



Macromolecular Nanotechnology

Poly(ethylene-co-butylene) functionalized multi walled carbon nanotubes applied in polypropylene nanocomposites

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ABSTRACT

A novel functionalized multi walled carbon nanotube (MWCNT) was prepared through grafting with α -azido-poly(ethylene-co-butylene) (PEB-N₃). The PEB-N₃ was prepared through a two step procedure and grafted onto an industrial grade multi walled carbon nanotube (MWCNT) through a highly efficient nitrene addition. This novel nano filler was melt mixed into polypropylene (PP) and the composite was characterized by FT-IR spectroscopy, Raman spectroscopy, Scanning Electron Microscopy (SEM), Rheology and Dielectric Relaxation Spectroscopy (DRS). The analyses showed that composites with the novel filler had a high degree of discharge from the surface and higher conductivity compared to the pristine filler, illustrating an efficient conductive network in the composites. The composites showed low percolation thresholds of 0.3 wt.% (0.15 vol.%) as well as improved stability at a range of temperatures from 25–135 °C.

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1. Introduction

A large number of nanocomposites employing different nanofillers have emerged during the last decade, where especially nanoclay and carbon nanotubes (CNTs) have been ascribed great potential [1]. The mechanical as well as the electrical properties that could be obtained through exploitation of CNTs have inspired much work on materials [2,3]. In particular the conductive properties of CNT fillers have led to a number of applications in electrics [4] such as in electrostatic charge dissipation (ESC) [5], electromagnetic interference screening (EMI) [6,7] or as bipolar plates in fuel cells [8]. For electric applications the low percolation thresholds generally observed for CNT fillers [9] enable lower loading of fillers compared to alternatives such as carbon black or graphite. In addition to this, CNT also contribute to the mechanical properties

through strengthening of the composite, which enables a number of novel applications. With the cost of CNT decreasing rapidly application of these materials as fillers in commodity plastics such as polypropylene (PP) has become increasingly attractive.

The most common method for dispersion of CNTs in PP has been melt mixing for prolonged periods of time. As an alternative to long mixing times, where the aspect ratio of the CNT can be reduced drastically through degradation, functionalization of CNTs is known to facilitate dispersion of fillers in polymer composites [10]. This approach has been proven to give mechanical improvements of PP composites, where e.g. amine functional MWCNT has been reacted with maleated PP [11] or butyl lithium has been used to activate the MWCNT surface and applied in subsequent grafting with chlorinated PP [12]. However, for electronic properties the functionalization approach has generally been found to result in a decrease of the conductivity of the CNT due to disruption of conjugation [13,14]. This result is heavily influenced by the method

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of functionalization as well as the extent of functionalization, and Lee et al. [15] has shown that a heat treatment or modification with low molecular weight compounds of the MWCNT could be applied to obtain an increased conductivity of a PP MWCNT composite. Often oxidative methods are involved in the purification or applied to introduce functional groups to the CNT. Such methods are known to cause degradation and shortening the tubes, which normally results in a substantial reduction of the conductive properties. Alternatively covalent functionalization of CNTs by non-oxidative methods can be performed through *in situ* generation of reactive species such as radicals, carbenes and nitrenes or by cycloaddition onto CNT as described in recent reviews [10,16]. For polymer grafting of CNTs [17] especially radical [18–21] and nitrene [22,23] approaches have been applied, since the reactive groups required for grafting can be introduced through common polymer endgroups. There are two examples of radical grafting of MWCNT in PP, where benzoyl peroxide has been applied in melt mixing [24,25]. In one case the material was used for drawing fibers and here a substantial improvement was observed [24], while in the other only moderate mechanical improvements were observed [25]. In these investigations the effects upon conductivity was not addressed.

Here a new concept with nitrene grafting of an azide functional PEB-N₃ onto a MWCNT was exploited to obtain a novel functional nano filler for PP. PEB is a well known compatibilizer for polyolefines, and this is to our knowledge the first application of it for functionalization of MWCNT. A low loading of PEB was targeted in order to preserve the conjugation of the system, while still striving for a compatibilizing effect to obtain a composite suitable for electronic applications.

2. Experimental

2.1. General methods and materials

MWCNTs with an average diameter of 9.5 nm and average length of 1.5 μm were purchased from Nanocyl S. A. (Belgium) and were used as received. Isotactic polypropylene was acquired from Lyondellbasell (HM562S, melt flow rate 30 g/10 min) Poly(ethylene-co-butylene)-OH (PEB-OH, $M_n = 7000$ g/mol, Kraton Liquid Polymer L-1203) was donated by Kuraray Co., Ltd. (Japan), all other chemicals were acquired from Sigma-Aldrich and used as received.

