



Localization of carbon nanotubes in polyamide 6 blends with non-reactive and reactive rubber



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ARTICLE INFO

Article history:

Received 21 March 2014

Received in revised form

28 April 2014

Accepted 2 May 2014

Available online 14 May 2014

Keywords:

Carbon nanotubes localization

Polymer-matrix blend

Electrical resistivity

ABSTRACT

Blending of two immiscible polymer matrices can be an effective way to combine favourable properties of both blend partners. The additional incorporation of multiwalled carbon nanotubes (MWCNTs) in such thermoplastic blends may further enhance the blend properties and especially generate electrical conductivity.

In the present study, 20 wt.% of non-reactive rubber and maleic anhydride functionalized rubber were melt blended with polyamide 6 and 3 wt.% MWCNTs by using different incorporation strategies. For the blends containing non-reactive rubber, the MWCNTs were always localized selectively in the thermodynamically preferred polyamide phase as shown by TEM images and electrical measurements. Interestingly, the different strategies resulted in different localization behaviours of the MWCNTs in case of the reactive rubber. These findings demonstrate the significant influence of maleic anhydride groups of the rubber component on localization of MWCNTs in the different blend phases which results in different values of electrical volume resistivity of the blends.

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1. Introduction

Blending of two immiscible polymer matrices can be an effective way to combine favourable properties of both blend partners. The incorporation of rubber in polymers is a concept to enhance the toughness of the blends which was described in the literature also for polyamides [1–4]. The additional incorporation of multiwalled carbon nanotubes (MWCNTs) in such thermoplastic blends may further enhance the blend properties and especially generate electrical conductivity.

Wang et al. [5] described the addition of ultra-fine rubber particles of carboxylic styrene–butadiene latex to PA6/MWCNT composites. For PA6/MWCNT composites an electrical percolation threshold at 6 phr MWCNT was found. However, if the PA6/MWCNT composites were filled with 16 phr rubber the percolation threshold decreased to 3 phr MWCNT. By variation of the rubber content for PA6/4 phr MWCNT/rubber composites an electrical percolation threshold at 8 phr rubber was found. Also González

et al. [6] described a decrease of the percolation threshold after rubber addition (styrene/ethylene-butylene/styrene triblock copolymer, SEBS) of 5–30%. The findings of both studies based on the volume exclusion effect.

In the literature same examples for reactive blending were found. The preparation of a polyamide 12 (58 wt.%)/maleated polyethylene–octene rubber (POE-g-MA, 40 wt.%)/graphene (2 wt.%) blend using different mixing strategies was described by Yan et al. [7]. It was found that the simultaneously melt mixing of all 3 components leads to randomly dispersed graphene sheets in both polymers, whereas the most sheets tend to distribute in PA12. The electrical conductivity was similar to the one of binary PA12/2 wt.% graphene composite. The graphene sheets are preferentially located in PA12 if the PA12/graphene composite was blended with the rubber. For such blend the highest conductivity was found. If the polyamide was melt mixed with a rubber/graphene composite the graphene was selectively located in the rubber and the lowest conductivity of the blend was obtained due to the fact that the graphene is not able to form a conductive network in the PA12 matrix. The MWCNT localization in PA6/POE-g-MA/MWCNT (75/20/5) blends is shown by Dasari et al. [8]. Such blends were prepared by twin-screw extrusion and

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simultaneously blending of all 3 components. The majority of the MWCNT are selectively located in the continuous PA6 matrix and a few MWCNT are in the rubber component. The electrical conductivities of the ternary blends are 1 decade higher than the binary composites without rubber at similar MWCNT loading indicating the volume exclusion effect.

That the blending sequence significantly influenced the blend properties like mechanical properties, microstructure, and filler location was also shown by Dasari et al. [9] for PA66/organoclay/SEBS-g-MA blends.

The role of maleic anhydride group in blend components for the nanotube localization was described from Gültner et al. [10] for PC/SAN (60 wt%/40 wt.%) blends containing 0.5 wt.% amino-functionalized MWCNT. It was found that the MWCNT localization was independent on the mixing strategy in the PC component if the blend was non-reactive (without a maleic anhydride functionalized component). The addition of a MA-functionalized component which was miscible only with the SAN component leads to a MWCNT localization in the SAN component. It was concluded that a chemical coupling or strong interactions between MWCNT and MA-functionalized component were the driving force for the MWCNT localization behaviour. Additionally, the content of the MA-functionalized component at a constant MWCNT concentration was varied. It was shown that a certain critical ratio of the MA-functionalized component and MWCNTs was required to achieve selective MWCNT localization in the SAN component.

The electrical percolation threshold for PA6/MWCNT composites in the literature varied by the preparation conditions. So, Kodgire et al. [11] and Krause et al. [12] found an electrical percolation threshold of 2–3 wt.% MWCNT on compression moulded PA6 films and Meincke et al. [13] found an electrical percolation threshold of around 5 wt.% on injection moulded test bars.

