kW m^{-2}), for unfilled EVA and the two related nanocomposites.

Formulation	PHRR [kW/m^2]
EVA	707
EVA + 3wt% MWNTs	315
EVA + 3wt% c-MWNTs	305

and combustion is complete after 300 s. The sample shows very strong bubbling during the combustion. The incorporation of 3 wt % MWNTs (both types) leads to a strong decrease of PHRR, which reaches a value of ca. 300 kW m^{-2}. The combustion time is also much longer (900 s). An important charring effect is observed for the two nanocomposites (photographs, Fig. 3).

Another interesting effect of the coating of the MWNTs by a thin layer of HDPE has been observed on the cohesion of the combustion residues. The photographs of Figure 3 present the residues obtained after the cone calorimeter tests. A fragile and cracked crust has been recovered in the MWNTs-based material, whereas the c-MWNTs-based composite gives rise to the formation of a cohesive, uniform, and even partially foamed carbonaceous residue. This better cohesion of the combustion residue of the nanocomposite based on c-MWNTs could be explained by the individually dispersed modified nanotubes forming a rigid network of MWNTs.

The samples did not show any bubbling during the combustion probably because of the much higher melt viscosity compared to the unfilled matrix. Such an increase in melt viscosity is clearly due to the presence of the long carbon nanotubes in the matrix. Similar behavior has been recently reported by Kashiwagi et al. for polymethylmethacrylate-based nanocomposites.[16] This seems to confirm our hypothesis for the delay in the first degradation step recorded during TGA analysis.

Interestingly enough, the recorded PHRR values appear significantly lower than values reported for other types of EVA-based nanocomposites tested at 35 kW m^{-2}. For instance, under the same conditions, the PHRR value obtained in a previous study for EVA/clay material, with well-dispersed organoclay,[7] reaches approximately 500 kW m^{-2} with a combustion time of 450 s. The formation of an intensive carbonaceous protective layer during the combustion test performed on the EVA/MWNT nanocomposites is most likely responsible for the observed reduction of PHRR. A more detailed characterization of such a protective layer is needed to understand how it reduces the heat-release rate. The combustion residues of the two composites have been analysed by X-ray diffraction (XRD). For the sake of comparison, native MWNTs and MWNTs calcinated in a furnace at 670 °C for 10 min have also been analyzed by XRD. As shown in Figure 4, the structures of the two carbonaceous crusts appear very similar to the structure of the MWNTs (calcined and non-calcined) with a peak at 25° corresponding to the (002) interplanar spacing, $d(002)$, characteristic of the graphitic structure. No other organized carbon structure is formed during the combustion of the EVA/MWNTs nanocomposites. Thus, the improved fire resistance displayed by the nanocomposites could be explained by the chemical structure of the nanofillers and the combustion products, and more precisely, by the stabilizing π–π electronic inter-

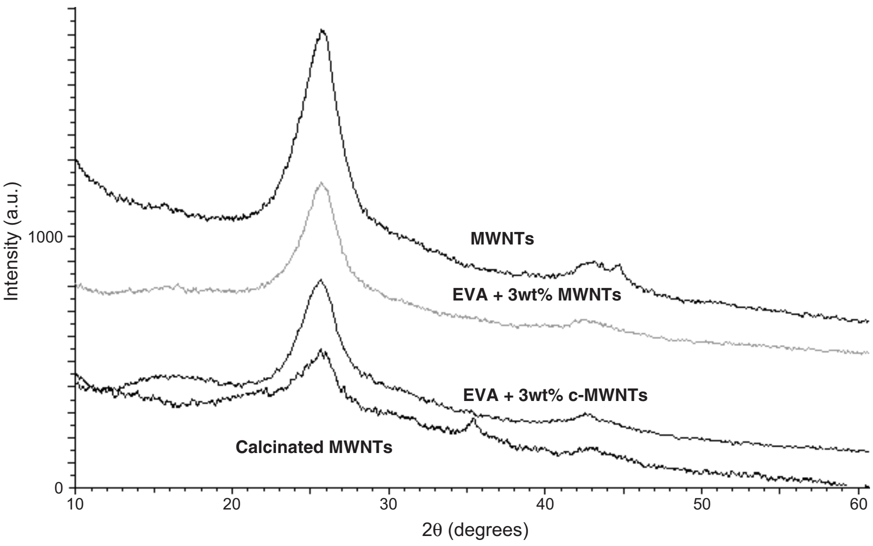

Figure 4. XRD patterns of the combustion residues of the two nanocomposites compared to the XRD patterns of the MWNTs before and after calcination at 670 °C for 10 min.

actions between the unsaturated structure of the carbonaceous amorphous char and the carbon nanotubes. Figure 5 presents a scanning electron microscopy (SEM) image of the residue of the burnt EVA/c-MWNT composite. The network formed by the coated MWNTs is clearly surrounded by char residue. This observation confirms that the dispersion state of the carbon nanotubes and the intimate HDPE–MWNT contact have a large effect on the cohesion of the combustion residue.

