



Interfacial chemistry using a bifunctional coupling agent for enhanced electrical properties of carbon nanotube based composites



Robert Socher^{a,b,1}, Lothar Jakisch^a, Beate Krause^a, Ulrich Oertel^a, Brigitte Voit^{a,b},
Petra Pötschke^{a,*}

^a Leibniz Institute of Polymer Research Dresden (IPF), Hohe Str. 6, 01069 Dresden, Germany

^b Organic Chemistry of Polymers, Technische Universität Dresden, 01062 Dresden, Germany

ARTICLE INFO

Article history:

Received 30 May 2013

Received in revised form

22 July 2013

Accepted 24 July 2013

Available online 31 July 2013

Keywords:

Carbon nanotubes

Polymer–matrix composites

Coupling agent

ABSTRACT

A bifunctional coupling agent (**BCA**) containing one oxazoline and one benzoxazinone group was applied to promote a reaction between polyamide 12 (PA12) and multiwalled carbon nanotubes (MWCNTs) during melt mixing. With this modification, the MWCNT content needed for the electrical percolation was significantly reduced by more than a factor of three. For amino functionalized MWCNT–PA12 composites adding 1 wt.% **BCA** electrical percolation was reached at only 0.37 wt.% MWCNTs compared to 1.0 wt.% without **BCA**. With the help of a model reaction, the covalent attachment of the **BCA** to the MWCNTs could be shown by thermogravimetric analysis (TGA) and via fluorescence spectroscopy. Model compounds were applied containing either only the oxazoline or the benzoxazinone group to show that the better electrical properties in the PA12–MWCNT composites were a result of a covalent bond between the polymer and the nanotube which only takes place when the **BCA** was used. In addition, significantly higher electrical conductivity values were obtained by the addition of **BCA** as well with amino functionalized as with nonmodified commercial MWCNTs. This surprising result was attributed to the significant hydroxy group content on the surface of those commercial MWCNTs.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Due to their extraordinarily high aspect ratio, carbon nanotubes (CNTs) can form electrically conductive networks in polymer nanocomposites at much lower content than the commonly used carbon blacks, for instance. With lower production costs for multiwalled carbon nanotubes (MWCNTs), increasingly more products are placed on the market. In the automotive sector an especially large market volume can be expected. Evonik Industries AG is already producing fuel lines with polyamide 12–MWCNT composites [1]. Since 2009, BASF supplies fuel filter housings based on polyoxymethylene filled with MWCNTs [2] to prevent electrostatic discharges. Melt mixing is the manufacturing method of choice of thermoplastic composites for these industrial applications. It is still a challenge to obtain a complete dispersion of the CNTs in the polymer by simple melt mixing because CNTs are usually synthesized in entangled agglomerates. Intensive investigations have been made to optimize the melt mixing conditions [3–7]. However,

in many cases the obtained electrical percolation thresholds are still much higher than the theoretical predicted ones [8]. Besides optimized processing conditions, different types of additives are applied. Surface active additives have been used for decades to improve the dispersion of agglomerated solids in the plastics processing industry. The use of additives to assist CNT dispersion in a composite can follow different approaches. It seems to be worthwhile to modify the surface properties of the CNTs with respect to a higher compatibility to the polymeric matrix. Furthermore, the application of a medium which easily infiltrates into the CNT agglomerates should lead to a reduction of the agglomerate strength and therefore to a better CNT dispersion. Usually, a differentiation is made between non-covalent and covalent additives. Ionic liquids with strong interactions to the π -systems of the carbon nanotubes are an example of non-covalent additives. An indication of the occurrence of these strong interactions was found by Fukushima et al. who described the formation of a gel of CNTs and imidazolium based ionic liquids [9,10]. The preparation of MWCNT–polystyrene composites with trialkylimidazolium tetrafluoroborate as an ionic liquid in a microcompounder led to nearly agglomerate free composites [11]. An example of the application of an additive with π – π interactions is the use of styrene–maleic anhydride copolymers

* Corresponding author. Tel.: +49 351 4658395; fax: +49 351 4658565.

E-mail address: poe@ipfdd.de (P. Pötschke).

¹ Present address: BASF SE, 67056 Ludwigshafen, Germany.

used in the manufacturing of PA6 [12] and PA12–SWCNT composites [13]. While the maleic anhydride-sites of the copolymer react with the endgroups of the polyamide, the styrene block interacts via π – π interactions with the SWCNTs. As a result, the composites showed a higher elongation at break in tensile tests. However, despite better nanotube dispersion the addition of an insulative polymer layer preventing nanotube–nanotube contacts caused by the strongly adhering polymer chains led to electrical insulating properties of the PA12 composites. Another example for the application of non-covalent additives during melt mixing is the wrapping of MWCNTs with polyethylene glycol in poly(L-lactide) composites resulting in better MWCNT dispersion as reported by Zou et al. [14].

In contrast to SWCNTs, for composites with MWCNT only a few results have been published concerning the use of additives resulting in covalent bonding. A “grafting to” approach where a reactive polymer is covalently attached to the carbon nanotubes is described for polypropylene (PP) composites. Using amino functionalized MWCNTs and maleic anhydride grafted polypropylene as a compatibilizer resulted in better dispersion of MWCNTs [15] and higher electrical conductivities [16] in PP based composites. Covalent bonding has several advantages compared to non-covalent additives: I) the improved interfacial interactions can result in mechanical reinforcement of the composites, and II) the chemical reaction leads to a fixation, which suppresses the exudation of the additive or an undesired phase separation in the composite.

