



Melt mixed nano composites of PA12 with MWNTs: Influence of MWNT and matrix properties on macrodispersion and electrical properties

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ABSTRACT

Nanocomposites containing four different polyamide 12 (PA12) types and three grades of multiwalled carbon nanotubes (MWNTs) were prepared via small-scale melt processing to study the effect of different MWNTs and the influence of polymer properties on the dispersion of the fillers and the electrical properties of the composites. Under the selected mixing conditions the lowest electrical percolation threshold of 0.7 wt.% was found for Nanocyl™ NC7000 in low viscous PA12. Moreover, big influences of the end group functionality (acid or amine excess) and the melt viscosity of the matrix were found. Composites of PA12 with acid excess showed lower percolation thresholds than those based on amine terminated materials. At constant end group ratio low viscous matrices resulted in lower percolation thresholds than high viscous materials. The best MWNT dispersion was obtained in both high viscous PA12 composites. In these systems the mixing speed was varied indicating an optimum concerning electrical conductivity at 150 rpm as compared to 50 and 250 rpm.

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1. Introduction

With the implementation of a 200 tons/year plant for Baytubes® [1] and the start up in 2010 of a 400 tons/year plant for Nanocyl™ NC7000 [2], the carbon nanotube (CNT) producers are on their way to the world-scale production of CNTs. In consequence, prices will drop and more and more potential applications [3–7] using the outstanding properties of CNTs like high mechanical strength [8] and electrical conductivity [8,9] can enter the market.

An enormous increase in number of studies in the field of CNT nano composites could be observed over the last years [10–12], but still some problems like the incomplete dispersion and distribution of primary CNT agglomerates or the insufficient adhesion between CNTs and the polymer matrix in nano composites have to be solved.

For composites of polyamide 12 (PA12) containing CNTs potential application areas are e.g. antistatic fuel pipes and parts in fuel pumps for the use in the automotive industry. Due to economic reasons a low electrical percolation threshold is desired.

The morphology of conductive fillers, like shape (spherical, rod-like, platelike, clustered) and the resulting aspect ratio, strongly influence their percolation threshold [13–15] in composites and thus for different kinds of fillers different electrical percolation threshold are observed [16]. Due to their very high aspect ratios

CNTs are favourable for achieving low percolation thresholds. For bulk applications, most commercially available CNTs represent multiwalled carbon nanotubes (MWNTs) produced by chemical vapour deposition where highly entangled MWNT agglomerates are formed.

For the dispersion and distribution of nanotubes in polymer matrices different techniques like solution mixing, in situ-polymerisation, the latex-approach, and melt mixing are applied. High mixing efficiency, working without solvents and short processing times make melt mixing the method of choice for industrial production of CNT composites. Hereby the dispersion of the nanotube agglomerates is influenced by many processing parameters like mixing speed, melt temperature, throughput or residence time [17–21]. Little attention has been paid to identify differences in the dispersion and electrical properties of different MWNT materials or the influence of polymer properties in melt mixed nano composites [22–28].

Most of the studies in literature concerning composites of polyamide and MWNTs are dealing with polyamide 6 (PA6) [18,29–31] or polyamide 6.6 (PA6.6) [18]. For PA6.6 a percolation threshold of 1 wt.% was reported, whereas those reported for PA6 appeared to be higher starting at about 2.5 wt.% for pressed plates when using Nanocyl™ NC7000 in small-scale melt mixing. For specially synthesized straight MWNTs having a low oxygen content on the surface and a high aspect ratio an ultralow percolation of 0.04 wt.% could be observed in melt mixed PA6.6 composites as measured on pressed plates [22]. For PA6, Kodgire et al. [32] reported an electrical percolation threshold of only 0.5 wt.% for

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MWNTs (Nanocyl, purity >95%, $L/D = 10\text{--}1000$) modified with sodium salt of 6-aminohexanoic acid (Na-AHA). In contrast, non-modified MWNTs showed a threshold between 2–3 wt.% when using small-scale melt mixing and pressed plates.

For PA12, only selected papers dealing with dispersion and/or electrical conductivity could be found. Ha et al. [33] found resistivity values lower than $10^7 \Omega \text{ cm}$ on pressed plates starting at 3 wt.% MWNTs (Nanocyl™ NC7000) in PA12 (Vestamid L1600 nf). The same value was reported by Bhattacharyya et al. [34,35] for non-modified single-walled carbon nanotubes (SWNTs, Nanoledge) when using a PA12 with equivalence of acid and amine end groups and a MFI of 154 g/10 min (275 °C, 5 kg). After encapsulating the nanotubes using styrene-maleic-anhydride in order to create a reactive coupling to the matrix much better dispersion was found, however the composites were non conductive due to a bonded polymer layer around the nanotubes.