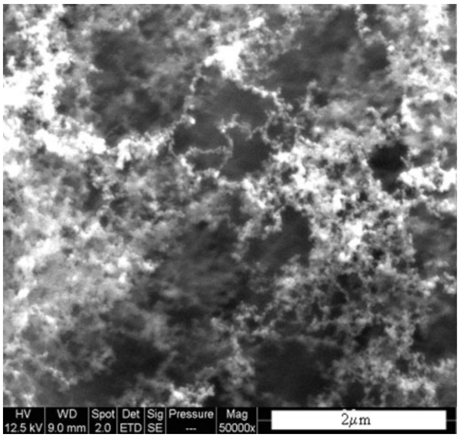

Figure 5. SEM image of MWNTs as observed in the combustion residues of the nanocomposite formed with c-MWNTS where the network formed by the c-MWNTs is covered by carbonaceous crust (magnification × 50 000).

3. Conclusions

De-aggregation of MWNTs bundles by applying PFT to the MWNTs to coat them with a layer of HDPE before melt-blending with EVA leads to material with enhanced mechanical properties and thermo-oxidative stability. Interestingly, a homogeneous dispersion of the HDPE-coated nanotubes has been observed throughout the polymer matrix. The presence of the carbon nanotubes modifies the thermo-oxidative degradation of the polymer matrix: the two degradation steps of the EVA matrix are shifted to higher temperature, as observed by TGA in air. The volatilization rate of the acetic acid is decreased and a stable char is formed.

As determined by cone calorimeter testing, two important parameters are influenced by adding coated MWNTs to EVA: heat-release rate, which is decreased, and cohesion of the combustion residue, which is largely improved. Even though, the nanotube surface coating only slightly improved the reduction of the heat-release rate with respect to the value recorded for untreated MWNTs, a much more cohesive combustion residue is generated in the presence of HDPE-coated nanotubes. This phenomenon can be attributed to the high quality of dispersion of the HDPE-coated nanotubes and to the chemical structure of the combustion products.

4. Experimental

A commercial EVA copolymer from ExxonMobil (Escorene UL00328), containing 27 wt % of vinyl acetate, was studied. The MWNTs studied in this work were produced at the Nuclear Magnetic Resonance Laboratory (FUNDP, Belgium) by catalytic decomposition of acetylene on transition-metal particles (Co, Fe) supported on Al$_2$O$_3$ [17]. They were purified after dissolution of the support in a boiling, concentrated sodium hydroxide aqueous solution and dissolution of the catalysts in concentrated hydrochloric acid aqueous solution. These MWNTs were characterized by an average inner diameter of 5 nm and an average outer diameter of 15 nm, corresponding to ca. 14–15 concentric layers. The average length was ca. 20 μm.

Coated MWNTs were obtained by a soft method derived from the polymerization-filling technique (PFT) initially developed for Ziegler–Natta catalysts [18,19] and more recently for metallocene catalysis [20–22]. PFT, as applied to carbon nanotubes [8], consists of anchoring methylaluminoxane (MMAO), a well-known cocatalyst used in the metallocene-based olefin polymerization process, onto the surface of the carbon nanotubes in suspension in dried heptane. A metallocene catalyst, Cp$_2$*ZrCl$_2$ in this study (where Cp stands for cyclopentadienyl), is then reacted with the surface-activated carbon nanotubes. Addition of ethylene leads to the synthesis of polyethylene (HDPE) exclusively at the surface of the carbon nanotubes. Such a coating limits the formation of airborne carbon-nanotube aggregates, making handling much safer. It allows for the preparation of a master batch of pre-dispersed carbon nanotubes that can be melt-blended by very conventional processing tools with polyolefins (polyethylene), but also any type of polymeric matrix, to form nanocomposites. The \ HDPE content in the master batch used in this study was around 40 wt %. The preparation of this master batch of HDPE-coated MWNTs was described elsewhere [8].

The EVA-based nanocomposites (filled with either MWNTs or c-MWNTs) were prepared in a Brabender internal mixer at 140 °C for 12 min with a speed of 45 rpm. The filler content was 3 wt % in terms of pure MWNTs.

Tensile properties were measured at 20 °C with a deformation rate of 50 mm min^{-1} on a Lloyd LR 10K tensile tester with dumbbell-shaped specimens, which were obtained from compression-molded samples, following the ASTM D638 type-V method. All tensile data were the average of five independent measurements; the relative errors committed on each data were reported as well.

Thermogravimetric analyses were performed on a TA instrument HiRes TGA 2950 thermogravimetric analyzer with a heating ramp of 20 K min^{-1} from room temperature to 625 °C under an air atmosphere.