Nuclear magnetic resonance (NMR) spectroscopy was performed on a 300 MHz Cryomagnat from Spectrospin & Bruker, at room temperature. Infrared spectroscopy (ATR-FTIR) was performed on a PerkinElmer Spectrum One model 2000 Fourier Transform Infrared system with a universal Attenuated Total Reflection sampling accessory on a ZnSe/diamond composite. Differential Scanning Calorimetry (DSC) was performed on a DSC Q1000 DSC from TA Instruments. The thermal analysis was performed at a heating and cooling rate of 10 °C/min. The glass transition temperatures (T_g 's) were measured at the inflection point. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere on a Q500 from TA instruments with a heating

rate of 10 °C/min from RT to 800 °C. Size Exclusion Chromatography (SEC) analyses were performed in THF on two Polymer Laboratories PLgel 5 μm Mixed-D columns (300 \times 7.5 mm) with a Shimadzu SIL-10AD auto injector, a Shimadzu LC10AD pump and a Viscotek 200 diffractometer detector. The number-average molecular weight (M_n) and polydispersity index (PDI) values were determined with polystyrene standards. Scanning Electron Microscopy (SEM) was performed on a Quanta 200F from FEI Instruments. Ultra sonication was performed with a Hielscher UP200S. Extrudates were prepared on a Haake mini lab extruder (7 min @ 50 RPM). Raman spectra were recorded on a Thermo DXR dispersive Raman microscope with a 780 nm laser. Small amplitude oscillatory shear measurements were made on an AR2000 rheometer from TA Instruments using parallel plate geometry with a diameter of 25 mm and a plate separation of 0.9 mm. The measurements were performed at 200 °C and frequency sweep between 0.01 rad/s and 100 rad/s were made at a low strain of 2%. Dielectric Relaxation Spectroscopy (DRS) was performed on a Novocontrol Alpha-A high performance frequency analyzer.

2.2. Preparation of PEB functionalized MWCNT

PEB-OH (0.493 g, $M_n = 7000$ g/mol, PDI = 1.04, 0.07 mmol OH group) was dissolved in distilled THF at 0 °C. Et₃N (0.06 mL, 0.43 mmol) and a solution of mesyl chloride (MsCl, 0.022 mL, 0.28 mmol, in 0.2 mL THF) was added dropwise to the reaction mixture. The mixture was stirred under nitrogen for 18 h while it was allowed to reach room temperature. The mixture was filtered and precipitated into MeOH. The solvent was decanted and the residue was dissolved in toluene and precipitated into MeOH again. PEB-OMs was recovered after decantation of the solvent as a clear viscous liquid (0.42 g, 83%) and used without further purification. PEB-OMs (0.400 g, 0.06 mmol functional group) was dissolved in THF (2.7 mL) and azidotrimethylsilane (0.031 mL, 0.24 mmol) as well as tetrabutylammonium fluoride (TBAF, 0.235 mL, 0.24 mmol) was added to the mixture, which was stirred under nitrogen at room temperature for 18 h. The crude was isolated by precipitation into MeOH, the solution was decanted and the residue was dissolved in toluene and precipitated again into MeOH. PEB-N₃ was isolated upon decantation of the MeOH solution and drying *in vacuo* as a viscous liquid (0.16 g, 39%).

IR (cm⁻¹): 3100–2800 (CH stretch); 2095 (N₃ stretch). ¹H-NMR (300 MHz) CDCl₃, δ_H (ppm): 0.6–2.0 (m, corresponds to polymer backbone); 3.27 (t, 2 H, ³J = 7.4 Hz, CH₂CH₂N₃).

The pristine MWCNT (0.5 g) and PEB-N₃ (0.05 g, 0.007 mmol) were suspended in xylene at 130 °C under a nitrogen atmosphere for 20 h. The suspension was filtered on a 0.4 μm filter, rinsed with CH₂Cl₂ and dried *in vacuo* to obtain PEB-MWCNT as a black powder in quantitative yield. TGA shows 7.4 wt.% of polymer on the MWCNT.

2.3. Preparation of MWCNT PP master batch

The pristine or functionalized MWCNT (0.5 g) was dispersed in xylene by ultra sonication (3 \times 30 s) and

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