In the present study, non-reactive rubber and maleic anhydride functionalized rubber were melt blended with polyamide 6 using four different mixing strategies. The influence of the maleic anhydride functionalization of the rubber, the mixing strategy on the electrical properties, and the nanotube localization were investigated.

2. Experimental part

2.1. Material

As polyamide 6 (PA6) matrix ULTRAMID® B27E (BASF SE, Germany) and as PA6-masterbatch PLASTICYL™ PA1503 (Nanocyl S.A., Sambreville, Belgium) containing 15 wt.% Nanocyl™ NC7000 (multiwalled carbon nanotubes, MWCNTs) were used. Two different rubbers were used for the blends: the non-reactive rubber AFFINITY™ EG8200G (ethylene copolymer, Dow Chemical Company) and the maleic anhydride functionalized rubber EXXELOR VA1803 (ethylene copolymer, Exxon Mobil Corporation) with a maleic anhydride content in the range of 0.5–1.0 wt.%. The commercially available multiwalled carbon nanotube materials Nanocyl™ NC7000 (Nanocyl S.A., Sambreville, Belgium) were employed. For Nanocyl™ NC7000 the carbon purity is given as 90% [14] and the bulk density was measured to be 66 kg/m³, and the mean agglomerate size was larger than 675 μm [15]. The outer diameter was determined to be 10 ± 3 nm [16]. The nanotube length distribution as determined by TEM was characterized by a x_{50} -value of 1341 nm and a x_{90} -value of 3314 nm [17].

The MWCNTs were annealed to reduce the degree of the functional groups on the surface of the nanotubes at 2600 °C in argon atmosphere for one hour (performed at the Leibniz Institute for Solid State and Materials Research Dresden).

2.2. Methods

The polyamide 6/rubber/MWCNT blends were produced using a small-scale DSM Xplore 15 twin screw microcompounder (DSM Xplore, Netherland) with a chamber volume of 15 cm³. The mixing conditions were 260 °C melt temperature, 80 rpm mixing speed, and 3 min mixing time. The extruded strands were compression moulded (260 °C, 50 kN) into plates (60 mm diameter, 0.3 mm thickness) using a hot press (Model PW 40 EH, Paul Otto Weber GmbH, Germany). The rubber-MWCNT masterbatch containing 7.2 wt.% MWCNT was prepared by melt mixing at 100 °C with a rotation speed of 200 rpm and with a mixing time of 5 min.

The electrical volume resistivity of the composite materials was determined according to the standards ASTM D 4496 and ASTM D 257. The resistivity measurements on the pressed plates with resistances >10⁷ Ohm were performed using a Keithley 8009 Resistivity Test Fixture (open symbols in the graphs). For resistances <10⁷ Ohm, strips (5 mm × 30 mm × 0.3 mm) were cut from the plates and measured using a 4-point test fixture (external source electrodes spacing 16 mm and measuring electrodes spacing 10 mm, filled symbols in the graphs). Both devices were combined with a Keithley electrometer 6517A or a Keithley multimeter DMM2000 (Keithley Instruments Inc., Cleveland, USA).

For transmission electron microscopy (TEM) investigations ultra-thin sections of the samples were cut with a diamond knife at –180 °C and observed using a Zeiss Libra200MS (IPF Dresden) or using a Zeiss Libra120 (at BASF).

X-ray photoelectron spectroscopy (XPS) measurements were performed on pressed powder film 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). An analyser having pass energy of 160 eV or 20 eV was used.

3. Results

The localization of the MWCNTs (3 wt.%) in immiscible polyamide 6/rubber blends has been investigated. A non-reactive and a maleic anhydride functionalized rubber were used to study the influence of a reactive group in the blend system on the blend morphology and the MWCNT localization. Furthermore, different mixing strategies for the blend preparation were used.

The different incorporation strategies were:

- a) The MWCNTs were added in the molten PA6/rubber blend.
- b) The MWCNTs, PA6, and rubber were dry premixed and melt mixed together.
- c) A PA6/MWCNT masterbatch was diluted with polyamide and rubber.
- d) A rubber/MWCNT masterbatch was diluted with PA6.

In the first three cases, a blend composition of rubber/PA6 of 20 wt./80 wt.% was chosen. Due to the low MWCNT content in the rubber masterbatch of 7 wt.% a PA6/rubber blend with 40 wt.% rubber was prepared to reach a MWCNT content of 3 wt.% in the blend. A higher MWCNT content in the rubber/MWCNT masterbatch could not be prepared due to the strong increase of the shear force during melt mixing with increasing MWCNT concentration.

The MWCNT concentration of 3 wt.% was used due to an electrical percolation threshold around 3 wt.% for PA6/MWCNT composites was found (see Fig. 1). At the percolation threshold, the electrical resistivity values of the polymer change very sensitively depending on conductive network formation of the MWCNT in the polymer.

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