Cone calorimeter tests (ISO 5660) were performed on 100 mm × 100 mm × 4 mm compression-molded samples placed horizontally with a flux of 35 kW m^{-2}. The results presented in this study correspond to mean values obtained from three experiments for each formulation, for which a typical variation of around 10 % was observed.

TEM images were obtained with a Philips CM200 TEM apparatus using an accelerating voltage of 100 kV. The samples were 70–80 nm thick and prepared with a LEICA Ultracut UCT ultracryomicrotome, cutting at –130 °C. SEM analysis was performed using an FEI company Quanta 200 FEG scanning electron microscope. Nanocomposite samples were directly observed without any prior surface treatment. XRD data were collected using a BRUKER D8 diffractometer with Cu Kα radiation ($\lambda = 1.5405$ Å). The scattering angle (2θ) domain studied ranged from 2° to 63°, with a rotation step scanning of 0.01° 2θ and a step time of 0.007 s.

Received: October 10, 2006
Revised: April 2, 2007

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[1] S. Iijima, *Nature* **1991**, *354*, 56.
[2] V. N. Popov, *Mater. Sci. Eng.* **2004**, *R43*, 61.
[3] D. Tasis, N. Tagmatarchis, A. Bianco, M. Prato, *Chem. Rev.* **2006**, *106*, 1105.
[4] T. Kashiwagi, F. Du, J.-F. Douglas, K. I. Winey, R. H. Harris, J.-R. Shields, *Nat. Mater.* **2005**, *4*, 928.
[5] T. Kashiwagi, E. Grulke, J. Hilding, K. Groth, R. Harris, K. Butler, J. Shields, J. Kharchenko, J. Douglas, *Polymer* **2004**, *45*, 4227.
[6] D. Gheysari, A. Bajhat, *Eur. Polym. J.* **2002**, *38*, 1087.
[7] S. Peeterbroeck, F. Laoutid, J.-M. Lopez-Cuesta, M. Alexandre, J. B. Nagy, N. Moreau, Ph. Dubois, *Macromol. Rapid Commun.* **2007**, *28*, 260.
[8] D. Bonduel, M. Mainil, M. Alexandre, F. Monteverde, Ph. Dubois, *Chem. Commun.* **2005**, 781.
[9] S. Peeterbroeck, B. Lepoittevin, E. Pollet, S. Benali, C. Broekaert, M. Alexandre, D. Bonduel, P. Viville, R. Lazzaroni, Ph. Dubois, *Polym. Eng. Sci.* **2006**, *46*, 1022.
[10] S. Peeterbroeck, M. Alexandre, J. B. Nagy, C. Pirlot, A. Fonseca, N. Moreau, G. Philippin, J. Delhalle, Z. Mekhalif, R. Sporken, G. Beyer, Ph. Dubois, *Compos. Sci. Technol.* **2004**, *64*, 2317.
[11] F. Gao, G. Beyer, Q. Yuan, *Polym. Degrad. Stab.* **2005**, *89*, 559.
[12] Y. S. Song, J. R. Youn, *Carbon* **2005**, *43*, 1378.
[13] A. Dufresne, M. Paillet, J. L. Putaux, R. Canet, F. Carmona, P. Delhaes, S. Cui, *J. Mater. Sci.* **2002**, *37*, 3915.
[14] M. Zanetti, G. Camino, R. Thomann, R. Mülhaupt, *Polymer* **2001**, *42*, 4501.
[15] M. Costache, D. D. Jiang, C. A. Wilkie, *Polymer* **2005**, *46*, 6947.
[16] T. Kashiwagi, F. Du, K. I. Winey, K. M. Groth, J. R. Shields, S. P. Bellayer, H. Kim, J. F. Douglas, *Polymer* **2005**, *46*, 471.
[17] S. Peeterbroeck, M. Alexandre, J. B. Nagy, N. Moreau, A. Destrée, F. Monteverde, A. Rulmont, R. Jérôme, Ph. Dubois, *Macromol. Symp.* **2005**, *221*, 115.
[18] E. G. Howard, *US Patent 4097447*, **1978**.
[19] L. A. Kostandov, N. S. Enikolopov, F. S. Dyachkovskii, L. A. Novokshonova, Y. A. Gavrilov, O. Kudinova, T. A. Maklakova, L. A. Akopyan, K.-M. A. Brikenstein,, *USSR Patent 763379*, **1980**.
[20] M. Alexandre, E. Martin, Ph. Dubois, M. Garcia-Marti, R. Jérôme, *Macromol. Rapid Commun.* **2000**, *21*, 931.
[21] M. Alexandre, E. Martin, Ph. Dubois, M. Garcia-Marti, R. Jérôme, *Chem. Mater.* **2001**, *13*, 236.
[22] M. Alexandre, M. Pluta, Ph. Dubois, R. Jérôme, *Macromol. Chem. Phys.* **2001**, *202*, 2239.