As other polyamides, PA12 can be synthesized with different ratios of the end groups, namely amine or acid, which influence different properties, like mechanical. The selection of the end group ratio depends on the application and the additives in formulations; however, most of the industrial types are acid group terminated. In literature, most of the papers do not name the end group ratio. Thus, a comparison of different results may be difficult, if the end group termination plays a role on dispersion and conductivity. To our knowledge, no comparative study exists concerning dispersion and electrical properties of composites based on different end group terminated PA12.

In this work, composites of different PA12 with diverse commercially available MWNTs were investigated to study the effect of the nanotube material as well as polymer matrix properties (especially end group functionalities and viscosity) on the nanotube macrodispersion and electrical properties. For this purpose PA12 types with preferential functionalities in two viscosity levels were used.

2. Experimental

2.1. Materials

Four different types of PA12 were supplied by Evonik Degussa GmbH (Marl, Germany). Among these types were two acid groups terminated and two amine group terminated PA12 with low or high viscosity. The materials are summarized in Table 1, showing also the end group contents as obtained by titration and melt viscosities at processing temperatures as studied using an ARES oscillatory rheometer (Rheometric Scientific Inc., Piscataway, NJ, USA) with parallel plate geometry in nitrogen atmosphere.

Table 1
Characteristics of the PA12 types (end group contents and melt viscosity).

PA12 type	[COOH] content (mmol/kg)	[NH ₂] content (mmol/kg)	$\eta_{\text{a}}^{\text{a}}$ at 100 rad/s (Pa s) @ T_{melt}
Low viscous, acid excess	104	4.2	140 (210 °C)
Low viscous, amine excess	26	126	100 (210 °C)
High viscous, acid excess	42	0.47	1240 (260 °C)
High viscous, amine excess	3	56	1140 (260 °C)

Table 2
Properties of the used CNTs according to the suppliers [45–47].

	Diameter (nm)	Length (μm)	Carbon purity (%)	Bulk density (kg/m ³)
Baytubes® C150P	13–16	1–>10	>95	120–170
Nanocyl™ NC7000	9.5 (average)	1.5 (average)	>90	66 [*]
FutureCarbon CNT-MW-K	15	–	90	28 [*]
Printex® XE2	30–35	n. a.	>99	100–400

^{*} According to Ref. [38].

The following multiwalled carbon nanotubes were employed: Baytubes® C150P (Bayer MaterialScience AG, Leverkusen, Germany), Nanocyl™ NC7000 (Nanocyl S.A., Sambreville, Belgium), and FutureCarbon CNT-MW-K (FutureCarbon GmbH, Bayreuth, Germany). For comparison, Printex® XE2 (Evonik Degussa GmbH, Marl, Germany) was used as Carbon Black (CB). This CB has a BET-surface area of 910 m²/g [36]. The properties of the MWNT materials and CB as given in the corresponding data sheets are shown in Table 2.

Octadecylamine (purity >90%) was supplied by Fluka (Fluka Chemie GmbH, Buchs, Switzerland) and was used without further purifications.

2.2. Processing

Melt mixing of the granular polymer (dried overnight at 80 °C) and the powdery MWNTs (dried overnight at 120 °C) was done in a DACA microcompounder (DACA Instruments, Santa Barbara, USA; inner volume: 4.5 ccm). Polymer and CNTs were alternatively added to the microcompounder (at least three portions). Melt mixing was performed at 210 °C with a mixing speed of 250 rpm for 5 min (low viscous PA12). In high viscous systems, a mixing temperature of 260 °C was used to enable processability. The relatively high mixing speed was selected as in [17,18] better dispersion was achieved at higher mixing speed; the mixing time was set considering the maximum mixing time achievable in industrial twin-screw extrusion. These mixing conditions do not represent optimized condition which may be different for diverse nanotube materials.

For some experiments, octadecylamine was used to prevent a cross-linking of PA12 and utilised in excess to the amine groups of the PA12. It was dispensed in the microcompounder at the end of the filling process.

The extruded strands were cut into pieces of some millimetres length and compression moulded into plates (30 mm diameter, 0.5 mm thickness) using a Weber hot press (Model PW 40 EH, Paul Otto Weber GmbH, Remshalden, Germany). Compression moulding was performed following the procedure given in [17] with a pressing temperature of 220 °C for low viscous PA12 composites, and 260 °C for high viscous PA12. The pressing speed was 6 mm/min with a pressing time of 1 min and the pressing force was increased in steps up to 100 kN.

2.3. Characterization

The electrical volume resistivity was measured using a Keithley Electrometer 6517A (Keithley Instruments Inc., Cleveland, USA)

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