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Influence of dry grinding in a ball mill on the length of multiwalled carbon nanotubes and their dispersion and percolation behaviour in melt mixed polycarbonate composites

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ABSTRACT

Ball milling of carbon nanotubes (CNTs) in the dry state is a common way to produce tailored CNT materials for composite applications, especially to adjust nanotube lengths. For Nanocyl™ NC7000 nanotube material before and after milling for 5 and 10 h the length distributions were quantified using TEM analysis, showing decreases of the mean length to 54% and 35%, respectively. With increasing ball milling time in addition a decrease of agglomerate size and an increase of packing density took place resulting in a worse dispersability in aqueous surfactant solutions. In melt mixed CNT/polycarbonate composites produced using masterbatch dilution step, the electrical properties, the nanotube length distribution after processing, and the nano- and macrodispersion of the nanotubes were studied. The slight increase in the electrical percolation threshold in the melt mixed composites with ball milling time of CNTs can be assigned to lower nanotube lengths as well as the worse dispersability of the ball milled nanotubes. After melt compounding, the mean CNT lengths were shortened to 31%, 50%, and 66% of the initial lengths of NC7000, NC7000-5 h, and NC7000-10 h, respectively.

1. Introduction

Besides solution casting and in situ polymerization, melt mixing is a highly convenient method to produce thermoplastic based nanocomposites as it uses industrially available processing devices. In order to benefit from the outstanding intrinsic properties of carbon nanotubes (CNTs), a high degree of dispersion within the thermoplastic matrix is needed. This aim is generally hindered by the strong interactions between neighboured CNTs caused by high van-der-Waals forces and physical entanglements. The probability of entanglements depends thereby on the aspect ratio and the flexibility of the CNTs. Therefore, a reduction of entanglements due to a mechanical CNT shortening could improve their dispersability. One route towards mechanically shortened CNTs is the dry-state steel ball milling process which can help to tailor CNT properties [1,2]. CNTs are filled together with steel balls into a rotating barrel for the milling process resulting in the grinding of the CNT material to the necessary fineness by friction and impact with the tumbling balls. Some authors discuss the effect of ball milling on the nanotube morphology [3–8]. Measurement of the nanotube lengths using transmission electron microscopy (TEM) shows that nanotubes break and their length decrease in dependence on the ball milling time [1,4–7]. Using X-ray Photoelectron Spectroscopy (XPS) measurements, an increase of oxygen proportion at long operation time was found caused by collision-induced cutting under ambient atmosphere introducing oxygen-containing functional groups to the cut nanotubes [4,7]. Ahn et al. [8] described that the multiwalled carbon nanotubes (MWCNTs) tend to be compacted by impact of the balls and form agglomerates with increased size during the ball milling process as observed by scanning electron microscopy (SEM). The compactness or strength of CNT agglomerates influenced their dispersability. Krause et al. [9] described the dispersability of commercial MWCNT materials in aqueous surfactant solutions using centrifugal separation analysis. It was found that with higher agglomerate density the dispersability of nanotubes worsened. Pegel et al. [10] described for two batches of the same MWCNTs different dispersabilities in aqueous surfactant solution. The incorporation of both kinds of MWCNTs in polycarbonate (PC) using melt mixing showed very different electrical percolation behaviours. The MWCNT material with the better dispersability leads to a significantly lower electrical percolation threshold in comparison to the MWCNTs with the worse dispersability. Comparable results were described by Krause et al. [11] for different kinds of CNTs and the electrical percolation behaviour of these CNTs in polyamide 6.6 and by Socher et al. [12] for composites based on polyamide 12. Nanotube materials with a good stability of their aqueous dispersions also showed a good

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dispersion after melt mixing as indicated by morphological investigations and exhibited low electrical percolation thresholds in the composites.

Concerning the length distribution of CNTs, some authors report measurements on pristine nanotubes using microscopic methods after dispersing nanotubes in suitable solvents or after dissolving them from a matrix. Albuerne et al. [13] dispersed pristine and functionalized multiwalled CNTs Baytubes® C150P in chloroform using ultrasound and determined the nanotube length distributions using scanning force microscopy (SFM). SEM investigations on nanotube lengths after incorporation in an epoxy resins were reported by Fu et al. [14] whereby the epoxy matrix was dissolved using dimethylformamide (DMF) and low energy ultrasound. A significant CNT shortening from 10–20 μm up to 1.4 μm was described. Chen et al. [15] measured MWCNT lengths after poly(methyl methacrylate) composite preparation by solution-mixing using field-emission SEM. The MWCNT composites were dissolved in tetrahydrofuran (THF). The comparison between the as-grown and processed MWCNTs indicated a strong shortening by up to 90% of the initial length during the sonication assisted composite preparation after a nanotube surface oxidation step. Duncan et al. [16] investigated the fragmentation aspect ratio of differently functionalized MWCNTs in PC composites prepared by a solvent precipitation method. For the fractured composites, PC was dissolved in THF and aspect ratio distributions of the partially broken nanotubes are shown. Lin et al. [17] determined MWCNT lengths after melt dilution of a PC based masterbatch using SFM whereby a relatively harsh solvent and ultrasound treatment was used to extract the nanotubes from the PC matrix. Using different small-scale mixers a comparable shortening of the nanotubes from 10–15 μm to 0.4–0.6 μm was measured. It has to be considered that ultrasonication of nanotube dispersions may lead to mechanical damage and shortening [18] changing the length to be studied. Krause et al. [19] performed SEM investigations on the remaining nanotubes after pyrolysis of small amounts of MWCNT-polyamide composites melt mixed in small-scale under different conditions. By this, changes in the nanotube lengths after melt compounding using different rotation speed could be estimated.