Concerning the electrical but also the mechanical properties of polymer–CNT composites it seems promising to covalently attach the carbon nanotubes to the polymer.

If the covalent bonding cannot be done directly between functional groups on the CNT surface and the polymer endgroups bifunctional coupling agents can be employed.

In this study, the influence of a bifunctional coupling agent (BCA) [17], as shown in Fig. 1, containing one benzoxazinone and one oxazoline group, on the electrical properties of melt mixed MWCNT–PA12 composites was investigated.

A possible advantage of this approach as compared to adding a second polymeric component as a compatibilizer is that a coupling between the nanotubes and the polymer chains of the matrix is provided which may prevent forming an insulative layer of a, chemically different, second polymeric component around the nanotubes.

In order to ensure covalent bonding via the bifunctional coupling agent, a PA12 type polymer with an excess of carboxylic acid endgroups and an amino functionalized MWCNT type were selected.

In this CNT–polymer system a direct reaction between the amino groups of the MWCNTs and the carboxylic groups of the polyamide 12 will only occur in very small extent due to the low reactivity at the used melt mixing conditions [18]. In contrast to that the oxazoline and benzoxazinone groups of the BCA react rapidly, selectively, and independently from each other with

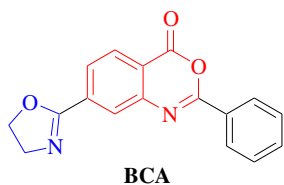


Fig. 1. Structure of the applied bifunctional coupling agent (BCA) with one benzoxazinone group (red) and one oxazoline group (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

carboxylic acid and amino groups [17]. Whereas the oxazoline groups react preferably with the carboxylic endgroups of the PA12, the oxazinone groups react with the amino groups of the MWCNTs. The selective reactions of this coupling agent were utilized in former works in chain extension of polyamides [19] and in synthesis of segmented block copolymers based on polyamide 12 [20,21]. As oxazoline and benzoxazinone groups are thermally stable at high temperatures, the BCA is ideal for the use in melt mixing processes. Another advantage of this heterobifunctional coupling agent as compared to a homobifunctional one is that bonding between the CNTs themselves or between two polymer endgroups will be diminished.

A special focus of this work was to prove the chemical reaction between the coupling agent and the applied MWCNTs. With the help of model compounds it is intended to show that the effectiveness of the chosen coupling agents lies in the covalent bonding between PA12 and MWCNTs.

2. Experimental

2.1. Materials

The applied polymers were a low viscous polyamide 12 (VESTAMID® L grade, Evonik Industries AG, Germany) with an excess of acid endgroups (for details see Ref. [22]), low density polyethylene (BPD2000, INEOS Olefins & Polymers Europe, United Kingdom) and polycarbonate (Makrolon® 2600, Bayer Material Science AG, Germany). Amino functionalized (Nanocyl™ NC3152), nominally unfunctionalized (Nanocyl™ NC7000) MWCNTs (Nanocyl S.A., Belgium), and SWCNTs SWeNT® CG100 (SouthWest NanoTechnologies, Inc., U.S.A.) carbon nanotubes were used. Whereas NC7000 represents the as-synthesized product with a carbon purity of <90%, NC3152 was obtained after purification (C purity > 95%) and functionalization (NH₂ content < 0.5%), according to the manufacturer. CG100 shows a carbon content >90 wt.%. All chemicals and solvents were received from Fluka and used without further purification. Tetrahydrofuran, chloroform and *N,N*-dimethylacetamide (DMAc) were dried over molecular sieves.

2.2. Analytical methods

NMR spectroscopy was performed on a Bruker Avance III 500 spectrometer. The ¹H NMR spectra were recorded at 500.13 MHz, the ¹³C NMR spectra at 125.74 MHz. Dimethyl sulfoxide-*d*₆ ($\delta(^1\text{H}) = 2.50$ ppm, $\delta(^{13}\text{C}) = 39.6$ ppm) was used for solvent, lock, and internal standard. Signal assignments were verified by ¹H–¹H and ¹H–¹³C correlated two-dimensional NMR spectra. The atom numbering within the aromatic rings corresponds to those given here for the compound **6** (see Fig. 2).

Fluorescence spectra were recorded with a Fluorolog 3 (Horiba Ltd. JobinYvon., U.S.A.) in steady-state mode. The samples were dissolved in ethanol (10^{−5} M), transferred into a cuvette and analyzed with a right-angle detector.

To record the Raman spectra, a LabRam 800 (Horiba Ltd. JobinYvon., USA) with a CCD detector was used. A red laser (He–Ne laser, 1.96 eV) was applied at an excitation wavelength of 633 nm.

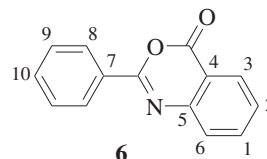


Fig. 2. Atom numbering within the aromatic rings for NMR signal assignments.

Download English Version:

<https://daneshyari.com/en/article/5182165>

Download Persian Version:

<https://daneshyari.com/article/5182165>

[Daneshyari.com](https://daneshyari.com)