A method to determine the CNT length of pristine CNTs and CNTs recovered from a composite using the same preparation and measurement method, namely by dispersing in chloroform, applying TEM on individualized nanotubes and performing image analysis, was recently described by Krause et al. [20]. In this way the obtained results concerning the CNT length are comparable and CNT shortening during processing could be assessed.

In our study, as-grown and ball milled CNTs were characterized with regard to their morphology, nanotube length distribution, and dispersability in aqueous dispersion. In addition, these nanotubes were melt mixed in PC and the electrical percolation thresholds as well as the morphology using TEM and light microscopy (LM) of the composites were determined. Furthermore, the nanotubes were dissolved from the PC and the nanotube length distributions after melt mixing were measured. In this way, the shortening during melt mixing could be quantified.

2. Experimental part

2.1. Materials

This study is based on Nanocyl™ NC7000 (Nanocyl SA, Sambreville, Belgium) MWCNT material, which was ball milled for 5 and 10 h. Nanocyl™ NC7000 is an as-grown material produced in an industrial large-scale chemical vapour deposition process. It is characterized by an average nanotube diameter of 10 ± 3 nm [21], a length of 1.5 μm, a carbon purity of 90%, and a surface area of 250–300 m^2/g [22]. The Nanocyl™ NC7000 material was ball milled using a 5 L jar half filled with stainless steel beads of 12 mm diameter. The remaining volume was filled with CNTs and the jar was rotated on two rubber rollers at a rotation speed of 50 revolutions per minute (rpm) for 5 (NC7000-5 h) and 10 h (NC7000-10 h).

The composites were processed by diluting a masterbatch containing 7.5 wt.% MWCNTs (Nanocyl® NC7000, NC7000-5 h, or NC7000-10 h) in PC (Lexan™ 141R, Sabic Innovative Plastics, The Netherlands) towards composites with different MWCNT contents. Both processing steps were performed using a co-rotating twin-screw extruder ZE25 (Berstorff, Germany) at a mean barrel temperature of 260 °C, 500 rpm, a throughput of 5 kg/h and an optimized screw configuration (SC5 in [23]). For the masterbatch production PC pellets and the powdery MWCNT material were fed simultaneously into the hopper by gravimetric dosing. For the masterbatch dilution, pellets of the masterbatch and the diluting PC were premixed.

2.2. Methods

2.2.1. Characterization of dry MWCNT powders

SEM of the MWCNT powders was performed using an Ultra plus microscope (Carl Zeiss GmbH, Oberkochen, Germany) on the as received material.

The agglomerate size distribution of the MWCNT powders was determined by laser diffraction using a Helos/BF particle size analyzer coupled with a RODOS dry dispersion unit and ASPIROS micro dose module (Sympatec GmbH, Clausthal-Zellerfeld, Germany). For the sample measurement a pressure of 0.5 bar was used. The measurement range is 4.5–875 μm. The volume weighted agglomerate size distributions were calculated in accordance to ISO 13320 combined with the Fraunhofer diffraction analysis [24–26]. Additionally, the parameters x_{10}, x_{50}, and x_{90} were calculated, indicating that 10%, 50%, and 90% of the particles are smaller than the given value.

All MWCNT materials were characterized by RAMAN spectroscopy using a Bruker FT-Raman spectrometer (excitation at 1064 nm). In order to assess the concentration of defects of multiwalled carbon nanotubes the area ratio D/G between the disorder band at 1284 cm^{-1} (D-band) and the band at 1609 cm^{-1} (G-band) assigned to the in-plane vibrations of the graphitic walls was analysed.

XPS studies were performed on small powder samples using an AXIS ULTRA system (Kratos Analytical, UK) combined with a Mono-Al $K\alpha_{1,2}$ X-ray-Source (300 W at 20 mA) and an analysator having a pass energy of 160 eV or 20 eV was used.

2.2.2. Preparation and characterization of aqueous MWCNT dispersions containing surfactant

To compare the dispersability of the three different kinds of MWCNTs the nanotubes were dispersed in an aqueous surfactant solution. According to previous investigations [11], the anionic surfactant sodium dodecyl benzene sulfonate (SDDBS) was used in this study. The carbon nanotubes were dispersed in a concentration of 0.07 g/l in an aqueous solution of the SDDBS surfactant (0.7 g/l). The formation of stable surfactant micelles is achieved since the concentration of SDDBS at 0.7 g/l is above the critical micelle concentration of 0.42 g/l [27]. The low concentration of CNTs was selected in order to ensure so-called swarm sedimentation of CNTs during the centrifugation step which means that the CNTs do not settle as a particle collective but move according to their size [28]. CNT dispersions were prepared in a beaker glass at room temperature using an ultrasonic processor UP 200S (Hielscher Ultrasonics, Germany, 24 kHz, 200 W) equipped with a Sonotrode S14 made of titanium. The amplitude was adjusted to 20% resulting